

**A Generalised Modular Framework
for the Synthesis of Nonideal Separation and
Reactive Separation Processes**

by

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*To my parents Rahim and Hasnah
who taught me patience*

Abstract

This thesis presents a systematic approach for the synthesis of azeotropic separation and combined reactive/separation systems, utilising a mass and heat transfer phenomena based representation. The developed framework does not explicitly prepostulate process alternatives but instead investigates them as mass and heat exchange possibilities. The building block of process alternatives is based on a mass/heat transfer module between two properly defined streams consisting of two parts: a mass/heat exchange block, whereby mass and heat transfer takes place between streams, and a pure heat exchanger, where only heat is exchanged and matching streams do not come into contact. In this work, the module is developed focusing on nonideal separation and separation reactive mass transfer phenomena. Gibbs free energy based constraints are derived and introduced in each block, to determine the direction of mass transfer for each component and ensure feasibility of both phase change and reactive mass transfer. Phase and reaction equilibria are not necessarily reached in the mass/heat transfer module but are instead utilised to define the limiting case.

Process operations are viewed as sets of mass and heat exchange, such that a set of properly connected blocks can be realised as process alternatives. The synthesis model is formulated as a mixed integer nonlinear optimisation problem, for which a decomposition strategy is developed for its solution. The main feature of this representation is that with no prepostulation of process units, different structures and mass transfer patterns, rather than detailed designs, are captured.

In the first part of this work, the proposed framework is developed for the synthesis of homogeneous azeotropic separation systems. For this class of systems, it is shown that sequencing and entrainer selection can be addressed in a single optimisation problem. Modelling aspects towards the synthesis of heterogeneous systems are outlined. The approach is further developed to encompass combined reaction and separation processes, where it is illustrated that process alternatives including hybrid process units, such as reactive separation units, as well as conventional separation and reaction units, can be generated within the framework. An application of the framework to an industrial methanol case study is also presented.

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Introduction

Process synthesis continues to be an active research area in chemical engineering, with significant advances achieved in terms of developing synthesis methods for subsystems (reactor networks, separation systems, heat exchange networks, mass exchange networks) and for total flowsheets. By definition, process synthesis is the determination of the topology of process units, as well as the type and design of the units within the flowsheet that will convert specified inputs into desired products. The synthesis task is usually driven by the optimisation of a specific objective, typically based on economics.

Systematic techniques for the synthesis and design of flowsheets are represented by two different approaches, hierarchical decomposition and mathematical programming, a recent overview of which is available in the book by Biegler *et al.* (1997). These two methodologies are concerned with different aspects of design and can be considered as complementary, and work to integrate them to exploit the advantages of the individual methods has been presented (Grossmann and Daichendt, 1998). The hierarchical decomposition technique breaks the synthesis procedure into five discrete decision levels, with the detail of design increasing at each level (Douglas, 1985; Douglas, 1988; Douglas, 1995). At each decision level beyond the first, the economic potential of the project is evaluated and a decision is made whether or not further work on the project is justified. Heuristics, short-cut design procedures and physical insight is utilised to develop an initial base-case design. Relying on heuristics, this approach cannot rigorously produce an optimal design. Furthermore, due to its sequential nature, interactions among the design variables at the various decision levels may not be properly accounted for as it is necessary to solve for them simultaneously. This is illustrated by Duran and Grossmann (1986), who considered simultaneous heat exchanger network and process synthesis. Despite these shortcomings the hierarchical approach method provides a powerful approach for quickly generating initial flowsheets and alternatives, and its implementation in a software system as presented by Douglas and Stephanopoulos (1995) contributes further to aid the engineer.

Emphasising the increasing use of algorithmic methods based on mixed integer nonlinear programming (MINLP) optimisation and their combination with other design methodologies, an extensive review of recent developments in the mathematical approach is given by Grossmann (1996). The mathematical programming approach to process synthesis utilises optimisation techniques to select the configuration and parameters of the processing system (Grossmann, 1985; Grossmann, 1990). A superstructure of alternative processing units and interconnections is modelled as an MINLP problem, with 0-1 binary variables representing the potential existence of units and their interconnections and continuous variables defining equipment sizes and operating conditions. In principle, the application of a solver to a superstructure with complete connectivity would yield the global solution. However, this is not always possible due to two associated difficulties with the solution of MINLP models - combinatorics due to the potentially large number of structural alternatives that arise, and local optima due to the nonconvexities inherent in nonlinear process models. The work addressing these problems is reviewed by Floudas and Grossmann (1995). A further inherent limitation of these techniques is their reliance on engineering knowledge for the construction of the superstructure, which only contains alternative processing units that are explicitly prepostulated. Hybrid process units and non-conventional process structures, that recently are proven favourable in industry, are only studied within an algorithmic superstructure based approach when prepostulated (Gumus and Ciric, 1997).

To overcome the implicit assignment of processing tasks to processing units, Papalexandri (1995) developed a general synthesis framework based on a mass and heat transfer representation. Utilising fundamental mass/heat transfer principles within a superstructure environment, this building block synthesis method exploits modelling concepts from the well defined heat exchanger network (HEN) and mass exchange network (MEN) problem. Synthesis alternatives are not prepostulated but instead embedded within a network of mass and heat exchanging modules that allow non-conventional, hybrid systems to be revealed. In terms of total process flowsheet alternatives, the potential of this approach has been illustrated through application to ideal systems including separation, reaction and heat integration operations. The approach has also been applied to the synthesis of flexible heat and mass exchange networks (Papalexandri and Pistikopoulos, 1994). However, the framework is not readily applicable to general multicomponent nonideal systems, lacking a fundamental theory for mass transfer within the building block module. For this modelling framework to be applicable to general nonideal systems, the mass/heat transfer module must be modified and developed.

In this thesis we face this challenge, presenting a synthesis framework within the mass/heat transfer representation for the synthesis of two topical subsystems : nonideal separation and combined reaction-separation systems. In terms of nonideal and azeotropic separations, apart from the pioneering work of Doherty and his coworkers there has been considerable activity in the development of systematic synthesis and design methodologies, excellent reviews of which are given by Malone and Doherty (1995), Widagdo and Seider (1996), Westerberg and Wahnschafft (1996) and chapter 14 of Biegler *et al.* (1997). A common feature of such advances is the emphasis on separation feasibility within a sequential framework typically based on analysis of residue curve maps and distillation lines. Generally, the synthesis task has been decomposed into subtasks of entrainer selection, sequencing of columns and design and optimisation of columns. A potential limitation of such a sequential approach is that there is often no guarantee that the resulting separation design is in fact optimal. In terms of integrated reaction and separation processes, academic interest has been recently fuelled by the superior performance of novel hybrid units such as membrane reactors over conventional units. Due to the complex interactions that occur in these classes of systems, however, advances in the modelling, design and synthesis of such systems have been mainly concentrated on the specific case of reactive distillation. The work presented herein focuses on the synthesis of these particular systems, within a generalised modular framework that is developed for application to general flowsheet synthesis.

1.1 Thesis Objectives and Outline

The objective of this work is to develop a systematic approach for the synthesis of general nonideal separation and combined reactive separation systems, utilising a mass and heat transfer synthesis framework. In particular, the aims of this thesis are as follows;

- ◇ For the synthesis of homogeneous azeotropic separations, to develop a framework by which entrainer and sequencing alternatives can be simultaneously explored. Entrainers, process units and structures are not determined sequentially but examined within one separation optimisation problem. Once promising schemes have been identified, they can then be considered further for detailed design optimisation.
- ◇ For the synthesis of combined reaction separation systems, to develop a framework whereby hybrid process units, such as reactive separation units with reactive and non-reactive sections, as well as conventional separation and reaction units can be generated.
- ◇ To develop a theoretical basis for the modelling of mass transfer between process streams, focusing on nonideal separation and reactive separation phenomena, thus providing a basis for the extension of the mass/heat transfer framework to other systems *i.e* heterogeneous and reaction network systems.

The building block of process alternatives is based on a multipurpose mass/heat transfer module, utilised to represent separation units and structures which are not explicitly prepostulated but rather investigated as mass and heat exchange possibilities. To ensure feasibility of both phase change and reactive mass transfer within the mass/heat transfer module, Gibbs free energy based constraints are derived and introduced. Phase and reaction equilibria are not necessarily reached within the module but are instead utilised to define the limiting case. The synthesis problem results in a network of mass/heat transfer modules within which all process alternatives are embedded. The superstructure model corresponds to a large scale mixed integer nonlinear programming (MINLP) problem, the solution of which is obtained via a proposed decomposition strategy. The synthesis task is driven by the minimisation of a cost function, usually consisting of utility costs and an approximation of capital costs.

This thesis is structured as follows. In chapter 2, the mass/heat transfer framework is introduced, and the mass transfer driving force constraints which constitute the basis for the synthesis representation are derived.

In chapter 3, the proposed framework is developed for the synthesis of homogeneous azeotropic separation systems. It is shown that through the use of driving force constraints and detailed thermodynamic models, nonideal behaviour can be sufficiently characterised. Separation feasibility is thus fully considered, enabling entrainer selection and separation sequencing to be determined in a single optimisation problem. In addition, modelling aspects to encompass the synthesis of heterogeneous azeotropic separations is outlined.

In chapter 4, the approach is further extended to encompass combined reaction and separation processes. Utilising reaction kinetics and thermodynamic models within the driving force constraints, it is shown that the complex interaction in this class of systems can be captured. Chemical and physical equilibrium is not assumed, and heat effects and multi-reactions can be considered. Without any prepostulation of units, hybrid structures and operating conditions can be generated, with the optimisation determining the complex mass transfer patterns.

In chapter 5, an application of the synthesis framework to an industrial methanol case study is presented, illustrating the ability of the approach to handle multicomponent nonideal systems. Finally, chapter 6 gives some concluding remarks and directions for future work.

The Mass/Heat Transfer Framework

2.1 Introduction

Popular approaches for the synthesis of entire flowsheets are governed by an implicit assignment of processing tasks to processing equipment, whereby a set of unit operations are prepostulated within a superstructure realisation of synthesis alternatives. The problem is thus reduced to one of determining interconnections between given alternatives. As a consequence, derived flowsheets are often limited by typical flow patterns, following the traditional hierarchical design guidelines. Hybrid process units and non-conventional process structures, that are recently proven favourable in industry, are only studied when explicitly prepostulated. Recent work by Papalexandri (1995) attempts to overcome these limitations through the development of a general process synthesis framework based on a mass and heat exchanger representation. The basic premise of the proposed framework is that all unit operations can be characterised as sets of operations involving heat and mass transfer. As a consequence, a network of mass and heat exchangers may be used to represent any chemical process without the prepostulation of specific unit operations. This framework is adopted and developed in this thesis, and in the following chapter the basic concepts and the developments made to encompass the class of synthesis problems addressed in the later chapters are presented.

2.2 The Mass/Heat Transfer Module

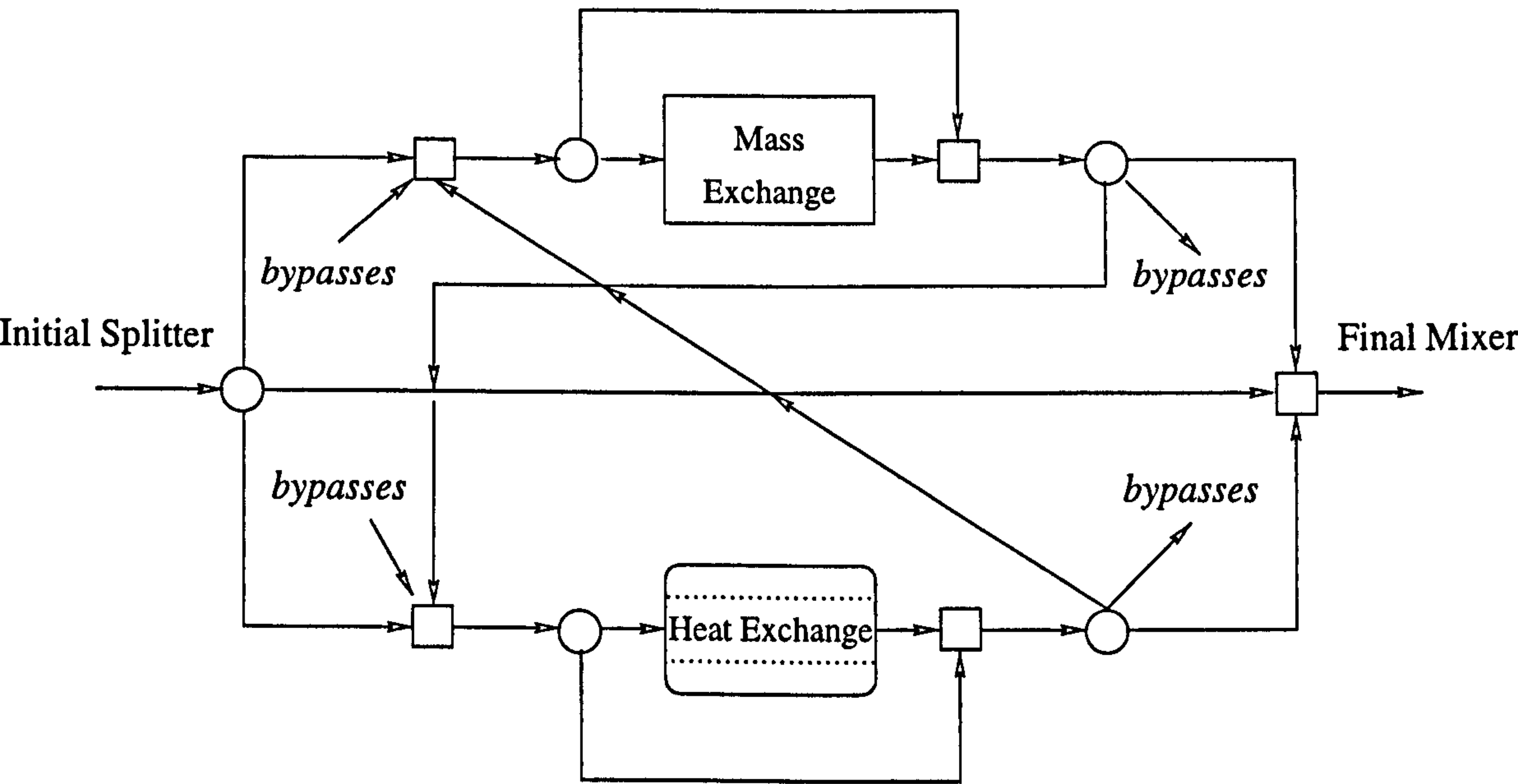
Broadly speaking, a process operation can be generally characterised by a set of mass and heat transfer phenomena, concerning mainly the mass transfer of a component from one substance or phase to another due to a difference in chemical potential. For example,

- in a reboiler, heat is transferred from the hot utility stream to the cold process stream
- in distillation, mass and heat are transferred between the contacting liquid and vapour phases of a mixture on a tray
- in a reactor, a generated component can be visualised as mass transfer of a species from a reactant stream to the product stream

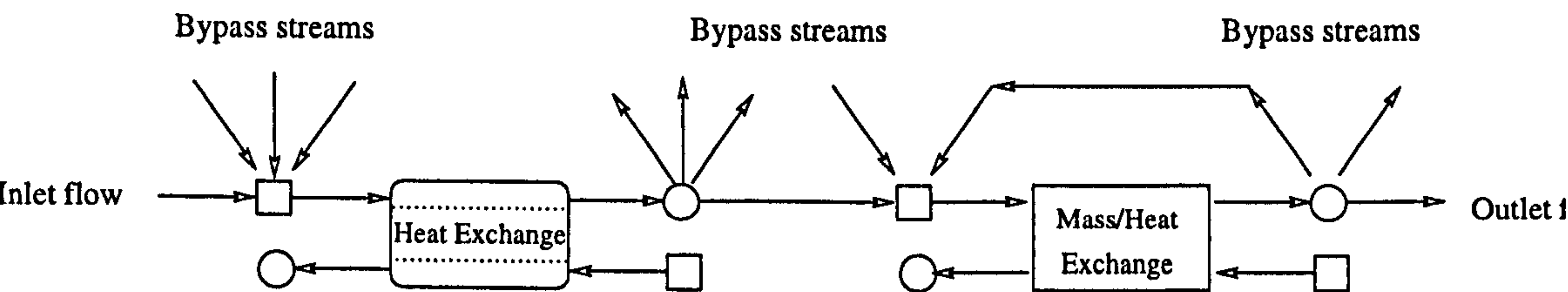
In order to capture mass and heat transfer phenomena in chemical processes, a mass and heat transfer module is proposed to form the basic building block of a network superstructure of process alternatives. Initially, the module was constructed from a heat exchanger and *pure* mass exchanger as shown in Figure 2.1(a) (Papalexandri and Pistikopoulos, 1994). However, as mass transfer can never occur without heat transfer, the two-exchanger module was modified to that shown in Figure 2.1(b) (Papalexandri and Pistikopoulos, 1995); a mass-and-heat exchanger whereby mass (and heat) transfer takes place between the exchanger defining streams, and a pure heat exchanger where matching streams only exchange heat and do not come into “mass active” contact. Side mixers and splitters are assigned to each mass/heat and pure heat exchanger, and block superstructure rules are applied allowing for all possible interconnections between exchangers.

2.3 Mass/Heat Transfer Representation Framework Concepts

Process operations are viewed as sets of heat and mass transfer between properly defined streams, and process units can be realised by sets of properly connected mass and heat exchange blocks (Papalexandri and Pistikopoulos, 1996). The streams appearing in process operations to participate in mass/heat transfer are defined by their phase (vapour, liquid, utility, organic, *etc.*) and chemical potential/composition (pure component, component mixture, mixture rich in a certain component, *etc.*). In general, a mixed stream containing all possible system components is considered. For example, in the distillation of a binary mixture of components AB where A is more volatile than B , streams participating in



(a) Mass Heat Transfer Module



Key

○ *Splitter*

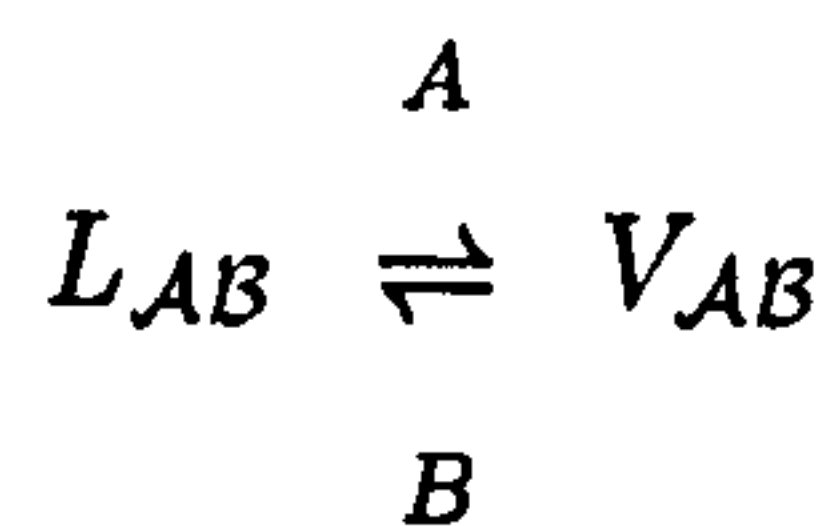
□ *Mixer*

(b) Mass Heat Transfer Module

Figure 2.1: Mass/ Heat Exchanger Module

the corresponding mass and heat transfer phenomena are a liquid and a vapour stream containing both components, denoted by L_{AB} and V_{AB} .

The mass and heat transfer in process operations take place between streams of different potential, which can be realised between different phases due to volatility differences, or when reactions take place (chemical potential). Mass/heat transfer stream matches are thus considered between streams of different phases and between reagent/product streams when reactions are possible. For example, in the distillation of a binary mixture AB , the more volatile component A is transferred from the liquid to the vapour and the heavier component B from the vapour to the liquid. Mass/heat transfer is thus realised between the liquid and vapour streams, which we denote as



In general possible mass transfer directions for each component in a multicomponent mixture define more than one mass exchange pattern, therefore multiple matches corresponding to multiple mass/heat exchange modules are considered.

Based on the definitions of streams and stream matches, a superstructure is constructed from the mass/heat transfer modules once the maximum number of matches of each type allowed is specified (for example, one may specify that at most three $L_{AB} - V_{AB}$ matches are permitted). An initial splitter is considered for each initial (feed) stream and a final mixer for each possible existing, intermediate and final stream. A full connectivity network is then developed between the initial splitters, final mixers, and the exchanger splitters and mixers.

No phase change is allowed at the mixers prior to each exchanger side and at the final mixers, therefore only stream flows of the same phase are merged. This assumption implies that no flash operations take place at mixers, and can only occur in the adjacent mass/heat exchanger block. In general phase properties cannot take values beyond the phase critical property values, therefore phase defining constraints are enforced. When the exchanging streams are of liquid or vapour phase, the inlet stream temperature is at most the mixture boiling point or at least the mixture dew point.

The mass/heat exchange superstructure is mainly described by mass and energy balances and constraints to ensure the existence of a driving force for mass and heat exchange. In particular the model requires the following constraints;

- **Stream Splitters** at the superstructure inlet of each initial stream and the outlet of each exchanger side are described by total stream flow mass balances.
- **Stream Mixers** at the inlet of each exchanger side and at the superstructure outlet of each product stream are described by total and component mass balances, energy balances and phase defining constraints.
- **Mass/Heat Exchangers** are described by component mass balances, energy balances, phase defining constraints and driving force constraints to ensure feasible mass transfer between exchanging streams. The driving force constraints for mass transfer is a function of stream component concentration and temperature, accounting for reaction and/or phase change phenomena.
- **Pure Heat Exchangers** are described by energy balances, phase defining constraints and driving force constraints for heat transfer. Feasible heat transfer is ensured by a minimum positive difference between the hot and cold streams at the inlet and outlet of the exchangers.

2.4 Representation Example

Based on the generalised network superstructure, process units can result as combinations of heat and mass transfer blocks. Revisit the separation of binary mixture $\mathcal{AB}$ in a distillation column into two liquid products, one of high purity $\mathcal{A}$ and the other of high purity $\mathcal{B}$, where $\mathcal{A}$ is more volatile than $\mathcal{B}$.

A distillation column for the separation may be realised by two mass/heat exchangers and two pure heat exchangers interconnected as shown in Figure 2.2. The top mass/heat exchanger $L_{\mathcal{AB}} - V_{\mathcal{AB}}$ corresponds to the rectifying section where the lean vapour stream is enriched in the more volatile component $\mathcal{A}$, to give a top product of high purity $\mathcal{A}$, which is represented by stream $L_{\mathcal{AB}}$ with $x_{\mathcal{A}} \approx 1, x_{\mathcal{B}} \approx 0$. The bottom exchanger $L_{\mathcal{AB}} - V_{\mathcal{AB}}$ corresponds to the stripping section, where the liquid stream is enriched in the heavier component $\mathcal{B}$, to give a bottom product of high purity $\mathcal{B}$, represented by stream $L_{\mathcal{AB}}$ with $x_{\mathcal{A}} \approx 0, x_{\mathcal{B}} \approx 1$. In both mass/heat exchangers, $\mathcal{A}$ is transferred from the liquid to the vapour stream, and $\mathcal{B}$ from the vapour to the liquid stream

The total condenser is realised as a pure heat exchange block between an inlet vapour stream and a cooling utility $V_{\mathcal{A}(\mathcal{B})} - U_{cold}$, whereby thermodynamic constraints ensure the inlet stream is of a vapour phase which is cooled to a liquid outlet stream. Similarly a reboiler is realised as heat exchange between a hot utility stream and an inlet liquid phase stream $U_{hot} - V_{(\mathcal{A})\mathcal{B}}$, whereby the inlet liquid stream is heated to a vapour stream.

2.5 The Rich and Lean Concept

Motivated by applications in waste recovery systems, El-Halwagi and Manousiouthakis (1989, 1990a, 1990b) introduced the concept of mass exchange networks (MEN) as a means of synthesising separation networks employing mass-separating agents. Given a number of *rich* process streams (undesirable wastes) and *lean* streams (process or auxiliary streams), and specifications on their compositions, the synthesis problem involves determination of an optimum MEN (stream matches and network topology) with respect to economics. Mass transfer from a set of rich streams to a set of lean streams is seen to be analogous to heat transfer from a set of hot streams to a set of cold streams. When concentration targets are specified for single components, analogies are thus drawn with the heat exchange network problem in terms of pinch point (El-Halwagi and Manousiouthakis, 1989) to ensure thermodynamically feasible mass exchange, and the MILP transshipment problem (El-Halwagi and Manousiouthakis, 1990) to determine the minimum number of mass transfer units.

Adopting the MEN terminology, the mass and heat transfer synthesis framework of Papalexandri (1995) is based upon the fundamental concept of ‘*rich*’ and ‘*lean*’ streams. Distinguishing a component of interest, exchanging streams in process operations are termed as ‘*rich*’ and ‘*lean*’, whereby the concentration of the component decreases in the former (*rich* and therefore able to give away), and increases in the latter (*lean* and thus able to accept component). Based on this definition, this terminology serves two main functions;

1. In the construction of the stream superset, the term is used to give a quantitative indication of the stream composition. *i.e.* $L_{A(B)}$ is described as a liquid stream *rich* in A , meaning containing mostly A .
2. To define the mass transfer direction of a component, which must be postulated. *i.e.* in the match $L_{A(B)} - V_{A(B)}$ where A is the component of interest transferred from the liquid to the vapour stream, the liquid is termed as the *rich* stream and the vapour the *lean* stream. Both streams are considered, however, as being *rich* in A !

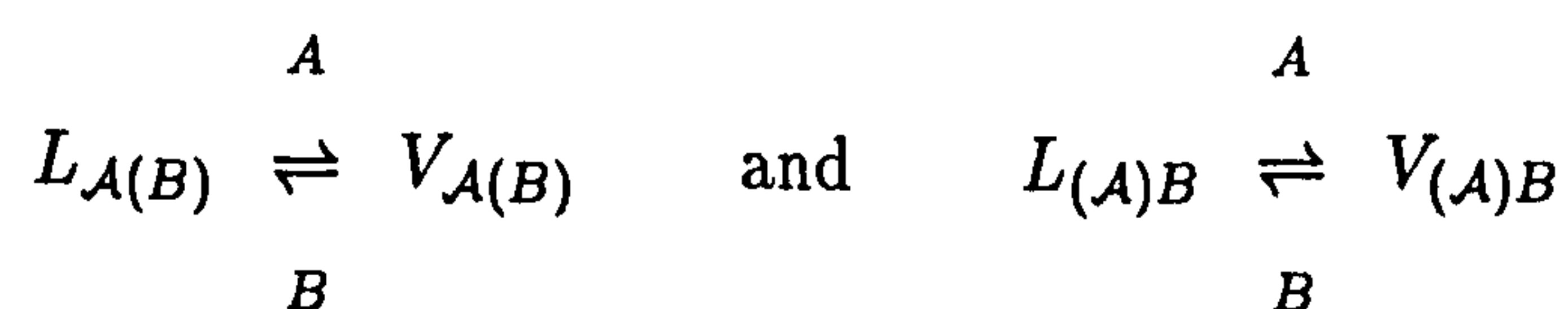
In this work, we find that labelling streams to give a quantitative indication of their composition is not necessary, and in fact complicates the framework and its extension to general multicomponent nonideal systems. As discussed in the previous section, considering general mixed streams in all possible phases is sufficient, with the final composition of the stream determining its contents.

Revisit the separation of binary mixture $\mathcal{AB}$, where $\mathcal{A}$ is more volatile than $\mathcal{B}$. Within the rich and lean terminology, streams participating in the corresponding mass and heat transfer phenomena are a liquid and a vapour stream rich in $\mathcal{A}$, and a liquid and vapour stream rich in $\mathcal{B}$. Disregarding pure heat exchange possibilities, the following four stream types are possible

- i) $V_{\mathcal{A}(\mathcal{B})}$ vapour stream rich in $\mathcal{A}$, lean in $\mathcal{B}$
- ii) $V_{(\mathcal{A})\mathcal{B}}$ vapour stream lean in $\mathcal{A}$, rich in $\mathcal{B}$
- iii) $L_{\mathcal{A}(\mathcal{B})}$ liquid stream rich in $\mathcal{A}$, lean in $\mathcal{B}$
- iv) $L_{(\mathcal{A})\mathcal{B}}$ liquid stream lean in $\mathcal{A}$, rich in $\mathcal{B}$

In theory, any stream of any type may exchange mass with any other stream, requiring $\binom{4}{2} = 6$ mass/heat transfer modules to allow for all potential stream transfers. Furthermore, if the order of volatility is not known, 2 of each type of match must be considered to account for each mass transfer direction, requiring a minimum of 12 mass/heat transfer modules. For the separation synthesis of a general n component mixture, the total number of stream types $\mathcal{S}$ possible is $\mathcal{S} = 2 \sum_{i=1}^{n-1} \binom{n}{i}$, with a total number of $\binom{\mathcal{S}}{2}$ matches required before any preprocessing. In general complex mixtures, the order of volatility can depend on the relative amounts of species in the streams. Thus the minimum number of mass/heat exchangers required to consider all mass/heat transfer possibilities is given by $n! \binom{\mathcal{S}}{2}$. In addition the pure heat transfer possibilities must be considered. It is plain to see that the combinatorial complexity of the problem could be considerable for general multicomponent chemical processes where multiple matches must be considered.

In practise, engineering knowledge is utilised to restrict the set of allowable matches and for homogeneous mixtures with no reaction, only liquid-vapour matches are required. For the small separation example discussed, knowing $\mathcal{A}$ to be the most volatile component, mass/heat transfer is realised between the liquid and vapour streams rich in $\mathcal{A}$, and the liquid and vapour streams rich in $\mathcal{B}$. Stream matches are thus restricted to



Note that in both these matches the concentration of $\mathcal{A}$ in the liquid stream is reduced, thus in terms of this component, the liquid streams act as the “rich” sides in mass transfer, whereas the vapour streams act as the “lean” sides.

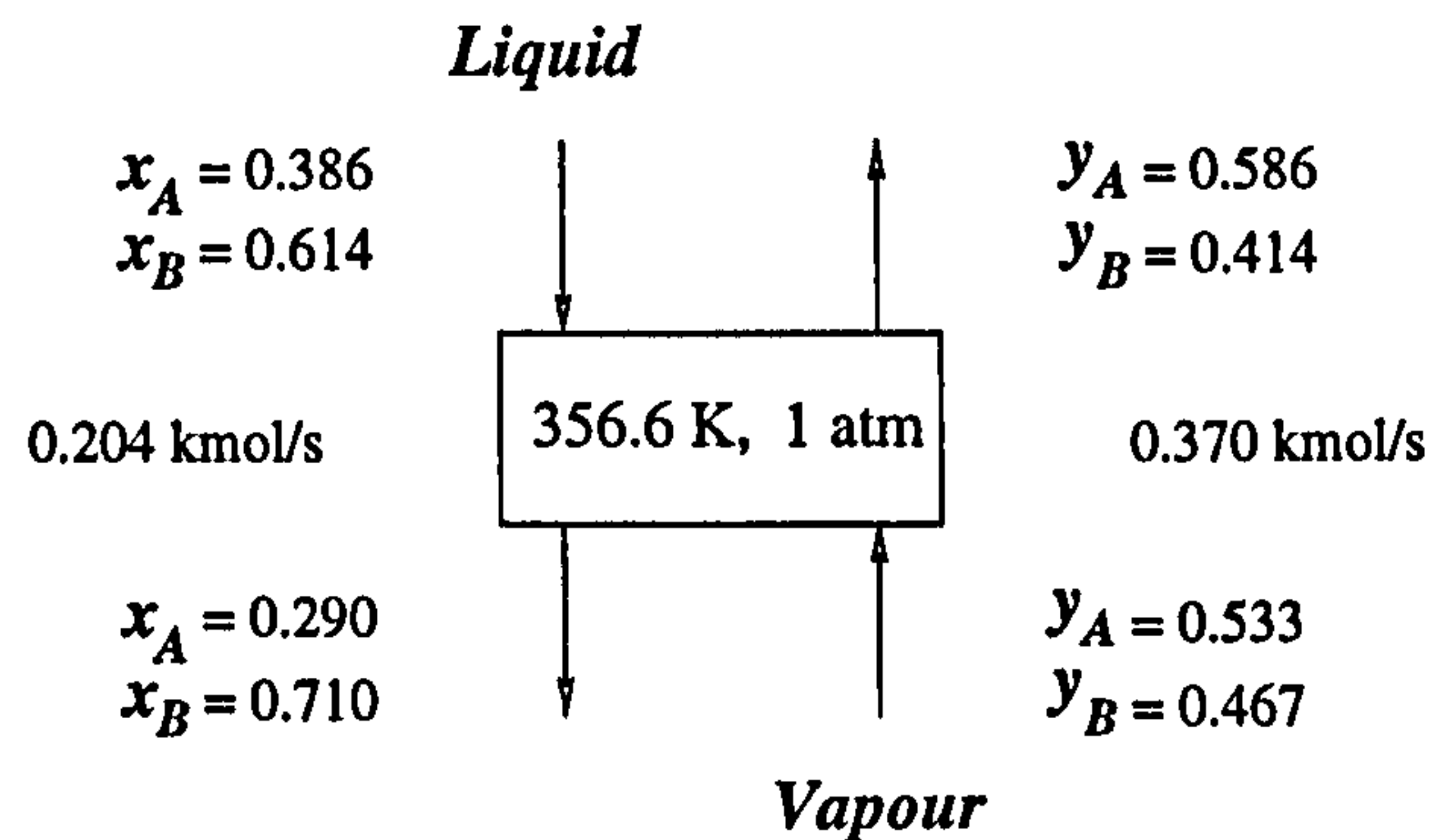


Figure 2.3: A Tray in the separation of Methanol and 1-Propanol

Consider at this point a tray in the rectifying section of a column separating an ideal mixture of Methanol A and 1-Propanol B shown in Figure 2.3. The more volatile component methanol is transferred to the vapour phase, whilst the propanol is transferred to the liquid phase. Through observation, one would say that the liquid stream contains mainly B and the vapour stream mainly A , thus labelling such a match as $L_{(A)B} - V_{A(B)}$. This match would not be implicitly considered according to Papalexandri and Pistikopoulos (1996) and in this simple example, the actual mass transfer phenomena are not actually lost but are captured through the other matches (for all the liquid vapour matches A is transferred to the vapour and B to the liquid). However, this is not necessarily the case for more complex, nonideal systems. Considering *a general mixed stream containing all components concerned in all possible phases* allows for easier formalisation of the identification of streams and possible stream matches for complex multicomponent systems.

For a n component system, $n!$ mass transfer directions are possible, and to account for these possibilities, in general $n!$ multiples of each stream match type are necessary. Feasible mass transfer between rich and lean streams has been ensured through driving force constraints based on the limiting case of equilibrium.

For mass transfer of component i from the rich to the lean stream

$$x_{lean,i} \leq x_{lean,i}^* \text{ where } x_{lean,i}^* = f(x_{rich,i})$$

For mass transfer of component i from the lean to the rich stream

$$x_{rich,i} \leq x_{rich,i}^* \text{ where } x_{rich,i}^* = f(x_{lean,i})$$

where x_i is the molar fraction of the stream, and x_i^* the equilibrium molar fraction of the stream which is a function of its exchanging stream.

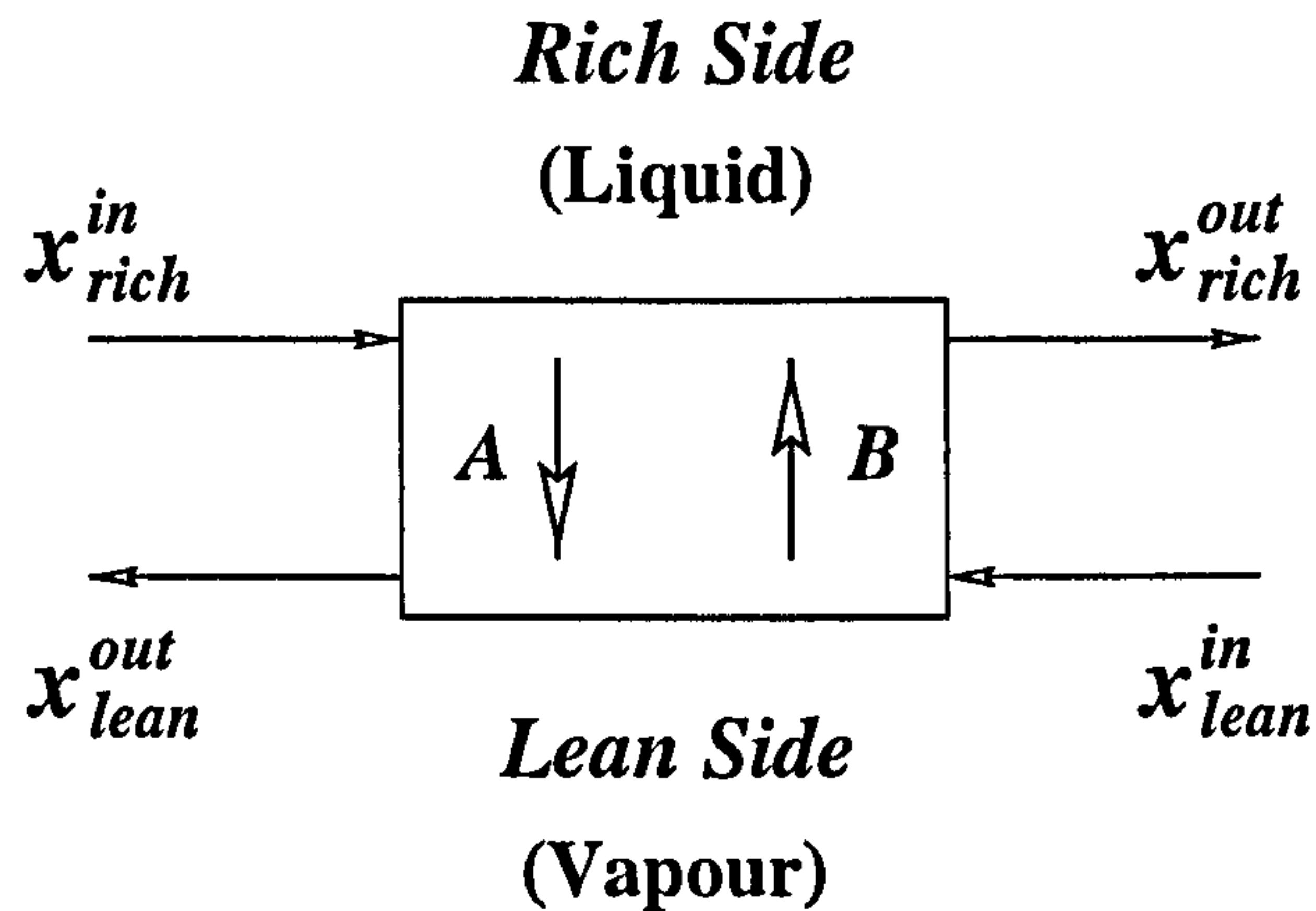


Figure 2.4: A Liquid-Vapour Match using the ‘rich’ and ‘lean’ terminology

For pure separation liquid-vapour matches, the equilibrium molar fraction is a phase equilibrium relation. To illustrate, consider a liquid-vapour match $L_{AB} - V_{AB}$ where A is the more volatile component, L is the rich stream and V the lean stream (see Figure 2.4). Postulating the mass transfer of A from the liquid to vapour and B from the vapour to the liquid, the following driving force constraints are enforced at each end of the mass/heat exchanger to ensure feasible mass transfer

$$x_{lean,A}^{out} \leq K_{rich,A}^{in} x_{rich,A}^{in} \quad (2.1)$$

$$x_{lean,A}^{in} \leq K_{rich,A}^{out} x_{rich,A}^{out} \quad (2.2)$$

$$x_{lean,B}^{out} \geq K_{rich,B}^{in} x_{rich,B}^{in} \quad (2.3)$$

$$x_{lean,B}^{in} \geq K_{rich,B}^{out} x_{rich,B}^{out} \quad (2.4)$$

A number of comments can be made;

- These constraints have been applied only to ideal systems, where the equilibrium constant K_i is a function of temperature. In general however, the equilibrium relation between a liquid and a vapour stream is a function of composition and temperature. Implementation of the constraint for nonideal separation systems as it stands is not valid.
- In the work of Papalexandri (1995), driving force constraints are enforced on ‘components of interest’ which must be identified. Usually the lightest and the heaviest components are selected, but even in ternary systems, this may not be sufficient for the intermediate component as will be shown in the next chapter. To utilise these

constraints, all possible mass transfer directions must be postulated and accounted for. For large multicomponent complex systems where prescreening is not possible, this indicates that a large number of mass/heat exchangers must be considered, exploding the combinatorial complexity of the already large MINLP problem.

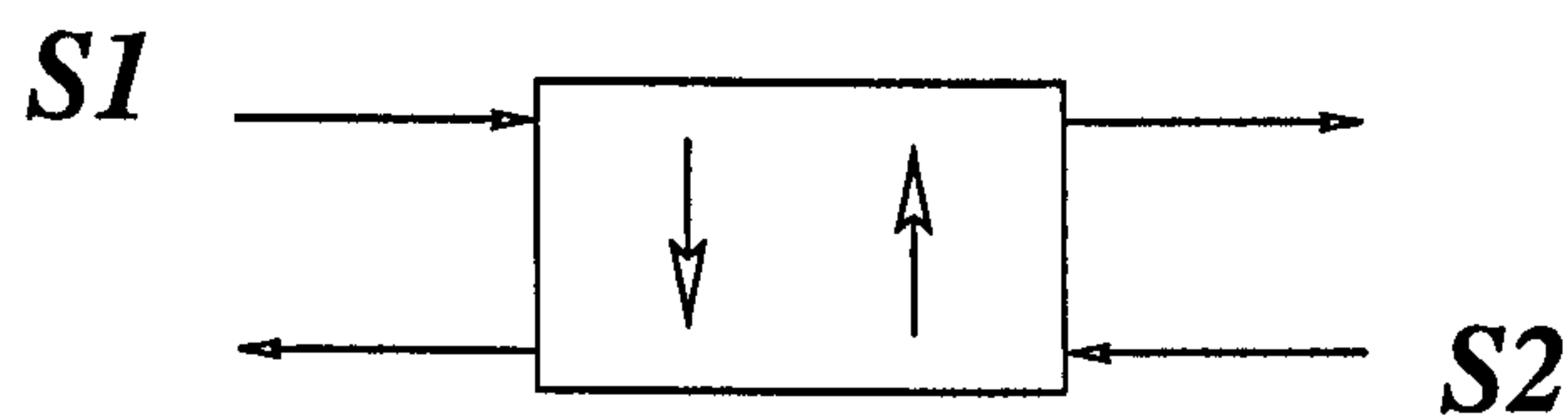
- No fundamental theory has been put forward for these constraints and therefore their extension to general nonideal reactive/separation systems is not possible. For example, what happens when both reaction and separation occurs within the module?

For these reasons, a more generic form of the driving force constraints is proposed, forming the heart of the synthesis framework proposed in this thesis. Derived from fundamental thermodynamic relations and presented in a compact mathematical form, the developed driving force constraints remove the need to define rich and lean streams and the prepostulation of mass transfer directions.

2.6 Driving Force Constraints

Within a mass/heat transfer module, mass transfer will take place between two participating streams of differing *potential*; that is, when two streams of different phase are not at equilibrium, and between reagent/product streams when reactions are possible. To ensure feasible mass transfer between streams, a set of constraints based on Gibbs free energy are imposed, the form of which is dependent on the type of stream match and phenomena taking place.

Consider a $S1 - S2$ mass/heat exchange block for a multicomponent system where in general, mass transfer between the streams can occur due to separation and reactive phenomena.



At constant temperature and pressure (taking the module to be a closed system) mass transfer will occur when the total Gibbs free energy $(nG)^{tot}$ of the system decreases, *i.e.*

$$d(nG)_{T,P}^{tot} \leq 0 \quad (2.5)$$

When the molar holdup of component i in one stream, say $S1$, in the system decreases ($dn_i^{S1} \leq 0$), either due to consumption in reaction and/or mass transfer from $S1$ to $S2$,

$$F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} x_{out,i}^{S1} \geq 0 \quad (2.6)$$

It follows from (2.5) that

$$\left[\frac{\partial (nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P} \geq 0 \quad (2.7)$$

When the molar holdup of the component i in stream $S1$ of the module is increased *i.e.* $dn_i^{S1} \geq 0$, it is trivial to see that the sign of the inequalities in equations (2.6) and (2.7) are reversed. Based on this, we propose the conjecture that in general, mass transfer within the module due to separation and/or reaction is consistently limited by (see Addendum at the end of this thesis)

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad \forall i = 1, \dots, C \quad (2.8)$$

where we define

$$\mathcal{G}1_i = F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} x_{out,i}^{S1} \quad (2.9)$$

$$\mathcal{G}2_i = \left[\frac{\partial (nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P} \quad (2.10)$$

The form of the constraint on the mass/heat transfer module is dependent on the type and phase of streams participating and the phenomena taking place. The constraints for liquid-vapour and liquid-liquid matches, with and without reaction, are derived in the following chapters. Since the fundamental basis of the constraints is generalised, however, in theory it can be extended to encompass any thermophysical phenomena.

An important feature of these constraints is that the mass transfer direction need not be postulated, and is instead determined and optimised to meet the synthesis objectives required. Through the use of detailed thermodynamic models, nonideal behaviour can thus be properly captured. The bilinear terms of the driving force constraints in equation (2.8) can be recasted in a linear form by the introduction of binary variables denoting the mass transfer direction of each component in the mass/heat transfer module.

2.7 Phase Defining Constraints

The streams participating in mass/heat transfer are of *postulated* phases, characterised by their molar composition, temperature and pressure. Phase defining constraints are enforced to ensure the stream conditions do not violate the phase critical property values.

For liquid phase, the stream conditions are constrained by the *bubble point* i.e. for a given pressure and composition, the temperature of the stream must be equal to or lower than the bubble point temperature. Consider a multicomponent liquid stream of molar composition x_i^L , temperature T^L and total pressure P^L , which has some vapour composition associated with it y_i^* . There are $5C+2$ variables associated with this stream:

$$x_i^L, y_i^*, P_{sat,i}^L, \gamma_i^L, \phi_i^L, T^L, P^L$$

And in general we have $4C+1$ equations

$$\gamma_i^L = \gamma_i(x_i^L, y_i^*, T^L, P^L)$$

$$\begin{aligned}
\phi_i^L &= \phi_i(x_i^L, y_i^*, T^L, P^L) \\
Psat_i^L &= Psat_i(T^L) \\
y_i^* &= \frac{\gamma_i^L Psat_i^L}{\phi_i^L P^L} x_i^L \\
\sum_i^C x_i^L &= 1
\end{aligned}$$

At equilibrium conditions,

$$\sum_i^C y_i^* = 1$$

Thus giving C degrees of freedom (*i.e.* specifying $C-1$ compositions x_i^L and P^L will determine the bubble point temperature T^L).

The temperature is thus constrained by

$$\sum_i^C y_i^* \leq 1$$

which can be rewritten as

$$\sum_i^C \frac{\gamma_i^L Psat_i^L}{\phi_i^L P^L} x_i^L \leq 1 \quad (2.11)$$

The condition of the vapour phase is constrained by the *dew point i.e.* for a given pressure and vapour composition, the temperature must be equal or greater than the dew point temperature. Similarly to the liquid phase, the vapour stream is characterised by x_i^V, T^V, P^V and it has some liquid composition associated with it x_i^* . Again we have $5C+2$ variables

$$x_i^V, x_i^*, Psat_i^V, \gamma_i^V, \phi_i^V, T^V, P^V$$

And $4C+1$ equations

$$\begin{aligned}
\gamma_i^V &= \gamma_i(x_i^V, x_i^*, T^V, P^V) \\
\phi_i^V &= \phi_i(x_i^V, x_i^*, T^V, P^V) \\
Psat_i^V &= Psat_i(T^V) \\
x_i^V &= \frac{\gamma_i^V Psat_i^V}{\phi_i^V P^V} x_i^*
\end{aligned}$$

$$\sum_i^C x_i^V = 1$$

The dew point is characterised by the case of equilibrium

$$\sum_i^C x_i^* = 1$$

Such that specifying C-1 compositions x_i^V and P^V will determine the dew point temperature T^V .

For the modular representation, we define the vapour phase by constraining its conditions to that of the dew point

$$\sum_i^C x_i^* \leq 1$$

or alternatively

$$\sum_i^C \frac{\phi_i^V P^V}{\gamma_i^V P_{sat_i}^V} x_i^V \leq 1 \quad (2.12)$$

For ideal mixtures, the phase defining constraints (2.11) and (2.12) reduce to a function of the stream temperature and composition only and are thus easy to utilise.

To define the liquid phase

$$\sum_i^C \frac{P_{sat_i}(T^L)}{P^L} x_i^L \leq 1$$

To define the vapour phase

$$\sum_i^C \frac{P^V}{P_{sat_i}(T^V)} x_i^V \leq 1$$

For nonideal mixtures, the calculation becomes more complex as in addition to the module balances and driving force constraints, ‘phase equilibrium’ calculations are indirectly required for the accurate determination of γ_i and ϕ_i .

In the bulk of this thesis, low pressure systems with nonideality in the liquid phase only are considered, such that $\phi_i = 1$. Consider a module with a liquid - vapour match.

In the liquid phase, $\gamma_i = f(x_i^L, T^L)$, which is easily incorporated as the variables are local to the stream. In the vapour phase however, $\gamma_i = f(x_i^*, T^V)$ which requires a phase equilibrium calculation to determine x_i^* . In an attempt to simplify this calculation the following approximations are considered

- The liquid activity coefficient calculated at the vapour composition

$$\gamma_i(x_i^*, T^V) \approx f(x_i^V, T^V)$$

- The liquid activity coefficient calculated at the liquid composition of the *adjacent* liquid stream.

$$\gamma_i(x_i^*, T^V) \approx f(x_i^{adj}, T^V)$$

The first approximation is not suitable, resulting in violation of the phase definition. The second approximation becomes an equality when the adjacent liquid stream is in equilibrium with the vapour stream; since generally the two adjacent streams are never too far from equilibrium, this approximation has proved to be adequate for the multicomponent systems that we have considered, and is currently utilised for the vapour stream in a liquid vapour match.

Note that this does not apply for the vapour streams around the heat exchangers *i.e.* vapour inlet to a cooler and vapour outlet from a heater. Streams through heat exchangers that consider total phase change have the same composition in and out, and thus here we use this composition to calculate the activity coefficient in both the liquid and vapour stream.

On their own, equations (2.11) and (2.12) are very loose and allow for a high level of superheating and supercooling. For most processes this is not desirable or physically feasible and a lower bound is imposed.

$$\sum_i^C \frac{\gamma_i^L P_{sat_i}^L}{\phi_i^L P^L} x_i^L \geq \mathcal{LB} \quad (2.13)$$

$$\sum_i^C \frac{\phi_i^V P^V}{\gamma_i^V P_{sat_i}^V} x_i^V \geq \mathcal{LB} \quad (2.14)$$

2.8 Synthesis Framework

Given the inlet streams (flowrate, temperature, composition), desired product specifications (flowrate, temperature, composition), available utility streams with their corresponding constraints, property and cost data and knowledge of the available technology to produce the desired products, the synthesis objective is to obtain an optimal process flowsheet, usually with respect to economics. The synthesis framework to meet this aim involves the following features (Figure 2.5):

- **Stream Superset**

A stream superset is constructed, including all initial and desired streams, as well as any intermediate streams that may result based on knowledge of physical properties and technologies used. A general mixture stream containing all possible components in all possible phases is considered.

- **Stream matches**

Having defined process streams, all possible mass/heat transfer matches are considered, defining the mass and heat transfer blocks in the superstructure. Since mass/heat transfer between streams may be realised in more than one way, multiple blocks are often considered for each stream match. Engineering knowledge may be employed at this stage to fathom out redundant stream matches and reduce problem dimensionality. Note that this should not imply any bias towards the final solution, but rather screen out any physically undesirable interconnections for the system.

- **Mass/heat exchange network superstructure**

Considering all the possible interconnections between stream splitters and mixers, again using engineering knowledge to disregard illogical connections, a mass/heat exchange network superstructure of process alternatives is developed.

- **Superstructure Model**

The mass/heat exchange network superstructure model is formulated as a mixed integer nonlinear programming problem (MINLP) involving

- *Total mass balances* at all splitters and mixers of the superstructure
- *Component mass balances* at all mixers and around the mass/heat and pure heat exchangers
- *Energy balances* at all mixers and around the mass/heat and pure heat exchangers. Negligible heat of mixing is assumed.
- *Phase Defining Constraints* for each superstructure stream

- *Heat transfer driving force constraints* at pure heat exchangers
 - *Mass transfer driving force constraints* at mass/heat exchangers
 - *Logical constraints* to account for the existence of modules, process constraints etc.
 - *Objective function* including the cost of raw materials, utilities and module cost as discussed in the next section.
- **Optimisation of mass/heat transfer superstructure.**

Conventional mixed integer nonlinear programming techniques may be employed for the resulting large scale optimisation problem. A nested MINLP decomposition strategy is developed for its solution as described in chapter 3. Optimisation is usually driven by the minimisation of the operating cost, corresponding to raw materials and utility consumption, and a pseudo - capital cost as discussed in the next section.

2.9 Capital Costing

As process units are not prepostulated, costing correlations such as Guthrie's cannot be directly applied. In the work of Papalexandri and Pistikopoulos (1996), a two step decomposition approach is proposed to cost a network of mass/heat transfer units without knowing the actual unit operations that they represent. In the first stage of the solution approach, the capital costs are ignored and the synthesis task is driven by the minimisation of the flowsheet operating and raw material costs. The resulting optimal network of modules is then inspected and the functionality of groups of modules are mapped onto actual units, *e.g.* modules as interconnected in Figure 2.2 are identified as a distillation column. Cost correlations are generated for these unit operations and the flowsheet is then re-optimised for this fixed set of process units, this time accounting for the capital costs of the flowsheet in the objective function. There is no evidence that this procedure will not eliminate a better flowsheet in the first stage where a higher operating cost may be offset by a lower capital cost, a feature which may lead to suboptimal solutions. An iterative bounding procedure could alleviate such problems.

A potential problem with this framework is that the derivation of an equivalent process flowsheet from the resulting network of mass/heat transfer blocks by looking for standard configurations is often not trivial.

The decomposition approach is not adopted, and instead a more direct method of accounting for the cost of each mass/heat transfer block is utilised. The cost of each block is based on its size and capacity, in order to obtain an order of magnitude estimate. In

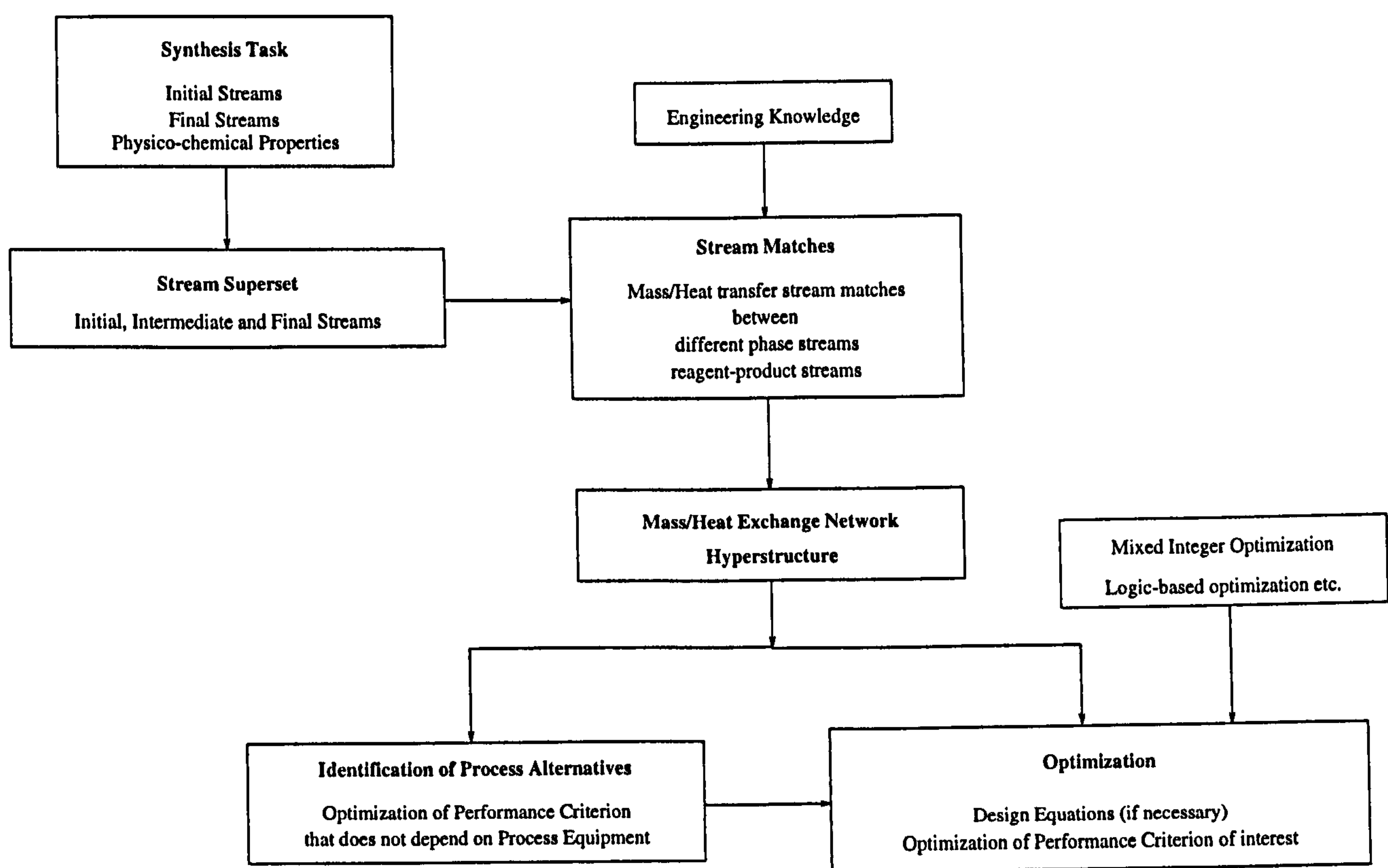


Figure 2.5: Synthesis Framework (Papalexandri and Pistikopoulos, 1996)

particular two types of mass/heat transfer modules are of interest, liquid - vapour and liquid - liquid matches.

- Liquid - Vapour Matches

A liquid-vapour match with inlet and outlet flows is essentially a separator. The cost of such a module is proportional to the vapour flowrate through it, the amount of separation involved, and the molar holdup.

- Liquid - Liquid Matches

A liquid-liquid match with one inlet and outlet with reaction is part of or a whole reactor. The cost of the module is proportional to the volume of the liquid holdup and/or volume of the catalyst if present. A liquid-liquid match with two inlets and outlets would be a separator, such as a liquid extractor. In this case the cost would be proportional to the liquid flowrate and the level of separation.

To derive cost correlations that capture the relative cost contributions of the module features, Guthrie's costing correlation for a pressure vessel is utilised as a base, where

$$\text{Installed Cost, \$} = \left(\frac{M\&S}{280} \right) 101.9 D^{1.066} H^{0.802} (2.18 + F_c) \quad (2.15)$$

where D = diameter in ft

H = height in ft

$F_c = F_m F_p$, function of shell material

2.9.1 Liquid-Vapour Module

Estimating liquid-vapour mass/exchanging modules as part of or a column, the diameter can be calculated by allowing the vapour velocity to be 80% of the flooding velocity. The flooding velocity can be calculated from the Francis Weir hydraulics equations (Coulson, 1990), or more simply it can be approximated by (Douglas, 1985)

$$v_{flood} \sqrt{\rho_{g,m}} = \text{constant} = 1.5 \quad (2.16)$$

where v_{flood} is in ft/s and $\rho_{g,m}$ is the vapour density in lb/ft^3 . This assumes a tower with 2-ft tray spacing and constant liquid density for all species. The cross sectional area of the unit is calculated by

$$A = \frac{\pi D^2}{4} = \frac{\text{Vapour volumetric flowrate}}{\text{Vapour velocity}} \quad (2.17)$$

The vapour volumetric flowrate is calculated from the division of the vapour molar flowrate by the vapour molar density. Taking the vapour velocity to be 80 % of the flooding velocity and allowing for 12% of the separator area to be taken up by internals, equation (2.17) can be rearranged to give

$$D = 0.2734 \left(\frac{MW_v}{\rho_v} \right)^{0.25} F_v^{0.5} \quad (2.18)$$

where D is in *ft*, F_v is the vapour flowrate in *kmol/h*, ρ_v the vapour mixture density in *mol/m³* and MW_v the vapour mixture molar mass in *g/mol*. ρ_v is easily estimated assuming an ideal gas.

The height of a separation column for use in equation (2.15) is usually calculated from the number of trays, the tray spacing and the liquid holdup on the trays. For a liquid-vapour module, the equivalent height is thus a function of the amount of separation, or the amount of mass transfer taking place within the module, and the liquid holdup *i.e.*

$$H = H(\mathcal{G}1) + \frac{4V}{\pi D^2} \quad (2.19)$$

$H(\mathcal{G}1)$ for pure separation can be derived as a linear function of $\mathcal{G}1$ that is system dependent and may be estimated as follows. For a given separation synthesis system, a section of a typical distillation column (N trays) is simulated using a phase equilibrium model. The amount of mass transfer of each component taking place in the column section $\mathcal{G}1N$ is then calculated and a tray spacing of 2 ft is assumed. Using the most or least volatile component transferred within the column section, the function can then be simply determined by

$$H(\mathcal{G}1) = 2 \left(\frac{N}{\mathcal{G}1N} \right) \mathcal{G}1 \quad (2.20)$$

Using an $M\&S$ value of 1000, $F_c = 1$ (carbon steel for pressures up to 3.4 atm), and taking $1.066 \approx 1$, from equation (2.15) the cost of the liquid-vapour module can thus be approximated by

$$\text{Cost}_{L-V} (\$) = 316.435 \left(\frac{MW_v}{\rho_v} \right) F_v^{0.5} H^{0.802} \quad (2.21)$$

where H (*ft*) is determined from equations (2.19) and (2.18).

2.9.2 Liquid-Liquid Module

A liquid-liquid module with reaction and a single inlet and outlet is approximated as part of a reactor and is costed as a pressure vessel. The cost of the module is a function of the liquid holdup, *i.e.* its capacity, and using the cost correlation in 2.15 as a basis, some geometry must be assumed to calculate D and H . Assuming a cylindrical vessel with a height to diameter ratio of 6, the volumetric holdup of the module is given by

$$V = \frac{\pi D^2}{4} H = \frac{6\pi D^3}{4} \quad (2.22)$$

Rearranging for the diameter,

$$D = \left(\frac{2V}{3\pi} \right)^{1/3} \quad (2.23)$$

Note that

$$D^{1.066} H^{0.802} = 6^{0.802} D^{1.868} = 6^{0.802} \left(\frac{2V}{3\pi} \right)^{0.623} = 1.602 V^{0.623}$$

From equation (2.15), the cost of the liquid-liquid module is given by

$$\$ = \left(\frac{M\&S}{280} \right) 101.9(2.18 + F_c) 1.602 V^{0.623} \quad (2.24)$$

Using an $M\&S$ value of 1000 and $F_c = 1$, the expression is simplified to

$$\text{Cost}_{L-L} (\$) = 1854.88 V^{0.623} \quad (2.25)$$

where V is in ft^3 .

2.10 Summary

The mass/heat exchange module can be utilised as the building block of process flowsheets, involving separators, reactors, heat exchangers *etc.* Previous work on the mass/heat transfer representation framework assumed ideal mixtures, requiring postulation of component mass transfer direction. In this chapter, driving force constraints based on Gibbs free energy are introduced, able to model mass transfer within the module without prepostulation of transfer direction. Based on the thermophysical properties of the mixtures, mass transfer direction can be determined and optimised. Such a theoretical basis allows the

application of the mass/heat transfer framework representation to be extended to general nonideal reactive/separation mixtures, as presented in the following chapters.

Separation of Homogeneous Azeotropic Mixtures

3.1 Introduction

This chapter details the extension of the mass/heat transfer framework for the synthesis of azeotropic separation systems through the addition of an homogeneous entrainer. To discriminate between promising entrainers for the separation of a given binary azeotrope, current approaches utilise a two stage procedure. Initially, graphical constructions are utilised to identify feasible separation sequences for each entrainer. In a second step, the separation systems are then designed, optimised and costed to compare entrainers on a common ground. The method proposed in this work considers feasibility of separation through systematic characterisation of the mixture using detailed thermodynamic models which in principle accounts for the presence of ‘distillation boundaries’. The multipurpose mass/heat exchange module as introduced in section 2.2 is employed as a building block to explore separation units and structures. Sequencing alternatives are embedded within a superstructure of mass and heat exchanging blocks which is modelled as a mixed integer nonlinear programming problem. In one optimisation step, the sequencing of feasible separation train for a given entrainer can be accomplished. This lays down the foundation for the potential of entrainers to be compared in a single optimisation step resulting in an optimal separation scheme.

3.2 Issues in Homogeneous Azeotropic Separation

Interest in nonideal separations, especially azeotropic operations has grown at a tremendous rate in the past decade, generating a large number of publications in the subject. Research is motivated by the need for a systematic procedure for the synthesis of nonideal separation systems which are often used in the chemical industry. Advances in methodologies for the synthesis, analysis and design of azeotropic distillations have substantially benefited from studies in nonlinear analysis such as bifurcation theory to explain unusual nonlinear effects. Excellent reviews for azeotropic separations are given by Widagdo and Seider (1996), Westerberg and Wahnschafft (1996) and Biegler *et al.* (1997) (chapter 14). A common feature of such advances is the emphasis on separation feasibility within a sequential framework typically based on analysis of residue curve maps and distillation lines. Sequencing is limited by the separation feasibility region defined in the first stage of entrainer selection. An obvious limitation of such an approach is that there is no guarantee that the resulting separation design is in fact optimal.

In this section, the important findings that have given greater understanding in the behaviour of homogeneous azeotropic distillation will be briefly outlined, along with the prominent methodologies developed for entrainer selection, separation train sequencing and column design.

3.2.1 Residue Curve Maps and Distillation Lines

Researchers have focussed on properties of fixed points to provide insights concerning the operation of azeotropic columns, and the mathematical and geometrical analyses have utilised simple distillation residue curves and distillation lines. From the geometry of such maps, limitations due to the presence of the azeotrope can be revealed. Therefore, until recently, analysis has been focussed on ternary mixtures - that is, the separation of a binary azeotropic mixture through the addition of an entrainer which alters the relative volatility of the constituents without inducing liquid-liquid phase separation.

First introduced by Schreinemakers (1901), a residue curve map (RCM) is a triangular diagram with the pure components at the vertices, showing the variation of the liquid composition of a ternary mixture with time during a simple distillation process. The liquid composition profile is modelled by a set of non-linear ordinary differential equations (Doherty and Perkins, 1978a; Doherty and Perkins, 1978b; Doherty and Perkins, 1979)

$$\frac{dx_i}{d\xi} = x_i - y_i \quad (3.1)$$

$$i = 1, \dots, C - 1$$

where x_i : mole fraction of component i in liquid
 y_i : mole fraction of component i in vapour in equilibrium with liquid
 ξ : an independent variable, nonlinear and dimensionless measure of time, increasing monotonically with time and temperature.

Starting from various initial values of x_i , integration of this equation in the positive and negative direction of ξ will give the residue curve map trajectories at a given pressure P . y_i is a function of x_i and can be calculated at a pressure P using an equilibrium relationship.

Residue curves represent the liquid composition profiles of *packed* columns at total reflux. Distillation lines, however, represent the liquid composition profile of a *staged* column operated at total reflux. At total reflux in a continuous distillation column, the composition of the vapour rising from a tray and the liquid coming from the tray above are equal. In addition, the vapour and liquid on a theoretical tray are in equilibrium. Therefore the distillation line is a smooth trajectory of a number of equilibrium steps connecting the liquid composition on each tray (Stichlmair *et al.*, 1989).

The relationship between residue curves and distillation lines is illustrated in Figure 3.1. At any given composition x_i , the vector joining the liquid and equilibrium vapour ('equilibrium vector') is tangent to the residue curve through x_i and crosses the distillation line at the equilibrium vapour composition y_i^* .

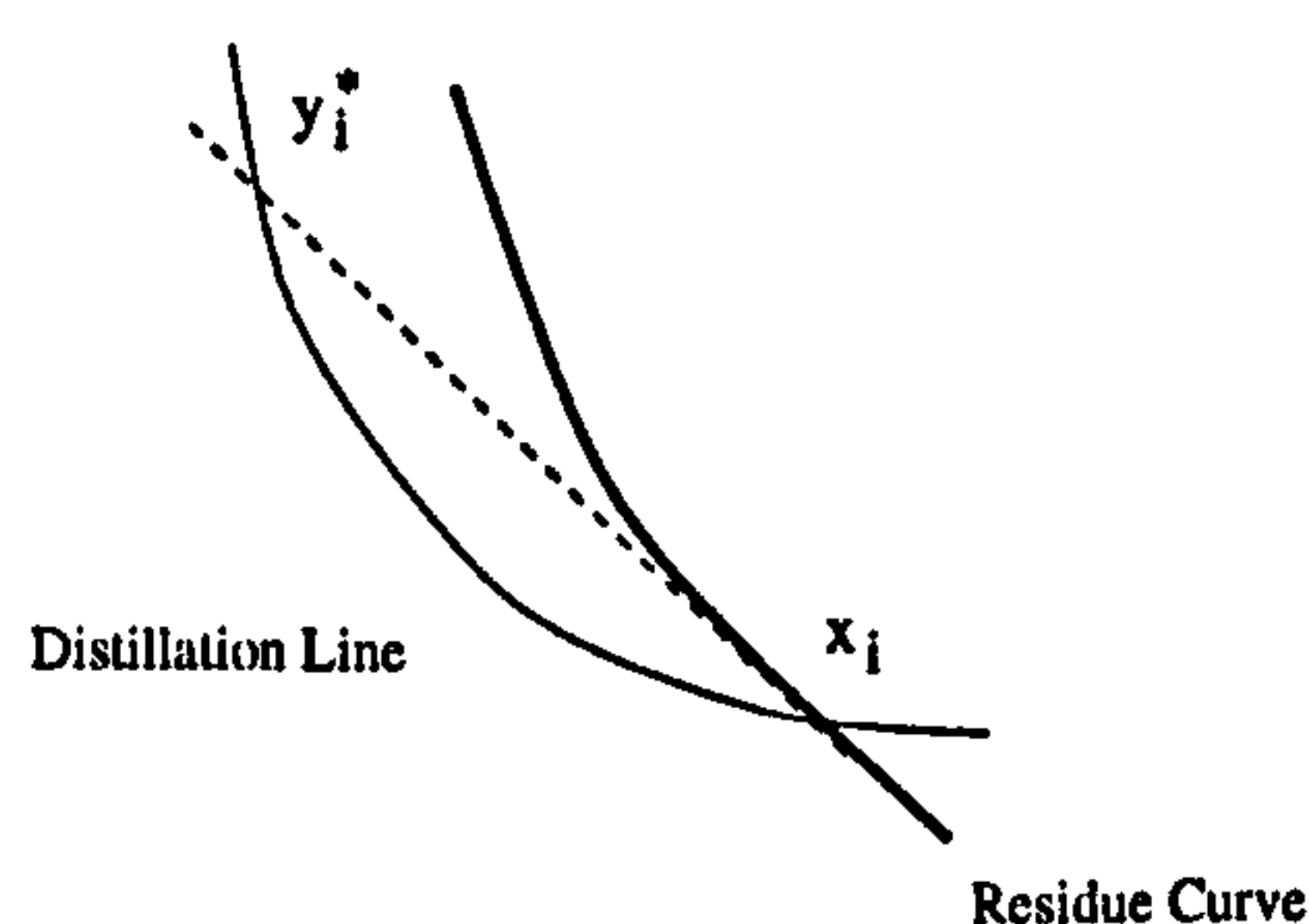


Figure 3.1: Relationship between residue curves and distillation lines

The singular (fixed) points of the residue curves described by equation 3.1 are points on the composition simplex where the driving force for change in the liquid composition is zero. This condition is trivially satisfied at the azeotrope and pure species vertices. For a ternary mixture with a binary azeotrope there are four fixed points on a triangular dia-

gram, the binary azeotrope and the three vertices. Mathematically, high order singularities introduce one or more simple distillation boundaries that separate two or more distillation regions in residue curve maps. Doherty and Perkins (1979) have shown that for the separation of homogeneous mixtures by simple distillation, these boundaries cannot be crossed. The separatrices on the maps of distillation lines are called distillation line boundaries. Although the fixed points of the maps of distillation lines and residue curves are in general identical, the residue curves and distillation lines do not coincide, as shown above, and nor do the simple-distillation and distillation-line boundaries. This has a vital impact on the methodologies developed for the design and synthesis of azeotropic separations. Many strategies for the synthesis and design of separation train sequences have assumed that operating lines cannot cross simple distillation boundaries. However, as Stichlmair *et al.* (1989) have pointed out, the distillation-line boundaries are the appropriate boundaries.

Doherty and Caldarola (1985) showed that residue curve maps can approximate the distillation line at total reflux by approximating finite difference equations in a single feed distillation column with differential models. When tray towers are modelled assuming vapour-liquid equilibrium, it is generally assumed that the residue curves are accurate representations of liquid composition profiles at total reflux (Van Dongen and Doherty, 1985; Bekiaris *et al.*, 1993). However, residue curves represent the liquid composition profiles of packed columns at total reflux and are at best an approximation to the liquid composition profiles for staged columns. Errors associated with residue curves are pronounced in wide boiling systems and regions of high curvature, where the total reflux profiles of staged columns are more bulged than the residue curve. Distillation line maps (DLM) represent the liquid composition profile of a staged column at total reflux.

The development of procedures for the design and synthesis of azeotropic distillation has been based on the topology of residue curves, and the approximation of distillation lines at total reflux by residue curves.

3.2.2 Prediction of Azeotropes

The ability to predict whether a given mixture will form azeotropes and its characteristics is important for the synthesis and modelling of nonideal separation processes. To test suitability and accuracy of thermodynamic models and parameters, the predicted azeotropes can be compared with experimentally determined data. Furthermore, azeotropic information is required for the construction of residue curve and distillation line maps.

Homogeneous azeotropes occur in a boiling mixture when the composition of the vapour phase is equal to the composition of the liquid phase. There are three thermody-

thermodynamic conditions which a system must meet in order for an azeotrope to exist;

- (1) Physical equilibrium. For a multicomponent mixture, this condition can be written in terms of the equality of fugacities

$$\hat{f}_i^V = \hat{f}_i^L \quad \forall i \in C \quad (3.2)$$

where $\hat{f}_i^V$ refers to the fugacity of component i in the vapour phase; $\hat{f}_i^L$ refers to the fugacity of component i in the liquid phase; and C is the set of components in question. In turn, these solution fugacities can be written as

$$y_i \hat{\phi}_i^V P_{tot} = x_i \gamma_i^L f_i^L \quad \forall i \in C \quad (3.3)$$

where y_i is the mole fraction of component i in the vapour phase; $\hat{\phi}_i^V$ is the mixture fugacity coefficient of component i in the vapour phase; P_{tot} is the system pressure; x_i is the mole fraction of component i in the liquid phase; γ_i^L is the activity coefficient of component i in the liquid phase; and f_i^L is the pure component fugacity of component i in the liquid phase. At low system pressure, the vapour phase can be assumed to behave ideally, and assuming Poynting correction factors of one

$$y_i P_{tot} = x_i \gamma_i^L P_i^{sat} \quad \forall i \in C \quad (3.4)$$

where P_i^{sat} is the vapour pressure of component i .

- (2) The composition of the vapour phase must be identical to the overall composition of the liquid phase

$$y_i = x_i \quad \forall i \in C \quad (3.5)$$

- (3) The component mole fractions in each phase must sum to unity and must be non-negative

$$\sum_i^C x_i - 1 = 0 \quad (3.6)$$

A summary of works reported in literature for the computation of homogeneous azeotropes from models of phase behaviour is given in Table 3.1, whereby the mathematical formulation of the methods involve the solution of the equations given above (often after manipulation). Due to the highly nonlinear form of the thermodynamic equations for phase equilibrium, the computation of azeotropes is a difficult problem. As such, the earlier methods do not guarantee locating all the azeotropes when one or more exists, or verify

when none exists. More recently, Fidkowski *et al.* (1993a) presented an efficient algorithm based on a homotopy-continuation method, applicable to multicomponent systems using any thermodynamic model. The continuation method of Westerberg and Wahnschafft (1996) has similar features. Although more reliable than the previous methods however, these procedure do not completely guarantee that all azeotropes are determined.

Facing this challenge, two differing methods have been presented that provide a mathematical guarantee for the determination of all azeotropes. Maranas *et al.* (1996) and Harding *et al.* (1997) developed a global optimisation approach based on a branch and bound framework with convex underestimating functions that are continuously refined as the domain in which the azeotropes may occur is narrowed. The success of this approach relies on the construction of valid convex lower bounds, and the authors develop tight bounding functions for the Wilson, NRTL, UNIQUAC and UNIFAC thermodynamic models (and assume ideal vapour behaviour). The alternative approach of Maier *et al.* (1998) is based on interval analysis, in particular the interval-Newton/generalised-bisection algorithm. As it does not require the construction of model-specific convex underestimators, this method can be applied with any thermodynamic model. The method is tested with the Wilson, NRTL and UNIQUAC models to describe the liquid phase nonidealities with ideal vapour phase.

3.2.3 Entrainer Selection

Screening of entrainers is a critical step, for an optimal design using an average entrainer can be considerably more costly than an average design using the best entrainer. Unlike zeotropic distillation, the achievable product compositions of azeotropic distillation is dependent on the feed composition and its relative position to the distillation line boundaries. Certain splits are therefore impossible to achieve. Criteria for the screening of entrainers are based on their potential for producing feasible designs with no consideration of economics.

When selecting an entrainer, the principal concern is the structure of the residue curve map and distillation lines that are associated with the mixtures involving it. To facilitate the screening of potential entrainers, Matsuyama and Nishimura (1977) classified all possible ternary mixtures. Since residue curves cannot cross the distillation boundaries, Van Dongen and Doherty (1985) suggest that as a first approximation, the compositions of distillation columns operating at finite reflux cannot cross the boundaries.

On this basis, Doherty and Caldarola (1985) assume that the overall mass balance line connecting the distillate, feed and bottom compositions cannot cross the distillation

Authors	Features
Earlier Works	
Aristovich and Stepanova (1970)	Calculated ternary homogeneous azeotropes using Wilson equation under isothermal conditions
Teja and Rowlinson (1973)	Calculated homogeneous azeotropes of binary mixtures using equation of state at constant temperature
Wang and Whiting (1986)	Extended the algorithm of above authors to multicomponent systems, but apply only to binary mixtures
Chapman and Goodwin (1993)	Presents search method for locating homogeneous and heterogeneous azeotropes using a Levenberg-Marquardt algorithm.
Fidkowski <i>et al.</i> (1993a)	Present homotopy continuation method for finding homogeneous azeotropes in multicomponent systems.
Westerberg and Wahnschafft (1996)	Presents a continuation method based on the relaxation of the azeotropy condition, similar to Fidkowski <i>et al.</i> (1993a).
Location of All Azeotropes	
Maranas <i>et al.</i> (1996) Harding <i>et al.</i> (1997)	Locates homogeneous azeotropes for multicomponent mixtures using a global optimisation approach. All solutions are guaranteed by the construction of convex underestimators for the thermodynamic model.
Maier <i>et al.</i> (1998)	Presents an interval-Newton/generalized-bisection-algorithm to determine all homogeneous azeotropes of multicomponent systems, and to verify when none exist. Can be applied to any thermodynamic model.

Table 3.1: Summary of methods for determining homogeneous azeotropes

boundary. According to them,

“the entrainer selected must be such that the pure components to be separated lie in the same distillation region on a residue curve.”

Approximating distillation lines at infinite reflux by residue curves, the proposed procedure involves sketching the residue curve map (as outlined by Doherty and Perkins, 1979), and should the resulting map obey this rule, the entrainer would be a viable candidate worthy of further study. Although simple, this procedure has a number of drawbacks. For certain systems, Van Dongen and Doherty (1985) and Levy *et al.* (1985) observe that when the distillation boundary is nonlinear (curved), the steady state composition profile in a homogeneous distillation may cross from the convex side. The entrainer selection strategy of Doherty and Caldarola (1985) is therefore conservative, rejecting many candidate entrainers that actually make the separation feasible. Furthermore, their procedure is limited to the separation of binary azeotropic mixtures, and as discussed in the previous section, residue curves are at best an approximation to the liquid composition profiles. This assumption is also used by Foucher *et al.* (1991) who propose a new methodology for the automatic screening of entrainers for the separation of binary azeotropic mixtures in homogeneous columns.

Stichlmair *et al.* (1989) propose another strategy for entrainer selection based on distillation lines and triangular diagrams as opposed to residue curves. By noting that only the most and least volatile component can be recovered in the distillation of a multi-component zeotropic, they extended this property to azeotropic mixtures by stating that only the constituents located at the end points of distillation lines could be obtained in their pure form. Thus, a candidate entrainer makes separation feasible if and only if the two azeotropic constituents are end points of distillation lines in the ternary diagram. To achieve this, they observe that

“If the binary mixture exhibits a high-boiling azeotrope, the entrainer must

1) be a high boiling substance or 2) form new high boiling binary azeotropes

If the binary mixture exhibits a low-boiling azeotrope, the entrainer must

1) be a low-boiling substance or 2) form new low-boiling binary azeotropes”

The analysis of feasibility of separation is limited to ternary mixtures, and a wrongful assumption in their criteria is the generalisation of the zeotropic case to azeotropic case. In fact, this criterion is necessary, but not sufficient to produce a feasible design (Laroche *et al.*, 1992a).

As shown by Laroche *et al.* (1992a), the criteria proposed by Doherty and Caldarola (1985) and Stichlmair *et al.* (1989) contradict each other. It is found that in all cases where an entrainer does not introduce a new azeotrope and has a lower boiling point than both azeotropic components or forms new low boiling binary azeotropes, there is a boundary separating the two azeotropic components in the residue curve, which violates the criterion set by Doherty and Caldarola (1985).

The criteria presented by Doherty and Caldarola (1985) and Stichlmair *et al.* (1989) are incomplete as they both wrongly assumed that infeasibility at infinite reflux implies infeasibility at finite reflux. Stichlmair and Herguajuela (1992) have taken this into account and assuming curved distillation boundaries, present rules for entrainer selection when the operating lines do and do not cross the distillation-line boundaries.

3.2.4 Bounding Strategies

Systematic approaches for the conceptual design require the ability to identify quickly feasible separations in the resulting systems. Methods for determining the range of the distillate and bottoms product compositions for distillation columns given the feed composition have been developed to aid the synthesis of separation sequences. Since the presented bounding strategies have involved graphical constructions (Stichlmair and Herguajuela, 1992; Fidkowski *et al.*, 1993b; Wahnschafft *et al.*, 1992a; Castillo *et al.*, 1998a), techniques have focussed on ternary and quaternary mixtures where it is possible to visualise the results. Recent work has produced the generalisation of geometric methods to equation based approach, giving methods for evaluating distillation feasibility of multicomponent systems (Safrit and Westerberg, 1997; Rooks *et al.*, 1998). However, a systematic procedure for generating alternative sequences of distillation columns for multicomponent mixtures is still not available. In this section, the basic bounding concepts developed and their limitations will be presented.

Bounding for Total Reflux Operation

The overall and component mass balance dictates that the feed, distillate and bottoms product compositions lie on a straight line (the mass balance line) with the distillation and bottoms compositions at the end points. A separation is feasible at total reflux if the bottoms and distillate composition are part of the same distillation line or, when residue curves are used to approximate the total reflux trajectories, part of one residue curve. Using distillation lines to represent operating lines, Stichlmair and Herguajuela

(1992) note that for a given feed, boundaries for distillate and bottoms compositions are determined by constructing

- the distillation line through the feed composition F
- the mass balance line through the pure distillate D (or the minimum boiling azeotrope) and the feed point F
- the mass balance line through the pure bottoms product B (or the maximum boiling azeotrope) and the feed point F

For a ternary zeotropic mixture, the feasible compositions are bounded by the shaded regions $DFB1$ and $BFD1$ as shown in Figure 3.2. Analogous bounding procedures at total reflux using residue curves instead of distillation lines are utilised, for example by Laroche *et al.* (1992a) and Doherty and Caldarola (1985).

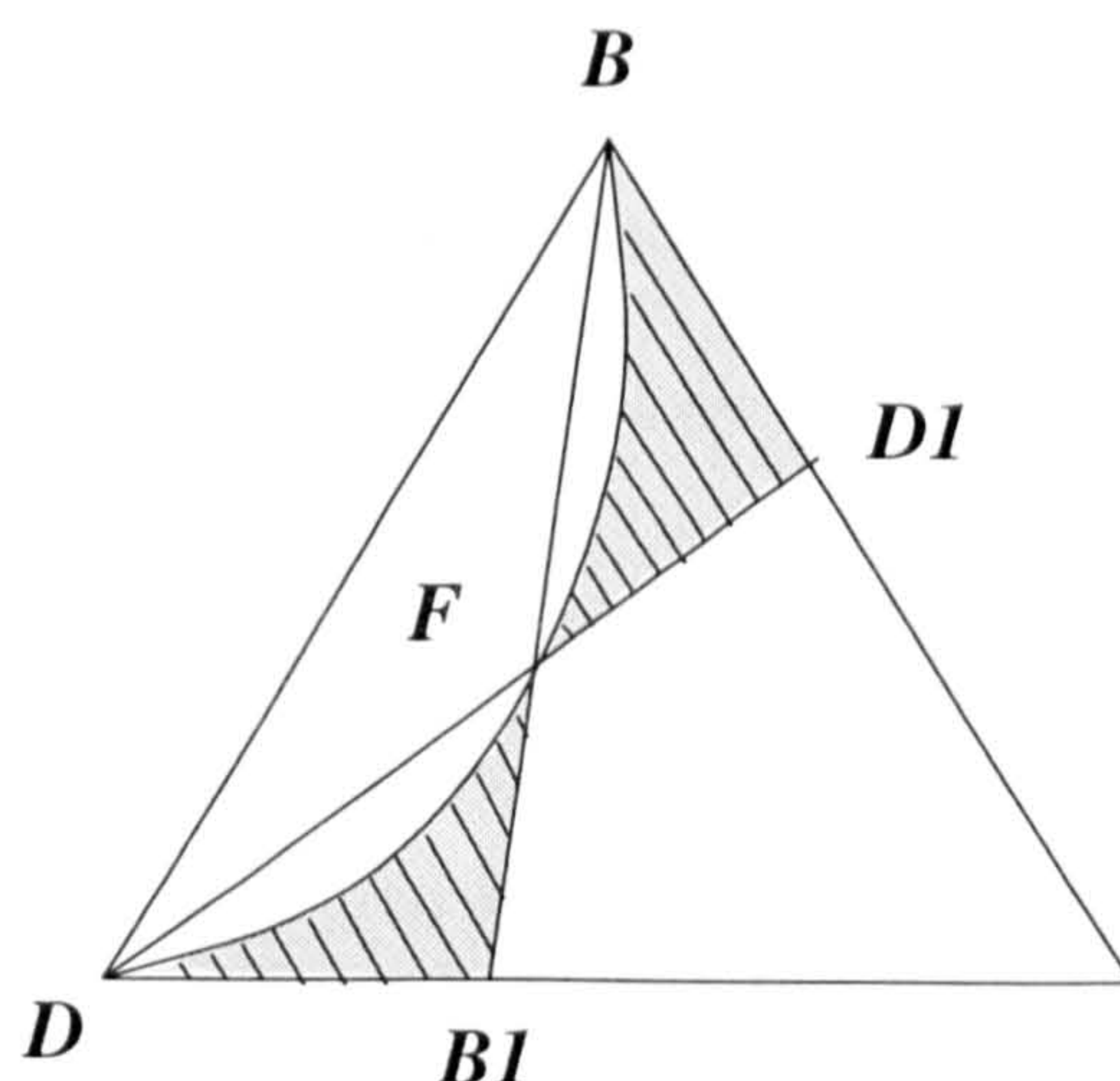


Figure 3.2: Total reflux bounding for a zeotropic mixture

Under certain circumstances, Stichlmair and Herguajuela (1992) show that for azeotropic mixtures,

- the product compositions recoverable in ternary mixtures do not have to be at the origin or terminus of a distillation line curve
- the distillation and bottom product can lie in different separation regions other than the feed *i.e.* the distillation boundary does not necessarily form a barrier

Figure 3.3 shows a ternary mixture XYZ (in decreasing volatility) with a minimum boiling azeotrope K . The system has no distillation boundaries and all the distillation line

curves originate at K and terminate at Z , with one of the curves tracing the perimeter of the composition space $KXYZ$. For a feed mixture F , the feasible distillate and bottoms compositions achievable in a single feed column can be constructed using the rules and are represented by the shaded areas R^D and R^B respectively. In this case, there exists an overall mass balance line through the feed F and pure vertex X . Thus although the pure species X is not at the end point of a distillation line, it can be recovered as the distillate product at total reflux.

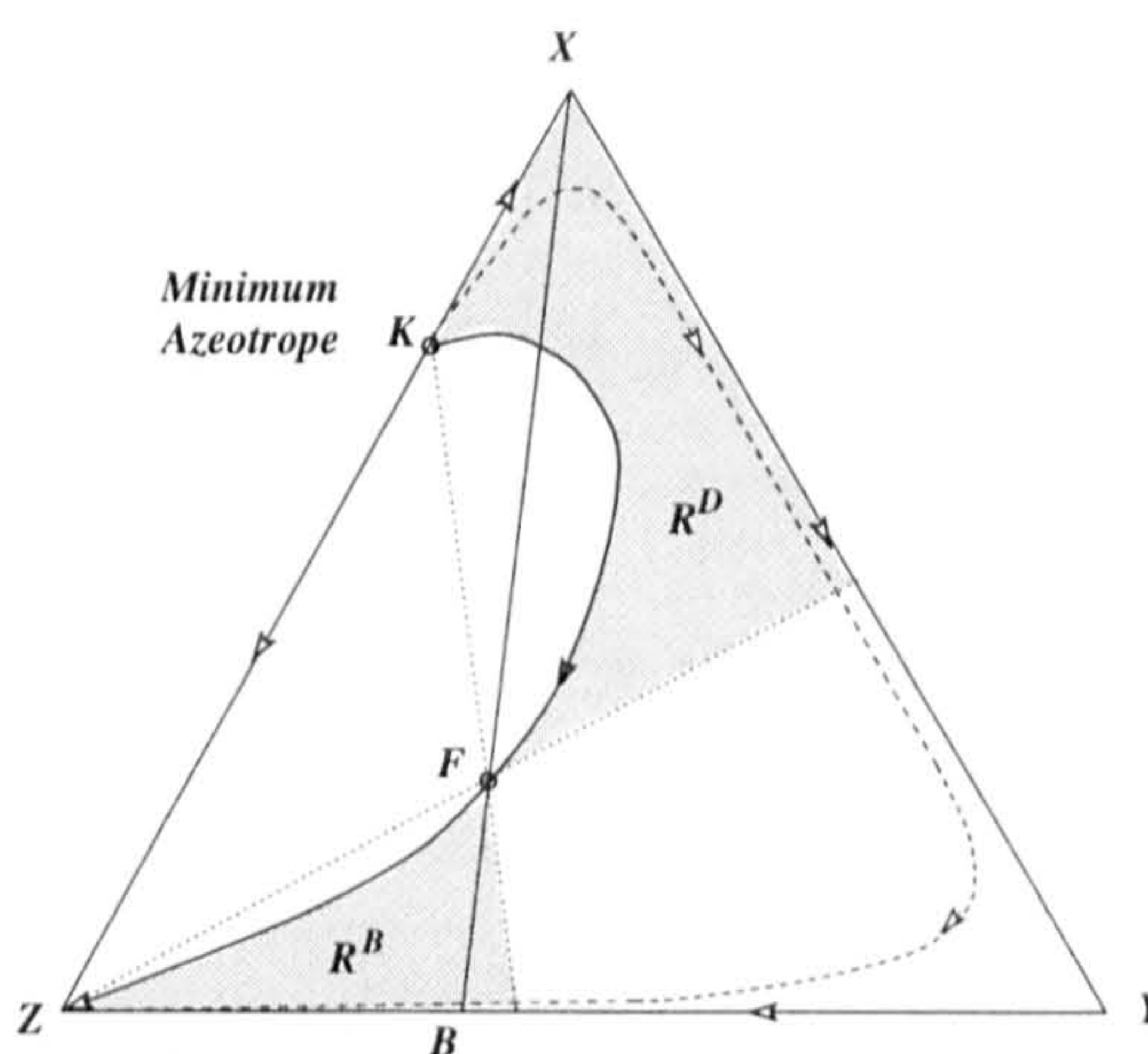


Figure 3.3: Separation regions of a ternary mixture with a minimum boiling azeotrope

Figure 3.4 shows a ternary mixture XYZ with a minimum boiling azeotrope K and a distillation boundary joining K and X . Two regions are formed, a concave region $XKZX$ and a convex region $XKYX$. For a feed F in the concave region, a mass balance line can be drawn such that a chord is formed with a distillation line curve in both the concave and the convex region. The feed F can produce a distillate D_1 and a bottoms product B_1 , which are both located in the same distillation region as F . It can also produce a distillate D_2 , with either B_2 or B_3 as its bottoms product, which is on a distillation line curve on the other side of the distillation boundary. In this case, the product compositions do not lie in the same distillation region as the feed and thus the distillation boundary can be crossed. In general however, the feed composition must be bracketed by the distillate and bottoms compositions and thus a distillation boundary can only be crossed from the concave to the convex side when moving from the feed to the product.

As shown by Laroche *et al.* (1992b) and Van Dongen (1983), finite reflux ratios may lead to better separation than at total reflux for multicomponent azeotropic mixtures. Further, there are compositions which are feasible from columns operated at finite reflux ratios but not at infinite reflux ratios. Consequently, methods determining feasible product compositions based on operating conditions at all reflux ratios, and not solely on the

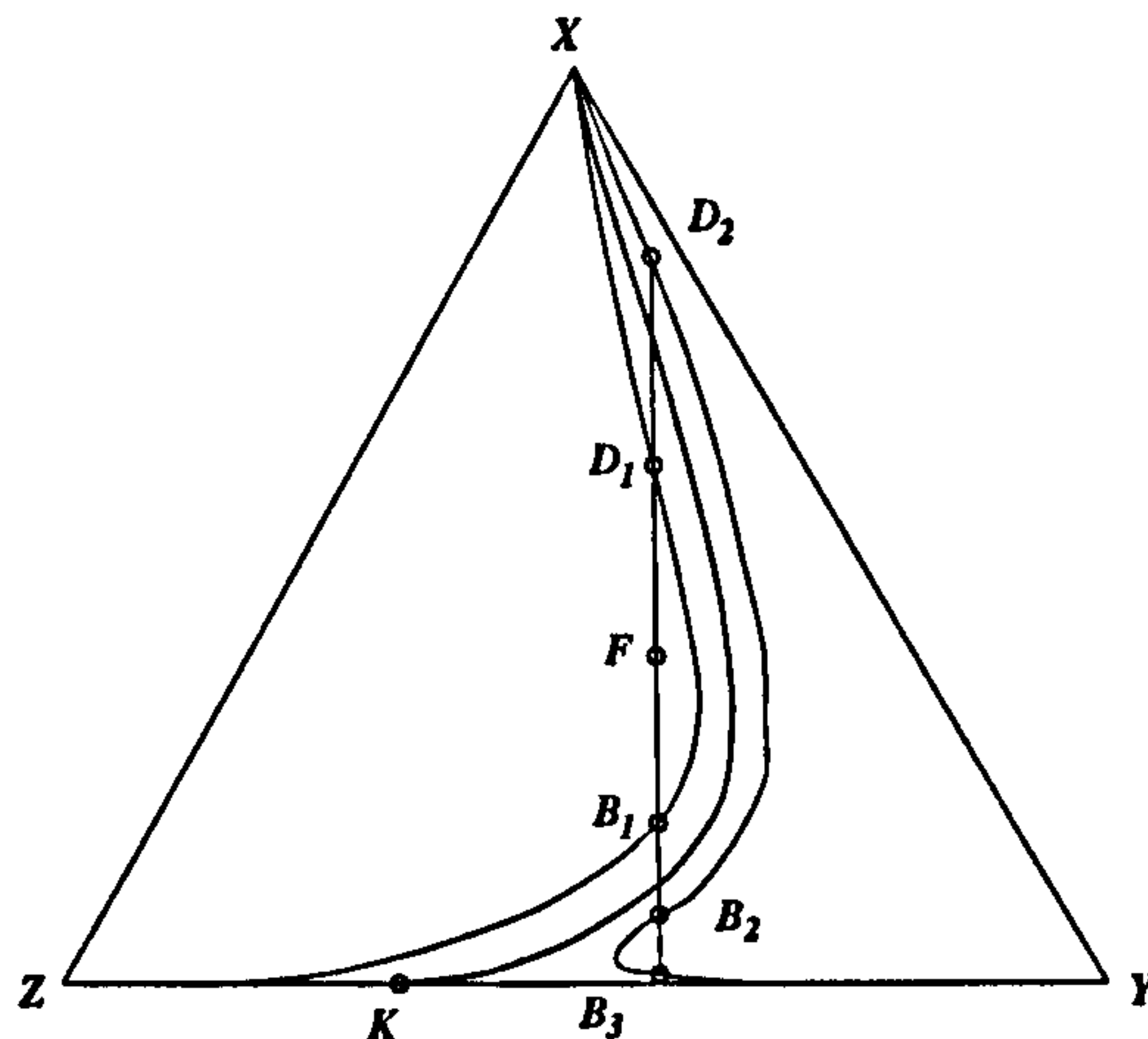


Figure 3.4: Crossing of a curved distillation line boundary for a ternary mixture

extreme condition of infinite reflux ratio, have been developed as an improvement to the works of Doherty and Caldarola (1985) and Stichlmair and Herguajuela (1992).

Bounding for Finite Reflux Operation

Recent work by Wahnschafft *et al.* (1992a, 1993), Fidkowski *et al.* (1993b) and Castillo *et al.* (1998b) have led to methodologies for improved estimations of regions of feasible product compositions at finite reflux. To further limit the regions of feasible product compositions, Wahnschafft *et al.* (1992a) utilises the *feed pinch-point trajectory*, Fidkowski *et al.* (1993b) introduces the *distillation limit* and Castillo *et al.* (1998a) defines the *operation leaf*. Note that these bounding and sequencing procedures are only applicable to ternary mixtures in single feed columns.

Wahnschafft *et al.* (1992a) argued that the range of products achievable in distillative separation of a given feed into two products is confined by the limits for the separations feasible at minimum work consumption and those achievable at maximum work consumption; that is, by the limiting operating conditions of total reflux and thermodynamically optimum operation. The limiting operating conditions at total reflux are approximated by residue curve maps, whilst thermodynamic optimum operation is represented by pinch point curves.

A pinch point occurs due to vanishing driving forces for mass exchange and in a distillation column it arises when the streams getting in contact on the trays approach equilibrium. Thermodynamically optimum operation is represented by pinch-point trajectories, which describe the possible compositions of pinch points in a column for all

conceivable values of reflux ratio. Analytically, pinch-point trajectories are determined as the compositions for which the material balance and the equilibrium line coincide. Wahnschafft *et al.* (1992a) showed that the tangent to the residue curve at the column pinch passes through the product composition. A product pinch point curve is thus the locus of points on residue curves whose tangents pass through the specified product composition (Figure 3.5). In a similar manner, the feed pinch point curve can be calculated.

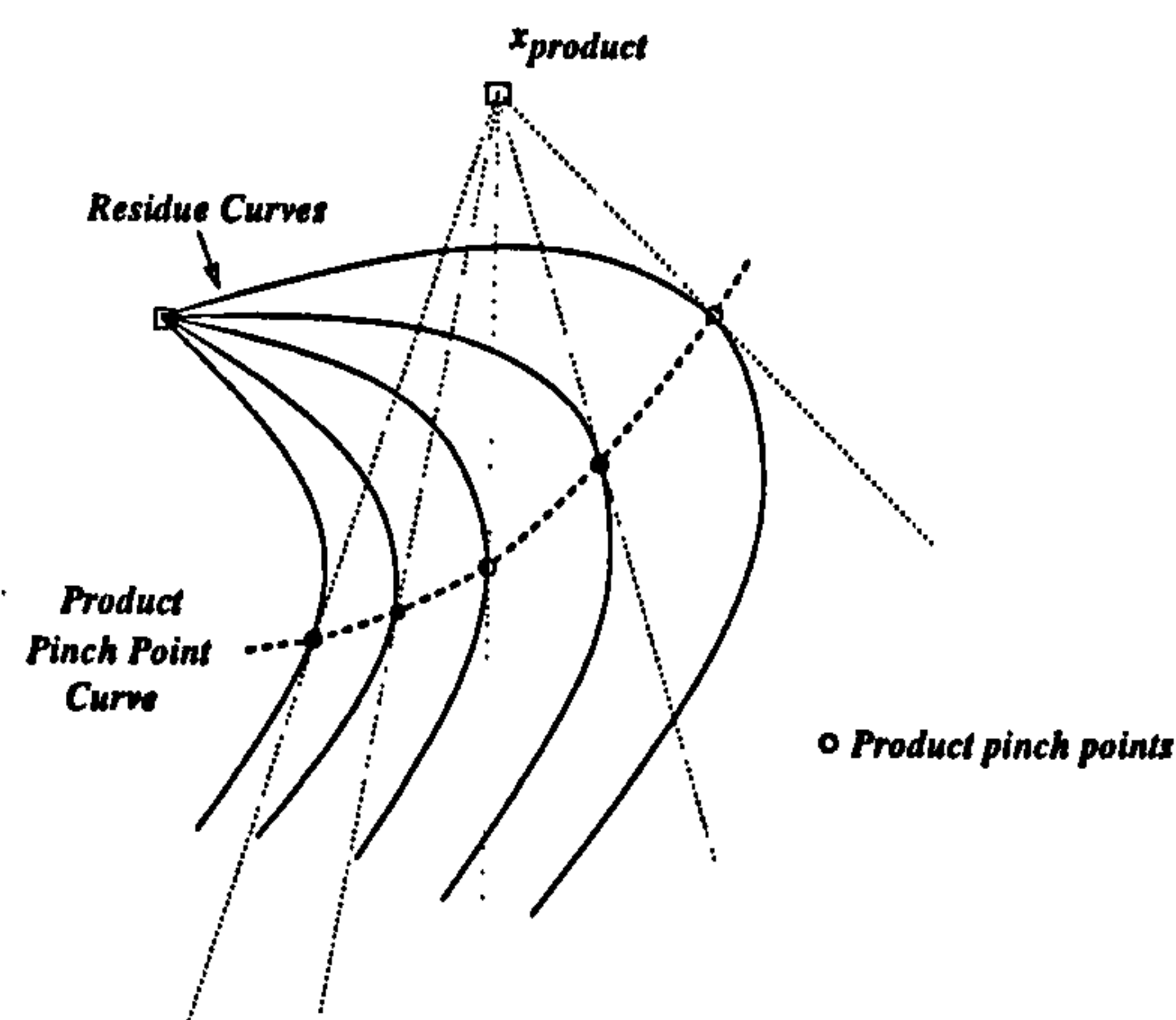


Figure 3.5: Product pinch-point curve

Wahnschafft *et al.* (1992a) developed their bounding criteria for a single feed column by the following analysis. For a given specification, the regions of possible finite concentration profiles in the stripping and rectifying sections are confined by

- The overall mass balance lines through the vertices and azeotropes
- Total Reflux Curve through the assumed product composition and
- *Branches* of the corresponding product pinch point curves.

For feasibility of separation, the profile regions for the two column sections must overlap. This criterion is applicable regardless of the physical property behaviour of a mixture and is a necessary, but not sufficient condition.

For an ideal system, there will only be one pinch point curve. However, for an azeotropic system, pinch point curves may exhibit bifurcations and multiple branches, as shown by Fidkowski *et al.* (1991) and Van Dongen (1983). Wahnschafft *et al.* illustrated that there may be more than one branch of pinch point curves if a product composition is just beyond a residue curve boundary, and is located on a residue curve with an inflection. As can be seen in Figure (3.6), one branch of the pinch point curve is in the distillation

region of the product and the other in the distillation region of the feed. Up to a certain reflux ratio, it is seen that the residue curve boundary can be crossed from the convex side, moving toward the feed (Curve I). However, increasing the reflux ratio beyond this point causes the profile to stay in the same distillation region and does not meet the required specifications (Curve II) due to too much energy being provided to the column. There is thus an associated maximum reflux ratio for feasibility when crossing a residue curve boundary, which can be determined.

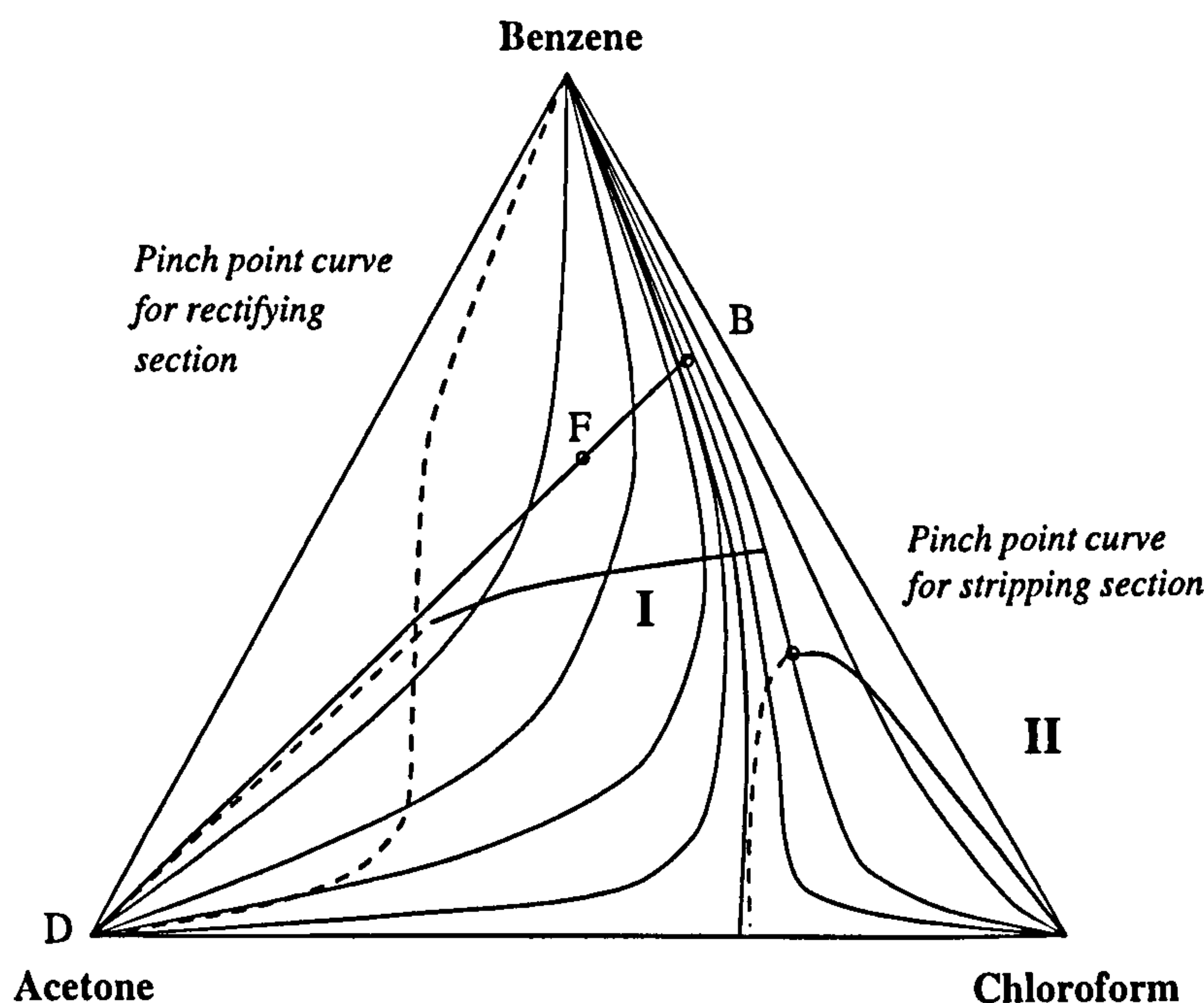


Figure 3.6: Multiple branches of pinch point curves

The only section of the material balance line where there is no feasible product is between the feed and the pinch point at which the product pinch point curves overlap *i.e.* a feed pinch point (the point at which the tangent to the residue curve goes through the feed). For ideal mixtures, separation is feasible for any products that are connected by a mass balance line that intersect the trajectory of feed pinch points twice, including at the given feed point. For non-ideal systems however, the mass balance line can cross the residue curve boundary if the feed is on the concave side of the boundary. The limit of feasible products on the other side of the boundary to the feed is given by the compositions whose pinch point trajectories do not cross the boundary. This is given by a tangent to a residue curve at the point of inflection. Thus to compose the feasible regions of product compositions, one must construct the limit on the convex side of the boundary by generating an envelope for the compositions whose pinch point curves completely remain in one distillation region. This is called the inflection point tangent.

According to Wahnschafft *et al.* (1992a), if the residue curve map has a curved separatrix and the feed is in the convex side, the product compositions feasible for a given feed are bounded by

1. The inflection point tangent
2. The liquid feed pinch point curve

and the composition profiles leading to feasible products can only intersect if the overall mass balance line intersects the feed pinch point twice, including at the feed point.

Fidkowski *et al.* (1993b) propose an analogous approach to the pinch point method, referring to the *feed pinch-point* curve as the *distillation limit*. The bottom composition is bounded by the liquid-feed pinch curve, and the distillate by the vapour feed pinch point curve, which passes through the composition of the vapour at equilibrium with the feed composition. The feasible product compositions are then further divided into separate regions for direct and indirect splits. A simple equation based procedure is developed for the calculation of the feasible separation regions. Accounting for the thermodynamic condition of the feed, these are the proper bounds for feasible products at finite reflux.

The advantage of the bounding procedures is in the ability to quickly assess the feasibility of a desired separation before trial and error calculations are used to determine the reflux ratio and number of stages needed in each column section. In practise, feasibility can be determined by rigorous simulation or by iterative design methods such as the boundary value procedure but these are time consuming and a tedious way to discover that a design specification is infeasible. In principle the criterion proposed by Wahnschafft *et al.* (1992a) and Fidkowski *et al.* (1993b) is a necessary but not sufficient condition and when an overlap of product regions is obtained, there is no guarantee that the product specification is feasible. Despite the overlap of regions, cases may arise where it is still impossible to produce an intersection of diabatic profiles due to the omission of enthalpy balances. This limitation was recognised by Wahnschafft *et al.* but the only suggestion was to satisfy the overall energy balance by 'strategic placement' of intermediate heat exchangers. It should also be noted that distillation lines should be used instead of residue curves when determining the bounds of a staged column.

Introducing the concept of *operation leaves*, Castillo *et al.* (1998b) proposed a method for bounding the possible liquid composition profiles in column sections. However, instead of determining all feasible products for a *given feed* as discussed above, they establish the feed compositions that will produce a *given product* when fed into a column section. Staged column sections are bounded by the limiting operating conditions of total and

minimum reflux. The distillation line through the desired product defines the former, whilst the product-pinch point curve defines the latter. Special attention is required when the products are not liquid, such as when a partial condenser is utilised. In such cases, the composition of the vapour product does not coincide with the liquid composition on the top stage and thus the vapour composition should be used to calculate the product pinch point curve, but the liquid composition of the top stage for the determination of the total reflux bound.

The operation leaf for a staged column section contains all the possible paths that a composition profile could follow to attain a given product and is defined as

“the area in the composition space bounded by the distillation line through the specified product and the product-pinch point curve for the specified product”

For a given product composition, two operating leaves can be defined - one for the rectifying section and one for the stripping section. The overlap of operation leaves of each column section for the desired products results in a necessary and sufficient condition for column feasibility at some finite reflux and reboil ratio. There are two exceptions to this rule. When the product pinch point curves and the distillation lines intersect each other, some composition profiles follow a path outside the total reflux bound. Secondly, when the specified product is close to a total reflux boundary, often the pinch point curve and the distillation line diverge toward different sides of a total reflux boundary. It is shown that distillation line boundaries can only be crossed when this phenomena occurs, and it is termed to form an ‘open leaf’.

Column Sequencing

Procedures for column sequencing are based on bounding procedures discussed in the previous section, and are limited to ternary mixtures due to the ease of visualisation of the composition space. Laroche *et al.* (1992b) and Doherty and Caldarola (1985) present methods based on residue curve maps and are restricted to separations operated at total reflux. Stichlmair and Herguajuela (1992) present flowsheets based on distillation line maps, and although they recognise that the conclusions drawn at total reflux are incomplete, they do not develop a procedure for column sequencing at finite reflux. Wahnschafft *et al.* (1992a) and Fidkowski *et al.* (1993b) extended these approaches to finite reflux, but again do not develop a systematic procedure for the synthesis of column sequences. Based on the concept of operating leaves to determine separation feasibility for staged columns,

Castillo *et al.* (1998b) developed a synthesis procedure for distillation sequences of ternary mixtures, incorporating insights such as the crossing of boundaries using complex column arrangements. Considering recycles, this non-iterative, graphical procedure is useful for the design of two-column sequences and complex column arrangements, such as columns with side strippers or rectifiers.

One obvious limitation to these procedures is that the pressure must be fixed for analysis, and therefore an iterative procedure is required to consider all possible pressures.

Bounding for Multicomponent Systems

Recent work is focussed on the generalisation of the geometrical methods discussed above to multicomponent mixtures. Ahmad and Barton (1996) developed tools for the analysis of multicomponent azeotropic homogeneous mixtures in batch distillation. Based on this work, Ahmad *et al.* (1998) developed an algorithm to identify the distillation regions of multicomponent systems which represent the topological structure of the composition simplex. From this information, all product sequences achievable in batch distillation can be extracted.

In terms of continuous distillation, there have been algorithmic advances in the determination of distillation regions for multicomponent systems, but no systematic procedure is available for the sequencing of columns.

Using the properties of distillation lines, Safrit and Westerberg (1997) proposed an algorithm to find all the distillation regions for continuous and batch distillation of multicomponent systems. The method determines the distillation regions in a stepwise manner, finding all $k - 1$ regions and using their properties to identify the k regions. The algorithm assumes straight distillation boundaries, not accounting for boundary crossing, and gives no indication of column sequencing.

Rooks *et al.* (1998) developed an equation based approach to determine the structure of distillation regions for multicomponent homogeneous mixtures, based on residue curve maps. Given a multicomponent system, the desired column pressure and a vapour-liquid equilibrium model, the algorithm has three stages;

1. Determine the structure of the residue curve map *i.e.* the singular points of equation (3.1), and the nature of the points *i.e.* stable or unstable nodes. This information is obtained through the *adjacency matrix*.
2. Determine the distillation regions and their structure. A distillation region is a

family of curves connecting one unstable node to one stable node, and has the same dimension in composition space as the original mixture.

3. Determine feasible splits, assuming that the mass-balance line connecting the distillate, feed and bottoms product composition must lie in a single distillation region.

Distillation sequences are generated from the determined feasible splits, and it is found that there are a surprising number of process alternatives for the distillation of azeotropic mixtures. The proposed method provides a sufficient condition for product feasibility, but as it assumes no boundary crossing, it rejects other feasible alternatives and is therefore not a necessary condition. Further, total reflux of staged columns are approximated by residue curve maps which are really lines of total reflux of packed columns.

3.2.5 Column Design

Once the synthesis alternatives for the separation of the given mixture are selected, *i.e.* the entrainer and corresponding distillation sequences, the separation systems must be designed, optimised and costed so that they can be compared. For each distillation column, the design decisions include the number of stages, the feed tray location and the reflux ratio at which to operate it. Approaches for azeotropic distillation columns have been developed by the analysis of the column geometry at minimum reflux ratio. Based upon these topological concepts, Doherty and coworkers have applied geometrical methods to ternary and higher order azeotropic mixtures to determine the minimum reflux ratio - and from this the operating reflux ratio and number of theoretical stages can be found.

To calculate the minimum reflux ratio given the distillate and bottoms mole fractions x_D and x_B , Levy *et al.* (1985) introduced a boundary-value design procedure (BVDP) utilising a differential column model. In its simplest form, the differential model assumes theoretical plates, constant molar overflow and a saturated liquid feed, and is a first order approximation to the finite difference mass balance equations. For a ternary mixture in a single-feed distillation column, the liquid-phase composition profile model consists of the following equations (Van Dongen and Doherty, 1985)

The rectifying section

$$\begin{aligned} \frac{dx_i^r}{dh^r} &= x_i^r - \frac{r+1}{r}y_i^r + \frac{1}{r}y_{D,i}^r \\ y_i^r &= f_{eq}(x_i^r) \end{aligned} \quad (3.7)$$

$$x_i^r(h^r = 1) = x_{i,D}$$

$$r = \frac{L_T}{D} \quad i = 1, 2$$

The stripping section

$$\frac{dx_i^s}{dh^s} = \frac{s}{s+1}y_i^s - x_i^s + \frac{1}{s+1}x_{B,i}^s \quad (3.8)$$

$$y_i^s = f_{eq}(x_i^s)$$

$$x_i^s(h^s = 1) = x_{i,B}$$

$$s = \frac{V}{B} \quad i = 1, 2$$

And the overall mass balance equation

$$s = (r + 1) \frac{x_{B,i} - x_{F,i}}{x_{F,i} - y_{D,i}} \quad (3.9)$$

where $x_{B,i}$ is the molar fraction of component i in the bottoms, $y_{D,i}$ is the molar fraction of component i in the distillate and $x_{F,i}$ is the molar fraction of component i in the feed. L_T is the molar liquid flow rate in the rectifying section, D is the molar flow rate of the distillate, V is the molar flow rate of the vapour stream throughout the column and B is the molar flow rate of the bottoms stream. Note that for a ternary system, only two of the three component mole fractions are independent and the last is determined by difference.

The boundary value design procedure involves specifying the product compositions (within the constraint of a mass balance) and integrating the equations above towards the middle of the column. A suitable vapour-liquid equilibrium model is required for y_i . In addition to the product compositions, for ternary mixtures the pressure must be defined and a value of reflux ratio guessed. Starting from the specified product compositions, equations 3.7 and 3.8 can be integrated by the fourth-order Runge-Kutta method to give the liquid composition profiles in the stripping and rectifying section of the column. The search for a feasible column involves an iterative procedure of changing ' r ' until the two profiles intersect. If the profiles cross and go further on, the reflux ratio is greater than minimum reflux, if the profiles do not cross, the reflux ratio is less than minimum reflux. At minimum reflux, one of the profiles just ends ('pinches') as it reaches the other. This condition can be found by iterative calculation of the composition profiles. Using the theory of differential equations to view the profiles, it is seen that the termination point of each profile is a stable node which can never be reached, except in the limit of infinite

plates. Thus when one profile ends on the other, an infinite number of trays are required to realise the column.

At operation of minimum reflux ratio, the rectifying and stripping section profiles have very sharp corners, corresponding to pinch zones. For all mixtures at R_{min} , the tangent to the saddle pinch profile (the rectifying profile for a direct split, stripping for indirect) at the feed pinch point (where the stripping profile just meets the rectifying profile for a direct split, vice versa for an indirect) is a straight line through the feed composition. For an ideal mixture, this implies that the saddle and feed pinch points $\hat{x}^{1,s}$ and $\hat{x}^{2,r}$ are collinear with the feed composition. This is an approximation for nonideal mixtures where the saddle pinch profile is often nonlinear.

To determine R_{min} , Levy *et al.* (1985) propose a search method in r to satisfy the second approximating condition. Alternatively, the equations describing this situation (Van Dongen and Doherty, 1985) may be solved simultaneously.

The method as described is for a single-feed column, but has been extended to design for multiple-feed columns (Levy and Doherty, 1986). The assumption of constant molar overflow has also been lifted to consider non negligible heat effects (Knight and Doherty, 1986).

The work of Levy *et al.* (1985) showed that for a direct split of a ternary mixture, the composition profiles start at the product compositions and end at the stable nodes, with an additional saddle fixed point close to the binary edge in each profile. This is illustrated for an ideal mixture (constant volatility) and saturated liquid feed in Figure 3.7. For $r \leq R_{min}$ (Figure 3.7a), the stripping and rectifying profiles do not intersect. For $r \geq R_{min}$ (Figure 3.7c), the stripping and rectifying profiles intersect transversely. At minimum reflux, the stripping profile ends on the rectifying profile, and the stripping node, the rectifying saddle and feed composition ($\hat{x}^{1,s}$, $\hat{x}^{2,r}$ and $\hat{x}_F$) are collinear (Figure 3.7b).

For highly non-ideal systems, the curve joining these points was found to be nearly linear. Julka and Doherty (1990) extended this methodology to higher dimensions. The rectifying profile starts at the distillate composition and approaches (c-2) saddles before ending at a stable node. A manifold of dimension (c-2) is spanned by these fixed points and is linear for constant volatility systems and nearly linear for many non-ideal systems. The stripping profile starts at the bottom composition and ends at the stripping node. At minimum reflux, the stripping node is located on the rectifying manifold. For an indirect split, the situation is symmetrically reversed with a manifold created by the stripping profile and the stable node in the rectifying profile ending on this manifold at

minimum reboil ratio. The fixed points can be used to find a close approximation to the minimum reflux (or reboil) ratio without calculation of the intermediate profiles. Using the finite difference mass balance equations, the fixed points are found as the roots of these equations, *i.e.*

$$F(\hat{x}) = 0 \quad (3.10)$$

where for the rectifying section

$$F(\hat{x}^r) = -y(\hat{x}^r) + \frac{r}{r+1}\hat{x}^r + \frac{1}{r+1}x_D$$

and for the stripping section

$$F(\hat{x}^s) = y(\hat{x}^s) - \frac{s+1}{s}\hat{x}^s + \frac{1}{s}x_B$$

For convenience the fixed points are labelled according to their position at total reflux. *E.g.* in the rectifying profile, fixed point 1 is the unstable node (lowest boiling), fixed point *c* is the stable node (highest boiling, and the rest of the points are saddles (intermediate boiling).

Julka and Doherty (1990) proposed an algebraic method for the calculation of minimum reflux ratio originally called the ‘zero volume’ method, and utilised this to determine the minimum flows in a single feed column assuming constant molar overflow for multi-component systems. The method involves constructing a set of vectors e_1 to e_{c-1} and at minimum reflux,

$$\det[e_1, e_2, \dots, e_{c-1}] = 0 \quad (3.11)$$

For a binary mixture this is the length between the end of the profiles on a x-y diagram, for a ternary mixture the area spanned between e_1 and e_2 (Figure 3.7b), for a quaternary mixture the volume spanned by e_1 , e_2 and e_3 and for mixtures with five or more components, it is a ‘fixed point volume’ To define the vectors $e_1, e_2, \dots, e_{c-1}$, *c* points must be chosen out of the *c*+1 fixed points (for direct split there is the feed point, the stripping node and $\hat{x}^{2,r}, \dots, \hat{x}^{c,r}$ in the rectifying profile), and the origin of the vectors. For a direct split, one can construct a set of vectors e_1 to e_{c-1} starting from the saddle point $\hat{x}^{2,r}$ to the feed, the stripping node and $\hat{x}^{3,r}, \dots, \hat{x}^{c-1,r}$. Reasons for this choice are detailed in the paper.

To calculate the minimum reflux, equation (3.11) must be solved in *r* with known fixed points. However, to determine the fixed points from equation (3.10), the value of *r*

is required. Thus an iterative procedure is required, with r as the tear variable. Julka and Doherty (1990) utilise this procedure to determine the minimum flows for nonsharp splits.

A more useful and robust alternative to tearing the information loop to solve equations (3.10) and (3.11) is to calculate the fixed points for all values of the reflux ratio and then solve (3.11). (Fidkowski *et al.*, 1991). The problem with tracking the branches of fixed points by, for example, starting at infinite reflux and decreasing r using the most recent value of $\hat{x}$ is that when a tangent pinch is encountered, there is a turning point and the Jacobian of $F(\hat{x})$ becomes singular.

Tangent pinches are often present in non-ideal mixtures and occur when there is an inflection in the equilibrium line. On a graph of $\hat{x}$ (fixed points) versus r , a tangent pinch is seen as a turning point. According to Julka and Doherty (1990), the minimum reflux occurs when the 'fixed point volume' is zero, but this is not necessarily true when the minimum reflux is controlled by a tangent pinch (Fidkowski *et al.*, 1993b).

Accounting for tangent pinches, Fidkowski *et al.* (1991) proposed a continuation method for finding fixed points using an 'arc length continuation'. This prevents the Jacobian from becoming singular at the turning point (tangent pinch). The algorithm to determine the minimum reflux involves finding the fixed points and solving the determinant in equation (3.11). If there are multiple zeroes of the determinant, then the one that controls is selected. Julka and Doherty (1993) also utilise an arc-length based continuation strategy to track all fixed points, and propose an algebraic, noniterative procedure to calculate the minimum reflux for multicomponent systems.

The methods described above have an advantage in that there is no need to calculate the intermediate profiles to determine the minimum reflux. The development of technique from Levy *et al.* (1985) to Fidkowski *et al.* (1991) use the same concept of 'pinch point', with the latter authors accounting for tangent pinches in their treatment which was previously neglected. The proposed method by Fidkowski *et al.* (1991) and Julka and Doherty (1993) is algebraic, with no need for lengthy iteration schemes, and is important as it is able to track *all* the fixed point branches inside the composition state space.

Note that equation (3.11) is only exact for ideal mixtures, as it assumes that the saddle pinch profile is linear at minimum reflux conditions. For some non-ideal systems this could lead to a substantial error.

These procedures for determining the minimum reflux are limited to single feed columns, and assume theoretical stages, constant molar overflow in each section, with known constant column pressure. In theory they are applicable to multicomponent sys-

tems, but have only been applied to quaternary systems.

Alternative design strategies for ternary mixtures in single feed columns are proposed by Stichlmair *et al.* (1993) and Castillo *et al.* (1998a).

Stichlmair *et al.* (1993) presents an alternative method for minimum reflux and reboil determination for single feed distillation of an azeotropic or zeotropic ternary mixture, exploiting the geometric characteristics of the column pinch. At minimum reflux and reboil ratio, pinches exist within the column whereby the vapour and liquid is in equilibrium. The authors classify ternary distillation into three types of separation and analyse the pinch properties as follows;

- *Preferred separation*, where the intermediate boiler exists in both the distillate and bottoms product. In this class a double pinch exists immediately above and below the feed point, with the pinch concentration coincidental with the feed concentration. Both the rectifying and stripping sections of the column are operated at minimum reflux and reboil respectively.
- *Lowboiler - rich distillate*, where the distillate is rich in the lower boiling component. In this class, the rectifying section is operated at increased reflux and the stripping section is operated at minimum reboil, thus there exists a single pinch in the stripping section immediately below the feed.
- *Highboiler - rich bottoms*, where the bottoms product is rich in the higher boiling component. In this class, the stripping section is operated at increased reboil, and the rectifying section displays a pinch immediately above the feed point.

Based on the fact that the pinch point concentration lies on a line between the transition point and the feed (Levy *et al.*, 1985), the pinch point is analytically determined. For the three classes of separation, this line is determined by the concentration profile immediately above or below the feed. In an ideal system, the concentration profile between the transition point and feed is straight, but for nonideal systems the profile is curved. The pinch point curve is thus approximated by linearising the concentration profile near the feed. From knowledge of the pinch point concentration, the minimum reflux and reboil ratios are then directly estimated

$$R_{min} = \frac{x_{D,i} - y_{P,i}^*}{y_{P,i}^* - x_{P,i}} \quad (3.12)$$

$$S_{min} = \frac{x_{P,i} - x_{B,i}}{y_{P,i}^* - x_{P,i}} \quad \text{for any component } i \quad (3.13)$$

where $x_{D,i}$ is the liquid distillate composition, $x_{B,i}$ the liquid bottoms product composition, $x_{P,i}$ the liquid pinch point composition and $y_{P,i}^*$ the vapour pinch point composition in equilibrium with $x_{P,i}$. This method is claimed to be faster and more reliable than the zero-volume method (Julka and Doherty, 1990), but is limited to ternary mixtures, assumes constant operating line and does not account for tangential pinches.

When a high boiling entrainer is selected for the separation of a binary azeotrope, the process requires at least two distillation columns, one to separate the azeotrope and the other to recover the entrainer. This process is often referred to as *extractive distillation*, and is the most common industrial application of homogeneous azeotropic distillation. Extractive distillations can only be performed in double-feed columns, and exhibits a maximum reflux above which the desired separation is not achievable, and a minimum entrainer flowrate, below which the separation is also impossible. Both these quantities correspond to a bifurcation pattern of the pinch point curves, and can be geometrically analysed.

Knapp and Doherty (1994) gives a bifurcation analysis of the finite difference equations describing the middle section of the column for ternary systems. Utilising arc-length continuation methods to track the fixed points, the minimum entrainer flow can be calculated from the column feed and desired product compositions. This allows the ranking of feasible entrainers according to their minimum entrainer flow to identify promising candidates. Numerical calculations for the analysis of pinch-point-curve bifurcation are available (Pollmann and Blass, 1994). Bauer and Stichlmair (1995) however, present a geometrical analysis of a residue curve map to calculate the minimum entrainer flow and the required reflux.

3.2.6 Summary

As nonideal behaviour has been mostly studied in a case dependent manner, nonideal separations and corresponding synthesis methods are much less advanced than that for ideal separation systems. The conceptual design of homogeneous azeotropic mixtures is typically sequential, with the synthesis problem decomposed into subtasks of entrainer selection, sequencing of columns and design and optimisation of columns. The representative developments in these areas, some of which has been reviewed and discussed in this section, are summarised in Table 3.2. Some of these works have been implemented in software codes *i.e.* MAYFLOWER (Malone and Doherty, 1995) and SPLIT (Wahnschafft *et al.*, 1991; Wahnschafft *et al.*, 1992b). Advances have focussed on distillation columns and to determine separation feasibility, analysis is based on residue curve maps or distillation

line maps representing distillation operating lines at total reflux. A limitation to these approaches apart from their sequential nature is that the findings are not readily applicable to different separation technologies and hybrid systems, and thus such non-conventional separation systems need to be studied separately.

In this work, the generalised modular framework is proposed for the separation of azeotropic systems by which entrainer selection and sequencing alternatives can be simultaneously explored in a single optimisation problem. Employing fundamental heat and mass transfer principles coupled with thermodynamic models, distillation columns are not explicitly prepostulated, and separation feasibility is consistently ensured.

Entrainer Selection	
Doherty and Caldarola (1985)	RCM, total reflux, ternary mixtures. Assumes linear distillation boundaries and no boundary crossing.
Stichlmair <i>et al.</i> (1989)	DLM, total reflux, linear distillation boundaries
Foucher <i>et al.</i> (1991)	RCM, total reflux, ternary. Automatic procedure.
Laroche <i>et al.</i> (1991, 1992a)	RCM, ternary. Analysis based on 'equivolatility curves'
Column Sequencing & Bounding Strategies	
Laroche <i>et al.</i> (1992b)	RCM, all reflux, ternary. Separability in single feed columns.
Wahnschafft <i>et al.</i> (1992a)	RCM, all reflux, ternary mixtures, single feed columns. Bounds by feed pinch point trajectories.
Fidkowski <i>et al.</i> (1993b)	DLM, all reflux, ternary, single feed. Introduces 'distillation limit', accounts for boundary crossing, algebraic based.
Stichlmair and Herguajuela (1992)	DLM, all reflux, ternary, single feed. Accounts for curved distillation boundaries.
Jobson <i>et al.</i> (1995)	Achieves attainable product region based on simple distillation and mixing for ternary mixtures
Safrit and Westerberg (1997)	RCM. Algorithm determining boundaries & distillation regions for n-component systems
Rooks <i>et al.</i> (1998)	RCM. Equation based approach to determine distillation region structures of multicomponent mixtures.
Design & Optimisation	
Boundary Value Design Procedure	
Levy <i>et al.</i> (1985)	Ternary mixtures, single feed columns, CMO Ternary, single feed with heat effects Multicomponent, single feed, CMO. Tracks fixed points Ternary, double feed column, CMO. Calculates R_{min} and R_{max} .
Knight and Doherty (1986)	
Julka and Doherty (1990)	
Knapp and Doherty (1994)	
Fidkowski <i>et al.</i> (1991)	Up to 4 components, single feed, CMO. Algebraic continuation arc method to locate tangent pinch
Stichlmair <i>et al.</i> (1993)	Ternary mixture, 'Pinch point' geometry
Bauer and Stichlmair (1995)	Combines pinch point analysis with process MINLP optimisation for ternary mixtures in single feed columns
Castillo <i>et al.</i> (1998a)	Introduces the concept of staged leaves for ternary mixtures in single feed.

Table 3.2: Summary of Design procedures for Homogeneous Azeotropic Separation

3.3 Problem Statement

The separation synthesis problem addressed in this chapter can be stated as follows;

Given

- A multicomponent feed mixture of known nonideal behaviour involving one or more azeotropes and given flowrate, composition and temperature
- A set of products with desired specifications.
- A set of available entrainers that may facilitate the separation and form a *homogeneous* mixture with the feed components.
- Available heat utility streams such as steam and cooling water and specifications on availability, supply temperatures and compositions.
- All thermodynamic property models and required cost data.

Synthesize an optimal separation system, *i.e.* sequence of separators and corresponding entrainer with respect to an overall separation cost. In this work, the separation cost comprises cost of utilities, cost of required separating agent and an approximation of capital costs based on the number and/or type of mass/heat separators as detailed in later sections.

The basic assumptions in this work are

- The thermodynamic state of the feed and product streams are known. As a first analysis saturated liquid feeds and products are considered.
- Total pressure of the system is constant and specified.
- Heaters and coolers are assumed to be total reboilers and condensers respectively
- There is no heat integration between the heaters and coolers

Within the proposed framework, all but the first of these assumptions can be easily relaxed, as detailed later. However, they are imposed to restrict the size of the resulting mathematical model.

3.4 The Mass/Heat Transfer Module

As introduced in Chapter 2, the building block of the proposed framework is based on the mass/heat transfer module whereby process operations are represented by sets of mass and heat transfer between properly defined streams. For simplification purposes, no stream heat integration is considered (all heating and cooling by utility) and the mass/heat exchange block is connected to a heater and a cooler as shown in Figure 3.8. Side mixers and splitters are assigned to each mass/heat exchange module, heater and cooler.

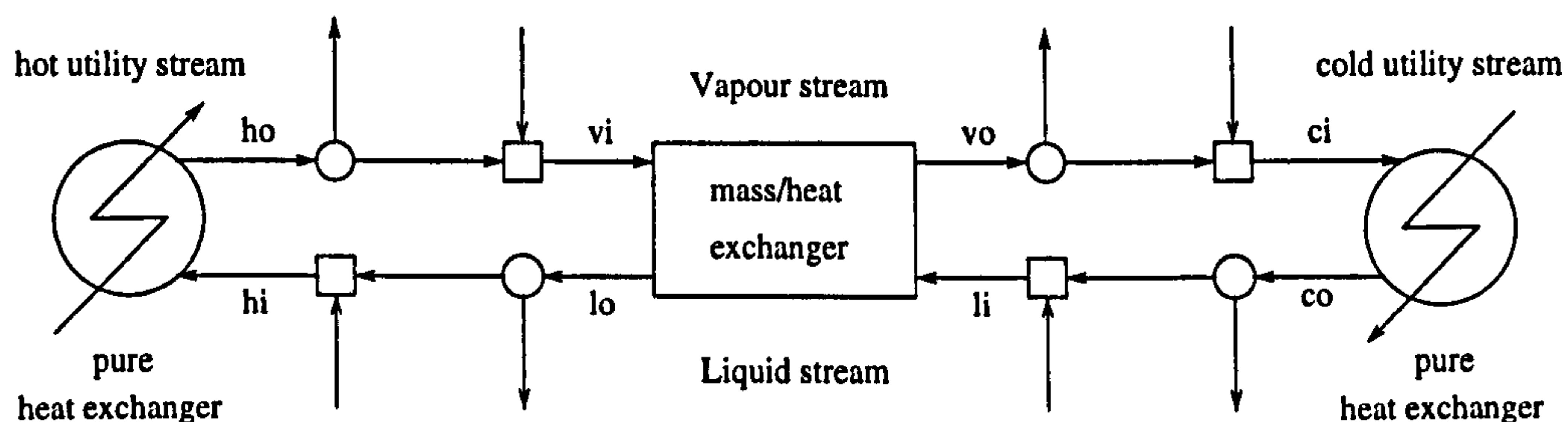


Figure 3.8: Mass/Heat Exchange Block

For the synthesis of homogeneous separation systems, each mass/heat exchanger corresponds to mass and heat transfer between a liquid stream and a vapour stream. To ensure feasible mass transfer within the block, driving force constraints are imposed at the inlet and outlet of the mass/heat exchanger, similar to the ΔT_{min} constraints in pure heat exchangers.

Consider a multicomponent liquid-vapour mixture, where the mixture is a closed system whilst the individual phases are open systems, allowing mass transfer between them. From classical thermodynamics, the change in total Gibbs free energy of the mixture is given by (Smith and Van Ness, 1987)

$$d(nG)^{tot} = (nV)^L dP^L - (nS)^L dT^L + (nV)^V dP^V - (nS)^V dT^V + \sum_{i=1}^C (\mu_i^L dn_i^L + \mu_i^V dn_i^V) \quad (3.14)$$

where $(nG)^{tot}$ is the total Gibbs free energy, V is the mixture volume, P the pressure, S the entropy, T the temperature, μ_i the chemical potential, n_i is the component number of moles, and the superscripts L and V denotes the liquid and vapour phase respectively.

Since no reaction takes place, mass conservation for each component i requires

$$n_i^L + n_i^V = \text{constant}$$

$$\text{and } dn_i^L + dn_i^V = 0$$

At this point, approximate the liquid and vapour phases to have the same temperature and pressure. Therefore at constant T and P ,

$$d(nG)^{tot} = \sum_{i=1}^C (\mu_i^L - \mu_i^V) dn_i^L \quad (3.15)$$

Analogous to the argument introduced in section 2.6, a component i is transferred from the liquid to the vapour phase when both the Gibbs free energy of the system decreases $d(nG)^{tot} \leq 0$, and the liquid holdup of i decreases $dn_i^L \leq 0$ i.e.

$$\frac{\partial(nG)^{tot}}{\partial n_i^L} \geq 0 \quad (3.16)$$

Similarly, for mass transfer of i from the vapour to the liquid,

$$\frac{\partial(nG)^{tot}}{\partial n_i^L} \leq 0 \quad (3.17)$$

Assuming $\partial\mu_i/\partial n_i^L \approx 0$, (3.15) is integrated from a reference state (denoted by $^\circ$),

$$\int_{(nG)^\circ}^{(nG)} d(nG)^{tot} = \int_{n_i^{L,\circ}}^{n_i^L} \sum_{i=1}^C (\mu_i^L - \mu_i^V) dn_i^L \quad (3.18)$$

$$(nG) - (nG)^\circ = \sum_{i=1}^C (\mu_i^L - \mu_i^V) (n_i^L - n_i^{L,\circ}) \quad (3.19)$$

Differentiating with respect to dn_i^L ,

$$\frac{\partial(nG)^{tot}}{\partial n_i^L} = \mu_i^L - \mu_i^V \quad (3.20)$$

The chemical potential of the liquid and vapour streams are given by

$$\mu_i^L = \Delta G_i^{f,L} + RT \ln (\gamma_i x_i^L) \quad (3.21)$$

$$\mu_i^V = \Delta G_i^{f,V} + RT \ln (\phi_i x_i^V P_{tot}) \quad (3.22)$$

where $\Delta G_i^{f,L}$ and $\Delta G_i^{f,V}$ is the Gibbs free energy of formation of pure component i of the liquid and vapour phase respectively at a standard state of 1 atm and temperature of the system, R the gas constant, γ_i the liquid phase activity coefficient, x_i the molar fraction, ϕ_i the vapour phase fugacity coefficient and P_{tot} the system pressure. Assuming negligible effect of pressure on $\Delta G_i^{f,L}$

$$\Delta G_i^{f,L} \approx \Delta G_i^{f,V} + RT \ln(P_i^{sat}) \quad (3.23)$$

Therefore from (3.20),

$$\begin{aligned} \frac{\partial(nG)^{tot}}{\partial n_i^L} &= \Delta G_i^{f,V} + RT \ln(P_i^{sat}) + RT \ln(x_i^L \gamma_i) - \Delta G_i^{f,V} - RT \ln(\phi_i^V x_i^V P_{tot}) \\ &= RT \left[\ln(x_i^L \gamma_i P_i^{sat}) - \ln(\phi_i x_i^V P_{tot}) \right] \end{aligned} \quad (3.24)$$

From (3.16), noting that the product RT is always positive and nonzero, transfer from liquid to vapour occurs when

$$\ln(x_i^L \gamma_i P_i^{sat}) \geq \ln(\phi_i x_i^V P_{tot}) \quad (3.26)$$

$$x_i^L \gamma_i P_i^{sat} \geq \phi_i x_i^V P_{tot} \quad (3.27)$$

$$K_i x_i^L \geq x_i^V \quad \text{where} \quad K_i = \frac{\gamma_i P_i^{sat}}{\phi_i P_{tot}} \quad (3.28)$$

Similarly, for mass transfer from the vapour to liquid, it must hold

$$K_i x_i^L \leq x_i^V \quad (3.29)$$

Extension of these constraints for general mass transfer direction in mass/heat transfer blocks is illustrated as follows. Consider a binary mixture AB in a liquid-vapour mass/heat exchange block $L_{AB} - V_{AB}$ (Figure 3.9). Mass transfer takes place between the liquid and vapour streams when they are not at equilibrium. A is transferred from L_{AB} to V_{AB} when the liquid composition is greater than the equilibrium composition (Figure 3.9(a)) i.e.

$$\begin{aligned} \mathcal{G}_{2A} &\geq 0 \\ \mathcal{G}_{3A} &\geq 0 \end{aligned} \quad (3.30)$$

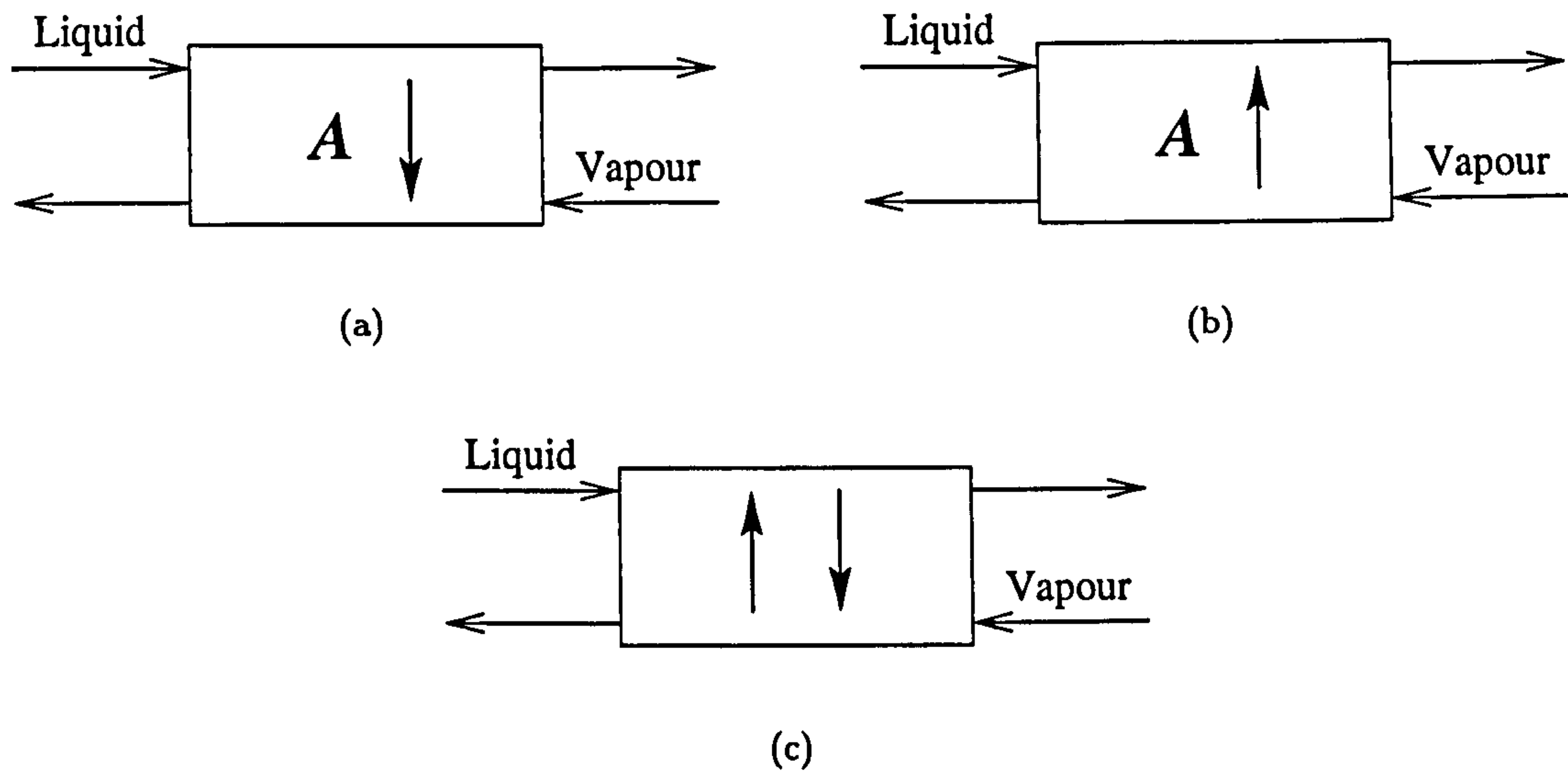


Figure 3.9: Mass transfer in mass/heat exchange block

For the reverse case (see Figure 3.9(b)) A is transferred from V_{AB} to L_{AB} and

$$\begin{aligned} \mathcal{G}_{2A} &\leq 0 \\ \mathcal{G}_{3A} &\leq 0 \end{aligned} \quad (3.31)$$

For the general case, when the mass transfer direction is to be determined, we have

$$\begin{aligned} \mathcal{G}_{1i} * \mathcal{G}_{2i} &\geq 0 \\ \mathcal{G}_{1i} * \mathcal{G}_{3i} &\geq 0 \end{aligned} \quad (3.32)$$

where

$$\mathcal{G}_{1i} = F^{LI} x_i^{LI} - F^{LO} x_i^{LO} \quad (3.33)$$

$$\mathcal{G}_{2i} = K_i^{LI} x_i^{LI} - x_i^{VO} \quad (3.34)$$

$$\mathcal{G}_{3i} = K_i^{LO} x_i^{LO} - x_i^{VI} \quad (3.35)$$

and $\mathcal{G}_{1i}$ denotes the transfer direction. Note that in either transfer direction, ($\mathcal{G}_{1A} \geq 0$ when A is transferred from liquid to vapour and $\mathcal{G}_{1A} \leq 0$ when A is transferred from vapour to liquid), mass transfer is consistently limited by equations (3.32).

$\mathcal{G}_2$ (3.34) and $\mathcal{G}_3$ (3.35) represents how far away the liquid and vapour streams are from phase equilibrium *i.e.* the ‘distance from equilibrium’. When the liquid and vapour

streams are at equilibrium *i.e.* when $\mathcal{G}_2 = \mathcal{G}_3 = 0$, no mass transfer occurs within the module *i.e.* $\mathcal{G}_1 = 0$.

When the relative volatility of the mixture components are known, the bilinear constraints (3.32) are not necessary and the appropriate directional constraints are imposed on the individual components. For example in the binary mixture AB , if A is more volatile than B , A will be transferred from the liquid to the vapour stream and B from the vapour to the liquid stream, and it holds that

$$\begin{aligned} \mathcal{G}_{2A} &\geq 0 & \mathcal{G}_{2B} &\leq 0 \\ \mathcal{G}_{3A} &\geq 0 & \mathcal{G}_{3B} &\leq 0 \end{aligned}$$

For general multicomponent nonideal systems however, the constraints (3.32) do not require prepostulation of mass transfer direction which is an important feature, accounting for phenomena such as

- in nonideal systems, the relative volatility, and thus mass transfer direction, can depend on the mixture conditions (composition, temperature and pressure)
- for azeotropic separation, the effect of the entrainer alters the relative volatility of the mixture and therefore mass transfer direction depends on the entrainer selected
- for general separation systems, the constraints are able to model direct/indirect splits and also nonsharp splits

To avoid the nonlinear, nonconvex constraints (3.32), a set of binary variables to denote the mass transfer direction of each component in a mass/heat exchange block can be introduced *i.e.*

$$y_{tei} = \begin{cases} 1, & \text{when } i \text{ is transferred from liquid to vapour in mass/heat exchange } e \\ 0, & \text{when } i \text{ is transferred from vapour to liquid in mass/heat exchange } e \end{cases}$$

enabling feasible mass transfer to be captured with the following set of mixed integer constraints

$$(y_{tei} - 1) \mathcal{U} \leq \mathcal{G}_{1i} \leq y_{tei} \mathcal{U} \quad (3.36)$$

$$(y_{tei} - 1) \mathcal{U} \leq \mathcal{G}_{2i} \leq y_{tei} \mathcal{U} \quad (3.37)$$

$$(y_{tei} - 1) \mathcal{U} \leq \mathcal{G}_{3i} \leq y_{tei} \mathcal{U} \quad (3.38)$$

where $\mathcal{U}$ is a (large) positive number.

3.5 Motivating Example: Separation of an Ideal Ternary System

To illustrate the necessity of driving force constraints on *all* components within a system, consider the separation of methanol (CH_3OH), ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) in a single distillation column operated at atmospheric pressure. The structure is fixed to 18 equilibrium trays / liquid-vapour modules as shown in Figure (3.10), with the feed location at the 9th tray, two liquid products and two pure heat exchangers corresponding to a total reboiler and condenser. Physical property parameters obtained from Reid (1987) are detailed in Appendix A, and the feed specifications are given in Table 3.3.

Three models are considered

- Tray by tray equilibrium model (Equil)
- Modular model with driving force constraints (3.32) enforced on the light and heavy component (2DF-mod)
- Modular model with driving force constraints (3.32) enforced all three components (3DF-mod)

Two cases are studied

Case I: Fixing the distillate rate at 166 mol/s and maximising the separation efficiency ξ

$$\xi = x_{CH_3OH}^{P1} + x_{C_3H_7OH}^{P2}$$

where $P1$ corresponds to the top distillate product and $P2$ the bottoms product.

Case II: Minimising operating cost

$$\$ / yr = C_{steam} Q_{heat} + C_{cw} Q_{cool}$$

where $C_{steam} = 137.27 \$ / kW yr$, $C_{cw} = 26.19 \$ / kW yr$ and Q_{heat} and Q_{cool} are the reboiler and condenser duties in kW respectively, subject to the product specifications

$$x_{CH_3OH}^{P1} \geq 0.33 \quad x_{C_3H_7OH}^{P2} \geq 0.96$$

3.5.1 Case I

For the tray by tray equilibrium model, maximising separation efficiency gives the composition profiles of Figure 3.11, achieved with a reflux ratio of 10.5. The values of G_1 (3.33) indicating mass transfer direction of each component is shown in Table 3.4. The concentration profile of methanol, the most volatile component, increases up the column to 33.37 %, being transferred from the liquid to the vapour phase on all trays ($G_1 \geq 0$). Propanol, the heaviest component, is transferred from the vapour to the liquid phase ($G_1 \leq 0$) and increases in concentration down the column to a maximum of 99.65 %. The concentration of intermediate component Ethanol increases the column to reach a maximum at tray 15, after which it decreases. On trays 1-15, the concentration of methanol is low and the primary separation operation is that between ethanol-propanol. Therefore on these trays ethanol is transferred from the liquid to the vapour (and propanol from vapour to the liquid). However, at tray 15, the concentration of propanol becomes negligible and that of methanol becomes important, such that the primary separation is that between methanol-ethanol. Ethanol thus features a switch in mass transfer direction, and is transferred from the vapour to the liquid on trays 15-18.

The composition and temperature profiles of the results obtained from the two modular models (with 2 and 3 driving force constraints) are compared to those of the equilibrium model in Figures 3.12. As illustrated, the modular models (2DF-mod and 3DF-mod) give similar profiles to that of the equilibrium model, with that constraining the mass transfer of *all* components giving a closer profile. Upon closer inspection, however, it can be seen that the mass transfer direction of the intermediate ethanol is not correctly described using 2DF-mod (incorrect mass transfer on trays 14-16, see Figure 3.12(b)). Furthermore, the liquid and vapour flowrates of 2DF vary significantly.

Flowrate	277 mol/s
x_{CH_3OH}	0.2
$x_{C_2H_5OH}$	0.4
$x_{C_3H_7OH}$	0.4
Temperature	353.0 K
Pressure	1 atm

Table 3.3: Feed Specifications for Separation of Ideal Ternary Mixture

Value of $G1 = F^{LI}x^{LI} - F^{LO}x^{LO}$			
Tray number	Methanol	Ethanol	Propanol
1	0.022794	5.897852	-5.688272
2	0.067836	11.067718	-10.692685
3	0.200550	20.582721	-19.936719
4	0.585673	37.638398	-36.600507
5	1.672554	66.727829	-65.285541
6	4.592149	111.918659	-110.610083
7	11.810937	170.700686	-171.834271
8	27.519424	223.416220	-233.492206
9	56.264468	232.175606	-264.112844
10	9.495152	230.035144	-219.835122
11	10.710600	192.716669	-185.248583
12	12.833352	130.547913	-129.526360
13	17.787378	70.556002	-78.826083
14	27.791633	22.885511	-43.858536
15	45.681921	-16.425651	-23.137310
16	75.127543	-55.938105	-11.820843
17	119.606820	-103.135267	-5.896954
18	178.792246	-160.288622	-2.861885

Table 3.4: Case I : Mass transfer direction in equilibrium model

	Equil	3DF-Mod
\$/yr		
Q_{steam} (kW)	15404.0	12722.1
Q_{cool} (kW)	15296.5	12677.8
Reflux ratio	2.85	2.48

Table 3.5: Case II : Optimal Results

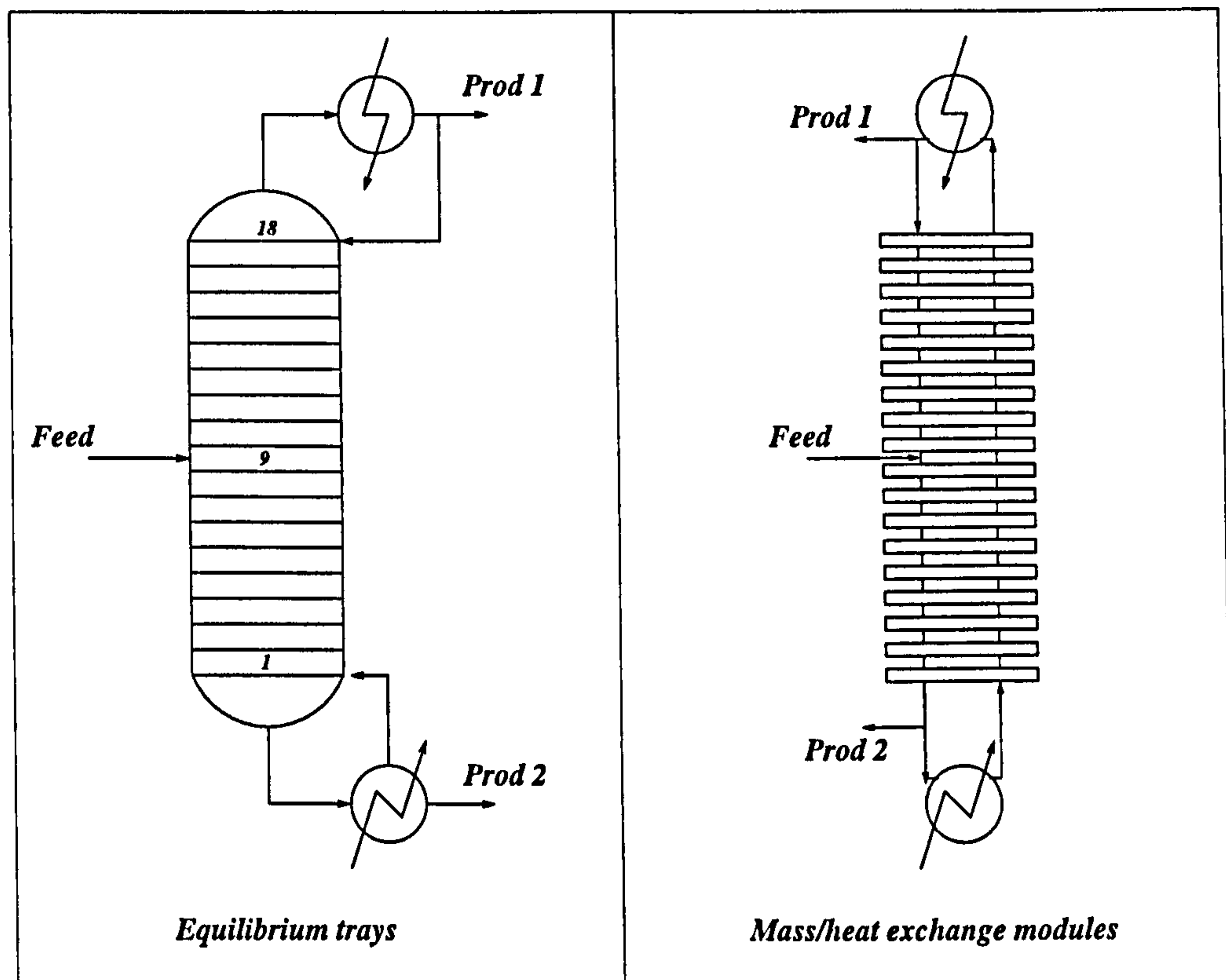


Figure 3.10: Separation of Methanol-Ethanol-1-Propanol

3.5.2 Case II

Minimising operating cost for the equilibrium model gives the composition profiles shown in Figure 3.13. Similar to Case I, the concentration of methanol increases up the column whilst that of propanol increases down the column. The composition profile of ethanol is somewhat flatter than that of Case I, due to the reduced optimal reflux ratio of 2.85 and thus reduced internal flows and separability. A much less distinct maximum is exhibited for the ethanol, but a switch in mass transfer direction for this component still occurs on the top tray.

With the modular model, constraining the mass transfer of only two components results in incorrect modelling of the separation mass transfer. This is illustrated in Figure 3.14, which shows the large deviations in the composition and temperature profiles of model DF2-mod as compared to the equilibrium model. When the mass transfer of all three components are constrained (DF3-mod), the composition and temperature profiles obtained are similar to that of the equilibrium model, capturing the switch in mass transfer direction of ethanol in the top stage. The optimal heat exchanger duties and reflux ratios of the equilibrium model and the full modular model are similar (Table 3.5), with the

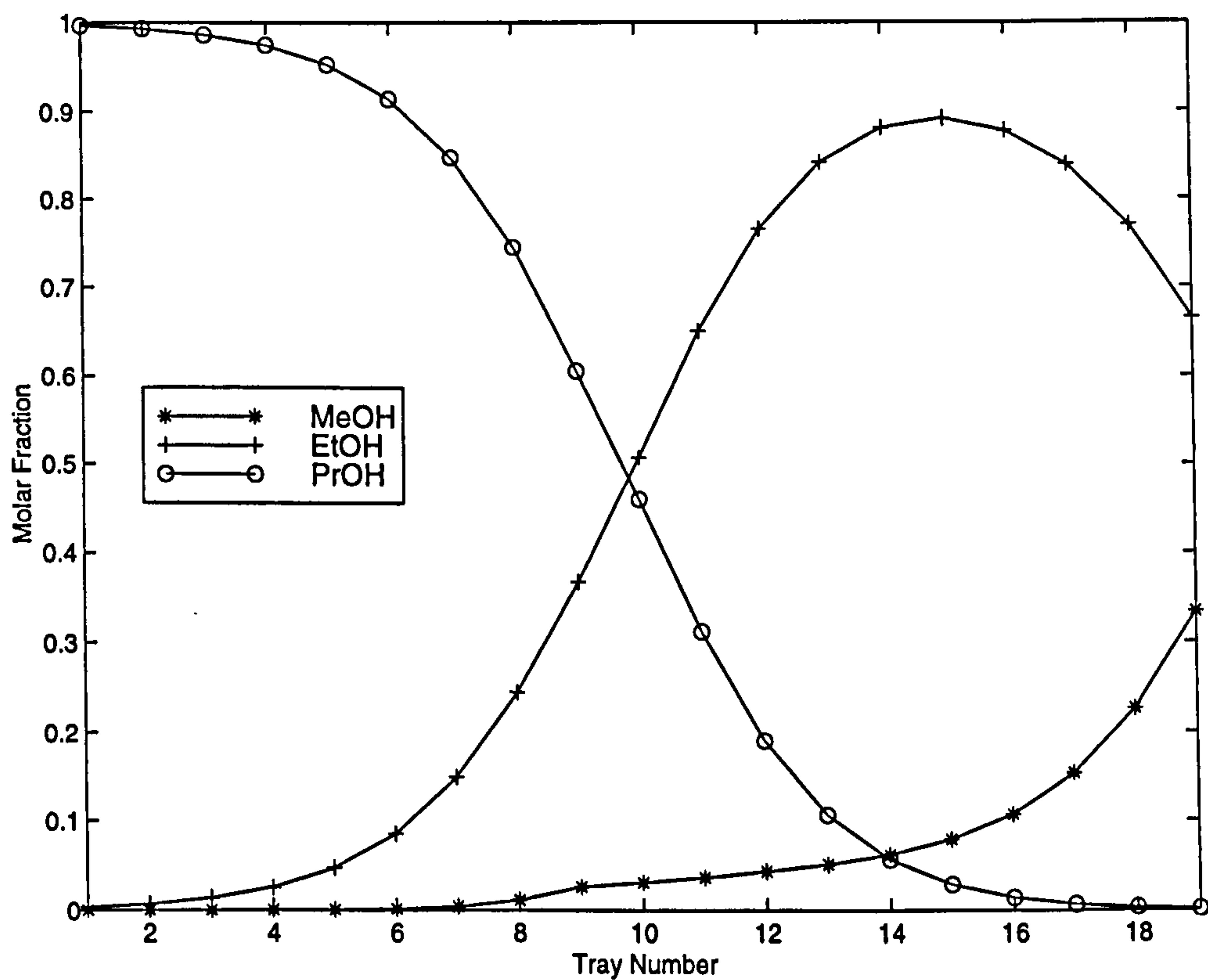
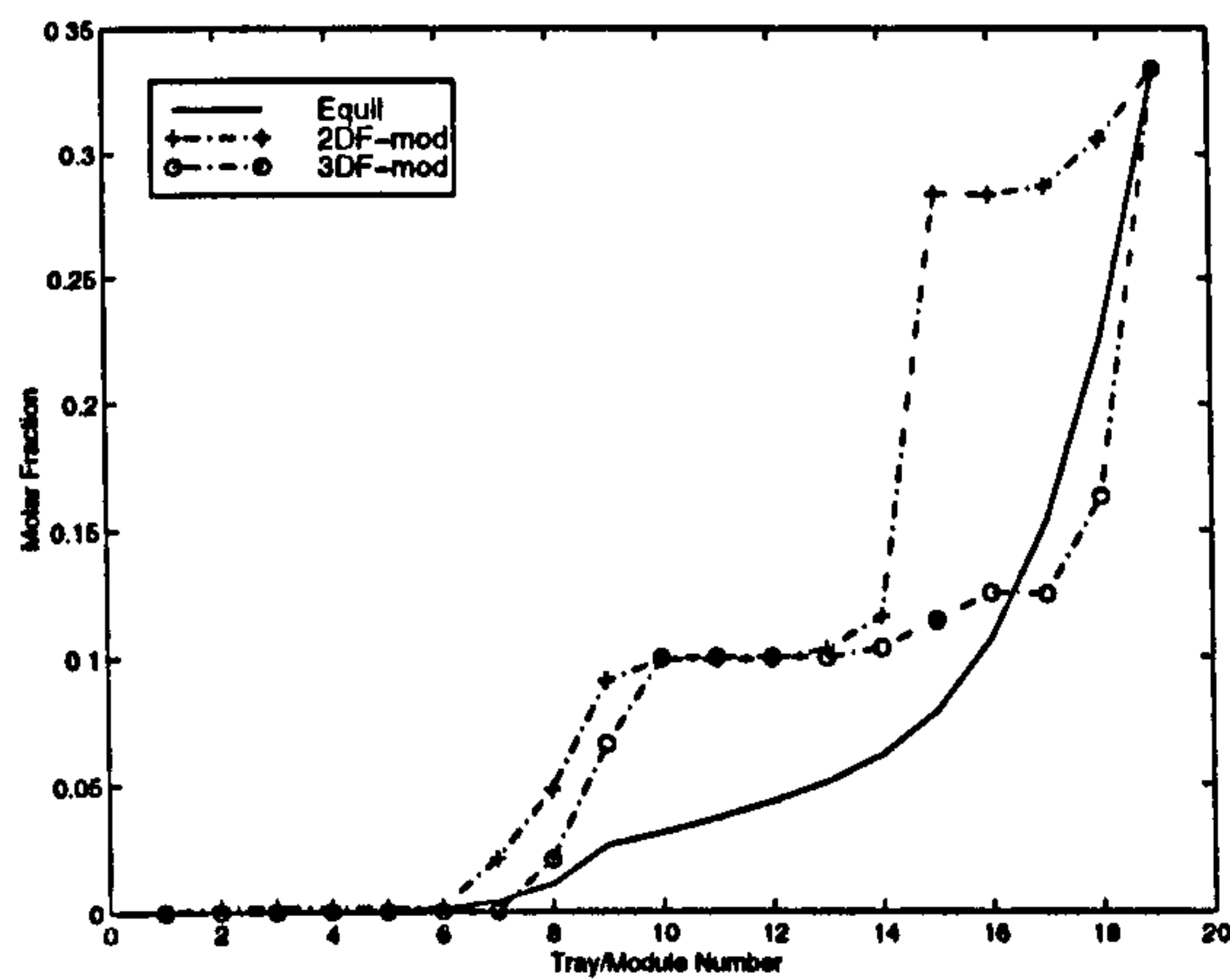


Figure 3.11: Case I : Equilibrium model composition profile

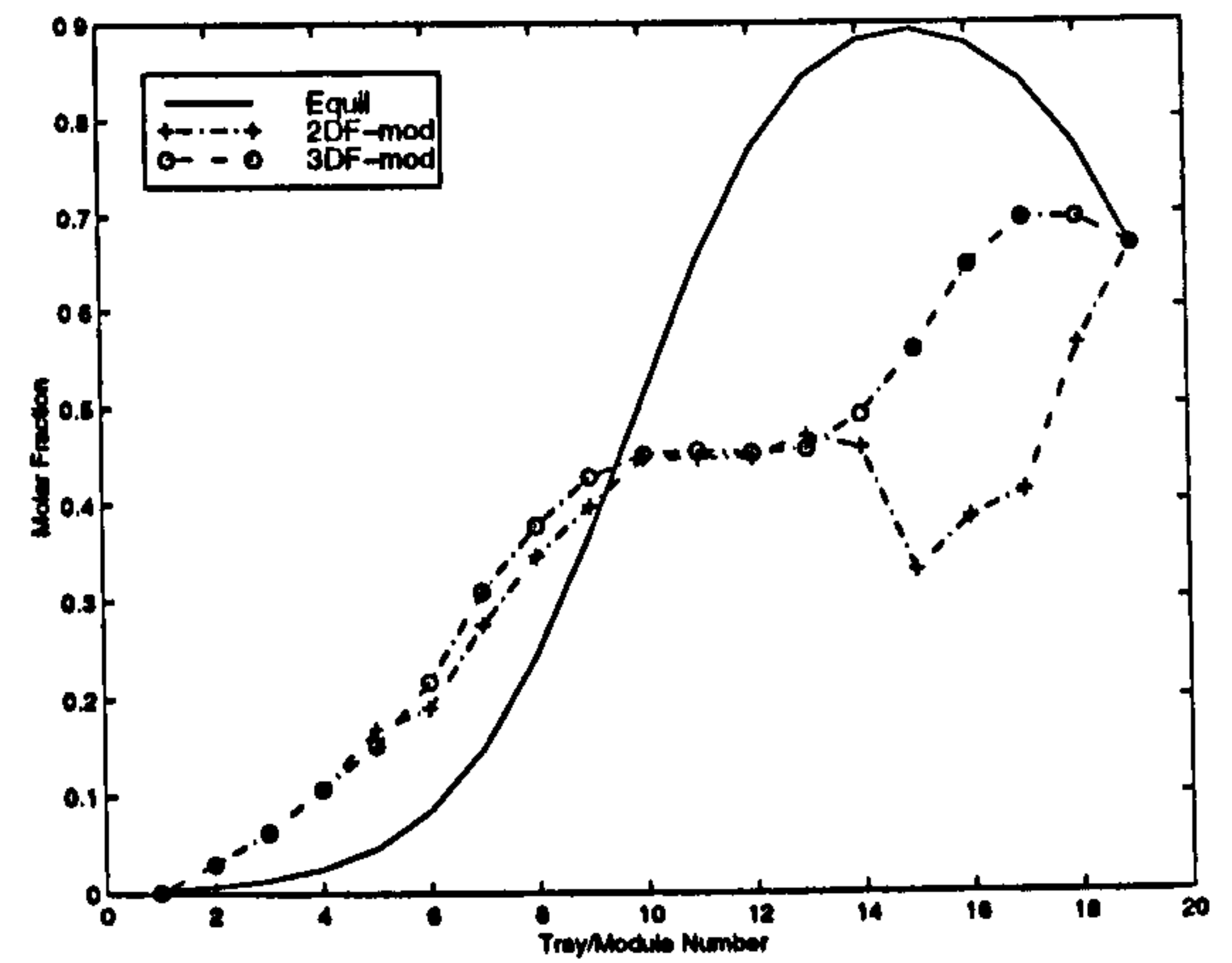
objective of the modular model slightly smaller. This is because in general, a module represents more than one tray, thus allowing the same separation to be achieved at slightly lower reflux.

3.5.3 Discussion

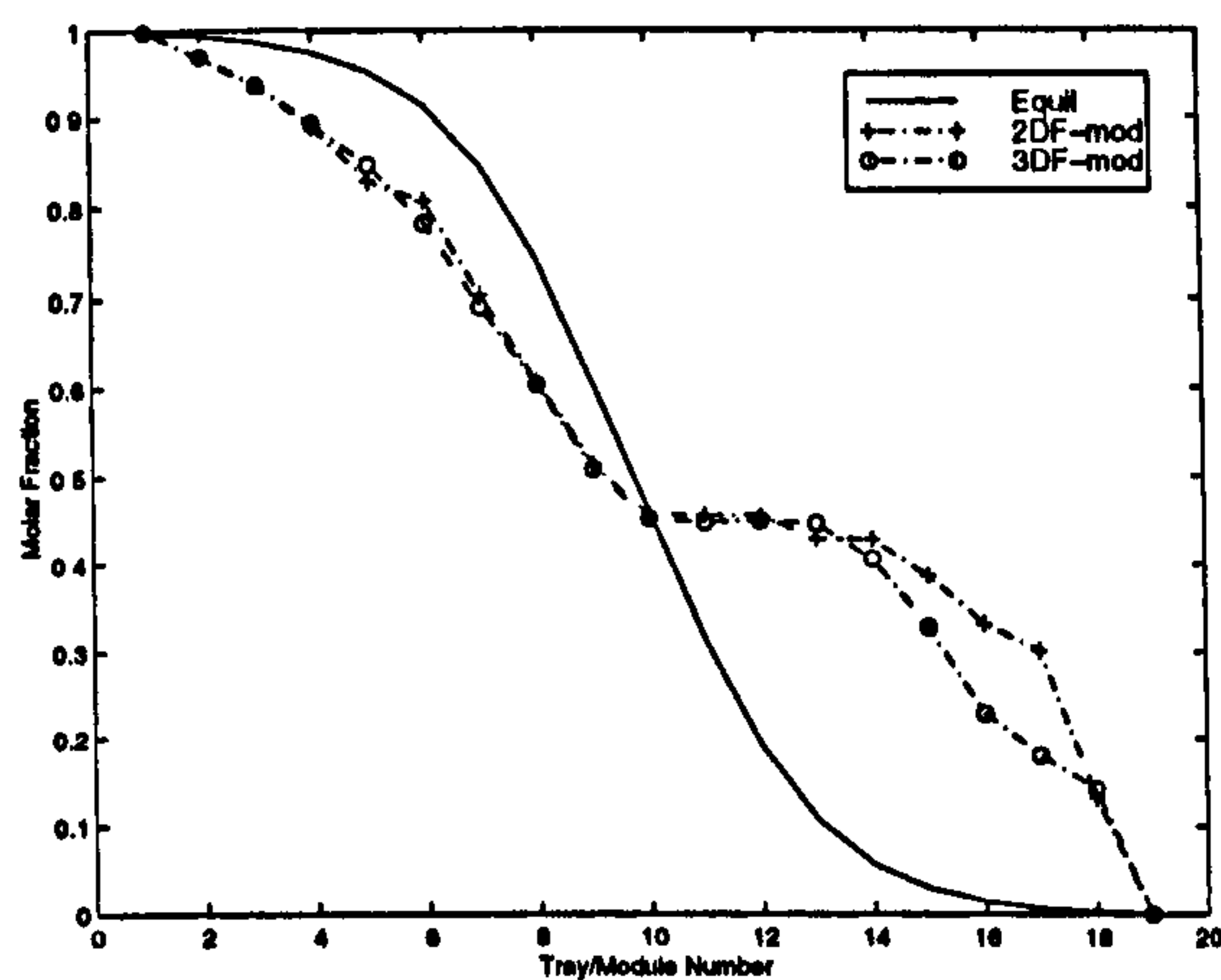
This example highlights that even for the separation of ideal ternary systems, the mass transfer direction of *all system components* must be modelled to correctly characterise mass transfer phenomena. Furthermore, the driving force constraints derived in section 3.4 are consistent with the phase equilibrium model, capturing the mass transfer trends.



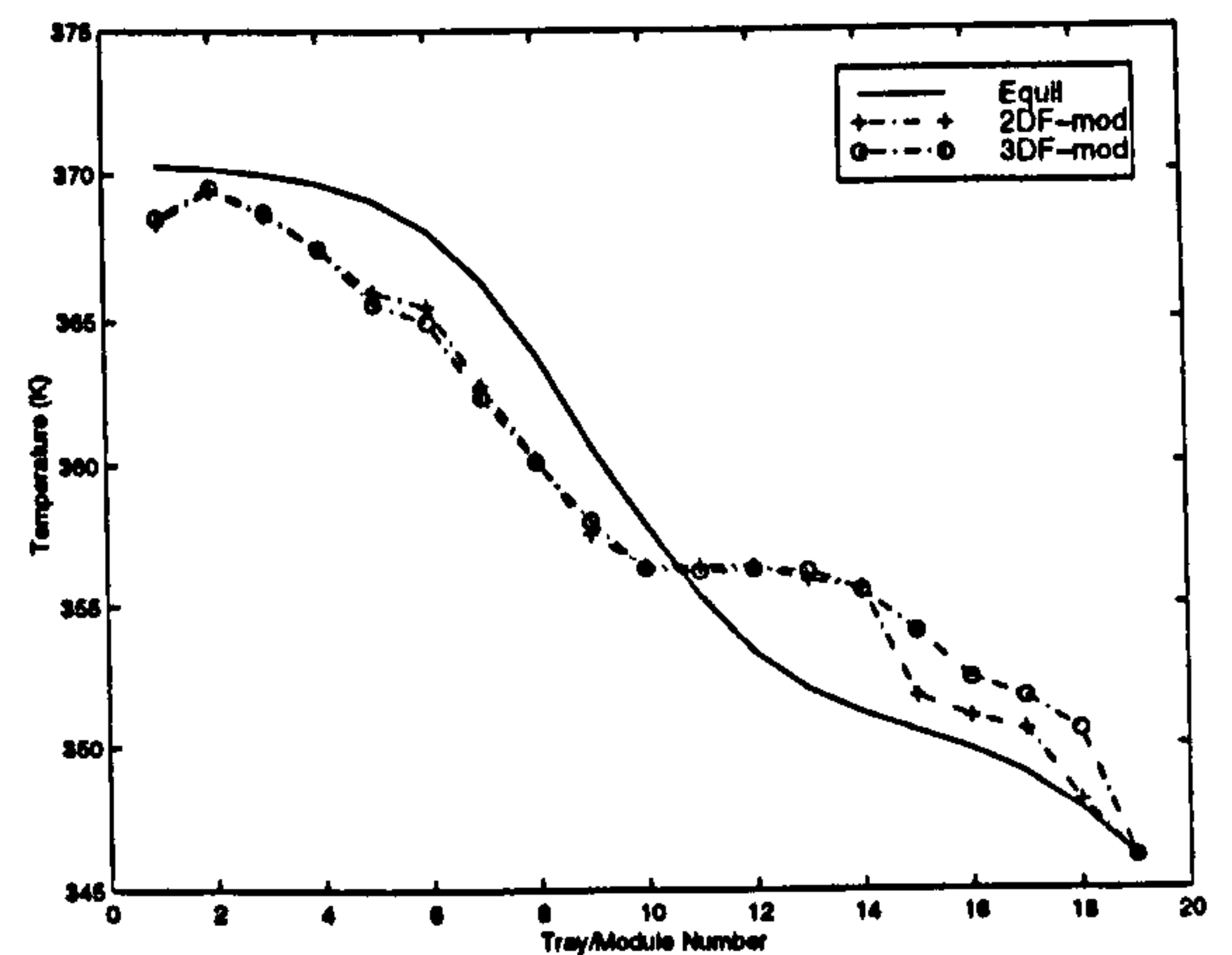
(a) Methanol Composition



(b) Ethanol Composition



(c) Propanol Composition



(d) Temperature Profile

Figure 3.12: Case I : Comparison of composition and temperature profiles for the modular and equilibrium models

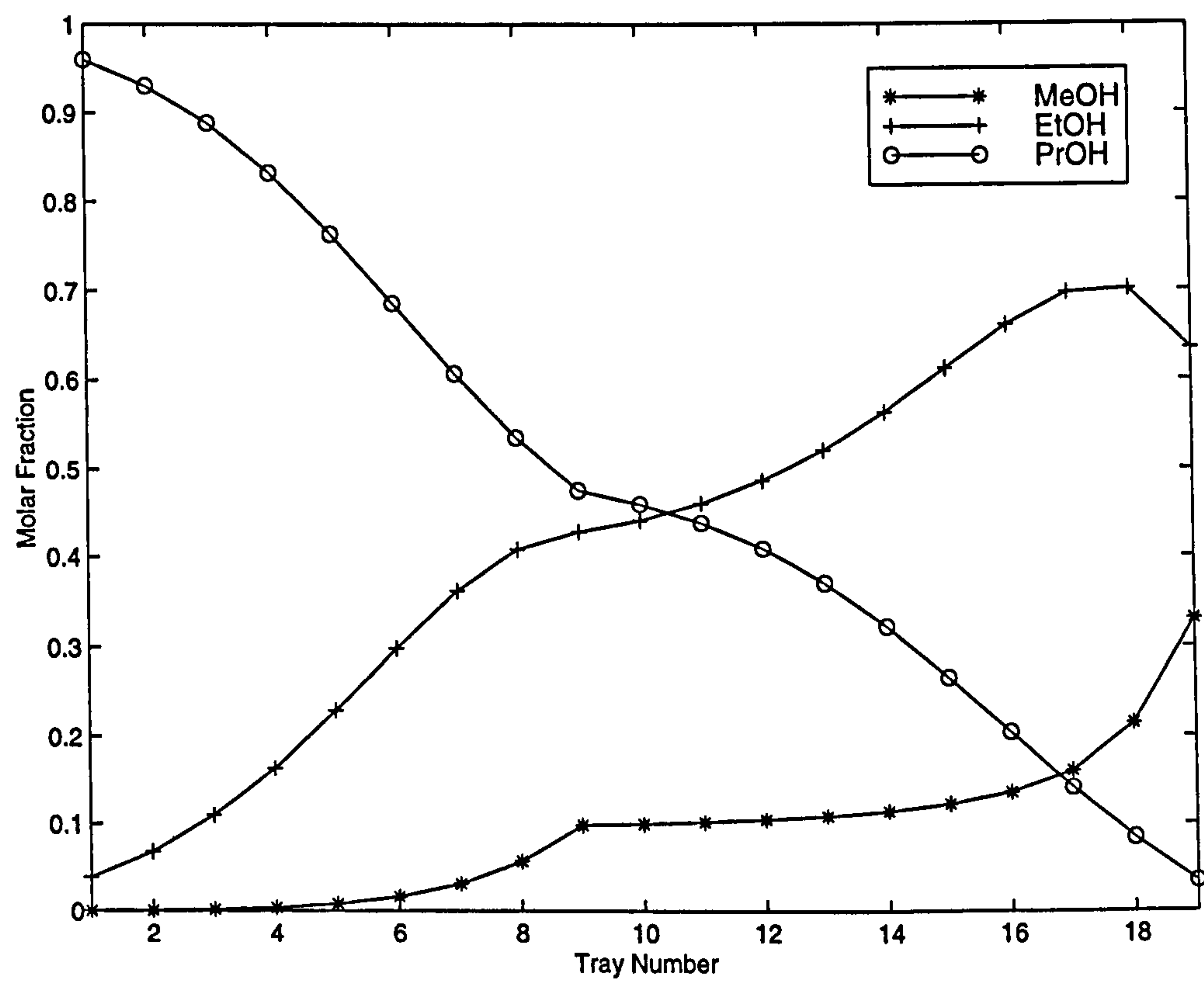
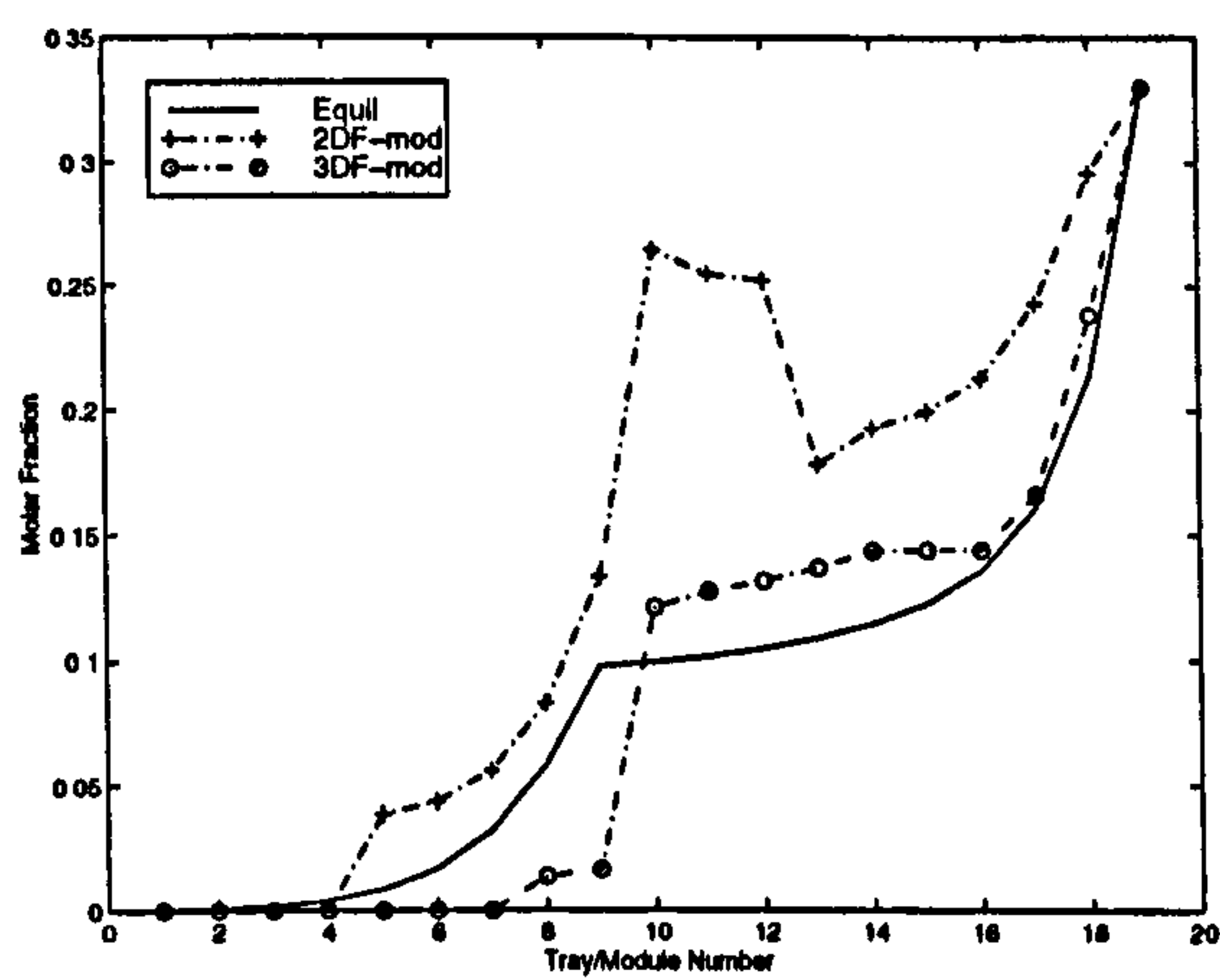
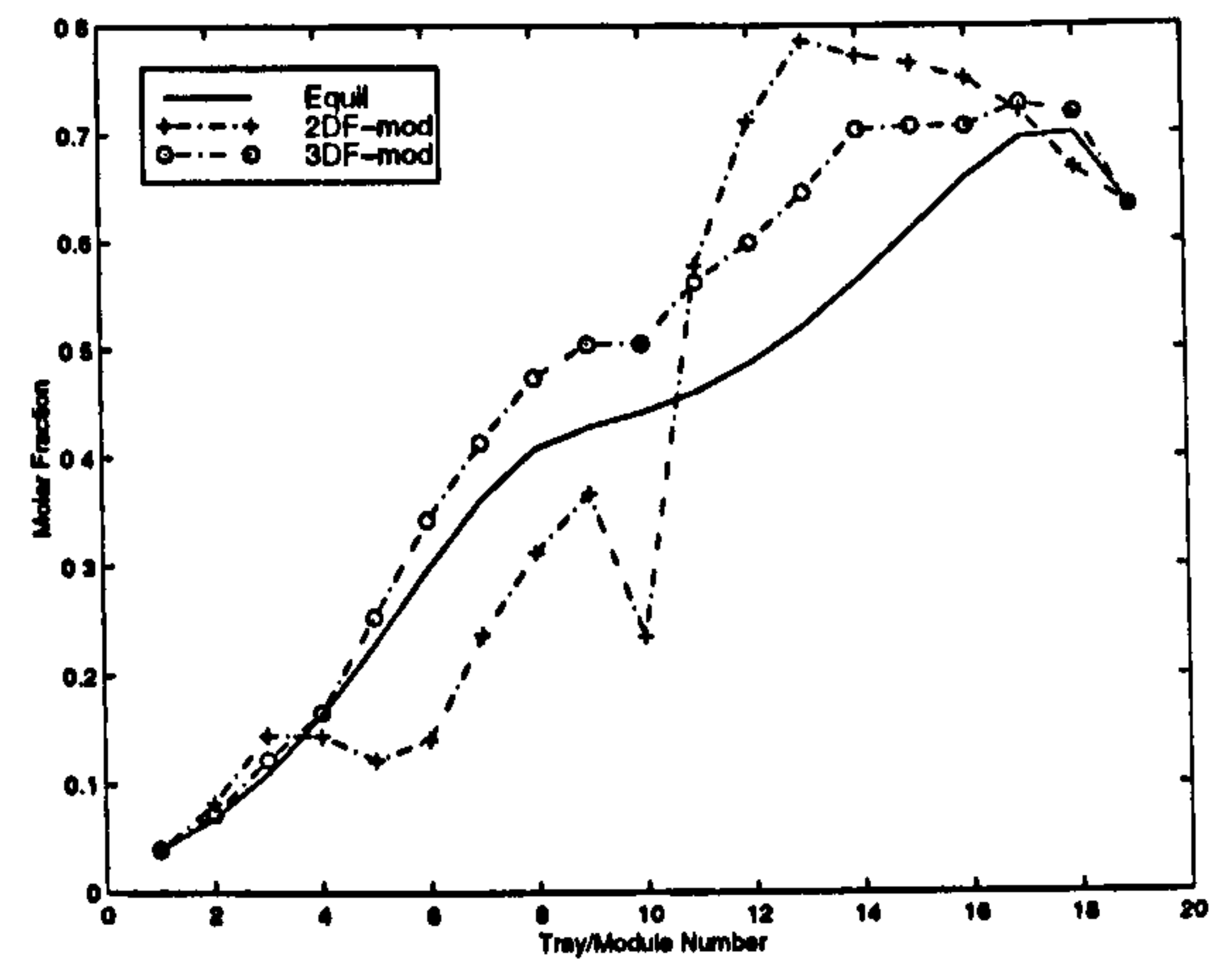


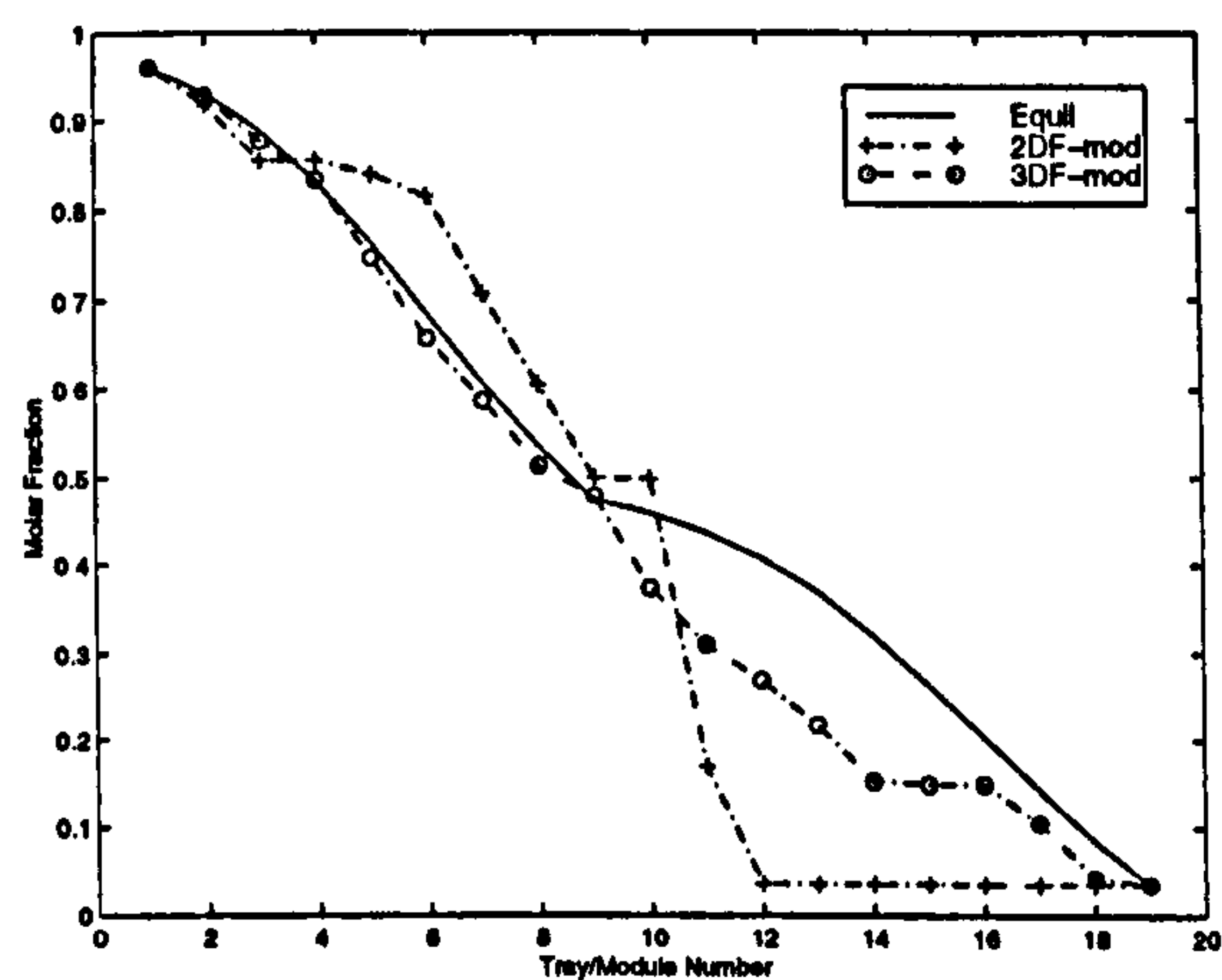
Figure 3.13: Case II: Equilibrium model composition profile



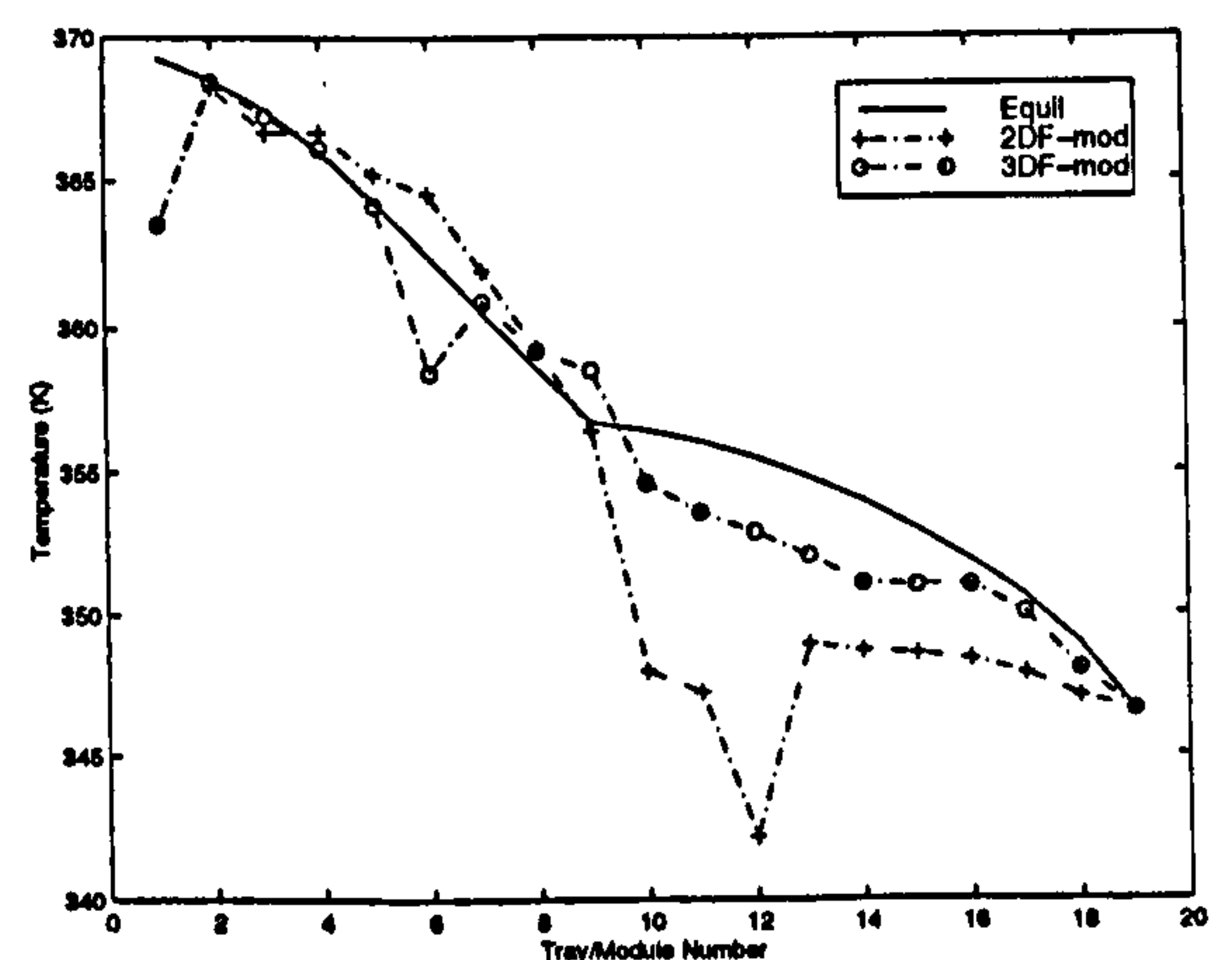
(a) Methanol Composition



(b) Ethanol Composition



(c) Propanol Composition



(d) Temperature Profile

Figure 3.14: Case II : Comparison of composition and temperature profiles for the modular and equilibrium models

3.6 Characterisation of Nonideal Mixtures

Nonideal behaviour can be captured employing detailed thermodynamic models for the calculation of the liquid phase activity coefficient γ_i and the vapour phase fugacity coefficient ϕ_i .

To test that the driving force constraints are sufficient to characterise a nonideal mixture and capture the presence of an azeotrope, consider a binary mixture of ethanol and water. The ethanol-water system has been studied extensively, and at a pressure of 1 atm and temperature of 78.15°C , a minimum boiling azeotrope is formed at 89.43 % mole ethanol. The separation of the binary mixture at 1 atm is considered in a configuration of 20 mass/heat exchanger modules simulating a distillation column (Figure 3.15). The NRTL equation as derived by (Renon and Prausnitz, 1968) is utilised to model the liquid phase nonidealities, and the pure component thermodynamic data is given in Appendix A. The vapour phase is assumed to behave ideally at this pressure ($\phi_i^V \approx 1$), as confirmed by the use of a semi-empirical equation of state (Black, 1958). The vapour-liquid equilibrium curves using these thermodynamic models is consistent with experimental data (Carey and Lewis, 1932), as shown in Figure 3.16. Maximising the ethanol concentration of the distillate results in the azeotropic mixture of 89.8 % ethanol concentration (Table 3.6), illustrating that the driving force constraints are able to properly capture the thermodynamic limitation (of the azeotrope).

	Feed	Distillate	Bottoms
T (K)	333.15	351.424	348.93
X_{eth}	0.7	0.898	0.314
X_{wat}	0.3	0.102	0.686
Flow (mol/s)	10.0	6.606	3.394

Table 3.6: Material balance for Ethanol-Water Separation

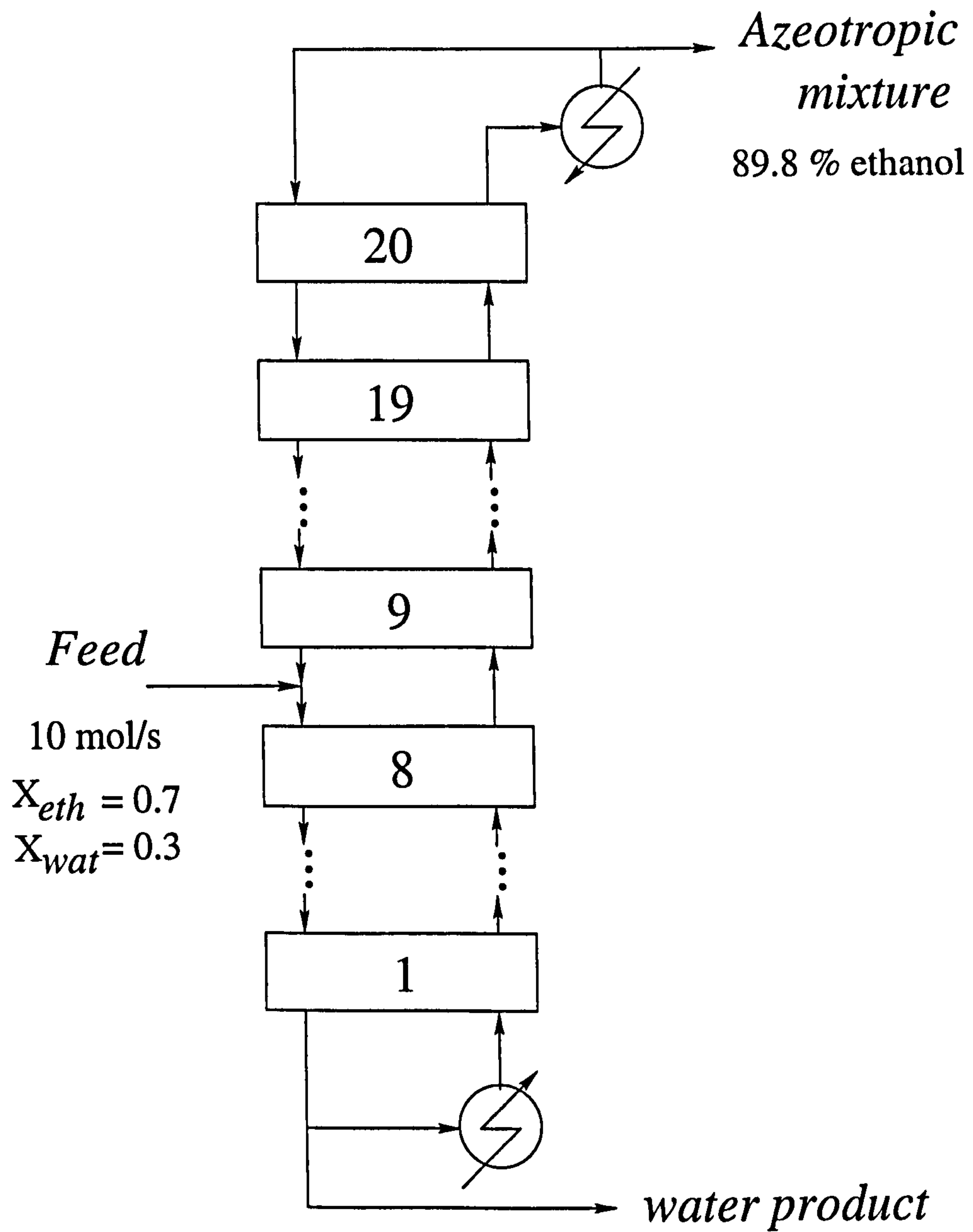


Figure 3.15: Separation of Ethanol-Water Mixture

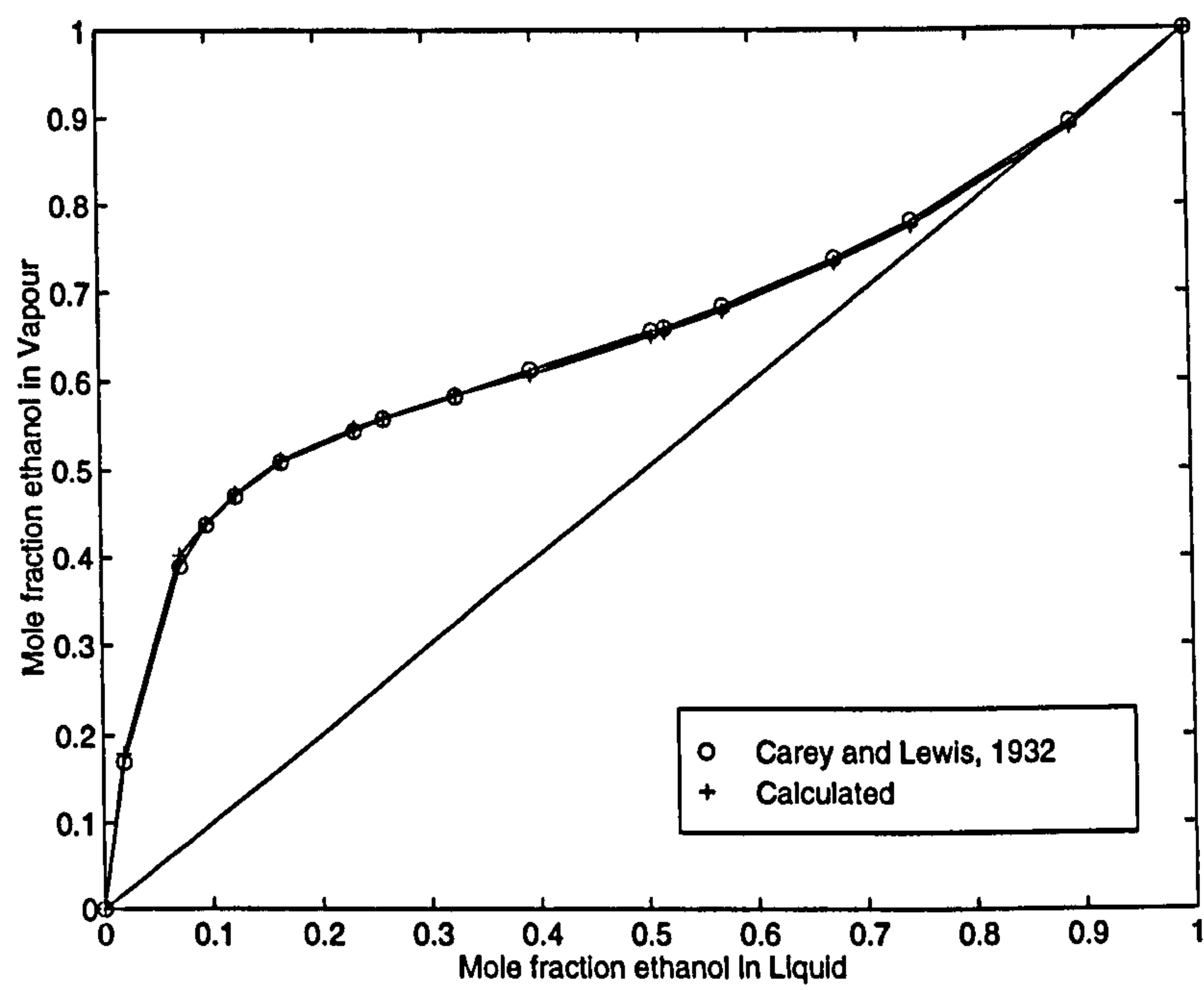


Figure 3.16: Vapour-liquid equilibrium diagram for Ethanol-water at 1 atm

3.7 Synthesis Framework for Azeotropic Separations

The main feature of the mass/heat exchange modular synthesis framework is that all feasible alternatives are considered in a mass/heat superstructure. For the separation of azeotropic mixtures, the framework as introduced in section 2.8 includes the following:

Stream Superset

Defining a stream by its phase, a general mixed stream containing all components concerned in all possible phases is considered to account for all possible initial, intermediate and final streams that may exist in a process. For homogeneous mixtures, only liquid and vapour streams are of interest, and therefore a liquid and vapour stream containing all possible components is accounted for.

Consider the separation of an azeotropic system AB whose separation may be facilitated by the addition of either a light entrainer L or a heavy entrainer H . The stream superset thus consists of a liquid and vapour mixed stream L_{LABH} and V_{LABH} which accounts for all possible streams as follows:

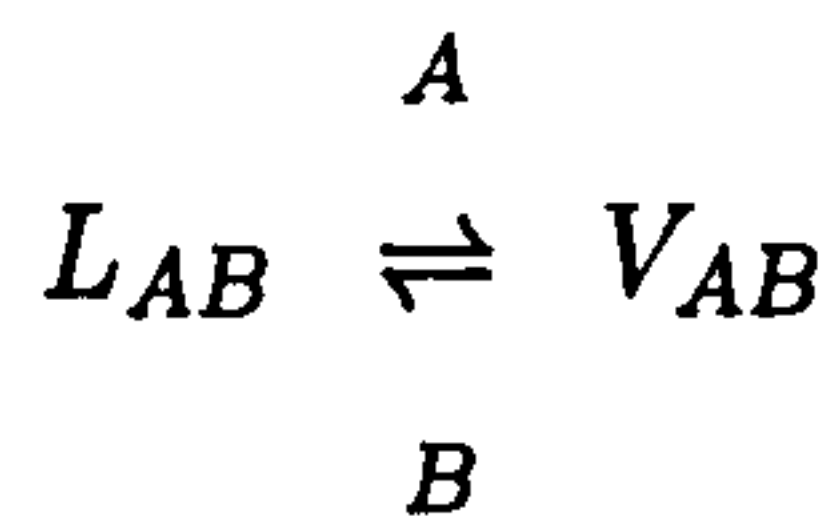
- the binary feed stream is an instance of the liquid mixed stream L_{LABH} with $x_L = x_H = 0$
- the feed of the light entrainer by setting $x_L = 1, x_A = x_B = x_H = 0$.
- a product stream of almost pure A will be an instance of a liquid stream with $x_A = 1, x_B = x_L = x_H = 0$

All possible intermediate streams are also considered in a similar fashion.

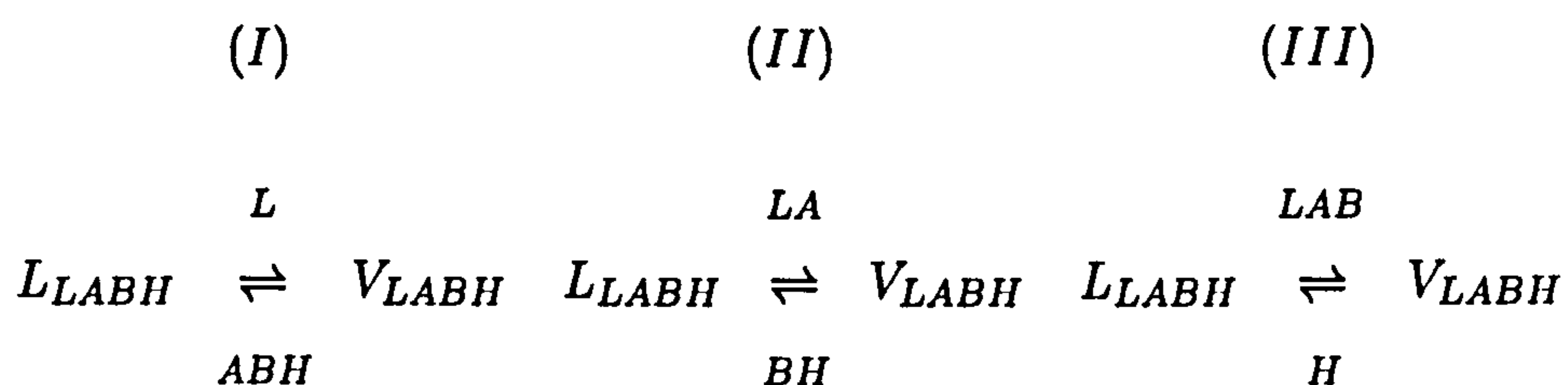
Mass/heat exchange matches

For the separation of a *homogeneous* mixture where no reaction occurs, mass transfer can only take place due to volatility differences between liquid and vapour streams; therefore only liquid-vapour stream matches are considered. Possible mass transfer directions for each component in a multicomponent mixture define more than one mass exchange pattern, thus multiple liquid-vapour matches corresponding to multiple mass/heat exchange modules are considered.

For the case of the binary system AB , multiple matches corresponding to mass transfer of A from the liquid to the vapour and that of B from the vapour to the liquid are considered, represented by



For a multicomponent system, such as $LABH$ described earlier, multiple $L_{LABH} - V_{LABH}$ matches are considered to allow for alternative mass transfer directions (and thus structures). Assuming for example $L > A > B > H$ in terms of volatility, we may have



Matches of type (I) corresponds to a L/ABH split, matches of type (II) to a LA/BH split, and so on.

Note however that mass transfer direction for each component, and thus order of volatility, is not prepostulated in the considered matches (as discussed in the previous section). This is of particular importance for nonideal separation whereby the order of volatility may change depending on the entrainer used.

Mass/heat exchange network superstructure model

To develop a superstructure we account for

- an initial splitter for each initial (feed) stream, from where flows are directed to the mixers of the modules that correspond to streams of the same phase and final mixers of product streams.
- a final mixer for each possible product stream, to where flows from the outlet splitters of the mass/heat exchange modules (that correspond to streams of the same phase) and initial stream splitters are merged towards a final product flow.
- interconnecting streams between the splitters and mixers of the mass/heat exchange modules. Note that only streams of the same phase are allowed to mix.

(Figure 3.17 for $I = 1$ initial splitters (liquid), $P = 1$ final products (liquid) and $e = 3$ mass/heat modules.) Furthermore, logic can be applied to screen out interconnections that cannot exist, thereby resulting in a reduced superstructure (*e.g.* recycling of a stream that has just been separated is illogical and not allowed, a stream that has just been heated should not be directed to a cooler). The mathematical model for the resulting network is formulated as a mixed integer nonlinear problem (MINLP), consisting of mass and energy balances, mass transfer driving force constraints, phase defining constraints for each stream, logical constraints to fathom out infeasible structures and an objective function. The full mathematical model is detailed in the next section.

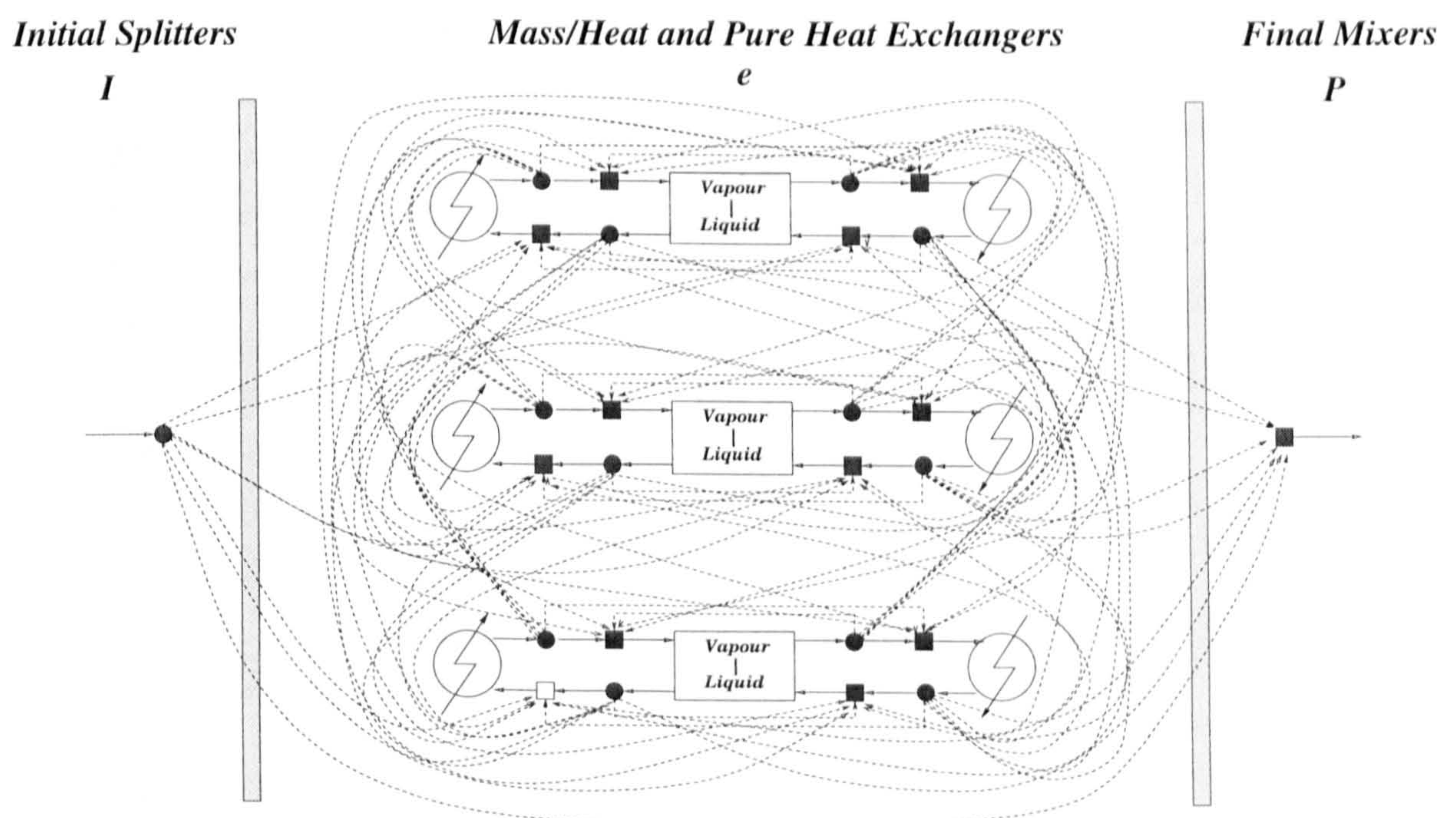


Figure 3.17: Superstructure Network

3.8 Mass/Heat Exchange Superstructure Model

Consider the mass/heat exchange module of Figure 3.8 and the reduced mass/heat exchange superstructure as described in the previous section. The existence (or not) of each module in the final flowsheet is denoted by a binary variable

$$y_e = \begin{cases} 1, & \text{if module } e \text{ exists} \\ 0, & \text{otherwise} \end{cases}$$

Considering liquid feeds and products, the following sets are introduced for the streams of the mass/heat exchange superstructure;

- I = $\{n/n$ initial stream including given feeds and possible entrainers $\}$
- P = $\{p/p$ product stream $\}$
- LI_e = $\{s/s$ liquid inlet stream li in mass/heat exchanger e $\}$
- LO_e = $\{s/s$ liquid outlet stream lo in exchanger e $\}$
- VI_e = $\{s/s$ vapour inlet stream vi in mass/heat exchanger e $\}$
- VO_e = $\{s/s$ vapour outlet stream vo in exchanger e $\}$
- HI_e = $\{s/s$ inlet stream hi of the utility heater of module e $\}$
- HO_e = $\{s/s$ outlet stream ho of the utility heater of module e $\}$
- CI_e = $\{s/s$ inlet stream ci of the utility cooler of module e $\}$
- CO_e = $\{s/s$ outlet stream co of the utility cooler of module e $\}$
- $LL_{ee'}$ = $\{s/s$ interconnecting stream from liquid outlet splitter of module e to liquid inlet mixer of module e' $\}$
- $VV_{ee'}$ = $\{s/s$ interconnecting stream from vapour outlet splitter of module e to vapour inlet mixer of module e' $\}$
- $LH_{ee'}$ = $\{s/s$ interconnecting stream from liquid outlet splitter of module e to utility heater of module e' $\}$
- $HV_{ee'}$ = $\{s/s$ interconnecting stream from utility heater of module e to vapour inlet mixer of module e' $\}$
- $VC_{ee'}$ = $\{s/s$ interconnecting stream from vapour outlet splitter of module e to utility cooler of module e' $\}$
- $CL_{ee'}$ = $\{s/s$ interconnecting stream from utility cooler of module e to liquid inlet mixer of module e' $\}$
- IL_{ne} = $\{s/s$ interconnecting stream from initial stream n to liquid inlet mixer of module e $\}$

$$\begin{aligned}
 IH_{ne} &= \{s/s \text{ interconnecting stream from initial stream } n \\
 &\quad \text{to utility heater of module } e\} \\
 IP_{np} &= \{s/s \text{ interconnecting stream from initial stream } n \\
 &\quad \text{to final mixer of product } p\} \\
 LP_{ep} &= \{s/s \text{ interconnecting stream from liquid outlet splitter} \\
 &\quad \text{of module } e \text{ to final mixer of product } p\} \\
 CP_{ep} &= \{s/s \text{ interconnecting stream from utility cooler of module } e \\
 &\quad \text{to final mixer of product } p\}
 \end{aligned}$$

$$\begin{aligned}
 \mathcal{S} &= I \cup P \cup LI_e \cup LO_e \cup VI_e \cup VO_e \cup HI_e \cup HO_e \\
 &\quad \cup CI_e \cup CO_e \cup LL_{ee'} \cup VV_{ee'} \cup LH_{ee'} \cup HV_{ee'} \\
 &\quad \cup VC_{ee'} \cup CL_{ee'} \cup IL_{ne} \cup IH_{ne} \cup IP_{np} \cup LP_{ep} \cup CP_{ep} \\
 \mathcal{S1}(\mathcal{S}) &= I \cup P \cup LI_e \cup LO_e \cup VI_e \cup VO_e \\
 &\quad \cup HI_e \cup HO_e \cup CI_e \cup CO_e
 \end{aligned}$$

The set of initial streams is made up of a set of given feed streams and possible entrainers

$$\begin{aligned}
 I &= I1 \cup I2 \\
 I1 &= \{n1/n1 \text{ set of initial existing feeds } \} \\
 I2 &= \{n2/n2 \text{ set of possible entrainers} \}
 \end{aligned}$$

The following set of continuous variables are introduced to describe the superstructure streams;

$$\begin{aligned}
 f^s &\text{ molar stream flow} & s \in \mathcal{S} \\
 x_i^s &\text{ molar fraction of component } i \text{ in stream } s \\
 h^s &\text{ enthalpy} & s \in \mathcal{S1} \\
 T^s &\text{ temperature}
 \end{aligned}$$

Since composition, temperature and enthalpy of streams coming out of the superstructure splitters are equal to composition, temperature and enthalpy of the stream entering the mixer, these variables are only defined for the liquid and vapour inlet and outlet streams of the mass/heat exchange modules, the inlet and outlet streams of the utility

heat exchangers and the initial and final product streams (subset $S1$). In addition, since no mass transfer occurs in the utility heat exchangers, the inlet and outlet stream flows and composition through them are unchanged and are described by one set of flow and compositions variables *i.e.* for the utility cooler, $f^C = f^{CI} = f^{CO}$ and $x_i^C = x_i^{CI} = x_i^{CO}$, for utility heater $f^H = f^{HI} = f^{HO}$ and $x_i^H = x_i^{HI} = x_i^{HO}$. Finally, variable heat loads of the utility exchanger (Qh_e, Qc_e) are defined, positive for heat input and negative for heat removal. As described in Table 3.7, binary variables are defined to denote the existence (or not) of superstructure streams in the final flowsheet. Note that these variables are not necessary, thus their presence does not increase the combinatorial complexity of the synthesis problem. They are utilised to simplify the solution of the nonlinear part of the superstructure model and to facilitate the introduction of logical constraints to the model.

Similarly, the utilisation (or not) of an entrainer is denoted by a binary variable

$$ysolv_n = \begin{cases} 1, & \text{if entrainer } n \text{ is utilized} \\ 0, & \text{otherwise} \end{cases}$$

Mass transfer direction for each component in each module is denoted by a binary variable

$$y_{tei} = \begin{cases} 1, & \text{when component } i \text{ is transferred from liquid to vapour in module } e \\ 0, & \text{otherwise} \end{cases}$$

Once again, this variable is not necessary. However, its inclusion simplifies the mass transfer driving force constraints.

The mass/heat exchange superstructure model involves:

◇ Mass balance for total stream flows at

- initial stream splitters $n \in I$

$$f_n^I - \sum_e f_{ne}^{IL} - \sum_e f_{ne}^{IH} - \sum_p f_{np}^{IP} = 0 \quad (3.39)$$

- splitters at the outlets of each side of module e

$$f_e^{LO} - \sum_{e'} (f_{ee'}^{LL} + f_{ee'}^{LH}) - \sum_p f_{ep}^{LP} = 0 \quad (3.40)$$

$$f_e^{VO} - \sum_{e'} (f_{ee'}^{VV} + f_{ee'}^{VC}) = 0 \quad (3.41)$$

$$f_e^H - \sum_{e'} f_{ee'}^{HV} = 0 \quad (3.42)$$

$$f_e^C - \sum_{e'} f_{ee'}^{CL} - \sum_p f_{ep}^{CP} = 0 \quad (3.43)$$

- mixers at the inlets of the mass/heat exchange module e

$$f_e^{LI} - \sum_n f_{ne}^{IL} - \sum_{e'} (f_{e'e}^{LL} + f_{e'e}^{CL}) = 0 \quad (3.44)$$

$$f_e^{VI} - \sum_{e'} (f_{e'e}^{VV} + f_{e'e}^{HV}) = 0 \quad (3.45)$$

- mixers of the utility exchangers e

$$f_e^C - \sum_{e'} f_{e'e}^{VC} = 0 \quad (3.46)$$

$$f_e^H - \sum_n f_{ne}^{IH} - \sum_{e'} f_{e'e}^{LH} = 0 \quad (3.47)$$

- final stream mixers $p \in P$

$$f_p^P - \sum_n f_{np}^{IP} - \sum_e f_{ep}^{LP} - \sum_e f_{ep}^{CP} = 0 \quad (3.48)$$

◇ Mass Balances for each component at

- mixers prior to liquid and vapour sides of each module e

$$f_e^{LI} x_{ei}^{LI} - \sum_n f_{ne}^{IL} x_{ni}^I - \sum_{e'} (f_{e'e}^{LL} x_{e'i}^{LO} + f_{e'e}^{CL} x_{e'i}^C) = 0 \quad (3.49)$$

$$f_e^{VI} x_{ei}^{VI} - \sum_{e'} (f_{e'e}^{VV} x_{e'i}^{VO} + f_{e'e}^{HV} x_{e'i}^H) = 0 \quad (3.50)$$

- mixers prior to utility exchangers e

$$f_e^C x_{ei}^C - \sum_{e'} f_{e'e}^{VC} x_{e'i}^{VO} = 0 \quad (3.51)$$

$$f_e^H x_{ei}^H - \sum_n f_{ne}^{IH} x_{ni}^I - \sum_{e'} f_{e'e}^{LH} x_{e'i}^{LO} = 0 \quad (3.52)$$

- final mixer of each product stream $p \in P$

$$f_p^P x_i^P - \sum_n f_{np}^{IP} x_{ni}^I - \sum_e (f_{ep}^{LP} x_{ei}^{LO} + f_{ep}^{CP} x_{ei}^C) = 0 \quad (3.53)$$

- around each mass/heat exchange block

$$f_e^{LI} x_{ei}^{LI} + f_e^{VI} x_{ei}^{VI} - f_e^{LO} x_{ei}^{LO} - f_e^{VO} x_{ei}^{VO} = 0 \quad (3.54)$$

◇ Energy balances at

- mixers prior to liquid and vapour sides of each module e

$$f_e^{LI} h_e^{LI} - \sum_n f_{ne}^{IL} h_n^I - \sum_{e'} \left(f_{e'e}^{LL} h_{e'}^{LO} + f_{e'e}^{CL} h_{e'}^{CO} \right) = 0 \quad (3.55)$$

$$f_e^{VI} h_e^{VI} - \sum_{e'} \left(f_{e'e}^{VV} h_{e'}^{VO} + f_{e'e}^{HV} h_{e'}^{HO} \right) = 0 \quad (3.56)$$

- mixers prior to utility exchangers e

$$f_e^C h_e^{CI} - \sum_{e'} f_{e'e}^{VC} h_{e'}^{VO} = 0 \quad (3.57)$$

$$f_e^H h_e^{HI} - \sum_n f_{ne}^{IH} h_n^I - \sum_{e'} f_{e'e}^{LH} h_{e'}^{LO} = 0 \quad (3.58)$$

- utility exchangers of each module e

$$Qh_e - f_e^H \left(h_e^{HO} - h_e^{HI} \right) = 0 \quad (3.59)$$

$$Qc_e - f_e^C \left(h_e^{CO} - h_e^{CI} \right) = 0 \quad (3.60)$$

- around each mass/heat exchange block e

$$f_e^{LI} h_e^{LI} + f_e^{VI} h_e^{VI} - f_e^{LO} h_e^{LO} - f_e^{VO} h_e^{VO} = 0 \quad (3.61)$$

- final mixers of each product stream $p \in P$

$$f_p^P h^P - \sum_n f_{np}^{IP} h_n^I - \sum_e \left(f_{ep}^{LP} h_e^{LO} + f_{ep}^{CP} h_e^{CO} \right) = 0 \quad (3.62)$$

◇ Summation of molar fractions

for superstructure streams $s \in S1$

$$\sum_i x_i^s - 1 = 0 \quad (3.63)$$

◇ Phase defining constraints

$$\text{for liquid streams :} \quad \mathcal{LB} \leq \sum_i K_i^s x_i^s \leq 1 \quad s \in S1 \quad (3.64)$$

$$\text{for vapour streams :} \quad \mathcal{LB} \leq \sum_i x_i^s / K_i^s \leq 1 \quad s \in S1 \quad (3.65)$$

where $\mathcal{LB}$ limits the level of superheating and supercooling ($\mathcal{LB} = 0.8$ is utilised) and

$$K_i^s = \frac{\gamma_i^s P_i^{sat,s}}{P_{tot}} \quad (3.66)$$

◇ Mass transfer driving force constraints for each component

Constraints (3.32) are rewritten as follows

$$[(y_e - 1) + (yt_{ei} - 1)] \mathcal{U} \leq f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO} \leq yt_{ei} \mathcal{U} + (1 - y_e) \mathcal{U} \quad (3.67)$$

$$[(y_e - 1) + (yt_{ei} - 1)] \mathcal{U} \leq K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO} \leq yt_{ei} \mathcal{U} + (1 - y_e) \mathcal{U} \quad (3.68)$$

$$[(y_e - 1) + (yt_{ei} - 1)] \mathcal{U} \leq K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI} \leq yt_{ei} \mathcal{U} + (1 - y_e) \mathcal{U} \quad (3.69)$$

where $\mathcal{U}$ is a (large) positive number. We impose without any loss of generality

$$yt_{ei} - y_e \geq 1 \quad (3.70)$$

such that in a nonexisting module, all components are transferred from the liquid to the vapour, making the above driving force constraints redundant.

◇ Thermodynamic property calculation

Stream properties are calculated as a function of its temperature and composition. Any thermodynamic model can be utilised to determine the enthalpy, activity coefficient and vapour pressure (stream equilibrium constant). Note that in this work constant total system pressure is assumed. If this is not the case, a variable pressure is also assigned to each stream.

◇ Process constraints and specifications on desired products

For example, given minimum specifications on product flows and purities $Fspec^P$, $Xspec_i^P$

$$f^P \geq Fspec^P$$

$$x_i^P \geq Xspec_i^P$$

◇ Logical constraints

- to define the existence of each module of each superstructure stream

$$[f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO}] - y_e \mathcal{F}^{max} \leq 0 \quad (3.71)$$

$$f_e^H - y_h \mathcal{F}^{max} \leq 0 \quad (3.72)$$

$$f_e^C - y_c \mathcal{F}^{max} \leq 0 \quad (3.73)$$

$$Qh_e - y_h \mathcal{Q}^{max} \leq 0 \quad (3.74)$$

$$Qc_e - y_c \mathcal{Q}^{max} \leq 0 \quad (3.75)$$

where $\mathcal{F}^{max}$ is an upper bound to stream flows and Q^{max} is an upper bound to heat flows.

- to define the existence of interconnecting streams

$$f_{ee}^{LL} - yll_{ee} \mathcal{F}^{max} \leq 0 \quad (3.76)$$

$$f_{ee}^{VV} - yvv_{ee} \mathcal{F}^{max} \leq 0 \quad (3.77)$$

$$f_{ee}^{LH} - ylh_{ee} \mathcal{F}^{max} \leq 0 \quad (3.78)$$

$$f_{ee}^{HV} - yhv_{ee} \mathcal{F}^{max} \leq 0 \quad (3.79)$$

$$f_{ee}^{VC} - yvc_{ee} \mathcal{F}^{max} \leq 0 \quad (3.80)$$

$$f_{ee}^{CL} - ycl_{ee} \mathcal{F}^{max} \leq 0 \quad (3.81)$$

$$f_{ne}^{IL} - yIl_{ne} \mathcal{F}^{max} \leq 0 \quad (3.82)$$

$$f_{ne}^{IH} - yIh_{ne} \mathcal{F}^{max} \leq 0 \quad (3.83)$$

$$f_{np}^{IP} - yIp_{np} \mathcal{F}^{max} \leq 0 \quad (3.84)$$

$$f_{ep}^{LP} - ylp_{ep} \mathcal{F}^{max} \leq 0 \quad (3.85)$$

$$f_{ep}^{CP} - ycp_{ep} \mathcal{F}^{max} \leq 0 \quad (3.86)$$

- to ensure that utility exchangers exist only if the module exists

$$yh_e - y_e \leq 0 \quad (3.87)$$

$$yc_e - y_e \leq 0 \quad (3.88)$$

- to ensure that interconnecting streams exist only if corresponding modules exist

$$yll_{ee'} - 0.5 [y_e + y_{e'}] \leq 0 \quad (3.89)$$

$$yvv_{ee'} - 0.5 [y_e + y_{e'}] \leq 0 \quad (3.90)$$

$$ylh_{ee'} - 0.5 [y_e + y_{h_{e'}}] \leq 0 \quad (3.91)$$

$$yhv_{ee'} - 0.5 [y_{h_e} + y_{e'}] \leq 0 \quad (3.92)$$

$$yvc_{ee'} - 0.5 [y_e + y_{c_{e'}}] \leq 0 \quad (3.93)$$

$$ycl_{ee'} - 0.5 [y_{c_e} + y_{e'}] \leq 0 \quad (3.94)$$

$$yIl_{ne} - y_e \leq 0 \quad (3.95)$$

$$yIh_{ne} - y_{h_e} \leq 0 \quad (3.96)$$

$$yIp_{ep} - y_e \leq 0 \quad (3.97)$$

$$ycp_{ep} - y_{c_e} \leq 0 \quad (3.98)$$

- to ensure that if a module exists there will be an inlet flow

$$y_e - \left[\sum_n yIl_{ne} + \sum_{e'} yll_{e'e} + \sum_{e'} ycl_{e'e} \right] \leq 0 \quad (3.99)$$

$$y_e - \left[\sum_{e'} yvv_{e'e} + \sum_{e'} yhv_{e'e} \right] \leq 0 \quad (3.100)$$

$$yh_e - \left[\sum_n yIh_{ne} + \sum_{e'} ylh_{e'e} \right] \leq 0 \quad (3.101)$$

$$yc_e - \left[\sum_{e'} yvc_{e'e} \right] \leq 0 \quad (3.102)$$

- to ensure that if a module exists there will be an outlet flow

$$y_e - \left[\sum_{e'} yll_{ee'} + \sum_{e'} ylh_{ee'} + \sum_p ylp_{ep} \right] \leq 0 \quad (3.103)$$

$$y_e - \left[\sum_{e'} yvv_{ee'} + \sum_{e'} yvc_{ee'} \right] \leq 0 \quad (3.104)$$

$$yh_e - \left[\sum_{e'} yhv_{ee'} \right] \leq 0 \quad (3.105)$$

$$yc_e - \left[\sum_{e'} ycl_{ee'} + \sum_p ycp_{ep} \right] \leq 0 \quad (3.106)$$

- to ensure at least one feed point per existing feed $n \in I1$

$$1 - \left[\sum_e yIl_{ne} + \sum_e yIh_{ne} + \sum_p yIp_{np} \right] \leq 0 \quad (3.107)$$

- to ensure at least one source per product $p \in P$

$$1 - \left[\sum_n yIp_{np} + \sum_e ylp_{ep} + \sum_e ycp_{ep} \right] \leq 0 \quad (3.108)$$

- to define the utilisation of an entrainer $n \in I2$

$$ysolv_n - \left[\sum_e yIl_{ne} + \sum_e yIh_{ne} + \sum_p yIp_{np} \right] \leq 0 \quad (3.109)$$

- non-redundancy constraints

$$y_{e+1} - y_e \leq 0 \quad (3.110)$$

◇ Objective Function

Synthesis of the separation system may be driven by

- maximisation of the molar fraction of a component C in a product stream (*i.e.* separation efficiency), or
- minimisation of a cost function, involving

- utility cost

$$Cost^{util} \sum_e (Qh_e + Qc_e)$$

- entrainer cost

$$Cost^{I2} \sum_{I2} f^{I2}$$

- “pseudo-capital” cost of each module, which may be a fixed cost or a function of stream flows and/or separation efficiency (see section 2.9)

The above mass/heat exchange superstructure model corresponds to a MINLP problem for which a nested MINLP decomposition strategy is developed for its solution, as described in section 3.9. The model is solved using GAMS (Brooke *et al.*, 1988), with solvers CONOPT employed for the primal problem and CPLEX for the master problems. The detailed formulation of the model for its solution is given in Appendix B, along with the model size statistics (Appendix B.2) for the example problems to follow. The complexity and size of the model increases with the total number of mass/heat modules e considered. In solving the MINLP, a conservative number of modules is considered and if all modules are selected, this number is increased. With the problems considered in this work it is found that a maximum of 10 is sufficient.

The basic assumptions listed in section 3.3 can be easily relaxed within this framework as follows. To consider liquid and vapour states of feeds and products, their corresponding interconnections must also be considered *i.e.* in addition to the stream sets listed earlier, account for the following sets;

Variable	Denoting the existence of
$y h_e$	utility heater prior to vapour inlet of module e
$y c_e$	utility cooler prior to liquid inlet of module e
$y l l_{ee'}$	interconnecting stream from liquid outlet splitter of module e to liquid inlet mixer of module e'
$y v v_{ee'}$	interconnecting stream from vapour outlet splitter of module e to vapour inlet mixer of module e'
$y l h_{ee'}$	liquid stream from liquid outlet splitter of module e to utility heater of module e'
$y h v_{ee'}$	vapour stream from utility heater of module e to vapour inlet mixer of module e'
$y v c_{ee'}$	vapour stream from vapour outlet splitter of module e to utility cooler of module e'
$y c l_{ee'}$	interconnecting stream from utility cooler of module e to liquid inlet mixer of module e'
$y I l_{ne}$	interconnecting stream from initial splitter of stream n to liquid inlet mixer of module e
$y I h_{ne}$	interconnecting stream from initial splitter of stream n to utility heater of module e
$y I p_{np}$	interconnecting stream from initial splitter of stream n to final mixer of product stream p
$y l p_{ep}$	interconnecting stream from liquid outlet splitter of module e to the final mixer of product stream p
$y c p_{ep}$	interconnecting stream from outlet utility cooler of module e to the final mixer of product stream p

Table 3.7: Structural Variables

IV_{ne} = {s/s interconnecting stream from initial stream n
to vapour inlet mixer of module e }

IC_{ne} = {s/s interconnecting stream from initial stream n
to utility cooler of module e }

VP_{ep} = {s/s interconnecting stream from vapour outlet splitter
of module e to final mixer of product p }

HP_{ep} = {s/s interconnecting stream from utility heater of module e
to final mixer of product p }

The superstructure model can then be appropriately altered. To consider variable system pressure, a variable pressure is assigned to each stream or to each module. To include heat exchangers without phase change, the building block module of Figure 3.8 can be modified to that shown in Figure 3.18, whereby three coolers and three heat exchangers are connected to the mass/heat exchanger. All heating and cooling possibilities are considered, accompanied by increased complexity of the model. Heat integration can be considered by accounting for utility and process streams to exchange heat. However, the problem is simplified to disregard heat integration when the dashed lines are utility streams.

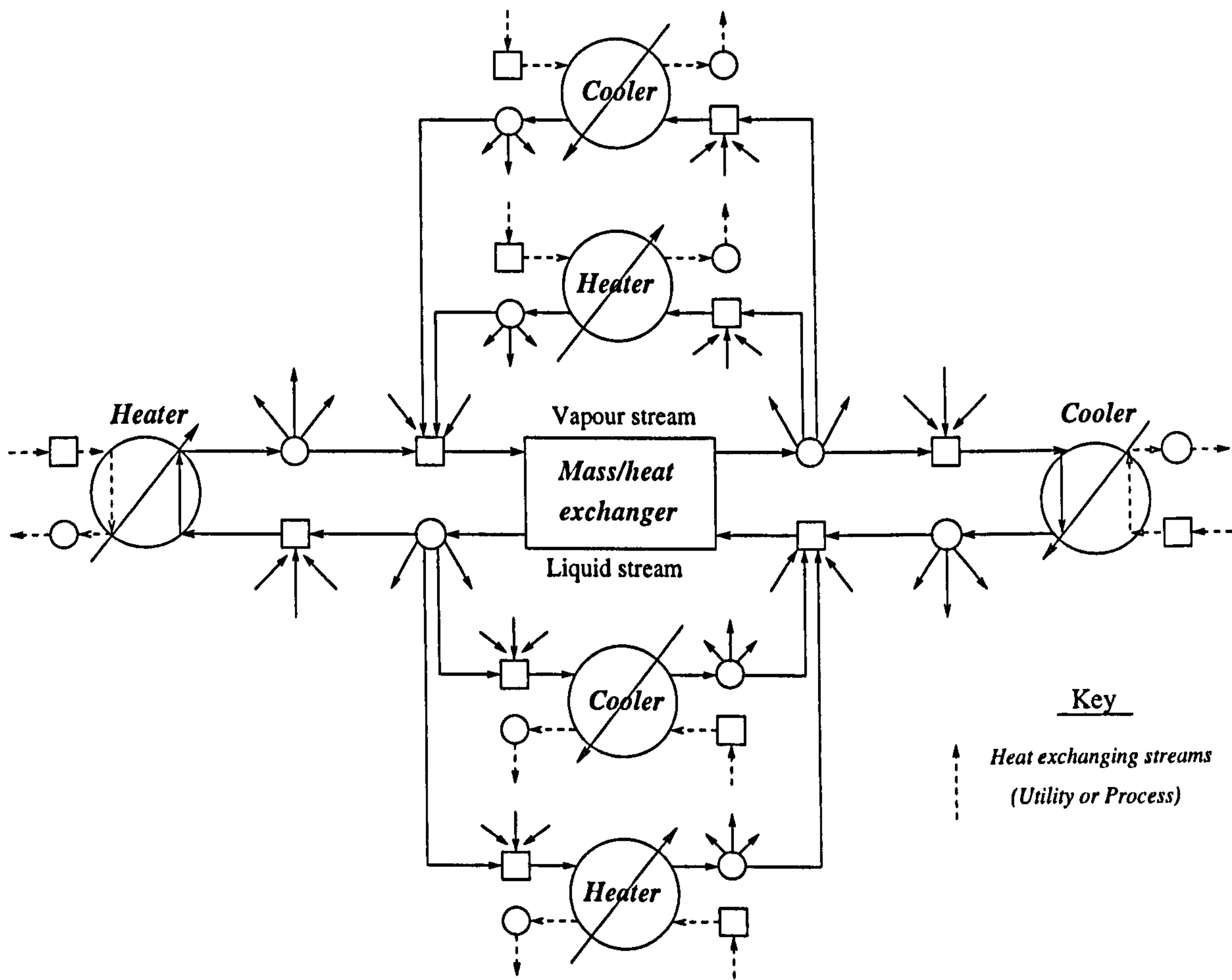


Figure 3.18: Complex heat exchange module

PRIMAL PROBLEM k

$$\begin{array}{lcl}
 U^k = \min & f(x, y_{k1}^s, y_k^t) & \\
 \text{s.t.} & h(x) = 0 & \\
 & g_1(x, y_{k1}^s, z_k) \leq 0 & \\
 & g_2(x, y_{k1}) \leq 0 &
 \end{array} \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{Upper Bound } U^k \\ \& \\ \text{Lagrange multipliers} \\ \lambda_1^{k(k1)}, \lambda_2^{k(k2)} \end{array}$$

where k corresponds to = $\begin{cases} k1, & \text{outer iteration} \\ k2, & \text{inner iteration} \end{cases}$

i.e. $k = 1, \dots, k2(k1)$

INNER MASTER SUBPROBLEM $k2$

$$\begin{array}{ll}
 \min & \mu \\
 \text{s.t.} & \mu \geq f(x^{k2}, y_{k1}, z) + \sum_{k2} \lambda_1^{k2} g_1(x^{k2}, y_{k1}, z) \\
 & k2 = 1, \dots, k2(k1)_{feasible} \\
 & (i.e. \text{ only from Primals of current } y_{k1}^s)
 \end{array}$$

$$\begin{array}{ll}
 \sum_{k2} \lambda_1 g_1(x^{k2}, y_{k1}, z) \leq 0 \\
 k2 = 1, \dots, k2(k1)_{infeasible}
 \end{array}$$

+ integer cuts for transfer direction z that

have been examined in current outer iteration $k1$

The solution of the inner master subproblem provides a lower bound to the solution of the primal problem with fixed current structure.

OUTER MASTER SUBPROBLEM k_1

$$\min \quad \mu$$

$$\text{s.t.} \quad \mu \geq f(x^{k_2(k_1)}, y, z) + \sum_k \lambda_1^{k_2(k_1)} g_1(x^{k_2(k_1)}, y, z) + \sum_k \lambda_2^{k_2(k_1)} g_2(x^{k_2(k_1)}, y)$$

$$\forall \quad k = k_2(k_1) \text{ feasible Primal}$$

$$\sum_k \lambda_1^{k_2(k_1)} g_1(x^{k_2(k_1)}, y, z) + \sum_k \lambda_2^{k_2(k_1)} g_2(x^{k_2(k_1)}, y) \leq 0$$

$$\forall \quad k = k_2(k_1) \text{ infeasible Primal}$$

$$g_3(y) \leq 0$$

+ integer cuts for combinations of structure and transfer directions
that have already been examined (*i.e.* including y, z).

The solution of the outer master subproblem provides a valid lower bound to the overall solution of problem (P).

Remarks

- (i) The inner iterations can stop when a feasible mass transfer pattern is found
- (ii) Integer cuts in the OUTER master subproblem must involve both structural and transfer binary variables when inner iterations stop before convergence. This is required so that a structure with a better z than the ones examined is not rejected. When, for a given structure y , the best z is found, then an integer cut for the structure can also be included.
- (iii) The OUTER master subproblem must involve variable z 's to provide a valid lower bound.
- (iv) Common assumptions for convexity are required to ensure convergence to the optimal solution.
- (v) Convergence in a finite number of iterations is guaranteed since only a finite number of combinations exist.

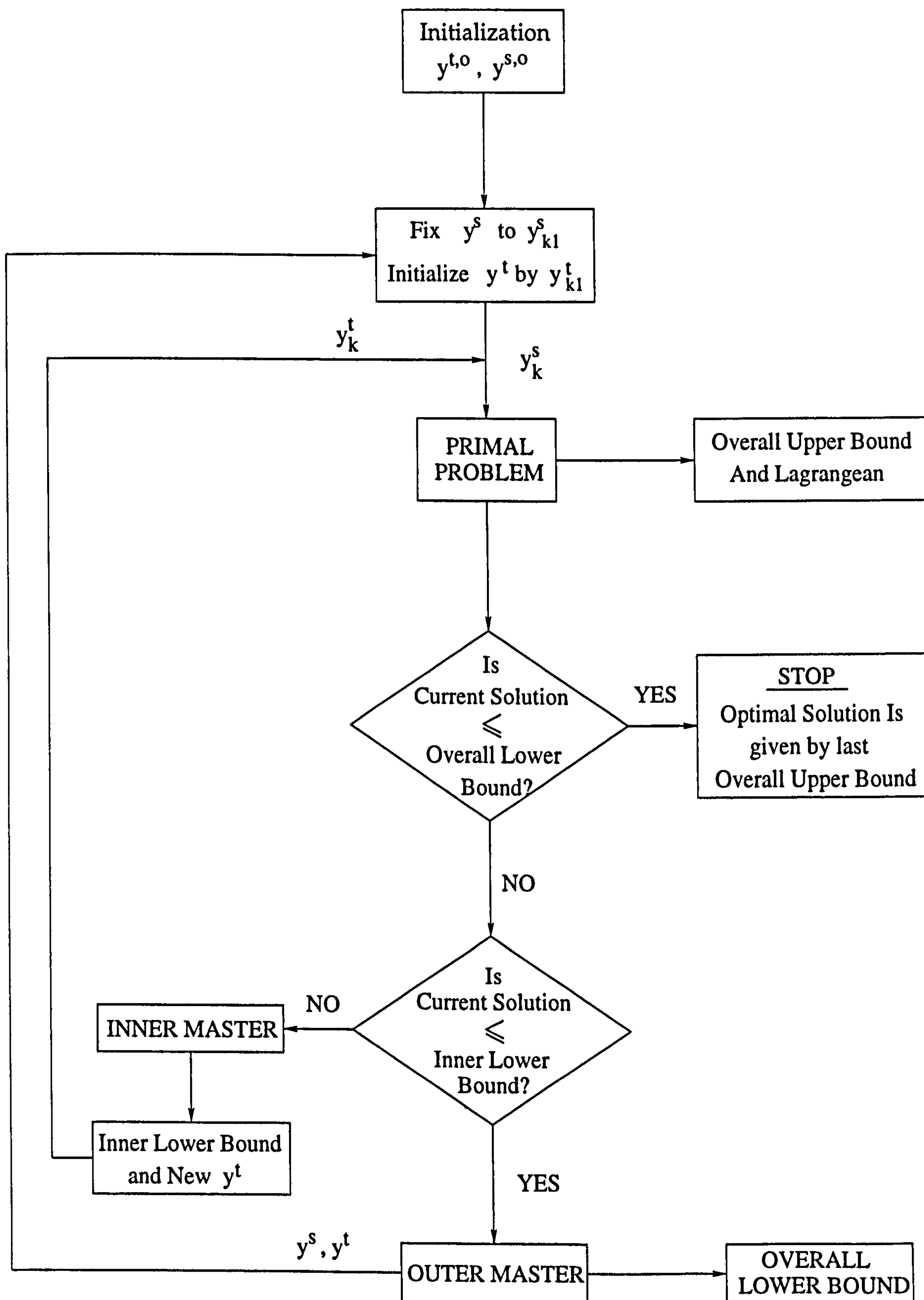


Figure 3.19: MINLP Decomposition Algorithm

Utility	Cost US\$ per kWyr
Cooling Water	26.19
Steam	137.27

Table 3.8: Utility Cost Data

3.10 Examples

In this section, the separation task for two azeotropic mixtures are considered in detail to illustrate the ability of the proposed synthesis framework to

- (i) consistently characterise separation feasibility
- (ii) identify the requirement (or not) of an (simultaneously depicted) entrainer and
- (iii) determine separation structure.

Utility cost data are given in Table (3.8), and pure component enthalpy data is detailed in Appendix A.

Note that for convenience in the presentation, we make a number of simplifying assumptions:

- (i) Saturated liquid feeds and liquid products are considered.
- (ii) The system is at constant atmospheric pressure.
- (iii) No heat integration between the separators is considered.

As already discussed, these assumptions can be easily relaxed.

3.10.1 Separation of Ethanol and Water

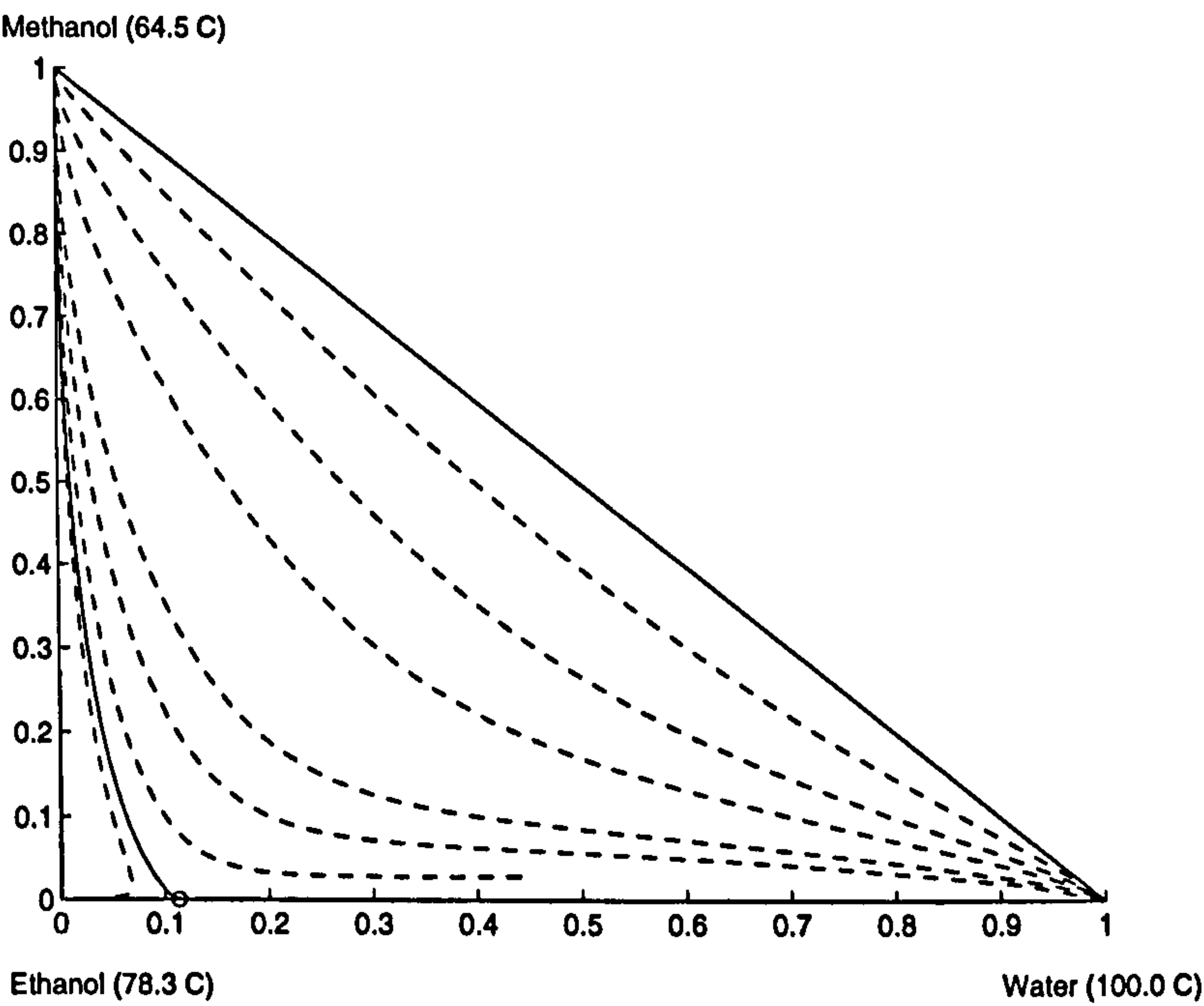
For the separation of ethanol (A) and water (B) mixture introduced earlier, ethylene glycol and methanol are considered as available candidate entrainers. Methanol (L) is a light entrainer with a lower boiling point than the azeotrope and introduces no new azeotrope, thus coming under case 020 under the entrainer classification of Doherty and Caldarola (1985). All the residue curves start from the methanol corner and end at a pure ethanol or water vertex, and a residue curve boundary runs from the entrainer to

the minimum boiling azeotrope (see Figure 3.20 (a)). Entrainers of this class always give feasible separation at infinite reflux under the analysis of Laroche *et al.*, (1992b). Ethylene glycol (H) is a heavy entrainer which does not introduce any new azeotropes or residue curve boundaries as shown in the residue curve map in Figure 3.20 (b), and is classified as case 100. From analysis of the residue curve map, separation in this case is infeasible at infinite reflux but feasible at finite reflux (see Laroche *et al.*, 1992b). Both these entrainers may facilitate the separation by forming a homogeneous mixture with the feed.

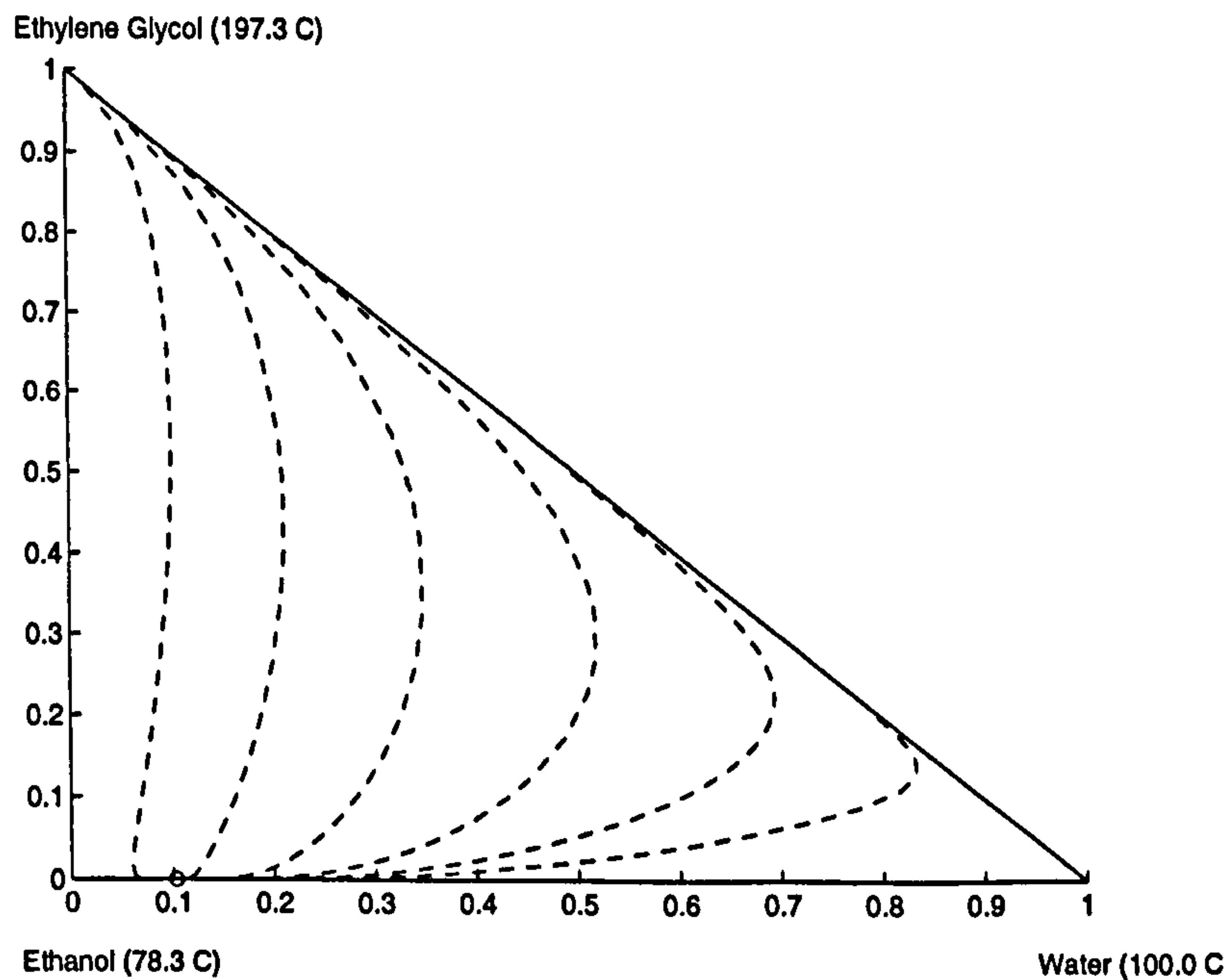
Four synthesis tasks (see Table 3.10) are considered for an ethanol and water liquid feed of composition $X_A = 0.85$ and $X_B = 0.15$ at a flowrate of 10 kmol/s and conditions of 351.3K, 1 atm. The NRTL equation was utilised to describe the liquid nonidealities, and the thermodynamic data utilised is detailed in Table 3.9. Since the total system pressure is fixed at 1 atm, the behaviour of the vapour phase is assumed to be ideal with $\phi_i = 1$. The product specifications for each synthesis task and the results obtained are summarized in Table 3.10.

Note that for tasks 1 and 2, the synthesis framework identifies the need for an entrainer to break up the azeotrope, as shown in Figure 3.21(a),(b). To achieve a pure ethanol product (see Figure 3.21(a), Task 1), the ethylene glycol entrainer is chosen to facilitate the separation which is realized in three $L_{AB} - V_{AB}$ matches, with mass transfer of ethanol from the liquid to the vapour stream. Three mass/heat exchange modules are interconnected in a configuration that can be recognized as a single extractive column. The ethylene glycol is fed above the feed (represented by a single module) at a solvent to feed ratio of 0.72, increasing the relative volatility of ethanol more than water and breaking up the azeotrope to achieve a pure ethanol liquid product emerging from the cooler. Figure 3.22 shows the temperature and composition profiles of the extractive column. Note that although the tray to tray details are lost, all the main features of an extractive column are captured: (i) maximum temperature in the extractive section due to the greater entrainer concentration in the liquid between the feed trays, (ii) The ethanol concentration changes abruptly and approaches zero at the bottom of the column and there is no ethylene glycol in the distillate product, (iii) in the extractive and most of the stripping section the liquid concentration of ethylene glycol is approximately constant, reaching a maximum at the bottom (see Meirelles *et al.*, 1992).

By specifying a high purity water product in task 2, the light methanol entrainer is selected resulting in the configuration shown in Figure 3.21(b). In this case, two liquid-vapour matches are sufficient to accommodate the separation, whereby methanol facilitates mass transfer of water from the vapour to the liquid to result in a pure water product emerging from the bottom of the column. Methanol and ethanol, having the greater



(a) Ethanol, water and methanol mixture



(b) Ethanol, water and ethylene glycol mixture

Figure 3.20: Residue Curve Maps for Ethanol-Water at 1 atm

	C1	C2	C3	C4	C5
Ethanol (1)	59.796	-6595.0	-5.0474	6.300e-7	2
Water (2)	72.550	-7206.7	-7.1385	4.046e-6	2
Ethylene Glycol (3)	194.64	-14615	-25.433	2.014e-5	2
Methanol (4)	109.93	-7471.3	-13.988	1.528e-2	1

$$\ln P^{sat} = C1 + \frac{C2}{T} + C3 \ln(T) + C4 T^{C5} \quad (Pa, K)$$

NRTL equation

$$\ln \gamma_i = \frac{\sum_{j \in C} \tau_{ji} G_{ji} x_j}{\sum_{j \in C} G_{ji} x_j} + \sum_{j \in C} \frac{G_{ij} x_j}{\sum_{l \in C} G_{lj} x_l} \left\{ \tau_{ij} - \frac{\sum_{l \in C} \tau_{lj} G_{lj} x_l}{\sum_{l \in C} G_{lj} x_l} \right\}$$

$$\tau_{ij} = \frac{\Lambda_{ij}}{RT} \qquad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\Lambda_{ii} = 0 \qquad \alpha_{ij} = \alpha_{ji}$$

Ethanol-Water System

$$\Lambda_{12} = 121.0 \text{ cal/mol} \qquad \Lambda_{21} = 1161.5 \text{ cal/mol} \qquad \alpha_{12} = 0.475$$

Ethanol-Water-Ethylene Glycol System

$$\Lambda_{ij} = \mathcal{A} \Lambda_{ij} + \mathcal{A} \mathcal{T}_{ij} * (T - 273.15)$$

<i>ij</i>	$\mathcal{A} \Lambda_{ij}$	$\mathcal{A} \mathcal{T}_{ij}$	$\mathcal{A} \Lambda_{ji}$	$\mathcal{A} \mathcal{T}_{ji}$	α_{ij}
12	-441.20	18.3280	3293.17	17.0471	0.475000
13	13527.42	-92.7391	-4351.97	53.3769	0.370400
23	1383.43	8.0409	-1445.97	-9.1506	0.185894

Ethanol-Water-Methanol System

$$\Lambda_{12}=206.7 \quad \Lambda_{21}=5270.3 \quad \Lambda_{41}=0$$

$$\Lambda_{14}=0 \qquad \Lambda_{24}=3641.5 \quad \Lambda_{42}=-788.20$$

$$\alpha_{ij} = 0.4$$

Table 3.9: Ethanol-Water Separation : Thermodynamic Properties

	Product Specification	Objective	Entrainer	$F_{entrainer}/F_{feed}$	No Mass/Heat Modules	No Pure Modules Heat Modules
Task 1	$X_{ethanol} \geq 0.99$	Minimize Cost	Glycol	0.72	4	2
Task 2	$X_{water} \geq 0.99$	Minimize Cost	Methanol	7.0	3	2
Task 3	(a) $X_{ethanol} \geq 0.99$ (b) $X_{water} \geq 0.99$	Minimize Cost $Cost_{glycol} \ll Cost_{methanol}$	Glycol	0.72	5	4
Task 4	(a) $X_{ethanol} \geq 0.99$ (b) $X_{water} \geq 0.99$	Minimize Cost $Cost_{methanol} \ll Cost_{glycol}$	Methanol	7.0	4	4

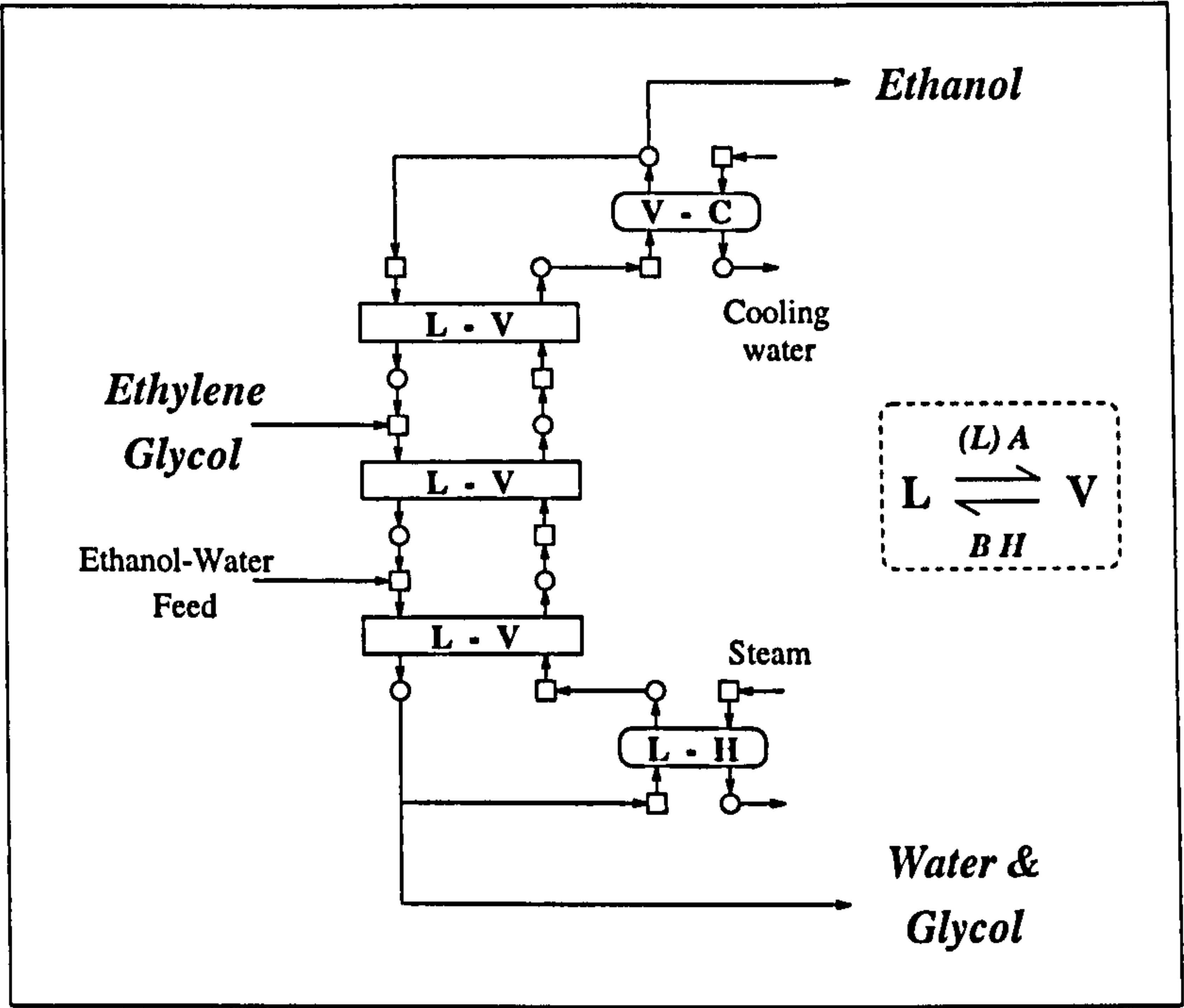
Table 3.10: Summary of Separation Tasks for Ethanol-Water Example

volatility, are transferred from the liquid to the vapour to appear in the distillate. A high solvent to feed ratio of 7 is required to achieve the required purity.

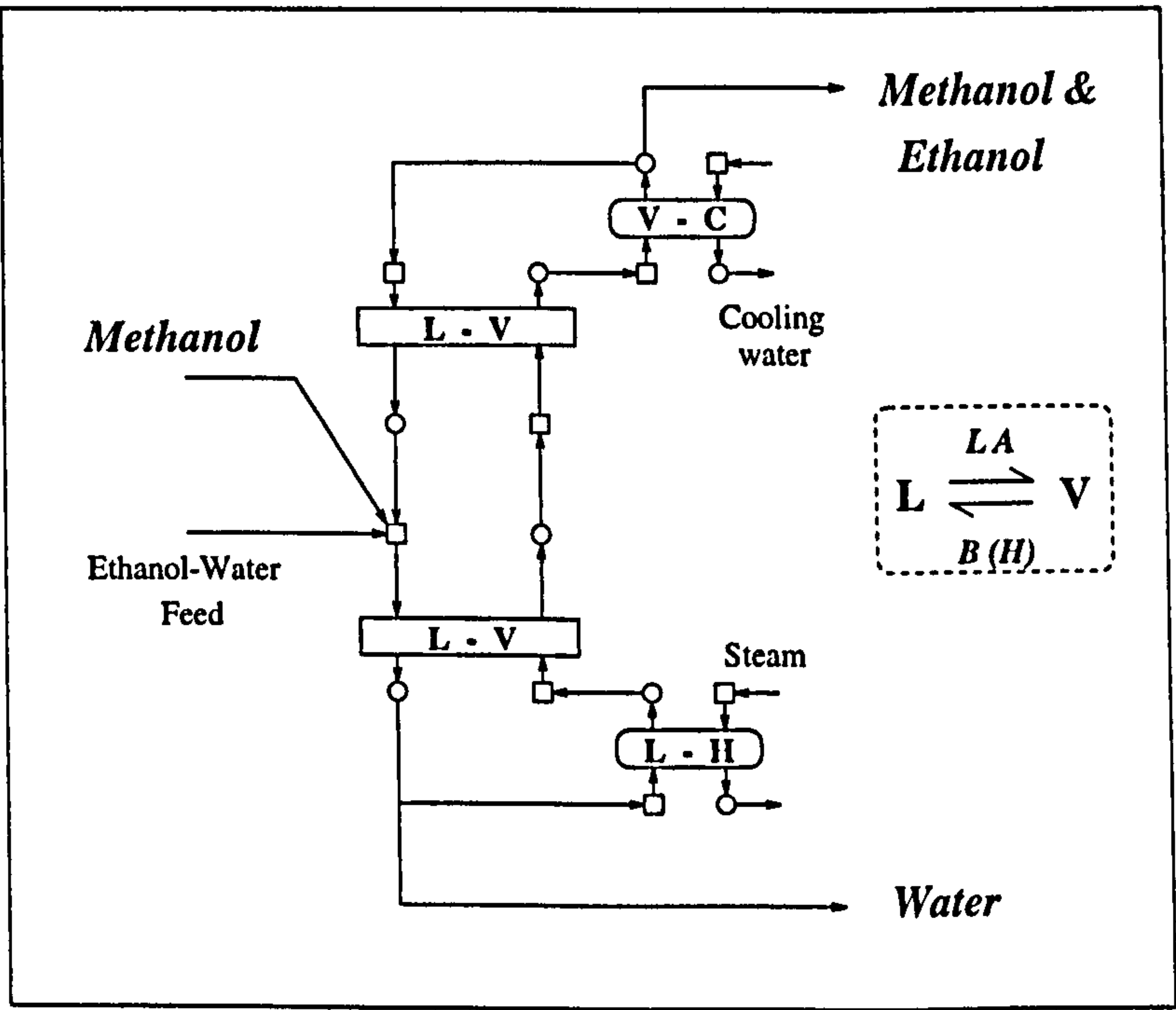
Tasks 3 and 4 are concerned with the case of high purity specifications required on both products. For the case that the choice of ethylene glycol is more economical *i.e.* $Cost_{ethylene\ glycol} \ll Cost_{methanol}$, the synthesis model results in the configuration shown in Figure 3.23(a) involving five liquid-vapour matches and four pure heat exchanger matches interconnected. Note that three liquid-vapour matches corresponding to mass transfer of *ethanol* to the vapour stream (and that of water and ethylene glycol to the liquid stream) represent the extractive column, whose composition profile is shown in Figure 3.24. Two matches corresponding to mass transfer of *water* to the vapour stream (and that of ethylene glycol to the liquid stream) represent the recovery column. Both the ethanol and water product streams appear as distillates in this configuration.

For task 4 when $Cost_{methanol} \ll Cost_{ethylene\ glycol}$, methanol is selected as the optimal choice in the optimal separation configuration shown in Figure 3.23(b) involving four mass/heat transfer modules. Two liquid-vapour matches whereby *water* is transferred from the vapour to the liquid stream (with ethanol and methanol transfer to the vapour stream) represents the azeotropic unit. In these matches, the addition of methanol increases the relative volatility between ethanol and water, resulting in a *LA/B* split with a pure water product appearing as the bottoms. The composition profile for this separator is given in Figure 3.25. The resulting ethanol and methanol mixture is fed to the next two mass/heat transfer modules corresponding to a *L/A* split. In these matches, mass transfer of methanol occurs towards the vapour stream whilst the liquid stream is enriched in ethanol. The configuration of these matches represent the recovery column whereby a pure ethanol product appears as bottom product and methanol is recycled.

In terms of utility cost, the separation scheme utilizing ethylene glycol as entrainer is more economical than that with methanol, as illustrated in Table 3.11. In order to achieve the product purity in the azeotropic column with methanol, a high entrainer to feed ratio of 7 is required to increase the relative volatility between ethanol and water sufficiently. In addition, the azeotropic column has high reboil ratios with large internal flowrates. These two factors lead to high heating and cooling duties in both the azeotropic and recovery column, and thus high operating cost. In contrast, the extractive column with glycol requires lower entrainer to feed ratio of 0.72 and relatively smaller internal flowrates in both columns (with low reflux and reboil ratios), thus a lower utility cost.



(a) Task 1 : specifying $X_{prod_{ethanol}} \geq 0.99$



(b) Task 2 : specifying $X_{prod_{water}} \geq 0.99$

Figure 3.21: Tasks 1 and 2 Results for Ethanol-Water separation

	Task 3 Ethylene Glycol		Task 4 Methanol	
F_{solv}/F_{feed}	0.72		7.0	
T_{solv} (K)	362		337	
Utility Cost/year \$ * 10 ³	159.2		1433.8	
	Col1	Col2	Col1	Col2
$Q_{heating}$ (kW)	658.9	337.3	3364.3	5579.3
$Q_{cooling}$ (kW)	670.9	184.7	3392.0	4477.9

Table 3.11: Summary of Results for Task 4 and 5

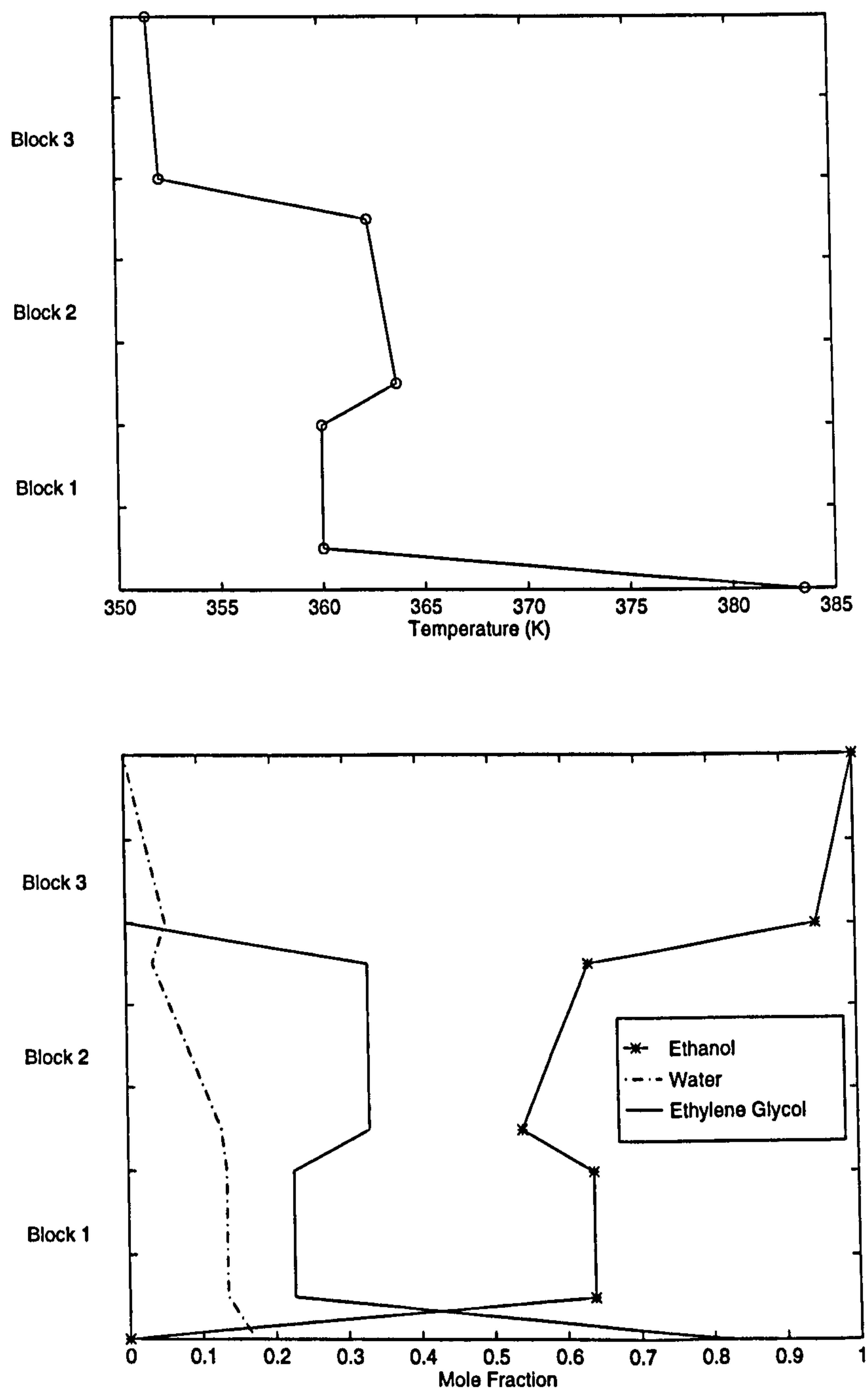
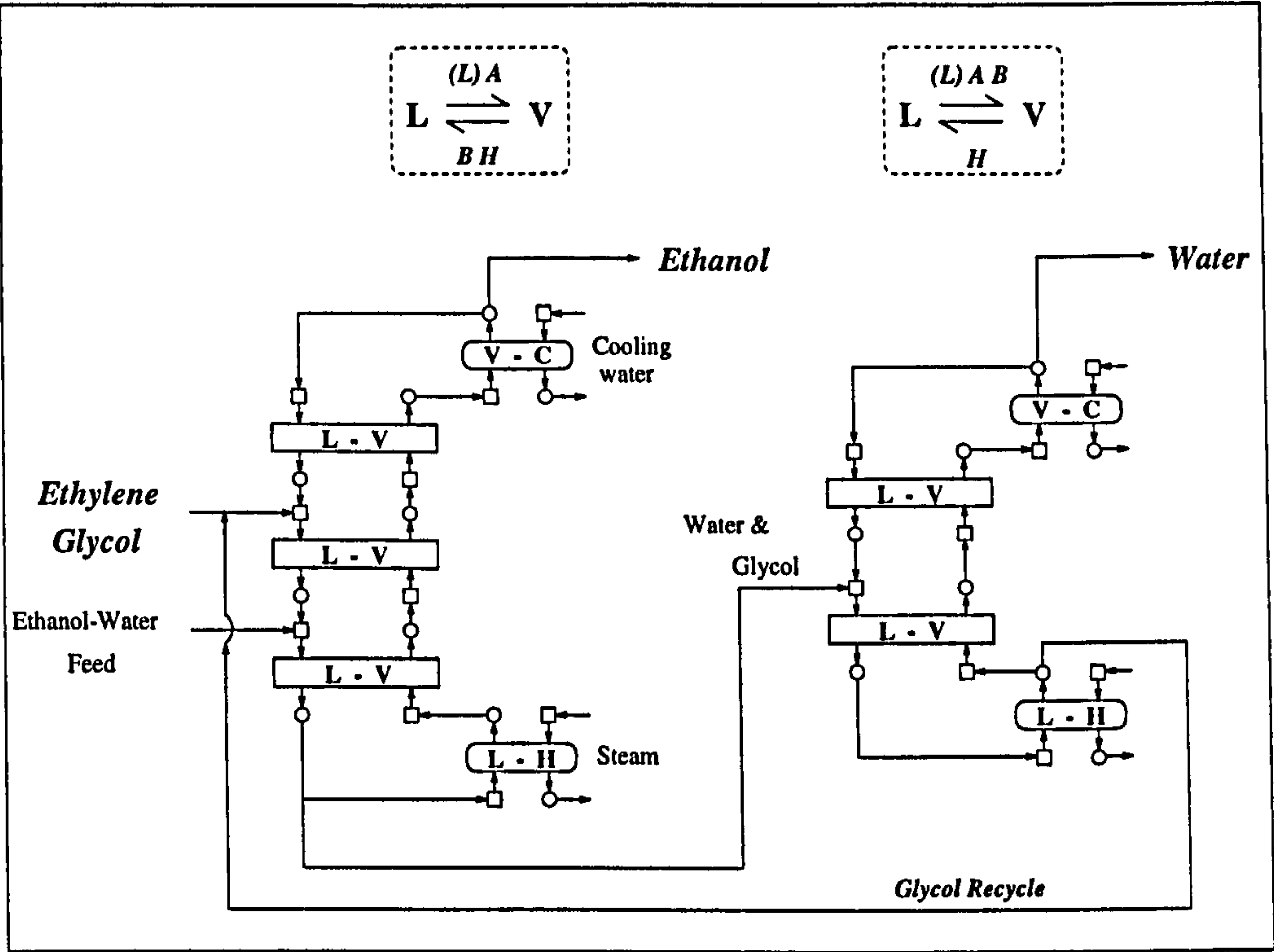
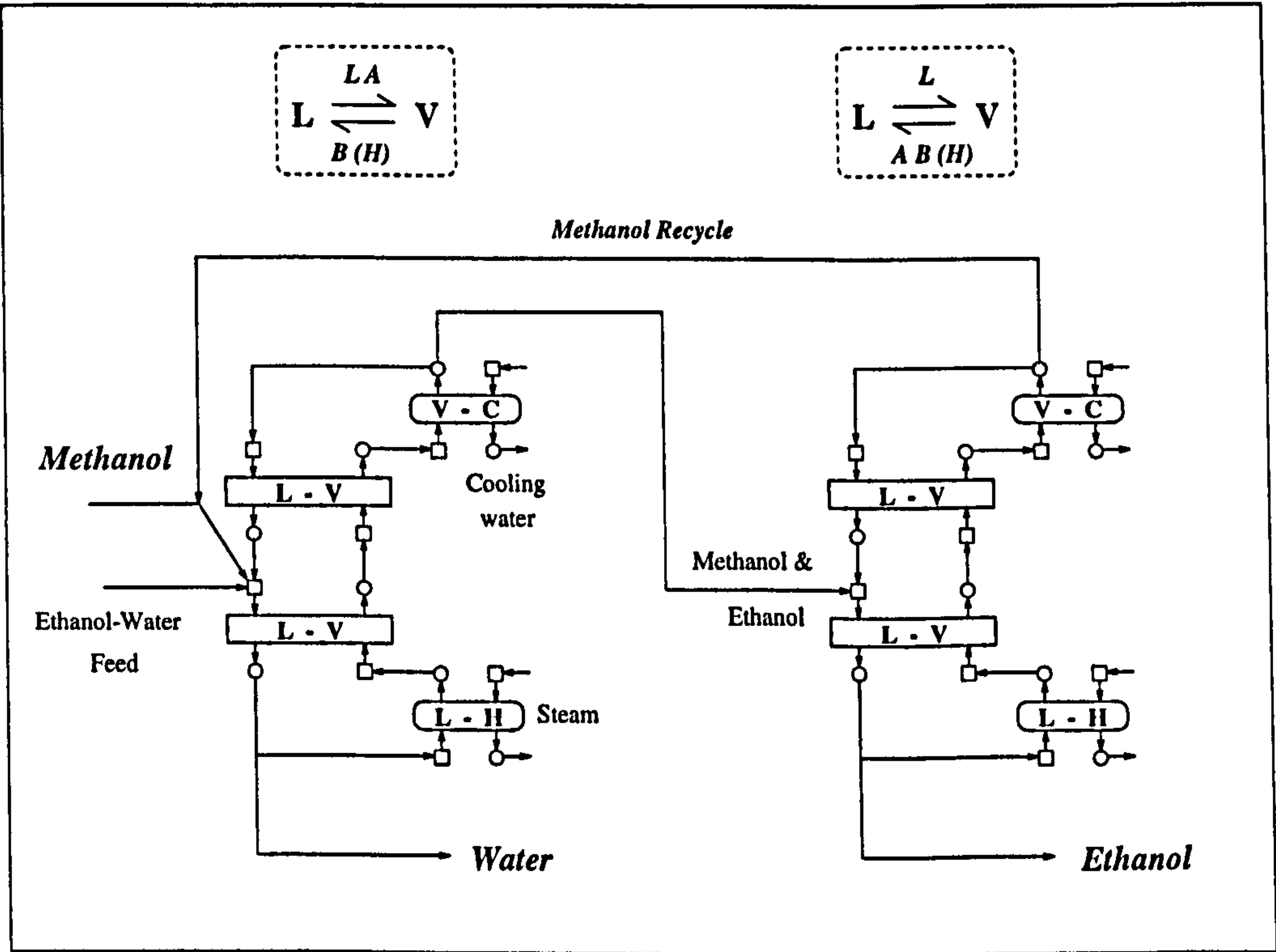


Figure 3.22: Task 1 Temperature-Composition Profiles



(a) Task 3 results



(b) Task 4 results

Figure 3.23: Task 3 and 4 Results for Ethanol-Water Separation

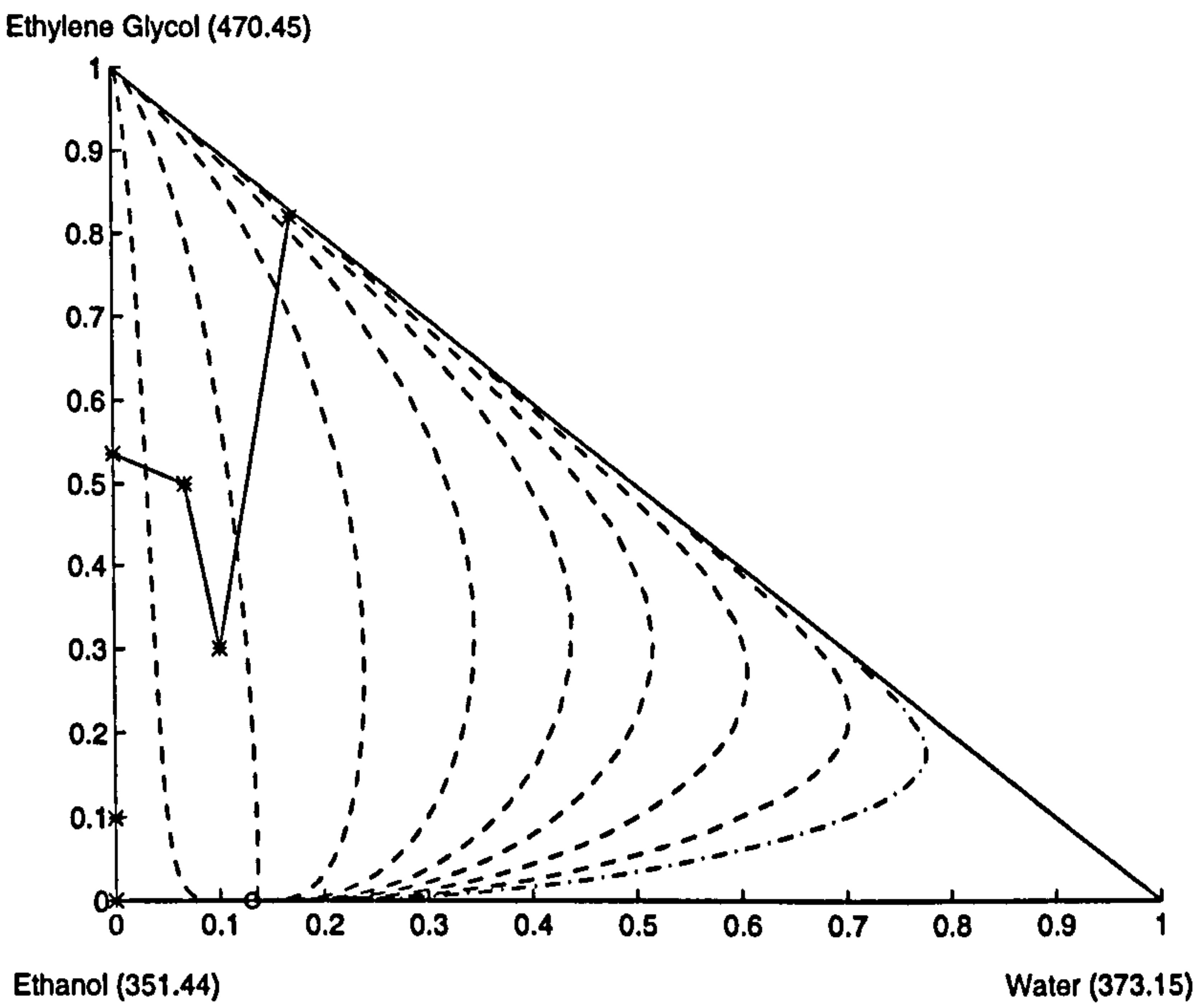


Figure 3.24: Task 3 : Composition Profile of Extractive Unit

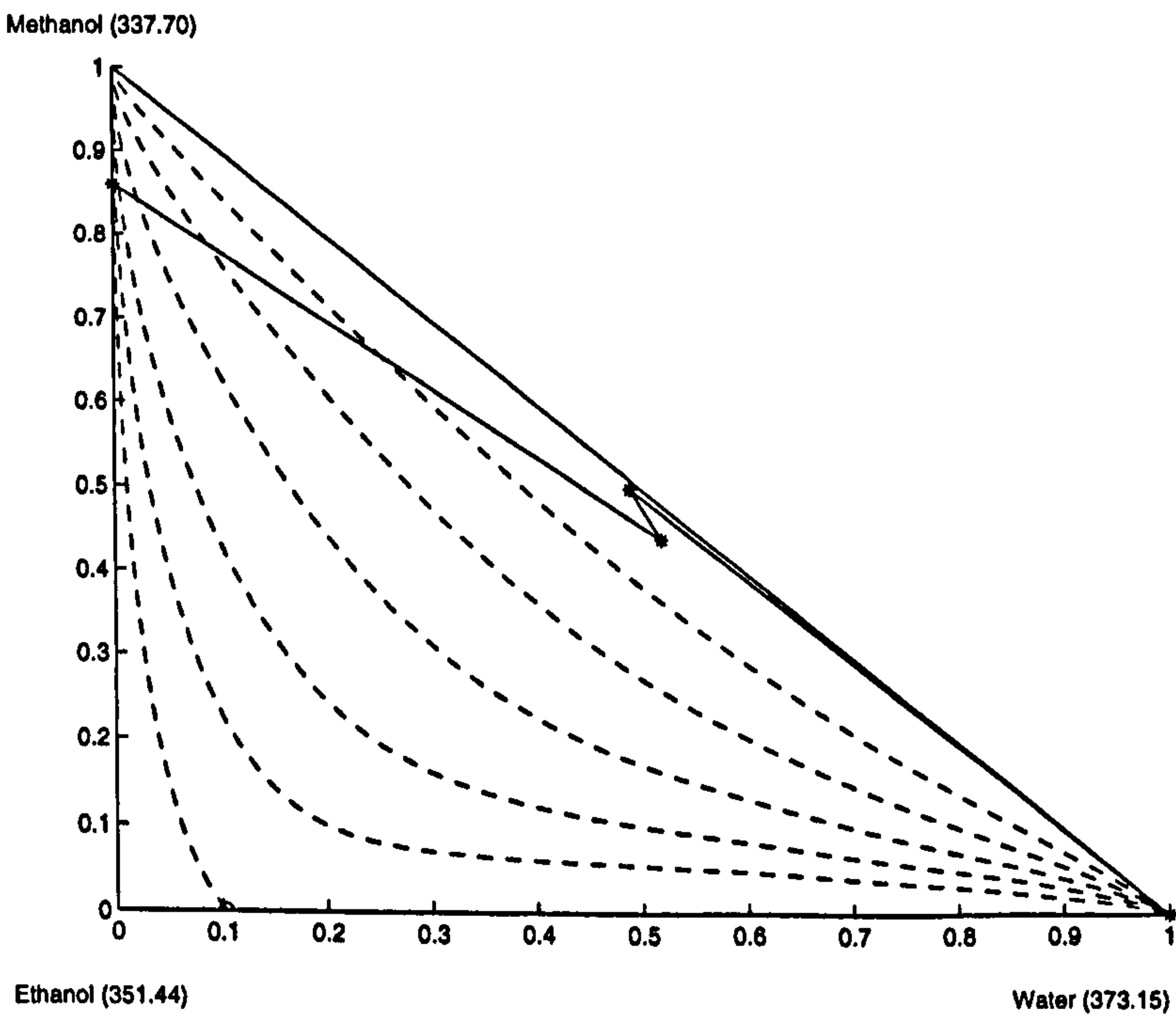


Figure 3.25: Task 4 : Composition Profile of Azeotropic Unit

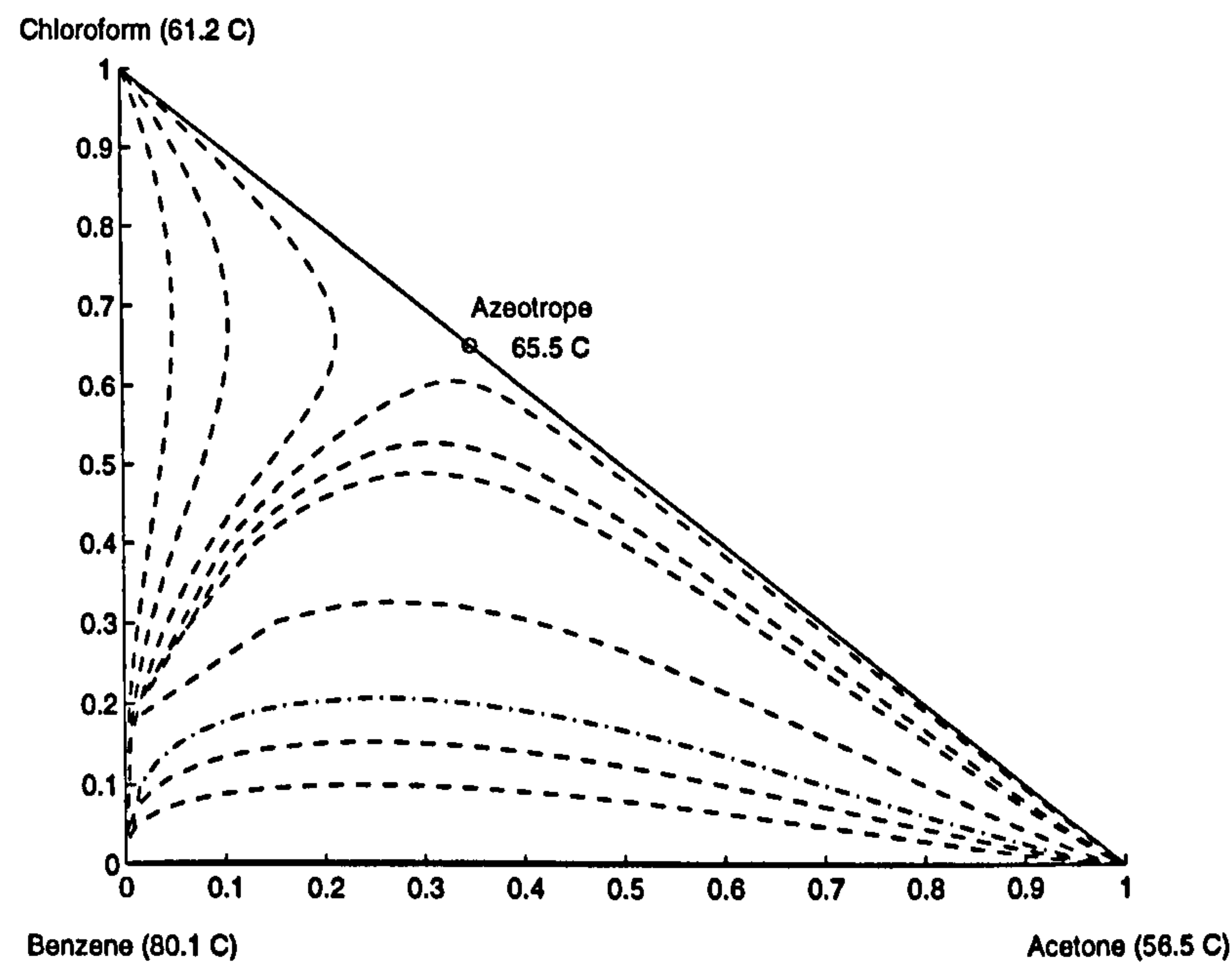
3.10.2 Separation of Acetone and Chloroform

The separation of an acetone (*A*) and chloroform (*C*) mixture is considered, given benzene (*B*) and methanol (*M*) as available entrainers. Acetone (normal b.p. of 329.25 K) and chloroform (normal b.p. 334.95 K) form a maximum boiling azeotrope of 34.5 mol% acetone at a temperature of 337.65 K (1 atm). Benzene introduces no new azeotropes to the system (see Figure 3.26(a)) while methanol introduces two new binary azeotropes and a ternary azeotrope as shown in Figure 3.26(b).

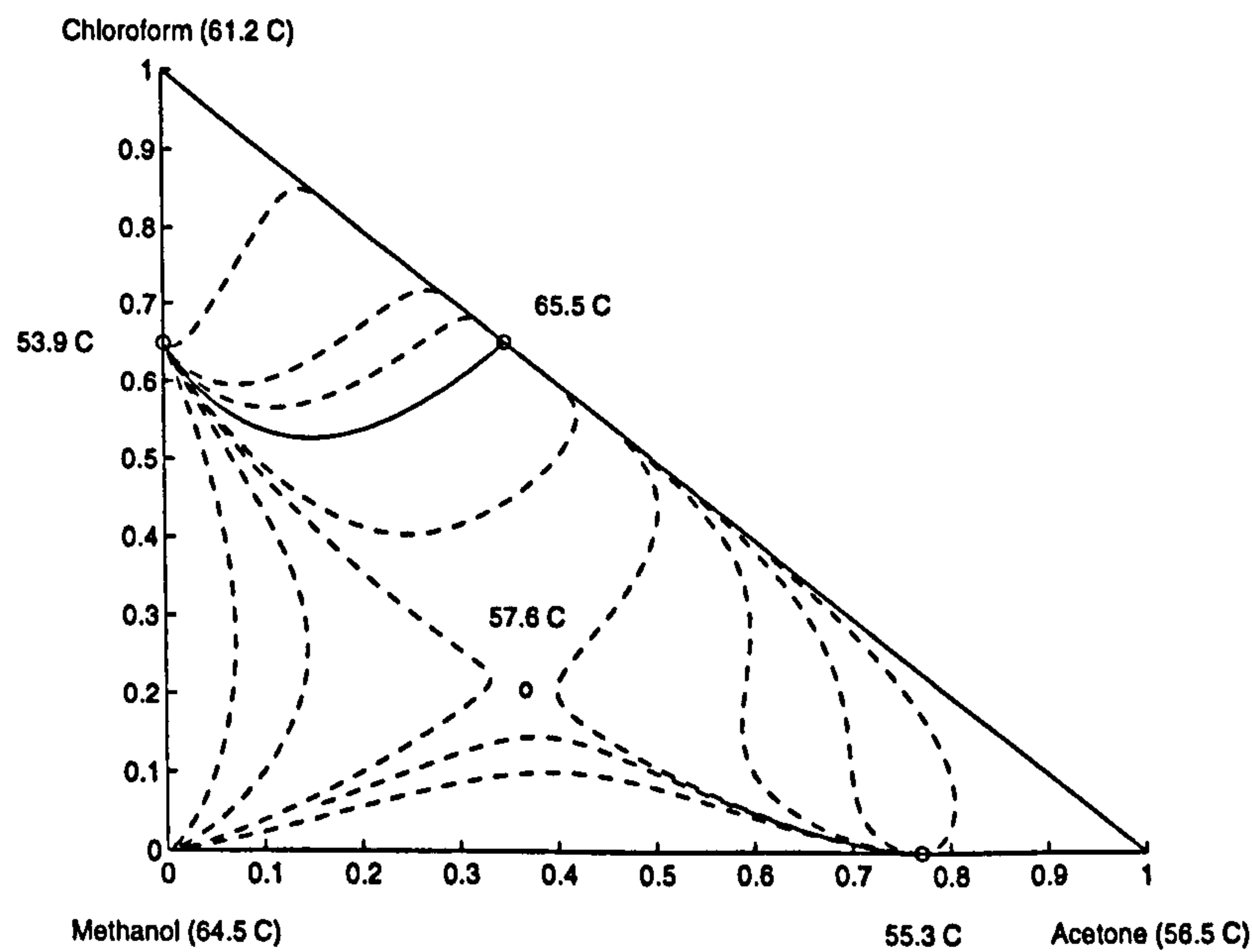
An atmospheric acetone-chloroform liquid feed of composition $X_{\text{acetone}} = 0.60$, $X_{\text{chloroform}} = 0.40$ at a flowrate of 10 kmol/s and a temperature of 330.15K is considered. The recovery of 99% of each component in two liquid products of 99% purity are specified. To describe the nonideality in the liquid phase, the Wilson model is used, and the vapour phase is assumed to be ideal. Thermodynamic data used is given in Table 3.12 and pure component enthalpies in Appendix A.

The synthesis model results in the selection of benzene as the optimal entrainer. When the mass/heat exchange module is heavily penalised in the cost function (indicating an important capital cost weighting function), the structure of Figure 3.27 is proposed for the separation. Four mass/heat modules are utilised interconnected in a configuration that can be realised as two distillation columns in series. The acetone-chloroform and benzene feed is fed into the liquid mixer of same mass/heat block. In the first two mass/heat exchangers, acetone is transferred to the vapour phase and chloroform and benzene to the liquid phase. A pure acetone product emerges from this separation “unit”. The liquid chloroform and benzene stream is then fed to the next two mass/heat exchange blocks where chloroform is transferred to the vapour phase and benzene to the liquid phase. The recovered benzene is recycled to the first separator and a pure chloroform product appears as the distillate of the second separator. Feasible separation in this system is achieved due to crossing of the simple distillation boundary, as shown in Figure 3.28. The cost of crossing the boundary is a high benzene recycle rate and high reboiler duties, as can be seen in Table 3.13.

When the cost of the mass/heat module is alleviated, the synthesis model results in an alternative separation structure, again utilising benzene as the entrainer. Shown in Figure 3.29 six mass/heat exchange modules are interconnected as in a three column sequence. In the first two mass/heat blocks, acetone is transferred from the liquid to the vapour stream. However, due to a lower ratio of benzene entrainer to fresh feed in this separator, not all the acetone emerges as the top product. Some acetone appears in the bottom liquid product with the chloroform and benzene, and the simple distillation



(a) Acetone, chloroform and benzene mixture



(b) Acetone, chloroform and methanol mixture

Figure 3.26: Residue Curve Maps for Acetone-Chloroform at 1 atm

Component	C1	C2	C3	v_i m^3/mol
Acetone	7.6313	1566.69	273.419	73.931×10^{-6}
Chloroform	7.44777	1488.99	264.915	80.662×10^{-6}
Benzene	6.87987	1196.76	219.161	89.503×10^{-6}
Methanol	7.97010	1521.23	233.970	40.691×10^{-6}

$$\log P^{sat} = C1 - \frac{C2}{C3 + T} \quad (mmHg, ^\circ C)$$

Wilson equation

$$\ln \gamma_i = 1 - \ln \left[\sum_j x_j \Lambda_{ij} \right] - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$
$$\Lambda_{ij} = \frac{v_j}{v_i} \exp \left(\frac{-A_{ij}}{RT} \right) \quad A_{ii} = 0$$

Binary Interaction Parameters A_{ij} (cal/mol)				
	Acetone	Chloroform	Benzene	Methanol
Acetone	0.0	28.8819	543.9352	-161.8813
Chloroform	-484.3856	0.0	-161.8065	-351.1964
Benzene	-182.5230	49.6010	0.0	183.0383
Methanol	583.1054	1760.6741	1734.4181	0.0

(Data from Gmehling *et al.*, 1979-1988)

Table 3.12: Acetone-Chloroform Separation : Thermodynamic properties

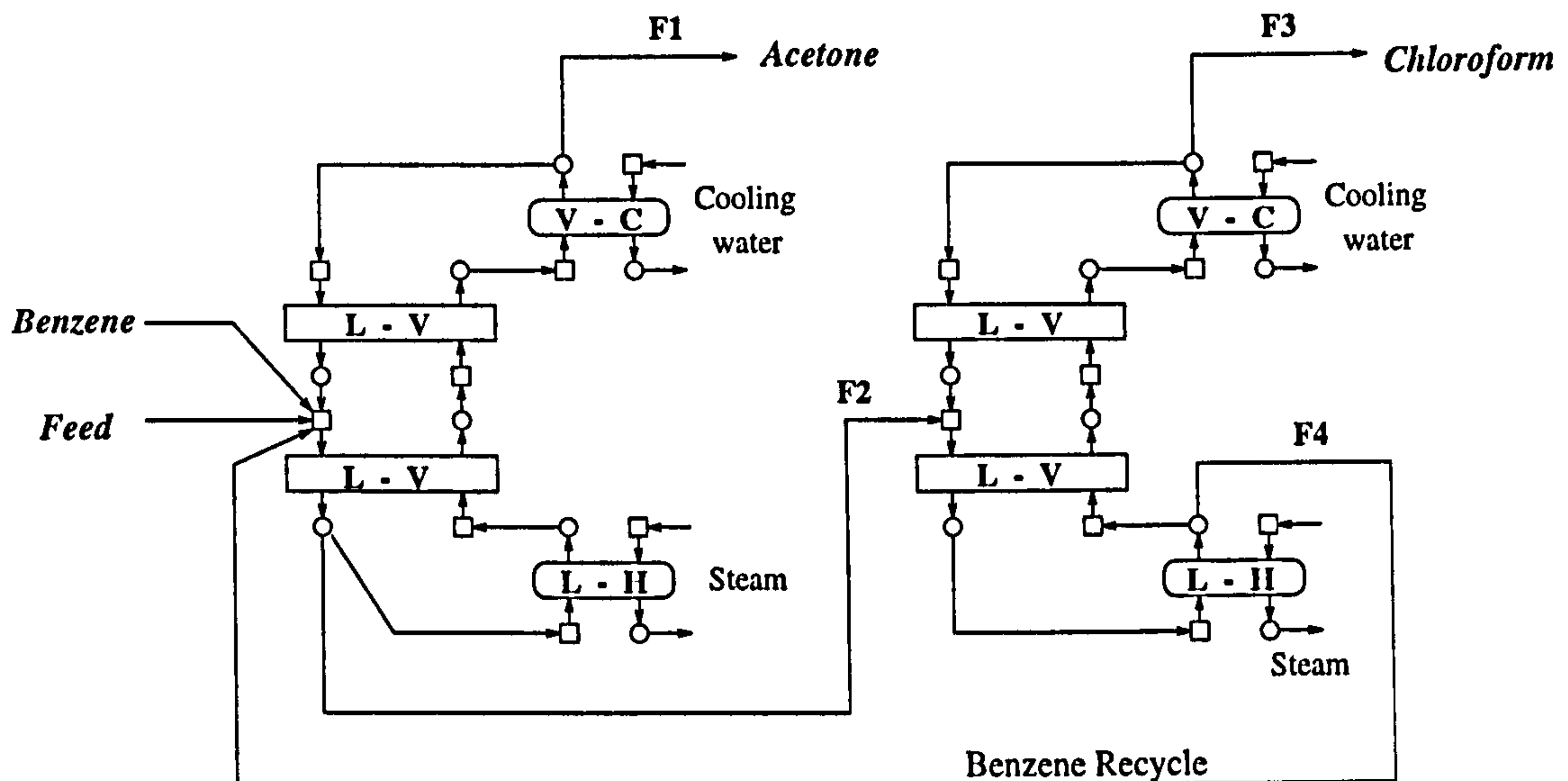


Figure 3.27: Acetone-Chloroform : Structure 1

boundary is *not* crossed (see the liquid profile of this separation sequence in Figure 3.30). This liquid is fed to a second separator consisting of two mass/heat modules and two pure heat blocks, where acetone and chloroform are transferred to the vapour stream and the benzene to the liquid stream. In this unit, pure liquid benzene is obtained as bottom and recycled to the first “unit”. The top product of this separator F3 is on the chloroform side of the azeotrope (Figure 3.30) and is fed to the next two mass/heat exchangers. In these blocks chloroform is transferred to the vapour phase to result in a desired pure chloroform stream, but the amount of mass transfer allowed is limited by the azeotropic composition which emerges as the bottom product. This stream F6 is recycled to the first separator.

It is interesting to note how the trade-offs between capital and operating cost can be captured within the proposed synthesis framework, even when exact capital cost functions cannot be employed. In the first case, when a high “capital cost” is considered for each mass/heat exchange module, the separation is achieved in a small number of modules (that can correspond to two separation units). However, in order to cross the distillation boundary, a high benzene recycle is required and thus high heating duties (see Table 3.13). When heating is penalised, the distillation boundary is not crossed and high purity chloroform is obtained at the cost of two extra mass/heat exchange modules (*i.e.* an extra separator). Furthermore, the “three column” sequence has better operational characteristics, and is not subject to the uncertainty of boundary crossing in the two column sequence (due to sensitivity of design to parameters in the thermodynamic model).

Stream	Total flow (kmol/s)	Component Molar Flows			Temp (K)
		Acetone	Chloroform	Benzene	
Feed	10.0000	6.0000	4.0000	0.0000	330.15
Makeup	0.0030	0.0000	0.0000	0.0030	353.30
F1	6.0026	5.9601	0.0396	0.0029	329.30
F2	60.8014	0.0399	3.9604	56.8011	352.80
F3	4.0004	0.0399	3.9604	0.0001	334.10
F4	56.8010	0.0000	0.0000	56.8010	353.30
		$Q_{heating,1}$		2843.49 kW	
		$Q_{heating,2}$		2660.79 kW	
		$Q_{heating,T}$		5504.28 kW	

Table 3.13: Acetone-Chloroform Structure 1 : Summary

Stream	Flow (kmol/s)	Composition			Temp (K)
		$X_{Acetone}$	$X_{Chloroform}$	$X_{Benzene}$	
Feed	10.000	0.600	0.400	0.000	330.15
F1	6.000	1.000	0.000	0.000	
F2	16.220	0.120	0.465	0.415	352.8
F3	9.550	0.210	0.790	0.000	
F4	6.670	0.000	0.000	1.000	353.3
F5	3.999	0.000	1.000	0.000	
F6	5.550	0.360	0.640	0.000	338.0
		$Q_{heating,1}$		1459.80	kW
		$Q_{heating,2}$		2059.70	kW
		$Q_{heating,3}$		1030.08	kW
		$Q_{heating,T}$		4549.58	kW

Table 3.14: Acetone-Chloroform Structure 2 : Summary

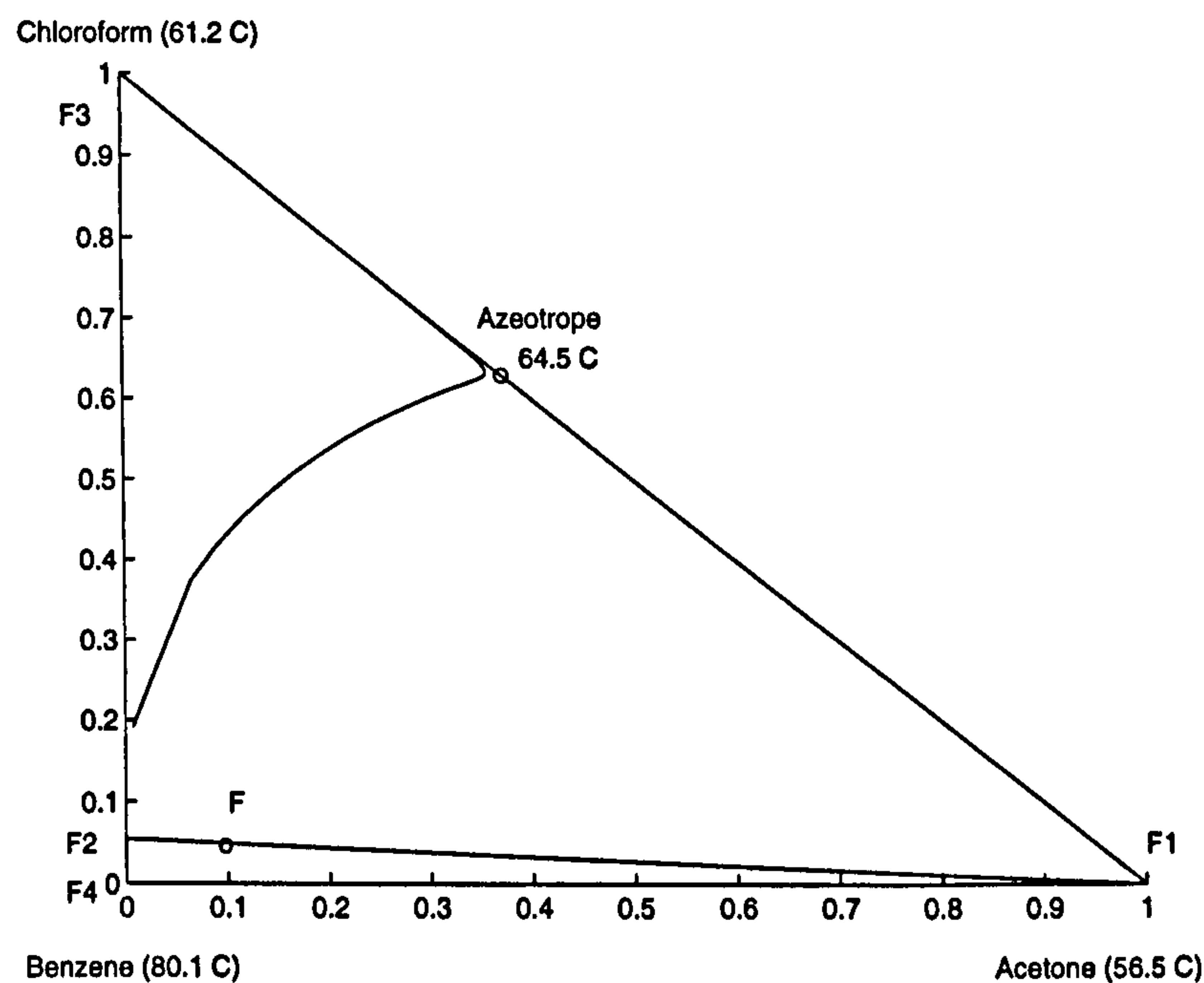


Figure 3.28: Acetone-Chloroform Structure 1: Liquid Composition Profile

3.11 Summary and Discussion

A mass/heat exchange superstructure modular representation for synthesising homogeneous azeotropic separation systems has been proposed in this work. The model features (i) generic expressions for the consistent determination of the mass transfer direction within the optimisation procedure, and (ii) multipurpose mass/heat exchange modules, through the combinations of which separation units and structures can be realized. As illustrated with two representative separation example problems, the proposed representation and synthesis methodology has the potential of identifying promising separation schemes *i.e.* columns, their sequence and required entrainers, in a simultaneous manner. Feasible alternatives optimal with respect to an economical objective function are achieved, and can be utilised as a starting point for more detailed design.

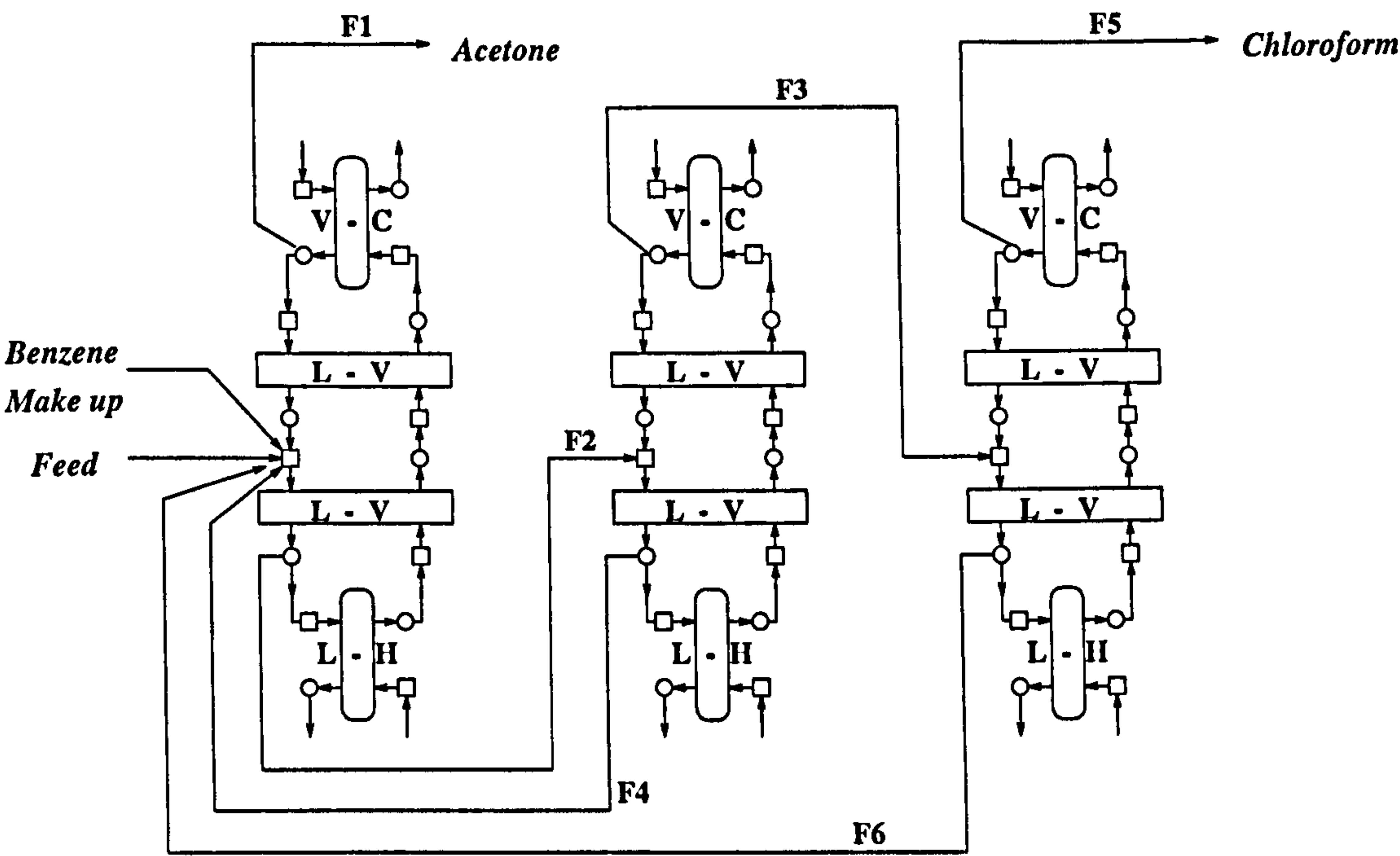


Figure 3.29: Acetone-Chloroform : Structure 2

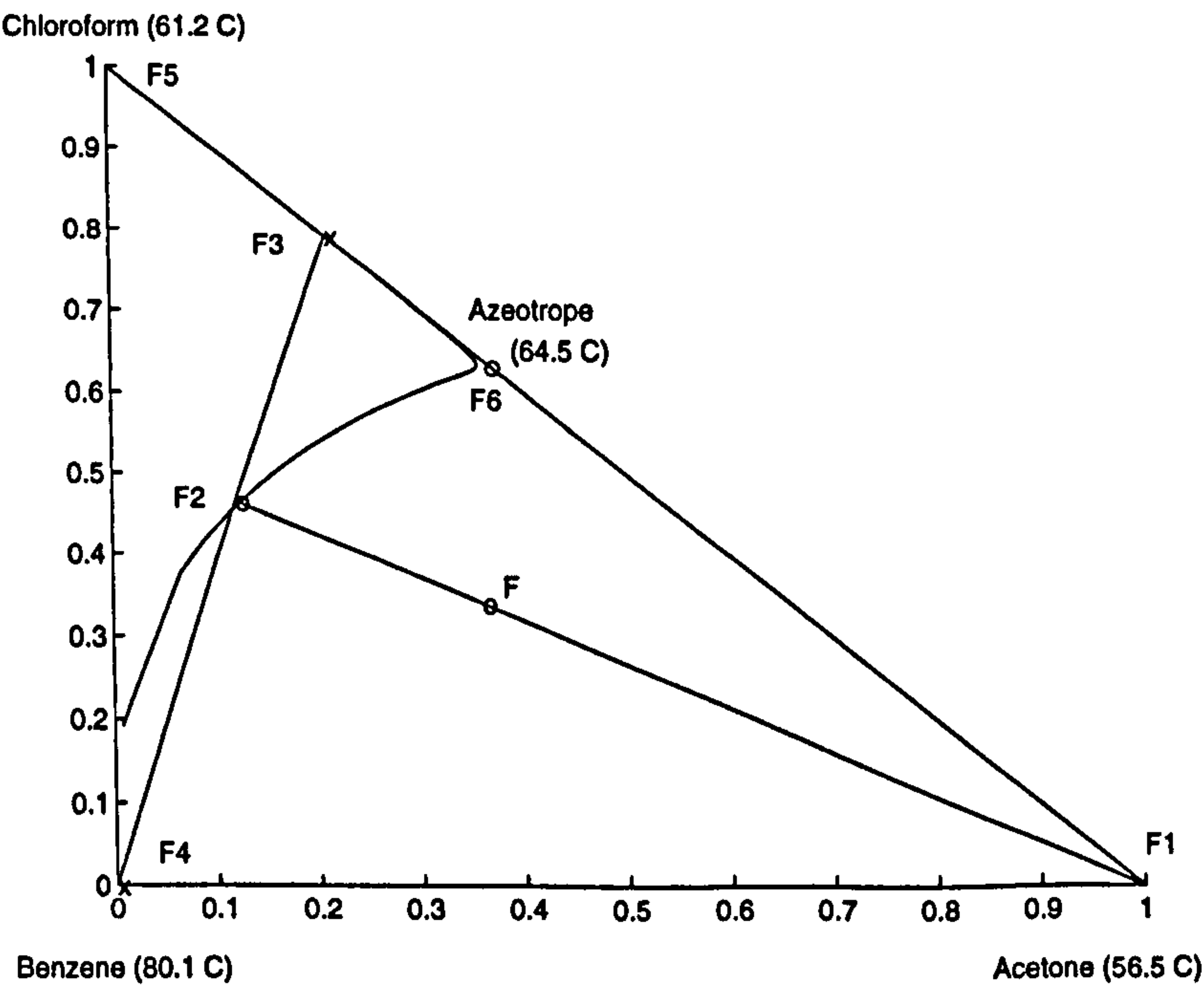


Figure 3.30: Acetone-Chloroform Structure 2 : Liquid Composition Profile

3.12 Extension to Heterogeneous Azeotropic Systems

Heterogeneous azeotropic distillation is a widely used technique for separating binary azeotropes into their pure components. Whilst homogeneous entrainers ensure feasible separation by removing or shifting the distillation boundaries between the desired components, heterogeneous entrainers induces liquid-liquid phase separation over a broad range of compositions and exploits this immiscibility to ‘jump’ across distillation boundaries Pham and Doherty (1990a).

Research in the analysis and design of heterogeneous azeotropic mixture is not as extensive as for homogeneous azeotropic separation systems. A summary of the studies in steady state behaviour and dynamic simulation is given by Widagdo and Seider (1996), and recent works have focussed in the existence of multiple steady states in heterogeneous azeotropic systems (Bekiaris *et al.*, 1996).

In terms of the synthesis and design of heterogeneous azeotropic systems, procedures using residue curve maps to assess feasibility of entrainers and corresponding column sequences have been developed in the same spirit as described in section 3.2 for homogeneous azeotropic systems. Procedures to construct heterogeneous residue curve maps for ternary systems and analyse its structure and properties are developed by (Pham and Doherty, 1990b). From this, rules for distinguishing between feasible and infeasible heterogeneous entrainers are presented (Pham and Doherty, 1990c) with illustrations on the generation of alternative feasible distillation sequences using residue curve maps. A boundary value design procedure (BVDP) (originally developed for homogeneous systems, see section 3.2.5) to determine the number of theoretical stages for heterogeneous distillation columns for ternary mixtures is presented by Pham *et al.* (1989), assuming constant molar overflow (CMO), liquid saturated feed and liquid-liquid separation only in the decanter. Although obviously incorrect for this class of systems, the CMO assumption enabled important geometrical aspects to be explored. Accounting for heat effects, Ryan and Doherty (1989) utilised this BVDP to design and optimise the separation system of ethanol and water through the addition of benzene. Within this study, a number of structural alternatives available through the literature were investigated and compared. For the optimisation, four main optimisation variables were identified. However, heuristics were developed to determine all but one set of the variables - the decanter temperature and composition. The structures were then optimised for this variable with respect to total annualised cost.

Available methods for synthesis and design of heterogeneous azeotropic mixtures are restricted to ternary mixtures and are based on separation feasibility analysis at total reflux. Although useful to quickly assess feasibility, these methods are not readily extendible

to multicomponent systems and only consider liquid-liquid separation in the decanter. Available optimisation studies have been conducted for a fixed structure with respect to one optimisation variable with the others determined from heuristics. Currently there are no procedures available for the optimal synthesis of heterogeneous azeotropic systems which are readily applicable to multicomponent systems. Extension of the proposed synthesis framework for homogeneous azeotropic separation to include heterogeneous separation would be beneficial, allowing the structure and operating conditions to be determined within a single optimisation problem. Although this is a topic left for future investigation, modelling concepts on a module level to encompass heterogeneous systems is suggested in this section.

3.12.1 Heterogeneous Azeotropes

The phenomenon of vapour/liquid/liquid equilibrium (VLLE) occurs when a liquid-liquid envelope intersects the vapour-liquid equilibrium bubble point curve. For a binary mixture exhibiting a minimum boiling azeotrope (Figure 3.31(a)), the resulting heterogeneous azeotropic phase diagram has the form shown in Figure 3.31(b). For a homogeneous azeotrope, the mixture boils at constant and equal composition in both the liquid and vapour phase such that $x_i = y_i = x_{i,AZ}$ (Figure 3.31(a)). At a heterogeneous azeotrope $x_{i,AZ}^o$ as shown in Figure 3.31(b), the mixture boils at constant, but not equal composition in the three coexisting phases. The vapour composition is equal to the overall liquid composition $y_i = x_{i,AZ}^o$, and the two liquid phases x_i^I and x_i^{II} are at equilibrium with one another at the end of the liquid-liquid tie line. A method for the determination of heterogeneous azeotropes is presented by Tolsma and Barton (1998), based on the extension of the homotopy-continuation method of Fidkowski *et al.* (1993a) for the determination of homogeneous azeotropes.

Although VLLE phase diagrams and phase equilibrium calculations are more complex than for homogeneous vapour liquid equilibria, the residue curve maps are only marginally more involved (Pham and Doherty, 1990a).

3.12.2 Modelling Concepts

In this section, initial modelling concepts to encompass heterogeneous mixtures within the modular framework will be discussed. In particular we consider the separation synthesis of a mixture whereby two liquid phases may form - for example the classical example of the separation of ethanol and water through the addition of a heterogeneous entrainer

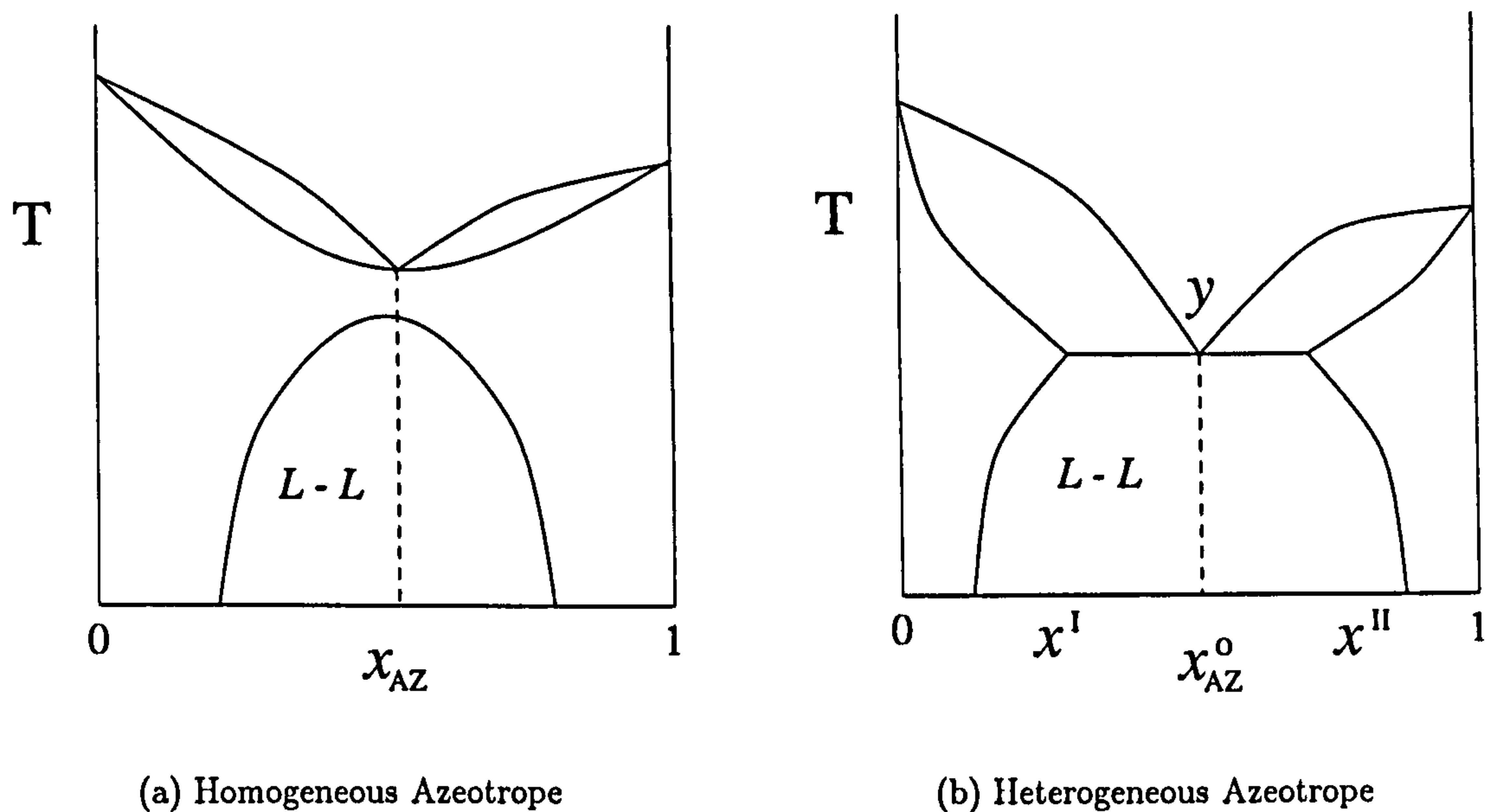


Figure 3.31: Binary Phase Diagrams

benzene.

For the separation of homogeneous mixtures, mass transfer occurs between the stable liquid phase and the vapour phase. Within the developed framework presented in this chapter, a liquid-vapour module is introduced as the building block of process alternatives (Figure 3.32(a)). When two liquid phases are formed, say for example on a tray of a heterogeneous azeotropic distillation column, mass transfer occurs between the two liquid phases and also between each of the liquid phases and the vapour phase. To account for this phenomena, the module can be amended as shown in Figure 3.32(b), consisting of two cocurrent immiscible liquid phases exchanging mass with a vapour phase. Individually, the phases $L1$ and $L2$ are stable but their combined overall liquid composition would be unstable. Due to mass transfer within the module between the liquid and vapour phases, a stable inlet liquid may become unstable and form two liquid phases as shown in Figure 3.32(c). Similarly an inlet two phase liquid may result in a single stable liquid phase (Figure 3.32(d)). Figure 3.32(c) and (d) can be considered as instances of Figure 3.32(b) with zero inlet and outlet $L2$ flows respectively.

Conceptually, Figure 3.32 represents all the possible mass transfer possibilities between a liquid that may form two phases, and a vapour. In terms of modelling the mass transfer of components within the module to ensure feasibility, mass transfer driving force constraints could be derived to describe the mass transfer between the two liquid streams (if they exist) and between each of the existing liquid streams and vapour streams. Decoupling the mass transfer between each of the streams, intuitive extension of the driving

force constraints would result in the following constraints:

- For mass transfer between the liquid streams $L1$ and $L2$ (see Appendix C.1)

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad (3.111)$$

$$\mathcal{G}1_i = (Fx_i)_{in}^{L1} - (Fx_i)_{out}^{L1} \quad (3.112)$$

$$\mathcal{G}2_i = (\gamma_i x_i)_{out}^{L1} - (\gamma_i x_i)_{out}^{L2} \quad (3.113)$$

- For mass transfer between the liquid streams $L1$ and V

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad (3.114)$$

$$\mathcal{G}1_i * \mathcal{G}3_i \geq 0 \quad (3.115)$$

$$\mathcal{G}1_i = (Fx_i)_{in}^{L1} - (Fx_i)_{out}^{L1} \quad (3.116)$$

$$\mathcal{G}2_i = (\gamma_i x_i P^{sat})_{out}^{L1} - (x_i)_{in}^V P_{tot} \quad (3.117)$$

$$\mathcal{G}3_i = (\gamma_i x_i P^{sat})_{in}^{L1} - (x_i)_{out}^V P_{tot} \quad (3.118)$$

- For mass transfer between the liquid streams $L2$ and V

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad (3.119)$$

$$\mathcal{G}1_i * \mathcal{G}3_i \geq 0 \quad (3.120)$$

$$\mathcal{G}1_i = (Fx_i)_{in}^{L2} - (Fx_i)_{out}^{L2} \quad (3.121)$$

$$\mathcal{G}2_i = (\gamma_i x_i P^{sat})_{out}^{L2} - (x_i)_{in}^V P_{tot} \quad (3.122)$$

$$\mathcal{G}3_i = (\gamma_i x_i P^{sat})_{in}^{L2} - (x_i)_{out}^V P_{tot} \quad (3.123)$$

To reduce the nonconvexities of the driving force constraints and also to allow the inclusion of logical constraints for the resulting synthesis problem, three types of mass transfer binary variables to denote the mass transfer direction of components between each pair of streams could be introduced. *i.e*

$$yt_{i,e}^{L1-L2} = \begin{cases} 1, & \text{when component } i \text{ is transferred from } L1 \text{ to } L2 \text{ in module } e \\ 0, & \text{when component } i \text{ is transferred from } L2 \text{ to } L1 \text{ in module } e \end{cases} \quad (3.124)$$

$$yt_{i,e}^{L1-V} = \begin{cases} 1, & \text{when component } i \text{ is transferred from } L1 \text{ to } V \text{ in module } e \\ 0, & \text{when component } i \text{ is transferred from } V \text{ to } L1 \text{ in module } e \end{cases} \quad (3.125)$$

$$yt_{i,e}^{L2-V} = \begin{cases} 1, & \text{when component } i \text{ is transferred from } L2 \text{ to } V \text{ in module } e \\ 0, & \text{when component } i \text{ is transferred from } V \text{ to } L2 \text{ in module } e \end{cases} \quad (3.126)$$

Then the driving force constraints could be rewritten as follows;

- For mass transfer between the liquid streams $L1$ and $L2$

$$\begin{aligned} (yt_{i,e}^{L1-L2} - 1) \mathcal{U} &\leq (Fx_i)_{in}^{L1} - (Fx_i)_{out}^{L1} \leq yt_{i,e}^{L1-L2} \mathcal{U} \\ (yt_{i,e}^{L1-L2} - 1) \mathcal{U} &\leq (\gamma_i x_i)_{out}^{L1} - (\gamma_i x_i)_{out}^{L2} \leq yt_{i,e}^{L1-L2} \mathcal{U} \end{aligned} \quad (3.127)$$

- For mass transfer between the liquid streams $L1$ and vapour V

$$\begin{aligned} (yt_{i,e}^{L1-V} - 1) \mathcal{U} &\leq (Fx_i)_{in}^{L1} - (Fx_i)_{out}^{L1} \leq yt_{i,e}^{L1-V} \mathcal{U} \\ (yt_{i,e}^{L1-V} - 1) \mathcal{U} &\leq (\gamma_i x_i P^{sat})_{out}^{L1} - (x_i)_{in}^V P_{tot} \leq yt_{i,e}^{L1-V} \mathcal{U} \\ (yt_{i,e}^{L1-V} - 1) \mathcal{U} &\leq (\gamma_i x_i P^{sat})_{in}^{L1} - (x_i)_{out}^V P_{tot} \leq yt_{i,e}^{L1-V} \mathcal{U} \end{aligned} \quad (3.128)$$

- For mass transfer between the liquid streams $L2$ and vapour V

$$\begin{aligned} (yt_{i,e}^{L2-V} - 1) \mathcal{U} &\leq (Fx_i)_{in}^{L2} - (Fx_i)_{out}^{L2} \leq yt_{i,e}^{L2-V} \mathcal{U} \\ (yt_{i,e}^{L2-V} - 1) \mathcal{U} &\leq (\gamma_i x_i P^{sat})_{out}^{L2} - (x_i)_{in}^V P_{tot} \leq yt_{i,e}^{L2-V} \mathcal{U} \\ (yt_{i,e}^{L2-V} - 1) \mathcal{U} &\leq (\gamma_i x_i P^{sat})_{in}^{L2} - (x_i)_{out}^V P_{tot} \leq yt_{i,e}^{L2-V} \mathcal{U} \end{aligned} \quad (3.129)$$

3.12.3 Heterogeneous mass/heat transfer module

Within the synthesis framework for the separation of homogeneous and heterogeneous mixtures, multiple instances of each module as shown in Figure 3.32 would be considered. In addition, initial splitters for all given and possible feeds and final mixers for all desired and possible products is considered. A superstructure of alternatives can then be constructed by considering all physically possible interconnections between splitters and mixers.

The following constraints would apply to each of the modules;

- Component mass balances *i.e* Figure 3.32(b)

$$(Fx_i)_{in}^{L1} + (Fx_i)_{in}^{L2} + (Fx_i)_{in}^V - (Fx_i)_{out}^{L1} - (Fx_i)_{out}^{L2} - (Fx_i)_{out}^V = 0 \quad (3.130)$$

- Energy balances *i.e* Figure 3.32(b)

$$(Fh)_{in}^{L1} + (Fh)_{in}^{L2} + (Fh)_{in}^V - (Fh)_{out}^{L1} - (Fh)_{out}^{L2} - (Fh)_{out}^V = 0 \quad (3.131)$$

- Summation of molar fractions for each stream *i.e.*

$$\sum_i x_{i,in}^{L1} = \sum_i x_{i,out}^{L1} = 1 \quad (3.132)$$

$$\sum_i x_{i,in}^{L2} = \sum_i x_{i,out}^{L2} = 1 \quad (3.133)$$

$$\sum_i x_{i,in}^V = \sum_i x_{i,out}^{L2} = 1 \quad (3.134)$$

- Driving force constraints between each pair of existing streams. *i.e* Equations (3.111) - (3.123) or (3.127) - (3.129) would apply to the module of Figure 3.32(b)
- Stability constraints on each of the liquid streams. Stability constraints would need to be imposed on the existing inlet and outlet liquid phase streams $L1$ and $L2$. Additionally, when both $L1$ and $L2$ exist, the overall liquid composition needs to be constrained by an instability constraint.

A reliable stability constraint would have to be investigated to correctly predict the right number of liquid phases. Derived from fundamental thermodynamic properties, the most reliable stability techniques are based on Gibbs free energy, and global stability tests have been proposed *i.e.* Michelsen (1982). A review of techniques is available in Heidemann (1983). Pham and Doherty (1990a) propose a simple test for the class of systems whereby there is at most two liquid phases. Alternatively, Gumus and Ciric (1997) proposed a nested optimisation problem to determine the number of phases.

Instead of explicitly considering all the liquid-vapour modules in Figure 3.32, a single module 3.32(b) can be considered. Note that when a module exists, the liquid stream $L1$ always exists and it is the presence of $L2$ that needs to be identified. A binary variable to denote the stability of the liquid phase could be introduced to account for all the possibilities. *i.e.*

$$ystab_e^{in} = \begin{cases} 1, & \text{when the inlet liquid stream to module } e \text{ is stable} \\ 0, & \text{when the inlet liquid stream to module } e \text{ is unstable} \end{cases} \quad (3.135)$$

$$ystab_e^{out} = \begin{cases} 1, & \text{when the outlet liquid stream to module } e \text{ is stable} \\ 0, & \text{when the outlet liquid stream to module } e \text{ is unstable} \end{cases} \quad (3.136)$$

Thus when $ystab_e^{in} = 1$ and $ystab_e^{out} = 1$, the module 3.32(b) collapses to 3.32(a), when $ystab_e^{in} = 0$ and $ystab_e^{out} = 1$ 3.32(b) collapses to 3.32(d), *etc.*

A potential combinatorial problem could result from this form of formulation, as for each liquid-vapour module, there are $3C + 2$ binary variables (3.135-3.136 and 3.124-

3.126) and thus 2^{3C+2} combinations. However, these variables aid the optimisation in the following way:

- Logical constraints can be introduced to reduce the allowable number of combinations

For example, when the inlet and outlet liquid streams are stable

$$ystab_e^{in} = ystab_e^{out} = 1$$

- (i) the binary variables $yt_{i,e}^{L1-L2}$ and $yt_{i,e}^{L2-V}$ are redundant, as are driving force constraints (3.127) and (3.129)
- (ii) continuous variables describing $L2$ such as flowrate and composition do not exist

Such constraints would aid the optimisation problem.

- To determine $ystab_e^{in}$ and $ystab_e^{out}$, a stability test can be handled in a separate step, for example a nested decomposition algorithm can be developed.

For completeness, possible mass transfer between the liquid phases would also be considered (Figure 3.33).

Whilst it is believed that stability criteria should be enforced on the liquid streams around the mass/heat exchangers, an open question would be how to handle the liquid streams around the heat exchangers. Within heat exchangers considered so far, no mass transfer occurs and thus the flowrate and composition of the stream is assumed constant. When more than one liquid phase exists, it may be necessary to couple mass transfer within the heat exchanger. A liquid phase heater or cooler can be represented as a heat exchanger between a utility stream and two liquid streams as shown in Figures 3.34(a)-(c), whereby mass exchange is allowed between the liquid streams, and heat between the liquid streams and the utility stream. Due to the amount of heat exchange between the utility stream and the liquid stream, the liquid streams may exchange mass to form one or two immiscible phases. A condenser followed by a decanter could be represented as shown in Figures 3.34(d), and a reboiler as Figure 3.34(e) illustrates.

3.12.4 Representation

For illustrative purposes, consider the configuration of modules as shown in Figure 3.35, representing a heterogeneous azeotropic column. The liquid feed stream and entrainer is

fed to a mixer of a $L1 - L2 - V$ module. Module $MH1$ represents the stripping section with a homogeneous outlet liquid stream. This stream is split to give the bottom liquid product and the inlet stream to heat exchanger $HX1$ representing a reboiler. Module $MH2$ and $MH3$ represents the rectifying section. The vapour outlet of $MH3$ is feed to $HX2$, whereby it is cooled to a liquid phase. Moreover, the liquid phase is unstable and splits into two immiscible phases. One phase is drawn off as a product, and the other phase is refluxed to $MH3$. Heat exchanger $HX2$ therefore represents the total condenser and the decanter.

3.12.5 Summary

In this section, the preliminary concepts for the extension of the framework for the synthesis of homogeneous azeotropic separation to encompass heterogeneous mixtures where two liquid phases may form is discussed. Such an extension would allow homogeneous and heterogeneous entrainers to be considered and compared within one optimisation problem, allowing the entrainer, structure and approximate operating conditions to be simultaneously determined. By amending the mass/heat transfer module to account for more than one liquid phase, and by derivation of appropriate driving force constraints to capture the VLLE mass transfer phenomena that can occur, the synthesis framework can be systematically extended.

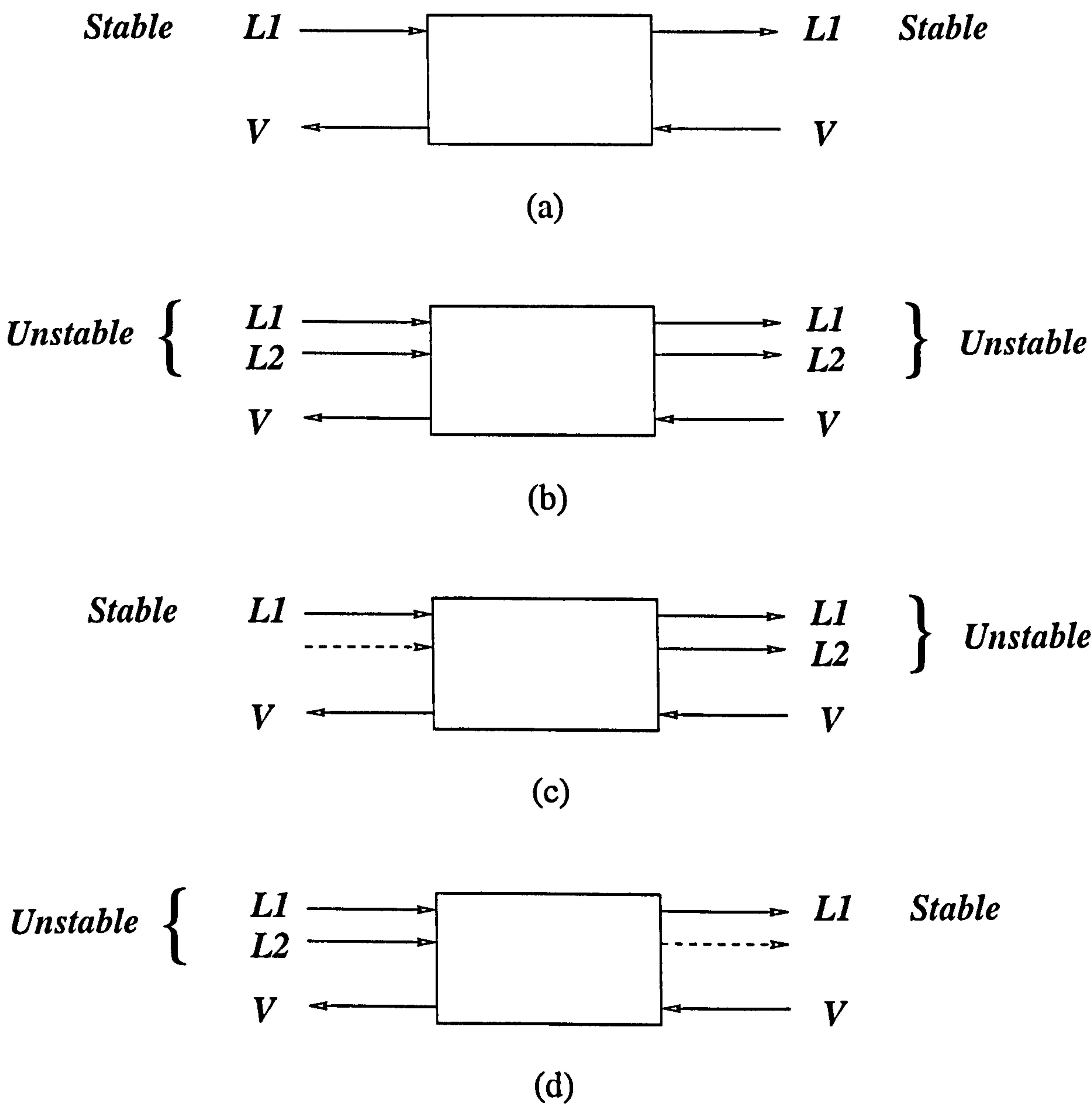


Figure 3.32: Possible Liquid-Vapour Modules

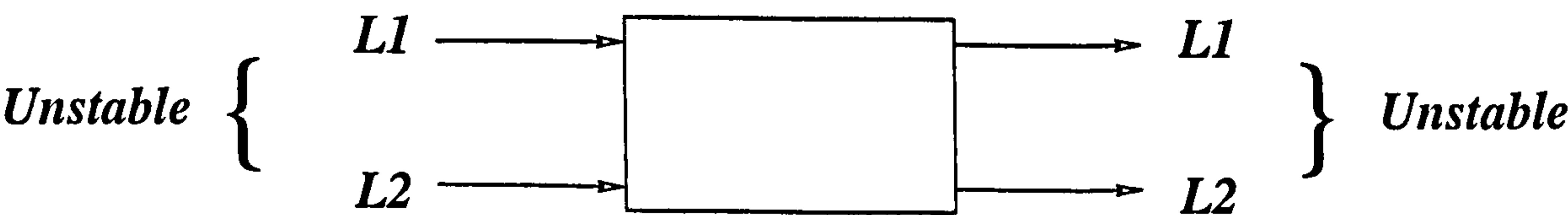


Figure 3.33: Possible Liquid-Liquid Modules

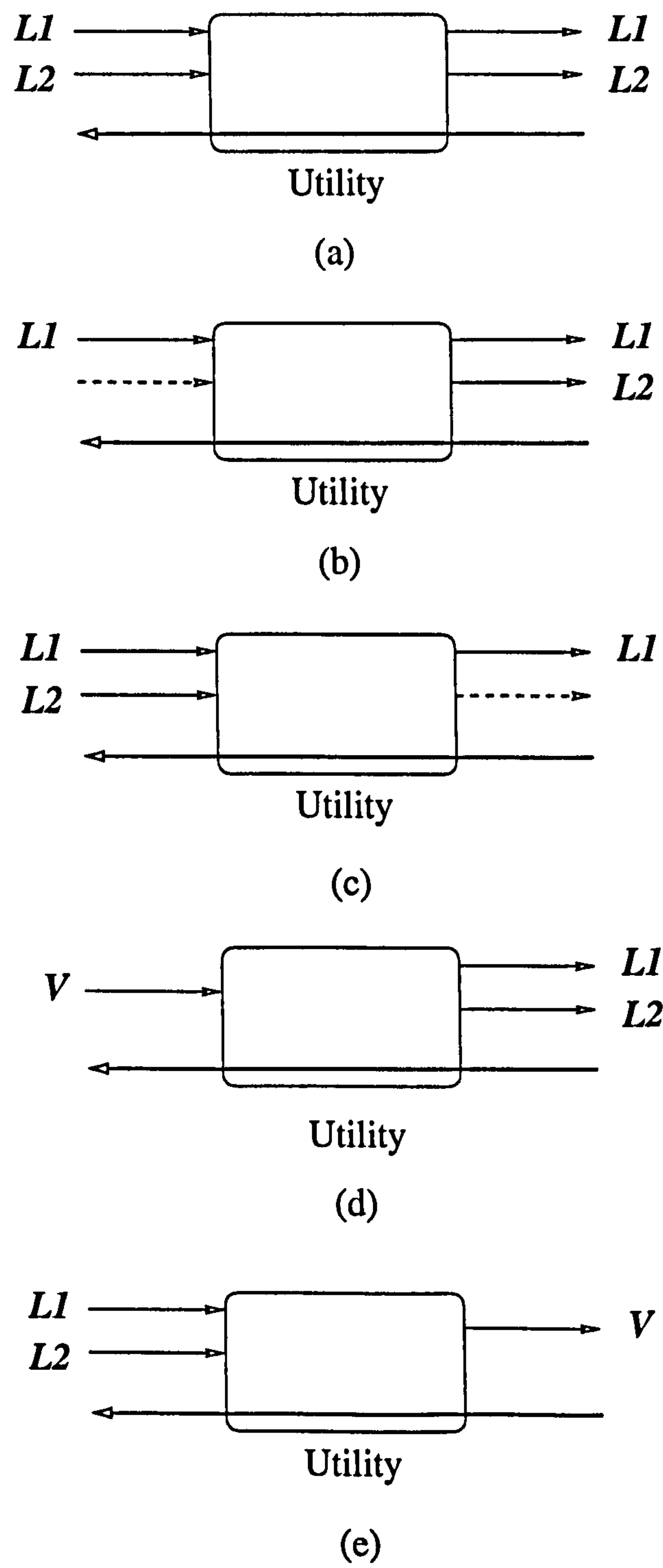


Figure 3.34: Heat Exchangers for Heterogeneous Systems

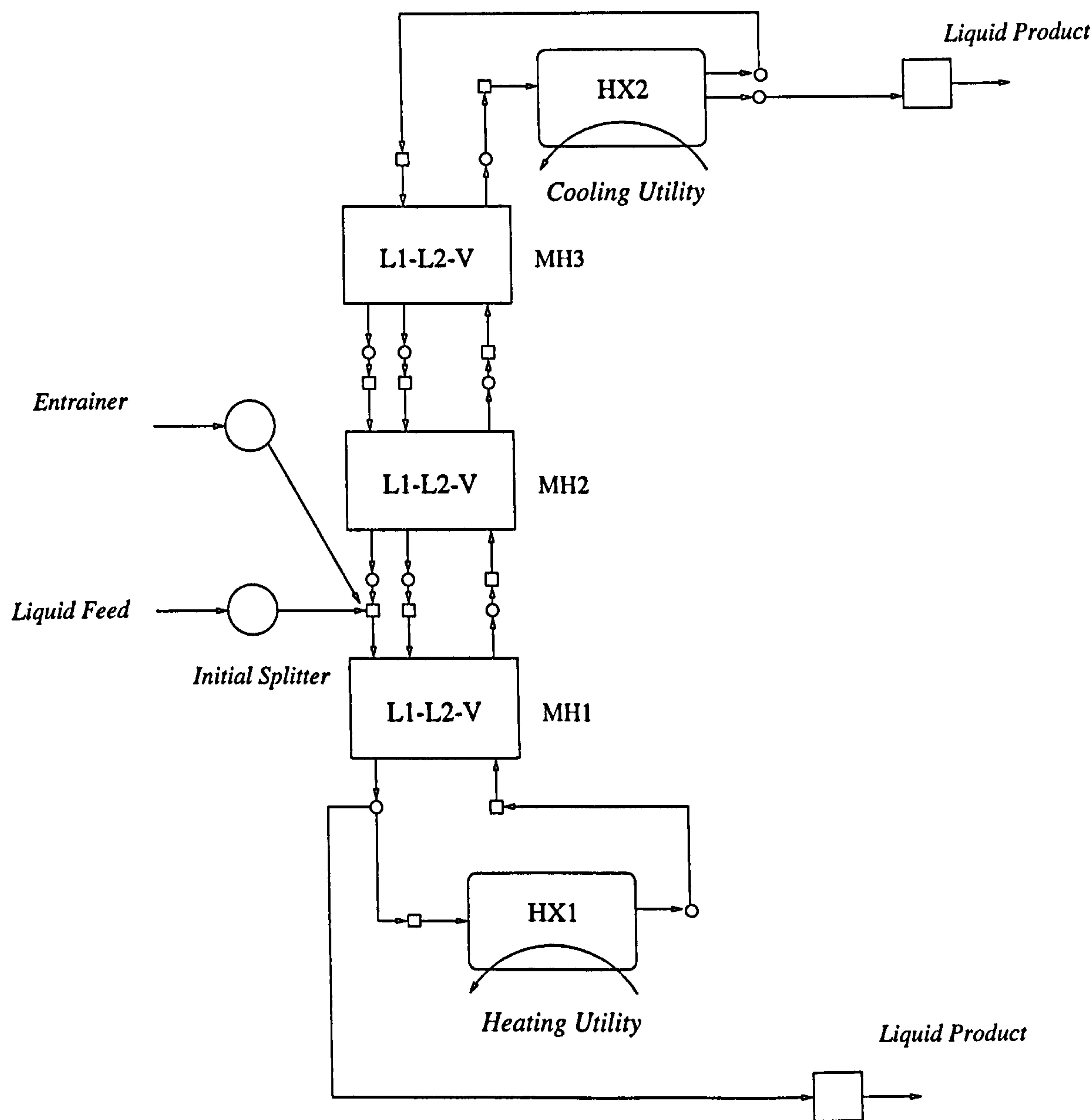


Figure 3.35: Representation of heterogeneous azeotropic column with phase splitting on the trays

Synthesis of Combined Reactive/Separation Systems

4.1 Introduction

In Chapter 3, the mass/heat transfer framework is applied to homogeneous azeotropic separation systems where it is shown that entrainer selection and separation structure can be revealed without any prepostulation of operation units. In this chapter, the methodology is extended to encompass combined reaction and separation processes. Accounting for the complex interactions which exist in these systems allows them to be exploited, leading to good process designs. Through the driving force constraints, combined reaction-separation phenomena can be captured, allowing integrated hybrid structures to be revealed. In section 4.1 a review of the works in this area is given. The driving force constraints for this class of system are then derived, and the synthesis framework is applied to three typical examples, illustrating the ability of this methodology to reveal hybrid processes with pure separation and combined separation-reaction operations.

4.2 State of Art in Reactive Separation Systems

Processes of integrated reaction and separation phenomena have been of recent academic interest, fuelled by the superior performance of novel hybrid units such as reactive distillation and membrane reactors over conventional units. Advances in the modelling, design and analysis of such systems has been mainly concentrated on the specific case of reactive distillation. To a lesser extent, there have been developments in the integration school of thought whereby separation and reaction is simultaneously synthesised with the rest of the flowsheet. An overview of both these approaches is given in the proceeding sections.

4.2.1 Reactive Distillation

Successful industrial application of reactive distillation in the production of chemicals such as MTBE and methyl acetate has maintained a high level of interest in research on various aspects of reactive separation. Reactive distillation is applied specifically to reversible chemical reactions in the liquid phase whereby the conversion of reactants is limited by the reaction equilibrium. By combining two operations in one unit, reactive distillation allows synergistic effects to occur, for example the shift of equilibrium by separation of the products, enhancing conversion by Le Chatelier's principle, and utilisation of the reaction heat for the separation of educts and products. Other advantages include the suppression of undesired side reactions, and the ability to achieve high conversions at stoichiometric feed flowrates. As a result, capital cost, recycle operating cost, and utility costs are minimised due to the reduction in the number of processing units and direct heat integration between separation and reaction.

Early research in reactive distillation focused upon computing a single steady-state solution of the system of equations that the simulation presents. A summary of the numerical methods developed is given by Chang and Seader (1988). Whilst the extension of simulation methods for non-reactive distillation to reactive distillation is relatively straightforward, the same cannot be said for the extension of design techniques. The bottleneck in the synthesis and of reactive distillation processes has been in the understanding of the interaction of reaction and distillation, a task with which many academics have dedicated intensive research. To our knowledge the approaches to the analysis and design of reactive distillation columns, as summarised in Table 4.1 and 4.2 can be classified into three categories which will be individually considered;

- Approach using transformed composition variables
- Element balance approach
- Superstructure based approach

In terms of non-equilibrium models, Higler *et al.* (1998) recently presented a simulation model for a single feed reactive column, utilising reaction kinetics and accounting for the coupling between chemical reaction and mass transfer. On a more conceptual level, Hauan and Lien (1998) take on a different approach and present an analytical framework for reactive distillation systems based on the notion of phenomena vectors. Similar to the '*attainable region concept*', as discussed later in this section, this approach seeks the optimal combination of the phenomena involved (in this case, separation, mixing and reac-

tion), then at a later stage derive the actual unit structure. This approach enables hybrid processes to be explored by providing synthesis targets rather than alternatives.

Transformed Composition Variables

The work of Doherty and coworkers has been based upon extending the design procedure for the separation of multicomponent nonideal and azeotropic mixtures to reactive mixtures. The means with which to achieve this is the introduction of a set of new composition variables, which reduce the conservation equations for simple reactive distillation mixtures to a form that is identical for non-reactive mixtures. The transformed variables are reaction invariant *i.e.* have the property of taking the same numerical value before and after reaction, and provide a mechanism for reducing the dimensionality of the phase and chemical equilibria problem in multicomponent reactive systems. These variables are especially convenient for visualising phase diagrams for multicomponent reactive mixtures.

The development of the tools for the analysis of reactive distillation columns by Doherty and coworkers is summarised in Table 4.1. The concept of transformed variables were introduced by Barbosa and Doherty (1987a) for multicomponent systems with a *single* reaction at *chemical equilibrium* with no inerts. From this, conditions for reactive azeotropy were studied (Barbosa and Doherty, 1987b), the influence of a single chemical reaction on the vapour-liquid diagram analysed (Barbosa and Doherty, 1988c), and a procedure for the calculation of residue curve maps developed, by deriving a set of autonomous ordinary differential equations describing the dynamics of homogeneous reactive simple distillation (Barbosa and Doherty, 1988d). These results were extended to multicomponent systems with or without inerts, undergoing *multiple* reactions at chemical equilibrium by Ung and Doherty (1995a,1995b,1995d), which are reviewed below.

For a mixture of a total of C components undergoing R chemical equilibrium reactions,

$$\sum_{i=1}^C \nu_{ir} A_i = 0 \quad \forall r \in R \quad (4.1)$$

where A_i are the reacting species and ν_{ir} is the stoichiometric coefficient of component i in reaction r . Note that by convention ν_{ir} is negative if component i is a reactant in reaction r , positive if component i is a product in reaction r and zero if component i does not participate in reaction r (or is an inert). The differential equation characterising the simple distillation of equilibrium reacting mixtures is given by (Ung and Doherty, 1995a) (Figure 4.1)

$$\frac{dX_i}{d\tau} = X_i - Y_i \quad (4.2)$$

$$i = 1, \dots, C - R - 1$$

where

$$X_i = \left(\frac{x_i - \nu_i^T N^{-1} \mathbf{x}_{\text{Fef}}}{1 - \nu_{\text{TOT}}^T N^{-1} \mathbf{x}_{\text{Fef}}} \right) \quad i = 1, \dots, C - R \quad (4.3)$$

$$Y_i = \left(\frac{y_i - \nu_i^T N^{-1} \mathbf{y}_{\text{Fef}}}{1 - \nu_{\text{TOT}}^T N^{-1} \mathbf{y}_{\text{Fef}}} \right) \quad i = 1, \dots, C - R \quad (4.4)$$

$$d\tau = \left(\frac{V}{H} \right) \left(\frac{1 - \nu_{\text{TOT}}^T N^{-1} \mathbf{y}_{\text{Fef}}}{1 - \nu_{\text{TOT}}^T N^{-1} \mathbf{x}_{\text{Fef}}} \right) dt \quad (4.5)$$

$$(4.6)$$

The transformed variables X_i, Y_i represent the overall compositions of the independent components in each phase and account for the total amount of these chemical species present in any chemical combination, whether it is in the form of a product or a reactant. H is the molar liquid holdup in the still and V the molar flowrate of the vapour evaporating.

Defining R reference components in the R reactions, $\mathbf{x}_{\text{Fef}}$ and $\mathbf{y}_{\text{Fef}}$ are the column vectors composed of the mole fractions of the R reference components,

$$\mathbf{x}_{\text{Fef}} = (x_{(C-R+1)}, x_{(C-R+2)}, \dots, x_C)^T \quad (4.7)$$

$$\mathbf{y}_{\text{Fef}} = (y_{(C-R+1)}, y_{(C-R+2)}, \dots, y_C)^T \quad (4.8)$$

ν_i^T is the row vector of stoichiometric coefficients of component i for each reaction, and ν_{TOT}^T is the row vector of the sum of the stoichiometric coefficients for each reaction

$$\nu_i^T = (\nu_{i1}, \nu_{i2}, \dots, \nu_{iR}) \quad (4.9)$$

$$\nu_{\text{TOT}}^T = (\nu_{T1}, \nu_{T2}, \dots, \nu_{TR}) \quad (4.10)$$

N is defined as the square matrix of stoichiometric coefficients for the R reference components in the R reactions. The components are ordered by rows and the reactions by columns

$$N = \begin{pmatrix} \nu_{(C-R+1)}^T \\ \vdots \\ \nu_C^T \end{pmatrix} = \begin{pmatrix} \nu_{(C-R+1)1} & \dots & \nu_{(C-R+1)R} \\ \vdots & \nu_{ir} & \vdots \\ \nu_{C1} & \dots & \nu_{CR} \end{pmatrix} \quad (4.11)$$

The reference components are chosen such that $\mathbf{N}$ is invertible, and τ , the warped time, goes in the same direction as the real time t . Rules for their choice are given in Ung and Doherty (1995d). The transformed variables have the additional property over those presented by Barbosa and Doherty that they sum to unity,

$$\sum_{i=1}^{C-R} X_i = 1 \quad (4.12)$$

such that there are only $(C - R - 1)$ independent transformed composition variables.

Equation (4.2) is in the same form as for non-reactive mixtures (equation 3.1), and can be integrated to give the residue curve map for reactive mixtures at chemical equilibrium (Ung and Doherty, 1995a), subject to the chemical equilibrium relation

$$K_{eq} = \exp\left(\frac{\Delta G^\circ}{RT}\right) = \prod_{i=1}^C (\gamma_i x_i)^{\nu_i} \quad (4.13)$$

and the phase equilibrium relation

$$y_i P_{tot} = \gamma_i P_i^{sat} x_i \quad (4.14)$$

The singular points of equation (4.2) correspond to all reactive azeotropes in the mixture, as well as the surviving non-reacting azeotropes and pure components. The necessary and sufficient conditions for reactive azeotropy for multiple reaction systems is given by (Ung and Doherty, 1995b)

$$X_i = Y_i \quad i = 1, \dots, C - R - 1 \quad (4.15)$$

Reactive azeotropes are defined as an equilibrium phenomena where the rate of vapourisation and condensation coupled with the rate of reaction of each species are such that vaporisation and condensation occurs without change of composition in either phase. The main difference with respect to non-reactive azeotropes is that in this case, the condition of equality of mole fractions for each species in the respective phases are not needed. The theoretical prediction of a reactive azeotrope has been confirmed by experiment by Song *et al.* (1997) for a mixture of acetic acid, isopropanol, isopropyl acetate and water at simultaneous reaction and phase equilibria.

For a single reaction system, Barbosa and Doherty (1988d) illustrate the effect that changes in the chemical equilibrium constant have on residue curve maps, observing

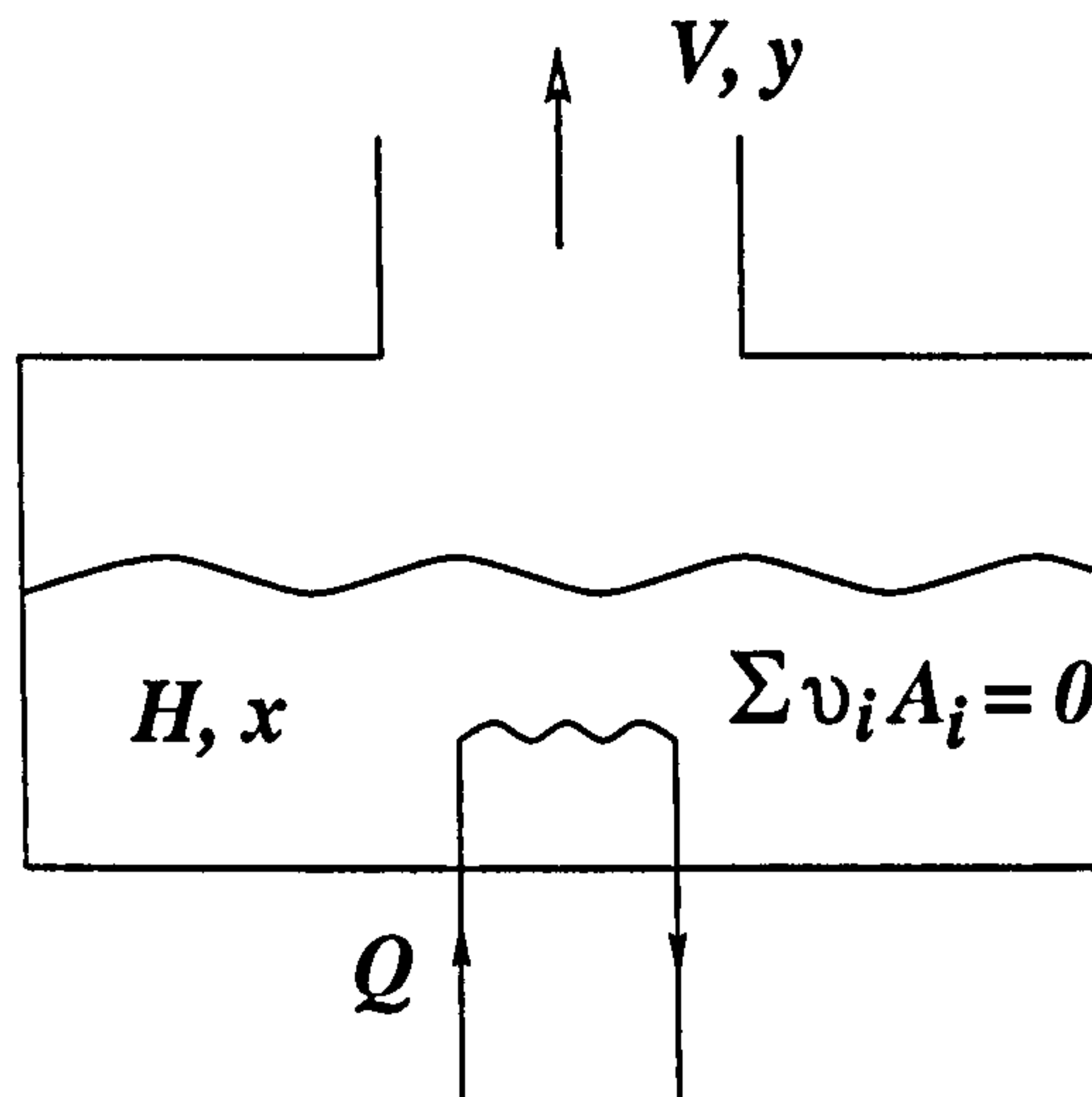


Figure 4.1: Simple reactive distillation process

the appearance and disappearance of reactive azeotropes. Using an arc-length continuation method, Okasinski and Doherty (1997) tracks solutions corresponding to reactive azeotropes as a function of the reaction equilibrium constant and portray the results in bifurcation diagrams. Investigating the effect of the reaction equilibrium constant on the existence and location of reactive azeotropes, this procedure highlights the sensitivity of thermodynamic uncertainty on the analysis of reactive distillation systems.

Although these works allow the phase equilibrium and limiting separation characteristics of quite complex mixtures to be represented in a relatively simple way, the variables can take negative values which are more difficult to interpret. In addition these works assume chemical equilibrium limited reactions and take no consideration of kinetics and liquid holdups.

Venimadhavan *et al.* (1994) analysed the effect of chemical *kinetics* on the residue curve map for reactive distillation for a ternary system with a single chemical reaction through the use of the Damköhler number. The Damköhler number is a dimensionless ratio of a characteristic liquid residence time to the characteristic reaction time, measuring the rate of reaction relative to product removal. For small Damköhler numbers, the obtained residue curve map corresponds to non-reactive residue curve maps, with the singular points corresponding to pure components and non-reactive azeotropes. Using a bifurcation analysis it is shown that in some cases, as the Damköhler number is increased, the equilibrium reactive residue curve map is recovered. The proposed bifurcation analysis can thus reveal the limitations of the equilibrium analysis for this class of systems. Experimental verification of residue curve maps generated from Damköhler numbers has

been recently presented by Song *et al.* (1998) for the esterification of methanol and acetic acid to methyl acetate.

Design procedures developed for reactive distillation columns utilising fixed point methods and related works are summarised in Table 4.2. A common approach is the adoption of design strategies for multicomponent non-reactive distillation for reactive distillation. Barbosa and Doherty developed procedures for the calculation of minimum reflux ratios and feasible designs for *single feed* (1988*b*) and *double feed* (1988*a*) multicomponent reactive distillation with a *single reaction*. The finite difference design equations are simplified utilising transformed variables and are approximated by a set of first order differential equations which are solved by a boundary value design method similar to that proposed for conventional distillation by Levy *et al.* (1985). Ung and Doherty (1995*c*) utilise a graphical procedure to determine feasible design and sequencing of reactive columns for multicomponent mixtures with *multiple reactions*. Both these procedures assume chemical and physical equilibrium on each tray, saturated liquid feed and constant molar overflow (CMO), which for reactive distillation guarantees constant vapour flow in each section and changes in liquid flow in each section only due to changes in total number of moles by reaction. In addition, these procedures are based on assessing feasibility at infinite reflux ratio and assume linear separatrix of saddle pinch profile, assumptions which are known to be invalid for the separation of nonideal non-reactive mixtures.

Espinosa *et al.* (1995) presents a graphical method to determine the product composition regions of a single-feed reactive distillation by analysing feasibility at the condition of both finite and infinite reflux, similar to the design procedure of Wahnschafft *et al.* (1992*a*) for non-reactive columns. Transformed variables of Barbosa and Doherty (1988*d*) are generalised for the calculation of residue curve maps, and the procedure is limited to a single chemical equilibrium reaction, with or without inerts.

Buzad and Doherty (1994) notes that it may not be desirable or realistic to operate reactive distillation at chemical equilibrium and presents a design procedure to determine feasible single feed columns for ternary mixtures with a single *kinetically controlled* reaction. To calculate the minimum flows in the column, a fixed-point method based on the novel design procedures of Fidkowski *et al.* (1991) for nonideal separations is adopted. However, heat effects are still ignored (CMO assumed), and equal holdups on each stage assumed, not allowing for the combination of reactive and non-reactive sections.

Recently, Bessling *et al.* (1997) developed the concept of reactive distillation lines based on the transformed variables of Barbosa and Doherty (1988*d*) and utilises them to assess feasibility reactive columns. In a first stage, geometric properties are utilised

to determine feasible design of single or double feed columns, allowing combinations of reactive and non-reactive sections. These alternatives are then used as starting points for rigorous simulation and optimisation. This procedure assumes liquid feeds and CMO and is limited to mixtures with a single chemical reaction. Although this allows great insight into the process, such a sequential approach does not guarantee an optimal design.

The developments in design procedures utilising transformed variables have provided a useful method with which to rapidly determine feasible reactive columns as well as giving an insight to the phenomena of simultaneous phase and chemical equilibria. However, most of the fixed point methods are greatly simplified, and do account for heat effects and are valid for systems close to chemical equilibrium. When any one of these assumptions are violated, the reaction kinetics, the heat of reaction, the liquid holdup and the residence times become major design parameters that cannot be accounted for. When reaction kinetics with physical equilibrium is considered, the combination of reactive and non-reactive zones can be accounted for. However, these procedures are currently restricted to single reaction systems, in single feed columns (Okasinski and Doherty, 1998).

Element Balance Approach

An alternative 'tool' developed for the calculation of simultaneous physical and chemical equilibrium of reactive systems for the analysis and design of reactive distillation is based on the elemental balance approach (Perez-Cisneros *et al.*, 1996). Similar to the transformed variables discussed above, the element balance variables reduces the dimension of the phase equilibrium problem, thus allowing the representation of multi-component reactive systems in two or three dimensional phase diagrams. The variables can be directly employed for analysis and design and unlike the transformed variables, the method of solution is similar to the well known non-reactive physical equilibrium problems. Algorithms for the computation of phase diagrams, reactive azeotropes, and the minimisation of Gibbs free energy have been developed (Perez-Cisneros *et al.*, 1997).

The element based model (or chemical model) reduces the dimensionality of the problem by exploiting the fact that the number of elements needed to represent a reactive system is less than the number of compounds in the system. For a mixture of a set of C components/molecules made up of a set of M elements in a single phase, the elemental composition b_j is given by

$$b_j = \sum_{i=1}^C A_{ji} n_i \quad (4.16)$$

where A_{ji} is the number of reaction invariant elements j in component i , and n_i is the molar composition of i .

Reactive phase diagrams and residue curves are computed in terms of element 'mole' fractions W_j , defined as

$$W_j = \frac{b_j}{\sum_{j=1}^M b_j} \quad (4.17)$$

For a two phase multicomponent system of R reactions, the dynamic material balances for the simple batch distillation of the mixture in terms of elements is given by

$$\frac{db_j^l}{dt} = \frac{d(b_T^l W_j^l)}{dt} = -V_T W_j^v \quad j = 1, \dots, M \quad (4.18)$$

where b_j^l is the element liquid holdup in the still, V_T is the element flowrate of vapour evaporating, W_j^l is the element mole fraction of element j in the liquid phase and W_j^v the element mole fraction of element j in the vapour phase. Equation (4.18) is a set of M ordinary differential equations which when integrated (given the pressure and an initial value of b_j^l), gives the reactive residue curve map. An algorithm for the computation of the residue curve map is developed (Perez-Cisneros, 1998), involving reactive bubble point calculations which enforce physical and chemical equilibrium.

To locate reactive azeotropes, in terms of the element balance approach *element azeotropes* are introduced, identical in principle to azeotropes found in non-reacting systems. The conditions for the existence of element azeotropes is given as the point where the compositions of element j ($j = 1, \dots, M$) in all coexisting phases are identical. Equivalently, this corresponds to unity element relative volatility of element j ($j = 1, \dots, M-1$) with respect to a reference element s (α_{js}) *i.e.*

$$\alpha_{js} = \frac{K_j}{K_s} = 1 \quad (4.19)$$

where K_j is the elemental separation factor defined by

$$K_j = \frac{W_j^v}{W_j^l} \quad (4.20)$$

Given the pressure and number of phases, the elemental mass fractions for element j and the corresponding temperature at which these conditions are satisfied for the existence of element azeotropes can be determined.

In an attempt to overcome difficulties associated with obtaining reliable and consistent models for properties prediction, reaction kinetics and process simulation for reactive distillation, Perez-Cisneros *et al.* (1996) proposed a systematic approach for the *analysis* of design and operation based on the element based approach. The approach involves three steps; in the first step appropriate models and parameters are validated. In the second step, the validated models are employed to generate relationships between the variables that have a large impact on the design of the process. In the third and final step, the relationships are employed to analyse their effect in the design. The first two stages identifies the sensitivity of model parameters to the prediction of the chemical-physical equilibrium and ensures that appropriate thermodynamic models are utilised for the analysis of reactive distillation design and operation.

The element based approach has provided a tool for the design of reactive columns, whereby well known *design* methods for the separation of non-reactive mixtures have been extended to reactive mixtures (Perez-Cisneros, 1998). For binary element reactive systems, a McCabe-Thiele method is presented to design feasible columns, assuming constant *element* molar overflow. For ternary element reactive systems, feasible product regions are determined for direct and indirect sharp splits using the 'bow-tie region' method. Once the feasible compositions have been determined, a stage by stage method may be applied to determine the number of reactive stages required.

Note that these graphical design methods assume chemical equilibrium and constant molar overflow (no heat effects) and does not allow for combinations of reactive and non-reactive sections in the column. Extensions to systems with more than 3 element fractions is not easily visualised. However, unlike Doherty's approach which utilises residue curve maps, feasibility is assessed at finite reflux, not the limiting case of infinite reflux.

Superstructure Approach

The MINLP approach to design reactive columns utilise a superstructure scheme which are readily applicable to multicomponent, multi-reaction systems in multi-feed columns. Accounting for heat effects, reaction kinetics are utilised to result in an optimal reactive column with respect to cost. Ciric and Gu (1994) developed a synthesis scheme for non-equilibrium reactive distillation processes featuring a rigorous tray-by-tray model combined with kinetic rate based expressions. The resulting optimisation model is a MINLP with the total annualised cost as the objective, the solution of which yields the optimal number of trays, reflux ratio, heat exchanger duties and liquid holdups on each tray. Recently, Gumus and Ciric (1997) extended this approach to the design of reactive

distillation columns with vapour/liquid/liquid equilibria, with the design problem formulated as a mixed integer nonlinear bilevel optimisation problem. Smith (1996) applied his synthesis procedure involving state-operator networks to the production of ethylene glycol. A network of reactive flash vessel building blocks was built up and complete connectivity assumed in the superstructure. An enumeration approach was then employed to solve the resulting MINLP.

The superstructure approach results in more realistic and accurate designs of distillation columns, allowing experimentally obtained kinetic rate expressions to be utilised and optimising all the vital variables. Reactive and non-reactive sections in columns can be optimised. However, these models are computationally demanding and can be difficult to solve.

4.2.2 Combined Reaction/Separation Systems

Developed procedures for the synthesis and simulation of general reaction-separation systems are summarised in Table 4.3, with approaches to simultaneously capture the two phenomena based on the extension of developed reaction network synthesis algorithms to encompass separation and mixing.

The synthesis of reactor networks has been studied using a variety of approaches, mostly based on optimisation techniques. For example, Kokossis and Floudas (1994) studied this problem for non-isothermal reactors by optimising a superstructure of continuously stirred-tank reactors (CSTR), plug-flow reactors (PFR) and heat exchangers in many possible configurations. From a completely different standpoint, the attainable region approach addresses reactor network feasibility based on geometric properties, identifying feasible but not optimal reactor sequences for production of the desired product. First introduced by Horn (1964), the attainable region has been extensively investigated by Hildebrandt, Glasser and coworkers for processes including reaction and mixing (Glasser *et al.*, 1987; Hildebrandt *et al.*, 1990; Hildebrandt and Glasser, 1990; Godorr *et al.*, 1994; Glasser *et al.*, 1994; Feinberg and Hildebrandt, 1997). For a given system of reactions with given reaction kinetics, the attainable region is defined as the portion of concentration space that can be achieved from a given feed composition by any combination of reaction and mixing. The attainable region has also been applied to determine the feasible products for the vapour-liquid separation of homogeneous ternary mixtures in separation-mixing processes (Jobson *et al.*, 1995). Recently, concepts for the extension of the attainable region results to consider separation and reaction have been presented for a binary system with a single reaction (McGregor *et al.*, 1997).

Transformed Variables Approach	
Barbosa and Doherty (1987a) (1988c) (1988d)	Developed tools for analysis of two-phase reactive mixtures with a <i>single equilibrium</i> limited reversible reaction without inerts. Introduction and derivation of transformed variables. Computation of reactive-phase diagrams and derivation of conditions for reactive-azeotropes. Computation of Residue Curve Map (RCM)
Ung and Doherty (1995a) (1995b) (1995d)	Extension of transformed variables to two-phase multicomponent mixtures with <i>multiple</i> equilibrium reversible chemical reactions, with or without inerts. Computation of RCM. General conditions for reactive azeotropes Computation of phase diagram.
Venimadhavan <i>et al.</i> (1994)	Computation of RCM accounting for the effect of chemical <i>kinetics</i> . Applicable to <i>ternary</i> mixtures with a <i>single reaction</i> .
Okasinski and Doherty (1997)	Analysis of the effect of reaction equilibrium constant on reactive azeotrope, illustrating the sensitivity of parameter uncertainty on design. Applicable to multicomponent mixtures with a <i>single chemical equilibrium</i> reaction.
Element Balance Approach	
Perez-Cisneros <i>et al.</i> (1996) (1997)	Development of tools based on element balance approach for the analysis and design of reactive mixtures with <i>multiple equilibrium</i> reactions Systematic approach for analysis of design and operation involving three steps; (i) validation of thermodynamic models (ii) identification of variables sensitive to design (iii) analysis of these effects on design and operation. Developed algorithms for reactive flash calculation, determination of reactive azeotropes and computation of phase diagrams.

Table 4.1: Analysis Tools for Reactive Distillation

Fixed Points Approach	
Barbosa and Doherty (1988 <i>b</i>) (1988 <i>a</i>)	Procedure for <i>feasible</i> reactive columns and calculation of minimum reflux ratio and number of trays. Limited to multicomponent mixtures with a <i>single reaction without inerts</i> , chemical equilibrium, liquid feed and no heat effects. Procedure for single-feed reactive distillation column Procedure for double-feed reactive distillation column
Buzad and Doherty (1994)	Design procedure for <i>feasible</i> single feed column, for <i>ternary</i> mixtures with single <i>kinetically</i> controlled reaction assuming equal liquid holdups on each stage & no heat effects.
Ung and Doherty (1995 <i>c</i>)	Graphical procedure for the <i>sequencing</i> of feasible single feed reactive and non-reactive columns. Applicable to multi-component mixtures with multiple reactions with or without inerts. Assumes sharp splits, chemical equilibrium and CMO.
Espinosa <i>et al.</i> (1995)	Graphical determination of feasible product composition regions of single feed reactive columns for multicomponent mixtures with a single equilibrium reaction, including inerts. Analyses case of both finite and infinite reflux ratios.
Bessling <i>et al.</i> (1997) (1998)	A two stage sequential approach for the optimal design of single or double feed columns with reactive and non-reactive sections. Limited to mixtures with a single equilibrium reaction and assumes liquid feeds and CMO.
Okasinski and Doherty (1998)	Design method for multicomponent system (+ inerts) with single kinetically controlled liquid phase reaction in single feed column. Accounts for heat effects and distribution of liquid holdups (reactive and non-reactive zones).
Superstructure Approach	
Ciric and Gu (1994)	MINLP to determine <i>optimal</i> reactive column wrt annualised cost for multicomponent non-equilibrium 2-phase mixtures.
Smith (1996)	Optimisation of a network of reactive flash vessels for optimal design of kinetically controlled columns. Enumeration approach employed to solve the resulting MINLP.
Gumus and Ciric (1997)	Mixed integer nonlinear bilevel optimisation problem for the optimal design of 3-phase columns for mixtures with either chemical equilibrium or kinetically controlled reactions.

Table 4.2: Design Procedures for Reactive Distillation

Synthesis Methods	
Balakrishna and Biegler (1993)	MINLP model for the synthesis of energy integrated reaction-separation systems using reaction-separation targets based on sharp splits.
Lakshmanan and Biegler (1996)	MINLP model for the synthesis of combined reaction -mixing-separation processes. Reactor network synthesis based on geometrically attainable concepts are combined with MEN concepts, allowing separation by one mass separating agent only.
Nisoli <i>et al.</i> (1997)	Geometric approach to generate feasible flowsheets for ternary systems with simultaneous separation and kinetic reaction. Attainable region approach for reaction-mixing are combined with geometric methods for separation feasibility.
McGregor <i>et al.</i> (1997)	Utilise attainable region results to synthesise alternative flowsheets for a binary system with a single liquid phase reaction. The flowsheets are optimised using a linear cost function, assuming packed columns and catalyst coated packing.
Modelling and Simulation	
Gani <i>et al.</i> (1998)	Developed a generalised reactive separation unit for the <i>simulation</i> of general reaction separation processes, applicable to multi-phase systems with kinetic or chemical controlled multi-reactions. Based on element based approach.

Table 4.3: Procedures for Combined Reaction/Separation Systems

Nisoli *et al.* (1997) developed feasibility analysis for systems with simultaneous reaction and separation, combining attainable region approach for reaction-mixing systems with geometric methods for the feasibility of separation. Based on CSTR and PFR models with vapour removal, a reaction-separation vector is derived in terms of the Damköhler number and the vapour fraction. Placed in the same form and as the reaction vector of Glasser *et al.* (1987), the separation-reaction vector is similar in terms of geometric properties and thus their developed procedure for constructing the attainable regions is applied. The regions are then graphically analysed in the composition space to determine feasibility. Valid for reactions in the liquid phase, this method allows the generation of feasible and not optimal flowsheets. Due to its graphical nature, this method is sensitive to parameter uncertainty in thermodynamic data. In addition, it is visually challenging to extend this method beyond systems of three components, and a range of Damköhler numbers must be screened. The models proposed by Balakrishna and Biegler (1993) and Lakshmanan and Biegler (1996) adopt a strategy of superstructure optimisation utilising targets based on attainable regions. In the latter work, the attainable region properties derived from Feinberg and Hildebrandt (1997) and mass exchange network concepts is incorporated within a superstructure formulation for reactor network synthesis, allowing for reaction, mixing and separation by a mass separating agent. Although able to capture some features of combined reaction-separation processes, these approaches focus on providing synthesis targets rather than deriving alternatives.

4.2.3 Summary

Although a much greater understanding of combined reaction separation systems have been gained, in terms of *synthesis*, there are still no generally accepted procedures for the generation of hybrid reactive/separation possibilities. The mass/heat transfer framework presents a phenomena based method within a superstructure environment that is able to capture hybrid reactive/separation possibilities. Based on fundamental mass and heat transfer principles, process alternatives are not explicitly prepostulated but instead generated based on the synthesis objectives.

4.3 Problem Statement

The synthesis problem addressed in this chapter is applicable to systems whereby reaction, separation and combined reaction and separation can take place. In this work, we consider systems with no liquid/liquid equilibrium and reactions occurring in the liquid phase only. Note that this is not a limitation of the approach, and extensions to such systems is discussed in later sections.

The synthesis problem can be stated as follows;

Given

- A set of feed streams of given temperature, pressure and composition
- Set of desired products with specifications on flowrate, temperature and purity
- A set of available mass utilities such as catalysts and mass exchange agents
- A set of available heat utilities such as cooling water and steam and specifications on availability, supply temperatures and compositions
- All reactions schemes and kinetics data
- Cost data of feeds and utilities
- All thermodynamic property models

Synthesize an optimal process system, *i.e.* sequence of reactors and/or separators. The system cost comprises of utilities, cost of required catalyst, cost of raw materials and an approximation of capital costs based on the number of mass/heat separator and reactor blocks.

4.4 Mass/Heat Transfer Module and Representation

The building block of process alternatives is the mass/heat transfer module as described in chapter 2 and chapter 3. Combined separation and reaction hybrid processes are represented by sets of connected modules whereby the correct phenomena is occurring. Consider for example a double feed reactive distillation column for the production of D from A and B according to the following reversible liquid phase reaction;



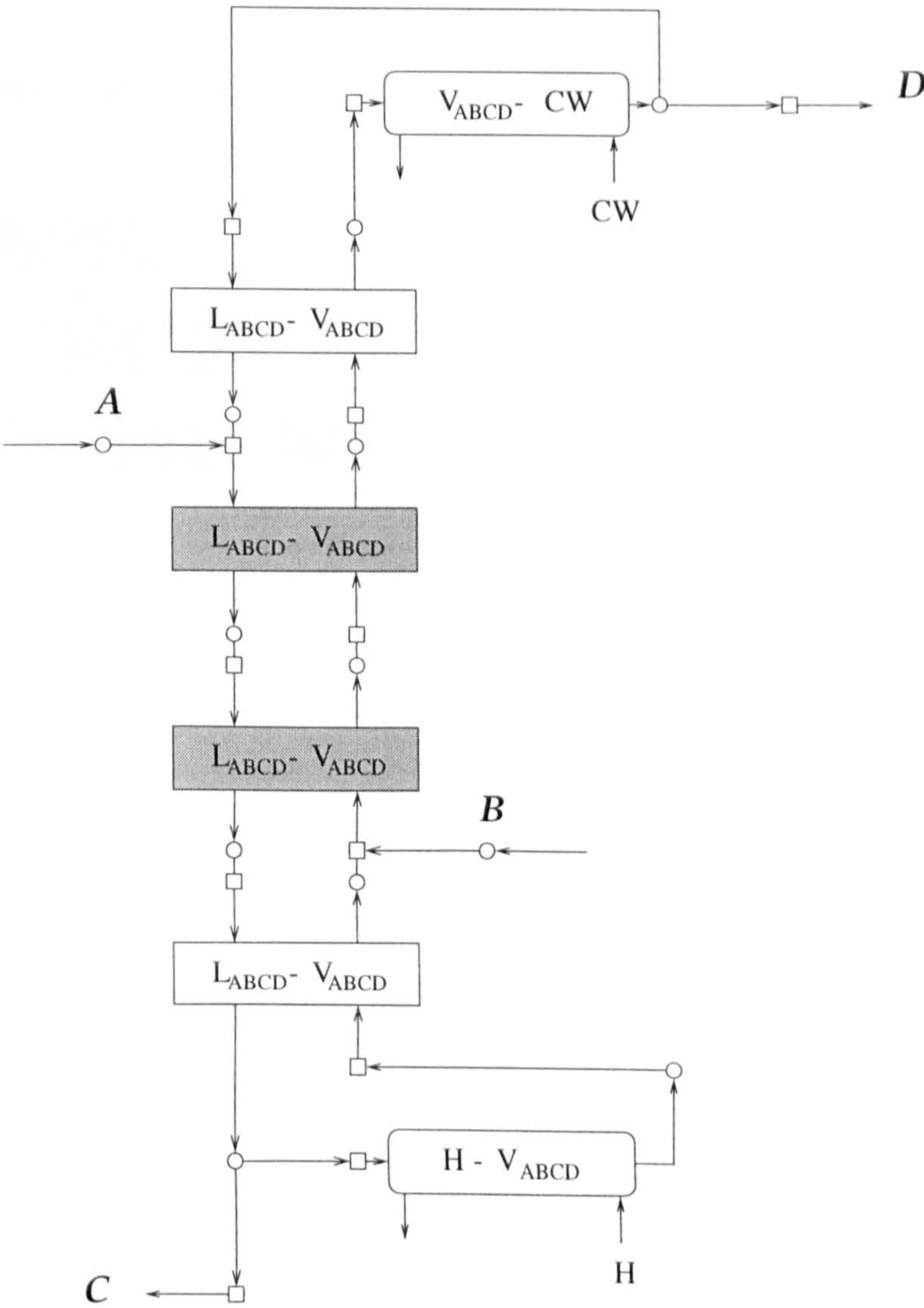
A reactive distillation tray involves mass and heat transfer within the liquid holdup due to reaction in addition to mass and heat transfer between the liquid and vapour mixtures (represented by L_{ABCD} and V_{ABCD}) due to volatility differences (figure 4.2(a)). On a non-reactive tray with only separation (figure 4.2(b)), mass and heat transfer occurs between the liquid and vapour contacting phases of a mixture. The reactive column is thus realised similarly to conventional distillation, as illustrated in Figure 4.2(c). The feeds enter the mixers of the mass/heat exchangers, A as a liquid and B as a vapour. The two liquid-vapour modules between the feeds represents the reactive section of the column where the bulk of the reaction occurs. In this section, reaction occurs in the liquid holdup of the module and the continual removal of the reaction products C and D drive the reaction forwards. Note that in order of relative volatility, $D > B > C > A$, thus overall we have mass transfer of D from the liquid to the vapour phase, and transfer of component C from the vapour phase to the liquid phase. The top $L_{ABCD} - V_{ABCD}$ mass/heat exchange block has no liquid holdup, representing the rectifying section, whereby D is transferred from the liquid to the vapour stream and ABC is transferred from the vapour to the liquid stream. Similarly, the bottom module has very little/no reaction due to a low concentration of A and no holdup, and represents the stripping section whereby water C is transferred to the liquid stream whilst methanol B is transferred to the vapour stream.

For the general synthesis problem for the production of D , alternative process structures featuring different operating conditions may result depending on the synthesis objective. Figure 4.3 shows a conventional alternative, featuring reaction in the liquid phase up to equilibrium followed by separation of D from the resulting mixture. Within each liquid-liquid module, mass/heat exchange occurs between a liquid reagent stream and a liquid reaction product stream which are assumed to be well mixed in order to define the reaction kinetics. Since each module corresponds to a continuous stirred tank reactor (CSTR), the series of modules represent a plug-flow reactor (PFR). The proceeding liquid-vapour modules separate the desired product from reactor exit stream, representing a separation column as discussed in the previous chapter.



(a) Reactive separation block

(b) Pure separation block



(c) Reactive Distillation Column

Figure 4.2: Representation of a Reactive Column

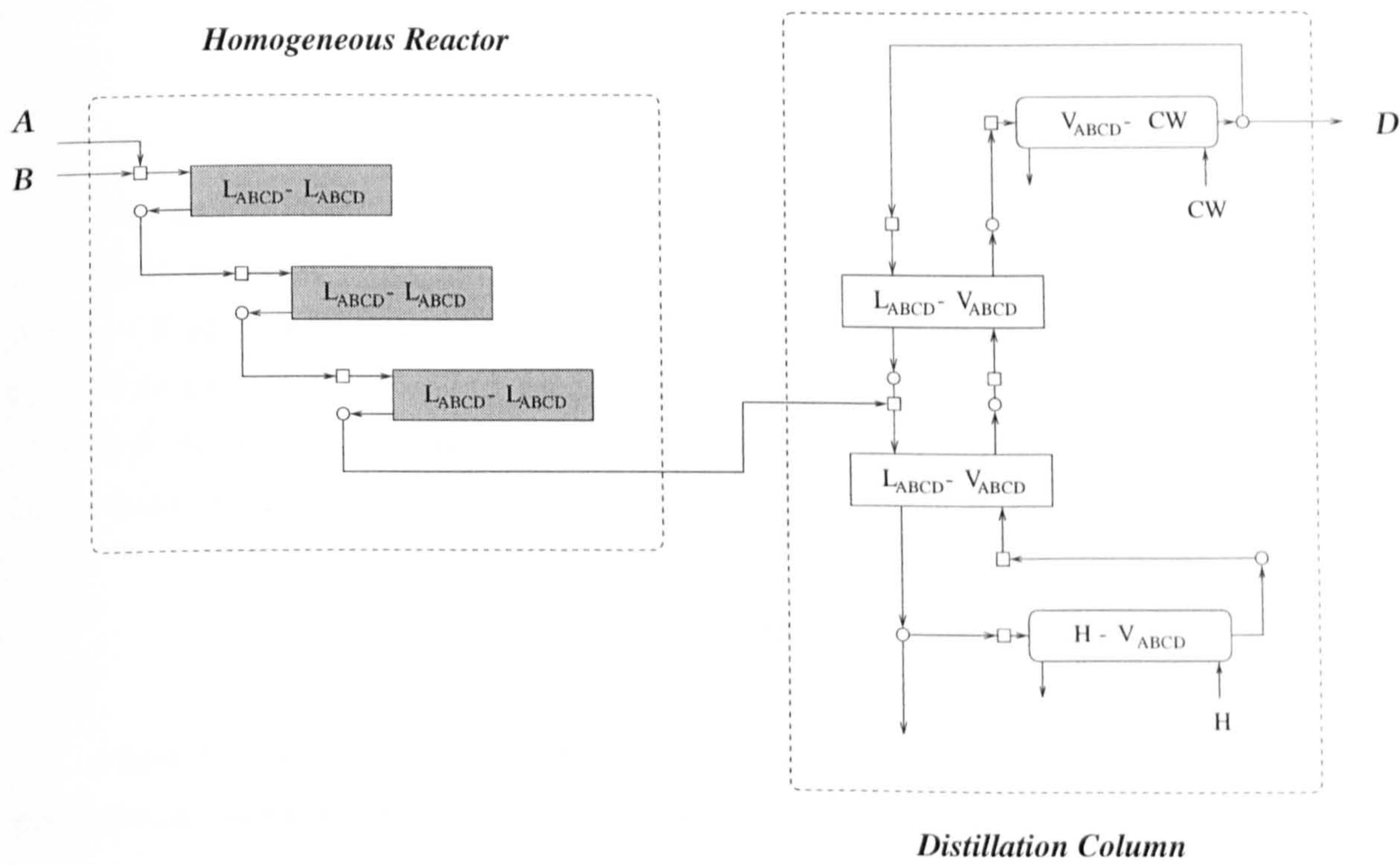


Figure 4.3: Conventional Alternative

4.5 Driving Force Constraints

As shown in section 2.6 and further discussed in the Addendum at the end of this thesis, we propose the conjecture that mass transfer between two streams $S1$ and $S2$ within a module is consistently limited by

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad \forall i = 1, \dots, C$$

where

$$\mathcal{G}1_i = F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} X_{out,i}^{S1}$$

$$\mathcal{G}2_i = \left[\frac{\partial (nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P}$$

The driving force constraints to ensure feasible mass transfer in a liquid-vapour mass/heat exchange block for pure separation systems is derived in section 3.4, where we show that $\left[\partial (nG)^{tot} / \partial n_i^L \right]$ represents the distance from phase equilibrium. To derive $\mathcal{G}2_i$ for combined reaction and separation systems, consider a multicomponent liquid-vapour mixture with k reactions occurring in the liquid phase. Mass conservation for each component requires

$$n_i^L + n_i^V = n_i^o + \sum_k \nu_{ik} \epsilon_k \quad (4.22)$$

where by convention the stoichiometric coefficient ν_{ik} for reaction r is positive for products, negative for reactants and zero for inerts.

Differentiating,

$$\begin{aligned} dn_i^L + dn_i^V &= \sum_{r=1}^R \nu_{ik} d\epsilon_k \\ dn_i^V &= -dn_i^L + \sum_k \nu_{ik} d\epsilon_k \end{aligned} \quad (4.23)$$

The fundamental relation for the Gibbs free energy of the mixture is given by (Smith and Van Ness, 1987)

$$d(nG)^{tot} = (nV)^L dP^L - (nS)^L dT^L + (nV)^V dP^V - (nS)^V dT^V + \sum_i (\mu_i^L dn_i^L + \mu_i^V dn_i^V) \quad (4.24)$$

At this point we approximate the temperature and pressure of the liquid and vapour streams to be the same. At constant T and P

$$d(nG)^{tot} = \sum_i (\mu_i^L dn_i^L + \mu_i^V dn_i^V) \quad (4.25)$$

$$= \sum_i \mu_i^L dn_i^L + \sum_i \mu_i^V (-dn_i^L + \sum_k \nu_{ik} d\epsilon_k) \quad (4.26)$$

$$= \sum_i (\mu_i^L - \mu_i^V) dn_i^L + \sum_i \sum_k \nu_{ik} \mu_i^V d\epsilon_k \quad (4.27)$$

Approximating $\partial\mu_i/\partial n_i^L \approx 0$,

$$\frac{\partial(nG)^{tot}}{\partial n_i^L} = \mu_i^L - \mu_i^V + \sum_i \sum_k \nu_{ik} \mu_i^V \frac{\partial\epsilon_k}{\partial n_i^L} \quad (4.28)$$

The chemical potential is given by

$$\mu_i^L = \Delta G_i^f + RT \ln(\gamma_i^L x_i^L P_i^{sat,L}) \quad (4.29)$$

$$\mu_i^V = \Delta G_i^f + RT \ln(\phi_i^V x_i^V P_{tot}) \quad (4.30)$$

where ΔG_i^f is the standard Gibbs function of formation of i from its elements at T and 1atm. Therefore

$$\begin{aligned} \frac{\partial(nG)^{tot}}{\partial n_i^L} = & RT \left[\ln(\gamma_i^L x_i^L P_i^{sat,L}) - \ln(\phi_i^V x_i^V P_{tot}) \right] \\ & + \sum_i \sum_k \nu_{ik} \left[\Delta G_i^f + RT \ln(\phi_i^V x_i^V P_{tot}) \right] \frac{\partial\epsilon_k}{\partial n_i^L} \end{aligned} \quad (4.31)$$

It is the sign of this expression that is of interest, and thus we can divide through by the positive product RT to obtain the expression required for the constraint in equation (2.8)

$$G2_i^{L-V} = \ln \left[\frac{\gamma_i^L x_i^L P_i^{sat,L}}{\phi_i^V x_i^V P_{tot}} \right] + \sum_i \sum_k \left[\frac{\nu_{ik} \Delta G_i^f}{RT} + \nu_{ik} \ln(\phi_i^V x_i^V P_{tot}) \right] \frac{\partial\epsilon_k}{\partial n_i^L} \quad (4.32)$$

A number of comments can be made;

- Reaction kinetics are utilised and the dimensionless term $(\partial\epsilon/\partial n_i^L)$ is system dependent and must be analytically derived.
- When no reaction occurs, the constraint for reactive liquid-vapour match is identical to that for non-reactive liquid-vapour match.

Liquid-Vapour Match : Pure Separation

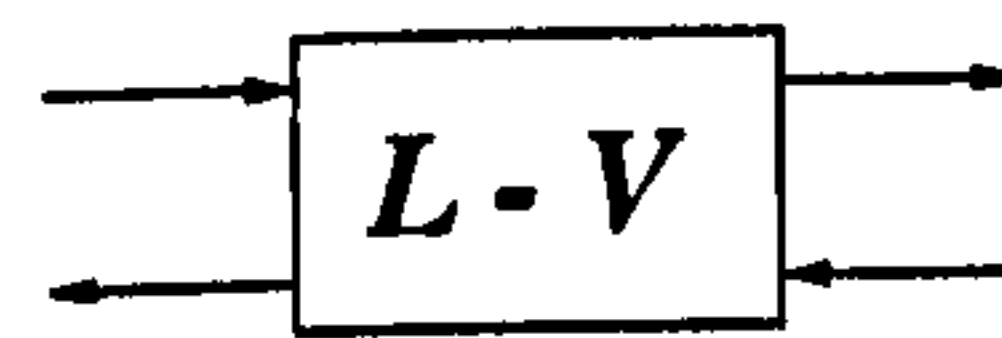


$$\begin{aligned} \mathcal{G}1_i &= F_{in}^L x_{in,i}^L - F_{out}^L x_{out,i}^L \\ \mathcal{G}2_i &= \gamma_{out,i}^L x_{out,i}^L P_{out,i}^{sat,L} - x_{in,i}^V P_{tot} \\ \mathcal{G}3_i &= \gamma_{in,i}^L x_{in,i}^L P_{in,i}^{sat,L} - x_{out,i}^V P_{tot} \end{aligned}$$

$$\mathcal{G}1_i \mathcal{G}2_i \geq 0$$

$$\mathcal{G}1_i \mathcal{G}3_i \geq 0$$

Liquid-Vapour Match : Reaction & Separation



$$\begin{aligned} \mathcal{G}1_i &= F_{in}^L x_{in,i}^L - F_{out}^L x_{out,i}^L \\ \mathcal{G}2_i &= \ln \left(\frac{\gamma_i^L x_i^L P_i^{sat,L}}{x_i^V P_{tot}} \right) + \sum_j \left[\frac{\nu_j \Delta G_j^f}{RT} + \nu_j \ln(x_j^V P_{tot}) \right] \frac{\partial \epsilon}{\partial n_i^L} \end{aligned}$$

$$\mathcal{G}1_i \mathcal{G}2_i \geq 0$$

Liquid-Liquid Match : Homogeneous Reaction



$$\begin{aligned} \mathcal{G}1_i &= F_{in}^{L1} x_{in,i}^{L1} - F_{out}^{L2} x_{out,i}^{L2} \\ \mathcal{G}2_i^{L1-L2} &= \sum_i \nu_i \left[\frac{\Delta G_i^f}{RT} + \ln (\gamma_i^{L2} x_i^{L2} P_i^{sat,L2}) \right] \frac{\partial \epsilon}{\partial n_i^L} \end{aligned}$$

$$\mathcal{G}1_i \mathcal{G}2_i \geq 0$$

Table 4.4: Summary of Driving Force Constraints

- The driving force constraints are recasted in a linear form by the introduction of binary variables as shown in section 3.4.

When simultaneous reaction and separation occur, mass transfer is constrained at the liquid outlet side of the module, as compared to the pure separation case where adjacent streams on both sides of the module are constrained. Driving force constraints can be analogously derived for liquid-liquid matches with reaction (Appendix C.2). In the classification of systems under consideration, mass transfer is possible between two liquid streams and between a liquid and a vapour stream (see section 4.6). Table 4.4 summarises the constraints utilised to define the limiting case for mass transfer within these modules.

4.6 The Synthesis Framework

The general synthesis framework as described in section 2.8 when applied to reactive-separation systems result in a superstructure of alternatives including distinct reaction and separation operations, and hybrid processes combining reactive and non-reactive operations. For illustrative purposes, consider the process synthesis for the production of pure D given A and B discussed previously, where reaction (4.21) occurs.

Stream superset

Given that the mixture $ABCD$ is homogeneous in the range of operating conditions considered, all possible streams can be represented as instances of a liquid stream, a vapour stream, a hot utility stream and a cold utility stream;

$$L_{ABCD}, V_{ABCD}, St, CW$$

Mass/heat exchange matches

Mass/heat exchange possibilities

For reactive/separation systems with reaction in the liquid phase, three types of matches whereby mass transfer can occur are possible

1. Liquid-liquid matches

Mass transfer between two liquid streams is possible, whereby a component is transferred from one stream to another due to 'consumption' or 'generation'. For example a liquid stream rich in reactants A and B will tend to 'give away' or 'transfer' C to a liquid product stream. Such a match would represent a reactor module.

2. Liquid-vapour matches without reaction

Mass transfer between a liquid stream and vapour stream is possible due to volatility differences, representing a pure separator module, such as an aggregate of distillation trays.

3. Liquid-vapour matches with reaction

Simultaneous mass transfer due to volatility differences and reaction results in such a match, representing a reactor/separator module, for example an aggregate of reactive distillation trays.

Multiple exchangers for each match are considered with the appropriate driving force constraints (Table 4.4) introduced to determine the mass transfer direction of a component within the block and ensure feasibility of reaction and phase change.

Pure heat exchange possibilities

To simplify the problem, only heat transfer between process and utility streams is considered *i.e.* no heat integration between process streams. For the synthesis problem considered, heat exchange matches are thus possible between each of the utility streams (St , CW) and the process streams (L_{ABCD} , V_{ABCD}). Feasibility of heat transfer is ensured by a minimum positive temperature difference between the hot and cold streams at the inlet and outlet of the exchanger. When phase change occurs in heat exchangers, the transferred heat includes vaporisation/condensation enthalpy.

Mass/heat Exchange Superstructure

Based on the postulated stream matches, the building blocks of the superstructure are shown in (Figure 4.4), with all possible interconnections between splitters and mixers defined.

Mathematical Model

Binary variables are introduced to denote

- (i) the existence or not of each mass/heat exchange and pure exchange module
- (ii) the existence (or not) of interconnecting streams between the splitters and mixers
- (iii) the mass transfer direction of each component in each module

Variables (ii) and (iii) are not necessary but are introduced to simplify the solution of the nonlinear part of the superstructure model and to facilitate the introduction of logical constraints to the model. The model involves

- mass balances at the splitters and mixers of the superstructure.
Total as well as component flow balances are required at mixers where stream compositions may change, whilst only total flow balances are required at splitters.
- component mass balances at the mass/heat exchangers. Since no mass exchange takes place at heat exchangers, flows through them are constant.
- energy balances at the mixers, pure heat and mass/heat exchangers, based on enthalpy calculations of the superstructure streams and assuming adiabatic stream mixing.
- summation of stream molar fractions

- phase defining constraints for each stream
- driving force constraints at mass/heat exchangers
- temperature-based driving force constraints for heat exchange at the inlet and outlet of heat exchange units.
A minimum temperature difference is imposed between the hot and cold side of the heat exchanger, to ensure feasible heat exchange in finite exchanger area.
- thermodynamic property calculation of each stream as a function of its temperature, composition and pressure. These include enthalpy, vapour pressure and activity coefficient calculation. Any thermodynamic model and correlation can be incorporated.
- mixed integer constraints to account for the existence of modules
- pure integer constraints corresponding to logical conditions or process constraints, reducing combinatorial complexity.
- Objective function, including the cost of raw materials, mass and heat utilities and module cost.

The detailed mathematical model is similar to that given in section 3.8, resulting in a MINLP which can be solved through the decomposition formulation described in section 3.9. However, a reaction term is implicitly considered in the mass and energy balances around the mass/heat exchanges. *i.e*

◇ Component Mass Balances around each mass/heat exchange block

$$f_e^{LI} x_{ei}^{LI} + f_e^{VI} x_{ei}^{VI} - f_e^{LO} x_{ei}^{LO} - f_e^{VO} x_{ei}^{VO} + \nu_i \epsilon = 0$$

where ϵ is the amount of product generated through reaction, calculated from reaction rate kinetics and liquid holdup (or amount of catalyst, *etc.*)

◇ Energy balance

$$f_e^{LI} h_e^{LI} + f_e^{VI} h_e^{VI} - f_e^{LO} h_e^{LO} - f_e^{VO} h_e^{VO} - \epsilon \Delta H_r = 0$$

where ΔH_r is the heat of reaction. The full model for the methyl acetate synthesis example is detailed in Appendix D.

Module Cost

Liquid-vapour modules are essentially a separator, and as derived in section 2.9.1, its cost is approximated by

$$\text{Cost}_{L-V} (\$) = 316.435 \left(\frac{MW^V}{\rho^V} \right) F^{V^{0.5}} H^{0.802} \quad (4.33)$$

The variable H is an equivalent height to a separator, and is a function of the amount of mass transfer within the module and the liquid holdup. Two levels of detail can be used to calculate H ;

Level 1. A constant parameter

Level 2. As a function of liquid holdup (capacity)

Liquid-liquid modules with one inlet and one outlet with reaction is part of or a whole reactor, and the cost is approximated by

$$\text{Cost}_{L-L} (\$) = 1854.88 V^{0.623} \quad (4.34)$$

In the next sections, three classical reactive distillation examples are considered; the esterification of methyl acetate, the esterification of ethyl acetate and the production of MTBE. These examples aim to illustrate;

- The consistency of the driving force constraints for combined reaction-separation phenomena with simulations based on phase equilibria and reaction kinetics.
- The ability of the synthesis framework to
 - capture the behaviour of nonideal mixtures with detailed thermodynamic models and reaction kinetics
 - capture the complex interaction of simultaneous reaction and separation
 - identify the combination of reactive and non-reactive processes in process units
 - determine a feasible separation/reaction structure

In the first two examples, the reaction is explicitly accounted for in the liquid phase holdup, where the liquid volumetric holdup within each module is determined through the optimisation. The third example, the production of MTBE, is a heterogeneous system

<u>Utilities</u>	
C_{cw}	26.19 US\$ per kWyr
C_{steam}	137.27 US\$ per kWyr
<u>Raw Materials</u>	
C_{AAcid}	4.767 US\$ per kmol
C_{EtOH}	26.28 US\$ per kmol
C_{MeOH}	0.393 US\$ per kmol
C_{Iso}	0.767 US\$ per kmol

Table 4.5: Cost Parameters

whereby a solid catalyst is considered. By explicitly considering the mass of catalyst as a variable, reactive heterogeneous systems can be accounted for when the reaction kinetics are given in terms of catalyst weight.

Cost parameters utilised are shown in Table 4.5 For convenience in the presentation, and to reduce the size of the resulting mixed integer nonlinear programming problem, a number of simplifying assumptions are made:

- (i) Saturated liquid products are considered.
- (ii) The system is at constant specified pressure.
- (iii) No heat integration between the mass/heat transfer modules is considered.

These assumptions can be relaxed, as discussed in section 3.8. For the solution of the MINLP synthesis problem, the nested MINLP decomposition based solution strategy developed in section 3.9 is adopted. The MINLP problems are solved using GAMS Brooke *et al.* (1988), with solvers CONOPT and MINOS5 for the NLPs and CPLEX for the MIPs.

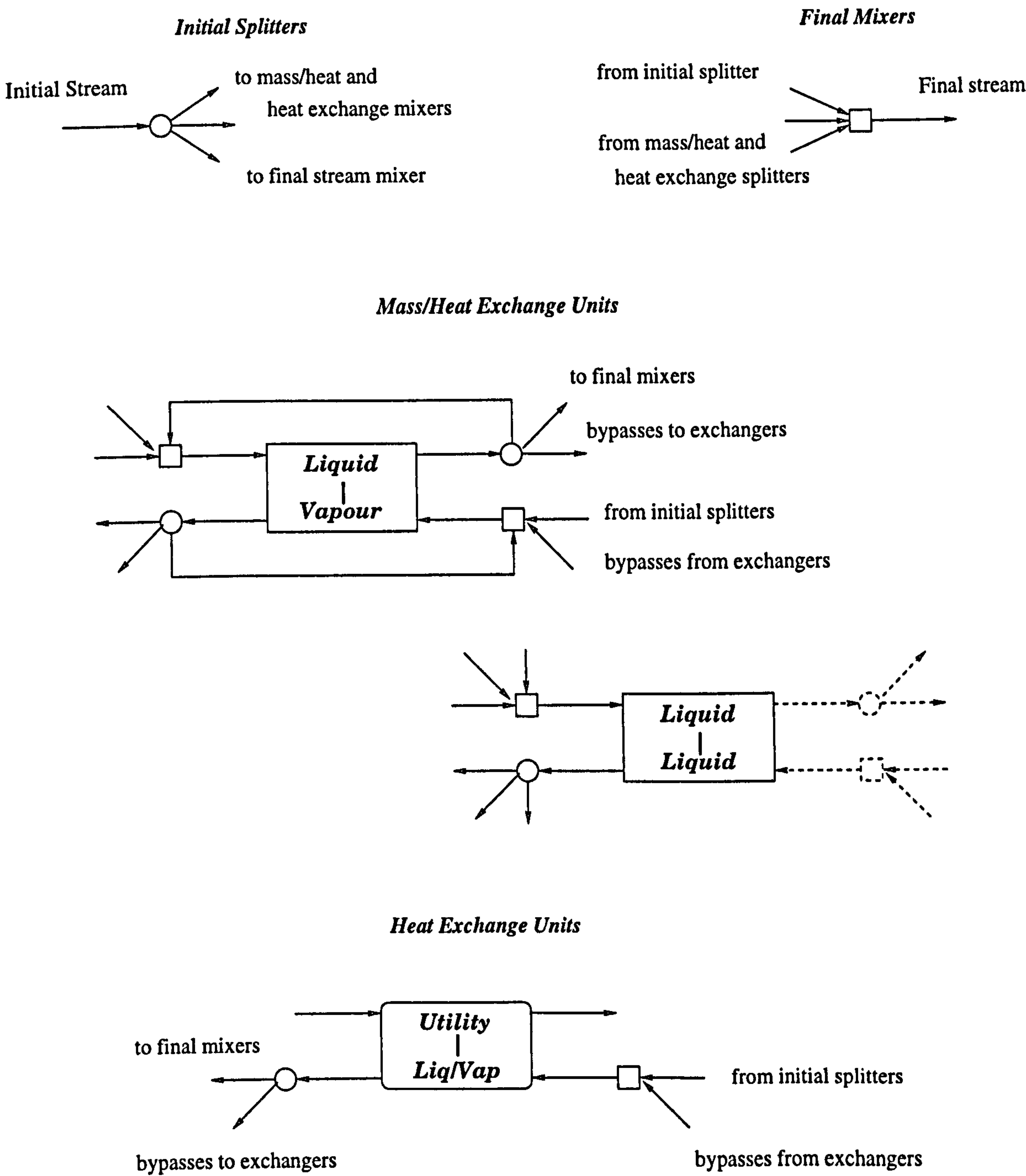
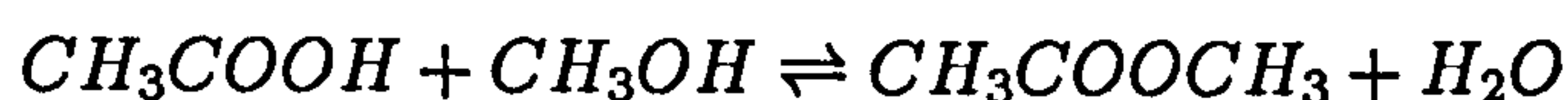


Figure 4.4: Superstructure Building Blocks for Reactive-Separation Systems

4.7 Production of Methyl Acetate

High purity methyl acetate is used in large amounts as an intermediate in the manufacture of a variety of polyesters (Mayfield and Agreda, 1986). The esterification of acetic acid (AAcid) with methanol (MeOH) in the liquid phase leads to methyl acetate (MeAc) and water (H₂O)



The production of high purity methyl acetate is limited by reaction equilibrium and the formation of two binary minimum boiling azeotropes methyl acetate/methanol ($x_{MeAc} = 0.66$) and methyl acetate/water ($x_{MeAc} = 0.92$). Conventional processes, working with a large excess of one reactant, require two reactors and eight distillation columns to overcome these limitations (Doherty and Buzad, 1992). High purity methyl acetate can also be produced with only one reactive distillation column with almost stoichiometric feed flows as invented and realised by Eastman Chemical Company (Agreda *et al.*, 1990). In a counter-current flow column with sulphuric acid as a homogeneous catalyst, chemical equilibrium limitations are overcome by vaporisation of the desired product. The minimum boiling azeotropes are broken by reaction of methanol and an integrated extractive distillation with the reactive entrainer acetic acid. The high purities of the products, methyl acetate as distillate and water as bottom product, are also achieved by a separation of products and reactants in non-reactive sections below and above the reactive section of the column.

Thermophysical Properties

In this system, dimerization of acetic acid occurs in the vapour phase, forming an equilibrium mixture of monomers, dimers and a small amount of higher polymers. The association of acetic acid molecules is strong enough to be considered as a chemical equilibrium reaction, but is simple enough to describe mathematically that it can be incorporated directly into the phase equilibrium equations. The method of Marek and Standart (1954) for calculating phase equilibrium considers a perfect gas phase and accounts for the associating component by introducing a correction factor (z_i) into the equilibrium relationship such that

$$y_i z_i P_{tot} = x_i \gamma_i P_i^{sat} \quad (4.35)$$

where

$$z_A = \frac{1 + (1 + 4KP_A^{\text{sat}})^{1/2}}{1 + [1 + 4KP_{\text{tot}}y_A(2 - y_A)]^{1/2}} \quad (4.36)$$

if A is the associating component and

$$z_B = \frac{2 \{1 - y_A + [1 + 4KP_{\text{tot}}y_A(2 - y_A)]^{1/2}\}}{(2 - y_A) \{1 + [1 + 4KP_{\text{tot}}y_A(2 - y_A)]^{1/2}\}} \quad (4.37)$$

if B is a non-associating component. K is the dimerization equilibrium constant for the associating component (Acetic Acid) given by

$$\log_{10}K = -12.5454 + \frac{3166}{T} \quad (\text{Pa}^{-1})$$

The Wilson equation was utilised to capture the nonidealities in the liquid phase. An alternative model for the activity coefficient is the Margules equation as developed for this system by Sawistowski and Pilavakis (1982). Pure component liquid density correlations and parameters are obtained from SEPSIM (Perregaard, 1992) databank, with liquid mixture density in the holdup calculated by the molar average,

$$\frac{1}{\rho_m} = \sum_{i=1}^C \frac{x_i}{\rho_i} \quad (4.38)$$

Pure component enthalpies were fitted linearly in the temperature range of 330-390K from the perfect gas heat capacities and heat of vaporisation correlations also obtained from SEPSIM. The thermodynamic models and parameters utilised are detailed in Table 4.6.

Reaction Kinetics

The liquid phase reaction for methyl acetate synthesis can be catalysed by inorganic acids like sulphuric acid or heterogeneously by strong acidic ion exchange resins. Recently, Song *et al.* (1998) developed kinetic rate expressions in terms of activities using a heterogeneous catalyst. In this work, the homogeneously catalysed esterification is considered, where the rate of formation of ester is given by the following concentration based rate expression (Sawistowski and Pilavakis, 1979)

$$r = \frac{k[H^+]C_{\text{AAcid}}C_{\text{MeOH}}}{K_1C_{\text{H}_2\text{O}} + C_{\text{MeOH}}} \quad (\text{kmol}/\text{m}^3\text{s}) \quad (4.39)$$

Component	C1	C2	C3	ΔG^f (kJ/kmol)	v_i m ³ /mol
Acetic acid	9.51271	1533.313	-50.851	-3.7405x10 ⁵	57.54x10 ⁻⁶
Methanol	10.20586	1582.271	-33.434	-1.6242x10 ⁵	40.73x10 ⁻⁶
Methyl acetate	9.19013	1157.63	-53.434	-3.2154x10 ⁵	79.84x10 ⁻⁶
Water	10.19620	1730.63	-39.734	-2.2859x10 ⁵	18.07x10 ⁻⁶

$$\log P^{sat} = C1 - \frac{C2}{C3 + T} \quad (Pa, K)$$

Wilson equation

$$\ln \gamma_i = 1 - \ln \left[\sum_j x_j \Lambda_{ij} \right] - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$
$$\Lambda_{ij} = \frac{v_j}{v_i} \exp \left(\frac{-A_{ij}}{T} \right) \quad A_{ii} = 0$$

Binary Interaction Parameters A_{ij} (K)				
	Acetic acid	Methanol	Methyl acetate	Water
Acetic acid	0.0	-7.0931	-204.3598	2.0311
Methanol	11.8097	0.0	453.5853	41.6934
Methyl acetate	433.9473	-65.4667	0.0	352.5512
Water	403.1564	262.1529	982.5402	0.0

Pure component enthalpy

$$H = AT + B \quad (J/mol, K)$$

	Acetic acid	Methanol	Methyl acetate	Water
Vapour A	76.1687	48.7023	93.0998	34.1335
B	-22964.9971	-14650.5741	-28102.0306	-10185.52543
Liquid A	64.7570	126.7599	170.0476	80.3012
B	-41942.0895	-77009.7147	-84201.9037	-68066.8819

Table 4.6: Methyl acetate production : Thermodynamic properties

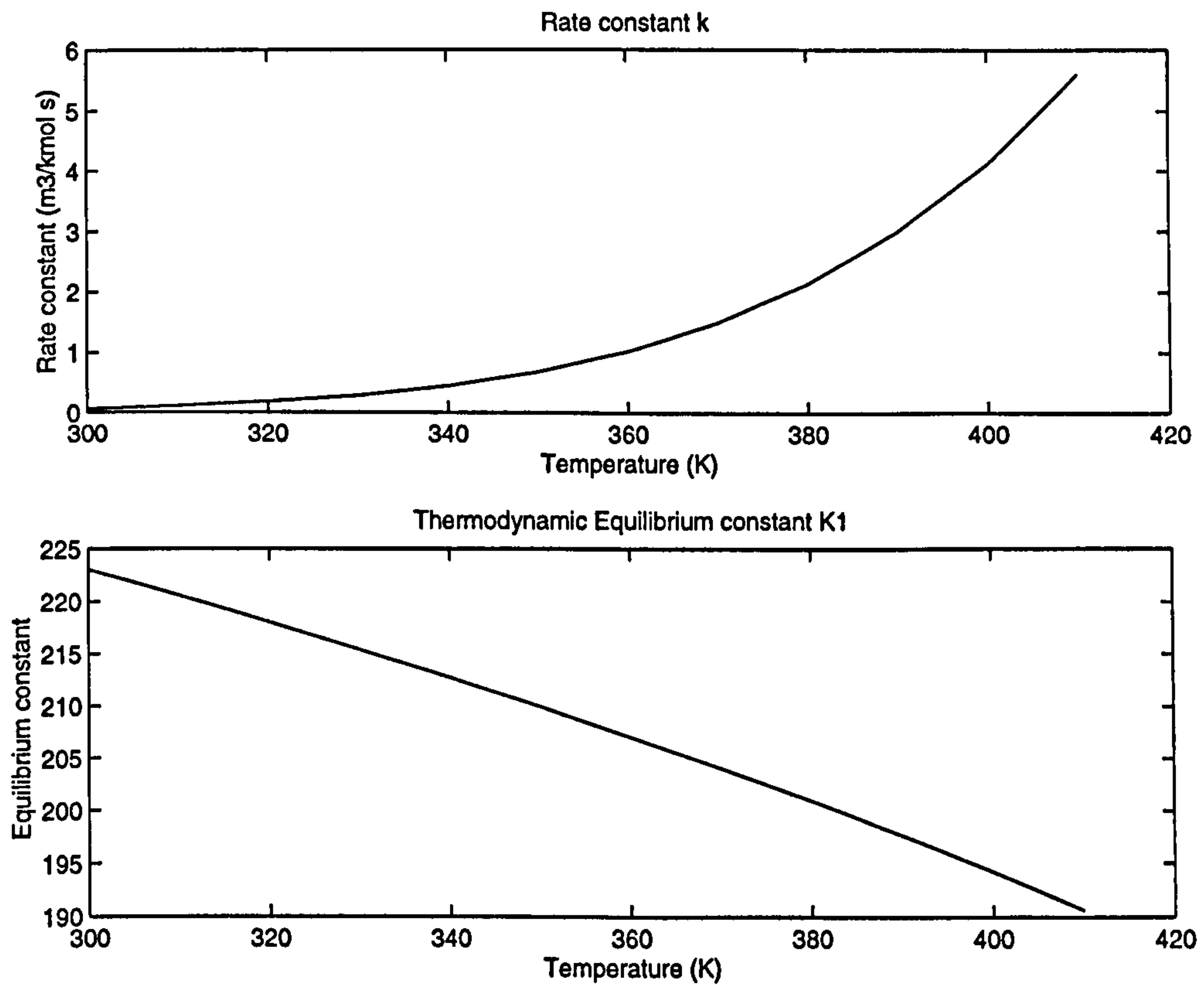


Figure 4.5: Reaction rate constant and thermodynamic equilibrium constant as function of temperature of esterification reaction to Methyl acetate

where the rate constant is given by (Smith, 1939)

$$k = 1.2 * 10^6 \exp \left[\frac{-10000}{RT} \right] \quad (\text{m}^3/\text{kmols}) \quad (4.40)$$

and the equilibrium constant is expressed as a function of temperature (Pilavakis, 1974)

$$K_1 = \frac{\rho_{\text{MeOH}}}{[0.11 + 0.0007043(T - 273.15)^{1.556}]} \quad (4.41)$$

where ρ_{MeOH} is in kmol/m^3 to make K_1 dimensionless. The dependence of the rate constant and the equilibrium constant on temperature is shown in Figure 4.5.

4.7.1 Driving force constraint and derivation of $(\partial\epsilon/\partial n_i^L)$

Expressions for $(\partial\epsilon/\partial n_i^L)$ are derived for use in the driving force constraints. The rate of production of species i for a homogeneous reaction is given by

$$r_i = \frac{\nu_i}{V} \frac{d\epsilon}{dt} \quad (4.42)$$

where $d\epsilon/dt$ is the rate of change of the extent of reaction in amount of moles per unit time. Integrating from the initial conditions of $t = 0$ when the reaction starts to $t = \theta$ when the reaction reaches its final extent of reaction ϵ ,

$$\begin{aligned} \int_0^\epsilon d\epsilon &= \int_0^\theta (rV) dt \\ \epsilon &= r * V * \theta \end{aligned} \quad (4.43)$$

θ is the active residence time *i.e.* time the mixture spends reacting in the liquid holdup. In a module, the residence time is calculated as the contact time of the mixture within the liquid holdup, which is evaluated by

$$\begin{aligned} \theta &= \frac{\text{Volume of liquid holdup in m}^3}{\text{Volumetric Flowrate of liquid through holdup}} \\ &= \frac{V}{\bar{V}} = \frac{n_{tot}^L / \rho_m^L}{F^L / \rho_m^L} \end{aligned} \quad (4.44)$$

$$= \frac{n_{tot}^L}{F^L} \quad (4.45)$$

where $n_{tot}^L = \sum_i n_i^L$ and n_i^L is the molar liquid holdup of component i in the reacting liquid mixture.

Utilising the reaction rate in equation (4.39) with (4.43), the extent of reaction for the methyl acetate system is given by

$$\epsilon = \frac{k [H^+] n_{AAcid}^L n_{MeOH}^L \theta}{K_1 n_{H_2O}^L + n_{MeOH}^L} \quad (4.46)$$

where $[H^+]$ is the concentration of catalyst hydrogen ions. Substituting for θ (4.45), equation (4.46) then becomes

$$\epsilon = \frac{k [H^+] n_{AAcid}^L n_{MeOH}^L n_{TOT}^L}{F^L (K_1 n_{H_2O}^L + n_{MeOH}^L)} \quad (4.47)$$

To differentiate this expression, the catalyst concentration is taken to be independent of changes in molar holdup of the reacting system components. Differentiating with respect to the molar holdup of acetic acid, (dropping the superscript L)

$$\begin{aligned}
 \frac{\partial \epsilon}{\partial n_{\text{AAcid}}^L} &= \frac{k[H^+]}{F(K_1 n_{\text{H}_2\text{O}} + n_{\text{MeOH}})} (n_{\text{MeOH}} n_{\text{TOT}} + n_{\text{AAcid}} n_{\text{MeOH}}) \\
 &= \frac{k[H^+]}{F(K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}}) n_{\text{TOT}}} (x_{\text{MeOH}} n_{\text{TOT}}^2 + x_{\text{AAcid}} x_{\text{MeOH}} n_{\text{TOT}}^2) \\
 &= \frac{k[H^+] n_{\text{TOT}}}{F(K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}})} x_{\text{MeOH}} (1 + x_{\text{AAcid}}) \quad (4.48)
 \end{aligned}$$

Differentiation with respect to the other components in a similar fashion leads to the following expressions

$$\frac{\partial \epsilon}{\partial n_{\text{MeOH}}^L} = \frac{k[H^+] n_{\text{TOT}}}{F(K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}})^2} x_{\text{AAcid}} (x_{\text{MeOH}}^2 + K_1 x_{\text{H}_2\text{O}} + K_1 x_{\text{H}_2\text{O}} x_{\text{MeOH}}) \quad (4.49)$$

$$\frac{\partial \epsilon}{\partial n_{\text{MeAc}}^L} = \frac{k[H^+] n_{\text{TOT}}}{F(K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}})} x_{\text{AAcid}} x_{\text{MeOH}} \quad (4.50)$$

$$\frac{\partial \epsilon}{\partial n_{\text{H}_2\text{O}}^L} = \frac{k[H^+] n_{\text{TOT}}}{F(K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}})^2} x_{\text{AAcid}} x_{\text{MeOH}} (K_1 x_{\text{H}_2\text{O}} + x_{\text{MeOH}} - K_1) \quad (4.51)$$

4.7.2 Simulation Study

Consider a liquid-vapour module/tray e in a reactive distillation column. A set of 4 streams s are introduced per module, denoting the liquid and vapour inlet and outlet streams *i.e.* $s = LI, LO, VI, VO$. The variables associated with this module/tray are as follows;

F^s	molar flowrate	4
T^s	temperature	4
x_i^s	molar composition	4C
P_{tot}	total pressure	1
V	volumetric liquid holdup	1
ϵ	molar extent of reaction	1
Total number of variables		11+4C

The equations describing each module/tray are summarised in Table 4.7. Both the (i) equilibrium model and (ii) modular model consist of generic mass and energy balances, summation of molar fractions and reaction kinetic description. However, whilst the equilibrium model assumes physical equilibrium between outlet streams, the modular model consists of driving force and phase defining constraints. A degree of freedom (DOF) analysis shows that the modular model has $C + 1$ more degrees of freedom than the equilibrium model *i.e.*

	Equilibrium Model	Modular Model
Variables	11+4C	11 +4C
Equalities	7+2C	6+C
Inequalities	-	C+4
DOF	4+2C	5+3C

Specification of the liquid and vapour inlet stream variables (F, T, x_{C-1}), the system pressure P_{tot} and the liquid holdup V gives a fully defined system for the equilibrium model. The same specifications corresponds to an optimisation problem for the modular model, constrained by $C + 4$ inequality constraints.

To compare the equilibrium and modular model, a set of five modules/trays in the reactive zone of a reactive distillation is considered, with fixed liquid inlet to the top tray and vapour inlet to the bottom tray. Using the specifications as given in Table 4.8, two cases are studied;

- Simulation considering physical equilibrium and reaction kinetics (Equilibrium model)
- Optimisation for maximum ethyl acetate fraction in the vapour outlet (Modular model).

Figure 4.6 shows the liquid and vapour composition profiles for the tray by tray simulation of methyl acetate. On all trays, methyl acetate is generated, giving a total extent of reaction of 1.18 mol/s. The methyl acetate profiles increase up the column section, whilst that of water decreases. The acetic acid profile remains almost constant, whilst that of methanol initially decreases up the first three trays, then increases on the top two tray. To analyse the mass transfer direction of each component more deeply, consider the value of $\mathcal{G}_{1i}$ for each component. We are reminded that $\mathcal{G}_{1i} \geq 0$ indicates a decrease in the liquid phase due to mass transfer from the liquid to the vapour phase, and/or consumption in reaction. Conversely, $\mathcal{G}_{1i} \leq 0$, indicates an increase in the liquid phase due to mass transfer from the vapour to the liquid phase, and/or generation in reaction. Table 4.9 gives the numerical values of $\mathcal{G}_{1i}$. Methyl acetate is generated on all trays, but due to its high volatility, it is simultaneously transferred to the vapour phase and $\mathcal{G}_{1i} \geq 0$. The intermediate component water, is relatively heavy and is transferred to the liquid phase as it is generated, giving $\mathcal{G}_{1i} \leq 0$ on all trays. Although the acetic acid is the heaviest component, due to its high concentration, its composition profile is almost constant and $\mathcal{G}_{1i} \geq 0$ due to its consumption on every tray. Methanol, the other intermediate component, exhibits interesting behaviour, with a switch in mass transfer

Component mass balances		
$F^{LI}x_i^{LI} + F^{VI}x_i^{VI} - F^{LO}x_i^{LO} + F^{VO}x_i^{VO} + \nu_i * \epsilon = 0$		C
Energy balance		
$F^{LI}h(T^{LI}) + F^{VI}h(T^{VI}) - F^{LO}h(T^{LO}) + F^{VO}h(T^{VO}) + \Delta H_r * \epsilon = 0$		1
Extent of reaction		
$\epsilon = f(T^{LO}, x_i^{LO}, V)$		1
Summation of molar fractions		
$\sum_i x_i^{LO} = 1 \qquad \sum_i x_i^{LI} = 1$		2
$\sum_i x_i^{VO} = 1 \qquad \sum_i x_i^{VI} = 1$		2
Equilibrium Model		
$T^{LO} = T^{VO}$		1
$x^{LO} = f(T^{LO}, x^{LO}, x^{VO}, P_{tot})x^{VO}$		C
Modular Model		
$\mathcal{G}1 * \mathcal{G}2 \geq 0$		C
$0.8 \leq \sum_i K(x_i^{LO}, T^{LO} P_{tot})x_i^{LO} \leq 1$		2
$0.8 \leq \sum_i x_i^{VO} / K(x_i^{VO}, T^{VO} P_{tot}) \leq 1$		2

Table 4.7: Summary of Model Equations

	Liquid Inlet	Vapour Inlet
Temperature (K)	344.941	347.537
Flowrate (mol/s)	29.301	27.732
X_{acid}	0.40776	0.07565
X_{MeOH}	0.00974	0.04036
X_{MeAc}	0.55274	0.75992
X_{Wat}	0.02977	0.12407
Pressure	1 atm	
Holdup	1 m^3 per tray	
Catalyst fraction	0.02 per tray	

Table 4.8: Methyl acetate simulation : Liquid and vapour inlet specifications

Tray Number	Acetic Acid	Methanol	Methyl acetate	Water
1	0.221108133	-0.129307298	0.998208080	-0.524649662
2	0.210425129	-0.033107885	0.732033293	-0.569051263
3	0.104303249	-0.005137650	0.648271832	-0.508305259
4	0.060741679	0.022389240	0.610288748	-0.481945726
5	0.243633916	0.257843315	0.513965533	-0.677968815

Table 4.9: Methyl acetate simulation: value of $\mathcal{G}_1$

direction between the third and fourth tray. On the first three three trays, the methanol profile decreases as it becomes depleted through reaction. However, due to the minimum boiling azeotrope between the methanol and methyl acetate, the unreacted methanol is drifted up the column, resulting in a slight increase in the composition profile due to mass transfer from the liquid to the vapour.

The mass transfer driving force constraints can consistently account for such effects due to the interaction between reaction and phase, as shown in Table 4.10 where the calculated value of $\mathcal{G}_1; * \mathcal{G}_2; \geq 0$ on each tray.

For the same specifications as for the simulation problem, the modular model is optimised for the maximum methyl acetate fraction in the vapour outlet and compared to the equilibrium model. The modular model allows for higher temperatures within the phase defining constraints, as shown in Figure 4.7(a). Although a slightly lower total generation rate of 0.93 mol/s than that achieved by the simulation model is obtained, as

Tray Number	Acetic Acid	Methanol	Methyl acetate	Water
1	0.008800572	0.170524377	0.075259432	0.023765024
2	0.048845240	0.045020790	0.035164388	0.058393798
3	0.025432167	0.007271367	0.025977162	0.071782392
4	0.013734119	0.014990529	0.023254237	0.079627602
5	0.053015157	0.445404723	0.018911730	0.145193106

Table 4.10: Methyl acetate simulation: value of $G1 * G2$

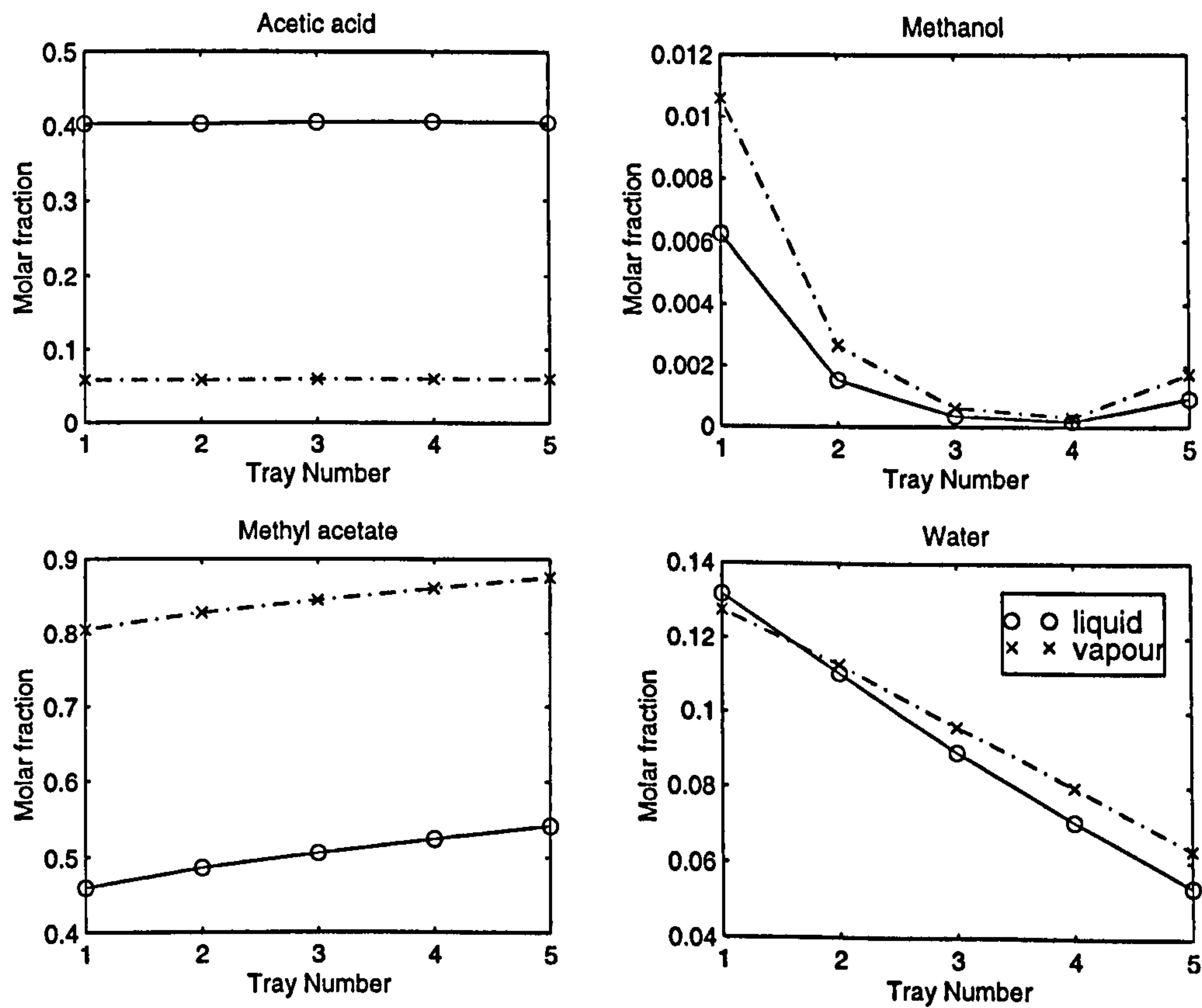


Figure 4.6: Methyl acetate simulation : Composition profiles

shown in Figure 4.7(b), a slightly purer vapour ethyl acetate is achieved. The composition profiles within the modular model are not smooth, but the general trend of the process can be generated.

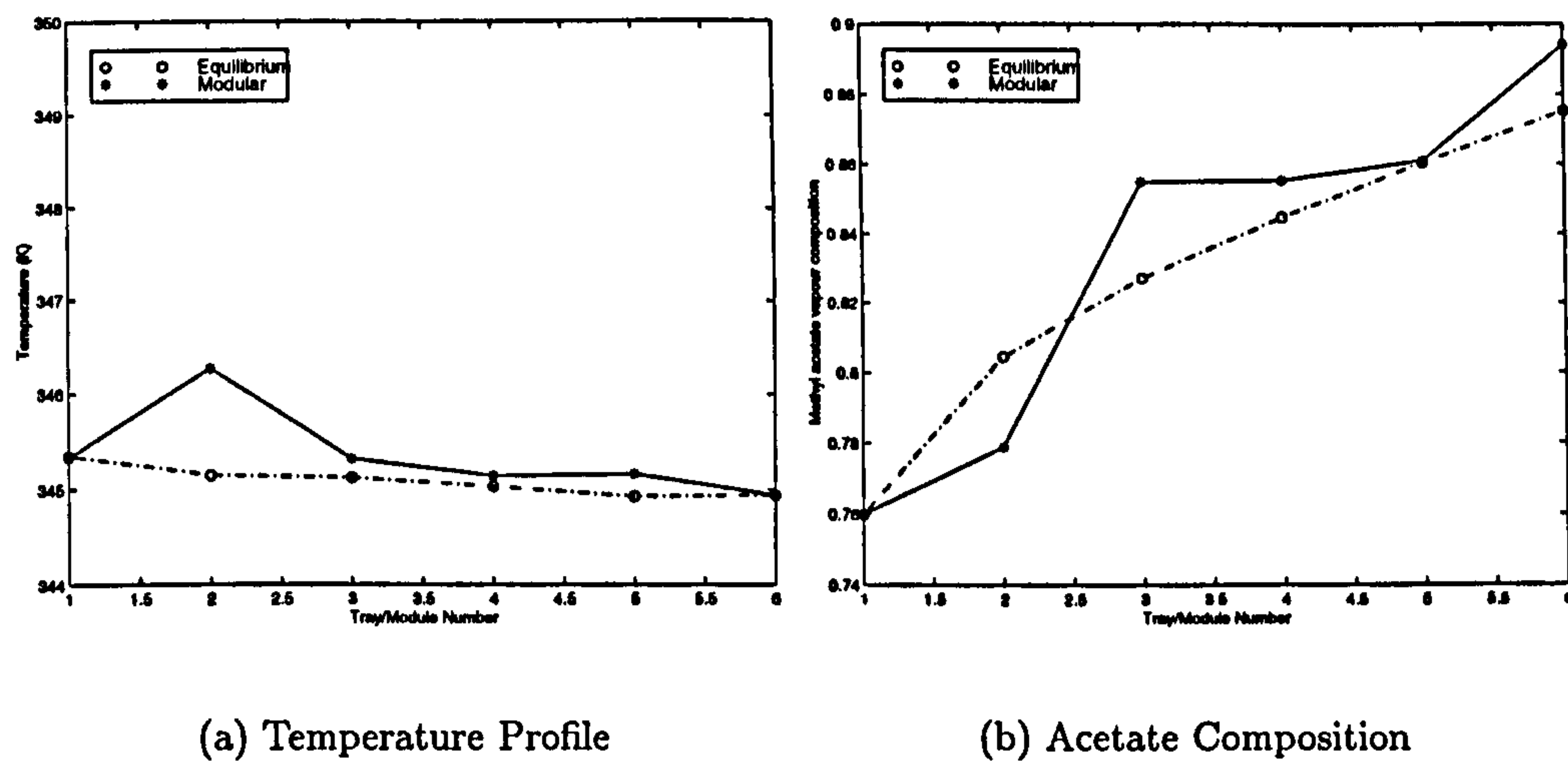


Figure 4.7: Methyl acetate: Comparison of Equilibrium and Modular Models

4.7.3 Synthesis Problem

We consider the synthesis task for the production of 9.8 mol/s of 98% pure methyl acetate at 1atm, given as raw products pure methanol and acetic acid. Homogeneous sulphuric acid is available as catalyst, and the maximum allowable mole fraction of sulphuric acid in each module was set at 0.02, since high concentrations can cause problems such as corrosion and product contamination. A total of 20 liquid-vapour mass/heat exchangers are considered, 10 pure separation and 10 with combined separation/reaction.

The synthesis task is driven by the minimisation of annualised cost ($\text{US\$}/\text{yr}$) based on plant operation of 7920 hrs/yr. Three cost functions are investigated;

- Obj1 : Utility cost (+ constant module cost)

$$Z = \sum C_{cw} * Q_{cool} + \sum C_{steam} * Q_{heat} \\ (+ \sum y_{L-V} * K_{cost_{L-V}})$$

- Obj2 : Utility and Raw material cost (+ constant module cost)

$$Z = \sum C_{cw} * Q_{cool} + \sum C_{steam} * Q_{heat} \\ + C_{AAcid} * F_{feed,AAcid} + C_{MeOH} * F_{feed,MeOH} \\ (+ \sum y_{L-V} * K_{cost_{L-V}})$$

- Obj3 : Utility, raw material and variable module cost

$$\begin{aligned}
 Z &= \sum C_{cw} * Q_{cool} + \sum C_{steam} * Q_{heat} \\
 &+ C_{AAcid} * F_{feed,AAcid} + C_{MeOH} * F_{feed,MeOH} \\
 &+ \sum y_{L-V} * Cost_{L-V}
 \end{aligned}$$

where $Cost_{L-V}$ is given by (4.33) with

$$\begin{aligned}
 H &= 2 + \frac{4V}{\pi D^2} \\
 D &= 0.98424 \sqrt{F^{VI}} \left(\frac{M^{VI}}{\rho^{VI}} \right)^{0.25}
 \end{aligned}$$

with F^{VI} is in mol/s , M^{VI} inlet vapour stream molarity and ρ^{VI} the density of the inlet vapour stream. *Obj1* and *Obj2* include a constant module cost $Kcost_{L-V}$ to penalise the number of modules chosen.

The initial structure consisting of 3 liquid-vapour modules each with 20 m^3 liquid holdup, in between 2 pure separation liquid-vapour modules is used Figure 4.8. This configuration is derived from the reactive column designed by Barbosa and Doherty (1988a), consisting of a total of 57 chemical and physical equilibrium trays to achieve pure methyl acetate distillate.

Minimization of all three cost functions results in the configuration shown in Figure 4.9, consists of 2 liquid-vapour modules with liquid holdups (separation and reaction) in between two pure separation liquid-vapour modules, and two pure heat exchangers. The solution represents a double feed reactive distillation column with reactive and nonreactive sections. The bulk of the reaction occurs within the two middle modules featuring catalyst fraction of 0.02. In the top liquid-vapour module, separation of methyl acetate and acid is achieved, giving almost pure methyl acetate product. The bottom pure separation module separates methanol and water, purifying the water product. Although the optimal structure of the three optimisation problems are similar, the operating conditions differ showing interesting features as detailed in Table 4.11. The lowest utility cost corresponding to the lowest reflux ratio is achieved with *Obj1*, at the expense of high methanol to acetic acid feed flow ratio of 5.6 and high liquid holdups, leading to a 3% loss of the methyl acetate produced. When the feed cost is considered (*Obj2*), a more efficient process results with almost stoichiometric feed rates of acetic acid and methanol, 99.96% conversion of acetic acid and negligible loss of methyl acetate produced. Considering utility, feed and capital cost (*Obj3*) results in significantly lower volumetric holdups (and thus smaller unit) at the expense of a slightly higher feed ratio of 1.02 to that of *Obj2*.

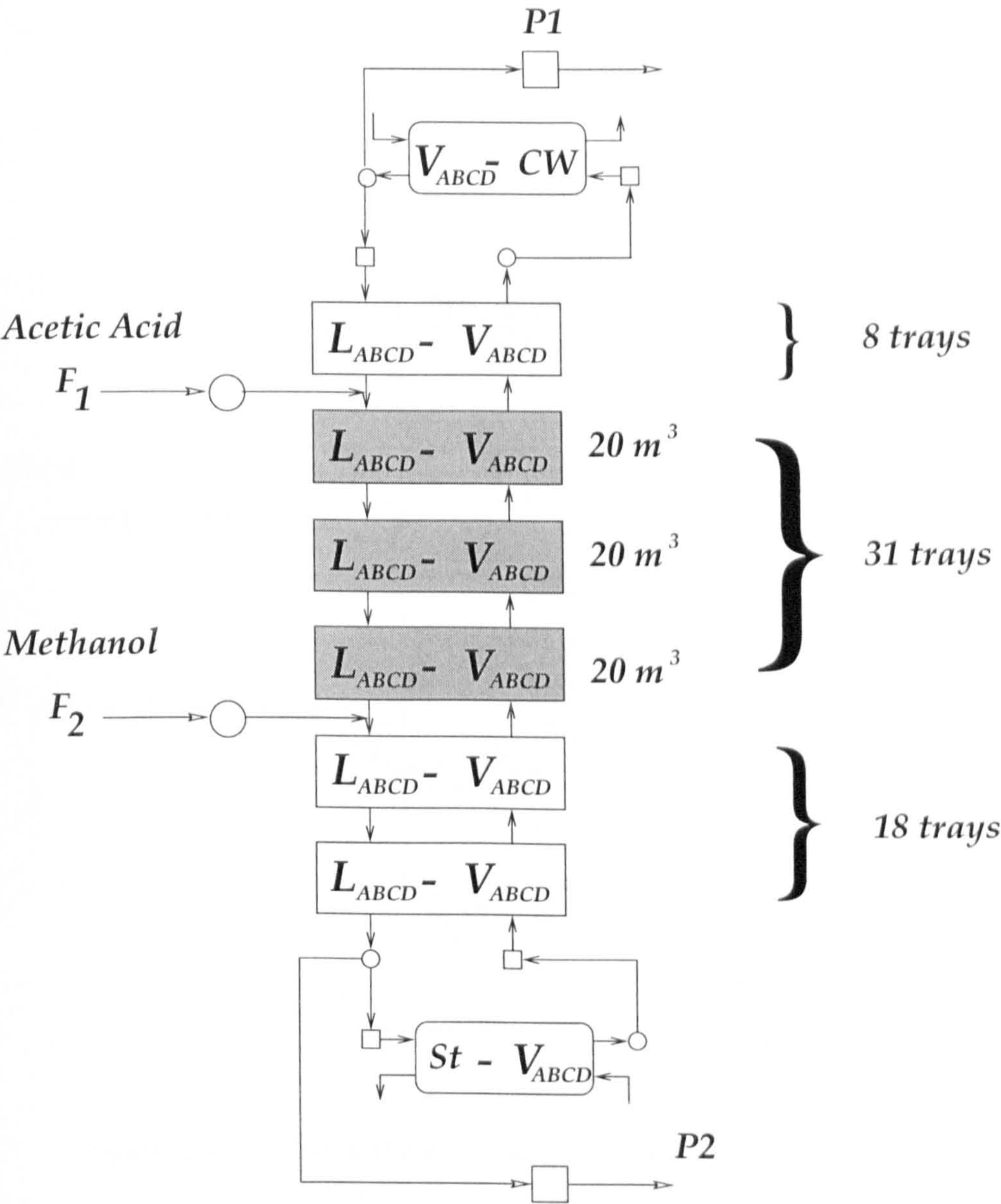


Figure 4.8: Methyl acetate synthesis : Initial Structure

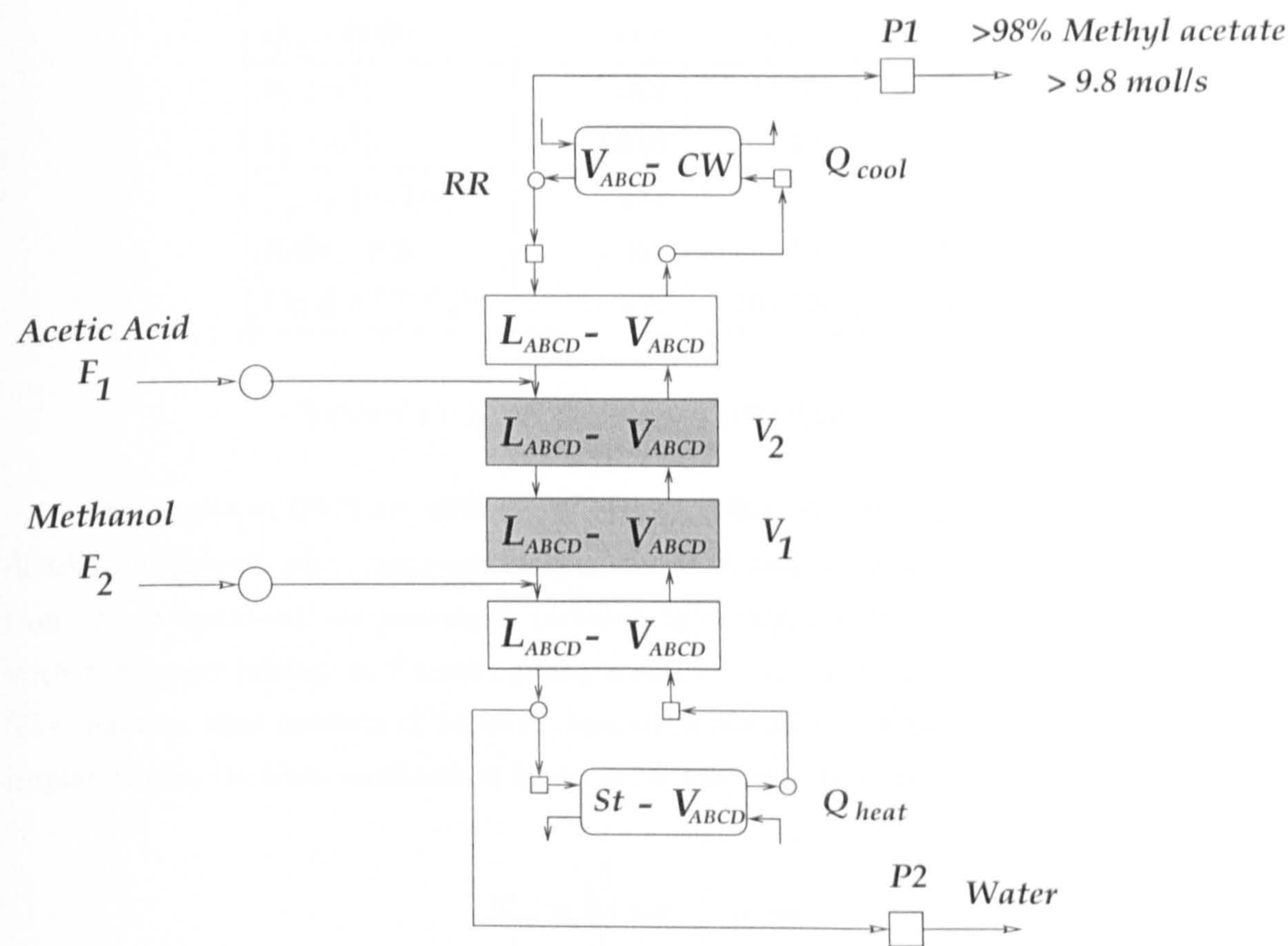


Figure 4.9: Methyl acetate production : Optimal configuration

	Obj1	Obj2	Obj3
Objective (\$/yr)	82 908	1 524 935	1 596 483
Utility Cost	82 908	111 503	122 577
Feed Cost	1 997 743	1 413 433	1 427 306
Module Cost	454 122	438 764	46 600
F_1^{Acid} (mol/s)	10.012	9.607	9.683
F_2^{MeOH} (mol/s)	56.847	9.604	9.923
Q_{heat} (kW)	465.9	649.3	716.6
Q_{cool} (kW)	723.6	854.2	924.6
V_1 (m ³)	17.962	22.001	0.847
V_2 (m ³)	32.038	27.999	1.182
$\sum_e \epsilon_e$ (mol/s)	9.914	9.604	9.604
Reflux RR	1.341	1.787	1.992
Final NLP CPU	88.889	102.536	116.352

Table 4.11: Synthesis results of Methyl Acetate

The results of *Obj3* are utilised as inlet specifications for a simulation of a reactive distillation column assuming simultaneous chemical and physical equilibrium for verification. Each liquid-vapour module is assumed to correspond to 6 trays, with the module with the larger holdup to 7 trays, giving a column with a total of 25 equilibrium trays. The reaction zone consists of 13 trays, and since the same reaction kinetics could not be implemented, chemical equilibrium is assumed whereby (Barbosa and Doherty, 1988b)

$$K_{eq} = \prod_i^C \gamma_i x_i^{\nu_i} = 14.6 \quad (4.52)$$

The column is simulated using AspenPlus and the rigorous steady state distillation module RADFRAC, with the Redlich-Kwong/UNIQUAC property set (SYSOP2). The comparative results are illustrated in Figure 4.12, with the reboiler and condenser duties of the aspen model recalculated utilising the same enthalpies. A number of comments can be made

- The reboiler within the modular model is a total reboiler with no mass exchange, and the liquid product is removed before being heated. The aspen model features a partial reboiler which heats the product to its bubble point, resulting in a higher reboiler duty.

- Although detail is lost within the mass/heat exchangers, the main features of the reactive column are captured in just four modules. This is illustrated in Figures 4.10 and 4.11, comparing the liquid composition and temperature profiles. Note that the liquid inlet and outlet module variables are plotted at the corresponding tray number within these plots (*i.e.* liquid inlet to module 1 corresponds to liquid inlet to tray 7, outlet of module 4 to outlet of tray 21).

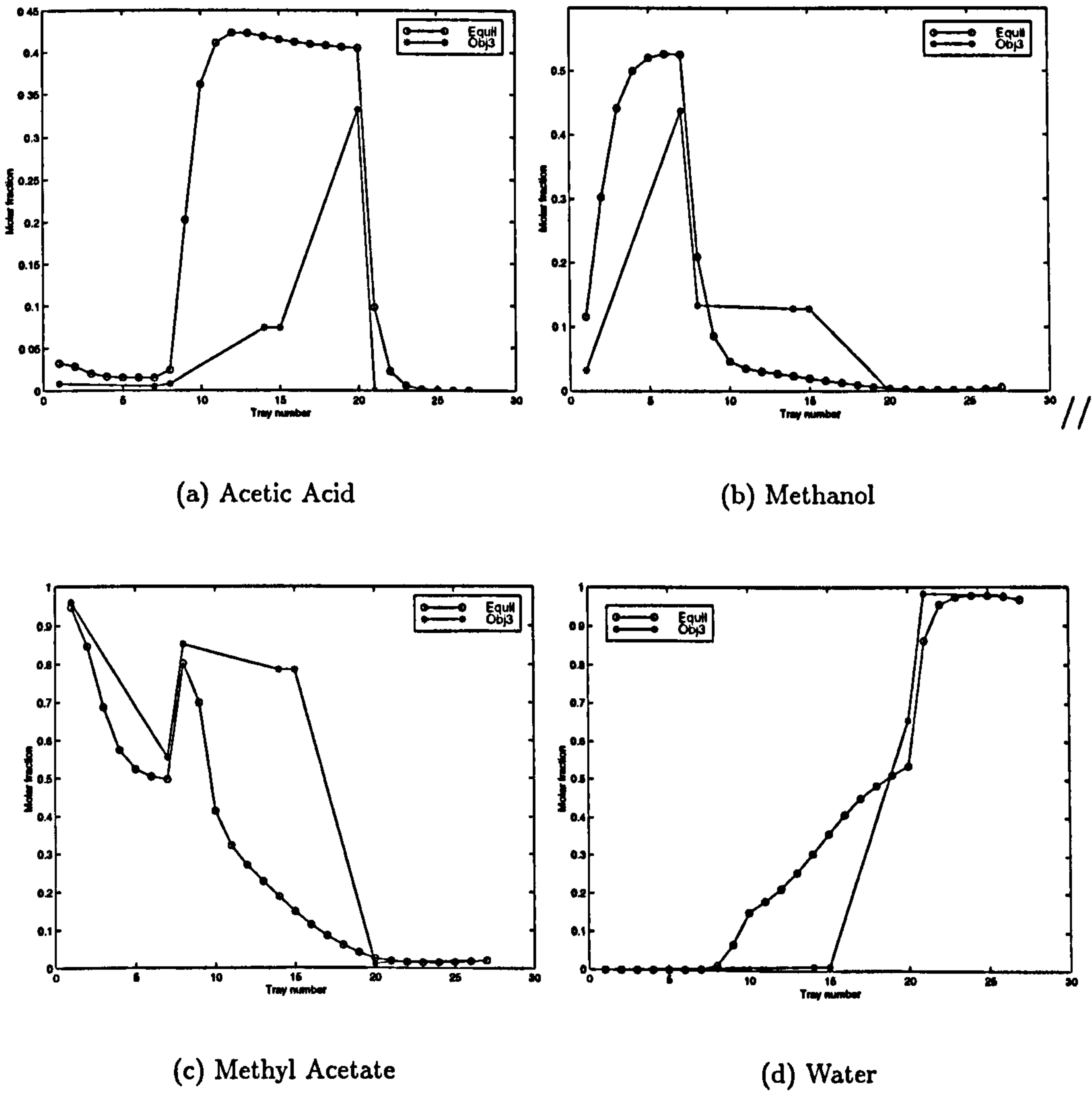


Figure 4.10: Comparison of Obj3 results with Equilibrium simulation

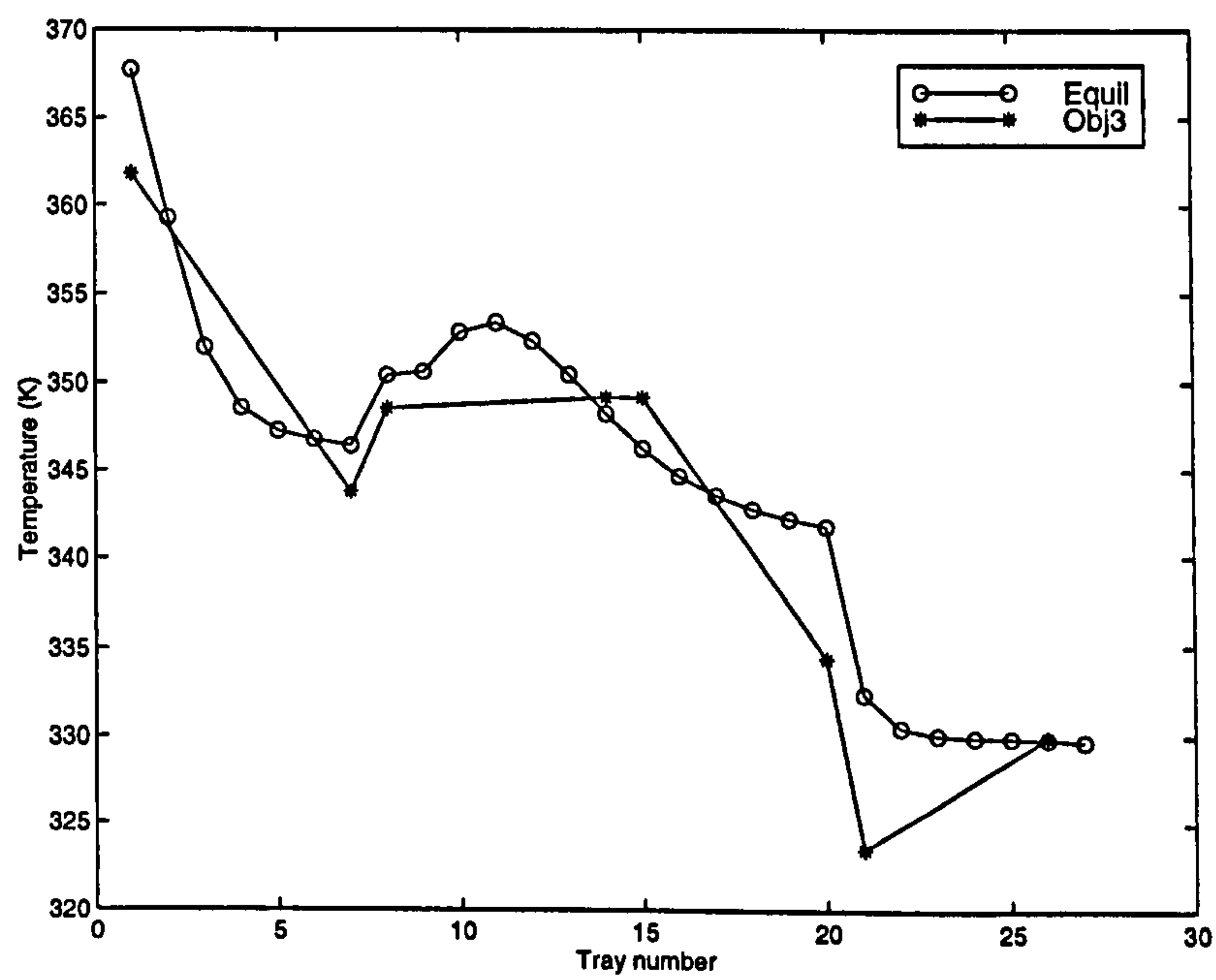


Figure 4.11: Comparison of Temperature profiles

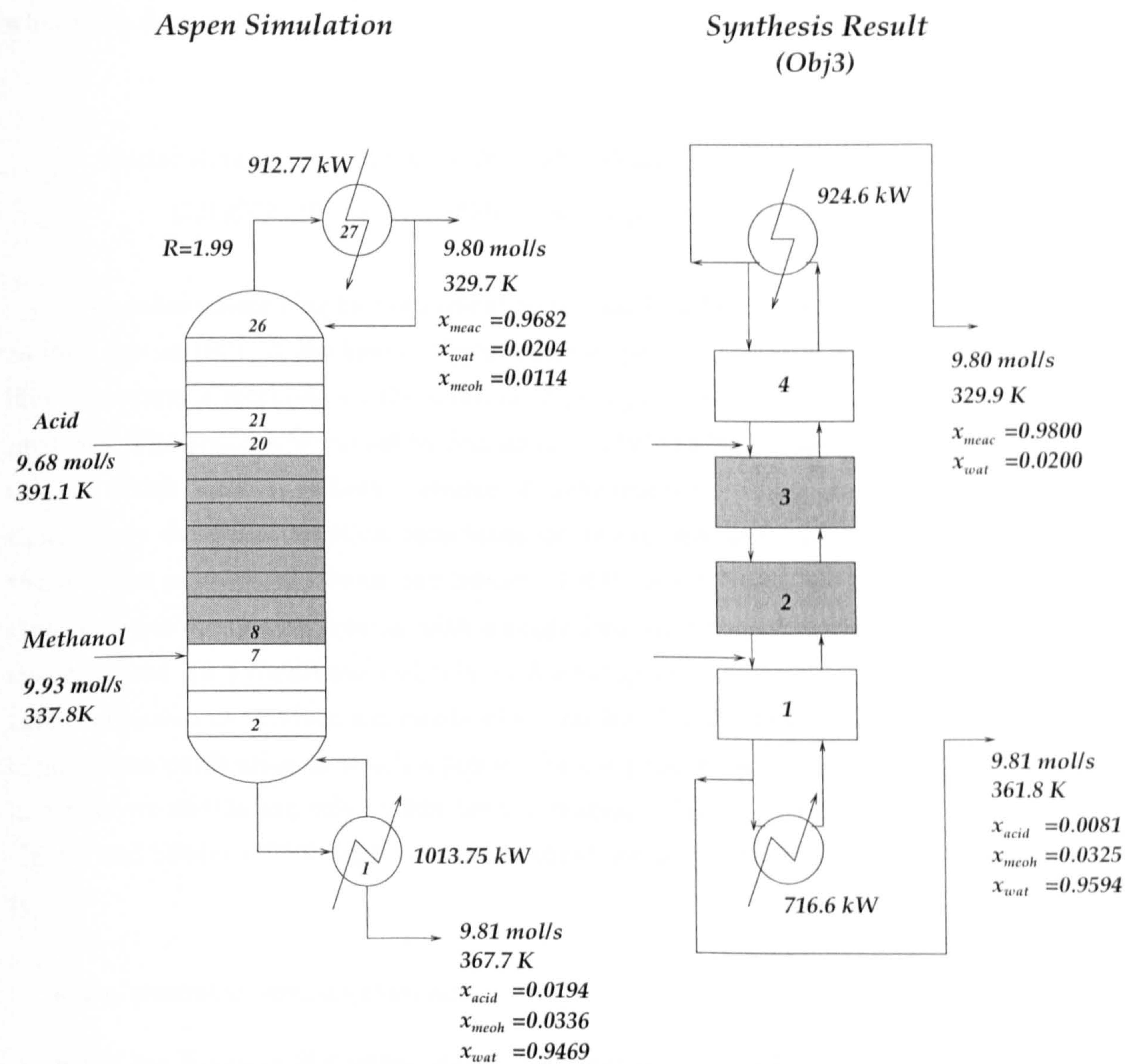
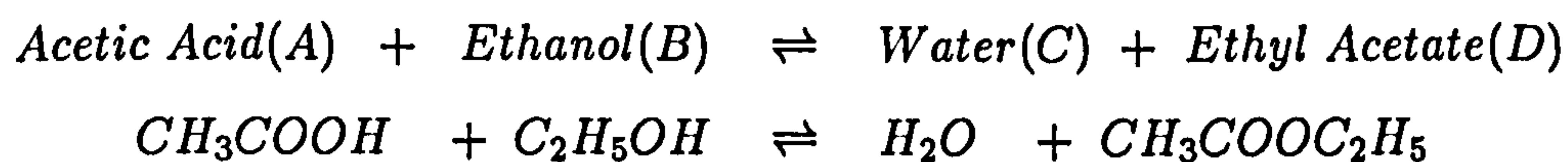


Figure 4.12: Verification of Obj3 results

4.8 Production of Ethyl Acetate

In the last few years, a large number of publications have been dedicated to reactive distillation, indicating the growing importance of the process as an alternative to conventional reaction separation processes. One of the most frequently considered reactive system in the literature is the esterification of acetic acid and ethanol to water and ethyl acetate, whose reaction is given by



The patent describing this esterification process in a distillation column was published as long ago as 1921 by Backhaus. Since then the process has been a popular example to illustrate various methods for the solution of the system of equations that the simulation presents. The precedence was set by Suzuki *et al.* (1971) who presented the first simulation results, which have since been a source of comparison for many authors demonstrating their newly developed solution techniques on the esterification process. A summary of these works is given by Chang and Seader (1988). All of these works simulate a steady state reactive distillation column with a single feed for a noncatalysed reaction, using the specifications (feed conditions and column design) given by Suzuki *et al.* (1971). However, these columns only produce a distillate of low purity of about 48 % ethyl acetate, and there is no known publication in which a process for the production of high purity ethyl acetate in a reactive distillation column has been developed using a rigorous model. According to Chang and Seader (1988), high conversion could not be achieved in a reactive column due to

- Unfavourable reaction conversion
- Similar K-values of ethanol, water and ethyl acetate, and
- the temperature profile in the column.

Recently, Bock *et al.* (1997) analysed the difficulties that arise in the uncatalysed esterification process using a rigorous model with reaction kinetics. They reported that reactive distillation appears to be unfavourable for this esterification, with low rise in conversion with increasing number of reactive stages due to

- The low reaction speed of the esterification leading to low formation of the product in the reactive stages
- Unfavourable phase equilibrium between the reactants and products which inhibits conversion.

However, they concluded that it is theoretically possible to obtain high purity ethyl acetate with different variants of the process. For example, a high excess of acetic acid gives a high proportion of acetic acid in the liquid phase, which results in a significant increase in the relative volatility between acetic acid and ethyl acetate as the number of separation stages increases.

Based on the assumption of chemical equilibrium and analysis of phase diagrams, Barbosa and Doherty (1988a) propose a number of alternative flowsheets for the production of esters by reactive distillation, where according to their analysis, a feed ratio of at least 7 (Acetic Acid to Ethanol flow) is required for a feasible design in a double feed column. By utilising acetic acid, a reactant, as the entrainer to break the ethyl acetate-ethanol entrainer, they propose a design configuration which can give complete conversion of the two reactants to products, obtaining pure ethyl acetate and water in a single column. However, their analysis is based on chemical equilibrium, neglecting heat effects and have no consideration of the difficulties that esterification present. This short cut method is not appropriate for this esterification process as it does not consider the hold up per stage which is a crucial factor for the conversion and thus for the design of this reactive column. In addition they propose the use of a catalyst but give no indication of the type of catalyst to use.

The esterification of acetic acid and ethanol to water and ethyl acetate is an interesting system as although there is a vast amount of open literature on the system, this has been confined to the simulation of single reactive columns and the synthesis task has not been addressed.

Thermophysical properties

The quaternary system features nonideal behaviour in the liquid phase caused by the polar molecules, and in the vapour phase due to the dimerization of the acetic acid. At a pressure of 1 atm, three minimum boiling binary azeotropes and a ternary azeotrope are possible in the system;

- ethyl acetate-water at 70.38°C
- ethyl acetate-ethanol at 71.81°C

Authors	VLE Models	Enthalpy calculations	Rate Equations
Suzuki <i>et al.</i> 1971	Case 1 : $K_i = f(T)$ fitted Case 2 : $y_i = \gamma_i P_i^{sat} x_i / P_{tot}$ P_i^{sat} - Antoine γ_i - modified Margules	Quadratic approximation $h_{i,vap} = f(T)$ $H_{i,liq}(T) = h_{i,vap}(T) - \lambda_i(T)$	Second Order, Irreversible $r_A = k_A C_A C_B$ $\log_{10} k_A = -2170/T + 3.70$
Izarraraz <i>et al.</i> 1980	$y_i = \gamma_i K_i x_i$ $K_i = f(T)$ as above γ_i - modified Margules	$h_{i,vap} = h_{i,pg} + \Omega$ $h_{i,pg} = \Delta H_{f,298} + \int_{298}^T C_{p,pg} dT$ $H_{i,liq} = h_{vap} - \lambda_i$ Ω using BWR EOS λ_i by Watson relation	Second Order, Reversible Arnika <i>et al</i> 1970 $r_A = k_f C_A C_B - k_b C_C C_D$ $k_f = 29000 \exp(-7150/T)$ $k_b = 7380 \exp(-7150/T)$ r_A in mol/liter min
Chang & Seader 1988	$y_i = \gamma_i P_i^{sat} x_i / p_{tot}$ γ_i modified Margules P_i^{sat} Antoine (from Suzuki <i>et al.</i> 1970)	As Izarraraz <i>et al.</i> 1980 i.e. referenced to elements	As Izarraraz <i>et al.</i> 1980
Alejski & Duprat 1996	$K_i = f(T, x_i)$ from Komatsu (1977)	From CHEMCAD database (Chemstations, Inc)	Second Order, Reversible Without catalyst - Arnika <i>et al</i> 1970 Sulphuric Acid catalyst -Alejski <i>et al.</i> 1989
Bock <i>et al.</i> 1997	γ_i - NRTL equation using parameters from Komatsu (1977)	Not Reported	Second Order, Reversible Arnika <i>et al</i> 1970

Table 4.12: Ethyl acetate production : Thermophysical Properties Used for Simulation

- ethanol-water at 78.17°C
- ethanol-ethyl acetate-water at 70.23°C

In the open literature, various thermodynamic and rate models have been utilised to simulate the reactive distillation column for the esterification of ethyl acetate. A sample of some of the correlations used are shown in Table 4.12. The thermodynamic models and parameters used in this work are detailed in Table 4.13 - the modified Margules equation developed by Suzuki *et al.* (1970) was used the system liquid nonidealities. Enthalpy and liquid density correlations and parameters are obtained from SEPSIM (Perregaard, 1992) databank, with liquid mixture density given by 4.38.

The esterification of acetic acid with ethanol is an endothermic, second order, reversible reaction. Uncatalysed, the reaction is slow but the rate can be significantly increased by the use of a homogeneous catalyst such as sulphuric acid. Two different kinetic equations are utilised;

For the noncatalysed reaction (Arnikar *et al.*, 1970)

$$\begin{aligned} r &= k_f C_A C_B - k_b C_C C_D \\ k_f &= 1.74 * 10^6 \exp(-7150/T) \\ k_b &= 4.428 * 10^5 \exp(-7150/T) \end{aligned} \quad (4.53)$$

For the sulphuric acid catalysed reaction (Alejski *et al.*, 1989)

$$\begin{aligned} r &= k_f C_A C_B - k_b C_C C_D \\ k_f &= 3.6 * 10^6 (4.195 C_k + 0.08815) \exp(-6500.1/T) \\ k_b &= 3.6 * 10^6 (4.195 C_k + 0.08815) \exp(-6500.1/T) / (7.558 - 0.012T) \end{aligned} \quad (4.54)$$

4.8.1 Driving force constraints

The reaction rate is of the form

$$\begin{aligned} r &= k_f C_A C_B - k_b C_C C_D \\ &= k_f \frac{n_A^L n_B^L}{V^2} - k_b \frac{n_C^L n_D^L}{V^2} \end{aligned} \quad (4.55)$$

From (4.43), the extent of reaction is thus given by (dropping the superscript L)

$$\epsilon = k_f \frac{n_A n_B}{V} - k_b \frac{n_C n_D}{V} \quad (4.56)$$

Component	C1	C2	C3	ΔG^f (kJ/kmol)
Acetic acid	7.55960	1644.05	233.52	-3.7405x10 ⁵
Ethanol	7.83124	1440.52	212.71	-1.6790x10 ⁵
Water	7.96681	1668.21	228.00	-2.2859x10 ⁵
Ethyl acetate	7.09808	1238.71	217.00	-3.2740x10 ⁵

$$\log P^{sat} = C1 - \frac{C2}{C3 + T} \quad (mmHg, ^\circ C)$$

Margules equation

$$\begin{aligned} \log \gamma_1 = & A_1 x_2^2 + A_2 x_3^2 + A_3 x_4^2 + A_4 x_2 x_3 \\ & + A_5 x_2 x_4 + A_6 x_3 x_4 + A_7 x_1 x_2^2 + A_8 x_1 x_3^2 \\ & + A_9 x_1 x_4^2 + A_{10} x_1 x_2 x_3 + A_{11} x_2 x_3 x_4 + A_{12} x_3 x_4 x_1 \\ & + A_{13} x_4 x_1 x_2 + A_{14} x_2 x_3^2 + A_{15} x_2 x_4^2 + A_{16} x_3 x_4^2 \end{aligned}$$

Activity coefficients for remaining components obtained
by rotating the subscripts 1 → 2 → 3 → 4 → 1

Constants	Acetic acid	Ethanol	Water	Ethyl acetate
A ₁	-0.554296	0.581778	0.688636	-0.0601367
A ₂	-0.324357	0.209245	0.0243031	0.229575
A ₃	-0.103685	-0.257329	0.375534	1.86575
A ₄	-0.705455	-0.562636	1.27548	0.355192
A ₅	-2.01335	-0.314853	1.77863	0.468416
A ₆	-2.25362	0.451732	0.696279	1.5111
A ₇	0.837926	-0.115411	0.936722	-0.0599682
A ₈	0.523760	0.0695310	0.449356	0.0673994
A ₉	0.434061	0.0740529	0.717790	-3.15997
A ₁₀	-0.534056	0.187010	1.44973	0.941858
A ₁₁	-3.25231	-0.369985	-2.11099	-1.92225
A ₁₂	5.90329	-0.0823390	0.746905	-0.755731
A ₁₃	3.354	-0.409472	1.12914	1.03791
A ₁₄	0.197296	1.09247	0.120436	0.365254
A ₁₅	-0.452660	0.192416	-1.64268	-1.36587
A ₁₆	0.0147152	-0.172565	0.330018	-2.13818

Table 4.13: Ethyl acetate production : Thermodynamic properties

Differentiating with respect to the molar holdup of component A,

$$\frac{\partial \epsilon}{\partial n_A} = \frac{k_f n_B}{\bar{V}} - \frac{k_f n_A n_B}{\bar{V}^2} \left(\frac{\partial \bar{V}}{\partial n_A} \right) + \frac{k_b n_C n_D}{\bar{V}^2} \left(\frac{\partial \bar{V}}{\partial n_A} \right) \quad (4.57)$$

Since

$$\bar{V} = \frac{F}{\rho_m} = \frac{F}{n_{tot}} \sum_i \frac{n_i}{\rho_i} \quad (4.58)$$

Differentiating with respect to n_i ,

$$\begin{aligned} \frac{\partial \bar{V}}{\partial n_i} &= \frac{F}{n_{tot} \rho_i} - \frac{F}{n_{tot}^2} \sum_i (n_i / \rho_i) \frac{\partial (n_{tot})}{\partial n_i} \\ &= \frac{F}{n_{tot}} \left(\frac{1}{\rho_i} - \frac{1}{\rho_m} \right) \end{aligned}$$

Substituting into (4.57) and noting that $n_i = x_i n_{tot}$,

$$\begin{aligned} \frac{\partial \epsilon}{\partial n_A} &= \frac{\rho_m}{F} \left[k_f n_B - \frac{k_f n_A n_B \rho_m}{n_{tot} \rho_A} + \frac{k_f n_A n_B}{n_{tot}} + \frac{k_b n_C n_D \rho_m}{n_{tot} \rho_A} - \frac{k_b n_C n_D}{n_{tot}} \right] \\ &= \frac{\rho_m n_{tot}}{F} \left[k_f x_B - \frac{k_f x_A x_B \rho_m}{\rho_A} + k_f x_A x_B + k_b x_C x_D \frac{\rho_m}{\rho_A} - k_b x_C x_D \right] \\ &= k_f x_B \rho_m \left[1 - \frac{x_A \rho_m}{\rho_A} + x_A \right] \theta + k_b x_C x_D \rho_m \left[\frac{\rho_m}{\rho_A} - 1 \right] \theta \end{aligned} \quad (4.59)$$

By similar analysis, differentiating equation 4.56 with respect to the other components give the following expressions;

$$\frac{\partial \epsilon}{\partial n_B} = k_f x_A \rho_m \left[1 - \frac{x_B \rho_m}{\rho_B} + x_B \right] \theta + k_b x_C x_D \rho_m \left[\frac{\rho_m}{\rho_B} - 1 \right] \theta \quad (4.60)$$

$$\frac{\partial \epsilon}{\partial n_C} = -k_f x_A x_B \rho_m \left[\frac{\rho_m}{\rho_C} - 1 \right] \theta - k_b x_D \rho_m \left[1 - \frac{x_C \rho_m}{\rho_C} + x_C \right] \theta \quad (4.61)$$

$$\frac{\partial \epsilon}{\partial n_D} = -k_f x_A x_B \rho_m \left[\frac{\rho_m}{\rho_D} - 1 \right] \theta - k_b x_C \rho_m \left[1 - \frac{x_D \rho_m}{\rho_D} + x_D \right] \theta \quad (4.62)$$

4.8.2 Simulation Study

For verification of thermodynamic property models and analysis of driving force constraints, an ethyl acetate reactive column is simulated with a tray-by-tray model. The features of the model are typical, i.e.

1. The liquid and vapour leaving each tray are assumed to be at physical equilibrium
2. Reaction is assumed to take place only in the liquid holdup of the tray
3. The condenser is a total condenser
4. Partial reboiler, with reaction
5. No pressure drop in column

Specifications utilised are given in Table 4.14, (similar to that of Chang and Seader (1988), Suzuki *et al.* (1971) and Izarraraz *et al.* (1980)) and the model is solved using the solver CONOPT in GAMS (Brooke *et al.*, 1988).

The simulation gives a vapour distillate product of 45.22% ethyl acetate (or 39.05% liquid distillate), comparable to that obtained by Bock *et al.* (1997) (45.27%) and Izarraraz *et al.* (1980) (46.29%). The composition, temperature, reaction extent and flowrate profiles obtained are shown in Figures 4.13 and 4.14. Figure 4.14 compares some profiles to those reported by Chang and Seader (1988), and as can be seen, they deviate slightly. These differences are attributed to differences in enthalpy and density correlations; the two simulations use the same vapour-liquid equilibrium models and reaction rate expression. The composition profiles also deviate slightly to those obtained by Suzuki *et al.* (1971) who only considered the forward rate in his reaction kinetics. In addition, the simulation model does not account for reaction in the condenser (assumes negligible holdup), and considers a liquid distillate as opposed to vapour distillate.

As shown in Figure 4.13, most of the reaction occurs in the bottom of the column. In trays 8-13 negligible reaction occurs and the primary operation is the separation between ethyl acetate and ethanol, with overall transfer of ethanol from the vapour to the liquid $G_1 \leq 0$ and from the liquid to the vapour for ethyl acetate. Trays 5-8 are operating at chemical equilibrium, with constant composition profiles for all the components indicating equal rates of generation and consumption. Below tray 5 there is complex interaction between ethanol and acetic acid, which are being consumed by reaction and simultaneously separated. The unreacted acid is transferred to the liquid whilst the more volatile ethanol is shifted upwards $G_1 \geq 0$. The driving force constraints for this system are consistent with the equilibrium model, where in a liquid-vapour module is

$$G_1 * G_2 \geq 0$$

where

$$G_{1i} = F_{in}^L x_{in,i}^L - F_{out}^L x_{out,i}^L$$

<u>Simulation Specifications</u>		
No of theoretical trays	13	
Column Pressure	1 atm	
Reflux Ratio	10	
Feed Conditions		
Flowrate	48.798 kmol/hr	
Temperature	365.529 K	(calculated bubble point)
$X_{Acetic\ Acid}$	0.4963	
$X_{Ethanol}$	0.4808	
X_{Water}	0.0229	
$X_{Ethyl\ Acetate}$	0.0000	
Liquid Distillate	9.433 kmol/hr	
Holdup Volumes	2.268 m ³	for trays
	7.560 m ³	for reboiler

Table 4.14: Ethyl acetate production : Simulation specifications

$$G_{2i} = \ln \left(\frac{\gamma_i^L x_i^L P_i^{sat,L}}{x_i^V P_{tot}} \right) + \sum_j \left[\frac{\nu_j \Delta G_j^f}{RT} + \nu_j \ln(x_j^V P_{tot}) \right] \frac{\partial \epsilon}{\partial n_i^L}$$

and $\partial \epsilon / \partial n_i^L$ is given by (4.59) - (4.62).

$G_1 * G_2$ is calculated for the simulated column at the liquid outlet of each equilibrium tray (tray numbers are 1 for reboiler, 13 for condenser). As shown in 4.15, $G_1 * G_2 \geq 0$ holds on all the trays, indicating a consistency of the constraints.

4.8.3 Synthesis Problem

We consider the synthesis task for the production of ethyl acetate, given as raw materials acetic acid and ethanol. A production rate of 2.52 kmol/h of a liquid stream 95% rich in ethyl acetate is desired, and the synthesis task is studied on the basis of minimum operating cost calculated as

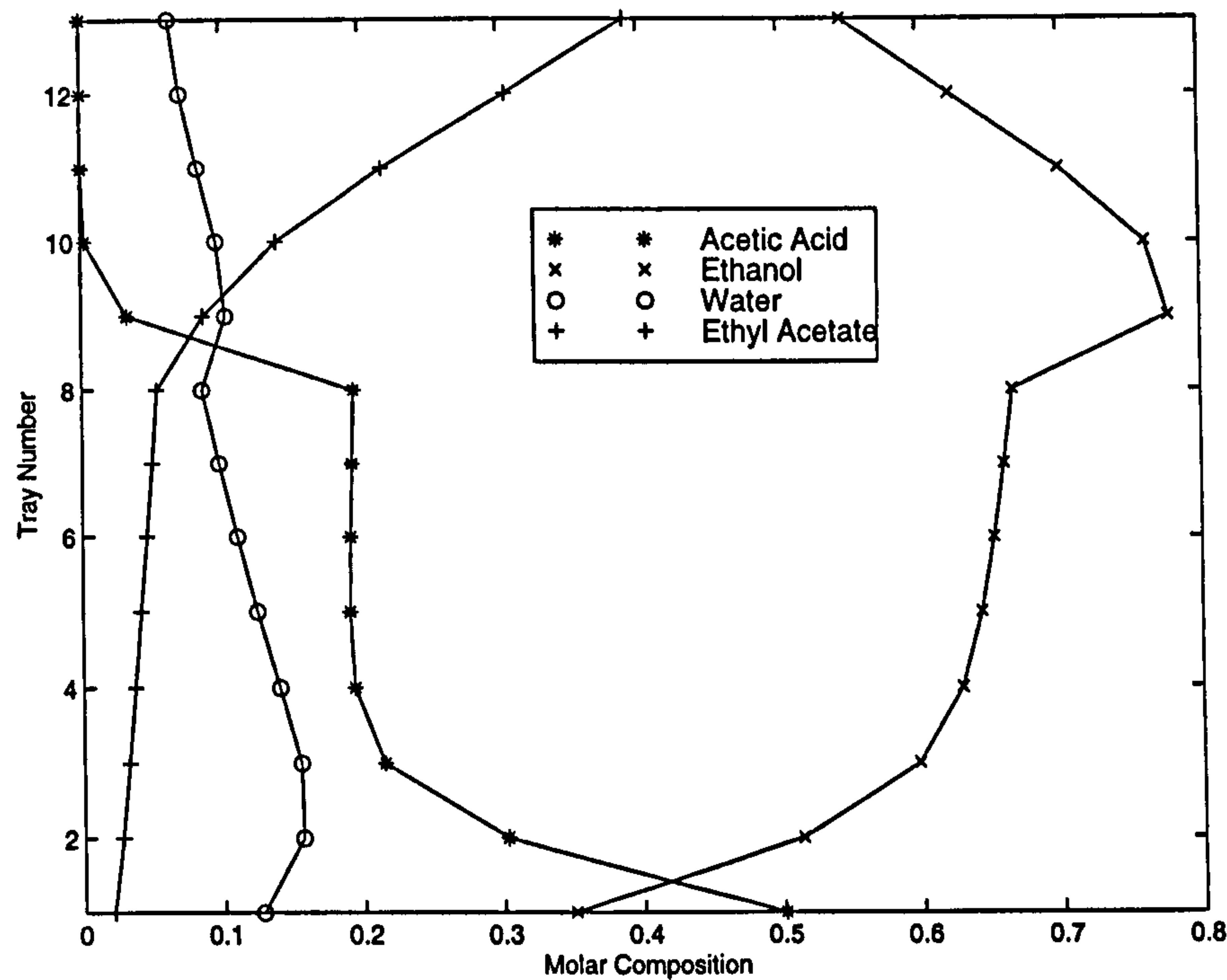


Figure 4.13: Ethyl acetate simulation : composition profiles

$$OpCost = 72.75 \sum Q_{cool} + 381.31 \sum Q_{heat} + 388510F_{feed,acid} + 214182F_{feed,etoh}$$

where Q_{cool} and Q_{heat} are the cooling and heating duties respectively in kJ/h . Five liquid-liquid mass/heat exchangers and 20 liquid-vapour mass/heat exchangers are considered (10 pure separation and 10 with combined separation/reaction). A maximum total holdup of 50 m^3 and a maximum sulphuric concentration of 2% in each reactive module is allowed. The synthesis model features 4587 continuous variables, and 4782 equations for the final Primal and 2580 binary variables and 2914 equations for the Master problem. Minimisation of operating cost results in the configuration shown in Figure 4.15, featuring a double feed reactive-separator and a separator unit represented by 5 liquid-vapour matches with liquid holdups (separation and reaction), 5 liquid-vapour matches with pure separation, 2 coolers with phase change and 2 heaters with phase change. The operating cost of the column is $2.5479 \times 10^6 \text{ USD/yr}$. The acid and ethanol are fed are at a ratio of 7.12 into the first set of modules where most of the catalysed reaction occurs in the modules between the two reactant feeds. These modules feature a high liquid holdup (total of 49.9 m^3) and 0.4 to 0.6 % catalyst concentration, with a total extent of 2.49 kmol/hr and 99.8% conversion of ethanol. The top module has no reaction occurring within it

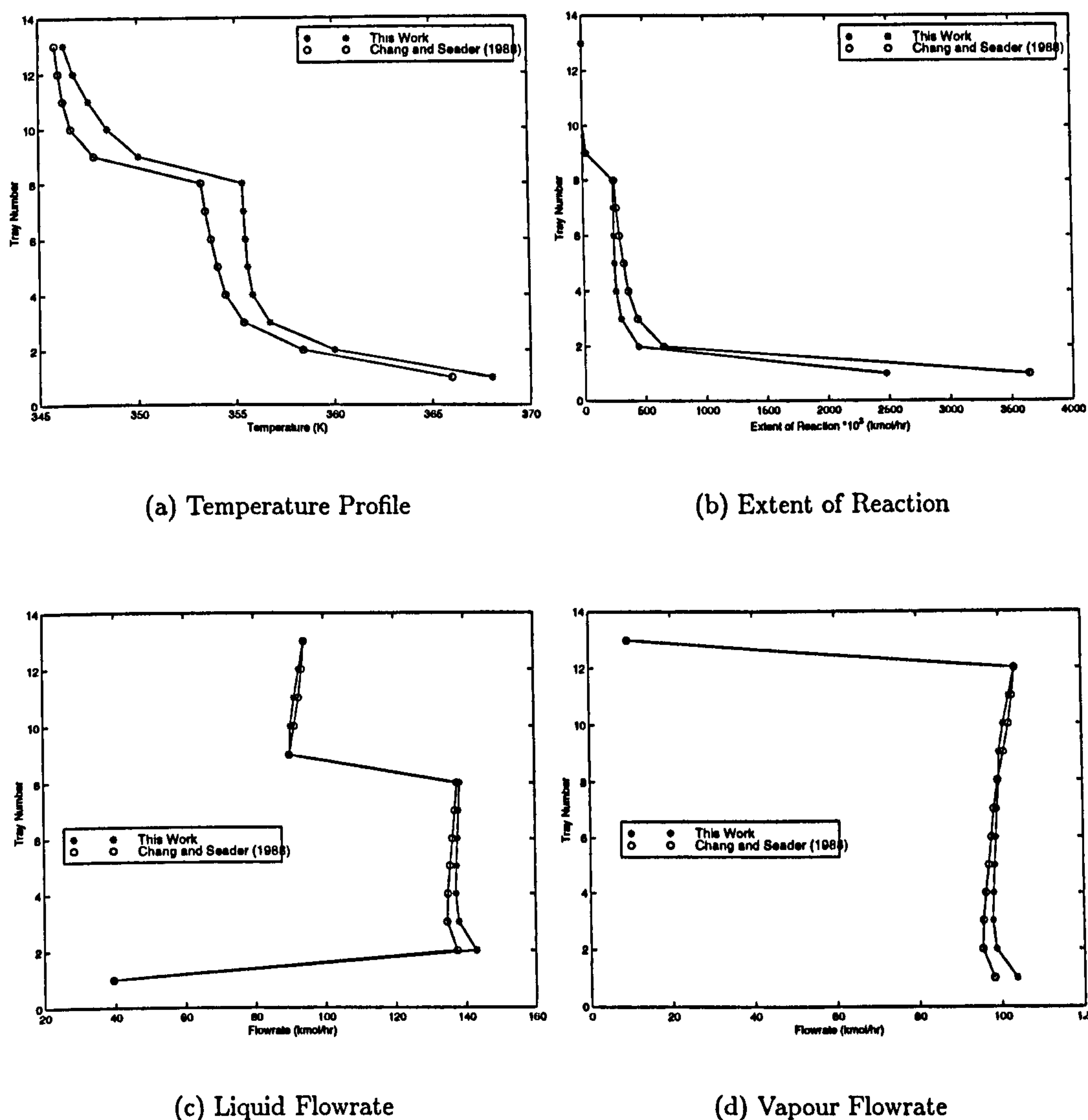


Figure 4.14: Ethyl acetate simulation : comparison of composition profiles with Chang and Seader (1988)

and acts as a rectifying section, purifying the ethyl acetate to the desired composition. A reflux of 14.3 is featured. The stream leaving the 1st module consists mostly of unreacted acetic acid and water product, with traces of ethanol and ethyl acetate, and is fed to the pure separator. This unit acts to recover 93% of the acetic acid and recycles it to the reactive-separator, whilst the rest is lost to the second product due to separation constraints. This recycle results in a low fresh feed ratio of 1.34 of the more expensive acetic acid to ethanol. Note that due to the nonconvexities in this model, this solution is likely to be locally optimal.

To illustrate the ability of the framework to identify process alternatives, two intermediate solutions obtained featuring higher operating costs are shown in Figure 4.16

Tray Number	Acetic Acid	Ethanol	Water	Ethyl Acetate
2	15.20407	1.33439	-0.00942	0.13552
3	2.17221	0.15090	0.21504	0.09679
4	0.09461	0.01632	0.25751	0.07819
5	-0.01335	-0.00143	0.23083	0.06567
6	-0.01366	-0.00512	0.20888	0.05375
7	-0.01255	-0.00604	0.19874	0.04077
8	1.05317	0.11381	0.34222	0.02756
9	7.22828	0.03171	0.03017	1.67559
10	0.60344	0.36214	0.14203	2.49900
11	0.04126	0.66781	0.14972	2.59725
12	0.00797	0.76889	0.06836	1.84868

Table 4.15: Product $G1 * G2$ for Simulation

and Figure 4.17. Alternative A in Figure 4.16 consists of similar modules to the optimal solution, but here an excess of ethanol is fed into the reactive-separator. Again, most of the reaction occurs in the middle and bottom section of the unit, but due to the excess of ethanol, the stream leaving the top module is consists of a mixture of ethyl acetate and ethanol, and is fed to a separator unit. An interesting feature of this system is that acetic acid also acts as an entrainer and is fed to the top of the separation unit. In this set of modules, the binary azeotrope is broken to give an ethyl acetate product of required specification, and the bottom stream is recycled to the first unit. This configuration has a higher operating cost of 2.7633×10^6 due to higher duties in the extraction column.

Alternative (B) in Figure 4.17 shows the conventional alternative for the esterification process, featuring a series of reactors (liquid-liquid matches) with intercoolers, followed by a number of separator units. The feed flowrates are higher than in the optimal solution and alternative (A), with excess acetic acid required to drive the reaction forwards in the reactors. This contributes to a significantly higher operating cost of 5.501×10^6 USD/yr for this configuration. The exit stream of the reactors consists of all the system components, which must then be separated to give pure ethyl acetate. Due to the azeotropes that exist in the system, a large number of separators, some azeotropic columns, are required. This complication is lifted in the reactive-separators where some of the azeotropes are reacted away.

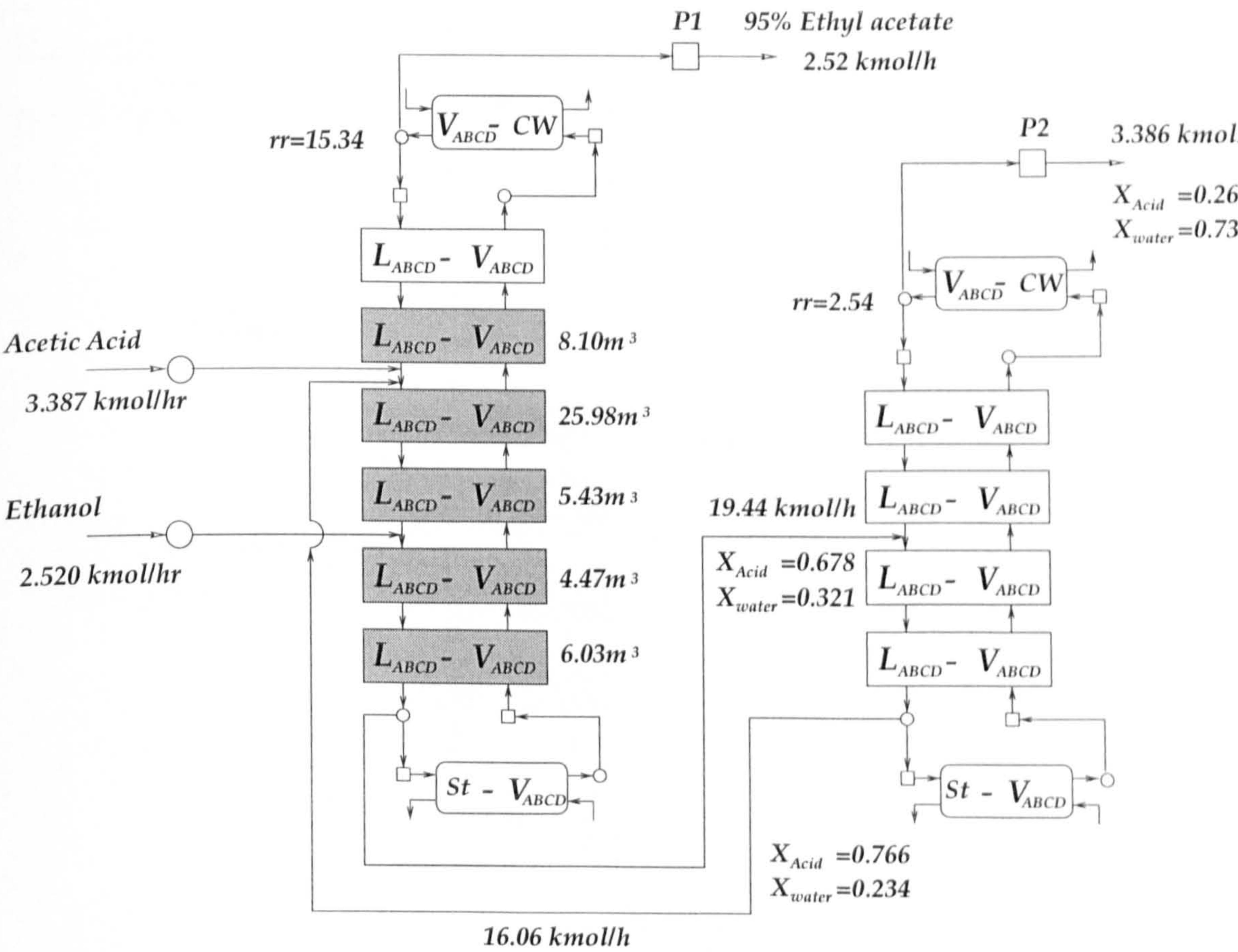


Figure 4.15: Ethyl acetate production : Optimal solution

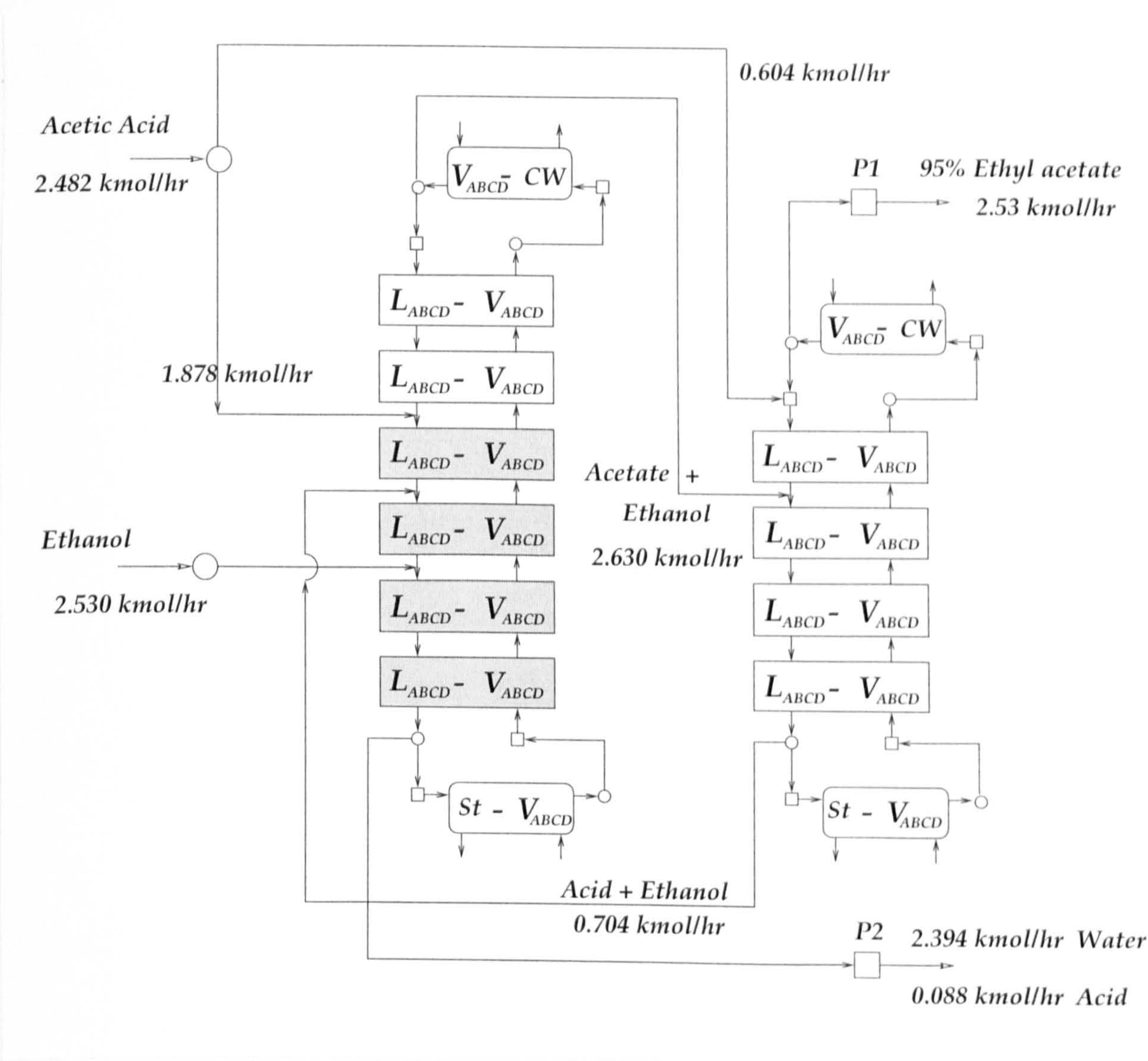


Figure 4.16: Ethyl acetate production : Alternative A

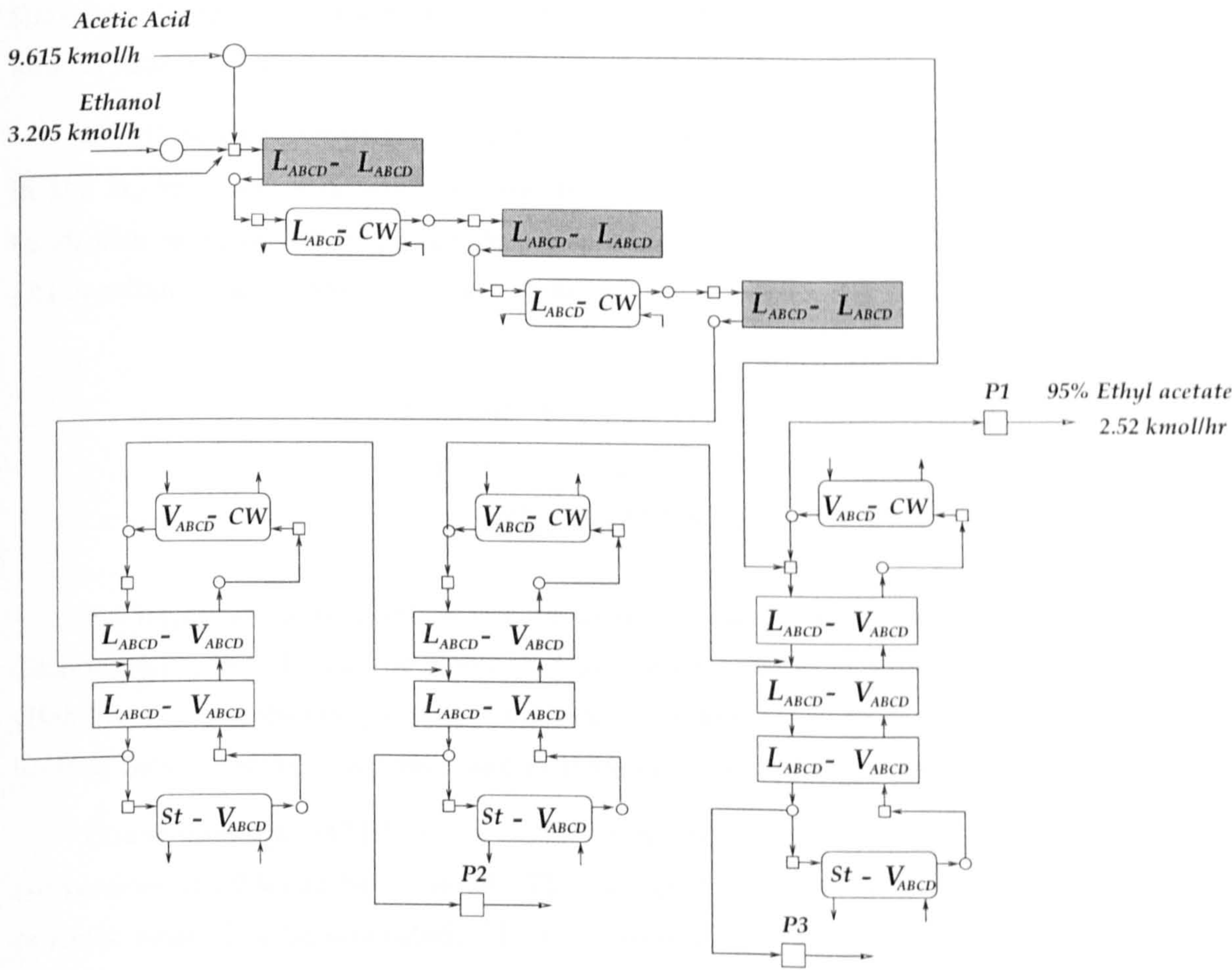
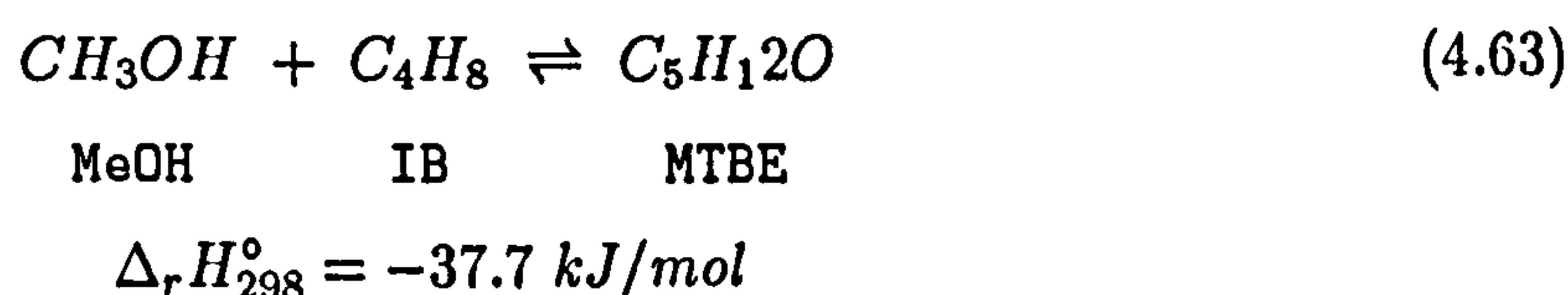


Figure 4.17: Ethyl acetate production : Conventional Alternative B

4.9 Production of MTBE

Exhibiting a high octane number, Methyl tert-butyl ether (MTBE) is an octane oxygenate and enhancer with clean burning properties. Due to these desirable properties and its compatibility with the existing gasoline distribution systems in the 1980s, its use to replace tetra ethyl lead (TEL) as an octane blending agent in gasoline made it the fastest growing chemical (Ainsworth, 1991). The increasing awareness of the risks in rising toxic emission levels and the tightening environmental regulations concerning gasoline composition continue to influence the production rate of MTBE, which has been steadily growing at an annual rate of 10-20 %.

MTBE is produced by the catalytic reaction of isobutene (*IB*) and methanol (*MeOH*) in the liquid phase with temperatures in the range of 40 to 100°C and pressures of 6.5 to 20 atm using an ion exchange resin (Rehfinger and Hoffmann, 1990) or sulphuric acid (Al-Jarallah *et al.*, 1988). The reaction scheme is



An important side reaction occurs when the isobutylene reacts with itself to form diisobutylene, but this can be eliminated by the selection of appropriate catalyst particles (Rehfinger and Hoffmann, 1990). As a result, the MTBE reaction was assumed not to be limited by intraparticle diffusion and is therefore kinetically controlled.

Conventionally, MTBE is produced in a packed bed reactor whereby single pass conversions of 90% can be achieved. The exit mixture of unreacted reactants, inerts and product must then be separated. The non-reactive mixture of methanol, isobutylene and MTBE is highly nonideal, exhibiting two binary minimum boiling azeotropes: one between methanol and isobutylene, one between methanol and MTBE. The separation task is thus nontrivial, requiring a number of distillation columns and separators.

Commercially, reactive distillation is an economically attractive method with which to produce MTBE, enabling high isobutylene conversion and high purity MTBE to be produced in a single unit. At chemical equilibrium, the reactive mixture exhibits no azeotropes due to the elimination of the distillation boundaries by reaction (Barbosa and Doherty, 1988*d*). This is due to the simultaneous decomposition of MTBE to methanol and isobutylene and conversion of methanol and isobutylene to MTBE, thereby not allowing

a binary mixture of MeOH-MTBE or MeOH-IB to exist. Therefore reaction equilibrium can be reached and azeotropes avoided.

An immense volume of literature is available on the production of MTBE by reactive distillation, with analysis and simulation studies providing insight into the process. Due to the nonlinear and complex nature of the system, multiple steady states are known to exist (Jacobs and Krishna, 1993; Nijhuis *et al.*, 1993; Hauan *et al.*, 1995), whereby more than one value of isobutylene conversion to MTBE may exist for a particular methanol feed stage location. Factors affecting the existence of multiple steady states include the concentration of inerts in the isobutylene feed, which is directly proportional to the attainable isobutylene conversion, and the methanol to isobutylene feed ratio which is shown to be the main factor (Eldarsi and Douglas, 1998a).

Reaction Kinetics

Several kinetic expressions have been proposed for the description of the MTBE reaction (4.63). In terms of component concentrations, Ancillotti *et al.* (1977), Gicquel and Torck (1983) and Al-Jarallah *et al.* (1988) developed rate expressions for the liquid phase reaction over catalyst Amberlyst 15. However, the reaction mixture is a strongly nonideal liquid due to the polarity of methanol, and therefore rate expressions in terms of component *activities* are preferred over those based on component concentrations or molar fractions. For the sulphuric catalysed reaction, Venimadhavan *et al.* (1994) obtained a kinetic model in terms of activities, utilising the Wilson equation to calculate the activity coefficients. Considering the ion exchange resin catalysed reaction (Amberlyst 15), this work utilises the intrinsic rate of MTBE formation as determined by Rehfinger and Hoffmann (1990), whereby

$$r = k \left[\frac{a_{IB}}{a_{MeOH}} - \frac{1}{Ka} \frac{a_{MTBE}}{a_{MeOH}^2} \right] \quad (4.64)$$

The reaction rate is related to the number of acid groups, such that r denotes rate per unit mass of dry catalyst resin.

The reaction equilibrium constant Ka is directly proportional to an attainable conversion of reactant components and increases exponentially with decreasing temperature, as expected for an exothermic reaction (see Figure 4.5). The expression proposed by Colombo *et al.* (1983) is utilised

$$\ln Ka = -112.3 + \frac{6314.89}{T} + 19.34 \ln T - 0.0451T \quad (4.65)$$

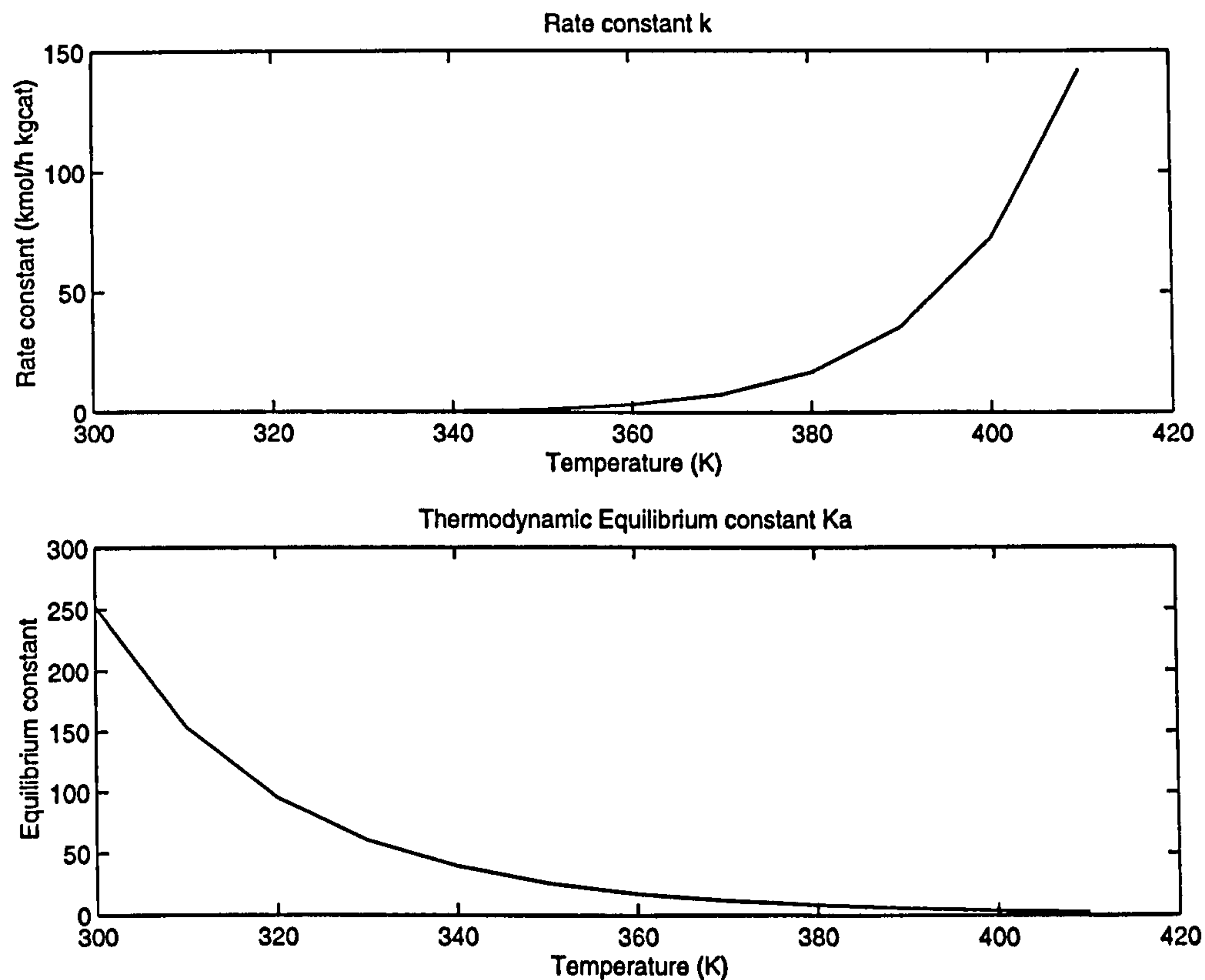


Figure 4.18: Reaction rate constant and thermodynamic equilibrium constant as function of temperature of MTBE reaction

The reaction rate constant k is much less temperature dependent (see Figure 4.5), and is given by

$$k = 8.3939 * 10^{13} \exp \left[\frac{-11112.85}{T} \right] \quad (\text{kmol/hr kgcat}) \quad (4.66)$$

The UNIQUAC equation is utilised to calculate the liquid activity coefficients, as given in Table 4.16 with the Antoine coefficients.

4.9.1 Derivation of $\partial \epsilon / \partial n_i^L$

The extent of reaction for this system is given by

$$\epsilon = r * \theta * M_{cat} \quad (4.67)$$

where M_{cat} is the mass of catalyst on a dry basis. Substituting for the rate (4.64) and residence time (4.45) (dropping the superscript L),

	C1	C2	C3	ΔG^f kJ/kmol
Meoh	23.49989	3643.31362	-33.434	-1.6242x10 ⁵
IB4	20.64556	2125.74886	-33.16	5.8074 x10 ⁴
NB4	20.64917	2132.42000	-33.15	-1.6560x10 ⁴
MTBE	20.71616	2571.5846	-48.406	-1.2544x10 ⁵

$$\ln P^{sat} = C1 - \frac{C2}{C3 + T} \quad (Pa, K)$$

Uniquac equation

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r$$
$$\ln \gamma_i^r = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_k \left(\frac{\theta_k \tau_{ik}}{\sum_j \theta_j \tau_{jk}} \right) \right]$$
$$\ln \gamma_i^c = 1 - J_i + \ln J_i - 5q_i \left[1 - \frac{J_i}{L_i} + \ln \left(\frac{J_i}{L_i} \right) \right]$$
$$J_i = \frac{r_i}{\sum_j r_j x_j} \qquad L_i = \frac{q_i}{\sum_j q_j x_j}$$
$$\tau_{ji} = \exp \left(\frac{-Int_{ji}}{RT} \right) \qquad \tau_{ii} = 1$$

Binary Interaction Parameters		Int_{ij} (kcal/kmol)		
	Meoh	IB4	NB4	MTBE
Meoh	0.0	-70.003	-70.003	-174.94
IB4	1403.5	0.0	0.0	103.73
NB4	1403.5	0.0	0.0	103.73
MTBE	931.43	-48.931	-48.931	0.0

Relative molecular volume and surface areas

	Meoh	IB4	NB4	MTBE
r_i	1.4311	2.9195	2.9209	4.0693
q_i	1.432	2.684	2.564	3.556

Table 4.16: MTBE production : Thermodynamic properties

$$\begin{aligned}
 \epsilon &= \left[\frac{\gamma_{IB}x_{IB}}{\gamma_{MeOH}x_{MeOH}} - \frac{1}{Ka} \frac{\gamma_{MTBE}x_{MTBE}}{\gamma_{MeOH}^2x_{MeOH}^2} \right] \frac{n_{tot}}{F} kM_{cat} \\
 &= \left[\frac{\gamma_{IB}n_{IB}n_{tot}}{\gamma_{MeOH}n_{MeOH}} - \frac{1}{Ka} \frac{\gamma_{MTBE}n_{MTBE}n_{tot}^2}{\gamma_{MeOH}^2n_{MeOH}^2} \right] \left(\frac{kM_{cat}}{F} \right) \quad (4.68)
 \end{aligned}$$

To obtain an analytical expression for $\partial\epsilon/\partial n_i$, this expression must be differentiated with respect to each component holdup n_i , keeping all $n_{j \neq i}$, T and P constant. The last bracketed term is constant, and we assume that the contribution of $\partial\gamma_i/\partial n_i \approx 0$ and can be neglected. Differentiating with respect to n_{IB} ,

$$\begin{aligned}
 \frac{\partial\epsilon}{\partial n_{IB}} &= \left[\frac{\gamma_{IB}}{\gamma_{MeOH}n_{MeOH}} \frac{\partial(n_{IB}n_{tot})}{\partial n_{IB}} - \frac{1}{Ka} \frac{\gamma_{MTBE}n_{MTBE}}{\gamma_{MeOH}^2n_{MeOH}^2} \frac{\partial(n_{tot}^2)}{\partial n_{IB}} \right] \left(\frac{kM_{cat}}{F} \right) \\
 &= \left[\frac{\gamma_{IB}}{\gamma_{MeOH}n_{MeOH}} (n_{IB} + n_{tot}) - \frac{1}{Ka} \frac{\gamma_{MTBE}n_{MTBE}}{\gamma_{MeOH}^2n_{MeOH}^2} 2n_{tot} \right] \left(\frac{kM_{cat}}{F} \right) \\
 &= \left[\frac{\gamma_{IB}}{\gamma_{MeOH}x_{MeOH}} + \frac{\gamma_{IB}x_{IB}}{\gamma_{MeOH}x_{MeOH}} - \frac{2}{Ka} \frac{\gamma_{MTBE}x_{MTBE}}{\gamma_{MeOH}^2x_{MeOH}^2} \right] \left(\frac{kM_{cat}}{F} \right) \quad (4.69)
 \end{aligned}$$

Similar treatment for MeOH and MTBE gives the following expressions

$$\frac{\partial\epsilon}{\partial n_{MeOH}} = \left[\frac{\gamma_{IB}x_{IB}}{\gamma_{MeOH}x_{MeOH}^2} (x_{MeOH} - 1) - \frac{2}{Ka} \frac{\gamma_{MTBE}x_{MTBE}}{\gamma_{MeOH}^2x_{MeOH}^3} (x_{MeOH} - 1) \right] \left(\frac{kM_{cat}}{F} \right) \quad (4.70)$$

$$\frac{\partial\epsilon}{\partial n_{MTBE}} = - \left[\frac{1}{Ka} \frac{\gamma_{MTBE}}{\gamma_{MeOH}^2x_{MeOH}^2} (2x_{MTBE} + 1) \right] \left(\frac{kM_{cat}}{F} \right) \quad (4.71)$$

For the inert component n-butene, $\partial\epsilon/\partial n_{NB4}^L = 0$.

4.9.2 Simulation Study

The simulation of a set of equilibrium trays in the reactive zone of a reactive distillation is considered, with fixed liquid inlet to the top tray and vapour inlet to the bottom tray. The inlet conditions, given in Table 4.17, are based upon the reproduction of the simulation results of Jacobs and Krishna (1993) for the production of MTBE by catalytic distillation in the simulator ASPEN PLUS (Venkataraman *et al.*, 1990). The composition profiles obtained are shown in Figure 4.19, highlighting some of the peculiarities which make reactive distillation feasible for MTBE production. On all the trays MTBE is generated

	Liquid Inlet	Vapour Inlet
Temperature (K)	348.790	355.413
Flowrate (kmol/h)	9611.644	9865.512
X_{MeOH}	0.02262	0.04434
X_{IB}	0.00184	0.04074
X_{NB4}	0.97344	0.86971
X_{MTBE}	0.00209	0.04521
Pressure	11 atm	
Catalyst mass	300 kg per tray	

Table 4.17: MTBE simulation : Liquid and vapour inlet specifications

by reaction (4.63) giving a total generation of 111.78 $kmol/h$, with the reaction rate increasing down the trays with the temperature (Figure 4.20). In terms of boiling point, the order of volatility of the pure components are (from lightest to heaviest) $IB(+NB4) > MTBE > MeOH$, thus one would expect $MeOH$ to be shifted towards the bottom tray, and IB towards the top tray. As shown in Figure 4.19, the composition profile of the unreacted methanol initially decreases, then increases up the trays, featuring a switch in its mass transfer direction. This is due to the existence of the minimum boiling non-reactive binary azeotrope between the inert n-butene and methanol, which tends to shift the methanol up the trays. In a complete column, this would eventually result in the heaviest component featuring in the distillate. The other minimum boiling azeotrope between methanol and MTBE also aids the upward movement of methanol in the column, resulting in more methanol being reacted away, and resulting in the MTBE composition profile to increase down the trays. The composition profile of isobutene decreases up the trays as it becomes depleted through reaction, whilst that of the inert increases due to its high volatility. Although affecting the behaviour of the system, the non-reactive azeotropes are ‘reacted’ away and do not appear.

The driving force constraints are evaluated on every tray and as shown in Table 4.18, they are consistent with the equilibrium model with $G1 * G2 \geq 0$, able to capture the complex effects between separation and reaction.

Tray Number	Methanol	Isobutene	n-butene	MTBE
1	73.97371681	312.62260194	43.90351270	1232.90237762
2	110.53589518	283.19826454	8.02517744	361.06933612
3	4.40159917	229.07033453	1.94048716	149.99958523
4	69.12648927	177.61180879	0.42641232	73.55549641
5	60.49890977	146.74944437	0.04870678	33.38083490

Table 4.18: MTBE simulation : value of $G1 * G2$

4.9.3 Synthesis Problem

The synthesis task for the production of 197 mol/s of at least 98% pure liquid MTBE is considered, with ion exchange resin Amberlyst 15 is available as catalyst. Raw materials are a pure liquid methanol at 320K, and a vapour isobutylene feed consisting of isobutylene $x_{IB} = 0.3558$ and n-butene inert $x_{NB4} = 0.6442$ at 350K. The feed flowrates are variables to be determined, with the methanol feed constrained to be less than 200 mol/s to avoid multiple steady states. A maximum vapour flowrate of 3000 mol/s around the mass/heat exchangers is enforced to constrain the equipment size (Eldarsi and Douglas, 1998b). A total system pressure of 11 atm is considered. The synthesis task is driven by the minimisation of operating and pseudo-capital cost as in the previous example, where

$$\begin{aligned}
 Cost(\$ / yr) = & \sum C_{cw} * Q_{cool} + \sum C_{steam} * Q_{heat} \\
 & + C_{MeOH} * F_{feed, MeOH} + C_{IB} * F_{feed, IB} \\
 & + \sum y_{L-V} * Cost_{L-V}
 \end{aligned}$$

where $Cost_{L-V}$ is given by (4.33) as a function of vapour flowrate only (Level 1) with $H = 2$. Cost parameters used are given in Table 4.5. A maximum of 10 pure separation and 10 combined separation/reaction liquid-vapour modules are allowed. The mass of catalyst within the module, if it exists, is considered on a dry-weight basis at a maximum mass of 2000 kg per module.

The initial structure is illustrated in Figure 4.21, similar to that shown in literature for the reactive distillation column for the synthesis of MTBE, featuring seven liquid-vapour mass/heat exchangers and two pure heat exchangers. The four modules with simultaneous reaction and separation make up the reactive section with a total of 4000 kg of catalyst. The optimal solution is obtained in two iterations taking 4133 CPU seconds, resulting in the configuration of modules as illustrated in Figure 4.22. The structure features four mass/heat transfer modules and two pure heat exchanger models, in a configuration rep-

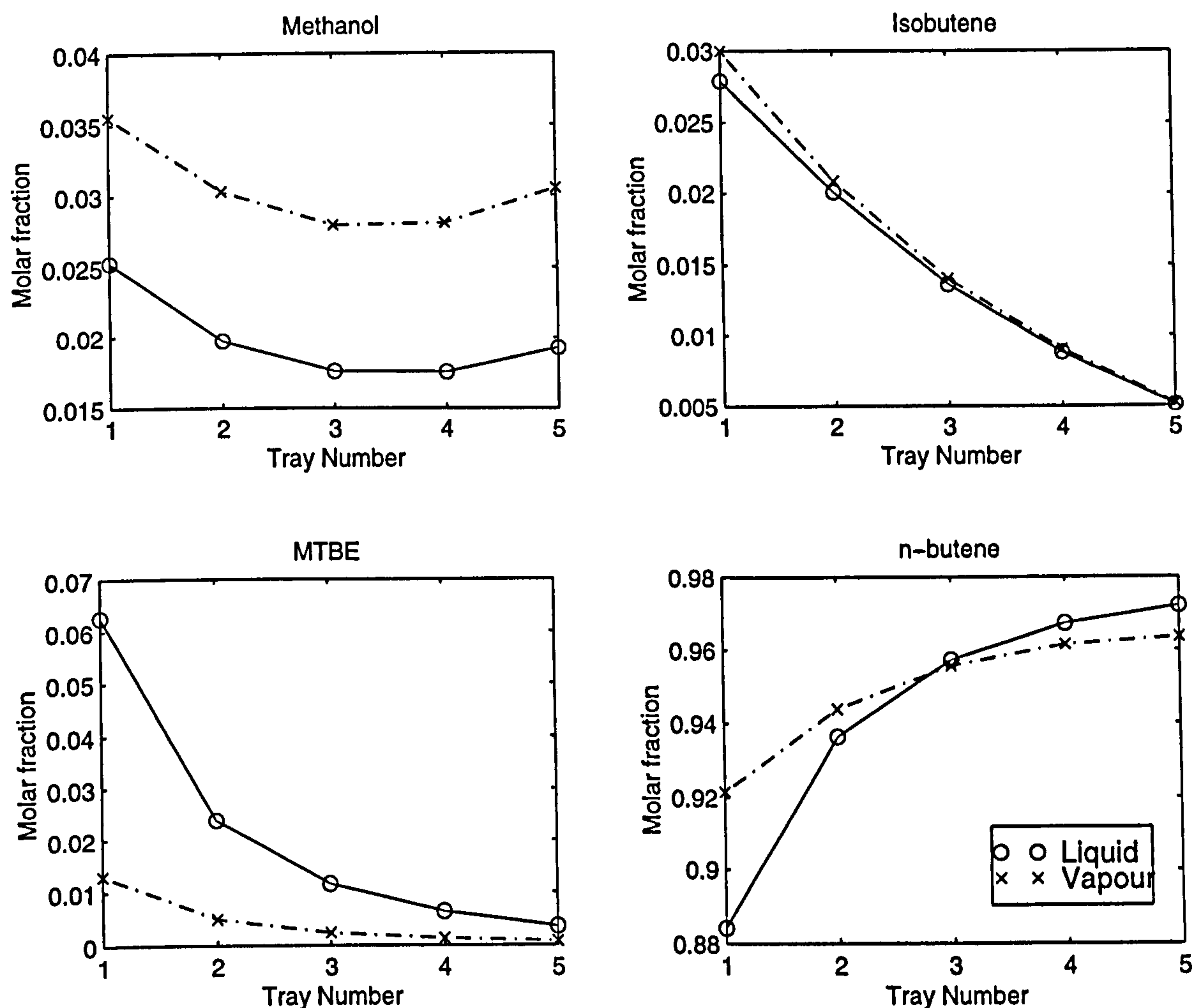


Figure 4.19: MTBE simulation : Composition profiles

representing a reactive separation column. The reactive section is made up of two modules, featuring a total of 3013 kg, whereby 193 mol/s of MTBE is generated. The pure separation module at the bottom of the unit separates the MTBE from the unreacted methanol, which is driven back into the reactive zone. Here MTBE is transferred to the liquid phase, and methanol to the vapour phase. In pure separation module at the top of the unit, the inert 1-butene is transferred to the vapour phase to give pure inert distillate. This solution features a total cost of 1.49609×10^7 USD/yr, corresponding mainly to feed cost of 1.40304×10^7 USD/yr, utility cost of 8.75494×10^5 USD/yr, and module cost of 54949 USD/yr.

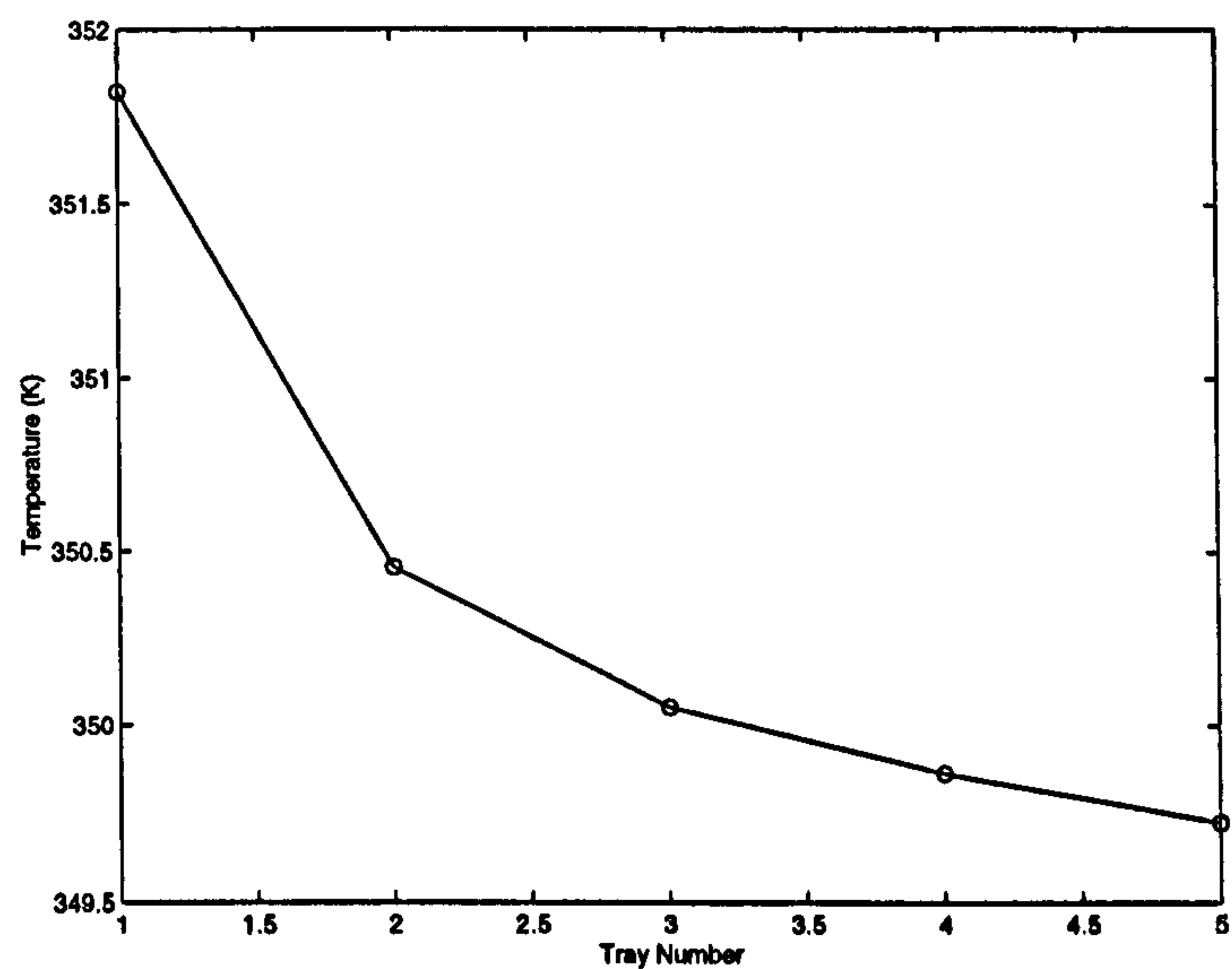


Figure 4.20: MTBE simulation : Temperature profile

4.10 Summary

In this chapter, a mass/heat transfer representation framework has been proposed for the synthesis of separation systems with reactions in the liquid phase. Driving force constraints to describe the mass transfer phenomena in reactive separation systems are shown to be consistent with equilibrium based models utilising reaction kinetics. Furthermore, when no reaction occurs in the liquid phase, the driving force constraints reduce to the form for pure separation. As illustrated with three representative reaction-separation example problems, this synthesis methodology is able to reveal hybrid structures combining reactive separation and pure separation operations without prior definition of units. The model is capable of handling system nonidealities and any number of reactions, given the reaction kinetics are available.

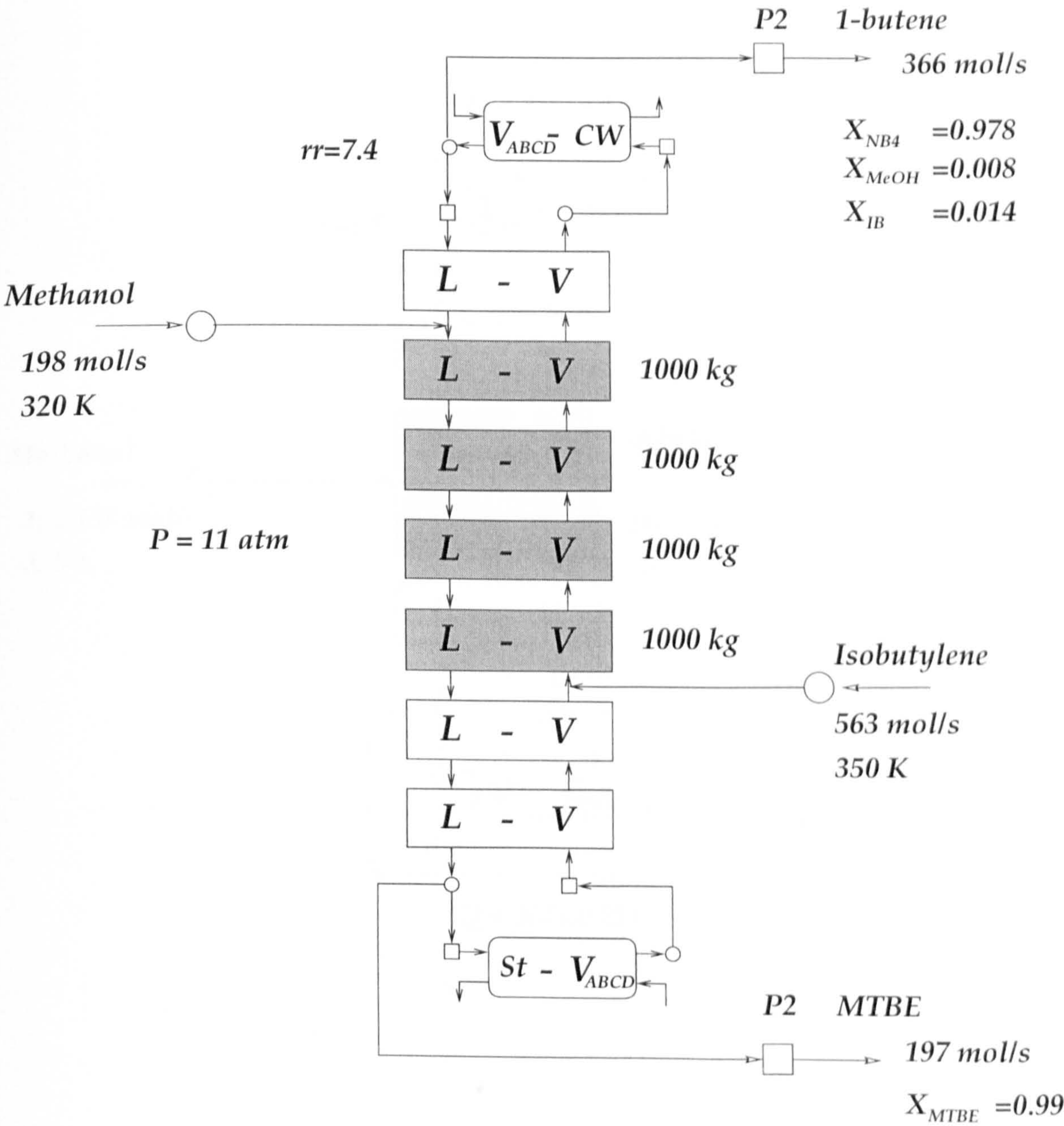


Figure 4.21: Synthesis of MTBE : Initial Structure

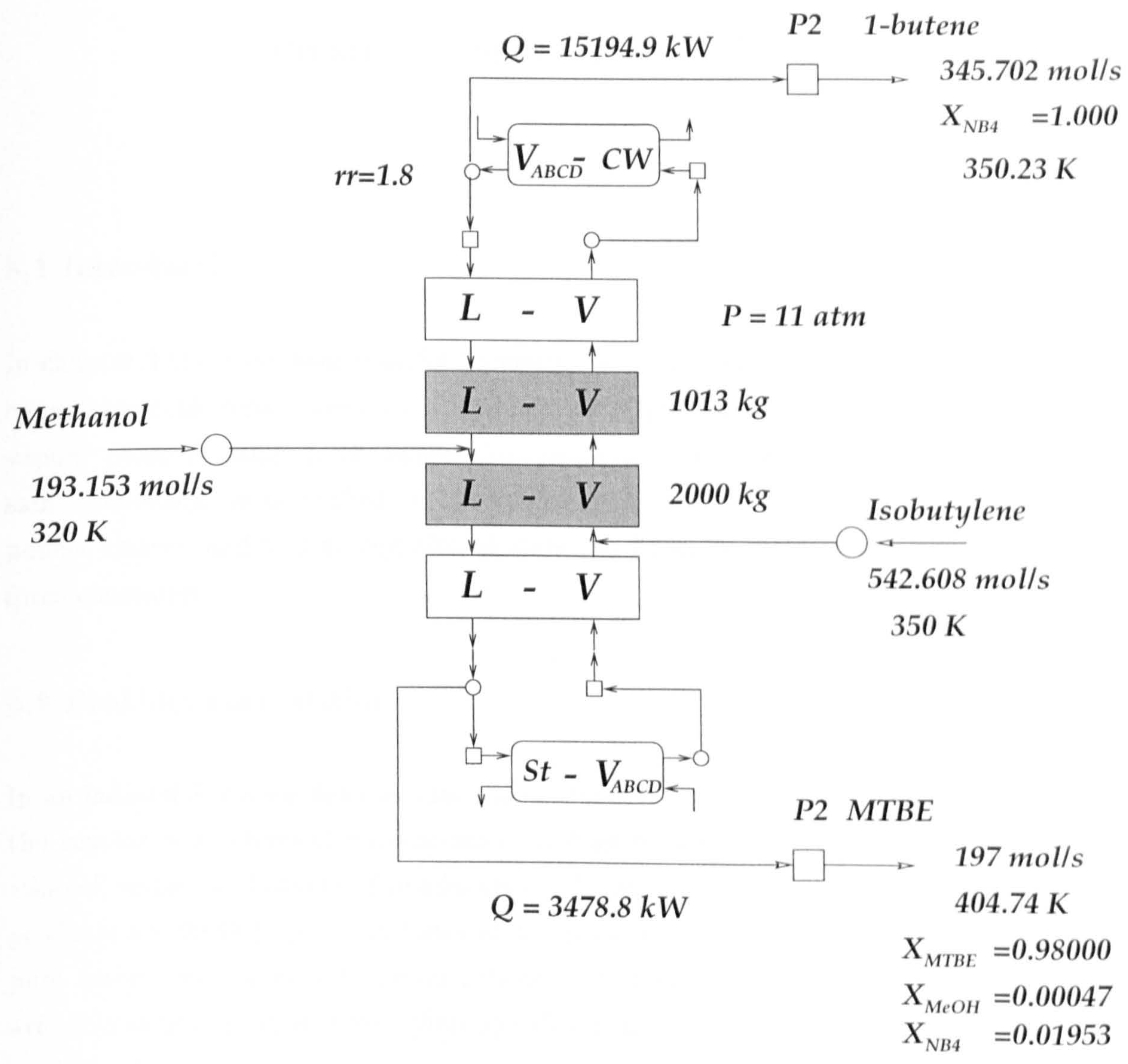


Figure 4.22: Synthesis of MTBE : Optimal configuration

Industrial Applications : Methanol Case Study

5.1 Introduction

In chapter 3 the mass/heat transfer framework is developed for the synthesis of homogeneous azeotropic separations, whereby a number of possible entrainers is given, and ideal vapour phase is assumed. By appropriate adaption, it is shown in this chapter that the same framework can be applied to the separation synthesis of a general nonideal multicomponent system, and that an equation of state can be easily incorporated into the driving force constraint.

5.2 Problem Formulation

In an industrial process flowsheet for the production of methanol, the outlet stream from the reactor is at chemical equilibrium consisting of methanol, carbon dioxide, acetone, ethanol, water and butanol. The mixture conditions is given in Table 5.1, and the desired products are 99.99 % pure methanol at a minimum flowrate of 3125 kmol/h, and 91 % pure carbon dioxide at a minimum rate of 9.399 kmol/h. Steam and cooling water are available as heat utilities. Given these specifications, the synthesis problem is to determine an optimal separation system with respect to energy requirements.

5.3 Thermodynamics

The mixture to be separated is a nonideal system with a number of polar associating components with three homogeneous binary azeotropes possible at 1 atm;

- Water-Ethanol at 351.2 K, 89.7 mol% ethanol

Component	Component flow (<i>kmol/h</i>)	Composition (mol %)
Carbon dioxide (<i>CO</i> ₂)	35.700	0.9052
Acetone (<i>Ace</i>)	0.052	0.0013
Methanol (<i>MeOH</i>)	3155.500	80.0024
Ethanol (<i>EtOH</i>)	1.450	0.0368
Water (<i>H</i> ₂ <i>O</i>)	750.000	19.0270
Butanol (<i>BuOH</i>)	1.079	0.0273
Total flowrate	3943.781 <i>kmol/h</i>	
Temperature	315 K	
Pressure	1 atm	

Table 5.1: Feed Conditions for Methanol Separation

- Water-Acetone at 329.2 K, 98.0 mol% acetone
- Methanol-Acetone at 328.4 K, 78.1 mol% acetone

In addition, a heterogeneous binary azeotrope exists for the water-butanol system at 365.9 K, 23 mol% butanol. Since liquid-liquid phase split cannot be currently handled within this representation, operation at these conditions is avoided, eliminating liquid-liquid extractors and decanters as separation alternatives.

In addition to the nonidealities in the liquid phase, the behaviour of the mixture is complicated by the presence of gaseous carbon dioxide which is a supercritical compound at normal conditions (298K, 1 atm). The Soave Redlich Kwong (SRK) equation of state (Soave, 1972) is an appropriate thermodynamic model for both phases of this system and is utilised with the MHV2-UNIFAC mixing rule (Dahl *et al.*, 1991).

The SRK equation of state may be written in terms of the compressibility factor as follows

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (5.1)$$

where

$$A = \frac{aP}{R^2T^2} \quad (5.2)$$

$$B = \frac{bP}{RT} \quad (5.3)$$

Given the temperature, pressure and composition of a stream, the compressibility factors for the liquid and vapour phase can be algebraically determined and utilised to

calculate the corresponding fugacity coefficients. The cubic equation (5.1) yields three roots, where

$$Z_{liq} \leq Z_i \leq Z_{vap}$$

Algebraic expressions for the roots of the cubic are found in Abramowitz and Stegun (1964), and the fugacity coefficient can be expressed in terms of the compressibility factor (Holland, 1981).

The pure component values of a and b can be deduced from the critical properties and the acentric factor;

$$a_i = \frac{0.428R^2T_{ci}^2}{P_{ci}} f(T_{ri}) \quad (5.4)$$

$$b_i = \frac{0.0866RT_{ci}}{P_{ci}} \quad (5.5)$$

where $f(T_{ri})$ is given by (Mathias and Copeman, 1983)

$$\begin{aligned} f(T_{ri}) &= \left[1 + Q_1(1 - \sqrt{T_{ri}}) + Q_2(1 - \sqrt{T_{ri}})^2 + Q_3(1 - \sqrt{T_{ri}})^3 \right]^2 & T_{ri} < 1 \\ &= 1 + Q_1(1 - \sqrt{T_{ri}}) & T_{ri} > 1 \end{aligned} \quad (5.6)$$

The mixture b parameter is derived from a linear mixing rule, whilst a is calculated according to the MHV2-UNIFAC mixing rule. The following equations apply,

$$b = \sum_i^C x_i b_i \quad (5.7)$$

$$a = \alpha b RT \quad (5.8)$$

where

$$q_1 \left(\alpha - \sum_i x_i \alpha_i \right) + q_2 \left(\alpha^2 - \sum_i x_i \alpha_i^2 \right) = \frac{g^E}{RT} + \sum_i x_i \ln \left(\frac{b}{b_i} \right) \quad (5.9)$$

where $q_1 = -0.47832$, $q_2 = -0.00469$. The excess Gibbs energy is calculated from the modified UNIFAC model (Larsen *et al.*, 1987) such that equation (5.9) yields α . The required parameters for the SRK and UNIFAC equations are given in Appendix A.7 along with the pure component parameters.

5.4 The Mass/heat Transfer Framework

To construct a superstructure of alternatives for the separation of methanol, the mass/heat transfer framework applied is similar to that detailed in section 3.7. Operating conditions whereby the components are miscible in all phases is considered, thus mass transfer occurs only between liquid and vapour streams. The building block is thus a liquid-vapour mass transfer module attached to two heat exchangers as described in section 3.4. To describe the mass transfer direction of all system components in the module, the driving force constraints of equations (3.32)-(3.35) are rewritten in terms of fugacity coefficients to give

$$\begin{aligned} \mathcal{G}_{1i} * \mathcal{G}_{2i} &\geq 0 \\ \mathcal{G}_{1i} * \mathcal{G}_{3i} &\geq 0 \end{aligned} \quad (5.10)$$

where

$$\mathcal{G}_{1i} = F^{LI} x_i^{LI} - F^{LO} x_i^{LO} \quad (5.11)$$

$$\mathcal{G}_{2i} = \phi_i^{LI} x_i^{LI} - \phi_i^{VO} x_i^{VO} \quad (5.12)$$

$$\mathcal{G}_{3i} = \phi_i^{LO} x_i^{LO} - \phi_i^{VI} x_i^{VI} \quad (5.13)$$

The phase defining constraints are also written in terms of fugacity coefficients to give

$$\text{For liquid streams} \quad \sum_i \frac{\phi_i^L}{\phi_{L^*}^L} x_i^L \leq 1 \quad (5.14)$$

$$\text{For vapour streams} \quad \sum_i \frac{\phi_i^V}{\phi_{V^*}^V} x_i^V \leq 1 \quad (5.15)$$

where ϕ^{L^*} (ϕ^{V^*}) is calculated at the vapour (liquid) in theoretical equilibrium with the liquid (vapour) stream.

A large difference in water solubility exists between carbon dioxide and the other mixture components, identifying water as a possible solvent. Carbon dioxide can also be utilised as a mass separating agent for the separation of the binary azeotropes in supercritical extraction, but is not considered in the first instance.

The given two phase feed (Table 5.1) is split into a vapour stream consisting only of carbon dioxide, and a liquid stream containing the remaining components. The building blocks of the superstructure include

- ◇ Three initial stream splitters for
 - I1. Liquid multicomponent feed stream (no C_{O2})
 - I2. Vapour feed stream of carbon dioxide
 - I3. Water as a possible solvent
- ◇ Two required product stream mixers for
 - P1. Vapour product of $\geq 91.00\%$ pure carbon dioxide ≥ 9.399 kmol/h
 - P2. Liquid product of $\geq 99.99\%$ pure methanol ≥ 3125 kmol/h
- ◇ A further four possible product stream mixers to account for intermediate streams, allowing for a possible product stream per component (three liquid and one vapour). This number is increased when all these products have an existing stream.
- ◇ A maximum of 10 mass/heat transfer modules, corresponding to 10 mass/heat exchangers and 20 pure heat exchangers. When all 10 modules are chosen, the upper bound of possible modules is increased.

A network is constructed by considering all possible interconnections between the splitters and mixers of the building blocks, noting that only same phases may be mixed. A maximum of five stream splits and five stream mixers are allowed at each splitter and mixer, limiting the resulting piping network.

5.5 The Mass/heat Transfer Model

Binary variables are introduced to denote

- (i) the existence of each mass/heat exchanger
- (ii) the existence of each pure heat exchanger
- (iii) the existence of interconnecting streams between the splitters and mixers

Note that variables (ii) and (iii) are not necessary, and are included to simplify the nonlinear part of the superstructure model and facilitate the introduction of logical constraints. Their presence therefore does not increase the combinatorial complexity of the synthesis problem.

The detailed model is similar to that given in section 3.8, including

- Equalities

- ◇ Total mass balances at all mixers and splitters
- ◇ Component mass balances at all mixers and around the mass/heat exchangers
- ◇ Energy balances at all mixers and around the pure heat and mass/heat exchangers
- ◇ Summation of molar fractions for all inlet and outlet streams of the exchangers and the product streams
- ◇ Enthalpy calculation of each stream as a function of its temperature, pressure and composition.
- ◇ Fugacity calculation of each stream as a function of its temperature, pressure and composition, utilising the SRK model described in section 5.3.

- Continuous variable inequalities

- ◇ Driving force constraints (5.10) - (5.13) at the inlet and outlet of mass/heat exchangers
- ◇ Phase defining constraints for each stream

- Mixed integer inequalities

- ◇ To ensure that mass and energy flows around the exchangers only exist if the exchanger exists
- ◇ To ensure that interconnecting stream flows only exist if the interconnecting stream exists

- Pure integer inequalities

- ◇ To ensure that the heat exchangers only exists if the mass exchanger exists
- ◇ To ensure that the interconnecting streams exist only if the corresponding modules exist
- ◇ To ensure that if an exchanger exists, there exists at least one inlet and one outlet flow
- ◇ To ensure that if an exchanger exists, the number of inlet flows to the mixer and number of outlet flows at the splitter does not exceed a defined maximum number.
- ◇ To ensure at least one feed point for the existing inlet feed mixture $I1$ and $I2$

- ◇ To ensure that both $I1$ and $I2$ enter mixers of the same module
 - ◇ To ensure at least one product source for the two required products $P1$ and $P2$
 - ◇ Non-redundancy constraints since all mass/heat exchange modules are the same.
- Objective Function
- The synthesis problem is driven by the minimisation of a cost function consisting of
- ◇ cost of heat utilities
 - ◇ constant module cost to penalise the number of resulting modules chosen.

Utility cost parameters of 24.5 \$/kWyr for cooling and 146.8 \$/kWyr for heating is utilised. The synthesis problem is a large scale MINLP involving 3483 continuous variables 1038 binary variables (of which only 10 are necessary), and is solved employing Generalized Benders Decomposition (Geoffrion, 1972) through the modelling system GAMS (Brooke *et al.*, 1988).

5.6 Initial Structure

To synthesise feasible flowsheets for the separation of methanol from the mixture, the thermodynamic based methodology as developed by Jaksland (1996) can be employed. Analysis of the mixture reveals that the most important separation is that between the components of greatest composition; carbon dioxide, methanol and water. From heuristics, separation of carbon dioxide is considered first. Based on the large differences in volatility and water solubility between carbon dioxide and the remaining components, flash operation and adsorption with water is identified as feasible separation techniques. Through simulation, a flash unit followed by an adsorption unit is found to be inefficient and instead a distillation unit is chosen (Figure 5.1(a)), followed by mixing with water and a flash unit to further purify the carbon dioxide product. The liquid from the flash consists of methanol and the other alcohols and is recycled to the first column (with a purge). The bottoms from the first column consists of the alcohols and water, and distillation is identified to separate the methanol from the mixture. The feasible flowsheet of Figure 5.1(a) is utilised as the initial structure for optimisation, consisting of 5 mass/heat exchangers and 4 pure heat exchangers as shown in Figure 5.1(b).

5.7 Optimal Solution

Obtained in 3 iterations, the optimal solution consists of 4 mass/heat modules and 4 pure heat exchangers, featuring a total utility cost of 33.017×10^6 \$/yr. The configuration of modules as illustrated in Figure 5.2 represents two separation columns, whereby in modules *MH1* and *MH2* carbon dioxide is separated from the mixture whilst *MH3* and *MH4* performs the main separation between methanol and water. In modules *MH1* – *MH2*, carbon dioxide exists mainly in the vapour phase and is removed between exchangers *MH2* and *C1* to result in a vapour product of 35.99 kmol/h of 99.47 % purity with traces of acetone and methanol. Exceeding the required specification, this results in almost no carbon dioxide in the second separator. In *MH3* and *MH4*, methanol (and acetone) is transferred from the liquid to the vapour stream, whilst water (and the remaining components) are transferred to the liquid stream. The liquid product *P2* consists of high purity methanol at 99.998 % with traces of acetone, ethanol and water, whilst the liquid product *P3* consists mainly of water and the remaining components. In total, only 0.92 % of the methanol is lost through *P2* and *P3*.

This structure is verified as feasible through simulation of two equilibrium distillation columns using the steady state simulator SEPSIM (Perregaard, 1992). For the first column, a reflux ratio of 1.3 is estimated based on the inlet liquid flowrates to *MH2*, whilst for the second column the obtained reflux ratio of 5 was used. Similar distillate purities and flowrates are obtained in two columns consisting of 10 trays and 35 trays, featuring similar reboiler duties as shown in Table 5.2. Differences between the modular and equilibrium model include the following;

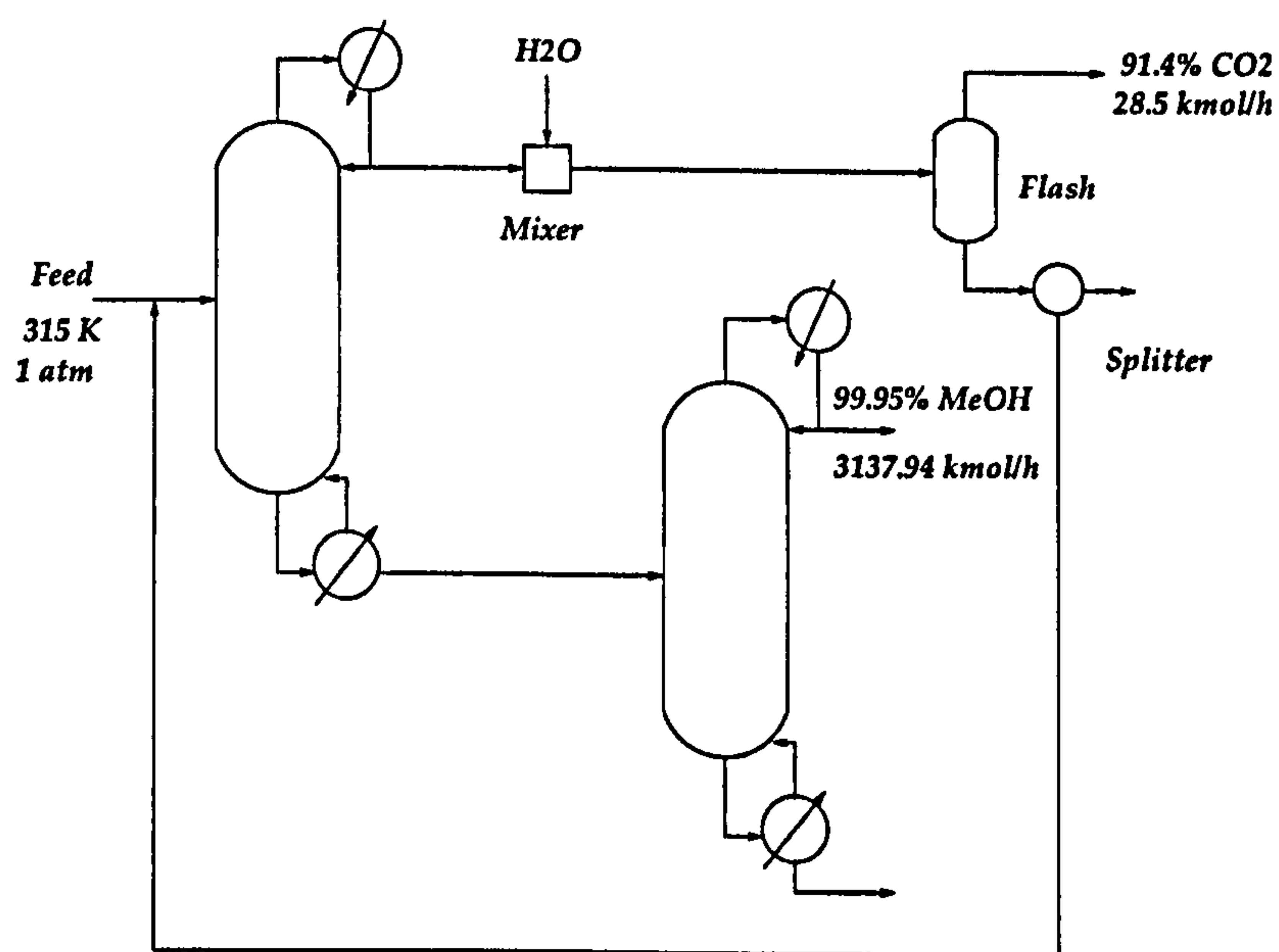
- The molar fraction does not change within the modular heat exchangers.
- Lower flow through the modular heaters as liquid product streams are removed prior it, leading to a lower product temperature than would be obtained in the equilibrium model.
- Lower flow of carbon dioxide through the modular cooler *C1* as the vapour product is removed prior to this unit, leading to lower condenser duties.

	Column 1	Column 2
No Stages	10	35
Feed location	5	18
Reflux ratio	1.3	35
Qheat (kW)	2815.4	177 759.7
Qcool (kW)	595.2	190 586.0
	C1 and H1	C2 and H2
Qheat (kW)	2821.2	191 387.5
Qcool (kW)	319.8	183 655.9

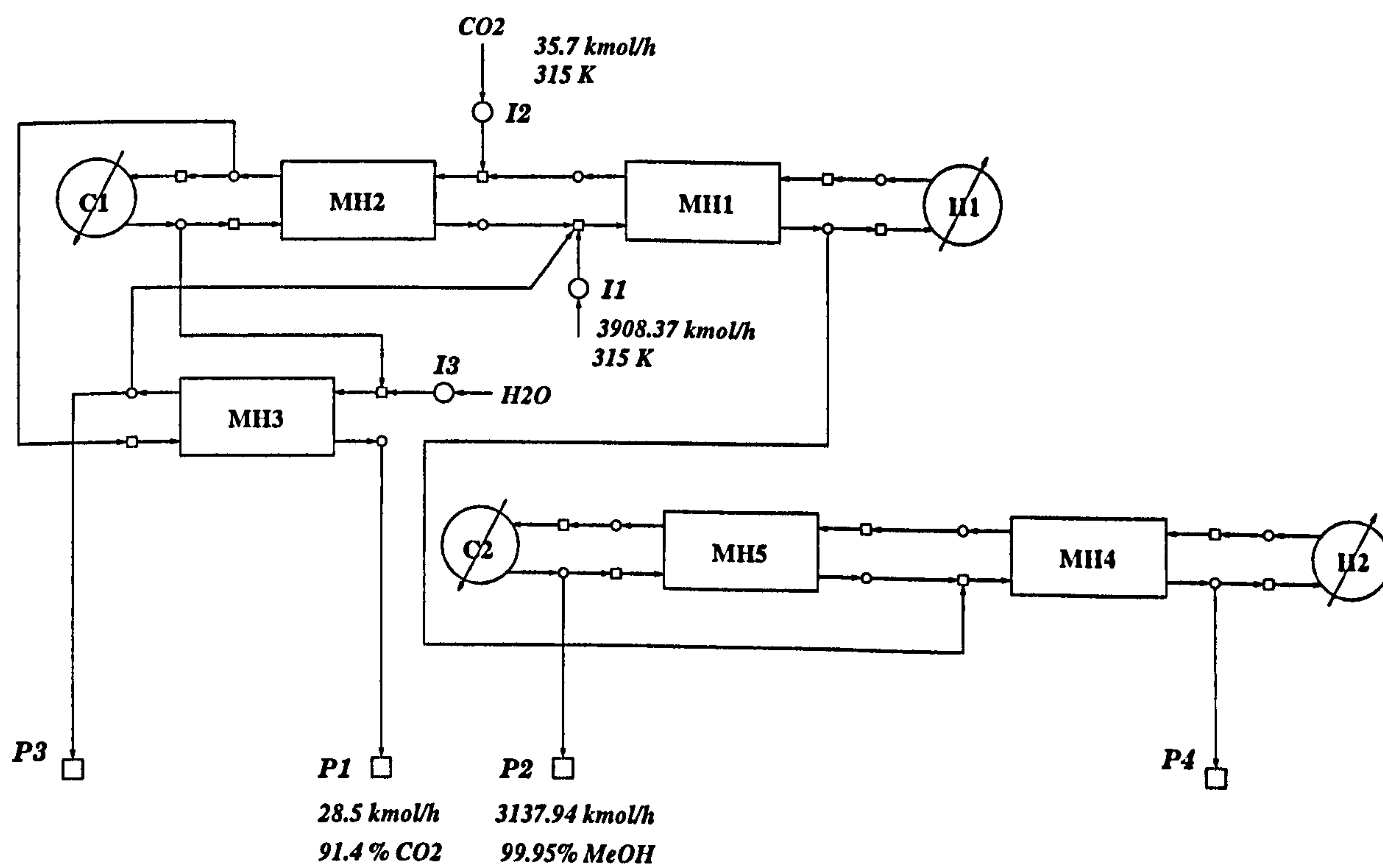
Table 5.2: Simulation results

5.8 Summary

In this chapter we have illustrated that the mass/heat transfer synthesis model can be successfully applied to the separation synthesis of general nonideal multicomponent mixtures. The use of an equation of state can be incorporated within the framework at the cost of increased model complexity for thermodynamic description.



(a)



(b)

Figure 5.1: Methanol Production : Initial Structure

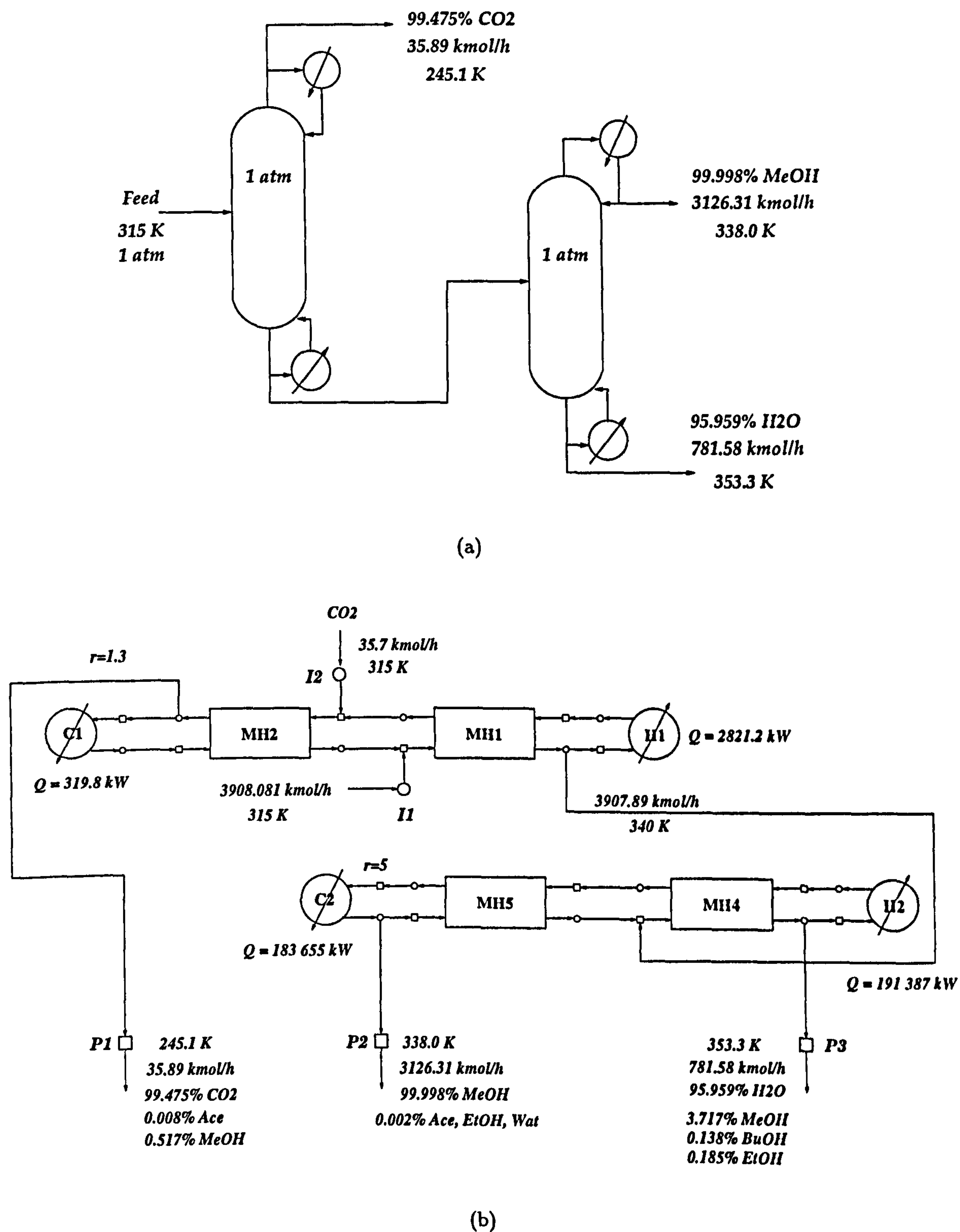


Figure 5.2: Methanol Production : Optimal Structure

Conclusions and Future Directions

6.1 Conclusions

This thesis has presented a mass and heat transfer modular framework for the synthesis of homogeneous azeotropic separation and combined reaction and separation systems. A review of the body of literature for these classes of systems has revealed that the design and synthesis procedures developed are typically case specific, and often of a graphical nature with focus on feasibility. The framework developed in this work is more of a generic nature, extendible to encompass general process synthesis problems and able to capture multifunctional units through optimisation.

The heart of this work is the multipurpose mass and heat transfer module as defined in chapter 2. Utilised as the building block of process alternatives, process units are not prepostulated but are instead investigated as mass and heat transfer between exchanging streams. Given the synthesis task (all possible inputs and desired outputs), and an objective to optimise, the framework can systematically develop a superstructure of mass and heat exchanging streams within which all possible flowsheet structures are embedded. Modelled as a MINLP, the optimal combinations of phenomena are then revealed as a network of mass/heat transfer modules, from which actual unit structures can be derived. The mass and heat transfer phenomena between streams is modelled through the introduction of Gibbs free energy based driving force constraints, laying the foundation for extension to all classes of systems. In a sense, the developed approach is similar to the attainable region approach (Hildebrandt and Glasser, 1990), or phenomena based design approach of Hauan and Lien (1998), whereby combinations of phenomena are determined to meet the objective. However, whilst those approaches provides the targets for process units to meet, this approach generates structural alternatives based on an economic or process objective. Accounting for no a priori knowledge of process units, capital costs are incorporated as a function of module capacity.

For the synthesis of multicomponent azeotropic mixtures, a framework is developed in chapter 3 whereby entrainer and sequencing alternatives are simultaneously explored for a given set of entrainers. Modules corresponding to mass and heat transfer between homogeneous liquid and vapour phases form the basic building block of the superstructure, whereby the limiting driving force constraint for mass transfer between the streams correspond to phase equilibrium. By constraining the mass transfer of *each process component*, it is shown that separation feasibility and its limitations due to the presence of pinch points can be captured within the mass/heat transfer module, similar to simple distillation region line boundaries in residue curve maps. Each module corresponds to a part or whole of a separation unit (*i.e.* such as an aggregate of trays) featuring a certain mass transfer pattern. Depending on the physical properties of the participating components, including the choice of entrainer, the optimal mass transfer pattern can be depicted to meet the objective. With no prepostulation of separation units, entrainers, process units and structures are thus simultaneously examined within one optimisation problem. Although illustrated on examples with constant total pressure and no heat integration, the framework can incorporate this at the cost of increased problem size and computational time.

In chapter 4, the mass/heat transfer framework is extended to encompass general nonideal separation systems whereby reaction may occur in the liquid phase. It is shown that by appropriate application of the driving force constraint, the complex interaction between reaction and separation can be modelled within a mass/heat transfer module. For simultaneous reaction and separation, a liquid-vapour module forms the superstructure building block whereby reaction is explicitly accounted for in the liquid holdup or catalyst mass within the module. When no reaction occurs, the module corresponds to a pure separation module. The synthesis framework is successfully applied to three typical reaction separation systems whereby it is shown that hybrid structures combining separation reaction and pure separation counterparts can be generated through optimisation of a cost function. Chemical equilibrium is not assumed but is utilised to define the limiting case; using reaction kinetics, the framework is capable of handling multi-reactions. Operating conditions and mass transfer patterns are obtained, and can be utilised as starting points for further detailed simulation, design and optimisation.

The capability of the framework to handle a general multicomponent nonideal mixture is illustrated in chapter 5, whereby the separation synthesis of a 6-component system is considered. An equation of state is incorporated within the driving force constraint, at the cost of increased model complexity for thermodynamic description.

The systematically generated superstructure of this framework results in a large scale mixed integer nonlinear problem. In principle, applying an available solver would yield a local solution. However, due to the nonideal nature of the problems considered, the model is nonconvex. A nested decomposition strategy is developed for the solution, but global optimality is not guaranteed. Where this work has focussed upon the modelling issues of general mixtures, future contributions are necessary for the development of efficient algorithms for the solution of the resulting problems.

In summary, the main contributions of this work have been:

- The introduction of a systematic representation framework for the synthesis of homogeneous azeotropic separations, whereby entrainers and sequencing are considered in one optimisation problem. When entrainers are not considered, the framework is applicable to general nonideal multicomponent separation synthesis allowing for the incorporation of any thermodynamic model.
- A synthesis framework for the synthesis of combined reaction and separation systems, able to identify hybrid processes as well as conventional processes. The approach is applicable to multicomponent systems with multi-reactions, whereby kinetics and heat effects are considered. Liquid holdups or catalyst mass, when a factor, are explicitly accounted for.
- The modelling of the mass transfer within the mass/heat transfer module based on Gibbs free energy constraints. For pure separation systems, the derived constraints can handle multicomponent mixtures with complex mass transfer patterns. For reactive separation systems, the constraints can model mass transfer due to simultaneous reaction and separation. Through the development of the driving force constraints, it is believed that the generic framework can be extended to encompass other complex systems.

6.2 Recommendations for future directions

A number of issues have been identified for further development;

(i) Mass/Heat Transfer Module

When each liquid-vapour mass/heat transfer module corresponds to a part or whole of a separation unit such as an aggregate of distillation trays, it features a certain mass transfer pattern. As many modules as the required mass transfer patterns are selected. When possible, the obtained separation structures have been simulated using equilibrium based models to map the number of trays corresponding to each separation module. However, this is not a trivial task and thus it would be beneficial to conduct a theoretical investigation into the correlation between number of trays and separation within a module.

Due to the nonconvex nature of the driving force constraints, although mass transfer may be feasible at the ends of the module, it may be violated within the module. Within this work, post analysis has been conducted to ensure that infeasible mass transfer did not take place. Methods to ensure this could be investigated - for example, each module could be further aggregated in an inner loop algorithm to check feasibility of mass transfer.

(ii) Analysis

Attempts to separate a minimum boiling binary azeotropic mixture beyond its azeotropic composition within the mass/heat transfer modules is detected through the driving force constraints, whereby the driving force constraint limits the separation. This suggests that the prediction of azeotropes within our framework may be possible and can be further explored.

For the separation of azeotropic mixtures, a set of alternatives entrainers is given. For the case when entrainers to facilitate the separation are unknown, it may be of interest to extend the framework model to choose or target the entrainer properties to achieve the desired separation, leading to material design.

Recently, analysis in the existence of multiple steady states in azeotropic and reactive separation systems has been of considerable interest. The ability for the framework to capture and evaluate this phenomena can be further explored.

(iii) Solution Procedure

To aid the solution of large-scale MINLP problems that result within the proposed framework, efficient algorithmic techniques can be explored. In particular, the incorporation of logic based methods (Raman and Grossmann, 1993) can be investigated

to exploit the underlying logic of the superstructure model and provide a formal procedure to formulate structural constraints which screen out infeasible configurations of modules.

In this work it is found that a good initial structure is essential to obtain a solution, and the effect of the initial structure on the final solution can be formally analysed. Due to the nonconvex nature of the problems addressed, global optima cannot be guaranteed. Global optimisation issues can be addressed by proper exploitation of the special structure of the underlying models. For example, the decomposition based technique of Floudas and Visweswaran (1990) can be examined for incorporation within this framework.

(iv) Modelling Issues

a. Heterogeneous Azeotropic Systems

The preliminary concepts for the extension of the synthesis framework to encompass heterogeneous systems where two liquid phases may form has been discussed in chapter 3. In particular, the following issues remain to be addressed;

- Driving Force constraints. It is suggested that the driving force constraints to describe the mass transfer between the two liquid phases and vapour phase are decoupled so that each pair of streams are constrained. The sufficient and accuracy of considering mass transfer of components between each pair of streams should be tested; otherwise a different single set of driving force constraints should be considered.
- Combinatorial complexity. Given the suggested constraints can be utilised, closer analysis of mass transfer within the vapour/liquid/liquid systems is required to investigate the possibility of screening out infeasible mass transfer patterns based on mixture properties. This could then be implemented as logical constraints which would reduce combinatorial problems.
- Stability Criteria. The ability to model accurately liquid-liquid split is vital, and methods available in the literature must be investigated for possible implementation to ensure liquid phase stability/instability. For example, a nested algorithm to determine the number of phases could be utilised.

b. Modelling of Non-conventional units

The modelling of non-conventional units such as double walled distillation columns and liquid-liquid membrane units can be considered, to investigate the ability of the framework to reveal new processes.

c. Reaction Network Systems

The driving force constraints for liquid-liquid module with reaction is derived in this work to illustrate the ability of the framework to reveal conventional reaction and separation units as well as hybrid units. The development of the module and framework to consider complex reaction network synthesis can be investigated, including vapour phase reactions.

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Presented Papers

- Rahim Ismail, S., Papalexandri, K.P and E.N. Pistikopoulos, "A Generalized Modular synthesis framework for Reactive Separation systems", Paper presented at AIChE annual meeting, Miami (1998)
- Rahim Ismail, S. and E.N. Pistikopoulos, "A Mass/Heat Transfer Representation for the Separation of Azeotropic Mixtures.", Paper presented at IChemE Jubilee research event (1997)
- Ismail, S.R., E.N. Pistikopoulos and K.P. Papalexandri, "Synthesis of Homogeneous Azeotropic Separation Systems based on Mass/Heat Exchange Principles,.", Paper presented at the AIChE Annual Meeting, Chicago (1996)

Reports

- *An Integrated Approach to the Design of Energy Efficient Process Systems (IDEES)*, Contract JOE3-CT95-0017 (JOULE), Final Report, July 1998.

Property Parameters

A.1 Ideal ternary system

Ideal gas heat capacity and heat of vapourisation

$C_p = A + BT + CT^2 + DT^3$ (cal/mol K)					ΔH_{vap} (cal/mol)
	A	B	C	D	
Methanol	3.052	1.694e-2	6.179e-6	-6.811e-9	8426
Ethanol	2.153	5.113e-2	-2.004e-5	0.328e-9	9260
Propanol	0.390	7.942e-2	-4.431e-5	1.026e-8	9980

Vapour Pressure

$\log(P_{sat}) = A - B/(C + T)$ (mmHg)			
	A	B	C
Methanol	18.5875	3626.35	-34.29
Ethanol	18.9119	3803.98	-41.68
Propanol	17.5439	3166.38	-80.15

A.2 Ethanol-water separation

Ideal gas heat capacity

$C_p = A + BT + CT^2 + DT^3$ (J/mol K)				
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Ethanol	9.014	0.2141	-8.39e-5	1.373e-9
Water	31.94	1.436e-3	2.432e-5	-1.176e-8
Ethylene Glycol	35.7	0.2483	-1.497e-4	3.01e-8
Methanol	21.15	0.07092	2.587e-5	-2.852e-8

Heat of Vapourisation

$\Delta H_{vap} = A(1 - T_r)^{(B+CT_r+DT_r^2)}$ (J/mol)				
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Ethanol	44150.0	-0.4134	0.75362	0.0
Water	57608.0	0.6964	-0.7797	0.47678
Ethylene Glycol	88200.0	0.397	0.0	0.0
Methanol	39700.0	-0.279	0.5080	0.084

A.3 Acetone - chloroform separation

Ideal gas heat capacity

$C_p = A + BT + CT^2 + DT^3$ (cal/mol)				
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
Acetone	1.505	0.06224	-2.992e-5	4.867e-9
Chloroform	5.733	0.04522	-4.397e-5	1.590e-8
Methanol	3.052	0.01694	6.179e-6	-6.811e-9
Benzene	-5.101	0.1133	-7.206e-5	1.703e-8

Heat of vapourisation

$\Delta H_{vap} = A(1 - T_r)^{(B+CT_r+DT_r^2)}$ (J/mol)				
	A	B	C	D
Acetone	49170	1.0360	-1.2940	0.6720
Chloroform	42970	0.3754	0.0000	0.0000
Methanol	39700	-0.279	0.5080	0.0840
Benzene	50730	0.76160	-0.5052	0.1564

A.4 Methyl acetate production

Liquid density

$\rho = \frac{A}{B^{1+[1-T/C]^D}}$ (kmol/m ³)				
	A	B	C	D
Acetic Acid	1.5791	0.26954	0.59271e3	0.26843
Methanol	1.2057	0.19779	0.51263e3	0.17272
Methyl Acetate	1.2090	0.2676	0.50680e3	0.2892
Water	4.6137	0.26214	0.64729e3	0.23072

A.5 Ethyl acetate production

Liquid heat capacity

$C_p = A + BT + CT^2 + DT^3 + ET^4$ (J/kmol K)					
	A	B	C	D	E
Acetic Acid	0.501e5	245.6	0.0	0	0
Ethanol	0.9456e5	-56.2	-0.329	0.2398e-2	0
Ethyl Acetate	0.15594e6	236.97	-1.9976	0.4592e-2	0
Water	0.27637e6	-2090.1	8.125	-0.14116e-1	0.93701e-5

Heat of Vapourisation

$\Delta H_{vap} = A(1 - T_r)^{(B+CT_r+DT_r^2)}$ (J/kmol)				
	A	B	C	D
Acetic Acid	0.126e8	-1.11	0.063	1.142
Ethanol	0.569e8	0.3359	0.0	0.0
Ethyl Acetate	0.4988e8	0.3935	0.0	0.0
Water	0.52053e8	0.3199	-0.212	0.25795

Liquid density

$\rho = \frac{A}{B^{1+[1-T/C]^D}}$ (kmol/m ³)				
	A	B	C	D
Acetic Acid	1.5791	0.26954	0.59271e3	0.26843
Ethanol	1.6480	0.27627	0.51392e3	0.23310
Ethyl Acetate	0.8866	0.25647	0.52325e3	0.27728
Water	5.459	0.30542	0.64713e3	0.08100

A.6 MTBE production

Ideal gas heat capacity

$C_p = A + BT + CT^2 + DT^3$ (J/mol K)					ΔH_{vap} (J/mol)
	A	B	C	D	
Methanol	21.15	0.07092	0.2587E-4	-0.2852E-7	37520
Isobutene	16.05	0.2804	-0.1091E-3	0.9098E-8	20600
n-butene	-2.994	0.3532	-0.199E-3	0.4463E-7	22422
MTBE	2.534	0.5136	-0.2569E-3	0.4303E-7	30400

A.7 Methanol case study

Critical parameters

	T_c (K)	P_c (atm)
Carbon dioxide	304.21	72.865
Acetone	508.20	46.400
Methanol	512.64	79.911
Ethanol	513.92	60.676
Water	647.13	217.666
Butanol	562.93	43.55

Ideal gas heat capacity

$C_p = A + BT + CT^2 + DT^3$ (J/mol K)				
	A	B	C	D
Methanol	21.15	7.092e-2	2.587e-5	-2.852e-8
Ethanol	9.014	2.141e-1	-8.39e-5	1.373e-9
Acetone	6.301	2.606e-1	-1.253e-4	2.038e-8
Water	32.24	1.924e-3	1.055e-5	-3.596e-9
Butanol	3.266	4.180e-1	-2.242e-4	4.685e-8
Carbon dioxide	19.80	7.344e-2	-5.602e-5	1.715e-8

Heat of Vapourisation

$\Delta H_{vap} = A(1 - T_r)^{(B+CT_r+DT_r^2)}$ (J/mol)				
	A	B	C	D
Methanol	52390	0.3682	0.0000	0.0
Ethanol	56900	0.3359	0.0000	0.0
Acetone	42150	0.3397	0.0000	0.0
Water	52053	0.3199	-0.212	0.25795
Butanol	67390	0.1730	0.2915	0.0
Carbon dioxide	21730	0.0000	0.0000	0.0

SRK parameters

	Q_1	Q_2	Q_3
Carbon dioxide	0.8653	-0.4386	1.3447
Acetone	0.9998	-0.4137	0.5345
Methanol	1.4450	-0.8150	0.2486
Ethanol	1.4252	0.1898	-1.3014
Water	1.0873	-0.6377	0.6345
Butanol	1.1345	1.7856	-2.8325

Modified UNIFAC parameters

Van der Waals volume of group g R_g and surface area of group g Q_g .

	R_g	Q_g
CO2	2.5920	2.5220
CH2	0.6744	0.5400
CH3	0.9011	0.8480
CH3CO	1.6724	1.4880
CH3OH	1.0000	1.0000
OH	1.0000	1.2000
H2O	0.9200	1.4000

Group interaction parameters, $T_o=298.15$							
$a_{mg} = a_{mg,1} + a_{mg,2}(T - T_o) + a_{mg,3} \left[T \ln \frac{T_o}{T} + T - T_o \right]$							
$a_{mg,1}$							
	CO2	CH2	CH3	CH3CO	CH3OH	OH	H2O
CO2	0	-55.69	-55.69	-0.0172	727.9	583.3	1067
CH2	123.9	0	0	414	1318	972.8	1857
CH3	123.9	0	0	414	1318	972.8	1857
CH3CO	81.51	71.93	71.93	0	263.3	179.6	272.4
CH3OH	-126.6	16.25	16.25	-29.4	0	66.34	-75.41
OH	261.7	637.5	637.5	161	29.5	0	155.6
H2O	226.6	410.7	410.7	40.2	265.5	-47.15	0
$a_{mg,2}$							
	CO2	CH2	CH3	CH3CO	CH3OH	OH	H2O
CO2	0	-0.4904	-0.4904	0	-1.331	-4.94	-0.418
CH2	-0.4065	0	0	-0.5165	-0.0126	0.2687	-3.322
CH3	-0.4065	0	0	-0.5165	-0.0126	0.2687	-3.322
CH3CO	0	-0.796	-0.796	0	-0.1553	-1.285	-1.842
CH3OH	-0.2024	-0.3005	-0.3005	-0.7294	0	-0.5845	-0.757
OH	5.381	-5.832	-5.832	0.7501	0.4043	0	0.3761
H2O	-0.2410	2.8680	2.8680	1.6680	3.54	-0.4947	0
$a_{mg,3}$							
	CO2	CH2	CH3	CH3CO	CH3OH	OH	H2O
CO2	0	0	0	0	0	0	0
CH2	0	0	0	1.8030	9.0	8.773	-9
CH3	0	0	0	1.8030	9.0	8.773	-9
CH3CO	0	-2.916	-2.916	0	1.768	-4.007	0.3303
CH3OH	0	0.6924	0.6924	-1.67	0	0	-4.745
OH	0	-0.8703	-0.8703	9.0	0	0	-9
H2O	0	9.0	9.0	-1.996	8.4210	8.65	0

MINLP details for Azeotropic Separation Model

B.1 Formulation of MINLP

Consider the mathematical model for the synthesis of azeotropic separations detailed in section 3.8. The MINLP is solved via a nested decomposition strategy as described in section 3.9 and illustrated in Figure 3.19, whereby the problem is decomposed into three subproblems;

- Primal Problem : by fixing all structural and mass transfer integer binaries, denoted by y and z respectively, solve the problem for the continuous variables x . This provides an upper bound to the overall problem solution and the lagrange multipliers for the master subproblems.
- Inner Master Subproblem : by fixing all structural integer binaries y and continuous variables x , determine the mass transfer binary integer binaries.
- Outer Master Subproblem : by fixing the continuous variables x , determine both structural y and mass transfer z integer binaries. This provides a lower bound to the overall problem solution.

The detailed formulation for the model of section 3.8 follows, whereby k corresponds to the iteration number, decomposed to $k1$ outer master and $k2$ inner master iterations. The model is solved through the modelling system GAMS (Brooke *et al.*, 1988) using CONOPT for the Primal and CPLEX for the master problems.

B.1.1 Primal Problem k

$$U^k = \min \sum_e \left(C^h * Qh_e + C^c * Qc_e \right) + C^{I2} \sum_{I2} f^{I2} + C^{module} \sum_e y_e^k$$

s.t.

$$\left. \begin{aligned} f_n^I - \sum_e f_{ne}^{IL} - \sum_e f_{ne}^{IH} - \sum_p f_{np}^{IP} &= 0 \\ f_e^{LO} - \sum_{e'} \left(f_{ee'}^{LL} + f_{ee'}^{LH} \right) - \sum_p f_{ep}^{LP} &= 0 \\ f_e^{VO} - \sum_{e'} \left(f_{ee'}^{VV} + f_{ee'}^{VC} \right) &= 0 \\ f_e^H - \sum_{e'} f_{ee'}^{HV} &= 0 \\ f_e^C - \sum_{e'} f_{ee'}^{CL} + \sum_p f_{ep}^{CP} &= 0 \\ f_e^{LI} - \sum_n f_{ne}^{IL} - \sum_{e'} \left(f_{e'e}^{LL} + f_{e'e}^{CL} \right) &= 0 \\ f_e^{VI} - \sum_{e'} \left(f_{e'e}^{VV} + f_{e'e}^{HV} \right) &= 0 \\ f_e^C - \sum_{e'} f_{e'e}^{VC} &= 0 \\ f_e^H - \sum_n f_{ne}^{IH} - \sum_{e'} f_{e'e}^{LH} &= 0 \\ f_p^P - \sum_n f_{np}^{IP} - \sum_e f_{ep}^{LP} - \sum_e f_{ep}^{CP} &= 0 \\ f_e^{LI} x_{ei}^{LI} - \sum_n f_{ne}^{IL} x_{ni}^I - \sum_{e'} \left(f_{e'e}^{LL} x_{e'i}^{LO} + f_{e'e}^{CL} x_{e'i}^C \right) &= 0 \\ f_e^{VI} x_{ei}^{VI} - \sum_{e'} \left(f_{e'e}^{VV} x_{e'i}^{VO} + f_{e'e}^{HV} x_{e'i}^H \right) &= 0 \\ f_e^C x_{ei}^C - \sum_{e'} f_{e'e}^{VC} x_{e'i}^{VO} &= 0 \\ f_e^H x_{ei}^H - \sum_n f_{ne}^{IH} x_{ni}^I - \sum_{e'} f_{e'e}^{LH} x_{e'i}^{LO} &= 0 \\ f_p^P x_i^P - \sum_n f_{np}^{IP} x_{ni}^I - \sum_e \left(f_{ep}^{LP} x_{ei}^{LO} + f_{ep}^{CP} x_{ei}^C \right) &= 0 \\ f_e^{LI} x_{ei}^{LI} + f_e^{VI} x_{ei}^{VI} - f_e^{LO} x_{ei}^{LO} - f_e^{VO} x_{ei}^{VO} &= 0 \\ f_e^{LI} h_e^{LI} - \sum_n f_{ne}^{IL} h_n^I - \sum_{e'} \left(f_{e'e}^{LL} h_{e'i}^{LO} + f_{e'e}^{CL} h_{e'i}^{CO} \right) &= 0 \\ f_e^{VI} h_e^{VI} - \sum_{e'} \left(f_{e'e}^{VV} h_{e'i}^{VO} + f_{e'e}^{HV} h_{e'i}^{HO} \right) &= 0 \\ Qh_e - f_e^H \left(h_e^{HO} - h_e^{HI} \right) &= 0 \\ Qc_e - f_e^C \left(h_e^{CO} - h_e^{CI} \right) &= 0 \\ f_e^{LI} h_e^{LI} + f_e^{VI} h_e^{VI} - f_e^{LO} h_e^{LO} - f_e^{VO} h_e^{VO} &= 0 \\ f_p^P h^P - \sum_n f_{np}^{IP} h_n^I - \sum_e \left(f_{ep}^{LP} h_e^{LO} + f_{ep}^{CP} h_e^{CO} \right) &= 0 \\ \sum_i x_i^s - 1 = 0 \quad \forall s = LI, LO, VI, VO, C, H, P \\ + \text{Thermodynamic Property Calculation} \quad \forall s \in S1 \end{aligned} \right\} h(x) = 0$$

$$\begin{array}{l}
\left. \begin{array}{l}
0.8 - \sum_i K_i^s x_i^s \leq 0 \\
\sum_i K_i^s x_i^s - 1 \leq 0 \\
0.8 - \sum_i x_i^s / K_i^s \leq 0 \\
\sum_i x_i^s / K_i^s - 1 \leq 0
\end{array} \right\} \begin{array}{l} \text{Phase Definition} \\ g_1(x) \leq 0 \end{array} \\
\\
\left. \begin{array}{l}
(y_e^k + yt_{ei}^k - 2) \mathcal{U} - [f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO}] \leq 0 \\
[f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO}] - (1 - y_e^k + yt_{ei}^k) \mathcal{U} \leq 0 \\
(y_e^k + yt_{ei}^k - 2) \mathcal{U} - [K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO}] \leq 0 \\
[K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO}] - (1 - y_e^k + yt_{ei}^k) \mathcal{U} \leq 0 \\
(y_e^k + yt_{ei}^k - 2) \mathcal{U} - [K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI}] \leq 0 \\
[K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI}] - (1 - y_e^k + yt_{ei}^k) \mathcal{U} \leq 0
\end{array} \right\} \begin{array}{l} \text{Driving Force Constraints} \\ g_2(x, y^k, z^k) \leq 0 \end{array} \\
\\
\left. \begin{array}{l}
[f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO}] - y_e^k \mathcal{F}^{max} \leq 0 \\
f_e^H - y h_e^k \mathcal{F}^{max} \leq 0 \\
f_e^C - y c_e^k \mathcal{F}^{max} \leq 0 \\
Q h_e - y h_e^k Q^{max} \leq 0 \\
Q c_e - y c_e^k Q^{max} \leq 0 \\
f_{ee}^{LL} - y l l_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ee}^{VV} - y v v_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ee}^{LH} - y l h_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ee}^{HV} - y h v_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ee}^{VC} - y v c_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ee}^{CL} - y c l_{ee}^k \mathcal{F}^{max} \leq 0 \\
f_{ne}^{IL} - y I l_{ne}^k \mathcal{F}^{max} \leq 0 \\
f_{ne}^{IH} - y I h_{ne}^k \mathcal{F}^{max} \leq 0 \\
f_{np}^{IP} - y I p_{np}^k \mathcal{F}^{max} \leq 0 \\
f_{ep}^{LP} - y l p_{ep}^k \mathcal{F}^{max} \leq 0 \\
f_{ep}^{CP} - y c p_{ep}^k \mathcal{F}^{max} \leq 0
\end{array} \right\} \begin{array}{l} \text{Logical Constraints} \\ g_3(x, y^k) \leq 0 \end{array}
\end{array}$$

The solution provides the lagrange multipliers λ_2^k and λ_3^k corresponding to the constraints $g_2(x, y^k, z^k)$ and $g_3(x, y^k)$ respectively.

B.1.2 Inner Master Subproblem $k2(k)$

$$\min \mu$$

s.t.

$$\left. \begin{aligned} \mu \geq & \left[\sum_e (C^h * Qh_e + C^c * Qc_e) + C^{I2} \sum_{I2} f^{I2} \right]^k + \sum_e y_e^{k1} \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \end{aligned} \right\} \text{Feasible Primal} \\ \text{of current } k1$$

$$\left. \begin{aligned} & \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e^{k1} + yt_{ei} - 2)\mathcal{U} - (K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k - (1 - y_e^{k1} + yt_{ei})\mathcal{U} \right] \leq 0 \end{aligned} \right\} \text{Infeasible Primal} \\ \text{of current } k1$$

$$1 - yt_{ei} + y_e^{k1} \leq 0$$

$$\left. \begin{aligned} & \sum_{ei \in A^{k2}} yt_{ei} - \sum_{ei \in B^{k2}} yt_{ei} - |A^{k2}| + 1 \leq 0 \\ & A^{k2} = \{ ei \mid yt_{ei}^{k2-1(k1)} = 1 \} ; B^{k2} = \{ ei \mid yt_{ei}^{k2-1(k1)} = 0 \} \end{aligned} \right\} \text{Integer cut for mass} \\ \text{transfer directions already} \\ \text{investigated in current} \\ \text{outer iteration } k1$$

The solution of the inner master subproblem provides a lower bound to the primal problem with current *fixed* structure. Note that the lagrange multipliers λ^k correspond to their respective constraints.

B.1.3 Outer Master Subproblem $k1(k)$

$$\min \mu$$

$$\text{s.t.}$$

$$\mu \geq \left[\begin{aligned} & \sum_e (C^h * Qh_e + C^c * Qc_e) + \sum_{n2} C^{n2} \sum_{n2} f_{n2}^{I2} \Big]^k + \sum_e y_e \\ & + \sum_e \lambda_e^k \left[(f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO}) - y_e \mathcal{F}^{max} \right] \\ & + \sum_e \lambda_e^k \left[f_e^H - y h_e \mathcal{F}^{max} \right] \\ & + \sum_e \lambda_e^k \left[f_e^C - y c_e \mathcal{F}^{max} \right] \\ & + \sum_e \lambda_e^k [Qh_e - y h_e Q^{max}] \\ & + \sum_e \lambda_e^k [Qc_e - y c_e Q^{max}] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{LL} - y l_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{VV} - y v_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{LH} - y l h_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{HV} - y h v_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{VC} - y v c_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{CL} - y c l_{ee} \mathcal{F}^{max} \right] \\ & + \sum_{ne} \lambda_{ne}^k \left[f_{ne}^{IL} - y l l_{ne} \mathcal{F}^{max} \right] \\ & + \sum_{np} \lambda_{np}^k \left[f_{np}^{IH} - y l h_{np} \mathcal{F}^{max} \right] \\ & + \sum_{np} \lambda_{np}^k \left[f_{np}^{IP} - y l p_{np} \mathcal{F}^{max} \right] \\ & + \sum_{ep} \lambda_{ep}^k \left[f_{ep}^{LP} - y l p_{ep} \mathcal{F}^{max} \right] \\ & + \sum_{ep} \lambda_{ep}^k \left[f_{ep}^{CP} - y c p_{ep} \mathcal{F}^{max} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - (f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO})^k - (1 - y_e + y t_{ei}) \mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - (K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO})^k - (1 - y_e + y t_{ei}) \mathcal{U} \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - (K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k \right] \\ & + \sum_{ei} \lambda_{ei}^k \left[(K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI})^k - (1 - y_e + y t_{ei}) \mathcal{U} \right] \end{aligned} \right] \quad \forall k \text{ of Feasible Primal}$$

$$\left. \begin{aligned}
& \sum_e \lambda_e^k \left[(f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO}) - y_e \mathcal{F}^{max} \right] \\
& + \sum_e \lambda_e^k \left[f_e^H - y h_e \mathcal{F}^{max} \right] \\
& + \sum_e \lambda_e^k \left[f_e^C - y c_e \mathcal{F}^{max} \right] \\
& + \sum_e \lambda_e^k \left[Q h_e - y h_e Q^{max} \right] \\
& + \sum_e \lambda_e^k \left[Q c_e - y c_e Q^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{LL} - y l l_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{VV} - y v v_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{LH} - y l h_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{HV} - y h v_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{VC} - y v c_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ee} \lambda_{ee}^k \left[f_{ee}^{CL} - y c l_{ee} \mathcal{F}^{max} \right] \\
& + \sum_{ne} \lambda_{ne}^k \left[f_{ne}^{IL} - y l l_{ne} \mathcal{F}^{max} \right] \\
& + \sum_{np} \lambda_{np}^k \left[f_{ne}^{IH} - y l h_{ne} \mathcal{F}^{max} \right] \\
& + \sum_{np} \lambda_{np}^k \left[f_{np}^{IP} - y l p_{np} \mathcal{F}^{max} \right] \\
& + \sum_{ep} \lambda_{ep}^k \left[f_{ep}^{LP} - y l p_{ep} \mathcal{F}^{max} \right] \\
& + \sum_{ep} \lambda_{ep}^k \left[f_{ep}^{CP} - y c p_{ep} \mathcal{F}^{max} \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - \left(f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO} \right)^k \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[\left(f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO} \right)^k - (1 - y_e + y t_{ei}) \mathcal{U} \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - \left(K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO} \right)^k \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[\left(K_{ei}^{LI} x_{ei}^{LI} - x_{ei}^{VO} \right)^k - (1 - y_e + y t_{ei}) \mathcal{U} \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[(y_e + y t_{ei} - 2) \mathcal{U} - \left(K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI} \right)^k \right] \\
& + \sum_{ei} \lambda_{ei}^k \left[\left(K_{ei}^{LO} x_{ei}^{LO} - x_{ei}^{VI} \right)^k - (1 - y_e + y t_{ei}) \right] \leq 0
\end{aligned} \right\} \quad \begin{array}{l} \forall k \text{ of} \\ \text{Infeasible Primal} \end{array}$$

$$\begin{aligned}
& y h_e - y_e \leq 0 \\
& y c_e - y_e \leq 0 \\
& y_{e+1} - y_e \leq 0 \\
& 1 - y t_{ei} + y_e \leq 0 \\
& y l l_{ee'} - 0.5 [y_e + y_{e'}] \leq 0 \\
& y v v_{ee'} - 0.5 [y_e + y_{e'}] \leq 0 \\
& y l h_{ee'} - 0.5 [y_e + y h_{e'}] \leq 0 \\
& y h v_{ee'} - 0.5 [y h_e + y_{e'}] \leq 0 \\
& y v c_{ee'} - 0.5 [y_e + y c_{e'}] \leq 0 \\
& y c l_{ee'} - 0.5 [y c_e + y_{e'}] \leq 0 \\
& y I l_{ne} - y_e \leq 0 \\
& y I h_{ne} - y h_e \leq 0 \\
& y l p_{ep} - y_e \leq 0 \\
& y c p_{ep} - y c_e \leq 0 \\
& y_e - [\sum_n y I l_{ne} + \sum_{e'} y l l_{e'e} + \sum_{e'} y c l_{e'e}] \leq 0 \\
& y_e - [\sum_{e'} y v v_{e'e} + \sum_{e'} y h v_{e'e}] \leq 0 \\
& y h_e - [\sum_n y I h_{ne} + \sum_{e'} y l h_{e'e}] \leq 0 \\
& y c_e - [\sum_{e'} y v c_{e'e}] \leq 0 \\
& y_e - [\sum_{e'} y l l_{ee'} + \sum_{e'} y l h_{ee'} + \sum_p y l p_{ep}] \leq 0 \\
& y_e - [\sum_{e'} y v v_{ee'} + \sum_{e'} y v c_{ee'}] \leq 0 \\
& y h_e - [\sum_{e'} y h v_{ee'}] \leq 0 \\
& y c_e - [\sum_{e'} y c l_{ee'} + \sum_p y c p_{ep}] \leq 0 \\
& 1 - [\sum_e y I l_{ne} + \sum_e y I h_{ne} + \sum_p y I p_{np}] \leq 0 \\
& 1 - [\sum_n y I p_{np} + \sum_e y l p_{ep} + \sum_e y c p_{ep}] \leq 0 \\
& y_{solv_n} - [\sum_e y I l_{ne} + \sum_e y I h_{ne} + \sum_p y I p_{np}] \leq 0
\end{aligned}$$

Structural Logical
Constraints
 $g_4(y, z) \leq 0$

+ integer cuts to exclude structures and mass transfer directions
already investigated

The solution provides a lower bound to the overall problem solution.

B.2 General Size Statistics

This section details the size of the superstructure model described in section 3.8, expressed in terms of the number of mass/heat transfer modules e , number of components in the system c , number of initial streams n (consisting of n_1 given feeds and n_2 possible entrainers) and number of product streams p considered.

- Continuous Variables

Flowrates	$n + p + 6e + 6ee + 2ne + 2np + 2ep$
Molar fractions	$pc + 6ec$
Temperatures	$p + 8e$
Heat loads	$2e$

$$\begin{aligned} \text{Number of continuous variables} \quad & 6ee + 6ec + 2ne + 2ep + 16e \\ & + n + 2p + 2np + pc \end{aligned}$$

In addition, continuous variables are introduced for the thermodynamic properties of $8e + p$ streams.

- Integer Variables

Mass/heat modules	e
Utility exchangers	$2e$
Mass transfer directions	ec
Entrainers	n_2
Interconnecting streams	$6ee + 2ne + 2ep + np$

$$\text{Number of binary integers} \quad 6ee + 3e + ec + n_2 + 2ne + 2ep + np$$

• Equality constraints

Total mass balances		
at feed splitters		n
at mass/heat module splitters		$4e$
at mass/heat module mixers		$4e$
at product mixers		p
Component mass balances		
at mass/heat module mixers		$4ec$
at product mixers		pc
around mass/heat exchanger		ec
Energy balances		
at mass/heat module mixers		$4e$
at product mixers		p
around mass/heat exchanger		e
around pure heat exchangers		$2e$
Summation of molar fractions		
for mass/heat exchanger streams		$4e$
for pure heat exchanger streams		$2e$
for product streams		p
Number of equality constraints	$21e + 5ec + n + 3p + pc$	

In addition, equality constraints are introduced to define the thermodynamic properties of $8e + p$ streams.

• Pure Continuous Inequality Constraints

Phase Defining Constraints, upper and lower limits		
for mass/heat module streams		$2 * 8e$
for product streams		$2 * p$
Number of Inequalities	$16e + 2p$	

- Mixed Integer Inequality Constraints

Driving force constraints	
for mass/heat exchangers	$6ec$
Existence of molar flows	
for mass/heat exchangers	e
for pure heat exchangers	$2e$
for interconnecting streams	$6ee + 2ne + np + 2ep$
Existence of heat flows	
for pure heat exchangers	$2e$
Number of Constraints	$6ee + 6ec + 2ne + 2ep + 5e + np$

- Pure Integer Inequality Constraints

Existence of	
utility exchangers	$2e$
interconnecting streams	$6ee + 2ne + 2ep$
mixer inlet streams	$4e$
splitter outlet streams	$4e$
initial interconnecting streams	n
product interconnecting streams	p
Others	
redundancy of mass transfer constraints	ec
non-redundancy constraint for module	e
Number of Constraints	$6ee + ec + 2ne + 2ep + 11e + n + p$

B.3 Size Statistics of Separation Examples

The synthesis examples given in section 3.10 involve a total of 10 possible mass/heat exchange modules, a given fresh feed and two possible entrainer feeds, and two desired products.

The overall synthesis task for the separation of ethanol and water (tasks 3 and 4) involves 2606 continuous variables (of which 1566 are thermodynamic variables) and 3100 equations (1940 equalities, 1160 inequalities) in the primal and 778 binary variables (including structural binaries for interconnections) and 861 equations in the outer master problem.

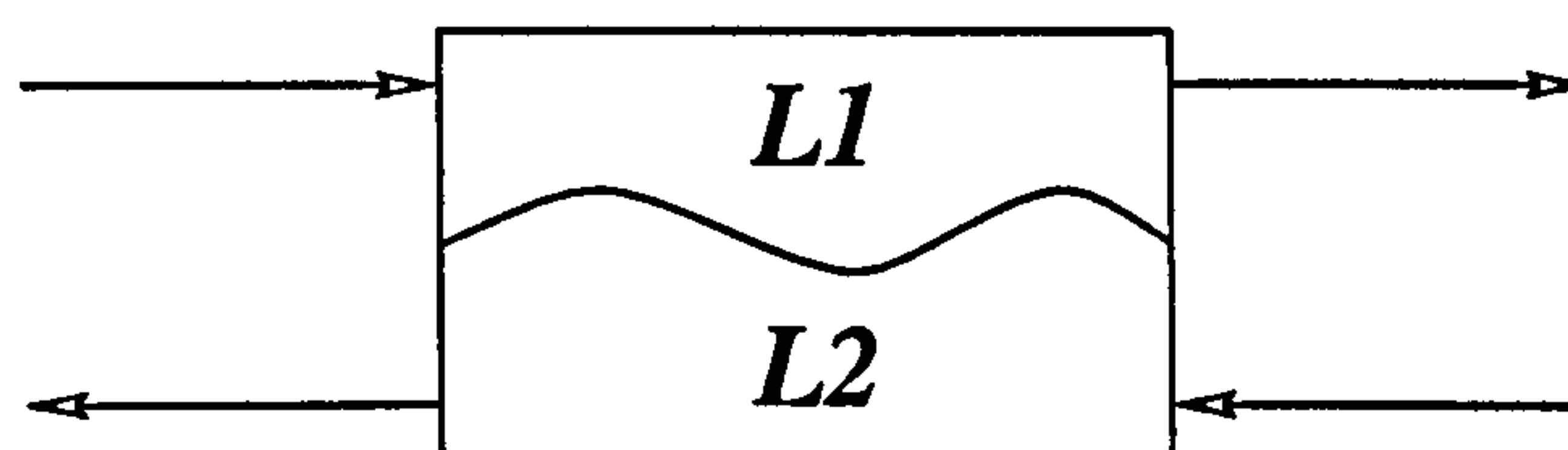
The final structure for task 3 was obtained in 3 outer master iterations and 5 inner master iterations (424 CPU seconds) whilst the final structure for task 4 required 4 outer iterations and 6 inner iterations (512 CPU seconds).

The synthesis model for the separation of acetone and chloroform involves 2210 continuous variables (of which 1170 are thermodynamic variables) and 2704 equations in the primal (1544 equalities, 1160 inequalities) , and 778 binary variables and 861 equations in the outer master problem. The first structure (Figure 3.27) was a result of 2 outer iterations and 4 inner iterations obtained in 381 CPU seconds, whilst the second structure (Figure 3.29) was a result of 4 outer iterations and 7 inner iterations, taking 520 CPU seconds.

Note that the binary variables in both examples correspond to 10 mass/heat exchangers, 20 pure heat exchangers, 2 possible entrainers, 40 mass transfer directions (possible 4 components in each block) and 706 interconnections.

Driving force constraint for Liquid-Liquid Match

C.1 Heterogeneous liquid with no Reaction



Consider a non-reactive multicomponent mixture whereby two liquid phases $L1$ and $L2$ are formed. Mass conservation for the mixture states that

$$n_i^o = n_i^{L1} + n_i^{L2} \quad (C.1)$$

$$\Rightarrow dn_i^{L2} = -dn_i^{L1} \quad (C.2)$$

$$(C.3)$$

where n_i^o is the initial molar holdup of component i in the system.

The Gibbs free energy of the mixture is given by

$$d(nG)^{tot} = (nV)dP - (nS)dT + \sum_i (\mu_i^{L1} dn_i^{L1} + \mu_i^{L2} dn_i^{L2}) \quad (C.4)$$

At constant T and P ,

$$d(nG)^{tot} = \sum_i (\mu_i^{L1} dn_i^{L1} + \mu_i^{L2} dn_i^{L2}) \quad (C.5)$$

$$= \sum_i (\mu_i^{L1} - \mu_i^{L2}) dn_i^{L1} \quad (C.6)$$

Component i will be transferred from liquid phase $L1$ to $L2$ (i.e. $dn_i^{L1} \leq 0$) when

$$\frac{\partial(nG)^{tot}}{\partial n_i^{L1}} \geq 0$$

Similarly for mass transfer from $L2$ to $L1$ (i.e. $dn_i^{L1} \geq 0$)

$$\frac{\partial(nG)^{tot}}{\partial n_i^{L1}} \leq 0$$

Differentiating (C.6) with respect to n_i^{L1} and substituting for the liquid chemical potentials (equation (3.21)),

$$\frac{\partial(nG)^{tot}}{\partial n_i^{L1}} = \mu_i^{L1} - \mu_i^{L2} \quad (C.7)$$

$$= \gamma_i^{L1} x_i^{L1} - \gamma_i^{L2} x_i^{L2} \quad (C.8)$$

Extending to a mass/heat transfer module between two two immiscible liquid phases, mass transfer may be consistently modelled by

$$\mathcal{G}1_i * \mathcal{G}2_i \geq 0 \quad (C.9)$$

$$\mathcal{G}1_i = (Fx_i)_{in}^{L1} - (Fx_i)_{out}^{L1} \quad (C.10)$$

$$\mathcal{G}2_i = (\gamma_i x_i)_{out}^{L1} - (\gamma_i x_i)_{out}^{L2} \quad (C.11)$$

where $(Fx_i)_{in}^{L1}$ and $(Fx_i)_{out}^{L1}$ is the inlet and outlet molar flow of component i in stream $L1$ respectively.

C.2 Homogeneous liquid phase with Reaction: $\partial(nG)^{tot}/\partial n_i^L$

Consider a homogeneous multicomponent liquid phase mixture with R reactions occurring. The Gibbs free energy of the mixture is given by

$$d(nG)^{tot} = (nV)dP - (nS)dT + \sum_i \mu_i^L dn_i^L \quad (C.12)$$

Changes in the molar holdup of each component is due to reaction only

$$n_i^L = n_i^o + \sum_k \nu_{ik} d\epsilon_k \quad (C.13)$$

$$dn_i^L = \sum_k \nu_{ik} d\epsilon_k \quad (C.14)$$

Therefore at constant T and P ,

$$d(nG)^{tot} = \sum_i \sum_k \mu_i^L d\epsilon_k \quad (C.15)$$

Assuming $\partial\mu_i/\partial n_i^L \approx 0$, differentiation gives

$$\frac{\partial(nG)^{tot}}{\partial n_i^L} = \sum_i \sum_k \nu_{ik} \mu_i^L \frac{\partial\epsilon_k}{\partial n_i^L} \quad (C.16)$$

$$= \sum_i \sum_k \nu_{ik} \left[\Delta G_i^f + RT \ln (\gamma_i^L x_i^L P_i^{sat,L}) \right] \frac{\partial\epsilon_k}{\partial n_i^L} \quad (C.17)$$

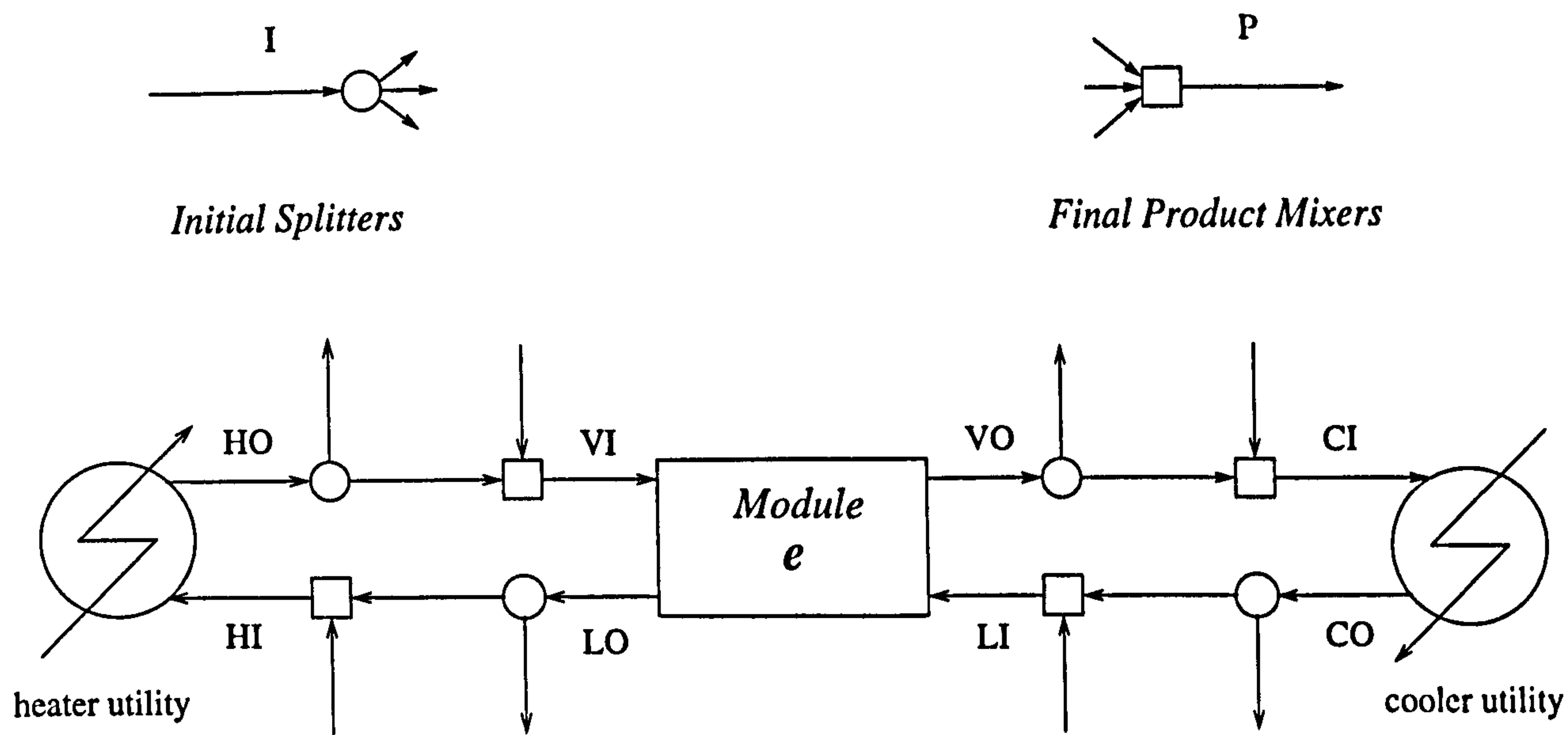
A reactant is consumed by reaction, i.e. $dn_i^L \leq 0$, when the Gibbs free energy is reduced, i.e. when $\partial(nG)^{tot}/\partial n_i^L \geq 0$. A product species is generated by reaction, i.e. $dn_i^L \geq 0$, when the Gibbs free energy is reduced, i.e. when $\partial(nG)^{tot}/\partial n_i^L \leq 0$. At chemical equilibrium, $\sum_i \nu_i \mu_i = 0$, there is no consumption or generation of components and $\partial(nG)^{tot}/\partial n_i^L = 0$.

Division by RT gives the expression for use in the driving force constraints as given in Table 4.4.

$$G2_i^{L-L} = \sum_i \sum_k \nu_{ik} \left[\frac{\Delta G_i^f}{RT} + \ln (\gamma_i^L x_i^L P_i^{sat,L}) \right] \frac{\partial\epsilon_k}{\partial n_i^L} \quad (C.18)$$

Mass/Heat Transfer Superstructure Model for Methyl Acetate Synthesis

The superstructure model for the synthesis of methyl acetate consists of 2 possible initial feed streams I , 2 desired product streams P and 20 mass/heat transfer modules e , 10 pure separation and 10 with combined separation/reaction.



In general, the initial streams and product streams can be liquid or vapour phase and the following sets are introduced for the streams of the mass/heat exchange superstructure;

I	=	{ n/n initial stream }
P	=	{ p/p product stream }
LI_e	=	{ s/s liquid inlet stream li in mass/heat exchanger e }
LO_e	=	{ s/s liquid outlet stream lo in exchanger e }
VI_e	=	{ s/s vapour inlet stream vi in mass/heat exchanger e }
VO_e	=	{ s/s vapour outlet stream vo in exchanger e }
HI_e	=	{ s/s inlet stream hi of the utility heater of module e }
HO_e	=	{ s/s outlet stream ho of the utility heater of module e }
CI_e	=	{ s/s inlet stream ci of the utility cooler of module e }
CO_e	=	{ s/s outlet stream co of the utility cooler of module e }
$LL_{ee'}$	=	{ s/s interconnecting stream from liquid outlet splitter of module e to liquid inlet mixer of module e' }
$LH_{ee'}$	=	{ s/s interconnecting stream from liquid outlet splitter of module e to utility heater of module e' }
LP_{ep}	=	{ s/s interconnecting stream from liquid outlet splitter of module e to final mixer of liquid product p }
$VV_{ee'}$	=	{ s/s interconnecting stream from vapour outlet splitter of module e to vapour inlet mixer of module e' }
$VC_{ee'}$	=	{ s/s interconnecting stream from vapour outlet splitter of module e to utility cooler of module e' }
VP_{ep}	=	{ s/s interconnecting stream from liquid outlet splitter of module e to final mixer of vapour product p }
IL_{ne}	=	{ s/s interconnecting stream from liquid initial stream n to liquid inlet mixer of module e }
IV_{ne}	=	{ s/s interconnecting stream from vapour initial stream n to vapour inlet mixer of module e }
IH_{ne}	=	{ s/s interconnecting stream from liquid initial stream n to utility heater of module e }
IC_{ne}	=	{ s/s interconnecting stream from vapour initial stream n to utility cooler of module e }
IP_{np}	=	{ s/s interconnecting stream from initial stream n to final mixer of product p }

- $HV_{ee'}$ = {s/s interconnecting stream from utility heater of module e
to vapour inlet mixer of module e' }
 HP_{ep} = {s/s interconnecting stream from utility heater of module e
to vapour final mixer of product p }
 $CL_{ee'}$ = {s/s interconnecting stream from utility cooler of module e
to liquid inlet mixer of module e' }
 CP_{ep} = {s/s interconnecting stream from utility cooler of module e
to liquid final mixer of product p }

For this synthesis model we have;

- | | | |
|----------------|------------------------------------|---|
| I , | Set of initial streams | $n = \text{AAcid, MeOH}$ |
| C , | Set of components | $i = \text{AAcid, MeOH, MeAc, H}_2\text{O}$ |
| P , | Set of products | $p = \text{P1, P2}$ |
| E , | Set of modules | $E = E^{sep} \cup E^{ressep}$ |
| E^{sep} , | Set of separation modules | $e^{sep} = 1, \dots, 10$ |
| E^{ressep} , | Set of separation/reaction modules | $e^{ressep} = 11, \dots, 20$ |

The following variables are introduced;

- | | | |
|-----------|--------------------------|---|
| f | molar flowrate | for all superstructure streams |
| x_i | molar fraction | for inlet & outlet streams of e , and p |
| T | temperature | for inlet & outlet streams of e , and p |
| $rate$ | reaction rate per volume | of each module $e \in E^{ressep}$ |
| V | volumetric liquid holdup | of each module $e \in E^{ressep}$ |
| C_{cat} | Catalyst concentration | of each module $e \in E^{ressep}$ |
| P_{tot} | Total system pressure | |

In this example, a total pressure of 1 atm is considered.

In addition for thermodynamic properties:

- | | | |
|-------------|--------------------------|--|
| h | enthalpy | for all inlet and outlet streams of module e |
| γ_i | activity coefficient | for all inlet and outlet streams of module e |
| P_i^{sat} | vapour pressure | for all inlet and outlet streams of module e |
| ρ | density of liquid holdup | for liquid outlet of module e |

The existence (or not) of each module, and the mass transfer direction of each component in the module is denoted by binary variables;

$$y_e = \begin{cases} 1, & \text{if module } e \text{ exists} \\ 0, & \text{otherwise} \end{cases}$$

$$y_{tei} = \begin{cases} 1, & \text{if component } i \text{ in module } e \text{ is transferred from} \\ & \text{liquid to vapour and/or consumed in reaction} \\ 0, & \text{otherwise} \end{cases}$$

Binary variables are also defined to denote the existence (or not) of superstructure streams in the final flowsheet as described in Table D.1. As these variables are not necessary their presence does not increase the combinatorial complexity of the synthesis problem. They are utilised to simplify the solution of the nonlinear part of the superstructure model and to facilitate the introduction of logical constraints to the model.

The mass/heat exchange superstructure model involves:

◇ Mass balance for total stream flows at

- initial stream splitters

$$f_n^I - \sum_e f_{ne}^{IL} - \sum_e f_{ne}^{IH} - \sum_{p \in \text{liq}} f_{np}^{IP} = 0 \quad \forall n \in \text{liquid} \quad (\text{D.1})$$

$$f_n^I - \sum_e f_{ne}^{IV} - \sum_e f_{ne}^{IC} - \sum_{p \in \text{vap}} f_{np}^{IP} = 0 \quad \forall n \in \text{vapour} \quad (\text{D.2})$$

- splitters at the outlets of each side of module e

$$f_e^{LO} - \sum_{e'} (f_{ee'}^{LL} + f_{ee'}^{LH}) - \sum_{p \in \text{liq}} f_{ep}^{LP} = 0 \quad (\text{D.3})$$

$$f_e^{VO} - \sum_{e'} (f_{ee'}^{VV} + f_{ee'}^{VC}) - \sum_{p \in \text{vap}} f_{ep}^{VP} = 0 \quad (\text{D.4})$$

$$f_e^H - \sum_{e'} f_{ee'}^{HV} - \sum_{p \in \text{vap}} f_{ep}^{HP} = 0 \quad (\text{D.5})$$

$$f_e^C - \sum_{e'} f_{ee'}^{CL} - \sum_{p \in \text{liq}} f_{ep}^{CP} = 0 \quad (\text{D.6})$$

- mixers at the inlets of each side of module e

$$f_e^{LI} - \sum_{n \in \text{liq}} f_{ne}^{IL} - \sum_{e'} (f_{e'e}^{LL} + f_{e'e}^{CL}) = 0 \quad (\text{D.7})$$

Variable	Denoting the existence of
yh_e	utility heater prior to vapour inlet of module e
yc_e	utility cooler prior to liquid inlet of module e
$yll_{ee'}$	interconnecting stream from liquid outlet splitter of module e to liquid inlet mixer of module e'
$ylh_{ee'}$	liquid stream from liquid outlet splitter of module e to utility heater of module e'
ylp_{ep}	interconnecting stream from liquid outlet splitter of module e to the final mixer of liquid product stream p
$yvv_{ee'}$	interconnecting stream from vapour outlet splitter of module e to vapour inlet mixer of module e'
$yvc_{ee'}$	vapour stream from vapour outlet splitter of module e to utility cooler of module e'
yvp_{ep}	interconnecting stream from vapour outlet splitter of module e to the final mixer of vapour product stream p
yIl_{ne}	interconnecting stream from liquid initial splitter of stream n to liquid inlet mixer of module e
yIv_{ne}	interconnecting stream from vapour initial splitter of stream n to vapour inlet mixer of module e
yIh_{ne}	interconnecting stream from liquid initial splitter of stream n to utility heater of module e
yIc_{ne}	interconnecting stream from vapour initial splitter of stream n to utility cooler of module e
yIp_{np}	interconnecting stream from initial splitter of stream n to final mixer of product stream p
$yhv_{ee'}$	vapour stream from utility heater of module e to vapour inlet mixer of module e'
yhp_{ep}	interconnecting stream from outlet utility heater of module e to the final mixer of vapour product stream p
$ycl_{ee'}$	interconnecting stream from utility cooler of module e to liquid inlet mixer of module e'
ycp_{ep}	interconnecting stream from outlet utility cooler of module e to the final mixer of liquid product stream p

Table D.1: Structural Variables

$$f_e^{VI} - \sum_{n \in \text{vap}} f_{ne}^{IV} - \sum_{e'} (f_{e'e}^{VV} + f_{e'e}^{HV}) = 0 \quad (\text{D.8})$$

$$f_e^C - \sum_{n \in \text{vap}} f_{ne}^{IC} - \sum_{e'} f_{e'e}^{VC} = 0 \quad (\text{D.9})$$

$$f_e^H - \sum_{n \in \text{liq}} f_{ne}^{IH} - \sum_{e'} f_{e'e}^{LH} = 0 \quad (\text{D.10})$$

- final product mixers

$$f_p^P - \sum_{n \in \text{liq}} f_{np}^{IP} - \sum_e f_{ep}^{LP} - \sum_e f_{ep}^{CP} = 0 \quad \forall p \in \text{liquid} \quad (\text{D.11})$$

$$f_p^P - \sum_{n \in \text{vap}} f_{np}^{IP} - \sum_e f_{ep}^{VP} - \sum_e f_{ep}^{HP} = 0 \quad \forall p \in \text{vapour} \quad (\text{D.12})$$

$$(\text{D.13})$$

◇ Mass Balances for each component at

- mixers prior to liquid and vapour sides and utility exchangers of each module e

$$f_e^{LI} x_{ei}^{LI} - \sum_{n \in \text{liq}} f_{ne}^{IL} x_{ni}^I - \sum_{e'} (f_{e'e}^{LL} x_{e'i}^{LO} + f_{e'e}^{CL} x_{e'i}^C) = 0 \quad (\text{D.14})$$

$$f_e^{VI} x_{ei}^{VI} - \sum_{n \in \text{vap}} f_{ne}^{IV} x_{ni}^I - \sum_{e'} (f_{e'e}^{VV} x_{e'i}^{VO} + f_{e'e}^{HV} x_{e'i}^H) = 0 \quad (\text{D.15})$$

$$f_e^C x_{ei}^C - \sum_{n \in \text{vap}} f_{ne}^{IC} x_{ni}^I - \sum_{e'} f_{e'e}^{VC} x_{e'i}^{VO} = 0 \quad (\text{D.16})$$

$$f_e^H x_{ei}^H - \sum_{n \in \text{liq}} f_{ne}^{IH} x_{ni}^I - \sum_{e'} f_{e'e}^{LH} x_{e'i}^{LO} = 0 \quad (\text{D.17})$$

- final mixer of each product stream

$$f_p^P x_i^P - \sum_{n \in \text{liq}} f_{np}^{IP} x_{ni}^I - \sum_e f_{ep}^{LP} x_{ei}^{LO} - \sum_e f_{ep}^{CP} x_{ei}^C = 0, \quad p \in \text{liquid} \quad (\text{D.18})$$

$$f_p^P x_i^P - \sum_{n \in \text{vap}} f_{np}^{IP} x_{ni}^I - \sum_e f_{ep}^{VP} x_{ei}^{VO} - \sum_e f_{ep}^{HP} x_{ei}^H = 0, \quad p \in \text{vapour} \quad (\text{D.19})$$

$$(\text{D.20})$$

- around each mass/heat exchange block

$$f_e^{LI} x_{ei}^{LI} + f_e^{VI} x_{ei}^{VI} - f_e^{LO} x_{ei}^{LO} - f_e^{VO} x_{ei}^{VO} + \nu_i * \text{rate}_e * V_e = 0 \quad (\text{D.21})$$

◇ Energy balances at

- mixers prior to liquid and vapour sides and utility exchangers of each module e

$$f_e^{LI} h_e^{LI} - \sum_{n \in \text{liq}} f_{ne}^{IL} h_n^I - \sum_{e'} (f_{e'e}^{LL} h_{e'}^{LO} + f_{e'e}^{CL} h_{e'}^{CO}) = 0 \quad (\text{D.22})$$

$$f_e^{VI} h_e^{VI} - \sum_{n \in \text{vap}} f_{ne}^{IL} h_n^I - \sum_{e'} \left(f_{e'e}^{VV} h_{e'}^{VO} + f_{e'e}^{HV} h_{e'}^{HO} \right) = 0 \quad (\text{D.23})$$

$$f_e^H h_e^{HI} - \sum_{n \in \text{liq}} f_{ne}^{IH} h_n^I - \sum_{e'} f_{e'e}^{LH} h_{e'}^{LO} = 0 \quad (\text{D.24})$$

$$f_e^C h_e^{CI} - \sum_{n \in \text{vap}} f_{ne}^{IV} h_n^I - \sum_{e'} f_{e'e}^{VC} h_{e'}^{VO} = 0 \quad (\text{D.25})$$

- around utility exchangers of each module e

$$Qh_e - f_e^H \left(h_e^{HO} - h_e^{HI} \right) = 0 \quad (\text{D.26})$$

$$Qc_e - f_e^C \left(h_e^{CO} - h_e^{CI} \right) = 0 \quad (\text{D.27})$$

- around each mass/heat exchange block e

$$f_e^{LI} h_e^{LI} + f_e^{VI} h_e^{VI} - f_e^{LO} h_e^{LO} - f_e^{VO} h_e^{VO} - \text{rate}_e * V_e * \Delta H_{\text{reac}} = 0 \quad (\text{D.28})$$

where ΔH_{reac} is the heat of reaction

- final mixers of each product stream

$$f^P h^P - \sum_{n \in \text{liq}} f_{np}^{IP} h_n^I - \sum_e f_{ep}^{LP} h_e^{LO} - \sum_e f_{ep}^{CP} h_e^{CO} = 0, \quad p \in \text{liquid} \quad (\text{D.29})$$

$$f^P h^P - \sum_{n \in \text{vap}} f_{np}^{IP} h_n^I - \sum_e f_{ep}^{VP} h_e^{VO} - \sum_e f_{ep}^{HP} h_e^{HO} = 0, \quad p \in \text{vapour} \quad (\text{D.30})$$

$$(\text{D.31})$$

◇ Summation of molar fractions

for superstructure streams $s = LI, LO, VI, VO, C, H, P$

$$\sum_i x_i^s - 1 = 0 \quad (\text{D.32})$$

◇ Phase defining constraints

$$\text{for liquid streams :} \quad 0.8 \leq \sum_i \frac{\gamma_i^s P_i^{\text{sat},s} x_i^s}{P_{\text{tot}}} \leq 1 \quad (\text{D.33})$$

$$\text{for vapour streams :} \quad 0.8 \leq \sum_i \frac{x_i^s P_{\text{tot}}}{\gamma_i^s P_i^{\text{sat},s}} \leq 1 \quad (\text{D.34})$$

◇ Mass transfer driving force constraints for each component

For $e \in E^{\text{sep}}$

$$(y_e + yt_{ei} - 2) \mathcal{U} \leq f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO} \leq (yt_{ei} + 1 - y_e) \mathcal{U} \quad (\text{D.35})$$

$$(y_e + yt_{ei} - 2) \mathcal{U} \leq \gamma_{ei}^{LI} P_{ei}^{\text{sat},LI} x_{ei}^{LI} - x_{ei}^{VO} P_{\text{tot}} \leq (yt_{ei} + 1 - y_e) \mathcal{U} \quad (\text{D.36})$$

$$(y_e + yt_{ei} - 2) \mathcal{U} \leq \gamma_{ei}^{LO} P_{ei}^{\text{sat},LO} x_{ei}^{LO} - x_{ei}^{VI} P_{\text{tot}} \leq (yt_{ei} + 1 - y_e) \mathcal{U} \quad (\text{D.37})$$

For $e \in E^{resep}$

$$(y_e + yt_{ei} - 2) \mathcal{U} \leq f_e^{LI} x_{ei}^{LI} - f_e^{LO} x_{ei}^{LO} \leq (yt_{ei} + 1 - y_e) \mathcal{U} \quad (D.38)$$

$$(y_e + yt_{ei} - 2) \mathcal{U} \leq G_{2ei} \leq (yt_{ei} + 1 - y_e) \mathcal{U} \quad (D.39)$$

$$G_{2ei} = \ln \left[\frac{\gamma_{ei}^{LO} x_{ei}^{LO} P_{ei}^{sat,LO}}{x_{ei}^{VI} P_{tot}} \right] + \sum_i \left[\frac{\nu_i \Delta G_i^f}{RT} + \nu_i \ln(x_{ei}^{VI} P_{tot}) \right] \frac{\partial \epsilon}{\partial n_{ei}} \quad (D.40)$$

where $\partial \epsilon / \partial n_{ei}$ is calculated at conditions of the liquid outlet of each module e and is given by equations (4.48)-(4.51). $\mathcal{U}$ is a (large) positive number. In a nonexisting module, the driving forces are made redundant by imposing

$$yt_{ei} - y_e \geq 1 \quad (D.41)$$

◇ Thermodynamic property calculation

- Reaction rate ;

$$rate_e = f(x_{ei}^{LO}, T_e^{LO}, C_{cat_e}) \quad (D.42)$$

where the rate expression is given by equations (4.39)-(4.41).

- Density ;

$$\rho_e^{LO} = f(x_{ei}^{LO}, T_e^{LO}) \quad (D.43)$$

where the component density correlation is detailed in Appendix A.4 and mixture density is given by ;

$$\frac{1}{\rho_e} = \sum_{i=1}^C \frac{x_{ei}}{\rho_{ei}} \quad (D.44)$$

- Vapour pressure, enthalpy and activity coefficient;

for $s = LI, LO, VI, VO, HI, HO, CI, CO, P$

$$P_{ei}^{sat,s} = f(T^s) \quad (D.45)$$

$$h^s = f(x_{ei}^s, T^s) \quad (D.46)$$

$$\gamma_{ei}^s = f(x_{ei}^s, T^s, P_{tot}) \quad (D.47)$$

Thermodynamic correlations are detailed in Table 4.6

◇ Specifications on desired products and constraints

$$\begin{aligned} f^{P1} &\geq 9.8 \\ x_{MeAc}^{P1} &\geq 0.98 \\ Ccat_e &\leq 0.02 \end{aligned}$$

◇ Logical constraints

- to define the existence of each module of each superstructure stream

$$\left[f_e^{LI} + f_e^{LO} + f_e^{VI} + f_e^{VO} \right] - y_e \mathcal{F}^{max} \leq 0 \quad (D.48)$$

$$f_e^H - y h_e \mathcal{F}^{max} \leq 0 \quad (D.49)$$

$$f_e^C - y c_e \mathcal{F}^{max} \leq 0 \quad (D.50)$$

$$Q h_e - y h_e \mathcal{Q}^{max} \leq 0 \quad (D.51)$$

$$Q c_e - y c_e \mathcal{Q}^{max} \leq 0 \quad (D.52)$$

where $\mathcal{F}^{max}$ is an upper bound to stream flows and $\mathcal{Q}^{max}$ is an upper bound to heat flows.

- to ensure that utility exchangers exist only if the module exists

$$y h_e - y_e \leq 0 \quad (D.53)$$

$$y c_e - y_e \leq 0 \quad (D.54)$$

- to ensure that if a module exists there will be an inlet flow

$$y_e - \left[\sum_{n \in liq} y I l_{ne} + \sum_{e'} y l l_{e'e} + \sum_{e'} y c l_{e'e} \right] \leq 0 \quad (D.55)$$

$$y_e - \left[\sum_{n \in vap} y I v_{ne} + \sum_{e'} y v v_{e'e} + \sum_{e'} y h v_{e'e} \right] \leq 0 \quad (D.56)$$

$$y h_e - \left[\sum_{n \in liq} y I h_{ne} + \sum_{e'} y l h_{e'e} \right] \leq 0 \quad (D.57)$$

$$y c_e - \left[\sum_{n \in vap} y I c_{ne} + \sum_{e'} y v c_{e'e} \right] \leq 0 \quad (D.58)$$

- to ensure that if a module exists there will be an outlet flow

$$y_e - \left[\sum_{e'} y l l_{ee'} + \sum_{e'} y l h_{ee'} + \sum_{p \in liq} y l p_{ep} \right] \leq 0 \quad (D.59)$$

$$y_e - \left[\sum_{e'} y_{vv_{ee'}} + \sum_{e'} y_{vc_{ee'}} + \sum_{p \in \text{vap}} y_{vp_{ep}} \right] \leq 0 \quad (\text{D.60})$$

$$yh_e - \left[\sum_{e'} y_{hv_{ee'}} + \sum_{p \in \text{vap}} y_{hp_{ep}} \right] \leq 0 \quad (\text{D.61})$$

$$yc_e - \left[\sum_{e'} y_{cl_{ee'}} + \sum_p y_{cp_{ep}} \right] \leq 0 \quad (\text{D.62})$$

- to ensure at least one feed point per initial stream

$$1 - \left[\sum_e y_{Il_{ne}} + \sum_e y_{Ih_{ne}} + \sum_{p \in \text{liq}} y_{Ip_{np}} \right] \leq 0, n \in \text{liquid} \quad (\text{D.63})$$

$$1 - \left[\sum_e y_{Iv_{ne}} + \sum_e y_{Ic_{ne}} + \sum_{p \in \text{vap}} y_{Ip_{np}} \right] \leq 0, n \in \text{vapour} \quad (\text{D.64})$$

- to ensure at least one source per product

$$1 - \left[\sum_{n \in \text{liq}} y_{Ip_{np}} + \sum_e y_{lp_{ep}} + \sum_e y_{cp_{ep}} \right] \leq 0, n \in \text{liquid} \quad (\text{D.65})$$

$$1 - \left[\sum_{n \in \text{vap}} y_{Ip_{np}} + \sum_e y_{vp_{ep}} + \sum_e y_{hp_{ep}} \right] \leq 0, n \in \text{vapour} \quad (\text{D.66})$$

- to constrain the number of streams allowed at existing mixers

$$\left[\sum_{n \in \text{liq}} y_{Il_{ne}} + \sum_{e'} y_{ll_{e'e}} + \sum_{e'} y_{cl_{e'e}} \right] - y_e N_{\text{mix}}^{\text{max}} \leq 0 \quad (\text{D.67})$$

$$\left[\sum_{n \in \text{vap}} y_{Iv_{ne}} + \sum_{e'} y_{vv_{e'e}} + \sum_{e'} y_{hv_{e'e}} \right] - y_e N_{\text{mix}}^{\text{max}} \leq 0 \quad (\text{D.68})$$

$$\left[\sum_{n \in \text{liq}} y_{Ih_{ne}} + \sum_{e'} y_{lh_{e'e}} \right] - y_h N_{\text{mix}}^{\text{max}} \leq 0 \quad (\text{D.69})$$

$$\left[\sum_{n \in \text{vap}} y_{Ic_{ne}} + \sum_{e'} y_{vc_{e'e}} \right] - y_c N_{\text{mix}}^{\text{max}} \leq 0 \quad (\text{D.70})$$

- to constrain the number of splits allowed at existing splitters

$$\left[\sum_{e'} y_{ll_{ee'}} + \sum_{e'} y_{lh_{ee'}} + \sum_{p \in \text{liq}} y_{lp_{ep}} \right] - y_e N_{\text{split}}^{\text{max}} \leq 0 \quad (\text{D.71})$$

$$\left[\sum_{e'} y_{vv_{ee'}} + \sum_{e'} y_{vc_{ee'}} + \sum_{p \in \text{vap}} y_{vp_{ep}} \right] - y_e N_{\text{split}}^{\text{max}} \leq 0 \quad (\text{D.72})$$

$$\left[\sum_{e'} y_h v_{ee'} + \sum_{p \in vap} y_h p_{ep} \right] - y_e N_{split}^{max} \leq 0 \quad (D.73)$$

$$\left[\sum_{e'} y_{cl} e_{e'} + \sum_p y_{cp} e_p \right] - y_e N_{split}^{max} \leq 0 \quad (D.74)$$

- to constrain the number of splits allowed at initial splitters

$$\left[\sum_e y_{Il} n_e + \sum_e y_{Ih} n_e + \sum_{p \in liq} y_{Ip} n_p \right] - N_{split}^{max} \leq 0, n \in \text{liquid} \quad (D.75)$$

$$\left[\sum_e y_{Iv} n_e + \sum_e y_{Ic} n_e + \sum_{p \in vap} y_{Ip} n_p \right] - N_{split}^{max} \leq 0, n \in \text{vapour} \quad (D.76)$$

- to constrain the number of product sources

$$\left[\sum_{n \in liq} y_{Ip} n_p + \sum_e y_{lp} e_p + \sum_e y_{cp} e_p \right] - N_{mix}^{max} \leq 0, n \in \text{liquid} \quad (D.77)$$

$$\left[\sum_{n \in vap} y_{Ip} n_p + \sum_e y_{vp} e_p + \sum_e y_{hp} e_p \right] - N_{mix}^{max} \leq 0, n \in \text{vapour} \quad (D.78)$$

Bounding the maximum number of stream splits and stream mixers allowed at splitters and mixers constrains the problem, aiding the solution. $N_{mix}^{max} = N_{split}^{max} = 5$ is utilised and is relaxed when the constraint is active. Note that placing an upper and lower bound on the number of mixers and splitters allowed at existing modules also ensures that interconnecting streams only exist if the corresponding modules exist.

- non-redundancy constraints

$$y_{e+1} - y_e \leq 0 \quad e \in E^{sep} \quad (D.79)$$

$$y_{e+1} - y_e \leq 0 \quad e \in E^{resep} \quad (D.80)$$

◇ Objective Function

Three objective functions are investigated;

- Utility cost and constant module cost

$$Z = \sum_e C_c * Qc_e + \sum_e C_h * Qh_e + \sum_e C^{mod} * y_e \quad (D.81)$$

- Utility and feed cost, and constant module cost

$$\begin{aligned}
 Z &= \sum_e C_c * Q_{c_e} + \sum_e C_h * Q_{h_e} + \sum_e C^{mod} * y_e \\
 &+ C_{AAcid} * f_{AAcid}^I + C_{MeOH} * f_{MeOH}^I
 \end{aligned} \tag{D.82}$$

- Utility and feed cost and variable module cost

$$\begin{aligned}
 Z &= \sum_e C_c * Q_{c_e} + \sum_e C_h * Q_{h_e} + \sum_e Cost_e * y_e \\
 &+ C_{AAcid} * f_{AAcid}^I + C_{MeOH} * f_{MeOH}^I
 \end{aligned} \tag{D.83}$$

$$\tag{D.84}$$

where

$$Cost_e = 316.435 \left(\frac{MW^{VI}}{\rho_e^{VI}} \right) \sqrt{f_e^{VI}} H_e^{0.802} \tag{D.85}$$

$$H_e = 2 + \frac{4V_e}{\pi D_e^2} \tag{D.86}$$

$$D_e = 0.98424 \sqrt{f_e^{VI}} \left(\frac{MW^{VI}}{\rho_e^{VI}} \right)^{0.25} \tag{D.87}$$

$$\rho_e = \frac{P_{tot}}{R_{gas} T_e^{VI}} \tag{D.88}$$

Addendum to Thesis

Driving Force Constraints

As detailed in section 2.6, mass transfer between two streams $S1$ and $S2$ at the same constant T and P will occur when

$$d(nG)_{T,P}^{tot} \leq 0$$

For the case of an increase or decrease in the molar component of i in stream $S1$, it holds that

$$\begin{aligned} dn_i^{S1} &\leq 0 & dn_i^{S1} &\geq 0 \\ \left[\frac{\partial(nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P} &\geq 0 & \left[\frac{\partial(nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P} &\leq 0 \end{aligned}$$

For a *differential* element, it holds that

$$\begin{aligned} dn_i^{S1} &\leq 0 & dn_i^{S1} &\geq 0 \\ F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} x_{out,i}^{S1} &\geq 0 & F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} x_{out,i}^{S1} &\leq 0 \end{aligned}$$

And thus the *conjecture* is proposed that in general, mass transfer between the two streams is consistently limited by equation (2.8), *i.e.*

$$\left[F_{in}^{S1} x_{in,i}^{S1} - F_{out}^{S1} x_{out,i}^{S1} \right] \left[\frac{\partial(nG)^{tot}}{\partial n_i^{S1}} \right]_{T,P} \geq 0$$

For mass transfer within a module, this expression is not rigorously derived and is not strictly true as a module is not a differential element - therefore there may be a spatial distribution of mass transfer within it. The inlet and outlet stream temperature through the module are in general different, and thus a temperature profile may exist within the module. Mass transfer within the module may thus not necessarily occur at one constant temperature. This approximation is alleviated when a small amount of mass transfer occurs within the module *i.e.* by increasing the number of modules for a given mass transfer pattern.

By constraining the mass transfer at the conditions at the ends of the module, it is found that this approximation (as applied in section 3.4 and 4.5) holds for the example problems considered within this thesis. For a more rigorous proof of the mass transfer driving force constraints, a spatially distributed mass transfer may be considered, and is a subject for future work.