UNIVERSITY OF EDINBURGH THESIS

Author (surname, initials): Abdul Manan, Z. Degree: Ph.D Year: 1998

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Process Synthesis for Waste Minimisation With Emphasis on the Synthesis of Cleaner and Cost Effective Distillation Sequences For Azeotropic Mixtures

[redacted]

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1998

Declaration

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Zainuddin Abdul Manan
Edinburgh
March, 1998

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Abstract

Waste minimisation, also known as pollution prevention, includes all activities to avoid, eliminate or lessen waste generation and release of pollutants to the environment. It encompasses not only safe onsite treatment practices but also addresses the root causes of waste generation, which include inefficient use of raw materials, energy and process solvents, and inefficient or inadequate recycling. The lack of emphasis on systematic elimination, reduction and recycling of waste during the *design stage* has motivated us to: (1) develop new tools for waste minimisation that can be integrated in a process design and synthesis environment, and (2) create a design and synthesis methodology that is conducive to opportunistic recycling between the reaction and separation sections. In this context, the main emphasis of this thesis is the development of a procedure for *synthesis of cleaner and cost effective distillation sequences for azeotropic mixtures.* This procedure is primarily based on reasoning over the geometric features of azeotropic mixtures ternary diagram known as *residue curve map (RCM).* This thesis offers significant contributions in two different but related areas. The major developments and new insights associated with each area are:

1. *Reaction-separation interactions.*
A *waste minimisation approach* to process design that promotes opportunistic recycling and includes a systematic technique for designing a recycle network in the context of an overall process.

2. *Azeotropic separation systems.*
a. A novel geometric approach for synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing. Important insights include:

- a geometric approach for synthesizing and screening the alternative separation sequences which results in a catalogue pairing the RCMs of the ternary systems with their most promising separation sequences.
- a novel procedure for entrainer minimisation for azeotropic distillation sequences.

- new evidences linking the *type of separation sequence, the azeotropic column feed-stage location* and *the volatility of an entrainer* with the separability of homogeneous azeotropic mixtures. These findings conclusively explain the peculiar dependencies of the separability of homogeneous azeotropic mixtures on the reflux ratio and the number of stages.

b. A geometric approach for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures which enables the graphical prediction of the *absolute minimum number of units, the region and the point of desirable entrainer flowrate, the optimum decanter tie line position, and the distillate composition for the entrainer recovery column.*

c. Guidelines for exploiting feed composition flexibility to improve azeotropic separation based on a novel geometric approach. Important insights include:

- the significance of the binary, ternary and desirable ternary feed compositions, and a procedure to achieve the desirable ternary feed composition.
- the development of a selection catalogue for feed preconcentration based on a novel geometric approach.
- the use of mixing and recycling for grassroot design and retrofit.

The achievement of minimum-waste designs often also results in cheaper azeotropic distillation sequences as a consequence of reduced capacity and lower effluent treatment costs. As the technique is primarily based on geometric reasoning and heuristics, these results can be achieved at the expense of minimum computations, thus making the approach particularly appropriate during the early stages of design.

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Chapter 1

Introduction

Efforts to improve the design and operation of chemical plants have intensified in the recent years with increased pressure on process industries to reduce pollution. Until the beginning of this decade, most chemical process industries (CPI) have relied on end-of-pipe treatment to reduce their wastes. However, the focus has now shifted towards waste minimisation. Waste minimisation, also known as pollution prevention, includes all activities to avoid, eliminate or lessen waste generation and release of polutants to the environment. It encompasses not only safe onsite treatment practices but also addresses the root causes of wastes which include inefficient use of raw materials, energy and process solvents, and inefficient or inadequate recycling.

Waste minimisation can often provide waste reductions comparable to (and sometimes greater than) those obtainable with end-of-pipe treatment. Even if waste minimisation cannot reduce wastes as much as end-of-pipe treatment, it can usually achieve a significant portion of the benefit at a much lower cost, and then even if further waste reductions are required, these can be achieved using conventional control with the advantage that they are applied to a smaller waste stream (see Figure 1.1). Thus, apart from helping the environment, waste minimisation can also yield numerous other benefits from

- increased production efficiency and reduced capital and operating costs

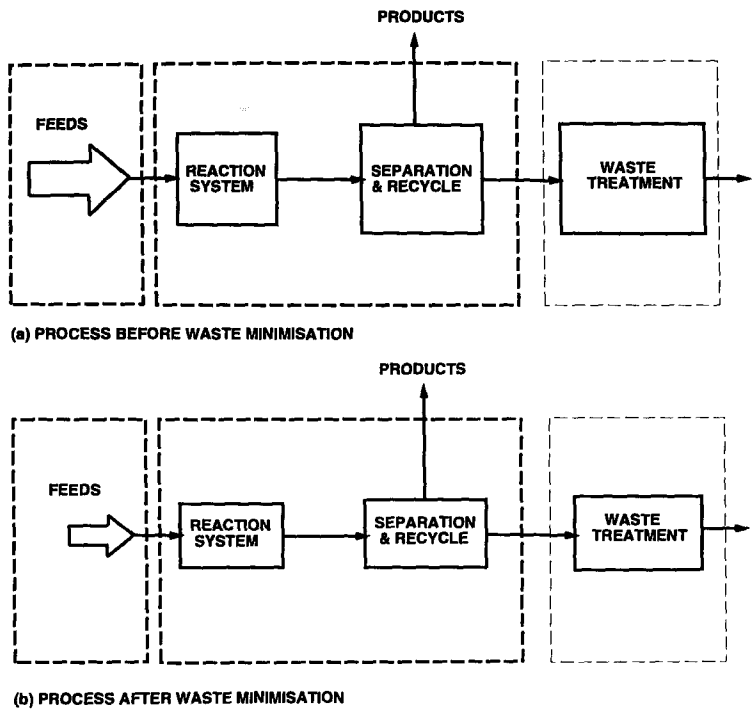


Figure 1.1: Waste minimisation can help achieve the dual benefit of lower effluent treatment costs and lower raw material costs. Process (a) before and (b) after waste minimisation [1].

- decreased liability
- decreased regulatory burden
- improved public attitude towards company
- improved health and safety for employees

Total elimination of waste is the ultimate goal of cleaner process designs. Unfortunately it is not always possible to eliminate waste completely. So, it is necessary to try to reduce its generation by making changes in process operations. After reduction, the remaining wastes can either be reused or treated in order to prevent or control their release to the environment. Figure 1.2 shows the hierarchy of waste management practices [3,4]. Waste minimisation is concerned with the *first, second and third* level of the hierarchy [4]. The significance of each level of the hierarchy will be described in detailed in Chapter 3 of this thesis.

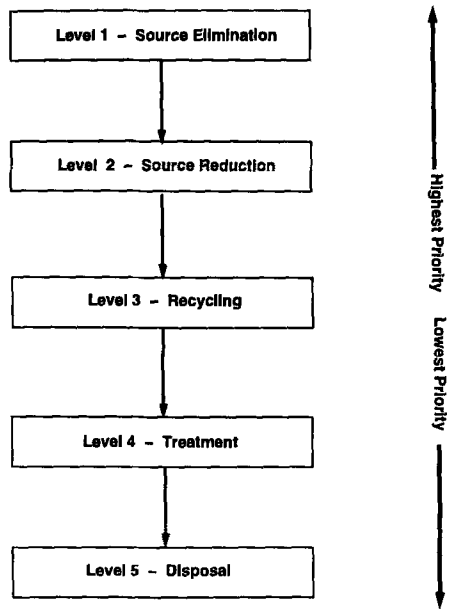


Figure 1.2: Hierarchy of waste management practices.

In line with the CPI progress on pollution prevention, and in the pursuit of cleaner processes, the majority of researches have focused on the development of end-of-pipe waste treatment technologies and on the use of environmental assessment as well as good housekeeping techniques to reduce process wastes[5-9], corresponding to the fourth and fifth levels of the hierarchy in Figure 1.2. Life cycle analysis (LCA) is a powerful and widely used assessment technique which consists of three components: a compilation of a waste inventory, an impact assessment, and an improvement analysis [10]. LCA can help designers assess the impacts of waste reduction options but they are time consuming, costly and typically require large amounts of detailed data which are seldom available during the early stages of design. Good housekeeping techniques involve operational improvements or administrative changes that can often be implemented relatively quickly but usually result in relatively smaller waste reductions as compared to technological changes.

In general, it is better to avoid waste generation during the design stages than to modify a process once it has been installed. To date, a number of proposals related to waste minimisation during the design stage have been developed, with the majority being focused on improving the raw materials efficiency and minimising the selectivity

losses in the reaction systems (refer to work by Glasser[11], Conti[12], Omtveit *et al.*[13,14] and Flower *et al.*[15]). Douglas extended his hierarchical design procedure to accomodate pollution considerations during the design stage[16]. Insights on the pollution prevention measures are, however, being left for designers to explore. El-Halwagi *et al.* developed the Mass Exchange Network (MEN) procedure that enables solvent usage in mass exchange operations to be minimised[17–19]. As far as improving the environmental performance of existing plants through retrofit, it has been found that many waste reduction measures proposed involve various forms of recycling[20–23], suggesting that recycling may well have received much less attention during the design stage than other waste reduction options from the other levels of the waste minimisation hierarchy of Figure 1.2.

Many designers regard stream recycling as a routine design exercise. It is easy to confuse recycle optimisation with *creative recycling.* The former involves a search for the best design parameter(s) for a given reactor-separator-recycle structure and is a relatively well established concept as mentioned in the previous studies made on reactor optimisation[11–15]. The latter, which is concerned with *finding alternative ways* to recycle has so far received very little attention during process design. The term *opportunistic recycling* will henceforth be used to reflect the creative aspect of recycling. It essentially refers to recycle exploration and exploitation and may result in waste elimination in addition to its traditional role of reducing the amount of waste being released to the environment.

The lack of emphasis on recycle exploration during process design is one of the prime reasons for its popularity during retrofit to minimise waste. Moreover, recycling involves relatively minor modifications i.e. small capital investments, hence it is easier to implement. Better opportunities and greater benefits for recycle exploration and exploitation can be anticipated during grassroots design as compared to retrofit since at an early stage, a process is not constrained to any particular design structure.

There are two motivations for this research:

1. to develop new tools for waste minimisation that can be applied within a process synthesis environment, and

2. to identify the issues for the creation of a synthesis environment that is conducive to opportunistic recycling, in addition to source elimination and reduction.

Both elements have been missing from Douglas' hierarchical design procedure[24]. In this context, the main emphasis of this thesis is the development of a procedure for synthesis of cleaner and cost effective distillation sequences for azeotropic mixtures. These procedures are based on geometric reasoning (an analysis of the azeotropic mixture thermodynamic properties that is built in the geometry of its ternary diagram known as *residue curve map* (RCM)) and heuristics derived from process simulation. The development of a process synthesis model that promotes opportunistic recycling, discussed in Chapter 3 of this thesis, plays a relatively minor role in this research.

With the work on waste minimisation covering the *reaction-separation interactions* and *azeotropic separation systems*, this thesis offers significant contributions in two different but related areas. Many new insights accompany the following major developments:

1. Reaction-separation interactions.

   - a process design procedure that promotes waste minimisation through opportunistic recycling.

2. Azeotropic separation systems.

   - a geometric and heuristic approach for synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing.
   - a geometric approach for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures.
   - guidelines for exploiting feed composition flexibility to improve separation and to reduce waste in the separation of azeotropic mixtures, which are applicable for grassroot design and retrofit.

The dissertation begins with a review of the literature on waste minimisation in general and an analysis of the work related to opportunistic recycling and waste minimisation for agent-based separation systems. A significant part of the review covers the work on synthesis of distillation sequences for azeotropic mixtures. Chapter 3 discusses the positions of the different classes of recycling techniques in the waste minimisation hierarchy and proposes some modifications and extensions to the Douglas hierarchical design procedure to promote opportunistic recycling. The final section of chapter 3 presents a case study which implements the opportunistic recycling procedure, resulting in the dual benefits of reduced waste and improved separation.

Chapters 4 and 5 focus on the development of a novel geometric approach for synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing. The new insights which have emerged from the studies can be summarized as follows:

- a geometric approach for synthesizing and screening the alternative separation sequences. This approach exploits valuable information extractable from the RCM which include the boiling points of pure components and azeotropes, the binary feed composition, the alternative separation structures and the relative quantity of entrainer for the purpose of synthesis and screening.
- a novel procedure for entrainer minimisation in the distillation sequences for separating the azeotropic mixtures mentioned. The procedure is also expected to be extendable to heterogeneous azeotropic systems. The minimum entrainer flowrate is used together with the most promising sequence in order to generate cleaner and cost effective distillation sequences for azeotropic mixtures.
- new evidences linking the type of separation sequence, the azeotropic column feedstage location and the volatility of an entrainer with the separability of homogeneous azeotropic mixtures. These findings conclusively explain the peculiar dependencies the separability of homogeneous azeotropic mixtures on the reflux ratio and the number of stages.
- generation of a catalogue pairing the RCMs of the ternary systems with the most

promising separation sequences. This catalogue, which covers a wide range of homogeneous mixtures enables a designer to identify the most promising separation sequence ahead of design.

Chapter 6 decribes a geometric approach for the synthesis of cleaner and cost effective distillation sequences for heterogeneous azeotropic mixtures. In addition to the properties relevant for homogeneous mixtures, this approach also exploits the essential RCM properties for heterogeneous mixtures[1] for synthesizing and screening the alternative separation sequences. These properties enable us to graphically predict the *absolute minimum number of units, the region and the point of desirable entrainer flowrate, the optimum decanter tie line position, and the distillate composition for the entrainer recovery column.*

The questions of when and how to exploit the feed composition flexibility to further improve the separation of azeotropic mixtures are addressed in Chapter 7. The development of a selection catalogue for feed preconcentration has been the major breakthrough in this chapter. This catalogue is developed based on a novel geometric approach that considers the effect of entrainer reduction and typical binary feed compositions. Other important new insights in Chapter 7 include:

- the significance of the binary, ternary and desirable ternary feed compositions, and a procedure to achieve the desirable ternary feed composition based on geometric reasoning.
- the use of mixing and recycling in grassroot design and retrofit of distillation sequences for azeotropic mixtures.

Figure 1.3 illustrates the conceptual links which exist between the chapters in the thesis.

In the bid to achieve favourable economics and environmental friendliness, it must be emphasized that no claim will be made for the final solution to represent the global

[1]these RCM properties include the nature of the binary and ternary azeotropes, distillation boundaries, liquid-liquid heterogeneous envelopes and the orientation and length of the heterogeneous tie lines.

economic optimum. However, the achievement of minimum-waste designs often also results in cheaper azeotropic distillation sequences as a consequence of reduced capacity and lower effluent treatment costs. As the technique is primarily based on geometric reasoning and heuristics, these results can be achieved at the expense of minimum computations, thus making the approach particularly appropriate during the early stages of design.

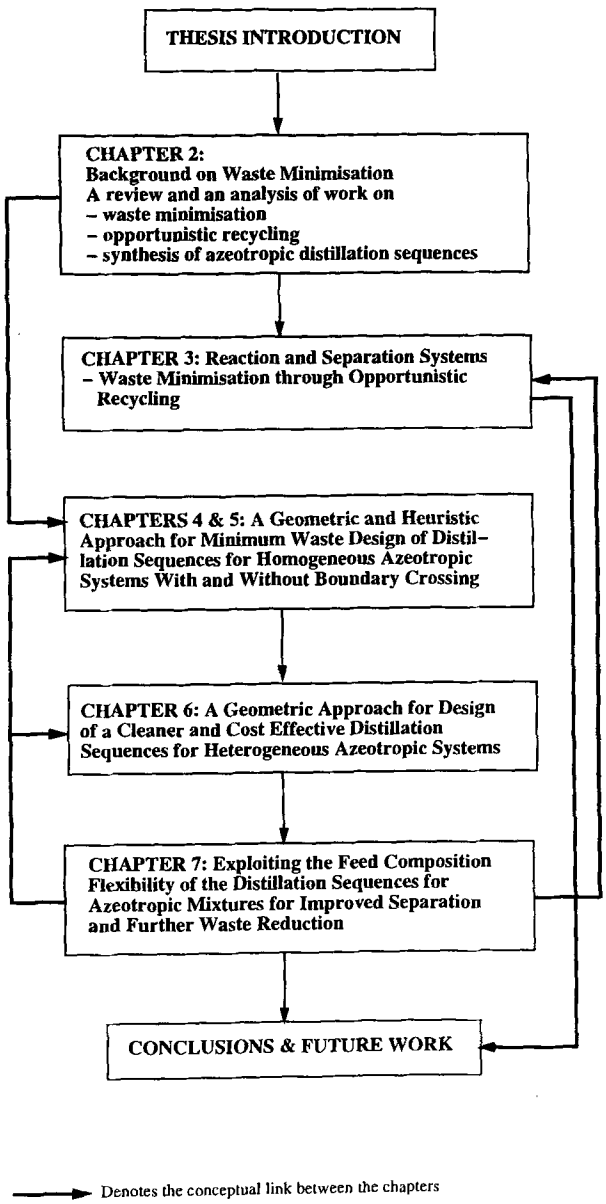


Figure 1.3: A flow diagram illustrating the conceptual links between the thesis chapters.

While it is hoped that these procedures can be of immediate use to those working towards cleaner as well as economical reaction-separation and azeotropic separation systems design, it also represents a step towards the development of more comprehensive waste minimisation approach covering the vast area of reaction and separation systems. With these in mind, the thesis concludes by pointing out possible directions of future work aimed at creating tools for waste minimisation in the reaction and heterogeneous azeotropic separation systems in particular, and other agent based separation systems in general.

Chapter 2

Background on Waste Minimisation

The majority of researches on pollution prevention have focused on the development of waste treatment technologies, environmental assessment and auditing methodologies [5-9]. Relatively little work is concerned with the systematic elimination, reduction and recycling of waste during the design stage. The development of systematic design techniques for pollution prevention covers four main areas - reactor design, overall synthesis procedure, separation synthesis and general retrofit of existing processes. The literature review in this chapter focuses on the development of systematic techniques for pollution prevention with specific highlights on the research emphasis for reactor waste prevention (Section 2.1), process synthesis for waste minimisation (Section 2.2), the techniques for retrofit to minimise waste (Section 2.3) and waste minimisation for agent-based separation processes (Section 2.4). Section 2.5 highlights the main contributions of this thesis.

2.1 Waste minimisation in the reaction systems

Research on reactor waste prevention is focused on improving materials efficiency and minimising selectivity losses. Efficient raw material usage can save capital and operating costs and reduce wastes generated from unwanted side reactions. The keys to improving raw material efficiency are improved conversion and selectivity. Both parameters are influenced by the type of reaction (kinetic or equilibrium controlled), choice

of reactor, operating conditions and reactor inlet and outlet concentrations. Hopper *et al.*[25] investigated the effects of choosing different reactor types and operating conditions on the selectivity of acrylonitrile production by means of process simulations. In other earlier studies, Conti [12] suggested that the optimum economic conversion for a process is typically bounded by conversion values giving maximum yield and maximum selectivity. Omtveit *et al.*[13,14,26] extended the idea of *attainable region* in concentration space[11] to search for optimum economic reactor-separator-recycle systems. This earlier work provided the basis for a modular mass-balance targeting approach for reactor and separator subsystems subject to environmental constraints (e.g. purge concentration limits and waste treatment costs) proposed by Flower *et al.*[15]. The modular approach employs the powerful graphical attainable region technique to search for optimal reactor outlet composition for systems with a maximum of four components. Optimisation for the modular approach is based on a fixed reactor-separator-recycle structure and sharp separations producing virtually pure products.

2.2 Process synthesis for waste minimisation

In preventing waste for *overall process design*, Douglas extended his hierarchical design procedure to include pollution considerations during the process synthesis stage [16,24]. A design is developed by proceeding through different levels of design abstractions while additional details are added at each level. To achieve the goal of waste minimisation, the idea is to identify potential pollution problems as design is developed, and make decisions not to introduce materials, chemistry, process conditions or techniques that could cause adverse environmental impact at each level of the design hierarchy. The different waste prevention alternatives are however left for designers to explore. Note that some alternatives related to material, chemistry and technological changes as proposed by Douglas may not be readily available hence are not always easy to implement.

2.3 Retrofit to minimise waste in existing processes

Retrofit guidelines and applications related to waste minimisation have been more widely reported [20–23]. Fonyo et al. [21] implemented the Douglas hierarchical approach to improve the environmental performance for a total of 26 existing sites. Results from the retrofit applications consistently point towards recycling as a popular means of reducing waste on existing plants, many of which are modern sites. As far as it could be identified, the only study that compares different recycle alternatives within a continuous process is found in Wahnschafft *et al.*[27] who study three cases of recycling to improve the performances of complex separation systems. *Primary recycling* improves separation through reduction in the number of required separation steps, *secondary recycling* eliminates redundant splits once the desired products are obtained, while *range extending recycling* enables operation at the absolute minimum number of units.

As will be shown in Chapters 3 and 7, the full benefits of the separation-enhancing recycles, however, cannot be realised when they are confined to the separation system. We also expect better opportunities and greater benefits for recycle exploration and exploitation (opportunistic recycling) during grassroots design as compared to retrofit since, at an early stage, a process is not constrained to any particular design structure. Moreover, recycling involves relatively minor modifications i.e. smaller capital investment, and hence is easier to implement. In bringing waste minimisation to the front end of the design process, it is also important to create an enviroment for process design that not only encourages source elimination or reduction but also is conducive to opportunistic recycling. In order to achieve this goal, we have proposed in Chapter 3 some modifications and extensions to the well established hierarchical design procedure developed by Douglas.

2.4 Waste minimisation for agent-based separation processes

Efforts to minimise effluent waste from separation processes have so far focused on processes which employ only mass separating agent (MSA)[1] to facilitate separation. For examples, El-Halwagi *et al.*[17–19] developed the Mass Exchange Network (MEN) procedure for systematic design of solvent recycle and reuse networks. Their aim is to minimise the solvent usage and capital investment for mass exchange operations such as liquid-liquid extraction, absorption, adsorption and ion-exchange. The same concept is later used by Wang and Smith on a more specific class of MEN problem involving only one lean stream, namely water[28]. As far as it could be found, this is the first study on waste minimisation for azeotropic distillation, a separation process which simultaneously employs mass *and* energy separating agents (ESA). One of our aims is towards the *cost-effective minimisation of the entrainer flowrate* for azeotropic distillation sequences. As a result, we have made a number of important findings in the areas of synthesis and optimisation of distillation sequences for azeotropic mixtures as well.

To date, research related to the *optimisation* of distillation sequences for azeotropic mixtures is very limited when compared to the extensive work done for zeotropic mixtures. Knight and Doherty[29], Ryan and Doherty[30], Pham and Doherty[31–33], Stichlmair et al.[34,35], Laroche et al.[36–38] and Wahnschafft et al.[27] provide the most recent contributions in the area of *synthesis* of separation sequences for azeotropic mixtures.

Knight and Doherty formulate a systematic procedure involving the numerical optimisation of entrainer to feed ratio for a homogeneous azeotropic mixture. They generalized that the procedure is applicable to nonideal and azeotropic separations even though it was applied only for the extractive distillation of the ethanol-water-ethylene glycol (high boiling entrainer) mixture. The procedure is later used with slight modifications by Knapp and Doherty [2] during the heat integration of the distillation columns for separating homogeneous azeotropic mixtures. However, their case studies are also

[1] i.e., an added stream, e.g. a solvent.

restricted to extractive distillation processes. Laroche et al., who use the optimum entrainer to feed ratio as one of the criteria for entrainer selection, extend the use of the entrainer optimisation procedure to other homogeneous azeotropic mixtures which do not introduce new azeotropes[38]. Ryan and Doherty[30] propose a useful technique involving numerical optimisation of the design and operating parameters for several alternative separation sequences for the ethanol-water-benzene (high boiling entrainer) heterogeneous azeotropic mixture.

Stichlmair and Herguijuela[39] focus their discussions on the basic concepts concerning the separation regions, entrainer selection and the resulting separation sequences for azeotropic mixtures without residue curve boundary crossing. Laroche *et al.*[36–38] provide some useful guidelines for selecting the entrainers for the separation of homogeneous azeotropic mixtures which do not introduce new azeotropes, and report how some unusual behaviours shown by these mixtures may affect entrainer selection. In another study, they also state the necessary conditions for separability of homogeneous azeotropic mixtures that use one, two, or three columns and discuss the synthesis of separation sequences for these mixtures. Their studies discuss separation synthesis in the context of entrainer selection but do not provide guidelines for screening between the alternative separation sequences. Among others, Wahnschafft *et al.*[27] assume that azeotropic mixtures generally result in a large number of separation sequences. The latter propose an automated approach for the synthesis of complex separation processes including heterogeneous azeotropic distillation.

From the abovementioned studies associated with the synthesis of distillation sequences for azeotropic mixtures, a number of issues remain unresolved:

1. Our analysis reveals that the procedures for optimisation of distillation sequences for azeotropic mixtures have so far been applied to homogeneous systems which do not introduce new azeotropes and only to the class of heterogeneous mixtures that is similar to the ethanol-water-benzene system. In Chapter 4, we explain under which conditions an entrainer minimisation procedure can be applied to more complex homogeneous systems. A geometric approach for the synthesis of cost

effective distillation sequences for heterogeneous systems is described in Chapter 6. From our literature survey we have found no evidence to support or disclaim that results from the optimisation studies performed by Knight and Doherty[29] as well as by Ryan and Doherty[30] are applicable to other types of homogeneous and heterogeneous mixtures. In view of the peculiarities of azeotropic mixtures, it is felt as important to show if these procedures can indeed be extended to more complex homogeneous and other heterogeneous systems.

2. We also question the need to automate the synthesis of the some complex separation processes as proposed by Wahnschafft *et al.*[27]. In Chapters 4 and 5, we show that it could be expensive and inefficient to search for the entire solution space to automate the synthesis of sequences for homogeneous azeotropic systems for which only a fixed and limited number of alternative sequences exist. We also show that, by geometric reasoning, it is possible to generate *every* desirable separation sequence for some common classes of homogeneous azeotropic mixture and to produce a catalogue of classes of homogeneous mixtures with their corresponding most promising separation sequences.

3. Other than conducting rigorous economics assessments, no guideline is available for eliminating inferior column sequences from alternative separation trains of homogeneous and heterogeneous azeotropic mixtures. As a result, designers often have to evaluate the economics of *every conceivable sequence* in order to find the most promising one. Such a task may prove very time consuming, for instance, when a number of different entrainers are being evaluated and a few separation options exist for each type of entrainer.

2.5 Contributions

With the work on waste minimisation covering the *reaction-separation interactions* and *azeotropic separation systems*, this thesis offers significant contributions in two different but related areas. The important developments and new insights associated with each area are summarized as follows:

Reaction-separation interactions.

1. *A waste minimisation approach to process design (Chapter 3).*

This approach provides an environment for process synthesis design that not only encourages source elimination and reduction, but is also conducive to opportunistic recycling. The approach includes a procedure for designing a recycle network in the context of an overall process.

Azeotropic separation systems.

1. *A novel geometric approach for synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing (Chapters 4 and 5). Important insights include:*

- a geometric approach for synthesizing and screening the alternative separation sequences. This approach exploits valuable information that can be extracted from the RCM which includes the boiling points of pure components and azeotropes, the binary feed composition, the alternative separation structures and the relative quantity of entrainer for the purpose of synthesis and screening.
- generation of a catalogue pairing the RCMs of the ternary systems with the most promising separation sequences.
- a novel procedure for entrainer minimisation in the distillation sequences for separating the azeotropic mixtures mentioned. The procedure is also expected to be extendable to heterogeneous azeotropic systems. The minimum entrainer flowrate is used together with the most promising sequence in order to generate cleaner and cost effective distillation sequences for azeotropic mixtures.
- new evidences linking the type of separation sequence, the azeotropic column feedstage location and the volatility of an entrainer with the separability of homogeneous azeotropic mixtures. These findings conclusively explain the peculiar dependencies of the separability of homogeneous azeotropic mixtures on the reflux

ratio and the number of stages.

2. *A geometric approach for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures (Chapter 6).*

A geometric approach for synthesizing and screening the alternative separation sequences. In addition to the properties relevant for homogeneous mixtures, this approach also exploits the essential RCM properties for heterogeneous azeotropic mixtures which include the nature of the binary and ternary azeotropes, distillation boundaries, liquid-liquid heterogeneous envelopes and the orientation and length of the heterogeneous tie lines. These properties enable us to graphically predict the *absolute minimum number of units, the region and the point of desirable entrainer flowrate, the optimum decanter tie line position, and the distillate composition for the entrainer recovery column.*

3. *Guidelines for exploiting feed composition flexibility to improve azeotropic separation (Chapter 7). Important insights include:*

- the significance of the binary, ternary and desirable ternary feed compositions, and a procedure to achieve the desirable ternary feed composition based on geometric reasoning.
- the development of a novel geometric approach for screening feed preconcentrators. This approach considers the effect of entrainer reduction and typical binary feed composition and leads to a selection catalogue for feed preconcentration (see Appendix E).
- the use of mixing and recycling for grassroot design and retrofit of distillation sequences for azeotropic mixtures.

The next chapter is concerned with the development of a design procedure that is geared towards waste minimisation through opportunistic recycling within the context of an overall chemical process.

Chapter 3

Waste Minimisation through Opportunistic Recycling

This chapter describes the conception and application of a design procedure for waste minimisation that promotes *opportunistic recycling*. The chapter begins with a review of the waste minimisation hierarchy, paying particular attention to the role of opportunistic recycling in eliminating, reducing and controlling waste, and to the appropriate position of each recycle technique in the waste minimisation hierarchy. Section 3.2 describes how the approach emerged from Douglas hierarchical design procedure, highlighting the proposed extension, modifications and the advantages of the approach over Douglas' procedure. The chapter ends with an application of the waste minimisation approach on a methyl acetate process, which also involves a procedure for designing a recycle network in the context of an overall process (Section 3.3).

3.1 The waste minimisation hierarchy

The waste minimisation hierarchy is a general guideline for pollution prevention. The US Environmental Protection Agency [40] describes the hierarchy as consisting of five levels, namely (1) source elimination, (2) source reduction, (3) recycling, (4) treatment and (5) disposal, each representing various waste management options. They are arranged in order of preference, from the most preferred option at the top of the hierarchy to the least preferred at the bottom. Figure 3.1 shows the hierarchy of waste manage-

ment practices [3,4]. Waste minimisation is concerned with the *first, second and third* level of the hierarchy [4].

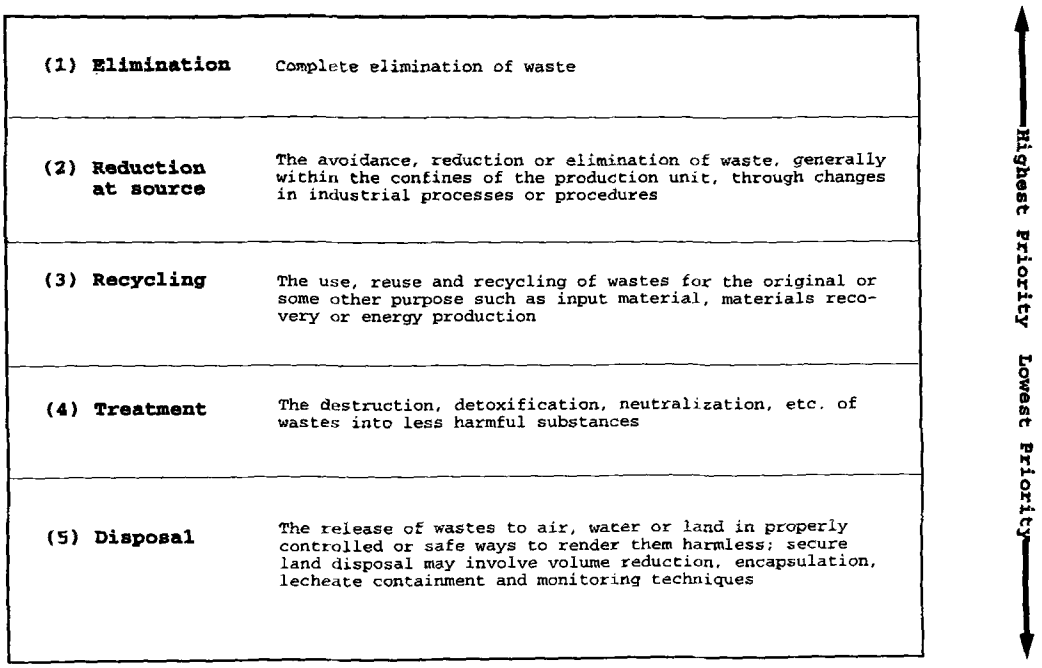


Figure 3.1: Hierarchy of Waste Management Practices.

In the following subsections, a detailed description of each level of the hierarchy as a pollution prevention option is focused on:

- the relative significance of each level of the hierarchy as an option for waste management, and
- the positions of various techniques for creative recycling in the hierachy.

3.1.1 Level 1 - Source elimination

It is always desirable to eliminate wastes rather than to reduce, recycle or treat them once they have been generated. The possible ways to eliminate the sources of wastes include changing the reaction chemistry, changing the process materials and finding "cleaner" separation techniques.

The reaction and separation sections offer the widest scope for source elimination and reduction and are closely associated with this level of the hierarchy. It is here that the reaction chemistry, process conditions, catalysts, inerts and solvents, reaction and separation structures and technologies are being specified. Therefore, it is here that wastes are being introduced into the entire process in various forms and quantities. It follows that the size, complexity and necessity for recycle and waste treatment hinges upon the decisions made at this level.

Once source elimination opportunities have been exhausted, a designer may proceed to the next level of the hierarchy. Waste generated at this stage will find exit at one or various points in the process. Hereafter, waste generation and release can be best minimised by means of source reduction and creative recycling.

3.1.2 Level 2 - Source reduction

Total elimination of waste is the ultimate goal of cleaner process designs. Because it is not always possible to eliminate waste completely, one must try the next best option, i.e. source reduction. Among the most effective means of reducing waste is to improve reactor raw materials usage, energy efficiency, process solvent usage and materials recycling. Whenever possible, it is best to improve the raw material usage by recycling the unconverted raw materials back to the reactor inlet. If this is difficult or not possible, then, it is necessary to improve the reactor conversion or selectivity by other means. Depending on the type of reaction (reversible, irreversible, parallel, consecutive, etc.), actions such as increasing the reactor residence times, changing the temperature, pressure, and the reactor inlet composition can help achieve the source reduction goal. A designer must however bear in mind that changes in the reaction parameters must be subject to equilibrium, kinetic and practical constraints.

3.1.3 Level 3 - Recycling

Recycling has been widely accepted as a method to control the release of waste which has already been created or introduced in a process. The idea that recycling can also prevent or reduce waste generation might be unfamiliar to those already accustomed to think about recycling at a level below source elimination and source reduction [41,42][1]. Attempts to strictly follow these established hierarchical classifications may steer designers away from using recycling as a viable means of eliminating and reducing wastes during design. It is thus useful to view recycling from a broader perspective and to emphasize its key role in eliminating and reducing waste in addition to its traditional role in controlling the release of waste. In general, recycling should include the possibilities of waste elimination, reduction and recovery.

Recycling for source elimination

Whenever possible, recycling to eliminate and reduce the sources of wastes should be considered before source reduction and recovery. The following set of general rules to *design for recyclability* outlined by Henshaw[43] may be implemented:

- when choosing the reaction chemistry, choose a system of easily separable components.
- the fewer types of components involved, the better.
- the fewer *secondary operations* required for a given system, the better.

Then, the possibilities to eliminate waste by recycling include:

- recycling byproducts formed by a secondary reversible reaction.

[1] other classifications combine source elimination and reduction on the first level and place recycling as the second level in the waste minimisation hierarchy.

- utilising a stream as a substitute material. This type of recycling is typically employed to replace an external solvent or inert. The stream to be recycled can be a byproduct, an inert or a solvent that is available elsewhere in a process.

Recycling for source reduction

The main techniques for recycling to reduce the sources of waste include:

1. *Recycling streams to improve reaction conversion and selectivity.* Whenever possible, unconverted raw materials should be recycled to the reactor. Apart from the common practice of recycling unconverted raw materials to the reactor to improve conversion, sometimes one can improve reaction selectivity by recycling an inert to the reactor to keep the concentration of the limiting reactants low, or to control the operating conditions. By reusing the inert, one can control the amount of inert released as waste, while at the same time reduce the formation of waste byproducts.

2. *Direct reuse of material.* The stream to be recycled is reused in contaminated form before purification. For example, depending on the concentration gradient, contaminated water from a scrubber may be reused in an absorber and then in a waste treatment facility. The effect is reduced water consumption and less wastes generation during waste water treatment. When there are many contaminated streams in the process, the *Mass Exchange Network (MEN)* synthesis technique may be employed to find the optimum recycle destination.

3. *Recycling streams to improve separation and to eliminate redundant splits* (discussed in Chapter 7).

Recycling for recovery

Recycling for recovery is classified into two classes based on the composition, properties and role of the streams to be recycled (the objective stream).

1. *Secondary recycling.* Reuse of a material in its original form. When an objective stream is reused after purification it is said to be reclaimed. A simple composition match will pinpoint streams that need to be reclaimed. In secondary recycling the objective stream can consist of reactants, solvents, catalysts, inerts or any combination of the materials thereof.

2. *Tertiary recycling.* Also termed as *sacrificial recycling.* Reuse of a material at a lower value. A tradeoff exist between reclamation and tertiary recycling. The main incentive for tertiary recycling is reduced environmental burden at no extra cost since reclamation is avoided. Common examples include use of an objective stream as fuel or animal feed. Materials properties, raw material costs and the treatment costs are needed in order to evaluate the economics.

The term *opportunistic recycling* will be used to reflect the recycle applications described above, i.e., as possible means to eliminate, prevent, reduce and control waste generation in an efficient manner. In Section 3.3.1, a systematic approach to generate a recycle network in the context of an overall process is described.

3.1.4 Levels 4 and 5 - Treatment and disposal

Treatment and disposal are the next two levels in the hierarchy to consider after waste recycling because materials that cannot be reused on-site have to undergo an *end of pipe* treatment before disposal to meet the environmental guidelines. Treatment and disposal are the least desirable options from the waste minimisation point of view and are to be avoided whenever possible. They are nevertheless necessary for many processes to control the amount of pollutants released. Using the modified hierarchical approach for design (described in the next section), the *end of pipe* treatment may not be eliminated, but will become an economically viable option.

3.2 Process design for waste minimisation - Synthesis with opportunistic recycling

3.2.1 Douglas Hierarchical Design Procedure

One of the most important considerations during the design of cleaner processes is to generate alternatives for pollution prevention. In preventing waste during process design, Douglas included pollution considerations in his hierarchical design procedure (shown in Table 3.1) [16,24]. A design is developed by proceeding through different levels of design abstractions while additional details are added at each level. To achieve the goal of waste minimisation, the idea is to identify potential pollution problems as design is developed, and make decisions not to introduce materials, chemistry, process conditions or techniques that could cause adverse environmental impact at each level of the design hierarchy. Douglas procedure, however, leaves the waste prevention alternatives for designers to explore. The aim of bringing waste minimisation to the *front end* of the design process and the emphasis on opportunistic recycling inspired the development of the *waste minimisation (WM) approach* hereby presented. This approach is essentially an extension of Douglas hierarchical design procedure. The following sections describe the proposed modifications and additions to Douglas' procedure.

Table 3.1: Douglas Hierarchical Decision Procedure

Level 1.	Input information
Level 2.	Input-output structure
Level 3.	Recycle structure
Level 4.	Separation system
	(a) Vapour recovery system
	(b) Liquid recovery system

3.2.2 The Waste Minimisation Approach to design

Note that the sequence of Levels 1 (Input information) and 2 (Input-output structure) of the design hierarchy shown in Table 3.1 is logically fixed by the availability of information during the early stages of process synthesis. These levels needed to be defined

before the structure of the recycle and separation systems are tackled, but, a designer may proceed either by specifying the recycle *or* the separation structure. Thus the hierarchical design procedure may branch in two possible direction:

1. Input information → Input-output structure → Recycle structure → Separation structure (original Douglas approach)
2. Input information → Input-output structure → Reaction system → Separation structure → Recycle structure (proposed waste minimisation approach, see Table 3.2)

To achieve the goal of waste minimisation, we propose to synthesize and add details to the separation structure before working on the recycle structure, thus departing from Douglas' established approach of fixing the recycle structure from the abstract (black box) reaction and separation blocks. Note that, assuming a black box separation when fixing the reactor recycles implies ignoring the "internal" separation recycles (e.g. separation solvent), and hence, their interactions with the reactor recycles, at least until the separation structure is decided. In contrast, developing the recycle structure based on a detailed reaction and separation schemes means that any solvent, inert and waste streams, both from the reaction and separation systems, may now be considered as potential recycles. Simultaneous consideration of the reaction and separation subsystems can promote opportunistic recycling and help achieve our waste minimisation goal.

Table 3.2: Waste Minimisation Approach.

Level 1.	Input Information
Level 2.	Input-output structure
Level 3.	Reaction system
Level 4.	Separation system
	(a) Vapour recovery system
	(b) Liquid recovery system
Level 5.	Global recycle network

Douglas described how a recycle structure is synthesized from the input-output information. What components to add, remove, replace or recycle are decided at this stage

before moving on to detailed separation separation sequence design. The following examples briefly illustrate the typical design decisions encountered when the recycle structure is being fixed and highlights the advantages of the waste minimisation procedure in generating cleaner designs.

Example 1. Ethylene production[16]. The ethylene production process can be represented by the following simplified set of reactions:

```
  C2H6          <==>      C2H4     +     H2
(ethane)                 (ethylene)   (hydrogen)

  C2H6    +     H2      <==>      2CH4
(ethane)  (hydrogen)             (methane)
```

Normally steam is added as an inert diluent to reduce byproduct methane because steam is easy to condense and separate. At level 3 (recycle structure) of Douglas hierarchical design procedure, an inert (e.g. steam) may be introduced to improve product distribution (see the decisions in Table 3.5 on page 32). Introduction of steam as an inert diluent however leads to an exit water stream that needs to be treated. It is suggested in the article steam be replaced by a different diluent that can be sent to a fuel supply or be recycled less expensively than water.

If the separation structure were defined, we could decide whether any solvent or diluent (in this case condensed steam) could be used internally either directly or indirectly before being sent to treatment facilities. This could reduce the water usage and waste treatment needs. Alternatively, a component from the separation system may be chosen to replace steam to improve product distribution. The disadvantage of Douglas' approach is that, at this stage, there is no way of knowing whether condensed steam can be used inside the separation or whether a substitute for steam exists, since the separation section is still undefined when the recycle structure is being fixed.

Example 2. Production of acrylonitrile [44] - Acrylonitrile is a building block for synthetic rubber. The once used acetylene production route has been replaced by the *Sohio Process* that utilizes cheaper raw materials:

```
 2 C3H6    +    3 O2    +      2NH3      --->    2C3H3N    +     6H2O
(propylene)     (oxygen)       (ammonia)        (acrylonitrile)  (water)
```

The reactor effluent consists of inerts (mainly nitrogen from air), unreacted propylene, propane, acrylonitrile, water and impurities. The notoriously difficult separation between propylene and propane is inevitable because propylene is used as a raw material. Conventional distillation is uneconomic due to the low relative volatility between the two hydrocarbons and the fact that propylene (the more volatile of the two) is five times more plentiful than propane. An indirect separation using acrylonitrile as a solvent was proposed by W.G. Johnson to overcome the separation problem. The use of acrylonitrile as a solvent eliminates the solvent recovery step and results in a simpler process (U.S. Patent 2,980,727 by W.G. Johnson).

This example shows the advantages of fixing the recycle structure only after the separation synthesis. Had the recycle structure been fixed first, acrylonitrile would be classified solely as a product to be removed from the process. The problem would need reworking when it is found later (during the separation synthesis) that acrylonitrile is also a potential solvent.

We can conclude that if we decide to add, remove or recycle certain components before the separation synthesis, we may have to answer the following questions later and possibly have to rework the problem:

1. Should a component be removed from the reactor or reused downstream? Can any component from the reactor be directly (or indirectly) reused downstream as an inert, solvent, etc.? Can further separation be avoided by reusing it downstream?

2. Is it necessary or convenient to add a new component in the reactor? Can any component from the separation section be reused in the reactor?

3. How does the *separator recycle* influences the reactor recycle? Can the recycle purges be independently designed? What would be the effects of independent recycle designs on plant performance and operability?

It is evident that in all cases a definite answer can only be obtained by delaying any recycle decisions until the separation structure is fixed. Detailing the separation structure before recycling, as proposed in the waste minimisation approach allow us to analyse *all* recycle streams simultaneously so that the possibility of waste exchange and recycle interactions can be assessed.

Four advantages can be expected from the waste minimisation approach:

- improving the scope for recycling and the ability to explore and exploit the waste minimisation alternatives,
- avoidance of design rework,
- effective prevention of trace accumulation that may cause operability problems, and
- reduction of excessive purge losses and waste release by eliminating unnecessary exit points.

There are two important points to draw from the preceding discussion. First, Douglas' model has originally been developed to be applicable for the general design case regardless of the design "theme" and is therefore not specifically directed towards recycling. Second, any recycle decisions made before fixing the separation structure via the Douglas synthesis model can still be revised and reworked. The modified model is an adaptation to process synthesis for waste minimisation, that has been designed to promote recycling. At best, it may prevent missed opportunities for recycling while guiding the design for better operability. At worst, it may only avoid design rework.

3.2.3 Design levels in the Waste Minimisation Approach

The hierarchical waste minimisation approach guides the user to systematically specify the input information, and the input-output, reaction, and separation-recycle structures sequentially. Waste potentials are analysed during each stage of the design and the design alternatives are generated.

Each stage is associated with the following waste minimisation problems:

- Input information and Input-output structure - source elimination.
- Reaction, Separation and Recycle structures - source elimination, reduction and recovery.

The decisions to be considered at each level are given in Tables 3.3, 3.4, 3.5 and 3.6. The differences between Douglas' approach and the waste minimisation approach are highlighted in these tables.

Level 1. Input information (Table 3.3). The most important decision at this level of detail is the choice of reaction route that will determine the type of reactants, the feed impurities and the byproducts. The sources of waste can be eliminated early by choosing a *cleaner* route to produce the desired product. For example, we may choose different reaction conditions, change the feedstock quality, use a different catalyst, or employ a different reaction route altogether. Whenever we decide to change the chemistry, we will have generated an alternative processing route. The stage is primarily concerned with *source elimination* and is the best opportunity to prevent waste.

Level 2. Input-output structure (Table 3.4). Based on the chemistry selected in the previous level, a graphical representation of the streams entering and leaving the overall process can provide a quick insight about the potential pollution problems associated with the chemistry chosen. Component destination is fixed at this level of the design hierarchy. In doing so, Douglas assumes distillation-based separation and sharp splits[24](no azeotropes formed). The waste minimisation approach takes account of

Table 3.3: A comparison between Douglas' Approach and the Waste Minimisation Approach. Level 1 - Input information.

Douglas' Approach	WM Approach
1. Reaction chemistry, conditions, conversion, selectivity, data on reaction rate and catalyst deactivation.	1. Reaction chemistry, conditions, conversion, selectivity, data on reaction rate and catalyst deactivation.
2. Feed streams, rates, conditions, compositions and cost.	2. Feed streams, rates, conditions, compositions and cost.
3. Products, byproducts, rates, purities.	3. Products, byproducts, rates, purities.
4. Product distribution and values, materials safety and hazardous properties, environmental impacts.	4. Product distribution and values, materials safety and hazardous properties, environmental impacts, emission limits.
5. Any processing constraints	5. Any processing constraints
6. Plant, site and physical property data.	6. Plant, site and physical property data.

mixture nonidealities (azeotrope formation, existence of immiscibility regions) during species allocation. It also make provision for the multiple roles that a given species may assume (e.g. a given species can either be a product and recycle).

Instead of recycling, Douglas suggests that sometimes we may decide to remove and not recycle some reactants and byproducts from the system. However, we choose not to make the decision to remove any materials at this stage and assume that all materials except for the feed impurities are recoverable somehow. Our decision with regard to recycling may change once the separation and recycle structures are defined. Douglas also stresses the desirability of a quick economic assessment (associated with raw materials, product, byproduct and estimated waste treatment costs) to eliminate poor routes early. We are aware that in our case the results of a pre-economic assessment will be totally different than that of Douglas. Had we chosen to remove the byproducts instead of recycling them, we would have been able to estimate the net material costs and treatment requirements and carry on with the assumptions based on the premise of the "cheapest route". However, there is no guarantee that removing the byproducts is more attractive than other actions that can be undertaken at lower levels of the design hierarchy such as changing the reactor operating conditions (source reduction) or recycling, which we have yet to explore. Thus, before we decide to remove a material,

we should ask ourselves the following questions:

Should we remove any materials at the input-output stage? Is it possible to recycle the materials *internally*? Can waste generation be reduced through a change in operations? What would be the effects of recycling and *source reduction* on the economics? How would this compare with the economics of "removing materials" and hence the additional cost of waste treatment? Has the economic assessment been meaningful at the input-output stage? Evidently we are unable to decide if the material is recoverable and prematurely eliminate this possibility simply because the separation and recycle structures are undefined. In essence, we may have prematurely screened the process without generating enough alternatives for evaluation. Therefore, it seems quite reasonable to delay any economic assessment until after the separation and recycle structures are defined.

Table 3.4: A comparison between Douglas' Approach and the Waste Minimisation Approach. Level 2 - Input-output structure.

Douglas' Approach	WM Approach
1. Purity of the feed streams?	1. Purity of the feed streams?
2. Do not recover & recycle some reactants?	2. Assume *all* reactants recyclable
3. Use a gas recycle and purge stream or vent gaseous reactants ?	3. Use a gas recycle and purge stream or vent gaseous reactants ?
4. Recover & recycle or remove a byproduct formed by a secondary reversible reaction?	4. Recover & recycle a byproduct formed by a secondary reversible reaction?
	5. Identify mixture nonidealities - e.g. azeotrope formation.
	6. New component required for agent-based separation?

Level 3. Reaction system (Table 3.5). The decisions to consider at this level are similar to those in level 3 (recycle structure) of Douglas' approach (see Table 3.5). We may come across the following decisions when we consider the reaction system:

- What reactor configuration should be used? - single or multiple reactors? Simultaneous reaction-separation?

- How to improve reactor conversion? How to achieve complete conversion? Is it possible to improve conversion by changing the temperature, pressure or feed ratio (relative concentration of the reactants) ?
- How to improve product distribution? Should we add new components, inerts or solvents? Can any of the components be recycled to improve product distribution?

It is important to recognize that, using the waste minimisation approach, the decisions made at this point are provisional and thus may not represent the final solution. They should regarded as alternative decisions to those to be made once the recycle structure is fixed. Therefore, all alternatives generated are not to be eliminated or screened at this stage until the recycle structure is fixed.

Table 3.5: A comparison between Douglas' Approach and the Waste Minimisation Approach. Level 3 - Recycle structure/reaction system.

Douglas' Approach	WM Approach
1. Reactor-separator (distillation, extraction, etc.)	1. Single or multiple reactor? Simultaneous reaction-separation?
2. Shift equilibrium conversion? how? diluent to improve product distribution?	2. Change temperature, pressure? feed concentration to improve product distribution?
3. Complete conversion to avoid separation?	3. Recycle to extinction? which material(s) to recycle? where to recycle?
4. Reactor or product solvents?	4. Add new materials or recycle to improve conversion or product distribution? which material to recycle? where to recycle?
	5. Add or recycle materials as reactor or product solvents?
	6. Reactor heat effects - adiabatic, isothermal, heat carrier ?

Level 4. Separation and recycle systems. (Table 3.6). The decisions to be made during the synthesis of separation and recycle structures are outlined in Table 3.5. Many new decisions in addition to those recommended by Douglas are added to account for the possibility of recycling between sections in the flowsheet. To further promote generation of alternatives it is necessary to recall information from the previous levels of detail and to combine it with the detail at the present level. Interactions between the

internal and external recycle loops can now be analysed more effectively. In Chapter 7,

Table 3.6: A comparison between Douglas' Approach and the Waste Minimisation Approach. Level 4 - Separation synthesis/separation & recycle synthesis.

Douglas' Approach	WM Approach
1. Vapour recovery system? (condensation, absorption, adsorption, reactive adsorption, membranes?)	1. vapour recovery system? (condensation, absorption, adsorption, reactive adsorption, membranes?)
2. Liquid separation system? (stripping, distillation (conventional, azeotropic, extractive and/or reactive distillation?))	2. Liquid separation system? (stripping, distillation (conventional, azeotropic, extractive and/or reactive distillation?))
	3. Recycle for source elimination? - recycle raw materials to extinction? find recycle material to substitute reactor solvent? substitute inerts? recycle to absorb heat of reaction?
	4. Recycle for source reduction? - (to improve conversion/selectivity) recycle raw materials? recycle byproducts formed reversibly? recycle solvent?
	5. Any materials from reactor to recycle to separator?
	6. Remove unrecoverable materials?
	7. Recycle and purge gas streams?
	8. Recycle and bleed aqueous streams?
	9. Locations or purges? how many purge /bleed/streams?
	10. Remove any byproducts? solvents? inerts?

ternary diagrams are used as a tool to visualise the scope for recycling and mixing in order to enhance separation and to generate cleaner alternative separation structures. In order to generate an efficient recycle network, the scope for mixing and recycling needs to be analysed in the context of an overall process. Application of the hierarchical waste minimisation approach on a methyl acetate production process is summarized in Appendix A.1 on page 189.

3.3 Global recycle network (GREEN) design

Once the reaction, separation and recycle structures (and their alternatives) have been specified in accordance with the waste minimisation approach, the next step is for a designer to come up with a structure that can best achieve the waste minimisation goal. For this purpose, it is useful to view mixing and recycling in the global process context, especially when an entrainer or a solvent is a component that comes from the process. Within the global process, there often exist a number of recycle options which may be classified according to their influence on the process. Therefore, it is necessary to be opportunistic in order to generate the best recycle scheme. The following factors may be considered for opportunistic recycling:

1. Options available for recycling,
   - recycling the byproducts of reversible reactions to extinction
   - recycling streams to improve reaction conversion and selectivity
   - recycling streams to improve separation, eliminate redundant splits and prevent waste release - include recycling internal or external solvents for separation
2. Alternative recycle destinations - often it may be possible to recycle streams to more than one section in a process, e.g. to the reactor and/or the separator sections
3. Possible constraints for recycling - Wahnschafft *et al.*[27] list two main constraints for recycling:
   - mass balance - mixing a recycle with the main feed to a separation step must bring the overall feed composition onto the mass balance line between the desired products.
   - possible product contamination from recycling.
4. Rules for getting the minimum waste mixing point. Whenever there exists more than one feasible destination, our criteria is that the best recycle scheme (mixing

point) generates the least amount of waste. The mixing point can therefore be decided on the basis of

- waste minimisation hierarchy - in the order of importance, emphasis is given on waste elimination, followed by reduction, recycling and treatment of waste streams, and
- the stream properties (operating conditions and composition)

In the next section a case study that describes opportunistic recycling, i.e. the process of determining the best mixing point, is presented.

3.3.1 GREEN design - A case study

Process Description

This case study illustrates a systematic procedure for designing a recycle network in the context of an overall process. Figure 3.2 represents an alternative flowsheet for methyl acetate production process. Most of the process stream data for this case study has been derived from the simulation studies performed by Guzman-Reyna and Bañares-Alcántara[45]. Methanol reacts reversibly with acetic acid to produce methyl acetate and water according to the following reaction:

```
  CH3OH    +    CH3COOH      <====>     CH3COOCH3      +    H2O
(methanol)   (acetic acid)              (methyl acetate)     (water)
```

In this case, excess acetic acid is required to force a high conversion of methanol. The reactor outlet which still contains some unreacted methanol and a large flowrate of unreacted acetic acid undergoes extractive distillation (using acetic acid as a solvent) to recover the lighter components including methanol, methyl acetate, and acetic acid overhead, while removing water and most of the acetic acid underflow (C1-B). The flowsheet and the ternary diagram[2]) representing the streams compositions for the

[2]the ternary diagram is better known as the *residue curve map (RCM)*. A reader is referred to the introduction to Chapter 4, page 43 for a definition of the RCM for azeotropic mixtures.

azeotropic separation section are shown in Figure 3.3. Part of the acetic acid in stream C1-B of Figure 3.2 is removed using column-3 in order to bring its composition from the *region of infeasible feed* to F1 as shown in Figure 3.3. This enables the heterogeneous azeotropic separation to be performed in a separation sequence which includes a liquid-liquid extractor. The overhead product from extractive distillation process (column-1)

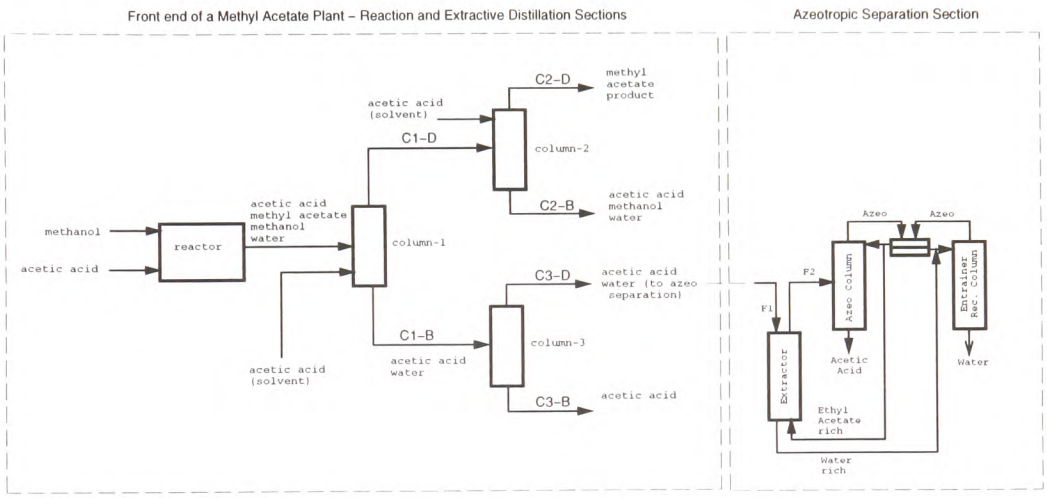


Figure 3.2: Option 1 - A methyl acetate production process with an acid removal column (column-3).

goes through another extractive column (column-2) to recover pure methyl acetate overhead, again using acetic acid as a solvent. The use of acetic acid as a solvent eliminates a column that would have been needed for an external solvent recovery. A very large flowrate of acetic acid is however required to satisfy its role as a reactant as well as a solvent.

Figure 3.6 shows that it is also possible to operate without column-3, in which case a water recycle stream may be used to bring the composition of C1-B to the region of feasible feed (see Figure 3.7 and a more detailed discussions in Chapter 7).

Mixing point analysis for the GREEN design

From the flowsheet in Figure 3.4, streams C2-B and C3-B, which are the bottom streams of column-2 and column-3 are the potential recycles. In order to find the best mixing point, the criteria for opportunistic recycling outlined previously are applied to each

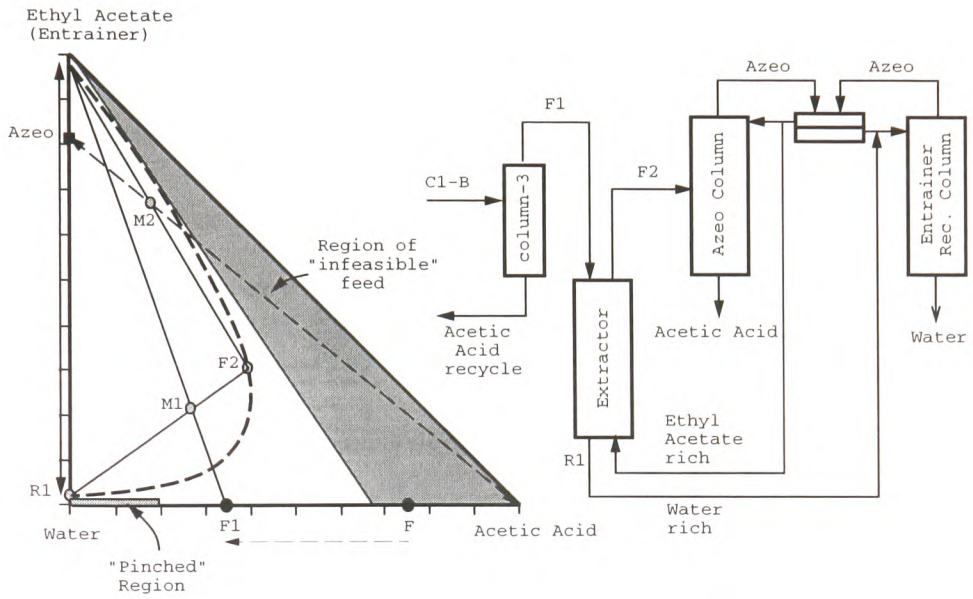


Figure 3.3: Acid removal brings the bottom composition of column-1 from the region of infeasible feed to F1, thus enabling separation in a sequence which include a liquid-liquid extractor.

recycle candidate. C2-B can be sent either to column-1 as a secondary recycle or to the reactor to participate in the reaction, or to column-2. In most chemical processes raw material is usually the most significant cost, comprising between 35 to 80% of the total product cost[24]. Therefore, recycling C2-B which contains 94% acetic acid and 6% methanol reactants directly to the reactor would be most desirable because this improves raw materials efficiency and, at the same time, reduce one of the sources of waste. The RCM and flowsheet for the extractive distillation of methanol-methyl acetate-acetic acid (with acetic acid as the entrainer) is shown in Figure 3.5.

Next, we compare the operating conditions of the recycle stream and each mixing point to further assess the suitability of the alternative mixing points. The operating pressure is assumed constant throughout the process. C2-B, with almost pure acetic acid, may be matched against the acetic acid feed to the reactor, or against one of the trays of column-1 whose composition profile matches the composition of stream C2-B. This makes the two options comparable with respect to the composition criteria. Finally in terms of the temperature, the reactor is preferred to column-1 (option b of Figure 3.4) due to the proximity of the reactor temperature to C2-B in comparison to the

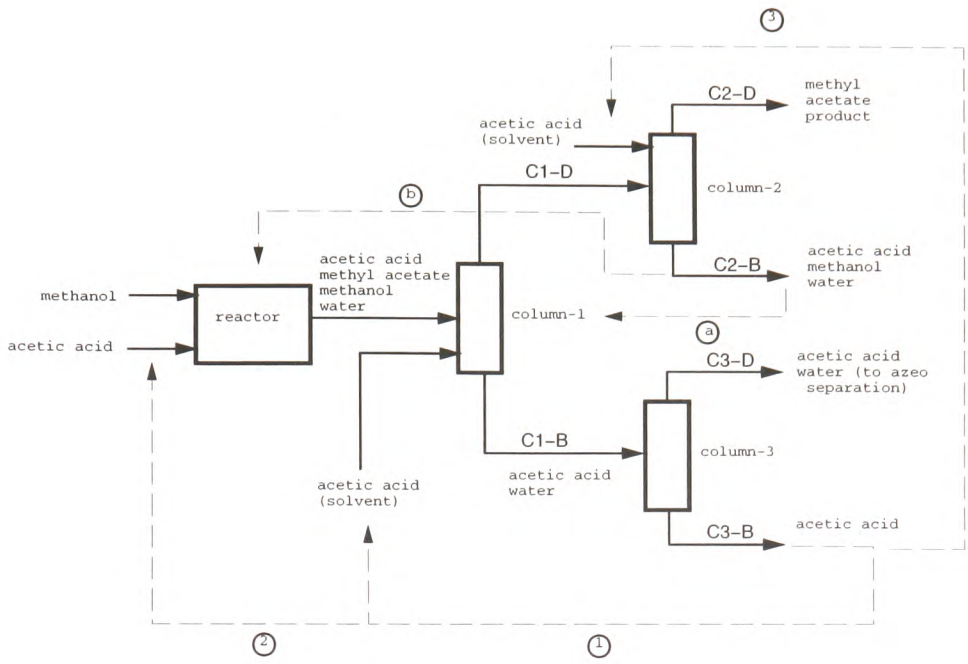


Figure 3.4: Front end of a methyl acetate production process.

temperature profile of column-1. We conclude that the outlined criteria unanimously favour the reactor as the mixing point for stream C2-B. In the event of a conflict, we propose that recycling to minimise waste should always be given the priority, followed by composition and temperature matching. Relative to composition, temperature criteria has the lower priority since unlike composition, it is usually much easier to modify a stream temperature to match the mixing point temperature (following the synthesis hierarchy outlined in Siirola[46]).

The second recycle candidate is stream C3-B which contains pure acetic acid. It can either be mixed with the pure solvents entering column-1 or column-2 or with the pure acetic acid feed to the reactor. Applying the same criteria for GREEN design, we find that all three mixing points give exactly the same reduction in the flowrate of external acetic acid. Thus, each option should result in equivalent saving in terms of the solvent cost and less potential waste from acetic acid utilisation. Note however, that, recycling C3-B to the reactor can help achieve three other benefits:

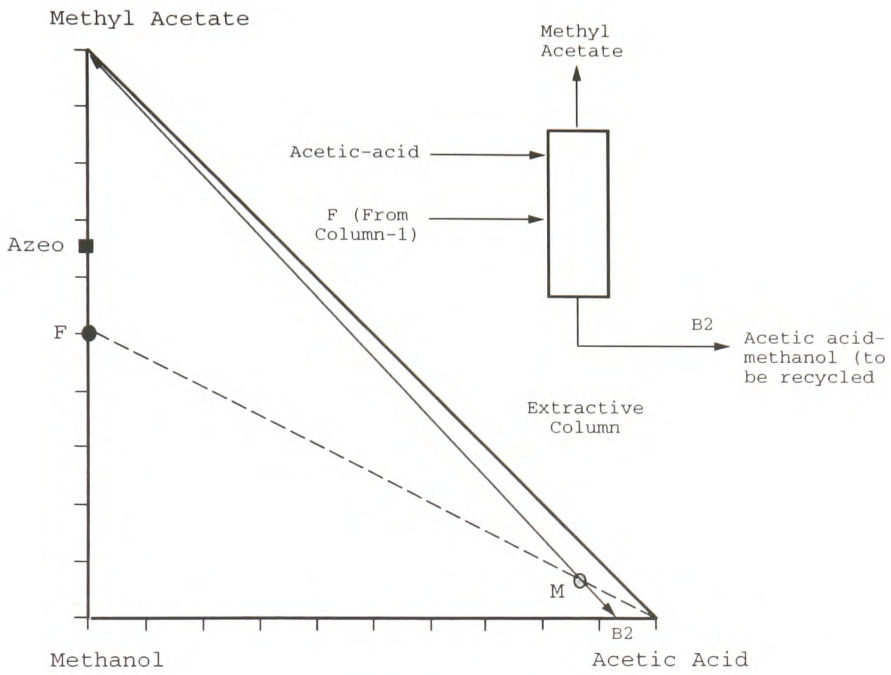


Figure 3.5: *Residue curve map* (RCM) and separation sequence for acetic acid-methanol-methyl acetate mixture

- it maximizes methanol conversion. This help saves raw material cost, in addition to reducing potential waste from unconverted methanol.
- it maintains a high concentration of acetic acid in the reactor effluent and results in reduced solvent requirements for column-2 and column-3,
- it reduces the amount of energy required to bring the reaction to its initiation temperature, as C3-B temperature perfectly matches that of the acetic acid feed to the reactor. Note that C3-B temperature is way outside the temperature ranges of column-1 and column-2.

On these basis, we choose the reactor as the most desirable mixing point for stream C3-B. Note that since the flowrates of acetic acid entrainer (or reactant) are flexible, the reactor and columns mass balance constraints can always be satisfied by appropriately adjusting the acetic acid flowrate.

Table 3.7 summarizes the alternative mixing points for the candidate recycle streams and the decisions made.

Table 3.7: Alternative mixing points for recycle streams

Stream to Recycle	Mixing Point	Class of Recycle	Matching Composition	Mixing Pt. Temp. (^oC)	Constraints
C2-B (T=96^oC) (94% Ac.Acid, 6% Methanol)	column-1	secondary recycle	column-1 bottom	60	temp.
	reactor	recycle to extinction	reactor	118	nil
C3-B (T=118^oC) (100% Ac.Acid)	column-1	secondary recycle	ac.acid feed	60	temp.
	column-2	secondary recycle	column-2 top	54	temp.
	reactor	recycle to extinction	ac.acid feed	118	nil

One of the most important applications for GREEN Design is for recycling process water which is a widely used solvent. As GREEN Design is used in the context of an overall process, it provides wider options for waste minimisation in comparison to the methods for recycle network design proposed by El-Halwagi *et al.*[17–19] and Wang and Smith[28]. It is also simpler to use, either for grassroots design or for retrofit of exisiting processes.

3.4 Summary

Opportunistic recycling is commonly employed during retrofit to minimise waste. However its systematisation is a subject that has received very little attention during process design. In this chapter, the Douglas hierarchical design procedure has been modified and extended to create a procedure for process design that is conducive to waste minimisation particularly through opportunistic recycling.

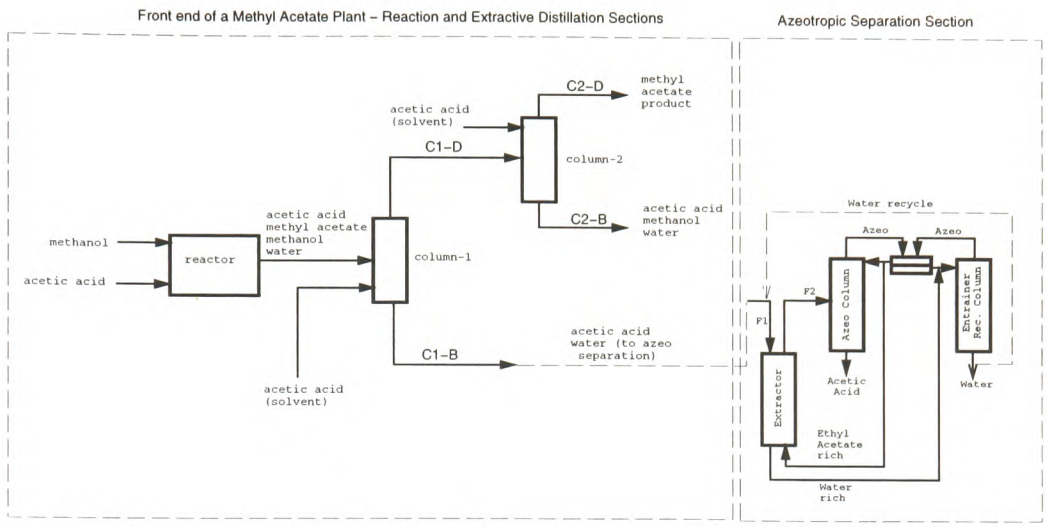


Figure 3.6: Option 2 - A methyl acetate production process with water recycle.

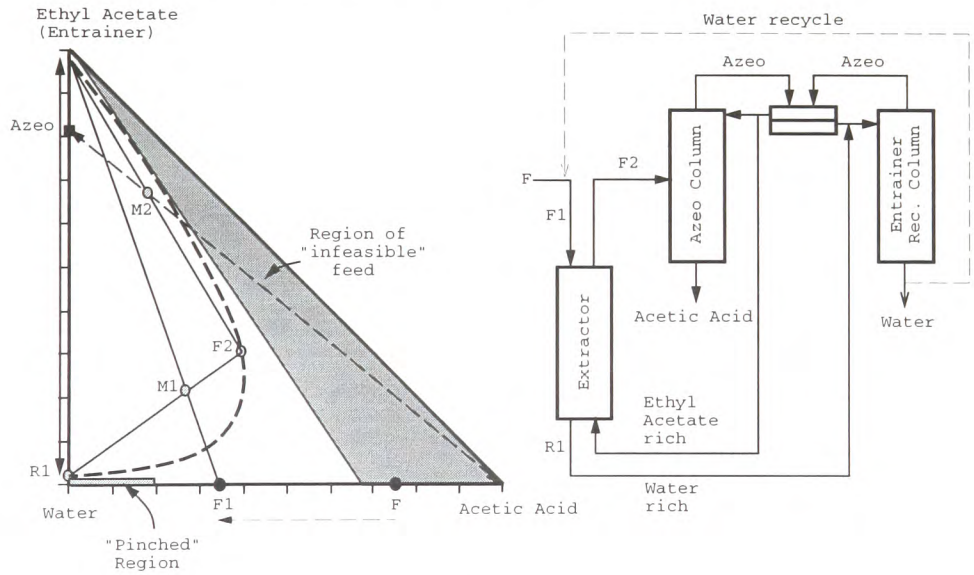


Figure 3.7: Water recycle brings the bottom composition of column-1 from the region of infeasible feed to F1, thus enabling separation in a sequence which include a liquid-liquid extractor.

Just as in Douglas' approach, a design is developed by proceeding through successive levels of design abstraction while additional details are added at each level. To achieve the goal of waste minimisation, the idea is to identify potential pollution problems as design is developed, and make decisions not to introduce materials, chemistry, process conditions or techniques that could cause adverse environmental impact at each level

of the design hierarchy.

The design procedure for waste minimisation which promotes opportunistic recycling includes the following key new features:

- identification of mixture noindealities (azeotrope formation, existence of immiscibility regions) during species allocation and inclusion of any external components (for agent-based separation) in the species allocation list.
- recognition of the multiple roles that a given species may assume (e.g. a given species can either be a product and a recycle), giving rise to alternative flowsheets.
- *intra* and *inter-level* recycling for the reaction and separation sections of the process and search for inert diluents, substitute materials and potential internal solvents.
- analysis and evaluation of alternative mixing points in the overall process context.
- visualisation of recycle and mixing scopes for enhanced separation and generation of cleaner alternative separation structures using ternary diagrams (detailed treatment in Chapter 7).

Chapter 4

Synthesis of Distillation Sequences for Homogeneous Azeotropic Mixtures - Systems Without Boundary Crossing

4.1 Introduction

Decision making during the synthesis and design of distillation sequences for ideal and slightly nonideal mixtures is influenced by variables such as the feed composition, volatility of the components to be separated, required product purities, column reflux ratios and number of stages. The presence of azeotropes introduce new variables such as the choice of entrainer, the type of azeotropes formed, the shape and locations of distillation boundaries and, in the case of heterogeneous systems, the properties of a liquid-liquid equilibrium region. This set of variables which affects the number and connectivity of the separation units, the flowrate of entrainer and the column design vary so much from one mixture to another as to make it impossible to formulate and solve a general numerical model for the optimal synthesis of separation sequences. For ternary mixtures, we can represent most of the azeotrope-related features on ternary diagrams known as *residue curve maps (RCMs)*. Schreinemakers [47] first defined RCMs as ternary diagrams displaying traces of the liquid composition remaining in a single-stage batch still as a result of vapourisation over a period of time. The liquid traces are better known as residue curves.

We shall limit our discussions to the synthesis of separation sequences for azeotropic mixtures with a maximum of three components. Unless stated otherwise, we use the following conventions for any given mixture:

- Every ternary diagram follows the convention for the location of pure components with respect to their boiling points shown in Figure 4.1: low boiling component at the top left corner, medium boiling at the bottom left and high boiling at the bottom right.
- The fractional composition of any given component ranges between 0 and 1. Reading any two composition from the horizontal and vertical edges of the right triangular diagram gives enough information to calculate the composition of the third component.
- Components are listed in the text according to their boiling points: light-medium-high boiling component, with the boiling characteristics of the entrainer shown in paranthesis. For example, ethanol-water-ethylene glycol (high boiling entrainer).
- "Azeotropic mixture" refers to an individual mixture whereas "azeotropic system" refers to a collection of similar azeotropic mixtures.

4.2 Classification of the synthesis problem

The notion of residue curve boundaries as limits of the range of feasible separation has been noted by Van Dongen and Doherty[48] as well as by Doherty and Caldarola[49]. Van Dongen and Doherty rationalise that the composition profile of a distillation column, which approximates the residue curves when the column operates at infinite reflux, cannot cross the residue curve boundaries. Doherty and Caldarola on the other hand use as a practical working assumption that the mass balance line linking the feed, distillate and bottoms compositions of a continuous distillation column must be located in the same distillation region no matter what the column operating conditions are. Laroche et al.[37] describe that the notion of residue curve boundaries has

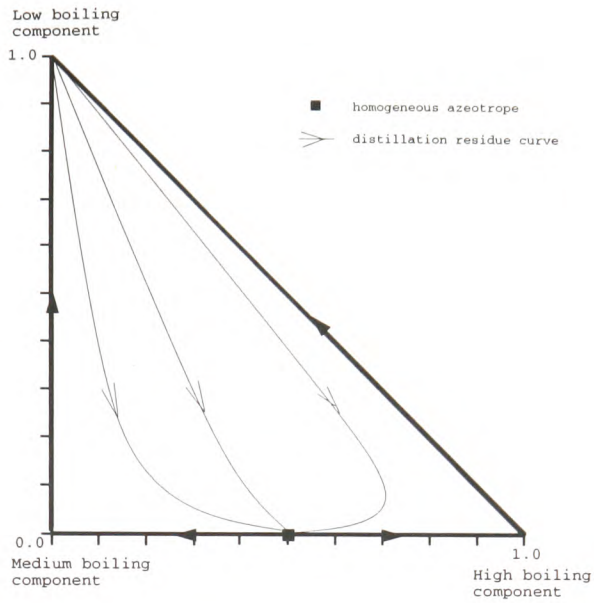


Figure 4.1: A typical residue curve map for homogeneous azeotropic mixtures.

meaning only for columns operating at infinite reflux and that finite reflux columns are almost always able to cross these boundaries, contrary to what have been reported by Doherty and coworkers. They add that even when operated at infinite reflux, the mass balance line of a column can still cross a residue curve boundary that is sufficiently curved.

We begin our analysis by distinguishing between two types of separation synthesis problems that emerge from two distinct classes of homogeneous azeotropic mixtures which are formed as a result of mixing a binary azeotropic mixture with a desired entrainer:

- a type I synthesis problem which deals with a homogeneous azeotropic mixture with *at least* one of the binary feed constituents as neither the origin nor the terminus of the residue curves. This implies that *at least* one of the binary feed constituents is medium boiling (a saddle) in relation to the entrainer and the azeotrope(s) (see any system in Figures 4.2 and 4.3). A homogeneous azeotropic mixture in this class either has no residue curve boundary or has a residue curve boundary that is linear, and therefore, *cannot* be crossed by the composition

profile of a continuous distillation column. In the case of the latter, the binary feed constituents are located in the *same* distillation region so that separation is feasible. A type I problem is referred to as *synthesis of separation sequences for homogeneous azeotropic systems without boundary crossing.*

- a type II synthesis problem which deals with a homogeneous azeotropic mixture whose binary feed constituents are either the origins or the termini of the residue curves. This implies that the boiling points of the binary feed constituents are either lower or higher than the boiling points of the azeotrope(s) and the entrainer (see any system in Figure 5.22 on page 118 of Chapter 5). A homogeneous azeotropic mixture in this class exists with the binary feed constituents located in two *separate* distillation regions. It has a residue curve boundary that is curved, and therefore, *can* be crossed by the composition profile of a continuous distillation column. This allows the binary feed constituents to lie in two *separate* distillation regions. A type II problem is referred to as *synthesis of separation sequences for homogeneous azeotropic systems with boundary crossing.*

It is well known that homogeneous azeotropic systems with or without boundary crossing exhibit distinctly different behaviour with respect to synthesis of their separation sequences. We expect a similar situation during screening and optimisation of the separation sequences for both types of systems. Optimisation of systems without boundary crossing has been studied by Knight and Doherty[29] and Knapp and Doherty[2]. In contrast, there is almost nothing available on the screening of the sequences for systems with boundary crossing. This chapter and Chapter 5 describe the procedure for synthesis of promising sequences for the homogeneous systems without and with boundary crossing respectively.

The synthesis procedure in this chapter begins with a classification of homogeneous mixtures without boundary crossing according to the boiling points of the entrainers relative to those of the binary feed constituents and the binary azeotropes. The alternative separation sequences for these homogeneous systems are then generated in Section 4.4 and screened by means of geometric reasoning (Section 4.5). The generation and screening process results in a catalogue featuring the systems' RCMs and

their corresponding most promising separation sequences. These sequences are used in conjunction with the minimum entrainer requirement (MER) described in Sections 4.6 and 4.8. Results of the study shows that the MER not only provides useful insights on the bounds and targets for the design of cleaner azeotropic separation systems but also proves instrumental in generating economical azeotropic distillation sequences.

4.3 Classification of homogeneous azeotropic mixtures with boundary crossing

The mixtures are grouped into classes of *homogeneous azeotropic systems* based on the type of entrainer used to break their azeotropes. Two most widely used criteria for the purpose are[39,50]:

1. *The boiling point of the entrainer relative to those of the binary feed constituents and the azeotropes*, e.g., high, low or medium boiling. To guarantee a feasible separation sequence, the entrainer may not form a homogeneous azeotropic mixture with a linear distillation boundary that divides the binary feed constituents into two separate regions[49]. This restriction, however, does not apply to entrainers forming liquid-phase heterogeneous regions and those which result in homogeneous mixtures with curved boundaries between the components to be separated. Liquid-phase immiscibility makes it possible to move from one region to another by using liquid-liquid phase separation. On the other hand, it is possible for a material balance line of a desired separation to cross a curved boundary by using appropriate combinations of mixing and splitting.

2. *The type of azeotrope introduced* (either maximum or minimum boiling), if any. The systems which are more common commercially are the ones with a minimum boiling binary azeotropes and an entrainer that does not add new azeotrope (i.e. systems WOBC-A1 and WOBC-A2 in Table 4.1, with system WOBC-A2 being the most common). The less common are those with maximum boiling binary azeotropes (i.e. systems WOBC-B1, WOBC-B2 and WOBC-B3 in Table 4.1, with system WOBC-B3 being the least common). We have so far come across very few

examples dealing with the separation of binary mixtures with maximum boiling azeotropes. Laroche *et al.*, who investigated over 400 homogeneous mixtures, report that binary mixtures with minimum boiling azeotropes are far more common than those with maximum boiling azeotropes[38]. This explains why most homogeneous azeotropic distillation usually separates minimum boiling azeotropes. Binary mixtures with maximum boiling azeotrope are nonetheless listed in Table 4.1 and Figure 4.3 as type WOBC-B mixtures, bearing in mind that they are of less importance commercially.

Table 4.1: Classes of ternary homogeneous azeotropic mixtures without boundary crossing.

	Entrainer for breaking the azeotrope[39,50]
WOBC-A. Binary mixture with a minimum boiling azeotrope	WOBC-A1. Medium boiler forming no new azeotrope WOBC-A2. High boiler forming no new azeotrope WOBC-A3. Low or medium boiler forming a maximum boiling azeotrope with either the the medium or low boiling constituent component respectively
WOBC-B. Binary mixture with a maximum boiling azeotrope	WOBC-B1. Low boiler forming no new azeotrope WOBC-B2. Medium boiler forming no new azeotrope WOBC-B3. High boiler forming a minimum boiling azeotrope with the high boiling constituent component

Entrainers for mixtures WOBC-A1, WOBC-A2, WOBC-B1 and WOBC-B2 in Table 4.1 results in feasible separation sequences because they neither add new azeotropes nor form distillation boundaries. The others add either a maximum or a minimum boiling azeotrope and form a linear distillation boundary which divides each of the RCMs into two distillation regions. Notwithstanding the distillation boundary, separation is still feasible since the binary feed constituents lie in the same distillation region.

In the next section, we generate the alternative separation sequences for each of the ternary systems listed in Table 4.1 and Figures 4.2 and 4.3. These sequences are then screened by means of geometric reasoning to produce a catalogue pairing the RCMs for classes of homogeneous azeotropic systems without boundary crossing and their most promising separation sequences (see Figures 4.9 and 4.10). Such catalogue provides a quick an essential guide for selecting the best separation sequence for a given

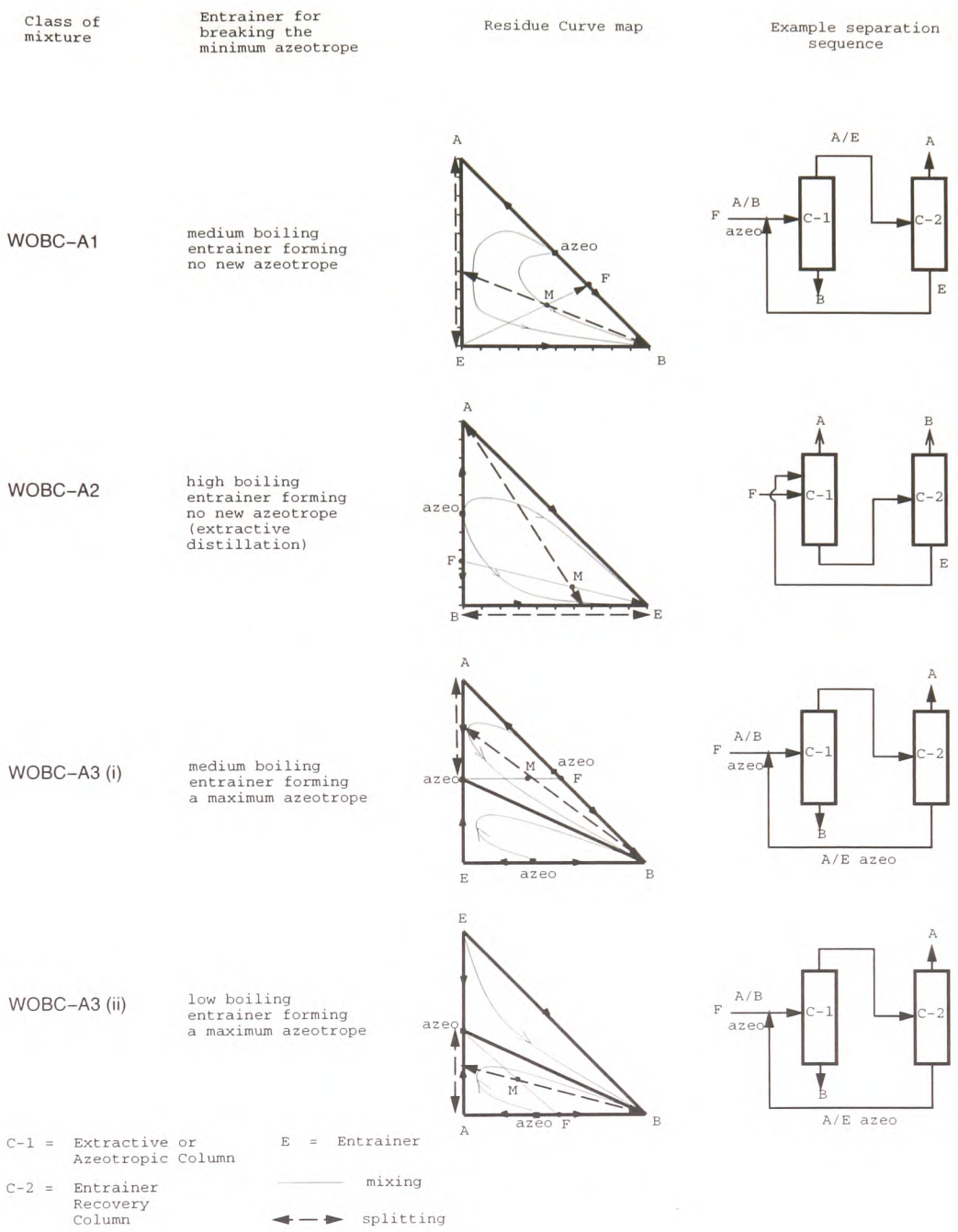


Figure 4.2: RCMs and the possible separation sequences for breaking minimum boiling azeotropes for classes of ternary homogeneous mixtures without boundary crossing.

homogeneous mixture during the early stages of flowsheet design.

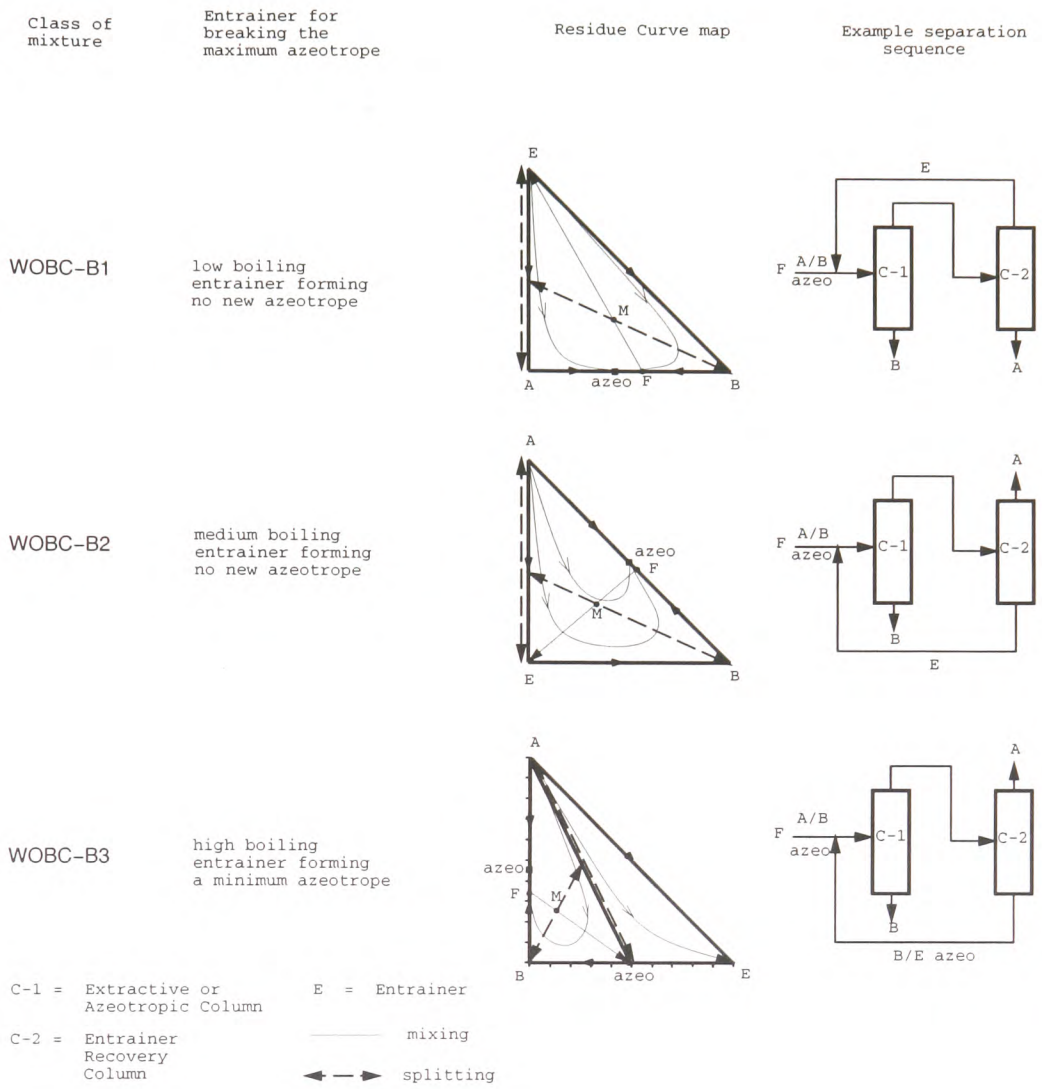


Figure 4.3: RCMs and the possible separation sequences for breaking maximum boiling azeotropes for classes of ternary homogeneous mixtures without boundary crossing.

4.4 The alternative column sequences

Synthesis of separation sequences for ideal mixtures may result in a combinatorially large number of feasible distillation sequences that can be narrowed down by using some well-established heuristics, such as the rank-ordered heuristics developed by Nadgir and Liu[51]. In contrast, the presence of residue curve boundaries and azeotropes prevent many splits that would have been feasible otherwise, drastically limiting them to a few feasible ones in the case of homogeneous mixtures in particular.

Separation of a binary homogeneous azeotrope into two essentially pure constituent components is normally performed in at least two distillation units consisting of the extractive (or homogeneous azeotropic distillation) and entrainer recovery columns[24,36,52] Laroche *et al.* also demonstrate the possibility of separating certain binary azeotropic mixtures into two pure products in only one column when both of the desired products compositions lie on the same residue curve[37]. This case is however too restrictive to the particular type of mixture mentioned. Moreover, because the entrainer goes through the azeotropic column only in a single pass, the entrainer requirement and the potential waste problems could prove expensive and detrimental in the long run even though the entrainer requirement is said to be relatively small. For these reasons, we limit our discussions to the general case of azeotropic separation which includes a separate column for entrainer recovery, i.e. a minimum of two distillation columns. Admittedly, the one-column scheme may be useful in the event that an entrainer is continuously available within the same process, as indicated in Chapter 7 of this thesis and in Manan and Bañares-Alcántara[53]. For the separation of a ternary azeotropic mixture, the number and types of alternative distillation sequences that can be generated depend on:

- *the species present in the ternary mixture.* Clearly, it is impossible to generate a priori the feasible sequences for every conceivable ternary homogeneous azeotropic mixture. Grouping these mixtures into classes, as described in Section 4.3 enable a wide range of homogeneous azeotropic mixtures to be considered.

- *the binary feed composition.* The effects of different binary feed compositions on the resulting separation structures has never been fully investigated. A synthesis study may begin with any one of the three possible binary feed compositions shown in Figure 4.4.

Laroche *et al.* [37] list some of those alternative sequences for the homogeneous azeotropic systems whose entrainers do not introduce new azeotropes. In the rest of this section, we generate every feasible distillation-based separation option for ternary homogeneous azeotropic systems without boundary crossing, including those which in-

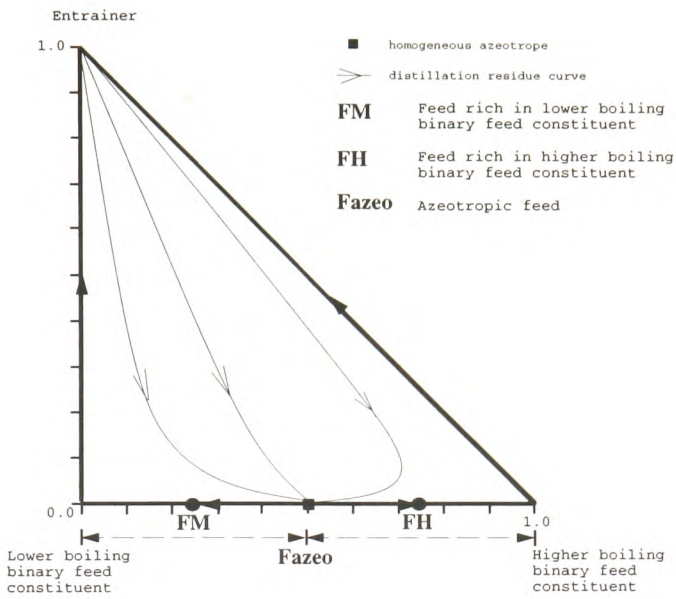


Figure 4.4: Typical binary feed compositions for synthesis of separation sequences for homogeneous azeotropic mixtures.

troduces new azeotropes (see for example, cases WOBC-A3(i) and WOBC-A3(ii) in Figure 4.2). As will be shown, each class results in a fixed number of feasible separation sequences. At this stage, we will exclude heat integration. Separation options for homogeneous azeotropic systems with boundary crossing are discussed in Chapter 5.

4.4.1 High boiling entrainer (extractive distillation, case WOBC-A2, Table 4.1)

The ethanol-water-ethylene glycol (high boiling entrainer) mixture is used as an example. Figure 4.5 shows that separation of such a system requires at least two columns. Except in the case of an azeotropic feed, any given binary feed should result in three possible sequences which include a direct sequence (options 1.1-1)[1], a direct sequence with a preconcentrator (option 1.2) and a non sharp split sequence (option 1.3). In the context of azeotropic distillation, a preconcentrator is a specific type of non-sharp split which partly removes one or more of the binary azeotrope constituents and bring the feed to the azeotropic composition before being sent to an azeotropic distillation

[1]Figure 4.6 of Section 4.4.2 illustrates the difference between a direct and an indirect sequence.

column (see Chapter 7). The first direct sequence removes ethanol overhead, water and ethylene glycol underflow. In this case, an indirect sequence is not feasible because water alone cannot be removed from the bottom of the extractive column since it is a medium boiling species.

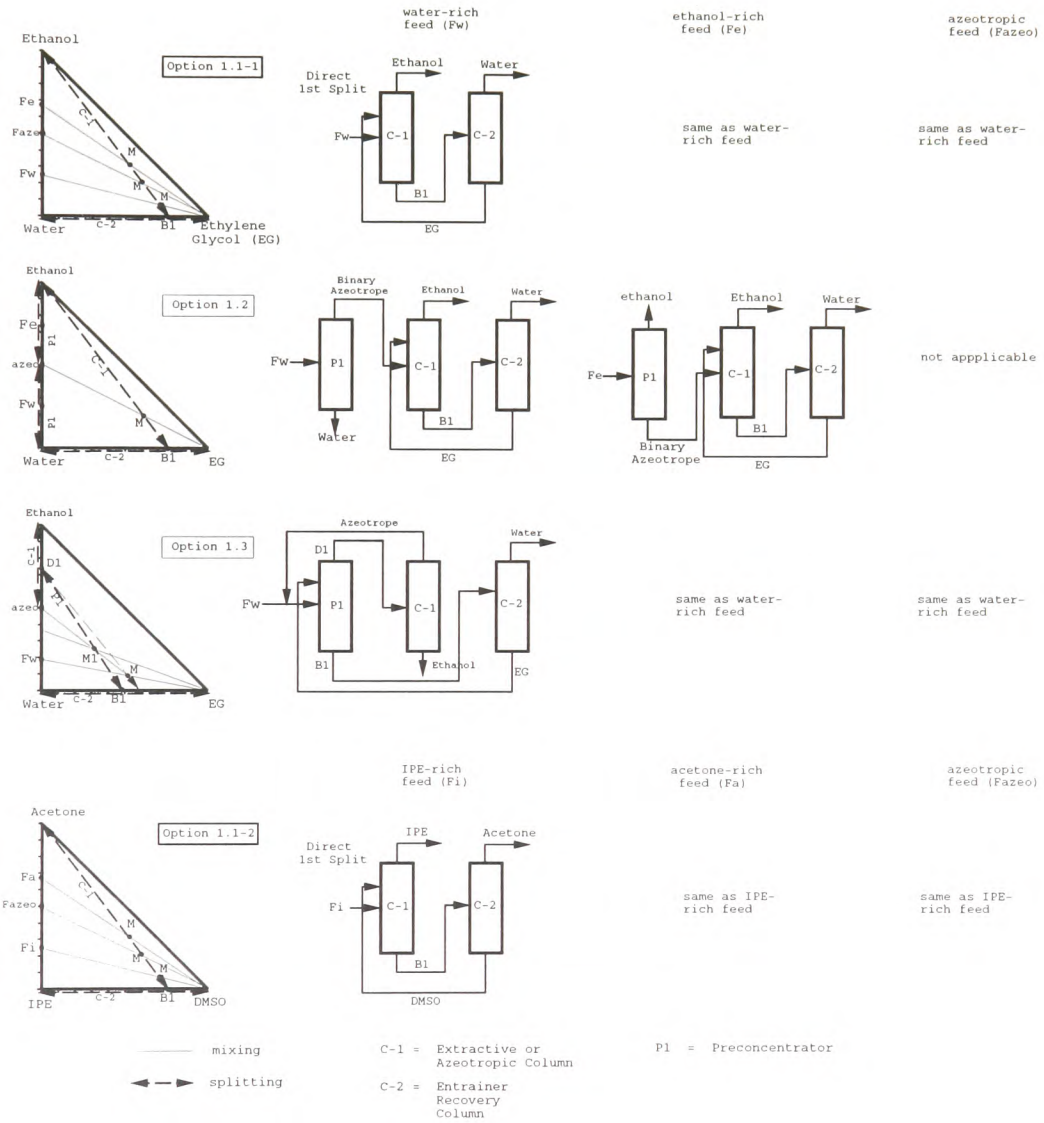


Figure 4.5: The separation options for the ethanol-water-ethylene glycol mixture (Case WOBC-A2, Table 4.1).

Another possible direct sequence (option 1.1-2) exists only for certain cases of homogeneous azeotropic mixtures which demonstrate the curious behaviour of *reversed volatility* between the binary feed constituents, making it possible to recover the me-

dium boiler overhead and the light and heavy boilers underflow. Acetone-isopropyl ether-dimethysulfoxide (DMSO) (high boiling entrainer) is an example of such system. Berg and Yeh[54] report that upon distillation, nearly pure isopropyl ether is found overhead while an acetone-DMSO mixture exits at the bottom of the extractive column.

An important final note concerns the separability and operability of extractive distillation. Separability of this system is highly dependent on the location of the entrainer feed in relation to the azeotropic feed. The high boiling entrainer feed is best placed near the top of an extractive column, above the azeotropic feed to ensure that a sufficient concentration of entrainer is available in the *extractive section* (i.e. between the entrainer and the azeotropic feed) to break the azeotrope. If a single feed is used instead, separation becomes infeasible because this eliminates the column extractive section[38]. Laroche *et al.* also state that where extraction does not play a role, e.g. for systems with medium and low boiling entrainers which add no new azeotropes, separation with a single feed is still feasible although in some cases multiple feeds may be required for optimal operations. Finally, the use of a high boiling entrainer that is far less volatile than the components to be separated leads to a bottom entrainer recycle loop which eliminates the risk of trace component accumulation.

4.4.2 Medium boiling pure or pseudo entrainer (cases WOBC-A1, WOBC-A3(i), WOBC-A3(ii),WOBC-B2 and WOBC-B3)

We may encounter one of the following ternary homogeneous azeotropic systems under this classification, i.e. the homogeneous azeotropic systems with

1. A medium boiling entrainer introducing no new azeotrope (the binary azeotrope can either be maximum or minimum boiling)(cases WOBC-A1 and WOBC-B2 shown in Figures 4.2 and 4.3 respectively)

2. A medium boiling entrainer which forms a maximum azeotrope with the light boiler (case WOBC-A3(i) in Figure 4.2)

3. A low boiling entrainer which forms a maximum azeotrope with the medium boiler (case WOBC-A3 (ii) in Figure 4.2)

4. A high boiling entrainer which forms a minimum azeotrope with the medium boiler (case WOBC-B3 in Figure 4.3)

We refer to the first one as the homogeneous azeotropic system with a medium boiling pure entrainer and the rest as the homogeneous azeotropic systems with medium boiling pseudo entrainers. The behaviour of the systems with medium boiling pseudo entrainer is *equivalent* to that of the system with a medium boiling pure entrainer.

It is quite well known that an entrainer does not have to be pure to enable separation. We define a *pseudo entrainer* to refer to the entrainers with impurities in excess of about ten percent.[2] In this case, the pseudo entrainers are either the maximum or minimum azeotropes formed between the entrainers and one of the binary azeotrope constituents, and result in distillation boundaries that separate the pure entrainers and one of the binary feed constituents into different distillation regions. Note that the first of the aforementioned systems, cases WOBC-A1 and WOBC-B2 use a *pure* medium boiling entrainer while the rest form *medium boiling pseudo entrainers.* Laroche *et al.*[36] list the possible sequences only for the cases that employ pure medium boiling entrainers. Our screening procedure include the systems with pseudo entrainers that also lead to a few other feasible separation sequences. These systems are among the common *feasible homogeneous azeotropic mixtures*[50], and are important to consider as they give designers more options in finding, for example, cleaner (environmentally friendly) *external* or *internal* entrainers (referring to either new species or species already present in the process respectively) for the purpose of minimising process waste.

Figure 4.6 shows that, except in the case of an azeotropic feed, a maximum of five alternative separation sequences may be generated for a homogeneous azeotropic mixture which employs a pure medium boiling entrainer that does not introduce new azeotropes. These include sequences with either direct or indirect sharp first splits

[2]This figure should be regarded as a mere estimate, and is chosen simply because this level of impurity is not normally acceptable in finished products.

leading to two-column designs (options 2.1 and 2.2 respectively), or with a preconcentrator (options 2.3 and 2.4) or with a nonsharp first split (option 2.5) leading to three-column designs. Figure 4.8 on page 65 shows that systems with medium boiling pseudo entrainers also result in the same type of sequences as those shown in Figure 4.6. The preceding analysis indicates that the available options for separating homogeneous azeotropic mixtures are fixed and limited. In particular, we learn that *both* the direct and indirect separation sequences exist only when the medium boiling pure or pseudo entrainer is used. In Chapter 5, we show that this finding can be generalised to homogeneous azeotropic systems with boundary crossing. The observation leads us to the following heuristic:

Heuristic 1.

> *Both the direct and indirect separation sequences exist only when the medium boiling pure or pseudo entrainer is used.*

Statements from Wahnschafft *et al.*[27] and Laroche *et al.* stating that azeotropic mixtures may result in a large number of possible separation sequences may be misleading *because homogeneous azeotropic mixtures do not normally lead to a large number of possible sequences*, as generally assumed. Therefore, it should be realised that the proposed automation of separation sequences in Wahnschafft *et al.*[55] may prove expensive and inefficient, at least as far as homogeneous mixtures are concerned. Because the number of separation options are naturally limited, *it is possible to produce a catalogue of the most promising separation sequences* for a wide range of homogeneous azeotropic mixtures commonly encountered in the process industry. Such "off-the-shelf" information would be valuable during the presynthesis stage as it eliminates potentially repetitive screening and optimisation tasks.

In the next section, the alternative separation sequences generated are screened by means of geometric reasoning in order to produce the most promising separation sequence for each class of homogeneous azeotropic system listed in Table 4.1 and Figures 4.2 and 4.3.

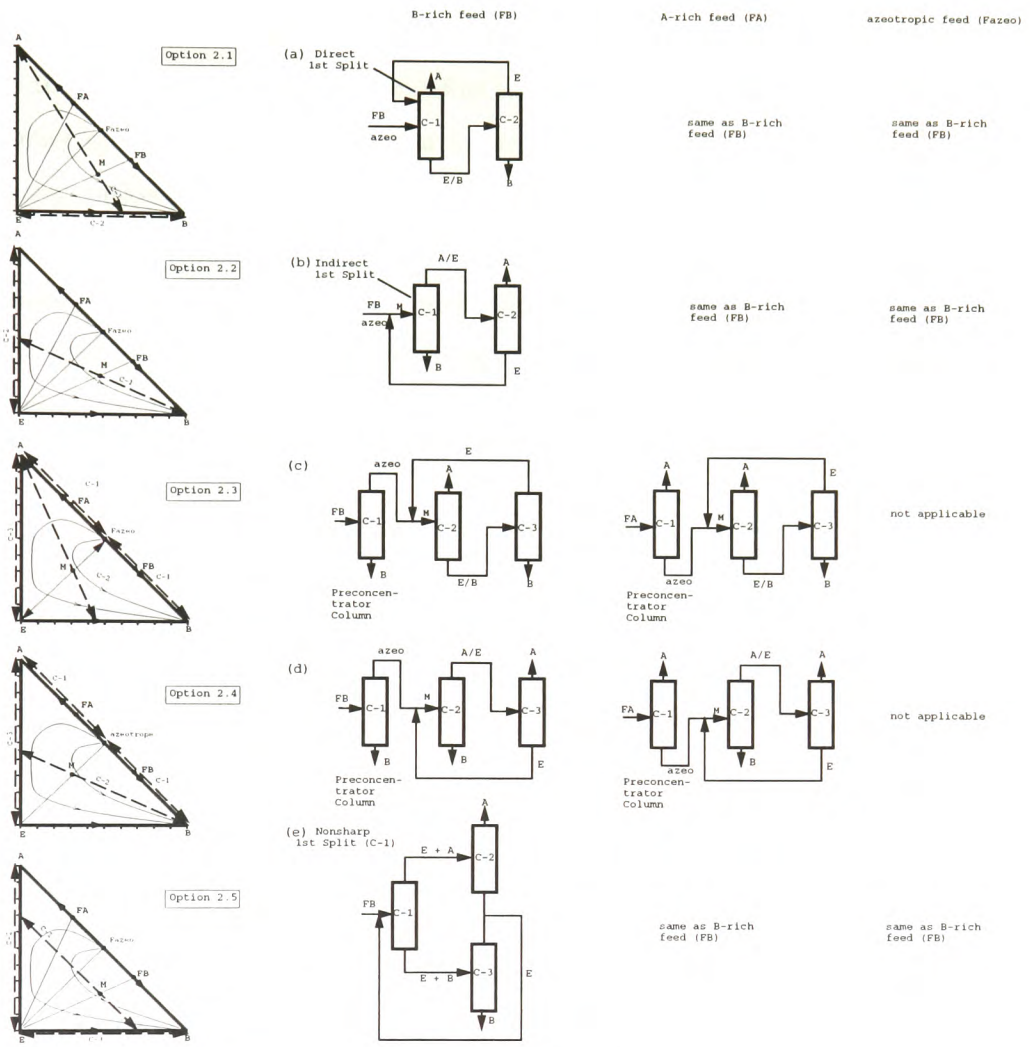


Figure 4.6: The separation options for case WOBC-A1 (and similar systems WOBC-A3, WOBC-B2 and WOBC-B3), Table 4.1. Mixture example:acetone-benzene (medium boiling entrainer)-heptane system.

4.5 Screening the alternative sequences

Two dominant synthesis parameters are proposed for the purpose of screening the alternative sequences:

1. *The number of separation units.*

The naturally high capital cost incurred by an extra column (e.g. for option 2.5) makes the *minimum unit sequence* attractive. This holds true to the extent that the entrainer

flowrate is small enough so as to avoid the increase in capital and operating costs due to the larger throughput. We define the *minimum unit sequence* as the minimum number of separation units required to achieve the desired product specifications for the separation of a ternary azeotropic mixture with a fixed feed composition. In our definition, we have used as a reference the number of units required for the sharp separation of an ideal, three component mixture by means of conventional distillation. Note that if we were to choose the most convenient feed composition, we must avoid selecting the feed that may result in a "local minimum" number of units in favour of the one giving the absolute minimum number of units.

2. *The amount of entrainer.*
Knight and Doherty prove that the entrainer to feed ratio is the dominant optimisation variable[29] by using rank ordered heuristics and proximity parameters[56]. Note that for a fixed binary feed flowrate, the entrainer to feed ratio can be changed by changing the entrainer flowrate.

In Section 4.8, we show that for the most promising sequence, the use of the minimum entrainer flowrate is cleaner and cost effective. Thus, for an azeotropic feed, the combination of minimum number of units and minimum entrainer flowrate results in a cleaner and cost effective azeotropic distillation sequence. However, feeding at other binary compositions may make the sequence with a preconcentrator (more than the minimum number of units) cleaner and cost effective (see Figure 4.2 which has been derived from the analysis in Chapter 7 and in Manan and Bañares-Alcántara[53]). A preconcentrator in those cases manage to further reduce the entrainer requirement and minimise separation difficulty, thus resulting in sequences that are cheaper than those with the minimum number of units. The preceding analysis leads to the following heuristic:

Heuristic 2.

When there is no scope for reducing the entrainer requirement, the combination of minimum number of units and minimum entrainer flowrate results

in a cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures without boundary crossing.

Separation with more than the minimum number of units is also more attractive for a number of homogeneous systems with boundary crossing due to their inherently lower entrainer requirement. Examples of such systems are discussed in Chapter 5.

In the next subsections, the alternative separation sequences for systems WOBC-A1, WOBC-A2, WOBC-A3(i) and WOBC-A3(ii) are screened. The screening procedure leads to a catalogue pairing the RCMs and the corresponding most promising separation sequences for the systems analysed (see Figures 4.9 and 4.10).

4.5.1 High boiling entrainer (extractive distillation, case WOBC-A2, Table 4.1)

The sequence with a preconcentrator (option 1.2 of Figure 4.5) with a water-rich feed is found by Knight and Doherty to be the most economical among the possible sequences for the ethanol-water-ethylene glycol system. This is true for a feed that is rich in the medium boiler (in this case, water) because the bulk of the energy required for removing the medium boiler overhead is eliminated by the use of a preconcentrator which removes the medium boiler underflow in the preconcentrator column. In Chapter 7 of this thesis, we use geometric reasoning to prove that preconcentration is not worthwhile in the case of a binary feed that is rich in the low boiler (in this case, ethanol). The sequence performing non sharp first split from option 1.3 leads to impure products. As a result, more units and recycle streams are required, thus making it an unattractive option. The RCMs and the corresponding most promising separation sequences for case WOBC-A2 at three typical binary feed compositions are represented in Figure 4.9.

4.5.2 Medium boiling pure or pseudo entrainer (cases WOBC-A1 and similar systems)

Figure 4.6 shows that the column performing a nonsharp split (option 2.5) unnecessarily results in impure products and ultimately, in more than the minimum number of columns. Unless azeotropes and distillation boundaries get in the way, we should always avoid distilling to an arbitrary composition and use sharp splits instead of nonsharp splits to minimize the number of columns. Thus, in the case of medium boiling pure and pseudo entrainers (case WOBC-A1 and similar cases), the nonsharp split sequence (option 2.5) is the first to be eliminated. The analysis in Chapter 7 proves that a feed preconcentrator for case WOBC-A1 manages to reduce the entrainer requirement, minimises separation difficulty and generally results in a sequence that is cheaper than the one with the minimum number of units.

An azeotropic feed, on the other hand, results in only three separation sequences (see Figure 4.6(c) and (d), azeotropic feed). In this case, the minimum unit sequence is the most promising since there is no scope for minimising the entrainer flowrate through feed preconcentration. The naturally high capital cost incurred by an extra column (e.g. for option 2.5) makes the minimum number of units attractive.

As previously mentioned, homogeneous systems with medium boiling pure and pseudo entrainers result in the direct and indirect sequences regardless of the binary feed composition. As far as screening the direct and indirect sequences is concerned, there are apparent contradictions among researchers, suggesting that the choice between the two is still unresolved. Laroche *et al.*[36], Buell and Boatright[57], Berg and Yeh[54] state that " the light boiler is often recovered first, but not always". Foucher and Doherty[50], on the other hand, imply the indirect sequence as preferable because it allows the use of a single-feed column and eliminate the problems of trace component accumulation.

Having shortlisted the number of possible sequences for systems with medium boiling pure and pseudo entrainers (case WOBC-A1 and similar cases) down to the direct and indirect sequences with a preconcentrator, we hereby compare them on the basis of the

following criteria: binary feedstream composition, amount of entrainer and operability constraints.

The binary feedstream composition

Information such as a mixture's binary feed composition, separation structure and the relative entrainer requirement for the alternative sequences can be obtained from the RCM. We use this information to determine which sequence leads to easier separation and less energy consumption. Note that this criteria does not apply in the case of an azeotropic feed.

Subcase WOBC-A1-1. Medium-boiling entrainer - Binary feed rich in heavy component.

Referring to Figure 4.7, the location of feedstream FB indicates that more heavy (B) than (A) component is present in the feed. The feed preconcentrators (C-1) remove B underflow in both the direct and indirect sequences. In the azeotropic column (C-2), the direct sequence recovers essentially pure A overhead and B/E mixture underflow of the azeotropic column. The B/E mixture is sent to an entrainer recovery column (C-3) which recycles the medium boiling entrainer overhead and recovers the heavy boiler B underflow. On the other hand, the indirect sequence recovers pure B and A/E as bottom and top products of the azeotropic column respectively. A/E is sent to an entrainer recovery column which removes the medium boiling entrainer underflow and light boiler A overhead.

The feed preconcentrator for the direct sequence reduces the entrainer requirement in the azeotropic column and results in less difficult B-E separation in the entrainer recovery column. On the other hand, the feed preconcentrator for the indirect sequence reduces the entrainer requirement in the azeotropic column and results in less difficult A/E-B separation in the azeotropic column (see Chapter 7 for a more detailed explanation on entrainer reduction). Note that the heavy and more plentiful component B is recovered underflow in one of the columns of each of the direct and indirect sequences. Since the heavier and more plentiful component (B) is removed underflow in both schemes and since a preconcentrator relieves the separation of one of the columns

of each scheme, we can see that both schemes are comparable from an energy point of view (assuming that all component rates are the same in both cases). Some other criteria must then be applied to screen the two schemes.

Subcase WOBC-A1-2. Medium boiling entrainer - Binary feed rich in light component.

As the binary feed approaches the pure light component (FA in Figure 4.7), the quantity of component A becomes dominant. A feed preconcentrator which removes A overhead reduces the entrainer and results in less difficult B-E separation for the direct sequence, and less difficult A/E-B separation for the indirect sequence. The energy consumption for the indirect sequence would be higher as a consequence of excess A being reboiled in two columns as compared to only one for the direct sequence.

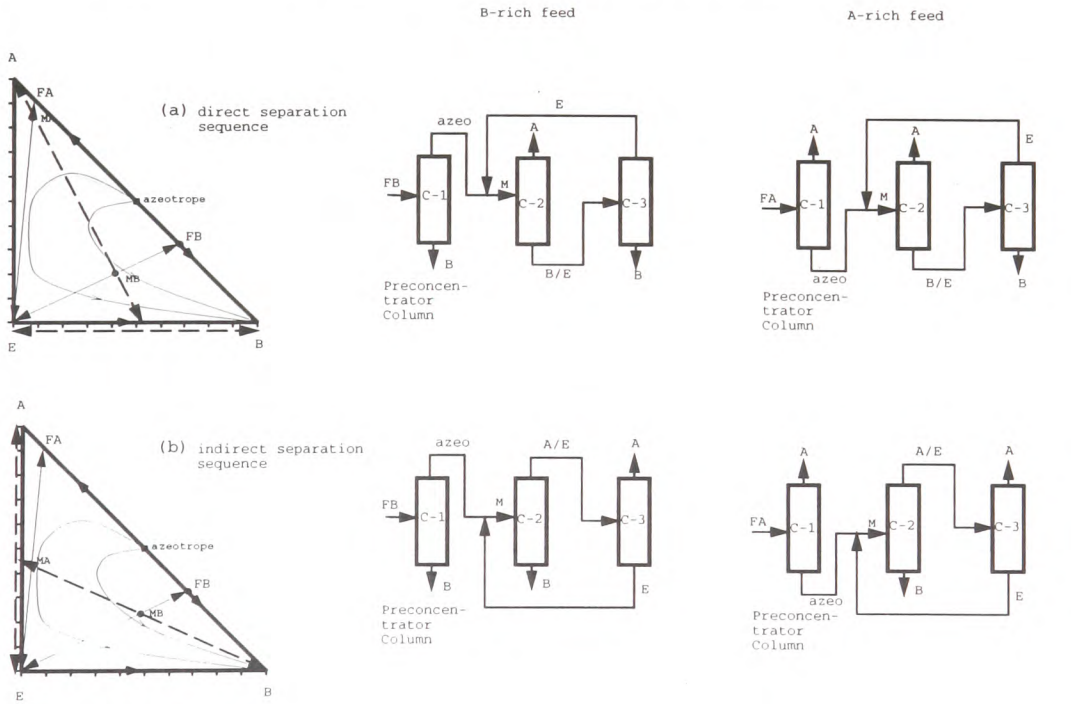


Figure 4.7: The influence of feedstream composition on energy consumption for direct and indirect separation sequences - Case WOBC-A1, Table 4.1.

The operability constraints

Azeotropic separation may cause additional problems related to separability and operability. However, since the extractive section does not play a major role in the case of a medium boiling entrainer (case WOBC-A1 and similar systems), separation with a single feed is still feasible even though multiple feeds may be required for optimal operations when a direct split is used. When a single feed is used in a direct split, a high concentration of the light component is found in the rectifying section while its concentration in the stripping section is negligible. As a result, the azeotropic column stripping section essentially performs a binary separation between the entrainer and the high boiling feed constituent. In such a case, feeding the entrainer *above* the azeotropic feed may enhance the mixture's separability.

A direct sequence is also more likely to cause trace components and light impurities to accumulate due to an overhead entrainer recycle loop. If trace component accumulation is a threat, the indirect sequence (option 2.2) should be favoured when the entrainer is a medium boiler. Note that the operability criteria applies to all feedstream composition, including an azeotropic feed.

Summary of the comparison

The advantages and disadvantages of the direct and indirect sequences are summarized in Table 4.2. From the preceding discussions it is clear that both sequences are comparable in terms of the number of units and energy consumption when the feed is rich in the heavy binary constituent. The direct sequence is however more energy efficient when the feed is rich in light component, but has clear disadvantages over the indirect sequence in terms of feed flexibility as well as operability when light impurities accumulation is a threat. We conclude that the final choice between the two sequences is largely dependent upon the process nature and operating conditions.

Table 4.2: Comparison between the direct and indirect sequences for separating homogeneous azeotropic mixtures (Case WOBC-A1 and similar)

Criteria	Direct Sequence	Indirect Sequence
Number of units	2	2
Energy consumption	more efficient when feed is rich in light component	comparable to direct when feed is rich in heavy component
Feed points	must be multiple	single or multiple
Operability	trace accumulation likely	trace accumulation unlikely

Example 4.5.1: Butanol-acetic acid-butyl acetate and water-acetic acid-methyl ethyl ketone (MEK) mixtures (medium boiling pure and pseudo entrainer system)

Figure 4.8 shows the RCMs and the alternative separation sequences for a medium boiling pseudo entrainer mixture. An example of this mixture is the butanol (A)-acetic acid (E)-butyl acetate (B) system. All three components are constituents of an esterification process, making the intermediate boiling acetic acid a very desirable candidate entrainer for breaking the minimum boiling butanol-butyl acetate azeotrope. Formation of a maximum boiling azeotrope on the butanol-acetic acid edge results in ternary a linear distillation boundary linking the maximum boiling azeotrope to pure butyl acetate, thereby dividing the map into two distillation regions. Separation between the constituent components is feasible since they lie in the same region.

Having eliminated the sequence whose non-sharp first split leads to more than the minimum number of units and impure top and bottom products (option 3.5), we are left with four possible topologies - i.e. direct or indirect sharp splits without a preconcentrator (options 3.1 and 3.2) and direct or indirect sharp splits with a preconcentrator (options 3.3 and 3.4). Since a preconcentrator is beneficial for the separation of a mixture with a medium boiling pseudo entrainer, sequences without a preconcentrator should be eliminated (see Chapter 7 and Manan and Bañares-Alcántara[53]). For a feed rich in butyl acetate (B), we find the indirect sharp split sequence comparable to the direct split in terms of energy consumption, but has advantage in terms of separ-

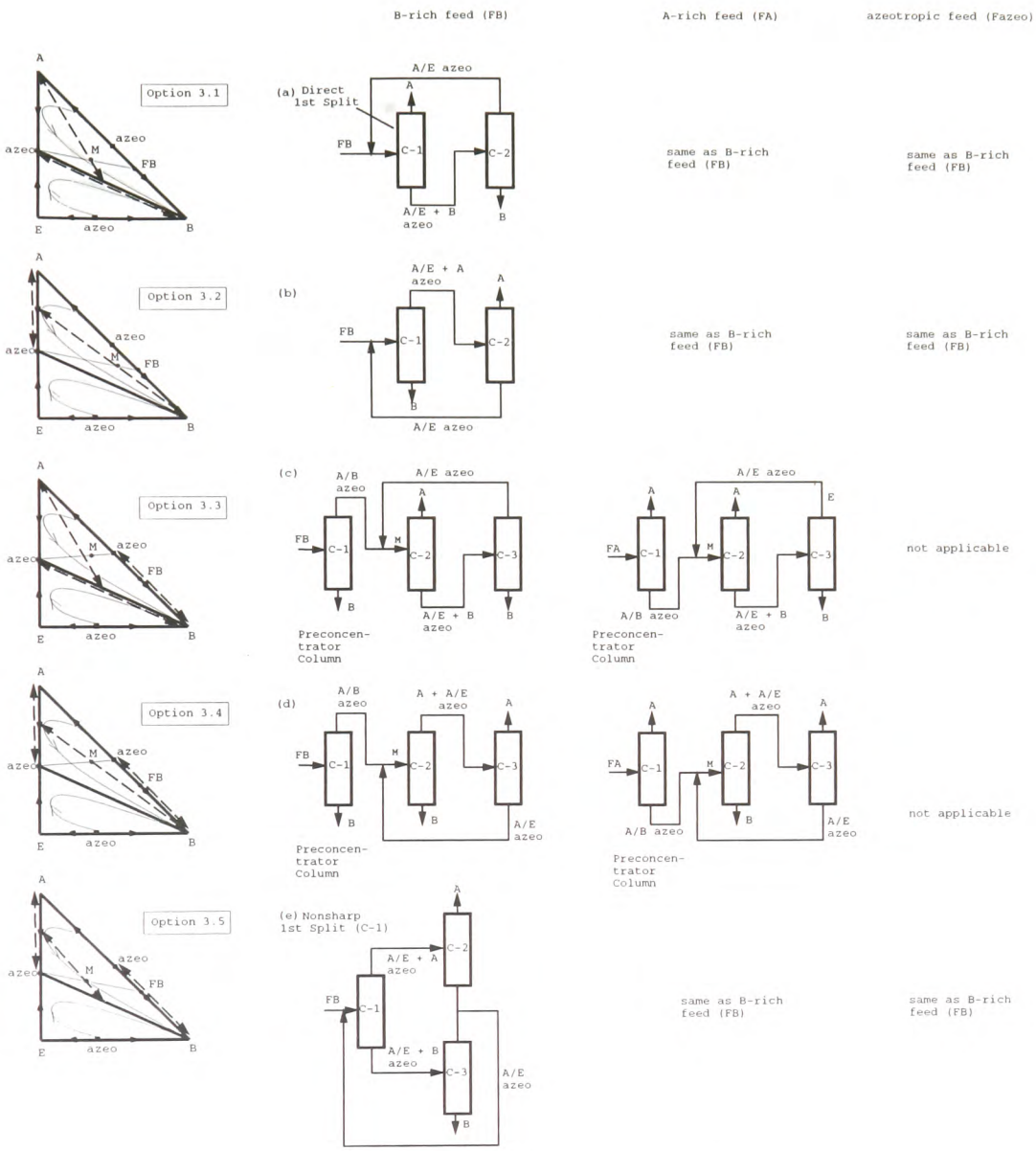


Figure 4.8: The separation options for case WOBC-A3(i), Table 4.1. Mixture example: butanol-acetic acid (medium boiling entrainer)-butyl acetate system.

ability and operability. The indirect split with a preconcentrator is proposed as the most promising sequence.

The alternative separation sequences in Figure 4.6 also apply for the separation of water-acetic acid (medium boiling entrainer)-methyl ethyl ketone (MEK) mixture. This mixture belongs to the same homogeneous azeotropic system as butanol-acetic acid-

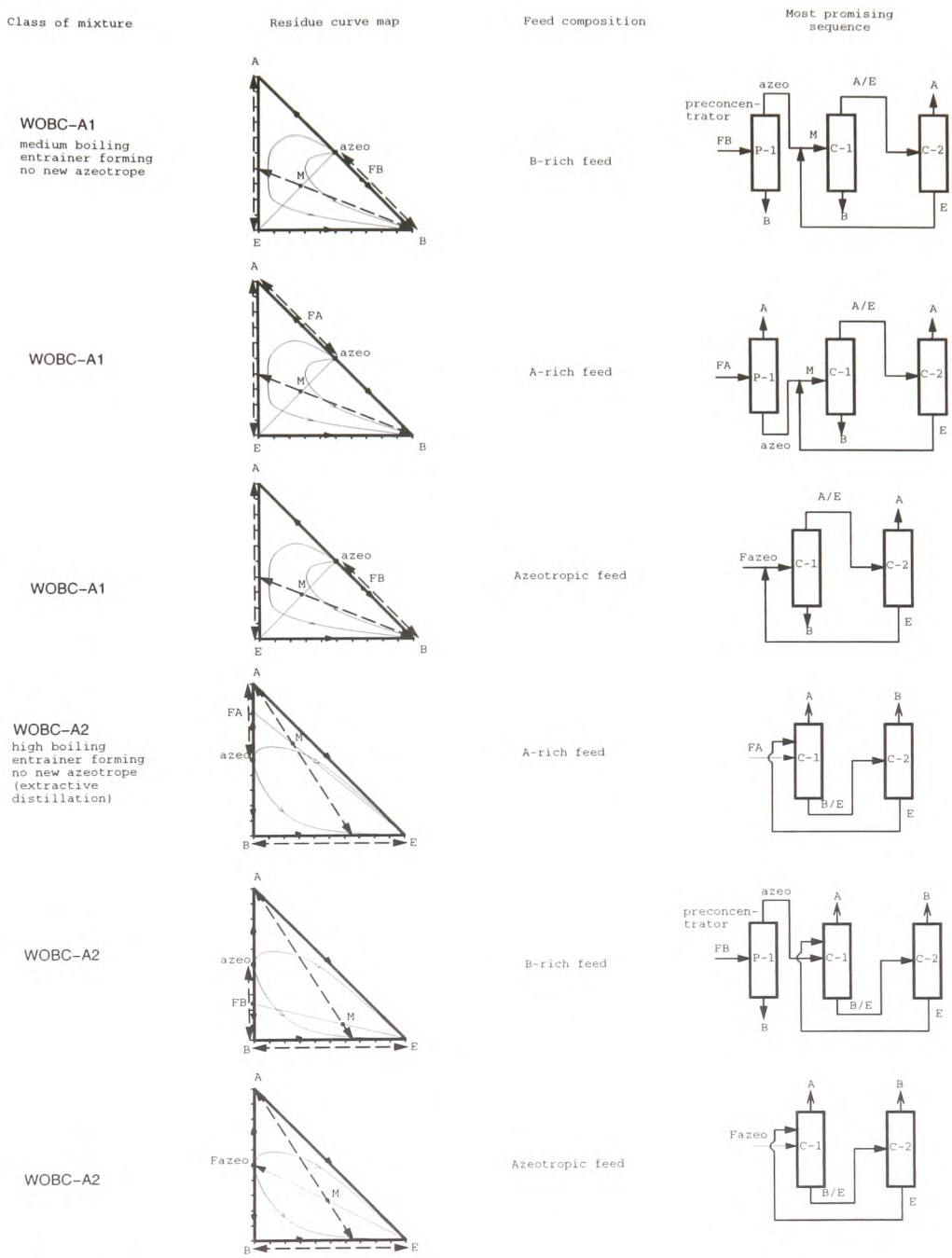


Figure 4.9: RCMs and the most promising separation sequences for breaking minimum boiling homogeneous azeotropes - cases WOBC-A1 and WOBC-A2.

butyl acetate mixture. In this case, the use of acetic acid as an entrainer *does not introduce new azeotrope* in addition to the minimum boiling azeotrope between MEK and water. Note that applying the same screening heuristics to this mixture yields the

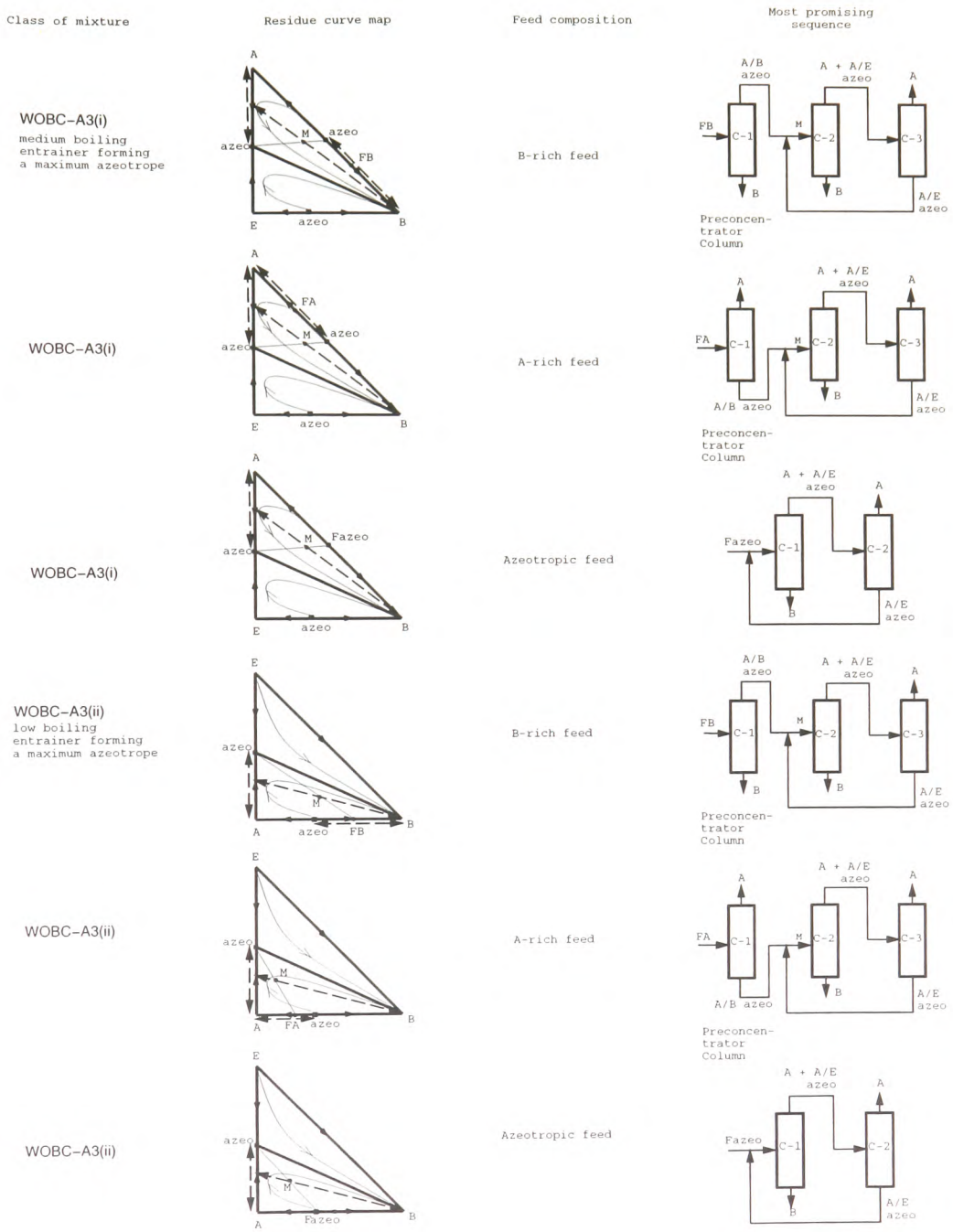


Figure 4.10: RCMs and the most promising separation sequences for breaking minimum boiling homogeneous azeotropes - cases WOBC-A3(i) and WOBC-A3(ii).

indirect sequence with a preconcentrator as the most promising separation option for a feed rich in MEK.

4.6 The minimum entrainer requirement[58]

Because entrainer usage during azeotropic separation can cause waste problems, it is best to avoid an indirect separation process (i.e. azeotropic separation; a separation process which uses an entrainer) in favour of a direct separation process (that which does not need an entrainer). In practice, it is seldom possible to eliminate this type of waste since very few direct separation processes exist as alternatives for azeotropic separation. Often, waste reduction is the more viable option. A three-way "separability tradeoff" exists among the entrainer flowrate, reflux ratio and number of stages. It means that it is possible to minimise waste by reducing the amount of entrainer, and, in order to meet the desired product specification, one must adjust the reflux ratio and number of stages. We define the minimum entrainer requirement (MER) as the lowest entrainer flowrate that allows a given product specification to be achieved in an azeotropic separation. The MER determined from the procedure described in this section will be the basis for a novel design of minimum waste and cost effective distillation sequences for homogeneous azeotropic mixtures. It will be used in conjunction with the most promising separation sequence determined by the geometric approach described in the previous sections.

In this section, we examine some of the curious and complex dependencies of separability on the *entrainer flowrate* (Section 4.6.1), on *reflux ratio* (Section 4.6.2), and on *number of stages* (Section 4.6.3). These relationships explains how these variables influence the MER, and establish their operating range during the determination of the MER. The procedure for entrainer minimisation is described in Section 4.7.

Thus far, the relations between reflux ratio and number of stages on separability has been thought to depend largely on the type of entrainer used[38]. In this section, we also report new insights explaining that the separability of homogeneous azeotropic mixtures is also strongly influenced by three other dominant parameters - the type of separation sequence, the azeotropic column feedstage location and the volatility of the entrainer. These new insights enable us to explain the peculiar dependencies of the separability of homogeneous azeotropic mixtures on the reflux ratio and the number of

stages that was until now, not yet well explained in the open literature.

4.6.1 The effect of entrainer flowrate on separability

Using ASPEN PLUS [59], a series of sensitivity analysis studies were performed on ethanol-water-ethylene glycol(EG) (high boiling entrainer), acetone-heptane-toluene (high-boiling entrainer), and acetone-benzene (medium boiling entrainer)-heptane mixtures to investigate the effects of entrainer flowrate on the separability of homogeneous azeotropic mixtures. The results of the study are shown in Figures 4.12, 4.13 and 4.14. Figure 4.11 shows the Residue Curve Map (RCM) and separation sequence for separating the ethanol-water-EG homogeneous azeotropic mixture, which is typical of all homogeneous mixtures with high boiling entrainers that do not introduce new azeotropes.

Note that two distinct trends are observed even though high boiling entrainers are used in both cases. Figure 4.12 shows ethanol purity in the distillate increasing monotonically with the flowrate of ethylene glycol until the maximum separation is achieved. In contrast, Figure 4.13 shows acetone purity increasing at low entrainer flowrates, passing a maximum, and decreasing at high entrainer flowrates. Figure 4.14 shows heptane purity passing a maximum at much lower entrainer flowrate.

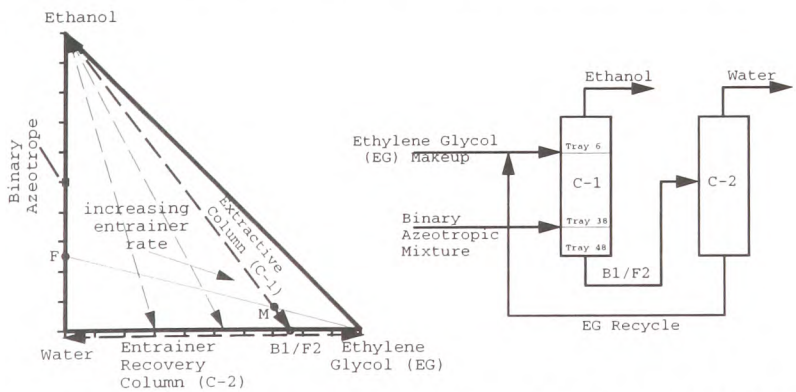


Figure 4.11: RCM and separation sequence for ethanol-water-EG (high boiling entrainer) mixture

These results suggest that the rate of entrainer being carried over with the product

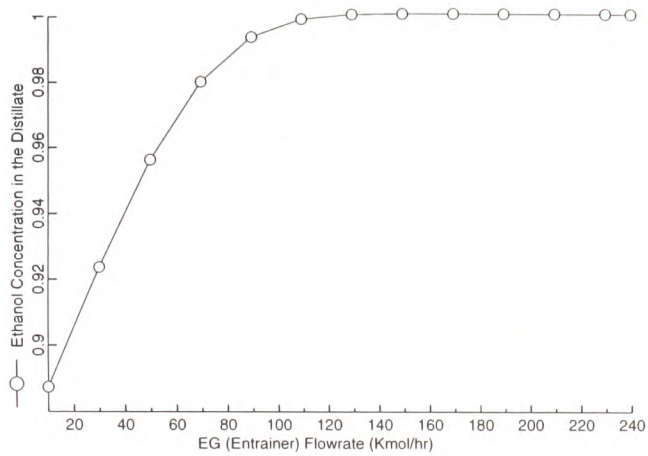


Figure 4.12: Entrainer flowrate versus ethanol concentration in the distillate for ethanol-water-EG (high boiling entrainer) mixture

has strong influence on the separability of homogeneous azeotropic mixtures. The carry over rate depends on the entrainer flowrate and the volatility of the entrainer relative to the binary feed constituents. Assuming all other things to be equal, the heavier the entrainer, the smaller the rate of carry over. For example, a high boiling entrainer like ethylene glycol (b.p. 197.4 ^oC) which is far less volatile than either of the binary feed constituents (water, b.p. 100 ^oC or ethanol, b.p. 78.3 ^oC) tends to concentrate at the bottom of the extractive column. Increasing the entrainer flowrate in this case causes negligible entrainment. In contrast, increasing the amount of

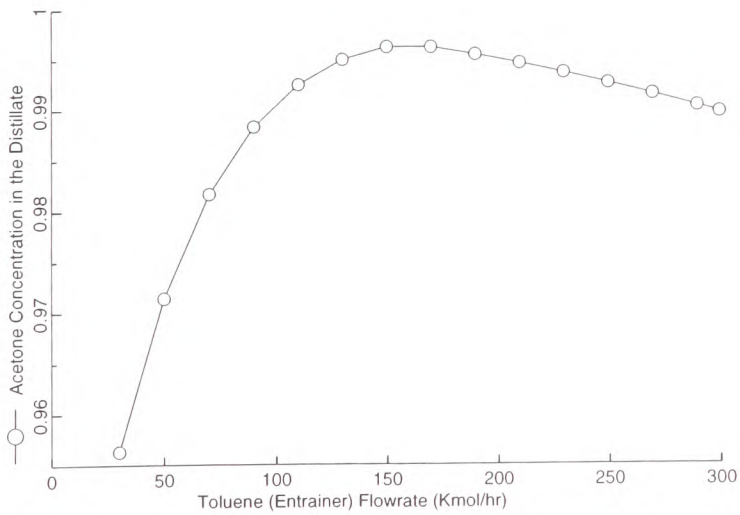


Figure 4.13: Entrainer flowrate versus acetone concentration in the distillate for for acetone-heptane-toluene (high boiling entrainer) mixture.

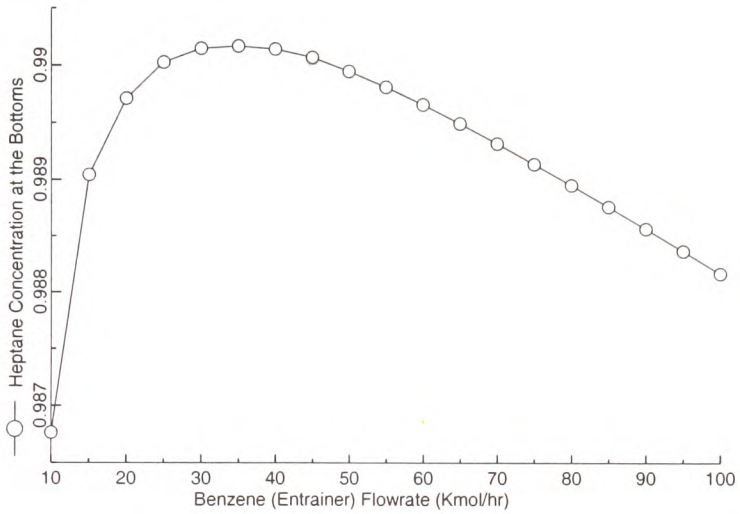


Figure 4.14: Entrainer flowrate versus heptane concentration at the bottom for for acetone-benzene (medium boiling entrainer)-heptane mixture. Number of stages: 30; feedstage locations: benzene (stage 8), binary feed (stage 27); reflux ratio: 1.5.

medium boiling entrainer, benzene (b.p. 80.2 ^oC), causes separation to decrease at high benzene flowrates as more and more benzene begin to escape with heptane (b.p. 98.4 ^oC) that is only slightly more volatile than benzene. Laroche *et al.*[38] had observed that, in some cases, increasing reflux ratio may decrease the entrainer concentration in the extractive section, ultimately causing separation to decrease. The results presented here show that the increase in entrainer flowrate (and hence, the entrainer concentration in the extractive section) can also cause separation to decrease. Depending on the volatilities of the entrainer and those of the binary feed constituents, a change in the entrainer flowrate may result in one of the following situations: 1. Separation increases monotonically with the entrainer flowrate when the entrainer is significantly less volatile than the binary feed constituents and tend to concentrate at the bottom of an extractive column. A "maximum" entrainer flowrate is reached once the entrainer versus purity curve levels off. An entrainer flowrate "working range" exists between zero and "maximum" entrainer flowrate. Separation may decrease *only* when the entrainer concentration in the extractive section becomes too low (i.e. when the reflux ratio is high, causing entrainer dilution).

2. Separation increases at low entrainer flowrates, then goes through a maximum,

and decreases at higher entrainer flowrates. This behaviour exists when the binary feed constituents are slightly more volatile than the entrainer, e.g. when a medium boiling entrainer is used. An entrainer flowrate working range exist between zero and the flowrate giving maximum separation. The maxima-type entrainer versus purity curve means that separation may decrease when the entrainer flowrate (and hence the entrainer concentration) is either too low or too high. The entrainer may become too low due to the effect of entrainer dilution. Depending on the feedstage location, carry over may result when the entrainer concentration is too high. Both phenomena, which tend to decrease separation are described in detail in the following sections.

4.6.2 The effect of reflux ratio on separability

Laroche *et al.*[38] report that, contrary to the separation of zeotropic mixtures, separation of some homogeneous azeotropic mixtures do not increase monotonically with reflux. They attribute this peculiar behaviour to two competing effects. While increasing reflux improves the operating lines in various sections of the column causing an increase in separation (positive effect), it also dilutes the entrainer in the column extractive section, decreasing the relative volatility, and thereby decreasing separation (negative effect). They further state that in the case of high boiling entrainers, the dilution effect (negative effect) becomes dominant at high reflux values. However, they fail to explain why dilution does not occur in the case of medium boiling entrainers. In the following section, we explain that the type of separation sequence (either direct or indirect split) and the feedstage location also have strong influence on the entrainer concentration in the azeotropic column extractive section, and hence, the reflux versus distillate (or bottoms) purity trend.

The influence of separation sequence and the reflux versus separability

In many cases, the relation between reflux ratio and separability depends on which type of separation sequence (direct or an indirect) is employed as opposed to the type of entrainer as Laroche *et al.*'s study suggested[38]. Figure 4.15 (a) and (b) show the direct and indirect separation sequences for acetone-benzene (medium boiling entrainer)-heptane mixture.

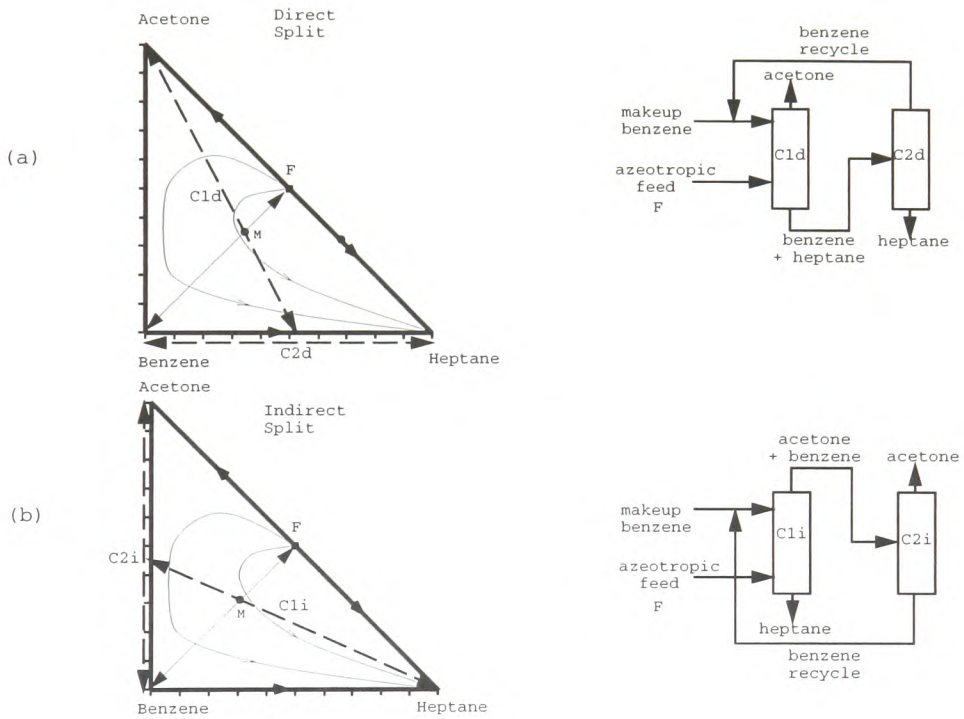


Figure 4.15: RCM and the (a) direct and (b) indirect sequences for separating acetone-benzene (medium boiling entrainer)-heptane mixture.

In a direct separation sequence, the distillate contains almost pure light component. The reflux stream which has the same concentration as the distillate tends to dilute the concentration of the entrainer in the extractive section. Figure 4.16 shows the distillate purity of an ethanol-water-EG (high boiling entrainer) mixture first increasing at lower reflux rates and decreasing at higher reflux rates as the effect of entrainer dilution becomes dominant. Note that in the case of a high boiling entrainer, only the maxima-type reflux curve is observed since only a direct separation sequence is feasible.

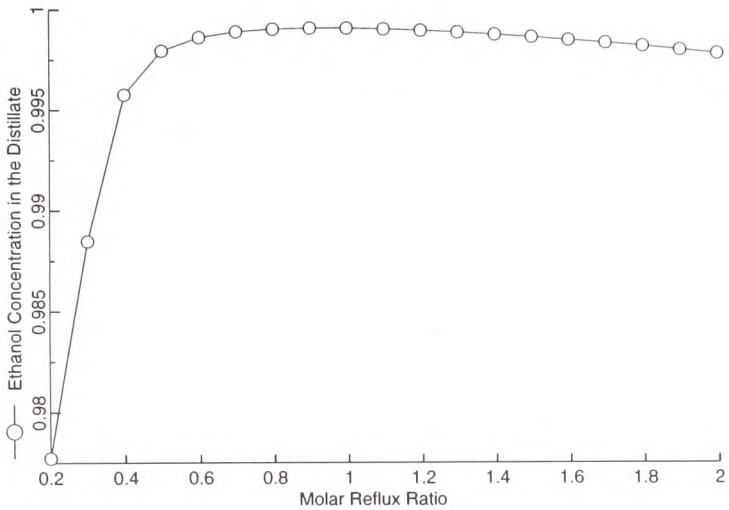


Figure 4.16: Molar reflux ratio versus ethanol concentration in the distillate for ethanol-water-EG (high boiling entrainer) mixture

When discussing a homogeneous system with a medium boiling entrainer, Laroche *et al.* assume an indirect separation sequence, for which a high entrainer concentration is present in the distillate[38]. Instead of causing entrainer dilution, Figure 4.17 shows that for the acetone-benzene (medium boiling entrainer)-heptane system, increasing the reflux maintains or increases the entrainer concentration in the extractive section, complement the improvement of the column operating lines and cause separation to increase monotonically. The maxima-type reflux trend is observed when the direct separation sequence is employed on this system (Figure 4.18). These results conclusively prove that the type of separation sequence, in combination with the type of entrainer together influence the reflux versus purity trend.

The influence of feedstage location and the reflux versus separability

The feedstage location has a strong influence on the separability of an azeotropic mixture and the reflux versus product purity trend. As a general rule, the high and medium boiling entrainers must be fed close to the top of the extractive column and the azeotropic mixture fed near the bottom so that there is sufficient entrainer concentration in the column extractive section (middle section) to break the azeotrope. Based on this rule, we have selected stage 8 and 27 as initial estimates for benzene and the azeotropic mixture feedstages in the previous example.

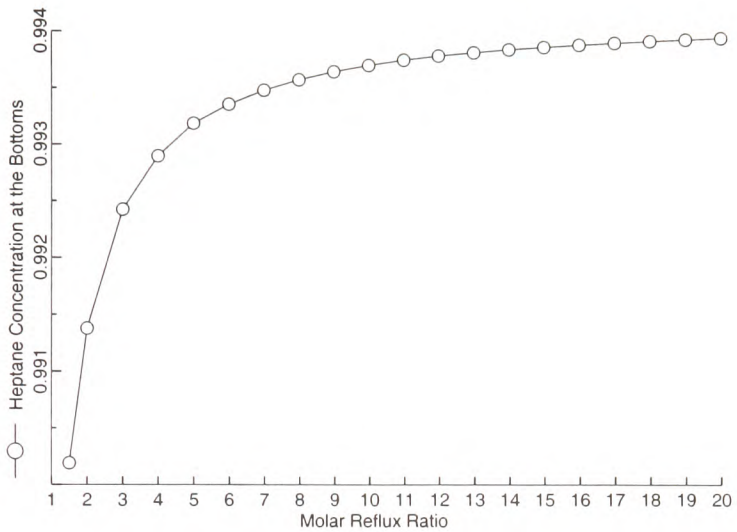


Figure 4.17: Molar reflux ratio versus heptane concentration at the bottoms for the separation of acetone-benzene (medium boiling entrainer)-heptane using an indirect separation sequence (Figure 4.15(b)).

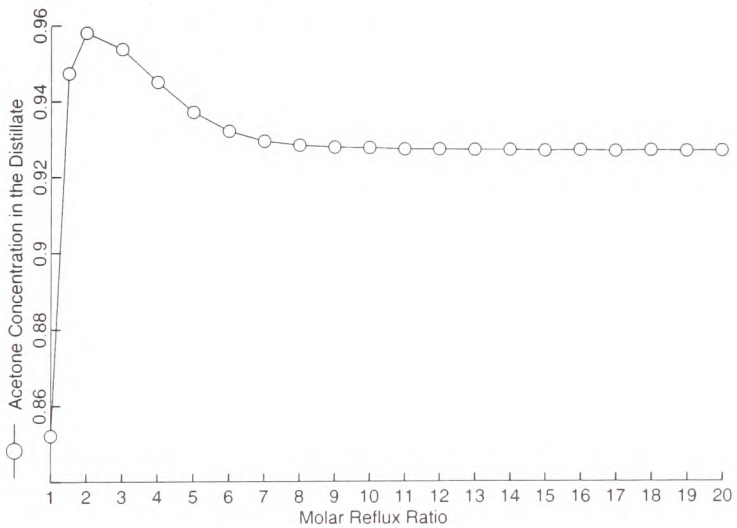


Figure 4.18: Molar reflux ratio versus acetone concentration in the distillate for the separation of acetone-benzene (medium boiling entrainer)-heptane using a direct separation sequence (Figure 4.15(a)).

We conduct a sensitivity analysis study to find the optimum feedstage combination (i.e. the one giving the highest distillate (or bottom) purity), by simultaneously varying the location of the entrainer and the azeotropic mixture feedstages, while the number of stages, reflux ratio and the entrainer flowrate are kept constant. The effect of reflux ratio on separability is investigated once the suitable feedstage locations are found.

Tray 2 and 29 are found to be the optimum for a 30-stage extractive column for separating acetone-benzene (medium boiling entrainer)-heptane mixture. Recall that Laroche *et al.*[38] suggested that increasing the reflux ratio *always* increased separation when a medium boiling entrainer is used. Results from our study show, however, that, depending on the feedstage location, increasing the reflux ratio *may or may not always* increase separation when a medium boiling entrainer is used.

Increasing reflux always increases separation with the feedstreams introduced on stages 8 and 27 (Figure 4.17) bearing in mind that separation begins to decrease as the entrainer flowrate exceeds 35 kmol/hr, as shown in Figure 4.14. However, when the feedstreams are introduced on stages 2 and 29, a maximum-type reflux versus purity curve is observed for entrainer flowrates greater than 25 kmol/hr, see for example, Figure 4.19. Figure 4.20 shows that entrainer flowrates of up to 25 kmol/hr still produce

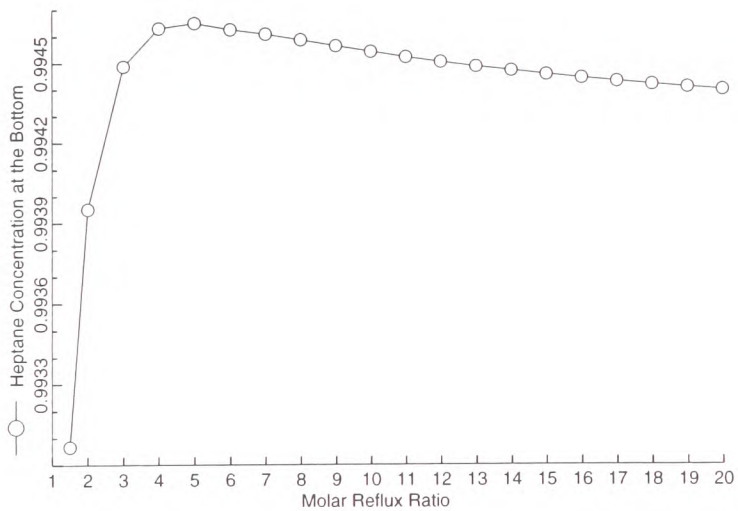


Figure 4.19: Molar reflux ratio versus heptane concentration at the bottoms for acetone-benzene-heptane mixture. Number of stages: 30; feedstage locations: benzene (stage 2), binary feed (stage 29); entrainer flowrate: 35 kmol/hr.

a monotonically increasing reflux curve for reflux ratios of up to 20. Such complex and intriguing behaviour exhibited by this mixture can be attributed to the effect of entrainer carryover described in Section 4.6.1. The rate of entrainer carryover primarily depends on (i) the entrainer flowrate (ii) the volatility of the entrainer relative to the binary feed constituents, (iii) the feedstage location and (iv) the reflux ratio. The

following analysis will focus on parameters (iii) and (iv) since (i) and (ii) have been discussed in detail in Section 4.6.1.

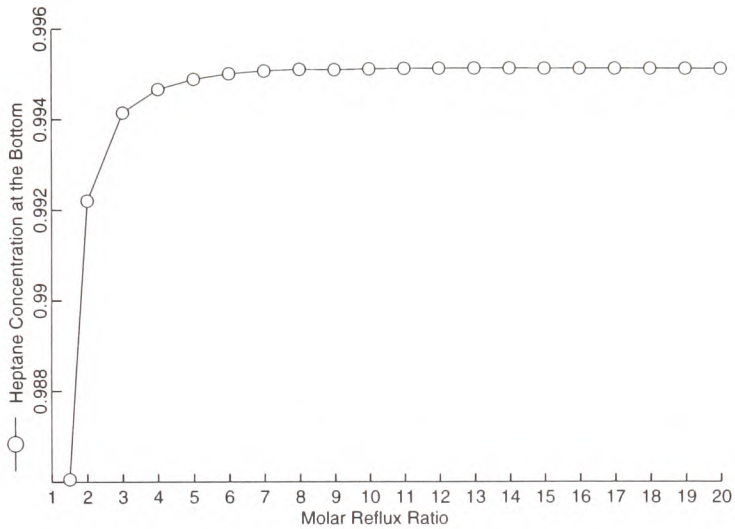


Figure 4.20: Molar reflux ratio versus heptane concentration at the bottoms for acetone-benzene-heptane mixture. Entrainer flowrate reduced from 35 to 15 kmol/hr.

The rate of entrainer carryover with the products increases at high reflux ratios as the feedstage approaches the product stage. This is due to the increase in the liquid and vapour throughput caused by the increase in reflux ratio, and the proximity of the feed and product stages. Introducing the feedstreams on the optimum stages, i.e. stage 2 and 29 gives rise two competing effects, and hence, the maximum type reflux versus purity curve. Figure 4.19 shows that feeding at the optimum stages causes heptane purity to increase at lower reflux ratios and to decrease at higher reflux ratios as the rate of carry over becomes dominant. While increasing the reflux ratio tends to improve the operating lines across the column (positive effect), the proximity of the feed to the product stages combined with the increase in reflux ratio causes entrainer carryover (negative effect). On the other hand, when the feedstreams are introduced on stages 8 and 27 there is virtually no entrainer carryover even at very high reflux because the feedstreams are distant enough from the product streams. The absence of a negative effect results in a monotonically increasing reflux trend. Notwithstanding the maximum type reflux curve, the heptane purity achieved with the feedstream introduced on stages 2 and 29 is always higher than when they are introduced on stages 8 and 27. This is because, feeding on the optimum stages results in an optimum entrainer concentration

in the extractive section which leads to maximum separability.

In determining the MER, the reflux ratio giving maximum separation must always be used for the maximum-type reflux curve. When the reflux versus purity curve increases monotonically, the reflux ratio to use occurs when the curve starts to level off.

4.6.3 The effect of the number of stages on separability

Laroche *et al.*[38] observe that for some homogeneous azeotropic mixtures, increasing the number of stages may decrease separation. They have used an acetone-heptane-toluene (high boiling entrainer) mixture to illustrate this phenomenon which they describe as unusual and inexplicable. Results from our study, however, show that as the number of stages is increased, the concentration of acetone in the distillate also increase monotonically, indicating an increase in separation, consistent with the behaviour observed in zeotropic mixtures. Figures 4.21 and 4.22 show that this behaviour is observed for both homogeneous azeotropic systems with high and medium boiling entrainers. In investigating the effect of the number of stages on separability, it is im-

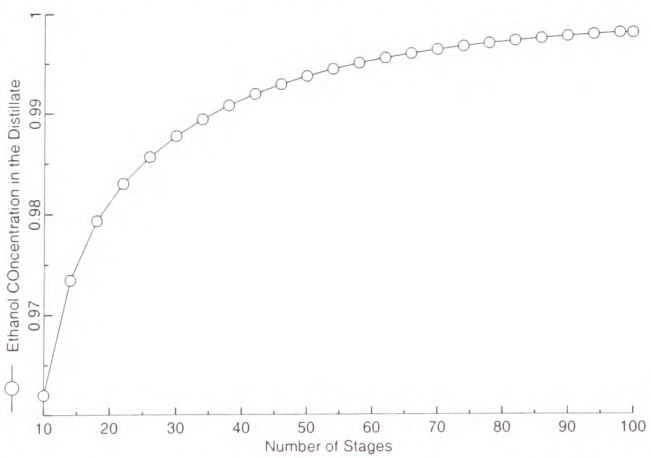


Figure 4.21: Number of stages versus ethanol concentration in the distillate for ethanol-water-EG (high boiling entrainer) mixture.

portant to compare the separation achieved with each increase in the number of stages using the same basis for the reflux ratio, entrainer flowrate, type of entrainer, type of separation sequence, and feedstage location. With these parameters fixed, the effect of entrainer dilution caused by the increase in reflux ratio and the effect of entrainment

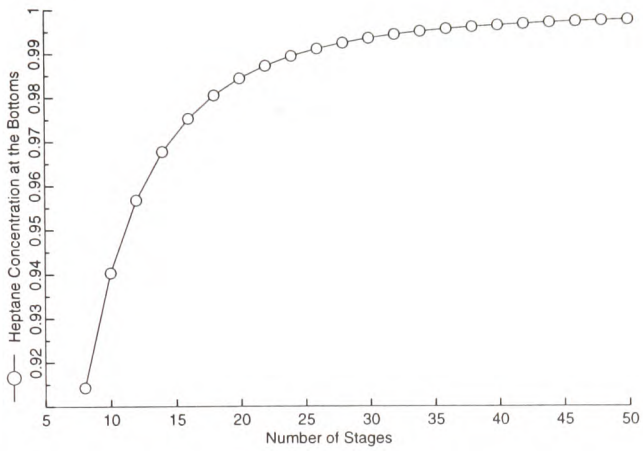


Figure 4.22: Number of stages versus heptane concentration at the bottoms for acetone-benzene (medium boiling entrainer)-heptane mixture.

caused by the increase in the amount of entrainer and the reflux ratio can thus be ruled out. As a result, any "unusual" behavior encountered in the previous sections are not expected with the increase in number of stages.The apparent contradiction between our results and that of Laroche *et al.*'s[38] may be due to the different emphasis given on feedstage location. In section 4.6.2 we emphasize the importance of specifying the optimum feedstage location to achieve maximum separability. The optimum feedstages are found through a rigorous sensitivity analysis study. In contrast, Laroche *et al.* only provide some qualitative guidelines for specifying the feedstage location.

Table 4.3 prove that suboptimal feedstage locations can cause separation to decrease dramatically even though the number of stages is increased. The results prove that for any change in the number of stages, a suboptimal feedstage specification runs the risk of getting spurious results.

Table 4.3: Increasing the number of stages may decrease separation when the feedstage is suboptimal.

Number of Stages	Suboptimal Feedstages*	Acetone Purity	Optimum Feedstages	Acetone Purity
10	4/9	0.9463	4/9	0.9463
20	5/16	0.9774	6/18	0.9811
30	5/24	0.9850	7/28	0.9900
40	4/38	0.9800	8/38	0.9931
50	3/44	0.9600	9/48	0.9945

*entrainer/azeotropic feed

4.7 Getting the minimum entrainer flowrate (MER)

The working ranges for entrainer flowrates, reflux ratio, number of stages and feedstage location and their influence on separability were establised previously and are useful in determining the MER. The procedure to establish the MER for azeotropic distillation can be best explained through a "simulated experiment" described as follows.

At zero entrainer flowrate, the distillate purity of a direct split column for separating an azeotropic mixture depends on the column reflux ratio and number of stages, and is limited by the binary azeotrope. At this point, further manipulations of the reflux ratio and number of stages can no longer improve the distillate purity until an appropriate entrainer is added to break the binary azeotrope. The effect of adding an entrainer and changing the reflux ratio on the distillate purity for an ethanol-water-EG mixture is shown in Figure 4.23. In this case, the number of stages is fixed. As a general rule, we choose the number of stages at the point where the number of stages versus the purity curve starts to level off (when not too many stages are required, e.g. in Figure 4.22), or the one which yields purity in excess of 99 percent (when it appears that many stages are required, e.g. in Figure 4.21). The entrainer flowrate and the reflux ratio are increased in a sequential manner until the product specification is reached. The optimum feedstage location must be determined for every change in the entrainer flowrate. Figure 4.23 shows that MER occurs at the optimum reflux ratio (i.e. the reflux ratio giving the maximum separation) and the desired product purity. Because different entrainer flowrates yield different optimum feed stage locations and optimum reflux ratios, it is necessary to perform a simultaneous search for the combination of these variables which lead to the MER. We accomplish this by using the Sequential Quadratic Programming (SQP) optimisation routine available in ASPEN PLUS. We specify the working range for the entrainer flowrate, reflux ratio, and number of stages[3] as the varied variables, choose the entrainer flowrate as the objective function to be minimised and the product purity as the constraint.

[3]Note that because the purity increases monotonically with the number of stages, the SQP routine will most likely pick the maximum number of stages (the upper range specified by a designer) in getting the MER. Thus the number of stages may also be fixed a priori.

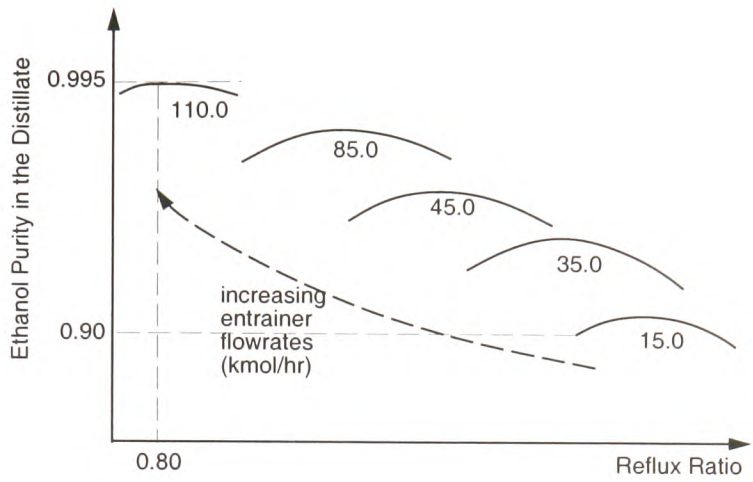


Figure 4.23: The MER is found by varying reflux ratio and the entrainer flowrate with respect to the purity of the light component in the distillate (not drawn to scale)

Optimisation yields the MER and the corresponding reflux ratio and the number of stages. The process flow diagram and input file for the separation of ethanol-water-EG mixture with minimum entrainer is included in Section B.1 of Appendix B. The optimum feedstage location is determined in a separate sensitivity study once the MER is found. The column profile giving the MER is represented on the RCM shown in Figure 4.24. Table 4.4 gives the optimisation results for homogeneous azeotropic mixtures with high and medium boiling entrainers that do not introduce new azeotropes.

Table 4.4: The MER, optimum reflux and number of stages.

Mixture	MER (kmol/hr)	Optimum Reflux	Number of Stages
ethanol-water-EG	115.5	1.163	48
acetone-benzene-heptane	2.364	40.	60
acetone-heptane-toluene	90.71	1.993	30

4.8 The MER versus the optimum entrainer flowrate

Using the rank ordered heuristics and proximity parameters developed by Fisher *et al.*[56], Knight and Doherty show that the entrainer to binary feed ratio is the dom-

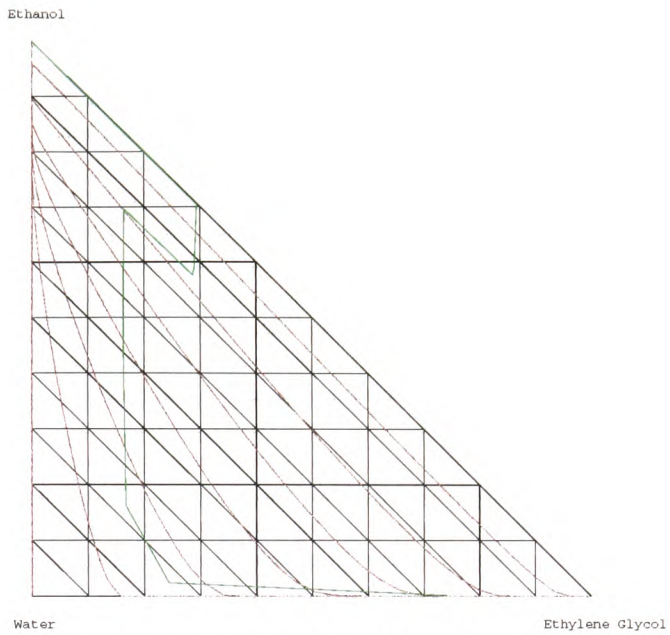


Figure 4.24: RCM and the extractive column profile. The column profile and residue curves are shown in *green and red lines respectively.*

inant optimisation variable in a distillation sequence for a homogeneous azeotropic mixture[29]. An optimum entrainer to feed ratio can be found using the optimisation procedure developed by them. This ratio yields an optimal distillation sequence for a homogeneous azeotropic mixture. In practice, azeotropic separation is performed by contacting an entrainer stream with a binary feed stream whose temperature, pressure, composition and flowrate are normally fixed by some upstream processes. Thus, during optimisation, it is possible to manipulate the entrainer to feed ratio just by changing the entrainer flowrate.

The entrainer flowrate leading to the optimum entrainer to feed ratio is the *optimum entrainer flowrate*, i.e., the one that gives the cheapest combined costs of capital and energy for a given separation sequence. The MER, On the other hand, is the lowest possible entrainer flowrate for a given product specifications. While the value of MER is absolute, the optimum entrainer flowrate depends on the following parameters:

1. *The entrainer cost.* This consists of the bulk entrainer and makeup entrainer costs. The bulk entrainer cost is a once-off investment if the entrainer is recycled. On the other hand, the annual cost of makeup entrainer is usually small due to its

small flowrate. Unless an expensive entrainer is used, or, if for some reason, the entrainer cannot be recycled, the entrainer cost should be insignificant in relation to the total annual operating cost. For most practical purposes, the optimum entrainer flowrate can be considered insensitive to the entrainer cost.

2. *The capital cost*, which include the cost of major equipment such as distillation columns, condensers, reboilers, etc.

3. *The utility cost*, which include the cost of steam, cooling water, and *electricity*. Electricity is roughly between 3 to 5 times more expensive than steam[60] and is consumed when the entrainer is continuously pumped from the recovery column back to the azeotropic column. The cost of electricity, which increases proportionally with the entrainer flowrate, constitutes a significant part of the total operating cost. Yet, is the type of cost that is quite often overlooked.

4. *Entrainer recovery and treatment costs.* Entrainer usage and handling cause stream contamination and waste problems. Note, that, in practice, entrainer recovery and treatment can seldom be accomplished in a single separation step (i.e., in a single distillation column). For mass separating agent (MSA)-based separation processes, the costs of entrainer recovery and stream treatment form a significant part of the overall investment cost and tend to increase with the increase in the amount of entrainer used.

5. *The nature of entrainer recovery.* The overhead recovery of an entrainer can be difficult and energy intensive, for example, when a large amount of entrainer is used or when the entrainer is a medium boiling component (see for example, the separation of acetone (low boiling entrainer)-IPA-toluene mixture in Section 7.3.2 of Chapter 7, and the separation of butanol-acetic acid (medium boiling entrainer)-butyl acetate mixtures in Section 4.5.2 of this Chapter). In these cases, a lower entrainer flowrate leads to a cheaper separation sequence.

Table 4.5 shows that optimum entrainer flowrate for an ethanol-water-EG separation leads to a sequence which is almost 30% cheaper in "utility cost" even though the entrainer flowrate itself is about 60% higher than the MER.[4] Such huge and unecpected

[4]The input files for these simulation runs are included in Appendix B.

discrepancy is due to the fact that, only the the capital and utility costs (excluding electricity) are considered in Knight and Doherty's optimisation study. Note that, in most cases, the optimum entrainer flowrate would approach the MER if factors 1, 3, 4 and 5 listed previously, are also considered. One must, however, bear in mind that, sometimes, low feed ratios can cause problems of operability and controllability[61]. In view of this constraint, and, of the aim of generating a cleaner and cost effective distillation sequence, we recommend that designers operate between the MER and the optimum entrainer flowrate whenever possible.

Table 4.5: A comparison between the cost of sequences operating with MER and with the optimum entrainer flowrate (OEF), obtained using the optimisation procedure of Knight and Doherty.

	sequence X, with MER	sequence Y, with OEF	% difference (X - Y)
entrainer flowrate (kmol/hr)	119.0	288.0	-59%
capital cost (x 10^6\$)	0.629	0.585	+7%
utility cost* (x 10^6\$/yr)	0.488	0.351	+28%

* cost of steam and cooling water combined (electricity excluded).

The preceding analyses lead us to the heuristic:

Heuristic 3.

> *For a cleaner, cost effective and more operable separation sequence, a designer should operate in the range between the MER and the optimum entrainer flowrate.*

The optimum entrainer flowrate gives the exact location of the *optimum ternary feed composition* (i.e., point M) on the binary feed-pure entrainer mixing line shown in Figure 4.25. From optimum ternary feed composition, it is possible to locate the *region of optimum product compositions* or the *optimum "bow-tie" region* which results from the use of direct and indirect separation sequences.

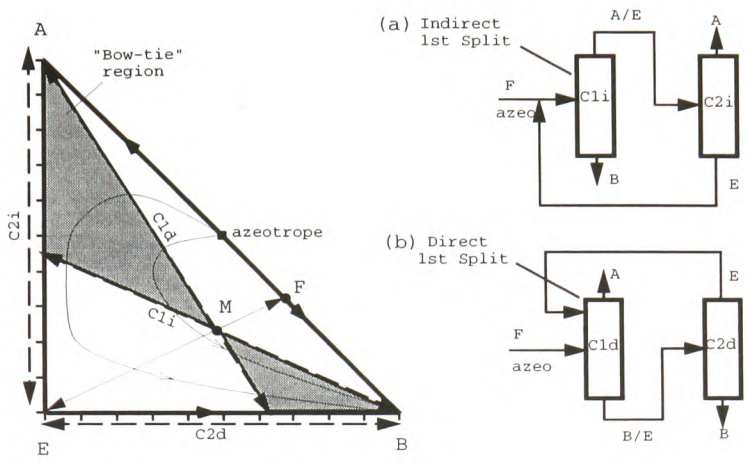


Figure 4.25: The optimum entrainer to feed ratio results in the optimum product composition region - case of a medium boiling entrainer introducing no new azeotrope (case WOBC-A1, Table 4.1).

4.9 Applicability of the entrainer minimisation and optimisation procedures

Knight and Doherty state that the procedure for entrainer optimisation "applies quite generally to nonideal and azeotropic separations" despite it having been applied only to classical extractive distillation processes which have no distillation boundary and only one minimum binary azeotrope[2,29] (see for example, Figure 4.5). Ryan and Doherty, on the other hand mention the possibility of extending the procedure to heterogeneous systems[30]. Given the influence of azeotropes and distillation boundaries on the synthesis of the separation sequences, and the wide spectrum of homogeneous azeotropic mixtures available in nature, the following fundamental issues concerning the generality of the approach appear unresolved: Is the entrainer minimisation or optimisation procedure applicable to more complex homogeneous mixtures with ternary azeotropes and mutiple binary azeotropes? How do these approaches deal with systems with or without boundary crossing, and cases with multiple distillation regions? Are the procedures directly applicable to heterogeneous systems? How to determine the optimal column sequence for the wide spectrum of homogeneous mixtures?

To be able to answer these questions, we begin by explaining the basic steps involved in

the optimal synthesis of distillation sequences for azeotropic mixtures. Synthesis may proceed in three sequential stages:

1. Selection or preliminary screening of entrainers to yield feasible separation sequences (see Table 4.1).
2. Search for feasible sequences.
3. Entrainer minimisation and optimisation.

The need to select a suitable entrainer for azeotropic separation essentially guarantees that only separable mixtures are formed. For homogeneous azeotropic systems, "separable mixtures" refer to those with a maximum of one ternary and three binary azeotropes with at most, two distillation regions[39,50]. Clearly, an appropriate entrainer precludes the synthesis of infeasible sequences.Some modifications are required to extend the entrainer flowrate optimisation procedure to homogeneous azeotropic systems with boundary crossing and to heterogeneous azeotropic systems. We propose a third heuristic:

Heuristic 4.

> *The entrainer flowrate minimisation and optimisation procedures are applicable to any industrially important azeotropic mixture for which suitable entrainers can be found. Where there are more than one feasible separation sequence for a homogeneous azeotropic mixture, it may be necessary to analyse each sequence individually in order to make a rational choice among the competing structures.*

Clearly, such practice becomes quite cumbersome as the number of possible sequences increases with the mixture complexity. To overcome this problem, we use the shortcut approach based on heuristics and geometric reasoning introduced in Section 4.5 to screen the sequences generated for homogeneous azeotropic mixtures without boundary

crossing. The entrainer flowrate is then optimised for the selected sequence to produce the most promising option.

In developing the procedure for generating the most promising separation sequence, no claim is made that the solution represents the global optimum. It is however clear that by minimising the number of units and by keeping the entrainer flowrate at a desirable value, we are able to minimize operating cost and capital investment. As a result, we can guarantee that the sequence generated is among the most promising design options, and that the computations involved are kept to a minimum.

Chapter 5

Synthesis of Distillation Sequences for Homogeneous Azeotropic Mixtures - Systems With Boundary Crossing (Systems With Curved Boundaries)

This chapter focuses on the synthesis of cleaner and cost effective separation sequences for homogeneous azeotropic systems with boundary crossing. Section 5.1 emphasizes the unique role played by systems with boundary crossing in the separation of homogeneous azeotropic mixtures. To enable us to consider a wide range of these mixtures, they are grouped into classes according to the magnitude of the boiling point of the entrainer relative to those of their binary feed constituents and binary azeotropes.

The synthesis of homogeneous systems with boundary crossing requires an accurate prediction of the distillation boundary. In Section 5.2, we combine process simulation and a geometric approach to enable us to predict the shape and extent of distillation boundary curvature, and to locate a curved distillation boundary with efficiency and accuracy. Once this is done, the alternative separation sequences for these systems are generated (Section 5.2.1). This is followed by elimination of inferior sequences (Section 5.3), leaving only a few promising ones. Synthesis and screening are done by means of geometric reasoning.

In order to screen between the shortlisted sequences, their capital and operating costs

are evaluated using ASPEN PLUS correlations[59] based on the minimum entrainer requirement (MER), and the optimum reflux ratios and component split fractions obtained from simulation. In Section 5.4, the procedure developed for systems *without* boundary crossing has been modified to determine the MER for the sequences shortlisted. Section 5.4 concludes with the analysis and comparison of the design and economic performances of the shortlisted sequences. The synthesis and screening process results in a catalogue pairing the systems RCMs with their corresponding most promising separation sequences.

5.1 Classes of systems with boundary crossing

It has been claimed that systems with curved boundaries are either too rare or that the curvature effects are rarely useful for engineering purposes[49,50]. However, studies done by Stichlmair *et al.*[34,35,39] and Laroche *et al.*[37,38] show quite the contrary. Stichlmair *et al.*[35] state that a system with a curved boundary may be formed by selecting an entrainer in such a way that the binary feed constituents are either the origins or the termini of the residue curves. This results in the binary constituents lying in different distillation regions.

A very useful survey completed by Laroche *et al.*[38] indicates that in 384 out of 416 cases the binary feed constituents are separated by a distillation boundary which is curved to a certain extent. 20 out of the 384 are cases of low boiling entrainers which do not introduce additional azeotropes, but, again, form curved distillation boundaries. This type of mixture is almost as common as the 31 extractive distillation cases out of the 416 mixtures investigated. In 362 out of the 384 cases mentioned, the binary azeotropes introduced by the entrainers are all minimum boiling. The survey indicates that it is quite common for two azeotropic constituents to be separated by a curved distillation boundary, which in principle permits separation across it, "even when the boundary looks almost straight". This is exemplified by the ethanol-water-methanol (low boiling entrainer) mixture in the study. In summary, the systems with curved boundaries are important to consider because they occur commonly and demonstrate

the classic effect of boundary crossing, posing a special type of synthesis problem for azeotropic systems. Interesting entrainers, and hence flowsheet alternatives may be overlooked if this effect is ignored.

Table 5.1 gives most classes of ternary homogeneous azeotropic systems with curved boundaries. Perhaps one of the major problems of considering systems with curved

Table 5.1: Classes of homogeneous azeotropic mixtures with boundary crossing.

	Entrainer to break the azeotrope[35]
BC-A. Binary mixture with a minimum boiling azeotrope.	BC-A1. Low boiler (lower than the binary feed constituents or their azeotrope). BC-A2. Medium boiler forming a minimum azeotrope with the low boiling binary feed constituent. BC-A3. High boiler forming minimum azeotropes with both binary feed constituents. At least one of the new azeotropes has to boil lower than the azeotrope formed between the binary feed constituents.
BC-B. Binary mixture with a maximum boiling azeotrope.	BC-B1. High boiler (higher than the binary feed constituents or their azeotrope). BC-B2. Medium boiler forming a maximum azeotrope with the high boiling binary feed constituent. BC-B3. Low boiler forming maximum azeotropes with both binary feed constituents. At least one of the new azeotropes has to boil higher than the azeotrope formed between the binary feed constituents.

boundaries is that only rigorous and exact methods are currently able to detect and accurately locate these boundaries. Unless a system possesses boundaries that are *sufficiently curved* so as to allow them to be crossed by columns operating at infinite reflux, a rigorous approach to locate these boundaries may prove unnecessary. Perhaps this is one of the reasons why some design and synthesis studies (including those of Doherty and co-workers) work on the assumption of linear boundaries which prohibit boundary crossing even for columns operating at finite reflux.

We emphasize that unless the mixtures with curved boundaries are analysed case by case, no conclusions can be drawn with regards to their potential separation schemes. It is quite well known, however, that only mixtures whose boundaries are strongly curved

always permit boundary crossing at infinite reflux, hence finite reflux. Thus, we make the practical working assumption that *a mixture whose binary feed constituents lie in different distillation regions must exhibit a strongly curved boundary in order to permit boundary crossing and guarantee a feasible separation sequence.* A direct consequence of this conservative assumption is that we need to quickly differentiate between ternary mixtures with strongly curved boundary from those with almost linear boundaries. For a given ternary mixture, it is useful to be able to predict (a) the boundary shape (either concave or convex with respect to the feed) and (b) when a boundary is likely to be strongly curved. Rigorous calculations to locate the exact boundaries are performed only when a strong curvature is anticipated. Otherwise, the method will reject a mixture as infeasible for boundary crossing.

In the next section we present a method which combines heuristics and simulation that allows us to *predict* the boundary shape and the extent of the boundary curvature, and to *locate* these boundaries with reasonable accuracy. Our method requires information which includes the boiling points of the pure components and azeotropes and vapor-liquid equilibrium data obtained from simulation.

5.2 A hybrid procedure for detecting and locating curved boundaries

Knowing the exact location and shape of the residue curve boundaries is crucial for the accurate prediction of the separability at infinite reflux. Van Dongen and Doherty[48] propose an exact and rigorous method to locate the positions of these boundaries by tracking the "pinches" (fixed points in the distillation model equations) as a function of the column parameters - e.g. reflux or reboil ratio, feed quality or entrainer to feed ratio. A detailed vapor-liquid equilibrium model is required for this purpose.

A set of heuristics based on the boiling points of the pure components as well as of the azeotropes and the RCM geometry were later developed by Foucher and Doherty to locate linear boundaries as an approximation to the actual residue curve boundaries[50]. This approach manages to eliminate detailed calculations and is said to be adequate

for the purpose of entrainer screening. Its major disadvantage is that the procedure is unable to detect boundary curvature and thus may yield erroneous results when used for systems with boundary crossing. Indirectly, Foucher's approach precludes the consideration of useful entrainers (and the systems with curved boundaries that they form) during the identification of feasible RCMs.

It is well known that a truly linear residue curve boundary can never be crossed by a profile of a continuous column operating at infinite reflux and that curved boundaries can be crossed only from the concave side. We utilize this information together with a set of entrainer selection guidelines such as the ones provided by Stichlmair and Herguijuela[35] to device a simple test for detecting the *shape and the extent* of a boundary curvature. It is hoped that such a quick and exact approach would allow the effect of boundary crossing to be fully exploited during the design and synthesis of azeotropic distillation sequences for the many mixtures exhibiting boundary curvature.

Referring to Figure 5.1 and using an acetone-chloroform-benzene(high boiling entrainer) mixture as an example, the hybrid approach, which combines geometric reasoning and simulation is described as follows:

Step 1. On a ternary diagram, place the residue curve boundaries according to the heuristics method proposed by Foucher and Doherty[50] which is based on the boiling points of pure components and the binary as well as ternary azeotropes. This heuristic procedure is necessary to help establish the appropriate boundary extreme points and focus the boundary search. Using the rule "there is a unique connection for each binary saddle" from Foucher and Doherty's method, we are able to identify the maximum boiling azeotrope and the high boiling entrainer (benzene) as the extreme points for the "linear boundary".

Step 2. Pick a 1:1 ratio between the entrainer to binary feed to get the base-case entrainer-binary feed mixing point (point F' in Figure 5.1). Place the first column material balance line, noting that the end with limited separability should lie along the "linear boundary" found in step 1 (point B1' in Figure 5.1).

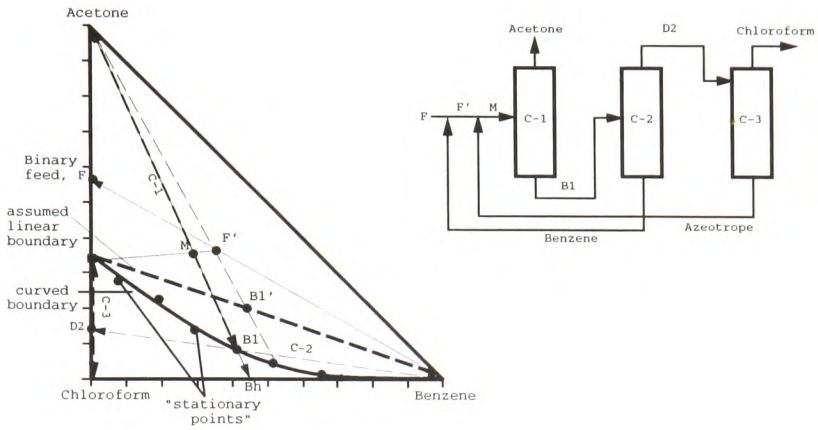


Figure 5.1: Predicting and locating a curved distillation boundary using a hybrid procedure.

For this ratio of entrainer to binary feed, note that acetone from the feed stream cannot be recovered completely as the distillate of the first column. The remaining acetone, which is distributed in the bottoms, will be recovered in successive columns. Therefore, the percentage recovery of acetone in the distillate of the first column, or the acetone distillate to feed ratio (D:F) should be specified between 0 and 1.

Step 3. Perform a *boundary shape* and *curvature* test in two steps:

- 3a. Predict if a boundary is curved. Use the entrainer selection criteria by Stichlmair and Herguijuela[35] (from Table 5.1).

  We identify the acetone-chloroform-benzene example as being of type BC-B1: acetone and chloroform form a maximum boiling azeotrope (A/C azeo) and benzene is an entrainer heavier than acetone, chloroform and A/C azeo, and does not form a new azeotrope.

- 3b. Test the shape and the extent of curvature. Use the following boundary curvature test:

  Based on the approximate boundary location found in step 1, it is expected that for this mixture the bottoms of the first column have limited separability. We then test the shape and extent of the boundary curvature by finding this column's separability limit. This limit is marked by a fixed (in this case, bottom) com-

position of a distillation column simulated at infinite reflux and an assumed D:F ratio. If the composition straddles the linear boundary, a curved boundary that is concave with respect to the feed is confirmed. We then compare this fixed point (on the material balance line) against the one intersecting the assumed linear boundary, B1'. If a strongly curved boundary is anticipated, proceed to steps 4 and 5 to determine the exact boundary location by steady-state simulation, otherwise assume a straight boundary.

Step 4. Estimate the component *split fraction*, i.e. the distillate D (or bottoms B) recovery relative to the feed F (D:F or B:F) for the product undergoing non-sharp split in the first column of the sequence. This is done by varying the D:F (or B:F) ratio of the species undergoing non-sharp split (in this example, acetone) with respect to the bottoms composition of the other binary feed constituent (in this case, chloroform). The number of stages, the feed stage location and reflux ratio must be fixed for this purpose. *Select the limiting D:F ratio, i.e. the one giving the highest bottoms purity for the second binary feed constituent (in this case, chloroform).*

Note that for a given entrainer flowrate, it is possible to estimate a component split fraction in the azeotropic column by geometric approach. Using the lever rule, the ratio of the length of acetone-B1 material balance line to that of a hypothetical acetone-Bh line in Figure 5.1 gives the acetone split fraction (D:F ratio) in the azeotropic column.

Step 5. Run mutiple simulation cases for columns operated at several different entrainer flowrates with the corresponding D:Fs determined from step 4, and at various reflux ratios. Watch for the situation when the recovery fraction of the bottom products remains constant, signifying the onset of a residue curve boundary. Points on the distillation boundary for the acetone-chloroform-benzene (high boiling entrainer) system are listed in Table 5.2. Figure 5.2 includes the distillation boundary and residue curves which have been plotted using a MAPLE application[62].

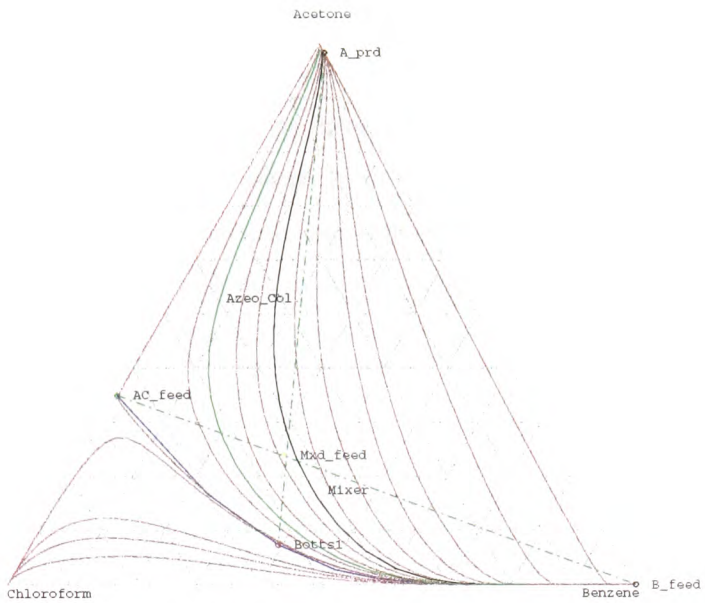


Figure 5.2: RCM and the distillation boundary generated using the hybrid approach. The distillation boundary is shown in *solid blue line.*

Table 5.2: Data for the distillation boundary of an acetone-chloroform-benzene system obtained from simulation runs. A/C binary feed = 170 kmol/hr.

Entrainer	D/F	reflux	azeo column bottoms composition		
(kmol/hr)	ratio	ratio	%Acetone	%Chloroform	%Benzene
40	0.65	16.0	16.78	59.82	23.39
80	0.77	15.0	7.44	53.30	39.25
120	0.89	11.0	2.80	46.49	50.70
160	0.95	10.0	1.10	40.29	58.59
200	0.98	9.0	0.51	35.34	64.14

5.2.1 The alternative column sequences

In generating and screening the alternative separation sequences for mixtures with boundary crossing we will focus our attention on the simpler and the more common of these systems, i.e. the mixtures with a low or a high boiling entrainer that do not introduce new azeotropes (cases BC-A1 and BC-B1 from Table 5.1). Acetone-chloroform-benzene (high boiling entrainer) and acetone (low boiling entrainer)-isopropanol (IPA)-toluene are used as examples.

The high boiling entrainer boils higher than the maximum boiling binary azeotrope and the low boiling entrainer lower than the minimum boiling binary azeotrope. In

the case of a high boiling entrainer, the residue curves begin at either of the pure components (acetone or chloroform) and converge at the entrainer (benzene). The residue curves move in the reverse direction when a low boiling entrainer is used. In each case, the residue curves result in a curved distillation boundary that separates the binary feed constituents into two different distillation regions. The alternative separation sequences for both mixtures are generated, analysed and evaluated by means of geometric reasoning. The steps taken lead us to four important observations:

Observation 1.

Each of the mixtures with a high or a low boiling entrainer leads to at least five desirable separation options. The binary feed constituents are recovered as either the top or the bottom products of different distillation columns in the case of high or low boiling entrainers respectively.

The alternative sequences for separating acetone-chloroform-benzene (high boiling entrainer) and acetone (low boiling entrainer)-IPA-toluene mixtures are shown in Figures 5.3, 5.4, 5.5 and 5.6.

For the acetone-chloroform-benzene mixture, we can start with (i) a direct sharp split (Figure 5.3(a)); or (ii) a non-sharp split (Figure 5.3(b)) which lead to three column designs; or (iii) we can first perform a direct sharp split leading to a two column design (Figure 5.3(c)); or, finally, (iv) we can start with a preconcentrator which leads to either three (Figure 5.4(d)) or four columns (Figure 5.4(e)). Figures 5.3, 5.4, 5.5 and 5.6 also show that changing the composition of the binary feed does not affect any of the separation structures except in the case of the sequence with a preconcentrator.

Observation 2.

Except when a preconcentrator is used, it is possible to achieve a desired split in the same separation sequence regardless of the composition of the binary feed with respect to the binary azeotrope.

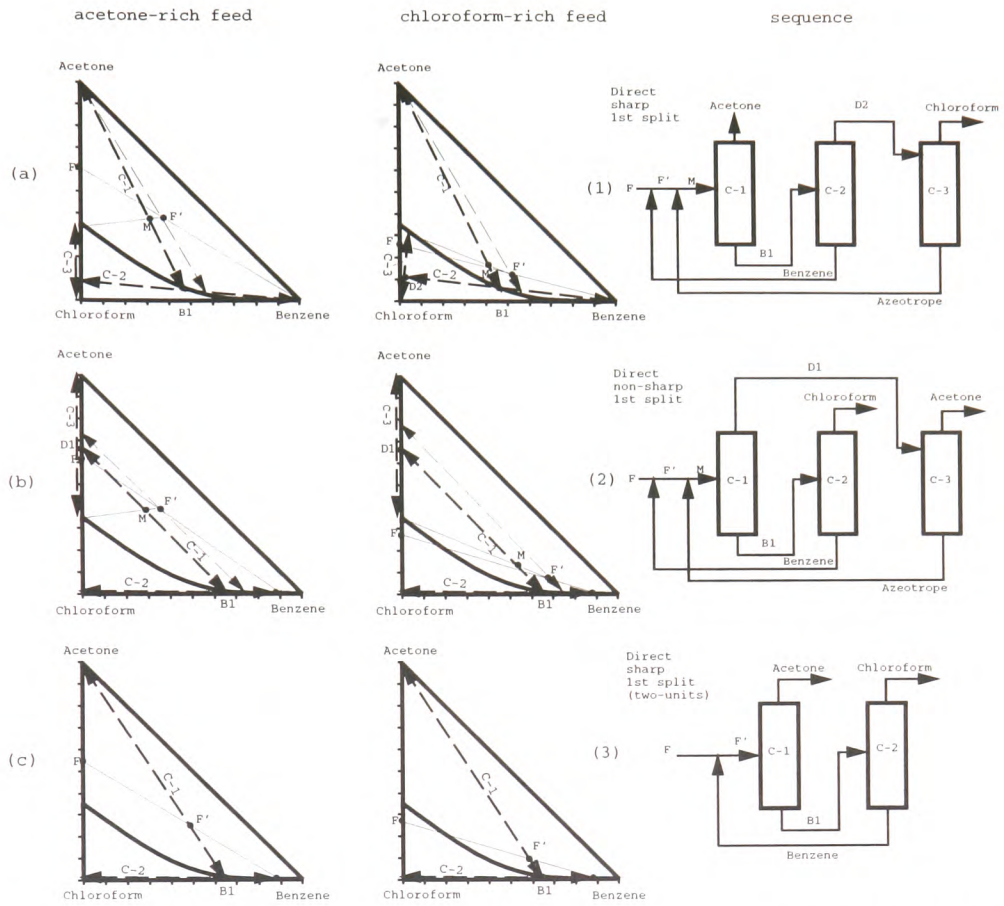


Figure 5.3: Separation sequences for mixtures with high boiling entrainers (Case BC-A1, Table 5.1) with acetone rich and chloroform-rich feeds - (a) three unit sequences with direct sharp and (b) nonsharp first splits, and (c) a two unit sequence with a direct sharp first split.

The following example clarifies observation 2:

Figure 5.7 illustrates the simulation case where the binary feed F (84% IPA, 16% toluene) lies on the *concave side* of the boundary. Mixing F with the light entrainer, acetone, gives a ternary feed, F', that is separated by column C-1 into pure toluene at the bottom and D1 mixture at the top. D1, which lies close to the distillation boundary, can be split by column C-2 to produce IPA mixture underflow and pure acetone overhead.

Simulation of an IPA-rich feed F containing 90% IPA and 10% toluene using the same separation sequence produces pure toluene and IPA as the bottom products of C-1 and C-2 respectively (Figure 5.8). Note that in this case, F lies on the *convex side* of the

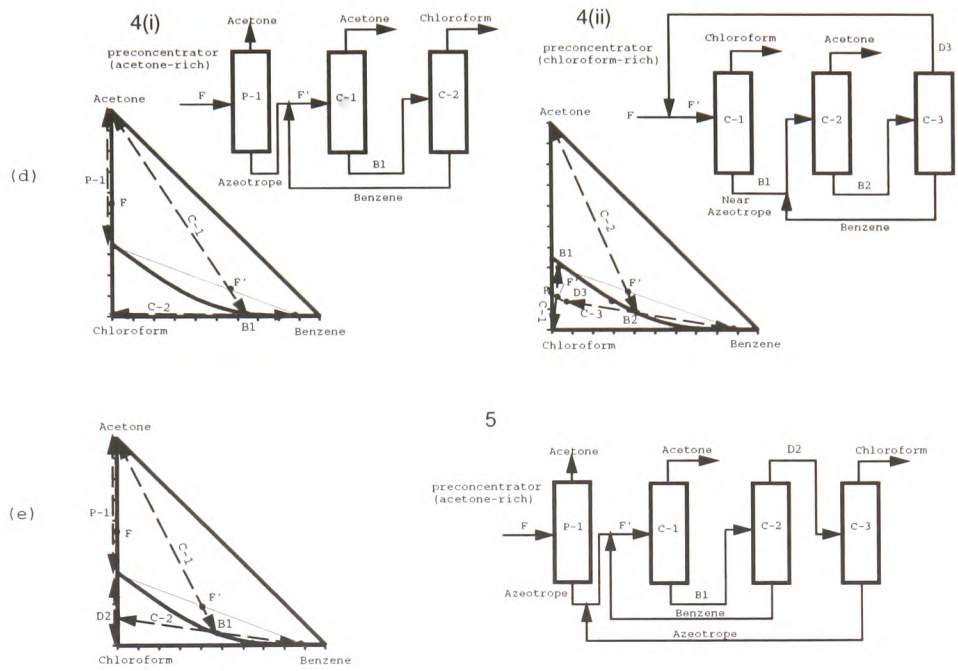


Figure 5.4: Separation sequences for mixtures with high boiling entrainers (Case BC-B1, Table 5.1) - (d) sequences with an acetone-rich (4(i)) and a chloroform-rich (4(ii)) feed preconcentrator and (e) four-unit sequence with an acetone-rich feed preconcentrator.

residue curved boundary. The process flow diagrams, stream data and input files for both simulation cases are included in Appendices C.1 and C.2.

Observation 3.

> *The mixtures with a high boiling and a low boiling entrainers are characterised by a change in the number of units along the curved distillation boundary.*

Figure 5.11 shows that for both types of entrainers, the number of units for the direct separation sequence changes from three to two at a *point of transition* described in detail in Sections 5.3 and 5.4.

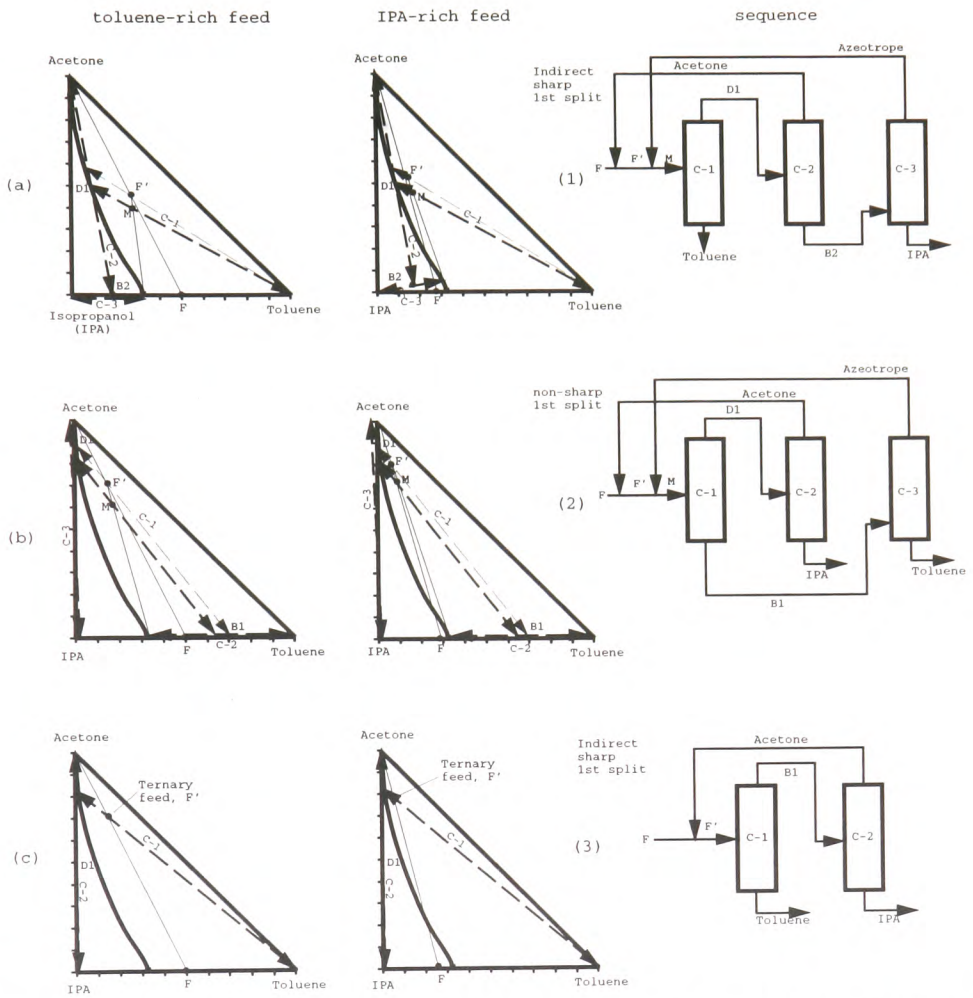


Figure 5.5: Separation sequences for mixtures with low boiling entrainers (Case BC-B1, Table 5.1) with toluene-rich and IPA-rich feeds - (a) three unit sequences with direct sharp and (b) nonsharp first splits, (c) two-unit sequence with an indirect sharp first split.

Observation 4.

For a given binary feed composition, either the direct or the indirect separation sequence is infeasible for the low and high boiling entrainer cases respectively. Because only a direct or an indirect sequence can exist at any binary feed composition, the criteria used to screen between the direct and the indirect splits do not apply for systems with boundary crossing.

Figures 5.9 and 5.10 respectively show that the indirect sequence is infeasible in the case of a high boiling entrainer, whereas the direct sequence is infeasible in the case of a low

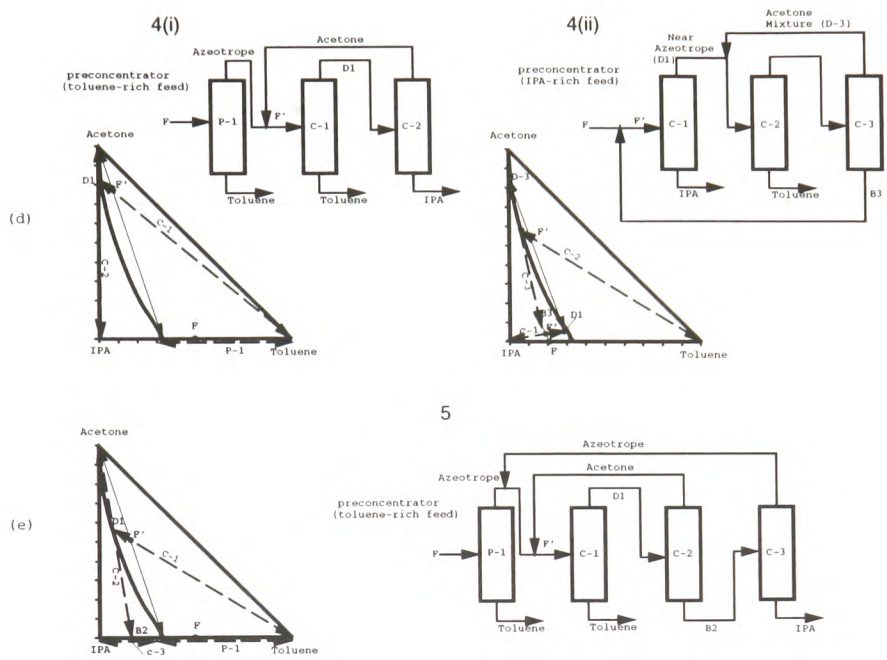


Figure 5.6: Separation sequences for mixtures with low boiling entrainers (Case BC-B1, Table 5.1) - (d) sequence with a toluene-rich (4(i)) and IPA-rich (4(ii)) feed preconcentrator (e) four unit sequence with a toluene-rich feed preconcentrator.

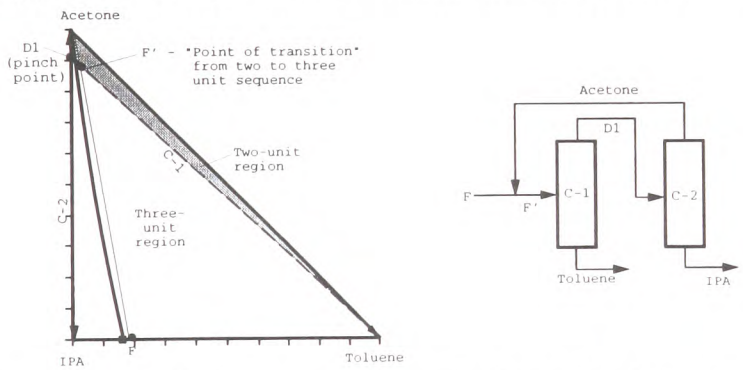


Figure 5.7: Separation sequence that results from a feed lying on a concave side of the residue curve boundary. Binary feed composition: 84% IPA, 16% toluene.

boiling entrainer regardless of the position of the binary feed in relation to the residue curve boundary. The infeasibility can be attributed to two constraints. Firstly, because one of the binary constituents lies on the convex side of a residue curve boundary (see for example, Figure 5.9). Secondly, because the presence of a maximum boiling azeotrope prevents the removal of the heavier constituent component underflow in the case of a high boiling entrainer (see for example, Figure 5.10(a)). Similarly, the presence of a minimum boiling azeotrope rules out a direct sharp split in the case of a low boiling

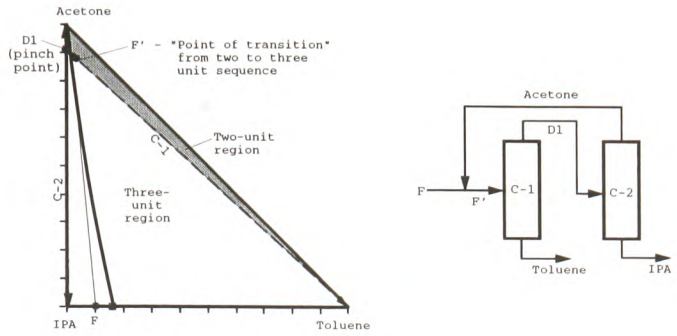


Figure 5.8: Separation sequence that results from a feed lying on a convex side of the residue curve boundary. Binary feed composition: 90% IPA, 10% toluene.

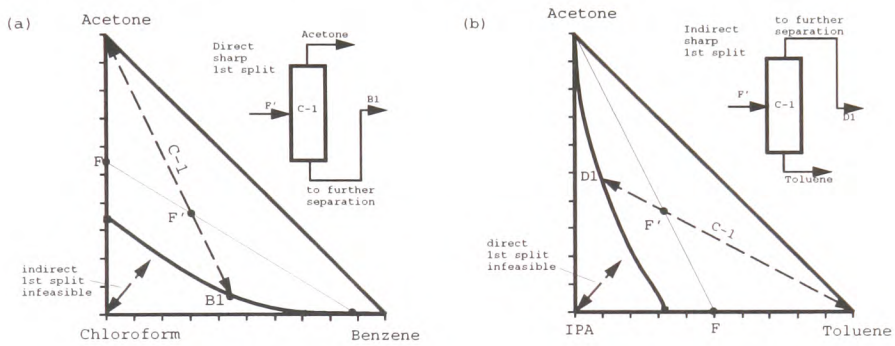


Figure 5.9: A binary feed lying on the concave side of the residue curve boundary results in an (a) infeasible indirect sequence (b) infeasible direct sequence because the residue curve boundary cannot be crossed from the convex side.

entrainer (see for example, Figure 5.10(b)). Note that both constraints apply when the binary feed is on the concave side of the residue curve boundary whereas only the second constraint apply when the binary feed is on the convex side of the boundary. Because only a direct or indirect sequence can exist at any given time, the criteria used to screen between the direct and indirect splits do not apply for systems with boundary crossing.

The next step is to screen the five typical sequences by use of geometric reasoning and heuristics which have been derived from the analysis of the results of process simulations.

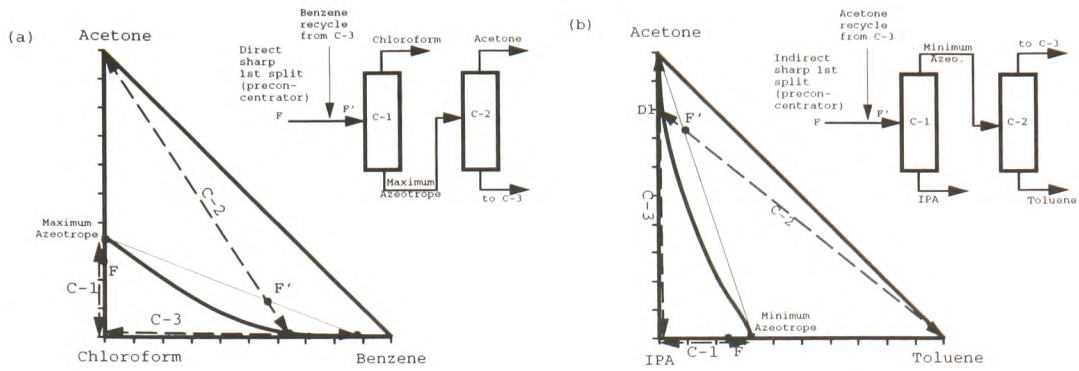


Figure 5.10: A binary feed lying on the convex side of the residue curve boundary results in an (a) infeasible indirect sequence (b) infeasible direct sequence due to the presence of either a maximum or minimum azeotrope respectively.

5.3 Screening the sequences

We refer to the examples previously presented for the high and low boiling entrainers which do not introduce new azeotropes, namely the acetone-chloroform-benzene (high-boiling entrainer) and acetone (low boiling entrainer)-IPA-toluene mixtures (cases BC-A1 and BC-B1 respectively, Table 5.1, page 90). We start by eliminating the sequences with non-sharp first splits (Figures 5.3(b) and 5.5(b) on pages 97 and 99 respectively) in order to avoid distilling to arbitrary compositions, and because this usually requires more than the minimum number of units.

In Chapter 7 of this work, we will show by geometric reasoning that, for the homogeneous systems with boundary crossing considered in this study, preconcentration is not worthwhile only for a mixture with a high boiling entrainer and low boiling component-rich feed because it merely serves to distribute the stripping duty and the capital requirement of the two column sequence into three columns (see Chapter 7 and Manan and Bañares-Alcántara[53]). Thus for this particular case, we can eliminate the three unit sequence which includes a preconcentrator (the sequence in Figure 5.4(d)-(i)). On the other hand, the four unit sequences shown in Figures 5.4(e) and 5.6(e) have two units more than the absolute minimum. These sequences can also be eliminated because they are clearly undesirable from the point of view of the capital cost.

When we use a low boiling entrainer or a high boiling entrainer with a high boiling component-rich feed, we are left with the three unit sequence with a preconcentrator, and the two and three unit direct separation sequences which exist in the shaded and unshaded regions of Figure 5.11 respectively. These regions are separated by a distillation column material balance line that connects the residue curve boundary "pinchpoint" (the point where the residue curve boundary becomes tangent to one of the edges of the ternary diagram) and one of the binary feed constituents corner. The

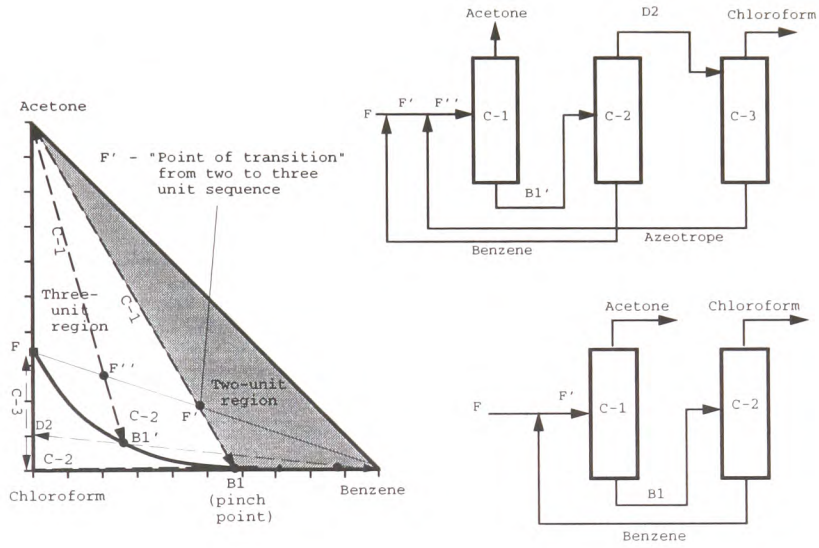


Figure 5.11: (a) Comparing the performances of the two and three-unit sequences by means of geometric reasoning.

main difference between the two and three unit sequences which exist along the curved distillation boundary is that sharp separation of one of the binary feed constituents and the entrainer is only possible in the case of the former, but not in the latter.

Figure 5.11 shows that at the pinch point, the distillation boundary begins to diverge from the chloroform-benzene edge as it moves away from the entrainer corner, thus making the complete recovery (sharp separation) of acetone in the distillate of the azeotropic column (C-1) more difficult. Fixing the acetone distillate to feed ratio to less than 1.0 tends to ease separation as some percentage of acetone is removed at the bottoms of C-1, but will result in an extra column. The "excess" acetone later forms an acetone-chloroform azeotrope that must be separated from pure chloroform in the extra

column (C-3) following the sharp separation of the entrainer (benzene) in column 2 (C-2). The acetone-chloroform binary azeotrope is recycled to C-1. A situation symmetric to case BC-B1 applies when a low boiling entrainer is used. Recall from Section 5.2 that the component *split fraction*, represented in the form of a distillate to feed (D:F) or bottoms to feed (B:F) ratio, describes the degree of sharpness of separation of a given component.

Stichlmair *et al.*[35] and Wahnschafft *et al.*[27] imply that the change from three to two unit sequence is generally desirable. The RCM geometry however suggests that a residue curve boundary pinch point approaching the entrainer corner may require a very high entrainer flowrate to achieve the desired product specifications in the minimum number of units. This could significantly increase the column throughput and hence, the column size, leading to high capital and operating costs. On the other hand, even though a three unit sequence has a lower entrainer requirement, it involves an extra column and an azeotrope recycle. In view of these competing effects, we believe that the relative advantages between the two and three column sequences can only be decided by performing detailed simulation. In Section 5.4, we describe the procedure to determine the MER for systems with boundary crossing. The MER, the optimum reflux ratio and the split fraction derived from our entrainer minimisation procedure are used as the design basis to evaluate the economics of the two and three unit sequences, and that of the two unit sequence which include a preconcentrator.

5.4 The MER and the most promising sequence

In Sections 5.4.1 and 5.4.2 we report some insights on how the entrainer flowrate, reflux ratio and the number of stages affect the separability and ultimately, the MER for homogeneous mixtures with boundary crossing. In Section 5.4.4, a procedure to determine the MER for the two and three unit sequences for cases BC-A1 and BC-B1 is outlined. In order to screen these sequences, their capital and operating costs are evaluated using ASPEN PLUS correlations[59] based on the MER, the optimum reflux ratios and split fractions obtained during simulation and optimisation. Section 5.4.4

concludes with the analysis and comparison of the design and economic performance of the two and three unit sequences, and that of the three unit sequence which include a preconcentrator.

5.4.1 The effects of entrainer flowrate on separability

In general, systems with boundary crossing exhibit a trend of entrainer versus separability that is similar to the one observed for systems without boundary crossing. Figure 5.12 shows that the separation of an acetone-chloroform-benzene mixture increases with the entrainer flowrate, reaches a maximum and begins to decrease at higher entrainer flowrates as the effect of entrainer carry over becomes dominant. In contrast, Fig-

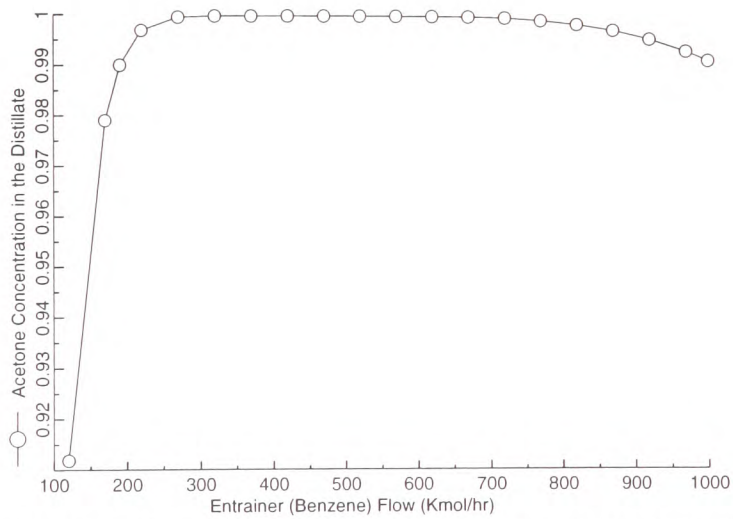


Figure 5.12: Entrainer flowrate versus acetone concentration in the distillate for the acetone-chloroform-benzene (high boiling entrainer) mixture.

ure 5.13 shows that when a low boiling entrainer is used to separate an IPA-toluene azeotropic mixture in a two unit sequence, it curiously causes the separability to decrease monotonically with the increase in entrainer flowrate. Such a peculiar trend results because the lower bound of the entrainer flowrate is a discrete point, i.e. the point of transition from two units (950 kmol/hr and above) to three units (below 950 kmol/hr). Entrainer flowrate of 950 kmol/hr is the MER, below which, it is not possible to achieve the desired product specifications in two units. Naturally, at such a

large MER the effect of entrainer carryover tends to predominate causing separation to decrease monotonically.

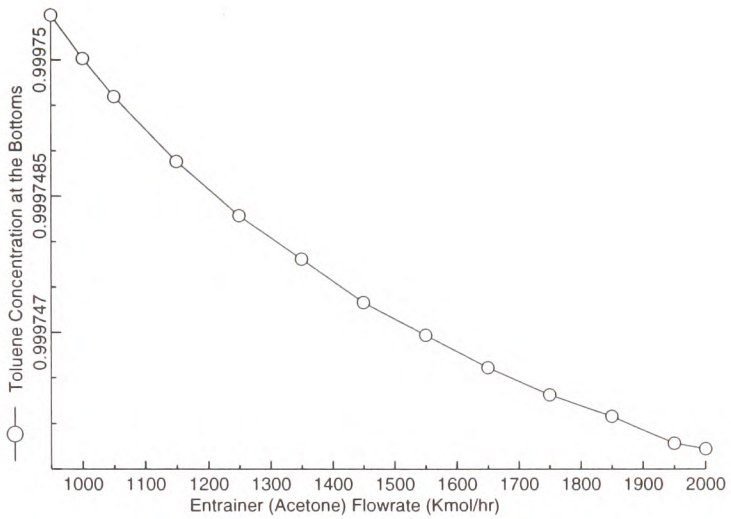


Figure 5.13: Entrainer flowrate versus toluene concentration at the bottoms for the acetone (low boiling entrainer)-IPA-toluene mixture.

5.4.2 The effects of reflux ratio on separability

Separation of an acetone-chloroform mixture using a high boiling entrainer, benzene, results in the typical maximum type reflux versus separability curve (Figure 5.14). Separation increases with entrainer flowrate, reaches a maximum and decreases thereafter. Note that the use of a direct separation sequence results in a behaviour that is qualitatively similar to the one shown by a mixture with a high boiling entrainer for systems without boundary crossing (case WOBC-A2, Table 4.1, page 48).

By the same reasoning, a low boiling entrainer which uses an indirect separation sequence produces a monotonically increasing reflux versus separability trend just like the one produced by a medium boiling entrainer for systems without boundary crossing (Figure 5.16). In this case the different types of entrainer naturally result in sensitivity differences between the reflux versus separability curves for each of the systems compared, but do not alter the general trend of the curves.

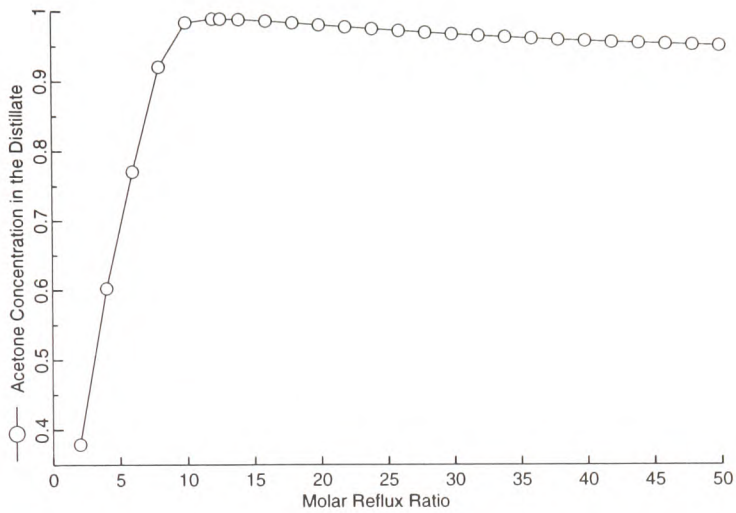


Figure 5.14: Molar reflux ratio versus acetone concentration in the distillate for the acetone-chloroform-benzene (high boiling entrainer) mixture.

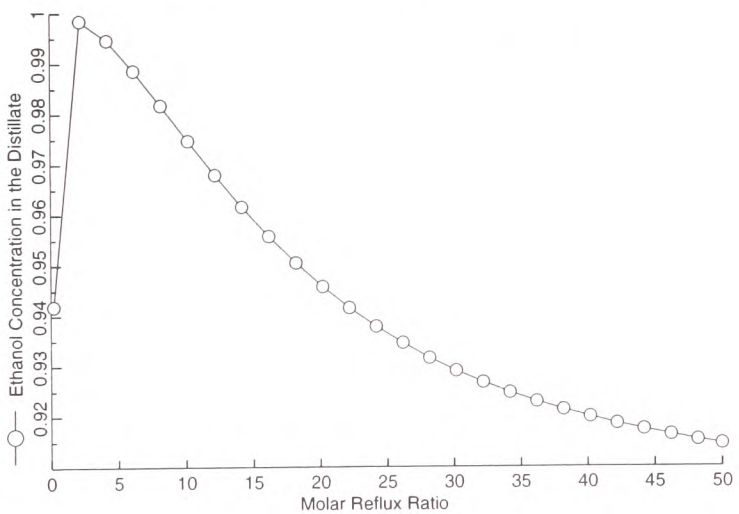


Figure 5.15: Molar reflux ratio versus ethanol concentration in the distillate for the ethanol-water-EG (high boiling entrainer) mixture, reproduced from Figure 4.16 with molar reflux ratio range between 1.0 and 50.0.

5.4.3 The effects of entrainer flowrate and reflux ratio on separability - the sensitivity differences between systems with and without boundary crossing

We observe some marked differences in the sensitivities of separability on the varied variables (i.e. entrainer flowrate and reflux ratio) between the systems with and without boundary crossing.

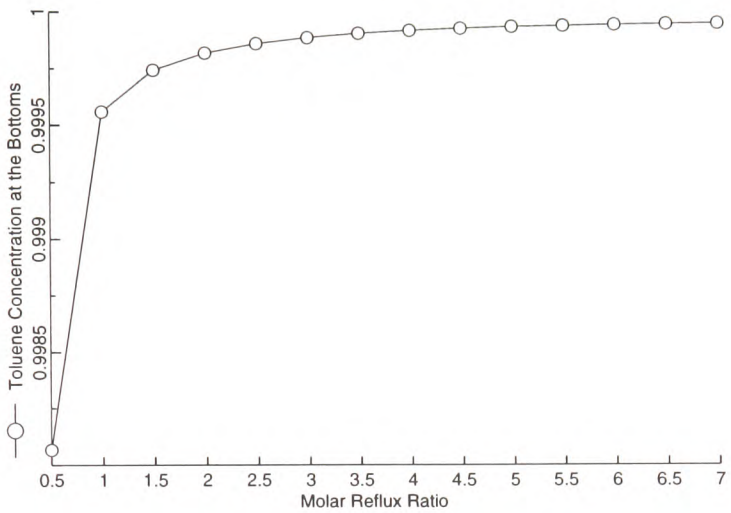


Figure 5.16: Molar reflux ratio versus toluene concentration at the bottoms for acetone(low boiling entrainer)-IPA-toluene mixture.

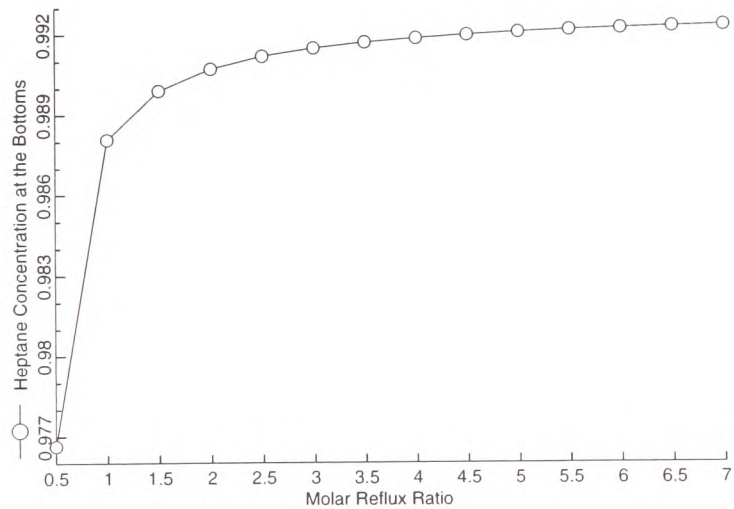


Figure 5.17: Molar reflux ratio versus heptane concentration at the bottoms for acetone-benzene (medium boiling entrainer)-heptane mixture, reproduced from Figure 4.17 for molar reflux ratio range between 0.5 and 7.0.

Consider, for example, the entrainer flowrate versus separability curves for systems with and without boundary crossing. A comparison between Figures 5.12 and 5.13 in this section and Figures 4.13 and 4.14 in Section 4.6.1 clearly show that the maxima occur at much higher entrainer flowrates for the systems with boundary crossing. In addition, Figures 5.12 and 5.13 show that the increase in entrainer flowrate for the systems with boundary crossing is accompanied by an almost negligible decrease in separation (see for example, the toluene concentration scale in Figure 5.13). The results suggest a very

strong resistance of the entrainer to carryover. This phenomenon appears to contradict the fact that the relative volatilities of the entrainers with respect to the binary feed constituents for both mixtures referred to in Figures 5.12 and 5.13 are smaller than those for the systems without boundary crossing.

Some noticeable differences in sensitivities are also observed when the reflux ratio versus separability curves for both systems are compared. From a comparison of Figures 5.14 and 5.16 for systems with boundary crossing with Figures 5.15 and 5.17 for systems without boundary crossing, it can be seen that some relatively large changes in reflux ratio cause smaller changes in separability for systems with boundary crossing.

The sensitivity differences can be attributed to the presence of distillation boundaries for systems with boundary crossing. In general, separation (and hence, the changes in separability) normally takes place along a single residue curve[37]. Figure 5.18 shows that, once the distillation boundary is crossed, the top and bottom products of the azeotropic column are located on separate residue curves, RC1 and RC2, and separate distillation regions. As a result, further changes in the entrainer flowrate and reflux ratio can cause little or no changes in the separability of the azeotropic column. Clearly, this does not happen for systems without boundary crossing.

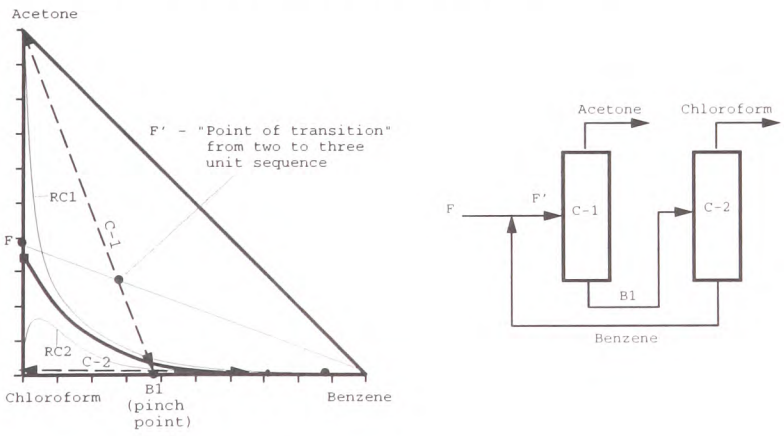


Figure 5.18: Boundary crossing results in a distillation column with its top and bottom products lying on separate residue curves, RC1 and RC2.

5.4.4 Getting the MER and the most promising sequence

Two separate procedures are implemented to determine the MER for systems with boundary crossing. These procedures handle sequences which involve sharp splits (two column sequences) and nonsharp splits (three column sequences).

Getting the MER for two column sequences

To determine the MER for two column sequences, we employ the entrainer minimisation procedure developed for systems without boundary crossing and described in Section 4.7. The binary feed constituents split fractions (D:F or B:F ratios) are fixed at or near 1.0 during the search for the MER so that each of the binary feed constituents will be completely recovered in only one column.

For example, to determine the MER for the separation acetone-IPA-toluene mixture in two units, the split fractions (B:F ratios) for the binary feed constituents in the azeotropic and entrainer recovery columns are fixed at 0.92 and 1.0 respectively. The entrainer flowrate is the objective function to be minimised. Since there is no analytical equation to represent the entrainer flowrate, we also specify the entrainer flowrate as a varied variable along with the reflux ratio to facilitate the search for the MER. The MER and the azeotropic column's bottom composition for the two unit sequence give the point of transition and the pinch point respectively. Recall from Section 5.3 that, given the entrainer and the feed flowrates, the intersection of the azeotropic column material balance line with the distillation boundary is defined, thus allowing the component split fraction in the azeotropic column to be found geometrically (i.e. by the lever rule) if the distillation boundary has been located.

Getting the MER for three column sequences

The need to perform nonsharp separation complicates the search for MER for three unit sequences. Since, in this case, entrainer minimisation involves nonsharp separation in the region below the pinch point (three unit region) where D:F (or B:F) ratio is less than 1.0, the MER procedure described in Section 4.7 cannot be used unless prior knowledge of the limiting component split fraction corresponding to a given entrainer

flowrate is available. The limiting split fraction can take the form of an analytical equation for the distillation boundary and must be supplied as a constraint to prevent possible errors due to boundary "overcrossing". Without this information, the MER can be determined based on knowledge of the effect of reflux ratio and entrainer flowrate on the separability as described in Sections 5.4.1 and 5.4.2.

To determine the MER for three column sequences using this alternative method, one may proceed through the following steps:

Step 1. Perform a sensitivity analysis study by varying the entrainer flowrate with respect to the product purities and production rates of the distillation columns in the sequence. For this purpose, the number of stages, the reflux ratios and the split fractions of these columns must be specified.

As initial estimates, choose the reflux ratios that give the highest separation from the reflux ratio versus separability curves like the ones shown in Section 5.4.2, and fix the number of stages. Note that the split fraction which corresponds to the MER should lie between the binary azeotropic composition and 1.0. Using the lower bound, i.e. the binary azeotropic composition as an initial estimate for the component split fraction can prevent possible errors due to boundary "overcrossing".

Step 2. Find the MER from the results of the sensitivity analysis. The MER is the lowest entrainer flowrate that allows the desired production rate and product purity to be achieved.

Step 3. Adjust the reflux and the split fractions by varying these parameters with respect to separability. Choose a reflux that is high enough to give the desired product specifications and the limiting split fraction (i.e. the one just before simulation error results). Note that the limiting split fraction takes the material balance line of the first column to the furthest point beyond the distillation boundary.

Finally, the capital and operating costs for the two and three column sequences are evaluated using ASPEN PLUS correlations[59] based on the MER, the optimum reflux

ratios and split fractions obtained during simulation and optimisation. The input files, process flow diagrams and stream data from simulation are presented in Sections C.2 to C.5 of Appendix C. These design and cost data are summarised in Tables 5.3 and 5.4.

Table 5.3: Economic comparison between the two and three unit sequences for acetone-chlorofom-benzene system

	two units		three units	
	size/ capacity	cost (x 10^6\$/yr)	size/ capacity	cost (x 10^6\$/yr)
AZEO-COL		0.640		0.634
shell (dia, m)	2.896		2.896	
# of trays (actual)	113		111	
reboiler (m^2)	107	0.027	91	0.025
condenser (m^2)	599	0.090	579	0.088
steam (x 10^6 kg/hr)	.008	0.228	0.008	0.214
cooling water (x 10^6 kg/hr)	0.521	0.193	0.498	0.184
ENT-CO1		2.172		1.107
shell (dia, m)	5.944		4.267	
# of trays (actual)	142		119	
reboiler (m^2)	900	0.122	472	0.074
condenser (m^2)	989	0.399	726	0.208
steam (x 10^6 kg/hr)	0.070	1.799	0.037	0.943
cooling water (x 10^6 kg/hr)	3.234	1.198	1.693	0.627
ENT-CO2				0.584
shell (dia, m)			3.353	
# of trays (actual)			65	
reboiler (m^2)			229	0.043
condenser (m^2)			982	0.132
steam (x 10^6 kg/hr)			0.023	0.585
cooling water (x 10^6 kg/hr)			1.050	0.389
MER (kmol/hr)	190.0		123.0	
Azeo-feed (kmol/hr)	170.0		259.0	
capital cost (x 10^6\$)	3.449		2.895	
steam (x 10^6\$/yr)	2.027		1.741	
cooling water (x 10^6\$/yr)	1.391		1.200	

Analysis and discussions

An analysis of the simulation results summarised in Tables 5.3 and 5.4 leads to two other important observations:

Observation 5.

In general, the MER is governed by the binary feed composition, the com-

Table 5.4: Economic comparison between the two and three unit sequences for acetone-IPA-toluene system

	two units		three units	
	size/ capacity	cost (x 10^6\$/yr)	size/ capacity	cost (x 10^6\$/yr)
COLUMN1		1.313		0.763
shell (dia, m)	4.572		3.048	
# of trays (actual)	112		112	
reboiler (m^2)	1874	0.292	831	0.131
condenser (m^2)	2157	0.327	906	0.141
steam (x 10^6 kg/hr)	.037	1.079	.017	0.503
cooling water (x 10^6 kg/hr)	2.186	0.927	1.012	0.429
COLUMN2		1.159		0.859
shell (dia, m)	5.182		3.962	
# of trays (actual)	64		64	
reboiler (m^2)	1491	0.242	781	0.125
condenser (m^2)	3736	0.582	2031	0.310
steam (x 10^6 kg/hr)	.059	1.736	.032	0.943
cooling water (x 10^6 kg/hr)	3.544	1.503	1.930	0.818
COLUMN3				0.425
shell (dia, m)			1.829	
# of trays (actual)			83	
reboiler (m^2)			129	0.035
condenser (m^2)			153	0.038
steam (x 10^6 kg/hr)			0.005	0.150
cooling water (x 10^6 kg/hr)			0.306	0.130
MER (kmol/hr)	950.0		516.0	
Azeo-feed (kmol/hr)	100.0		141.0	
capital cost (x 10^6\$)	3.915		2.826	
steam (x 10^6\$/yr)	2.815		1.596	
cooling water (x 10^6\$/yr)	2.430		1.376	

position of the azeotrope, the pinch point location, the desired production rate and product purity.

a. Effect of the binary feed composition on MER.

The MER increases with an increase in the concentration of the *first cut* in the binary feed. The first cut is the binary feed constituent to be removed in the azeotropic column (C-1). The other binary feed constituent which is to be removed in either the second or the third column is hereby termed the *final cut*. Acetone and toluene are the first cuts, whereas chloroform and IPA are the final cuts for acetone-chloroform-benzene and acetone-IPA-toluene mixtures respectively (see Figures 5.19(a) and (b)).

Table 5.5 shows that for the separation of acetone-IPA-toluene mixture in three columns,

the MER for an equimolar IPA-toluene binary feed is 722kmol/hr, compared to only 516 kmol/hr for an azeotropic binary feed (84%IPA, 16% toluene). With the B:F ratio of the first cut (toluene) specified at 90% in the azeotropic column, only 10% of the first cut is transferred to column 3 for further separation. In contrast, an equimolar IPA-toluene binary feed leads to a higher concentration of the first cut in the final column compared to the case of azeotropic binary feed. An equimolar IPA-toluene binary feed results in a more difficult separation due to larger overhead entrainer and azeotrope recycles and ultimately, a larger MER to achieve the desired product specifications.

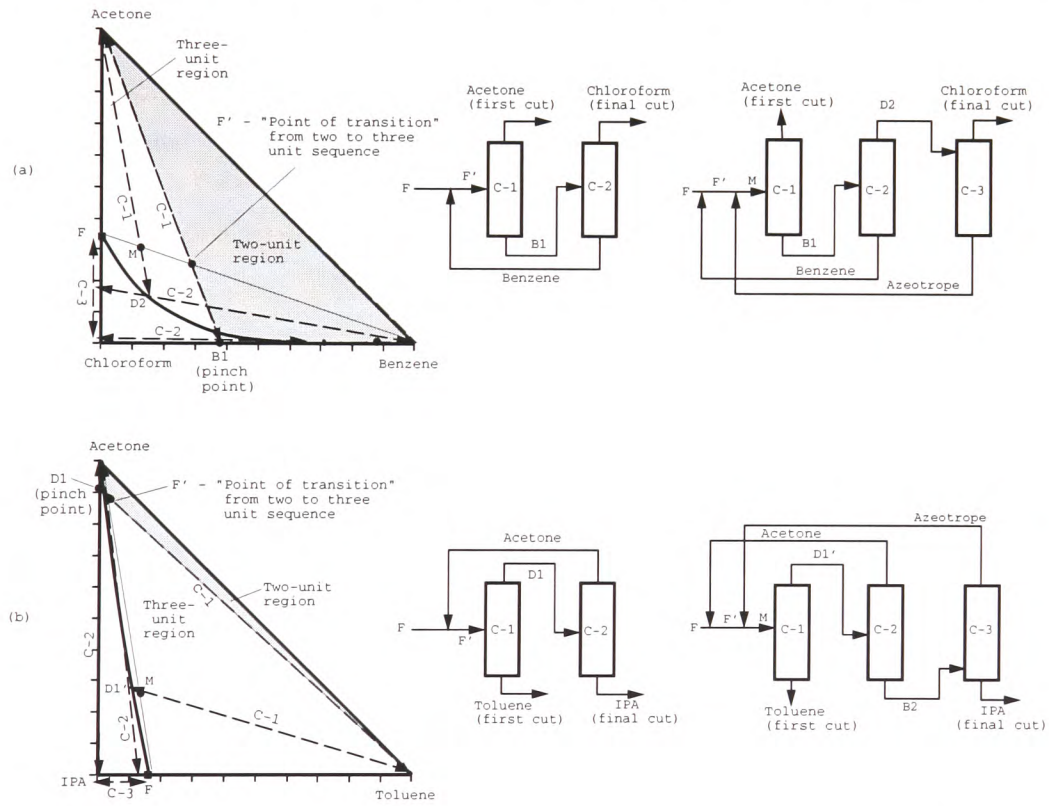


Figure 5.19: Two and three column sequences, the points of transition and pinchpoint locations for (a) acetone-chloroform-benzene mixture (b) acetone-IPA-toluene mixture.

When a low boiling entrainer that introduces no new azeotrope is used for a system with boundary crossing, it is desirable to have the binary feed as near the azeotropic composition as possible. The results in Table 5.5 prove that a savings of 20% in capital cost and almost 30% in utility cost can be achieved by changing the IPA-toluene binary feed from equimolar to the azeotropic composition (preconcentrated feed). This is done

by removing part of the first cut, toluene, at the bottom of a preconcentrator column. However, it is important to note that preconcentration, which results in lower MER, may not be economical for certain types of mixtures. Figures E.1 and E.2 of Appendix E list other cases where it is economical to preconcentrate a binary feed to its azeotropic composition.

Table 5.5: The effects of binary feed composition on the overall economics of two and three unit separation sequences for acetone-IPA-toluene mixture.

		equimolar feed	azeotropic feed	preconc. feed
2-units	MER (kmol/hr)	1435.0	950.0	950.0
	capital cost (x 10^6\$)	5.468	3.915	4.400
	utility cost* (x 10^6\$/yr)	7.505	5.245	5.354
3-units	MER (kmol/hr)	722.0	516.0	
	capital cost (x 10^6\$)	3.380	2.826	
	utility cost* (x 10^6\$/yr)	4.065	2.972	
	recycle (kmol/hr)	53.0	44.0	

* cost of steam and cooling water combined.

b. Effect of the composition of the binary azeotrope on MER.

Because the MER increases with an increase in the concentration of the first cut in the binary feed, any changes that leads to a higher concentration of the first cut tend to increase the MER. For example, for the separation of acetone-methanol-water (high boiling entrainer) system which has to maintain an azeotropic binary feed, a shift in pressure from 1 to 8 bar leads to an azeotrope composition which "moves" towards the methanol tip. This increases the concentration of methanol (the first cut) and ultimately, the MER (see Figure 5.20).

c. Effect of the pinch point location on MER.

Recall that the MER and the azeotropic column bottoms composition for the two unit sequence give the point of transition and the pinch point location respectively. The stronger a boundary curvature, the further the pinch point is from the entrainer corner, the closer the pinch point is to the binary feed edge, and the lower the MER for the two unit sequence. The acetone-chloroform-benzene mixture, which has a strongly curved boundary, has a pinch point at 37% chloroform and 63% benzene on the chloroform-

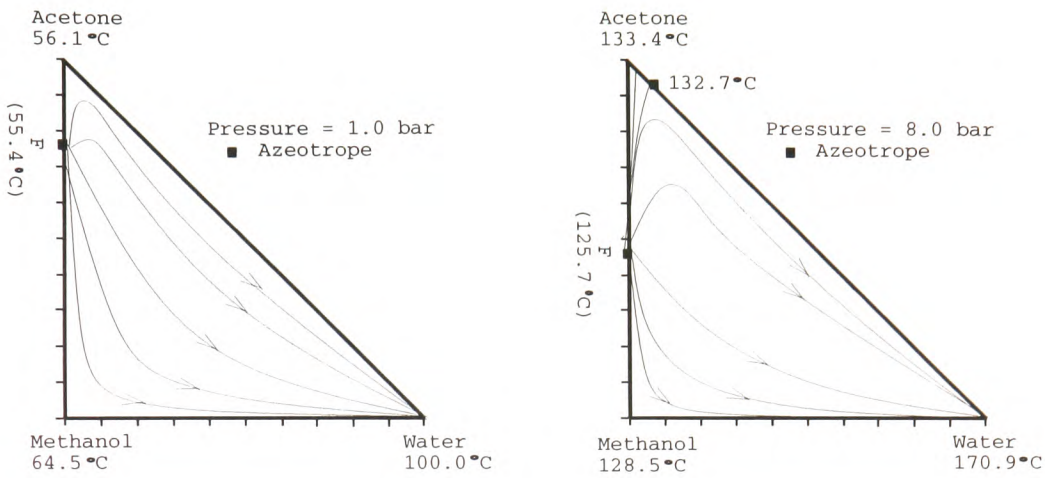


Figure 5.20: The effect of pressure on the binary azeotrope composition for the acetone-methanol-water (high boiling entrainer) mixture[2].

benzene edge (Figure 5.19(a)). This leads to an MER that is only 10% more than the azeotropic feed flowrate for its two unit sequence. In contrast, the acetone-IPA-toluene mixture with an almost linear distillation boundary has a pinch point at 92% acetone and 8% IPA, leading to a MER that is 850% more than the azeotropic feed flowrate for its two unit sequence (Figure 5.19(b)). The hydrochloric acid-water-sulfuric acid (high boiling entrainer) and ethyl ethanoate (low boiling entrainer)-isopropanol-toluene mixtures shown in Figures 5.21(a) and (b) respectively, are other examples of the mixtures whose residue curve boundary pinch points are nearer the binary feed edge, that naturally result in lower MER.

d. Effect of the production rate and product purity on MER.

The MER for the two unit sequence is naturally higher than that of the three unit sequence since the material balance line of the former is always closer to the entrainer corner. The MER for the three unit sequence is 35% less in the case of acetone-chloroform-benzene mixture, and only 46% less in the case of acetone-IPA-toluene mixture even though a 9.5:1 ratio of entrainer to azeotropic feed is required in the latter. This shows that the pinch point location has little or no effect on the *difference* between the MERs for the two and three-unit sequences. The need to maintain a desired production rate and product purity in either the two or three column sequences is the reason why the two resulting MERs are not significantly different from one another.

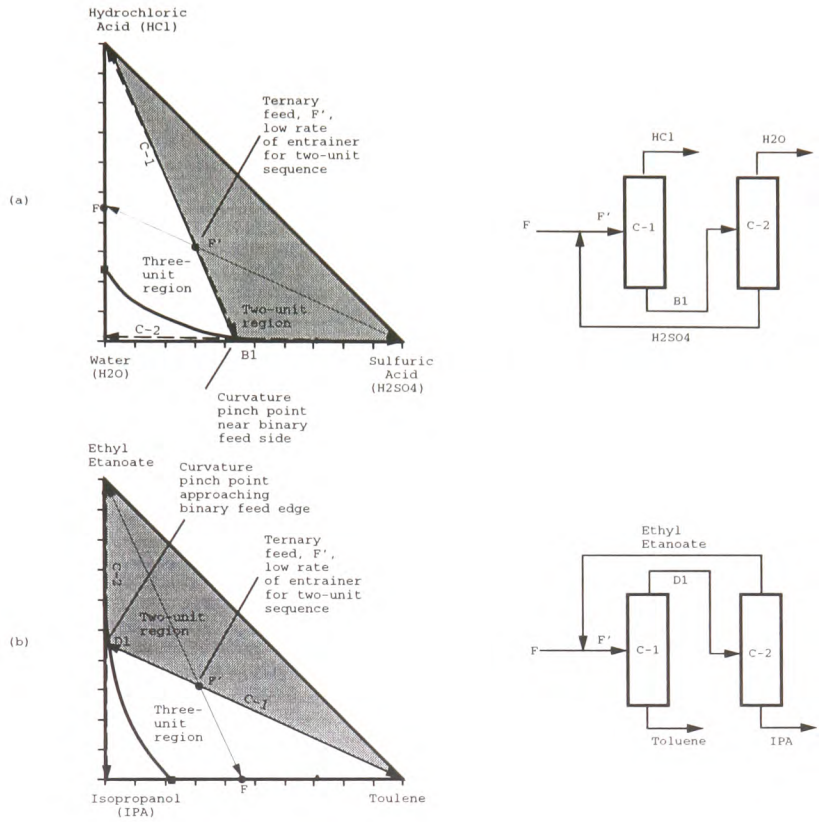


Figure 5.21: Examples of mixtures with a curved boundary pinch point near the binary feed edge (a) high boiling entrainer (b) low boiling entrainer, which do not introduce new azeotropes.

Observation 6.

Lower MER leads to a cheaper three column sequence.

Results from Tables 5.3 and 5.4 show that lower entrainer flowrates may reduce the azeotropic column separation load and the entrainer recovery column (i.e. the second column) separation difficulty. In particular, a lower entrainer flowrate results in cheaper entrainer recovery columns for the three column sequences. In the case of the acetone-chloroform-benzene mixture, the savings obtained in the entrainer recovery column are much higher than the investment required for the third column.

Figure 5.22 shows the RCM and the corresponding most promising separation sequences for systems with boundary crossing that results from the preceding screening procedure.

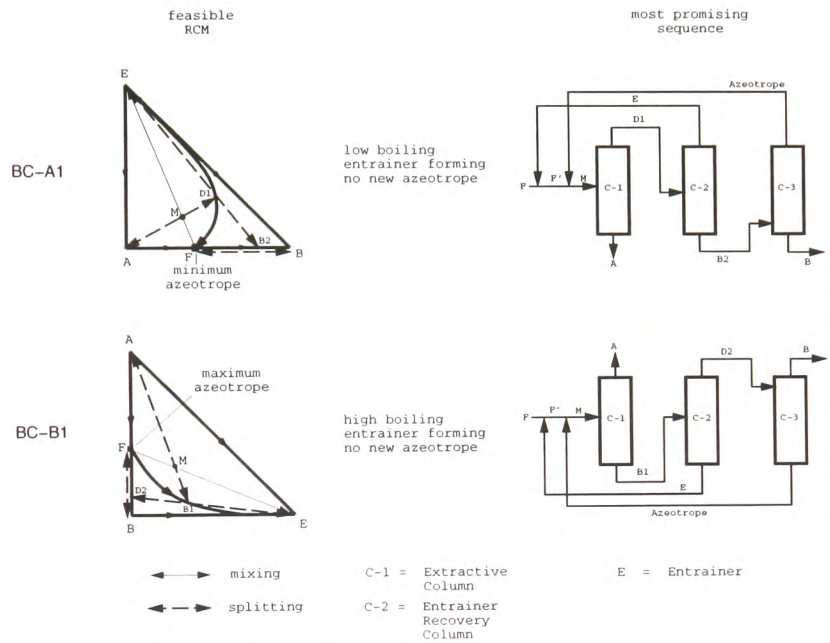


Figure 5.22: RCMs and their corresponding most promising separation sequences for the more common types of mixtures with boundary crossing.

5.5 Summary

To date, research related to the optimisation of distillation sequences for azeotropic mixtures is very limited when compared to the extensive work done for zeotropic mixtures. As far as it can be found, no guidelines are currently available to screen alternative column sequences for azeotropic mixtures in general. The available procedures for optimisation of distillation sequences for azeotropic mixtures are specific to simple homogeneous mixtures and a particular class of heterogeneous mixtures[29,30]. When using these techniques to determine the most promising sequence, it is necessary to optimise and evaluate the economics of every sequence generated. The approach becomes cumbersome when a number of different entrainers are being evaluated and when a few separation options exist for each type of entrainer. To overcome these problems,

in Chapters 4 and 5 we have produced a catalogue of homogeneous azeotropic mixtures with their corresponding most promising separation sequences. This catalogue enables a designer to identify the most promising separation sequence ahead of design, given the azeotropic mixture RCM properties, which include the boiling points of pure components and azeotropes. The screening technique, which is based on heuristics and reasoning over the geometric features of the RCMs, allows designers to consider a wider range of ternary homogeneous azeotropic mixtures than was previously possible.

In Chapters 4 and 5, the concept of a MER and the procedure to minimise the required amount of entrainer for distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing have been introduced for the first time. Results of the study show that the MER not only provides insights for waste minimisation but also proves instrumental in generating economical azeotropic distillation sequences. In addition, the entrainer minimisation study has led to new evidences linking the type of separation sequence, the azeotropic column feedstage location and the volatility of an entrainer with the separability of homogeneous azeotropic mixtures.

In summary, the major developments and new insights in Chapters 4 and 5 include:

- a geometric approach for synthesizing and screening the alternative separation sequences for azeotropic systems with and without boundary crossing. This approach exploits valuable information that can be extracted from the RCM which include the boiling points of pure components and azeotropes, the binary feed composition, the alternative separation structures and the relative quantity of entrainer for the purpose of synthesis and screening.
- generation of a catalogue pairing the RCMs of the ternary systems with the most promising separation sequences.
- a novel procedure for entrainer minimisation in the distillation sequences for separating the azeotropic systems mentioned. The procedure is also expected to be extendable to heterogeneous azeotropic systems. The MER is used together with the most promising sequence in order to generate cleaner and cost effective distillation sequences for azeotropic mixtures.

- new evidences linking the type of separation sequence, the azeotropic column feedstage location and the volatility of an entrainer with the separability of homogeneous azeotropic mixtures. These findings conclusively explain the peculiar dependencies of the separability of homogeneous azeotropic mixtures on the reflux ratio and the number of stages.

An approach for generating promising sequences for heterogeneous mixtures is described in the next chapter, and in Manan and Bañares-Alcántara[63].

Chapter 6

Synthesis of Distillation Sequences for Azeotropic Mixtures - Heterogeneous Systems

6.1 Introduction

In Chapters 4 and 5 of this thesis, emphasis has been placed on the importance of considering the mixture peculiarities and the use geometric reasoning to gain insights from residue curve maps (RCMs) to formulate a general procedure for the synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures. The similarities and differences that exist between the homogeneous and heterogeneous mixtures' RCMs and from one heterogeneous mixture RCM to another indicate that mixture peculiarities and geometric reasoning also have important roles to play in the synthesis of separation sequences for heterogeneous azeotropic mixtures. To enable separation, the entrainer for heterogeneous mixtures must form immiscible liquid-liquid regions straddling the distillation boundaries. In this case, a point on a residue curve inside the heterogeneous region results in two equilibrium liquid phases lying in different distillation regions, thus allowing the use of liquid-liquid phase separation to "move" across the heterogeneous distillation boundary in a way that is not possible for homogeneous systems. Consequently, there is practically no limit on the number of distillation regions a heterogeneous system may form in order for distillation to remain feasible. Recall from Chapter 4 that a homogeneous system without boundary crossing

may only form a maximum of two regions. From one heterogeneous system to another, we find that peculiarities of the heterogeneous azeotropes, distillation boundaries, heterogeneous liquid boiling envelopes and liquid-liquid tie lines have significant influence on the design and optimisation of separation sequences and is the subject of detailed discussions in this chapter and in Manan and Bañares-Alcántara[63].

Some related work was reported by Ryan and Doherty[30], who use the reflux ratio for the azeotropic column, the position of the tie lines in the decanter and the distillate composition in the entrainer recovery column as the main optimisation variables to compare five alternative sequences for the ethanol-water-benzene heterogeneous mixture. Also, an automated procedure for the synthesis of distillation sequences was developed by Wahnschafft *et al.*[27], but it assumes a *fixed ternary feed* composition, implying that an internal entrainer is available from within a process (see Section 7.2 of Chapter 7 for a detailed explanation).

To find the best sequence, it is currently necessary to optimise the parameters of every conceivable sequence and to compare their economics. So far, the entrainer flowrate has not been considered in the optimisation of heterogeneous sequences, even though it is expected to be one of the dominant optimisation variables[30]. It is important to realise that a "generate and test" approach that is based on a fixed ternary feed or a suboptimal entrainer flowrate cannot guarantee a global optimum solution. Issues concerning the flexibility of feed composition in azeotropic separations are discussed in detail in Chapter 7.

This chapter describes a short cut approach for generating promising distillation sequences for heterogeneous azeotropic mixtures based on reasoning over the geometric features of an RCM. The approach involves a search along two dominant synthesis parameters, namely:

- the absolute minimum number of units, and
- the optimum entrainer flowrate.

Observation of the RCM trends for a wide variety of azeotropic mixtures enables the identification of some essential RCM properties, an explanation for previous observations made by other researchers and, ultimately, the formulation of some general synthesis rules covering a much wider variety of azeotropic mixtures than what is currently possible. This chapter explains how geometric reasoning can be used to find:

- *the absolute minimum unit sequence* using the *collinearity rule* (Section 6.2),
- *the region* and *point of optimum entrainer flowrate* (Section 6.3),
- *the optimum decanter tie line position* (Section 6.4),
- and *the distillate composition for the entrainer recovery column* (Section 6.5).

In contrast to the assumption of an "internally available entrainer" leading to a fixed ternary feed used by Wahnschafft *et al.*[27], the present study is based on the fact that, in practice, a suitable entrainer required for the separation of an azeotropic mixture seldom comes from within the process. To enable separation, an external entrainer is usually added in a predetermined quantity to an azeotrope-forming binary mixture whose composition is normally fixed by some upstream processes. A critical analysis of the internal entrainer assumption and a study of the implications of fixed binary and ternary feeds for various distillation regions of a RCM can be found in Chapter 7.

It must be emphasized that in formulating the synthesis guidelines no claim is made for the solution to represent the global optimum. It is, however, clear that by making sure that the number of units is kept to a minimum and the entrainer flowrate is maintained at a desirable value, one can guarantee that the sequence generated is among the most promising design options. Also, the computations involved are kept to a minimum, thus making the use of these techniques particularly appropriate during the early stages of design. An algorithm for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures is presented in Appendix D. As in Chapter 4, Chapter 5, and in Manan and Bañares-Alcántara[64], the technique presented is limited to azeotropic mixtures with a maximum of three components. Every ternary diagram

follows the particular convention set in the introduction to Chapter 4 with respect to the boiling points and the fractional compositions of the pure components involved.

We begin with a review of the definition of the absolute minimum-unit sequence and an explanation of its crucial role during the synthesis of promising sequences for heterogeneous azeotropic mixtures. The first synthesis step is to exploit the geometric features of a RCM in locating the absolute minimum-unit sequence. A fixed *binary feed* is used as a basis for the study.

6.2 The absolute minimum-unit sequence

In Chapter 4 and in Manan and Bañares-Alcántara[64], the *absolute minimum-unit sequence* has been defined as the minimum possible number of distillation units required to achieve the desired product specifications for the separation of a ternary homogeneous azeotropic mixture, whatever the feed composition may be. In doing so, the number of units for the sharp separation of an ideal three component mixture by means of *conventional distillation* has been used as a reference. The same reference will be used for heterogeneous systems with two modifications to account for liquid heterogeneity. First, the definition will strictly refer to the number of distillation units and, as such, will exclude decanters which usually consist of a simple atmospheric or pressure vessel. Second, there is a special case where the absolute minimum number of units may be one less than the reference number, i.e. for mixtures whose heterogeneous liquid boiling envelope "endpoints" approach near pure components. Figure 6.1 is an example of a mixture with such liquid boiling envelope.

Ryan and Doherty[30] compare five alternative sequences for the heterogeneous distillation of an ethanol-water-benzene mixture and shortlist the two and three unit sequences as the most competitive and deserving detailed optimisation studies. Results from these studies report the three unit sequence which includes a preconcentrator to be advantageous with respect to the energy costs (but not capital). In terms of the combined capital and energy costs, the three unit sequence is found to be marginally cheaper only

when the binary feed contains less than 4 percent ethanol, with the savings beginning to diminish at a slightly higher percentage of ethanol in water. Note that, in practice, it is necessary for the feed to be more flexible and to add the costs of installation and control for the preconcentrator column of the three unit sequence, making the marginal estimated cost savings difficult to justify. With these additional considerations, it could be argued that the two unit sequence (the absolute minimum) may prove to be the more sensible option across all binary feed compositions. Chapter 7 further explains why, for heterogeneous azeotropic distillation, the absolute minimum-unit sequence may be generally preferred to the sequence with a preconcentrator.

From the preceding analysis, it can be concluded that for all practical purposes and for most binary feed compositions, the sequence with absolute minimum number of units is the more sensible alternative than the three unit sequence which includes a preconcentrator. Thus, any sequence with more than the absolute minimum number of units can be eliminated from detailed optimisation study since they cannot be advantageous. Hence, among the primary goals of this study is to find the absolute minimum-unit sequence from the RCM and to ensure that the corresponding entrainer flowrate is desirable so that the sequence generated is among the most (if not the most) cost-effective.

In the next subsections, we describe two general classes of heterogeneous mixtures and relate them to the problem of locating the minimum-unit sequence and optimum entrainer flowrate. The first is classified as *complex heterogeneous mixture* with heterogeneous azeotropes (with or without distillation boundaries) and the second is the *simple heterogeneous mixture* without any heterogeneous azeotropes or distillation boundaries.

6.2.1 Complex heterogeneous mixtures

The mixtures with heterogeneous azeotropes with or without distillation boundaries are classified as *complex heterogeneous mixtures*. It can be concluded from Pham and Doherty[31–33], Wahnschafft *et al.*[27,55,65] and Fien and Liu[66] that complex heterogeneous mixtures are more commonly encountered in practice than mixtures without

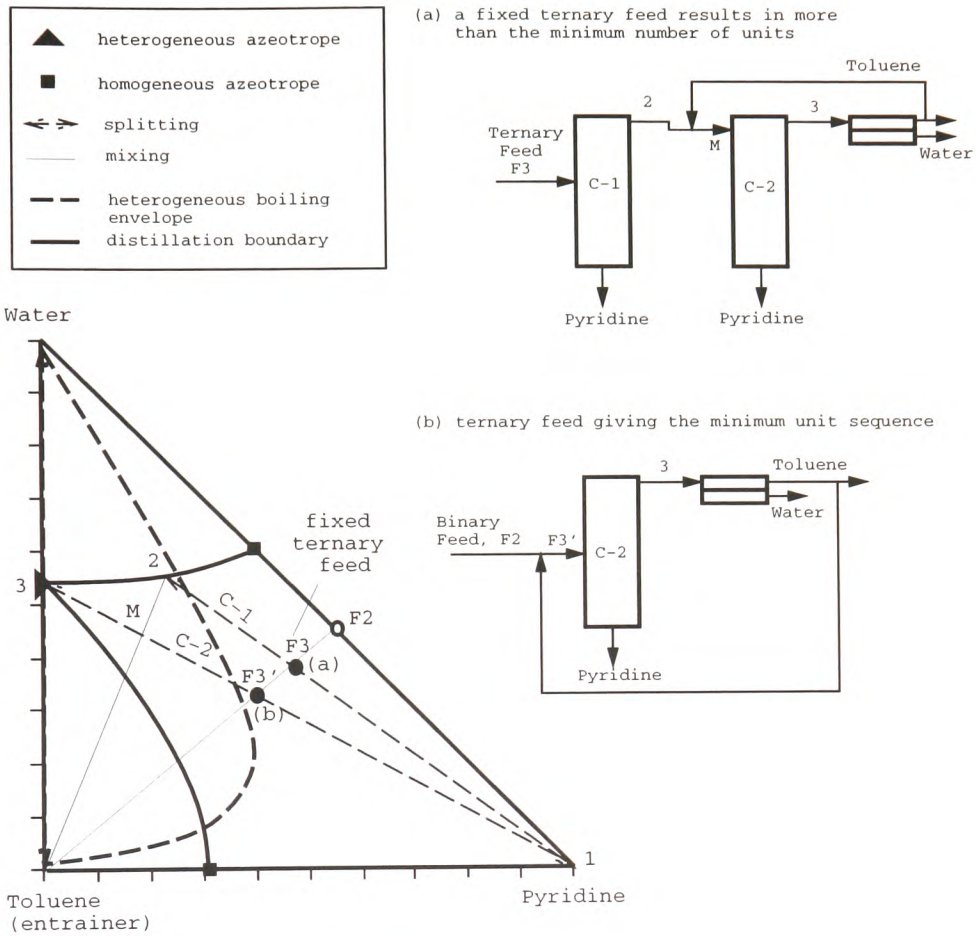


Figure 6.1: A ternary feed that is collinear with a pure component and a heterogeneous azeotrope leads to a sequence with an absolute minimum number of units.

heterogeneous azeotropes.

Siirola suggests drawing an azeotropic column mass balance line that links the overall column feed composition (e.g., point F3' in Figure 6.1(b)) to the pure heterogeneous azeotrope (point 3 in Figure 6.1(b)) and the relevant pure component (pyridine in Figure 6.1(b)) since this tends to maximize the temperature difference between the column's bottoms, which recovers the pure component, and the column's top, which recovers the heterogeneous azeotrope (note that heterogeneous azeotropes must be minimum boiling[31]). He presumes that such arrangement may reduce the separation difficulties[46]. The above implies that the *optimum decanter tie line* position must always go through (or be placed near) the heterogeneous azeotrope. An optimisation

study on decanter tie lines position performed Ryan and Doherty, however, show that this may not necessarily be the case[30].

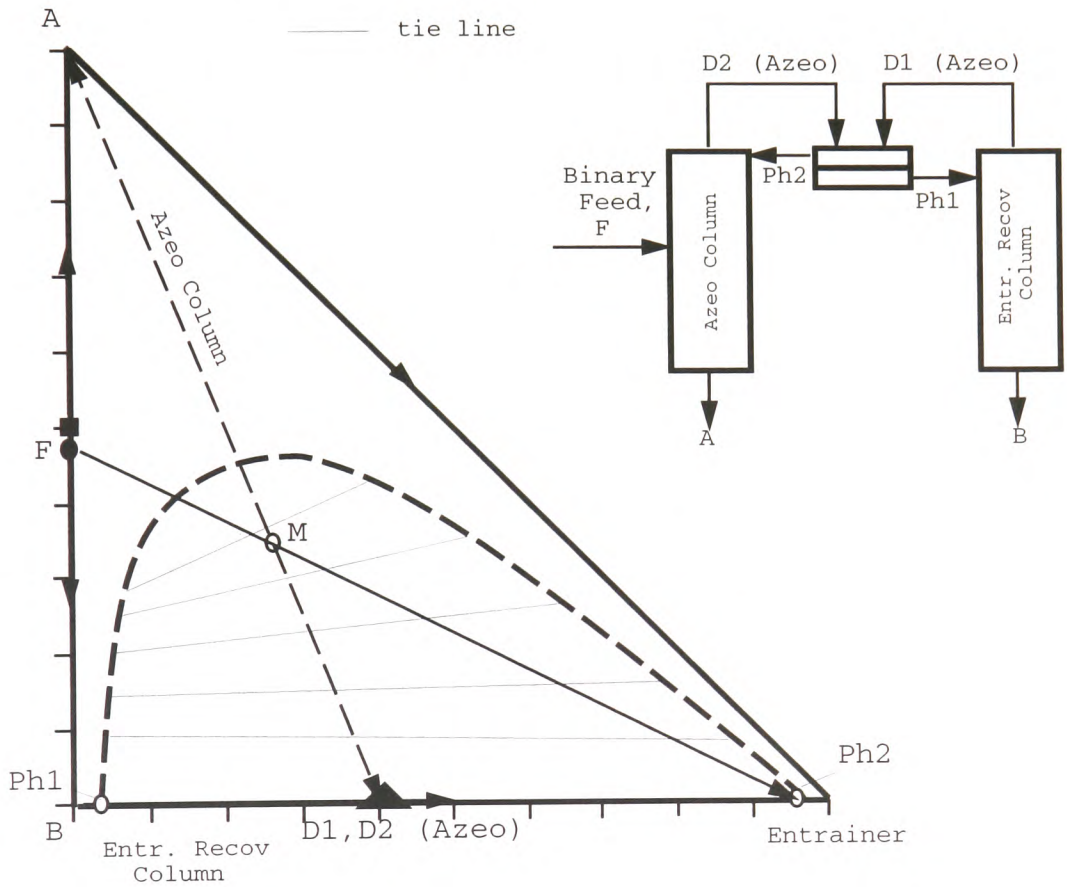


Figure 6.2: Minimum unit sequence for complex heterogeneous systems with a binary heterogeneous azeotrope.

In summary, we define the *collinearity rule* as the practice of placing the azeotropic column mass balance line collinear with the pure component and heterogeneous azeotrope, but with endpoints that do not necessarily coincide with the pure component and the heterogeneous azeotrope. It is also observed that this may involve adjusting the entrainer to binary feed ratio such that the overall ternary feed composition is collinear with either the binary heterogeneous azeotrope (when there is no ternary heterogeneous azeotrope) or the ternary heterogeneous azeotrope and one of the pure components to be separated. Figure 6.1(b) is an example of the collinearity rule applied to a system with a binary heterogeneous azeotrope.

Perhaps the most important implication of the collinearity rule is that it affects the number of units required to achieve a separation objective. Figure 6.1 illustrates a case where the distillation boundary for the complex mixture is located in such a way that following the rule essentially guarantees the absolute minimum number of units while ignoring it will usually lead to sequences with more units than the absolute minimum. For this reason, it is strongly encouraged that the collinearity rule is strictly followed in locating the absolute minimum-unit sequence for complex heterogeneous mixtures even though, admittedly, the absolute minimum-unit sequence can sometimes be achieved without the collinearity rule.

6.2.2 Simple heterogeneous mixtures

Figure 6.3 represents a simple ternary azeotropic mixture with only one binary homogeneous azeotrope, no heterogeneous azeotrope and no distillation boundary. It is possible to separate the ternary mixture using a minimum of two distillation columns (the absolute minimum number of units).

In order to get the *base case* absolute minimum-unit sequence, one should begin by adding an approximately equal amount of entrainer to the binary feed, setting an overall column composition for the azeotropic column at a point midway between the pure entrainer and the binary feed. A cost effective sequence can be achieved once the region and point of desirable entrainer flowrate, and the optimum decanter tie line position are found using the geometric approach outlined in Sections 6.3 and 6.4 respectively.

6.2.3 General rules for achieving the absolute minimum-unit sequence

The following are additional rules to ensure that the absolute minimum unit sequence is achieved. The rules apply for both types of mixtures (simple and complex heterogeneous).

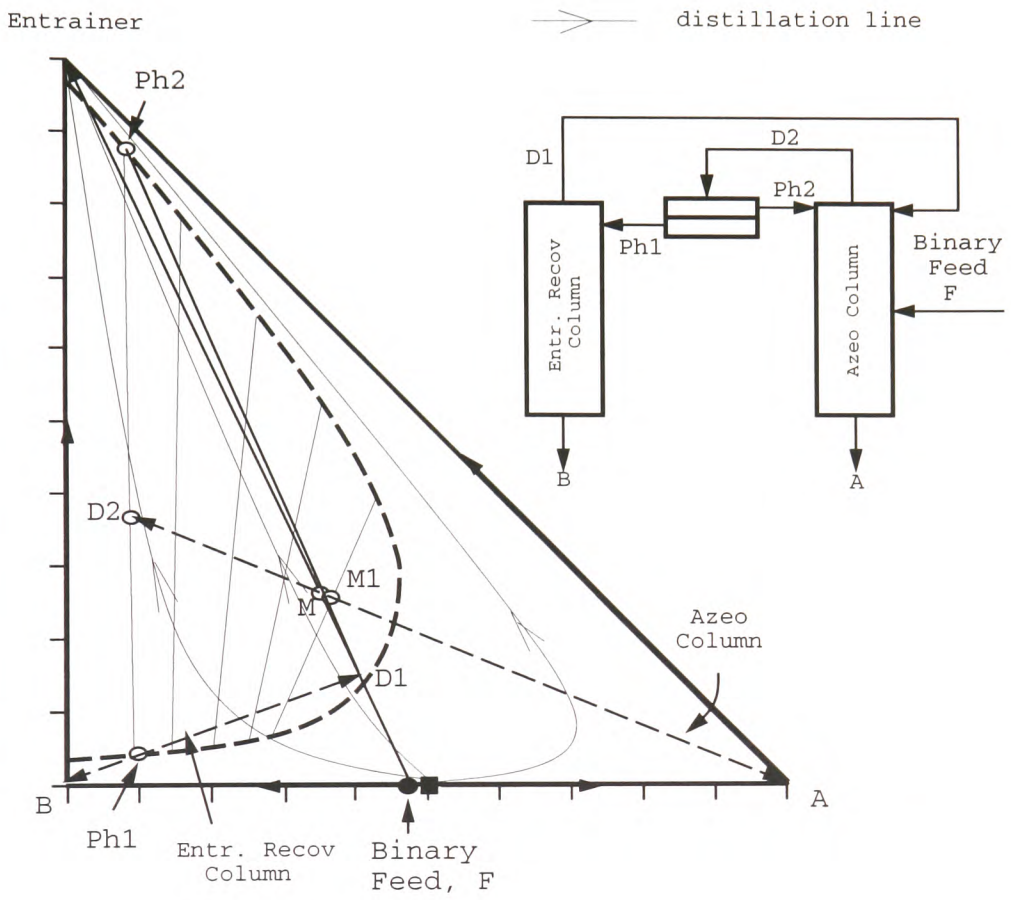


Figure 6.3: Minimum unit sequence for simple heterogeneous mixtures.

- Do not preconcentrate the binary feed. For all practical purposes, preconcentration is not worthwhile for heterogeneous azeotropic distillation[53].

- Whenever possible, recycle a stream to change the inlet composition of a column to allow additional separation to be performed, i.e. a separation that is not initially designed for the column. Wahnschafft *et al.* refer to this as *range extending recycle* [27].

- Recycle an "unrefined" stream to a column whose range of separation covers that of the recycle stream once all the required separation tasks has been performed. Wahnschafft *et al.* term this as *secondary recycling*[27].

6.3 The optimum entrainer flowrate

The phrase *optimum entrainer flowrate* defined in Section 4.8 for homogeneous systems also applies to heterogeneous systems. For heterogeneous systems however, this phrase refers to the lowest possible entrainer flowrate that results in the cheapest combined capital and energy costs for the *absolute minimum-unit sequence*. This definition confines the search for the optimum entrainer flowrate, and hence, the resulting desirable overall azeotropic column composition to the sequence with the absolute minimum number of units. For this reason, the search procedure follows the same classifications used for locating the absolute minimum-unit sequence for heterogeneous mixtures. In Section 6.3.1, we show that the *simple heterogeneous mixtures* lead to an entrainer optimisation problem. In Section 6.3.2 we explain that it may not be necessary to optimise the entrainer flowrate for *complex heterogeneous mixtures* in order to achieve a cost effective azeotropic distillation sequence. Recall that only the optimisation problem exists for homogeneous systems.

6.3.1 Case 1. Optimisation problem for simple heterogeneous mixtures

Figure 6.4[1] represents a relatively simple generic heterogeneous system exhibiting a liquid-liquid heterogeneous region and no distillation boundary. Only one binary homogeneous azeotrope exists between the binary feed constituents A and B. It is possible to recover components A and B in pure form in at least two columns. A binary feed mixture, F, consisting of the binary feed constituents A and B is first distilled to reach its binary azeotropic composition, D1, which is then mixed in the azeotropic column, initially with a specified amount of fresh entrainer, and thereafter with the entrainer-rich mixture, Ph2, coming from the organic layer of the decanter. The resulting ternary mixture with an overall column composition M1 (later M1') is distilled in the azeotropic distillation column to recover pure A as the bottom product, and D2 as the top product that condenses and splits into two liquid phases in the decanter. Note that for startup purposes, a designer may choose any entrainer to (binary) feed ratio that lies within

[1] adapted from Pham and Doherty's heterogeneous entrainer selection scheme[33].

the shaded region enclosed by the *binary feed (F)-binary azeotrope-pure entrainer* triangle. Once the process reaches a steady state, the "peak" of the shaded triangle will shift from the pure entrainer tip to the composition of the entrainer-rich liquid phase (Ph2). The shaded triangle represents an area of *feasible overall azeotropic column compositions* for a given binary feed F and the selected flowsheet sequence.

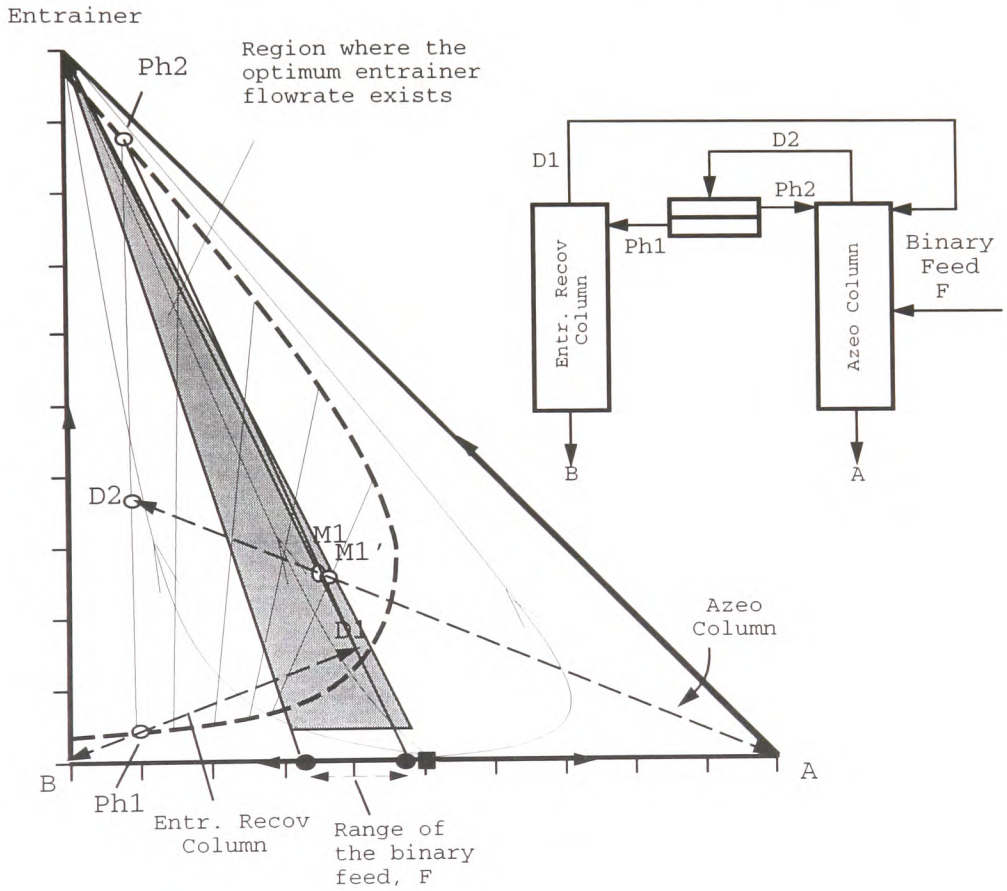


Figure 6.4: A simple heterogeneous mixture exhibiting a region for entrainer optimisation

The boundary at the base of the triangle essentially guarantees that only the entrainer to feed ratios that enable heterogeneous separation are chosen. Note from Figure 6.4 that an entrainer to feed ratio below this boundary leads to an azeotropic column with an overhead composition lying *outside* the heterogeneous liquid boiling region, thus preventing two-phase separation. In practice the binary feed flowrate, F, is normally fixed by some upstream processes. For this reason we have chosen to vary the entrainer

to feed ratio simply by varying the entrainer flowrate.

Changes in the entrainer flowrate results in a trade off between the capital and operating costs of the sequence similar to the one observed for homogeneous systems as discussed in Section 4.8. It can be concluded that for the simple heterogeneous mixture shown in Figure 6.4, optimisation of the entrainer flowrate using the procedure described by Knight and Doherty[29] is expected to yield a desirable overall column composition within the shaded region of the RCM. Note however, that, the optimum entrainer to feed ratio can only be found once the decanter tie line position is fixed using the geometric approach outlined in Section 6.4 of this chapter. Fixing the decanter tie line position followed by optimisation of the entrainer flowrate fixes the decanter liquid-liquid distribution at the point marked by D2, hence the reflux ratio in the azeotropic column, the distillate composition (D1 or D1') from the entrainer recovery column and, ultimately, the design of each column in the separation sequence.

6.3.2 Case 2. Non-optimisation problem - complex heterogeneous mixtures

Earlier, it has been shown that whenever a heterogeneous azeotrope exist, it is desirable to adjust the overall azeotropic column composition on the RCM so that the azeotropic column mass balance line is collinear with the pure component product and the heterogeneous azeotrope. This implies the existence of a *unique entrainer flowrate.* Figure 6.5 shows the *closed-loop* overall azeotropic column composition existing at the intersection between the azeotropic column mass balance line and the mixing line between the optimum distillate composition from the entrainer recovery column (D1) and the entrainer-rich liquid composition (Ph2) from the decanter. The overall azeotropic column composition leading to the desirable entrainer flowrate exists within the locus of possible overall azeotropic column compositions which results from different decanter tie line positions. The desirable entrainer flowrate can be determined once the optimum decanter tie line position and distillate composition from the entrainer recovery column are found from the methods described in Sections 6.4 and 6.5 respectively.

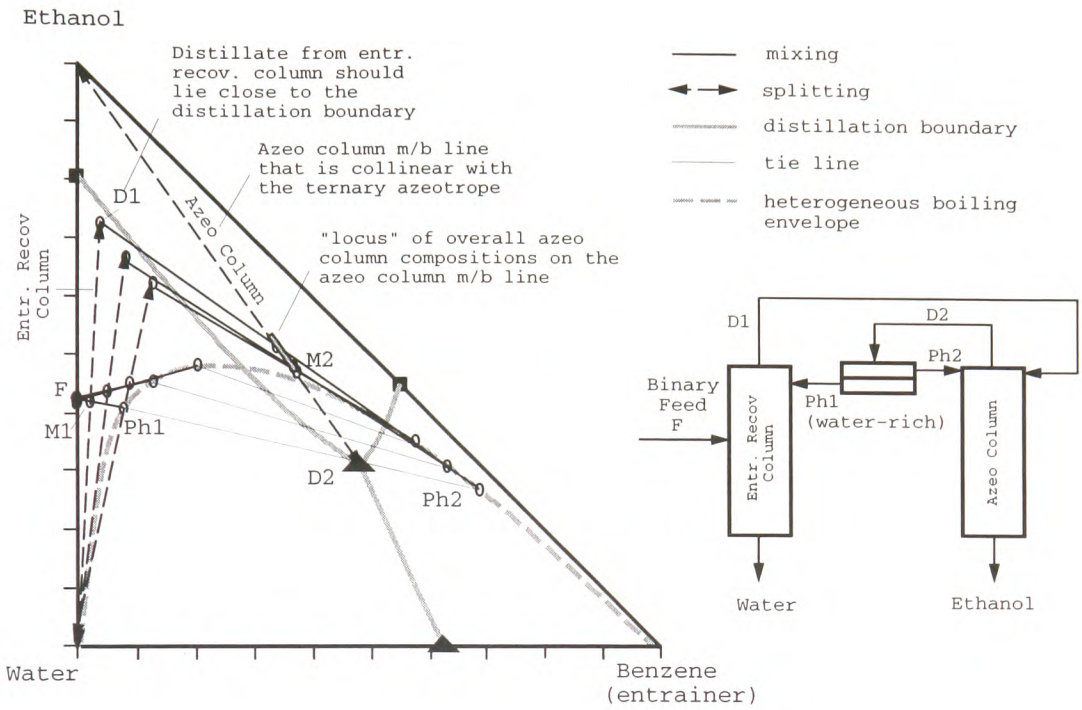


Figure 6.5: Complex heterogeneous mixture with a ternary heterogeneous azeotrope exhibiting a fixed entrainer flowrate.

Application of the collinearity rule yields a unique entrainer flowrate for the absolute minimum-unit sequence, thus allowing a designer to avoid entrainer flowrate optimisation for complex heterogeneous mixtures. This discovery leads to an important heuristic applicable to the large number of mixtures exhibiting heterogeneous azeotropes:

> *Whenever there is at least one heterogeneous azeotrope*[2]*, there exists a desirable overall azeotropic column composition for the minimum unit sequence at the intersection of the azeotropic column mass balance line and the mixing line between the optimum distillate composition from the entrainer recovery column and the composition of the entrainer-rich phase from the decanter.*

Figures 6.1, 6.2 and 6.5 are examples of heterogeneous systems observing this rule.

[2]the heteroazeotrope can be a binary or a ternary azeotrope.

6.4 The optimum decanter tie line position

Ryan and Doherty[30] studied the effects of the decanter tie line position on the azeotropic column energy consumption by approximating the vapour rate leaving the reboiler according to the relation

$$V = (r + 1)D$$

with V representing the vapour rate, r the reflux ratio and D the distillate rate for the azeotropic column.

Results from the study show that the choice of decanter tie line not only affects the azeotropic column distillate rate, reflux ratio and the vapour rate but also the economics of the entire separation sequence. For an ethanol-water-benzene separation sequence, they find that moving from the *lower to the upper tie lines*, the azeotropic column reflux ratio decreases while the distillate rate increases resulting in an overall cost that is more or less insensitive to the decanter tie line position. They attribute this result to the "fortuitous cancellation of large but opposite effects" between the azeotropic column reflux ratio and distillate flowrate. They conclude that such trend is specific to the ethanol-water-benzene mixture and therefore cannot be expected to occur in general, and predict that the position of the decanter tie line would become the main optimisation variable in most new problems.

In making the crucial discoveries for decanter tie line optimisation, Ryan and Doherty might have possibly overlooked some equally crucial geometric features linking the length and position of the decanter tie lines as well as the azeotropic column mass balance line to its reflux ratio and distillate rate. The following sections describe how geometric variations of the decanter tie lines, azeotropic column mass balance line and the properties of the heterogeneous liquid boiling envelope influence the azeotropic column reflux ratio and distillate rate, and hence, the overall economics of the separation sequence. We include some examples derived from the studies of Ryan and Doherty[30], Pham and Doherty[33] and Siirola[46]. In principle, it is possible to use the geometric

reasoning approach described in the next section to determine the optimum decanter tie line position for any heterogeneous azeotropic mixture given the liquid boiling envelope and the equilibrium tie lines. This will ultimately allow a designer to produce a "catalogue of effects" leading to some useful guidelines for a *graphical optimal selection* of the decanter tie line.

6.4.1 Heterogeneous systems with tie lines of type 1 (ternary heterogeneous azeotrope in the entrainer-rich region)

Figure 6.6 represents the RCM for the ethanol-water-benzene (entrainer) heterogeneous mixture from Ryan and Doherty's study showing tie lines that have been classified in this study as "type 1" tie lines, i.e. those which slant from the entrainer-lean to the entrainer-rich region. The separation schemes in this study are represented in the manner described by Fien and Liu[66], i.e., to treat the azeotropic column and decanter separately as opposed to combining them in one mass balance envelope (as is done by Ryan and Doherty) in order to avoid the confusion that might arise as a result of an azeotropic column which appears to cross the homogeneous distillation boundary[30].

For mixtures similar to the ethanol-water-benzene system, an azeotropic column mass balance line that is placed collinear with the pure component and heterogeneous azeotrope guarantees the overhead vapour to remain within the wedged-shaped region enclosed by the distillation boundaries and the heterogeneous liquid boiling envelope (the shaded region in Figure 6.6). Fixing the azeotropic column mass balance line fixes the decanter liquid-liquid composition on the *base case* tie line, which we have chosen as the one going through the heterogeneous azeotrope for this type of mixture. It has been observed during this study that shifting from *the base case (lower) to the upper tie lines* reveals some geometric links between:

- the tie line position and the distillate rate as well as the azeotropic column reflux ratio
- the length of tie line and the azeotropic column reflux ratio

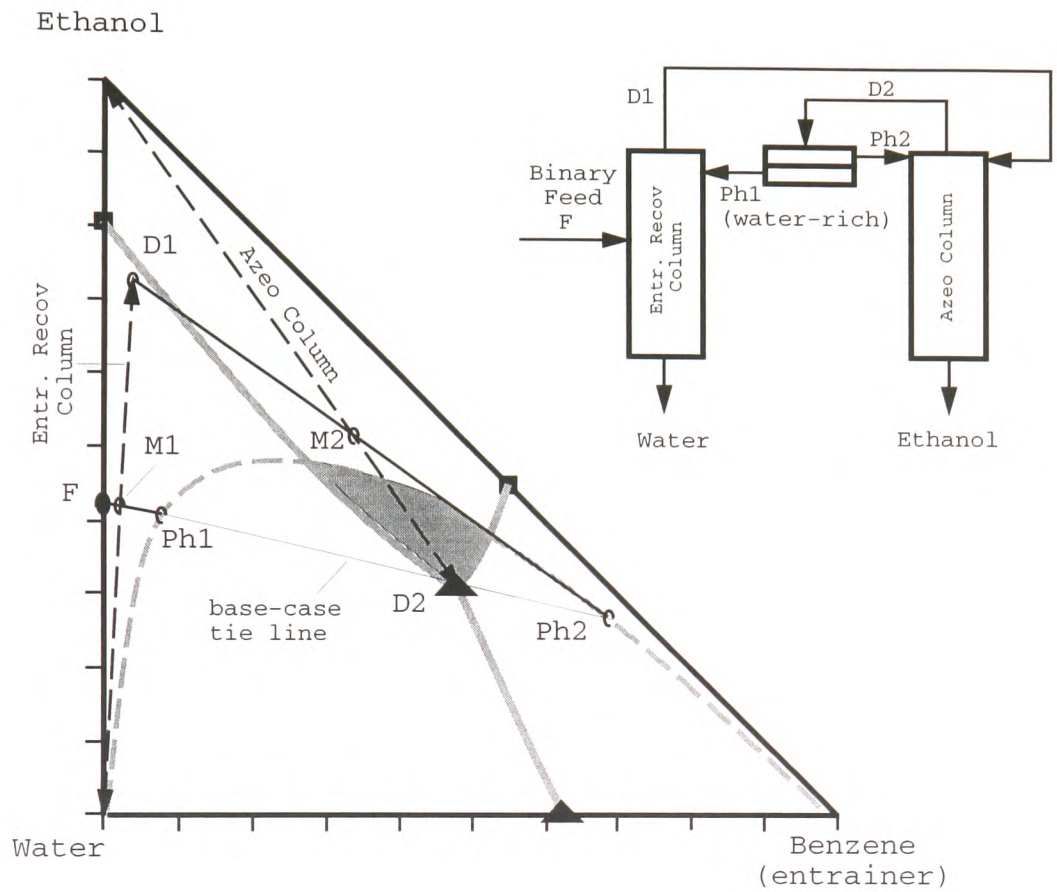


Figure 6.6: A RCM and a separation sequence for the ethanol-water-benzene (entrainer) system.

Figure 6.7 shows that the overall azeotropic column composition tends to shift closer towards the heterogeneous azeotrope as one moves from the *base case (lower) to the upper tie lines.* By the lever rule, the overall azeotropic column composition shift in the direction of the heterogeneous azeotrope physically matches a decrease in ethanol flowrate at the bottoms and an increase in the flowrate of the overhead vapour, hence an increase in the decanter condensate (and the entrainer-rich and entrainer-lean phases in equilibrium). This ultimately *increases* the azeotropic column distillate flowrate as one moves from the *base case to the upper* tie lines. Note that decreased ethanol flowrate at the bottoms (moving from the base case to the upper tie line) also means that more ethanol is being entrained in the vapour leaving in the distillate stream as evident from the resulting two liquid phases of the upper tie lines with relatively higher percentage ethanol in comparison to that of the lower tie lines. Bear in mind that

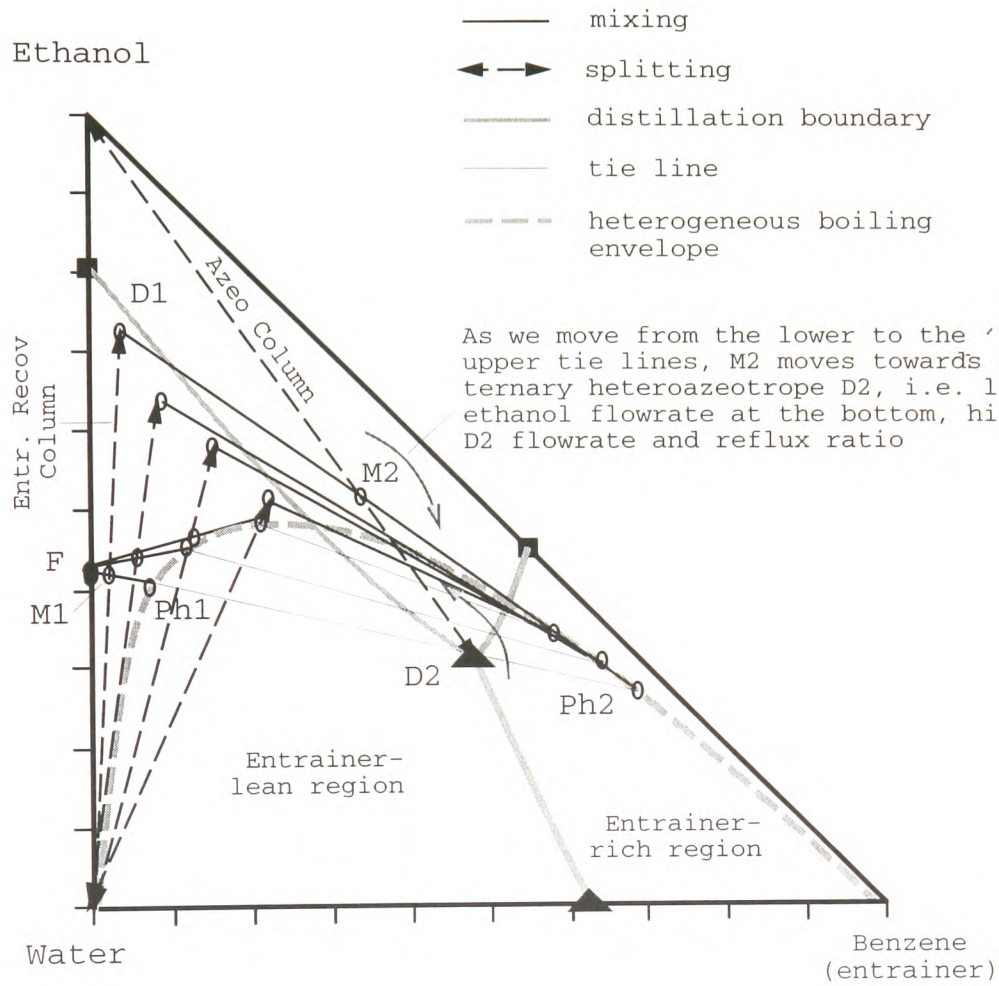


Figure 6.7: Geometric links between the decanter tie line positions and the distillate rate and reflux ratio.

higher ethanol entrainment can also be attributed to poorer vapour-liquid separation, which is expected when the liquid reflux is lower. The geometric relationship that exists between the position of the decanter tie lines and the distillate flowrate yields results that are consistent with the ones obtained from the numerical optimisation studies performed by Ryan and Doherty but were not conceptually explained by them.

Pham and Doherty[32] suggest that a practical azeotropic column reflux ratio should be larger than the value of "ϕ", which is defined as the ratio between the flowrates of the entrainer-rich and entrainer-lean phases whose compositions are located at the endpoints of a decanter tie line. From the lever rule, it can be concluded that the

azeotropic column reflux ratio is *proportional to the ratio of the length of the tie line segments for the entrainer-lean phase and the entrainer-rich phase.* Note that ternary systems exhibiting a liquid-liquid region typically have tie lines which decrease in length from the *lower to the upper part* of the liquid-liquid envelope.

For the ethanol-water-benzene mixture shown in Figure 6.7, it is clear that the use of the *collinearity rule* and the position of heterogeneous azeotrope in the entrainer-rich region yield reflux ratios that decrease with decrease in the lengths of the decanter tie lines, i.e. *from the heterogeneous azeotrope to the top of the liquid-liquid envelope.* For a given tie line, the exact reflux ratio may also be calculated from the *actual* compositions of the two liquid phases at the endpoints of the tie line, and the top liquid composition for the azeotropic column which occurs at the intersection between the tie line and the azeotropic column mass balance line. This geometric relationship between the *length* of the decanter tie line and the reflux ratio supports the previous conclusions derived from the physical relationship between the decanter tie line position and the reflux ratio.

From the correlation for the estimation of the vapour rate leaving the reboiler presented at the beginning of this section, it is clear that the decrease in reflux ratio *towards the top tie line* coupled by the increase in distillate rate explains the cancellation effect observed by Ryan and Doherty.

Summary of the geometric links for Section 6.4.1:

From lower to upper tie lines:

- *Overall azeo column composition moves towards heteroazeotrope→ distillate rate* $\Uparrow$,
- *Ratio of entrainer-lean to entrainer-rich tie line segments* $\Downarrow$ *→reflux ratio* $\Downarrow$,
- *Overall cost insensitive to tie line position due to the cancellation effect.*

6.4.2 Heterogeneous systems with tie lines of type 2 (ternary heterogeneous azeotrope in the entrainer-rich region)

Figure 6.8 represents the isopropanol-water mixture with benzene as the entrainer, showing strikingly similar distillation boundary trends and liquid-liquid envelope shape to that of the ethanol-water-benzene mixture. The only difference in terms of geometry is that the decanter tie lines within the liquid-liquid envelope are now slanted from the entrainer-rich to the entrainer-lean region in direct contrast to the tie line trend displayed by the ethanol-water-benzene (entrainer) mixture. It is possible to predict the azeotropic column distillate rate and reflux ratio trends using geometric reasoning in order to assess their overall effect on the economics without having to perform detailed simulation and optimisation.

For this system, note that the overall feed composition on the azeotropic column mass-balance lines in Figure 6.8 tends to move away from the ternary heterogeneous azeotrope, decreasing the distillate rate, as one moves from the *lower (longer) to the upper (shorter) tie lines.* As the lengths of the tie lines decrease from the *bottom to the top* of the liquid-liquid region, one would expect the reflux ratio to decrease in the same direction like in the case of type 1 tie lines. A closer look however reveals that for this mixture, the *rate of decrease* of the tie lines' lengths on the entrainer-rich side appear slightly higher compared to that for the entrainer-lean side. From the lever rule, this implies a slightly higher decrease in the flowrate of the entrainer-lean phase as compared to that for the entrainer-rich phase. The net effect is an *increasing reflux ratio trend towards the top* of the envelope, contrary to the case of type 1 tie lines. Again, this can be verified by taking the exact tie line compositions to calculate the reflux ratios. The decrease in distillate rate accompanied by an increase in reflux ratio *towards the upper tie lines* results in the cancellation effect similar to the one observed for the systems with tie lines of type 1. This finding shows that the trend is not specific to the ethanol-water-benzene mixture but much more generic, against the expectations of Ryan and Doherty[30].

Summary of the geometric links for Section 6.4.2:

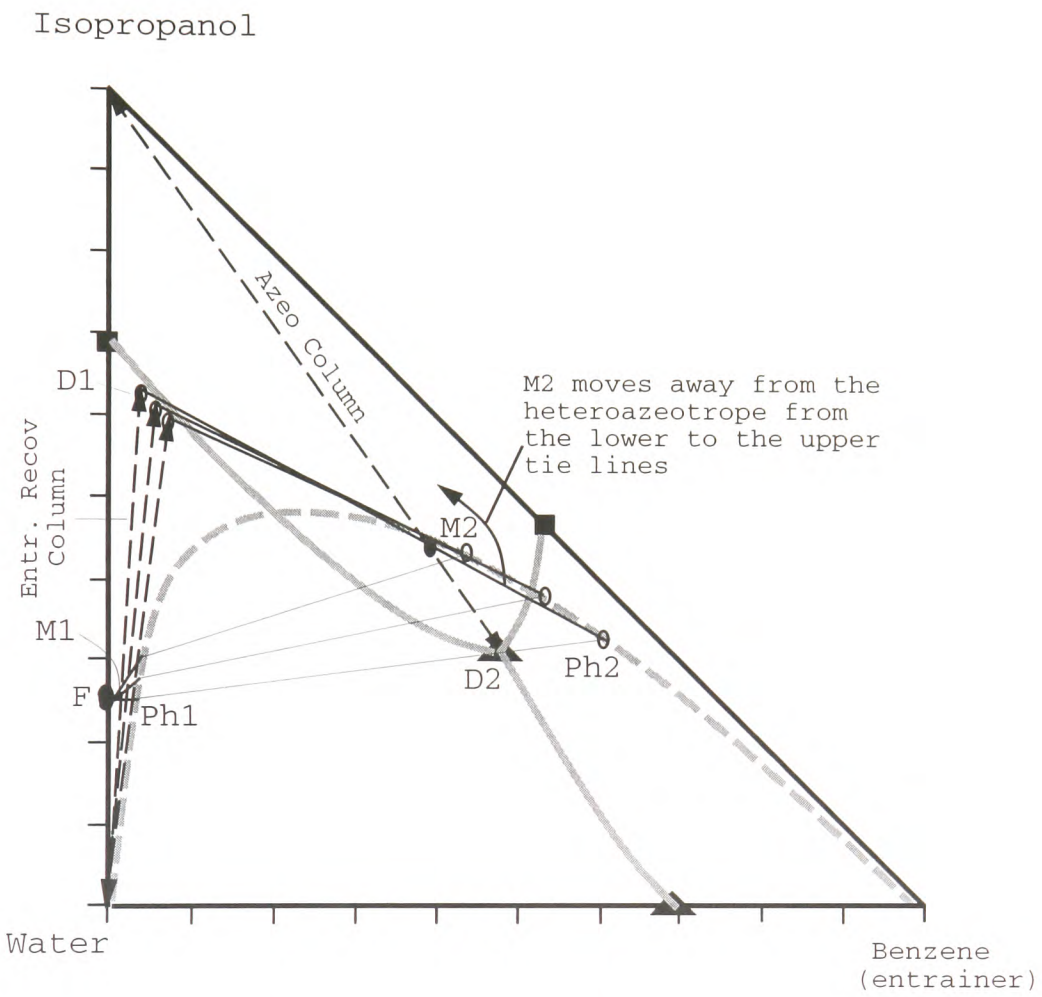


Figure 6.8: Isopropanol-water-benzene (entrainer) system exhibiting "type 2" decanter tie lines orientation.

From lower to upper tie lines:

- *Overall azeo col. composition moves away from heteroazeotrope→ distillate rate* $\Downarrow$,
- *Ratio of entrainer-lean to entrainer-rich tie line segments* $\Uparrow$ *→reflux ratio* $\Uparrow$,
- *Overall cost insensitive to tie line position due to the cancellation effect.*

6.4.3 Heterogeneous systems with a ternary heterogeneous azeotrope in the entrainer-lean region

A third possible variation to the problem of positioning the decanter tie line is exemplified by the ethanol-water system with toluene as the entrainer, shown in Figure 6.9. Unlike the two previous cases, the ternary heterogeneous azeotrope for this system is located in the entrainer-lean region instead of the entrainer-rich region. The tie line is of *type 1*, but now the flowrate of the entrainer-lean phase is always higher than that of the entrainer-rich phase, causing the azeotropic column reflux ratio to increase as the length of the tie line decreases from the *lower to the upper tie lines* (the lowest tie line in this case goes through the ternary azeotrope). The tie lines of *type 1* always lead to distillate rates that increase from the *lower to the upper tie lines.* The overall effect is a net increase in both the reflux-ratio and distillate rates, ultimately increasing the total annual costs towards the top of the liquid-liquid region. For such a system, the lower tie lines represent the economically better choice.

Summary of the geometric links for Section 6.4.3:

From lower to upper tie lines:

- *Overall azeo column composition moves towards heteroazeotrope→ distillate rate* $\Uparrow$,
- *Ratio of entrainer-lean to entrainer-rich tie line segments* $\Uparrow$ *→reflux ratio* $\Uparrow$,
- *Overall cost increases towards top tie line. Lower tie line economical.*

6.4.4 Heterogeneous systems with only a binary heterogeneous azeotrope and no distillation boundary

A final example involves the acetic acid-water-ethyl acetate (entrainer) system with no distillation boundary and only a binary heterogeneous azeotrope, shown in Figure 6.10. As we move from the *lower to the upper tie lines*, a type 2 tie line trend (similar to that of the isopropanol-water-benzene system discussed in Section 6.4.2) gives decreasing distillate rates and increasing reflux ratios. This ultimately results in a cancellation effect, as has been observed for the type 2 tie lines (i.e., for isopropanol-water-benzene

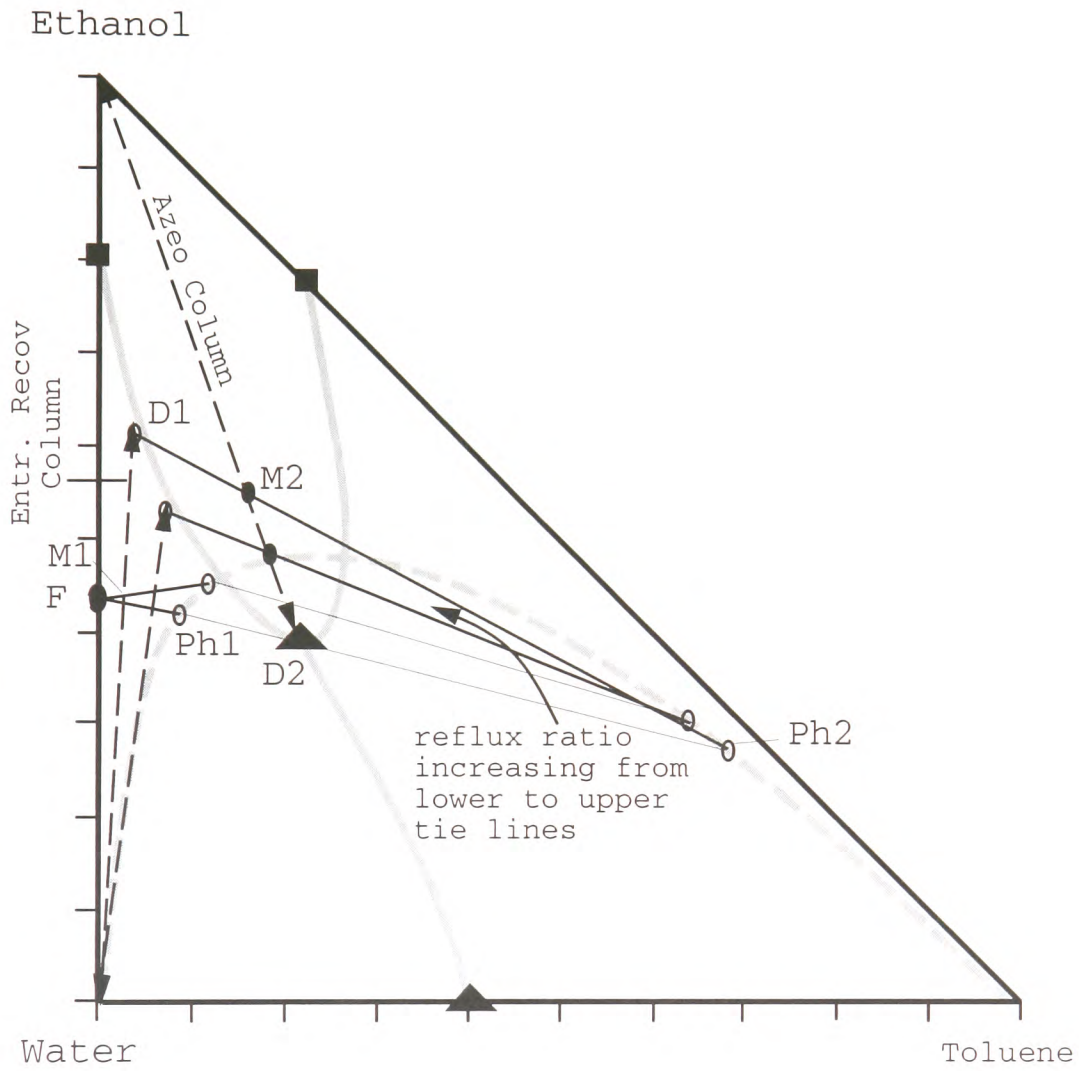


Figure 6.9: Heterogeneous system with a ternary heteroazeotrope located in the entrainer-lean region.

system).

Summary of the geometric links for Section 6.4.4:

From lower to upper tie lines:

- *Overall azeo col. composition moves away from heteroazeotrope→ distillate rate* $\Downarrow$,
- *Ratio of entrainer-lean to entrainer-rich tie line segments* $\Uparrow$ *→reflux ratio* $\Uparrow$,
- *Overall cost insensitive to tie line position due to the cancellation effect.*

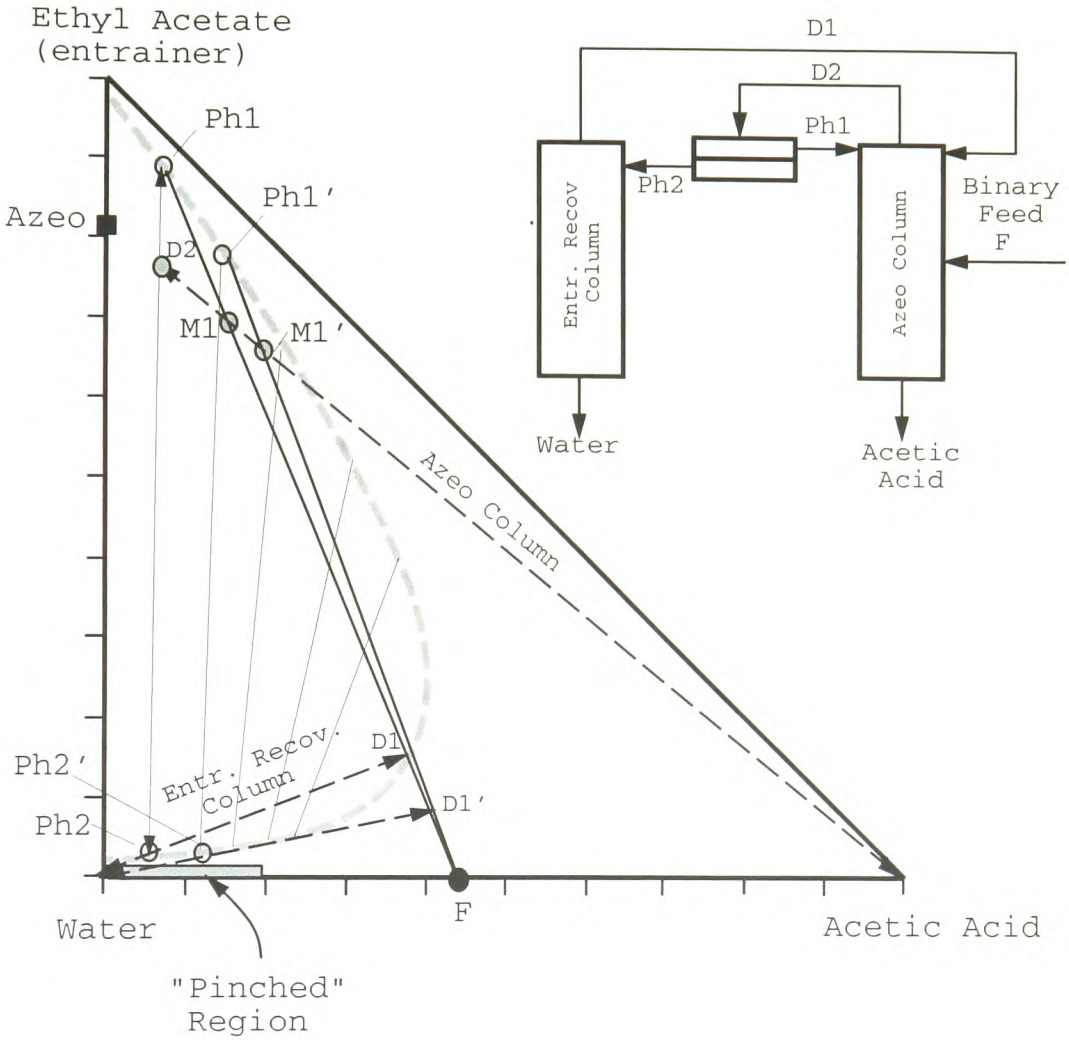


Figure 6.10: Tie line positioning for complex heterogeneous azeotropic mixtures with a binary heterogeneous azeotrope.

6.4.5 Conclusions for decanter tie line positioning

Using geometric reasoning, it is possible to predict the effects of the decanter tie line position on the reflux ratio and the distillate rate (hence the azeotropic column reboiler rate) and assess these effects on the overall economics without the need of numerical calculations (other than, obviously, the ones needed to predict the azeotropes, distillation boundaries and liquid-liquid equilibria). Thus far, it has been found that the orientation and the intersection of the azeotropic column mass balance line with the decanter tie lines, the location of distillation boundaries and heterogeneous azeotropes

are the main parameters influencing the optimum selection of the decanter tie line.

The following trends have been observed as the position of the selected tie line moves from the *lower to the upper* part of the heterogeneous liquid boiling envelope:

- type 1 tie lines always result in increasing distillate rate, and conversely, type 2 tie lines always result in decreasing distillate rate.
- type 1 tie lines cause the reflux ratio to increase when the ternary azeotrope is in the entrainer rich-region, and to decrease when the ternary azeotrope is in the entrainer-lean region.
- the reflux ratio trend is reversed for the RCMs with type 2 tie lines.

Where uncertainties exist with regards to the length of the segments of the tie lines used to estimate the reflux ratio, the exact reflux ratio must then be calculated (and its trend verified) from the tie line liquid phase compositions and the tie line intersection with the azeotropic column mass balance line. The preceding observations enable the identification of three categories of mixtures, classified according to the way they affect the distillate rate and reflux ratio as the selected tie lines move from the *lower to the upper* part of the heterogeneous liquid boiling envelope:

- cancellation effect - distillate rate decreases and reflux ratio increases. Tie line position does not significantly influence overall design. The findings from Ryan and Doherty[30] confirm this observation.
- combined "positive" effect - distillate rate and reflux ratio increase. Lower tie lines advantageous.
- combined "negative" effect - distillate rate and reflux ratio decrease. Upper tie lines advantageous.

Similar reasoning can also be used to decide the optimum tie line position for *any* mixture whose distillation boundaries, liquid-liquid heterogeneous envelope, tie line

orientation and azeotrope location can be predicted from vapour-liquid-liquid equilibrium data.

Table 6.1: The effects of tie line selection on the azeotropic column reflux ratio, r, and distillate rate, D, as we move from bottom to the top of heterogeneous liquid boiling envelope.

heteroazeotrope position	entrainer-rich region		entrainer-lean region	
tie line type	type 1	type 2	type 1	type 2
predicted effects	r $\Downarrow$, D $\Uparrow$	r $\Uparrow$, D $\Downarrow$	r $\Uparrow$, D $\Uparrow$	r $\Downarrow$, D $\Downarrow$
best tie line	any[3]	any[3]	base	top

[3]base tie line is preferred since it maximizes the temperature difference between the top and the bottom section of a column.

6.5 The optimum distillate composition for the entrainer recovery column

A heuristic derived from the Ryan and Doherty's optimisation study states that the *optimum* distillate composition from the entrainer recovery column is always close to the distillation boundary[30,66]. In its current form, the heuristic appears confined to systems with distillation boundary trends similar to the mixture for which it is derived, thus may not appear applicable in general given the peculiarities of azeotropic mixtures leading to systems with either no distillation boundaries or very different boundary locations. One must, however, realise that setting a target composition close to the distillation boundary entails making the distillate composition as lean as possible in the amount of component the entrainer recovery column is supposed to remove from its bottom stream, and as rich as possible in the amount of component to be removed from the bottom of the azeotropic column. We emphasize that these important implications arising from the heuristic derived by Ryan and Doherty[30] hold for *all* heterogeneous mixtures and are the basis for the new heuristics presented in this section.

Once again, geometric reasoning have an important role to play in the sequencing of separators for heterogeneous azeotropic mixtures. Figures 6.11 and 6.12 represent two generic classes of systems typifying many other heterogeneous mixtures not covered by

the distillate composition heuristic of Ryan and Doherty. Figure 6.11 represents a *complex heterogeneous mixture* with a binary heterogeneous azeotrope and no distillation boundary. For such mixtures the optimum decanter tie line position is at the base of

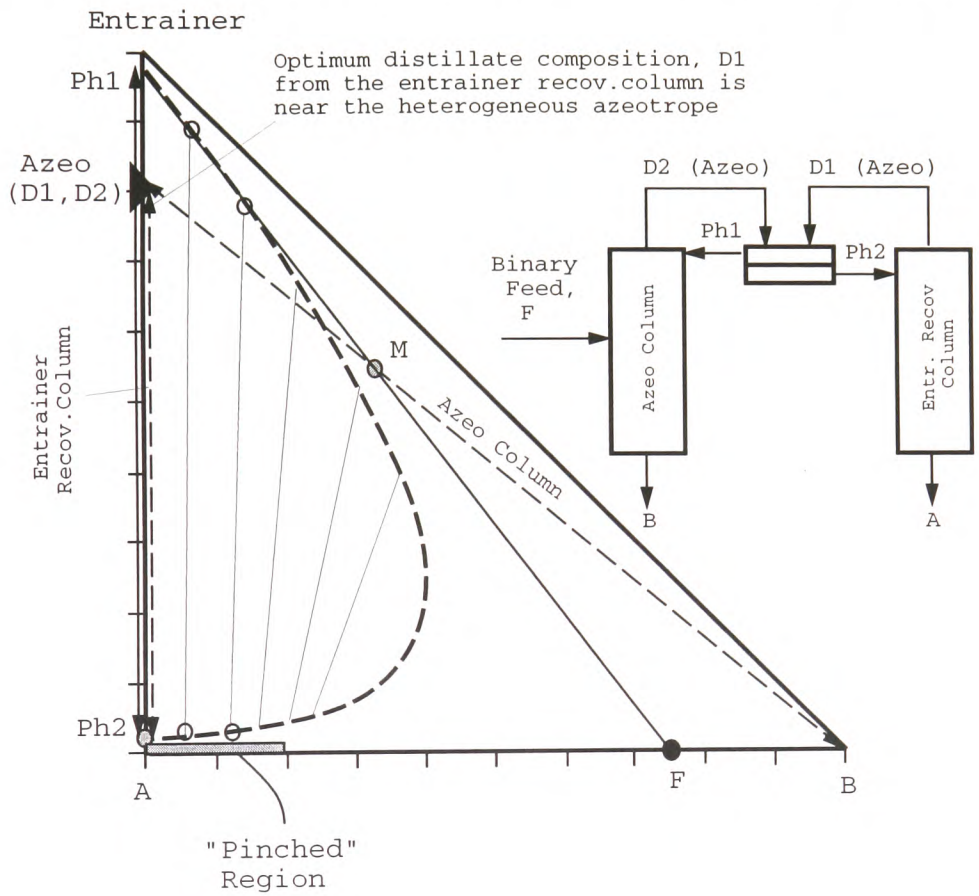


Figure 6.11: The optimum distillate composition for mixtures with a heterogeneous azeotrope but no distillation boundary.

the heterogeneous liquid boiling envelope. Siirola[46] states that there exists a "pinched region" at a particular binary composition for which the relative volatility between the binary feed constituents (A and B) approaches unity, making conventional distillation very expensive. Note that although no distillation boundary exists, the distillate composition from the entrainer recovery column is limited by the heterogeneous azeotrope. It can be concluded that the optimum distillate composition for the entrainer recovery column in this system is near the heterogeneous azeotrope as shown in the figure. An example of such system is the ethyl acetate (low boiling entrainer)-water-acetic acid mixture.

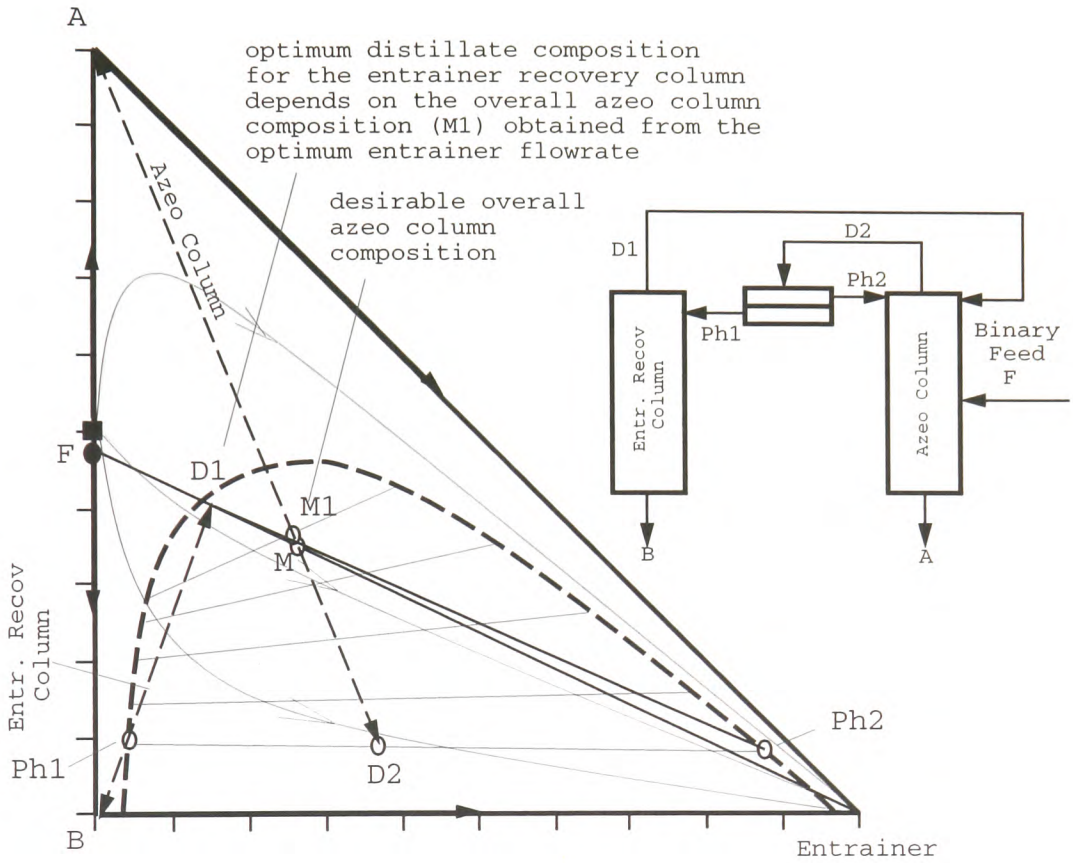


Figure 6.12: The optimum distillate composition for simple heterogeneous mixtures mixtures with neither distillation boundary nor heterogeneous azeotrope.

Figure 6.12 represents a *simple heterogeneous mixture* with only a binary homogeneous azeotrope and no distillation boundary. Recall that, for such mixtures, optimisation of the entrainer flowrate gives the desirable ternary feed composition for the azeotropic column, thereby fixing its mass balance line and the intersection of the mass balance line with the best decanter tie line. Assuming that the best tie line lies near the base of the heterogeneous liquid envelope, the distillate composition from the entrainer recovery column, D1 *must lie on the line linking M with the entrainer-rich phase, Ph2* in order to satisfy the azeotropic column mass balance. Thus, in the absence of a heterogeneous azeotrope, the distillate composition is dependent upon the desirable overall azeotropic column composition which is obtained from the optimum entrainer flowrate.

In general, it can be concluded that the optimum distillate composition from the en-

trainer recovery column is always

- at or near a *stationary point* (azeotropes, distillation boundaries) on a RCM for *complex heterogeneous mixtures* (i.e. systems with heterogeneous azeotropes and/or distillation boundaries),
- at or near the binary feed-pure entrainer mixing line for *simple heterogeneous mixtures* (i.e. systems without heterogeneous azeotrope and distillation boundaries), once the optimum entrainer flowrate is fixed.

The overall procedure for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures by geometric reasoning is presented in Appendix D.

6.6 Summary

An automated procedure for the synthesis of distillation sequences developed by Wahnschafft *et al.* [55] assumes a *fixed ternary feed* composition, implying that an internal entrainer is available from within a process. To find the best sequence, it is currently necessary to optimise the parameters of each of the sequences generated and to compare their economics. So far, in the literature, the entrainer flowrate has not been considered during the optimisation of heterogeneous sequences even though it has been identified as one of the dominant optimisation variables. It is important to realise that a "generate and test" approach that is based on a fixed ternary feed or a suboptimal entrainer flowrate cannot guarantee a global optimum solution, thus may yet be an expensive way of isolating a promising sequence.

The proposed procedure for the synthesis of cost effective distillation sequences for homogeneous azeotropic mixtures, which is based on reasoning over the geometric features of a RCM, has been extended to heterogeneous mixtures with modifications to account for liquid heterogeneity. The approach guides the search for two dominant synthesis parameters, namely:

1. The absolute minimum number of units.

2. The optimum entrainer flowrate.

An analysis of the RCM trends for a wide variety of heterogeneous mixtures allow us to identify a set of essential RCM properties which influence the synthesis of separation sequences, to provide explanation for previous unexplained observations by other researchers and ultimately, to formulate a set of general rules for the synthesis of promising sequences across a wide variety of heterogeneous mixtures. These essential properties include the nature of the binary and ternary azeotropes, distillation boundaries, liquid-liquid heterogeneous envelopes and the orientation and length of the heterogeneous tie lines. As a result, it is possible to predict the effects of such properties on the *absolute minimum number of units* using the *collinearity rule*, the *region and the point of minimum economic entrainer flowrate*, the *optimum decanter tie line position*, and the *distillate composition for the entrainer recovery column* without need of numerical calculations other than the ones needed to predict the features of the ternary diagram.

Note that the solution may or may not represent the global economic optimum. The main aim is however, to generate some of the most promising design options at the expense of minimum possible computation, thus making the use of the technique particularly appropriate during the early stages of design. To achieve these goals, it is important to make sure that the number of separation units is kept to a minimum and that the entrainer flowrate is maintained at a desirable value.

Chapter 7

Feed Modification for Improved Separation and Reduced Waste for Azeotropic Distillation Sequences

7.1 Introduction

Given the peculiarities and the wide spectrum of azeotropic mixtures, a numerical procedure for the synthesis and optimisation of distillation sequences for azeotropic mixtures can fall short of providing a general solution, in which case a geometric approach also has an important role to play. In Chapters 4, 5 and 6 of this thesis, a set of methods based on heuristics and geometric reasoning have been developed to generate cleaner and cost effective sequences for separating homogeneous and heterogeneous azeotropic mixtures. Note, however, that the separation sequence generated is the best only for the given binary or ternary feed.

Sometimes, there may be room to improve the separation performance of an azeotropic mixture by modifying the given binary or ternary feed composition by means of feed preconcentration, mixing and recycling. Such modifications may result in simpler separation sequences, reduced entrainer requirement, capital as well as operating costs. Using heuristics and geometric reasoning, this chapter provides some simple guidelines for designers to assess when such changes in the feed composition might be appropriate and advantageous. The chapter begins by analysing the implications of a binary or

a ternary feed initialisation in an azeotropic separation synthesis study (Section 7.2). Sections 7.3.1, 7.3.2 and 7.3.3 identify the cases where preconcentration may be advantageous for homogeneous azeotropic mixtures with or without boundary crossing, and for heterogeneous mixtures respectively. The chapter concludes with Section 7.4 in which geometric reasoning is employed to examine the possible mixing and recycling schemes that may lead to improved azeotropic separation.

As in the previous chapters, the techniques presented here are limited to azeotropic mixtures with a maximum of three components. Unless stated otherwise, the same conventions used in the previous chapters are maintained. In the next section, the implications of assuming a binary or a ternary feed during the synthesis of separation sequences for azeotropic mixtures are compared. Results from the comparison explain why a binary feed or its resulting *desirable ternary feed* is the natural choice in most cases.

7.2 Binary and ternary feeds - Assumptions and implications

This study is based on the premise that most azeotropic separation problems are specified in terms of a binary mixture of a given composition that forms an azeotrope at another composition beyond which, further separation by distillation is impossible. Separation of the original binary mixture into two essentially pure components is achievable if a suitable entrainer is added in an appropriate quantity to the binary mixture to form a ternary system.

Wahnschafft *et al.*[27] proposed an automated procedure for the synthesis of azeotropic distillation sequences. In most cases, they assume that an azeotropic separation task begins with a ternary instead of a binary feed specification. They present an example of a heterogeneous mixture which results in many separation options and conclude that the generation of every conceivable separation sequence for azeotropic mixtures can become a complex task. For the separation of homogeneous azeotropic mixtures, we have shown that only a fixed and limited number of desirable separation options exist (see Chapters

4 and 5). However, heterogeneous mixtures may lead to a large number of separation options because they are generally more complex than homogeneous mixtures due to the presence of heterogeneous liquid-liquid regions.

It should be realised that assuming a fixed ternary feed entering an azeotropic column is justified only when the entrainer is a component already present in the process, i.e. when an internal entrainer is used. This is because, with an internal entrainer, the composition of the ternary feed is dictated by some upstream process conditions and can be rather arbitrary. In practice, however, an entrainer is very seldom available within a process, and when it is, it is rarely found in the right quantity required for the separation. Separation is usually achieved by adding an external entrainer to a binary azeotropic mixture. For an azeotropic mixture, there exists a *desirable ternary feed composition* that results in the minimum number of units and the minimum economic entrainer flowrate. A separation sequence is best synthesized by searching for the desirable ternary feed at the outset, as described in Chapters 4, 5 and 6. Thus, with an external entrainer, we suggest that synthesis should not be initiated with ternary feeds other than the desirable ternary feed because doing so may lead to inferior designs even though other ternary feeds may be justified from the mass balance point of view.

Figure 7.1 shows that when the entrainer is an *external component*, a ternary feed other than the desirable one may lead to a sequence with more units though slightly smaller entrainer requirement. Note from Figures 7.1 and 7.2 that (i) the closer the feed is to the entrainer tip, the larger the entrainer rate for a given binary feed and, (ii) the desirable ternary feed may still be achieved with a water rich binary feed. Figure 7.2 reiterates the important insight presented in Chapters 4, 5 and 6 which suggests that, in many cases it is possible to design using the absolute minimum number of units and the minimum economic entrainer flowrate at the outset of a sequence synthesis. Given the binary feed and product specifications, the minimum unit-minimum entrainer heuristics provide a short cut alternative technique to arrive at one of the most (if not the most) desirable separation options with a minimal amount of computation. One must, however, realise that given the large number of feasible ternary compositions to operate with, any procedure for the synthesis of distillation sequences for azeotropic mixtures,

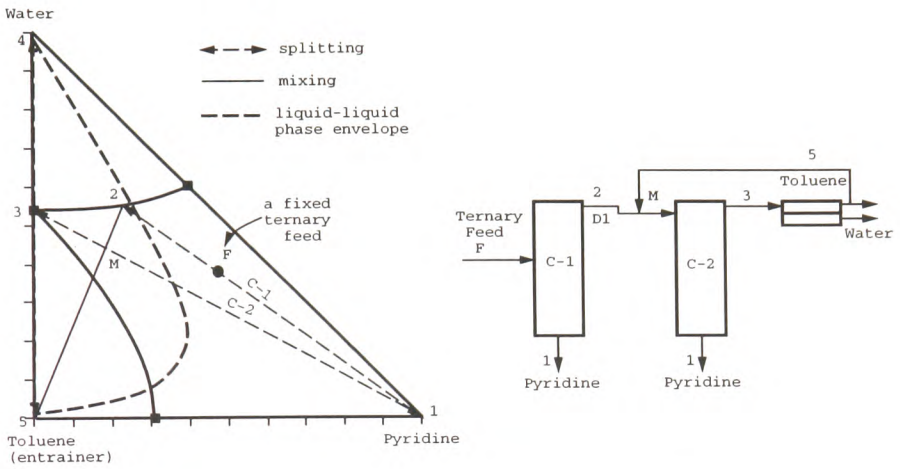


Figure 7.1: RCM and a possible separation sequence for a fixed ternary feed

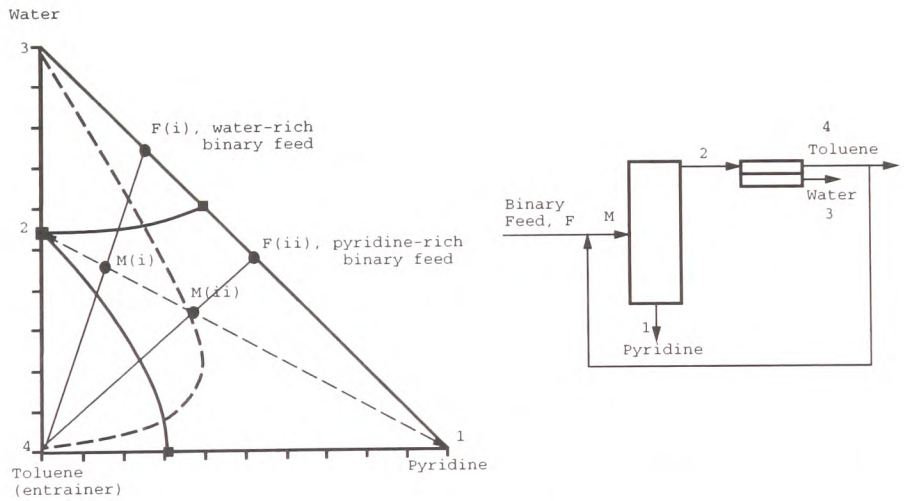


Figure 7.2: RCM and the sequence resulting from a desirable ternary feed

automated or otherwise, cannot guarantee a global optimum solution if the ternary feed composition results in more units and suboptimal entrainer flowrate. If, on the other hand, the entrainer happens to be an internal component, a fixed ternary feed may be acceptable. It may then be worthwhile to modify the feed through internal recycling in order to arrive at an attractive sequence bearing in mind that the modifications would incur extra cost. For this reason, this chapter will provide a brief review of the concept

of internal recycling and extend its application to retrofit situations.

The preceding analysis can be summarized as follows:

1. In most cases, the synthesis of separation sequences for azeotropic systems begins with a binary mixture of fixed composition that must be mixed with an appropriate amount of an external entrainer. The binary and the resulting ternary feeds may be favourably modified either by preconcentration or recycling.

2. The synthesis of separation sequences for azeotropic mixtures may begin with a fixed ternary feed if and only if the entrainer is a component that is already present in a process. In this case, the feed may be favourably modified to a certain extent by partially recycling one or more of the components from the ternary mixture to the appropriate column in the separation sequence. A major disadvantage of using a fixed ternary feed is that, in many cases, mixing the recycle stream (whose composition is usually beyond control) and the feed stream may not result in the desired composition (the composition target). As a result, the desired separation improvement cannot be implemented.

3. The desirable ternary feed composition is proposed as the overall column composition target for the synthesis of separation sequences for azeotropic mixtures. This composition can be produced by mixing a binary feed with an entrainer, keeping in mind that a large number of feasible but not desirable entrainer flowrates are possible. A synthesis procedure which works from ternary feeds other than the desirable one, automated or otherwise, may lead to inferior sequences.

The new insights from this study and the results from previous studies associated with the necessity of feed preconcentration are presented in the next section.

7.3 Feed preconcentration

A binary feed mixture forming an azeotrope may undergo distillation (preconcentration) to partly remove one of the azeotrope-forming components and bring the feed to the azeotropic composition before being sent to the azeotropic distillation columns. The practice can sometimes result in substantial energy savings. The economics of azeotropic distillation sequences with and without preconcentrators have been compared by Knight and Doherty as well as by Ryan and Doherty for two common ternary mixtures. Knight and Doherty report a 400 percent savings in the total annual cost when a preconcentrator is included in the extractive distillation of an ethanol-water system with ethylene glycol as the entrainer[29], concluding that it is *always* economical to preconcentrate a dilute feed. Ryan and Doherty, who studied several sequences for the heterogeneous separation of ethanol-water-benzene (with benzene as the entrainer), however, state that preconcentration manage to save *only* energy cost (but not capital) when the feed contains less than four percent ethanol[30]. This last study reports a marginal 7 percent net savings in the annual energy cost after deducting the capital investment for a preconcentrator column. The savings tend to diminish at a slightly higher ethanol percentage. In practice some feed flexibility is required. This, in addition to the cost of equipment installation and control for the sequence with a preconcentrator (three unit sequence), it may be argued that the sequence without a preconcentrator (the two unit sequence) is the more sensible option for such marginal savings.

The discrepancy between both findings related to the advantages of preconcentration can be attributed to the peculiarities of azeotropic mixtures, in which case optimisation is an obvious means of deciding when preconcentration might be economically attractive, on a case by case basis. It is clear, however, that for preconcentration to be considered, it must result in a sequence that is much cheaper than the two unit sequence. With this goal in mind, the merit of preconcentration can be assessed based on:

1. *Its ability to minimise separation difficulty.* Preconcentration usually leads to sub-

stantial savings if, for example, it manages to remove part of a heavy and more plentiful component at the bottom of a preconcentrator column instead of the top of an azeotropic or an entrainer recovery column, or, if it manages to reduce the size of an overhead product stream containing a heavy or more plentiful component.

2. *Its ability to minimise the specific entrainer requirement (SER).* Note that preconcentration *always* reduces the *total amount of entrainer* required in an azeotropic column as a result of its reduced binary feed load. However, due to the disproportionate reduction between the amount of entrainer and that of the binary feed, the entrainer requirement per unit of binary feed to the azeotropic column (the *specific entrainer requirement*), may increase or decrease. For example, before preconcentration, 100 kmol/hr of entrainer is required to separate 100kmol/hr of an A-B binary azeotropic mixture (SER = 1.0). Upon preconcentration, only 80 kmol/hr of entrainer is required to separate 70 kmol/hr of the preconcentrated mixture (SER = 1.14). In this case the entrainer has decreased even though the SER increased. The reduction in the amount of entrainer can be estimated if the flowrate of either the entrainer or the binary feed before preconcentration is known.

Regardless of the value of the SER, preconcentration is worthwhile if it can be established that it minimises the separation difficulty in the manner described by criterion 1. In such a case, the SER complements criterion 1 by providing a quantitative comparison between the entrainer consumption for sequences with and without a preconcentrator. Thus, the SER is most useful in indicating whether or not the effect of entrainer flowrate reduction would be of significance when preconcentration does not prevent any difficult separation.

Example 7.3.1 illustrates a simple procedure to calculate the SER from the geometry of a RCM. It also shows that, for a constant azeotropic column bottoms composition, the SER decreases when the composition of a binary feed changes along the constituent components' edge of a ternary diagram in the direction of the pure light component.

Compliance with the preceding set of criteria for preconcentration can be established from the RCM geometric features which include the boiling points of pure components

and azeotropes, the binary and ternary feed compositions to the distillation columns, the relevant stream compositions, the lengths of the segments of the azeotropic column mixing line, and vapor liquid equilibrium data (this is required only when a curved distillation boundary is anticipated from the boiling points of the pure components and azeotropes).

Example 7.3.1. Determination of the SER

From Figure 7.3, it can be seen that, for a constant azeotropic column bottoms composition, B1, the *ratio of the lengths* of the azeotropic column mixing line segments, $\frac{|M-F|}{|E-M|}$ essentially *decreases* when the binary feed composition changes along the A-B edge of the ternary diagram in the direction of pure A (e.g. from F to F1). Since, by the lever rule, this ratio represents the SER (i.e. the entrainer to binary feed ratio), it can be concluded that *the SER tends to decrease in the same direction.*

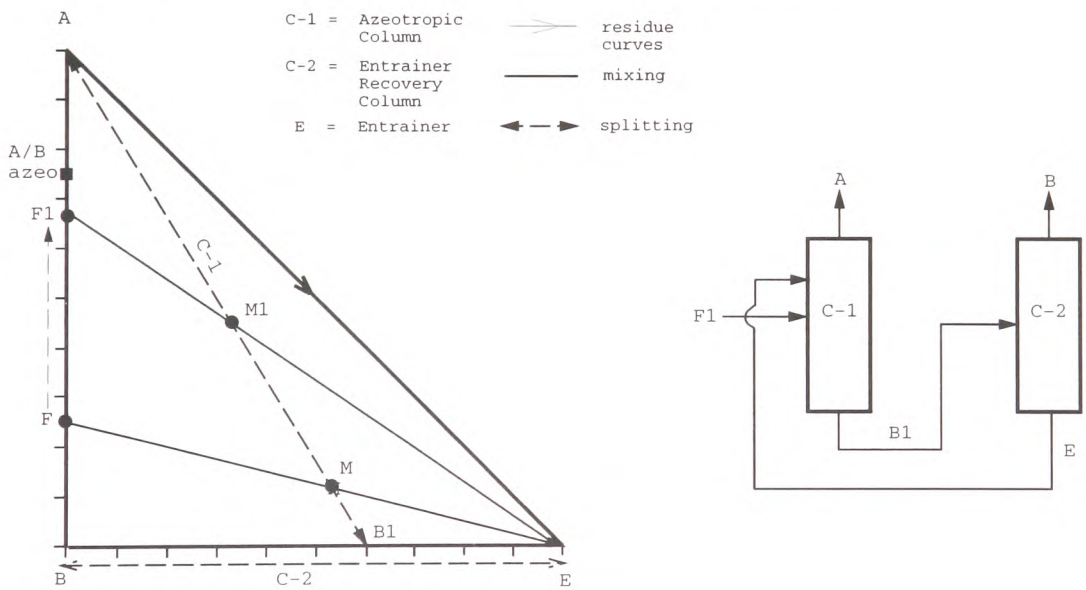


Figure 7.3: The SER decreases as the binary feed changes along A-B edge of the ternary diagram, in the direction of pure A.

The preceding conclusion is supported by the following example:

A hypothetical azeotrope-forming binary mixture A-B, which is rich in B, can be sep-

arated in a two unit azeotropic distillation sequence shown in Figure 7.4, using a high boiling entrainer, E. When a feed preconcentrator (P-1) is added to the sequence, it changes the composition of the binary feed, F1, to the azeotropic composition, A/Bazeo (A/Bazeo = 0.5). At a constant azeotropic column bottoms composition, the SER for the sequence with and without a preconcentrator can be calculated as follows:

(i) for the sequence *without* a preconcentrator, $\frac{|M1-F1|}{|E-M1|}$

$$= \frac{\sqrt{(x_{M1}-x_{F1})^2+(y_{M1}-y_{F1})^2}}{\sqrt{(x_E-x_{M1})^2+(y_E-y_{M1})^2}}$$

$$= \frac{\sqrt{(0.62-0)^2+(0.1-0.25)^2}}{\sqrt{(1.0-0.62)^2+(0-0.1)^2}}$$

$$= \frac{0.6379}{0.3929}$$

$$= 1.6236$$

(ii) for the sequence *with* a preconcentrator, $\frac{|M1'-A/Bazeo|}{|E-M1'|}$

$$= \frac{\sqrt{(x_{M1'}-x_{A/Bazeo})^2+(y_{M1'}-y_{A/Bazeo})^2}}{\sqrt{(x_E-x_{M1'})^2+(y_E-y_{M1'})^2}}$$

$$= \frac{\sqrt{(0.52-0)^2+(0.25-0.5)^2}}{\sqrt{(1.0-0.52)^2+(0-0.25)^2}}$$

$$= \frac{0.5770}{0.5412}$$

$$= 1.066$$

$\frac{|M1-F1|}{|E-M1|}$ in (i) is greater than $\frac{|M1'-A/Bazeo|}{|E-M1'|}$ in (ii), showing that the entrainer per unit of binary feed is reduced from (i) to (ii).

Laroche *et al.*[36] provide a brief account of the merit of preconcentration for homogeneous azeotropic systems, (i) without boundary crossing and high boiling entrainers that do not introduce new azeotropes, and (ii) with boundary crossing and low boiling entrainers that do not introduce new azeotropes. They conclude that, in (i), preconcentration is economical when the feed is rich in the higher boiling binary feed constituent

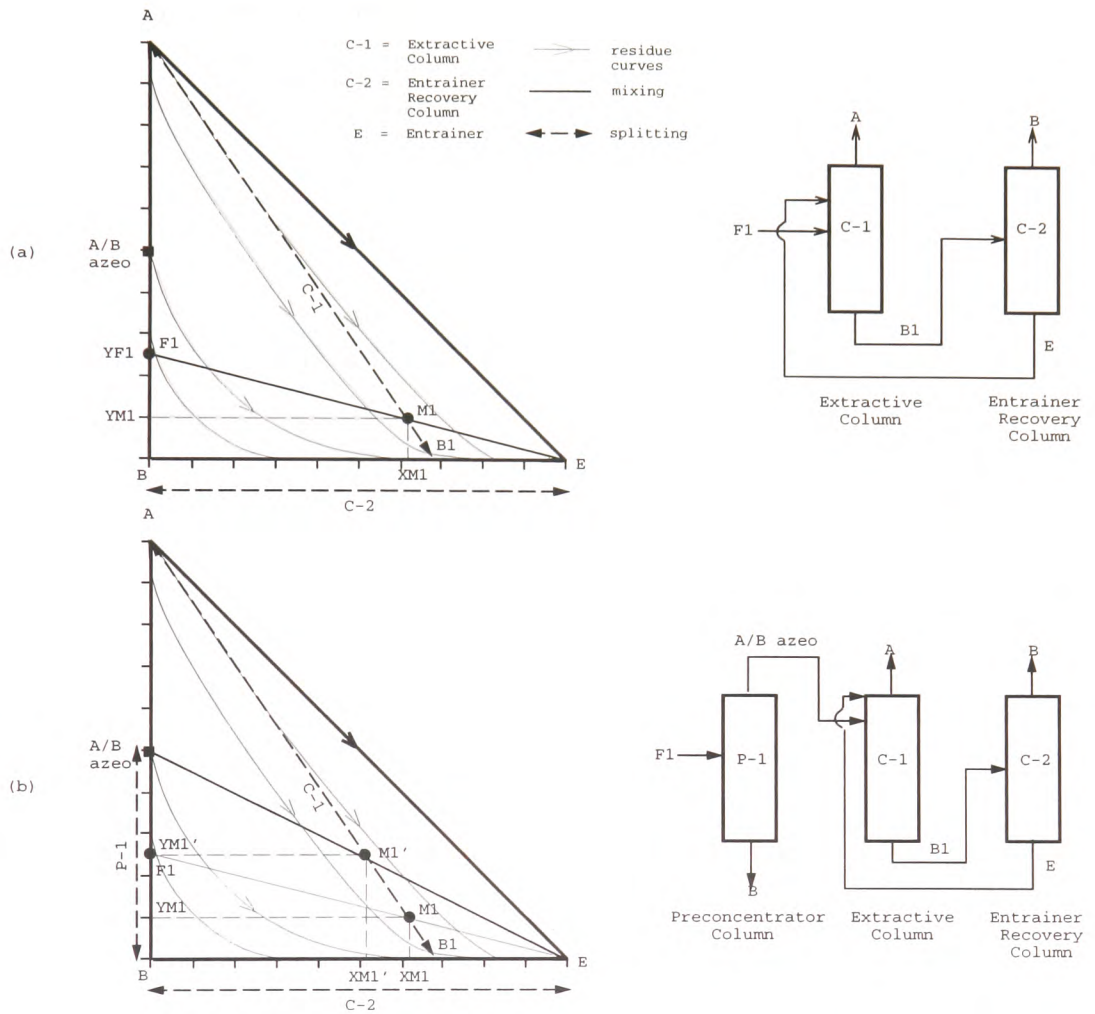


Figure 7.4: Effect of preconcentration on the SER for homogeneous systems without boundary crossing when a high boiling entrainer is employed, with the binary feed rich in the medium boiler B; (a) without (b) with a preconcentrator.

and, in (ii), when the feed is rich in the lower boiling binary feed constituent. However, in (ii), they have failed to reach the same conclusion for a feed rich in the higher boiling binary feed constituent because the effect of feed preconcentration on the amount of entrainer required in the azeotropic column was not considered.

The previous findings will now be revised and extended to three other important classes of azeotropic mixtures, i.e., to (iii) homogeneous azeotropic systems without boundary crossing, with medium boiling pure and pseudo entrainers, (iv) homogeneous azeotropic systems with boundary crossing, and a high boiling entrainer that does not introduce

new azeotropes and (v) to heterogeneous azeotropic systems.

The analysis will be organized as follows:

- Section 7.3.1 - feed preconcentration for *homogeneous systems without boundary crossing.*
- Section 7.3.2 - feed preconcentration for *homogeneous systems with boundary crossing.*
- Section 7.3.3 - feed preconcentration for heterogeneous mixtures.

To enable a wide range of homogeneous azeotropic mixtures to be considered, these mixtures have been grouped into typical classes based on the entrainer selection criteria described in Chapter 4. Heterogeneous mixtures (Section 7.3.3) are treated as a separate group. The analysis with regards to the merit of preconcentration for azeotropic mixtures is summarized in a selection catalogue presented in Appendix E.

7.3.1 Homogeneous systems without boundary crossing

Case 1. Homogeneous azeotropic distillation with a high boiling entrainer (classical extractive distillation)

A RCM for an extractive distillation process and the resulting two column sequence is shown in Figure 7.5(a). The RCM depicts a ternary mixture with an entrainer E as the highest boiling species that introduces no new azeotrope, and the light boiler A and the medium boiler B as the constituents of a binary mixture contained in a stream coming from an upstream process. An example of this system is an ethanol-water mixture with a high boiling entrainer, ethylene glycol (EG). A binary feed which is rich in the medium boiler yields the sequence shown in Figure 7.5(a). Such system requires the medium boiler (i.e. water, from the example) to be removed from the top of the entrainer recovery column if a two column sequence is chosen. The sequence with a preconcentrator shown in Figure 7.5(b) achieves two advantages: (i) it allows some water to be removed at the bottom of the preconcentrator column (P-1), thereby

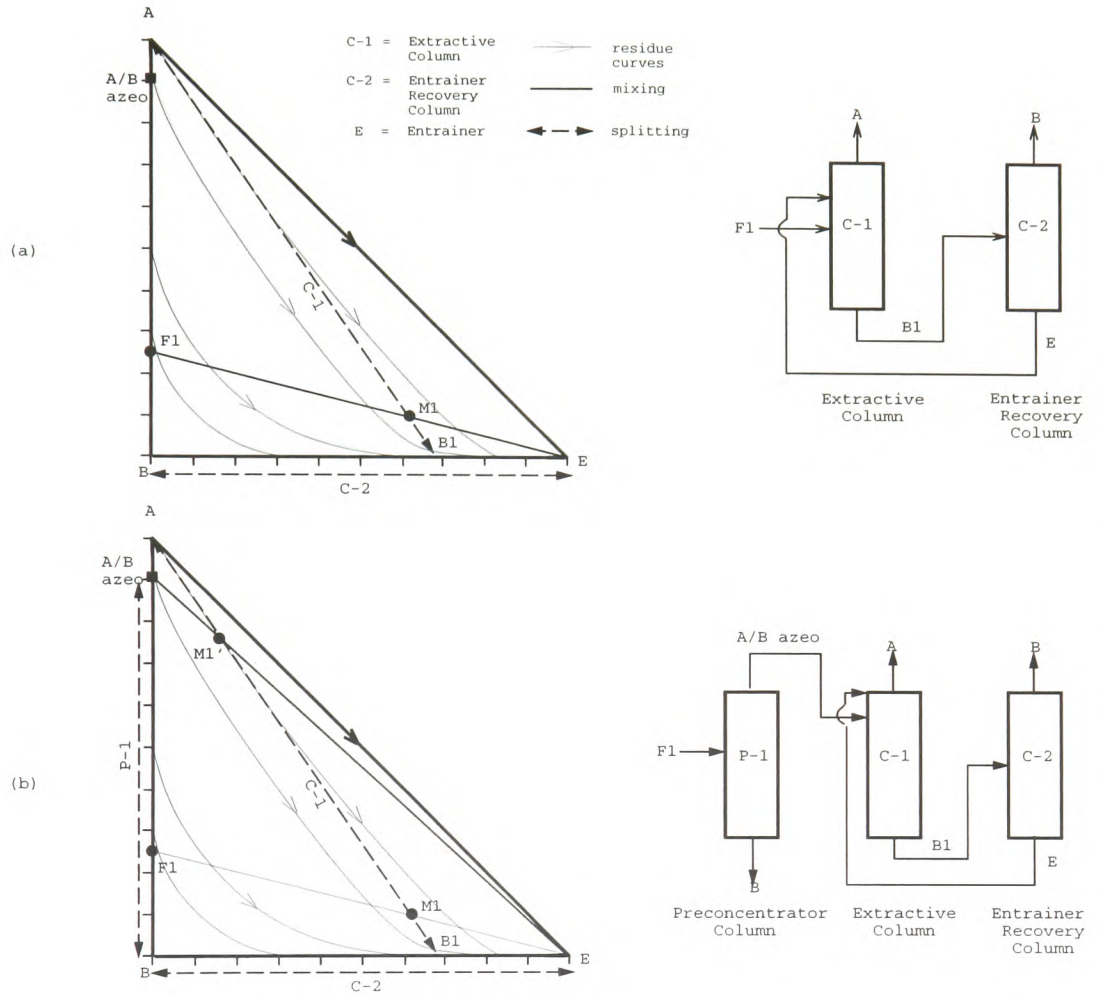


Figure 7.5: Effect of preconcentration for homogeneous systems without boundary crossing when a high boiling entrainer is employed, with the binary feed rich in the medium boiler B; (a) without (b) with a preconcentrator.

partly avoiding the more difficult overhead removal of water in the entrainer recovery column (C-2), and (ii) it reduces the amount of entrainer required in the extractive column (C-1). Note that, as the overall composition of the extractive column moves away from the entrainer tip, i.e., from M1 to M1', less entrainer is required per unit flowrate of binary feed.

For a feed that is rich in water, these changes could result in a substantial amount of savings in energy costs in excess of the capital investment required for the preconcentrator column. Knight and Doherty[29] prove that this is indeed the case for the

ethanol-water-EG (high boiling entrainer) system. In this case, preconcentrating is consistent with two well-known heuristics which suggest the *removal of the more plentiful and heavier component at the bottom.* In conclusion, for extractive distillation, preconcentration is generally advantageous when the binary feed is rich in the medium boiling component.

The changes in the extractive column composition are represented geometrically in the RCM of Figure 7.5(b). In this case, a preconcentrator (P-1) which removes part of the medium boiling component B (i.e. water from the example) changes the overall extractive column composition from M1 to M1'. M1' is significantly richer in A and leaner in B and the entrainer. Note that, since the amount of B is significantly reduced, the *total amount of entrainer*, and hence, the SER for extractive separation is also significantly reduced for a constant extractive column bottoms composition (B1), thereby leading to a much easier separation.

Figure 7.6 represents the same homogeneous azeotropic system with the feed now rich in the low boiling component, A. In this case, a preconcentrator which removes part of the low boiling component, A, (i.e. ethanol from the example) changes the overall extractive column composition from M1 to M1'. M1' is slightly leaner in A and richer in B and the entrainer. The flowrate of component B at the top of C-2 is the same for the sequences with and without a preconcentrator, but the amount of entrainer per unit of binary feed (SER) has slightly increased (see Figure 7.6(b)).

Note also, that in this case, no difficult separation has been prevented. Apart from increasing the overall capital cost, a preconcentrator in this case increases the SER and results in a more difficult extractive separation. Thus, there is no advantage of adding a feed preconcentrator for extractive distillation when the feed is rich in the low boiling binary feed constituent. Conclusions for the preceding geometric analysis are supported by the simulation results presented in Section E.1 of Appendix E.

Another possible direct sequence exists only for special types of homogeneous azeotropic mixtures which exhibit an unusual behaviour of *reversed volatility* between the binary feed constituents in the presence of special entrainers. Acetone-isopropyl ether

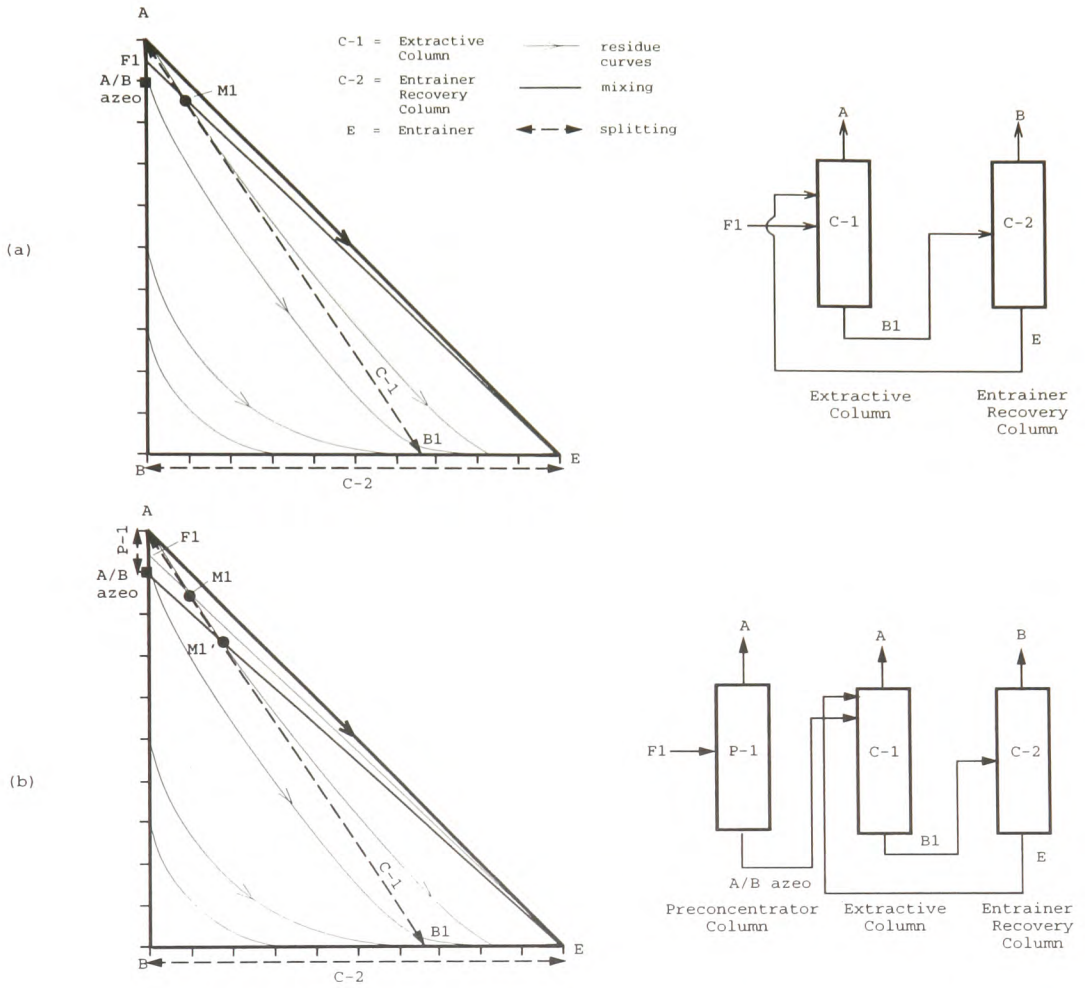


Figure 7.6: Effect of preconcentration for homogeneous systems without boundary crossing when a high boiling entrainer is employed, with the binary feed rich in the low boiler A; (a) without (b) with a preconcentrator.

(IPE)-dimethysulfoxide (DMSO)(high boiling entrainer) is an example of such system. Berg and Yeh[54] report that upon distillation, nearly pure IPE (medium boiling component) is found overhead while an acetone-DMSO mixture exists at the bottom of the extractive column. A schematic representation of the mixture RCM and the separation sequence with a medium boiling component-rich feed (in this case, IPE-rich feed) is shown in Figure 7.7.

Note that the "role reversal" (in which IPE becomes the "lighter" while acetone the "heavier" of the binary feed constituents) occurs only in the extractive column where

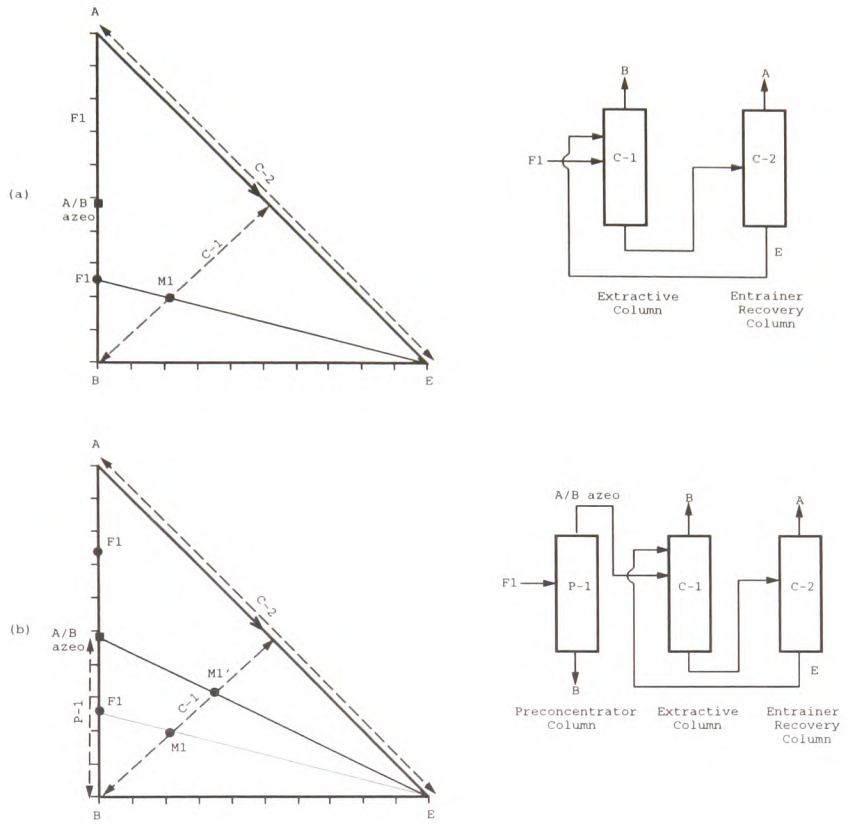


Figure 7.7: Homogeneous mixture showing reversed volatility, with a high boiling entrainer and a binary feed that is rich in the light boiler A; (a) without (b) with a preconcentrator.

the binary feed constituents and the entrainer are present in appreciable amounts. DMSO, which has a higher affinity[1] towards IPE as compared to acetone, "carries" IPE down the extractive column. Separation of the "pseudo-binary" mixtures[2] in the entrainer recovery and preconcentrator columns (if a preconcentrator is required) are expected to obey the normal relative volatility constraint.

In this case, even though the medium boiling IPE is recovered overhead of the extractive column, preconcentrating a binary feed that is rich in IPE is not advantageous since its overhead recovery in the extractive column has been made easier by the presence of the high boiling entrainer, DMSO. In fact, preconcentrating an acetone-IPE binary feed in

[1] Affinity can be measured by comparing the polar interaction and hydrogen bonding of the entrainer with the polar interactions and hydrogen bondings of the binary feed constituents.

[2] When a binary separation is assumed, since the quantity of the other components present are relatively negligible.

the absence of DMSO tends to make separation even more difficult, and results in a net increase in the energy cost in addition to the cost of the preconcentrator column. Note that the same situation applies when a low boiling component-rich feed is used (i.e. an acetone-rich feed). In both instances preconcentration is not worthwhile because it makes separation more difficult than the one which takes place in the extractive column in the presence of DMSO which reverses the relative volatility of acetone-IPE. The preceding analysis leads to the heuristic:

> *For classical extractive distillation, preconcentration is advantageous only when the binary feed constituents exhibit a normal relative volatility behaviour and when the binary feed is rich in the higher boiling constituent.*

Case 2. Homogeneous azeotropic distillation with a medium boiling entrainer

Figure 7.8 shows the direct sequences for separating a homogeneous azeotropic mixture with a medium boiling entrainer, and a low and high boiling component-rich feeds. Each sequence results in an overhead removal and recycle of the medium boiling entrainer, making separation in the entrainer recovery column difficult. In this case, preconcentration can minimise separation difficulty if it can reduce the entrainer flowrate, or if it results in partial removal of the medium boiling component underflow (as in the case of ethanol-water-EG separation). Figure 7.8(a) and (b) show that feed preconcentration increases the SER for a low boiling component-rich feed but decreases the SER for a high boiling component-rich feed. The SER values suggest more reduction in the *total entrainer flowrate* for case (b) as compared to case (a). Nonetheless, in both cases, decreased *total entrainer flowrate* in the azeotropic column reduces the size of the overhead entrainer recycle streams and minimizes separation difficulty. This makes feed preconcentration very desirable for both cases (a) and (b) in Figure 7.8.

The indirect sequences shown in Figures 7.9(a) and (b), on the other hand, are faced with difficult azeotropic separation tasks as a result of the overhead recovery of the entrainer-component A mixture. Feed preconcentration is desirable in these cases because it reduces the *total entrainer flowrate* and results in much less difficult azeotropic

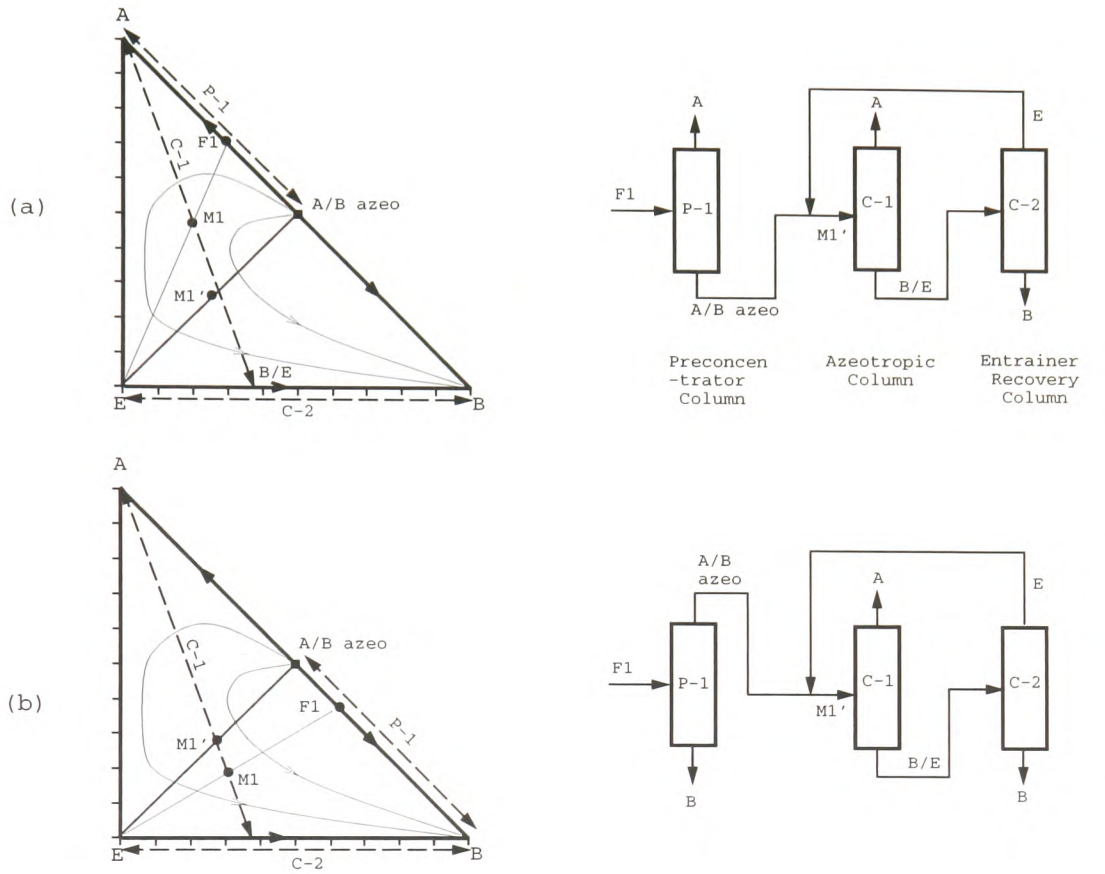


Figure 7.8: Effect of preconcentration for homogeneous systems without boundary crossing when a medium boiling entrainer is employed. (a) and (b) are the direct sequences with low and high boiling component-rich feeds.

separation. An indirect sequence which removes the entrainer and low boiling component overhead is often preferred over a direct sequence (see Section 4.5 of Chapter 4).

Case 3. Homogeneous systems with multiple distillation regions

Figure 7.10 presents three other RCMs which feature homogeneous systems with more than one distillation region. In order to have a feasible separation sequence, most common homogeneous azeotropic systems without boundary crossing may have two regions at the most (see Section 4.5 of Chapter 4). These systems employ either a light or medium boiling entrainer that is able to "group" the binary feed constituents into the same distillation region to permit separation. These systems, which are referred to as "homogeneous azeotropic systems with medium boiling pseudo entrainers" in Chapter

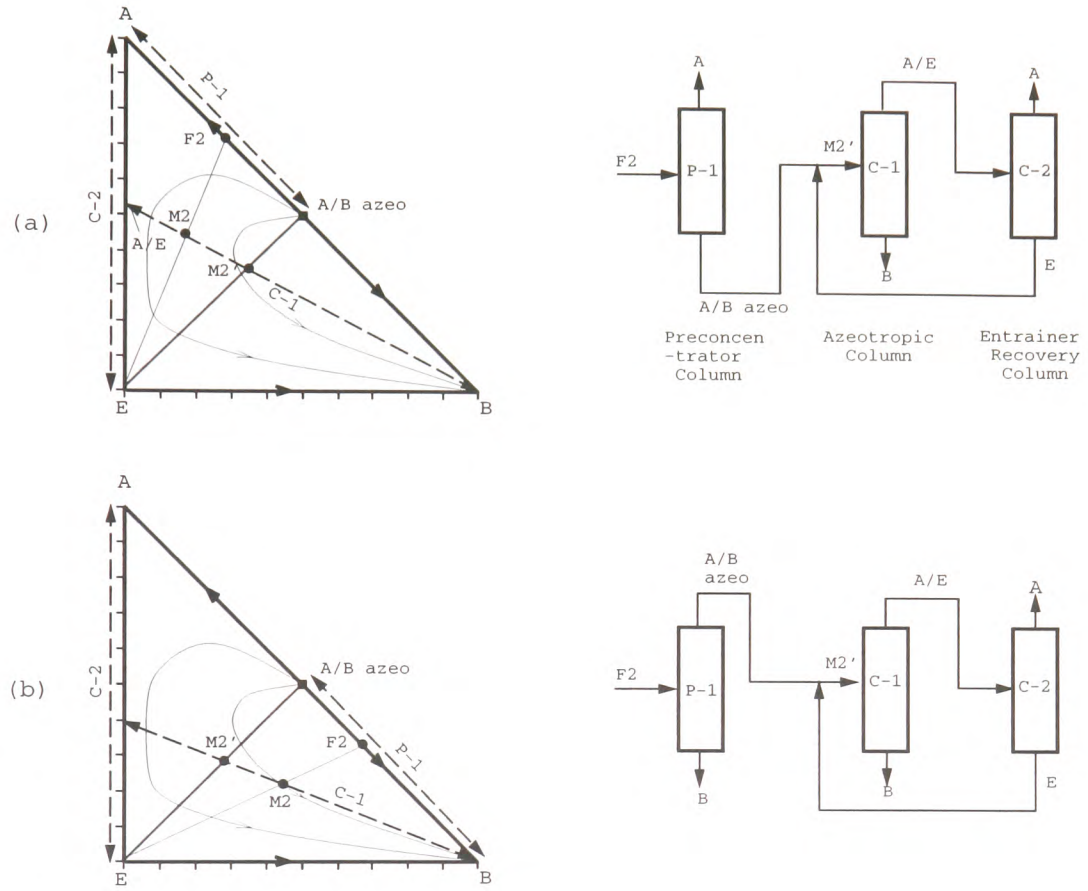


Figure 7.9: Effect of preconcentration for homogeneous systems without boundary crossing when a medium boiling entrainer is employed. (a) and (b) are the indirect sequences with low and high boiling component-rich feeds.

4, result in the similar direct and indirect sequences with a preconcentrator as those generated for the mixture with a medium boiling pure entrainer. As in the case of a medium boiling pure entrainer, a preconcentrator can minimise separation difficulty, and, is thus desirable regardless of the binary feed composition, or of whether a direct or an indirect separation sequence is being used. The direct sequence, however, is often less preferred because its overhead entrainer recycle may pose problems due to the accumulation of trace components (see Section 4.5 of Chapter 4).

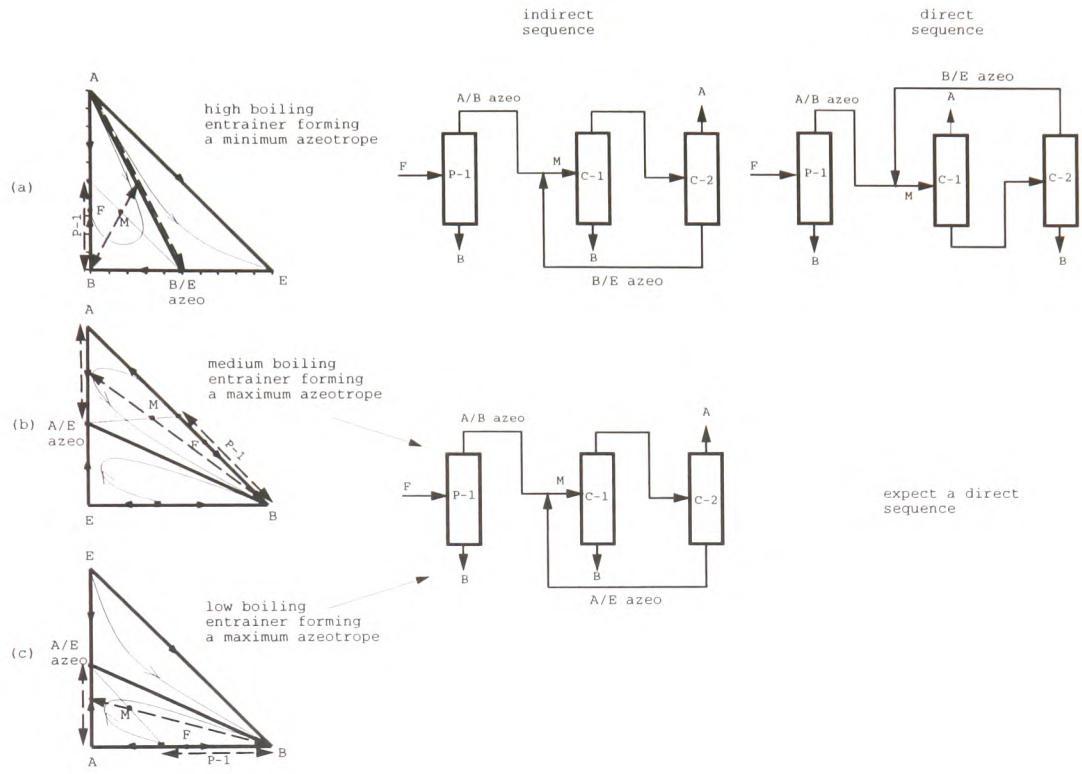


Figure 7.10: Homogeneous systems with multiple distillation regions.

7.3.2 Homogeneous systems with boundary crossing

In Chapter 5, we have derived a set of heuristics for the synthesis of the most promising sequence for homogeneous azeotropic systems with boundary crossing whose low and high boiling entrainers do not introduce new azeotropes. Synthesis results in symmetric separation structures due to the symmetry of the residue curves between the low and the high boiling entrainers. Examples of the homogeneous azeotropic systems with boundary crossing that do not introduce new azeotropes are shown in Figures 7.11 and 7.12. Figure 7.11 shows the RCM and the corresponding separation sequence (with a preconcentrator) for the acetone (low boiling entrainer)-IPA-toluene mixture for the case of (a) toluene-rich and (b) IPA-rich feed. Recall from Chapter 5 that a two column sequence for such azeotropic system requires a very large amount of entrainer due to the distillation boundary pinch point approaching the entrainer tip. A feed preconcentrator (P-1) in the case of a toluene-rich feed increases the SER but reduces the flowrate of the

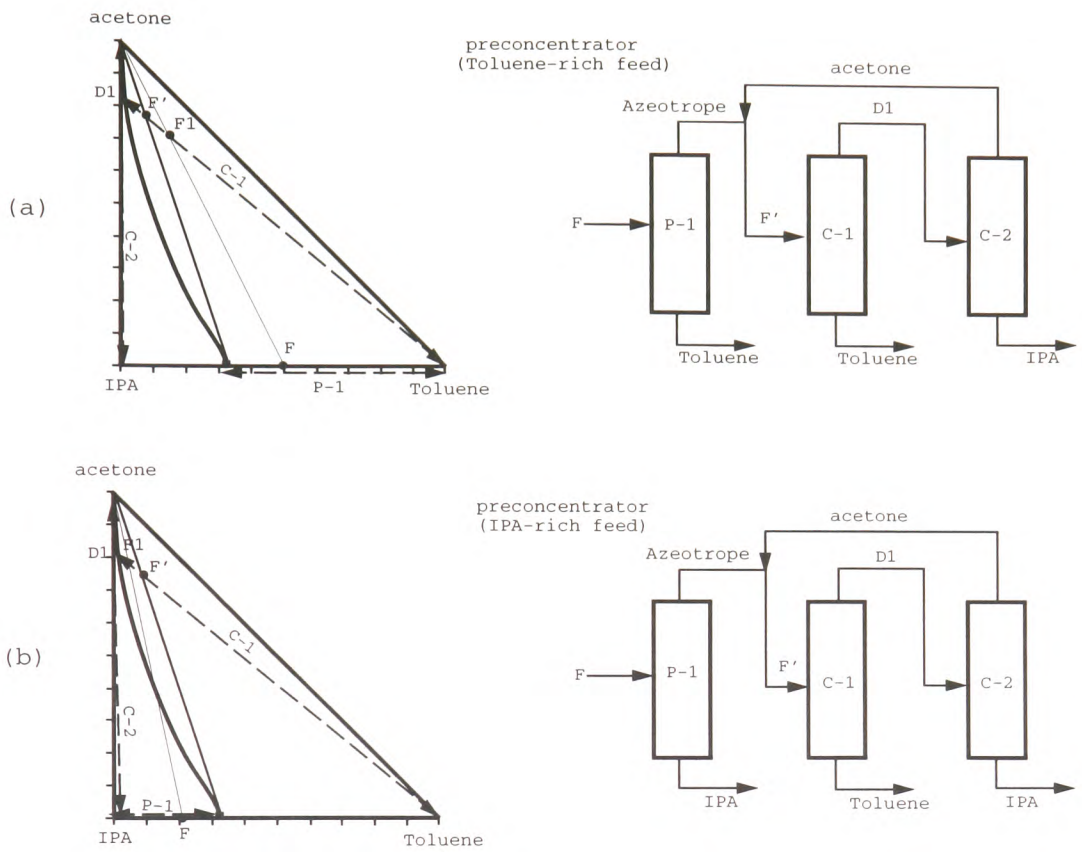


Figure 7.11: RCM and the separation sequence with a preconcentrator for acetone (low boiling entrainer)-IPA-toluene mixture - (a) toluene-rich (b) IPA-rich feed.

entrainer in the azeotropic column (C-1) as well as the size of the overhead entrainer recycle stream (see Figure 7.11(a)). Reduction in the flowrate of the most plentiful component (i.e., the entrainer) minimises separation difficulty and results in savings in both the capital and operating costs. This geometric reasoning is supported by the simulation results presented in Table 5.5 on page 115 of Chapter 5. On the other hand, a preconcentrator in the case of the IPA-rich feed is desirable because it not only reduces the SER but also results in the bulk of IPA being removed underflow instead of overhead of the azeotropic column (C-1). In this case, preconcentration partly avoids the difficult overhead removal (see Figure 7.11(b)) and results in substantial savings in capital and operating costs. Note that this case is similar to the one for the extractive distillation of ethanol-water-EG (high boiling entrainer) mixture with a water-rich binary feed (see Section 7.3.1, Case 1).

Figure 7.12 shows the RCMs and the resulting separation sequences with a preconcentrator for an acetone-chloroform-benzene (high boiling entrainer) mixture with (a) acetone-rich, and (b) chloroform-rich feed.

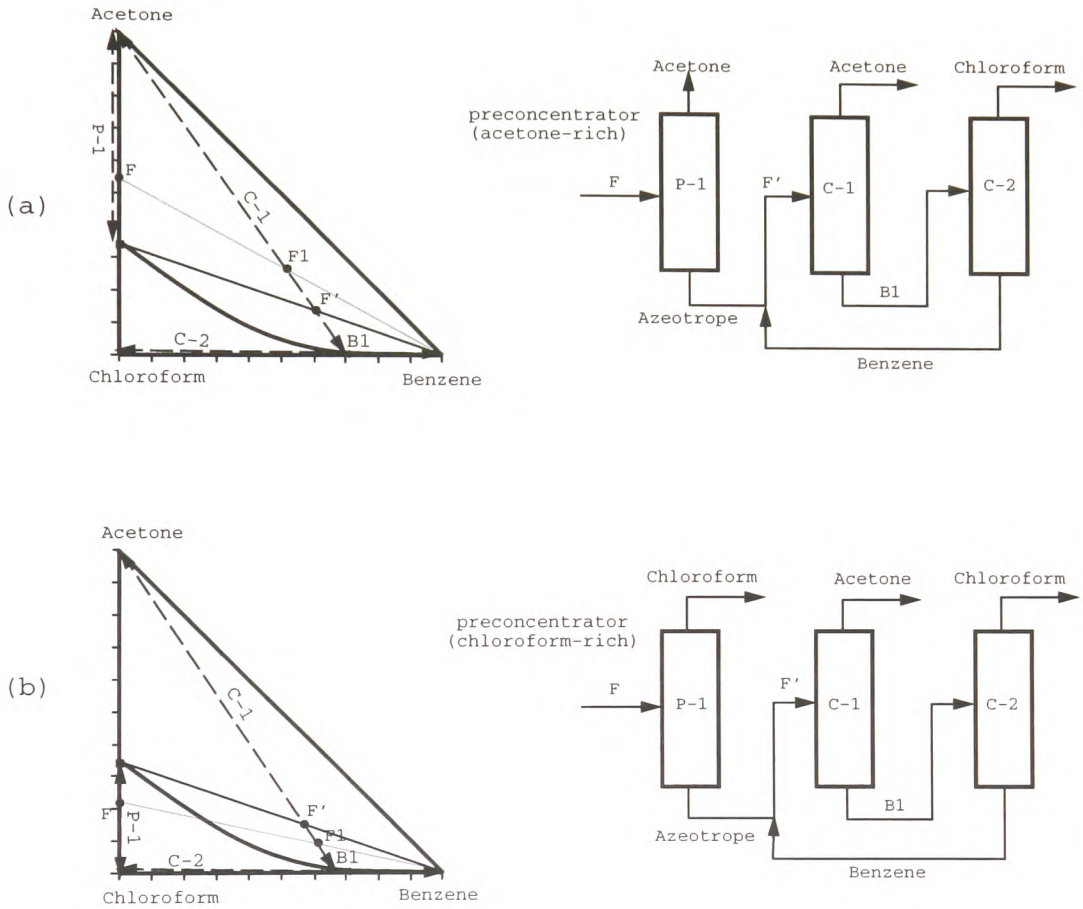


Figure 7.12: RCM and separation sequence with a preconcentrator for acetone-chloroform-benzene (high boiling entrainer) mixture - (a) acetone-rich (b) chloroform-rich feed.

Note that through the overhead removal of the low boiling component (acetone), the azeotropic column with an acetone-rich feed performs an easy direct first split (see Figure 7.12(a)). Adding a preconcentator (P-1) which partially removes acetone overhead does not prevent any difficult separation. Instead, it causes the ternary feed to move from F1 to F' in the direction of increasing SER, suggesting only a marginal reduction in the total entrainer flowrate and at best, a minor improvement in the overall sequence cost. In this case preconcentration merely distributes the stripping duty and

capital requirement of the two column sequence into three columns. Note that this case resembles the separation ethanol-water-EG (high boiling entrainer) system with an ethanol (low boiling component)-rich binary feed (see Section 7.3.1, Case 1).

In contrast, Figure 7.12(b) shows that a feed preconcentrator decreases the SER when a chloroform-rich feed is used. Even though no difficult separation has been prevented, decreased SER results in a substantial decrease in the entrainer flowrate and an improvement in the overall preformance of the sequence.

The preceding analyses are supported by the simulation results presented in Sections E.2 and E.3 of Appendix E.

7.3.3 Heterogeneous systems

We refer to the economic comparison made by Ryan and Doherty between the three and two-unit sequences (with and without a preconcentrator respectively) for the heterogeneous separation of ethanol-water with benzene as the entrainer[30]. Why is there a stark contrast in the overall savings derived from the presence of a preconcentrator between extractive distillation (a special case of homogeneous distillation) and heterogeneous distillation? To be able to answer this question, it is necessary to look at the fundamental differences between the two separation techniques.

Two fundamental requirements for heterogeneous azeotropic distillation essentially guarantee that the entrainer is recovered overhead:

1. the use of a light boiling entrainer
2. the formation of minimum boiling heterogeneous azeotropes

Pham and Doherty prove that the heterogeneous azeotropes formed must be minimum boiling in order that the entrainer mixture may be recovered overhead to enable phase separation in the decanter[31]. These requirements mean that, for heterogeneous sys-

tems, an entrainer mixture[3] is always the light boiler recoverable overhead whereas the two constituent components are always the heavier boilers recoverable at the bottom of an azeotropic distillation sequence.

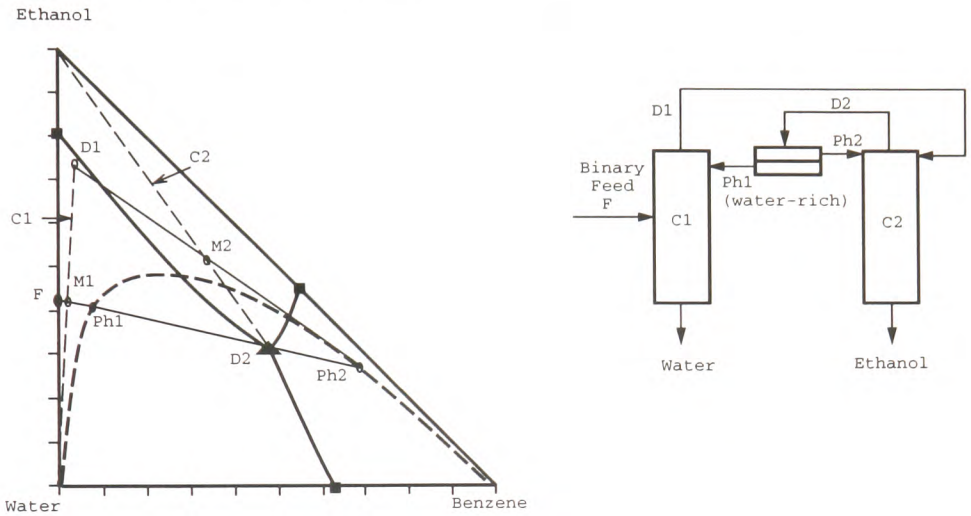


Figure 7.13: RCM and the minimum number of unit separation sequence for ethanol-water-benzene (high boiling entrainer) mixture.

On the other hand, recall from Section 7.3.1 (Case 1) that the two-unit classical extractive distillation of a dilute ethanol-water-EG (high boiling entrainer) system must operate at a high reflux and pumping costs due to the large amount of the heavier boiler (water) that must be recovered at the top of the entrainer recovery column. Preconcentrating the dilute ethanol-water feed allows the bulk of the water to be removed at the bottom of the preconcentrator instead, resulting in significant energy savings for the extractive distillation case.

In contrast, for the heterogeneous mixture in question, the higher boilers, water and ethanol are removed at the bottom of the azeotropic and entrainer recovery columns respectively, while the minimum boiling heterogeneous azeotrope is recovered overhead. As a consequence, adding a preconcentrator to remove part of a heavy component and to bring the binary feed to its azeotropic composition yields only about 7 percent overall cost savings in the very narrow feed range of less than 4.2 percent ethanol[30]. Due to

[3]the entrainer may not necessarily be a pure component.

such marginal savings, one can expect the "break-even point" for the two-unit sequence to become favourable to occur at a concentration of ethanol in water that is not much higher 4 percent. For a binary feed stream that fluctuates between a low and a high concentration of ethanol, the two-unit sequence is clearly the sensible choice.

Thus, it can concluded that *for most practical purposes*, preconcentration *will not* yield an overall economic benefit for heterogeneous azeotropic distillation.

7.4 Mixing and recycling

Recycles can improve separation by allowing the use of fewer unit operations and in some cases, by reducing the requirement of mass separating agent. Stichlmair *et al.*[35] emphasize the importance of optimising the entrainer recycle rate but made no mention about the need to reduce the initial entrainer flowrate. Knight *et al.* [29], on the other hand, report the entrainer to feed ratio as the dominant optimisation variable in the synthesis of azeotropic distillation sequences, stressing on the need to keep the ratio at an optimum level. The last study is in line with one of our prime synthesis concerns - i.e. in generating azeotropic distillation sequences with inherently lower entrainer flowrates that will give rise to naturally smaller recycle rates.

Wahnschafft *et al.*[27] discuss in detail the role of various forms of recycles in enhancing complex separation processes. They divide the techniques for recycling into three classes:

- Primary recycles
- Secondary recycles
- Range-extending recycles

In the next sections we review and report new insights related to these recycle techniques.

7.4.1 Primary recycles

We refer to the example presented in Chapter 5 of this thesis on the homogeneous azeotropic separation of acetone-chloroform-benzene (high boiling entrainer) mixture, derived from Wahnschafft *et al.* In Chapter 5, benzene is assumed as an external mass separating agent. Let us now analyse the idea that is first proposed by Wahnschafft's *et al.*, which assumes that all components, including the entrainer, are actually present within the azeotropic separation sequence. In such a case, the feed to the separation sequence is more likely to be a ternary (as opposed to a binary) mixture with a composition that is fixed by some upstream processes. Figure 7.14 shows a three unit sequence for separating an acetone-chloroform-benzene (high boiling entrainer) mixture with feed F' which results from mixing F with the azeotrope recycle. It is possible to operate with one less unit and still achieve the desired outlet product qualities if the overall inlet composition can be changed from F to F", for example, through addition of any stream whose composition lies within the shaded region of Figure 7.15. From the RCM and the corresponding process flowsheet, it is clear that recycling benzene from the bottom of the second column can accomplish the total shift in the inlet composition enabling operation with two units instead of three.

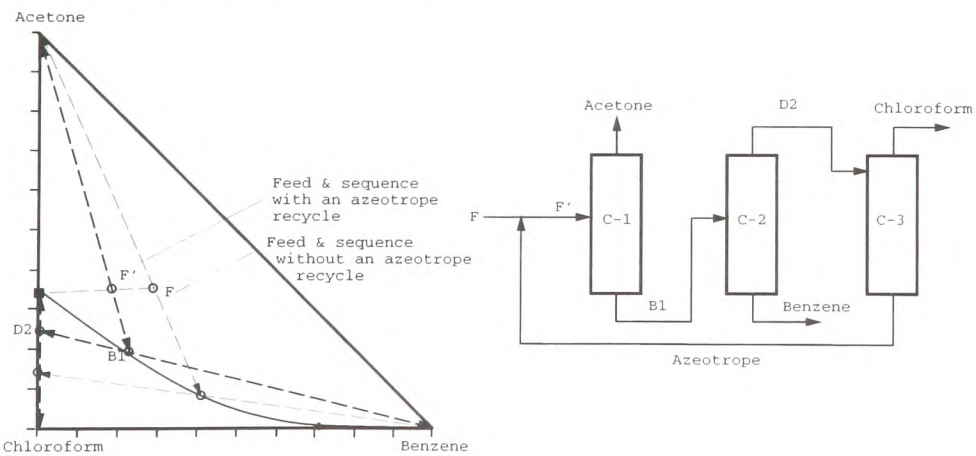


Figure 7.14: Three-unit sequence for the separation of acetone-benzene-chloroform mixture.

Wahnschafft *et al.* termed a recycle stream that changes the overall inlet feed compos-

ition to improve separation and thus to reduce the number of separation steps required as *primary recycle.* Note that, in many instances Wahnschafft *et al.* use only part of an entrainer stream as a primary recycle in order to achieve a desirable change in the ternary feed composition. Figure 7.15 shows that for the acetone-benzene-chloroform mixture, only part of the benzene product is recycled to the first column of the sequence to top the quantity of benzene that is continuously available from the process to form a ternary feed leading to the sequence with the absolute minimum number of units. Partially recycling benzene implies that the entrainer is *continuously present in a process* together with acetone and chloroform, in a quantity that depends on the upstream process operations. As has been mentioned in the introduction to this chapter,

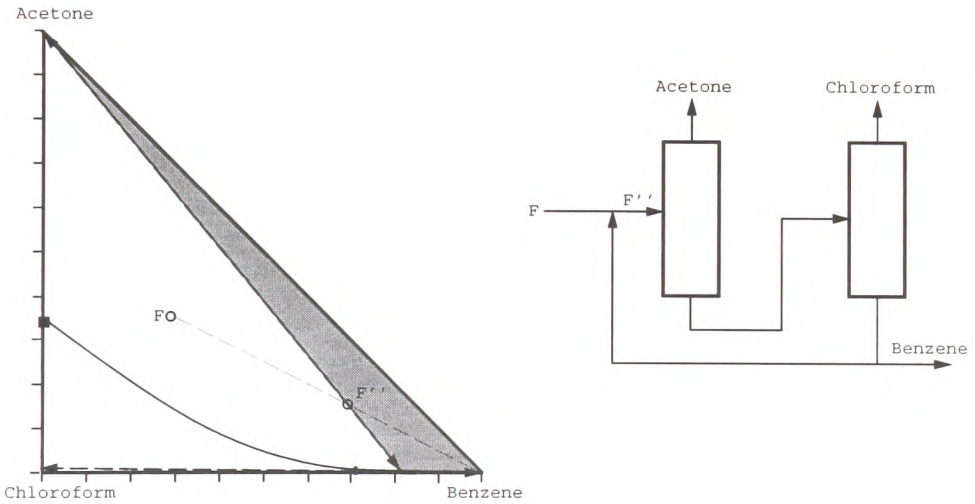


Figure 7.15: Primary recycle reduces the number of separation units

a suitable entrainer for azeotropic separation is seldom found from within a process. Thus naming benzene as the entrainer and partially recycling it to the inlet of the acetone-benzene-chloroform separation sequence implies the existence of a very specific process (yet to be named) which includes acetone, benzene and chloroform among the process components. To be more realistic, in Chapter 5, benzene has been assumed as an *external* mass separating agent as opposed to an agent available from the process. Note that using the entrainer as a primary recycle may be relevant only in the relatively few cases where all the components in a ternary mixture, including the entrainer, is available within the same process. In such a case, it is reasonable to assume a fixed ternary feed composition as has been described in Section 7.2 of this chapter. If on the

other hand, an external entrainer is used, a designer should aim to achieve the desirable ternary composition at the outset. This can be done by employing an appropriate amount of entrainer. In such a case, the need for a primary recycle to change the feed composition does not arise.

In order for the primary recycle to have a wider applicability, it should not be confined to the recycle of entrainer streams and to the terms of "reducing the number of separation steps" as originally defined by Wahnschafft *et al.* We propose to include under the category of primary recycle another important class of recycling which has received far less emphasis in complex separation synthesis - the use of streams other than the entrainer to change the feed composition. The aim is to either improve or enable separation even though the number of separation steps may not necessarily be reduced. We name this class of recycling as *type-II primary recycle* since it also involve *partial recycling* of an internal component to change the overall feed composition, and is therefore identical in nature to the primary recycle case presented by Wahnschafft *et al.* The type-II primary recycle is important and arguably more practical than the *entrainer primary recycle* for two main reasons. Firstly, compared to internal entrainers which are seldom available from a process, it is quite reasonable to use the constituent components as primary recycles since they are readily available in pure form as products of azeotropic separation. Secondly, the type-II primary recycle causes a smaller change to the process structure because it usually involves stream rerouting and does not result in a change in the number of separation steps, thus is appropriate not only for design but also for retrofit purposes.

To illustrate the type-2 primary recycle, a reader is referred to the acetic acid-water-ethyl acetate ternary diagram and its corresponding flowsheet sequence shown in Figure 7.16 which has been adapted from Siirola[46]. There exists a "pinched region" at a particular binary composition for which the relative volatility between acetic acid and water approaches unity, making conventional distillation very expensive. To allow the recovery of pure water, an external entrainer, ethyl acetate, is mixed with the acetic acid-water binary feed in an extractor to produce the binary raffinate stream, R1 and a ternary extract stream, F2 shown in the diagram. The extract stream is fed to a

distillation column where just enough entrainer mixture (ethyl acetate rich stream) is recycled from the decanter so that the overall feed composition is exactly collinear with the bottom product acetic acid, and the overhead product, the heterogeneous azeotrope. The azeotrope is decanted into two immiscible liquid layers whose relative quantities are determined by the tie line going through the azeotrope. While the aqueous layer (water-rich stream) is fed to the entrainer recovery column, the organic layer (ethyl acetate-rich stream) is recycled to the azeotropic and extraction columns at exactly the same composition required for the azeotropic entrainer and extraction solvent.

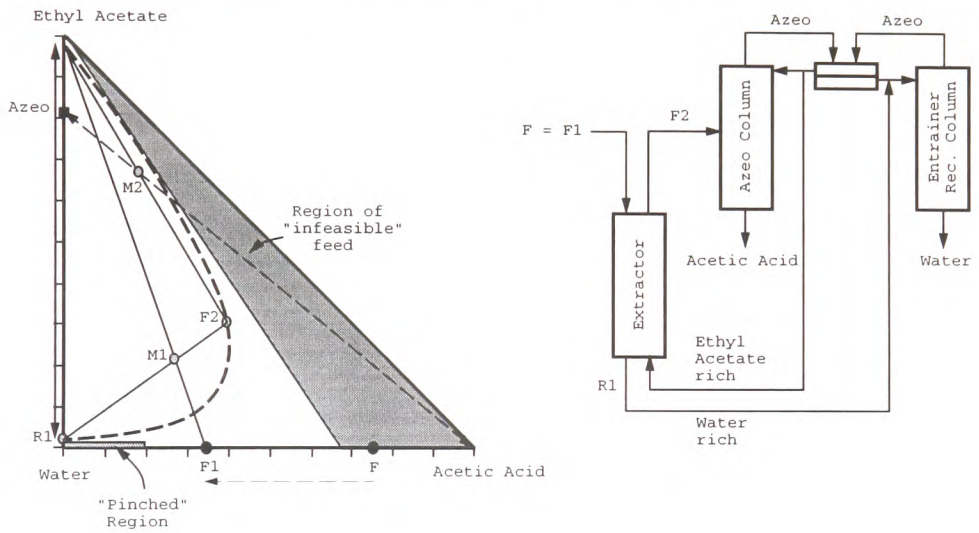


Figure 7.16: Acetic acid-water separation with ethyl acetate as an entrainer, employing an extractor.

Note from Figure 7.16 that drawing a line from the point of pure entrainer and tangent to the heterogeneous liquid boiling envelope all the way to the acetic acid-water axis yields a "border line" that divides the RCM into two separate triangular regions. Mixing between the pure entrainer and a binary feed containing more than about 68 percent acetic acid (where the border line intersects the acetic acid-water axis) will result in an overall ternary feed composition that lies in the shaded triangular region, outside the heterogeneous liquid-liquid region of the RCM. Because the shaded region is homogeneous, an extractor for removing water is "infeasible". The shaded triangle is hereafter termed the *region of infeasible feed.* Notice that this region has meaning only if an extractor is employed as one of the separation steps, apart from distillation

columns.

It is extremely important to recognise the existence of these two regions since in practice, it is quite normal for a binary feed to fluctuate from a low to high concentration of solute thus changing from a feasible to an "infeasible" feed. If the binary feed lies in the infeasible region, separation can be enabled by employing two distillation columns and eliminating the extractor in a synthesis scenario, or by changing the feed composition so that acetic acid content is reduced in either a synthesis or a retrofit scenario. There are two ways to reduce the acetic acid content. One is to use a preconcentrator to remove some acetic acid, and the other is to use water recovered from the bottom of the entrainer recovery column to dilute the acetic acid content. Both schemes are shown in Figure 7.17 and Figure 7.18. Figure 7.18 illustrates the use of a non-entrainer stream as a *type-II primary recycle* to change the feed composition to enable separation.

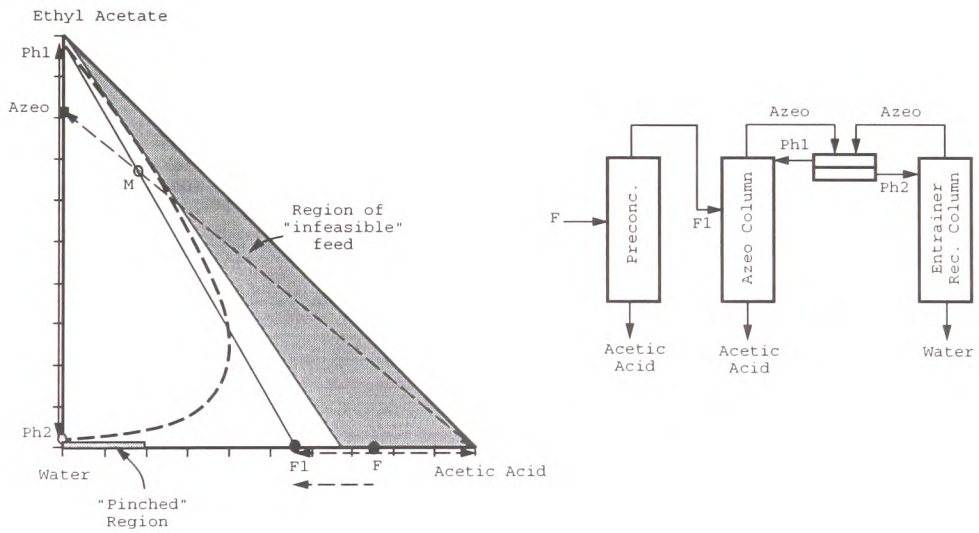


Figure 7.17: Use of a preconcentrator to enable separation.

7.4.2 Secondary recycles

Due to the presence of distillation boundaries that prevent sharp split, separation of azeotropic mixtures may result in process streams which consist of mixtures of components already recovered in pure form by appropriate columns in a given sequence. Clearly, it would make sense to recycle these streams back to the particular columns

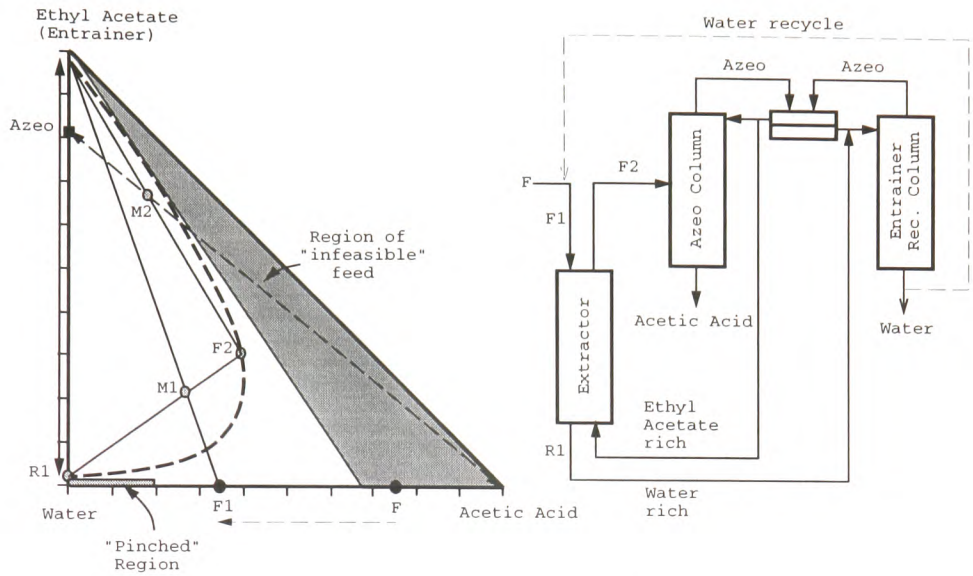


Figure 7.18: *Type-II primary recycle* - use of a non-entrainer component recycle to enable separation.

whose separation range encompass the stream composition. Wahnschafft *et al.* refer to the acetone-chloroform-benzene example shown in Figure 7.19 to illustrate the significance of the stream which they define as *secondary recycle.* This process alternative uses the first column to produce acetone overhead and a ternary mixture containing a non-negligible amount of acetone as the bottom product. This stream is further processed into pure benzene as the bottom product and a mixture of acetone and chloroform as the distillate which is then fed to a third column producing pure chloroform overhead and a bottom stream whose composition lies near the maximum-boiling acetone-chloroform binary azeotrope. Since the relative composition of the mixture of the original feed and the azeotropic stream lies in the range of separation performed by the first unit, it is fed there as secondary recycle, changing the overall feed composition towards the direction of the maximum binary azeotrope.

7.4.3 Range-extending recycles

It is sometimes possible to recycle a stream even though not all splits required for the stream has been performed in the sequence. Cases exist where a particular column in

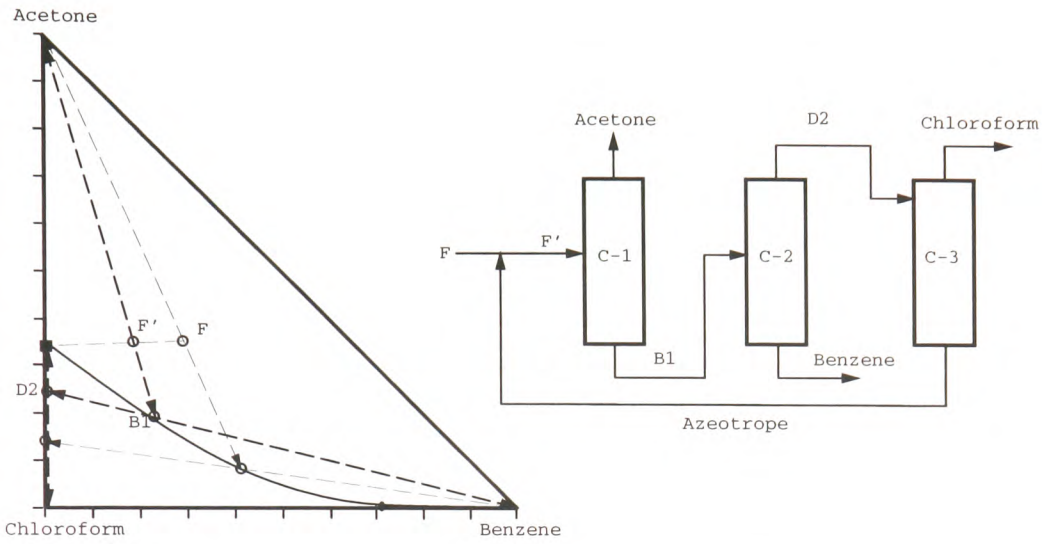


Figure 7.19: Secondary recycle (adapted from Wahnschafft *et al.*)

the sequence is able do more than what is expected of it (i.e. to perform splits it is not initially designed to handle) so long as the "new load" is small in comparison to the column capacity. To illustrate the idea, the heterogeneous separation of an ethanol-water-benzene ternary mixture is used as an example. For the ternary diagram shown in Figure 7.13, at least three distillation columns may be needed to recover water, ethanol and benzene in pure form. However, because it is not necessary to recover the benzene entrainer in pure form, a sequence with two columns and a decanter (shown in the same figure) may therefore be feasible. For this sequence, the combination of columns C1 and C2 separates ethanol and water and the decanter the benzene-rich and the water-rich (aqueous) layer. The benzene-rich layer need not be purified further as it readily satisfies the entrainer composition constraint, and can be recycled to column C2 (azeotropic column).

All required separation tasks are now covered, except for the recovery of the entrainer (benzene) which is present in a non-negligible amount in the aqueous layer leaving the decanter. Wahnschafft *et al.* show that the aqueous layer should be recycled to the first column because it normally lies within the separation range performed by the column. When the aqueous stream is recycled to the first column, it changes the overall feed composition there so that the separation between benzene and water is also performed

in addition to the ethanol-water separation. Wahnschafft *et al.*[27] describe this as the *range extending recycle* that eliminates a third column which might be required in more conventional process flowsheets. They, however, imply that a point may be reached when range extending recycle may adversely affect the product quality as the quantity of entrainer in the aqueous phase is beyond a "tolerable" amount. In such a case, a third column is unavoidable.

7.5 Summary

In azeotropic distillation sequences, the binary and ternary feed composition have significant influence on the overall economics unlike in ideal distillation. Sometimes it is possible to improve the economics of these sequences by modifying a given binary or ternary feed composition by means of preconcentration and recycling. The use of reasoning over the geometric features of RCMs which may involve analysis of the composition space, boiling points of pure components and azeotropes, and distillation boundary location allows a designer to decide when a feed composition change may prove beneficial. The important contributions from this chapter include:

- the significance of the binary, ternary and desirable ternary feed compositions, and a procedure to achieve the desirable ternary feed composition.
- development of a selection catalogue for preconcentration of azeotropic mixtures (presented in Appendix E) using a novel geometric approach which includes a simple procedure to determine the change in specific entrainer requirement (SER) affecting the amount of entrainer reduced.
- insights on the use of mixing and recycling in grassroot design and retrofit of distillation sequences for azeotropic mixtures.

Chapter 8

Conclusions and Future Work

Many waste reduction techniques have been proposed since the beginning of the 1990s with the increased pressure on chemical process industry to reduce pollution. Most of the research on waste reduction has focused on the development of waste treatment technologies and environmental audit and assessment methodologies for new designs and existing processes. Few techniques related to the systematic elimination, reduction and recycling of waste during the design stage have so far been developed. This last type of research on waste minimisation can be divided into three areas covering the overall process design, the design of reaction systems and the design of the separation systems. In preventing waste from the overall process design, Douglas has extended his hierarchical design procedure to include pollution considerations during the process design stage[16]. Research on waste prevention from the reaction system has emphasized the improvement of raw materials efficiency and minimisation of reactor selectivity losses. For separation systems, a design technique which reduces waste for mass separating agent (MSA)-based processes has been developed[17–19].

This thesis addresses two of the three main areas mentioned above. In Chapter 3, a process synthesis procedure that is geared towards waste minimisation in general and opportunistic recycling in particular has been developed as an alternative to Douglas' hierarchical process design procedure. Some modifications and extensions to the original approach developed by Douglas, and a systematic procedure for recycling in the context of an overall process have been proposed in order to promote internal recycling

between the reaction and separation subsystems. Development of an overall process synthesis procedure, however, plays a relatively minor role in this thesis. The main focus of the thesis is on the development of procedures for synthesis of cleaner and cost effective distillation sequences for homogeneous and heterogeneous azeotropic mixtures, an area of process design which has received very little attention. The proposed procedures are based on geometric reasoning and heuristics which have been derived from the analysis of the results of process simulations. Design of cleaner and cost effective azeotropic distillation systems is organized into four chapters covering the (i) synthesis of distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing (Chapters 4 and 5); (ii) synthesis of heterogeneous azeotropic mixtures (Chapter 6); and (iii) feed modifications to improve azeotropic separation (Chapter 7).

In Chapters 4 and 5, the concept of a minimum entrainer requirement (MER) and the procedure to minimise the required amount of entrainer for distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing were introduced for the first time. Naturally, during the course of the research, a detailed study on synthesis and optimisation of the distillation sequences for azeotropic mixtures has led to a number of important findings in the areas of synthesis and optimisation as well. Results of the study show that the MER not only provides insights for waste minimisation but also proves instrumental in generating economical azeotropic distillation sequences. In addition, the entrainer minimisation study has led to new evidences linking the type of separation sequence, the azeotropic column feedstage location and the volatility of an entrainer with the separability of homogeneous azeotropic mixtures. These findings conclusively explain the peculiar dependencies of the separability of homogeneous azeotropic mixtures on the reflux ratio and the number of stages, that was until now, not well explained in the open literature.

To date, research related to the optimisation of distillation sequences for azeotropic mixtures is very limited when compared to the extensive work done for zeotropic mixtures. As far as we are aware, no guidelines are currently available to screen alternative column sequences for azeotropic mixtures in general. The available procedures for optimisation of distillation sequences for azeotropic mixtures are specific to simple

homogeneous mixtures and a particular class of heterogeneous mixtures[29,30]. When using these techniques to determine the most promising sequence, it is necessary to optimise and evaluate the economics of every sequence generated. The approach becomes cumbersome when a number of different entrainers are being evaluated and when a few separation options exist for each type of entrainer. To overcome these problems, in Chapters 4 and 5 we have produced a catalogue of homogeneous azeotropic mixtures with their corresponding most promising separation sequences. This catalogue enables a designer to identify the most promising separation sequence ahead of design, given the azeotropic mixture RCM properties, which include the boiling points of pure components and azeotropes. The MER and optimum entrainer flowrate are then determined for the most promising separation sequence selected from the catalogue. The screening technique, which is based on heuristics and reasoning over the geometric features of the RCMs, allows designers to consider a wider range of ternary homogeneous azeotropic mixtures than was previously possible.

A procedure for synthesis of promising separation sequences for heterogeneous mixtures that is based on geometric reasoning is described in Chapter 6. The formation of a minimum boiling heterogeneous azeotrope and the presence of a liquid-liquid region for heterogeneous azeotropic mixtures result in a large number of feasible sequences. For this reason, a catalogue of the most promising separation sequences cannot be produced as in the screening procedure developed for homogeneous mixtures. The synthesis problem is thus classified into those involving simple and complex heterogeneous mixtures, based on the properties of the heterogeneous RCMs. These properties guide the search of two dominant synthesis parameters, namely, *the absolute minimum number of units* and the *region or point of minimum economic entrainer flowrate.* Geometric reasoning also enables the determination of the optimum decanter tie-line position and the optimum distillate composition for the entrainer recovery column for some common classes of heterogeneous mixtures.

Note, however, that the separation sequences generated for the homogeneous and heterogeneous azeotropic mixtures described so far are "optimal" only for the given binary or ternary feeds. Sometimes, it may be possible to improve the economics of these se-

quences by modifying a given binary or ternary feed composition by means of preconcentration and recycling. Once again, geometric reasoning allows a designer to decide when feed composition changes might be feasible and beneficial. Important insights for exploiting feed composition flexibility to improve separation of azeotropic mixtures are highlighted in Chapter 7.

In summary, this thesis offers important contributions in the areas of waste minimisation and process synthesis covering the reaction-separation interactions and azeotropic separation systems. Many new insights accompany the following major developments:

- a process design procedure that promotes waste minimisation through opportunistic recycling,
- a geometric and heuristic approach for the synthesis of cleaner and cost effective distillation sequences for homogeneous azeotropic mixtures with and without boundary crossing,
- a geometric approach for the synthesis of promising distillation sequences for heterogeneous azeotropic mixtures,
- guidelines for exploiting feed composition flexibility to improve separation and to reduce waste in the separation of azeotropic mixtures, which are applicable for grassroot design and retrofit.

Admittedly, the proposed synthesis approach does not guarantee a global economic optimum solution. However, the primary goal of generating minimum-waste designs often results in cheaper azeotropic distillation sequences due to reduced capacity and lower effluent treatment costs, i.e. in an overall reduction of capital and operating costs. As the technique is largely based on geometric reasoning and heuristics, the results can be achieved at the expense of little computation, thus making the approach particularly appropriate during the early stages of design.

Three possible directions of future research are hereby anticipated. Firstly, the catalogue of the most promising distillation sequences presented in this work, though not

exhaustive, covers the homogeneous systems that are most commonly encountered in practice. Nonetheless, the proposed geometric approach and the catalogue of the most promising distillation sequences are readily extendable to homogeneous systems of less practical importance.

Some work is left to be done to improve the RCM classifications for heterogeneous systems. We have classified the heterogeneous systems into the simple and complex heterogeneous systems based on some *observable* geometric properties (e.g. the existence of heterogeneous azeotropes, distillation boundaries etc.) as opposed to the *manipulable* geometric properties (e.g. the type of entrainer). Our classification results in two distinct, but rather broad and lopsided classes of synthesis problems. The main disadvantage of such classification is that a problem mixture may not be readily matched since the relationship between the entrainer and the RCM properties is unknown. In view of the drawbacks mentioned, it would be useful to classify heterogeneous systems based on a set of manipulable geometric properties such as the volatility of the entrainer in relation to that of the binary feed constituents (i.e., in the manner done for homogeneous systems). This can be accomplished by conducting a detailed survey on a wide range of heterogeneous mixtures, aimed at exploring the effect of entrainer volatility and type of entrainer on (i) the type of azeotropes and distillation boundaries generated, and (ii) the properties of the heterogeneous liquid boiling envelope (e.g. the tie line orientation and the composition of heterogeneous azeotropes).

A second possible direction of future research concerns simulation and optimisation. Note that, the simulation-based entrainer minimisation procedure developed for homogeneous systems is also extendable to heterogeneous systems. The presence of a liquid-liquid region in the RCMs of heterogeneous mixtures complicates simulation and the search for the MER. The optimisation variables in this case include the decanter tie line position (the temperature in the decanter), the liquid composition in the decanter and the distillate composition for the entrainer recovery column in addition to those applicable for homogeneous systems. The appropriate optimisation bounds for the decanter tie line position and decanter liquid composition can be established from the heterogeneous liquid boiling envelope that can be generated from the vapour-

liquid-liquid equilibrium (VLLE) data obtained from simulation. During the search for the MER, it would be useful to investigate the effects of entrainer volatility, reflux ratio and the number of stages on heterogeneous azeotropic mixtures separability, which are, until now, not yet well understood.

Finally, the work in this thesis could culminate in the development a computer-based library of alternative separation sequences for a wide range of homogeneous and heterogeneous azeotropic systems. We envision a system, which, by virtue of search, pattern matching and geometric reasoning, is capable of screening the alternative azeotropic separation sequences and rationalise the choice of the most promising sequence, given the minimal information[1] about the entrainer and the binary feed constituents. With this information in hand, it is also possible for the knowledge-based system to recommend the feasible and beneficial feed composition changes.

In summary, the current and future developments have three mutually complementary objectives:

1. *RCM classification.* This is aimed at extending the applicability of the geometric approach for synthesis of the distillation sequences.

2. *Simulation and optimisation.* To address the balance between the issue of environment and economy, provide explanation about the peculiar behaviour of azeotropic mixtures, generate heuristics and furnish the necessary information for geometric and numerical analysis.

3. *Automation.* To enhance the documentation, reproducibility and to minimise repetitive synthesis and design work.

With the proposed current and future developments, it is hoped that this thesis can significantly contribute towards the generation of cleaner and cost effective distillation sequences for azeotropic mixtures in particular, and provide valuable assisstance for

[1] i.e. the boiling points of the pure components and azeotrope, the binary feed composition and the product requirements.

designers working in the relatively less established and highly complex area of azeotropic separation in general.

Appendix A

A.1 A Waste Minimisation Approach for process synthesis

Figures A1 and A2 summarizes the design procedure for waste minimisation with emphasis on opportunistic recycling. A design is developed by proceeding through successive levels of design abstractions (input information, input-output structure, reaction system, separation and recycle system) while additional details are added at each level. To achieve the goal of waste minimisation, the idea is to identify potential pollution problems as design is developed, and make decisions not to introduce materials, chemistry, process conditions or techniques that could cause adverse environmental impact at each level of the design hierarchy.

Input Information

- raw materials - methanol, acetic acid
- desired product - methyl acetate, water
- production rate & product distribution - nil
- catalyst type - sulfuric & hydrochloric acid
- data on catalyst deactivation
- reactor solvent or inerts - nil
- reaction chemistry:

  methanol + acetic acid <===> methyl acetate + water

Input–Output structure

- feeds - methanol, acetic acid
- products - methyl acetate, water

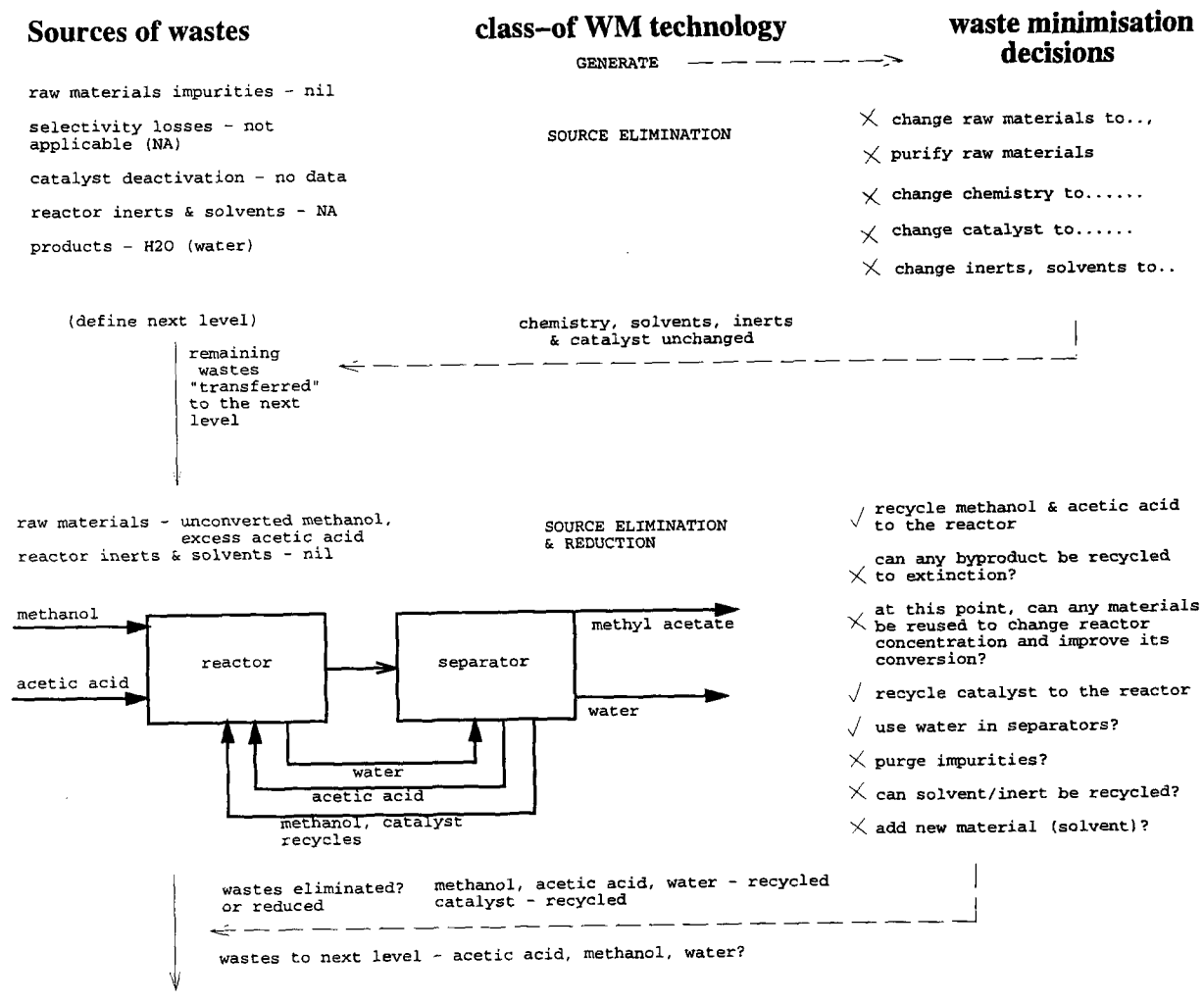


FIGURE A1. WASTE MINIMISATION APPROACH FOR PROCESS SYNTHESIS

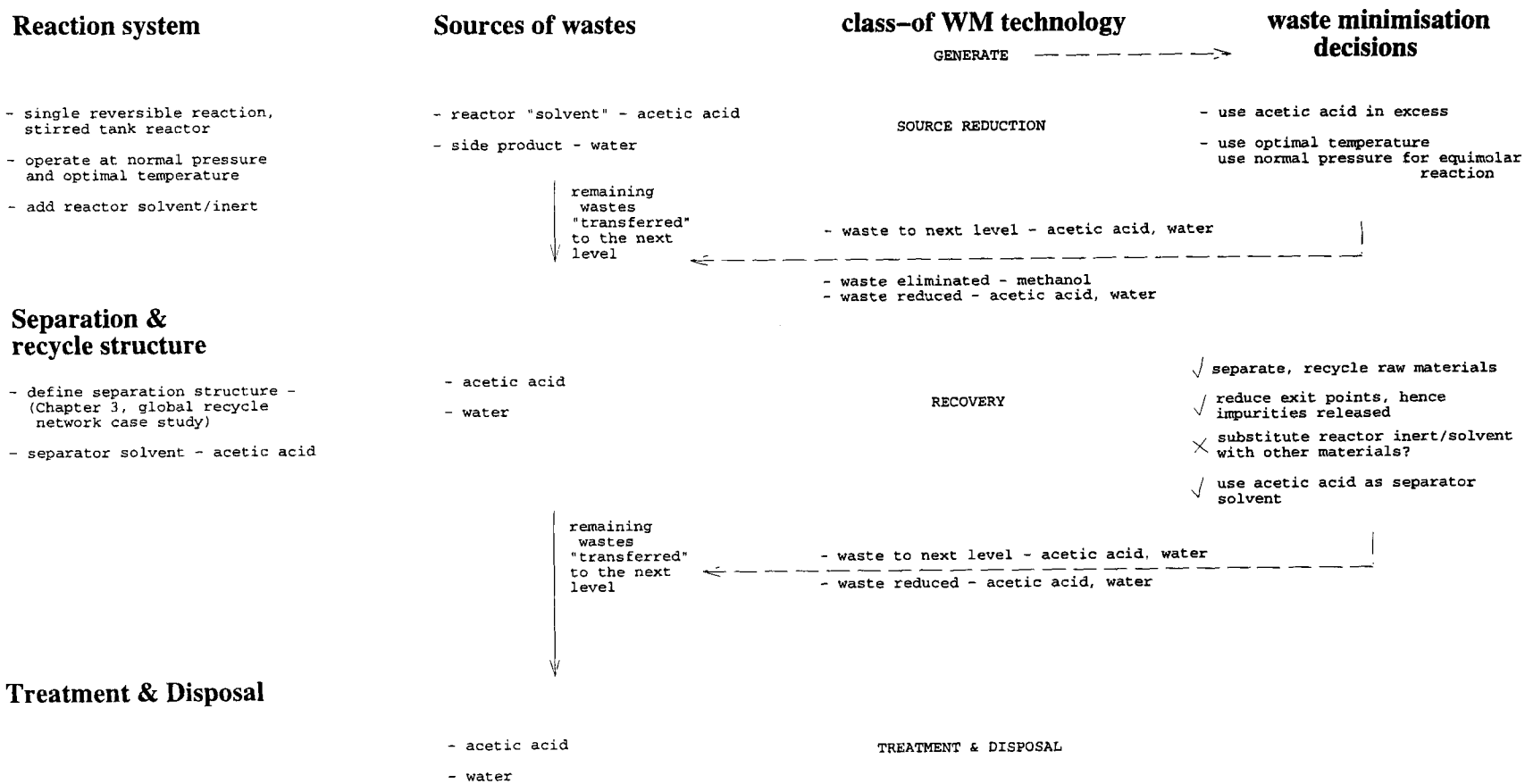
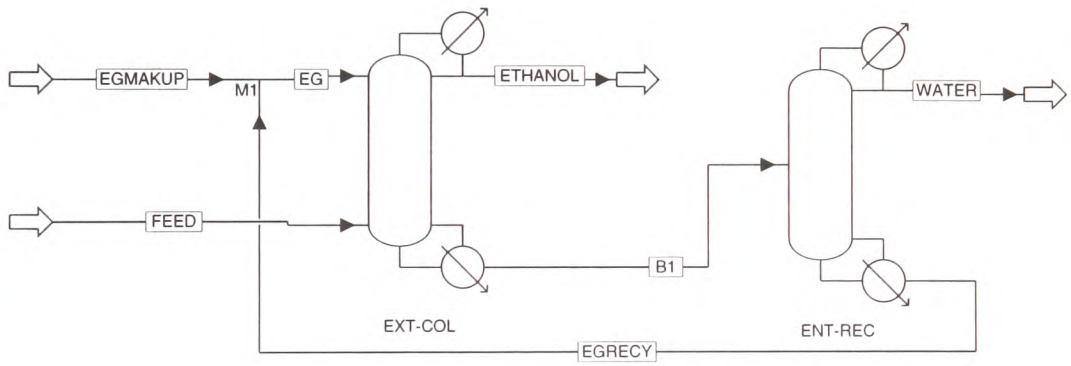


FIGURE A2.. WASTE MINIMISATION APPROACH FOR PROCESS SYNTHESIS

Appendix B

B.1 Process flow diagram, stream data and input file for ethanol-water-ethylene glycol separation



Heat and Material Balance Table								
Stream ID		B1	EG	EGMAKUP	EGRECY	ETHANOL	FEED	WATER
Temperature	C	144.2	196.6	25.6	199.3	80.4	44.0	100.4
Pressure	BAR	1.100	1.014	1.014	1.100	1.100	1.100	1.100
Vapor Frac		0.000	0.011	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	171.369	130.789	0.001	130.788	242.019	282.600	40.581
Mass Flow	KG/HR	8844.640	8106.195	0.062	8106.133	11142.145	11880.649	738.507
Volume Flow	CUM/HR	9.450	63.702	< 0.001	9.179	15.788	15.566	0.809
Enthalpy	MMKCAL/HR	-16.170	-13.136	> -0.001	-13.136	-15.583	-18.645	-2.714
Mole Flow	KMOL/HR							
EHTANOL		0.265	trace		trace	241.754	242.019	0.265
WATER		40.581	0.265		0.265	0.264	40.581	40.317
EG		130.523	130.524	0.001	130.523	< 0.001		trace
Mole Frac								
EHTANOL		0.002	trace		trace	0.999	0.856	0.007
WATER		0.237	0.002		0.002	0.001	0.144	0.993
EG		0.762	0.998	1.000	0.998	92 PPB		2 PPB

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 12:15:14 Sat Jan 17, 1998
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG/ewegrecy.inp
```

```
COMPONENTS
    EHTANOL C2H6O-2 EHTANOL /
    WATER H2O WATER /
    EG C2H6O2 EG
PROPERTIES UNIQUAC

STREAM EGMAKUP
    SUBSTREAM MIXED TEMP=25.55556 PRES=1.013529
    MOLE-FLOW EG .4535923
STREAM FEED
    SUBSTREAM MIXED TEMP=44 PRES=1.1
    MOLE-FLOW EHTANOL 242.0186 / WATER 40.5814

BLOCK ENT-REC RADFRAC
    PARAM NSTAGE=18
    FEEDS B1 7
    PRODUCTS WATER 1 L / EGRECY 18 L
    P-SPEC 1 1.1
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=1.5
    DB:F-PARAMS COMPS=WATER
BLOCK EXT-COL RADFRAC
    PARAM NSTAGE=48
    FEEDS FEED 38 / EG 6
    PRODUCTS ETHANOL 1 L / B1 48 L
    P-SPEC 1 1.1
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=0.95
    DB:F-PARAMS COMPS=EHTANOL
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 47 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=EHTANOL HEAVY-KEY=WATER

;Design Specs for converging entrainer recycle
DESIGN-SPEC DS-1
    DEFINE EGRATE MOLE-FLOW STREAM=EG SUBSTREAM=MIXED  &
        COMPONENT=EG
    DEFINE NPEG PARAMETER 1
    SPEC "EGRATE" TO "NPEG "
    TOL-SPEC "0.01"
    VARY MOLE-FLOW STREAM=EGMAKUP SUBSTREAM=MIXED COMPONENT=EG
    LIMITS "0.001" "50.0"

;fortran block to store the transient value of entrainer flowrate
;as a parameter that changes during optimisation.  This value is used
;continuously in the Design Specs DS-1
FORTRAN F-2
```

```
    DEFINE EG MOLE-FLOW STREAM=EG SUBSTREAM=MIXED COMPONENT=EG
    DEFINE NPEG PARAMETER 1
F       EG=NPEG
    READ-VARS NPEG
    WRITE-VARS EG

;minimising entrainer
CONSTRAINT C-2
    DEFINE ETFRAC MOLE-FRAC STREAM=ETHANOL SUBSTREAM=MIXED  &
        COMPONENT=EHTANOL
    SPEC "0.999" LE "ETFRAC"
    TOL-SPEC "0.001"

OPTIMIZATION O-2
    DEFINE ENFLO MOLE-FLOW STREAM=EG SUBSTREAM=MIXED  &
        COMPONENT=EG
    DEFINE NPEG PARAMETER 1
    MINIMIZE "ENFLO"
    CONSTRAINTS C-2
    VARY BLOCK-VAR BLOCK=EXT-COL VARIABLE=MOLE-RR  &
        SENTENCE=COL-SPECS LABEL="MOLERR"
    LIMITS "0.2" "20.0 "
    VARY PARAMETER 1 LABEL="ENTFLO"
    LIMITS "20.0" "350.0"
```

B.2 Input file for entrainer minimisation of an ethanol-water-EG system

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG/eaenop.inp
;
TITLE 'Entrainer optimisation for an ethanol-water-EG system.'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP=BAR

DEF-STREAMS CONVEN ALL

SIM-OPTIONS ATM-PRES=1.013529
```

```
DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    EHTANOL C2H6O-2 EHTANOL /
    WATER H2O WATER /
    EG C2H6O2 EG

FLOWSHEET
    BLOCK EXT-COL IN=FEED EG OUT=ETHANOL B1
    BLOCK ENT-REC IN=B1 OUT=WATER EGRECY
    BLOCK M1 IN=EGMAKUP OUT=EG

PROPERTIES UNIQUAC

PROP-DATA UNIQ-1

STREAM EGMAKUP
    SUBSTREAM MIXED TEMP=70.0 PRES=1.1
    MOLE-FLOW EG 50.0

STREAM FEED
    SUBSTREAM MIXED TEMP=100.0 PRES=1.1
    MOLE-FLOW EHTANOL 242.0186 / WATER 40.5814

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK ENT-REC RADFRAC
    PARAM NSTAGE=18
    FEEDS B1 7
    PRODUCTS WATER 1 L / EGRECY 18 L
    P-SPEC 1 1.1
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=1.5
    DB:F-PARAMS COMPS=WATER
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 17 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=WATER HEAVY-KEY=EG

BLOCK EXT-COL RADFRAC
    PARAM NSTAGE=48
    FEEDS FEED 38 / EG 6
    PRODUCTS ETHANOL 1 L / B1 48 L
    P-SPEC 1 1.1
```

```
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=0.95
    DB:F-PARAMS COMPS=EHTANOL
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 47 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=EHTANOL HEAVY-KEY=WATER

CBLOCK ENTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-REC STAGE=TOP

CBLOCK ENTREB HEATX
    REFERENCE TUBE UTILITY=ST-300
    REFERENCE SHELL BLOCK=ENT-REC STAGE=BOTTOM

CBLOCK EXTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=EXT-COL STAGE=TOP

CBLOCK EXTREB HEATX
    REFERENCE TUBE UTILITY=ST-100
    REFERENCE SHELL BLOCK=EXT-COL STAGE=BOTTOM

CBLOCK ENT-REC TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-REC

CBLOCK EXT-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=EXT-COL

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167
```

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UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONSTRAINT C-1
    IN-UNITS ENG
    DEFINE ETREC MOLE-FRAC STREAM=ETHANOL SUBSTREAM=MIXED  &
        COMPONENT=EHTANOL
    SPEC "0.999" EQ "ETREC"
    TOL-SPEC "0.001"

CONSTRAINT C-2
    DEFINE EGRECY MOLE-FRAC STREAM=EGRECY SUBSTREAM=MIXED  &
        COMPONENT=EG
    SPEC "1.000" LE "EGRECY"
    TOL-SPEC "0.005"

CONSTRAINT C-3
    DEFINE ETFRAC MOLE-FRAC STREAM=ETHANOL SUBSTREAM=MIXED  &
        COMPONENT=EHTANOL
    SPEC "1.000" LE "ETFRAC"
    TOL-SPEC "0.005"

CONSTRAINT C-4
    DEFINE WATFRC MOLE-FRAC STREAM=WATER SUBSTREAM=MIXED  &
        COMPONENT=WATER
    SPEC "1.000" LE "WATFRC"
    TOL-SPEC "0.001"

CONSTRAINT C-5
    DEFINE EGFRAC MOLE-FRAC STREAM=EGRECY SUBSTREAM=MIXED  &
        COMPONENT=EG
    SPEC "1.000" LE "EGFRAC"
    TOL-SPEC "0.005"

OPTIMIZATION O-2
    DEFINE ENFLO MOLE-FLOW STREAM=EGMAKUP SUBSTREAM=MIXED  &
        COMPONENT=EG
    MINIMIZE "ENFLO"
```

```
    CONSTRAINTS C-1
    VARY MOLE-FLOW STREAM=EGMAKUP SUBSTREAM=MIXED COMPONENT=EG  &
        LABEL="ENTFLO"
    LIMITS "10.0" "300.00"
    VARY BLOCK-VAR BLOCK=EXT-COL VARIABLE=MOLE-RR  &
        SENTENCE=COL-SPECS LABEL="REFCL1"
    LIMITS "0.05" "20.00"

STREAM-REPOR MOLEFLOW MOLEFRAC
```

B.3 Input file for optimisation of an ethanol-water-EG separation sequence

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG/eacsop.inp
;
TITLE 'Cost optimisation of ethanol-water-EG separation system.'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP=BAR

DEF-STREAMS CONVEN ALL

SIM-OPTIONS ATM-PRES=1.013529

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    EHTANOL C2H6O-2 EHTANOL /
    WATER H2O WATER /
    EG C2H6O2 EG

FLOWSHEET
    BLOCK EXT-COL IN=FEED EG OUT=ETHANOL B1
    BLOCK ENT-REC IN=B1 OUT=WATER EGRECY
    BLOCK M1 IN=EGMAKUP OUT=EG
```

```
PROPERTIES UNIQUAC

PROP-DATA UNIQ-1

STREAM EGMAKUP
    SUBSTREAM MIXED TEMP=70.0 PRES=1.1
    MOLE-FLOW EG 40.0

STREAM FEED
    SUBSTREAM MIXED TEMP=100.0 PRES=1.1
    MOLE-FLOW EHTANOL 242.0186 / WATER 40.5814

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK ENT-REC RADFRAC
    PARAM NSTAGE=18
    FEEDS B1 7
    PRODUCTS WATER 1 L / EGRECY 18 L
    P-SPEC 1 1.1
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=1.5
    DB:F-PARAMS COMPS=WATER
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 17 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=WATER HEAVY-KEY=EG

BLOCK EXT-COL RADFRAC
    PARAM NSTAGE=48
    FEEDS FEED 38 / EG 6
    PRODUCTS ETHANOL 1 L / B1 48 L
    P-SPEC 1 1.1
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=0.95
    DB:F-PARAMS COMPS=EHTANOL
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 47 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=EHTANOL HEAVY-KEY=WATER

CBLOCK ENTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-REC STAGE=TOP

CBLOCK ENTREB HEATX
    REFERENCE TUBE UTILITY=ST-300
    REFERENCE SHELL BLOCK=ENT-REC STAGE=BOTTOM
```

```
CBLOCK EXTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=EXT-COL STAGE=TOP

CBLOCK EXTREB HEATX
    REFERENCE TUBE UTILITY=ST-100
    REFERENCE SHELL BLOCK=EXT-COL STAGE=BOTTOM

CBLOCK ENT-REC TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-REC

CBLOCK EXT-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=EXT-COL

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONSTRAINT C-2
    DEFINE EGRECY MOLE-FRAC STREAM=EGRECY SUBSTREAM=MIXED  &
```

```
        COMPONENT=EG
    SPEC "1.000" LE "EGRECY"
    TOL-SPEC "0.005"

CONSTRAINT C-3
    DEFINE ETFRAC MOLE-FRAC STREAM=ETHANOL SUBSTREAM=MIXED  &
        COMPONENT=EHTANOL
    SPEC "1.000" LE "ETFRAC"
    TOL-SPEC "0.005"

CONSTRAINT C-4
    DEFINE WATFRC MOLE-FRAC STREAM=WATER SUBSTREAM=MIXED  &
        COMPONENT=WATER
    SPEC "1.000" LE "WATFRC"
    TOL-SPEC "0.001"

OPTIMIZATION O-1
    DEFINE CST100 UTILITY-VAR UTILITY= ST-100 VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE CST300 UTILITY-VAR UTILITY= ST-300 VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE CCW UTILITY-VAR UTILITY= WATER VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE CEXTCL CBLOCK-VAR CBLOCK= EXT-COL VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE CENTCL CBLOCK-VAR CBLOCK= ENT-REC VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE CEXTRE CBLOCK-VAR CBLOCK= EXTREB VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE CENTRE CBLOCK-VAR CBLOCK= ENTREB VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE CEXTCO CBLOCK-VAR CBLOCK= EXTCOND VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE CENTCO CBLOCK-VAR CBLOCK= ENTCOND VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    MINIMIZE  &
        "CST100+CST300+CCW+CEXTCL+CENTCL+CEXTRE+CENTRE+CEXTCO+CENTCO"
    CONSTRAINTS C-2
    VARY MOLE-FLOW STREAM=EGMAKUP SUBSTREAM=MIXED COMPONENT=EG  &
        LABEL="ENT-RATE"
    LIMITS "10.0" "300.0"
    VARY BLOCK-VAR BLOCK=EXT-COL VARIABLE=MOLE-RR  &
        SENTENCE=COL-SPECS LABEL="REFLC1"
    LIMITS "0.05" "20.0"
    VARY BLOCK-VAR BLOCK=ENT-REC VARIABLE=MOLE-RR  &
        SENTENCE=COL-SPECS LABEL="REFC2"
    LIMITS "0.01" "10.0"
```

Appendix C

C.1 Input file summary and process flow diagram for acetone-IPA-toluene separation - two column sequence with IPA-rich feed

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-isop-tou
;Filename ~/zain/aspenrun/ace-isop-tou/acisoto5.inp

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    IPROPANL C3H8O-2 IPROPANL /
    TOLUENE C7H8 TOLUENE

FLOWSHEET
    BLOCK C-1 IN=MIXAZEO OUT=D1 TOLUENE
    BLOCK C-2 IN=D1 OUT=ACERECY IPA
    BLOCK M2 IN=AZEO MIXACE OUT=MIXAZEO
    BLOCK M1 IN=ACETONE ACERECY OUT=MIXACE

PROPERTIES UNIQUAC

STREAM ACETONE
    SUBSTREAM MIXED TEMP=40 PRES=1
    MOLE-FLOW ACETONE 0.001

STREAM AZEO
    SUBSTREAM MIXED TEMP=70.0 PRES=1
    MOLE-FLOW IPROPANL 90.0 / TOLUENE 10.0

STREAM MIXACE
```

```
    SUBSTREAM MIXED TEMP=56.5 PRES=1.01325
    MOLE-FLOW ACETONE 1250.0

BLOCK M1 MIXER

BLOCK M2 MIXER

BLOCK C-1 RADFRAC
    PARAM NSTAGE=50 MAXOL=25
    FEEDS MIXAZEO 47
    PRODUCTS D1 1 L / TOLUENE 50 L
    P-SPEC 1 1
    COL-SPECS B:F=0.95 MOLE-RDV=0.0 MOLE-RR=1.5
    DB:F-PARAMS COMPS=TOLUENE

BLOCK C-2 RADFRAC
    PARAM NSTAGE=30
    FEEDS D1 20
    PRODUCTS ACERECY 1 L / IPA 30 L
    P-SPEC 1 1.0
    COL-SPECS B:F=1.00 MOLE-RDV=0.0 MOLE-RR=3.5
    DB:F-PARAMS COMPS=IPROPANL

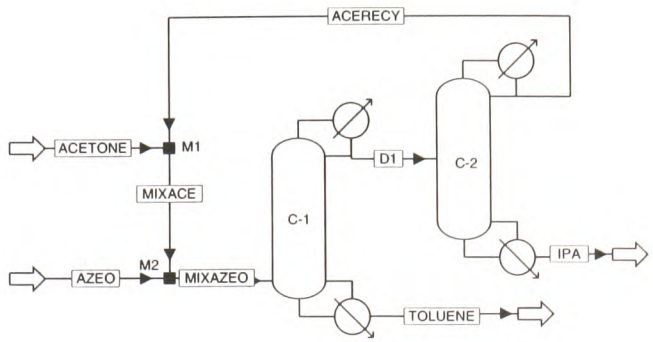
DESIGN-SPEC DS-1
    DEFINE MIXACE MOLE-FLOW STREAM=MIXACE SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    SPEC "MIXACE" TO "1250.0"
    TOL-SPEC "0.05"
    VARY MOLE-FLOW STREAM=ACETONE SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    LIMITS "0.01" "10.0"

STREAM-REPOR MOLEFLOW MOLEFRAC
```

C.2 Input file summary and process flow diagram for acetone-IPA-toluene separation - two column sequence with toluene-rich feed

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-isop-tou
;Filename ~/zain/aspenrun/ace-isop-tou/acisoto4.inp

SIM-OPTIONS ATM-PRES=1.01325
```



Heat and Material Balance Table									
Stream ID		ACERECY	ACETONE	AZEO	D1	IPA	MIXACE	MIXAZEO	TOLUENE
Temperature	C	55.8	40.0	70.0	56.6	82.0	55.8	54.7	110.0
Pressure	BAR	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	1250.547	0.010	100.000	1341.049	90.503	1250.549	1350.549	9.500
Mass Flow	KG/HR	72632.812	0.581	6330.038	78087.750	5454.936	72632.961	78963.000	875.254
Volume Flow	CUM/HR	97.048	0.001	8.399	104.390	7.529	97.048	105.060	1.123
Enthalpy	MMKCAL/HR	-72.564	-0.001	-6.591	-79.106	-6.588	-72.564	-79.156	0.061
Mole Flow	KMOL/HR								
ACETONE		1250.044	0.010		1250.044	< 0.001	1250.047	1250.047	0.002
IPROPANL		0.503		90.000	90.503	90.000	0.503	90.503	< 0.001
TOLUENE		trace		10.000	0.502	0.502	trace	10.000	9.498
Mole Frac									
ACETONE		1.000	1.000		0.932	4 PPM	1.000	0.926	241 PPM
IPROPANL		402 PPM		0.900	0.067	0.994	402 PPM	0.067	9 PPM
TOLUENE		trace		0.100	375 PPM	0.006	trace	0.007	1.000

Figure C.1: Process flow diagram and stream data for acetone-IPA-toluene separation - two column sequence with IPA-rich feed.

```
PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    IPROPANL C3H8O-2 IPROPANL /
    TOLUENE C7H8 TOLUENE /
    WATER H2O WATER

FLOWSHEET
    BLOCK C1 IN=MIXAZEO OUT=D1 TOLUENE
    BLOCK C2 IN=D1 OUT=ACERECY IPA
    BLOCK M2 IN=AZEO MIXACE OUT=MIXAZEO
    BLOCK M1 IN=ACETONE ACERECY OUT=MIXACE

PROPERTIES UNIQUAC
```

```
STREAM ACETONE
    SUBSTREAM MIXED TEMP=50.0 PRES=1.01325
    MOLE-FLOW ACETONE 0.001

STREAM AZEO
    SUBSTREAM MIXED TEMP=70.0 PRES=1.01325
    MOLE-FLOW IPROPANL 84.0 / TOLUENE 16.0

STREAM MIXACE
    SUBSTREAM MIXED TEMP=55.6 PRES=1.01325
    MOLE-FLOW ACETONE 950.0

BLOCK M1 MIXER

BLOCK M2 MIXER

BLOCK C1 RADFRAC
    PARAM NSTAGE=50 MAXOL=25
    FEEDS MIXAZEO 47
    PRODUCTS D1 1 L / TOLUENE 50 L
    P-SPEC 1 1.01325
    COL-SPECS B:F=0.95 MOLE-RDV=0.0 MOLE-RR=1.5
    DB:F-PARAMS COMPS=TOLUENE
    SIZE-DATA COND=YES REB=YES

BLOCK C2 RADFRAC
    PARAM NSTAGE=30
    FEEDS D1 20
    PRODUCTS ACERECY 1 L / IPA 30 L
    P-SPEC 1 1.01325
    COL-SPECS B:F=1.00 MOLE-RDV=0.0 MOLE-RR=3.5
    DB:F-PARAMS COMPS=IPROPANL
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=NOVEMBER YEAR=1996
    PURCHASE MONTH=NOVEMBER YEAR=1997
    START-UP MONTH=NOVEMBER YEAR=1998

CBLOCK COND1 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=C1 STAGE=TOP

CBLOCK COND2 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=C2 STAGE=TOP

CBLOCK REB1 HEATX
```

```
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=C1 STAGE=BOTTOM

CBLOCK REB2 HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=C2 STAGE=BOTTOM

CBLOCK C1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=C1

CBLOCK C2 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=C2

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=38.00

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

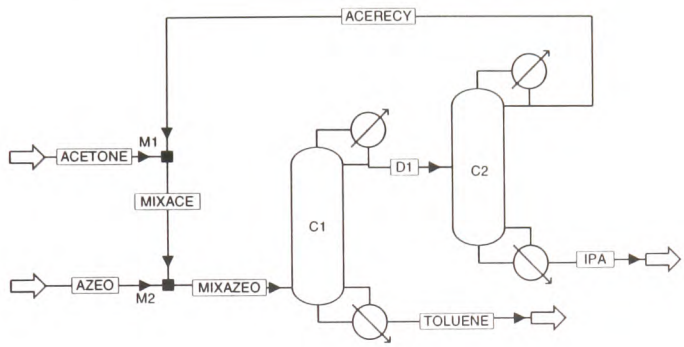
UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

DESIGN-SPEC DS-1
    DEFINE MIXACE MOLE-FLOW STREAM=MIXACE SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    DEFINE MP PARAMETER 1
```

```
    SPEC "MIXACE" TO "950.0"
    TOL-SPEC "0.05"
    VARY MOLE-FLOW STREAM=ACETONE SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    LIMITS "0.01" "10.0"

STREAM-REPOR MOLEFLOW MOLEFRAC
```



Heat and Material Balance Table									
Stream ID		ACERECY	ACETONE	AZEO	D1	IPA	MIXACE	MIXAZEO	TOLUENE
Temperature	C	56.1	50.0	70.0	57.2	82.3	56.1	55.1	110.5
Pressure	BAR	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	950.806	0.010	100.000	1035.610	84.804	950.810	1050.810	15.200
Mass Flow	KG/HR	55224.496	0.581	6522.306	60346.613	5122.117	55224.715	61747.020	1400.406
Volume Flow	CUM/HR	73.836	0.001	8.566	80.729	7.068	73.836	82.046	1.798
Enthalpy	MMKCAL/HR	-55.166	-0.001	-6.118	-61.269	-6.146	-55.166	-61.284	0.098
Mole Flow	KMOL/HR								
ACETONE		950.003	0.010		950.003	< 0.001	950.006	950.006	0.004
IPROPANL		0.804		84.000	84.804	84.000	0.804	84.804	< 0.001
TOLUENE		trace		16.000	0.804	0.804	trace	16.000	15.196
WATER									
Mole Frac									
ACETONE		0.999	1.000		0.917	625 PPB	0.999	0.904	242 PPM
IPROPANL		845 PPM		0.840	0.082	0.991	845 PPM	0.081	11 PPM
TOLUENE		trace		0.160	776 PPM	0.009	trace	0.015	1.000
WATER									

Figure C.2: Process flow diagram for acetone-IPA-toluene separation - two column sequence with toluene-rich feed.

C.3 Input file summary and process flow diagram for acetone-IPA-toluene separation - three column sequence with an azeotropic feed

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
```

```
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-isop-tou
;Filename ~/zain/aspenrun/ace-isop-tou/acisoto1.inp

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    IPROPANL C3H8O-2 IPROPANL /
    TOLUENE C7H8 TOLUENE /
    WATER H2O WATER

FLOWSHEET
    BLOCK C1 IN=AZEOMX OUT=D1 TOLUENE
    BLOCK C2 IN=D1 OUT=ACERECY B2
    BLOCK C3 IN=B2 OUT=AZEORECY IPA
    BLOCK M1 IN=AZEO AZEORECY ACMIX OUT=AZEOMX
    BLOCK M2 IN=ACETONE ACERECY OUT=ACMIX

PROPERTIES UNIQUAC

STREAM ACETONE
    SUBSTREAM MIXED TEMP=40 PRES=1.01325
    MOLE-FLOW ACETONE 0.001

STREAM ACMIX
    SUBSTREAM MIXED TEMP=56.2 PRES=1.01325
    MOLE-FLOW ACETONE 400.0

STREAM AZEO
    SUBSTREAM MIXED TEMP=70.0 PRES=1.01325
    MOLE-FLOW IPROPANL 84.00 / TOLUENE 16.00

BLOCK M1 MIXER

BLOCK M2 MIXER

BLOCK C1 RADFRAC
    PARAM NSTAGE=50 MAXOL=25
    FEEDS AZEOMX 47
    PRODUCTS D1 1 L / TOLUENE 50 L
    P-SPEC 1 1.01325
    COL-SPECS B:F=0.71 MOLE-RDV=0.0 MOLE-RR=0.80
    DB:F-PARAMS COMPS=TOLUENE
    SIZE-DATA COND=YES REB=YES

BLOCK C2 RADFRAC
    PARAM NSTAGE=30
    FEEDS D1 12
```

```
    PRODUCTS B2 30 L / ACERECY 1 L
    P-SPEC 1 1.01325
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=3.5
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES

BLOCK C3 RADFRAC
    PARAM NSTAGE=40
    FEEDS B2 25
    PRODUCTS IPA 40 L / AZEORECY 1 L
    P-SPEC 1 1.01325
    COL-SPECS B:F=0.70 MOLE-RDV=0.0 MOLE-RR=5.5
    DB:F-PARAMS COMPS=IPROPANL
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=NOVEMBER YEAR=1996
    PURCHASE MONTH=NOVEMBER YEAR=1997
    START-UP MONTH=NOVEMBER YEAR=1998

CBLOCK COND1 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=C1 STAGE=TOP

CBLOCK COND2 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=C2 STAGE=TOP

CBLOCK COND3 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=C3 STAGE=TOP

CBLOCK REB1 HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=C1 STAGE=BOTTOM

CBLOCK REB2 HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=C2 STAGE=BOTTOM

CBLOCK REB3 HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=C3 STAGE=BOTTOM

CBLOCK C1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=C1
```

```
CBLOCK C2 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=C2

CBLOCK C3 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=C3

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=38.00

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

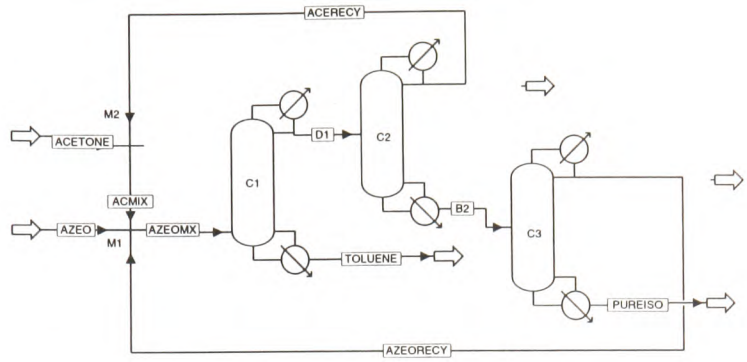
UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

DESIGN-SPEC DS-1
    DEFINE ACEMIX MOLE-FLOW STREAM=ACMIX SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    SPEC "ACEMIX" TO "400.0"
    TOL-SPEC "0.01"
    VARY MOLE-FLOW STREAM=ACETONE SUBSTREAM=MIXED  &
        COMPONENT=ACETONE
    LIMITS "0.001" "40.00"

STREAM-REPOR MOLEFLOW MOLEFRAC
```



Heat and Material Balance Table

Stream ID		ACERECY	ACETONE	ACMIX	AZEO	AZEOMX	AZEORECY	B2	D1	IPA	TOLUENE
Temperature	C	56.2	40.0	56.2	70.0	55.7	79.8	81.2	58.8	82.3	110.2
Pressure	BAR	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	517.049	0.001	517.050	100.000	660.767	43.702	128.132	645.181	84.431	15.586
Mass Flow	KG/HR	30032.484	0.058	30032.543	6522.306	39370.496	2814.818	7902.686	37935.172	5087.868	1435.323
Volume Flow	CUM/HR	40.154	< 0.001	40.154	8.568	52.102	3.773	10.791	50.715	7.028	1.843
Enthalpy	MMKCAL/HR	-30.009	> -0.001	-30.009	-6.118	-38.844	-2.716	-8.865	-38.830	-6.147	0.099
Mole Flow	KMOL/HR										
ACETONE		515.920	0.001	515.921		517.066	1.129	1.129	517.049	trace	0.018
IPROPANL		1.129		1.129	84.000	121.749	36.619	120.615	121.744	83.996	0.005
TOLUENE		< 0.001		< 0.001	16.000	21.952	5.954	6.389	6.389	0.435	15.563
WATER											
Mole Frac											
ACETONE		0.998	1.000	0.998		0.783	0.026	0.009	0.801	trace	0.001
IPROPANL		0.002		0.002	0.840	0.184	0.838	0.941	0.189	0.995	313 PPM
TOLUENE		24 PPB		24 PPB	0.160	0.033	0.136	0.050	0.010	0.005	0.999
WATER											

Figure C.3: Process flow diagram for acetone-IPA-toluene separation - three column sequence with an azeotropic feed.

C.4 Input file summary and process flow diagram for acetone-chloroform-benzene separation - two column sequence with an azeotropic feed

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-isop-tou
;Filename ~/zain/aspenrun/ace-chlo-benz/abc6bopt.inp

SIM-OPTIONS
    IN-UNITS ENG
    SIM-OPTIONS ATM-PRES=1.01325 <BAR>

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
```

```
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=MC6H6 MFEED OUT=ACETONE B1
    BLOCK ENT-CO1 IN=B1 OUT=D2 C6H6RECY
    BLOCK ENT-COL2 IN=D2 OUT=CHLRFM AZEORECY
    BLOCK M-1 IN=C6H6 C6H6RECY OUT=MC6H6
    BLOCK M-2 IN=FEED1 AZEORECY OUT=MFEED

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR

STREAM C6H6
    SUBSTREAM MIXED TEMP=62.77779 PRES=1.013529
    MOLE-FLOW BENZENE 0.0001

STREAM FEED1
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 60. / CHLOROFM 110.

STREAM MC6H6
    SUBSTREAM MIXED TEMP=62.8 PRES=1.01325
    MOLE-FLOW BENZENE 123.518

BLOCK M-1 MIXER
    IN-UNITS ENG

BLOCK M-2 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS MC6H6 26 / MFEED 36
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=0.68 MOLE-RDV=0 MOLE-RR=12.00
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=50
    FEEDS B1 8
    PRODUCTS D2 1 L / C6H6RECY 50 L
    P-SPEC 1 1.013529
    COL-SPECS B:F=1.0 MOLE-RDV=0 MOLE-RR=12.00
    DB:F-PARAMS COMPS=BENZENE
```

```
    SIZE-DATA COND=YES REB=YES

BLOCK ENT-COL2 RADFRAC
    PARAM NSTAGE=28
    FEEDS D2 18
    PRODUCTS CHLRFM 1 L / AZEORECY 28 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=0.65 MOLE-RDV=0 MOLE-RR=14.00
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK COND-3 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-COL2 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK REB-3 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-COL2 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
```

```
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-CO1

CBLOCK ENT-COL2 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-COL2

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

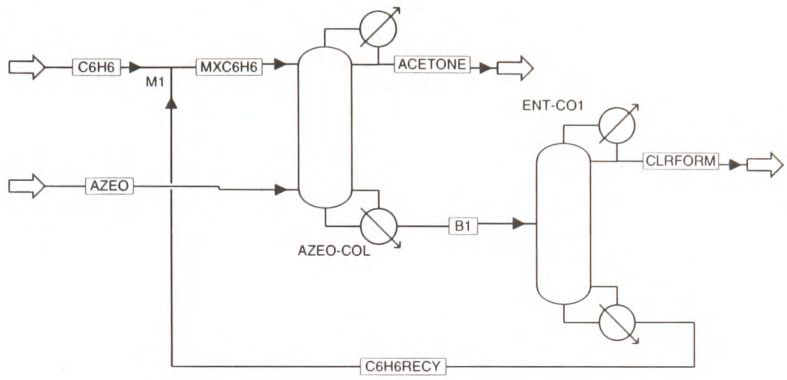
UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

DESIGN-SPEC DS-1
    DEFINE MFLO MOLE-FLOW STREAM=MC6H6 SUBSTREAM=MIXED  &
        COMPONENT=BENZENE
    DEFINE MP PARAMETER 1
    DEFINE MIXB MOLE-FLOW STREAM=MC6H6 SUBSTREAM=MIXED  &
        COMPONENT=BENZENE
    SPEC "MFLO" TO "123.518"
    TOL-SPEC "0.05"
    VARY MOLE-FLOW STREAM=C6H6 SUBSTREAM=MIXED COMPONENT=BENZENE
```

```
    LIMITS "0.0" "5.00"

CONV-OPTIONS
    WEGSTEIN MAXIT=80
    SQP TOL=0.001

STREAM-REPOR MOLEFLOW MOLEFRAC
```



Separation of Acetone-Benzene-Chloroform System								
Stream ID		ACETONE	AZEO	B1	C6H6	C6H6RECY	CLRFORM	MXC6H6
Temperature	C	56.3	68.3	77.0	62.8	80.1	61.3	80.1
Pressure	BAR	1.014	1.014	1.014	1.014	1.014	1.014	1.014
Vapor Frac		0.000	1.000	0.000	0.000	0.000	0.000	0.000
Mole Flow	KMOL/HR	60.000	170.000	300.979	0.581	190.397	110.582	190.979
Mass Flow	KG/HR	3522.388	16616.277	28035.811	45.379	14896.477	13139.335	14941.922
Volume Flow	CUM/HR	4.665	4762.220	27.712	0.054	18.211	9.336	18.267
Enthalpy	MMKCAL/HR	-3.464	-5.669	-0.867	0.008	2.574	-3.425	2.582
Mole Flow	KMOL/HR							
ACETONE		59.385	60.000	0.615		trace	0.615	trace
BENZENE		0.003		190.397	0.581	189.818	0.579	190.399
CHLOROFM		0.612	110.000	109.967		0.579	109.388	0.579
WATER								
Mole Frac								
ACETONE		0.990	0.353	0.002		trace	0.006	trace
BENZENE		44 PPM		0.633	1.000	0.997	0.005	0.997
CHLOROFM		0.010	0.647	0.365		0.003	0.989	0.003
WATER								

Figure C.4: Process flow diagram for acetone-chloroform-benzene separation - two column sequence with an azeotropic feed.

C.5 Input file summary and process flow diagram for acetone-chloroform-benzene separation - three column sequence with an azeotropic feed

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1
```

```
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-isop-tou
;Filename ~/zain/aspenrun/ace-chlo-benz/abc7a.inp

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=AZEO MXC6H6 OUT=ACETONE B1
    BLOCK ENT-CO1 IN=B1 OUT=CLRFORM C6H6RECY
    BLOCK M1 IN=C6H6 C6H6RECY OUT=MXC6H6

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR

STREAM AZEO
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 60.0 / CHLOROFM 110.0

STREAM C6H6
    SUBSTREAM MIXED TEMP=62.77779 PRES=1.013529
    MOLE-FLOW BENZENE 0.001

STREAM MXC6H6
    SUBSTREAM MIXED TEMP=79.44446 PRES=1.013254
    MOLE-FLOW BENZENE 190.3548

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS AZEO 28 / MXC6H6 28
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0 MOLE-RR=12.5920
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=60
    FEEDS B1 14
    PRODUCTS C6H6RECY 60 L / CLRFORM 1 L
```

```
    P-SPEC 1 1.013529
    COL-SPECS B:F=1.0 MOLE-RDV=0 MOLE-RR=44.7748
    DB:F-PARAMS COMPS=BENZENE
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-CO1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056
```

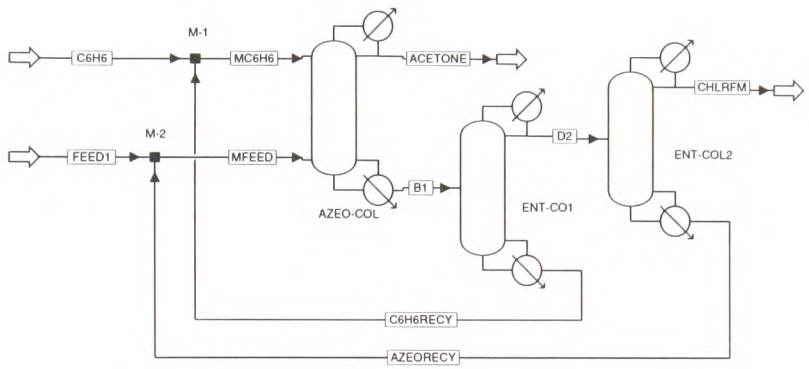
```
UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

DESIGN-SPEC DS-1
    DEFINE MC6H6 MOLE-FLOW STREAM=MXC6H6 SUBSTREAM=MIXED  &
        COMPONENT=BENZENE
    SPEC "MC6H6" TO "190.4"
    TOL-SPEC "1.50"
    VARY MOLE-FLOW STREAM=C6H6 SUBSTREAM=MIXED COMPONENT=BENZENE
    LIMITS "0.0001" "20.0"

STREAM-REPOR MOLEFLOW MOLEFRAC
```



Separation of Acetone-Benzene-Chloroform System											
Stream ID		ACETONE	AZEORECY	B1	C6H6	C6H6RECY	CHLRFM	D2	FEED1	MC6H6	MFEED
Temperature	C	56.1	64.3	71.1	-188.8	80.1	61.1	63.1	68.3	80.1	64.2
Pressure	BAR	1.014	1.014	1.014	1.014	1.014	1.014	1.014	1.014	1.014	1.014
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.664
Mole Flow	KMOL/HR	60.012	88.525	323.057	0.026	124.525	110.007	198.532	170.000	124.551	258.525
Mass Flow	KG/HR	3485.880	8793.552	31694.932	2.011	9769.576	13131.803	21925.355	16616.277	9771.587	25409.828
Volume Flow	CUM/HR	4.660	7.352	28.612	0.002	11.905	9.283	16.651	4762.220	11.907	4760.955
Enthalpy	MMKCAL/HR	-3.480	-3.485	-5.275	< 0.001	1.654	-3.415	-6.910	-5.669	1.655	-9.154
Mole Flow	KMOL/HR										
ACETONE		59.991	28.252	28.261		trace	0.008	28.261	60.000	trace	88.252
BENZENE		0.020	1.029	124.525	0.026	123.496	trace	1.029		123.522	1.029
CHLOROFM		trace	59.243	170.271		1.029	109.999	169.242	110.000	1.029	169.243
WATER											
Mole Frac											
ACETONE		1.000	0.319	0.087		trace	77 PPM	0.142	0.353	trace	0.341
BENZENE		338 PPM	0.012	0.385	1.000	0.992	trace	0.005		0.992	0.004
CHLOROFM		2 PPB	0.669	0.527		0.008	1.000	0.852	0.647	0.008	0.655
WATER											

Figure C.5: Process flow diagram for acetone-chloroform-benzene separation - three column sequence with an azeotropic feed.

Appendix D

D.1 Algorithm for synthesis of cost effective distillation sequences for heterogeneous azeotropic mixtures by geometric reasoning

The overall procedure for optimal synthesis of distillation sequences for heterogeneous azeotropic mixtures based on geometric reasoning can be summarized as follows:

1. Find the sequence with the absolute minimum number of units using the *collinearity rule* for mixtures with heterogeneous azeotropes. Otherwise, select an entrainer rate such that the overall ternary feed composition lies midway between the binary feed and pure entrainer for the base case design, and proceed with the next steps to refine this assumption.

2. Find the optimum entrainer flowrate for the minimum-unit sequence, carefully differentiating between the optimisation and non-optimisation problems. For optimisation problems, locate the region where the optimum entrainer flowrate lies and use the entrainer optimisation method developed by Knight and Doherty[29] to find this flowrate.

3. Select the best decanter tie line position based on the properties of the heterogeneous RCM (the presence of distillation boundaries and heterogeneous azeotropes, tie line orientation, location of the binary or ternary heterogeneous azeotropes). This step also fixes the decanter liquid-liquid distribution and the purity of the recycled entrainer mixture from the decanter.

4. Set the distillate composition for the entrainer recovery column either close to a *stationary point* (azeotropes or distillation boundaries, depending on the mixture) on an RCM, or on the azeotropic column mixing line for systems without heterogeneous azeotropes or distillation boundaries.

5. Find the *closed loop* overall azeotropic column composition from the intersection of the azeotropic column mass balance line and the mixing line between the optimum distillate composition from the entrainer recovery column and the entrainer-rich decanter liquid composition. The overall azeotropic column composition gives the *minimum unit-optimum entrainer target.*

Appendix E

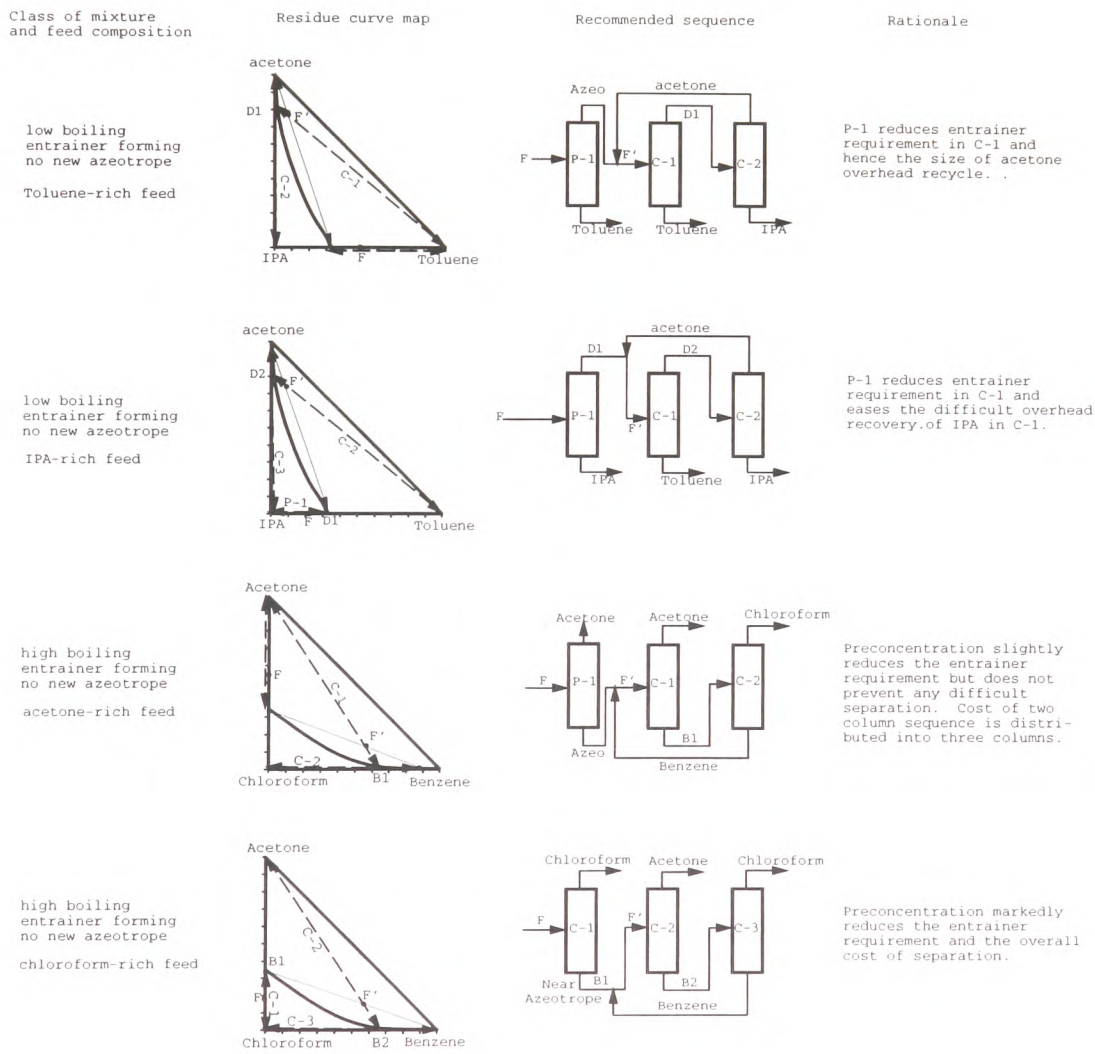


Figure E.1: Decision catalogue for preconcentration for homogeneous azeotropic system with boundary crossing.

E.1 An economic comparison between the sequences with and without a preconcentrator (P-1): - Case of ethanol-water-EG (high boiling entrainer) mixture with an ethanol-rich binary feed.

Table E.1: An economic comparison between the sequences with and without a preconcentrator (P-1): - Case of ethanol-water-EG (high boiling entrainer) mixture with an ethanol-rich binary feed (ratio of ethanol to water flowrate = 500:40).

	sequence without P-1	sequence with P-1	% difference $(X - X_{(P-1)})$
entrainer flowrate (kmol/hr)	300.0	250.0	-17.0%
capital cost (x 10^6\$)	0.688	0.853	-19.0%
utility cost* (x 10^6\$/yr)	1.176	1.240	-5.2%

* cost of steam and cooling water combined.

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:03:22 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG/eweg-c.inp
;
TITLE 'Sequence with a preconcentrator and an ethanol-rich feed.'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP=BAR

DEF-STREAMS CONVEN ALL

SIM-OPTIONS ATM-PRES=1.013529

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    EHTANOL C2H6O-2 EHTANOL /
    WATER H2O WATER /
    EG C2H6O2 EG

FLOWSHEET
    BLOCK EXT-COL IN=EG AZEO OUT=D1 B1
```

```
    BLOCK ENT-REC IN=B1 OUT=D2 B2
    BLOCK M1 IN=EGMAKUP OUT=EG
    BLOCK P1 IN=FEED OUT=ETHANOL AZEO

PROPERTIES UNIQUAC

PROP-DATA UNIQ-1

STREAM EGMAKUP
    SUBSTREAM MIXED TEMP=65.55557 PRES=1.013529
    MOLE-FLOW EG 250.00

STREAM FEED
    SUBSTREAM MIXED TEMP=44 PRES=1.1
    MOLE-FLOW EHTANOL 500.0 / WATER 40.5814

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK ENT-REC RADFRAC
    PARAM NSTAGE=18
    FEEDS B1 7
    PRODUCTS D2 1 L / B2 18 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=2.0
    DB:F-PARAMS COMPS=WATER
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 17 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=WATER HEAVY-KEY=EG

BLOCK EXT-COL RADFRAC
    PARAM NSTAGE=30
    FEEDS EG 3 / AZEO 26
    PRODUCTS D1 1 L / B1 30 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=0.89
    DB:F-PARAMS COMPS=EHTANOL
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 29 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=EHTANOL HEAVY-KEY=WATER

BLOCK P1 RADFRAC
    PARAM NSTAGE=30
    FEEDS FEED 3
```

```
    PRODUCTS ETHANOL 1 L / AZEO 30 L
    P-SPEC 1 1.013259
    COL-SPECS D:F=0.18 MOLE-RDV=0.0 MOLE-RR=1.0
    DB:F-PARAMS COMPS=EHTANOL
    SIZE-DATA COND=YES REB=YES

CBLOCK C1 HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=P1 STAGE=TOP

CBLOCK ENTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-REC STAGE=TOP

CBLOCK ENTREB HEATX
    REFERENCE TUBE UTILITY=ST-300
    REFERENCE SHELL BLOCK=ENT-REC STAGE=BOTTOM

CBLOCK EXTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=EXT-COL STAGE=TOP

CBLOCK EXTREB HEATX
    REFERENCE TUBE UTILITY=ST-100
    REFERENCE SHELL BLOCK=EXT-COL STAGE=BOTTOM

CBLOCK R1 HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=P1 STAGE=BOTTOM

CBLOCK ENT-REC TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-REC

CBLOCK EXT-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=EXT-COL

CBLOCK P1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=P1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
```

```
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

STREAM-REPOR MOLEFLOW MOLEFRAC


;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:03:57 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/eth-wat-EG/eweg-c2c.inp
;
TITLE 'Sequence without a preconcentrator, with an ethanol-rich feed.'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP=BAR

DEF-STREAMS CONVEN ALL

SIM-OPTIONS ATM-PRES=1.013529

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC
```

```
COMPONENTS
    EHTANOL C2H6O-2 EHTANOL /
    WATER H2O WATER /
    EG C2H6O2 EG

FLOWSHEET
    BLOCK EXT-COL IN=EG AZEO OUT=D1 B1
    BLOCK ENT-REC IN=B1 OUT=D2 B2
    BLOCK M1 IN=EGMAKUP OUT=EG

PROPERTIES UNIQUAC

PROP-DATA UNIQ-1

STREAM AZEO
    SUBSTREAM MIXED TEMP=78.2 PRES=1.1
    MOLE-FLOW EHTANOL 500.0 / WATER 40.5814

STREAM EGMAKUP
    SUBSTREAM MIXED TEMP=65.55557 PRES=1.013529
    MOLE-FLOW EG 300.00

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK ENT-REC RADFRAC
    PARAM NSTAGE=18
    FEEDS B1 7
    PRODUCTS D2 1 L / B2 18 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=2.0
    DB:F-PARAMS COMPS=WATER
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
    TRAY-SIZE 1 2 17 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=WATER HEAVY-KEY=EG

BLOCK EXT-COL RADFRAC
    PARAM NSTAGE=30
    FEEDS EG 3 / AZEO 26
    PRODUCTS D1 1 L / B1 30 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0.0 MOLE-RR=0.89
    DB:F-PARAMS COMPS=EHTANOL
    COND-HCURVE 1
    REB-HCURVE 1
    TRAY-REPORT TRAY-OPTION=BRIEF
```

```
    TRAY-SIZE 1 2 29 SIEVE
    SIZE-DATA COND=YES REB=YES LIGHT-KEY=EHTANOL HEAVY-KEY=WATER

CBLOCK ENTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-REC STAGE=TOP

CBLOCK ENTREB HEATX
    REFERENCE TUBE UTILITY=ST-300
    REFERENCE SHELL BLOCK=ENT-REC STAGE=BOTTOM

CBLOCK EXTCOND HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=EXT-COL STAGE=TOP

CBLOCK EXTREB HEATX
    REFERENCE TUBE UTILITY=ST-100
    REFERENCE SHELL BLOCK=EXT-COL STAGE=BOTTOM

CBLOCK ENT-REC TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-REC

CBLOCK EXT-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=EXT-COL

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
```

```
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

STREAM-REPOR MOLEFLOW MOLEFRAC
```

E.2 An economic comparison between the sequences with and without a preconcentrator: - Case of acetone-chloroform-benzene (high boiling entrainer) mixture with an acetone-rich binary feed.

Table E.2: An economic comparison between the sequences with and without a preconcentrator (P-1): - Case of acetone-chloroform-benzene (high boiling entrainer) mixture with an acetone-rich binary feed (ratio of acetone to chloroform flowrate = 200:100).

	sequence without P-1	sequence with P-1	% difference $(X - X_{(P-1)})$
entrainer flowrate (kmol/hr)	220.0	200.0	-9.1%
capital cost (x 10^6\$)	3.882	3.603	+7.1%
utility cost* (x 10^6\$/yr)	4.187	4.177	+0.2%

* cost of steam and cooling water combined.

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:19:59 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz/abc7.inp

TITLE 'Sequence without a preconcentrator, with an acetone-rich feed'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP-PER-HT='MBAR/M' PDROP=BAR

DEF-STREAMS CONVEN ALL

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD
```

```
PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=AZEO MXC6H6 OUT=ACETONE B1
    BLOCK ENT-CO1 IN=B1 OUT=CLRFORM C6H6RECY
    BLOCK M1 IN=C6H6 OUT=MXC6H6

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR

PROP-DATA NRTL-1

STREAM AZEO
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 200.00 / CHLOROFM 100.00

STREAM C6H6
    SUBSTREAM MIXED TEMP=62.77779 PRES=1.013529
    MOLE-FLOW BENZENE 215.00

STREAM MXC6H6
    SUBSTREAM MIXED TEMP=79.44446 PRES=1.013254
    MOLE-FLOW BENZENE 190.3548

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS AZEO 28 / MXC6H6 28
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0 MOLE-RR=12.5920
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=60
    FEEDS B1 14
    PRODUCTS C6H6RECY 60 L / CLRFORM 1 L
```

```
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.00 MOLE-RDV=0 MOLE-RR=44.7748
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-CO1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056
```

```
UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONV-OPTIONS
    PARAM SPEC-LOOP=OUTSIDE USER-LOOP=INSIDE

STREAM-REPOR MOLEFLOW MOLEFRAC


;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:20:34 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz/abc7pc.inp

TITLE 'Sequence with a preconcentrator and an acetone-rich feed'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP-PER-HT='MBAR/M' PDROP=BAR

DEF-STREAMS CONVEN ALL

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
```

```
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=MXC6H6 AZEO OUT=ACETONE B1
    BLOCK ENT-CO1 IN=B1 OUT=CLRFORM C6H6RECY
    BLOCK M1 IN=C6H6 OUT=MXC6H6
    BLOCK PREC1 IN=ACE-RICH OUT=PACETONE AZEO

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR

PROP-DATA NRTL-1

STREAM ACE-RICH
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 200.00 / CHLOROFM 100.00

STREAM C6H6
    SUBSTREAM MIXED TEMP=62.77779 PRES=1.013529
    MOLE-FLOW BENZENE 200.0

STREAM MXC6H6
    SUBSTREAM MIXED TEMP=79.44446 PRES=1.013254
    MOLE-FLOW BENZENE 200.00

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS MXC6H6 28 / AZEO 28
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0 MOLE-RR=12.5920
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=60
    FEEDS B1 14
    PRODUCTS C6H6RECY 60 L / CLRFORM 1 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.00 MOLE-RDV=0 MOLE-RR=44.7748
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES
```

```
BLOCK PREC1 RADFRAC
    PARAM NSTAGE=25
    FEEDS ACE-RICH 10
    PRODUCTS PACETONE 1 L / AZEO 25 L
    P-SPEC 1 1.013259
    COL-SPECS D:F=0.40 MOLE-RDV=0.0 MOLE-RR=7.0
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK CONDP HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=PREC1 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK REBP HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=PREC1 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
```

```
    REFERENCE BLOCK=ENT-C01

CBLOCK PREC1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=PREC1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONV-OPTIONS
    PARAM SPEC-LOOP=OUTSIDE USER-LOOP=INSIDE

STREAM-REPOR MOLEFLOW MOLEFRAC
```

Table E.3: An economic comparison between the sequences with and without a preconcentrator (P-1): - Case of acetone-chloroform-benzene (high boiling entrainer) mixture with a chloroform-rich binary feed (ratio of chloroform to acetone flowrate = 80:20).

	sequence without P-1	sequence with P-1	% difference $(X - X_{(P-1)})$
entrainer flowrate (kmol/hr)	165.0	80.0	-52%
capital cost (x 10^6\$)	2.508	1.986	+21%
utility cost* (x 10^6\$/yr)	2.379	1.496	+37%

E.3 An economic comparison between the sequences with and without a preconcentrator: - Case of acetone-chloroform-benzene (high boiling entrainer) mixture with a chloroform-rich binary feed.

* cost of steam and cooling water combined.

```
;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:18:28 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz/abc-rich.inp
;
TITLE 'Sequence without a preconcentrator, with a chloroform-rich feed'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP-PER-HT='MBAR/M' PDROP=BAR

DEF-STREAMS CONVEN ALL

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=AZEO MXC6H6 OUT=ACETONE B1
```

```
    BLOCK ENT-CO1 IN=B1 OUT=CLRFORM C6H6RECY
    BLOCK M1 IN=C6H6 OUT=MXC6H6

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR

PROP-DATA NRTL-1

STREAM AZEO
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 20.00 / CHLOROFM 80.00

STREAM C6H6
    SUBSTREAM MIXED TEMP=62.77779 PRES=1.013529
    MOLE-FLOW BENZENE 165.00

STREAM MXC6H6
    SUBSTREAM MIXED TEMP=79.44446 PRES=1.013254
    MOLE-FLOW BENZENE 190.3548

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS AZEO 28 / MXC6H6 28
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0 MOLE-RR=20.00
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=60
    FEEDS B1 14
    PRODUCTS C6H6RECY 60 L / CLRFORM 1 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.00 MOLE-RDV=0 MOLE-RR=44.7748
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
```

```
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-CO1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557

UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
```

```
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONV-OPTIONS
    PARAM SPEC-LOOP=OUTSIDE USER-LOOP=INSIDE

STREAM-REPOR MOLEFLOW MOLEFRAC


;Input Summary created by ASPEN PLUS Rel. 9.3-1 at 16:19:00 Sat Feb 21, 1998
;Directory /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz
;Filename /a/lyne/export/home/ecosse0/zain/aspenrun/ace-chlo-benz/abc-rpc.inp
;
TITLE 'Sequence with a preconcentrator and a chloroform-rich feed'

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR'  &
        HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C  &
        VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM'  &
        MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL'  &
        MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L'  &
        PDROP-PER-HT='MBAR/M' PDROP=BAR

DEF-STREAMS CONVEN ALL

DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD

PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
    ACETONE C3H6O-1 ACETONE /
    BENZENE C6H6 BENZENE /
    CHLOROFM CHCL3 CHLOROFM /
    WATER H2O WATER

FLOWSHEET
    BLOCK AZEO-COL IN=MXC6H6 AZEO OUT=ACETONE B1
    BLOCK ENT-CO1 IN=B1 OUT=CLRFORM C6H6RECY
    BLOCK M1 IN=C6H6 OUT=MXC6H6
    BLOCK PREC1 IN=CHL-RICH OUT=PCHLRFOR AZEO

PROPERTIES NRTL
    PROPERTIES NRTL-RK / VANLAAR
```

```
PROP-DATA NRTL-1

STREAM C6H6
    SUBSTREAM MIXED TEMP=68. PRES=1.013529
    MOLE-FLOW BENZENE 75.00

STREAM CHL-RICH
    SUBSTREAM MIXED TEMP=68.33334 PRES=1.013529
    MOLE-FLOW ACETONE 20.00 / CHLOROFM 80.00

STREAM MXC6H6
    SUBSTREAM MIXED TEMP=79.44446 PRES=1.013254
    MOLE-FLOW BENZENE 200.00

BLOCK M1 MIXER
    IN-UNITS ENG

BLOCK AZEO-COL RADFRAC
    PARAM NSTAGE=50 MAXOL=60
    FEEDS MXC6H6 28 / AZEO 28
    PRODUCTS ACETONE 1 L / B1 50 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.0 MOLE-RDV=0 MOLE-RR=12.5920
    DB:F-PARAMS COMPS=ACETONE
    SIZE-DATA COND=YES REB=YES
    PROPERTIES NRTL

BLOCK ENT-CO1 RADFRAC
    PARAM NSTAGE=60
    FEEDS B1 14
    PRODUCTS C6H6RECY 60 L / CLRFORM 1 L
    P-SPEC 1 1.013529
    COL-SPECS D:F=1.00 MOLE-RDV=0 MOLE-RR=44.7748
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES

BLOCK PREC1 RADFRAC
    PARAM NSTAGE=25
    FEEDS CHL-RICH 10
    PRODUCTS PCHLRFOR 1 L / AZEO 25 L
    P-SPEC 1 1.013259
    COL-SPECS D:F=0.50 MOLE-RDV=0.0 MOLE-RR=11.0
    DB:F-PARAMS COMPS=CHLOROFM
    SIZE-DATA COND=YES REB=YES

PROJECT-DATE
    START MONTH=DECEMBER YEAR=1994
```

```
    PURCHASE MONTH=NOVEMBER YEAR=1995
    START-UP MONTH=NOVEMBER YEAR=1996

CBLOCK COND-1 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=TOP

CBLOCK COND-2 HEATX
    SIZING-DATA U=488.2428
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=TOP

CBLOCK CONDP HEATX
    REFERENCE TUBE UTILITY=WATER
    REFERENCE SHELL BLOCK=PREC1 STAGE=TOP

CBLOCK REB-1 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=AZEO-COL STAGE=BOTTOM

CBLOCK REB-2 HEATX
    SIZING-DATA U=732.3642
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=ENT-CO1 STAGE=BOTTOM

CBLOCK REBP HEATX
    REFERENCE TUBE UTILITY=ST-50
    REFERENCE SHELL BLOCK=PREC1 STAGE=BOTTOM

CBLOCK AZEO-COL TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=AZEO-COL

CBLOCK ENT-CO1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=ENT-CO1

CBLOCK PREC1 TRAY-TOWER
    SIZING-DATA
    REFERENCE BLOCK=PREC1

UTILITY WATER WATER
    PROPERTIES STEAM-TA
    COST PRICE=3.52740E-5
    PARAM COMPONENT=WATER TIN=29.44445 TOUT=40.55557
```

```
UTILITY ST-50 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=3.15261E-3 MONTH=NOVEMBER YEAR=1996
    PARAM COMPONENT=WATER PRES=3.447379 TIN=137.9611  &
        TOUT=137.4056

UTILITY ST-100 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=4.29901E-3
    PARAM COMPONENT=WATER PRES=6.894758 TIN=164.0722  &
        TOUT=163.5167

UTILITY ST-300 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.01862E-3
    PARAM COMPONENT=WATER PRES=20.68427 TIN=214.0723  &
        TOUT=213.5167

UTILITY ST-500 STEAM
    PROPERTIES STEAM-TA
    COST PRICE=6.30522E-3
    PARAM COMPONENT=WATER PRES=34.47379 TIN=241.2945  &
        TOUT=240.7389

CONV-OPTIONS
    PARAM SPEC-LOOP=OUTSIDE USER-LOOP=INSIDE

STREAM-REPOR MOLEFLOW MOLEFRAC
```

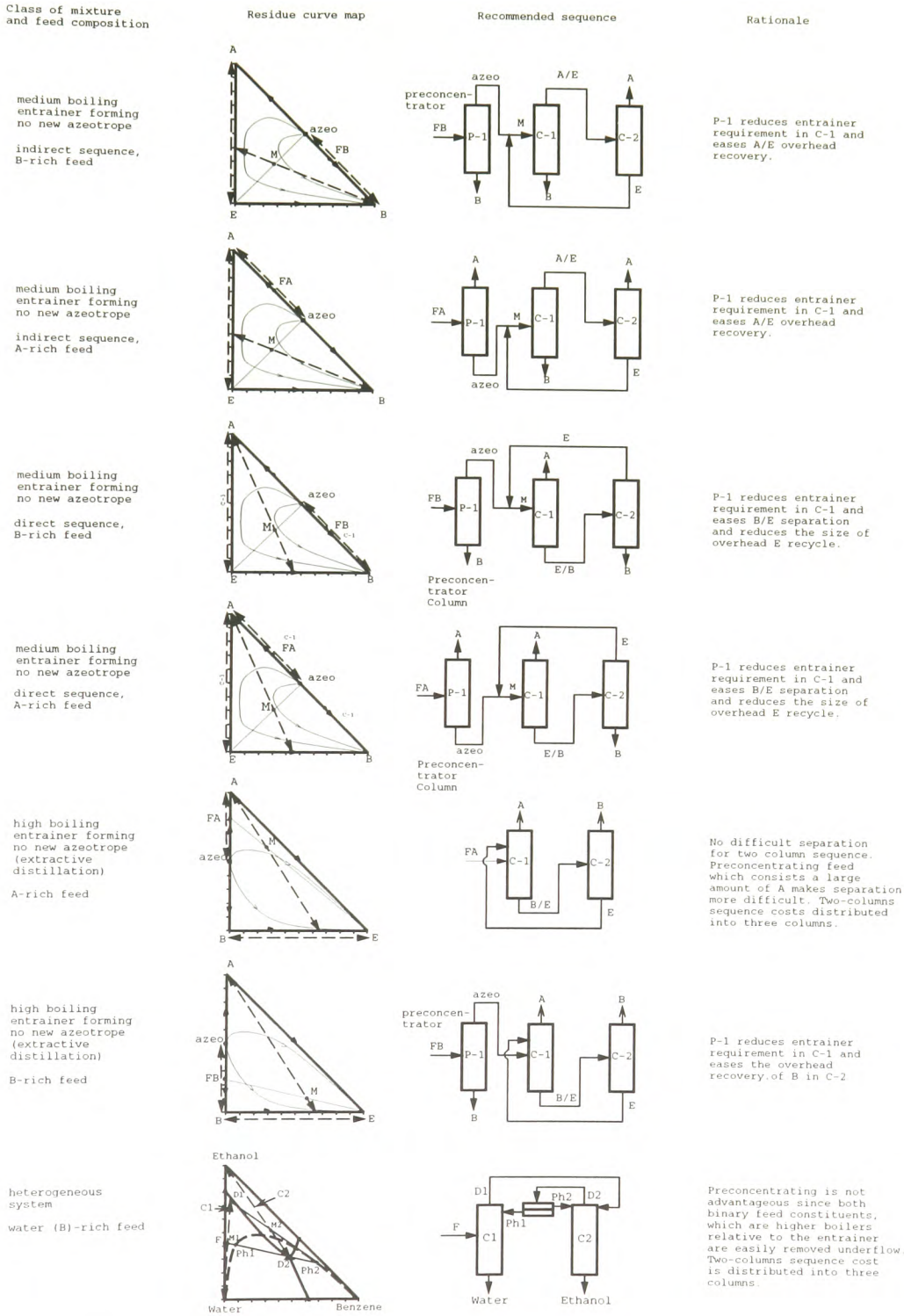


Figure E.2: Decision catalogue for preconcentration for homogeneous azeotropic systems without boundary crossing and for heterogeneous azeotropic systems.

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