Design Of Integrated Batch Processes

by

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To My Parents

Abstract

This thesis presents a framework for the optimal design of integrated batch processes, taking into account equipment design, scheduling and the detailed operating procedure of the individual processing tasks.

A mathematical characterisation of the integrated batch process design problem based on the State-Task Network (STN) process representation is presented. The formulation introduces the concept of a "super-STN" as a superstructure within which a number of process alternatives are embedded. The concept is based on a fully connected set of generic unit operations described by detailed dynamic models. An important characteristic of the approach is that the number of distinct process structure alternatives that need to be considered is relatively small. As a result, a complete enumeration procedure is adopted for determining the optimal structure.

The second key feature of our formulation is that it considers discrete decisions relating to equipment design. Such decisions arise, for instance, in the selection of equipment from a set of standard "off-the-shelf" items, and in determining the number of trays in batch distillation columns.

An algorithm using a two-level approach based on a complete enumeration procedure coupled with an outer approximation/augmented penalty decomposition scheme is proposed for the solution of the resulting complex mixed integer dynamic optimisation problem.

The approach has been used to address a wide variety of batch process design problems that have not been previously explored using detailed dynamic models. One such problem is the determination of the number of trays in batch distillation columns. This involved developing and employing a novel superstructure for the batch distillation column. It is also shown that the algorithm can be applied to the problem of selecting equipment from a set of standard "off-the-shelf" items. Finally, optimal structures and operating policies are determined for two classes of batch process design problems involving reactor networks and reactor-separator networks respectively.

Acknowledgments

I count myself in nothing else so happy
As in a soul remembering my good friends.

Shakespeare (1564 - 1616), Richard II Act ii, sc. 3, I.46

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Chapter 1

Introduction

The growing importance of batch processes for the production of speciality and fine chemicals, polymers, pharmaceuticals and bioproducts is now well recognised (Parakrama, 1985; Stinson, 1993). The flexibility and diversity of batch processes offer distinct advantages over continuous processes, specifically when the market demand is uncertain or changing with time, when small quantities of high value-added products are needed or when several different products are required over a short period of time. The on-going trend towards custom-made rather than commodity chemicals and the increasing cost pressures due to over-capacity problems with high volume continuous plants is likely to increase further the importance of batch processing.

1.1. Batch Process Development

A *process* is defined as a set of physical, chemical and/or biological transformations that convert a set of raw materials to the final products, usually via one or more intermediate materials (Charalambides, 1996). A *batch operation* occurs when inputs are charged to an appropriate unit before the start of a processing step and are discharged from the vessel after the end of the step. A *semi-batch* operation is when at least part of the input is added to the unit during processing, either as a continuous or discrete form; similarly part of the product may also be removed from the unit during the operation.

The goal of batch process development is primarily the design of an efficient process (Allgor *et al.*, 1996). The design of *any* processes is driven by economic factors and is subject to product specifications, facility limitations, safety concerns, environmental regulations and short time horizons.

The currently prevailing market conditions highlight the need for rapid process development. This provides a competitive advantage by facilitating faster market penetration, by exploiting patent protection (especially in the important pharmaceuticals sectors) and by meeting customer expectations. Also, the processes must be efficient. Increasing the economic efficiency of manufacture is necessary to allow companies to compete on a cost basis. Higher efficiencies may lead to an increase in the profit margin or determine whether a test-marketed product is adopted. An efficient process also allows the revenue stream for a product to continue despite competition once a patent has expired; equally importantly, it permits current and expected future environmental regulations to be met. Both of these are growing concerns in the speciality chemical and pharmaceutical industries. All of these factors pose a need for the improvement in the methodologies used for the development and operation of batch processes.

1.2. The Batch Process Design Problem

The batch process design problem consists of several interacting facets that need to be addressed simultaneously. Figure 1.1 highlights some of the most important of these. The interactions among them are discussed in this section.

One is often faced with the problem of designing a large-scale process for a recently created or modified product. Information, such as the properties of the raw materials required, the reaction kinetics, *etc.*, obtained from the original synthesis of the product, is commonly based on experimental procedures and serves only as a starting point since the process is driven by economic factors and constraints that are not considered at the laboratory level. The final products are usually subject to market specifications, for instance, the final concentrations of the main product and impurities. However, the various process operations as well as the intermediates in the process are not so well defined and neither is the precise manner in which each processing step is operated. In other words, the processing steps and the operating policy of these steps are not known *a priori*. Moreover, the interconnections between the tasks are usually not fully explored at the experimental level; this is particularly true regarding possible recycle streams. A further complication in the design problem is that the process is often subject to operational safety constraints (Dimitriadis *et al.*, 1997) and environmental regulations (Linninger *et al.*, 1996; Stefanis *et al.*, 1997; Calderón *et al.*, 1998).

The various batch processing steps are carried out in equipment items, such as reactor vessels, distillation columns, *etc.*, and clearly the characteristics of these units will have a substantial effect on the operating policy for the corresponding processing step. For example,

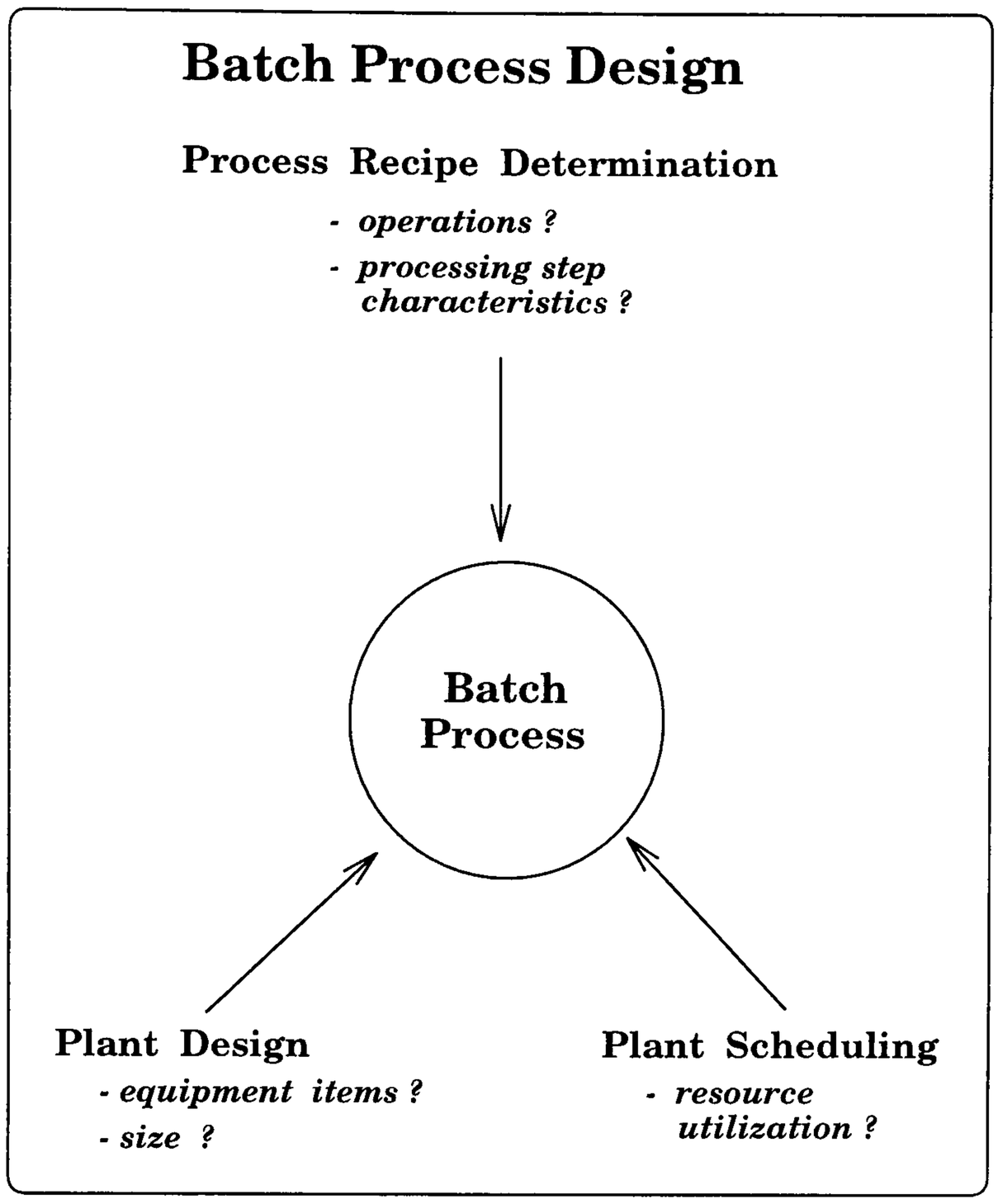


Figure 1.1: Batch process design problem

the initial charge for a batch distillation column must not exceed the capacity of the reboiler.

For the reasons mentioned in the previous section, it is often the case that a new process has to be implemented in an existing plant. In such cases, there is a selection of equipment items that are available in certain standard sizes, so the physical characteristics of the processing units are given, but one still has to determine which equipment items to use from the inventory, and also determine the operating policy for each processing step and the nature of the materials in the process as well as the overall process topology.

In addition to the operating units, most processes require the use of utilities such as steam, cooling water, electricity, *etc.*, the precise requirements of which must also be determined. In some cases, there will be restrictions on the availability of the utilities as well as environmental constraints, for instance, the temperature of the cooling water leaving a heat exchanger should not exceed a maximum temperature. Plants will also require auxiliary hardware, such as storage units, pipes, pumps, conveyor belts and other transport facilities.

Another problem that has be considered is *scheduling* the plant operation over a given time

horizon. This involves the determination of the number, size and timing of the batches of material undergoing each processing step so as to achieve the required production targets and maximise the economic returns arising from production. The complications of this problem are due to the interactions between successive processing steps in terms of the overall material balance and the detailed timing considerations. Also, activities overlapping in time will place restrictions on shared resources, such as multipurpose equipment items, utilities and input materials.

There are also strong interactions between production scheduling and the operating policy of individual processing steps. Incorporating the operating policy in the overall design exploits the trade-offs that exist between processing time and intensity of processing, and the effects of the quality of the intermediate materials on the operation of downstream processing steps.

One further complication that escalates the degree of complexity of the design problem is the presence of uncertainty. Uncertainty in the data, such as the composition of raw materials or reaction kinetics, is often neglected in the design of the process (see Terwiesch *et al.*, 1994; Walsh *et al.*, 1995). Uncertainty is also present in market demands (Subrahmanyam *et al.*, 1994; Ierapetritou and Pistikopoulos, 1995; Petkov and Maranas, 1998) and there is always the risk of equipment failure (Sanmartí *et al.*, 1997; Vassiliadis and Pistikopoulos, 1998). Neglecting the issues of uncertainty leads to the "ill-definedness" (Rippin, 1991) of the batch optimisation problem. Hence, robustness is an important issue that needs to be addressed (Uesbeck *et al.*, 1998). Consider, for example, a batch distillation unit operating with an "optimal" policy which was determined by the optimisation of the nominal model and then subject to an uncertain initial charge composition. The presence of this uncertainty will affect the objective function, the purity specification, the overall behaviour of the column, *etc.* A robust operating policy is one that when faced with uncertainty, the constraint violations (*e.g.* purity, temperature rise, *etc.*) as well as batch-to-batch variability will be minimal.

1.3. Batch Process Modelling

Several techniques are available to analyse the different aspects of batch design problems. For example, batch process development typically involves the extensive use of laboratory scale experiments and test runs in pilot plants. However, this is a very time consuming and expensive process. Therefore, over the past few years, there has been a rapid increase in the use of simulators together with dynamic optimisation techniques (Barton and Park, 1997). However, the use of simple mathematical models to reflect the complex aspects of batch processes is the major shortfall of the current batch process design techniques. Batch

processes are characterised by their inherently time-dependent behaviour which, together with the numerous combinations of process alternatives in the design, results in a complex combinatorial problem. Thus, most of the research involves solving a simplified version of the problem. These simplifications result in solutions which are suboptimal — the modelling activity generates at best a feasible solution rather than a "true" optimal solution; at worst, the use of simplified models results in "solutions" that actually violate important process constraints.

An optimal design for an integrated batch process involves production planning and scheduling, equipment selection and sizing for the plant construction, determination of operating policies of the individual processing steps, and the treatment of uncertainty in these tasks, all of which are subject to constraints, for instance, limited number of equipment items available, limited capacity, purity specifications, *etc.* All these factors should, in theory, be addressed simultaneously; however, this is practically impossible to achieve with the mathematical algorithms and the computer hardware that are currently available. Most of the research is, therefore, dedicated to solving particular aspects of the problem, mainly production scheduling and equipment selection (Barbosa-Póvoa, 1994; Shah, 1998), and optimal process operation under uncertainty (Terwiesch, 1994; Ruppen *et al.*, 1995).

1.4. Objectives of this Work

From the previous section, it is clear that there is a need to develop a systematic methodology to solve the batch process design problem. Although the importance of incorporating uncertainty in the design of batch processes is evident, nonetheless, we feel that it is more imperative to first develop efficient techniques to address all the aspects of a *deterministic* batch process model before we even attempt to incorporate uncertainty into the design problem. Therefore, this thesis is primarily concerned with establishing a comprehensive framework for batch process design in which the optimal structure of the process, and the detailed design and operating conditions of the individual processing tasks can be determined simultaneously.

This work will pay particular attention to the handling of discrete decisions in the batch process design problem, which makes it possible to address a wide variety of important problems that have not been previously explored using detailed dynamic models. In particular, we consider discrete decisions relating to:

(i) *Equipment design*: Here, the process structure is fixed *a priori* but the operating policies for the individual processing steps are unknown. The discrete decisions

that need to be taken are usually related to the design of the equipment items, *e.g.* the determination of the optimal number of trays in batch distillation columns and the selection of "off-the-shelf" equipment items available in standard sizes for batch process design.

(ii) *Process structure*: This problem considers the determination of the optimal structure for a batch process required to produce a set of products from a set of raw materials using a set of potential unit operations — in other words determining the process topology.

The structure of the thesis is outlined as follows:

- Chapter 2 provides a critical literature review of earlier work on the design of integrated batch processes. The main emphasis is placed on work that has considered the details of the operation of the individual processing steps as a part of the decisions that have to be made.

- Chapter 3 is concerned with the mathematical characterisation of the integrated batch process design problem based on the State-Task Network (STN) process representation. The formulation presented allows the determination of the optimal process structure embedded within a given superstructure, as well as the detailed design and operating policies for the individual processing equipment items. A two-level algorithm for the solution of this complex mixed integer dynamic optimisation problem is proposed.

- Chapter 4 considers the application of our algorithm to the design of networks of multicomponent batch distillation columns. The structure of these networks is fixed. The number of trays in each column is treated as an integer-valued design decision. Three examples are presented to illustrate the performance of the algorithm.

- Chapter 5 applies the algorithm to the design of networks of batch reaction-separation devices. The structure of these networks is fixed *a priori*, but the equipment items under consideration are available only in certain standard sizes.

- Chapter 6 considers the issue of establishing appropriate superstructures for the determination of optimal process structures within the framework of Chapter 3. It is shown that a methodology that was recently proposed by Smith (1996) for the design of continuous processes can be extended to batch process design. The main advantage of this approach is the automatic generation of general superstructures that involve only a relatively small number of discrete alternatives.

- Chapters 7 and 8 apply the ideas of Chapter 6 to the design of batch reaction networks and reaction-separation networks respectively.

- Finally, Chapter 9 summarises the contributions of this work to the area of integrated batch design and highlights some areas for future research in this field.

Chapter 2

Literature Review

This chapter presents a critical review of earlier work on the design of integrated batch processes. The main emphasis is placed on work that has considered the optimal design of batch processes involving multiple processing steps.

2.1. Introduction

The development of design methodologies for batch processes has been a subject of extensive research over the past several years. Most of the research deals with specific areas relating to batch processes. In particular, almost all studies deal either with the problem of planning and scheduling the operation of a given plant, or with the design of a plant to implement a given process recipe. Comprehensive reviews of these areas have recently been presented by Reklaitis (1989, 1992), Barbosa-Póvoa (1994), Papageorgiou (1994) and Shah (1998).

The following section reviews earlier work on the optimal design of batch processes with particular emphasis on research that has considered the details of the operation of individual processing steps as part of the decisions that have to made — this is our main area of interest.

2.2. Optimal Design of Batch Processes

There is now a substantial amount of literature available on the optimal design of batch processes, especially in the area of plant planning and scheduling as well as the operation of

individual batch units. However, relatively little has been done to address the issues associated with the design of integrated batch process involving *multiple* processing steps. The transient nature and the dimensionality of multistep batch processes result in a complex combinatorial problem. Most of the existing batch process design techniques rely on simple mathematical models to describe what is essentially a complex process. Two approaches that are commonly used are:

1. Use *simple* models which take account of the combined continuous and discrete nature of the problem; the dynamic nature of the problem is simplified by using algebraic models. These techniques usually do not represent in detail the dynamic nature of the problem.

2. Use *detailed* dynamic models but simplify the problem by relaxing the discrete decisions and treating them as continuous variables.

In section 2.2.1, we will review the work based on the first approach. The second approach is reviewed in section 2.2.2.

2.2.1. Optimisation of Batch Processes Using Non-Dynamic Models

2.2.1.1. The Work of Iribarren and Co-workers

Iribarren (1985) adopted a hierarchical decomposition approach to cope with the large number of decision variables involved in designing batch processes. The nature of each processing stage, the intermediate storage provisions, the duplication of the equipment items and the merging of stages were among the decisions that were tackled in the design of multiproduct batch plants. The operational behaviour of each stage was described in terms of simple algebraic (posynomial) design equations that relate the conversion achieved to the size factors and the cycle time of the stage. Equations that relate capital costs to key design variables were also included. The determination of the nature of each processing step and the possibility of merging conformable stages were the first steps in the hierarchical procedure. The total annualised capital cost was used as criterion to compare the various alternatives. Dynamic simulation was used in the final step of the design procedure to compare the most promising design alternatives. Iribarren *et al.* (1994) proposed a systematic way of generating the various alternatives using heuristic rules during the search procedure. The rules favoured the merging of consecutive stages, stages with similar size factors and merging of stages that yield a cycle time that is smaller than the limiting one.

The effect of process variables on the design of single product batch plants with fixed structural decisions was considered by Salomone and Iribarren (1992). A posynomial model was proposed that was later generalised to take into account batch intensive, semi-continuous and batch extensive processing steps (Salomone *et al.*, 1994). The distinction between the three types of processing steps was based on the effect of intensive properties (*e.g.* temperature, pressure) and inlet batch size on processing time and equipment volume. The authors argued that the posynomial models provide a process description of a level of complexity that is appropriate for the purposes of batch process synthesis. The detail offered by considering more rigorous models was considered to be undesirable at this stage due to the increased problem size, computational requirements and the present status of process optimisation techniques. They suggested that the process of optimisation should and could be applied *only* to the refinement of the design of individual units. Montagna *et al.* (1994) developed this work further by considering the multiproduct case.

More recently, Chiotti *et al.* (1996) considered the development of an approach for the design of batch chemical plants with adaptive operating policies to cope with varying parameters such as the kinetics of crystallisation and filtration, fouling of heat exchanger surfaces, catalyst deactivation, seasonal sea water temperature variations, *etc.* The operation of the plant was divided into periods, with the parameters being constant over each period. The unit size was taken to be a hard constraint (*i.e.* one that must never be violated), whilst the production demands were soft constraints (*i.e.* they can be relaxed). The key factor influencing the complexity of the model is the number of periods into which the varying parameters are discretised. The number of periods was a design decision that traded off the degree of adaptation to varying parameters against the complexity of the plant operation schedule.

2.2.1.2. The Work of Barrera

Barrera (1990) considered process performance issues and equipment sizing decisions in an optimisation framework. The optimisation consisted of selecting the equipment units to be used at each stage of the process and choosing the operating conditions and operating times in order to optimise a suitable objective function. The process recipe was fixed.

The objective function used was the minimisation of the total manufacturing cost including raw materials, energy, *etc.*, as well as a fixed allocated cost of capital. Barrera used algebraic equations to describe the behaviour of the individual batch processing units. This may be inaccurate for some transient processes. The problem was formulated as a Mixed Integer Non-

Linear Programming (MINLP) which was solved using a decomposition strategy. The set of the decisions was divided between two simpler subproblems : a "performance" subproblem and a "structure" subproblem.

The *Performance Subproblem* involved the optimisation of operating conditions and times for a process with fixed equipment. A sequential simulation approach was adopted to model the process. The key input variables such as unit sizes and operation times were specified for each unit. By supplying the initial conditions, the calculations flowed from the first unit through each successive unit. After determining the process performance for a given set of key input variables, the total manufacturing cost was calculated. The problem was formulated as a Non-Linear Programming problem (NLP) and was solved using a Successive Quadratic Programming (SQP) algorithm. Derivatives of the objective function and the constraints with respect to the decision variables were calculated numerically by finite differences. Multiple starting points were used in an attempt to obtain a global optimum, but if the nature of the problem is non-convex, no guarantee of global optimality can be made.

The *Structure Subproblem* involved the assignment of equipment units to stage locations for a fixed process performance to minimise total manufacturing charges. The number and sizes of all equipment items available for the process was known. The problem was formulated as a MINLP problem and was solved using the Outer Approximation/Equality Relaxation (OA/ER) method. However, to avoid potentially large solution times, an approximate method was adopted based on local search techniques. The approximate method required less computational time and generated near optimal solutions.

Two types of decomposition strategy were investigated. The first was to embed the performance subproblem inside the structure (SOPI); in the second, the structure subproblem was nested inside the performance shell (POSI). Figure 2.1 shows the steps involved in the two strategies.

The testing criteria in comparing the two nesting strategies were:

- the closeness of the solution to the global optimum value,
- the computational effort required in terms of the number of simulations,
- the quality and availability of the methods for solving each nesting strategy.

Investigations showed that the SOPI method was favoured in terms of expected solution quality but a large computational time was required to solve the complex performance sub-

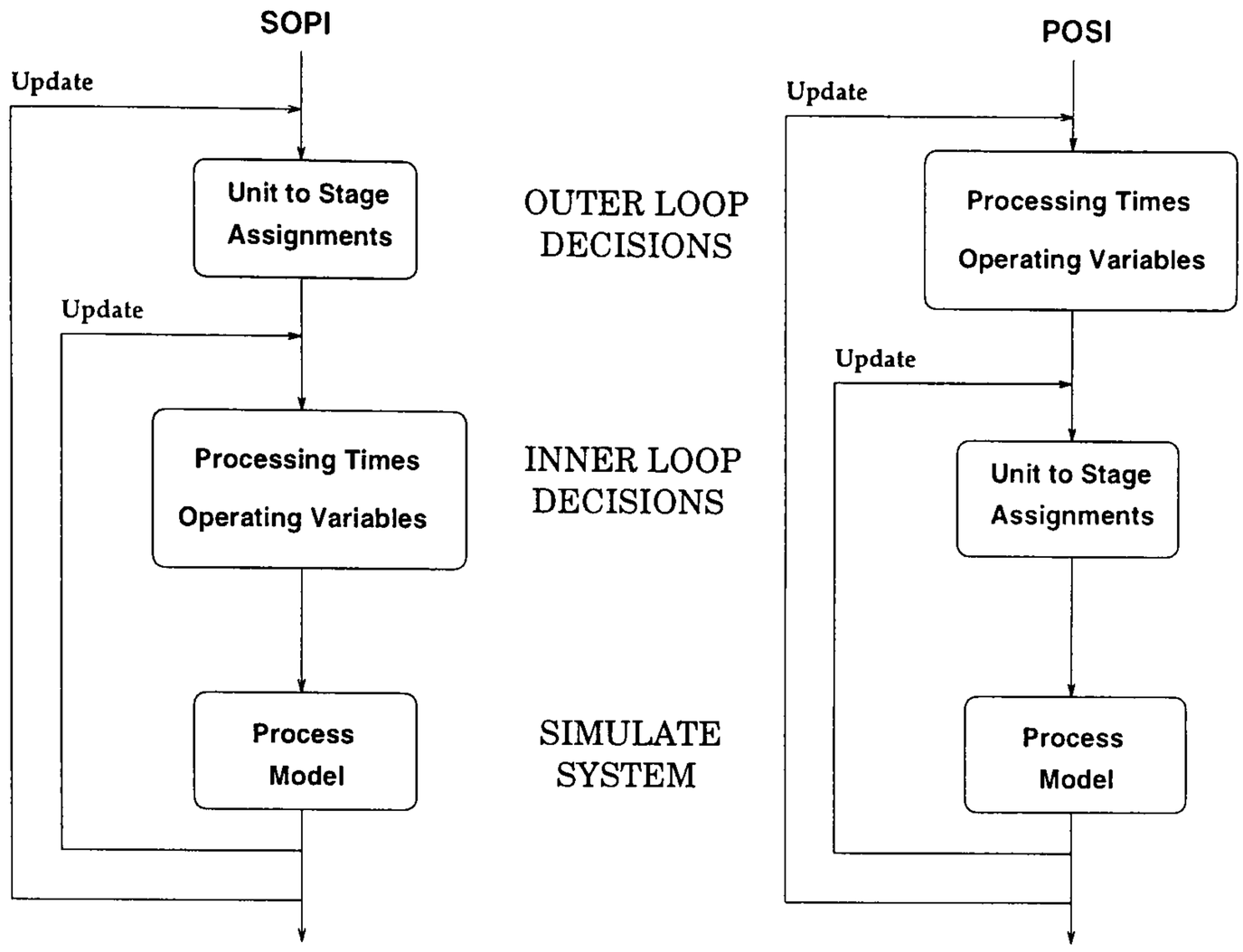


Figure 2.1: SOPI and POSI nesting strategies (Barrera, 1990)

problem for each structural alternative. On the other hand, the POSI method was fast but its solution accuracy was unclear, particularly for large problems.

2.2.1.3. The Work of Tricoire and Malone

The development of flexible procedures based on a simulated annealing algorithm to provide a global treatment of scheduling, design, synthesis and retrofit of multi-product batch plants was considered by Tricoire (1992). In this study, scheduling was addressed in a preliminary design context, where the emphasis was based on the global flowsheet structure and the most expensive equipment items.

Tricoire (1992) defined a scheduling problem as a combination of the following four aspects:

- The production requirements: these are generated by customer orders or stock replenishment decisions.
- The scheduling objective: for example, the minimisation of lateness or earliness, inventory levels, make-span time, *etc.*
- The plant configuration: there are numerous plant configurations of increasing complexity such as the single stage of one unit, the flowshop, the network flowshop, the single

stage of parallel units and the multipurpose plant.

- The transfer mode: this deals with the storage capacity and the maximum holding times between consecutive stages.

The problem of designing multiproduct batch processes was defined as follows:

Given:

- Demand Patterns: product slate, production requirements, due dates, uncertainties.
- Process specification for each product: sequence of processing tasks to proceed from raw materials to final products and a list of the possible types of equipment to perform these tasks.

Determine:

- The best type of equipment to perform each task.
- The batch times and operating conditions for each task.
- The equipment network: parallel units in or out of phase, location of intermediate storage, merging and splitting of tasks in units and interactions between different production lines.
- The scheduling and planning of the production.
- The equipment sizes.

The production of chain growth polymers was investigated to identify the sequence of tasks that were needed to obtain the final products from the raw materials, to list the possible types of units to perform these tasks and to isolate important design variables. A hierarchical approach based on heuristics and simple simulation was used to develop simple single-product plant designs.

Due to the difficulty of optimising all of the operating conditions, only variables which have a significant impact on the global design were examined. Global variables such as conversion were incorporated in the design optimisation. Tricoire and Malone (1992) argued that considering all of the possible operating variables will result in a highly complex and computationally demanding problem. Hence, variables such as the temperature profile of the

reactor were considered as local, having an impact on the reactor performance only. Although the reactor itself has an impact on the overall design, it was argued that this impact was adequately represented only in terms of batch size, batch time and the initial and final batch compositions. Conversion was found to be the most important design variable and accordingly the sizing factors and batch times were correlated with conversion. Batch times and batch sizes were obtained from kinetic data, physical properties and process specifications. When the kinetics were not exactly known, the operating conditions were determined empirically from pilot plant experiments.

The economic objective for the optimisation was a cost function which included labour, changeover, capital, operating and recycle. Shortage penalties and inventory costs were included in the objective function only when the due dates and inventory costs were significant. However, if none of the above items were significant, the objective was altered to improve productivity through reduced production time by minimising make-span.

Multi-product plant structures were optimised by first finding the optimal structure for each individual product and then attempting to find the overall optimal structure of the plant by optimising all of the individual optimal product structures.

2.2.1.4. The Work of Xia and Macchietto

Xia and Macchietto (1997) presented a stochastic based solution methodology where the structural aspects of very general batch plants and the associated production schedules were optimised simultaneously. Simple models were used to describe the behaviour of the processing tasks. The design variables included the existence of the storage vessels and the capacities of the processing units, storage vessels and utilities. The main operation variables included the time of event, the operation sequence of the tasks in the units, the batch sizes, the utility requirements of the tasks, the starting time of each task, the material in a particular storage at the time of event, and the start and finish times of each processing task.

The non-convex mixed integer non-linear programming problems was solved by the **EASY** method which is a stochastic optimiser based on an Evolutionary Algorithm (EA) with Simulated Annealing (SA). The main advantage of this stochastic technique is that it is a global search method where no gradient information is required. The method is based on a guided stochastic generation of alternative "vectors" of the decision variables which explore all regions of the search space, and exponentially exploit promising areas through selection, crossover,

and mutation operations applied to individual solution candidates. In principle, it can be used to deal with non-convex, non-differentiable and multiple local optima function optimisation problems. However, the solution optimality of the stochastic technique is not guaranteed within a finite computing time. Two examples were used to demonstrate and test the applicability and the features of the design procedure. The dynamic nature of each of the processing tasks was not considered and, therefore, the operating policy of each task was not determined in detail.

2.2.2. Optimisation of Batch Processes Using Dynamic Models

2.2.2.1. The Work of Barton and Ahmad

Barton and Ahmad (1995) considered the challenges posed by pollution prevention caused by the use of solvents in the bulk synthesis operations characteristic of the pharmaceutical and speciality chemical industries. Increasingly, restrictive legislation and growing concern over environmental impacts are forcing chemical manufacturers to reassess their use of solvents. The traditional use of end-of-pipe control alone will not be acceptable. Current environmental legislation is mainly focused on continuous processing and dedicated batch manufacturing, and does not fully recognise the unique problems faced by the flexible batch manufacturers. For example, closed loop recycling is usually infeasible for batch systems. According to the authors, a more appropriate objective for pollution prevention in multi-product batch facilities would be the task of integrating source reduction and recovery of materials in such a way that any waste treatment or disposal is made redundant.

Some of the features of batch processes that influence emissions levels are:

- the chemistry including the choice of solvents, reagents and catalysts,
- the task network (or recipe),
- operating policies.

Ideally, all of these aspects should be considered simultaneously. In order to reduce the complexity, the authors considered only the latter two aspects, with special emphasis on how to improve solvent recovery and recycling within a manufacturing facility. A prototype technology was proposed involving the following steps:

1. Rigorous dynamic models and/or plant data were used to predict the compositions and magnitude of waste-solvent streams.

2. Recent research results from the analysis of residue curve maps were exploited and extended to target for the maximum feasible recovery when using batch distillation.

3. The information was then used to suggest design modifications. The new design was then modified for further improvements, returning to step 2 if necessary.

The proposed methodology was applied to a batch distillation for the rapid automated prediction of the product sequence and maximum feasible recovery in each product.

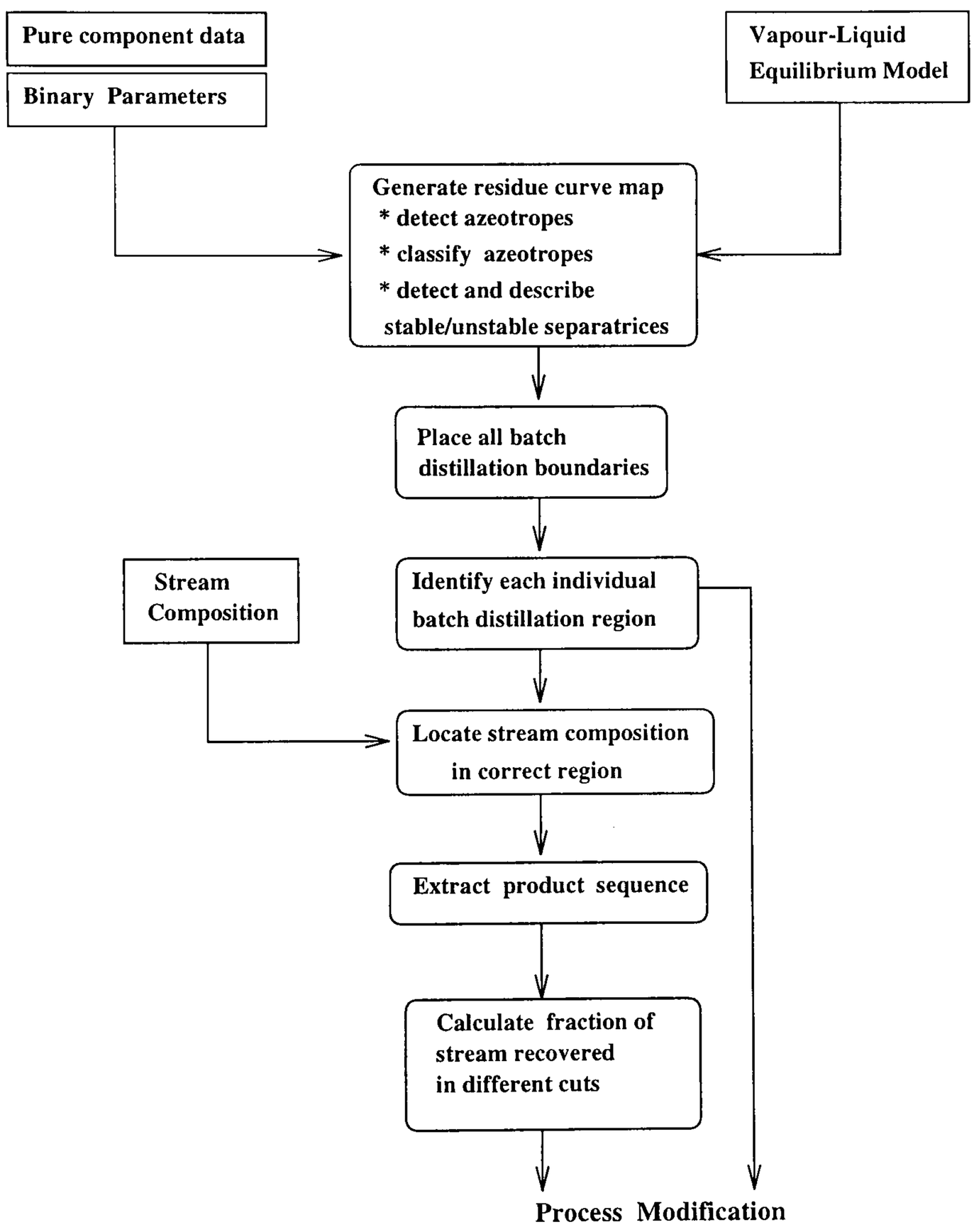


Figure 2.2: Batch distillation solvent recovery targeting (Barton and Ahmad, 1995)

An outline of the technique is presented in figure 2.2. The approach which was applied to an

industrial case study, reflected a significant reduction in emission levels by simply integrating recovery and recycling of solvent as part of the process flowsheet. Although residue curve maps can be derived for any number of components, their graphical representation becomes increasingly difficult as the number of components increases. For systems with more than four components, there is no straightforward way of studying the separation behaviour of a mixture.

2.2.2.2. The Work of Bhatia and Biegler

Bhatia and Biegler (1996) considered incorporating dynamic processing conditions for products in a multi-product batch plant, in the broader context of equipment design, production planning, scheduling and inventory considerations. This extended previous work in that the process recipe was no longer fixed. The objective used was a general function of fixed design costs, operating costs, production revenues, *etc.* The decision variables included:

- *Processing:*
  - optimal stage operations,
  - state and control variable profiles,
  - stage processing times,
  - final batch state at each production stage.
- *Design:*
  - continuous equipment sizes,
  - continuous design parameters.
- *Production Planning:*
  - production capacity,
  - batch sizes and number of batches.
- *Scheduling:*
  - production span or cycle time,
  - production sequence.

The mathematical formulation proposed was an infinite dimensional optimal control problem which was solved for each operation using collocation over finite time elements. To simplify the scheduling problem, only a special class of batch problems was addressed. These included flowshop plants with unlimited intermediate storage (UIS) and zero wait (ZW) transfer policies and with one unit per stage. The work focused on the trade-offs between equipment and batch size decisions versus production span for a limited class of batch operations. It also involved various simplifications; for instance, all the integer variables (*e.g.* the number of column trays, batches, *etc.*) were either fixed or treated as continuous. The approach was illustrated by its application to a three-stage process where only one of the stages was considered to be transient and a four-stage recipe where only two of the stages were modelled dynamically; the operation of the other stages was fixed. Therefore, the solutions provided do not always represent a realistic picture of the complexity of the problems associated with the modelling of batch processes.

Incorporating processing decisions adequately requires sufficiently accurate non-linear process models and methods that deal with process model uncertainty. Recently, the above approach was extended (Bhatia and Biegler, 1997) to address dynamic processing and planning decisions for multiproduct batch plants, with uncertainty in process parameters. Instances of uncertain parameters were used to construct planning scenarios that were handled using a multiperiod formulation. In addition, dynamic processing under uncertainty was addressed via a closed loop state feedback correction strategy. Furthermore, to provide an implementation advantage, parameters in the feedback law were determined in an open loop manner, as design variables that remain invariant across the scenarios in the multiperiod formulation. The main drawback with this approach is the explosive growth in the problem size as the number of periods increases.

2.2.2.3. The Work of Charalambides

The integrated design of general batch processes using detailed dynamic models to describe the behaviour of individual batch operations was considered by Charalambides (1996). The study showed that the State-Task Network (STN) representation which was originally introduced for the development of the general plant scheduling formulations (Kondili *et al.*, 1993), also provides a natural framework for the complete characterisation of the process recipes for the batch systems. By representing the design of integrated batch processes as a STN structure, the formulation of the design problem for processes of arbitrary complexity (*e.g.* those with material recycles) was simplified.

The mathematical formulation regarded both the design (*e.g.* equipment capacities) and the operational characteristics (*e.g.* control variable profiles) of each task as degrees of freedom, the values of which were selected to optimise a particular objective function. The solution may be restricted by inequality constraints which hold throughout the task (*e.g.* upper bounds on temperature), or at the end of the task (*e.g.* end-product purity specification). The mathematical formulation took only limited account of plant scheduling considerations, essentially ensuring that the aggregate production capacity of the processing equipment was not exceeded. The formulation was applicable to processes with both mixed unlimited intermediate storage and zero-wait storage policies.

A number of examples presented by Charalambides (1996) highlighted the fact that it is both desirable and feasible to consider a dynamic optimisation framework for the optimal design of batch processes. The examples included processes involving both single and multiple processing steps, multiple recycles of material, plant operation subject to limited availability of utilities as well as multiple purpose equipment items.

Despite its relative generality, this algorithm assumed that the number, nature and interconnections of the individual tasks are known *a priori*. Moreover, the approach can not deal with discrete decisions such as the number of trays in a distillation column.

2.3. Conclusions

This chapter has summarised some of the important recent work in the field of batch processes that is of particular interest to this project. Most of this work deals individually with the three main areas of planning and scheduling, optimal operation of individual processing steps and plant design. However, to obtain a *truly* optimal design, one must address the three areas simultaneously. This is by no means a trivial task. It is this challenge, together with the potential economic benefits of batch processes, that provide the motivation for the current research in the field of batch process design.

A summary of the literature reviewed in this chapter is shown in table 2.1. It can be seen that all the papers reviewed made at least one of the following assumptions:

- Process structures were fixed a priori.
- Simple algebraic models were used to describe process operations.

Chapter 3

Mathematical Formulation of the Integrated Batch Process Design Problem

In this chapter, we present a mathematical characterisation of the integrated batch process design problem. A two-level algorithm for the solution of the resulting complex mixed integer dynamic optimisation problem is proposed.

3.1. Introduction

The design of integrated batch processes generally involves the determination of the network of processing tasks required to convert a set of raw materials into a set of products. It also involves the determination of the nature of all intermediate materials, and a suitable operating policy for each individual task.

An assumption common to all the studies reviewed in Chapter 2 is that the process recipe is fixed and known *a priori*. This means that the structure of the processing network is predetermined, as are the precise characteristics of the individual processing tasks. For some batch processes (*e.g.* those involving complex biological transformations), such simplifying assumptions are necessary since many of the processing tasks involved are poorly understood, and the need for reproducible quality of the final products implies that the operating strategy must be kept as close as possible to that determined by experience. However, many other processes involve standard unit operations for which detailed and relatively accurate models *are* available. It is possible in such cases, to consider the use of such models for the design of the process itself.

Another aspect of the batch design problem that has received only limited attention is that related to the handling of discrete decisions at the equipment design level. This includes, for instance, considering the use of "off-the-shelf" equipment items available in certain standard sizes, or finding the optimal number of trays in distillation columns. One approach (reviewed in section 2.2.1) is to use simple models which combine both the continuous and discrete nature of the problem. However, these models are, generally, not detailed enough to reflect the dynamic nature of the problem accurately. Another approach (see section 2.2.2) is to use detailed dynamic models and simplify the problem by relaxing the discrete decisions and treating them as continuous variables allowed to vary within appropriate ranges. This methodology, clearly, does not fully capture the discrete nature of the problem.

Kondili *et al.* (1993) have shown that the conventional process flowsheet diagram (PFD) may lead to ambiguous representations when applied to complex batch process recipes. They, therefore, proposed the general State-Task Network (STN) process representation for batch chemical processes. The digraph representation distinguishes two types of node, namely tasks and states, corresponding to the processing operations and the different types of material respectively. Each task transforms one or more input states into one or more output states.

The authors were mainly concerned with scheduling the operation of a *fixed* plant implementing a *fixed* recipe. They used a simple mathematical model to describe the transformations taking place, expressed in terms of:

- The fixed processing time of the task.
- The total resource amounts required for carrying out a single batch of the task. The resources included utilities (*e.g.* cooling water, steam, *etc.*) and raw materials. The amounts required were expressed as simple linear functions of the batchsize.
- The proportion of the batchsize transformed into each output state, and the relative time of its production with respect to the start of the task.

In our work, we will also use the State-Task Network (STN) representation for the mathematical characterisation of batch processes. However, in contrast to the simple characterisation of tasks and states adopted by Kondili *et al.* (1993), we will employ detailed models to describe the behaviour of the processing tasks. Our characterisation is similar to that presented by Charalambides *et al.* (1995) who were primarily concerned with the process design stage where neither the processing times, nor the detailed operating policy of each task are known. However, in their work, they assumed that the structure (*i.e.* the set of nodes and

arcs) of the STN representing the process under consideration was given, in other words, the process recipe structure was *fixed.* Furthermore, they did not address the issues related to the handling of discrete decisions in the batch design problem.

In the rest of this chapter, we will review the mathematical characterisation of the tasks and the states as well as the interactions between them as proposed by Charalambides (1996). We will also formally present a general mathematical formulation for the design of integrated batch processes where both the structure and the operating policy of the process are to be determined simultaneously. The structure of the process recipe will not, therefore, be specified *a priori.* Moreover, the design of individual equipment items may involve discrete decisions.

3.2. Definition of a State

Each state s corresponds to a different material and is characterised by a vector of intensive properties z_s which may include its composition, temperature, pressure, particle size distribution, *etc.* Commercial (*e.g.* product purity) and/or safety (*e.g.* stability of intermediates) considerations often restrict the properties z_s to lie within specified bounds:

$$z_s^{min} \leq z_s \leq z_s^{max} \quad \forall \ s \tag{3.1}$$

It is also possible to have specifications on derived properties of a state (*e.g.* pH, colour, *etc.*) that depend on the variables z_s. These are usually formulated as more general constraints of the form:

$$C_s(z_s) \leq 0 \quad \forall \ s \tag{3.2}$$

3.3. Definition of a Task

A task is defined as a processing operation which transforms material from one or more input states to one or more output states. The behaviour of most processing operations (such as reaction, distillation, filtration) used in typical batch processes is described by mixed sets of differential and algebraic equations (DAEs) which generally represent the fundamental laws of conservation of mass and energy and any associated equations such as phase equilibrium relations and the definition of the relevant thermodynamic properties and reaction rates. Certain batch/semi-batch unit operations (*e.g.* chromatographic separations) involve properties varying with respect to both time and spatial position. The models describing the behaviour of such tasks consist of partial differential and algebraic equations (PDAEs). In such cases, it

is usually possible to reduce these to DAE models by discretising the spatial variations (see, for example, Samsatli, 1997).

A batch process design will typically consider a set $\mathcal{T}$ of candidate tasks that may be employed in the process. The mathematical model for each task $i \in \mathcal{T}$ takes the general form:

$$f_i(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.3}$$

where t_i^f is the processing time of the task, $x_i(t)$ and $\dot{x}_i(t)$ represent the variables describing the task behaviour and their time derivatives respectively, and $\kappa_i(t)$ represent the algebraic variables. The variables $u_i(t)$ denote the control variables (such as reflux ratios, steam flowrates, *etc.*), *i.e.* manipulations that can be applied to the task by some external agent (*e.g.* a human operator or an automatic control system); all of these typically vary over time. On the other hand, v_i are time invariant parameters. These are also at the disposal of some external agent (*e.g.* the process designer); however, unlike control variables, they are not functions of time. Examples include the sizes of equipment items and the (initial) charges of material into batch equipment.

The mathematical models of some of the tasks considered in this thesis may also involve discrete (*i.e.* binary or general integer) decisions y_i. Some examples include:

- Models of batch distillation in which the number of stages is not fixed *a priori* (*cf.* Chapter 4). In this case, the variables y_i characterise the tray to which the reflux stream is returned to the column and thus, indirectly, the actual number of trays in it.

- Models of equipment which are available only in a finite set of standard sizes. In this case, the variables y_i determine which of these options will be selected for the actual design, thereby specifying the size of the equipment; as we have seen already, the latter is typically one of the time invariant parameters v_i.

Generally, the discrete design decisions y_i are related to each other and to the continuous design decisions v_i via equality constraints of the form:

$$\mathcal{H}(v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T} \tag{3.4}$$

We will see examples of such constraints in Chapters 4 and 5.

In addition to the fundamental equations that describe the behaviour of the process, the operation of the task itself may be subject to safety considerations. For instance, the temperature of exothermic reactors is usually restricted not to exceed an upper limit so as

to prevent thermal runaway. These constraints must be enforced at *all* times during the processing of task i and take the general form:

$$h_i(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) \leq 0 \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.5}$$

Other considerations may result in point equality and/or inequality constraints which must be enforced only at a *finite* set of times $\{t_{i\omega}, \omega = 1, 2, \ldots\}$. Often, these constraints pertain to the final condition of the task (*end-point* constraints), in other words they are expected to hold at time t_i^f. For instance, the final conversion or selectivity of a reaction task may be restricted in order to avoid undesirable side reactions. These constraints are of the following form:

$$g_{i\omega}^{e}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), u_i(t_{i\omega}), v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \tag{3.6}$$

$$g_{i\omega}^{ie}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), u_i(t_{i\omega}), v_i, y_i) \leq 0 \quad \forall\ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \tag{3.7}$$

There are also bounds on the time invariant parameters; for example, in a reaction task, the reactor capacity is bounded not to exceed the upper and lower limits.

$$v_i^{min} \leq v_i \leq v_i^{max} \quad \forall\ i \in \mathcal{T} \tag{3.8}$$

Similarly, the control variables are also bounded. The corresponding bounds may be functions of the design parameters v_i and y_i; for instance, the cooling water flowrate in the condenser of a distillation column will depend upon pump and pipework details:

$$u_i^{min}(v_i, y_i) \leq u_i(t) \leq u_i^{max}(v_i, y_i) \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.9}$$

3.4. State-Task Interactions

We now proceed to characterise the interactions between a task and its input and output states. Consider task i shown in figure 3.1. The set of states S_i^{IN} are those consumed by the task and the set of states S_i^{OUT} are those produced by the task.

3.4.1. Input State

In figure 3.1, the total amount of state $s \in S_i^{IN}$ consumed by task i during its operation is denoted by B_{is}^{IN}. The latter may comprise a discrete amount B_{is}^{d} which is added as an initial

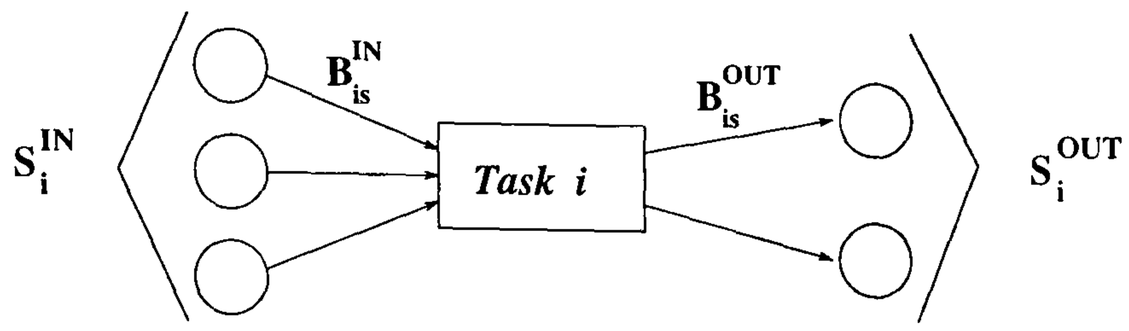


Figure 3.1: Interactions between a task and its input and output states

charge at the start of the operation, and/or an amount B_{is}^c which can be added continuously (not necessarily at a constant flowrate) during the operation. Therefore, the total amount of material added is given by:

$$B_{is}^{IN} = B_{is}^d + B_{is}^c \quad \forall\ i \in \mathcal{T}, s \in S_i^{IN} \tag{3.10}$$

The initial charge determines the initial condition for the operation via equations of the form:

$$I_i\left(x_i(0), \dot{x}_i(0), \kappa_i(0), u_i(0), v_i, y_i, \{z_s, B_{is}^d, s \in S_i^{IN}\}\right) = 0 \quad \forall\ i \in \mathcal{T} \tag{3.11}$$

Equations (3.11) are assumed to be a complete and non-redundant set of initial conditions that, together with the model equations (3.3), allow the determination of the initial values $(x_i(0), \dot{x}_i(0), \kappa_i(0))$ provided all other quantities occurring in them are specified.

Safety and other operability considerations may impose certain restrictions on the amounts of various materials initially charged to the task. These restrictions may also depend on the equipment design (*e.g.* size) and/or control systems. In general, they will lead to constraints of the form:

$$\hat{I}_i\left(u_i(0), v_i, y_i, \{z_s, B_{is}^d, s \in S_i^{IN}\}\right) \leq 0 \quad \forall\ i \in \mathcal{T} \tag{3.12}$$

The further addition of material during the operation is generally treated as a control variable $u(t)$ and is related to the final values of the task variables via an end-point constraint of the form:

$$B_{is}^c = B_{is}^c(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \tag{3.13}$$

For example, if an input state $s \in S_i^{IN}$ is allowed to be added continuously to a task i during the operation of the latter, then we can introduce within the task model (3.3):

- a control variable $u_i^{[s]}(t)$ corresponding to the rate of addition of s;

- a differential variable $x_i^{[s]}$ defined via the equation:

$$\dot{x}_i^{[s]} = u_i^{[s]} \quad \forall \ t \in [0, t_i^f] \tag{3.14}$$

Then (3.13) takes the simple form:

$$B_{is}^c = x_i^{[s]}(t_i^f) \tag{3.15}$$

3.4.2. Output State

The outputs of a task can be produced at the end and/or during its operation. The intensive properties z_s together with the total amount B_{is}^{OUT} of each state $s \in S_i^{OUT}$ produced by task i can usually be expressed in terms of the final values of the variables in the task model:

$$B_{is}^{OUT} = B_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \quad \forall \ i \in \mathcal{T}, s \in S_i^{OUT} \tag{3.16}$$

and similarly,

$$z_s = z_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \quad \forall \ i \in \mathcal{T}, s \in S_i^{OUT} \tag{3.17}$$

For instance, if the output of the task is the material that remains in the equipment at the end of processing, then B_{is}^{OUT} and z_s will most probably correspond to a subset of the variables $x_i(t_i^f)$ and $\kappa_i(t_i^f)$. On the other hand, if the output material is withdrawn continuously from the task into an accumulator during processing, then we can augment the task model (3.3) with additional variables and equations characterising this accumulator; in this case, B_{is}^{OUT} and z_s will be related to the final values of the variables describing the accumulator. In many cases, the rate of withdrawal of material will be treated as an extra control variable u_{is}.

3.5. State-Task Network Constraints

In the previous section, we defined and characterised the relationship between task i and its associated input and output states. In this section, we consider the interactions between the various tasks and states in the entire batch process network.

As proposed by Charalambides (1996), we will assume that the task in the recipe under consideration may be partitioned into a number $\mathcal{N}$ of disjoint subsets $\mathcal{P}_n, n = 1, 2, .., \mathcal{N}$:

$$\mathcal{T} = \bigcup_{n=1}^{\mathcal{N}} \mathcal{P}_n \ ; \quad \mathcal{P}_n \bigcap \mathcal{P}'_n = \emptyset \quad \forall \ n, n' \neq n \tag{3.18}$$

The tasks $i \in \mathcal{P}_n$ form a linear sequence ("train"), with an output state of one being an input state of the next. These materials are assumed to be unstable and therefore the tasks operate in a "zero-wait" mode (Reklaitis, 1992). This method of operation establishes a cycle time t_n^{cycle} which cannot be less than the processing time of any task in the process:

$$t_n^{cycle} \geq t_i^f \quad \forall \; n, i \in \mathcal{P}_n \tag{3.19}$$

The *idle time* is the delay which task i incurs between successive batches. It is given by:

$$t_i^{idle} = t_n^{cycle} - t_i^f - t_i^{set} \quad \forall \; n, i \in \mathcal{P}_n \tag{3.20}$$

where t_i^{set} is the set-up time (*i.e* time for charging and discharging).

To help illustrate the different features of the interactions between the tasks and states, we consider a batch process with a *given* recipe shown in figure 3.2. The process consists of 5 tasks and 11 states. The process involves two modes of operation:

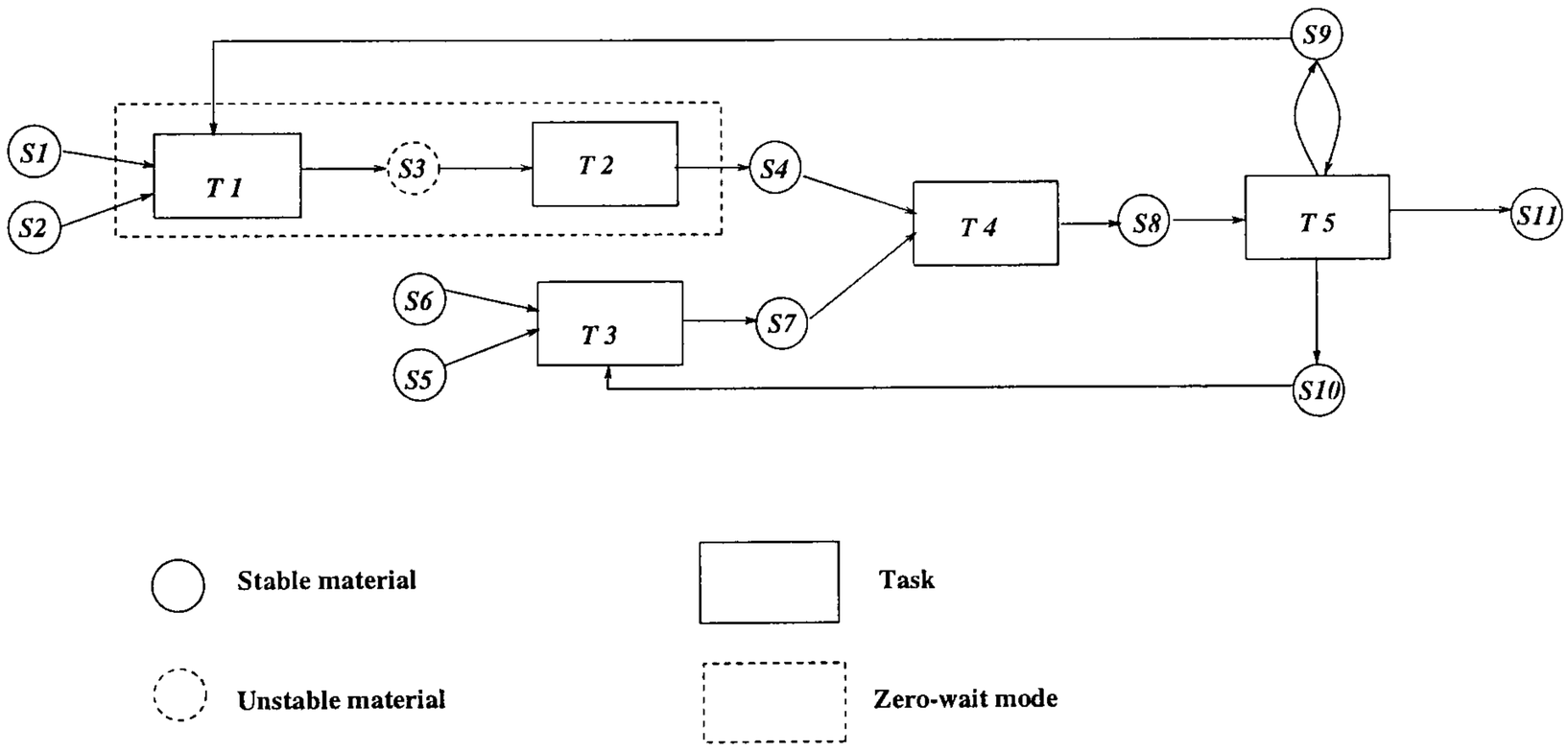


Figure 3.2: State-Task Network for a batch process of *fixed* recipe

- "Zero-wait" where the batch of material produced by task $T1$ is immediately taken up by task $T2$ for further processing. This may be necessary if, for example, intermediate material $S3$ is unstable and cannot be stored for any significant length of time.

- Unlimited/finite storage where the batch of material produced, for instance by task $T3$, is stable. There is no urgency for it to be taken up immediately by the succeeding task and it can, therefore, be stored. There might, however, be limits on the storage capacity available.

We note that in this example $\mathcal{N} = 4$, with $\mathcal{P}_1 = \{T1, T2\}, \mathcal{P}_2 = \{T3\}, \mathcal{P}_3 = \{T4\}, \mathcal{P}_4 = \{T5\}$.

An additional complication in this thesis, beyond what was considered by Charalambides (1996), arises from the fact that the recipe structure is not fixed *a priori*. The manner in which we propose to address this issue is by considering a process "superstructure" (Grossmann and Sargent, 1978) which will embed in it all possible process alternatives. In our case, this superstructure will take the form of a "super-STN", parts of which may be deleted by the design procedure[†].

At this point, we introduce the further assumption that the design procedure will always include or exclude from the process design an *entire* zero-wait sequence $\mathcal{P}_n$ but never part of it. This is justified since omitting one or more individual tasks from such a sequence would usually render it inoperable. We, therefore, introduce in our formulation the following binary variables:

$$\theta_n = \begin{array}{ll} 1, & \text{if sequence } \mathcal{P}_n \text{ is included in the final process design;} \\ 0, & \text{otherwise.} \end{array}$$

3.5.1. Material Balance Constraints

Consider, first, the set of stable states $\mathcal{SS}$ in the STN under consideration (*e.g.* states $S4$, $S7$, $S8$ in figure 3.2). The stable state s is consumed by a subset $\mathcal{N}_s$ of the zero wait trains in the STN and produced by another subset $\bar{\mathcal{N}}_s$. The stable states usually also include raw materials (*e.g.* $S1$, $S2$, $S5$ and $S6$) and final products ($S11$). The material balance is written as:

$$\sum_{n \in \bar{\mathcal{N}}_s} \theta_n \underbrace{\sum_{i \in \mathcal{P}_n} \frac{B_{is}^{OUT}}{t_n^{cycle}}}_{(a)} = \sum_{n \in \mathcal{N}_s} \theta_n \underbrace{\sum_{i \in \mathcal{P}_n} \frac{B_{is}^{IN}}{t_n^{cycle}}}_{(b)} + R_s \quad \forall \ s \in \mathcal{SS} \tag{3.21}$$

Note that the quantity $\frac{B_{is}^{OUT}}{t_n^{cycle}}$ is the average rate of production, since the amount B_{is}^{OUT} of material s is produced every t_n^{cycle} time units by task i in the "zero-wait" train n. The term (a) in equation (3.21) is the summation over all tasks in the train n capable of producing state s. The summation is a general term and in most practical cases B_{is}^{OUT} will be zero for

[†]In the approach considered in this thesis, this design procedure involves the solution of a mathematical optimisation problem. However, the concept of a super-STN may, in principle, be used within other (*e.g.* heuristic-based) approaches.

all but one of the tasks i in the train n. Similarly, the term (b) in equation (3.21) represents the total average consumption rate of state s. We note that *both* terms are multiplied by the binary variable θ_n; clearly, if a train n is *not* included in the final process design, then it will make no contribution to the generation or consumption of material in the process.

The quantity R_s in the material balance equation (3.21) denotes the net rate of production of material state s. R_s is negative for raw materials and positive for end-products. In the case of intermediate materials, R_s can be either zero or a positive number depending on whether the material is allowed to accumulate or not. More generally, the quantity R_s will be restricted to lie within given minimum and maximum limits:

$$R_s^{min} \leq R_s \leq R_s^{max} \qquad \forall \ s \tag{3.22}$$

If the net accumulation of the intermediate material s is undesirable, then setting $R_s^{min} = R_s^{max} = 0$ will ensure that this does not take place.

In the case where unstable material in state s_{kn} (*e.g.* state $S3$) between tasks i_{kn} and $i_{k+1,n}$ is present in a zero-wait train, it is necessary to ensure that the amount of this unstable material produced by task $i_{kn}, k = 1, .., m_n - 1$ is equal to the amount consumed by task $i_{k+1,n}$. We then have:

$$B^{OUT}_{i_{kn},s_{kn}} = B^{IN}_{i_{k+1,n},s_{kn}} \qquad \forall \ n, k = 1, .., m_n - 1 \tag{3.23}$$

Here the m_n tasks in $\mathcal{P}_n$ are denoted as $i_{kn}, k = 1, 2, .., m_n$, and the state that effects the coupling between the tasks i_{kn} and $i_{k+1,n}$ as s_{kn}.

3.6. Objective Function

The average net revenue achieved by the process per unit time of operation is used as the main performance criterion for our design procedure. The objective function takes account of:

- the capital cost of the equipment items used,
- the operating costs of the various tasks, including the cost of utilities such as steam, cooling water and electricity,
- the cost of raw materials,
- the disposal cost of waste materials,

- the revenue from the products.

3.6.1. Cost of States

The set of product states in $\mathcal{S}_{\mathcal{P}}$ can be divided into the desired product(s) $\mathcal{S}_{\mathcal{P}_{\mathcal{D}}}$ which have a positive unit value C_s^{prod}, and those which are unwanted by-products $\mathcal{S}_{\mathcal{P}_{\mathcal{W}}}$ and have a unit disposal cost C_s^{waste} associated with it. Similarly, each raw material state $\mathcal{S}_{\mathcal{RM}}$ has an associated unit cost C_s^{rm}.

Overall, the total net revenue associated with material production and utilisation per unit time of operation of the process is given by:

$$\sum_{s \in \mathcal{S}_{\mathcal{P}_{\mathcal{D}}}} C_s^{prod} R_s - \sum_{s \in \mathcal{S}_{\mathcal{P}_{\mathcal{W}}}} C_s^{waste} R_s - \sum_{s \in \mathcal{S}_{\mathcal{RM}}} C_s^{rm} R_s \tag{3.24}$$

3.6.2. Cost of Tasks

There are two main contributions to the cost of each task i that is included in the process:

(i) *Capital cost*

This is a function of the size and other design characteristics of the equipment. These are included in our formulation in the form of the time invariant parameters v_i and integer variables y_i. Therefore, the capital cost of task i is expressed (on an annualised basis) as $C_i^{cap}(v_i, y_i)$.

(ii) *Utility costs*

The *instantaneous* rate of consumption $r_{\mu i}(t)$ of a utility μ by a batch task i will generally vary over the duration of the latter. In principle, it can be expressed in terms of the values of the variables describing the task[‡]:

$$r_{\mu i}(t) = r_{\mu i}(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) \quad \forall \ \mu, i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.25}$$

The *total* amount of utility μ consumed over the duration of a batch of task i is, therefore, given by:

$$\mathcal{U}_{\mu i}(t_i^f) = \int_0^{t_i^f} r_{\mu i}(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) dt \quad \forall \ \mu, i \in \mathcal{T} \tag{3.26}$$

[‡]In fact, it will often correspond to one of the control variables $u_i(t)$.

which can be expressed in a more conventional, differential equation form as:

$$\frac{d\mathcal{U}_{\mu i}}{dt} = r_{\mu i}(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i); \qquad \mathcal{U}_{\mu i}(0) = 0 \qquad \mu, i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.27}$$

Overall, the average cost of operating the task train $\mathcal{P}_n$ per unit time is given by:

$$\sum_{i \in \mathcal{P}_n} \left(C_i^{cap}(v_i, y_i) + \frac{1}{t_n^{cycle}} \sum_{\mu} C_\mu \mathcal{U}_{\mu i}(t_i^f) \right) \tag{3.28}$$

where C_μ is the unit cost of utility μ[§]. Of course, this cost will be incurred *only if* this train is actually included in the final process design, *i.e.* if $\theta_n = 1$.

3.6.3. Overall Objective Function

The combination of the above contributions yields the overall objective function for the process as a measure of the average profit achieved per unit time of operation:

$$\max \left\{ \begin{array}{l} \underbrace{\sum_{s \in \mathcal{S}_{\mathcal{P}_\mathcal{D}}} C_s^{prod} R_s}_{products} - \underbrace{\sum_{s \in \mathcal{S}_{\mathcal{RM}}} C_s^{rm} R_s}_{raw\ materials} - \underbrace{\sum_{s \in \mathcal{S}_{\mathcal{P}_\mathcal{D}}} C_s^{waste} R_s}_{waste\ disposal} \\ \underbrace{-\sum_{n=1}^{\mathcal{N}} \theta_n \sum_{i \in \mathcal{P}_n} \left(C_i^{cap}(v_i, y_i) + \frac{1}{t_n^{cycle}} \sum_{\mu} C_\mu \mathcal{U}_{\mu i}(t_i^f) \right)}_{task\ costs} \end{array} \right\} \tag{3.29}$$

[§]In some cases (*e.g.* "green field" design), this cost may also include a component reflecting the cost of setting up a utility provision infrastructure.

3.7. Summary of the Mathematical Formulation

$$
\begin{aligned}
\max\ \Phi = & \left\{ \begin{array}{l} \sum_{s\in\mathcal{S}_{\mathcal{P}_\mathcal{D}}} C_s^{prod} R_s - \sum_{s\in\mathcal{S}_{\mathcal{P}_\mathcal{D}}} C_s^{waste} R_s - \sum_{s\in\mathcal{S}_{\mathcal{RM}}} C_s^{rm} R_s \\ -\sum_{n=1}^{\mathcal{N}} \theta_n \sum_{i\in\mathcal{P}_n} \left(C_i^{cap}(v_i, y_i) + \frac{1}{t_n^{cycle}} \sum_{\mu} C_\mu \mathcal{U}_{\mu i}(t_i^f) \right) \end{array} \right\} \\
& \text{Subject to :} \\
& \text{State constraints :} \\
& z_s^{min} \le z_s \le z_s^{max} \quad \forall\ s \\
& C_s(z_s) \le 0 \quad \forall\ s \\
& \text{Task constraints :} \\
& f_i(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \\
& \mathcal{H}(v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T} \\
& h_i(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i) \le 0 \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \\
& g_{i\omega}^{e}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), u_i(t_{i\omega}), v_i, y_i) = 0 \quad \forall\ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \\
& g_{i\omega}^{ie}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), u_i(t_{i\omega}), v_i, y_i) \le 0 \quad \forall\ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \\
& v_i^{min} \le v_i \le v_i^{max} \quad \forall\ i \in \mathcal{T} \\
& u_i^{min}(v_i, y_i) \le u_i(t) \le u_i^{max}(v_i, y_i) \quad \forall\ i \in \mathcal{T}, t \in [0, t_i^f] \\
& I_i(x_i(0), \dot{x}_i(0), \kappa_i(0), u_i(0), v_i, y_i\{z_s, B_{is}^d, s \in S_i^{IN}\}) = 0 \quad \forall\ i \in \mathcal{T} \\
& \text{State} - \text{Task interaction constraints :} \\
& B_{is}^{IN} = B_{is}^{d} + B_{is}^{c} \quad \forall\ i \in \mathcal{T}, s \in S_i^{IN} \\
& B_{is}^{c} = B_{is}^{c}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \\
& \hat{I}_i\left(u_i(0), v_i, y_i, \{z_s, B_{is}^d, s \in S_i^{IN}\}\right) \le 0 \quad \forall\ i \in \mathcal{T} \\
& B_{is}^{OUT} = B_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \quad \forall\ i \in \mathcal{T}, s \in S_i^{OUT} \\
& z_s = Z_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), u_i(t_i^f), v_i, y_i) \quad \forall\ i \in \mathcal{T}, s \in S_i^{OUT} \\
& \text{Other constraints :} \\
& t_n^{cycle} \ge t_i^f \quad \forall\ n, i \in \mathcal{P}_n \\
& \sum_{n\in\bar{\mathcal{N}}_s} \theta_n \sum_{i\in\mathcal{P}_n} \frac{B_{is}^{OUT}}{t_n^{cycle}} = \sum_{n\in\mathcal{N}_s} \theta_n \sum_{i\in\mathcal{P}_n} \frac{B_{is}^{IN}}{t_n^{cycle}} + R_s \quad \forall\ s \in \mathcal{SS} \\
& B_{i_{kn}, s_{kn}}^{OUT} = B_{i_{k+1,n}, s_{kn}}^{IN} \quad \forall\ n, k = 1, .., m_n - 1 \\
& R_s^{min} \le R_s \le R_s^{max} \quad \forall\ s \\
& \frac{d\mathcal{U}_{\mu i}}{dt} = r_{\mu i}(x_i(t), \dot{x}_i(t), \kappa_i(t), u_i(t), v_i, y_i); \quad \mathcal{U}_{\mu i}(0) = 0 \quad \mu, i \in \mathcal{T}, t \in [0, t_i^f] \\
& \theta_n \in \{0, 1\}; \quad y_i \in \{0, 1\}, \quad \forall\ i \in \mathcal{T}
\end{aligned}
\tag{3.30}
$$

The above mathematical formulation is a mixed integer non-linear programming problem (MINLP). The maximisation of the objective function is achieved by manipulating decisions regarding:

- Process recipe structure:
  - the binary variables θ_n.
- Materials:
  - the intensive properties z_s,
  - the rate of external supply or delivery, R_s, of stable materials.
- Operations:
  - the equipment design decisions, v_i, y_i,
  - the task durations, t_i^f and train cycle times, t_n^{cycle},
  - the initial state charges, B_{is}^d, $s \in S_i^{IN}$,
  - the control variables, $u_i(t)$, $t \in [0, t_i^f]$.

An important property of the formulation is that the above decisions, coupled with the *equality* constraints in the formulation, completely determine all other variables as well as the value of the objective function (3.29). Of course, there is no guarantee that any particular choice of values for these decisions will satisfy the *inequality* constraints in the formulation.

Before proceeding to consider methods for the solution of the above problem, it is worth considering the main simplifying assumptions that have been introduced to reduce its complexity:

- *Plant Design:* our design formulation does not take into account the possibility of multipurpose equipment items, so each task is assumed to take place in a single dedicated item of equipment, the size and other characteristics of which may be either fixed or determined by the optimisation.
- *Plant Operation:* all batches of material undergoing the same task in a particular equipment item are assumed to be identical, being processed in exactly the same way.
- *Plant Scheduling:* only simple interactions between plant scheduling and design are considered. The formulation considers the case where the materials are unstable and, therefore, cannot be stored, leading to a zero-wait operating policy; and the case where the materials are stable and can be stored to unlimited amounts. The case where only finite storage resources are available is not considered.

3.8. Solution Methodology

Formulation (3.30) is a complex infinite dimensional multistage mixed integer dynamic optimisation problem. The first major difficulty that one has to address is the infinite dimensional nature of this problem. This is mainly due to the fact that the variables describing the behaviour of each task i, namely $x_i(t)$, $\kappa_i(t)$ and $u_i(t)$ are functions of time t over the finite domain $[0, t_i^f]$. Similarly, certain constraints such as (3.3) and the inequality constraints (3.5) must hold at *all* times $t \in [0, t_i^f]$ rather than just at finite number of distinct points.

In the following subsection, we will describe the two main solution methodologies that have emerged over the past two decades for handling the infinite dimensional nature of such dynamic optimisation problems by reducing them to finite dimensional ones.

3.8.1. Complete Parameterisation Approach

This approach (Cuthrell and Biegler, 1987; Renfro *et al.*, 1987) approximates all the time-varying variables in the model $(x_i(t), \kappa_i(t), u_i(t))$ in terms of finite sets of parameters:

$$\left.\begin{array}{rcl} x_i(t) & = & X_i(t, \alpha_i^x) \\ \kappa_i(t) & = & \mathcal{K}_i(t, \alpha_i^\kappa) \\ u_i(t) & = & \Psi_i(t, \alpha_i^u) \end{array}\right\} \quad t \in [0, t_i^f] \tag{3.31}$$

where $X_i(.,.)$, $\mathcal{K}_i(.,.)$ and $\Psi_i(.,.)$ are functions of a given, relatively simple mathematical form (*e.g.* piecewise polynomials defined over a finite element partition of the domain $t \in [0, t_i^f]$). On the other hand, α_i^x, α_i^κ and α_i^u are finite sets of parameters that are to be determined by the optimisation.

When the variables are discretised in the above manner, the infinite dimensional constraints (3.3) and (3.5) can be replaced by finite approximations. This can be achieved by enforcing these constraints at a finite number of collocation points in each finite element. Consequently, the infinite dimensional problem (3.30) is transformed into a large mixed integer non-linear programming (MINLP) problem.

One of the disadvantages of this approach is the size of the MINLP that it generates. This becomes important when handling processes comprising several complex tasks which are of particular interest to this thesis; using the complete parameterisation approach will result in MINLPs involving tens of thousands of constraints and equations. An alternative to the complete parameterisation is the control vector parameterisation approach.

3.8.2. Control Vector Parameterisation Approach

This approach (Sargent and Sullivan, 1977; Morison and Sargent, 1986; Vassiliadis, 1993) applies parameterisation to the control variables $u_i(t)$ only:

$$u_i(t) = \Psi_i(t, \alpha_i) \tag{3.32}$$

expressing them in terms of a finite vector of parameters α_i for each task i. More specifically, the domain $[0, t_i^f]$ is partitioned into a number of finite elements and the control variables are expressed as piecewise constant or linear polynomials within these partitions.

The piecewise constant control variables are described by a single parameter ξ_{ki} per finite element, while two parameters (ξ_{ki}, ξ'_{ki}) are necessary for piecewise linear controls. The length of each finite element δ_{ki} is also treated as an optimisation parameter. Therefore, for the piecewise constant case, the set of control parameters (*cf.* equation (3.32)) is given by:

$$\alpha_i \equiv \{\xi_{ki}, \delta_{ki}, k = 1, .., \mathcal{NE}_i\} \tag{3.33}$$

and for the piecewise linear ones:

$$\alpha_i \equiv \{\xi_{ki}, \xi'_{ki}, \delta_{ki}, k = 1, .., \mathcal{NE}_i\} \tag{3.34}$$

where $\mathcal{NE}_i$ is the total number of finite elements for task i. These two forms of control parameterisation, although might appear somewhat restrictive, correspond to the forms of control action used in most practical batch applications.

One desirable characteristic of the control variable parameterisation is that the variable bound constraints (3.9) can be expressed directly in terms of the corresponding parameters; for the piecewise constant case, this is written as:

$$u_i^{min}(v_i, y_i) \leq \xi_{ki} \leq u_i^{max}(v_i, y_i) \quad \forall \ i \in \mathcal{T} \tag{3.35}$$

and for the piecewise linear case:

$$\left.\begin{array}{l} u_i^{min}(v_i, y_i) \leq \xi_{ki} \leq u_i^{max}(v_i, y_i) \\ u_i^{min}(v_i, y_i) \leq \xi'_{ki} \leq u_i^{max}(v_i, y_i) \end{array}\right\} \quad \forall \ i \in \mathcal{T}, \ k = 1, .., \mathcal{NE}_i \tag{3.36}$$

In both cases, the following constraint is imposed:

$$\sum_{k=1}^{\mathcal{NE}_i} \delta_{ki} = t_i^f \quad \forall \ i \in \mathcal{T} \tag{3.37}$$

A lower bound is imposed on the length of the elements to avoid the problem of one or more elements vanishing and consequently giving rise to numerical difficulties:

$$\delta_{ki} \geq \epsilon \quad \forall \ i \in \mathcal{T}, k = 1, .., \mathcal{NE}_i \tag{3.38}$$

where ϵ is a small positive quantity.

3.8.3. Elimination of Task Variables and Equations

We now examine the application of the control vector parameterisation approach to our formulation. In particular, consider a task i and the following set of decision variables:

- the processing time, t_i^f;
- the control variable discretisation parameters, α_i;
- the time invariant parameters, v_i;
- the discrete design decisions, y_i;
- the intensive properties z_s for each input state $s \in S_i$;
- the amounts B_{is}^d, $\forall\ s \in S_i$ that form the initial charge(s) to this task.

We denote the above set by Γ_i:

$$\Gamma_i \equiv \left\{\alpha_i, v_i, y_i, t_i^f, \{t_{i\omega}, \forall\omega\}, \{z_s, B_{is}^d, s \in S_i^{IN}\}\right\}, \quad \forall \ i \in \mathcal{T} \tag{3.39}$$

The initial conditions (3.11), now written as:

$$I_i(x_i(0), \dot{x}_i(0), \kappa_i(0), \Psi_i(0, \alpha_i), v_i, y_i, \{z_s, B_{is}^d, s \in S_i\}) = 0 \quad \forall \ i \in \mathcal{T} \tag{3.40}$$

can be solved together with the model equations (3.3) at time $t = 0$:

$$f_i(x_i(0), \dot{x}_i(0), \kappa_i(0), \Psi_i(0, \alpha_i), v_i, y_i) = 0 \tag{3.41}$$

to determine the initial values:

$$\{x_i(0), \dot{x}_i(0), \kappa_i(0)\} \tag{3.42}$$

of the variables of task i. Once this initialisation is completed, and given the task processing time t_i^f, the DAE system (3.3) which is written as:

$$f_i(x_i, \dot{x}_i, \kappa_i, \Psi_i(t, \alpha_i), v_i, y_i) = 0 \quad \forall \ i \in \mathcal{T}, \ t \in [0, t_i^f] \tag{3.43}$$

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can be integrated to determine $x_i(t), \dot{x}_i(t), \kappa_i(t), \ \forall \ t \in [0, t_i^f]$.

From the above solution, the residuals of the path constraints (3.5) and point constraints (3.6) - (3.7) can also be evaluated as follows:

$$h_i(x_i(t), \dot{x}_i(t), \kappa_i(t), \Psi_i(t, \alpha_i), v_i, y_i) \leq 0 \quad \forall \ i \in \mathcal{T}, t \in [0, t_i^f] \tag{3.44}$$

$$g_{i\omega}^{e}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), \Psi_i(t_{i\omega}, \alpha_i), v_i, y_i) = 0 \quad \forall \ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \tag{3.45}$$

$$g_{i\omega}^{ie}(x_i(t_{i\omega}), \dot{x}_i(t_{i\omega}), \kappa_i(t_{i\omega}), \Psi_i(t_{i\omega}, \alpha_i), v_i, y_i) \leq 0 \quad \forall \ i \in \mathcal{T}, t_{i\omega} \in [0, t_i^f], \omega = 1, 2, \ldots \tag{3.46}$$

We adopt the approach proposed by Vassiliadis *et al.* (1994a) and later adopted by Charalambides (1996) for the finite representation of the inequality path constraints (3.44). This involves replacing the latter by:

- A single end-point inequality constraint:

$$\chi_i(t_i^f) \leq \epsilon \tag{3.47}$$

where ϵ is a small positive tolerance and χ_i is a new variable defined by the differential equation:

$$\dot{\chi}_i = \left[max\left(0, h_i(x_i(t), \dot{x}_i(t), \kappa_i(t), \Psi_i(t_i^f, \alpha_i), v_i, y_i)\right)\right]^2 \tag{3.48}$$

subject to the initial condition: $\chi_i = (0)$.

- A set of interior point inequality constraints:

$$h_i\left(x_i(t_{ik}), \dot{x}_i(t_{ik}), \kappa_i(t_{ik}), \Psi_i(t_{ik}, \alpha_i), v_i, y_i\right) \leq 0, \qquad k = 0, .., \mathcal{NE}_i \tag{3.49}$$

where t_{ik} are selected to be the boundaries of the finite elements used for the control parameterisation *i.e.*:

$$\begin{aligned} t_{i0} &= 0 \\ t_{ik} &= \sum_{k'=1}^{k} \delta_{k'i}, \qquad k = 1, .., \mathcal{NE}_i \end{aligned} \tag{3.50}$$

The amounts B_{is}^c of input states $s \in S_i$ fed to task i in a continuous form during the operation and the amounts B_{is}^{OUT} and the intensive properties z_s of all the output states $s \in S_i^{OUT}$ of task i can also be calculated using equations (3.13) and (3.16)-(3.17):

$$B_{is}^c = B_{is}^c(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), \Psi_i(t, \alpha_i), v_i, y_i) \tag{3.51}$$

$$B_{is}^{OUT} = B_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), \Psi_i(t_i^f, \alpha_i), v_i, y_i) \quad \forall \ i \in \mathcal{T}, \ s \in S_i^{OUT} \tag{3.52}$$

$$z_s = z_{is}^{OUT}(x_i(t_i^f), \dot{x}_i(t_i^f), \kappa_i(t_i^f), \Psi_i(t_i^f, \alpha_i), v_i, y_i) \quad \forall\ i \in \mathcal{T},\ s \in S_i^{OUT} \tag{3.53}$$

The amounts B_{is}^{IN}, $\forall\ s \in S_i^{IN}$ can then be computed as $B_{is}^{d} + B_{is}^{c}$.

Finally, the contribution of the task to the operating cost can be obtained by evaluating the utility consumption (3.26):

$$\mathcal{U}_{\mu i}(t_i^f) = \int_0^{t_i^f} r_{\mu i}(x_i(t), \dot{x}_i(t), \kappa_i(t), \Psi_i(t_i^f, \alpha_i), v_i, y_i)dt \quad \forall\ \mu, i \in \mathcal{T} \tag{3.54}$$

Overall, then, the parameterisation of the controls (3.32) has enabled us to express the quantities $\{B_{is}^{IN},\ \forall\ s \in S_i^{IN}\}$, $\{B_{is}^{OUT}, z_s\ \forall\ s \in S_i^{OUT}\}$ and $\mathcal{U}_{\mu i}$ as functions of the finite vector Γ_i. We denote these functions as $\{\tilde{B}_{is}^{IN}(\Gamma_i),\ \forall s \in S_i^{IN}\}$, $\{\tilde{B}_{is}^{OUT}(\Gamma_i), \tilde{z}_{is}(\Gamma_i),\ \forall\ s \in S_i^{OUT}\}$ and $\tilde{\mathcal{U}}_{\mu i}(\Gamma_i)$. Furthermore, the parameterisation, together with the conversion of the infinite dimensional constraint (3.44) into a finite set of constraints (3.47) and (3.49), has enabled us to convert (3.5) - (3.7) into equality and inequality constraints in Γ_i:

$$\begin{aligned} \mathcal{G}_{i\omega}^{e}(\Gamma_i) &= 0 \\ \mathcal{G}_{i\omega}^{ie}(\Gamma_i) &\leq 0 \end{aligned} \tag{3.55}$$

3.8.4. Mixed Integer Non-Linear Programming Problem (MINLP)

The elimination described in section 3.8.3 allows the infinite dimensional mixed integer dynamic optimisation (3.30) problem to be transformed into a finite mixed integer non-linear programming problem (MINLP). This is summarised below:

$$\max_{\substack{\{\Gamma_i,\,\forall i\},\{t_n^{cycle},\,\forall n\},\\ \{R_s,\,\forall s\in\mathcal{SS}\}}} \Phi = \left\{ \begin{array}{l} \sum_{s\in\mathcal{S}_{\mathcal{PD}}} C_s^{prod} R_s - \sum_{s\in\mathcal{S}_{\mathcal{PD}}} C_s^{waste} R_s - \sum_{s\in\mathcal{S}_{\mathcal{RM}}} C_s^{rm} R_s \\ -\sum_{n=1}^{\mathcal{N}} \theta_n \sum_{i\in\mathcal{P}_n} \left(C_i^{cap}(v_i,y_i) + \frac{1}{t_n^{cycle}} \sum_{\mu} C_\mu \mathcal{U}_{\mu i}(t_i^f) \right) \end{array} \right\}$$

Subject to :

$$z_s^{min} \le z_s \le z_s^{max} \quad \forall\ s$$

$$\mathcal{C}_s(z_s) \le 0 \quad \forall\ s$$

$$\mathcal{H}(v_i,y_i) = 0 \quad \forall\ i \in \mathcal{T}$$

$$\mathcal{G}_{i\omega}^{e}(\Gamma_i) = 0 \quad \forall\ i \in \mathcal{T},\ \omega = 1,2,\ldots$$

$$\mathcal{G}_{i\omega}^{ie}(\Gamma_i) \le 0 \quad \forall\ i \in \mathcal{T},\ \omega = 1,2,\ldots$$

$$v_i^{min} \le v_i \le v_i^{max} \quad \forall\ i \in \mathcal{T}$$

$$or: \left. \begin{array}{c} u_i^{min}(v_i,y_i) \le \xi_{ki} \le u_i^{max}(v_i,y_i) \\ u_i^{min}(v_i,y_i) \le \xi_{ki} \le u_i^{max}(v_i,y_i) \\ u_i^{min}(v_i,y_i) \le \xi'_{ki} \le u_i^{max}(v_i,y_i) \\ \delta_{ki} \ge \epsilon \end{array} \right\} \quad \forall\ k = 1,..,\mathcal{NE}_i,\ i \in \mathcal{T}$$

$$\sum_{k=1}^{\mathcal{NE}_i} \delta_{ki} = t_i^f \quad \forall\ i \in \mathcal{T}$$

$$B_{is}^{IN} = B_{is}^{d} + \tilde{B}_{is}^{c}(\Gamma_i) \quad \forall\ i \in \mathcal{T}, s \in S_i^{IN}$$

$$B_{is}^{OUT} = \tilde{B}_{is}^{OUT}(\Gamma_i) \quad \forall\ i \in \mathcal{T}, s \in S_i^{OUT}$$

$$\hat{I}_i\left(u_i(0), v_i, y_i, \{z_s, B_{is}^{d}, \forall s \in S_i^{IN}\}\right) \le 0 \quad \forall\ i \in \mathcal{T}$$

$$z_s = \tilde{z}_{is}^{OUT}(\Gamma_i) \quad \forall\ i \in \mathcal{T}, s \in S_i^{OUT}$$

$$t_n^{cycle} \ge t_i^f \quad \forall\ n, i \in \mathcal{P}_n$$

$$\sum_{n\in\bar{\mathcal{N}}_s} \theta_n \sum_{i\in\mathcal{P}_n} \frac{B_{is}^{OUT}}{t_n^{cycle}} = \sum_{n\in\mathcal{N}_s} \theta_n \sum_{i\in\mathcal{P}_n} \frac{B_{is}^{IN}}{t_n^{cycle}} + R_s \quad \forall\ s \in \mathcal{SS}$$

$$B_{i_{kn},s_{kn}}^{OUT} = B_{i_{k+1,n},s_{kn}}^{IN} \quad \forall\ n, k = 1,..,m_n - 1$$

$$R_s^{min} \le R_s \le R_s^{max} \quad \forall\ s$$

$$\mathcal{U}_{\mu i} = \tilde{\mathcal{U}}_{\mu i}(\Gamma_i) \quad \forall\ i \in \mathcal{T}$$

$$\theta_n \in \{0,1\};\quad y_i \in \{0,1\}, \quad \forall\ i \in \mathcal{T} \qquad (3.56)$$

Overall, then, the above optimisation problem is expressed in terms of a relatively small

set of decision variables:

$$\Gamma \equiv \bigcup_{i \in \mathcal{T}} \Gamma_i \bigcup_{n=1}^{\mathcal{N}} t_n^{cycle} \bigcup_{s \in \mathcal{SS}} R_s \tag{3.57}$$

Note that the sets Γ_i may not necessarily be disjoint since two or more tasks may share one or more input states and, hence, the same z_s.

Although the size of the problem has been substantially reduced by applying control vector parameterisation to the original problem (3.30), solving the MINLP problem (3.56) is by no means a trivial task. The nature of the problem (*i.e.* the combination of integer and continuous decisions) makes the problem particularly challenging. Furthermore, an added complication is that there are potentially two "levels" of binary variables; those that describe the existence of the processing task trains, θ_n; and those that describe the characteristics of individual equipment items, y_i.

There are two solution strategies which may be adopted:

- an enumeration-based approach;
- standard MINLP solution techniques.

3.8.4.1. Enumeration-Based Approach

This approach is based on the optimisation of each individual discrete alternative of the problem. This approach is favourable in cases where the number of discrete alternatives is so small that the algorithmic overheads of standard MINLP solution techniques[††] outweigh the benefits of not considering all discrete alternatives explicitly. We shall return to use this approach to determine the optimal process structure, which is described mathematically by the binary variables θ_n, in more detail in Chapter 6.

3.8.4.2. Standard MINLP Solution Techniques

More systematic MINLP solution techniques are especially favourable for cases where the number of discrete alternatives is large. In our case, they are particularly useful for finding the integer variables y_i that determine the characteristics of the equipment items (such as the optimal selection of equipment items or the optimal number of trays) since the large number of distinct alternatives renders the total enumeration approach impractical.

One such technique is the branch-and-bound method (Beale, 1977); its main drawback is that it can require the solution of a large number of NLP subproblems. Alternatively, the MINLP problem can be solved using the extended cutting plane method which relies only on the iterative solution of a mixed integer linear programming (MILP) problem constructed by

[††]E.g. the cost of solving the MILP master problem in outer approximation algorithms (see section 3.8.4.2).

successively adding the most violated constraint at the predicted solution point (Westerlund and Pettersson, 1995; Westerlund *et al.*, 1998). However, this method may require a large number of iterations in order to find the optimal solution.

The most popular methods to solve MINLP problems are those that require solving a sequence of non-linear (NLP) and mixed integer linear programming (MILP) problems. They include Generalised Benders decomposition (GBD, Benders, 1962; Geoffrion, 1972) and Outer Approximation (OA, Duran and Grossmann, 1986; Kocis and Grossmann, 1987). GBD has the disadvantage that it may require a significant number of major iterations of the NLP subproblem and the MILP master problem. The main advantage of using OA is that it typically requires fewer iterations to reach a solution since its MILP master problem contains more information than the GBD. On the other hand, because the OA master problem is richer, it is also more difficult to solve. A detailed review of the various MINLP algorithms is given by Floudas (1995).

In this work, we consider the approach based on the Outer Approximation since the algorithm typically requires fewer iterations when compared to the other MINLP techniques. Also its modified version (Outer Approximation/Augmented Penalty (OA/AP), Viswanathan and Grossmann, 1993) has been found to be capable of handling mild non-convexities present in the MINLP problems.

3.8.5. A Combined Complete Enumeration and Outer Approximation Algorithm

For the purposes of solving the MINLP problem (3.56), we adopt a two-level approach:

- We deal with the decision variables θ_n that determine the structure of the process recipe using a complete enumeration approach. The efficiency of the latter depends crucially on being able to construct a super-STN that involves only a very small number of discrete alternatives. We shall see how this is achieved in Chapter 6.

- For each one of the alternative process structures considered by the above enumeration procedure, we employ the OA/AP approach for the determination of the optimal values of the discrete y_i variables, as well as all other continuous decisions.

The basic idea of the OA algorithm is that the MINLP is solved using a two stage iterative procedure:

- The first stage involves fixing the integer variables to given values, thereby, reducing the MINLP to a *non-linear programming (NLP) subproblem.*

- The next stage involves solving a *master problem* which is based on the outer approximation (linearisation) of the non-linear objective function and constraints around a solution point for fixed integer variables. This generates a new set of integer variable values.

3.8.5.1. Subproblem

As already noted above, the subproblem involves fixing the y_i variables to given values. In our formulation, this corresponds to fixing some aspects of the design of the individual item of processing equipment such as:

- the number of trays in batch distillation columns (*cf.* Chapter 4);
- the size of equipment items available in a discrete range of standard capacities (*cf.* Chapter 5).

In all these cases, we can easily eliminate the binary variables y_i from the formulation, and also eliminate or greatly simplify the various constraints in which they occur. Hence, the set of decision variables Γ_i (3.39) is reduced to:

$$\tilde{\Gamma}_i \equiv \left\{ \alpha_i, \tilde{v}_i, t_i^f, \{t_{i\omega}, \forall \omega\}, \{z_s, B_{is}^d, s \in S_i^{IN}\} \right\}, \quad \forall\ i \in \mathcal{T} \tag{3.58}$$

where $\tilde{v}_i$ is the subset of the time invariant parameters v_i which are *not* determined by constraints (3.4) once the y_i variables are fixed.

The DAE model (3.43) is now written as:

$$\tilde{f}_i(x_i, \dot{x}_i, \kappa_i, \Psi_i(t, \alpha_i), \tilde{v}_i) = 0 \quad \forall\ i \in \mathcal{T},\ t \in [0, t_i^f] \tag{3.59}$$

and is subject to the following reduced initial conditions:

$$\tilde{I}_i(x_i(0), \dot{x}_i(0), \kappa_i(0), \Psi_i(0, \alpha_i), \tilde{v}_i, \{z_s, B_{is}^d, s \in S_i\}) = 0 \quad \forall\ i \in \mathcal{T} \tag{3.60}$$

The resulting problem is, in fact, precisely the same as that solved by Charalambides (1996) who did not consider any discrete decisions. We can, therefore, adopt his solution strategy which is illustrated schematically in figure 3.3.

At the highest level, the standard dynamic NLP optimisation problem is formulated and solved using Vassiliadis' (1993) DAEOPT code interfaced to the *gPROMS/gOPT* modelling tool (Process Systems Enterprise Ltd., 1997). DAEOPT code implements the control vector

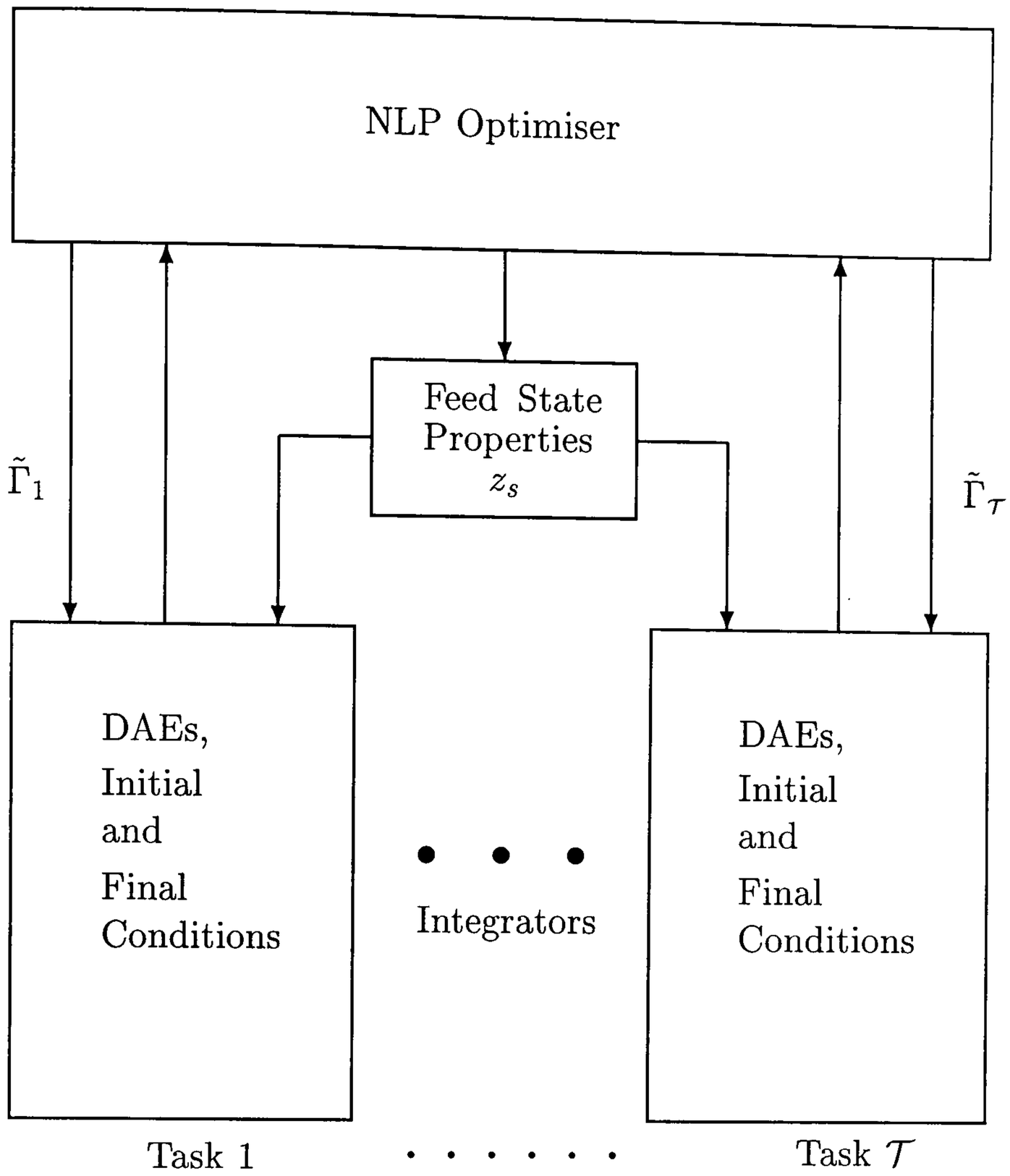


Figure 3.3: Overview of subproblem solution methodology (Charalambides, 1996)

parameterisation approach described in section 3.8.2. The optimisation uses the SRQPD code (Chen and Macchietto, 1989), which is a dense-matrix implementation of the sequential quadratic programming algorithm proposed by Chen (1988).

The calculation of the values of the objective function and the constraints in the NLP problem involves the integration of the reduced model equations (3.59) subject to the initial conditions (3.60). The DASOLV code (Jarvis and Pantelides, 1992) is used to perform the integration. This is an efficient implementation of the Backward Differentiation Formulae (BDF) integration methods (Gear, 1971) for large sparse DAE systems. Once these integrations are carried out for each task i, we can use the final values of the variables $x_i(t_i^f)$, $\dot{x}_i(t_i^f)$ and $\kappa_i(t_i^f)$ to compute the following quantities:

- $\mathcal{G}_{i\omega}^{e}$ from equation (3.45),
- $\mathcal{G}_{i\omega}^{ie}$ from equation (3.46), (3.47) and (3.49),

- $\tilde{B}^{c}_{is}$ from equation (3.13),
- $\tilde{B}^{OUT}_{is}$ from equation (3.16),
- $\tilde{z}^{OUT}_{is}$ from equation (3.17),
- $\tilde{\mathcal{U}}_{\mu i}$ from equation (3.26).

Moreover, the gradients of these quantities with respect to the reduced optimisation decision variables $\tilde{\Gamma}_i$ may be computed by integrating the sensitivity equations:

$$\frac{\partial \tilde{f}_i}{\partial x_i}\frac{\partial x_i}{\partial \tilde{\Gamma}_i} + \frac{\partial \tilde{f}_i}{\partial \dot{x}_i}\frac{\partial \dot{x}_i}{\partial \tilde{\Gamma}_i} + \frac{\partial \tilde{f}_i}{\partial \kappa_i}\frac{\partial \kappa_i}{\partial \tilde{\Gamma}_i} + \frac{\partial \tilde{f}_i}{\partial u_i}\frac{\partial \Psi_i}{\partial \alpha_i}\frac{\partial \alpha_i}{\partial \tilde{\Gamma}_i} + \frac{\partial \tilde{f}_i}{\partial \tilde{v}_i}\frac{\partial \tilde{v}_i}{\partial \tilde{\Gamma}_i} = 0, \quad \forall\ i \in \mathcal{T},\ \ t \in [0, t^f_i] \tag{3.61}$$

subject to the initial conditions:

$$\frac{\partial \tilde{I}_i}{\partial x_i}\frac{\partial x_i}{\partial \tilde{\Gamma}_i}(0) + \frac{\partial \tilde{I}_i}{\partial \dot{x}_i}\frac{\partial \dot{x}_i}{\partial \tilde{\Gamma}_i}(0) + \frac{\partial \tilde{I}_i}{\partial \kappa_i}\frac{\partial \kappa_i}{\partial \tilde{\Gamma}_i}(0) + \frac{\partial \tilde{I}_i}{\partial u_i}\frac{\partial \Psi_i}{\partial \alpha_i}\frac{\partial \alpha_i}{\partial \tilde{\Gamma}_i} + \frac{\partial \tilde{I}_i}{\partial \tilde{v}_i}\frac{\partial \tilde{v}_i}{\partial \tilde{\Gamma}_i} = 0, \quad \forall\ \ i \in \mathcal{T} \tag{3.62}$$

for each task i given the values of the variables $\tilde{\Gamma}_i$ (*cf.* equation (3.58)). At the end of the integration, the quantities $\frac{\partial x_i}{\partial \tilde{\Gamma}_i}(t^f_i)$, $\frac{\partial \dot{x}_i}{\partial \tilde{\Gamma}_i}(t^f_i)$ and $\frac{\partial \kappa_i}{\partial \tilde{\Gamma}_i}(t^f_i)$ may be used to compute the gradients:

$$\frac{\partial \mathcal{G}^{e}_{i\omega}}{\partial \tilde{\Gamma}_i},\ \ \frac{\partial \mathcal{G}^{ie}_{i\omega}}{\partial \tilde{\Gamma}_i},\ \ \ldots,\ \ \frac{\partial \mathcal{U}_{\mu i}}{\partial \tilde{\Gamma}_i} \tag{3.63}$$

via the simple application of the chain rule of differentiation to the equations listed above.

If the MINLP is a maximisation problem, then the *globally optimal* solution of the sub-problem will provide a lower bound to the parent MINLP since it is solved for a fixed choice of binary variables. Of course, in reality, obtaining global solutions of large NLPs of the type considered here is impracticable. We, therefore, make use of locally optimal solutions. The implication of this is that the solutions obtained by the OA/AP algorithm may not be globally optimal solutions of the original MINLP problem. On the other hand, they are, at least, feasible with respect to all constraints that are taken into consideration.

3.8.5.2. Master Problem

The MILP master problem solves a linear approximation to the MINLP problem. It is constructed by accumulating linearisations of the constraints and objective function at the solutions of all previous subproblems so as to produce an increasingly better approximation of the original MINLP problem. At each iteration, the master problem predicts new values for the binary variables. It also generates an upper bound to the objective function, provided that

the non-linear objective function and the constraints are convex. When the latter is not true, the master problem constraints may cut into the feasible region excluding some candidate integer solutions; hence, the final solution cannot be guaranteed to be optimal.

As already mentioned in section 3.8.5.1, $\tilde{\Gamma}_i$ excludes all discrete variables y_i (since these are now fixed) as well as any variables v_i that are fully determined by the choice of y_i via constraints (3.4). However, the master problem used by the OA/AP algorithm requires the values of the gradients of the objective function and the constraints with respect to *all* members of the set Γ_i. These gradients have to be evaluated at the solution point of the subproblem. Hence, once the optimal solution of the subproblem is found, the gradients are then computed by integrating the sensitivity equations for the model equation (3.43) with respect to Γ_i (and not just $\tilde{\Gamma}_i$).

In view of the possibility that the MINLP problem (3.56) is non-convex, we adopt the approach proposed by Viswanathan and Grossmann (1990) where the master problem is modified to handle mild non-convexities. This involves an augmented penalty version of the MILP master problem which tries to avoid cutting off feasible mixed integer solutions. At the Kth iteration, this modified MILP has the following form:

$$\max_{\Gamma} \quad \Upsilon - \sum_{k=1}^{K} w_k q_k \tag{3.64}$$

subject to:

$$\Upsilon \leq \tilde{\Phi}(\Gamma^{(k)}) + \left.\frac{\partial \tilde{\Phi}}{\partial \Gamma}\right|_{\Gamma^{(k)}} (\Gamma - \Gamma^{(k)}) \quad \forall \quad k = 1, .., K \tag{3.65}$$

$$\tilde{C}(\Gamma^{(k)}) + \left.\frac{\partial \tilde{C}}{\partial \Gamma}\right|_{\Gamma^{(k)}} (\Gamma - \Gamma^{(k)}) \leq q_k \quad \forall \quad k = 1, .., K \tag{3.66}$$

$$\sum_{i \in A^k} y_i - \sum_{i \in B^k} y_i \leq |A^k| - 1 \quad \forall \quad k = 1, .., K \tag{3.67}$$

$$q_k \geq 0 \tag{3.68}$$

where $\tilde{\Phi}$ and $\tilde{C}$ are the objective function and the constraints of formulation (3.56) evaluated at the solution point of the subproblem respectively. In addition to the linearisations (3.65) and (3.66) about the solutions of all the subproblems $k = 1, .., K$, the master problem involves an integer cut constraint (3.67) to exclude all previously selected solutions for the integer variable. The slack variables q_k are introduced to relax the constraint linearisations, and are then penalised in the objective function. The weights w_k are large but finite and are often set to 1000 times the Lagrange multipliers of the corresponding constraints at the optimal solution of the subproblem (Viswanathan and Grossmann, 1990). However, our experience

with the type of problem of interest to this thesis indicates that a slightly better performance is obtained by setting w_k to be equal to the Lagrange multipliers.

The modified master problem cannot, in general, be guaranteed to produce valid upper bounds for the objective function of the problem. The termination criterion used by Viswanathan and Grossmann (1990) is to stop the search when there is no further improvement in the solution of the subproblem. However, our experience indicates that a slightly better solution is sometimes determined if the search is terminated when the upper bound provided by the MILP master problem becomes lower than the current best lower bound of the NLP subproblem (see examples in Chapters 4 and 5).

3.8.5.3. Algorithm Steps

The summary of the main steps of the OA/AP algorithm are as follows:

1. Set $K = 1$ and the lower bound of the objective $\Phi^* = -\infty$. Either fix the integer values y_i to given values (*i.e.* initial guesses), or treat them as continuous variables (*i.e.* $y_i \in [0, 1]$).

2. Solve the NLP subproblem to obtain the objective function Φ^{SB}. If infeasible, go to step 4.

3. If $\Phi^{SB} > \Phi^*$, then set $\Phi^* := \Phi^{SB}$ and $\Gamma^* := \Gamma$.

4. Solve MILP master problem to determine $\Gamma^{(K+1)}$ and the objective function value Φ^{MP} (excluding the penalty terms). If infeasible, then go to step 6.

5. If $\frac{\Phi^{MP}-\Phi^*}{\Phi^*} \leq \epsilon$, then go to step 6, else set $K := K + 1$, fix y_i at the values they have in $\Gamma^{(K+1)}$, and go to step 2.

6. If $\Phi^* > -\infty$, then the optimal solution is Γ^* with an objective function value of Φ^*; otherwise, the problem is infeasible.

In our implementation, we solve the MILP master problem using the *CPLEX MILP* solver (CPLEX Optimization Inc., 1995).

It is important to note that there is no theoretical guarantee that the algorithm will find the global optimum despite the augmented penalty provisions for trying to overcome the effect of non-convexities.

3.9. Conclusions

A general formulation for the design of batch processes based on the State-Task Network (STN) has been proposed in this chapter. This aims to determine:

- the structure of the process recipe;
- the precise nature of the materials handled in the process;
- the operating policies of the various processing stages;
- the characteristics of the equipment items.

The formulation (3.30) presented is a complex infinite dimensional multistage mixed integer dynamic optimisation problem. In addition to the inherently time-dependent behaviour of the system, there are two other aspects that add to the complexity of the problem. The first is the existence of numerous alternatives for the process recipe structure. The second is that many problems involve discrete quantities or decisions at the equipment design level, *e.g.* the optimal number of trays in batch distillation columns or the choice of equipment items that are available only in certain standard sizes. Overall, these characteristics impart a combinatorial character to the problem.

The infinite dimensionality of formulation (3.30) is handled using the control vector parameterisation which transforms the problem to a mixed integer non-linear programming problem (MINLP) in a finite and relatively small set of decision variables (*cf.* equation (3.56)). We propose to solve this problem using a two-level approach:

I. An enumeration procedure that considers all feasible process recipe structures that are embedded within a given superstructure.

II. An outer approximation/augmented penalty decomposition scheme that handles all discrete decisions associated with individual equipment items within a fixed process recipe structure.

In Chapters 4 and 5 of this thesis, we will consider two classes of application of the Level II algorithm above. Then, in Chapter 6, we will present a superstructure that can be used by the Level I algorithm. Its application to specific batch process design problems will be considered in Chapters 7 and 8.

Chapter 4

Design of Batch Distillation Column Networks

In this chapter, we apply the formulation and solution methodology introduced in Chapter 3 to the design of batch distillation columns, both individually and where these are arranged in networks. The structure of these networks is fixed but the number of trays and other design characteristics of each unit are to be determined by the optimisation, together with the column operating procedures.

4.1. Introduction

In Chapter 3, we highlighted that there are two levels of discrete decisions associated with the design of batch problems: equipment design level and process structure level. In this chapter, we will focus on a problem where the process structure is *fixed* and the discrete decisions that need to be taken are those related to the design of the equipment items. In addition to finding the optimal operating policy and the characteristics of the tasks, our aim is also to determine the optimal design parameters of each of the equipment items used.

In particular, we consider the problem of designing networks of multicomponent batch distillation columns. Here, in addition to determining the optimal values or time variations of the continuous variables (such as the size of the reboiler or the reflux ratio profiles), one must also determine the values for the discrete decisions, in particular the optimal number of trays in the distillation column.

Batch distillation has received extensive attention in the recent past, partly due to the fact that it is frequently used in the production of small quantities of chemical and biochemical

products of high value. Its main advantage in this context is its versatility. However, it is precisely this flexibility and the inherently unsteady-state nature of its operation that pose challenging design and operation problems.

The behaviour of a batch distillation column can be translated into a mathematical model involving a set of differential material and energy balances, with algebraic equations representing the phase equilibria and other thermodynamic relationships. The stiffness of this system and its size which grows with the number of stages and components, often render even the simulation of these processes a non-trivial task. This has led to the development of alternative models that attempt to reduce the computational time without affecting the overall accuracy of the results. Diwekar and Madhavan (1991) approached the problem by applying an extended shortcut method commonly used for continuous distillation and based on the assumption that the batch column can be regarded as a continuous column with a changing feed. The authors proposed solving the model using the Fenske-Underwood-Gilliland (FUG) method assuming equimolar overflow, constant relative volatility and negligible column holdup. Simplified column dynamics and augmented short-cut models were also considered by Diwekar (1994). The effects of the various modelling assumptions for both rigorous and short-cut methods were examined by Bosley and Edgar (1994).

Numerous studies have sought to determine optimal reflux policies for batch distillation columns. This is usually achieved by the solution of one of the following optimisation problems:

- *Maximum distillate problem* : maximise the amount of product of a specified purity produced over a prescribed period of time (Mujtaba, 1989; Logsdon and Biegler, 1993).
- *Minimum time problem* : minimise the amount of time needed to produce products of specified quantity and quality (Diwekar, 1992; Mujtaba, 1989).
- *Maximum profit* : maximise an economic profit function subject to product purity and quantity constraints (Diwekar *et al.*, 1989; Logsdon *et al.*, 1990; Mujtaba and Macchietto, 1993; Charalambides, 1996).

Salimi and Depeyre (1998) compared the dynamic behaviour of a batch packed column with a plate column. Dynamic mathematical models were developed for both packed and plate columns and the model was applied to a batch system that separates a benzene-toluene-xylene mixture. The objective was to compare the effect of the hydraulic equations which include the liquid holdup, dry pressure drop and total pressure drop on the dynamic simulation of the two columns under identical operating policies.

Mujtaba and Macchietto (1997) presented a framework for the dynamic optimisation of

batch distillation where chemical reaction and separation take place simultaneously. The objective of the dynamic optimisation problem was to maximise the conversion of the limiting reactant, and parametric solutions of the problem were obtained. Polynomial curve fitting techniques were then applied to the results of the dynamic optimisation problem. The polynomials were used to formulate a non-linear algebraic maximum profit problem which was solved efficiently using a non-linear optimisation solver. This provided a framework which could be used for on-line optimisation of batch distillation within scheduling programs for batch processes.

Most studies dealing with the optimisation of the operation of batch distillation columns have been based on fixed equipment characteristics (*e.g.* the number of trays in a column, still capacity, *etc.*). However, it is often possible for a given set of separation requirements to be met using a column with a large number of equilibrium stages and short batch times at low reflux ratio, or alternatively, one with fewer equilibrium stages operated over longer batch times at a higher reflux ratio. It is clear that the design issues (*e.g.* the number of stages) and the operating policies (such as the reflux ratio variations) are interdependent and have to be considered simultaneously in the optimisation calculations.

Of course, one way of finding the optimal number of trays is to determine the optimal operating policy for each possible number of trays and then simply choose the one that corresponds to the best objective function value. Clearly, this is very tedious and time consuming. This is particularly the case when the optimisation of integrated batch processes involving multiple distillation columns is to be considered (see section 4.6). There is, therefore, a need for a more efficient and systematic way of determining the optimal number of trays which will be less time consuming than exhaustive enumeration.

To our knowledge, there has been only one systematic attempt to date, that by Mujtaba and Macchietto (1994, 1996), to treat the number of trays as a decision variable in the design and operation of batch distillation columns. The optimisation problem sought to determine optimal values for:

- design decision variables such as the number of trays and the vapour flow to the condenser; the latter indirectly determines the size of the reboiler;
- operating control variables such as the reflux ratio variation and cut times;

so as to maximise an annualised profit function for a given set of product specifications and constraints.

A two-level optimisation algorithm was proposed, with both the operating decisions and

the design decisions being optimised in an outer loop while only the operating control variables were optimised in the inner loop. Except for the number of trays N, the problem was formulated as a standard non-linear programming problem, where an inner optimisation problem was effectively solved to compute the values for the outer problem objective function and constraints. In the outer problem, N was considered as a continuous optimisation variable; in the inner loop problem, its value was rounded off to the nearest integer. The gradients with respect to N, required by the outer loop, were evaluated by finite differences using the function and constraint values at the *rounded off* values of N and $N+1$. If the outer problem converged to a non-integral value of N, the latter was fixed at the immediately lower and higher integer values, the inner problem was solved for each of these values and the better of the two solutions was taken as the optimum solution.

In the next section, we propose a mathematical formulation which generates the optimum number of trays for a distillation column by treating N directly as an *integer variable*. This is followed by the description of an algorithm for the solution of the resulting mathematical problem. Finally, examples are presented to demonstrate the application of the algorithm and examine its performance.

4.2. Mathematical Formulation

In principle, the design methodology to be presented in this section can be used in conjunction with *any* dynamic tray-by-tray model of a batch distillation column. Here, we consider a model in which the molar holdups on each tray and in the condenser are constant and the tray energy dynamics are fast. This is a common set of assumptions in the batch distillation literature (see, for example, Mujtaba and Macchietto, 1993). Recently, however, there has been increasing evidence that some, if not all, of these assumptions are not justified (see, for example, Tomazi, 1997; Mujtaba and Macchietto, 1998; Furlonge *et al.*, 1998). We could relax the assumptions to form a more realistic model, which would inevitably result in a more complex optimisation problem. With such increasing complexity there is, all the more, a need to develop an efficient methodology to find the optimal solution. In this study, we are primarily interested in developing this methodology; in the interests of simplicity of presentation, we will therefore retain the assumptions stated above.

We initially restrict our attention to the optimisation of a single batch distillation column. This allows us to introduce the basic ideas. The extension of the latter to network of batch distillation columns is entirely straightforward (see section 4.6).

In general, the standard batch distillation column model has to be modified to reflect

the fact that N is an unknown integer bounded between an upper limit N_{max} and a lower limit N_{min}. The basic idea of our approach is similar to that used by Viswanathan and Grossmann (1993) for the design of continuous distillation columns. Thus, the reflux stream for the condenser is allowed to return to any one of the candidate trays, as shown schematically in figure 4.1.

Mathematically, this is achieved by the introduction of the binary variable set ζ_n, $n \in \tau \equiv [N_{min},\ N_{max}]$ where:

$$\zeta_n = \begin{array}{ll} 1, & \text{if the reflux return stage is } n; \\ 0, & \text{otherwise.} \end{array}$$

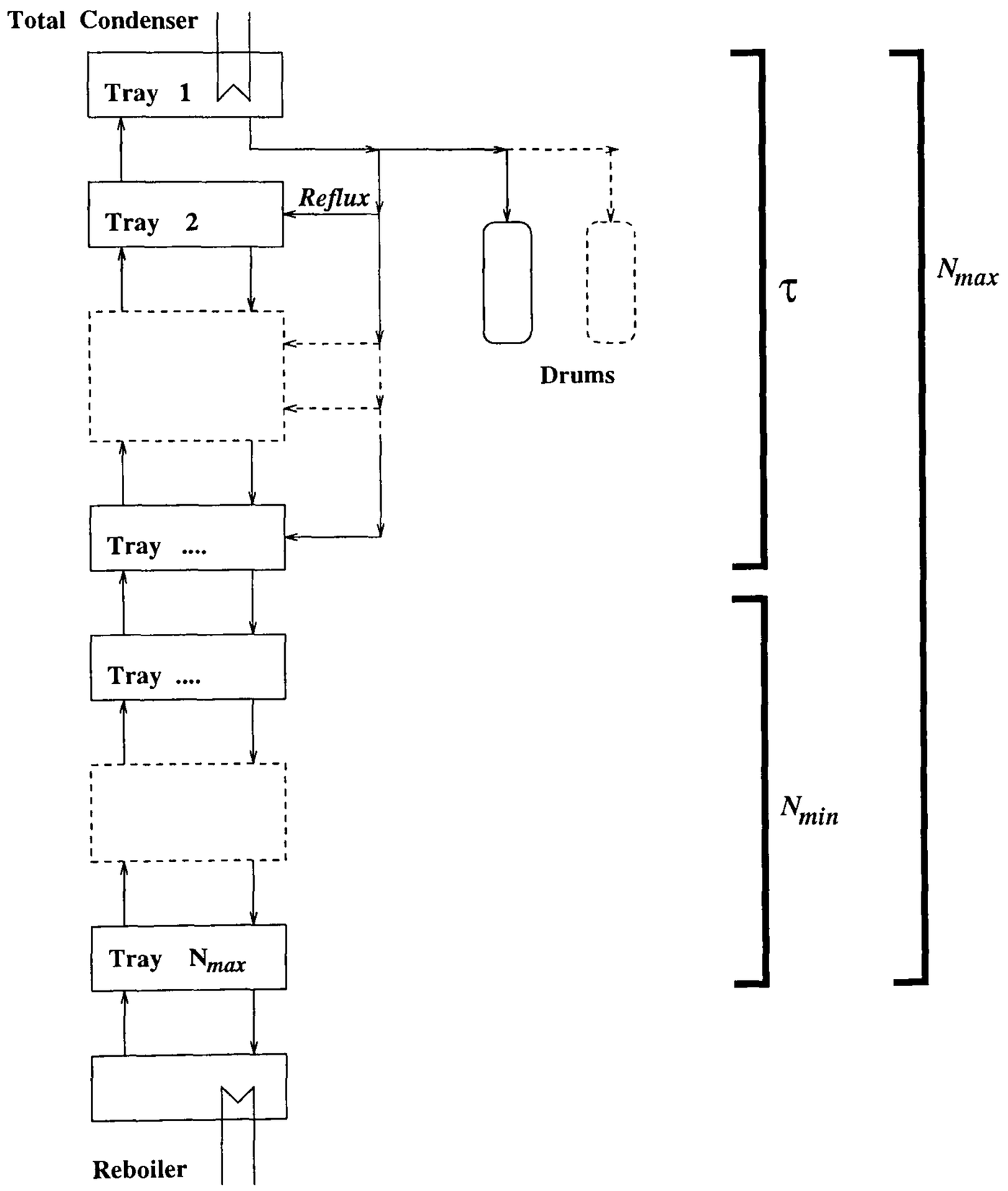


Figure 4.1: Batch column superstructure (based on Viswanathan and Grossmann, 1993)

In the final column design, the reflux must be returned to a single tray. Therefore, exactly one of the variables ζ_n will take a value of 1, all others being zero. This is achieved via the

logical constraint:

$$\sum_{n \in \tau} \zeta_n = 1 \tag{4.1}$$

For the case of the design of *continuous* columns considered by Viswanathan and Grossmann (1993), no separation is effected in the trays above the reflux return position since the vapour flowing through them does not encounter any liquid stream flowing downwards. Thus, fixing the reflux position effectively removes all these trays from the design, which is the desired effect. However, this is not the case with batch distillation columns. In particular, the vapour flowing through the trays above the reflux return position still comes into contact with the liquid holdup in these trays, and this may result in mass transfer which is clearly fictitious since in reality these trays do not exist. On the other hand, *not* including any liquid holdup on these trays would most probably result in severe numerical problems caused by the intensive properties (*e.g.* temperature and composition) on these trays becoming undefined.

In order to resolve the above difficulty, we modify the Viswanathan and Grossmann (1993) column superstructure shown in figure 4.1 to include additional vapour streams that may be used to by-pass all trays above the reflux return position (see figure 4.2).

We now proceed to formulate an optimisation problem based on this superstructure. The variables in our model are:

i : component index
L_d : molar distillate flowrate
L_n : liquid molar flowrate leaving tray n
M_c : condenser holdup
M_n : molar holdup on tray n
n : tray index
N : number of trays in a column
N_{max} : maximum number of trays in a column
N_{min} : minimum number of trays in a column
Q_c : condenser heat duty
q_k : slack variables for constraint linearisations
r : normalised reflux ratio
t_f : duration of the distillation task
t_I : idle time
t_s : set-up time for column
V_n : vapour molar flowrate leaving tray n
x_{ic} : mole fraction of component i in the condenser
x_{in} : liquid mole fraction of component i on tray n
y_{in} : vapour mole fraction of component i on tray n
ζ : binary variables determining reflux return position (see text)
τ : set of possible candidate trays

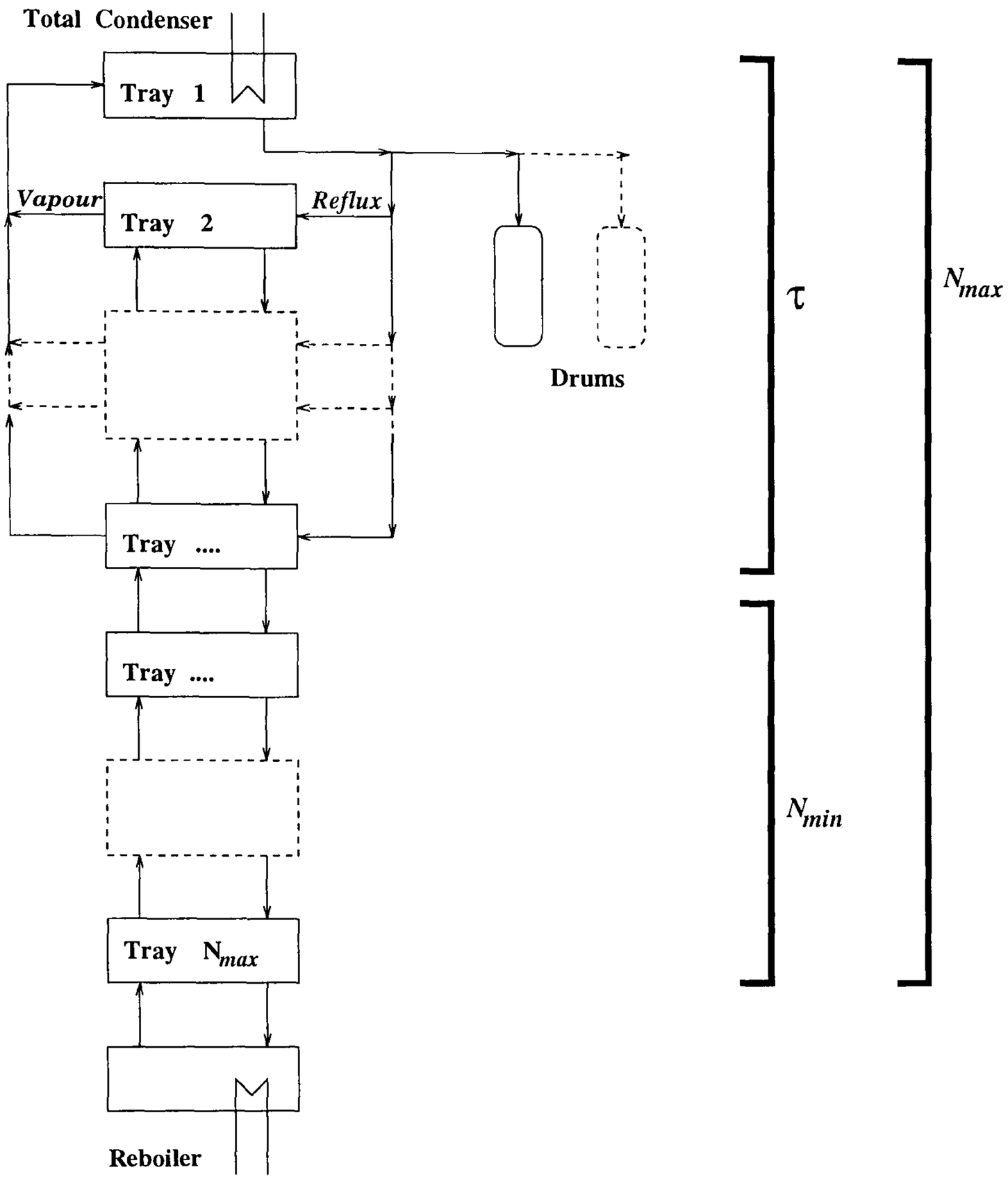


Figure 4.2: Modified batch column superstructure

Overall, the standard tray material and energy balance equations (see Appendix A.1) for all trays $n \in \tau$, that are eligible to receive the reflux return stream, have to be modified to:

- Overall tray mass balance:

$$L_{n-1} + V_{n+1}(1 - \sum_{n'=n+1}^{N_{max}-N_{min}} \zeta_{n'}) + L_c\zeta_n = L_n + V_n \quad \forall\ n \in \tau \tag{4.2}$$

- Tray component mass balance:

$$M_n \frac{dx_{in}}{dt} = L_{n-1}x_{i,n-1} - L_n x_{in} + L_c x_{ic}\zeta_n + V_{n+1}y_{i,n+1}(1 - \sum_{n'=n+1}^{N_{max}-N_{min}} \zeta_{n'}) - V_n y_{in} \quad \forall\ n \in \tau,\ i \tag{4.3}$$

- Tray energy balance:

$$L_{n-1}h^l_{n-1} + V_{n+1}h^v_{n+1}(1 - \sum_{n'=n+1}^{N_{max}-N_{min}} \zeta_{n'}) - L_n h^l_n - V_n h^v_n + L_c h^l_c \zeta_n = 0 \quad \forall\ n \in \tau \tag{4.4}$$

Note that the quantity:

$$\sum_{n'=n+1}^{N_{max}-N_{min}} \zeta_{n'}$$

appearing in all of the above equations has a value of 1 if the reflux return position is below tray n, and 0 otherwise. In the former case, the form of the above equations ensures that no contribution of mass or energy is made to tray n from the tray below it. Thus, tray n is effectively by-passed.

The total condenser equations are also modified to reflect the fact that the condenser can receive its vapour input from any one of the trays $n \in \tau$:

- Overall condenser mass balance:

$$\sum_{n\in\tau} \zeta_n V_n = L_c + L_d \tag{4.5}$$

- Condenser component mass balance:

$$M_c \frac{dx_{ic}}{dt} = \sum_{n\in\tau} \zeta_n V_n (y_{in} - x_{ic}) \quad \forall \quad i \tag{4.6}$$

- Condenser reflux ratio calculation:

$$L_c = r \sum_{n\in\tau} \zeta_n V_n \tag{4.7}$$

- Condenser duty:

$$Q_c = \sum_{n\in\tau} \zeta_n V_n (h_n^v - h_c^l) \tag{4.8}$$

The actual number N of trays in the column is given by:

$$N = N_{max} - \sum_{n\in\tau} n\zeta_n + 1 \tag{4.9}$$

In general, the objective of the optimisation is to determine the column design and operating policy that maximise an objective function:

$$P(X(t_f), N, v, t_f) \tag{4.10}$$

while satisfying one or more constraints on the mean production rate and/or the product purities. Here, t_f is the duration of the distillation task, v is a set of other design parameters (*e.g.* column diameter) and $X(t)$ represents the set of all variables describing the operation of the column.

4.3. Solution Methodology

The mathematical problem to be solved involves the maximisation of the objective function (4.10) subject to:

- A mixed set of differential and algebraic equations:

$$f(X(t), \dot{X}(t), u(t), v, \zeta) = 0 \quad \forall \quad t \in [0,\ t_f] \tag{4.11}$$

  where $u(t)$ are control variables such as the reflux ratio and the heat input to the reboiler. Equations (4.2)-(4.8) are a subset of these equations f. The latter also include thermodynamic equilibrium relations, physical property calculations, as well as the model of the column reboiler and accumulator tank(s).

- The logical constraints (4.1) and the definition of the number of trays (4.9).

- Constraints on the product purity and recovery. These are of the general form:

$$C(X(t_f)) \leq 0 \tag{4.12}$$

- Bounds on the control variables u and the time invariant parameter v:

$$u_{min} \leq u(t) \leq u_{max}\ , \qquad \forall\ t \in [0, t_f] \tag{4.13}$$

$$v_{min} \leq v \leq v_{max} \tag{4.14}$$

In view of the binary nature of the variables ζ_n, the above is a mixed integer dynamic optimisation problem. Recently, Mohideen *et al.* (1996, 1997) presented an algorithm for the solution of this type of problem based on a Generalised Benders decomposition approach, the discretisation of (4.11) using an implicit Runge-Kutta scheme and the calculation of the required gradients via the integration of the adjoint equations. Allgor and Barton (1997) used targeting techniques to decompose the mixed integer dynamic optimisation problem into subproblems which provide rigorous upper and lower bounds on the objective function. Here, we adopt the approach described in section 3.8 of this thesis. It will be recalled that this is based on a combination of an outer approximation/augmented penalty (OA/AP) algorithm (Viswanathan and Grossmann, 1990) for the solution of mildly non-convex mixed integer nonlinear programming problems (MINLPs) with the control vector parameterisation approach for the solution of dynamic optimisation problems (Vassiliadis *et al.*, 1994b, 1994a). The

latter involves expressing the control variables $u(t)$ in terms of a finite set of parameters α:

$$u(t) \equiv \Psi(t, \alpha) \quad \forall \quad t \in [0,\ t_f] \tag{4.15}$$

where $\Psi(.)$ are functions of a *given* form with respect to time. We assume that the form of these functions is sufficiently simple (*e.g.* piecewise constant) for the bounds (4.13) on the control variables $u(t)$ to be translated into bounds on the parameters α:

$$\alpha_{min} \leq \alpha \leq \alpha_{max} \tag{4.16}$$

The vector of the decision variables:

$$Z \equiv \{\alpha,\ v,\ t_f,\ \zeta\}$$

fully determines the values of the objective function $P(.)$ and the constraints $C(.)$ since, once these are given, we can solve the DAEs (4.11) to obtain $X(t_f)$. We, therefore, define the functions:

$$\tilde{P}(Z) \equiv P(X^*(t_f, Z),\ N,\ v,\ t_f) \tag{4.17}$$

$$\tilde{C}(Z) \equiv C(X^*(t_f, Z)) \tag{4.18}$$

where $X^*(t, Z)$ is the solution of $f(X(t),\ \dot{X}(t),\ \Psi(t, \alpha),\ v,\ \zeta) = 0$ for given Z. The original infinite dimensional problem is now reduced to the following finite dimensional problem:

$$\max_{Z \equiv \{\alpha, v, t_f, \zeta\}} \quad \tilde{P}(Z) \tag{4.19}$$

subject to:

$$\tilde{C}(Z) \leq 0 \tag{4.20}$$

$$\sum_{n \in \tau} \zeta_n = 1 \tag{4.21}$$

$$N = N_{max} - \sum_{n \in \tau} n\zeta_n + 1 \tag{4.22}$$

$$\alpha_{min} \leq \alpha \leq \alpha_{max} \tag{4.23}$$

$$v_{min} \leq v \leq v_{max} \tag{4.24}$$

The finite dimensional problem above is a mixed integer non-linear programming (MINLP) problem. In view of the possibility that the MINLP problem is non-convex, the problem is solved via the OA/AP two-stage iterative procedure outlined in the next two subsections (*cf.* section 3.8.5).

4.3.1. Subproblem

The *Kth subproblem* of the OA/AP algorithm applied to the batch distillation problem involves fixing the discrete decision variables ζ_n to a given set of values $\zeta_n^{(K)}$. It is, therefore, equivalent to optimising a column with a given number of trays, $N^{(K)}$. This is a standard dynamic optimisation problem; we solve it using Vassiliadis' (1993) DAEOPT code interfaced to the *gPROMS/gOPT* modelling tool (Process Systems Enterprise Ltd., 1997). Since the optimisation is carried out for a *fixed* number of trays, the solution of the subproblem is a lower bound P^{LB} on the solution of the overall optimisation design problem.

In fact, since in the Kth subproblem the number of trays $N^{(K)}$ is known, there is no need to introduce any of the inactive trays ($n = 1, .., N^{max} - N^{(K)} + 1$) in the model or, indeed, to modify the original equations to include the ζ_n variables (as we have done in equations (4.2)-(4.8)). Instead, we solve a standard optimisation problem for a batch column of $N^{(K)}$ trays aiming to determine optimal values $\alpha^{(K)*}$, $v^{(K)*}$ and $t_f^{(K)*}$.

Of course, the master problem (see section 4.3.2) still requires the gradients of the objective function $\tilde{P}$ and constraints $\tilde{C}$ with respect to the ζ_n variables. These gradients have to be evaluated at the solution of the subproblem. Therefore, once the optimal subproblem solution is obtained, we calculate the gradients of $\tilde{P}$ and $\tilde{C}$ by integrating the sensitivity equations of the *modified* DAE model (*i.e.* the one involving the modified equations (4.2)-(4.8)) with respect to the vector:

$$Z^{(K)} \equiv \{\alpha^{(K)*}, \quad v^{(K)*}, \quad t_f^{(K)*}, \quad \zeta^{(K)}\} \tag{4.25}$$

4.3.2. Master Problem

The *master problem* at the Kth iteration of our OA/AP algorithm involves linearisation of the functions $\tilde{P}(.)$ and $\tilde{C}(.)$ about the solutions of all subproblems $k = 1, .., K$ considered so far:

$$\max_{Z} \quad \Upsilon - \sum_{k} w_k q_k \tag{4.26}$$

subject to:

$$\Upsilon \leq \tilde{P}(Z^{(k)}) + \left.\frac{\partial \tilde{P}}{\partial Z}\right|_{Z^{(k)}} (Z - Z^{(k)}) \quad \forall \quad k = 1, .., K \tag{4.27}$$

$$\tilde{C}(Z^{(k)}) + \left.\frac{\partial \tilde{C}}{\partial Z}\right|_{Z^{(k)}} (Z - Z^{(k)}) \leq q_k \quad \forall \quad k = 1, .., K \tag{4.28}$$

$$\sum_{n \in \tau} \zeta_n = 1 \tag{4.29}$$

$$N = N_{max} - \sum_{n \in \tau} n\zeta_n + 1 \tag{4.30}$$

$$\zeta_{n_k} = 0, \quad \forall \quad k = 1, .., K \tag{4.31}$$

$$Z_{min} \leq Z \leq Z_{max}; \quad q_k \geq 0 \tag{4.32}$$

$$\zeta_n \in \{0, 1\} \quad \forall \quad n \in \tau \tag{4.33}$$

In addition to the linearisations (4.27) and (4.28), the master problem involves constraint (4.29) enforcing a unique selection for the reflux return position, and equation (4.30) defining the number of trays N in each column. Moreover, constraint (4.31) ensures that reflux return positions that have already been considered are not selected again. Here, the index n_k is such that ζ_{n_k} had a value of 1 in the solution of the master problem at the kth iteration.

In view of the potential non-convexity of the problem, the OA/AP algorithm relaxes the constraint linearisations (4.28) via the introduction of slack variables q_k which are then penalised in the objective function (4.26) (for details see section 3.8.5.2).

The master problem is a Mixed Integer Linear Programming (MILP) problem. We solve it using the *CPLEX MILP* solver (CPLEX Optimization Inc., 1995). In addition to the number of trays to be fixed at the next subproblem, the solution also provides initial guesses for the control variable variations (in terms of the parameters α), the time invariant parameters v and the processing time t_f in the next subproblem.

4.3.3. Outer Approximation Algorithm

The overall OA/AP algorithm is summarised below:

1. Set $K = 1$ and $P^* = -\infty$. Guess number of trays N, thereby fixing $\zeta_n^{(1)} \quad \forall \ n$.
2. Solve the subproblem for fixed $\zeta_n^{(K)}$ to obtain the objective function P^{SB}. If infeasible, go to step 4.
3. If $P^{SB} > P^*$, then set $P^* := P^{SB}$ and $Z^* := Z$.
4. Solve the MILP master problem to determine $Z^{(K+1)}$ and the objective function P^{MP} (value excluding penalty terms). If infeasible, then go to step 6.
5. If $\frac{P^{MP} - P^*}{P^*} \leq \epsilon$, then go to step 6, otherwise set $K := K + 1$ and go to step 2.

6. If $P^* > -\infty$, then the optimal solution is Z^* with an objective function value of P^*; otherwise, no feasible solution to the problem could be found.

Our experience indicates that, for this type of problem, slightly better results are obtained with the termination criterion used in step 5 above than with that originally suggested by Viswanathan and Grossmann (1990).

4.4. Example 1: Ternary Batch Distillation

To illustrate the methodology presented in the previous section, we consider a ternary batch distillation system process involving the separation of 2.93 $kmol/batch$ of feed mixture consisting of 40.7% cyclohexane (component 1), 39.4% n-heptane (component 2) and 19.9% toluene (component 3). This distillation operation was initially studied by Nad and Spiegel (1987) who simulated a column with 20 theoretical trays, with the pressure varying from 1.013 bar at the bottom to 0.962 bar at the top. The UNIQUAC model was used for the vapour-liquid equilibrium calculations. They neglected the enthalpy effects on the system.

The optimal design and operation of this ternary system was further considered by Mujtaba and Macchietto (1996). The number of trays, processing time, cut location and the reflux ratio were treated as decision variables. The vapour flow to the condenser was fixed at 2.75 $kmol/hr$. The DAE model formulated took account of both material and energy balances, with constant vapour flow to the condenser. The vapour-liquid equilibrium calculations were performed using the Soave-Redlich-Kwong (SRK) equation of state (see section B.1.1 in Appendix B for details). The objective function used was the maximisation of the annual profit taking into account net revenues (products and raw materials), operating cost and annualised capital costs.

The same system was also considered by Charalambides (1996). In his study, the number of trays was fixed at 17, and different policies for the recycling of the off-cuts was investigated.

4.4.1. Process Description

The process is set up as shown in figure 4.3. The distillation column consists of N theoretical trays. The products are the first and the second main cuts which are collected in the drums $D1$ and $D2$, and the residue left in the reboiler at the end of the operation which is collected in the drum Bf. Final product purities of 89.5% cyclohexane in $D1$, 86.3% of n-heptane in $D2$ and 99.0% of toluene in Bf are required. The off-cuts collected in $R1$ and $R2$ have no economic value.

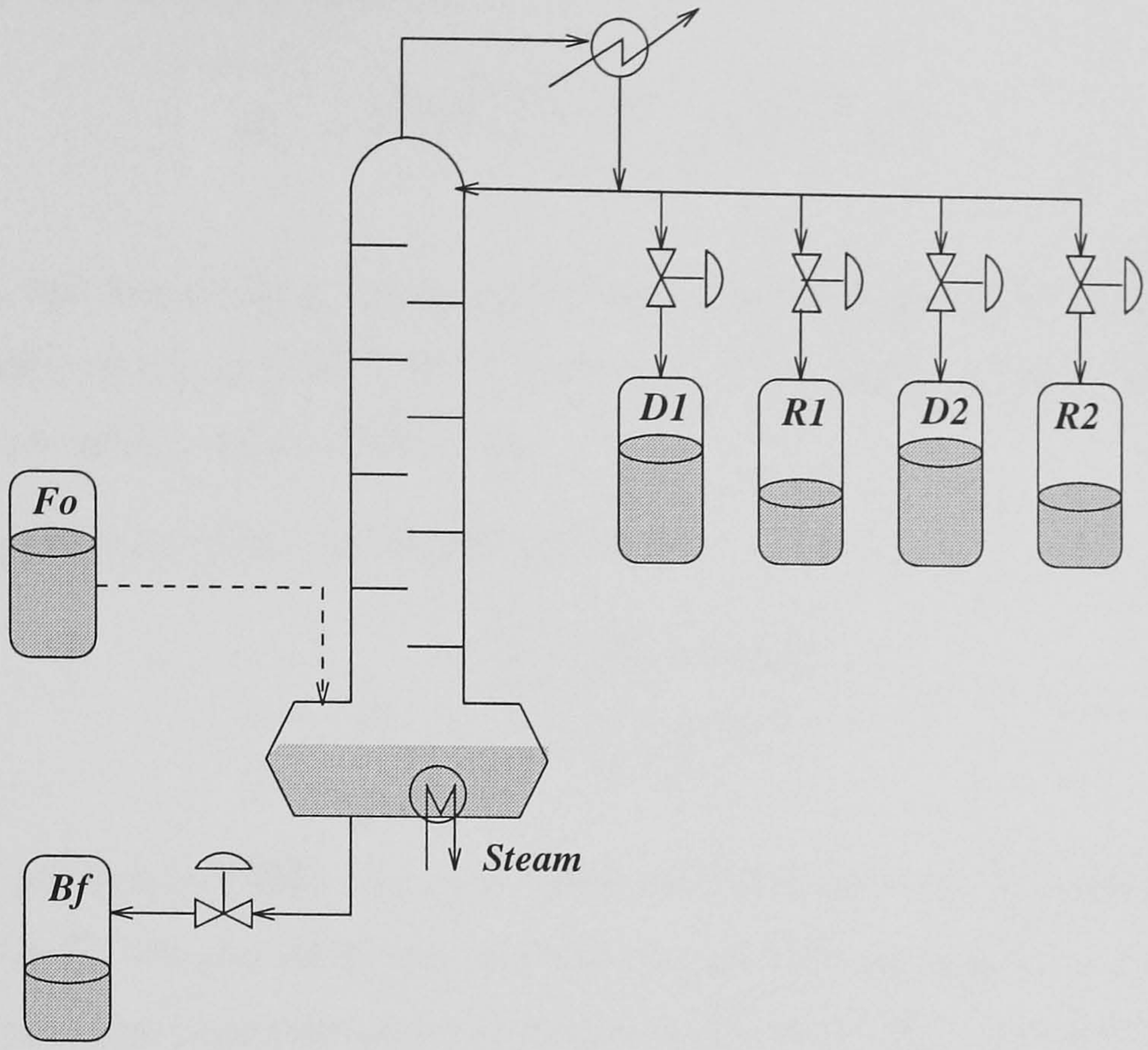


Figure 4.3: Ternary batch distillation process

The reboiler, the trays and the condenser are filled with liquid at the initial charge composition and at a temperature of 365 K. A molar charge of 3.28 *moles* is assumed for each column tray and 31.52 *moles* for the total condenser. The inlet and outlet temperatures of the cooling water in the condenser are fixed at 288 K and 328 K. A constant column pressure of 1.025 *bar* is used. Non-ideal Soave-Redlich-Kwong (SRK) vapour-liquid equilibrium models are used (for more details, see section B.1.1 in Appendix B). The normalised reflux ratio, defined as the ratio of the flowrate of the reflux stream to that of the vapour stream entering the condenser, is allowed to vary between 0.75[¶] and 0.99. The number of trays is bounded between 10 and 25.

4.4.2. Costing

The annualised capital cost ($\$/hr$) is calculated using the formula:

$$C_c = 0.1875V^{0.5}N^{0.8} + 1.1875V^{0.65} \tag{4.34}$$

where V $(kmol/hr)$ is the condenser vapour load and N is the number of trays. Equation (4.34) is of the same form as that used by Mujtaba and Macchietto (1996).

[¶]A fairly high lower bound on the reflux ratio is necessary in order to ensure that the column will be operable at the solution determined by the optimisation; this would have been unnecessary if flooding and weeping constraints had been imposed explicitly in the column model.

The operating cost ($\$/hr$) is calculated by:

$$C_o = \frac{C_w \int_0^{t_f} F_{cw}\, dt + C_s \int_0^{t_f} F_s\, dt}{t_f + t_s} \tag{4.35}$$

where F_{cw} and F_s are the cooling water and steam flowrates in kg/hr respectively. The cost coefficients are taken as $C_w = 8.33 \times 10^{-6}$ $\$/kg$ and $C_s = 0.01038$ $\$/kg$. The set-up time, t_s, is taken as constant with a value of 30 min.

The operating revenue ($\$/hr$) is calculated by:

$$R_o = \frac{\sum_s C_s B_s - C_0 B_0}{t_f + t_s} \tag{4.36}$$

where C_s and B_s are respectively the unit value and the amount of product s produced per batch, while C_0 and B_0 are the unit cost and the amount of raw material consumed per batch. The values for these cost parameters are given in table 4.1. The negative unit values for $R1$ and $R2$ reflect the undesirability of building up stocks of these materials. The objective is to maximise the overall profit rate calculated by:

$$Profit = R_o - C_c - C_o \tag{4.37}$$

Material	Unit value ($\$/kmol$)
F_o	2.0
$D1$	50.0
$D2$	26.0
$R1$	-1.0
$R2$	-1.0
Bf	24.0

Table 4.1: Unit values for process materials

4.4.3. Optimisation Calculations

4.4.3.1. Subproblem

In the studies by Mujtaba and Macchietto (1993; 1994) and Charalambides (1996), the vapour flow to the condenser was always fixed at a value of 2.75 $kmol/hr$. Here, however, this is

treated as a piecewise constant control variable to be determined by the optimisation. Its variation is bounded between 2.0 $kmol/hr$ and 2.90 $kmol/hr$. Also, the minimum cyclohexane recovery constraint of 95% used by Charalambides (1996) is replaced by an inequality constraint on the mean[§] production rate of the first cut $D1$ of at least 0.06 $kmol/hr$. The purity constraints are treated as inequality constraints, and the reflux ratio as another piecewise constant control variable, allowed to vary between a lower bound of 0.75 and an upper bound of 0.99.

The processing time of the distillation operation is divided into 6 control intervals of varying durations. The first cut is produced at the end of interval 2, the second, third and fourth cuts are produced at the ends of intervals 3, 5 and 6 respectively.

4.4.3.2. Problem Solution

The first iteration was performed using ζ_{12}= 1.0, *i.e.* a column with 14 trays. The initial guess for the processing time is 8.00 hr. The reflux ratio and vapour flowrate to the condenser are initially set at uniform values of 0.85 and 2.75 $kmol/hr$ respectively. The solution of the MILP master problem generated an upper bound for the objective function and also the values for the reflux ratio at each time interval, the duration of the intervals, the value of the vapour flow V_1 and a new value for ζ, *i.e.* the number of trays. The subproblem was then formulated and solved using the latter values, and the steps were repeated.

Table 4.2 shows the steps and the results of the OA/AP algorithm for the ternary batch distillation column. The optimisation required 3 outer approximation iterations and a total of approximately 3.78 hr of CPU time on a *SUN SPARC10* workstation.

OA Iteration	**1**	**2**	**3**
Subproblem			
N	14	16	**19**
P^* ($/hr)	6.016	6.670	**7.421**
NLP Iterations	39	20	26
CPU(s on *SUN SPARC10*)	5606.3	3211.6	4806.2
Master problem			
N	16	19	18
P^{MP} ($/hr)	17.137	16.734	0.068
P^{MP} - P^*	11.121	10.064	-7.353
Branch & Bound nodes	0	2	0
CPU(s on *SUN SPARC5*)	0.05	0.05	0.05

Table 4.2: OA/AP algorithm performance

[§]Averaged over the duration of a batch, including the set-up time, t_s.

4.4.3.3. Results and Discussion

The solution obtained indicates that a column with 19 trays will achieve the highest profit rate. The processing time is 6.23 *hr* with a 30 *min* set-up time; therefore, the total batch cycle time is 6.73 *hr*. An economic breakdown of the optimal solution[‡] is shown in table 4.3. The details of the optimal recipe are presented in the form of an *annotated* State-Task Network (STN) in figure 4.4. As these diagrams are used to show the optimal solutions throughout this thesis, it is essential to understand the various items of information presented in them:

> *As is the usual STN convention, each rectangle corresponds to a task. The information below the name of the task i is the processing time t_i^f per batch (typically in hours). If the task incurs some idle time t_i^{idle} between successive batches (cf. section 3.5), this is also shown on the diagram directly below the task rectangle (for example, see figure 4.12).*
>
> *Circles represent the state s of materials, again conforming with the standard STN convention. The information presented in a rounded dashed box next to each state is the vector of intensive properties, z_s. In this thesis, unless otherwise stated, these correspond to the mole fractions of the various components.*
>
> *The arrow from a state node s to a task node i in the diagram is annotated with B_{is}^{IN}, the total amount of material of state s fed to each batch of task i (cf. section 3.4.1).*
>
> *The arrow from a task node i to a state node s is annotated with B_{is}^{OUT}, the amount of material of state s that is produced by each batch of task i (cf. section 3.4.2). In the case of tasks producing multiple product at different times, the time after which the entire amount of each product is generated is also shown on the corresponding arrow.*

The key features of the optimal STN are:

- 0.435 *kmol/hr* of F_o are separated to produce 0.184 *kmol/hr* of distillate $D1$ which consists of 89.5% of cyclohexane, hence satisfying the purity and the minimum mean production rate (0.06 *kmol/hr*) constraints. The composition profiles in the first accumulator tank are shown in figure 4.5(a).

[‡]Based on the assumption that the column is operating for 8000 *hr* per annum.

- 0.154 $kmol/hr$ of $D2$ containing 86.3% of n-heptane is produced in the second main cut. The composition profiles in the third accumulator tank are shown in figure 4.5(b).
- Only 0.02 and 0.03 $kmol/hr$ of the off-cuts $R1$ and $R2$ respectively are produced and are discarded as waste.
- Finally, 0.05 $kmol/hr$ of reboiler residue containing 99% of toluene is produced by the process. The variation of the composition of the contents of the reboiler during the process operation and the reflux ratio are shown in figure 4.6(a).

The optimal operating policies for the steam and cooling water flowrates are presented in figure 4.6(b). The vapour flow to the condenser V_1 is held at its upper bound of 2.90 $kmol/hr$ during the entire operation.

Material	Net Production rate ($kmol/yr$)	Revenue ($/yr$)
Fo	−3482.91	−6965.82
$D1$	1469.47	73473.50
$D2$	1230.07	31981.82
$R1$	128.48	−128.48
$R2$	237.35	−237.35
Bf	418.05	10033.20
Total Production Revenue		**108156.87**
Total Annualised Capital Cost		**46179.28**
Utility	Mean consumption rate (te/yr)	Cost ($/yr$)
Cooling water	3986.226	33.20
Steam	248.225	2576.58
Total Utility Cost		**2609.78**
Total Net Profit		**59367.81**

Table 4.3: Economic breakdown of optimal solution

The optimal values/variations of the decision variables are summarised in table C.1 in Appendix C.

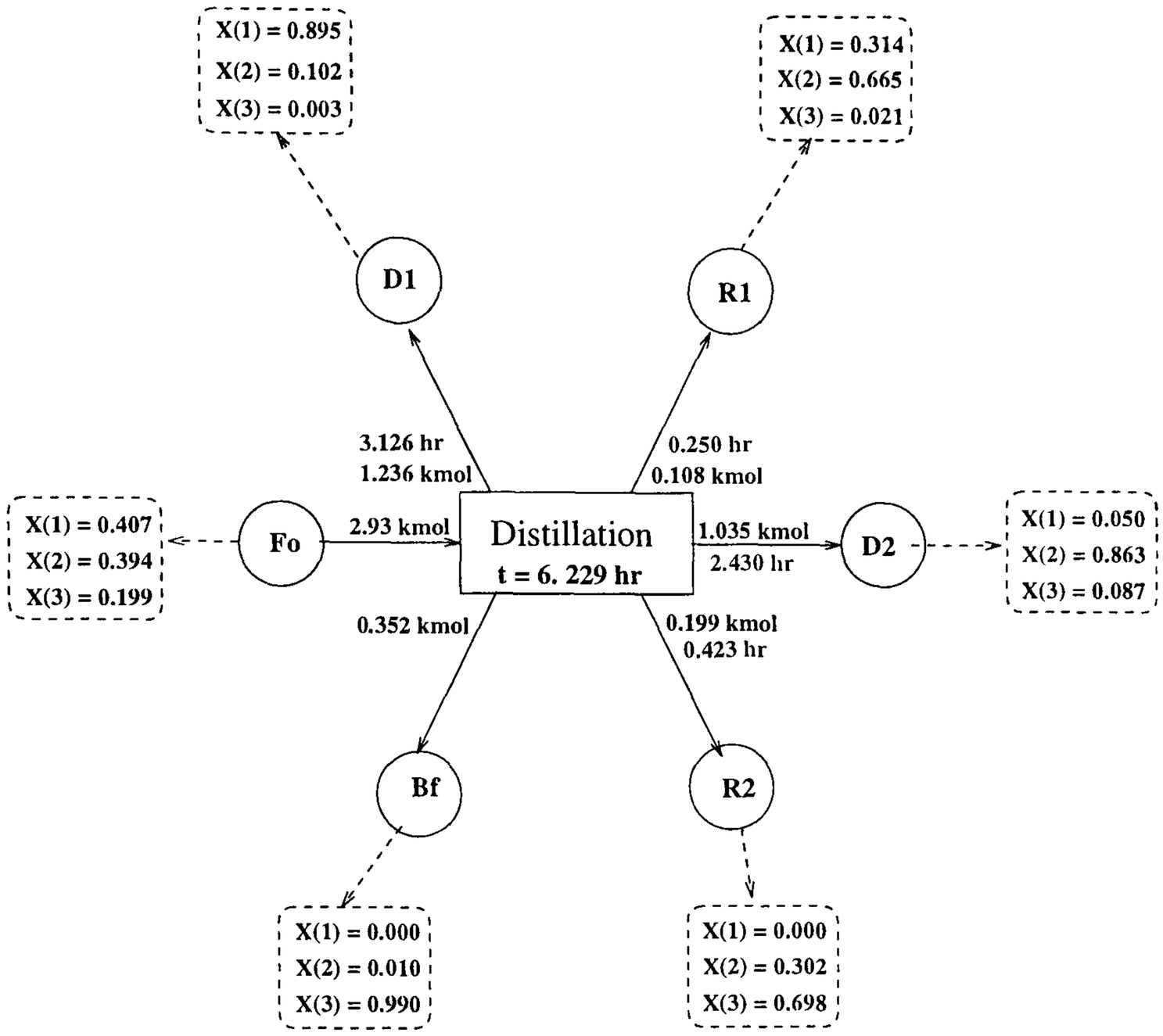
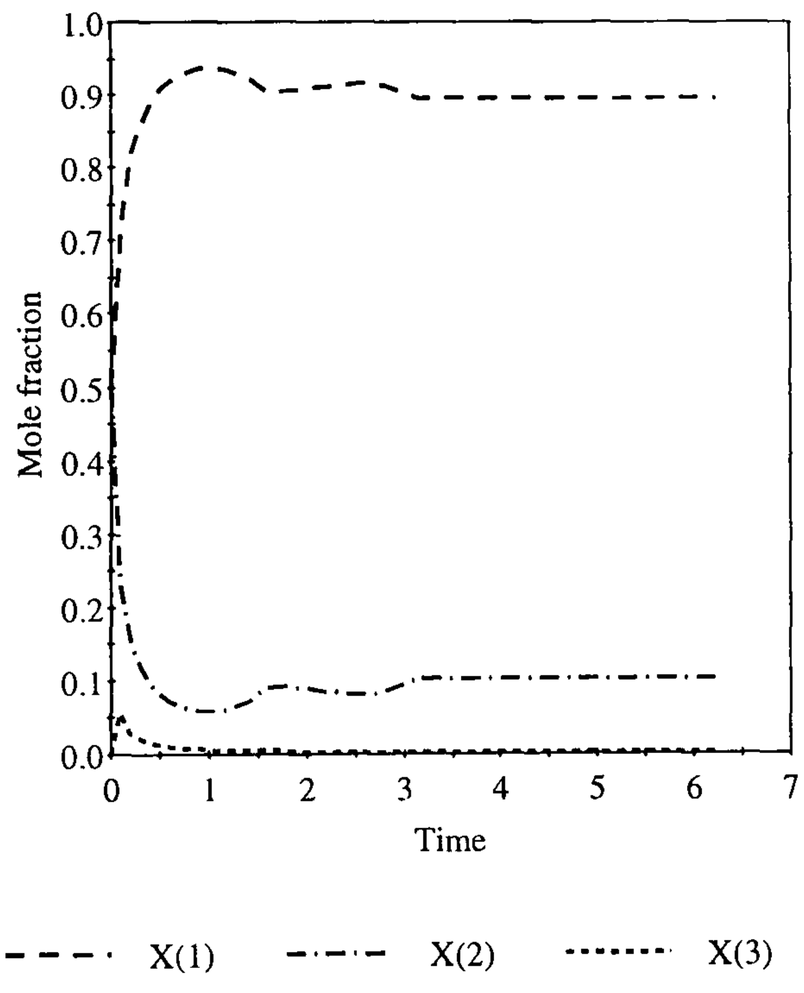
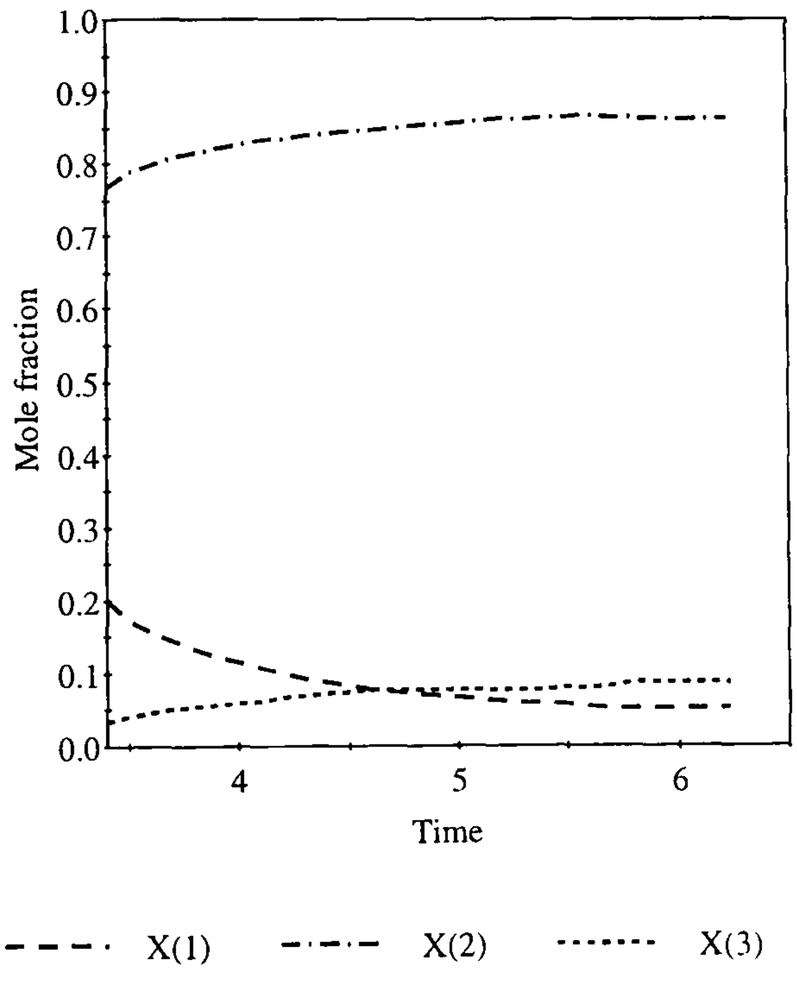


Figure 4.4: Optimal process recipe for 19 tray column

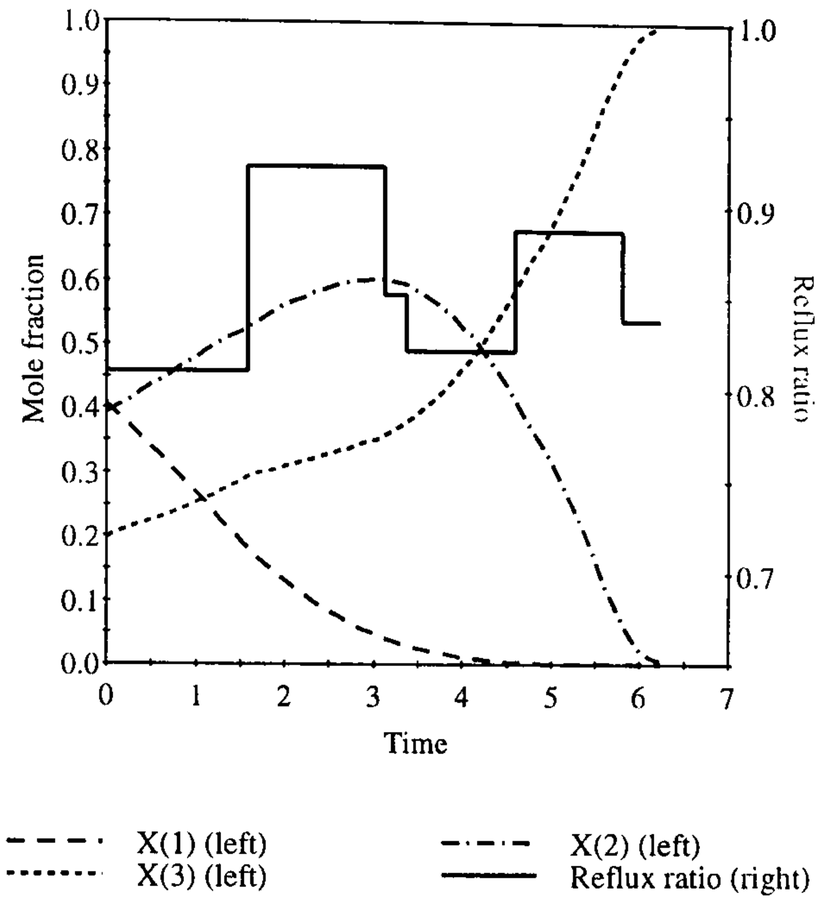


(a) Mole fraction profiles in the first accumulator tank

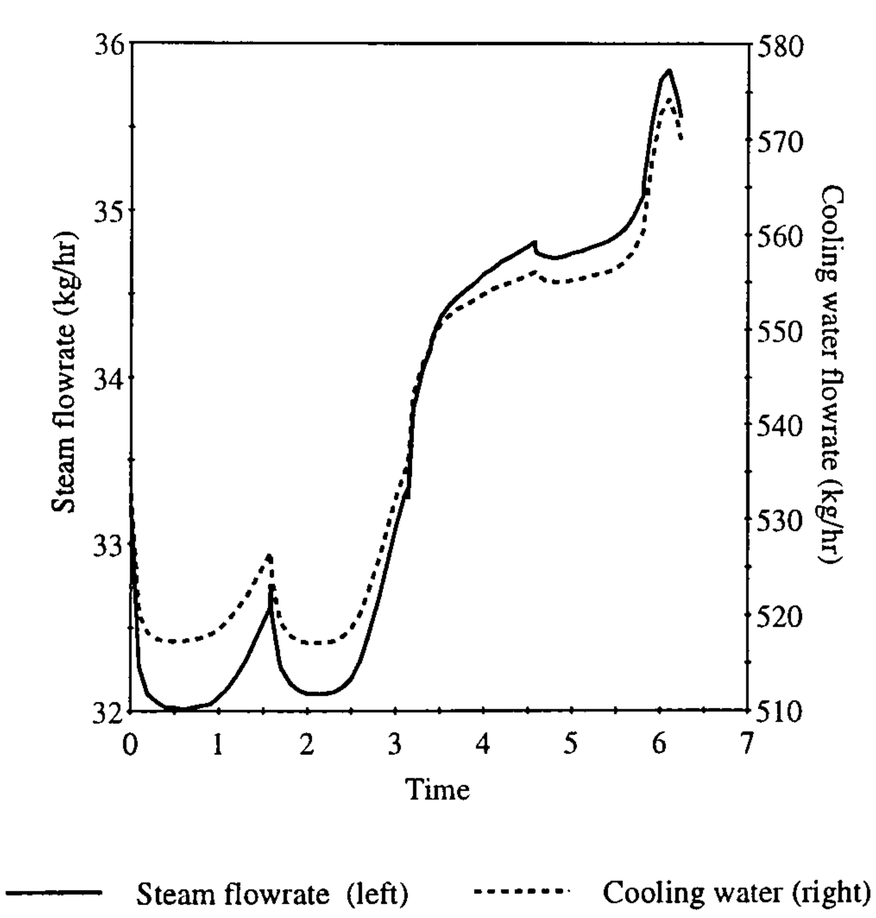


(b) Mole fraction profiles in the third accumulator tank

Figure 4.5: Accumulator tank composition profiles



(a) Mole fraction profiles in the reboiler and the optimal reflux ratio policy



(b) Steam and cooling water flowrates (kg/hr) in the reboiler and condenser respectively

Figure 4.6: Column optimal operating policy

4.5. Example 2: Batch Distillation of Isomers

This example is based on an industrial project carried out for a major chemical company. The distillation operation involves the separation of 625 $kg/batch$ of 3 isomers consisting of 99.2% (mass basis) of isomer A, 5000 ppm of isomer B and 3000 ppm of isomer C. The structure of the process is shown in figure 4.7. The product is the first (and only) distillate cut collected in drum D_t, and the residue left in the reboiler is collected in drum D_b. The product is required at a purity of at least 99.85% of isomer A and must contain less than 1000 ppm and 500 ppm of isomers B and C respectively. Also, a recovery of 90% of isomer A is required. The mean production rate must not exceed 0.270 $kmol/hr$ and must not be less than 0.250 $kmol/hr$.

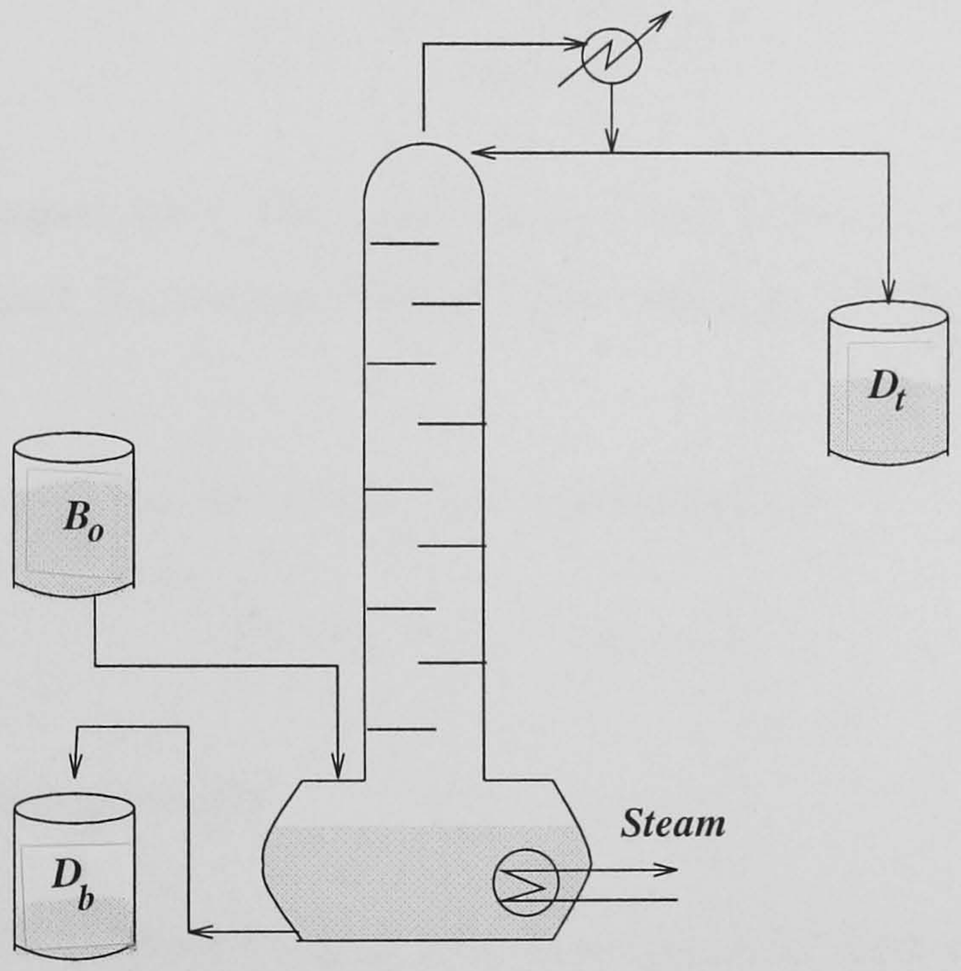


Figure 4.7: Multicomponent batch distillation column structure

The reboiler, trays and condenser are filled with liquid at the initial charge composition at a temperature of 366 K. A molar charge of 2.375 $moles$ is assumed for each column tray and 86.450 $moles$ for the total condenser. The inlet and outlet temperatures of the cooling water to the condenser are fixed at 288 K and 320 K respectively. The column is operated at constant pressure of 50 $Torr$ (6.67×10^3 Pa).

4.5.1. Economic Considerations

The annualised capital cost ($/hr) of the column is calculated by the following formula:

$$C_c = 0.125V^{0.3}N^{0.89} + 0.775V^{0.65} \tag{4.38}$$

where V is the vapour flowrate to the condenser (in $kmol/hr$) and N is the number of trays.

The operating cost ($\$/hr$) of the column is calculated by:

$$C_o = \frac{C_w \int_0^{t_f} F_{cw}\, dt + C_s \int_0^{t_f} F_s\, dt}{t_f + t_s} \tag{4.39}$$

where F_{cw} (te/hr) is the cooling water flowrate and F_s (te/hr) is the steam flowrate. The cost coefficients are taken as $C_w = 1.5$ $\$/te$ and $C_s = 20$ $\$/te$. The set-up time t_s is fixed at 1.0 hr.

The operating revenue is determined by:

$$R_o = \frac{\sum_p C_p D_t - C_0 B_0}{t_f + t_s} \tag{4.40}$$

where C_p and D_t are respectively the unit value (100 $\$/kmol$) and amount of product p produced. Similarly, C_0 and B_0 are respectively the unit cost (10 $\$/kmol$) and amount of raw material consumed.

The objective is to maximise the profit rate calculated by:

$$Profit = R_o - C_o - C_c \tag{4.41}$$

4.5.2. Modelling Considerations

The distillation column is modelled using standard material and energy balance equations. Ideal vapour-liquid equilibrium models are used (see section B.1.2 for data). The vapour flow to the condenser V (in $kmol/hr$) and the normalised reflux ratio r (defined as the flowrate of the reflux stream to that of the vapour stream entering the condenser) are both treated as piecewise constant control variables in the ranges [2.5 $kmol/hr$, 4.0 $kmol/hr$] and [0.5, 1.0] respectively. The operating time of the distillation process is divided into 6 control intervals of varying durations. Appropriate inequality constraints are imposed on the recovery, mean production rate and purity.

The number of trays in the column is allowed to vary between 70 and 100 trays. In the initial guess, the number of trays in the column is fixed at 78 trays. The initial guess for the processing time is 20 hr. The reflux ratio and vapour flowrate to the condenser are initially set at uniform values of 0.98 and 4.0 $kmol/hr$ respectively.

4.5.3. Results and Discussion

Table 4.4 shows the steps taken by the OA/AP algorithm. The solution obtained indicates that 81 trays in the distillation column will achieve the highest profit rate. The optimisation required 5 iterations and a total of about 2.82 *hr* of CPU time on a *SUN ULTRA* workstation.

OA/AP Iteration	**1**	**2**	**3**	**4**	**5**
Subproblem					
N	78	77	79	80	**81**
P^* ($/hr$)	9.18	9.16	9.23	9.25	**9.29**
NLP Iterations	27	18	34	26	35
CPU(s on *SUN ULTRA*)	1816	1095	2868	1809	2550
Master problem					
N	77	79	80	81	75
P^{MP} ($/hr$)	159.12	125.91	40.49	17.25	7.07
P^{MP} - P^*	149.94	116.73	31.26	8.00	-2.22
Branch & Bound nodes	0	0	0	14	14
CPU(s on *SUN SPARC5*)	0.067	0.067	0.100	0.116	0.117

Table 4.4: OA/AP algorithm performance

The process achieves a net profit of 9.29 $/hr$. The details of the optimal recipe are presented in the form of a State-Task Network (STN) in figure 4.8. The economic breakdown of the optimal solution is presented in table 4.5. The mean throughput of feed being separated is 0.3021 $kmol/hr$, with a processing time of 13.31 hr and a fixed set-up time of 1.0 hr. The distillation task produces a mean flowrate of 0.27 $kmol/hr$ of a top product which is 99.89% rich in isomer A. The composition profiles of the isomers in the accumulator tank are shown in figure 4.9(a). 0.032 $kmol/hr$ of residue is left in the reboiler and is discarded as waste at no cost. The composition profiles of the isomers in the reboiler are shown in figure 4.9(b).

Material	Net production revenue ($kmol/hr$)	Revenue ($/hr$)
B_0	0.3021	−3.02
D_t	0.2700	27.00
Total Capital Cost		**11.35**
Total Operating Cost		**3.34**
Total Net Profit		**9.29**

Table 4.5: Economic breakdown of optimal solution

The optimal variation of the vapour flowrate to the condenser is shown in figure 4.9(b).

The vapour flowrate is maintained at its upper limit of 4.0 $kmol/hr$, over almost the entire operation. This ensures that most of the valuable product (isomer A) is distilled and collected in the accumulator tank. However, during the last 0.5 hr of the operation, the vapour flowrate is lowered to 3.4 $kmol/hr$ so as to prevent the accumulation of isomer B in the distillate cut, hence satisfying the requirement that no more than 1000 ppm of isomer B are to be present in the final product.

The optimal variation of the normalised reflux ratio in the distillation column is also shown in figure 4.9(a). The reflux ratio is maintained above 0.90 during the entire operation: isomers by nature have close boiling points and consequently, the vapour entering the condenser is relatively rich in all three isomers; hence, a high reflux is required.

The optimal values/variations of the decision variables are summarised in table C.2 in Appendix C.

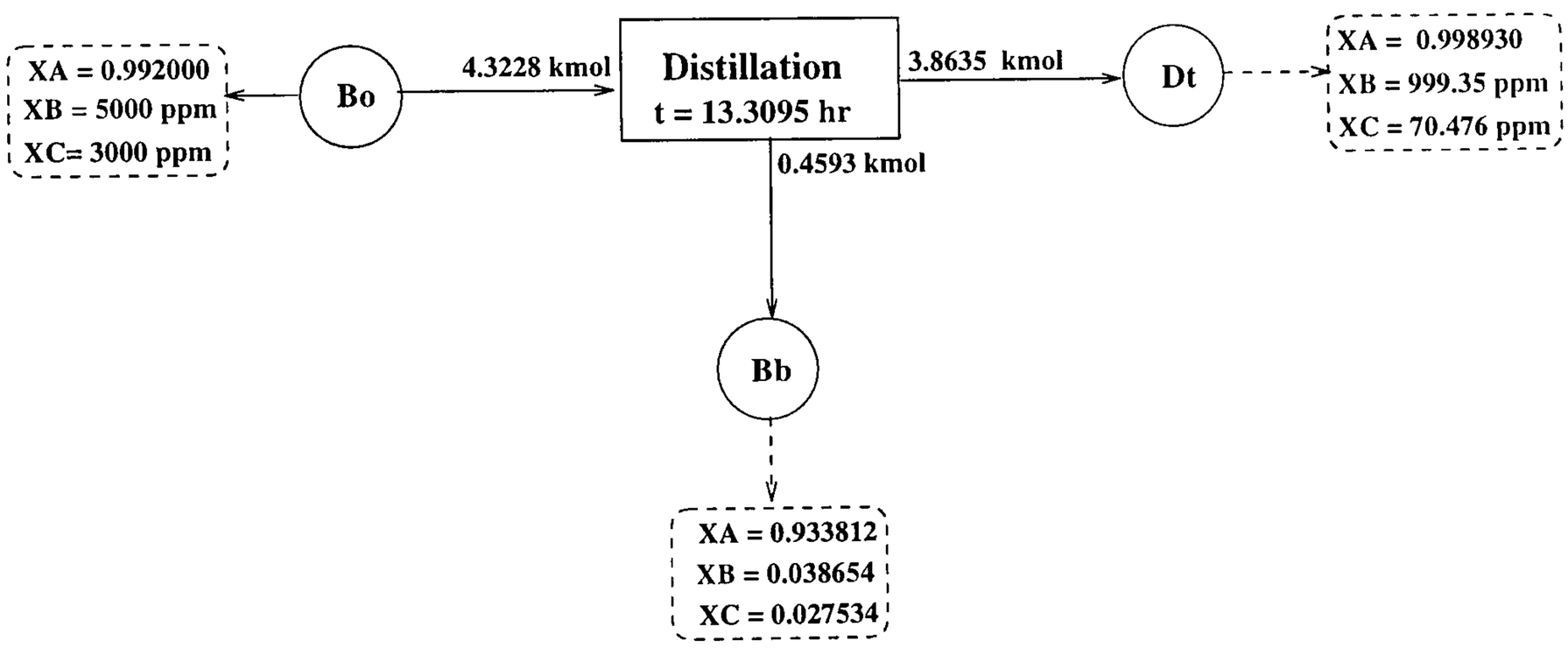
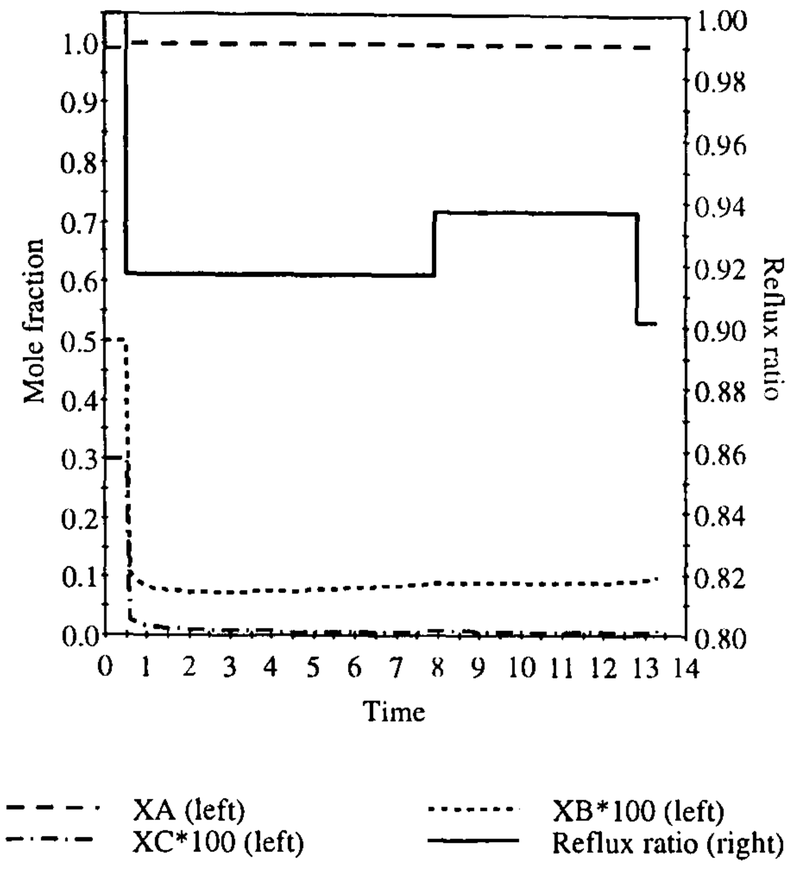
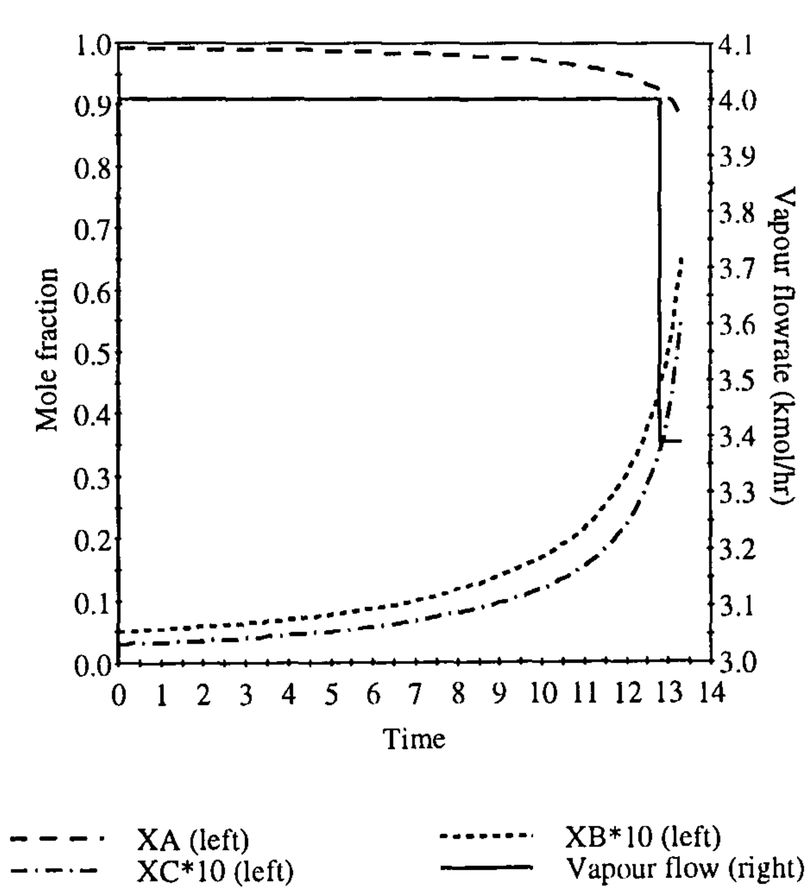


Figure 4.8: State-Task Network of the optimal operating policy for a column with 81 trays



(a) Mole fraction profiles in the accumulator drum and the optimal reflux ratio policy



(b) Mole fraction profiles in the reboiler and vapour flowrate ($kmol/hr$) to condenser

Figure 4.9: Optimal operating policy for isomer separation

4.6. Optimisation of Multicomponent Batch Distillation Column Networks

So far in this chapter, we have considered the optimal design and operation of a single batch distillation column. We now proceed to consider the optimisation of integrated batch processes comprising multiple batch distillation units. This is entirely within the scope of the formulation presented in Chapter 3. As in the case of a single column, the subproblem involves optimising columns with a fixed number of trays.

The master problem is very similar to the one presented in section 4.3.2, except that the integer cut constraint (4.31) is replaced by:

$$\sum_{c=1}^{NC} \zeta_{n_k,c} \leq NC - 1, \quad \forall \quad k = 1, .., K \tag{4.42}$$

Here, the summation is taken over all NC batch distillation columns in the process and $\zeta_{n_k,c}$ is the ζ variable for column c that had a value of 1 in the solution of the master problem at the kth iteration. This constraint excludes any combination of numbers of trays that has already been considered at previous iterations of the algorithm.

4.6.1. Example 3: Multicomponent Two Column Batch Distillation

The algorithm is applied to a process utilising a sequence of two batch distillation columns (see figure 4.10) for the separation of 22.86 $kmol/batch$ of a mixture of eight components with mole fractions 0.0262, 0.0004, 0.1867, 0.4777, 0.0007, 0,0505, 0.2571 and 0.0007 respectively. The product is the residue left in the reboiler of the second distillation column, with a mass purity requirement of 99% of component 7 and a mean production rate requirement of 500 kg/hr.

Distillation column I is operated at constant atmospheric pressure. Distillation column II is operated at 0.036 bar as it is used to separate a heavier mixture. The numbers of trays in both columns are bounded between 6 and 15.

The reboiler, trays and condenser of both columns are filled with liquid at the initial charge composition. The holdup of each tray and the condenser is fixed at 100 $moles$.

The distillation columns are modelled assuming constant liquid holdups on the trays, negligible vapour holdups and tray hydraulics, fast energy dynamics, no reactions between the components and perfect mixing. Ideal vapour-liquid equilibrium models are used (see table B.4 in Appendix B). The time for charging and discharging each batch, t_s, is fixed at 30 min.

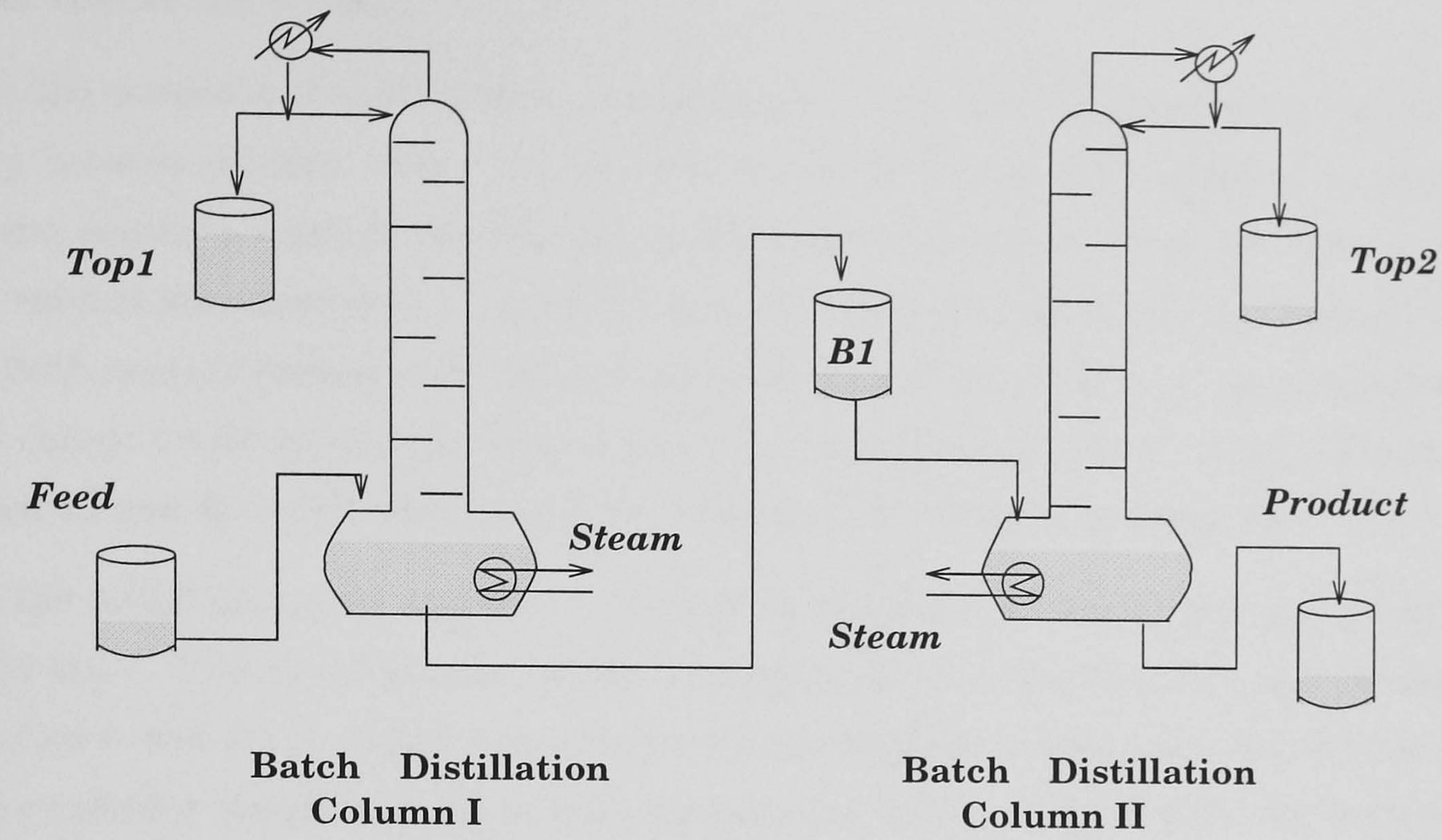


Figure 4.10: Multicomponent two column batch distillation columns

The *capital cost* C_c of the distillation columns is calculated on an hourly basis ($\$/hr$) as:

$$C_c = \alpha_r V_D^{0.6} + \alpha_n V_D^{0.533} N^{0.802} + \alpha_p (760 - Pr)^2 \tag{4.43}$$

incorporating both size and pressure dependent terms. Here, Pr, the operating pressure of the column in $mmHg$, is assumed to remain constant throughout the distillation task. V_D is the reboiler volume in dm^3, N the number of trays, and α_r, α_n and α_p the cost coefficients with values of 1.35, 0.0663 and 0.00033 respectively. The last term in equation (4.43) represents the extra capital cost incurred when operating at sub-atmospheric pressures.

The operating cost C_o ($\$/hr$) takes into account the reboiler load, expressed in terms of the vapour flowrate to the condenser (V, mol/hr), the operating pressure (Pr, $mmHg$) and the condenser cooling load (Q_c, kJ/hr) (Charalambides, 1996):

$$C_o = 0.0177V + 0.0011(760 - Pr)^2 + 0.0001552Q_c \tag{4.44}$$

The contribution of column c to the overall objective function is given by:

$$C_c + \frac{\int_0^{t_f} C_o(t).dt}{t_f + t_s + t_I} \tag{4.45}$$

where t_s is the set-up time (fixed at 30 min) and t_I is the idle time between batches.

The unit value of the feed is taken as 250 $\$/kmol$ while that of the product as 15 $\$/kg$ (3756.48 $\$/kmol$). The two light by-products *Top1* and *Top2* are treated as wastes with a

disposal cost of 100 $\$/kmol$.

For the purposes of optimisation, the processing time for each distillation task is allowed to vary between 0.5 and 10 hr. The maximum vapour flow to the condenser is treated as a piecewise constant control variable varying between 12.5 and 20 $kmol/hr$. The normalised reflux ratio is also treated as a piecewise constant control variable varying between 0.70 and 0.99. Both control variables are defined over four control intervals of varying durations. The initial charge to the reboiler is treated as a time invariant parameter, being allowed to vary between 15 and 45 $kmol$. This indirectly determines the reboiler volume, V_D.

In the initial guess, the number of trays N in column I is fixed at 9 trays and in column II at 12 trays. The initial guesses for the processing times t_f for column I and column II are 2.6 $hr/batch$ and 2.5 $hr/batch$ respectively. The normalised reflux ratio and vapour flowrate to the condenser are initially set at uniform values of 0.70 and 16 $kmol/hr$ for both columns, and the initial charges at 26.91 $kmol$.

4.6.2. Results

Table 4.6 shows the steps of our OA/AP algorithm when applied to this problem. The solution of the algorithm indicates that 7 trays in column I and 8 trays in column II will achieve the highest profit rate. The optimisation required 10 outer approximation iterations and a total of about 16 hr of CPU time on a *SUN ULTRA* workstation. The process achieves a net profit of 4043 $\$/hr$. The details of the optimal recipe are presented in the form of a State-Task Network (STN) in figure 4.12. The economic breakdown of the optimal solution is presented in table 4.7.

Distillation column I separates 7.7 $kmol/hr$ of feed with a processing time of 2.47 hr and a fixed set-up time of 0.5 hr. It produces 4.99 $kmol/hr$ of distillate which is discarded as waste material. The material in the reboiler residue which is produced at 2.71 $kmol/hr$ forms intermediate $B1$ and undergoes further separation. The reboiler volume for column I is 2983 dm^3. The vapour flowrate to the condenser is maintained at its upper limits of 20 $kmol/hr$ and the normalised reflux ratio is maintained at its lower limit. This mode of operation ensures that most of the light components are separated from the initial feed charge. Figure 4.11(a) shows the profiles of the optimal normalised reflux ratio variations and also the optimal vapour flowrates to the condenser for distillation column I.

2.71 $kmol/hr$ of intermediate $B1$ are separated in distillation column II, which requires a processing time of 45 min and a fixed set-up time of 30 min and an idle time of 4.55 hr. The light components are collected in the distillate tank at 0.71 $kmol/hr$. The heavy material

OA Iteration	**1**	**2**	**3**	**4**	**5**
Subproblem					
N (Column I)	9	6	7	8	7
N (Column II)	12	6	6	6	7
P^* ($/hr$)	4005	4025	4034	4035	4039
NLP Iterations	9	17	15	13	31
CPU(s on *SUN ULTRA*)	4396	5446	3265	2867	8133
Master problem					
N (Column I)	6	7	8	7	8
N (Column II)	6	6	6	7	7
P^{MP} ($/hr$)	24678	12750	11883	10798	7832
P^{MP} - P^*	20673	8725	7849	6763	3793
Branch & Bound nodes	0	0	0	2	0
CPU(s on *SUN ULTRA*)	0.117	0.133	0.150	0.133	0.150

OA Iteration	**6**	**7**	**8**	**9**	**10**
Subproblem					
N (Column I)	8	9	10	6	**7**
N (Column II)	7	7	7	8	**8**
P^* ($/hr$)	4042	4040	4037	4028	**4043**
NLP Iterations	25	22	20	22	21
CPU(s on *SUN ULTRA*)	7041	6369	6135	6489	6323
Master problem					
N (Column I)	9	10	6	7	8
N (Column II)	7	7	8	8	8
P^{MP} ($/hr$)	7062	6796	6186	5926	2344
P^{MP} - P^*	3020	2756	2149	1898	-1699
Branch & Bound nodes	2	2	0	0	14
CPU(s on *SUN ULTRA*)	0.117	0.133	0.117	0.133	0.150

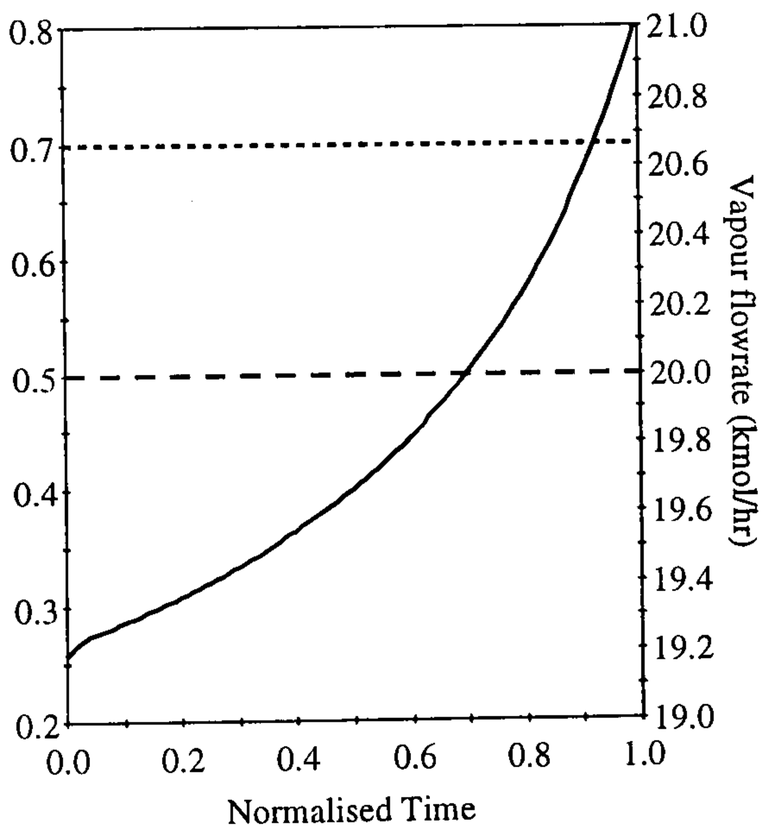
Table 4.6: OA/AP algorithm performance

remaining in the reboiler of the column forms the final product and is produced at a mean rate of 500 kg/hr, as required by the problem specification. The reboiler volume is 2839 dm^3. At the initial stages of the distillation task, the normalised reflux ratio is at its upper limit of 0.99. This is due to the fact that, at the start of the operation, the condenser, trays and reboiler are filled with the initial charge of intermediate $B1$; since the latter contains over 70% of the heavy product component 7, most of the material entering the condenser has to be refluxed back into the column so that this component is collected in the reboiler. Also, the vapour flowrate to the condenser is maintained at its lower limit of 12.5 $kmol/hr$ at the beginning of the process to prevent the accumulation of the heavy component 7 in the condenser. During the rest of the operation, the normalised reflux ratio is maintained at 0.70 and the vapour flowrate is varied as shown in figure 4.11(b). Composition profiles of component 7 (the product) are also shown in figure 4.11.

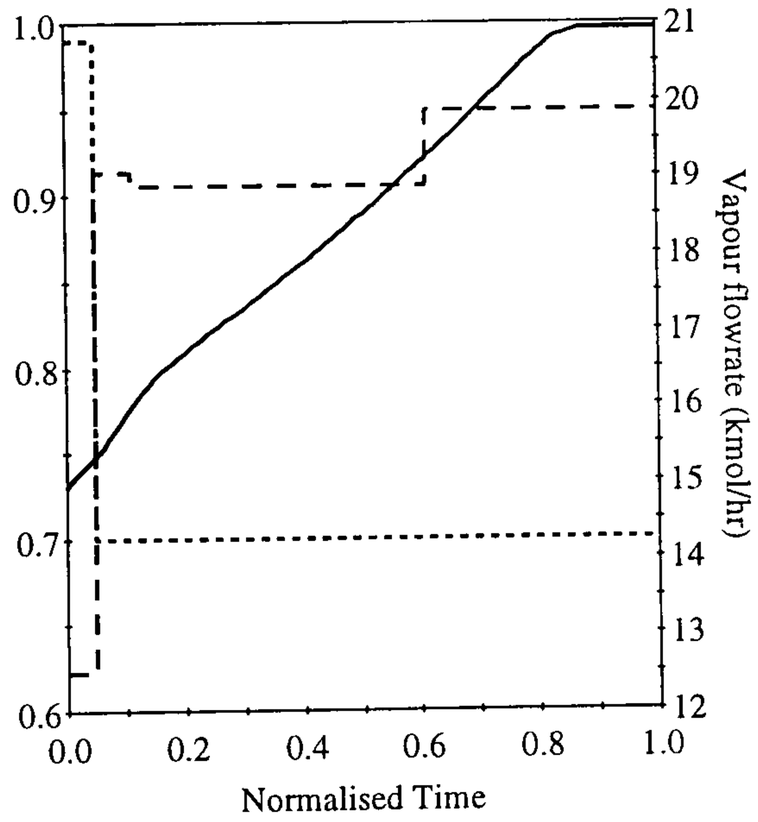
The optimal values/variations of the decision variables are summarised in table C.3 in Appendix C.

Total Capital Cost		**546.97** $\$/hr$
Total Operating Cost		**414.82** $\$/hr$
Material	Net production rate $(kmol/hr)$	Revenue $(\$/hr)$
Feed	7.70	-1925.00
Top1	4.99	-499.00
Top2	0.71	-71.00
Product	500 kg/hr	7500.00
Total Production Revenue		5005.00
Total Net Revenue		**4043.21** $\$/hr$

Table 4.7: Economic breakdown of optimal solution



(a) Column I



(b) Column II

Figure 4.11: Optimal policies for the reflux ratio and vapour flowrate $(kmol/hr)$ and the mole fraction for component 7 in the reboiler

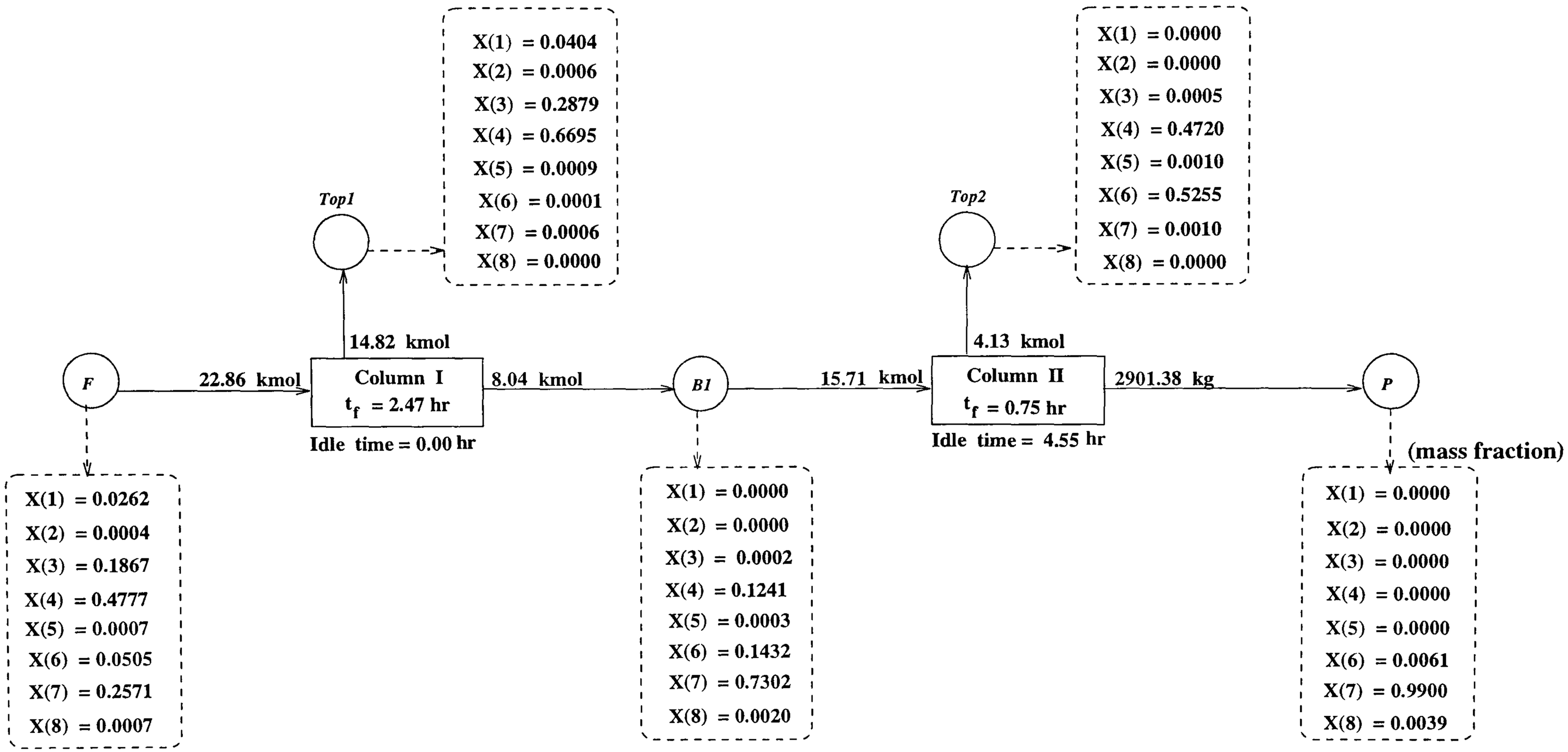


Figure 4.12: State-Task Network for optimal solution with 7 trays in column I and 8 trays in column II

4.7. Conclusions

This chapter has presented an algorithm for the simultaneous design and operational optimisation of batch distillation columns. Its novel feature is that it is based on a superstructure that allows the determination of the optimal number of trays together with other design and control decision variables. The algorithm is applicable both to individual distillation columns and to integrated batch processes involving one or more such columns.

Each subproblem of the optimisation algorithm is equivalent to the optimisation of a process in which all batch columns have fixed numbers of trays. The total computational time is completely dominated by these subproblem optimisations. Therefore, the proposed algorithm will practically always be more efficient than complete enumeration of all the possible tray number combinations. This was certainly found to be the case for the problems examined here. For instance, in the example in section 4.6, the solution was found in just 10 iterations while complete enumeration would have required 100 $(= (N_{max} - N_{min} + 1)^2)$ iterations.

The algorithm can be used effectively with any *tray-to-tray dynamic* batch distillation model. In fact, the more detailed the model being used, the greater the complexity of the optimisation problem and, therefore, the more beneficial the use of an efficient methodology such as the one presented here.

Although the number of trays in a distillation column does not always have a major effect on the overall cost, the use of a systematic algorithm is essential to prevent excessive over- or even under-designing of batch distillation columns. Moreover, although the OA/AP does not generally guarantee detection of the global optimum of non-convex MINLPs, the examples presented in this chapter indicate that it is a useful tool for the rapid determination of improved column designs.

Our algorithm could also be used in cases where the batch distillation column is used as a multipurpose equipment item, in other words, when the same column is used to perform several different separation tasks in the plant. In this case, the batch column should be designed for the most difficult separation task, *i.e.* the task that requires the most number of trays. The algorithm can also be adapted to determine the optimal number of trays in more complex batch distillation column structures such as multivessel batch distillation columns (see Skogestad *et al.*, 1997; Furlonge *et al.*, 1998).

Chapter 5

Design of Integrated Batch Processes With Discrete Equipment Sizes

This chapter considers the design of batch processes and plants where one or more of the equipment items are available only from a selection of standard sizes. The design of a three-stage batch plant consisting of a jacketed reactor, a plain reactor and a distillation column with a recycle stream is considered as an illustrative example.

5.1. Introduction

A basic assumption of most existing methodologies for the design of batch processes that utilise detailed dynamic models (see Charalambides *et al.*, 1995) is that the equipment capacity or volume can be treated as a continuous variable. However, many equipment items are available in standard sizes from the suppliers; equipment items that have to be custom-made to non-standard size specifications are usually more expensive.

Although the present thesis puts emphasis on the design of *new* plants, it is increasingly the case in industry that new processes are retrofitted into existing equipment. In such cases, one is often called upon to select the most appropriate equipment items out of a given inventory. This type of problem may be accommodated within the framework that will be presented in this chapter: clearly, the existing equipment is available only in certain sizes; the cost of such equipment may notionally be considered to be zero or, in any case, much lower than that of new hardware.

5.2. Handling Discrete-Sized Equipment

In general, the batch process design problem has to reflect the fact that the capacity of a processing unit is an unknown. In the cases of interest to this chapter, this is a discrete decision to be made by choosing from a selection of units available in certain sizes only.

As an example, let us consider the case where we need to use a jacketed batch reactor which is available in four standard sizes as shown in figure 5.1. The question that needs to be addressed is which one of the four available sizes we should use in the process. Of course, it is possible to treat the reactor volume as a continuous variable and then choose the available reactor with the capacity equal to or immediately above the value arising from the optimisation. However, this does not necessarily lead to an optimal solution, especially if the process comprises several such units. One may well end up with a process where the equipment is operating at low capacities, hence incurring unnecessary high capital and maintenance costs. Another option is to determine the optimal answer for each one of the various combinations and adopt the one that satisfies the objective function the best, *e.g.* highest profit rate. However, this option is time consuming and impractical. It is, therefore, essential to develop a systematic framework to address this problem.

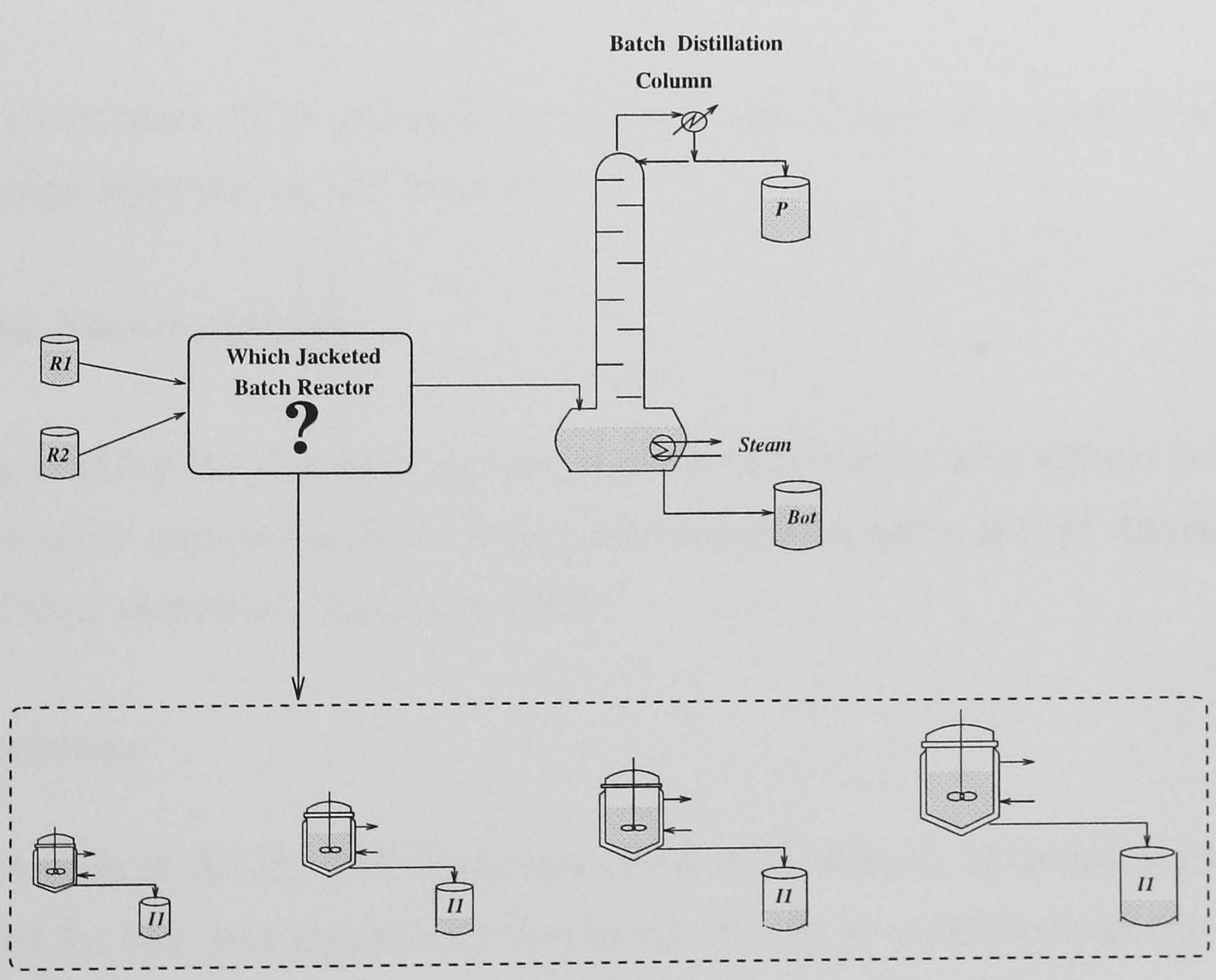


Figure 5.1: Plant flowsheet with discrete equipment sizes

Let $\mathcal{P}_{\mathcal{D}}$ denote the subset of batch unit operations p in the process, the equipment for

which is available only in finite sets of discrete choices. We introduce a binary variable set ζ_{ep} $e \in \mathcal{V}_p$ defined as:

$$\zeta_{ep} = \begin{array}{ll} 1, & \text{if choice } e \text{ is selected for unit } p; \\ 0, & \text{otherwise.} \end{array}$$

The final design will involve only one of these choices, therefore only one of the variables ζ_{ep} will take a value of 1, all others being zero. This is enforced via the logical constraint:

$$\sum_{e \in \mathcal{V}_p} \zeta_{ep} = 1, \quad \forall\ p \in \mathcal{P}_\mathcal{D} \tag{5.1}$$

The design characteristics (*e.g.* size) of the equipment items used for operation p generally form (a subset of) the time invariant parameters v_p associated with this operation (*cf.* section 3.3). Let the equipment characteristics for standard choice e for item p be denoted by the (given) vector V_{ep}. Then, the characteristics V_p of the item that is *actually* incorporated in the design will be determined by the constraint:

$$V_p = \sum_{e \in \mathcal{V}_p} \zeta_{ep} V_{ep} \quad \forall\ p \in \mathcal{P}_\mathcal{D} \tag{5.2}$$

We note that constraints (5.1) and (5.2) are an example of the constraints (3.4) appearing in the general design formulation of Chapter 3.

5.3. Solution Methodology

The algorithm used for the design of an integrated batch process with a fixed recipe but which involves one or more equipment items being selected out of finite sets of discrete choices is a special case of that described in section 3.8.5.

5.3.1. Subproblem

The *first subproblem* of the OA/AP algorithm involves solving an optimisation problem where the requirement for the unit equipment characteristics V_p to match one of the discrete alternatives V_{ep} is relaxed. Instead, V_p is allowed to take any value between a lower bound of $\min_{e \in \mathcal{V}_p} V_{ep}$ and an upper bound of $\max_{e \in \mathcal{V}_p} V_{ep}$. Because of this relaxation, the objective function value of the *globally optimal* solution of this subproblem is an upper bound on the optimal objective function value of the original problem.

The *Kth subproblem* ($K > 1$) involves fixing the discrete decision variable ζ_{ep} to a given set of values $\zeta_{ep}^{(K)}$. It is, therefore, equivalent to optimising a process where the equipment volumes are fixed. Hence, there is no need to introduce the logical constraints (5.1) and (5.2), or the discrete variables ζ_{ep}. Again, just like the optimal number of tray problem, the gradients of the objective function $\tilde{P}$ and the constraints $\tilde{C}_p$ required by the master problem are calculated by integrating the sensitivity equations of the *modified* DAE model (which includes equations (5.2) and (5.1)) with respect to the vector:

$$Z^{(K)} \equiv \bigcup_p \{\alpha_p^{(K)*}, \quad v_p^{(K)*}, \quad t_p^{f(K)*}, \quad \zeta_p^{(K)}\} \tag{5.3}$$

It will be recalled from section 3.8.2 that α_p are the parameters used to discretise the control variables associated with operation p.

5.3.2. Master Problem

The master problem is formed from the linearisations of the objective and constraints at the solution points of the subproblems $k = 1, .., K$:

$$\max_Z \quad \Upsilon - \sum_{k=1}^{K} w_k q_k \tag{5.4}$$

subject to:

$$\Upsilon \leq \tilde{P}(Z^{(k)}) + \left.\frac{\partial \tilde{P}}{\partial Z}\right|_{Z^{(k)}} (Z - Z^{(k)}) \quad \forall \quad k = 1, .., K \tag{5.5}$$

$$\tilde{C}_p(Z^{(k)}) + \left.\frac{\partial \tilde{C}_p}{\partial Z}\right|_{Z^{(k)}} (Z - Z^{(k)}) \leq q_k \quad \forall \quad p \in \mathcal{P}_\mathcal{D},\ k = 1, .., K \tag{5.6}$$

$$\sum_{e \in \mathcal{V}_p} \zeta_{ep} = 1 \quad \forall \quad p \in \mathcal{P}_\mathcal{D} \tag{5.7}$$

$$V_p = \sum_{e \in \mathcal{V}_p} \zeta_{ep} V_{ep} \quad \forall \quad p \in \mathcal{P}_\mathcal{D} \tag{5.8}$$

$$Z_{min} \leq Z \leq Z_{max}; \quad q_k \geq 0 \tag{5.9}$$

$$\sum_{p \in \mathcal{P}_\mathcal{D}} \zeta_{e_{kp}p} = |\mathcal{P}_\mathcal{D}| - 1, \quad \forall \quad k = 2, .., K \tag{5.10}$$

$$\zeta_{e_{kp}p} \in \{0, 1\} \quad \forall \quad e \in \mathcal{V}_p \tag{5.11}$$

Constraint (5.10) ensures that any discrete choice combinations for the units $p \in \mathcal{P}_\mathcal{D}$ that have already been considered are not selected again. Here, $|\mathcal{P}_\mathcal{D}|$ denotes the cardinality of set $\mathcal{P}_\mathcal{D}$, and the index e_{kp} is such that $\zeta_{e_{kp}p}$ had a value of 1 in the solution of the master problem at the *kth* iteration. Note that this constraint is enforced from $k = 2, .., K$ since in

the first iteration the variables ζ are treated as continuous decisions.

5.3.3. Algorithm Summary

The steps of the algorithm are as follows:

1. Set $K = 1$ and $P^* = -\infty$. Relax the discrete choices, thereby treating ζ_{ep} as continuous variables in the range [0,1].

2. Solve the relaxed NLP subproblem for continuous ζ_{ep} to obtain the solution point Z^R with the corresponding objective function value P^R. If infeasible, go to step 4.

3. If all ζ_{ep} happen to take integer values at the solution, then set $P^* := P^R$ and $Z^* := Z^R$. Go to step 8.

4. Solve the MILP master problem to determine $Z^{(K+1)}$ and the objective function P^{MP} (excluding the penalty terms). If infeasible, then go to step 8.

5. If $\frac{P^{MP}-P^*}{P^*} \leq \epsilon$, then go to step 8, else set $K := K + 1$.

6. Form the NLP subproblem for fixed $\zeta_{ep}^{(K+1)}$, and solve it to obtain the objective function value P^{SB}. If infeasible, go to step 4. Otherwise, compute the gradients of the objective function and constraints with respect to $Z^{(K+1)}$ and use them to create constraints of the form (5.5) and (5.6) to be appended to the master problem.

7. If $P^{SB} > P^*$, then set $P^{SB} := P^*$ and $Z := Z^*$. Go to step 4.

8. If $P^* > -\infty$, then the optimal solution is Z^* with a corresponding objective function value of P^*; otherwise, the problem is infeasible.

In the following section, the methodology is illustrated by its application to the design of a three-stage batch plant consisting of a jacket reactor, a plain reactor and a distillation column with a recycle stream.

5.4. Example: Batch Reaction and Distillation

5.4.1. Process Description

The feedstocks A, B and E are converted to product F and undesirable side-product D via the exothermic liquid phase reaction scheme:

$$A + B \rightarrow 2C \tag{5.12}$$

$$B + C \rightarrow D \tag{5.13}$$

$$C + E \rightarrow 2F \tag{5.14}$$

The process structure is shown in figure 5.2. The total amount of reactant A added to the first reactor must exceed the total amount of reactant B by at least 50%. The reactor contents must be kept below a maximum temperature of 350 K at all times in order to avoid vaporisation of the reacting mixture. Also, the final reaction temperature must not exceed 310 K so as to ensure that the reaction is quenched. The temperature can be controlled by manipulating the flowrate of the cooling water available at 288 K in the cooling jacket of the first reactor up to a maximum of 2.0 te/hr.

Figure 5.2: Plant flowsheet for the example problem

The output from the first reactor is mixed with reactant E in a second reactor operating adiabatically. To avoid undesirable side reactions, the total amount of component C added to the reactor must exceed by at least 50% of the total amount of reactant E, and the temperature must not exceed 310 K.

The output of the second reactor contains a mixture of unreacted raw materials A, B, E and products D and F. These are to be separated by a distillation task which produces two distillate cuts. The volatility of the six components decreases in the order $E > B > A > C > D > F$. Consequently, the first cut recovers the unreacted reactants A, B and E, and these are recycled back into the first reactor. The second cut is rich in the undesirable product D and is discarded. The distillate cuts are cooled down to 310 K via a cooler using cooling water at 288 K before entering their respective accumulator tanks. The desired product F is material remaining in the column reboiler, trays and condenser at the end of the distillation task with a specified minimum purity of 96%. The normalised reflux ratio is allowed to vary between 0.60 and 0.99, and the reboiler load between 550 and 1050 MJ/hr.

All process materials are assumed to be stable and can be stored in unlimited amounts.

The detailed unit operation models and kinetic and physical property data used are given in Appendix A and section B.2 in Appendix B respectively.

5.4.2. Equipment and Cost Data

For the design of this process, we assume that a single equipment item is dedicated to each task. The capacity of each equipment item can be selected from a choice of four alternatives as shown in table 5.1. The corresponding (annualised) capital costs are also shown in this table.

Jacketed Reactor				
Volume (m^3)	1.25	1.50	2.00	2.25
Capital cost ($/hr)	12.67	14.66	18.46	20.28
Plain Reactor				
Volume (m^3)	2.00	2.50	3.00	3.50
Capital cost ($/hr)	9.45	11.29	13.07	14.78
Column Reboiler				
Volume (m^3)	1.25	2.25	3.25	4.25
Capital cost ($/hr)	21.20	34.26	46.27	57.62

Table 5.1: Data on available plant equipment choices

The column has 10 theoretical trays. The unit values of various materials in the process

are shown in table 5.2. The unit cost of cooling water used in the first reactor and in the condenser of the distillation column is taken as 8 $\$/te$. The unit cost of steam used in the column reboiler is 40 $\$/te$.

Material	Unit value ($\$/kmol$)
A	7.0
B	7.0
E	3.0
$Waste$	1.0
F	40.0

Table 5.2: Unit values for process materials

5.4.3. Modelling

The operation of the jacketed reactor is modelled in terms of a set of standard dynamic material and energy balances. The cooling driving force is taken as the difference between the outlet cooling water temperature and the temperature of the reactor contents which are assumed to be well mixed. The cooling water flowrate is varied in a piecewise constant fashion over the duration of the reaction. The initial charge, reactor volume and processing time of each reactor unit are treated as time invariant optimisation variables. Inequality path constraints (*cf.* equation (3.5)) are imposed to ensure that the capacity of the reactor is not exceeded[§] and that the temperature limit is not violated at any point during the reaction. The limitation on the feed ratio of A and B is treated as an additional inequality constraint.

The plain reactor is operated adiabatically using standard material and energy balances and assuming a well mixed vessel. The reaction temperature is constrained not to exceed 310 K. The intermediate I_1 and reactant E are added as initial charges. The limitation on the feed ratio of C to E is treated as an inequality constraint.

The operation of the distillation column is modelled assuming constant liquid holdups on the trays and condenser, negligible vapour holdup and fast energy dynamics. The initial charge to the column fills the reboiler, trays and total condenser with liquid at the charge composition. A molar holdup of 50 *moles* is assumed for each of the column trays and the total condenser. The vapour-liquid mixture is assumed to be ideal. A 40 K and 10 K temperature rise in the cooling water is assumed for the total condenser and cooler respectively. Both the

[§]For ideal liquid mixtures in a reactor from which no product withdrawal takes place *during* the processing, an *end-point* constraint would suffice since the volume of the reactor cannot decrease with time.

reflux ratio and the reboiler load are treated as piecewise constant control variables. For the purposes of the optimisation, the operating time for each unit is divided into 4 intervals of variable durations.

In the initial guess for the optimisation, the processing times are set at 1.5, 2.5 and 1.5 *hr* for reaction I, reaction II and the distillation task respectively. The initial charges to the jacketed reactor are set at 4.9, 4.5 and 7.25 *kmol/batch* of reactant A, B and I_3 respectively; the cooling water flowrate is set at 1.0 *te/hr* during the duration of the process. The initial charge to the plain reactor is set at 25 and 8.5 *kmol/batch* of intermediate I_1 and reactant E respectively. The initial charge to the distillation column is set at 25 *kmol/batch* and the reflux ratio and reboiler heat duty are set at uniform values of 0.6 and 1050 MJ/hr respectively.

5.4.4. Results

Table 5.3 shows the steps and results of the algorithm when applied to this problem.

OA/AP Iteration	**1**	**2**	**3**	**4**	**5**
Subproblem					
Jacketed reactor volume (m^3)	1.701	1.25	1.25	1.50	**1.50**
Plain reactor volume (m^3)	2.374	2.00	2.50	2.00	**2.50**
Reboiler volume (m^3)	1.683	1.25	1.25	1.25	**1.25**
P ($/hr$)	83.48	70.82	67.36	78.40	**79.29**
NLP Iterations	74	47	93	29	198
CPU(s on *SUN ULTRA*)	12309.30	6426.70	12750.30	3941.70	27123.20
Master problem					
Jacketed reactor volume (m^3)	1.25	1.25	1.50	1.50	1.25
Plain reactor volume (m^3)	2.00	2.50	2.0	2.50	2.00
Reboiler volume (m^3)	1.25	1.25	1.25	1.25	2.25
P^{MP} ($/hr$)	753.03	151.22	104.56	93.10	76.56
P^{MP} - P^*	669.55	80.40	33.74	14.70	-2.73
Branch & Bound nodes	0	0	2	2	7
CPU(s on *SUN SPARC5*)	0.150	0.250	0.330	0.417	0.483

Table 5.3: OA/AP algorithm performance

The optimisation required 5 OA/AP iterations and a total of approximately 17.4 *hr* of CPU time on a *SUN ULTRA* workstation. The highest net profit rate of 79.29 $/hr$ with a mean production rate of 5.86 *kmol/hr* is achieved using 1.50, 2.50 and 1.25 m^3 for the volumes of the jacketed reactor, plain reactor and reboiler respectively. A detailed economic breakdown of the optimal solution obtained is presented in table 5.4. The characteristics of the recipe are shown in the State-Task Network in figure 5.3. It can be seen that intermediates

$I1$, $I2$ and $I3$ are not allowed to accumulate but the accumulation of off-cut $I4$ is unavoidable, leading to the production of some waste material.

Material	Net production rate $(kmol/hr)$	Revenue $(\$/hr)$
A	−2.674	−18.72
B	−2.234	−15.64
$I1$	0.000	0.00
E	−2.879	−8.64
$I2$	0.000	0.00
$I3$	0.000	0.00
$I4$ $(waste)$	1.93	−1.93
F	5.859	234.36
Total production revenue		**189.43**
Operator	Volume (m^3)	Capital cost $(\$/hr)$
Jacketed reactor	1.50	14.66
Plain reactor	2.50	11.29
Distillation column	1.25	21.20
Total capital cost		**47.15**
Utility	Mean consumption rate (te/hr)	Cost $(\$/hr)$
Cooling water	5.844	46.75
Steam	0.406	16.24
Total utility cost		**62.99**
Total net profit		**79.29**

Table 5.4: Economic breakdown of optimal solution

The jacketed reactor requires 2.67, 2.23 and 3.75 $kmol/hr$ of reactants A and B and intermediate $I3$ respectively, with a processing time of 1.86 hr and a fixed set-up time of 15 min. The constraint on the ratio of reactants A to B in the total amount fed to the reactor is satisfied at 1.5. The operating constraint of not allowing the reacting mixture to exceed 350 K is satisfied and the temperature profile together with the cooling water policy can be seen in figure 5.4(a). There is a high cooling water flowrate towards the end of the operation to ensure that the temperature of the reacting mixture is brought down to 310 K by the end of the processing step. The composition profiles (molar basis) of the components in the reacting mixture are shown in figure 5.4(b).

The plain reactor consumes mean flowrates of 8.66 and 2.88 $kmol/hr$ of intermediate $I1$ and reactant E respectively. The processing time is 1.95 hr and the set-up time is fixed at 15

min. The constraint on the feed ratio of C to E is satisfied. The temperature does not exceed 310 K as shown in figure 5.5(a). The variations in the mole fractions of the components can be seen in figure 5.5(b).

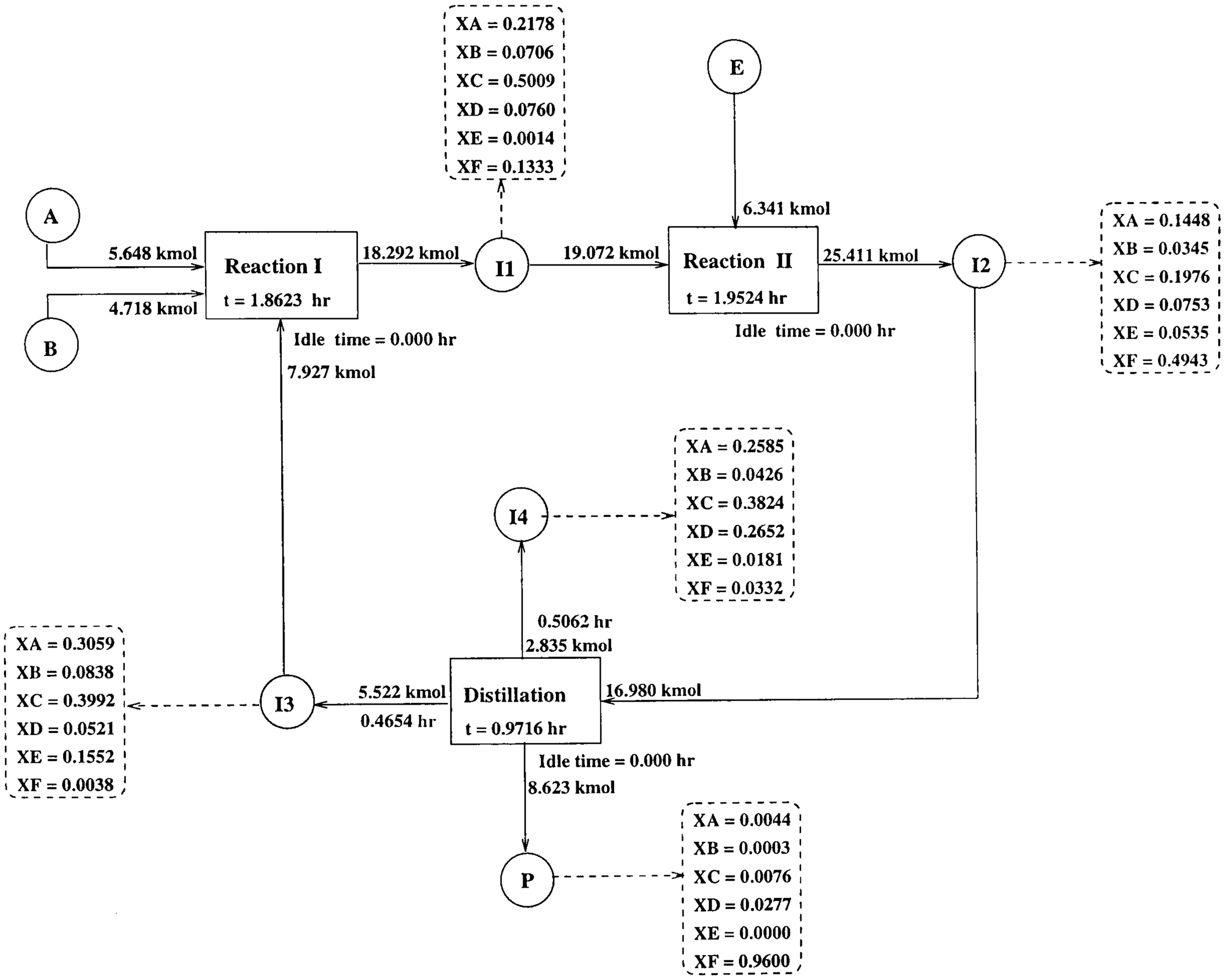
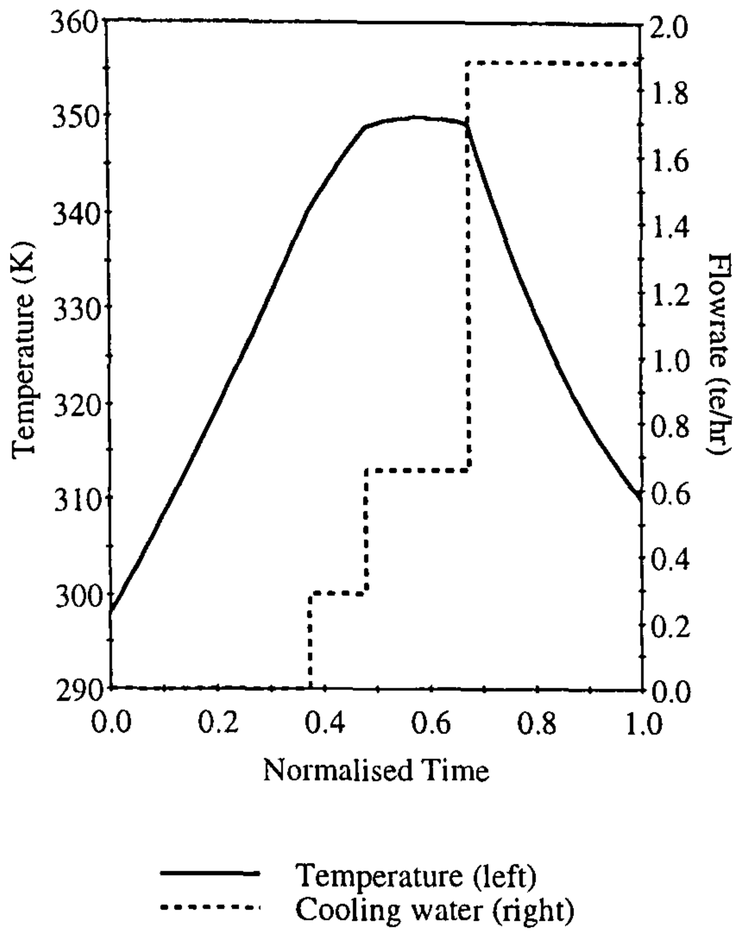


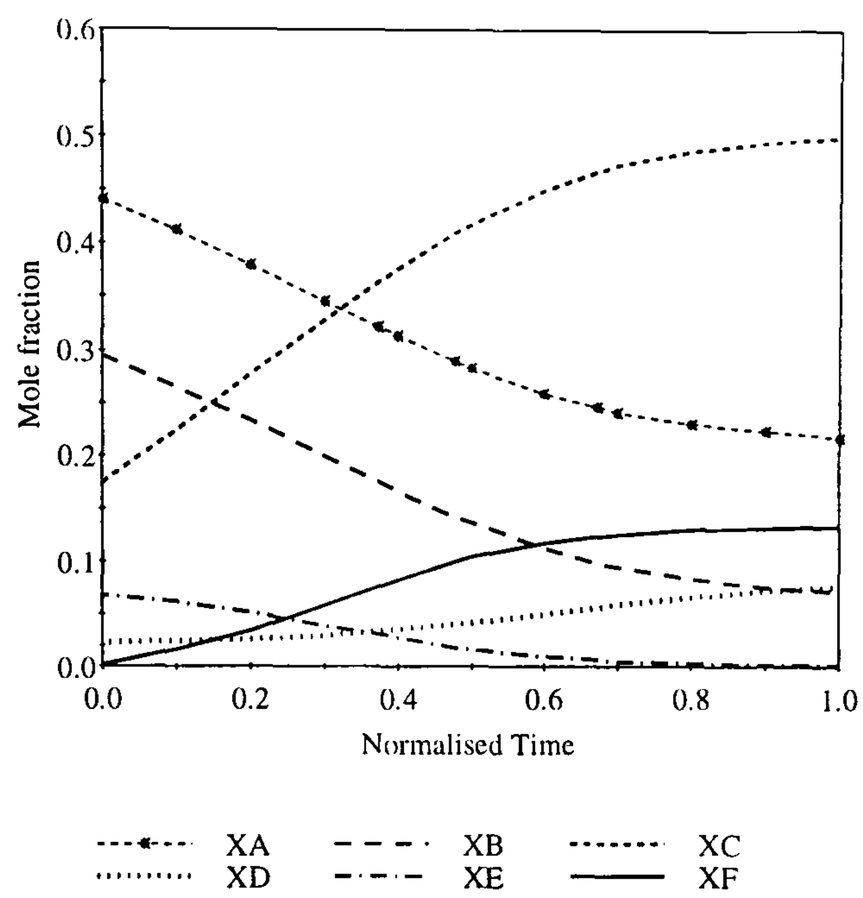
Figure 5.3: State-Task Network of the optimal recipe

The distillation column is operated with an initial charge of 16.98 *kmol/batch* with a processing time of 0.97 *hr* and a fixed set-up time of 30 *min*. The mole fraction trajectories of the components in the reboiler are shown in figure 5.6(a). At the optimal solution, the reboiler heat load is held at its maximum value of 1050 MJ/hr throughout the operation of the task. The optimal variation of the normalised reflux ratio in the distillation column is shown in figure 5.6(b). The operating policies for the cooling water flowrates in both the condenser and the cooler are shown in figure 5.7.

The optimal values/variations of the decision variables are summarised in table C.4 in Appendix C.

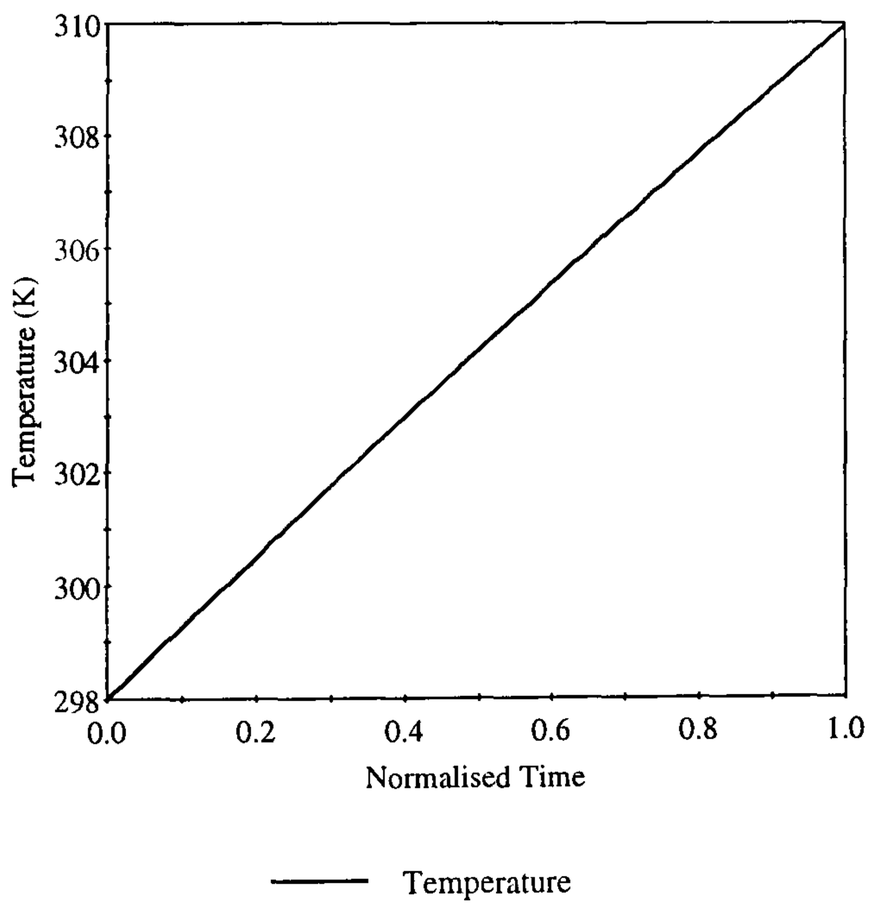


(a) Temperature profile and cooling water policy

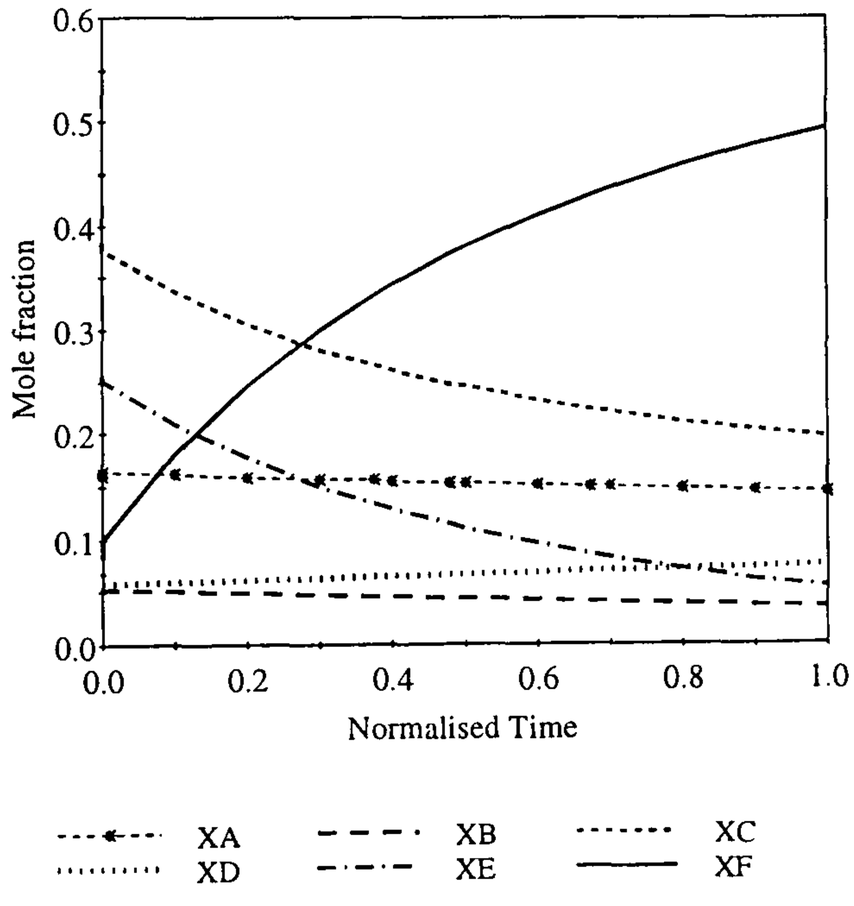


(b) Mole fraction profiles

Figure 5.4: Jacketed reactor operating policy

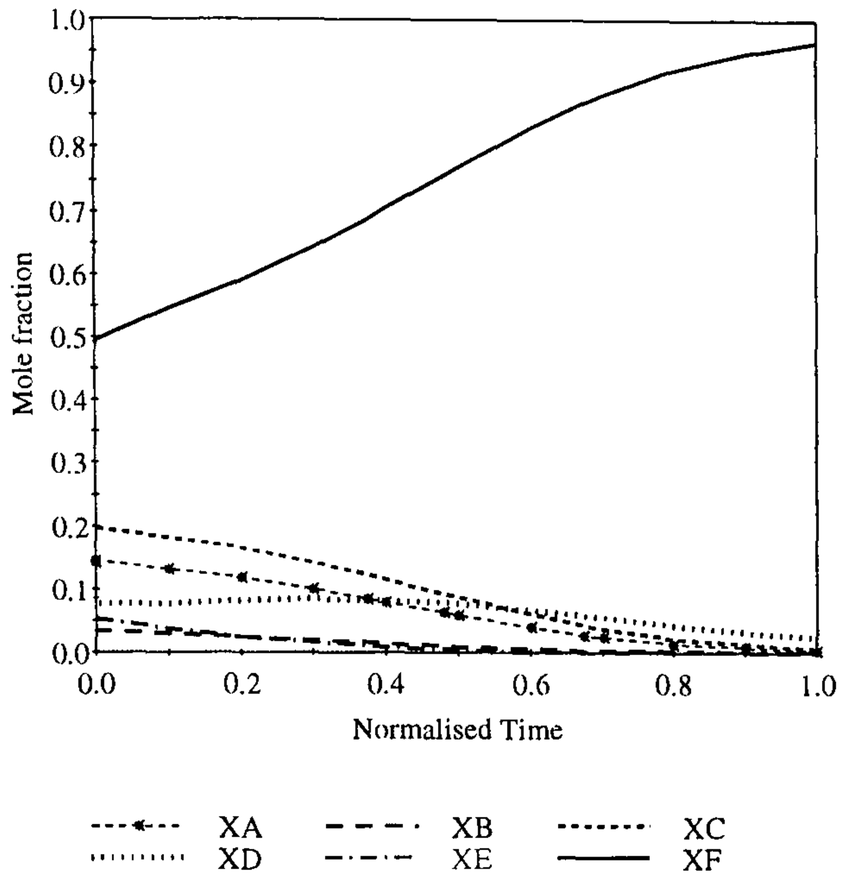


(a) Temperature profile

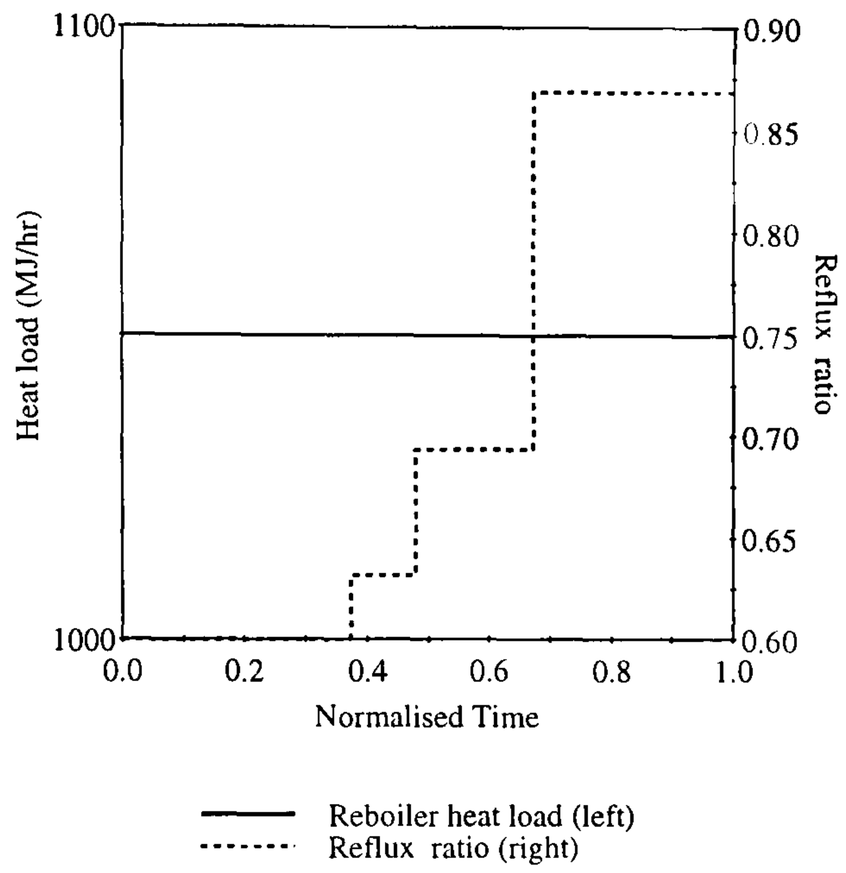


(b) Mole fraction profiles

Figure 5.5: Plain reactor operating policy



(a) Mole fraction profiles in the reboiler



(b) Heat load and reflux ratio policies

Figure 5.6: Column operating policy

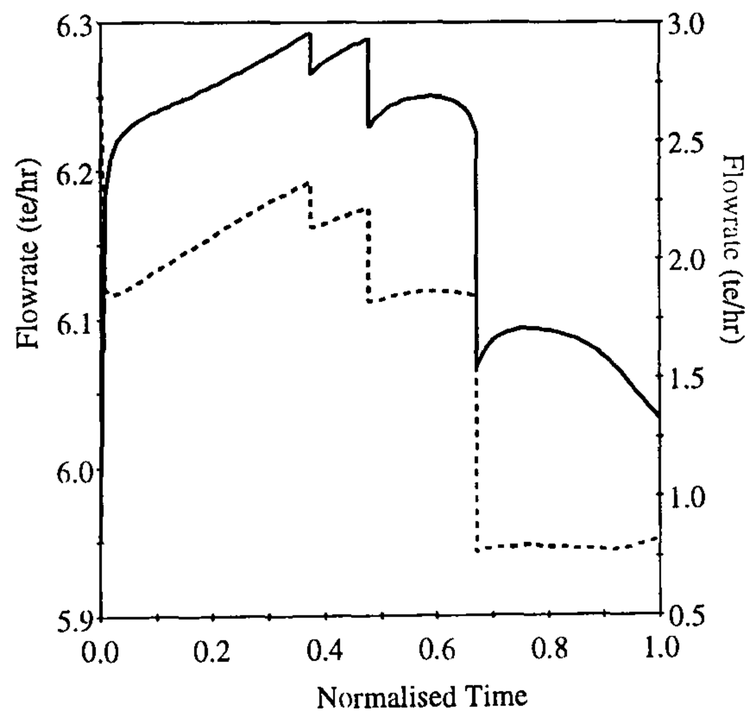


Figure 5.7: Cooling water profiles for the distillation column

5.4.5. Remarks

The first subproblem of the optimisation algorithm is equivalent to optimising a process where the unit volumes are treated as continuous variables; hence, this is a relaxation of the original problem, and the resulting value of the objective function (assuming it is determined to global optimality) is an upper bound to the true optimal objective function. However, all the succeeding subproblems are equivalent to the optimisation of a process for fixed unit volumes; therefore, the resulting value of the objective function is a *lower* bound on the true optimum.

The total computational time is completely dominated by the subproblem optimisations. Therefore, the proposed algorithm will practically always be more efficient than complete enumeration of all possible unit volume combinations. This was certainly found to be the case in the example considered: here, the optimal solution was found in just 5 iterations while complete enumeration would have required 64 ($= |\mathcal{V}_{jr}| \times |\mathcal{V}_{pr}| \times |\mathcal{V}_{d}|$) iterations, where $\mathcal{V}_{jr}$, $\mathcal{V}_{pr}$ and $\mathcal{V}_{d}$ are the sets of possible candidates for the jacketed reactor, the plain reactor and the reboiler of the distillation column respectively. Even though the OA/AP does not generally guarantee detection of the global optimum of non-convex MINLPs, it provides a useful means for determining improved and feasible batch process designs.

5.5. Modifying the OA/AP Algorithm

The steps of the algorithm described in section 5.3.3 are strictly sequential as each master problem is formed from linearisations carried out at the solution of the previous subproblem, and each subproblem (except the first one) uses equipment selected by the immediately preceding master problem.

On the other hand, if multiple computer processors are available, then it is highly desirable to be able to explore a number of subproblems simultaneously. One way of generating these subproblems is by solving the master problem repeatedly, each time using the same objective function and constraint linearisations but adding an integer cut constraint (*cf.* equation (5.10)) excluding all previously selected equipment combinations. This type of strategy is particularly attractive for the MINLPs considered here where the time required to solve the master problem is generally negligible compared to that for the subproblem.

The number of subproblems that will be created and considered simultaneously is determined by the number, NP, of available processors. The algorithm of section 5.3.3 is now modified as follows:

1. Set $K = 1$ and $P^* = -\infty$. Relax the discrete choices, thereby treating ζ_{ep} as continuous variables in the range [0,1].

2. Solve the relaxed NLP subproblem for continuous ζ_{ep} to obtain the solution point Z^R with the corresponding objective function value P^R. If infeasible, go to step 4.

3. If all ζ_{ep} happen to take integer values at the solution, then set $P^* := P^R$ and $Z^* := Z^R$. Go to step 9.

4. Create a MILP master problem involving the linearisations of objective function and constraints at the optimal solution of subproblem 1.

5. Set $NSP = 0$.

6. Master problem solution:

   6.1 Solve the MILP master problem to obtain the solution point $Z^{(K+i)}$ and the corresponding objective function value P^{MP}.

   6.2 If the master problem is infeasible or $P^{MP} - P^* \leq \epsilon$, then go to step 9.

   6.3 Set $NSP := NSP + 1$.

   6.4 Add integer cut to exclude equipment selection determined at step 6.1 from future master problems.

   6.5 If $NSP < NP$, then go to step 6.1.

7. For $i := 1$ to NSP do *in parallel* for all i:

   7.1 Form the NLP subproblem for fixed $\zeta_{ep}^{(K+i)}$, and solve it to obtain the objective function value P^{SB}. If feasible, compute the gradients of the objective function and constraints with respect to $Z^{(K+i)}$ and use them to create constraints of the form (5.5) and (5.6) to be appended to the master problem.

   7.2 If $P^{SB} > P^*$, then set $P^{SB} := P^*$ and $Z := Z^*$.

8. If $NSP = NP$, then set $K := K + NP$; go to step 5.

9. If $P^* > -\infty$, then the optimal solution is Z^* with a corresponding objective function value of P^*; otherwise, the problem is infeasible.

We note that steps 1-3 of the above algorithm involve the construction and solution of the first (fully-relaxed) subproblem, steps 4-6 are concerned with the master problem, and step 7 with all later subproblems.

The main task of step 6 is to determine up to NP equipment selection candidates. The *actual* number of such candidates generated is denoted by NSP. We note that NSP can be lower than NP; this is a consequence of step 6.2 which terminates the search for further candidates if the master problem becomes infeasible or generates an objective function value P^{MP} that is no better than that of the best feasible solution, P^*, available already.

Step 7 solves the NSP subproblems corresponding to the NSP candidate equipment selections generated by step 6. All these subproblems may be solved in parallel. We note that this step will automatically be by-passed if NSP has a value of 0 following step 6.

Step 8 returns control to step 6 to generate more equipment selection candidates; of course, this is unnecessary if the previous execution of step 6 already failed to generate the maximum number of such candidates (*i.e.* if $NSP < NP$).

Finally, it is interesting to note that this algorithm reduces to that described in section 5.3.3 if the number of processors NP is set to 1.

5.5.1. Results and Discussion

The example in section 5.4 is solved using the modified master problem for the case where the number of processors, NP, available is three. The steps of the algorithm are shown in table 5.5:

- We start by solving the single fully-relaxed subproblem 1.
- By linearising the objective function and the constraints at the solution of this subproblem, we form the first master problem.
- We then solve this master problem *three* times *in sequence* to generate three different equipment selections; each time, we use the integer cut constraints (5.10) to exclude all previous selections.
- We then solve the three subproblems (corresponding to the above equipment selections) *in parallel.* By the end of this step, the best feasible solution determined is that generated by subproblem 4 with an objective function value of 78.40 $\$/hr$.
- We linearise the objective function and the constraints around the solutions of the three subproblems above, and add these linearisations to the master problem.
- We now solve the master problem three more times in sequence to generate the three more equipment selections.

Subproblem	1			2	3	4				5	6	7	
Reactor I volume (m^3)	1.701			1.25	1.25	1.50				**1.50**	1.50	1.50	
Reactor II volume (m^3)	2.374			2.00	2.50	2.00				**2.50**	3.00	3.50	
Reboiler volume (m^3)	1.683			1.25	1.25	1.25				**1.25**	1.25	1.25	
P ($/hr$)	83.48			70.82	67.36	78.40				**79.29**	77.41	75.06	
NLP Iterations	74			47	93	29				198	70	105	
CPU(s on *SUN ULTRA*)	12309			6427	12750	3942				27123	9966	14252	
Master problem	1	2	3				4	5	6				7
Reactor I volume (m^3)	1.25	1.25	1.50				1.50	1.50	1.50				1.25
Reactor II volume (m^3)	2.00	2.50	2.00				2.50	3.00	3.50				3.50
Reboiler volume (m^3)	1.25	1.25	1.25				1.25	1.25	1.25				1.25
P^{MP} ($/hr$)	753.03	752.22	751.13				93.10	91.43	89.12				60.75
P^{MP} - P^*	669.55	681.40	680.31				14.70	12.14	9.83				-18.54
Branch & Bound nodes	0	0	2				2	4	4				13
CPU(s on *SUN SPARC5*)	0.150	0.216	0.417				0.200	0.290	0.221				0.391

Table 5.5: The parallelised algorithm performance

- We solve the three subproblems corresponding to the above equipment selection *in parallel.* An improved feasible solution (with the objective function of 79.29 $\$/hr$) is determined by subproblem 5.

- We linearise the objective function and constraints around the solutions of the three subproblems above, and add these linearisations to the master problem.

- We now attempt to solve the master problem to generate three more subproblems. However, the first master problem solution has an objective function value of 60.78 $\$/hr$ which is already lower than the best feasible solution available. Therefore, in accordance with step 6.2 of the algorithm, we terminate the computation at this point.

The optimal solution found using the parallelised algorithm is the same as that found by the original sequential algorithm (*cf.* section 5.3.3). The advantage is that the modified algorithm generates *"batches"* of NP subproblems that are solved in parallel, which results in a reduction in the (elapsed) time required by the computation. The total elapsed time is approximately[‡] equal to the CPU time of the first (fully-relaxed) subproblem plus the maximum CPU time required for the solution of any subproblem in each batch. In this example, this leads to:

$$\begin{pmatrix} \text{Elapsed} \\ \text{Time} \end{pmatrix} = 12309 + \max(6427, 12750, 3942) + \max(27123, 9966, 14252) \approx 14.5\ hr \tag{5.15}$$

which compares well with the elapsed time of the sequential algorithm (*cf.* table 5.3) which was 17.4 hr. The overall elapsed time is reduced by approximately 3 hr despite the fact that the parallelised algorithm solves two more subproblems than the original.

5.6. Conclusions

In this chapter, we presented an algorithm for the simultaneous design and operational optimisation of integrated batch processes with *fixed* recipes. The main feature of the algorithm is that it is based on a superstructure that allows the determination of the optimal equipment size from a selection of potentially available units together with other design and control decision variables.

[‡]We ignore the time required for the solution of the master problems, as well as any communication overhead that would be involved in a parallel implementation of this algorithm. Both of these are negligible in comparison with the time required by the subproblems.

Our algorithm is based on an OA/AP approach. The first subproblem is equivalent to the optimisation of a process where the equipment sizes are treated as continuous variables; successive subproblems are equivalent to the optimisation of processes where the equipment sizes are fixed. The total computational time is completely dominated by the solutions of these subproblems. Consequently, the algorithm will always be more efficient than complete enumeration of all the possible equipment sizes. This was certainly found to be true for the example considered.

In view of the high computational cost of the subproblems, we proposed a modification of the OA/AP algorithm which allows the solution of several subproblems in parallel. The results obtained with the parallelised algorithm are encouraging. However, further improvements may be possible (see section 9.2).

Chapter 6

Batch Process Network Synthesis and Design

In this chapter, we consider the problem of determining the optimal structure for a batch process required to produce a set of products from a set of raw materials using a set of potential unit operations. A representation based on a fully connected set of generic unit operations described by detailed dynamic models is adopted. The main discrete decisions considered in this optimisation concern the number of instances of each type of unit operation to be included in the design. The total number of discrete alternatives is relatively small. A complete enumeration approach is, therefore, adopted for the determination of the optimal process network.

6.1. Earlier Work on Synthesis of Batch Processes

Process synthesis has been described as *"the act of determining the optimal interconnection of processing units as well as the optimal type and design of the units within a process system"* (Nishida *et al.*, 1981) and more recently as *"the systematic generation of alternative process flowsheets and the selection of a design whose configuration and parameters optimise a given objective function that is commonly economic in nature"* (Grossmann and Daichendt, 1996).

The development of process design methodologies has been the subject of extensive research over the past two decades. The current state of flowsheet synthesis is primarily represented by two different approaches:

- Hierarchical decomposition approaches,
- Mathematical programming approaches.

6.1.1. The Hierarchical Decomposition Approach

The *hierarchical* approach, advocated by Douglas (1988), decomposes the flowsheet synthesis problem into the five decision levels shown in table 6.1. The decision at each level, with the exception of the first, is made based on the economic potential of the process which in turn justifies whether the project warrants further development or terminates the project completely. This approach develops an initial base case design using heuristic rules or ("rules of thumb"), short-cut design procedures and physical insight, but does not search rigorously through all alternatives to produce an optimal design.

Level	Decision
1	Batch vs. continuous process
2	Input-output structure of the flowsheet
3	Reactor and recycle structure
4	Separation structure:
	- Vapour recovery system
	- Liquid recovery system
5	Energy integration of flowsheet

Table 6.1: Douglas' (1988) process synthesis decision hierarchy

It can be seen from table 6.1 that the choice between a batch or a continuous process is the first decision that has to be made. In fact, this is common to both the hierarchical and the mathematical programming based approaches. We will return to consider this issue again in section 6.1.3.

Unfortunately, Douglas' (1988) methodology concentrates almost entirely on continuous processes, and little consideration is given to batch operations beyond Level 1 of the hierarchy.

6.1.2. Mathematical Programming Based Batch Process Synthesis

In the *mathematical programming approach*, the configuration and parameters of the process system are evaluated using optimisation techniques. Process design involves both continuous decisions (*e.g.* operating policies such as reflux ratios, cooling water flowrates, *etc.*) and discrete decisions (*e.g.* flowsheet structure, "off-the-shelf" equipment sizes). Mathematically, this is translated into a mixed integer non-linear programming (MINLP) problem (*cf.* section 3.7).

The superstructure representation of process alternatives has become a favourable approach since it allows the synthesis alternatives to be systematically evaluated and optimised.

Most of the research on superstructure optimisation focuses on synthesis of individual process subsystems ("homogeneous systems") such as separation networks, heat-exchanger networks and reactor networks. There is already a vast amount of literature on the application of this type of approach to the synthesis of *continuous* processes (see the recent review by Smith (1996), and also the textbook by Biegler *et al.* (1997)). Here, we concentrate on the much smaller literature on the synthesis of batch processes.

Irribarren and Malone (1985) proposed a systematic approach for the design of batch processes. They suggested that the best approach to design a batch process is to design a continuous one first since it is simpler to screen for process alternatives and to determine the best process flowsheet if one does not have to address the dynamic nature of batch processes. Once the continuous plant was designed, the authors used a hierarchical procedure which involved replacing the continuous units with batch units. It was claimed that this eventually led to the best batch process design. However, this approach does not search rigorously through all alternatives to obtain the optimal design since it uses the continuous process as the initial starting point.

Bernot *et al.* (1991) addressed the problem of developing a systematic procedure for assessing the feasibility and separation sequences of multicomponent azeotropic mixtures. Various levels of alternatives were considered. The first level of alternatives were those which reduce the cost of the separation system by merging the separation tasks into as few columns as possible. Another level of alternatives were those generated by the methods used to break azeotropes such as pressure-swing techniques, reactive distillation, and homogeneous and heterogeneous azeotropic distillation.

Sundaram and Evans (1993) considered the problem of determining the recipe for separations systems via batch distillation. They addressed the problem of determining the separation step sequence, the allocation of equipment items to processing steps and the operating policy of each processing step (reflux ratio, cut location), given the feed composition, product purity and equipment item inventory. The superstructure was represented as shown in figure 6.1. The synthesis problem was modelled as a non-linear programming problem (NLP) with integer decisions concerning the existence of any separation step modelled using the cut location, defined as the fraction of feed which ends up as top product. In this way, the separation step is deemed to exist if a top product is produced. The Fenske-Underwood-Gilliland (FUG) short-cut method was used to describe the operation of the distillation columns. This allowed for the fast enumeration of the various structural alternatives, which is an important consideration since even the simplest separation can yield a large number of alternatives. When n components are to be separated into n products, with M distillation columns available, the

total number of alternatives is given by:

$$N_{structure} = \frac{1}{2n-1}\frac{(4n-4)!}{((2n-2)!)^2}M^{2n-2} \tag{6.1}$$

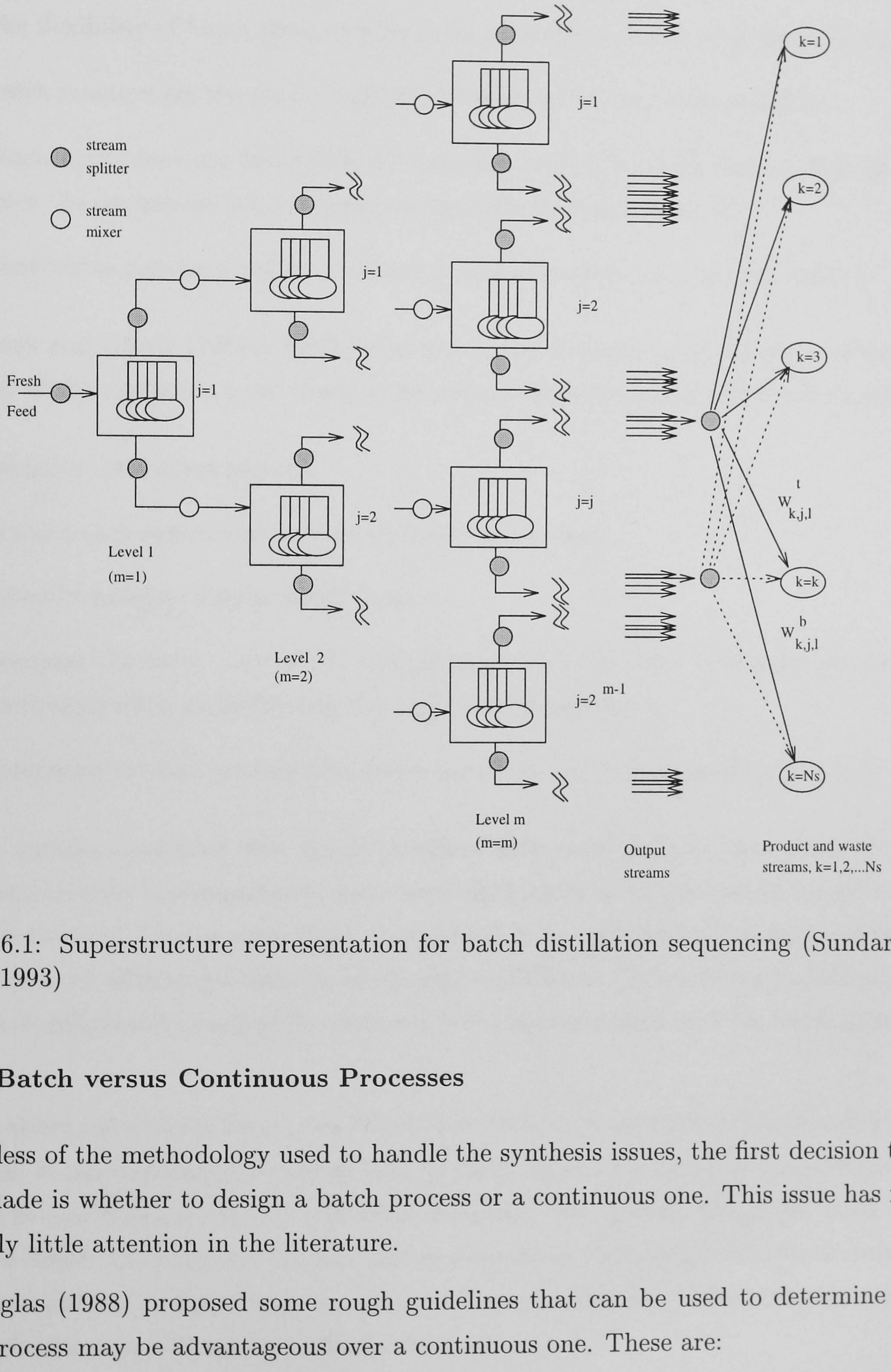


Figure 6.1: Superstructure representation for batch distillation sequencing (Sundaram and Evans, 1993)

6.1.3. Batch versus Continuous Processes

Regardless of the methodology used to handle the synthesis issues, the first decision that has to be made is whether to design a batch process or a continuous one. This issue has received relatively little attention in the literature.

Douglas (1988) proposed some rough guidelines that can be used to determine when a batch process may be advantageous over a continuous one. These are:

- Plants having a capacity greater than 5000 te/yr are usually continuous whereas plants with a capacity less than 500 te/yr are likely to be batch; under certain conditions, a combined continuous/batch is appropriate.
- Batch plants are preferable for products with a seasonal demand.
- The flexibility of batch plants makes them ideal for products with short life cycles.
- Batch reactors are the only reasonable alternative for very slow reactions.
- Batch operations are favourable for handling materials which foul equipment rapidly, since the equipment is periodically started, stopped and cleaned.
- Continuous processes exhibit a difficulty when handling low capacity slurries.

Goršek and Glavič (1997a; 1997b) also considered the important factors that govern the selection of the operation mode (batch/continuous). They proposed the following approach:

1. Design a continuous process.
2. Replace each continuous process unit by a batch unit.
3. Consider merging similar batch units.
4. Compare the total costs of the merged units with the costs of comparable batch and continuous units including recycles and energy integration.
5. Determine the best process alternative based on the economics of steps 1 to 4.

The authors concluded that batch processes with multi-purpose equipment are usually less expensive than continuous ones since fewer equipment items, and hence lower investment costs, are required. On the other hand, they argued that continuous plants are more profitable when compared with single-purpose batch plants. However, for small production capacities, the overall difference in profitability between the continuous plant and the batch plant is very small.

The above research highlights the effect of economies of scale on the economics of individual processes. It can be reasonably argued that, in many cases, to make a fair comparison between continuous and batch processes, one must determine the optimal design for both types of processes rather than rely on simple rules or procedures. This thesis will focus only on the issue of the optimal design of batch processes and the detailed comparison between continuous and batch processes will not be addressed further.

6.2. Batch Process Network Synthesis Problem

Most of the mathematical techniques used for process design in the literature consider a set of candidate unit operations, each of which is used to achieve a specific pre-specified function within the process; for instance:

- a distillation task used to split between components A and C;
- a reaction task used to carry out the specific chemical reaction $A + 3B \rightarrow 2C$.

As a result of this, each task or unit operation model has an *identity* or a specific *role* to perform in a process flowsheet. Such representations (often called *"one-to-one"*) may lead to combinatorial explosion when used in the context of process synthesis, rendering the solution of large problems intractable due to the increasing size of the discrete component.

In this section, a solution technique for the process design of integrated batch problem based on the methodology of *"one-to-many"* representation is developed. The basic idea of our approach is similar to that used by Smith (1996) for the optimal design of *continuous* processes.

6.2.1. One-to-Many Representation

The concept of the *"one-to-many"* representation (Smith, 1996) of our batch process design methodology is as follows:

1. A batch process comprises material states and processing tasks.
2. Each raw material, end-product and intermediate is described by a *state* of material s. The intensive properties of the state s (*e.g.* composition, temperature, pressure, particle size distribution, colour, *etc.*) are treated as optimisation variables in the mathematical formulation, *i.e.* their values are not specified *a priori*.
3. Each *task* is performed using processing unit operator(s) transforming a set of input states into a set of output states.
4. *Full* connectivity between the states and the tasks is allowed. Thus, the material fed to each task (either as part of the initial charge or continuously during the task operation) may comprise:
    - raw materials,

- products of this task,
- products of any other task.

Similarly, the end-products of the process may be formed by blending raw materials and/or the outputs of the unit operations in the process.

5. The amount of each material s consumed by each task i in the process is treated as a continuous optimisation variable in the mathematical formulation.

In the above formulation, there are no preconceptions about the "role" of each task in the process. Indeed, the only discrete decisions associated with the process structure are the existence or not of the various tasks. In a process plant where the raw materials are specified and the desired end-products are known *a priori*, the input required from the design engineer is to specify the different types of processing units that *may* be used by the process, and the maximum number of instances of each type of processing unit allowable within the optimum flowsheet. In general, if there are n^t different types of processing unit to be considered, and the plant design is allowed to include up to n^p_{max} instances of processing unit $p = 1, .., n^t$, the maximum number, Ψ, of distinct flowsheets which needs to be considered is:

$$\Psi = \prod_{p=1}^{n_t} (n^p_{max} + 1) \tag{6.2}$$

These ideas are best explained through the use of an example. Let us consider the design of a batch process to transform three raw materials $R1$, $R2$ and $R3$ into an end-product P satisfying given specifications, for instance, a minimum purity of 99% for the product P. To achieve the transformation, we need to determine:

- the tasks to be performed;
- the type, number and size of the processing units;
- the operating policy for performing individual tasks in the selected equipment.

As stated in section 3.7, we assume that each task takes place in a single dedicated equipment item. Therefore, the number of different types of candidate tasks available for the process is equal to the number of different types of candidate processing units available. In this case, suppose that we can use a plain reactor, a jacketed reactor and a distillation column, *i.e.* there is a potential of having two reaction tasks and one separation task to perform the

Flowsheet	Plain reactor	Jacketed reactor	Distillation column	Feasible ?
a	0	0	0	$\times$
b	1	0	0	$\times$
c	0	1	0	$\times$
d	0	0	1	$\times$
e	1	1	0	$\times$
f	1	0	1	$\surd$
g	0	1	1	$\surd$
h	1	1	1	$\surd$

Table 6.2: Alternative flowsheets

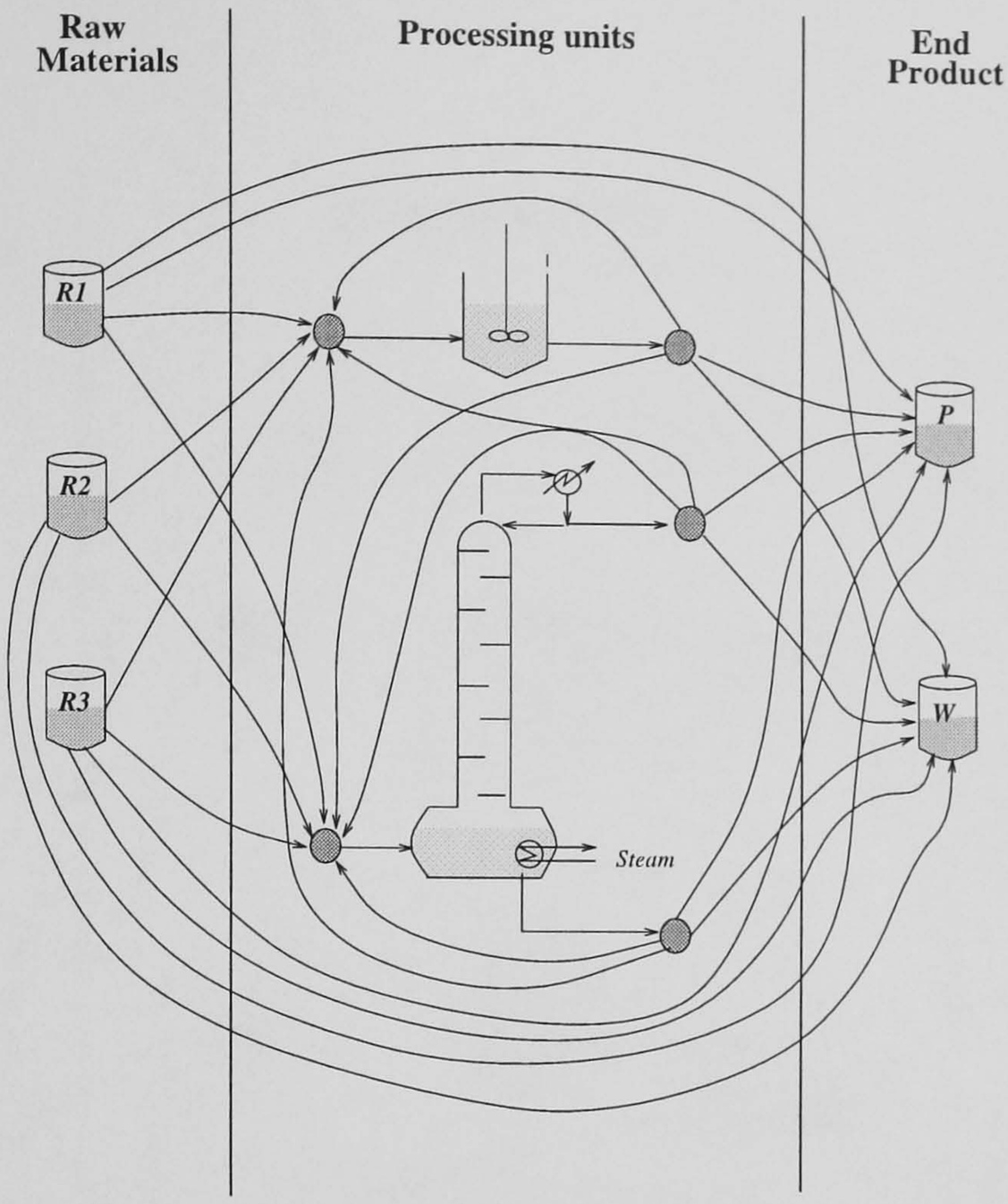
process. Noting that each unit item can be used only once, the possible flowsheets that need to be considered are enumerated in table 6.2.

It is clear from the list that there are a total of eight potential flowsheets (a to h). We note that this number is in accordance with equation (6.2):

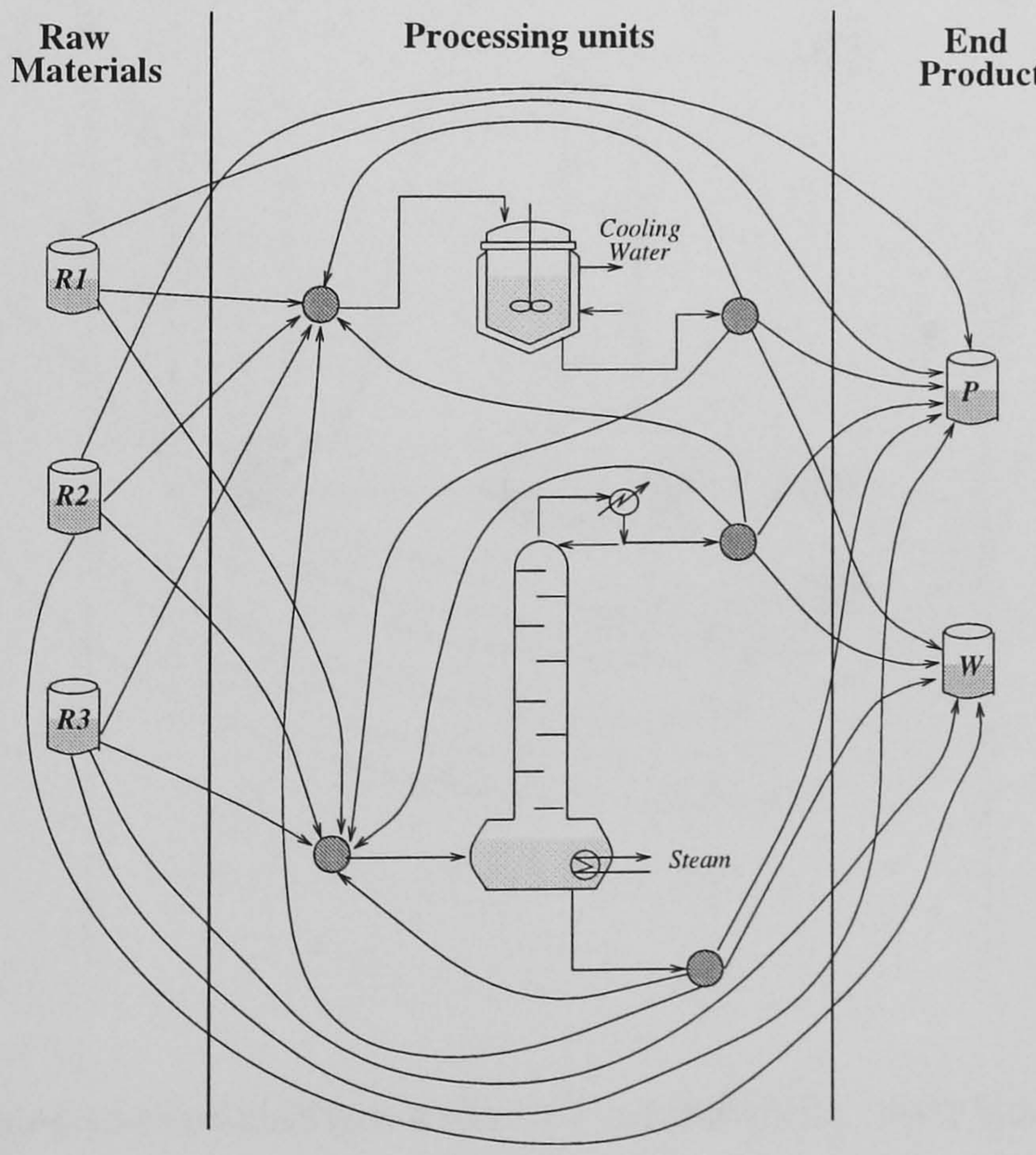
$$\underbrace{(1+1)}_{\substack{\text{plain reactor}\\ \text{alternatives}}} \times \underbrace{(1+1)}_{\substack{\text{jacketed reactor}\\ \text{alternatives}}} \times \underbrace{(1+1)}_{\substack{\text{distillation column}\\ \text{alternatives}}} = 8 \tag{6.3}$$

i.e. $n^t = 3$; n^p_{max} =1, $p = 1,\ 2,\ 3$. However, flowsheet a is obviously infeasible, unless of course the composition of the raw materials is such that these can be blended to produce the right product. Flowsheets b, c and e do not involve any separation and will also be infeasible unless the reactors operate at very high conversions to achieve 99% purity of the product. Flowsheet d does not involve a reactor and will also be practically infeasible unless the product appears in substantial amounts as a component in the raw materials. Hence, the only realistic alternatives are the three distinct flowsheets (f, g and h). The full connectivity superstructures of the flowsheets f and g are shown in figures 6.2(a) and (b) respectively. The superstructure for flowsheet h and its respective State-Task Network are presented in figures 6.3 and 6.4 respectively.

The final product P is generated by mixing the output states (*i.e.* $Int1$, $Int2$, $Int3$ and/or $Int4$) of the processing units and raw materials (*i.e.* $R1$, $R2$ and/or $R3$). However, in most practical cases, the product is likely to be the output state of one of the processing units rather than a mixture of several output states, in which case the mixing task is not required. For this example, in view of the high purity required, the product will almost certainly be an output from the distillation column.



(a) Plain reactor and one column superstructure



(b) Jacketed reactor and one column superstructure

Figure 6.2: Flowsheets with full connectivity with two processing units

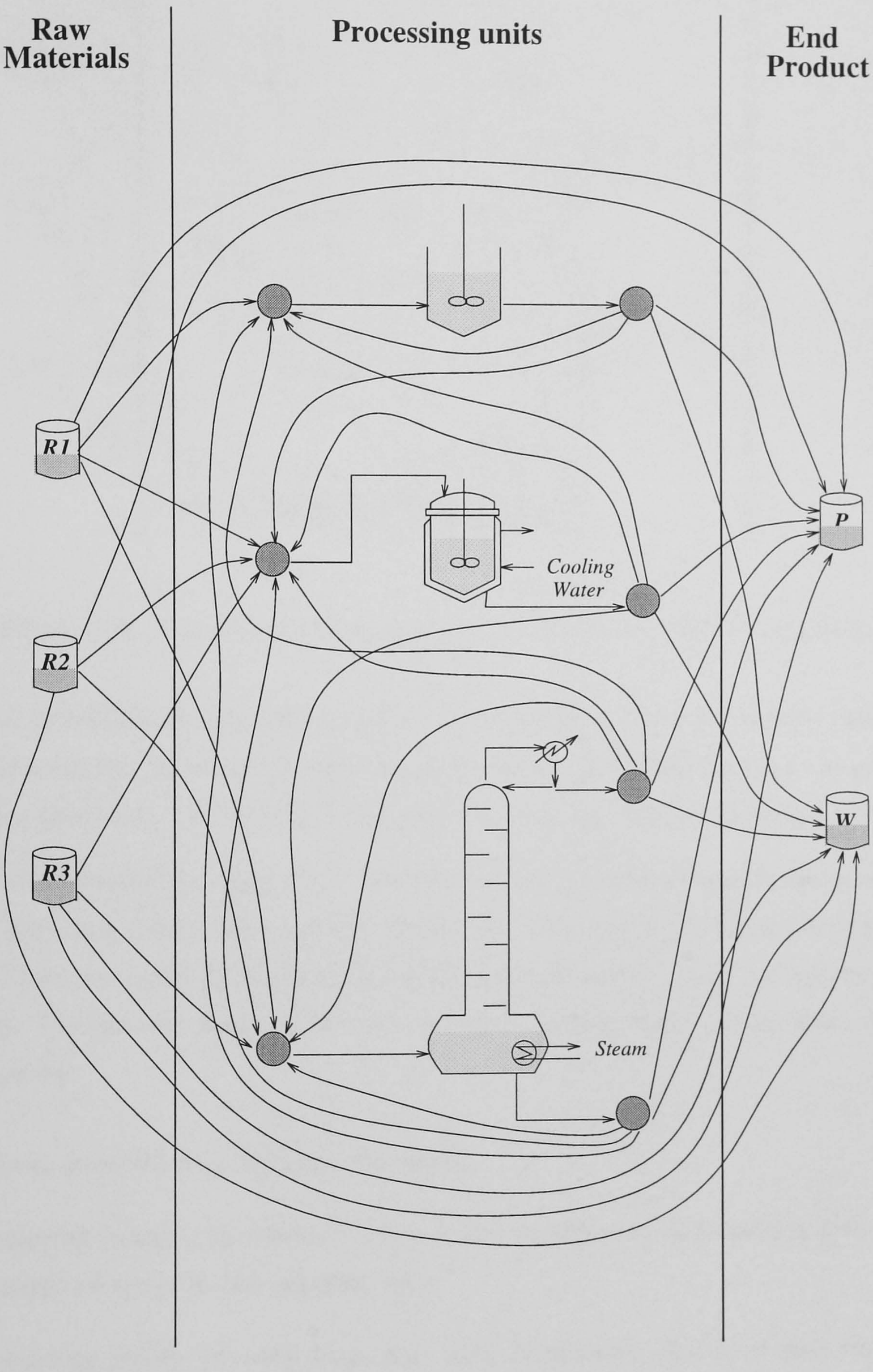


Figure 6.3: Flowsheet superstructure with full connectivity with three processing units

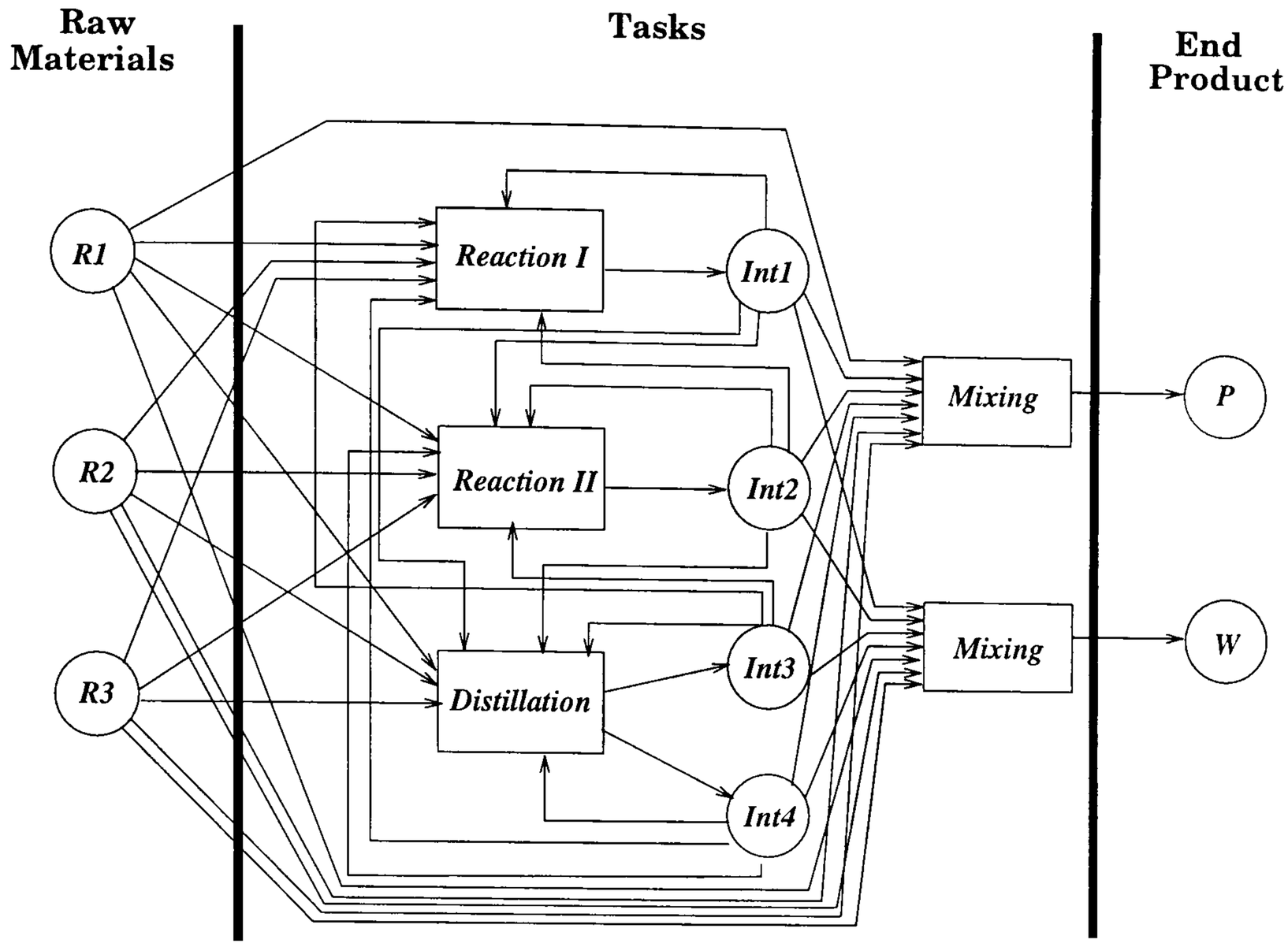


Figure 6.4: State-Task Network superstructure with full connectivity

Note that, in addition to the main product P, we have introduced a second (waste) product W. This will comprise all material *other* than P produced by the process. In general, many process design problems will be infeasible without the introduction of such a waste state.

We note that the STN in figure 6.4, as well as those corresponding to the processes shown in figures 6.2(a) and 6.2(b), are entirely consistent with the type of representation used in Chapter 3. Thus, we could optimise each one of these processes using the approach described in Chapter 3. The precise function of each of the operating tasks in the optimal design will be determined by:

- the actual material flow between the units;
- the equipment design characteristics, *e.g.* the volumes of the reactors and the reboiler, the number of trays in the column, *etc.*;
- the operating policy for each task, *e.g.* their batch size, duration and time profiles of control variables such as the cooling water flowrate in the jacketed reactor and the condenser of the column, the heat load on the reboiler of the column, the reflux ratio policy, *etc.*

6.3. An Enumeration-Based Solution Approach

As we have seen in section 3.8.4, there are several sophisticated algorithms for the solution of mixed integer non-linear programming (MINLP) problems. However, here we adopt an enumeration solution approach based on the optimisation of each individual discrete alternative flowsheet of the process design. In contrast to the problems considered in Chapters 4 and 5 where the number of discrete alternatives could be quite large, here, as we have seen, there are only relatively few discrete alternative flowsheets. In fact, there are two potential advantages for using a complete enumeration approach in preference to the more sophisticated MINLP techniques. First, the optimisations of the individual alternative flowsheets are completely decoupled since no transfer of information from the solution of one flowsheet optimisation is required for the optimisation of another. Consequently, the solution of this set of optimisation problem allows a parallelised solution approach where the optimisation of the multiple discrete alternative flowsheets is carried out simultaneously using multiple computer processors.

The second advantage of the enumeration-based approach arises from the changing configuration of the actual mathematical problem being solved for each flowsheet. Only the constraints and variables from those processing units that actually exist in the discrete alternative flowsheet to be optimised need to be included in the formulation, *i.e.* the problem size varies with each distinct alternative flowsheet being optimised. This is in contrast with the direct MINLP method where the makeup of the subproblem remains the same regardless of the existence (or not) of the processing tasks. The fact that the optimisation problems solved in the enumeration approach are of variable makeup may lead to the average computational time required for the solution of each problem being *less* than that required for the solution of the problems in the direct MINLP approach. Moreover, the removal of the constraints/variables describing the performance of non-existing processing units from these optimisation problems eliminates some of the numerical difficulties which may arise during the solution of the direct MINLP subproblems. Although some of the numerical difficulties may be overcome by using the modelling-decomposition strategy such as the one developed and applied by Kravanja and Grossmann (1997), the processes of interest to us tend to be more complex because of the existence of two *levels* of binary variables: those that denote the existence (or not) of the processing tasks (θ_i) and those associated with the design of each unit (y_i) performing task i. The application of the modelling-decomposition strategy in this context is far from a trivial task.

It is important to note that the optimisation of each individual discrete alternative flowsheet may still require the solution of an MINLP due to the presence of discrete design variables

y characterising the performance of individual processing units (see example of section 7.5).

6.4. Conclusions

A general process methodology is considered in this chapter for the design of integrated batch processes where in addition to determining the operating policies and the equipment sizes, the optimal process structure is also found. The methodology requires the following information:

- the potential raw materials and the possible restrictions on their availability;
- the end-product specifications, such as the purity and production rate requirements;
- the types of processing units that *may* be used to perform the tasks in the batch process;
- the objective function which is to be optimised by the process.

The above are the fundamental components of *any* process design problem specification and are independent of the methodology proposed here. The methodology presented in this work imposes two additional requirements:

- a mathematical model of the physical, chemical and biological behaviour of each type of available processing unit;
- the *maximum* number of instances of each type of equipment item that may be used in the process.

The use of a full connectivity superstructure eliminates the combinatorial complexity associated with the interconnections between processing steps in the process. In particular, it obviates the need for any further definition of an *appropriate* structure on behalf of the process designer. Moreover, provided the mathematical models used are sufficiently accurate, the designs produced using the method will give rise to flowsheets that are realisable and whose performance can be accurately predicted through the use of detailed models of the individual processing units. This is an essential requirement for any process design methodology that is to be of any practical value.

Finally, the approach can be used for both batch and continuous processes (*cf.* Smith, 1996). The distinction between the two types of processes is reflected in the mathematical model of each of the processing units; for continuous processes, the units operate at steady-state whereas in batch processes, the operating units are inherently time-dependent.

Chapter 7

Synthesis and Design of Batch Reactor Networks

This chapter is concerned with the application of the process design approach described in Chapter 6 to the problem of designing networks of batch reactors. Three case studies are used to illustrate the ability of our methodology to take account of complex process trade-offs and to produce novel designs.

7.1. Batch Reactor Network Synthesis

Batch and semi-batch reactors are widely used for the production of low volume, high value products such as pharmaceuticals, polymers, fine chemicals or other biotechnological chemicals. They are especially suited to performing very slow reactions in relatively small amounts.

In order to produce products of high quality and purity with strict control of polluting waste materials and losses of raw materials, it is necessary to optimise the batch operating conditions (*e.g.* temperature, inlet concentrations, processing time, *etc.*). The optimisation of batch reactors has been studied for a long time. The literature has mainly focused on the determination of optimal temperature profiles, feed flow rate profiles, pH, *etc.* (Rippin, 1983). Levien (1992) proposed a methodology based on kinetic insight that optimises the product distribution obtained from competing chemical reactions which take place in parallel. Vassiliadis *et al.* (1994) addressed the problem of optimising the operation of discrete charge batch reactors within a general framework which is independent of the form of the kinetic mechanism and any non-idealities that might be present. Garcia *et al.* (1995) formulated the optimisation problem as a non-linear programming (NLP) problem and solved it by the generalised reduced gradient procedure together with the golden search method for the

minimisation of the total batch time. The objective was to optimise simultaneously different variables and to take into account the bounds on the variables as well as the linear and/or non-linear constraints such as the restrictions on the temperature gradients, the reactant fed and/or the amount of by-products.

Recently, Carrasco and Banga (1997) proposed two algorithms based on stochastic optimisation (*i.e.* incorporating an element of random search) and used them to solve four case studies in batch reactor optimisation. The advantages of these techniques include ease of implementation, global convergence properties and computational efficiency. Also, the growing importance of pollution prevention as a necessary environmental protection strategy prompted Calderón *et al.* (1998) to present an integrated methodology to compare the process waste generation for different operating conditions in batch reactors. The methodology involved the optimisation of an objective function including environmental costs.

The literature reviewed above either deals with single batch reactors or assumes that the structure of the batch reactor networks are *fixed*. The structure of the recipe is not considered within the optimisation framework. However, a fair amount of work has been carried out on the design of optimal networks of *continuous* reactors. Most of this work has been based around two reactor types, namely continuous stirred tank reactor (CSTR) and the tubular reactor. Kokossis and Floudas (1990, 1994) used standard CSTR models, with tubular reactors being modelled as sequences of large numbers of CSTRs of equal size. The existence of each CSTR was modelled using a binary variable, and the volume of each unit was optimised. The reactor synthesis problem was formulated as a mixed integer non-linear programming (MINLP) that can handle both thermodynamic and economic objective functions. Their approach allows arbitrary general network configuration but leads to large MINLP formulations. Lakshmanan and Biegler (1996) took advantage of attainable-region properties derived from geometric targeting techniques to design a concise reactor module for reactor network synthesis. An MINLP algorithm was used to identify parallel reactor structures and by-passes, if they exist for the optimal network. Smith (1996) used a fully connected superstructure approach to solve reactor network design problems where detailed unit operation models were used to ensure the practical realisability and the optimality of the derived systems.

In the following section, we apply the methodology described in Chapter 6 to find the optimal recipe and operating policies of batch reactor networks. Two basic forms of batch reactors are considered: plain reactor and jacketed reactor. The unit operation models used to describe their behaviour are presented in detail in section A.2 of Appendix A.

7.2. Example: Exothermic Batch Reaction Network

This example problem is similar to the first two reaction steps of the Reaction-Distillation II process described in section 7.2 (pp. 111-123) of Charalambides' (1996) PhD thesis.

7.2.1. Process Description

Feedstocks R_1, R_2 and R_3 are transformed into products A and E via the exothermic liquid phase reaction scheme:

$$R_1 + R_2 \rightarrow I_1 \tag{7.1}$$

$$R_1 + I_1 \rightarrow A \tag{7.2}$$

$$I_1 \rightarrow C \tag{7.3}$$

$$C + R_3 \rightarrow E \tag{7.4}$$

A side reaction also takes place:

$$I_1 + C \rightleftharpoons I_2 \tag{7.5}$$

The reactions make use of catalyst Cat which undergoes deactivation to an inert state Cat^*:

$$Cat \rightarrow Cat^* \tag{7.6}$$

The reactions take place in a solvent S in the presence of active catalyst particles Cat which are supplied in a slurry form. The reactor is operated in a semi-batch mode allowing both discrete initial charges and the continuous supply of pure feedstocks R_1, R_2 and catalyst Cat. Reactant R_3 and pure solvent S are available only as discrete initial charges. The deactivation of the catalyst is also taken into account, with the deactivation rate being a function of the concentration of the active catalyst only.

The reactor operation has to satisfy several constraints. The molar ratio of solvent S to feed R_2 in the total amount fed to the reactor must always exceed 1.35. The maximum supply flowrates for R_1 and R_2 are 1.0 $kmol/hr$ and for the catalyst 500 dm^3/hr. All feeds are available at 338 K. The reaction temperature is constrained to lie between 338 and 380 K at all times. The temperature of the mixture at the end of the reaction process must not exceed 350 K. The temperature is controlled by manipulating the cooling water flowrate with a fixed inlet temperature at 293 K in the jacket.

The physical and reaction kinetic data used in this example are provided in section B.3 of Appendix B.

7.2.2. Reactor Network

We start by specifying the number of instances of each type of operator to be allowed within the "optimal" flowsheet. In this example, we allow a maximum of two jacketed reactors and two plain reactors with a maximum combination of only three reactors that could be used at any one time. The fully connected superstructure for the above example is shown in figure 7.1.

The temperature of the reaction is controlled by manipulating the cooling water flowrate in the jacket. The maximum cooling water flowrate in the jacket is 8.0 te/hr. The plain reactor is operated adiabatically. The reactor volumes can vary between 1.875 m^3 and 3.785 m^3.

7.2.3. Economic Data

The capital cost ($\$/hr$) is calculated using the following correlation (Charalambides, 1996):

$$C_c = \alpha_r V_R^{0.6} \tag{7.7}$$

where V_R is the reactor volume in litres and α_r is a cost coefficient with values of 0.95 and 0.54 for jacketed and plain reactors respectively.

The operating cost ($\$/hr$) for the jacketed reactors is calculated by (Charalambides, 1996):

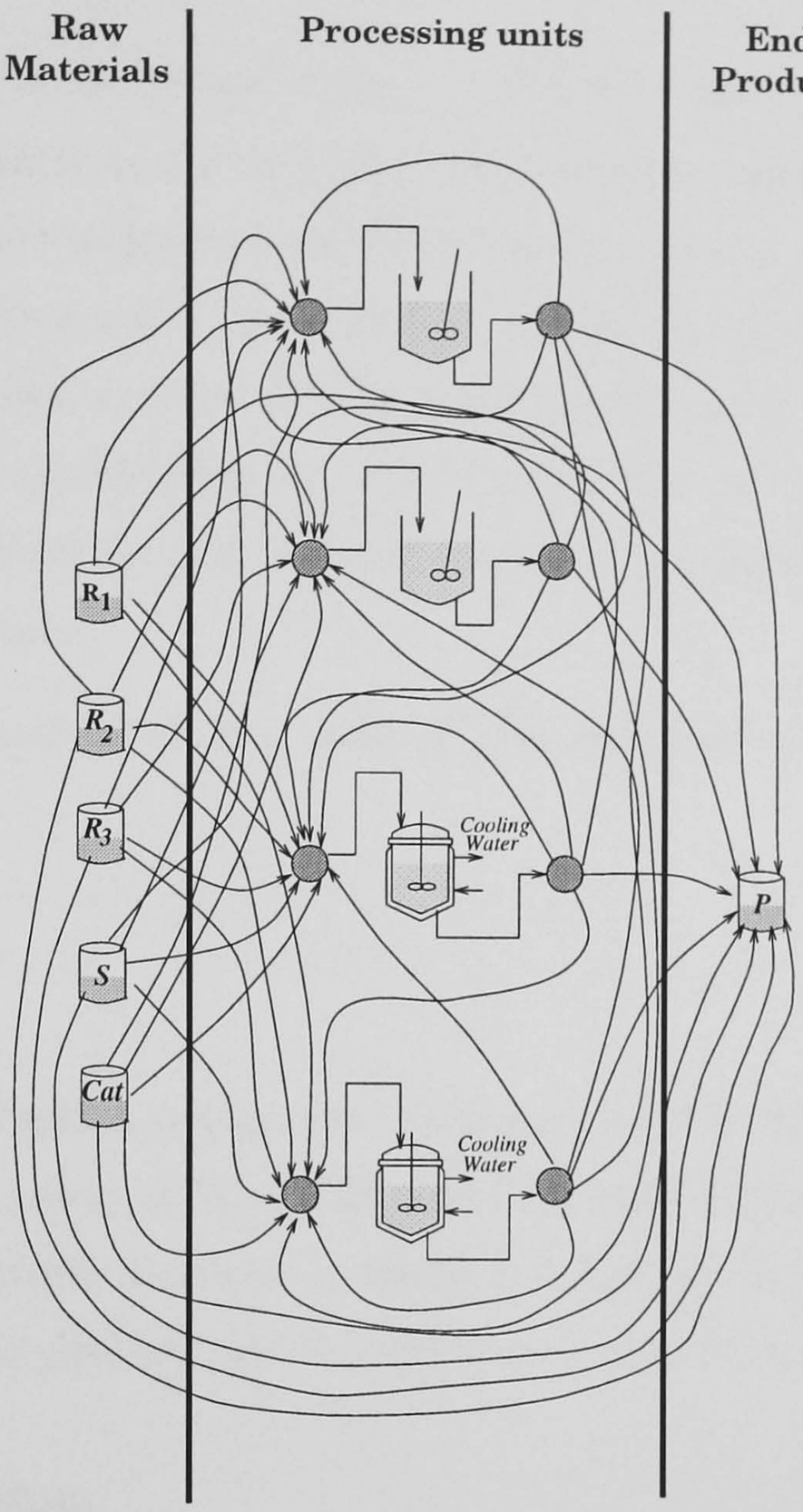
$$C_o = 0.01920 Q_c \tag{7.8}$$

where Q_c is the mean cooling jacket load in kJ/hr. The plain reactor is operated adiabatically at effectively no operating cost.

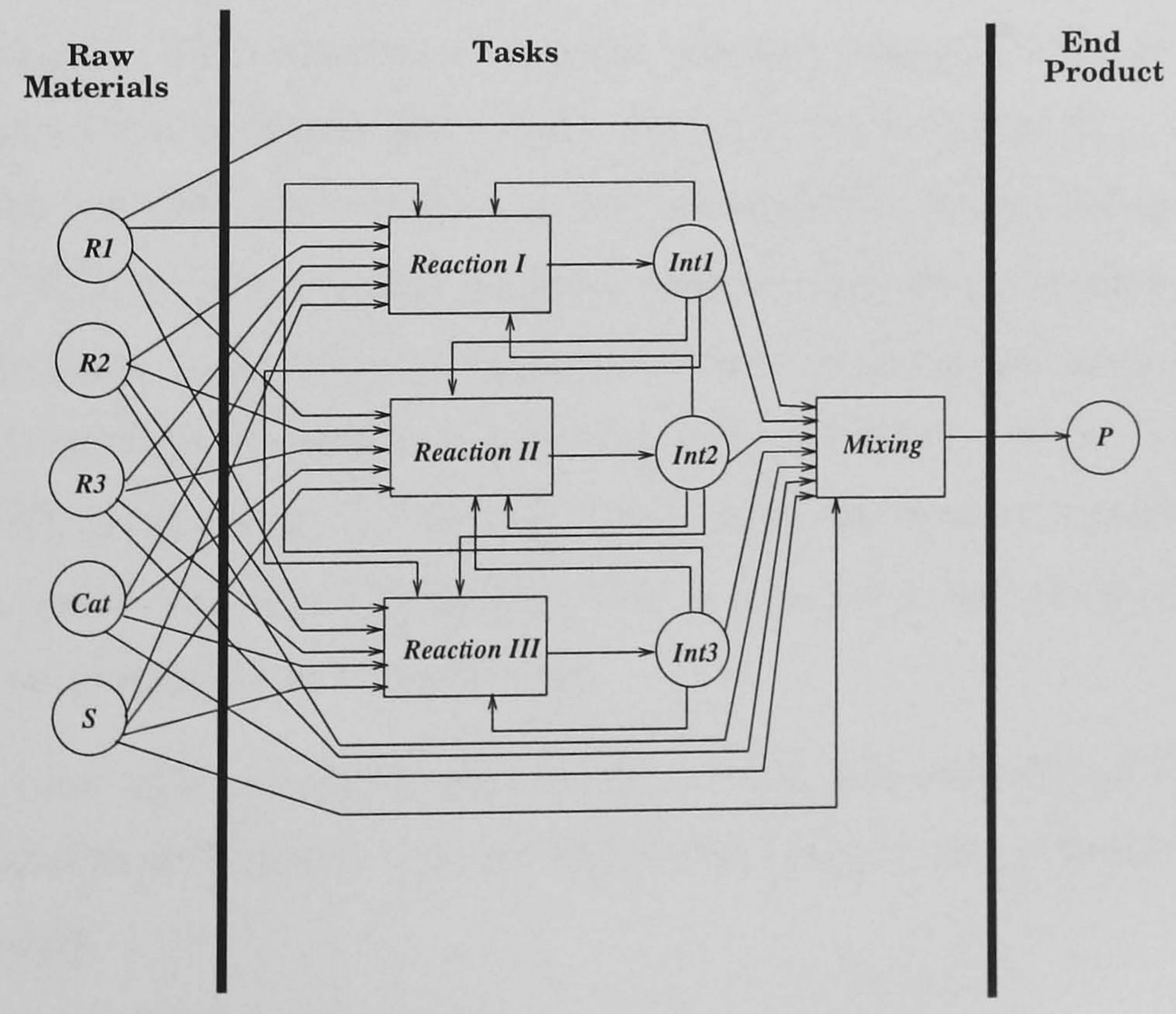
The cost parameter values for the various materials are shown in table 7.1.

Material	Unit value ($\$/kmol$)
R_1	238.7088
R_2	1186.608
R_3	39.41166
S	134.89442
P	1356.27
Cat	35 ($\$/dm^3$)

Table 7.1: Unit values for process materials



(a) Flowsheet superstructure



(b) State-Task Network superstructure

Figure 7.1: Superstructure with full connectivity for batch reactors

7.2.4. Modelling

The reactors incorporate material and energy balances to form standard DAE models. The cooling driving force is taken as the difference between the outlet cooling water temperature and the temperature of the reactor contents which are assumed to be well mixed. The flowrates of the feeds and the cooling water are varied as piecewise constant functions of time. The initial charge to the reactors, reactor volume and the processing time of each reactor unit are treated as time invariant optimisation variables. Inequality constraints are introduced to deal with the imposed limitations on product quality, mean production rate, feed ratio of S and R_2, volume and temperature.

The detailed mathematical models used in this example are provided in section A.2 of Appendix A.

7.3. Case Study 1

In this example, the production requirement is similar to that used by Charalambides (1996) with the product P containing at least 0.25 and 0.04 mole fractions of components A and E respectively. The mean production rate is fixed at 7.5 $kmol/hr$. The operating time of each operation in the process is divided into 4 control intervals of varying durations.

7.3.1. Base Case Solution

For the sake of comparison, we will consider the structure used by Charalambides as the base case for this example. This consists of a *fixed* network comprising a jacketed reactor and a plain reactor as shown in figure 7.2. Since reactant R_3 is not added to the first reactor, reaction (7.4) does not take place there. In fact, Charalambides assumed that reactions (7.1 - 7.3) and (7.5 - 7.6) take place in the jacketed reactor, and *only* reaction (7.4) occurs in the plain reactor. The latter assumption is not strictly correct since reactants R_1 and R_2 are still present. We will relax this assumption in our model of the plain reactor by allowing all of the reactions (7.1 - 7.6) to take place. Moreover, Charalambides assumed isothermal operation in the plain reactor; again, we relax this assumption by operating the plain reactor adiabatically with constraints on the reaction temperature.

The optimal base case structure results in a total net revenue of 5268.96 $\$/hr$. The corresponding State-Task Network and the economic analysis are presented in figure 7.3 and table 7.2 respectively.

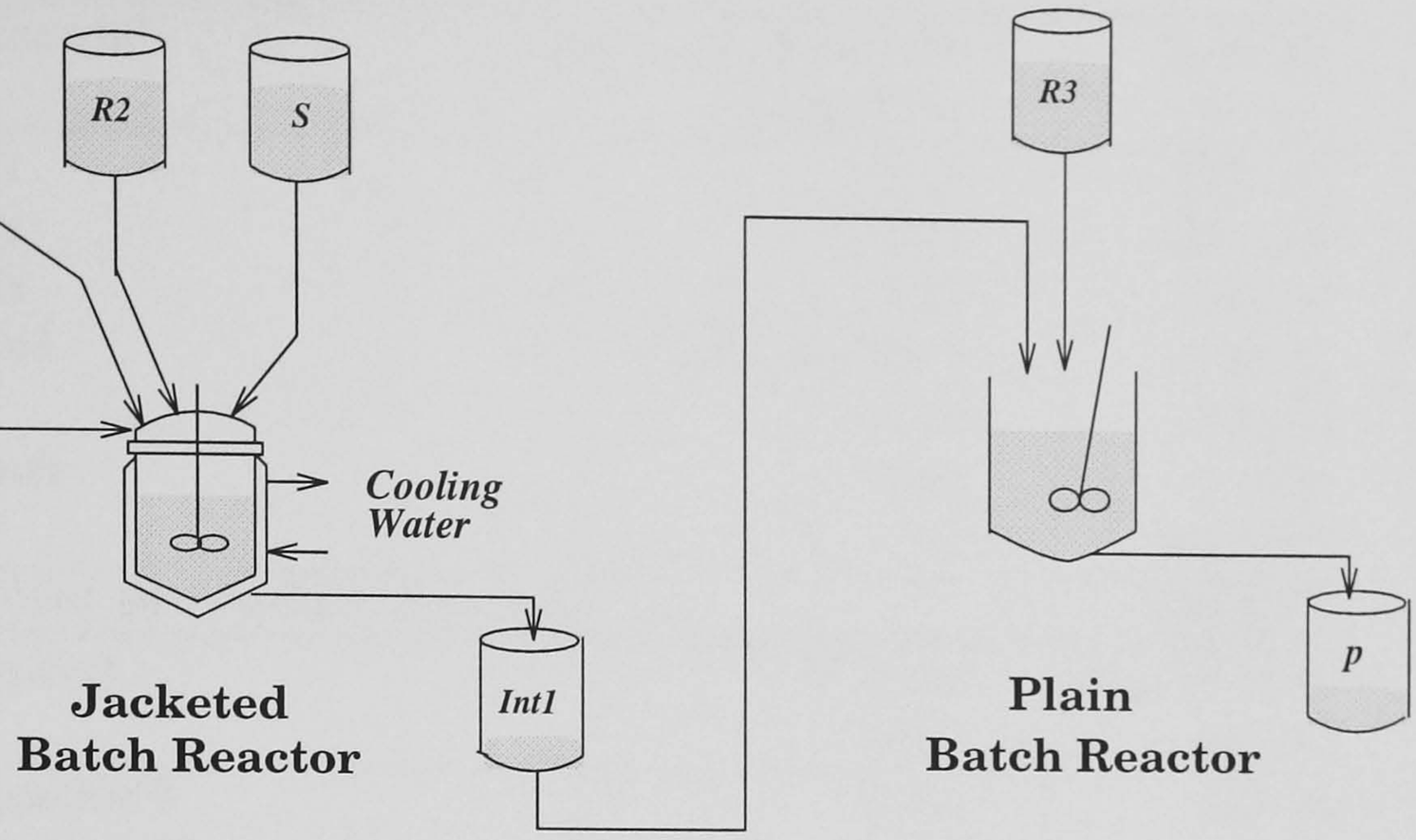


Figure 7.2: Base Case: Original structure

The jacketed reactor requires initial charges of 10.84, 4.68 and 7.97 $kmol/batch$ of reactants R_1 and R_2, and solvent S respectively and 0.28 $dm^3/batch$ of the catalyst with a processing time of 2.16 hr and a (fixed) set-up time of 15 min. There is practically no idle time. Further amounts of R_1, R_2 and the catalyst are added continuously during the first half of the operation as shown in figure 7.4(a). The molar ratio of S to R_2 in the total charge to the reactor is 1.42, thereby satisfying the constraint that it must exceed 1.35.

The variation in the reaction temperature and the corresponding cooling water flowrate are shown in figure 7.4(b). A high cooling water flowrate is adopted at the beginning of the process in order to dampen the initial rate of temperature rise, and at the end to cool down the mixture to the required temperature of 350 K rapidly.

At the initial stages of the operation, the concentrations of the reactants R_1 and R_2 are high, thereby favouring the generation of I_1. As the concentration of I_1 increases, reaction $R_1 + I_1 \rightarrow A$ takes place. The temperature in the reactor is kept below 350 K in the first half of the process to reduce the rate of the forward reaction of $I_1 + C \rightleftharpoons I_2$, thereby enhancing the generation of the desirable product A. However, in the final stages of the process, there is a quick rise in temperature; this helps to form C via the reaction $I_1 \rightarrow C$ and the backward part of the reaction $I_1 + C \rightleftharpoons I_2$, both of which are favoured by high temperature. By the end of the operation, the jacketed reactor produces 3.82 $kmol$ (1.577 $kmol/hr$) or about 84% of the total amount of A required.

The plain reactor requires 4.65 and 27.24 $kmol/batch$ of reactant R_3 and intermediate $Int1$ respectively, and operates for 3.67 hr with a fixed set-up time of 15 min. The reactor

Material	Net production rate ($kmol/hr$)	Revenue ($/hr)
R_1	−5.16	−1231.74
R_2	−2.31	−2741.06
R_3	−1.19	−46.90
Cat	−1.25 (dm^3/hr)	−43.75
S	−3.29	−443.80
$Int1$	0.00	0.00
P	7.5	10172.02
Total production revenue		**5664.77**
Operator	Volume (m^3)	Capital cost ($/hr)
Reactor I	2.404	101.45
Reactor II	3.781	75.68
Total capital cost		**177.13**
Task		Operating cost ($/hr)
Reaction I (Reactor I)		218.68
Reaction II (Reactor II)		0.0
Total operating cost		**218.68**
Total net profit		**5268.96**

Table 7.2: Base Case: Economic breakdown for optimal solution

is operated adiabatically with the final temperature of the mixture rising to 348 K. By the end of the operation, the plain reactor produces 1.176 $kmol/batch$ (0.300 $kmol/hr$) of E and 1.169 $kmol/batch$ (0.298 $kmol/hr$) of A.

The optimal values/variations of the decision variables are summarised in table C.5 in Appendix C.

Using the design approach described in Chapter 6, it can be shown that a reactor network structure can be obtained that is more cost effective that the conventional structure. We consider this next.

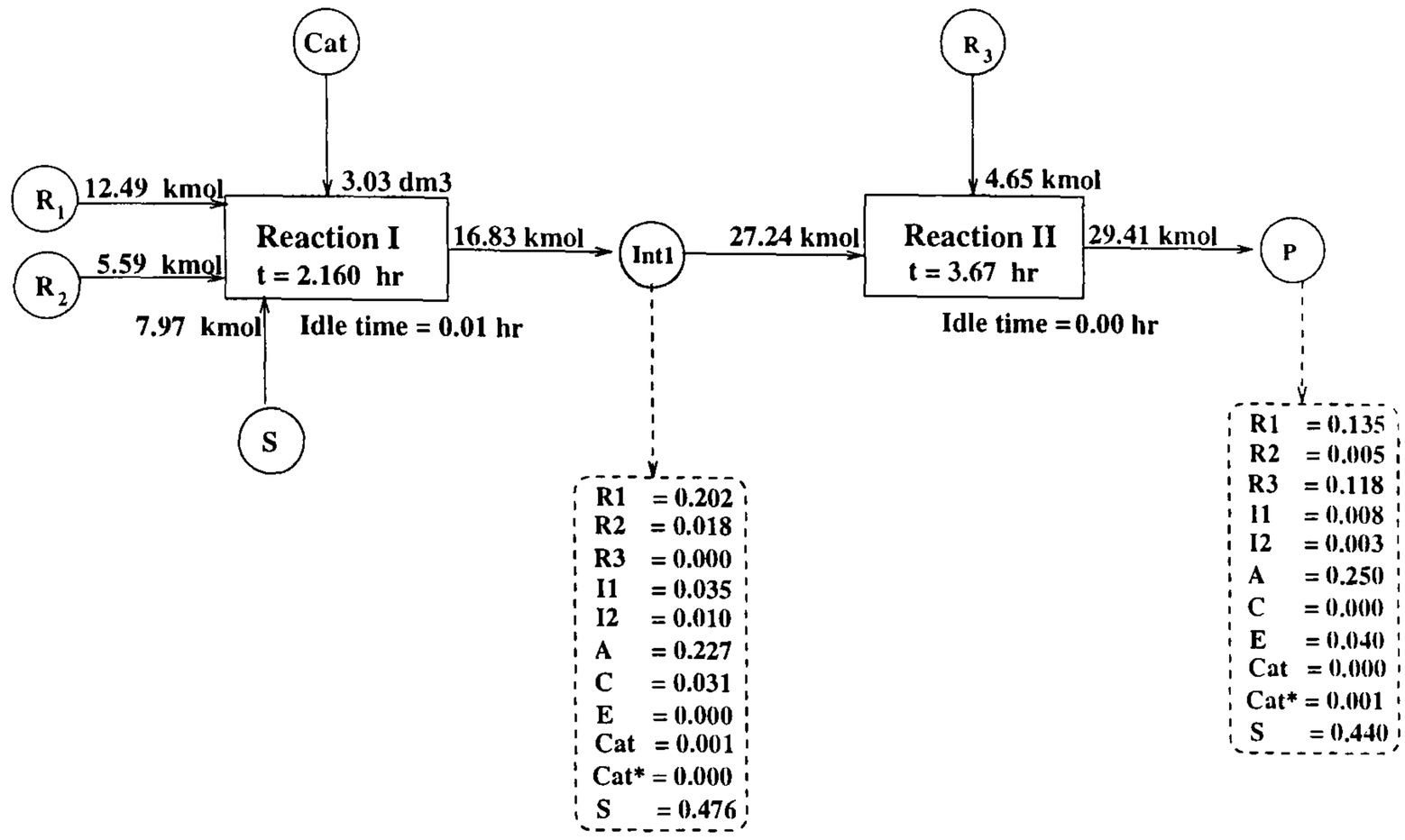
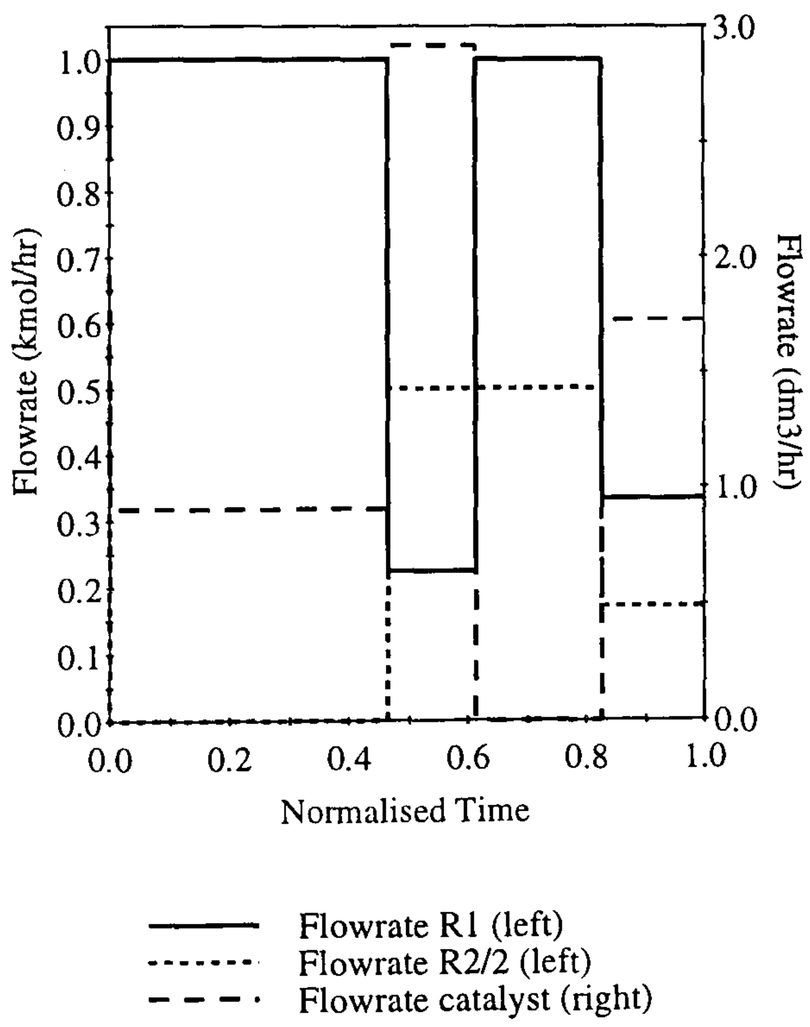
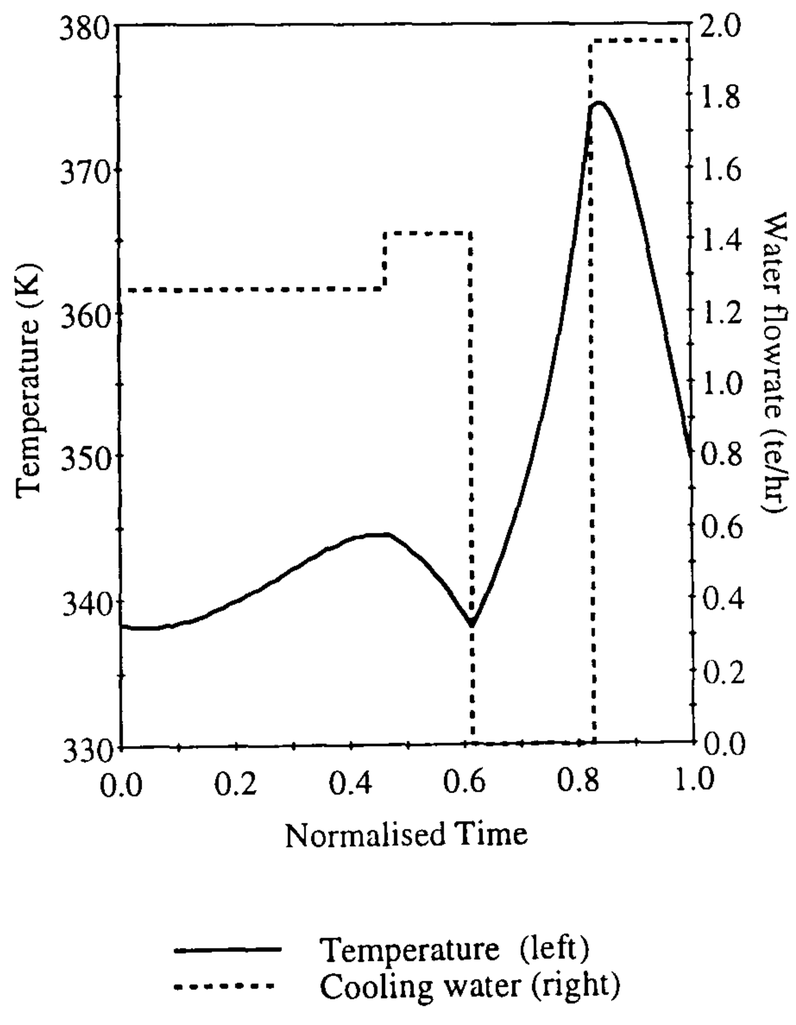


Figure 7.3: Base Case: State-Task Network for the optimal solution



(a) Feed addition rates of R_1, $R_2/2$ in $kmol/hr$ and the catalyst in dm^3/hr for the jacketed reactor



(b) Temperature and cooling water flowrate profiles in jacketed reactor

Figure 7.4: Base Case: Optimal operating policy

7.3.2. Optimal Reaction Network

Given that only three reactors could be used at any one time and that there are two jacketed reactors and two plain reactors available, there are eight potential alternatives. All of the potential flowsheets were individually optimised. The results are shown in table 7.3:

Plain reactor	Jacketed reactor	Total net profit ($/hr)	CPU(s) (on *SUN ULTRA*)	NLP Iterations
0	0	INFEASIBLE	–	–
1	0	INFEASIBLE	–	–
0	1	5601.80	647.7	123
1	1	5833.88	14477.7	185
2	0	INFEASIBLE	–	–
0	**2**	**5882.16**	6726.9	190
2	1	5817.09	90095.2	350
1	2	5872.68	116830.0	428

Table 7.3: Case 1: Enumeration results

The structure associated with the maximum net profit comprises two jacketed reactors as shown in figure 7.5.

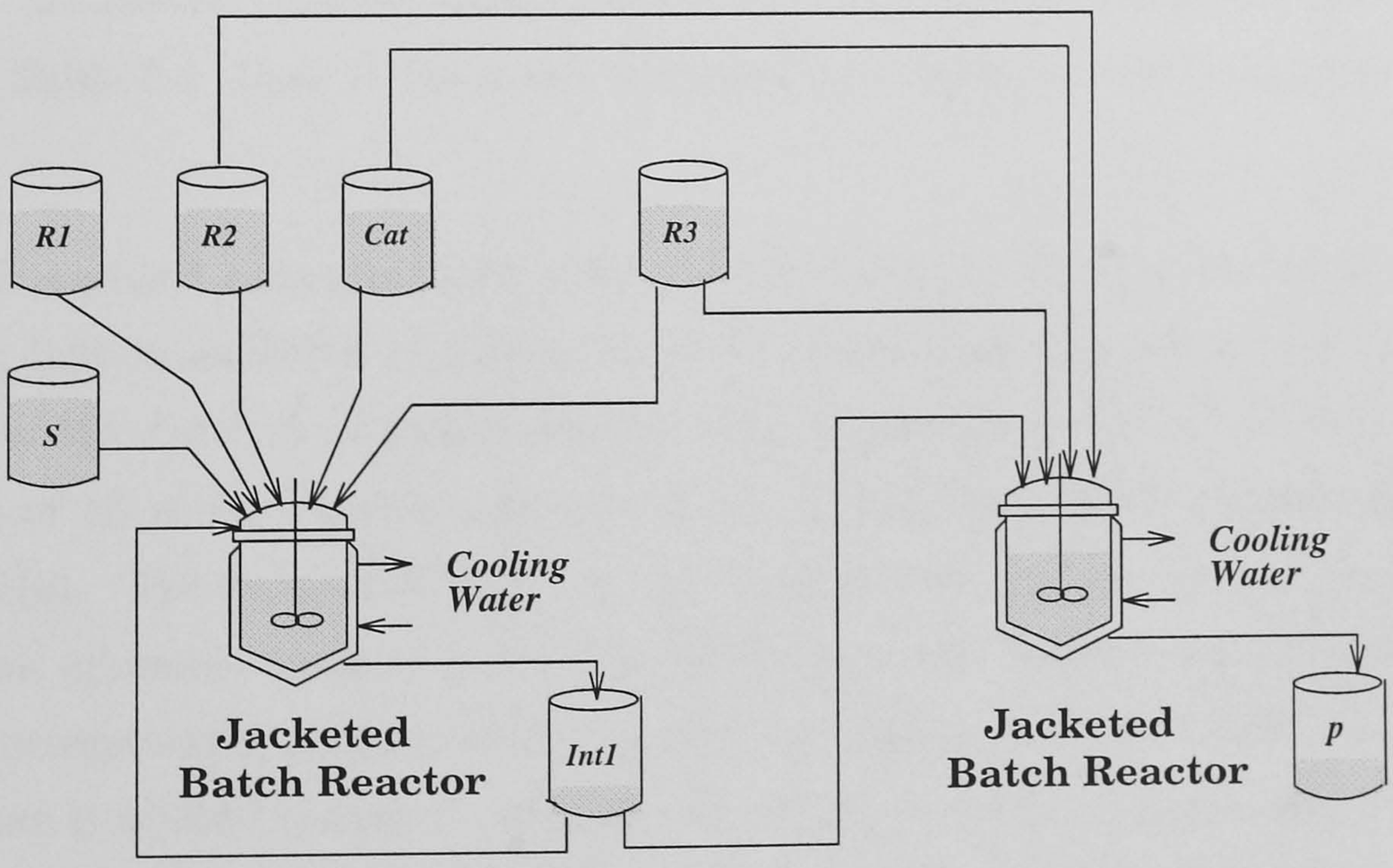


Figure 7.5: Case 1: Optimal reactor network structure

The process requires 4.48, 2.16 and 4.57 $kmol/hr$ of reactants R_1, R_2 and R_3 respectively, 0.18 dm^3/hr of catalyst and 0.58 $kmol/hr$ of solvent S. The total net revenue of the process is

5882.16 $\$/hr$. The economic breakdown and the optimal recipe for the process are presented in table 7.4 and figure 7.6 respectively.

Material	Net production rate $(kmol/hr)$	Revenue $(\$/hr)$
R_1	−4.48	−1069.42
R_2	−2.16	−2563.07
R_3	−4.57	−180.11
Cat	−0.18 (dm^3/hr)	−6.30
S	−0.58	−78.24
$Int1$	0.00	0.00
P	7.5	10172.02
Total production revenue		**6274.88**
Operator	Volume (m^3)	Capital cost $(\$/hr)$
Reactor I	3.785	133.21
Reactor II	2.484	103.46
Total capital cost		**236.67**
Task		Operating cost $(\$/hr)$
Reaction I (Reactor I)		120.20
Reaction II (Reactor II)		35.85
Total operating cost		**156.05**
Total net profit		**5882.16**

Table 7.4: Case 1: Economic breakdown for optimal reactor network

Jacketed reactor I consumes 3.87, 1.65 and 1.37 $kmol/batch$ of reactants R_1, R_2 and R_3 respectively, 0.58 $kmol/batch$ of solvent S, 27.77 $kmol/batch$ of intermediate $Int1$ and 0.07 $dm^3/batch$ of the catalyst as initial charges with a processing time of 45 min and a fixed set-up time of 15 min. Further amounts of R_1 and R_2 are added continuously as shown in figure 7.7(a). The ratio of S to R_2 in the total amount fed to the reactor is at exactly the minimum allowable value of 1.35. The variation in the reaction temperature of reactor I and the corresponding cooling water flowrate are shown in figure 7.7(b). A high cooling water flowrate is utilised during the middle part of the process to prevent side reactions from depleting I_1. The reaction produces 1.459 $kmol/hr$ or 77.8% of the total amount of A required, and 0.121 $kmol/hr$ or 40.3% the total amount of E required.

Jacketed reactor II consumes 0.88, 10.66 and 16.82 $kmol/batch$ of R_2, R_3 and $Int1$ respectively, and 0.38 $dm^3/batch$ of the catalyst as initial charges with a processing time of 3.08 hr and a fixed set-up time of 15 min. The ratio of S to R_2 fed to the reactor is 1.36.

The temperature profile together with the optimal cooling water consumption of the reactor are shown in figure 7.8. The operation generates 0.415 $kmol/hr$ (1.38 $kmol/batch$) or the remaining 22.2% of A required and 0.179 $kmol/hr$ (0.595 $kmol/batch$) or 59.7% of E.

The new structure results in an increase in the overall profit rate of 613.20 $\$/hr$, an improvement of 11.6% from the original base case structure.

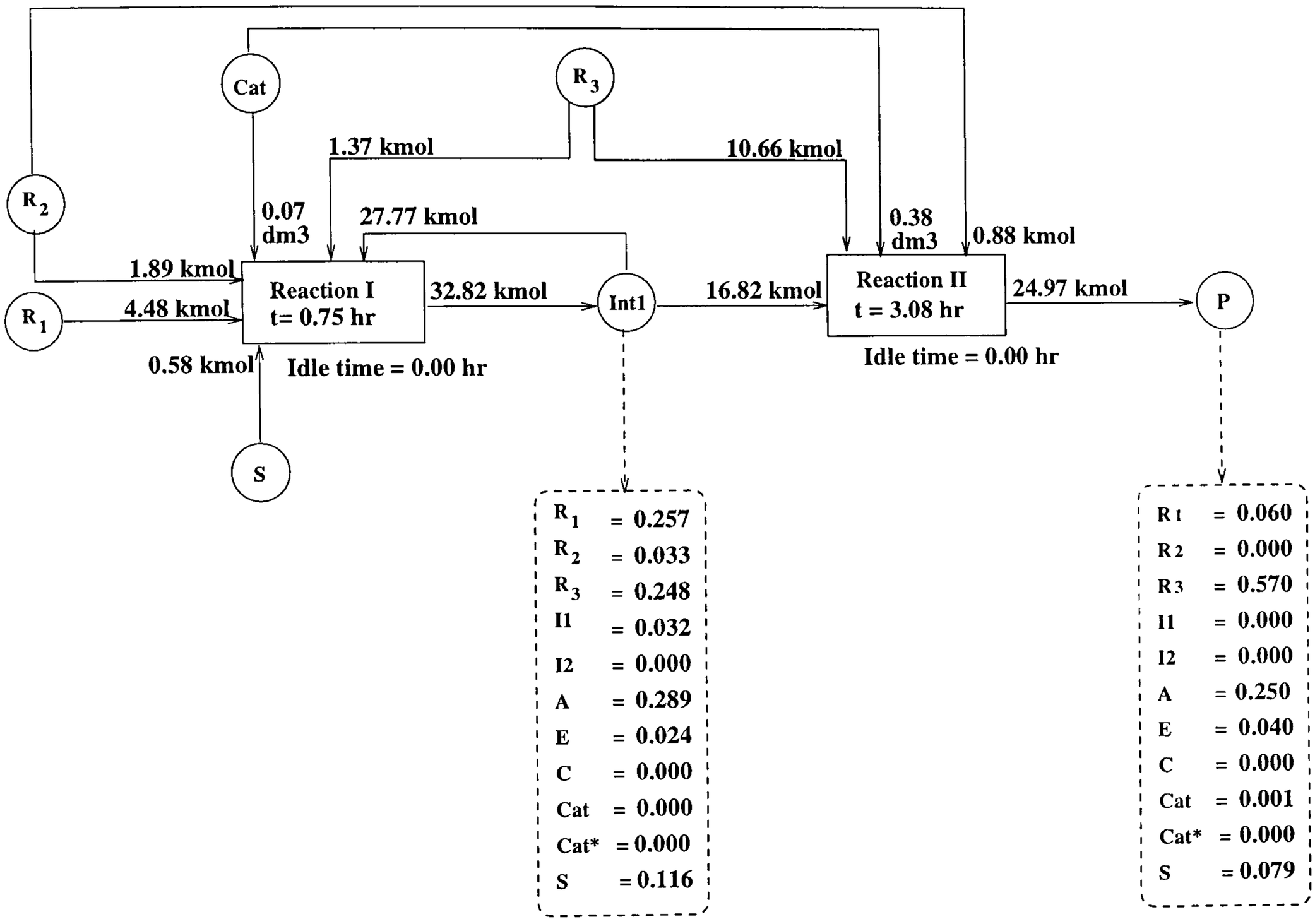
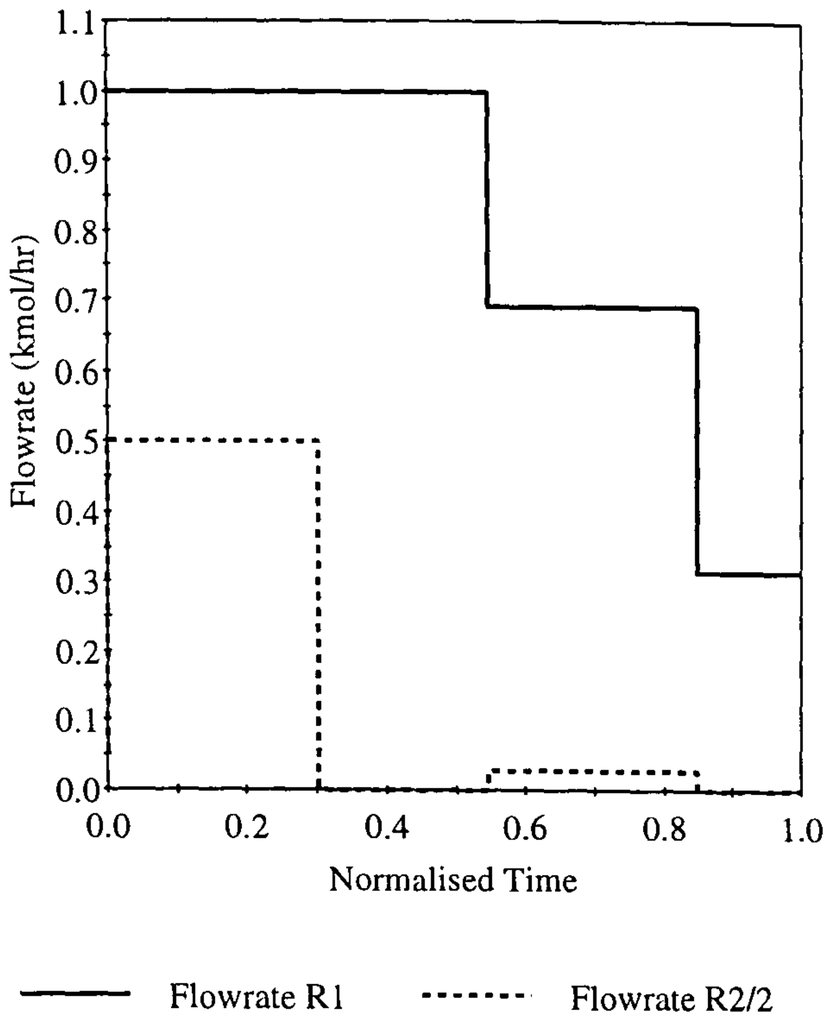
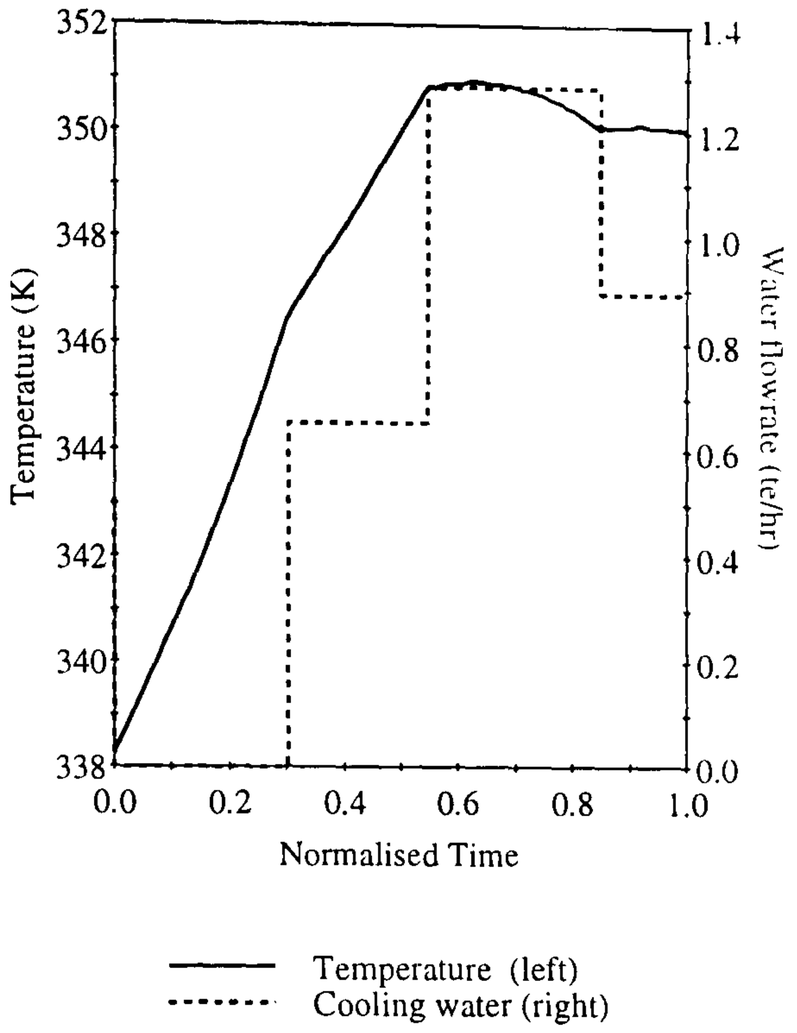


Figure 7.6: Case 1: State-Task Network for the optimal reactor network

The optimal values/variations of the decision variables are summarised in table C.6 in Appendix C.



(a) Feed addition rates of $R1$ and $\frac{R2}{2}$ in $kmol/hr$



(b) Temperature and cooling water flowrate profiles

Figure 7.7: Case 1: Optimal operating policy for reactor I

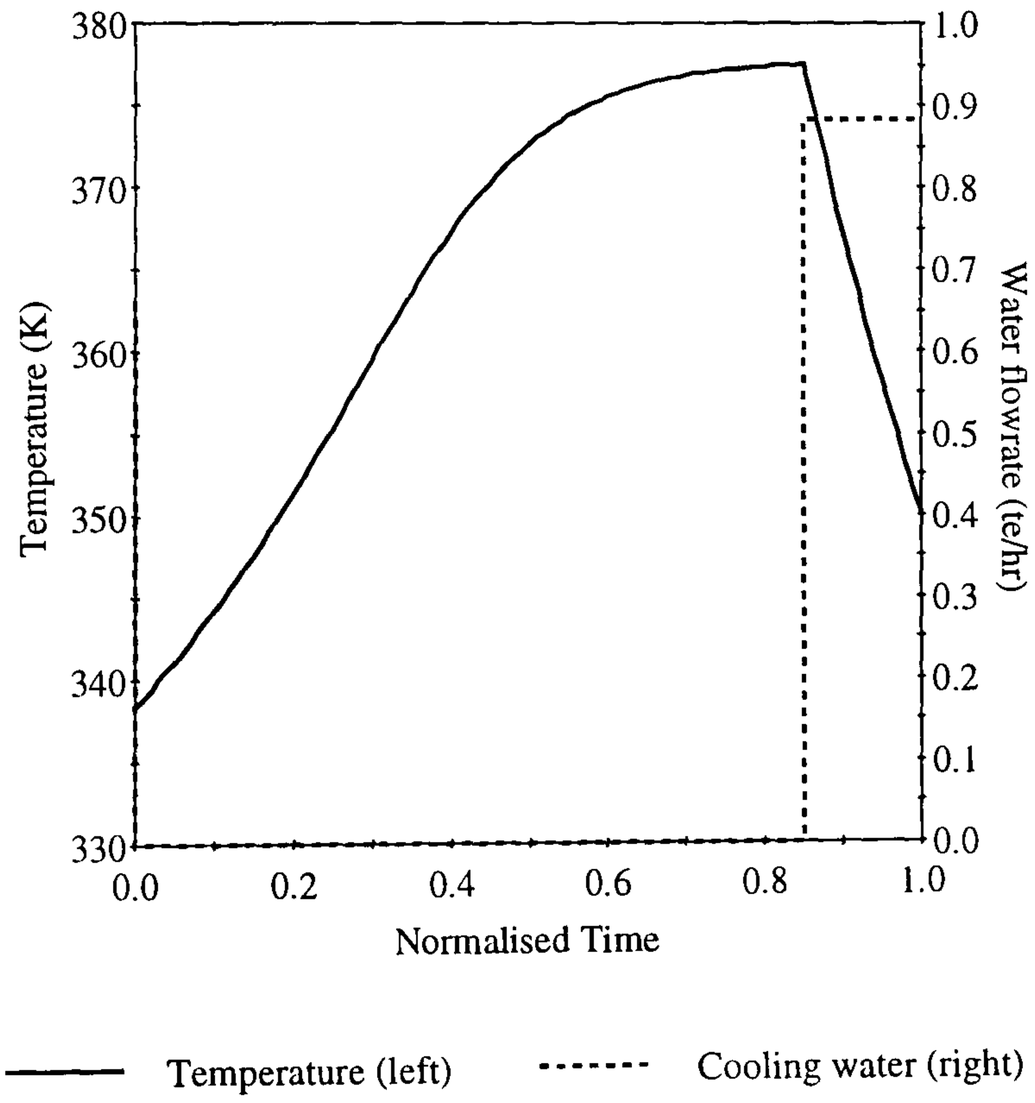


Figure 7.8: Case 1: Temperature and cooling water flowrate profiles for reactor II

7.4. Case Study 2

In this case study, the required mole fractions of product A and E are increased to at least 0.35 and 0.1 respectively, and the reactor volumes can vary between 1.875 m^3 and 5.375 m^3. All other constraints are exactly the same as those of Case Study 1.

The base case structure described in Case Study 1 cannot achieve the new production requirements. Therefore, we use the full connectivity method in order to obtain a feasible structure with maximum profit.

As in the previous case, we assume that a maximum of three reactors can be used at any one time, with up to two jacketed and plain reactors being available.

7.4.1. Results

The results for the complete enumeration of potential flowsheets are shown in table 7.5:

Plain reactor	Jacketed reactor	Total net profit ($\$/hr$)	CPU(s) (on *SUN ULTRA*)	NLP Iterations
0	0	INFEASIBLE	–	–
1	0	INFEASIBLE	–	–
0	1	3651.06	1355.1	75
1	1	3734.37	5231	68
2	0	INFEASIBLE	–	–
0	**2**	**3886.05**	2538.7	32
2	1	3807.81	24434.4	103
1	2	3813.55	90982.5	302

Table 7.5: Case 2: Enumeration results

Just like the previous case, the structure with the highest net profit consists of two jacketed reactors as shown in figure 7.5 with the only difference being that in this case reactant R_1 is added to both reactors. The State-Task Network for the optimal solution is presented in figure 7.9.

The process utilises 6.66, 4.45, 12.24 and 1.01 $kmol/batch$ of reactants R_1, R_2 and R_3 and solvent S respectively, and 1.25 $dm^3/batch$ of the catalyst with a total net profit of 3886.05 $\$/hr$. The economic breakdown is shown in detail in table 7.6.

The first jacketed reactor requires 5.45, 2.57, 0.41, 1.01 and 30.00 $kmol/batch$ of R_1, R_2, R_3, solvent S, and intermediate $Int1$ respectively, and 0.07 $dm^3/batch$ of the catalyst as

initial charges, with a processing time of 45 min and a fixed set-up time of 15 min. Additional amounts of R_1 and R_2 are added as shown in figure 7.10(a). The molar ratio of solvent S to reactant R_2 in the total amount fed to the reactor is 1.35. The variations in the temperature trajectories and the optimal cooling water policy are shown in figure 7.10(b). At the end of the operation, the reactor produces 2.057 $kmol/hr$ (or 78.5%) of the total amount of A required and 0.284 $kmol/hr$ (or 37.9%) of the total amount of E required.

Material	Net production rate ($kmol/hr$)	Revenue ($/hr$)
R_1	−6.19	−1477.61
R_2	−3.36	−3987.00
R_3	−3.62	−142.67
Cat	−0.39 (dm^3/hr)	−13.65
S	−1.01	−136.24
$Int1$	0.00	0.00
P	7.5	10172.02
Total production revenue		**4414.85**
Operator	Volume (m^3)	Capital cost ($/hr$)
Reactor I	5.075	158.85
Reactor II	3.569	128.60
Total capital cost		**287.45**
Task		Operating cost ($/hr$)
Reaction I (Reactor I)		183.39
Reaction II (Reactor II)		57.96
Total operating cost		**241.35**
Total Net Profit		**3886.05**

Table 7.6: Case 2: Economic breakdown for optimal reactor network

Jacketed reactor II consumes 0.64, 1.49, 11.83 and 20.16 $kmol/batch$ of R_1, R_2, R_3 and intermediate $Int1$ respectively, and 1.18 $dm^3/batch$ of the catalyst as initial charges. It operates for 3.43 hr with a fixed set-up time of 15 min. The molar ratio of S to R_2 fed to the reactor has a value of 1.35. The temperature profile and the optimal cooling water policy for the reactor are shown in figure 7.11. At the end of the process, the reactor produces 0.566 $kmol/hr$ (or 21.5%) of A and 0.465 $kmol/hr$ (or 62.1%) of E.

The optimal values/variations of the decision variables are summarised in table C.7 in Appendix C.

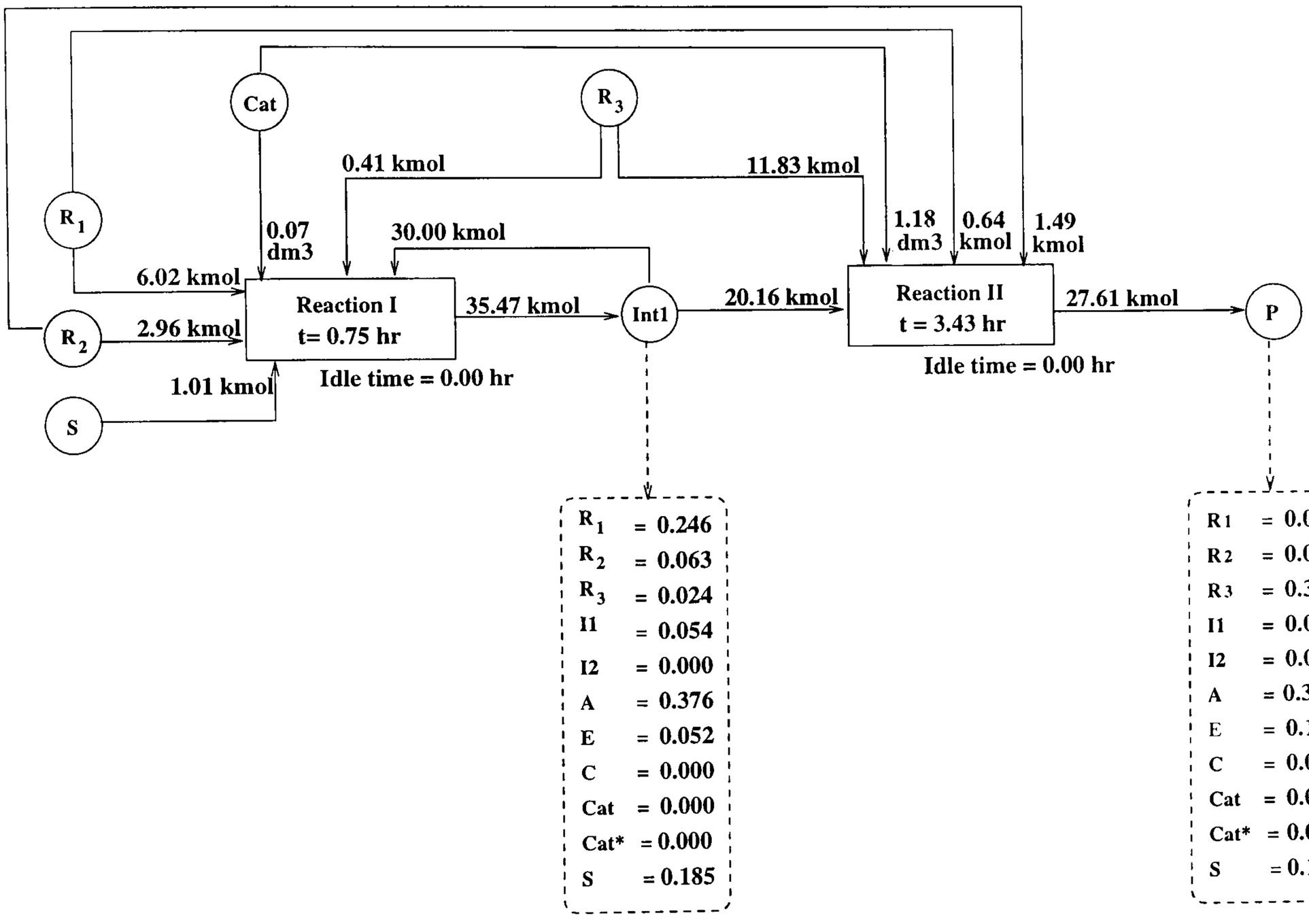
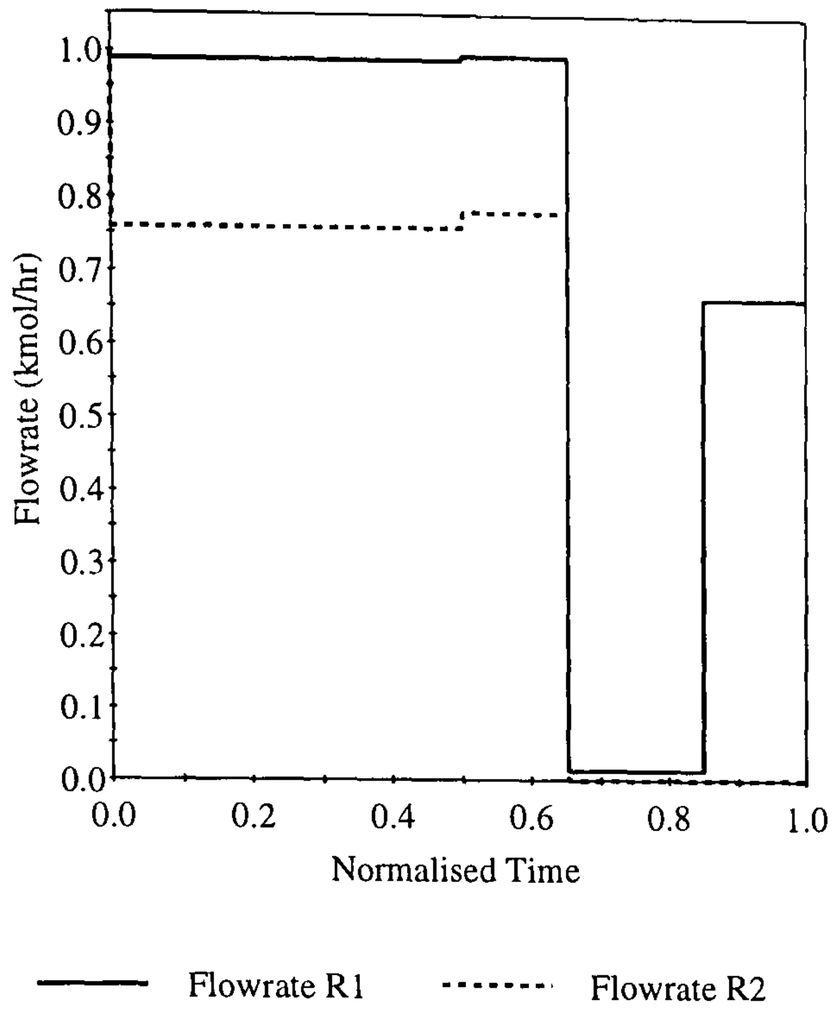
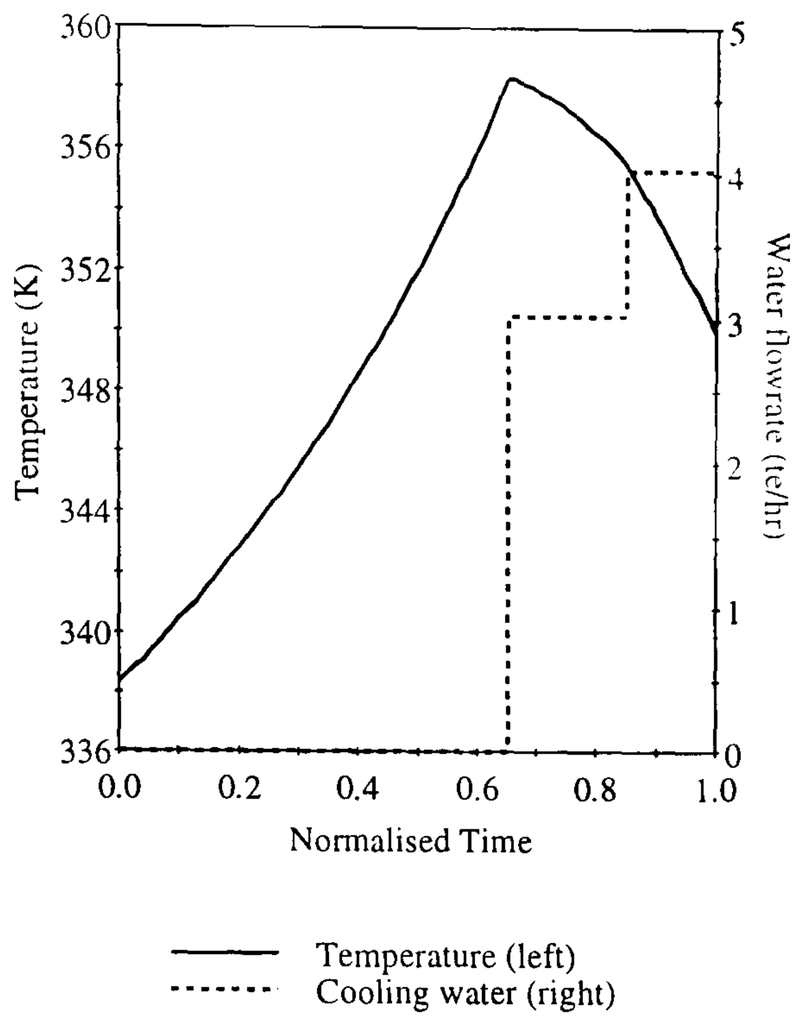


Figure 7.9: Case 2: State-Task Network for optimal reactor network



(a) Feed addition rates of $R1$ and $R2$ in $kmol/hr$



(b) Temperature and cooling water flowrate profiles

Figure 7.10: Case 2: Operating policy for reactor I

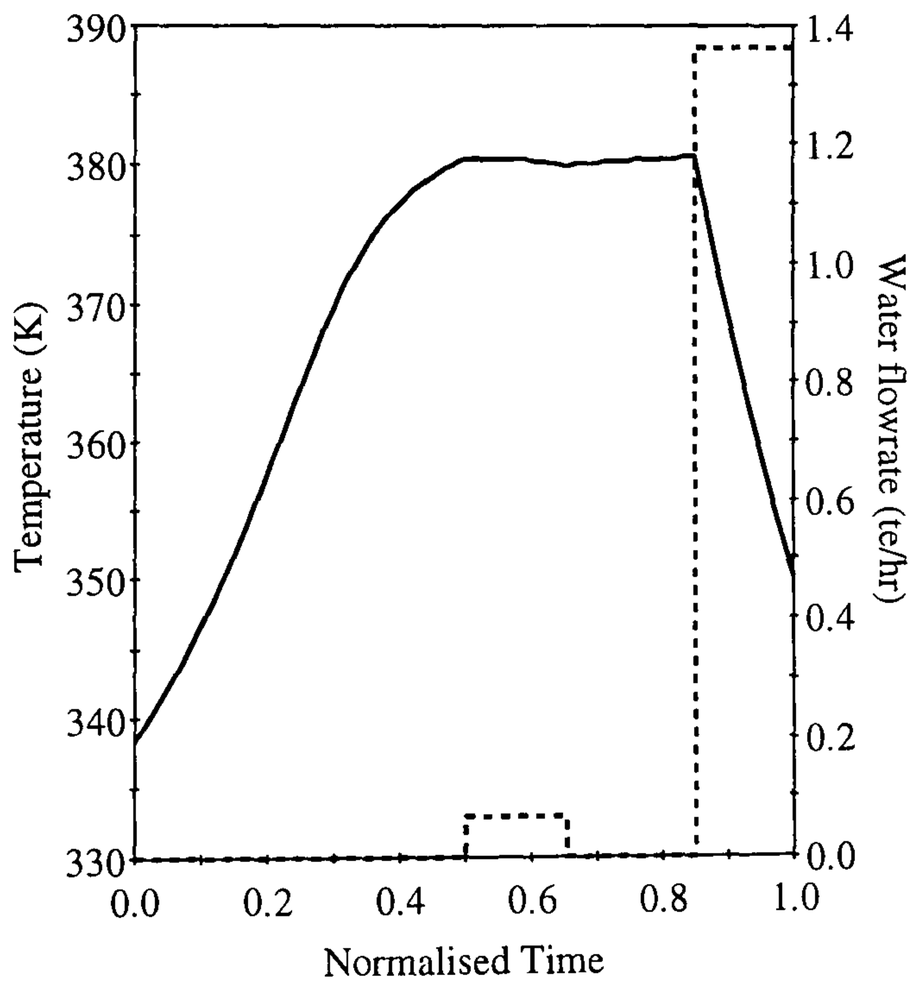


Figure 7.11: Case 2: Temperature and cooling water flowrate profiles for reactor II

7.5. Case Study 3

In Case Study 2, the reactor volumes are treated as continuous variables varying between 1.875 m^3 and 5.375 m^3. Here, we consider a modified problem in which the capacity of each reactor can be selected from a choice of five alternatives which are shown in table 7.7 together with the corresponding (annualised) capital costs. In the interests of comparability, the range of the reactor sizes considered are the same as those for Case Study 2 (*i.e.* from 1.875 m^3 to 5.375 m^3). Moreover, the annualised capital costs in table 7.7 were generated using correlation (7.7).

Jacketed Reactor					
Volume (m^3)	1.875	3.375	3.875	4.785	5.375
Capital cost ($/hr)	87.40	124.36	135.11	153.34	164.42
Plain Reactor					
Volume (m^3)	1.875	3.375	3.875	4.785	5.375
Capital cost ($/hr)	49.68	70.69	76.80	87.16	93.46

Table 7.7: Data on available reactor choices

As we have already seen in section 7.4, if the reactor volumes are allowed to take relaxed values, the highest net profit is achieved by a flowsheet consisting of two jacketed reactors. We now proceed to determine the optimal flowsheet where the reactors are available in discrete sizes only. Thus, this case study brings together the concepts of Chapters 5 and 6.

7.5.1. Results

To solve this problem, we adopt the two-level approach described in section 3.8.5. Thus, we have:

- an outer enumeration of all possible process structures in accordance with the methodology of Chapter 6;
- for each candidate process structure, the application of an OA/AP algorithm for the determination of the optimal equipment selection as well as the characteristics of the corresponding optimal recipe (*cf.* Chapter 5).

We note that, notwithstanding the discrete nature of the equipment options available, the process structures to be examined are exactly the same as those considered in sections 7.3 and 7.4. Moreover, the optimisation problem solved in section 7.4.1 for each particular process

structure (*e.g.* 1 jacketed reactor, 1 plain reactor) represents a relaxation of the corresponding optimisation problem considered here. This is because:

- every feasible point of the problem with discrete equipment capacities has a corresponding point in the problem with continuous capacities;
- the objective function values corresponding to the two feasible points above are the same[†].

Consequently, we can use the results in table 7.5 as upper bounds on the corresponding results to be obtained here. This obviates the need to solve the fully relaxed subproblem at step 2 of the OA/AP algorithm for each candidate process structure (*cf.* section 5.3.3).

Since the process structure involving two jacketed reactors has the highest objective function value (3886.05 $\$/hr$, see table 7.5) in the relaxed case, we choose to consider it first. Table 7.8 shows the steps and results of the OA/AP algorithm (*cf.* section 5.3) when applied to this problem. As already noted, subproblem 1 corresponds to the optimal solution of Case Study 2 (*cf.* table 7.6). The algorithm required 5 iterations and a total of approximately 7.6 *hr* of CPU time on a *SUN ULTRA* workstation.

OA/AP Iteration	**1**	**2**	**3**	**4**	**5**
Subproblem					
Jacketed reactor I volume (m^3)	5.075	5.375	4.785	5.375	**4.785**
Jacketed reactor II volume (m^3)	3.569	5.375	5.375	4.785	**3.875**
P ($\$/hr$)	3886.06	3853.24	3863.01	3869.30	**3879.30**
NLP Iterations	32	21	30	27	21
CPU(s on *SUN ULTRA*)	2538.70	1418.10	5830.30	13395.20	4053.30
Master problem					
Jacketed reactor I volume (m^3)	5.375	4.785	5.375	4.785	3.875
Jacketed reactor II volume (m^3)	5.375	5.375	4.785	3.875	3.875
P^{MP} ($\$/hr$)	46794.37	15959.30	7157.68	4366.37	3317.64
P^{MP} - P^*	42908.31	12106.06	3294.67	497.07	-561.66
Branch & Bound nodes	0	0	1	0	1
CPU(s on *SUN ULTRA*)	0.050	0.060	0.080	0.080	0.070

Table 7.8: OA/AP algorithm performance

The highest net profit rate of 3879.30 $\$/hr$ is achieved using two jacketed reactors of sizes 4.785 m^3 and 3.875 m^3 to perform reaction tasks I and II respectively. Since the profit rate for this structure (which takes account of the *discrete* nature of the equipment capacities)

[†]This is a consequence of the fact that the annualised capital costs in table 7.7 are consistent with the correlation (7.7).

is already higher than the profit rates of the other flowsheet structures with *relaxed* reactor capacities (see table 7.5), it is, therefore, unnecessary to determine the integer optimal answers for the other process structures candidates by applying the OA/AP algorithm to them.

The process requires 6.77, 4.67 and 13.74 $kmol/batch$ of reactants R_1, R_2 and R_3 respectively, and 0.97 $kmol/batch$ of solvent S and 1.12 $dm^3/batch$ of the catalyst. A detailed economic breakdown of the optimal solution is presented in table 7.9. The details of the recipe are shown in the STN in figure 7.12.

Material	Net production rate ($kmol/hr$)	Revenue ($/hr)
R_1	−6.20	−1480.00
R_2	−3.36	−3987.00
R_3	−3.68	−145.03
Cat	−0.54 (dm^3/hr)	−18.90
S	−0.94	−126.80
$Int1$	0.00	0.00
P	7.5	10172.02
Total production revenue		**4414.29**
Operator	Volume (m^3)	Capital cost ($/hr)
Reactor I	4.785	153.34
Reactor II	3.875	135.11
Total capital cost		**288.45**
Task		Operating cost ($/hr)
Reaction I (Reactor I)		191.80
Reaction II (Reactor II)		54.74
Total operating cost		**246.54**
Total Net Profit		**3879.30**

Table 7.9: Case 3: Economic breakdown for optimal reactor network

Jacketed reactor I consumes 5.37, 2.44, 0.36, 0.93 and 27.61 $kmol/batch$ of R_1, R_2, R_3, solvent S and intermediate $Int1$ respectively, and 0.34 $dm^3/batch$ of the catalyst as initial charges. The reaction has a processing time of 45 min and a fixed set-up time of 15 min. Additional amounts of R_1 and R_2 are added continuously as shown in figure 7.13(a). The ratio of S to R_2 in the total amount fed to the reactor is 1.35. The variation in the reaction temperature of reactor I and the corresponding cooling water flowrate are shown in figure 7.13(b). The reaction produces 2.066 $kmol/hr$ or 78.7% of the total amount of A required, and 0.319 $kmol/hr$ or 42.5% of the total amount of E required.

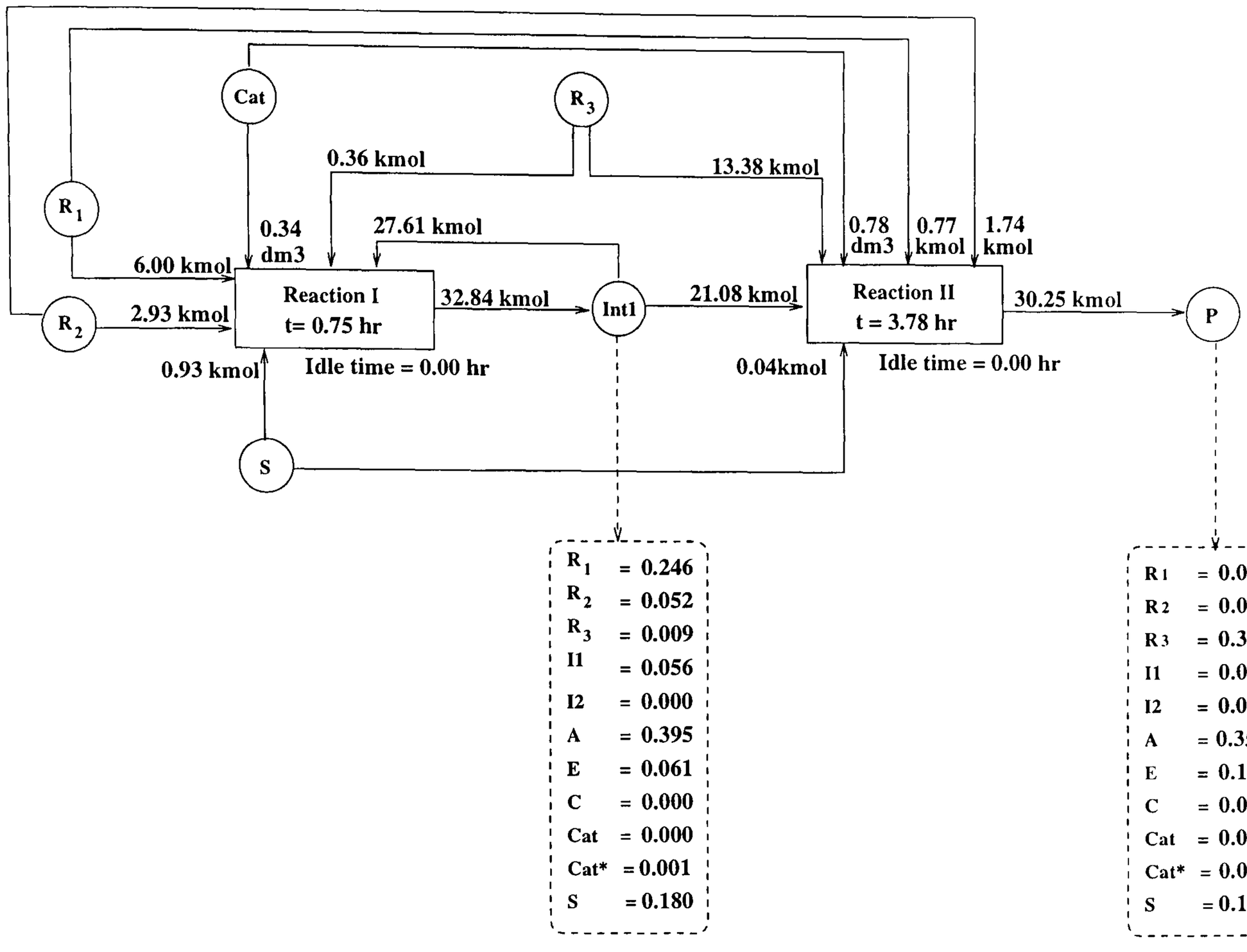
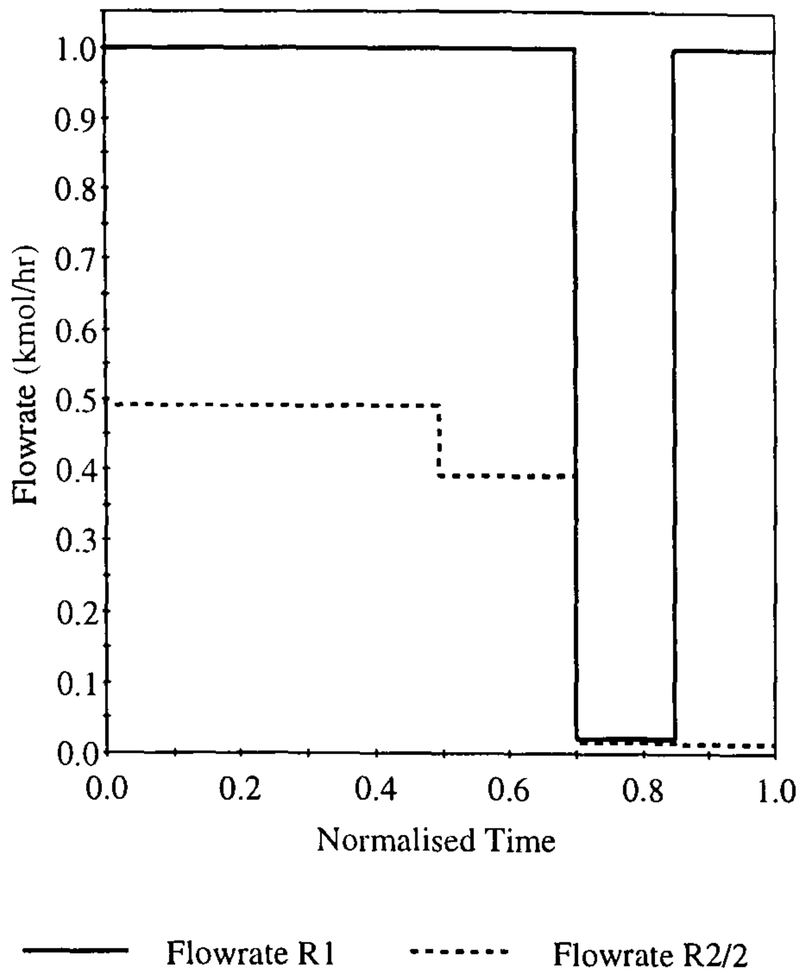


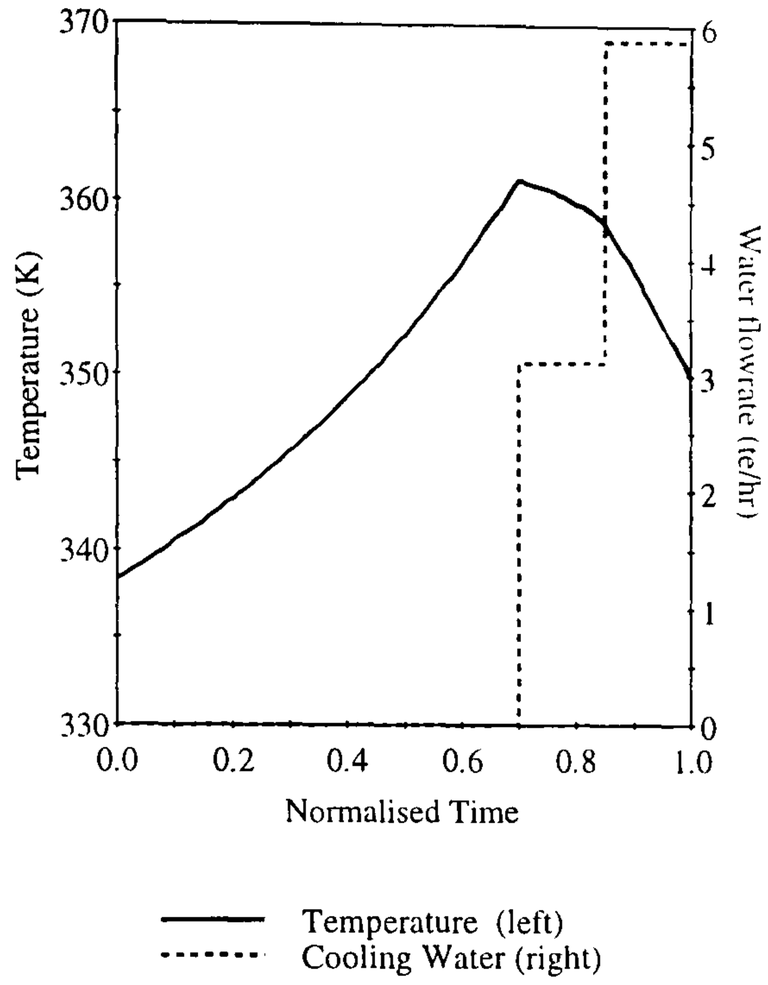
Figure 7.12: Case 3: State-Task Network for optimal reactor network

Jacketed reactor II utilises 0.77, 1.74 and 13.38 $kmol/batch$ of reactants R_1, R_2 and R_3 respectively, 0.04 $kmol/batch$ of solvent S, 21.08 $kmol/batch$ of intermediate $Int1$ and 0.78 $dm^3/batch$ of the catalyst as initial charges with a processing time of 3.78 hr and a fixed set-up time of 15 min. The ratio of S to R_2 in the total amount fed to the reactor is 1.35. The temperature profile together with the optimal cooling water consumption of the reactor are shown in figure 7.14. The process generates 0.561 $kmol/hr$ (2.26 $kmol$) or the remaining 21.3% of A required and 0.431 $kmol/hr$ (1.74 $kmol$) or the remaining 57.5% of E required.

The optimal values/variations of the decision variables are summarised in table C.8 in Appendix C.



(a) Feed addition rates of $R1$ and $\frac{R2}{2}$ in $kmol/hr$



(b) Temperature and cooling water flowrate profiles

Figure 7.13: Case 3: Operating policy for reactor I

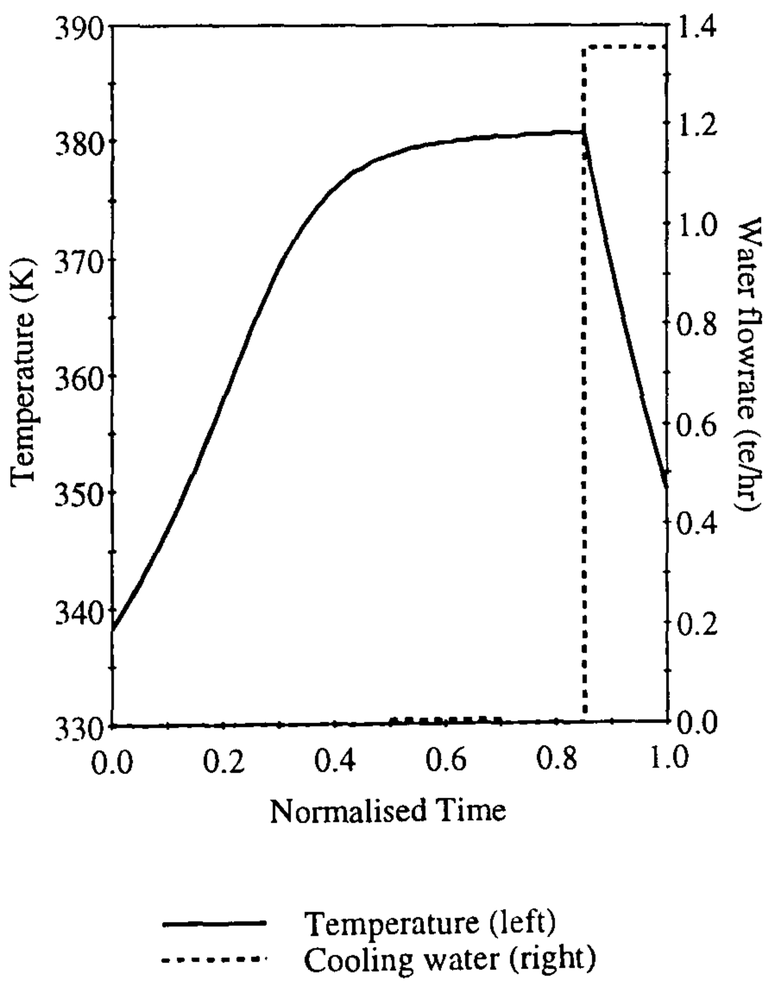


Figure 7.14: Case 3: Temperature and cooling water flowrate profiles for reactor II

7.6. Remarks

Although the structures of Case Study 1 and Case Study 2 are identical, the increase in the production requirements of A and E has resulted in a 2008 $\$/hr$ decrease in the profit rate. This decrease is mainly caused by the increase in the consumption and, hence, cost of raw materials. Consequently, the capital cost of this process is also higher than in the previous case. In order to achieve the production requirements of A and E, the reaction tasks in Case Study 2 operate at higher temperatures and therefore incur a higher operating cost, since the final temperature of the mixture for both cases is constrained not to exceed 350 K.

A comparison of the STNs in figures 7.9 and 7.12, and the process economic breakdowns in tables 7.6 and 7.9 of Case Study 2 and Case Study 3 respectively, shows how the restrictions on the equipment capacities can affect the overall performance of the task. In Case Study 3, the profit was lower at 3879.30 $\$/hr$, a reduction of 6.75 $\$/hr$ or 54000 $\$/yr$[‡]. This reduction is mainly due to the increase of 8.41 $\$/hr$ in the operating cost of the first reaction task. Reaction task I of both case studies produces similar amounts of products A and E as shown in table 7.10. In Case Study 3, however, the reactor volume is smaller at 4.785 m^3 and therefore, the initial charges are smaller and the task has to operate more extensively in order to achieve the production rates. Therefore, the reactor operates at a higher temperature (see figure 7.13(b)); thus, the increase in the cooling water consumption. Reaction task II is performed in a larger reactor with a volume of 3.875 m^3 and therefore, the reaction task is less extensive; hence, the slightly lower operating cost; a reduction of 3.22 $\$/hr$. The cost of raw materials for the two case studies are similar since the production rate and purity specifications are the same. The capital cost is only slightly higher (an increase of 1 $\$/hr$) and this is mainly due to the fact that the decrease in the volume of first reactor is counteracted by the increase in the volume of the second reactor. We note that the discrete equipment sizes selected by Case Study 3 are those that would be obtained from the results of Case Study 2 by adjusting its optimal volumes to the nearest discrete alternative. However, this is not generally true.

	Case Study 2 $(kmol/hr)$	Case Study 3 $(kmol/hr)$
Product A	2.056	2.066
Product E	0.285	0.319

Table 7.10: Comparison of reaction task I

[‡]Based on 8000 hr of operation per annum.

An interesting feature of the process structure of the three case studies, shown in figure 7.5, is the recycling of the intermediate $Int1$ back to the first reactor. Although there is no point in operating a recycle around a *continuous* stirred tank reactor (CSTR) under steady-state operation, this is not necessarily the case for a batch reactor. To justify further the presence of the recycle streams, a fixed network with two jacketed reactors without any recycle was also optimised. For Case study 1, the optimal flowsheet without the recycle generates a total net profit of 5701.86 $\$/hr$, a reduction of 3% in the profit from the original case (see table 7.4 for details). Removing the recycle stream leads to loss of 180.3 $\$/hr$ or 1.44×10^6 $\$/yr$. The optimal operating policy of the structure without recycle is shown in figure 7.15.

	With Recycle ($\$/hr$)	Without Recycle ($\$/hr$)
Total raw material cost	3897.14	4030.51
Total capital cost	236.67	219.21
Total operating cost	156.05	220.62
Total net profit	5882.16	5701.86

Table 7.11: Comparison of Case Study 1 - with and without recycle

It is clear from table 7.11 that the main reason for the decrease in the net profit rate of the optimal solution of the structure without recycle is the increase in the cost of raw materials - 133.37 $\$/hr$. The recycling of intermediate $Int1$, which is rich in reactants R_1 and R_2, gives rise to the better overall utilisation of the raw materials when compared to the optimal solution for the structure without recycling. With recycling (see figure 7.6), component I_1 is present in the initial charge to the first reactor; the relatively high concentration of I_1 favours the reaction $I_1 \rightarrow C$ and consequently, the reaction $C + R_3 \rightarrow E$. Without recycling (see figure 7.15), extra amounts of R_1 and R_2 have to be added, leading to the increase in the overall cost of the system. In this case, the processing time of the first reaction task is higher to allow for the formation of I_1 before it can be converted. Thus, although both systems achieve the final mole fraction and production requirements, the reaction tasks have to be much more extensive without the recycle, thus leading to higher operating costs (an increase of 64.57 $\$/hr$). Without recycling, the overall capital cost is lower by 17.46 $\$/hr$, however, this is relatively small when compared to the substantial increase in the costs of raw material and the operating cost.

Similar patterns of results were observed for Case Study 2 where optimal solution of the structure without recycling generates a total net profit of 3556.86 $\$/hr$. This corresponds to

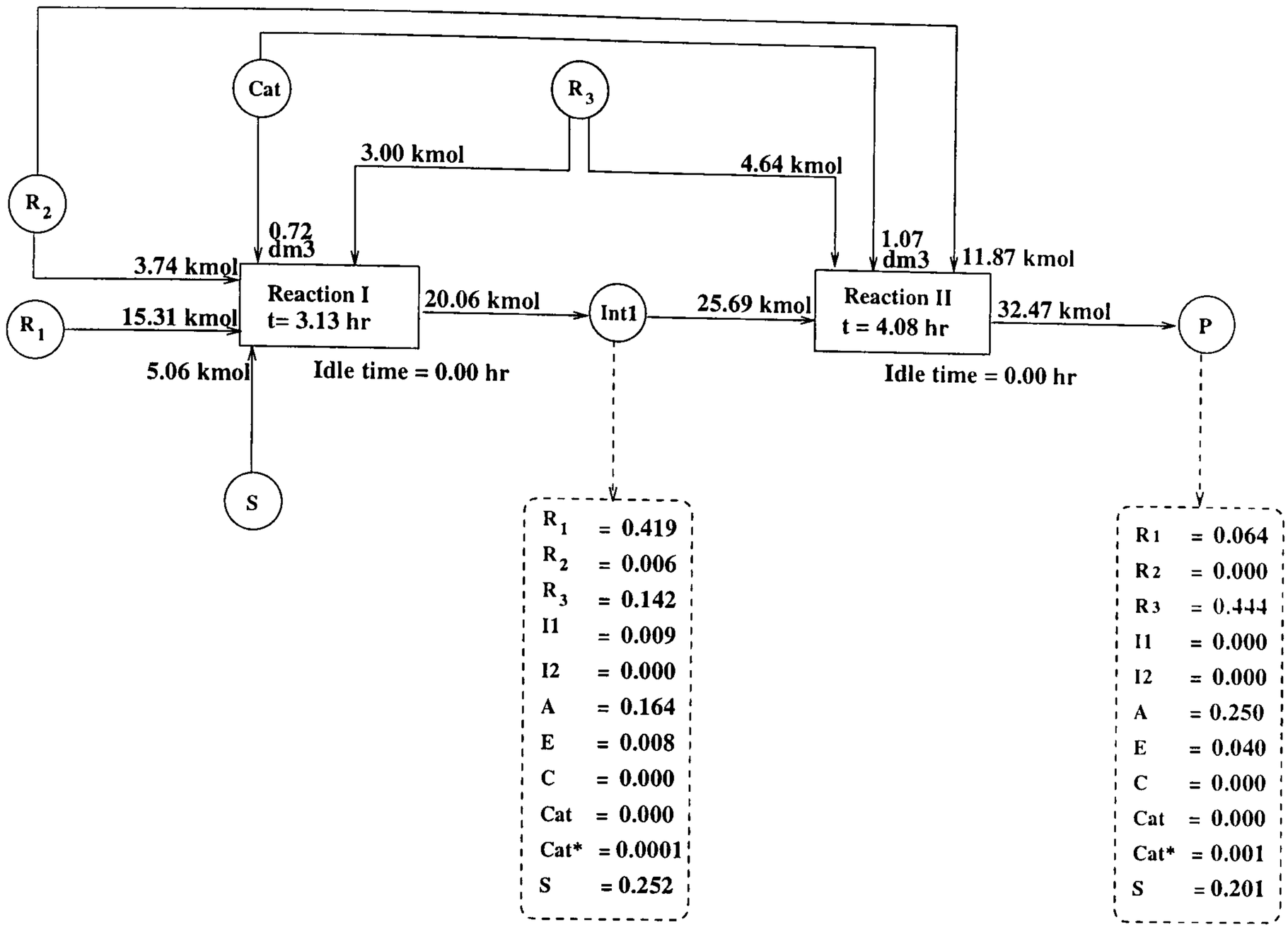


Figure 7.15: Case 1: State-Task Network of optimal solution without recycle

a reduction of 8.5% from the structure with recycling (see table 7.6), or a loss of 329.19 $\$/hr$ (or 2.63×10^6 $\$/yr$). A comparison of the economic breakdowns are shown in table 7.12.

	With Recycle ($\$/hr$)	Without Recycle ($\$/hr$)
Total raw material cost	5757.17	6030.20
Total capital cost	287.45	255.42
Total operating cost	241.35	329.54
Total net profit	3886.05	3556.86

Table 7.12: Comparison of Case Study 2 - with and without recycle

As for Case Study 3, the optimal solution without recycling generates a total net profit of 3434.38 $\$/hr$, a reduction of 11.5% or loss of 444.92 $\$/hr$ (or 3.6×10^6 $\$/yr$) from the structure with recycling. Table 7.13 shows the comparison of the economic performance of the two structures.

Although the partial recycling of the reactor output back to the reactor itself is somewhat unusual, for these case studies it proves to be effective. It is interesting, then, that the

	With Recycle ($/hr$)	Without Recycle ($/hr$)
Total raw material cost	5757.73	6120.71
Total capital cost	288.45	245.85
Total operating cost	246.54	371.08
Total net profit	3879.30	3434.38

Table 7.13: Comparison of Case Study 3 - with and without recycle

approach presented in Chapter 6 can lead to structures that have not been previously seen in conventional batch process flowsheets.

7.7. Conclusions

This chapter has presented three examples of the application of the process design technique described in Chapter 6 to batch reactor network design problem. Some evidence for the effectiveness and usefulness of the design technique has been provided by the results which exhibit some unconventional features.

However, the design of reactor networks in isolation is often not entirely justified from the engineering point of view. In particular, the presence of a separation system offers the possibility of reactant separation and recycle which is not considered when the reactor network is optimised in on its own. There are many complex trade-offs involved in the simultaneous design of reactor-separator system. Some of these are highlighted by the examples in Chapter 8.

Chapter 8

Synthesis and Design of Batch Reactor-Separator Networks

This chapter tackles the more complex batch processes involving reactor and separator networks and explores the complex interactions which exist between the design of the two subsystems. Three examples involving jacketed reactors and distillation columns are considered.

8.1. Batch Reactor-Separator Network Synthesis

The previous chapter presented examples of the application of the process design methodology proposed in Chapter 6 to reactor networks. However, in order to design integrated batch processes, one needs to consider both reactor and separator networks and explore the complex interactions between these individual subsystems.

To yield both realistic and optimal designs for integrated batch processes, it is essential to use detailed dynamic models which accurately represent the behaviour of such processes. Bhatia and Biegler (1996) and Charalambides (1996) used dynamic models to determine optimal recipes for processes of known structure (see section 2.2.2). Each task takes place in a pre-specified equipment item. For instance, Charalambides (1996) dedicated exothermic reaction tasks to take place in jacketed reactors and assigned reactions with negligible heat generation to plain reactors despite the fact that the reactants responsible for the exothermic reactions are often present throughout the process. Moreover, the number of tasks and interactions between the process recipe and process structure are not considered as part of the optimisation problem.

In the following section, we address such interactions in the problem of designing integrated batch processes comprising reactor-separator networks. The types of unit operators that will be considered are jacketed reactors and distillation columns. There are a maximum of two jacketed reactors and two columns that are available at any given time. The flowsheet and State-Task Network superstructures are presented in figures 8.1 and 8.2.

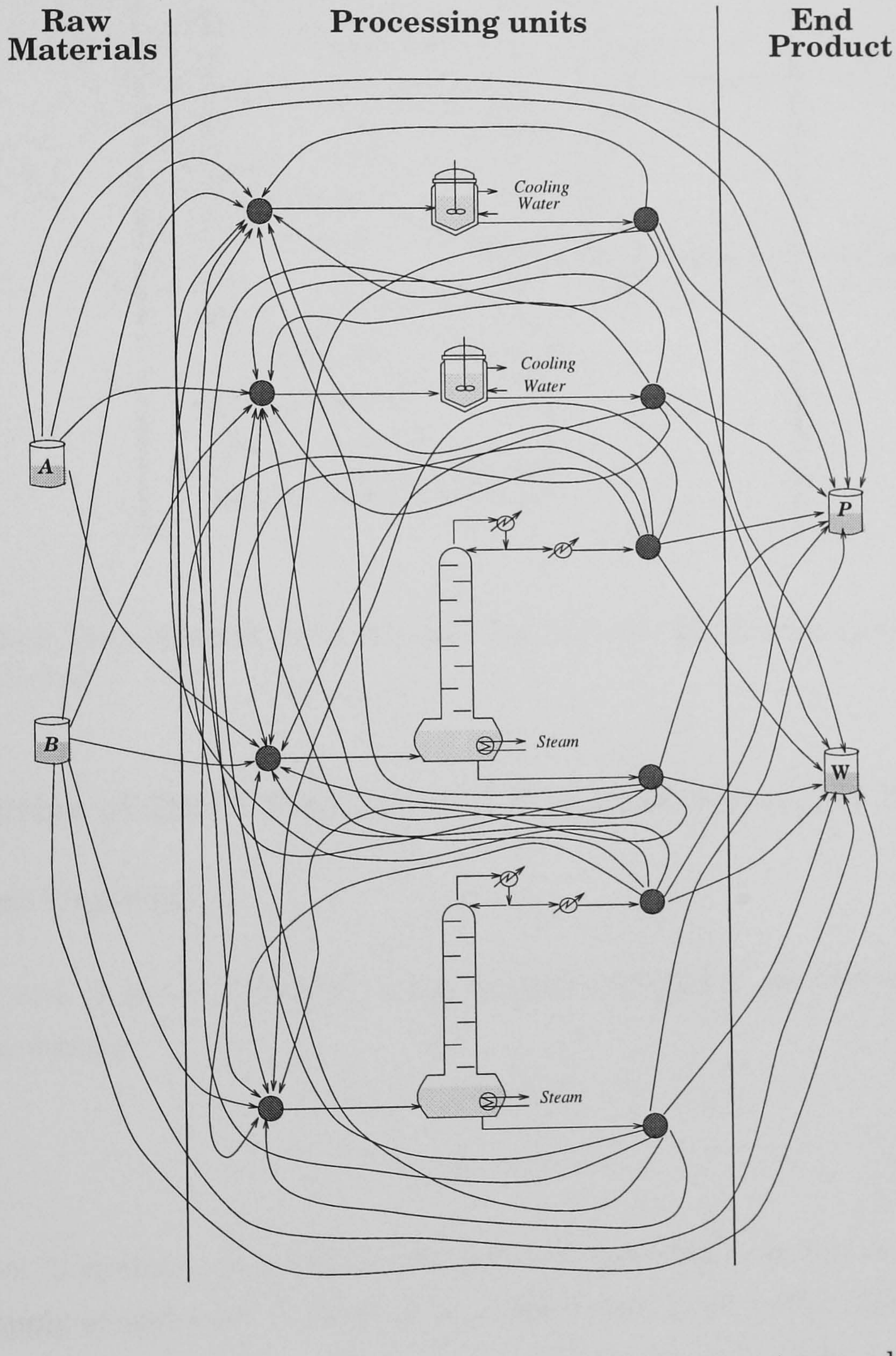


Figure 8.1: Fully connected flowsheet for a system with two reactors and two distillation columns

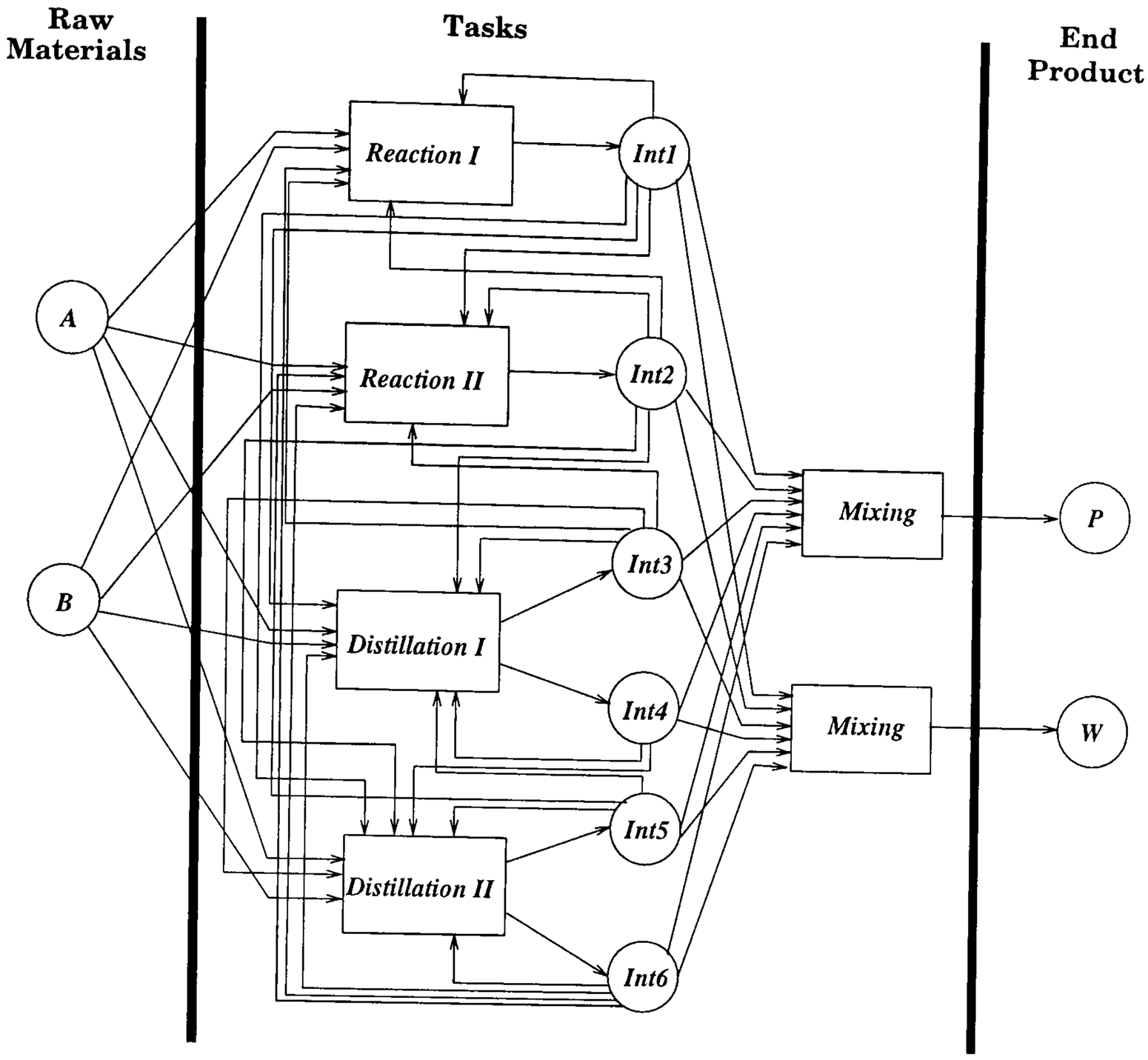


Figure 8.2: State-Task Network for a two reaction and two distillation system (only partial connectivity shown)

8.2. Description of Batch Reaction and Distillation Example Problem

8.2.1. Process Description

Feedstocks A and B are transformed to the desirable product C via the exothermic liquid phase reaction scheme:

$$A + B \rightarrow 2C \tag{8.1}$$

$$B + C \rightarrow D \tag{8.2}$$

The reactor is operated in a semi-batch mode allowing both discrete initial charges and continuous supply of feed stock B. Feed A is available only as an initial charge. The temperature of the reactor mixture must always be kept below 350 K to avoid vaporisation of the reacting mixture; the temperature is controlled by manipulating the cooling water flowrate in the jacket. The cooling water supply temperature is 288 K. The temperature of the mixture leaving the reactor must not exceed 310 K. The molar ratio of reactant A to reactant B in the total amount fed to the reactor must always exceed 1.5. The maximum supply flowrate

for B is 1.0 $kmol/hr$. All feeds are available at 298 K.

The volatility of the components in the process decreases in the order of $C > A > B > D$. The desired product C is required at a specified minimum purity. The distillate cut is cooled down to 310 K via a cooler using cooling water at 288 K. Saturated steam at 4 bar is used in the reboiler. The normalised reflux ratio is allowed to vary between 0.70 and 0.99 and the reboiler load between 550 and 1200 MJ/hr. The allowable temperature rise for the cooling water is 40 K in the condenser and 10 K in the cooler.

The necessary reaction kinetic and physical properties data are given in section B.4 of Appendix B.

8.2.2. Economic Data

The unit values of various materials in the process are shown in table 8.1.

Material	Unit value ($/kmol)
A	9.0
B	9.0
$Waste$	3.0
$Product$	40.0

Table 8.1: Unit values for process materials

The cost of cooling water used in the reactor and distillation column condenser is 0.16 $/te, while that of the steam used in the column reboiler is 20 $/te.

The capital cost ($/hr) of the reactors is calculated using the following correlation:

$$C_c = \alpha_r (11V)^{0.8} \tag{8.3}$$

where V is the volume of the reactor (in m^3) and α_r is the cost coefficient with a value of 0.43.

In the case of the distillation columns, the capital cost ($/hr) is of the form:

$$C_c = \alpha_b (11V_D)^{0.8} + \alpha_c N^{0.65} (11V_D)^{0.9} \tag{8.4}$$

where V_D is the volume of the reboiler (in m^3) and N is the number of trays in the column. The cost coefficients α_b and α_c are 0.325 and 0.105 respectively.

8.2.3. Modelling

The reactor operation is modelled in terms of a set of standard dynamic material and energy balances. The cooling driving force is taken as the difference between the outlet cooling water temperature and the temperature of the reactor contents which are assumed to be well mixed. The cooling water flowrate and the flowrate of reactant B are varied in a piecewise constant fashion over the duration of the reaction. The initial charges, reactor volume and the processing time of each reactor unit are treated as a time invariant optimisation variables. The restrictions on the volume, temperature and feed ratio of A to B are treated as inequality constraints. The reactor volume is bounded between 1.5 m^3 and 2.75 m^3. The maximum cooling water flowrate available for the jacketed reactor is 5.0 te/hr.

The operation of the distillation column is modelled assuming constant liquid holdups on the trays and condenser, negligible vapour holdup and fast energy dynamics. The column has 12 theoretical trays. The volume of the reboiler is bounded between 1.0 m^3 and 8 m^3. The initial charge to the column fills the reboiler, trays and total condenser with liquid at the charge composition. A molar holdup of 50 *moles* is assumed for each of the column trays and the total condenser. The vapour-liquid mixture is assumed to be ideal. A 40 K and 10 K temperature rise in the cooling water is assumed for the total condenser and cooler respectively. Both the reflux ratio and the reboiler load are expressed as piecewise constant control variables. The maximum cooling water flowrate available of each column condenser is 9.0 te/hr, and 5.0 te/hr is available for each cooler.

The initial charge in both the reactor and the reboiler is constrained to occupy at least 75% of the equipment volume to ensure the proper operation of these units.

For the purposes of the optimisation, the operating time for each unit is divided into 5 intervals of variable durations.

The mathematical models of the processing units utilised in this example are described in Appendix A.

8.3. Case Study 1

In this example, the minimum purity specification for the desired product is set at 95%. The mean production rate is fixed at 9.5 $kmol/hr$ and the objective is to minimise cost. Given that there are only two jacketed reactors and two distillation columns available, in principle, there are nine potential alternatives. In reality, since flowsheets that consist only of reactors or only of distillation columns are clearly not feasible for this example, there are only four

feasible flowsheets that have to be considered.

8.3.1. Results

All the potential flowsheets were optimised and the results are shown in table 8.2:

Jacketed reactor	Distillation column	Total cost ($/hr$)	CPU(s) (on *SUN ULTRA*)	NLP Iterations
0	0	INFEASIBLE	–	–
1	0	INFEASIBLE	–	–
2	0	INFEASIBLE	–	–
0	1	INFEASIBLE	–	–
0	2	INFEASIBLE	–	–
1	1	177.40	7659.0	68
2	1	170.70	16087.1	91
1	2	151.27	26264.7	75
2	**2**	**142.06**	125622.4	106

Table 8.2: Case 1: Enumeration results

It is clear from the above enumeration procedure that the flowsheet with the lowest cost consists of two jacketed reactors and two distillation columns, as shown in figure 8.3. Its key features are:

- the plant comprises two distinct parts, each involving a reactor and a distillation column with a recycle between the two;
- the first reactor uses pure A and B feedstocks;
- the second reactor makes use of pure B and the bottom product from the first distillation column;
- the product is formed by blending the top products from the two distillation columns as well as the product of the second reactor.

The optimal State-Task Network for the process is shown in figure 8.4. An economic breakdown of the optimal solution is shown in table 8.3; the process net profit is 237.94 $\$/hr$.

The first reactor consumes 5.278 and 4.409 $kmol/batch$ of reactants A and B with a processing time of 45 min and a fixed set-up time of 15 min. The constraint on the ratio of the reactants A to B fed to the reactor is satisfied. The variations of the mole fractions of

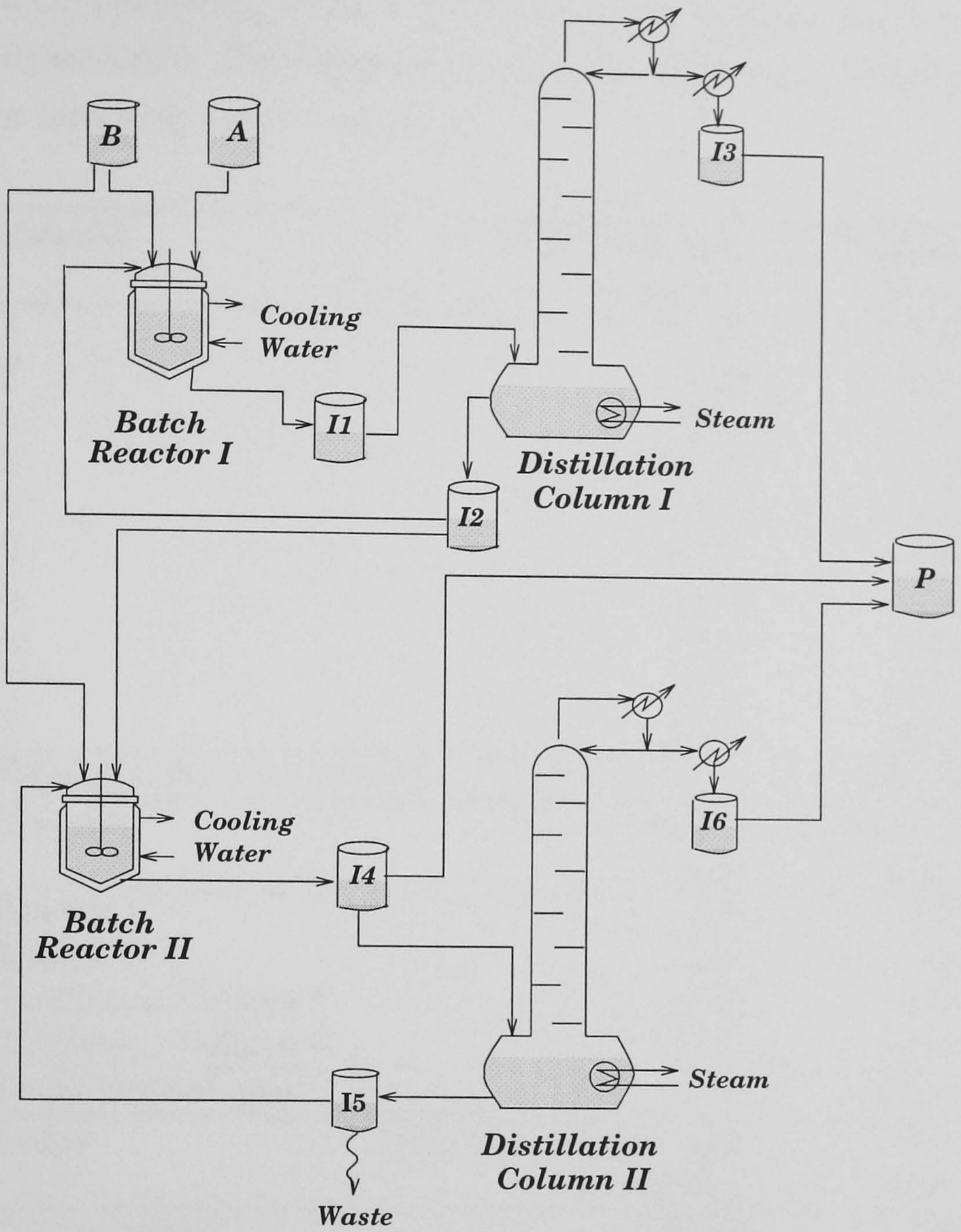


Figure 8.3: Case 1: Optimal process structure

the components in the reactor are shown in figure 8.5(a). A point to note is that, although the temperature of the mixture in the reactor is allowed to reach 350 K, reactor I chooses to operate at a lower temperature (below 343 K). This reduces the rate of reaction $B + C \rightarrow D$, thus preventing the production of the undesirable product D. The temperature profile and the optimal cooling water policy for the reactor are shown in figure 8.5(b).

The output of reactor I is then processed in the first of the distillation columns. Distillation column I separates 20.28 $kmol/batch$ of intermediate I_1 and operates for 45 min with a fixed set-up time of 30 min. The product C is recovered in the distillate tank at 98% purity. The composition of the material in the reboiler and the variation in the reflux ratio policy are shown in figure 8.6(a). The reboiler load is maintained at its higher bound of 1200 MJ/hr throughout the operation in order to reduce the processing time by rapidly vapourising the

light component C. The cooling water policies in both the condenser and the cooler of column I are shown in figure 8.6(b). The cooler ensures that the temperature of the product entering the accumulator tank does not exceed 310 K.

Material	Net production ($kmol/hr$)	Revenue ($/hr)
A	−5.278	−47.50
B	−5.493	−49.44
I_1	0.000	0.00
I_2	0.000	0.00
I_3	0.000	0.00
I_4	0.000	0.00
I_5	0.000	0.00
I_6	0.000	0.00
W	0.770	−2.31
P	9.500	380.00
Total Production revenue		**280.75**
Operator	Volume (m^3)	Capital cost ($/hr)
Reactor I	1.500	4.05
Reactor II	1.500	4.05
Distillation Column I	1.843	11.53
Distillation Column II	1.174	7.80
Total capital cost		**27.43**
Utility	Mean Consumption rate (te/hr)	Cost ($/hr)
Cooling water	10.231	1.64
Steam	0.687	13.74
Total utility cost		**15.38**
Total net profit		**237.94**

Table 8.3: Case 1: Economic breakdown for optimal solution

The reboiler residue of column I undergoes further reaction. Reactor II consumes 4.789, 9.299 and 1.536 $kmol/batch$ of I_2, I_5 and B respectively, with a processing time of 1.167 hr and a fixed set-up time of 15 min. The constraint on the ratio of A to B in the total amount fed to the reactor is satisfied. The variation of molar composition of the mixture in the reactor is presented in figure 8.7(a). The reactor temperature profile and the cooling policy are shown in figure 8.7(b). A high cooling water flowrate is utilised towards the end of the reaction task to prevent the mixture from exceeding the upper limit of 350 K and also to cool down the mixture to the end-point temperature of 310 K. The mixture leaving reactor II is then separated in distillation column II.

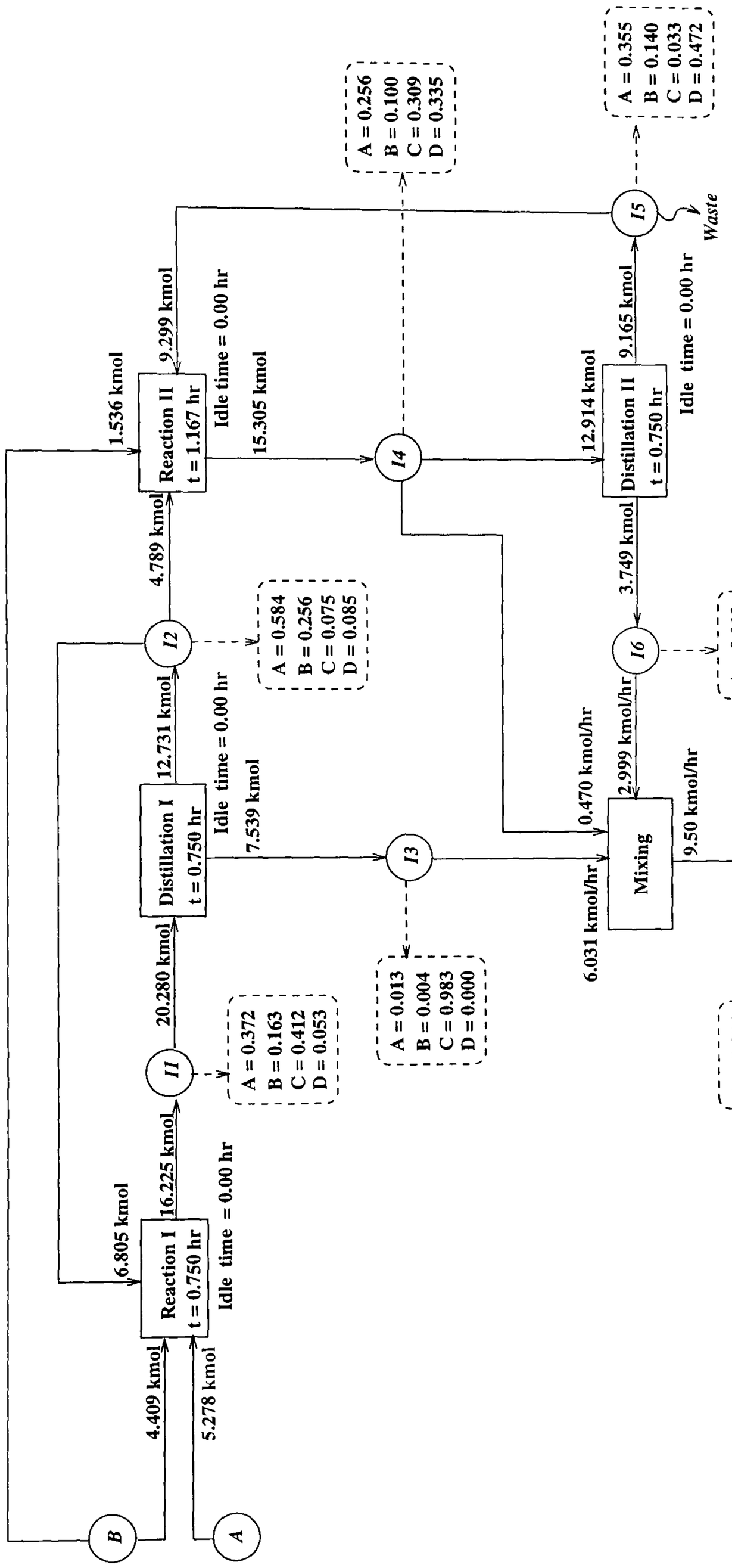
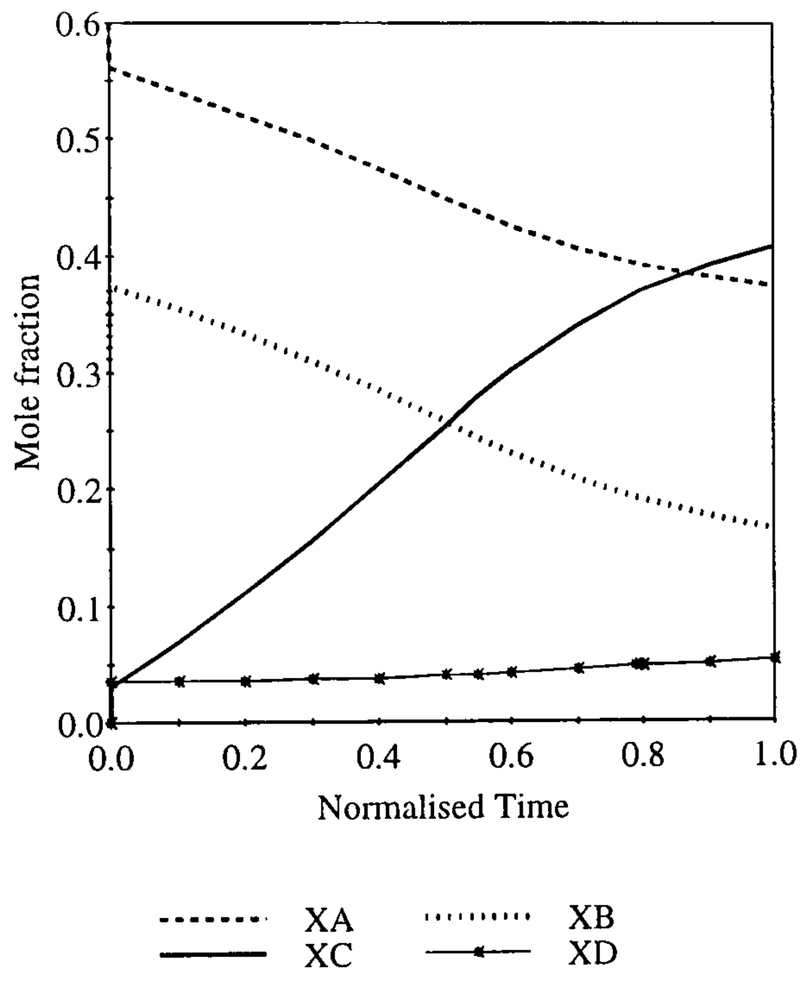


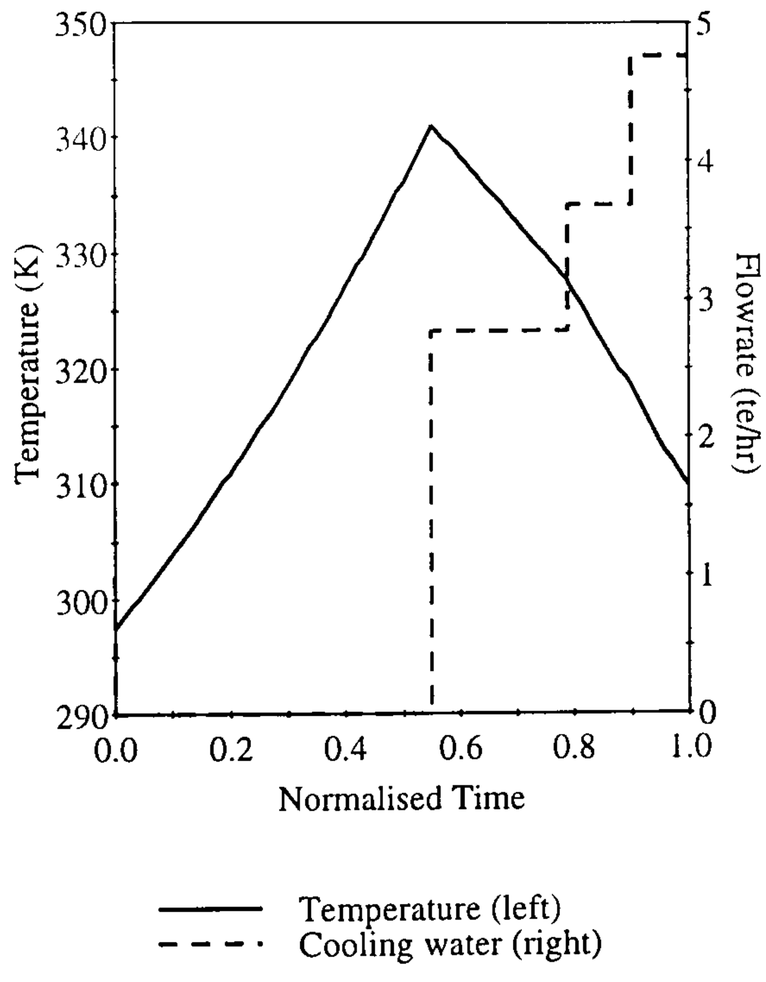
Figure 8.4: Case 1: State-Task Network for the optimal solution

Distillation column II separates 12.914 *kmol/batch* of intermediate I_4 with a processing time of 45 *min* and a fixed set-up time of 30 *min*. The product C is collected in the accumulator tank at a temperature of 310 K. The reflux ratio policy together with the mole fractions of the components in the reboiler are presented in figure 8.8(a). The cooling water flowrates for both the condenser and the cooler together with the reboiler heat load are shown in figure 8.8(b). At the beginning of the operation, the column is operated at a lower reboiler duty and hence, a lower cooling water flowrate is required in the condenser. As the operation progresses, a higher reboiler duty and cooling water flowrates are utilised to ensure that most of the product is distilled. The reboiler residue (*i.e.* intermediate I_5) consists of over 50% of the reactants A (35.5%) and B (14.0%). Therefore, 89% of the amount of I_5 generated is recycled back to reactor II; the rest is discarded as waste.

The optimal values/variations of the decision variables are summarised in table C.9 in Appendix C.

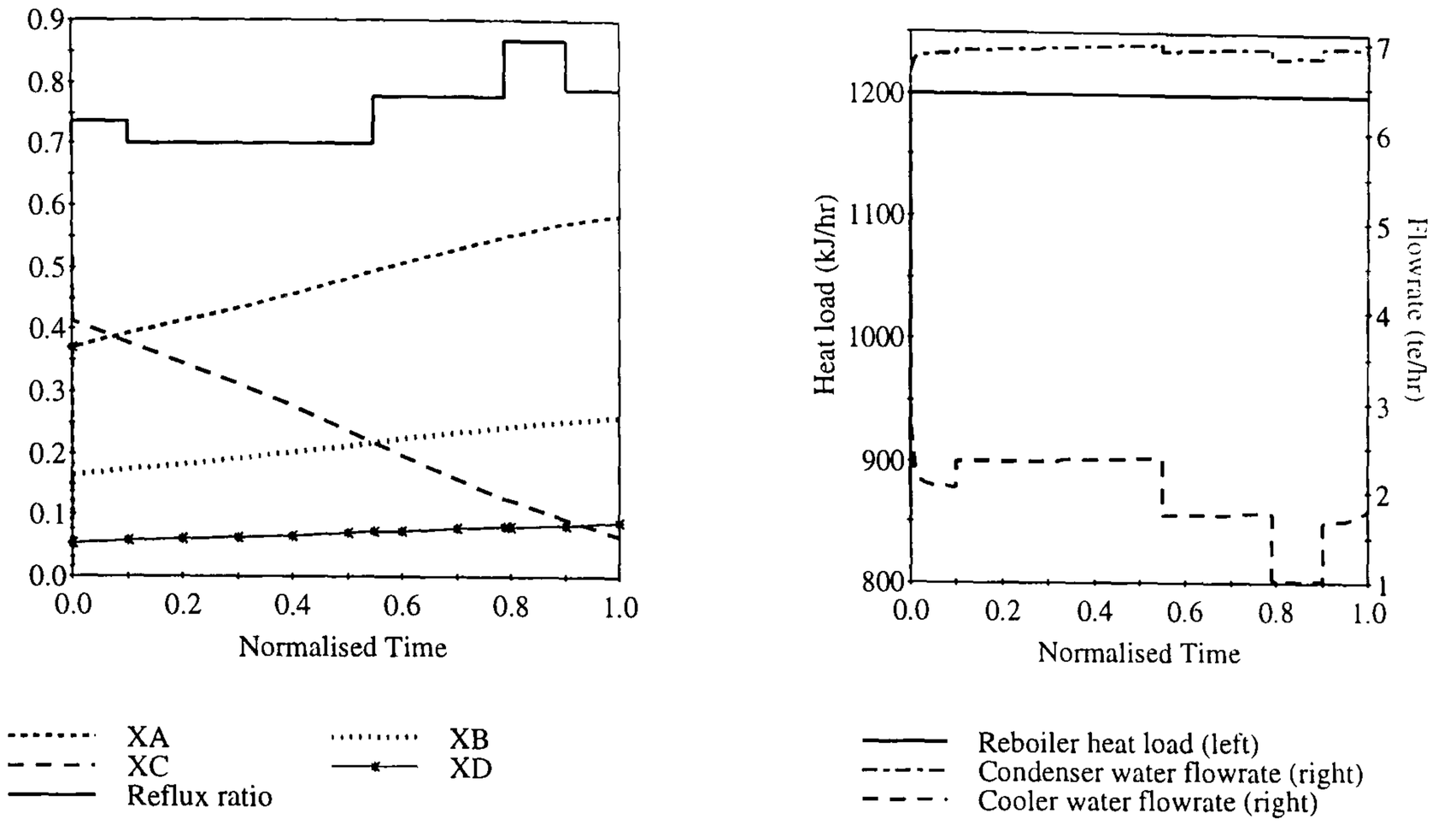


(a) Mole fraction profiles



(b) Temperature profile and cooling water policy

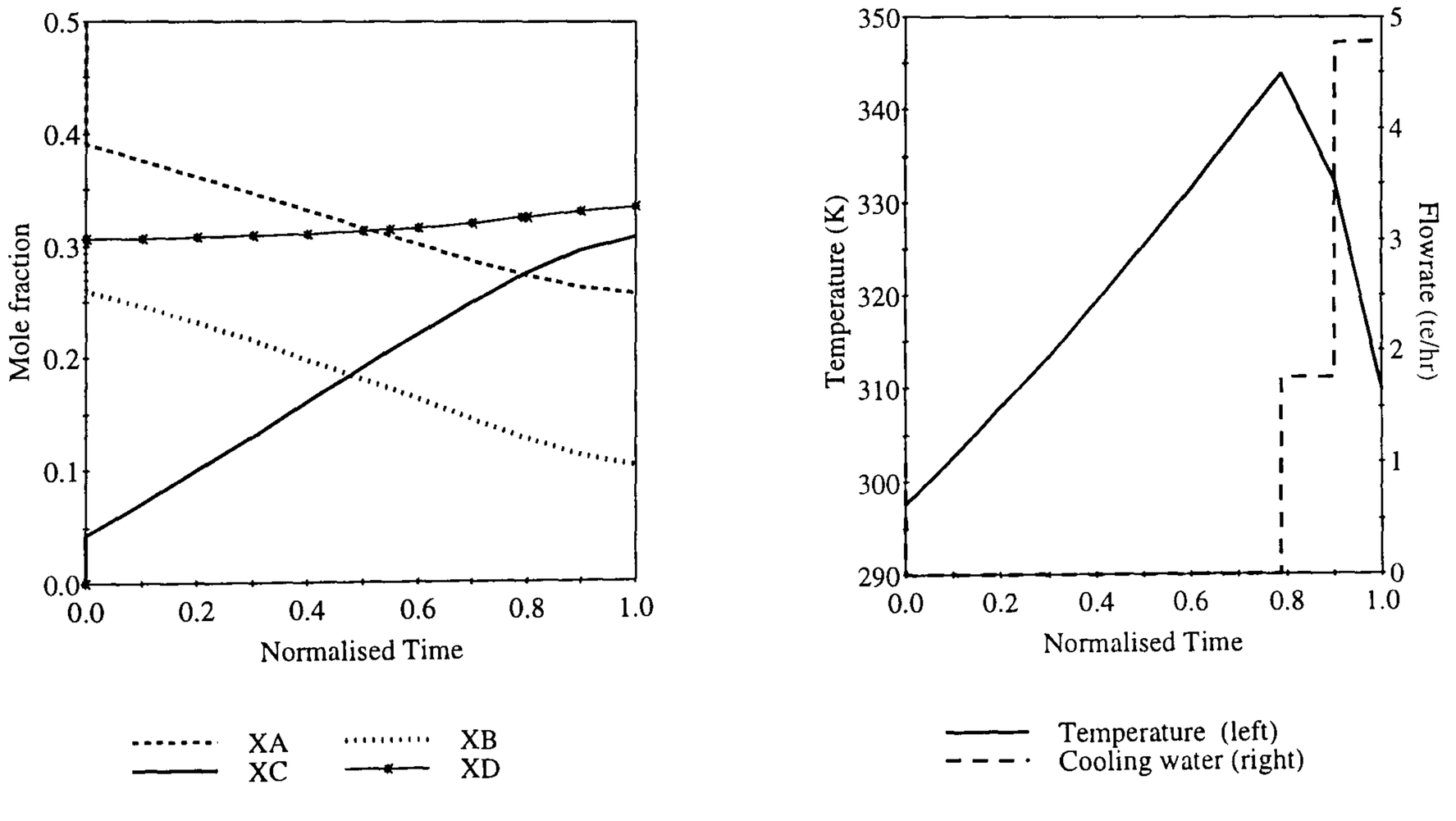
Figure 8.5: Case 1: Reactor I operating policy



(a) Reboiler composition and reflux ratio profiles

(b) Reboiler heat load (kJ/hr), condenser and cooler cooling water flowrates (te/hr)

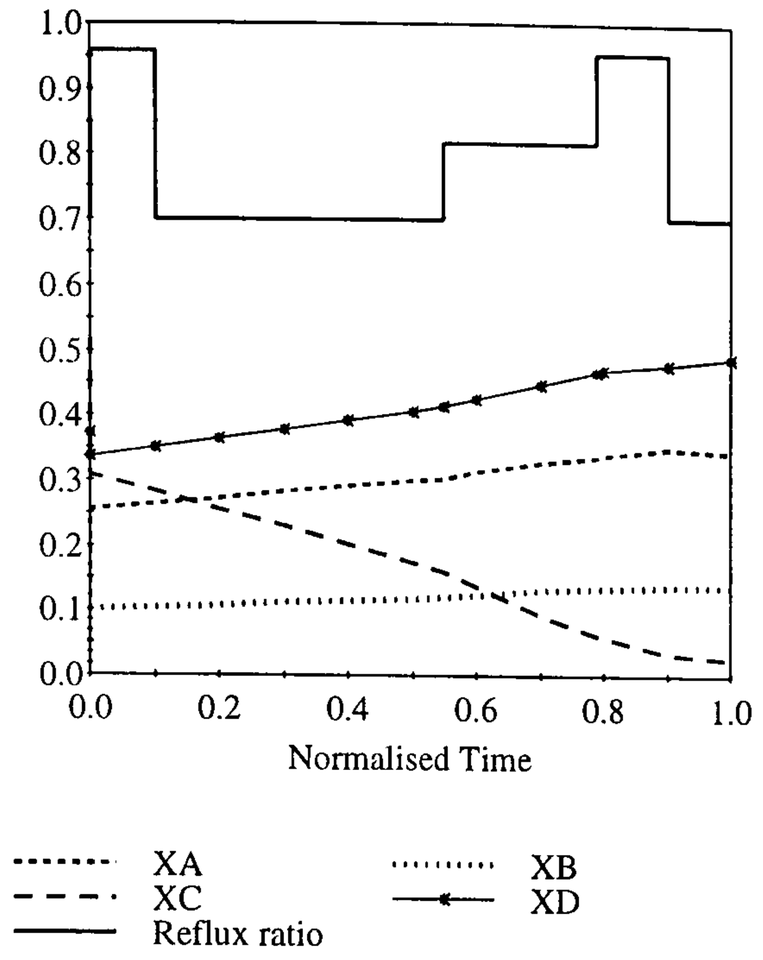
Figure 8.6: Case 1: Column I operating policy



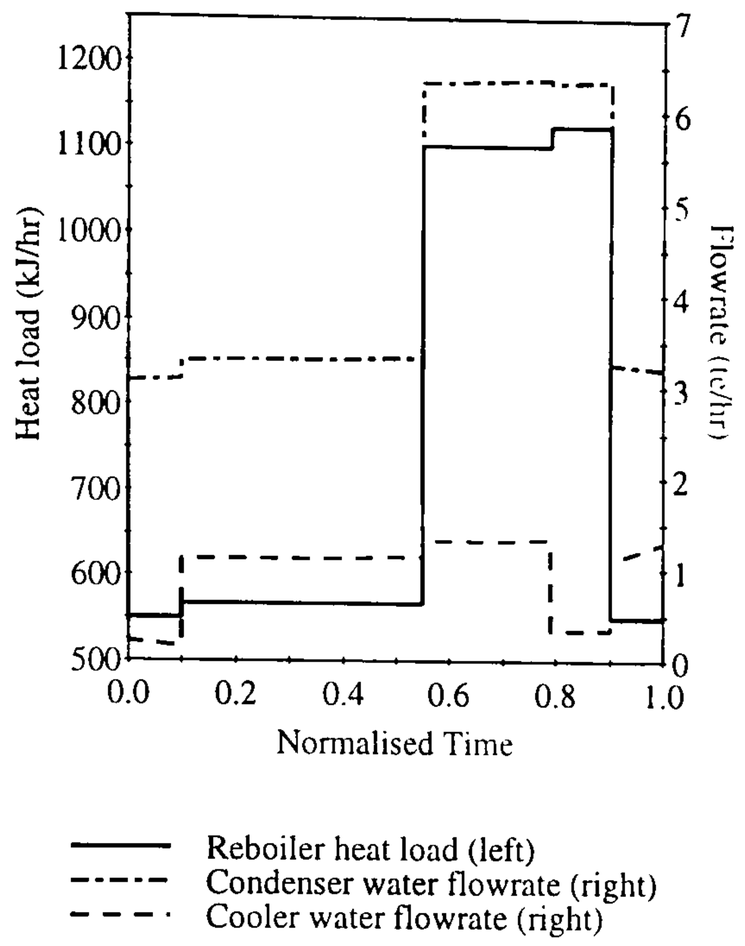
(a) Mole fraction profiles

(b) Temperature profile and cooling water policy

Figure 8.7: Case 1: Reactor II operating policy



(a) Reboiler composition and reflux ratio profiles



(b) Reboiler heat load (kJ/hr), condenser and cooler cooling water flowrates (te/hr)

Figure 8.8: Case 1: Column II operating policy

8.3.2. Discussion

It is interesting to note that the final product C is formed by blending the product in the accumulator tank of column I (*i.e.* intermediate I_3) and column II (*i.e.* intermediate I_6) as well as the intermediate I_4 produced by reactor II. Although it is easy to understand why the intermediates I_3 and I_6 (both of which are more than 98% pure in product C) are used in this manner, it is not so clear why intermediate I_4 is blended in as well. This may be justified by the fact that the product is required at only 95% purity; there are at least two ways of achieving this *without* involving the intermediate I_4:

- The first option is to terminate the distillation task as soon as the purity of the product reaches 95% in the accumulator tank; however, in this case, the mean production rate specification may be impossible to achieve.

- The alternative is to operate the distillation task with a higher reboiler heat load to distill most of the product as well as some of the heavier components to lower the composition down to 95%. In this case, the required mean production rate is attained but the operating cost of the distillation task is higher.

However, the optimisation has discovered that it is better to terminate the operation at higher purity but lower production rate and then to blend in some intermediate I_4, thus achieving the specified mean production rate at the required purity. The reason for using intermediate I_4 rather than some other intermediate (*e.g.* I_1, I_2 or I_5) can be explained by the fact that all of these intermediates are richer in reactants A and B; therefore, it is preferable either to separate the material (as is the case for I_1) or to recycle it completely (like intermediates I_2 and I_5).

In order to provide a more quantitative justification for the above argument, an optimisation was performed with fixed structure in which the reactor products and the reboiler residues are *not* allowed to contribute to the overall product; in other words, the product formed is only a mixture of the distillate cuts of the two columns. Table 8.4 shows a comparison between the economics of the flowsheet with mixing of intermediate I_4 and without any mixing. The total cost of the optimal flowsheet without mixing is 148 $\$/hr$, an increase of 6 $\$/hr$ from the optimal structure. Without mixing, the process operates using the first conventional mode of operation mentioned earlier, *i.e* the distillation tasks are terminated as soon as the product purity of 95% is achieved and hence the operating cost is lower by 1.42 $\$/hr$. However, as a direct result of this conventional mode of operation, the cost of raw materials is higher by 5.07 $\$/hr$ since the reaction tasks need to produce more of the product C to achieve the production rate specification. Moreover, since the intermediate stream is not allowed to mix with the final product, the initial charge that has to be separated by the second distillation column is larger, and this is reflected by the increase in the capital cost of the process. Also, the waste material produced by the column is slightly higher as a result of the higher initial charge, and this results in an increase in the cost of waste disposal. Overall, the decrease in the operating cost is overwhelmed by the increase in the cost of raw materials, capital cost and the waste disposal cost.

	With mixing of I_4 ($\$/hr$)	Without mixing of I_4 ($\$/hr$)
Total raw material cost	96.94	102.01
Total capital cost	27.43	28.09
Total utility cost	15.38	13.96
Total waste cost	2.31	3.90
Total net profit	237.94	232.20

Table 8.4: Case 1: Comparison of economic performance with and without mixing of intermediate I_4

In conclusion, although the mixing of the reactor output with the distillate product is rather unusual, for this particular case it proves to be effective resulting in a 4% reduction in the overall cost of the process.

8.4. Case Study 2

Here, we consider the same problem as in Case Study 1, but set the minimum purity specification for the desired product at 99%. All other conditions are the same as in Case Study 1.

8.4.1. Results

The results for the complete enumeration of potential flowsheets are shown in table 8.5:

Jacketed reactor	Distillation column	Total cost ($\$/hr$)	CPU(s) (on *SUN ULTRA*)	NLP Iterations
0	0	INFEASIBLE	–	–
1	0	INFEASIBLE	–	–
2	0	INFEASIBLE	–	–
0	1	INFEASIBLE	–	–
0	2	INFEASIBLE	–	–
1	1	213.20	4395.6	37
2	1	191.70	31703.3	78
1	2	162.67	29737.3	94
2	**2**	**150.57**	90505.2	136

Table 8.5: Case 2: Enumeration results

As in Case Study 1, the flowsheet with the minimum cost consists of two reactors and two columns with a net profit of 229.42 $\$/hr$. The flowsheet structure and the State-Task Network characteristics are respectively shown in figures 8.9 and 8.10. The economic breakdown of the optimal solution is presented in table 8.6.

The initial charge to reactor I consists of 5.545, 4.513 and 6.431 $kmol/batch$ of reactants A and B, and intermediate I_2 respectively. The constraint on the ratio of A to B added to the reactor is satisfied. The reaction task requires a processing time of 45 min with a fixed set-up time of 15 min, and it produces 16.233 $kmol/batch$ of intermediate I_1. The reactor temperature rises to a maximum of only 336 K despite the upper limit on the temperature being 350 K. The lower temperature reduces the rate of the undesirable side-reaction of

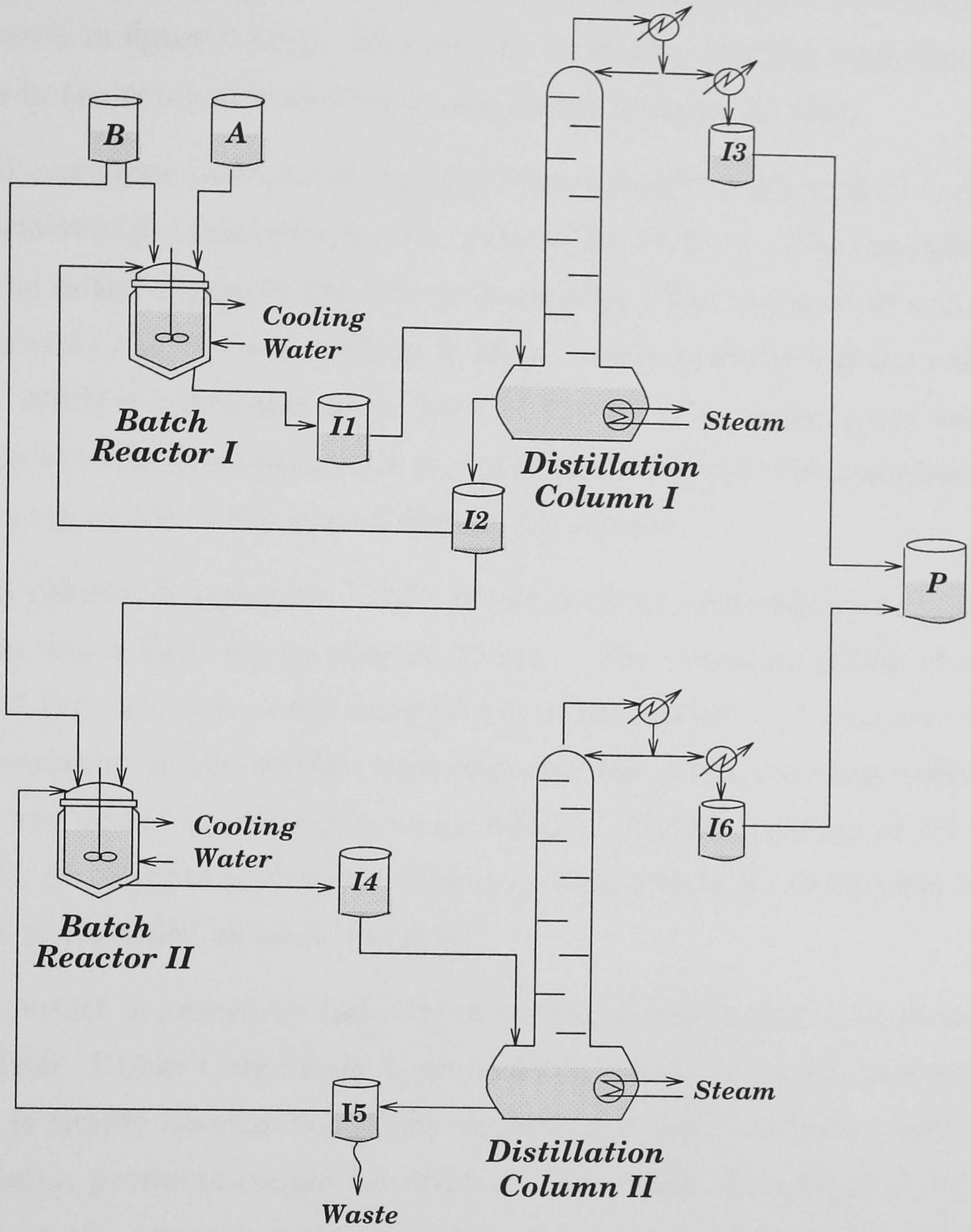


Figure 8.9: Case 2: Optimal process structure

$B + C \rightarrow D$. The molar composition profiles in the reacting mixture are shown in figure 8.11(a). The temperature profile and the optimal cooling water policy are shown in figure 8.11(b).

20.192 $kmol/batch$ of intermediate I_1 are separated in distillation column I which requires a processing time of 45 min with a fixed set-up time of 30 min. The distillation task produces 7.297 $kmol/batch$ of intermediate I_3 containing 98.9% of product C. The material in the reboiler residue forms intermediate I_2 which is partly recycled back to the first reaction task and partly forms the input to the second reaction task. The reboiler heat duty is maintained at its upper limit of 1200 MJ/hr to ensure that most of the product C is distilled and collected in the accumulator tanks to form the intermediate state I_3. The optimal variation of the

normalised reflux ratio in the distillation column and the resulting composition profiles in the reboiler are shown in figure 8.12(a). The reboiler heat duty and the variations of the cooling water flowrate in the condenser and cooler are shown in figure 8.12(b).

Reaction II consumes 1.632, 5.176 and 9.677 $kmol/batch$ of reactant B and intermediates I_2 and I_5 respectively as initial charge, and operates for 1.073 hr. The constraint on the ratio of A to B in the initial charge to the reactor is satisfied. The variation of the composition of the reacting mixture can be seen in figure 8.13(a). The temperature of the reaction does not exceed 347 K which is below the upper limit of 350 K. The temperature variation profiles and the cooling water flowrate policy are shown in figure 8.13(b). Intermediate I_4, the output of reactor II, is separated in the second distillation column.

Distillation column II separates 15.277 $kmol/batch$ of intermediate I_4 with a processing time of 45 min and a fixed set-up time of 30 min. The operating policy of the normalised reflux ratio and the variation in the composition of the reboiler contents are shown in figure 8.14(a). The variation in the reboiler heat load and the optimal cooling water flowrates for the condenser and cooler are shown in figure 8.14(b). The top product of the column forms intermediate I_6. 85.5% of the reboiler residue ($i.e$ intermediate I_5) is recycled back to reactor II and the rest is discarded as waste material.

The final product is formed by blending of intermediates I_3 and I_6 in proportions 61.5%: 38.5% respectively. Unlike Case Study 1, no blending of reactor products is employed in this process. This is simply because the purity requirement (99%) is higher and, therefore, the distillation column products cannot be diluted. Otherwise, the overall flowsheet structure is very similar to the previous example and so are the operating policies of the individual processing units. The difference in the cost arises from higher material costs (an increase of 4.30 $\$/hr$), utility consumptions and capital cost (a rise of 2.79 $\$/hr$), since the same production rate is required but at a higher purity to the previous case study.

The optimal values/variations of the decision variables are summarised in table C.10 in Appendix C.

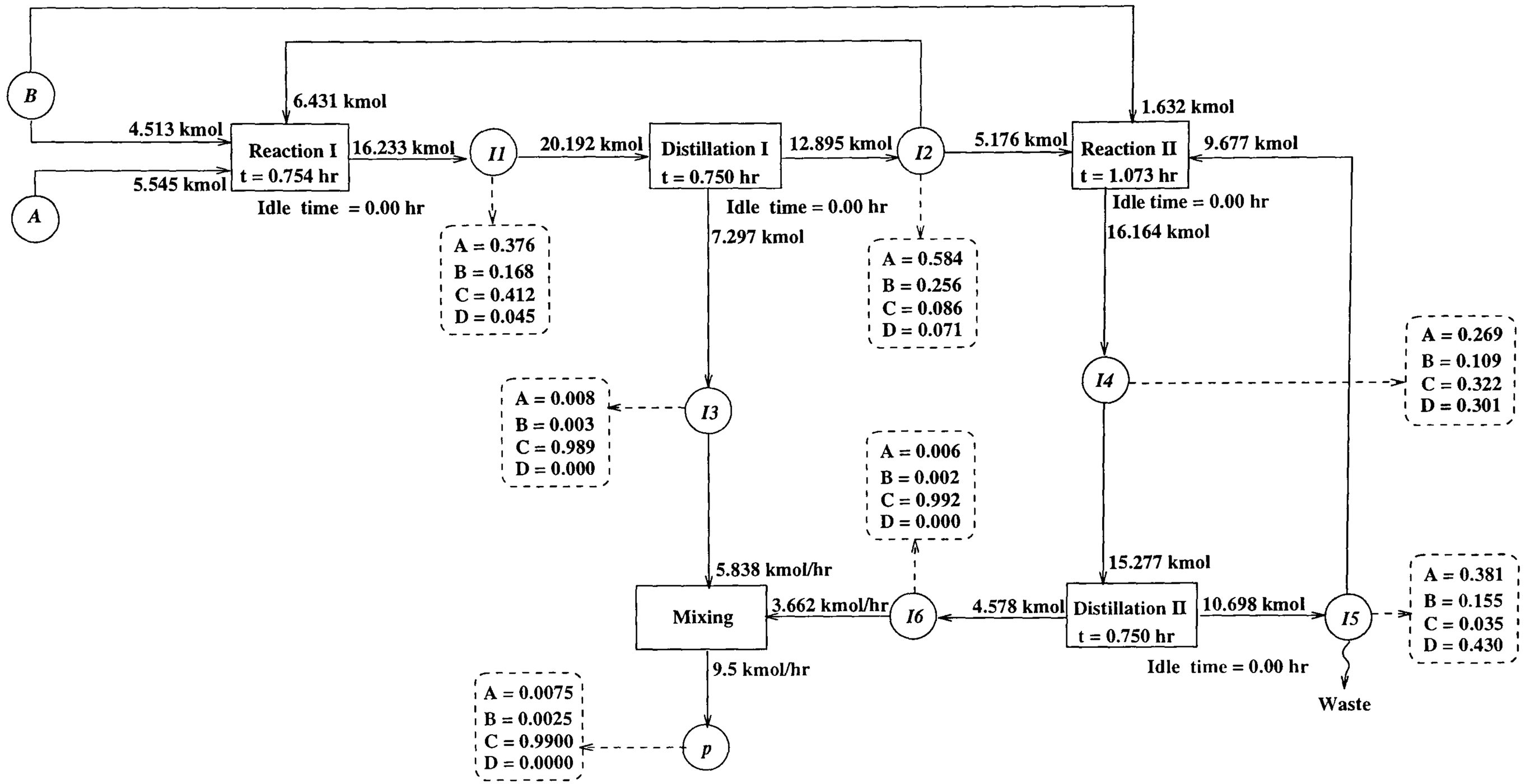
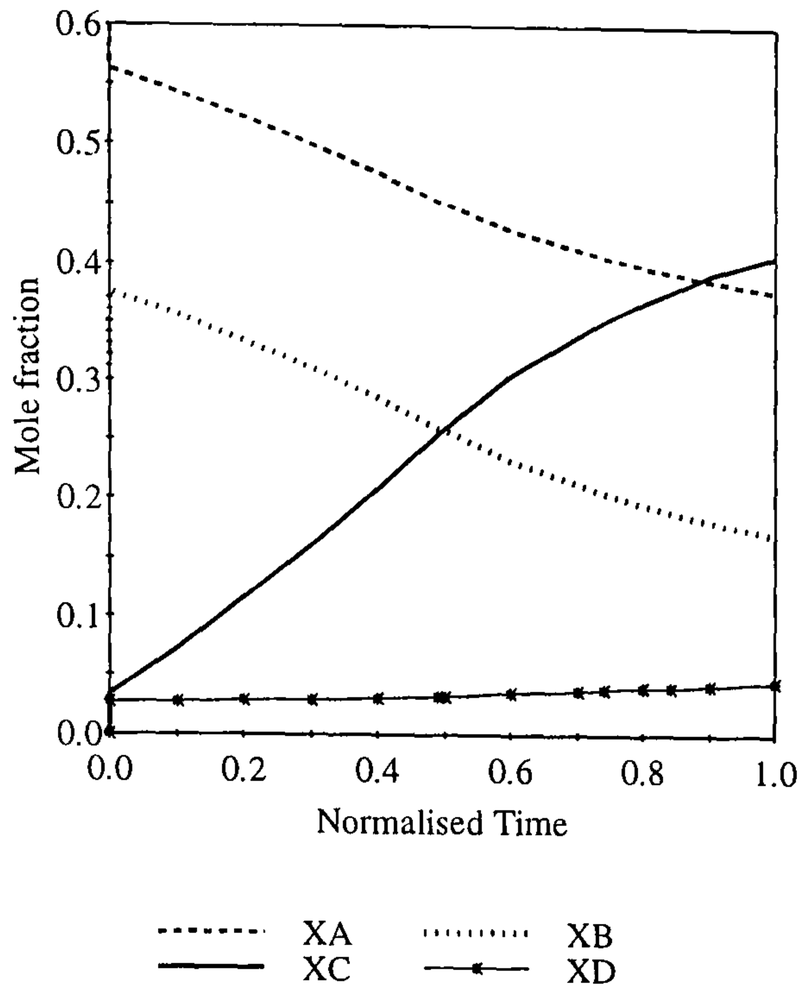


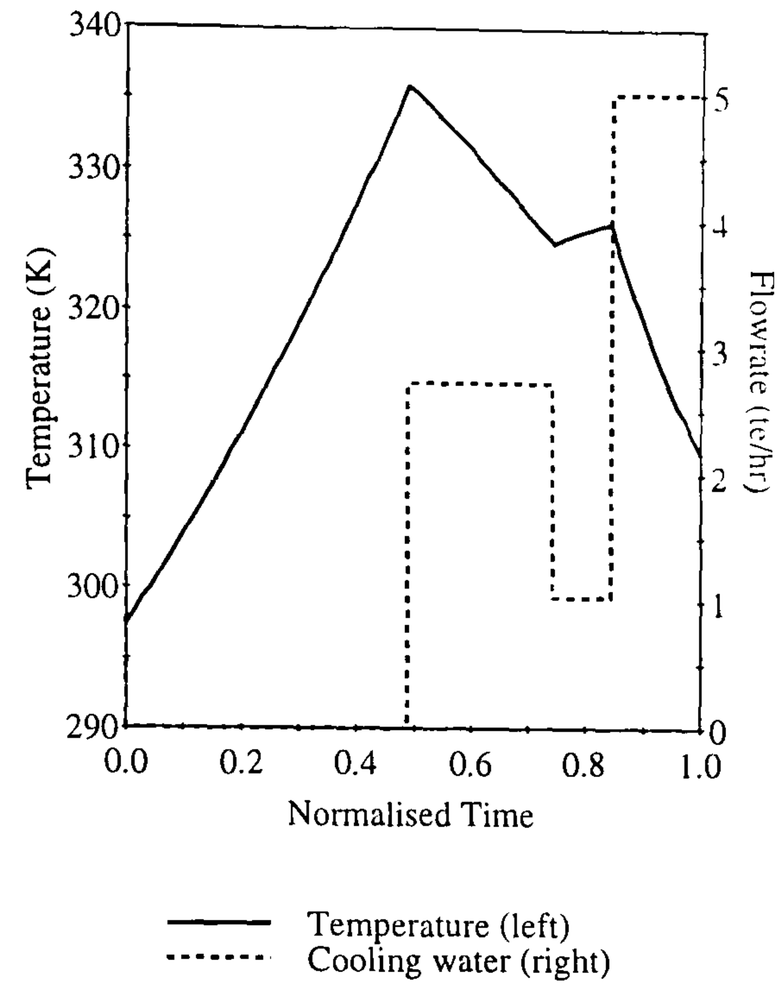
Figure 8.10: Case 2: State-Task Network for the optimal solution

Material	Net production rate ($kmol/hr$)	Revenue ($/hr)
A	−5.521	−49.69
B	−5.729	−51.56
I_1	0.000	0.00
I_2	0.000	0.00
I_3	0.000	0.00
I_4	0.000	0.00
I_5	0.000	0.00
I_6	0.000	0.00
$Waste$	1.243	−3.73
P	9.500	380.00
Total production revenue		**275.03**
Operator	Volume (m^3)	Capital cost ($/hr)
Reactor I	1.500	4.05
Reactor II	1.500	4.05
Distillation Column I	1.836	11.50
Distillation Column II	1.389	9.02
Total capital cost		**28.62**
Utility	Mean consumption rate (te/hr)	Cost ($/hr)
Cooling water	11.138	1.78
Steam	0.760	15.20
Total utility cost		**16.98**
Total Net Profit		**229.42**

Table 8.6: Case 2: Economic breakdown for optimal solution

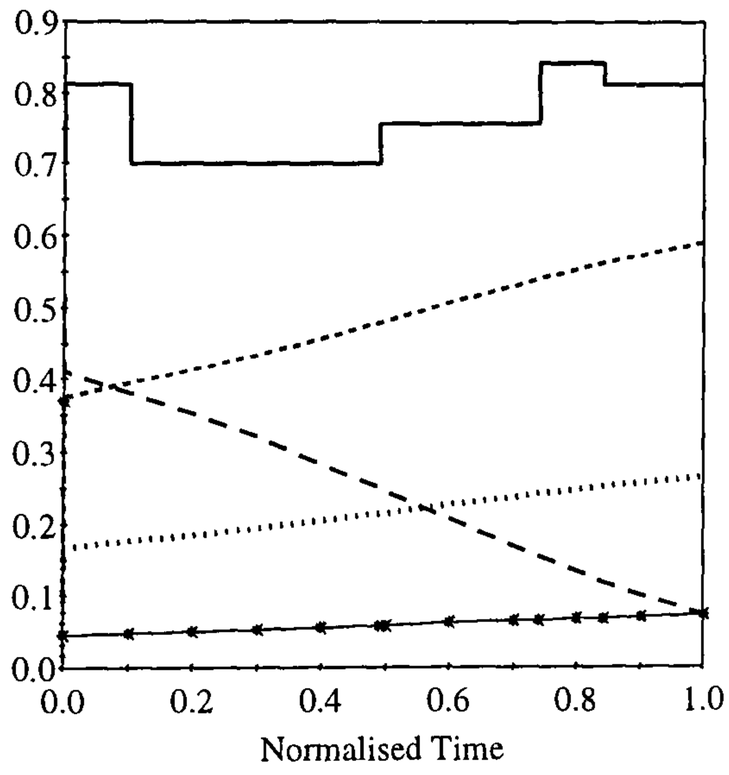


(a) Mole fraction profiles

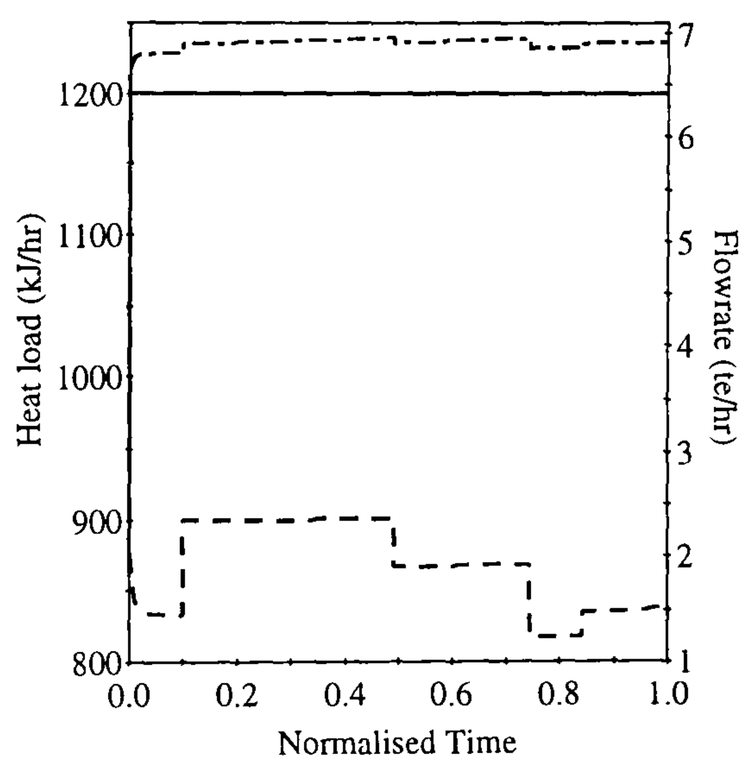


(b) Temperature profile and cooling water policy

Figure 8.11: Case 2: Reactor I operating policy

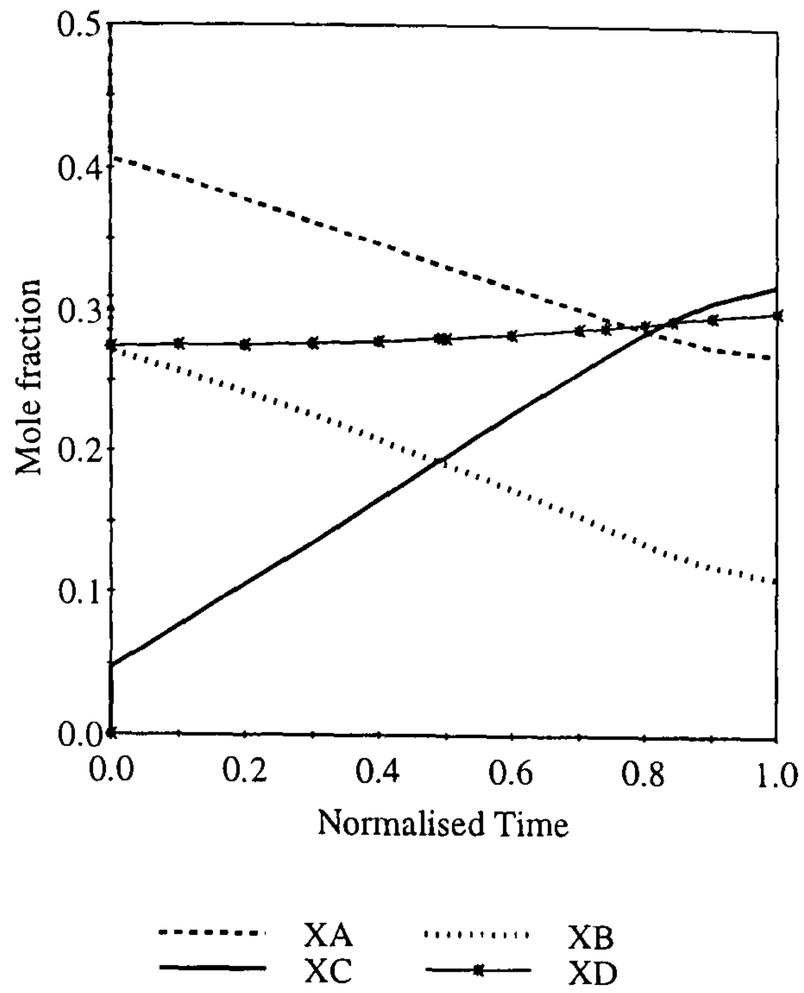


(a) Reboiler composition and reflux ratio profiles

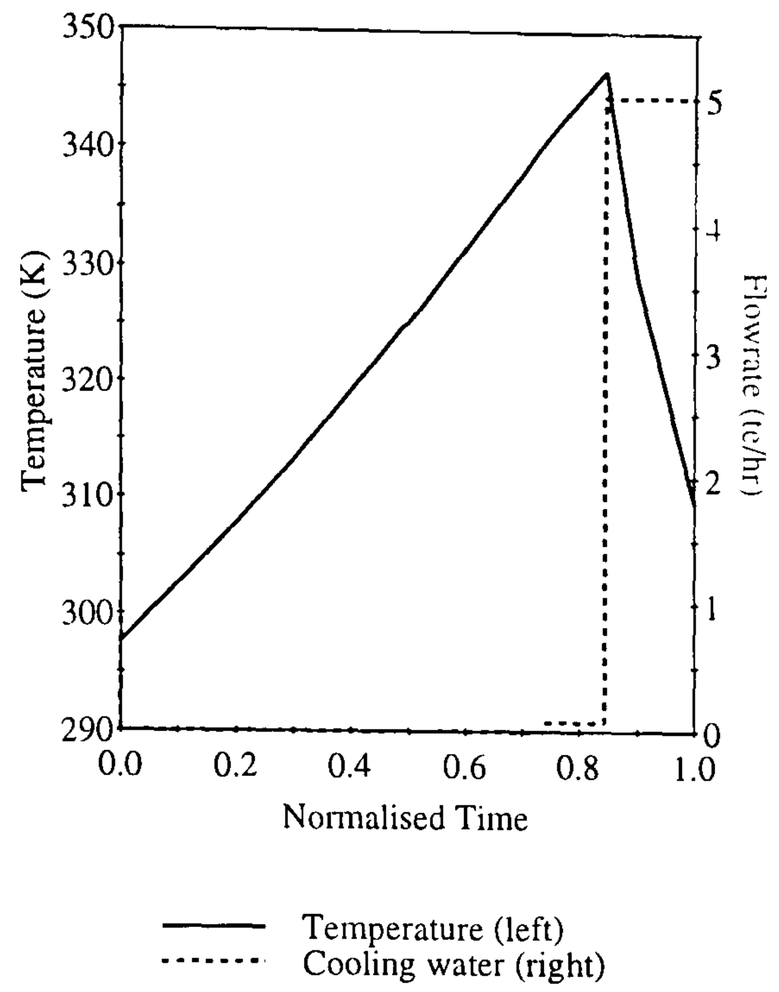


(b) Reboiler heat load (kJ/hr), condenser and cooler cooling water flowrates (te/hr)

Figure 8.12: Case 2: Column I operating policy

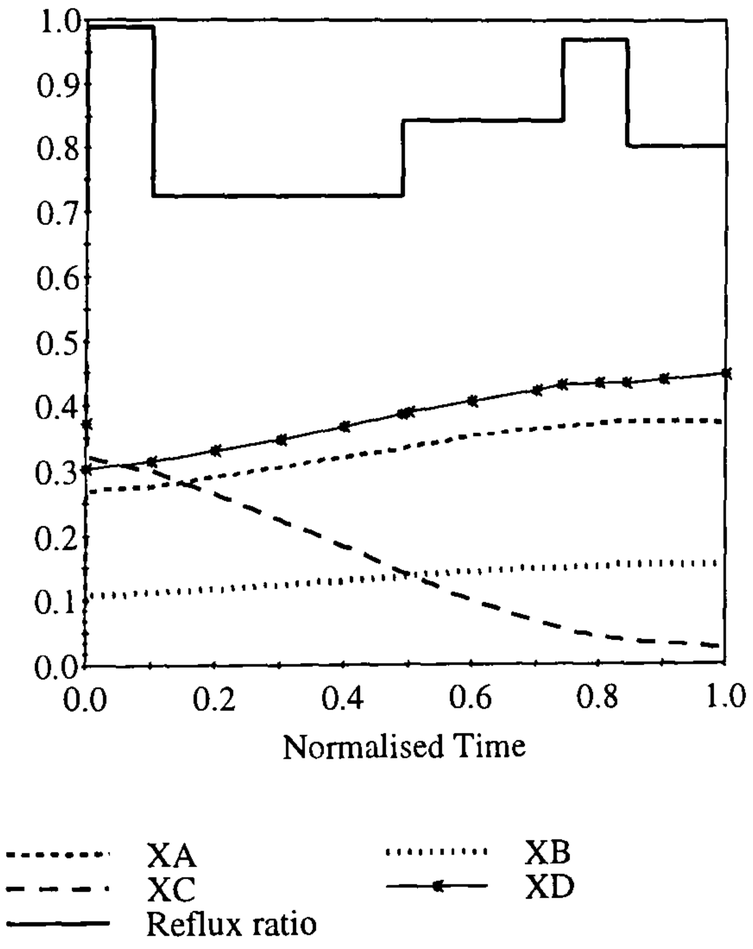


(a) Mole fraction profiles

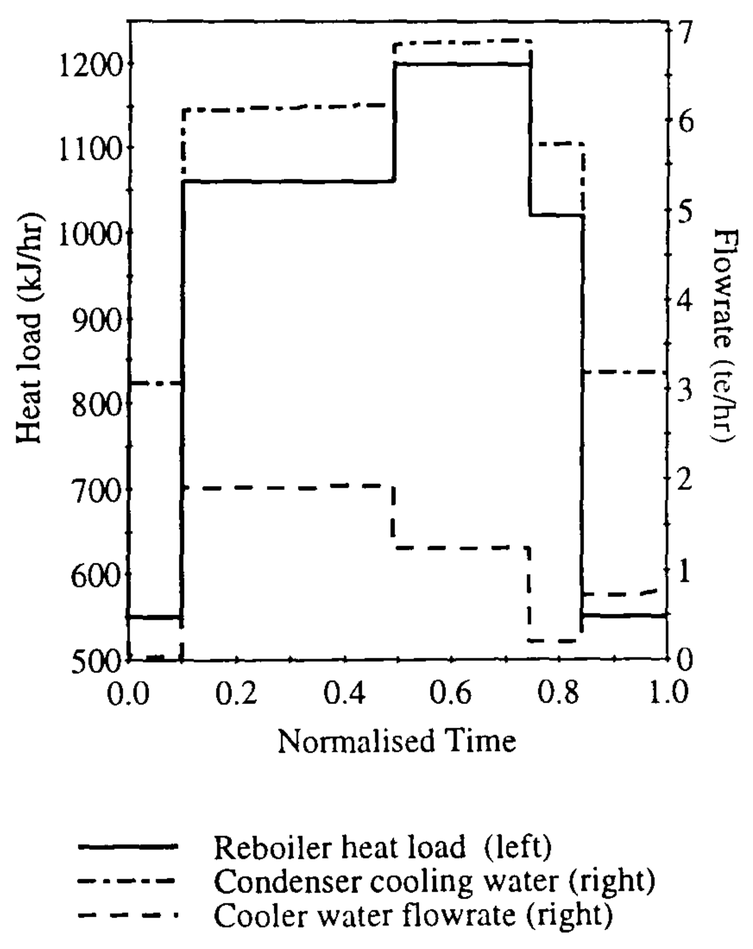


(b) Temperature profile and cooling water policy

Figure 8.13: Case 2: Reactor II operating policy



(a) Reboiler composition and reflux ratio profiles



(b) Reboiler heat load (kJ/hr), condenser and cooler cooling water flowrates (te/hr)

Figure 8.14: Case 2: Column II operating policy

8.5. Case Study 3

In this case study, the values of the parameters for the operating cost, capital cost and raw material costs have been changed from the previous two case studies (*cf.* table 8.1) and are shown in table 8.7. In particular, we note that the cost of raw materials A and B is reduced from 9 $\$/kmol$ to 7 $\$/kmol$, and the waste disposal cost is reduced from 3 $\$/kmol$ to 1 $\$/kmol$. The values of the cost coefficients α_r and α_b are increased from the original values of 0.86 and 0.325 respectively, and α_c is decreased from 0.105 to 0.08. The unit cost of steam is twice the value used in the previous two case studies and the unit cost of cooling water has been increased substantially from its original value of 0.16 $\$/hr$.

Material	Unit value ($\$/kmol$)
A	7.0
B	7.0
$Waste$	1.0
$Product$	40.0
Cost Coefficients	**Value**
α_r	1.68 $\$/hr.m^{2.4}$
α_b	2.35 $\$/hr.m^{2.4}$
α_c	0.08 $\$/hr.m^{2.7}$
Utilities	**Unit value ($\$/te$)**
C_{cw}	8.0
C_{steam}	40

Table 8.7: Economic cost data for Case Study 3

The minimum purity specification for the desired product is at least 99% with a mean production rate specification of 7.5 $kmol/hr$ (instead of 9.5 $kmol/hr$ as in the previous cases). Also, the reboiler volume is bounded between 1.5 m^3 and 3.0 m^3 rather than between 1.0 m^3 and 8.0 m^3. 9.0 te/hr of cooling water is available for each reactor, distillation column condenser and heat exchanger, as opposed to 5.0 te/hr for the reactors and exchangers, and 9.0 te/hr for the condensers in the previous examples. All other conditions are identical to the previous two case studies.

8.5.1. Results

The results for the complete enumeration of potential flowsheets are shown in table 8.8:

Jacketed reactor	Distillation column	Total cost ($/hr)	CPU(s) (on *SUN ULTRA*)	NLP Iterations
0	0	INFEASIBLE	–	–
1	0	INFEASIBLE	–	–
2	0	INFEASIBLE	–	–
0	1	INFEASIBLE	–	–
0	2	INFEASIBLE	–	–
1	**1**	**224.90**	5442.4	55
2	1	232.50	11650.8	91
1	2	238.67	16281.3	66
2	2	230.01	50038.6	113

Table 8.8: Case 3: Enumeration results

The structure with the lowest cost for the given production rate consists of a single reaction and a single distillation task as shown in figure 8.15; the corresponding detailed STN can be seen in figure 8.16. It is clear that the different economics and specifications of this process have a dramatic effect on the optimal flowsheet structure. The increase in the operating and capital costs (*cf.* tables 8.3, 8.6 and 8.9) and the reduction in the mean production rate as well as the restriction on the reboiler volumes means that the flowsheet with two reactors and two columns is no longer economically attractive.

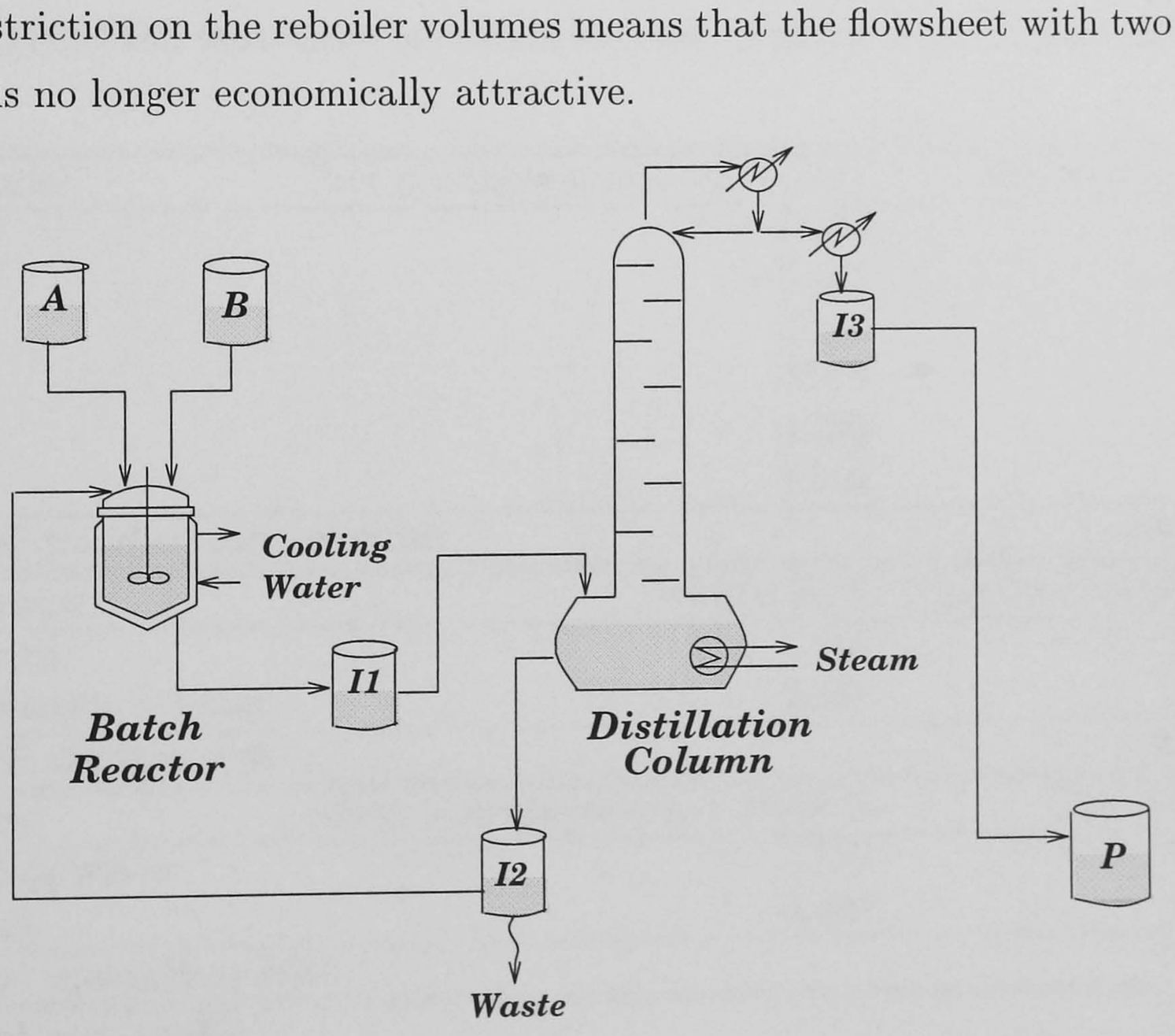


Figure 8.15: Case 3: Optimal process structure

The jacketed reactor consumes 8.23, 7.50 and 9.32 $kmol/batch$ of reactants A and B and intermediate I_2 respectively, and requires a processing time of 1.12 hr. The composition profiles are shown in figure 8.17(a). As the cost of cooling water is much higher than in the preceding case studies, the temperature of the reactor is allowed to reach its upper limit of 350 K and is maintained there for almost half of the duration of the reaction task (see figure 8.17(b)). Consequently, the production of the undesirable product D is high in reactor I (14% of the total reaction I product). Towards the end of the reaction process, a high flowrate of cooling water is utilised to lower the reaction temperature very rapidly, thus satisfying the final temperature constraint.

The distillation column requires 26.37 $kmol/batch$ of intermediate I_1 with a processing time of 1.00 hr and has a fixed set-up time of 30 min. The column produces 15.10 $kmol/batch$ of intermediate I_2; 67.8% of this is recycled to the reactor since it is rich in reactants A and B; the rest is treated as waste. The column also produces 11.27 $kmol/batch$ (7.5 $kmol/hr$) of distillate 99% rich in product C. The variations in the reboiler composition together with the optimal normalised reflux ratio policy are shown in figure 8.18(a). The optimal operating policies of the cooling water flowrate in the condenser and cooler, and the reboiler heat load are given in figure 8.18(b). The reboiler heat load is maintained at the maximum of 1200 MJ/hr throughout the separation operation in order to shorten the processing time.

Material	Net production rate ($kmol/hr$)	Revenue ($/hr$)
A	−6.021	−42.15
B	−5.486	−38.40
I_1	0.000	0.00
I_2	0.000	0.00
W	3.230	−3.23
P	7.500	300
Total production revenue		**216.22**
Operator	Volume (m^3)	Capital cost ($/hr$)
Reactor	2.275	22.08
Distillation column	2.397	39.86
Total capital cost		**61.94**
Utility	Mean consumption rate (te/hr)	Cost ($/hr$)
Cooling water	7.553	60.42
Steam	0.469	18.76
Total operating cost		**79.18**
Total net profit		**75.10**

Table 8.9: Case 3: Economic breakdown for optimal solution

The optimal values/variations of the decision variables are summarised in table C.11 in Appendix C.

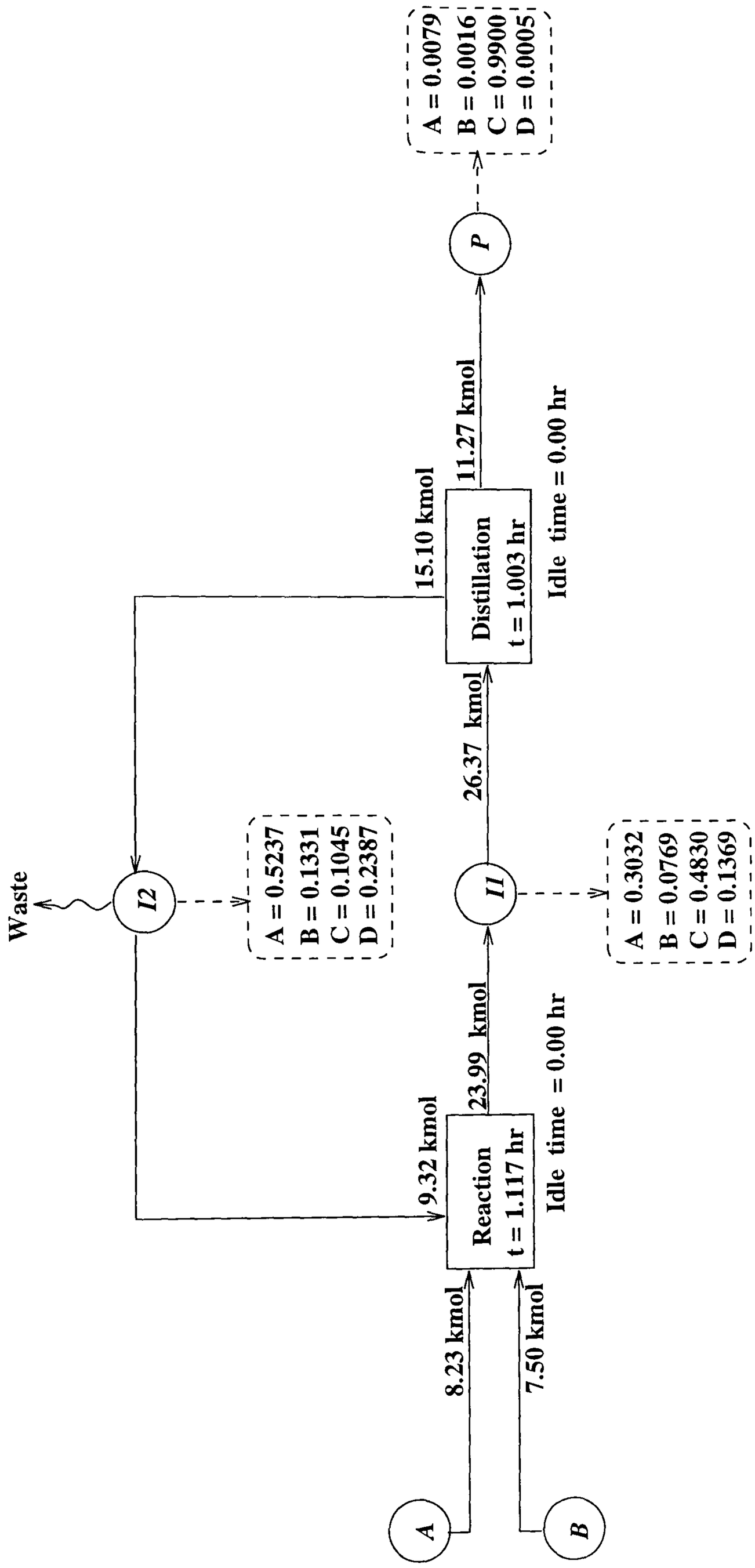
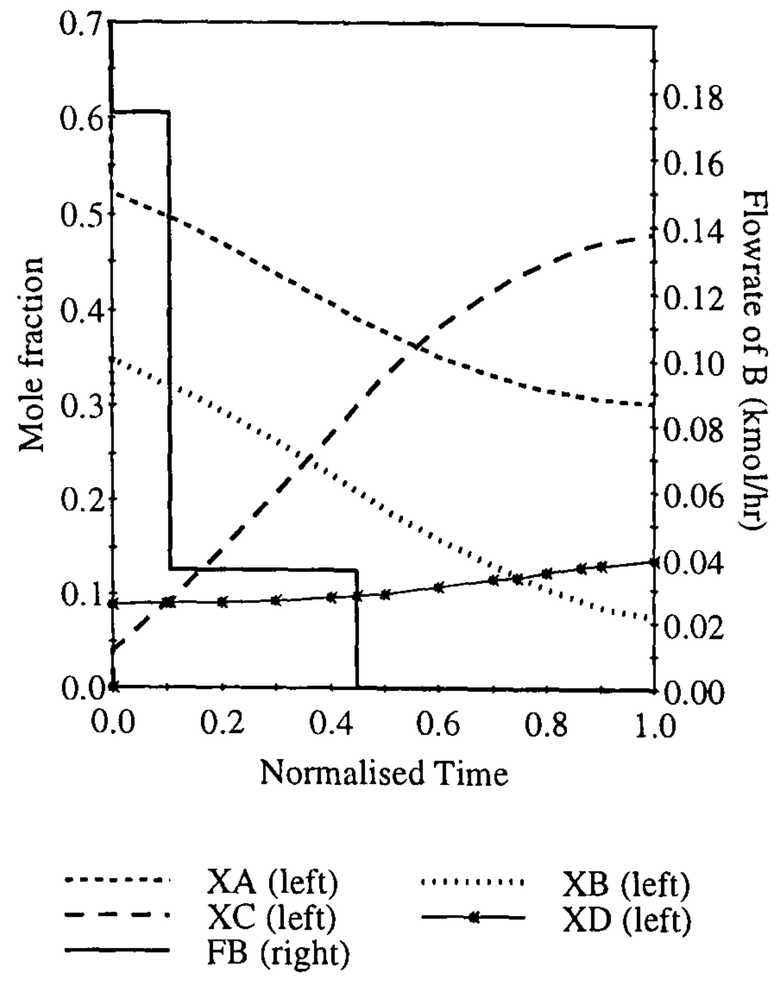
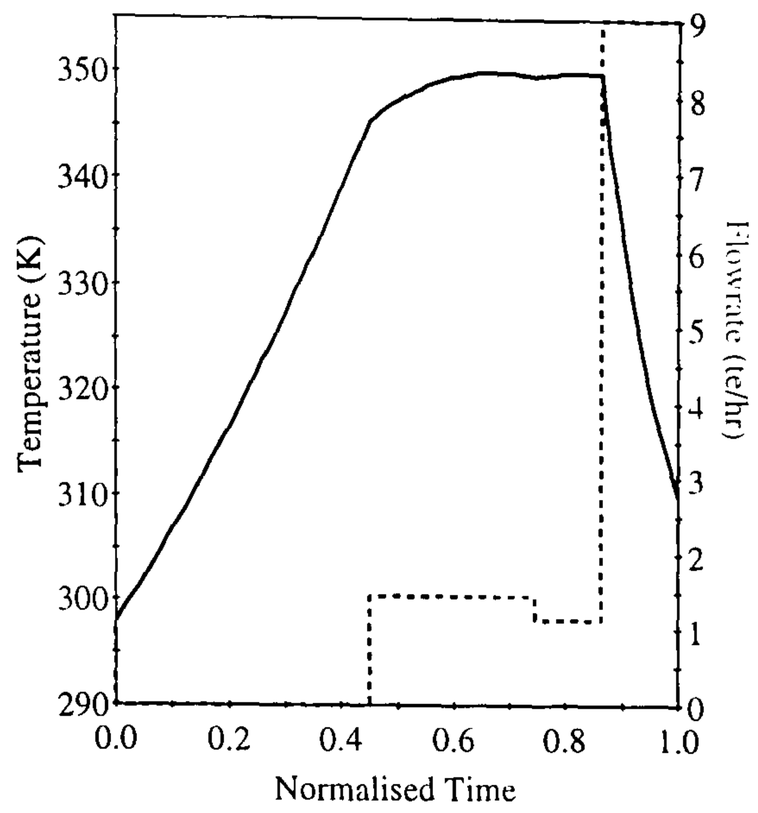


Figure 8.16: Case 3: State-Task Network for the optimal solution

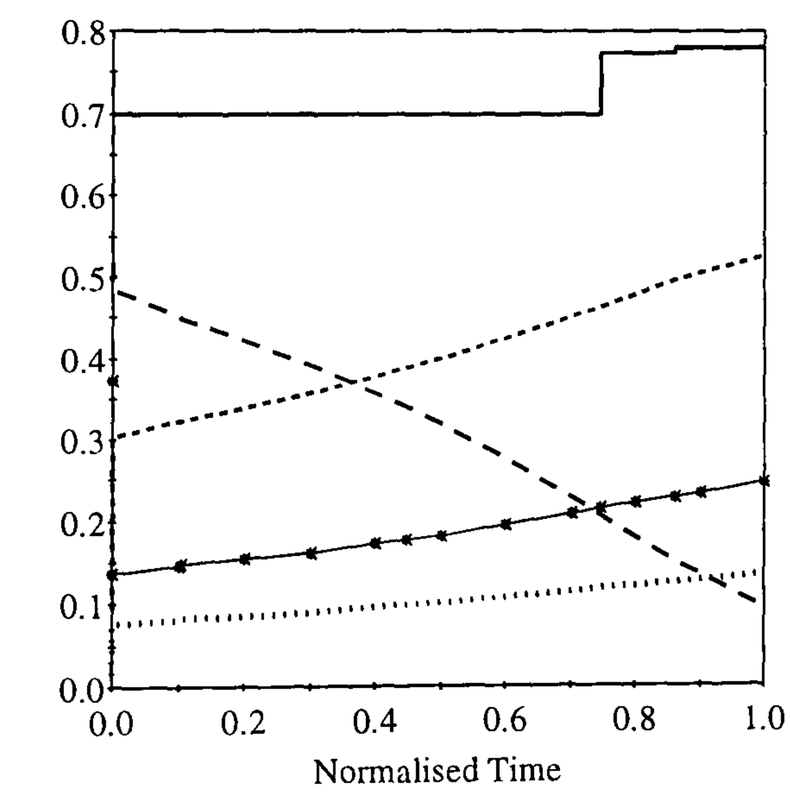


(a) Mole fraction profiles

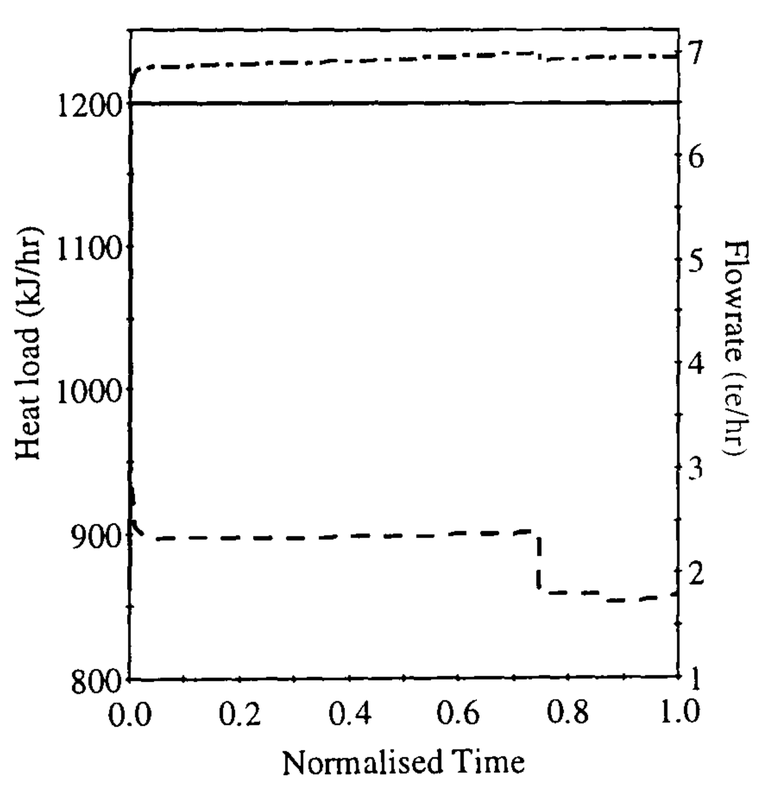


(b) Temperature profile and cooling water policy

Figure 8.17: Case 3: Reactor operating policy



(a) Reboiler composition and reflux ratio profiles



(b) Reboiler heat load (kJ/hr), condenser and cooler cooling water flowrate (te/hr)

Figure 8.18: Case 3: Column operating policy

8.6. Conclusions

This chapter has considered the problem of designing batch processes involving networks of reaction and separation tasks. Three case studies were presented and tackled using the design methodology in Chapter 6 of this thesis.

The recovery of unreacted raw materials which are recycled for further processing is widely used in batch operations to improve the process economics. This characteristic was observed in all of the optimal designs obtained; yet there was no need for *a priori* assumptions about the flowsheet structure or connectivity; in other words, our methodology automatically determines which of the recycle streams would improve the process performance and introduces them accordingly.

An interesting point that is raised by a comparison of the three optimal designs presented in this chapter is the strong influence of continuous parameters (such as the design specifications and cost data) on the optimal *structure* of the process. It is precisely this influence that makes batch process design based on qualitative or very approximate quantitative task models highly problematic.

Chapter 9

Conclusions and Directions for Future Research

This chapter summarises the work presented in this thesis. The contributions of this research to the design of integrated batch process are presented. This is followed by a discussion of the limitations that may hinder its immediate practical application. Finally, some possible directions for future development are indicated.

9.1. Contributions of this Thesis

This thesis has presented a framework for the design of integrated batch processes in which the optimal structure of the process is determined simultaneously with the detailed design and operating policies for the individual processing tasks.

The approach of Charalambides (1996) has been adopted in this work. Thus, it makes use of a State-Task Network (STN) process representation where "states" correspond to different types of material characterised by arbitrary vectors of intensive properties, and "tasks" are processing steps described by detailed dynamic models. We believe that the latter are essential in order to ensure that any design obtained is both feasible (*i.e.* it satisfies all important process constraints) and economical.

Charalambides' work considered the design of integrated batch processes, the structure of which was described by a *given* STN. One major contribution of our work has been in introducing the concept of a "super-STN", *i.e.* a superstructure within which a number of alternative process structures are embedded. Moreover, by extending the recent work of Smith (1996) from continuous to batch processes, we have shown that such super-STNs may be constructed *automatically* from:

- a description of the raw material states,
- a description of the end-product states,
- models for each type of batch unit operation at the disposal of the designer,
- a specification of the *maximum* number of the instances of each unit operation that may be incorporated in the design.

An important characteristic of the approach is that the number of alternative process structures embedded within the super-STN is relatively small. Hence, a complete enumeration procedure may be adopted for determining the optimal structure.

The second major contribution of our work has been the formal consideration of discrete equipment design decisions within the above framework. The introduction of such decisions leads to a complex mixed integer dynamic optimisation problem. A methodology based on control vector parameterisation (CVP) coupled with an outer approximation/augmented penalty (OA/AP) algorithm was proposed for solving this type of problem.

The new algorithm has enabled us to address new classes of batch process design problems, such as those involving the determination of the optimal number of trays in batch distillation columns, or the selection of equipment from a set of standard "off-the-shelf" items. In the former case, a novel superstructure for a batch distillation column was devised and used.

9.2. Limitations to the Practical Implementation of our Approach

The work presented in this thesis represents a general and detailed methodology for the design of integrated batch processes. However, its immediate practical implementation is hindered by several factors:

- *The lack of detailed unit operation models*
  The use of detailed dynamic models of batch unit operations is central to our approach. Although, in principle, much simpler models (*e.g.* based on purely algebraic correlations) could also be used within the framework that we have established, it is doubtful whether such models can provide the accuracy required to guarantee the feasibility of any solution obtained or to take account of the complex trade-offs inherent in many integrated batch processes.

  Unfortunately, detailed models are not always available in practice. This is especially true at the early stages of process design; the use of approaches based on simpler models

(such as those proposed by Linninger *et al.*, 1995; Linninger *et al.*, 1997) may be more appropriate in these cases. However, a number of current trends indicate that this situation may change in the longer term. These include improvements in process modelling tools and methodologies, the tighter integration of laboratory experimentation within process modelling, and the increasing use of computational chemistry techniques for the generation of some of the data needed for process design.

- *The lack of guarantees for global optimality*

  Although the optimisation formulations presented in this thesis are entirely general, the techniques used for their solution do not guarantee that the designs obtained are the *globally* optimal ones*. Thus, there may well exist designs that deliver considerably better economic performance than those presented here.

  From a practical point of view, it can be said that our approach at least provides solutions that are feasible (within the accuracy of any model used) and, therefore, practically implementable. Provided these solutions are better than those that could be obtained using currently available techniques, then some important progress *has* been made, notwithstanding the lack of formal guarantees of global optimality.

  In the longer term, developments in the global solution of dynamic optimisation problems, such as those recently described by Esposito and Floudas (1998) may address such concerns in a more rigorous fashion. However, it is unlikely that these techniques will be applicable to problems of the size of interest to our work in the near future.

- *The high computational cost*

  The computational statistics provided with the various examples in this thesis indicate that the solution of our optimisation problems, even to *local* optimality, entails very significant computational cost, often of the order of many hours on typical desktop workstations.

  Our results also indicate that almost all of the computational cost is incurred in the solution of dynamic optimisation problems where any discrete decisions have already been fixed. Fortunately, dynamic optimisation is an area where rapid progress is currently being made. For instance, new algorithms have recently been proposed (Feehery *et al.*, 1997; Keeping and Pantelides, 1998) for the computationally expensive task of computing sensitivities (*cf.* section 3.8.5.1) of systems of differential-algebraic equations (DAEs). These developments, together with advances in integration methods and codes

*Our use of techniques such as the Augmented Penalty (AP) modification of the Outer Approximation (OA) algorithm are aimed at improving the *probability* of obtaining globally optimal solutions.

for DAEs and the underlying linear algebra computations will have an immediate and proportional impact on improving the efficiency of our design computations.

Moreover, there is significant potential for the use of parallel computation in our solution algorithms:

- As already noted by Charalambides (1996), in the context of the type of CVP algorithm used here, the DAEs describing each unit operation (and the corresponding sensitivity equations) can be solved independently of those describing every other operation (*cf.* section 3.8.5.1).
- The modified OA/AP algorithm described in section 5.5 is designed for implementation on multiple computer processors. Further improvements to this algorithm are worth investigating. For instance, there may be significant differences in the computational times required by the various subproblems being solved in parallel at step 7 of the algorithm (see results in table 5.5); hence, some of the processors may be left idle while waiting for the one dealing with the most difficult subproblem to finish. It may, therefore, be advantageous to follow an alternative strategy: as soon as any subproblem is solved, its linearisations are added to the master problem; the latter is then solved again to generate a new subproblem, the solution of which may start immediately.
- The procedure used for enumerating all possible process structures (*cf.* section 6.3) can be parallelised by considering several candidate structures simultaneously.

9.3. Possible Directions for Future Research

The previous section has already identified several key areas for possible development. These are aimed at removing some of the limitations to the application of our methodology within the scope considered in this thesis. Here, we consider some further directions which aim at widening the scope of our methodology.

The first area that can benefit from more detailed consideration is that of the interactions of scheduling with design. In our work, the amount of scheduling information used in the design stage is rather limited, based on aggregate models of plant utilisation. This is usually sufficient for the case where a new plant is constructed to implement a new process since it covers the two important cases of unstable intermediates (zero-wait policy) and stable materials (for which unlimited storage is assumed to be available). However, it may not be adequate for the case where a new process is to be implemented within an existing plant with

finite storage facilities.

The second area that needs to be addressed is the derivation of "robust" recipes within the context of uncertainty (*cf.* section 1.2). Our optimal recipes are determined for a nominal set of process parameters (*e.g.* raw material composition) with no consideration of the sensitivity of the key process outputs (*e.g.* product quality) with respect to these parameters. However, a primary technical objective in many sectors of the process industries today is the reproducibility of the final product composition; in fact, this is often accorded a higher importance than more traditional criteria such as the maximisation of yield (Terwiesch, 1994). In the pharmaceutical and speciality chemical industries, the end-product of each individual batch must be guaranteed to meet given specifications. Batch-to-batch variations (*e.g.* due to raw material impurities or upstream disturbances) are a major cause for concern. Maintaining safe operating conditions is another important factor that must not be violated, which in the presence of impurities or inaccurate reaction kinetics may not be easy to achieve.

Robustness is characterised by the reduction of the sensitivity of the objective function and constraints caused by uncertainties in the model and its data. Overall, then, an important extension of this work will be to consider approaches that ensure that the derived process and design is able to perform satisfactorily over a range of possible operating conditions. The handling of uncertainty in dynamic processes has only recently begun to attract some attention (see Terwiesch *et al.*, 1994; Walsh *et al.*, 1995; Diwekar and Kalagnanam, 1996; Terwiesch *et al.*, 1998; Samsatli *et al.*, 1998). However, despite the progress that has been made, it must be recognised that the types of systems that have been studied so far are much simpler than the large-scale multistage processes of interest to our work.

References

Allgor, R. J., M. D. Barrera, P. I. Barton and L. B. Evans (1996). Optimal batch process development. *Computers chem. Engng. 20*, 885–896.

Allgor, R. J. and P. I. Barton (1997). Mixed-integer dynamic optimization. *Computers chem. Engng. 21*, S451–S456.

Barbosa-Póvoa, A. P. F. D. (1994). *Detailed Design and Retrofit of Multipurpose Batch Chemical Plants.* PhD thesis, University of London.

Barrera, M. D. (1990). *Optimal Design and Operation of Batch Processes.* PhD thesis, Massachusetts Institute of Technology.

Barton, P. I. and B. Ahmad (1995). Solvent recovery targetting for pollution prevention in pharmaceutical and specialty chemical manufacturing. *AIChE Symposium Series 90*, 59–73.

Barton, P. I. and T. Park (1997). Analysis and control of combined discrete/continuous systems: Progress and challenges in the chemical process industries. *AIChE Symposium Series 93*, 102–114.

Beale, E. M. L. (1977). In D.A.H. Jacobs, editor. *The state of the art of numerical analysis*, 409–448, Academic Press, London.

Benders, J. F. (1962). Partitioning procedures for solving mixed variable programming problems. *Numerische Mathematik 4*, 238–252.

Bernot, C., M. F. Doherty and M. F. Malone (1991). Feasibility and separation sequencing in multicomponent batch distillation. *Chem. Eng. Science 46*, 1311–1326.

Bhatia, T. and L. T. Biegler (1996). Dynamic optimization in the design and scheduling of multiproduct batch plants. *Ind. Eng. Chem. Res. 35*, 2234–2246.

Bhatia, T. and L. T. Biegler (1997). Dynamic optimization of batch design and scheduling with process model uncertainty. *Ind. Eng. Chem. Res. 36*, 3708–3717.

Biegler, L. T., I. E. Grossmann and A. W. Westerberg (1997). *Systematic methods of chemical process design.* Prentice Hall International.

Bosley, J. R. and T. F. Edgar (1994). Appropriate modeling assumptions for batch distillation optimization and control. *Proceedings of the 5th International Symposium on Process Systems Engineering, Seoul, S. Korea*, 477–482.

Calderón, Z., A. Espuña and L. Puigjaner (1998). Waste analysis and minimization in batch and semibatch reactor operation through dynamic simulation and neural networks. *Computers chem. Engng. 22*, S977–S980.

Carrasco, E. F. and J. R. Banga (1997). Dynamic optimization of batch reactors using adaptive stochastic algorithms. *Ind. Eng. Chem. Res. 36*, 2252–2261.

Charalambides, M. S. (1996). *Optimal Design of Integrated Batch Processes.* PhD thesis, University of London.

Charalambides, M. S., N. Shah and C. C. Pantelides (1995). Synthesis of batch reaction/distillation processes using detailed dynamic-models. *Computers chem. Engng 19*, S167–S174.

Chen, C. L. (1988). *A Class of Successive Quadratic Programming Methods for Flowsheet Optimisation.* PhD thesis, University of London.

Chen, C. L. and S. Macchietto (1989). SRQPD - successive reduced quadratic programming. Technical report, Centre for Process Systems Engineering, Imperial College.

Chiotti, O. P., H. E. Salomone and O. A. Iribarren (1996). Batch plants with adaptive operating policies. *Computers chem. Engng. 20*, 1241–1256.

CPLEX Optimization Inc. (1989-1995). *Using the CPLEX Callable Library.* CPLEX Optimization Inc.

Cuthrell, T. E. and L. T. Biegler (1987). On the optimization of differential-algebraic process systems. *AIChE J. 33*, 1257–1270.

Daubert, T. E. and R. P. Danner (1985). *Data Compilation Tables of Properties of Pure Compounds.* AICHE-DIPPR.

Dimitriadis, V. D., N. Shah and C. C. Pantelides (1997). Modeling and safety verification of discrete/continuous processing systems. *AIChE J. 43*, 1041–1059.

Diwekar, U. M. (1992). Unified approach to solving optimal design-control problems in batch distillation. *AIChE J. 38*, 1551–1562.

Diwekar, U. M. (1994). How simple can it be? - a look at the models for batch distillation. *Computers chem. Engng. 18S*, S451–S457.

Diwekar, U. M. and J. R. Kalagnanam (1996). Robust design using an efficient sampling technique. *Computers chem. Engng. 20*, S389–S394.

Diwekar, U. M. and K. P. Madhavan (1991). BATCH – DIST: A comprehensive package for simulation, design, optimization and optimal control of multicomponent, multifraction batch distillation columns. *Computers chem. Engng. 15*, 833–842.

Diwekar, U. M., K. P. Madhavan and R. E. Swaney (1989). Optimization of multicomponent batch distillation columns. *Ind. Eng. Chem. Res. 28*, 1101–1017.

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

Duran, M. A. and I. E. Grossmann (1986). A mixed integer nonlinear programming algorithm for process systems synthesis. *AIChE J. 32*, 592–606.

Esposito, W. R. and C. A. Floudas (1998). Global optimization of nonconvex problems with differential and algebraic constraints. *Paper presented at the AIChE Annual Meeting, Miami, FL.*, Paper No.236b.

Feehery, W. F., J. E. Tolsma and P. I. Barton (1997). Efficient sensitivity analysis of large-scale differential-algebraic systems. *Applied Numerical Mathematics 25*, 41–54.

Floudas, C. (1995). *Nonlinear and Mixed-Integer Optimization: Fundamentals and Applications.* Oxford University Press.

Furlonge, H. I., E. Sørensen and C. C. Pantelides (1998). Optimal operation of multivessel batch distillation columns. *AIChE J.* (submitted for publication).

Garcia, V., M. Cabassud, M. V. Le Lann, L. Pibouleau and G. Casamatta (1995). Constrained optimization for fine chemical productions in batch reactors. *The Chemical Engineering Journal 59*, 229–241.

Gear, C. W. H. (1971). Simultaneous numerical solution of differential-algebraic equations. *IEEE Transactions on Circuit Theory CT-18*, 89–95.

Geoffrion, A. M. (1972). Generalized Benders' decompostion. *Journal of Optimization Theory and Application 10*, 237–260.

Goršek, A. and P. Glavič (1997a). Design of batch versus continuous processes - part I: Single-purpose equipment. *Chem. Eng. Res. & Des. 75*, 709–717.

Goršek, A. and P. Glavič (1997b). Design of batch versus continuous processes - part II: Multi-purpose equipment. *Chem. Eng. Res. & Des. 75*, 718–723.

Grossmann, I. E. and M. M. Daichendt (1996). New trends in optimization-based approaches to process synthesis. *Computers chem. Engng. 20*, 665–683.

Grossmann, I. E. and R. W. H. Sargent (1978). Optimum design of heat exchanger networks. *Computers chem. Engng. 2*, 1–7.

Gundersen, T. (1982). Numerical aspects of the implementation of cubic equation of state in flash calculation routines. *Computers chem. Engng. 6*, 245–255.

Ierapetritou, M. G. and E. N. Pistikopoulos (1995). Design of multiproduct batch plants with uncertain demands. *Computers chem. Engng. 19*, S627–S632.

Iribarren, O. A. (1985). *Batch Chemical Process Design.* PhD thesis, University of Massachusetts.

Iribarren, O. A., M. F. Malone and H. E. Salomone (1994). A heuristic approach for the design of hybrid batch-continuous processes. *Chem. Eng. Res. & Des. 72*, 295–306.

Irribarren, O. A. and M. F. Malone (1985). A systematic procedure for batch process synthesis. *Paper presented at the AIChE Annual Meeting, Chicago.*

Jarvis, R. B. and C. C. P. Pantelides (1992). DASOLV - a differential algebraic equation solver. Technical report, Centre for Process Systems Engineering, Imperial College.

Keeping, B. R. and C. C. P. Pantelides (1998). A distributed memory parallel algorithm for the efficient computation of sensitivities of differential-algebraic systems. *Mathematics and Computers in Simulation 44*, 545–558.

Kocis, G. R. and I. E. Grossmann (1987). Relaxation strategy for the structural optimization of process flowsheets. *Ind. Eng. Chem. Res. 26*, 1869–1880.

Kokossis, A. C. and C. A. Floudas (1990). Optimization of complex reactor networks - I: Isothermal operation. *Chem. Eng. Sci. 45*, 595–614.

Kokossis, A. C. and C. A. Floudas (1994). Optimization of complex reactor networks - II: Nonisothermal operation. *Chem. Eng. Sci. 49*, 1037–1051.

Kondili, E., C. C. Pantelides and R. W. H. Sargent (1993). A general algorithm for short-term scheduling of batch operations I - MILP formulation. *Computers chem. Engng. 27*, 211–227.

Kravanja, Z. and I. E. Grossmann (1997). Multilevel-hierarchical MINLP synthesis of process flowsheets. *Computers chem. Engng. 21*, S421–S426.

Lakshmanan, A. and L. T. Biegler (1996). Synthesis of optimal chemical reactor networks. *Ind. Eng. Chem. Res. 35*, 1344–1353.

Levien, K. L. (1992). Maximising the product distribution in batch reactors. *Chem. Eng. Sci., 47*, 1751–1760.

Linninger, A. A., E. Salomone, S. A. Ali, E. Stephanopoulos and G. Stephanopoulos (1997). Pollution prevention for production systems of energetic materials. *Waste Management 17*, 165–173.

Linninger, A. A., A. A. Shahnin and G. Stephanopoulos (1996). Knowledge-based validations and waste management of batch pharmaceutical process designs. *Computers chem. Engng. 20*, S1431–S1436.

Linninger, A. A., E. Stephanopoulos, S. A. Ali, C. Han and G. Stephanopoulos (1995). Generation and assessment of batch processes with ecological considerations. *Computers chem. Engng. 19*, S7–S13.

Logsdon, J. S. and L. T. Biegler (1993). Accurate determination of optimal reflux policies for the maximum distillate problem in batch distillation. *Ind. Eng. Chem. Res. 32*, 692–700.

Logsdon, J. S., U. M. Diwekar and L. T. Biegler (1990). On the simultaneous optimal-design and operation of batch distillation. *Chem. Eng. Res. & Des. 68*, 434–444.

Mohideen, M. J., J. D. Perkins and E. N. Pistikopoulos (1996). Optimal design of dynamic systems under uncertainty. *AIChE J. 42*, 2251–2272.

Mohideen, M. J., J. D. Perkins and E. N. Pistikopoulos (1997). Towards an efficient numerical procedure for mixed integer optimal control. *Computers chem. Engng. 21S*, S457–S462.

Montagna, J. M., O. A. Iribarren and F. C. Galiano (1994). The design of multiproduct batch plants with process performance models. *Chem. Eng. Res. & Des. 72*, 783–791.

Morison, K. R. and R. W. H. Sargent (1986). Optimisation of multistage processes described by differential-algebraic equations. *Lecture notes in Mathematics, 1230:86-102, Springer Verlag, Berlin.*

Mujtaba, I. M. (1989). *Optimal Operational Policies in Batch Distillation.* PhD thesis, University of London.

Mujtaba, I. M. and S. Macchietto (1993). Optimal operation of multicomponent batch distillation-multiperiod formulation and solution. *Computers chem. Engng. 17*, 1191–1207.

Mujtaba, I. M. and S. Macchietto (1994). Optimal design of multicomponent batch distillation columns - single and multiple separation duties. *Proceedings of the 5th International Symposium on Process Systems Engineering, Seoul, S. Korea*, 179–184.

Mujtaba, I. M. and S. Macchietto (1996). Simultaneous optimization of design and operation of multicomponent batch distillation column-single and multiple separation duties. *J. Proc. Cont. 6*, 27–36.

Mujtaba, I. M. and S. Macchietto (1997). Efficient optimization of batch distillation with chemical reaction using polynomial curve fitting techniques. *Ind. Eng. Chem. Res. 36*, 2287–2295.

Mujtaba, I. M. and S. Macchietto (1998). Holdup issues in batch distillation-binary mixtures. *Chem. Eng. Science 53*, 2519–2530.

Nad, N. and L. Spiegel (1987). Simulation of batch distillation by computer and comparison with experiments. *Proceedings of Chemical Engineering Fundamentals, Italy*, 737–742.

Nishida, N., G. Stephanopoulos and A. W. Westerberg (1981). A review of process synthesis. *AIChE J. 27*, 321–351.

Papageorgiou, L. G. (1994). *Optimal Scheduling of Multipurpose Batch/Semi Continuous Plants*. PhD thesis, University of London.

Parakrama, R. (1985). Improving batch chemical processes. *The Chemical Engineer*, 24–25.

Petkov, S. B. and C. D. Maranas (1998). Design of multiproduct batch plants under demand uncertainty with staged capacity expansions. *Computers chem. Engng. 22*, S789–S792.

Process Systems Enterprise Ltd. (1997). *gPROMS Advanced Users' Guide*. London, UK: Process Systems Enterprise Ltd.

Reid, R. C., J. M. Prausnitz and B. E. Poling (1987). *The Properties of Gases and Liquids*. R. R Donnelley and Sons Company, 4th edition.

Reklaitis, G. (1989). Progress and issues in computer aided batch process design. *Proceedings of the Conference on Foundations of Computer-Aided Process Operations (FOCAPO '89)*, Snowmass, Colorado, USA, 241–276.

Reklaitis, G. V. (1992). Overview of scheduling and planning of batch process design. *NATO Advanced Study Institute on Batch Processing Systems Engineering, Antalya, Turkey*.

Renfro, J. G., A. M. Morshedi and O. A. Asbjornsen (1987). Simulaneous optimization and solution of systems described by differential/algebraic equations. *Computers chem. Engng. 11*, 503–517.

Rippin, D. W. T. (1983). Simulation of single and multiproduct batch chemical plants for the optimal design and operation. *Computers chem. Engng. 7*, 137–156.

Rippin, D. W. T. (1991). Batch process planning. *Chem. Engng. 98*, 101–107.

Ruppen, D., C. Benthack and D. Bonvin (1995). Optimization of batch reactor operation under parametric uncertainty - computational aspects. *J. Proc. Cont. 5*, 235–240.

Salimi, F. and D. Depeyre (1998). Comparison between dynamic behaviour of a batch packed and plate column. *Computers chem. Engng. 22*, 343–349.

Salomone, H. E. and O. A. Iribarren (1992). Posynomial modelling of batch plants: A procedure to include process decision variables. *Computers chem. Engng. 16*, 173–184.

Salomone, H. E., J. M. Montagna and O. A. Iribarren (1994). Dynamic simulations in the design of batch processes. *Computers chem. Engng. 18*, 191–204.

Samsatli, N. J. (1997). *Optimal Design and Operation of Biochemical Processes.* PhD thesis, University of London.

Samsatli, N. J., L. G. Papageorgiou and N. Shah (1998). Robustness metrics for dynamic optimisation models under parameter uncertainty. *AIChE J. 44*, 1993–2006.

Sanmartí, E., A. Espuña and L. Puigjaner (1997). Reliability and maintenance considerations in process design under uncertainty. *Computers chem. Engng. 21*, 1157–1168.

Sargent, R. W. H. and G. R. Sullivan (1977). The development of an efficient optimal control package. *Proceedings of the 8th IFIP conference on Optimisation Technology, London, UK*.

Shah, N. (1998). Single- and multisite planning and scheduling: Current status and future challenges. *Proceedings of the Conference on Foundations of Computer-Aided Process Operatons (FOCAPO '98)*, Snowbird, Utah, USA.

Skogestad, S., B. Wittgens, R. Litto and E. Sørensen (1997). Multivessel batch distillation. *AIChE J. 43*, 971–978.

Smith, E. M. B. (1996). *On the Optimal Design of Continuous Processes.* PhD thesis, University of London.

Soave, G. (1989). Equilibrium constants form a modified Redlich – Kwong equation of state. *Chem. Eng. Sci. 27*, 1197–1203.

Stefanis, S. K., A. G. Livingston and E. N. Pistikopoulos (1997). Enviromental impact considerations in the optimal design and scheduling of batch processes. *Computers chem. Engng. 21*, 1073–1094.

Stinson, S. (February 8, 1993). Custom chemicals. *Chemical & Engineering News*, 34–59.

Subrahmanyam, S., J. F. Pekny and G. V. Reklaitis (1994). Design of batch chemical-plants under market uncertainty. *Ind. Eng. Chem. Res. 33*, 2688–2701.

Sundaram, E. and L. B. Evans (1993). Shortcut procedure for simulating batch distillation operations. *Ind. Eng. Chem. Res. 32*, 511–518.

Terwiesch, P. (1994). *Dynamic Optimization of Batch Process Operations with Imperfect Modeling.* PhD thesis, Swiss Federal Institute of Technology, Zurich.

Terwiesch, P., M. Agarwal and D. W. T. Rippin (1994). Batch unit optimization with imperfect modelling: A survey. *J. Proc. Cont. 4*, 238–258.

Terwiesch, P., D. Ravemark, B. Schenker and D. W. T. Rippin (1998). Semi-batch process optimization under uncertainty: Theory and experiments. *Computers chem. Engng. 22*, 201–213.

Tomazi, K. G. (1997). Limitations and dynamics imposed on multicomponent batch distillation by tray hydraulics. *Ind. Eng. Chem. Res. 36*, 4273–4281.

Tricoire, B. (1992). *Design and Scheduling of Multiproduct Batch Plants with Application to Polymer Production.* PhD thesis, University of Massachusetts.

Tricoire, B. and M. F. Malone (1992). Design of multiproduct batch processes for polymer production. *Paper presented at the AIChE Annual Meeting, Miami, FL.*, Paper No.134e.

Uesbeck, F., N. J. Samsatli, L. G. Papageorgiou and N. Shah (1998). Robust optimal fermentation operating policies. *Computers chem. Engng. 22*, S167–S174.

Vassiliadis, C. G. and E. N. Pistikopoulos (1998). Reliability and maintenance considerations in process design under uncertainty. *Computers chem. Engng. 22*, S521–S528.

Vassiliadis, V. S. (1993). *Computational Solution of Dynamic Optimization Problems with General Differential-Algebraic Constraints.* PhD thesis, University of London.

Vassiliadis, V. S., C. C. Pantelides and R. W. H. Sargent (1994). Optimization of discrete charge batch reactors. *Computers chem. Engng. 18*, S415–S419.

Vassiliadis, V. S., R. W. H. Sargent and C. C. Pantelides (1994a). Solution of a class of multistage dynamic optimization problems - II: Problems with path constraints. *Ind. Eng. Chem. Res. 33*, 2123–2133.

Vassiliadis, V. S., R. W. H. Sargent and C. C. Pantelides (1994b). Solution of a class of multistage dynamic optimization problems - I: Problems without path constraints. *Ind. Eng. Chem. Res. 33*, 2111–2122.

Viswanathan, J. and I. E. Grossmann (1990). A combined penalty function and outer-approximation method for MINLP optimization. *Computers chem. Engng. 32*, 2942–2949.

Viswanathan, J. and I. E. Grossmann (1993). An alternative MINLP model for finding the number of trays required for a specified separation objective. *Computers chem. Engng. 17*, 949–955.

Walsh, S., I. M. Mujtaba and S. Macchietto (1995). Optimal design of operating procedures for batch distillation columns with uncertainty. *Acta Chimica Slovenica 47*, 69–74.

Westerlund, T. and F. Pettersson (1995). An extended cutting plane method for solving convex MINLP problems. *Computers chem. Engng. 19*, S131–S136.

Westerlund, T., H. Skrifvars, I. Harjunkoski and R. Porn (1998). An extended cutting plane method for a class of non- convex MINLP problems. *Computers chem. Engng. 22*, 357–365.

Xia, Q. and S. Macchietto (1997). Design and synthesis of batch plants - MINLP solution based on stochastic method. *Computers chem. Engng. 21*, S697–S702.

Appendix A

Models for Batch Unit Operations

This Appendix provides the mathematical models of the processing units used in our case studies.

A.1. General Model For Batch Distillation

Figure A.1 shows a distillation column which is modelled assuming the following:

- constant liquid holdups on the trays, reflux drum and reboiler,
- negligible vapour holdups,
- fast energy dynamics,
- negligible tray hydraulics,
- no reactions,
- perfect mixing,
- adiabatic tray operation.

A.1.1. Accumulator Model

Consider a distillation process producing z distillate cuts. The distillate flow is directed to the assigned accumulator tank via control valves. The control variable ν_z is set to 1 when the corresponding valve is open and 0 if the valve is shut.

Overall mass balance:

$$\frac{dM_z}{dt} = \nu_z L_d \quad \forall z \tag{A.1}$$

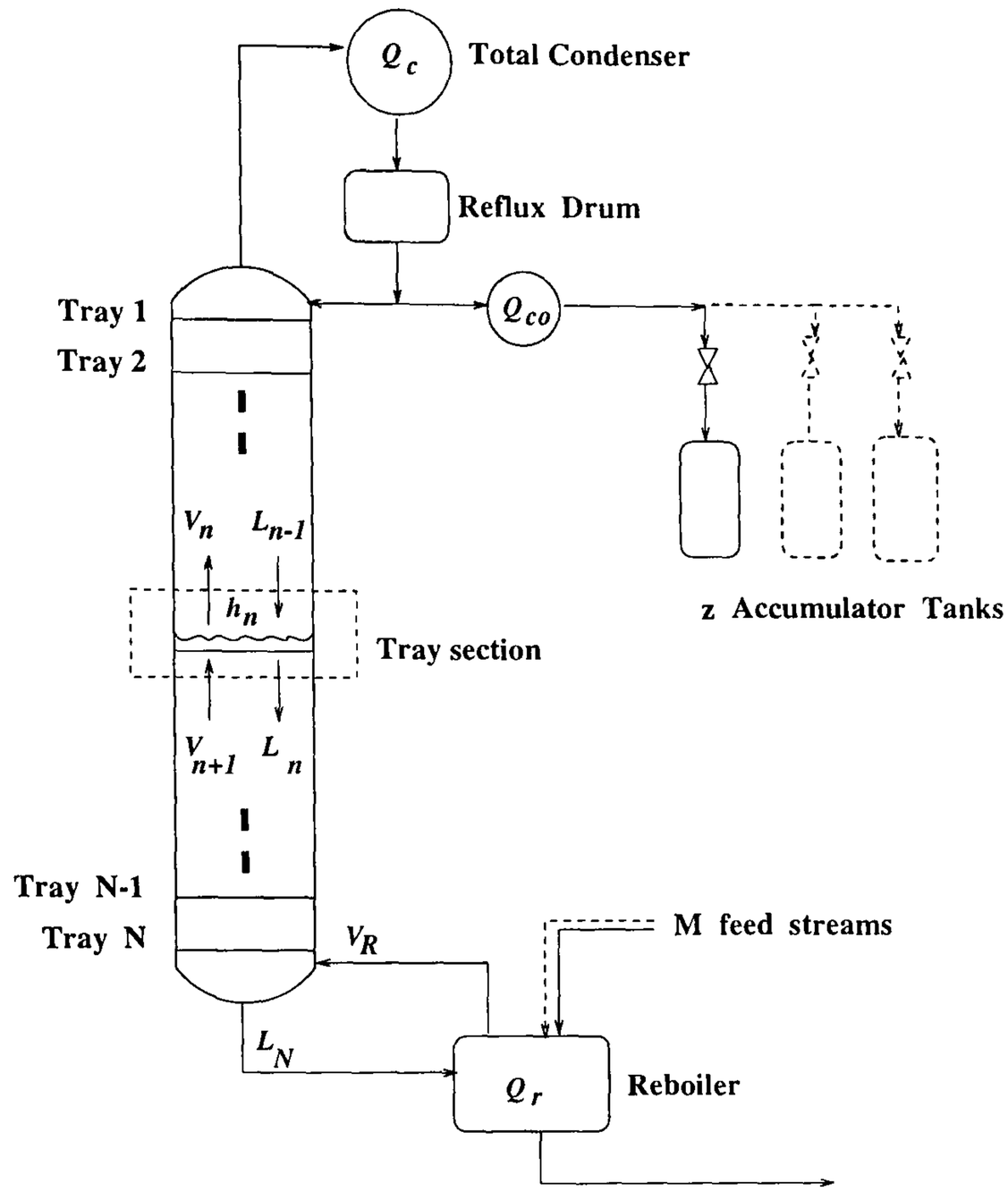


Figure A.1: General batch distillation column

Component balance

$$M_z \frac{dx_{iz}}{dt} = \nu_z L_d (x_{ic} - x_{iz}) \quad \forall \quad i, \quad z \tag{A.2}$$

A.1.2. Total Condenser Model and Reflux Drum

Mass balance

$$M_c \frac{dx_{ic}}{dt} = V_1 (y_{i1} - x_{ic}) \quad \forall \quad i \tag{A.3}$$

Reflux calculations

$$V_1 = L_c + L_d \tag{A.4}$$

$$L_c = V_1 r \tag{A.5}$$

Condenser duty

$$Q_c = V_1 (h_1^v - h_c^l) \tag{A.6}$$

Bubble point calculation

$$\sum_i K_{ic} x_{ic} = 1 \tag{A.7}$$

A.1.3. Tray Model

Overall mass balance

$$L_{n-1} + V_{n+1} = L_n + V_n \quad \forall \quad n \tag{A.8}$$

Component mass balance

$$M_n \frac{dx_{in}}{dt} = L_{n-1}x_{i,n-1} - L_n x_{in} + V_{n+1}y_{i,n+1} - V_n y_{in} \quad \forall \quad i,n \tag{A.9}$$

Energy balance

$$L_{n-1}h^l_{n-1} - L_n h^l_n + V_{n+1}h^v_{n+1} - V_n h^v_n = 0 \quad \forall \quad n \tag{A.10}$$

Equilibrium

$$y_{in} = K_{in}x_{in} \quad \forall \quad i,n \tag{A.11}$$

Vapour mole fraction normalisation

$$\sum_i y_{in} = 1 \quad \forall \quad n \tag{A.12}$$

A.1.4. Reboiler Model

Overall mass balance

$$\frac{dM_R}{dt} = L_N - V_R \tag{A.13}$$

Component mass balance

$$M_R \frac{dx_R}{dt} = L_N(x_{iN} - x_{iR}) - V_R(y_{iR} - x_{iR}) \quad \forall \quad i \tag{A.14}$$

Energy balance

$$L_N(h^l_N - h^l_R) + V_R(h^l_R - h^v_R) + Q_R = 0 \tag{A.15}$$

Equilibrium

$$y_{iR} = K_{iR}x_{iR} \quad \forall \quad i \tag{A.16}$$

Vapour fraction normalisation

$$\sum_i y_{iR} = 1 \tag{A.17}$$

A.1.5. Physical Properties

$$h^l_s = h^l(x_{is}, T_s) \quad \forall \quad s \in \{z,\ c,\ n,\ R\} \tag{A.18}$$

$$h^v_s = h^v(y_{is}, T_s) \quad \forall \quad s \in \{z,\ c,\ n,\ R\} \tag{A.19}$$

$$K_{is} = K_i(T_s, P_s) \quad \forall \quad s \in \{z,\ c,\ n,\ R\} \tag{A.20}$$

A.1.6. Notation

Accumulator

M_z : Molar holdup in tank z
ν_z : Control variable for valve of tank z
L_d : Molar distillate flowrate
x_{iz} : Mole fraction of component i in tank z

Condenser

x_{ic} : Mole fraction of component i in the condenser
M_c : Condenser holdup
V_1 : Vapour flowrate leaving the first tray
L_c : Molar reflux flowrate
y_{i1} : Vapour phase mole fraction of component i on the first tray
r : Normalised reflux ratio
Q_c : Condenser heat duty
h_1^v : Specific vapour enthalpy on first tray
h_c^l : Specific liquid enthalpy in the condenser
K_{ic} : Equilibrium constant of component i in the condenser

Trays

L_{n-1} : Liquid molar flowrate leaving tray n
V_n : Vapour molar flowrate leaving tray n
M_n : Molar holdup on tray n
x_{in} : Liquid mole fraction of component i on tray n
y_{in} : Vapour mole fraction of component i on tray n
h_n^l : Specific liquid enthalpy on tray n
h_n^v : Specific vapour enthalpy on tray n
K_{in} : Equilibrium constant of component i on tray n

Reboiler

M_R : Molar holdup in the reboiler
L_N : Liquid molar flowrate leaving tray N
V_R : Vapour molar flowrate leaving the reboiler
x_{iN} : Liquid mole fraction of component i leaving tray N
x_{iR} : Liquid mole fraction of component i in the reboiler
y_{iR} : Vapour mole fraction of component i in the reboiler
h_N^l : Specific liquid enthalpy on tray N
h_R^l : Specific liquid enthalpy in the reboiler
h_R^v : Specific vapour enthalpy in the reboiler
Q_R : Reboiler heat duty
K_{iR} : Equilibrium constant of component i in the reboiler

A.2. General Batch Reactor Models

Our batch reactor models are based on assumptions of perfect mixing and ideal liquid mixture behaviour. Only the liquid phase is modelled.

A.2.1. Jacketed Reactor

The mathematical model describing the transient behaviour of a multicomponent liquid phase jacketed reactor, shown in figure A.2 with both discrete and continuous reactant composition is described below.

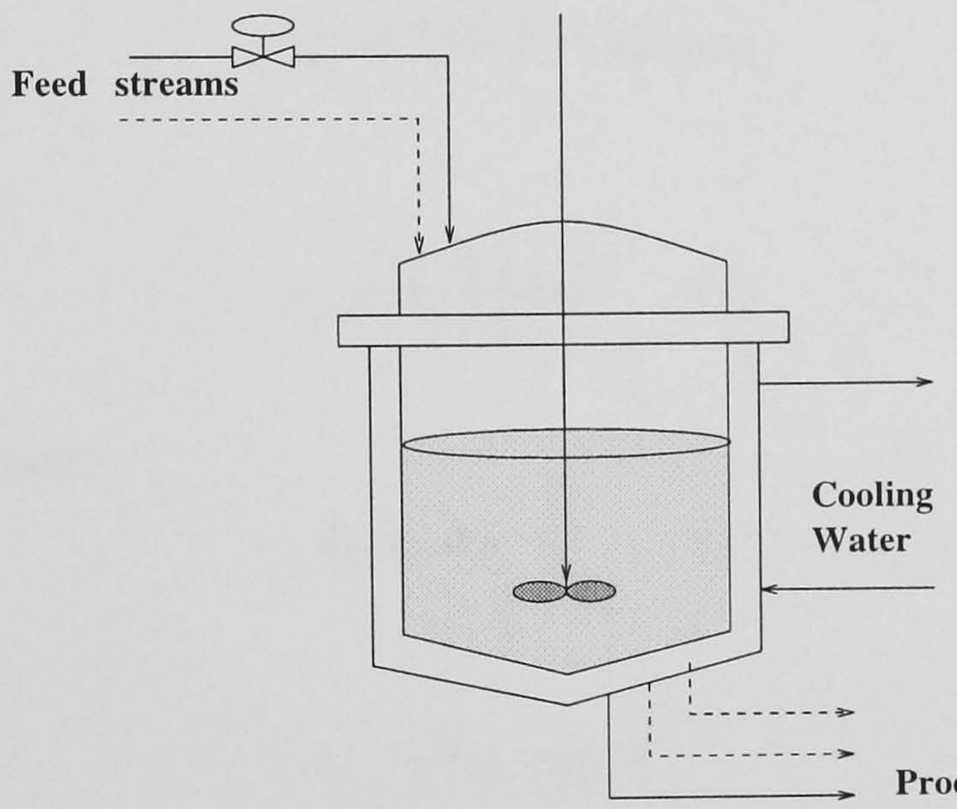


Figure A.2: Jacketed batch reactor

Mass balance

$$\frac{dM_i}{dt} = \sum_s x_{is}^{in} F_s^{in} + V \sum_j r_j \nu_{ji} \qquad \forall i \tag{A.21}$$

Total holdup

$$M = \sum_i M_i \tag{A.22}$$

Mole fractions

$$x_i = \frac{M_i}{M} \qquad \forall i \tag{A.23}$$

Molar concentrations

$$C_i = \frac{M_i}{V} \qquad \forall i \tag{A.24}$$

Reaction mixture volume

$$V = \sum_i \frac{M_i}{\rho_i^o} \tag{A.25}$$

Energy balance

$$\frac{dH}{dt} = \sum_s F_s^{in} h_s^{in} + V \sum_j r_j(-\Delta H_{Rj}) - Q_c \tag{A.26}$$

Total enthalpy

$$H = \sum_i M_i h_i^o \tag{A.27}$$

Heat transfer via external cooling system

$$Q_c = Ua(T - T_{cwout}) \tag{A.28}$$

Reaction rates

$$r_j = k_j \prod_i C_i^{\beta_{ij}} \qquad \forall j \tag{A.29}$$

Reaction rate constants

$$k_j = A_j e^{\frac{-E_j}{RT}} \qquad \forall j \tag{A.30}$$

Physical properties

$$h_i^o = h_i^o(T) \tag{A.31}$$

A.2.2. Plain Reactor

The batch plain reactor shown in figure A.3 is modelled in a similar way to the jacketed reactor, with the only difference being in the energy balance and heat transfer equations. More specifically, the plain reactor is operated adiabatically. Hence, the energy balance equation (A.26) is modified to omit the heat removal term:

$$\frac{dH}{dt} = \sum_s F_s^{in} h_s^{in} + V \sum_j r_j(-\Delta H_{Rj}) \tag{A.32}$$

The heat transfer equation (A.28) is also omitted.

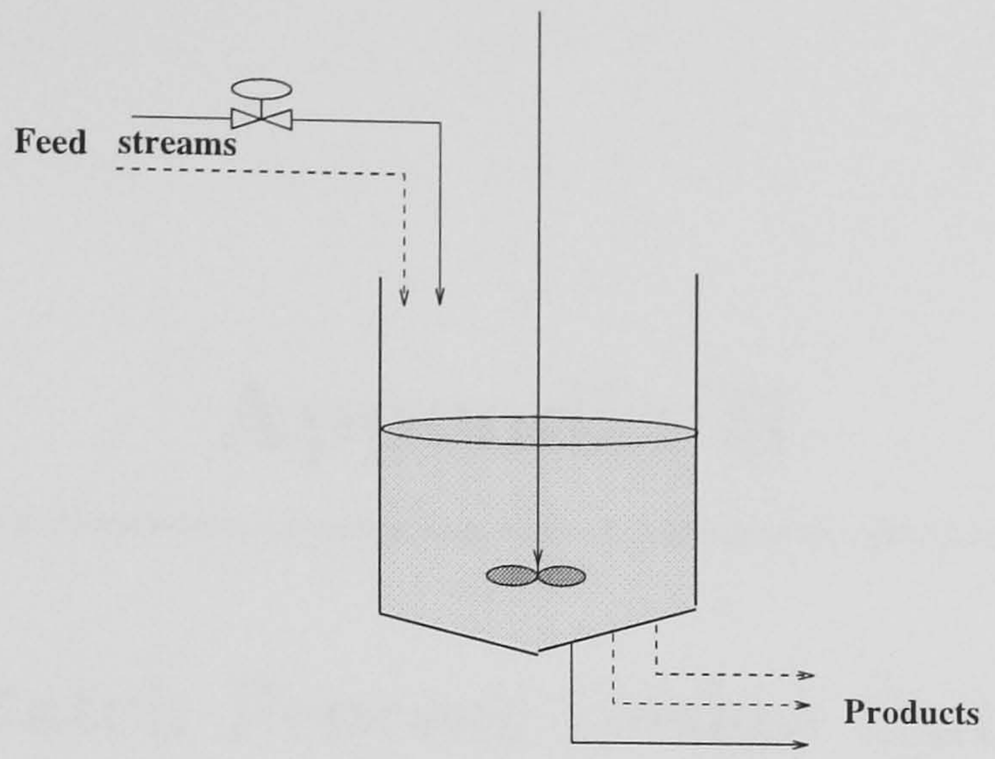


Figure A.3: Plain batch reactor

A.2.3. Notation

The model variables and parameters for the batch reactor models are as follows:

M_i	: Molar holdup for component i
V	: Volume of reactor contents
ν_{ji}	: Stoichiometric coefficient of component i in reaction j
r_j	: Reaction rate for reaction j
F_s^{in}	: Feed stream s
x_{is}^{in}	: Mole fraction of component i in the feed stream s
M	: Total molar holdup
H	: Total enthalpy content of the system
h_s^{in}	: Specific enthalpy of the feed stream
ΔH_{Rj}	: Enthalpy of reaction for reaction j
Q_c	: Energy removed by the external cooling system
x_i	: Mole fraction of component i in the system
C_i	: Concentration of component i in the system
ρ_i^o	: Density of pure component i
h_i^o	: Specific enthalpy of pure component i
k_j	: Reaction rate constant for reaction j
β_{ij}	: Order of the reaction j with respect to component i
A_j	: Pre-exponential Arrhenius constant for reaction j
E_j	: Activation energy for reaction j
R	: Universal gas constant
T	: Temperature of the reaction mixture
T_{cwout}	: Temperature of the cooling water
U	: Heat transfer coefficient of the jacket
a	: Heat exchange area

Appendix B

Batch Process Design Data

This Appendix provides the detailed input data used in our case studies.

B.1. Case Studies of Chapter 4

B.1.1. Physical Properties for Example 1 (section 4.4)

Vapour-liquid equilibria

The vapour-liquid equilibrium calculations are based on the Soave-Redlich-Kwong (SRK) equation of state. Using the cubic equation of state and simple mixing rules, it is possible to derive an analytical expression for the fugacity coefficient (ϕ) of each component i in the liquid or vapour phase s (Reid *et al.*, 1987):

$$\begin{aligned} log(\phi_i^s) &= \left(\frac{b_i}{b_s^m}(Z_s - 1)\right) - \ln(Z_s - B_s^*) \\ &+ \frac{A_s^*}{B_s^*}\left(\frac{b_i}{b_s^m} - 2\left(\frac{a_i}{a_s^m}\right)^{0.5}\right)\ln\left(\frac{Z_s + B_s^*}{Z_s}\right) \qquad \forall\ i = 1,..,NC \end{aligned} \tag{B.1}$$

where Z_s is the compressibility factor of phase s. Given the critical temperature T_{ci} and pressure P_{ci} and the acentric factor ω_i of each component i, the parameters a_i, b_i, b_s^m, a_s^m, A_s^*, B_s^* as functions of composition z_i[§] are given by:

$$A_s^* = \frac{a_s^m P_t}{R_g^2 T^2} \qquad \forall\ s \tag{B.2}$$

[§] z_i can be either liquid or vapour composition.

where R_g is the universal gas constant.

$$B_s^* = \frac{b_s^m P_t}{R_g T} \quad \forall \ s \tag{B.3}$$

$$a_s^m = \sum_i \sum_j z_i z_j (a_i a_j)^{0.5} \quad \forall \ s \tag{B.4}$$

$$b_s^m = \sum_i z_i b_i \quad \forall \ s \tag{B.5}$$

$$a_i = \frac{0.42748 R_g^2 T_{ci}^2}{P_{ci}} \left(1 + f_{wi}\left(1 - \left(\frac{T}{T_{ci}}\right)^{0.5}\right)\right)^2 \quad \forall \ i = 1, .., NC \tag{B.6}$$

$$f_{\omega_i} = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \quad \forall \ i = 1, .., NC \tag{B.7}$$

$$b_i = \frac{0.0866 R_g T_{ci}}{P_{ci}} \quad \forall i = 1, .., NC \tag{B.8}$$

where T_{ci}, P_{ci} and ω_i are pure component critical temperature, critical pressure and acentric factor respectively.

Equation (B.1) depends on the compressibility factor of both the liquid and vapour phases, calculated from the cubic equation of state (Soave, 1989) written in the form:

$$Z_s^3 - Z_s^2 + \left(A_s^* - B_s^* - B_s^{*2}\right) Z_s - A^* B^* = 0 \quad \forall \ s \tag{B.9}$$

Unfortunately, the solution of the cubic equation of state sometimes results in calculation failures with the equilibrium constant collapsing ($K_i \rightarrow 1.0$), in particular for a bad initial guess at high pressures and when the wrong root is selected (Gundersen, 1982). To overcome these difficulties, Gundersen (1982) proposed an algorithm that calculates the correct root of the equation based on the values of Q_s and R_s, and the residual of the equation (B.9) at $Z_s = \frac{1}{3}$. Assuming that only low pressure vapour-liquid equilibria calculations are required, selecting the largest root for the vapour phase and the smallest one for the liquid phase would suffice.

Heat of vaporisation

Chen's method (Reid *et al.*, 1987) is adopted for the calculation of the specific enthalpy of vaporisation (ΔH_{vb} in J/mol):

$$\Delta H_{vb} = R_g T_c T_{br} \left(\frac{3.978 T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}}\right) \tag{B.10}$$

where T_{br}, T_c and P_c denote the reduced boiling temperature, critical pressure and critical temperature. The pure component critical parameter data (Daubert and Danner, 1985) used

are given in Table B.1.

Component	T_c K	P_c bar	ω
Cyclohexane	553.5	40.7	0.273
n-Heptane	540.3	27.4	0.263
Toluene	591.8	41.0	0.263

Table B.1: Batch distillation example 1: Critical parameter data

The normal boiling temperatures (T_b) of cyclohexane, n-heptane and toluene are 353.5 K, 371.6 K and 383.8 K respectively.

Specific enthalpy

The pure component specific enthalpy (J/mol) is given by the following equation:

$$h_k^v = \int_{T_{ref}}^{T} \left(a + bT + cT^2 + cT^3\right) dT \quad \forall \quad k \tag{B.11}$$

A reference temperature of 298 K is used. The values of the coefficients (Daubert and Danner, 1985) are given in table B.2.

Coefficient	Cyclohexane	n-Heptane	Toluene
a	-3.7810E+1	-5.1466	-2.4350E+1
b	5.5390E-1	6.7620E-1	5.1250E-1
c	-1.9530E-4	-3.6510E-4	-2.7650E-4
d	-1.5340E-8	7.6580E-8	4.9110E-8

Table B.2: Batch distillation example 1: Specific enthalpy data

B.1.2. Physical Properties for Example 2 (section 4.5)

Vapour pressure

The vapour pressure of the components are calculated using Antoine's equation:

$$\ln P = a + \frac{b}{T + c} \tag{B.12}$$

where P is pressure in Pa and T is temperature in K. The values of the coefficients are in table B.3. Equation (B.12) is valid for T between 363 K and 418 K, and P between 6.67

$\times 10^3$ Pa (50 $Torr$) and 4.60 $\times 10^4$ Pa (345 $Torr$). The boiling point temperatures of the components A, B, and C are 366.05 K, 368.13 K and 369.07 K respectively.

i	A	B	C
a	23.7149	22.8568	22.3781
b	-5460.085	-4842.725	-4500.10
c	-3.05E-05	-23.6482	-37.6818

Table B.3: Batch distillation example 2: Vapour pressure data

Enthalpy of vaporisation

The enthalpy of vaporisation (J/mol) is calculated using the Clausius-Clapeyron equation:

$$\Delta H_v = \frac{-bRT^2}{(T+c)^2} \tag{B.13}$$

where R is the universal gas constant (8.31441 $J/mol.K$) and T is temperature in K. The values of the coefficient b and c for each component are shown in table B.3.

Specific heat capacity

The ideal gas specific heat capacity ($J/kmol.K$) is calculated by:

$$C_p^{ig} = D_1 + D_2 \left(\frac{D_3/T}{\sinh(D_3/T)} \right)^2 + D_4 \left(\frac{D_5/T}{\cosh(D_5/T)} \right)^2 \tag{B.14}$$

where T is temperature in K. Note the ideal gas enthalpy is the same for all 3 isomers.

Ideal gas specific enthalpy

The ideal gas specific enthalpy ($J/kmol$) is calculated by the following equation:

$$h^{ig} = D_1 T + D_2 D_3 \left(\frac{1}{\tanh(D_3/T)} \right) - D_4 D_5 \tanh\left(\frac{D_5}{T} \right) \tag{B.15}$$

where T is the temperature in K and the reference temperature is 298.15 K.

The values of the coefficients D_1 to D_5 are 8.847E+04, 2.56530E+05, 1.45140E+03, 1.85330E+05 and 6.80200E+02 respectively.

B.1.3. Physical Properties for Example 3 (section 4.6.1)

Table B.4 includes all the physical properties data used in example 3 for the design of multi-component batch distillation columns (Charalambides, 1996).

i	1	2	3	4	5	6	7	8
Vapour Pressure (Pa): $\ln P_i^0 = a + \frac{b}{T} + cT + d\ln T + eT^f$								
a	58.71	61.623	58.959	71.77	100.41	128.43	156.62	127.31
b	-6364.7	-5620.8	-5591.9	-6413.3	-8482.7	-11654.0	-17059.0	-16097.0
c	-0.0023901	0.0	0.0	0.0041663	0.0043966	0.0	0.0	0.0
d	4.7344	-5.7449	-5.3538	-7.5054	-11.435	-14.768	-18.041	-13.991
e	0.20888E-16	0.21E-16	0.16714E-16	0.542E-17	0.13959E-16	0.29E-16	0.93E-17	0.31E-17
f	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Specific Heat Capacity ($J/kmol.K$): $Cp_i^0 = \alpha + \beta T + \gamma T^2 + \delta T^3$								
α	21152.0	-135420.0	-29644.0	-24355.0	-1105.3	1143.0	-20884.0	-6784.0
β	70.924	1522.70	783.51	512.46	314.64	1113.1	1400.30	1941.70
γ	0.02587	-1.4824	-0.57862	0.27654	-0.20319	0.6722	-0.9224	-1.1714
δ	0.16647E-4	0.62E-3	0.17853E-3	0.49111E-4	0.53214E-4	0.15E-3	0.24E-3	0.26E-3
Enthalpy of Vaporisation ($\times 10^8$ $J/kmol$)								
	0.35278	0.28323	0.39984	0.333201	0.29694	0.45471	0.62857	0.60603
Mean Molecular Weight ($kg/kmol$)								
	32.042	158.24	58.08	383.80	134.33	222.43	250.48	366.72
Specific Volume (dm^3/mol)								
	0.0435	0.13159	0.07614	0.11833	0.13578	0.17095	0.19257	366.72

Table B.4: Batch distillation example 3: Physical property data

B.2. Case Study of Chapter 5 (section 5.4)

Physical properties

Table B.5 includes all the physical properties data used in this example (Charalambides, 1996).

i	A	B	C	D	E	F
Vapour Pressure (Pa): $\ln P_i^0 = -\frac{a}{T} + b$						
a	3325.26	3246.00	3361.42	3540.19	3274.56	4642.15
b	9.42	9.40	9.4688	9.4405	9.9404	11.0104
Liquid Phase Specific Enthalpy $(kJ/kmol)$: $h_k^v = \int_{T_{ref}}^{T} \alpha dT \quad \forall k$						
α	172.3	172.3	200.0	155.0	200.0	160.0
Enthalpy of Vaporisation $(kJ/kmol)$						
	33430.74	33741.43	34000.0	44560.38	44091.48	49587.02
Density $(kmol/m^3)$						
	16.0	10.4	11.0	10.0	11.0	16.0

Table B.5: Batch process design with discrete equipment sizes: Physical property data

A reference temperature of 296 K is used in the calculation of the liquid and vapour specific enthalpies of the pure components.

Reaction kinetics

$$main \quad reaction \quad rate = k_1 C_A C_B \quad (kmol/hr.m^3) \tag{B.16}$$

$$side \quad reaction \quad rate = k_2 C_C \quad (kmol/hr.m^3) \tag{B.17}$$

$$main \quad reaction \quad rate = k_3 C_C C_E \quad (kmol/hr.m^3) \tag{B.18}$$

where C_A, C_B, C_C and C_E are the concentrations $(kmol/m^3)$ of components A, B, C and E respectively.

The kinetic rate constants are of the Arrhenius form:

$$k_1 = 300.0e^{\frac{-20000}{R_g T}} \tag{B.19}$$

$$k_2 = 100.0e^{\frac{-20000}{R_g T}} \tag{B.20}$$

$$k_3 = 200.0e^{\frac{-17000}{R_g T}} \tag{B.21}$$

where T is the reaction temperature (K) and R_g the universal gas constant $(8.314\ kJ/kmol.K)$. The enthalpy of reaction for reaction (B.19) and reaction (B.20) are -60000 and -50000 $kJ/kmol$ respectively. The enthalpy of reaction associated with reaction (B.21) is assumed to be negligible.

External cooling system

The cooling jacket in the reactor vessel has a surface area of 50 m^2. An overall heat transfer coefficient of 5088.16 $kW/m^2.K$ is assumed for heat transfer between the reacting mixture and the cooling water. The inlet temperature of the cooling water is 288 K with a constant heat capacity of 4200.0 $kJ/te.K$.

B.3. Case Studies of Chapter 7 (section 7.2)

Reaction kinetics data

The following reaction scheme is utilised (Charalambides, 1996):

$$\begin{aligned}
R_1 + R_2 &\rightarrow I_1 \quad \Delta H_R = -23.0\ kcal/mol \\
R_1 + I_1 &\rightarrow A \quad \Delta H_R = -15.0\ kcal/mol \\
I_1 &\rightarrow C \quad \Delta H_R = -5.0\ kcal/mol \\
C + R_3 &\rightarrow E \\
I_1 + C &\rightleftharpoons I_2 \\
Cat &\rightarrow Cat^*
\end{aligned}$$

with the associated reaction rates:

$$\begin{aligned}
rate \quad rxn1 &= k_1 C_{R_1} C_{R_2} \frac{C_{Cat}}{k_8 + C_{Cat}} \\
rate \quad rxn2 &= k_2 C_{R_1} C_{I_1}
\end{aligned}$$

$$rate \quad rxn3 = k_3 C_{I_1}$$

$$rate \quad rxn4(fwd) = k_4 C_{I_1} C_C$$

$$rate \quad rxn4(bwd) = k_5 C_{I_2}$$

$$rate \quad rxn5 = k_6 C_{R_3} C_C$$

$$rate \quad rxn6 = k_7 C_{Cat}$$

where all concentrations are in mol/m^3 and the rates in $mol/m^3.hr$.

The rate constants are of the Arrhenius form, with the pre-exponential factors and activation energies given in Table B.6. (Charalambides, 1996).

	Pre-exponential Factor	Activation Energy
k_1	2.7E+8	18700.0
k_2	3.63E+3	10900.0
k_3	4.4E+14	24700.0
k_4	1.29E+2	7700.0
k_5	2.64E+13	21800.0
k_6	1.0	0.0
k_7	5.0E-1	0.0
k_8	7.0E-4	0.0

Table B.6: Reactor network: Reaction data

External cooling system

The cooling jacket in the reactor vessel has a surface area of 7.2 m^2. An overall heat transfer coefficient of 5088.16 $kW/m^2.K$ is assumed for the heat transfer between the reaction mixture and the cooling water. The inlet temperature of the cooling water is 293 K with a constant specific heat capacity of 4200.0 $J/kg.K$.

Enthalpy and specific volume

The ideal gas specific enthalpy ($J/kmol.K$) is calculated using equation (B.11) at a reference temperature of 298.3 K. Table B.7 provides the values of the relevant coefficients (Charalambides, 1996).

B.4. Case Studies of Chapter 8 (section 8.2)

Physical properties

Table B.8 includes all the physical properties data used in the three case studies (Charalambides, 1996).

	$R1$	$R2$	$R3$	I_1
Coefficient	Specific Heat Capacity $(J/kmol.K)$			
a	-29644.0	-1105.3	21152.0	-657.0
b	783.51	314.64	70.924	961.38
c	-0.57862	-0.20319	0.02587	-0.5602
d	0.17853E-03	0.53214E-04	0.16647E-04	0.12E-03
	Specific Volume (dm^3/mol)			
	0.07614	0.13578	0.0435	0.13591
	Mean Molecular Weight (g/mol)			
	58.08	134.33	32.042	18.015

	I_2	A	C	S
Coefficient	Specific Heat Capacity $(J/kmol.K)$			
a	-6784.0	-20884.0	-0.13542E+06	-24355.0
b	1941.7	1400.3	1522.7	512.46
c	-1.1714	-0.9224	-1.4824	0.27654
d	0.26E-03	0.24E-03	0.62E-03	0.49111E-04
	Specific Volume (dm^3/mol)			
	0.19257	0.13159	0.11833	0.43351
	Mean Molecular Weight (g/mol)			
	250.48	158.24	383.80	366.72

Table B.7: Reactor network: Enthalpy and specific volume data

i	A	B	C	D
Vapour Pressure (Pa): $\ln P_i^0 = -\frac{a}{T} + b$				
a	3881.88	3874.56	4142.75	4543.71
b	9.9915	9.9404	11.58	11.2599
Liquid Phase Specific Enthalpy $(kJ/kmol)$: $h_k^v = \int_{T_{ref}}^{T} \alpha dT \quad \forall k$				
α	200.0	160.0	172.3	155.0
Enthalpy of Vaporisation ($kJ/kmol$)				
	26000.0	28000.0	31000.0	34000.0
Density $(kmol/m^3)$				
	11.0	11.0	11.0	11.0

Table B.8: Reactor-separator network: Physical property data

A reference temperature of 296 K is used in the calculation of the liquid and vapour specific enthalpies of the pure components.

Reaction kinetics

$$main \quad reaction \quad rate = k_1 C_A C_B \quad (kmol/hr.m^3) \tag{B.22}$$

$$side \quad reaction \quad rate = k_2 C_C \quad (kmol/hr.m^3) \tag{B.23}$$

where C_A, C_B and C_C are the concentrations $(kmol/m^3)$ of components A, B and C respectively.

The kinetic rate constants are of the Arrhenius form:

$$k_1 = 350.0e^{\frac{-20000}{R_g T}} \tag{B.24}$$

$$k_2 = 150.0e^{\frac{-20000}{R_g T}} \tag{B.25}$$

where T is the reaction temperature (K) and R_g the universal gas constant (8.314 $kJ/kmol.K$). The enthalpy of reaction for reaction (B.24) and reaction (B.25) are -60000 and -50000 $kJ/kmol$ respectively.

External cooling system

The cooling jacket in the reactor vessel has a surface area of 50 m^2. An overall heat transfer coefficient of 5088.16 $kW/m^2.K$ is assumed for heat transfer between the reacting mixture and the cooling water. The inlet temperature of the cooling water is 288 K with a constant heat capacity of 4200.0 $kJ/te.K$.

Appendix C

Summary of Results for Case Studies

This Appendix provides the summary tables of the optimal values/variations of the decision variables for our case studies.

C.1. Case Studies of Chapter 4

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Processing time (hr)	Time invariant parameter	0.500	20	6.229
Number of trays	Time invariant parameter	10	25	19
Vapour flow ($kmol/hr$)	Time invariant parameter	2.00	2.90	2.90
Reflux ratio	Control variable	0.75	0.99	[(1.582, 0.81), (1.544, 0.92), (0.250, 0.85), (1.199, 0.82), (1.231, 0.89), (0.423, 0.84)]

Table C.1: Batch distillation example 1: Results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Processing time (hr)	Time invariant parameter	2	50	13.31
Number of trays	Time invariant parameter	70	100	81
Vapour flow ($kmol/hr$)	Control variable	2.5	4.0	[(0.51, 4.0), (7.41, 4.0), (4.89, 4.0), (0.50, 3.4)]
Reflux ratio	Control variable	0.5	1.0	[(0.51, 1.0), (7.41, 0.92), (4.89, 0.94), (0.50, 0.90)]

Table C.2: Batch distillation example 2: Results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Column I				
Processing time (hr)	Time invariant parameter	0.50	10	2.47
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Number of trays	Time invariant parameter	6	15	7
Vapour flow ($kmol/hr$)	Control variable	12.5	20.0	[(2.47, 20.0)]
Reflux ratio	Control variable	0.70	0.99	[(2.47, 0.70)]
Column I				
Processing time (hr)	Time invariant parameter	0.50	10	0.75
Idle time (hr)	Time invariant parameter	0.0	20	4.55
Number of trays	Time invariant parameter	6	15	8
Initial charge ($kmol$)	Time invariant parameter	15	45	15.71
Vapour flow ($kmol/hr$)	Control variable	12.5	20.0	[(0.04, 12.5), (0.05, 19.1), (0.37, 18.9), (0.29, 19.9)]
Reflux ratio	Control variable	0.70	0.99	[(0.04, 0.99), (0.05, 0.70), (0.37, 0.70), (0.29, 0.70)]

Table C.3: Batch distillation example 3: Results

C.2. Case Study of Chapter 5

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Jacketed reactor				
Processing time (hr)	Time invariant parameter	0.75	9.0	1.86
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.5	18	5.648
Initial charge B ($kmol$)	Time invariant parameter	0.5	18	4.718
Initial charge $I3$ ($kmol$)	Time invariant parameter	2.0	35	7.927
Volume (m^3)	Time invariant parameter	1.25	2.25	1.50
Cooling water (te/hr)	Control variable	0.0	2.0	[(0.70, 0.0), (0.20, 0.29), (0.35, 0.66), (0.61, 1.88)]
Plain reactor				
Processing time (hr)	Time invariant parameter	0.75	9.0	1.95
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge E ($kmol$)	Time invariant parameter	0.5	14	6.341
Initial charge $I1$ ($kmol$)	Time invariant parameter	2.0	35	19.072
Volume (m^3)	Time invariant parameter	2.0	3.50	2.50
Distillation column				
Processing time (hr)	Time invariant parameter	0.75	9.0	0.97
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge ($kmol$)	Time invariant parameter	5.0	95	16.980
Reboiler volume (m^3)	Time invariant parameter	1.25	4.25	1.25
Reboiler load (MJ/hr)	Control variable	550	1050	[(0.97, 1050)]
Reflux ratio	Control variable	0.60	0.99	[(0.36, 0.60), (0.10, 0.63), (0.19, 0.69), (0.32, 0.87)]

Table C.4: Batch process design with discrete equipment sizes: Results

C.3. Case Studies of Chapter 7

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Jacketed reactor				
Processing time (hr)	Time invariant parameter	0.75	7.50	2.16
Idle time (hr)	Time invariant parameter	0.0	18	0.01
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	10.84
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	4.68
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	7.97
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.28
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(1.00, 1.0), (0.32, 0.22), (0.46, 1.0), (0.37, 0.33)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(1.00, 0.0), (0.32, 1.0), (0.46, 1.0), (0.37, 0.34)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(1.00, 0.91), (0.32, 2.91), (0.46, 0.0), (0.37, 1.72)]
Volume (m^3)	Time invariant parameter	1.875	3.785	2.404
Cooling water (te/hr)	Control variable	0.0	8.0	[(1.00, 1.26), (0.32, 1.41), (0.46, 0.0), (0.37, 1.95)]
Plain reactor				
Processing time (hr)	Time invariant parameter	0.75	9.0	3.67
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	4.65
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	27.24
Volume (m^3)	Time invariant parameter	1.875	3.785	3.781

Table C.5: Reactor networks: Base case results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	7.50	0.75
Idle time (hr)	Time invariant parameter	0.0	18	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	3.87
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	1.65
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	1.37
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	0.58
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.07
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	27.77
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(0.23, 1.0), (0.18, 1.0), (0.23, 0.69), (0.11, 0.31)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(0.23, 1.0), (0.18, 0.0), (0.23, 0.06), (0.11, 0.0)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(0.75, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	3.785	3.785
Cooling water (te/hr)	Control variable	0.0	8.0	[(0.23, 0.0), (0.18, 0.65), (0.23, 1.29), (0.11, 0.90)]
Jacketed reactor II				
Processing time (hr)	Time invariant parameter	0.75	9.0	3.08
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	0.0
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	0.88
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	10.66
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	0.0
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.38
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	16.82
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(3.08, 0.0)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(3.08, 0.0)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(3.08, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	3.785	2.484
Cooling water (te/hr)	Control variable	0.0	8.0	[(2.618, 0.0), (0.462, 0.88)]

Table C.6: Reactor networks: Case 1 results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value/ variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	7.50	0.75
Idle time (hr)	Time invariant parameter	0.0	18	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	5.45
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	2.57
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	0.41
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	1.01
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.07
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	30.0
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(0.38, 0.98), (0.11, 0.99), (0.15, 0.01), (0.11, 0.67)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(0.38, 0.76), (0.11, 0.78), (0.15, 0.0), (0.11, 0.0)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(0.75, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	5.375	5.075
Cooling water (te/hr)	Control variable	0.0	8.0	[(0.38, 0.0), (0.11, 0.0), (0.15, 3.0), (0.11, 4.0)]
Jacketed reactor II				
Processing time (hr)	Time invariant parameter	0.75	9.00	3.43
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	0.64
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	1.49
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	11.83
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	0.0
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	1.18
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	20.16
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(3.43, 0.0)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(3.43, 0.0)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(3.43, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	5.375	3.569
Cooling water (te/hr)	Control variable	0.0	8.0	[(1.72, 0.00), (0.52, 0.07), (0.68, 0.00), (0.51, 1.36)]

Table C.7: Reactor networks: Case 2 results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	7.50	0.75
Idle time (hr)	Time invariant parameter	0.0	18	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	5.37
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	2.44
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	0.36
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	0.93
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.34
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	27.61
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(0.37, 1.0), (0.15, 1.0), (0.12, 0.02), (0.11, 1.0)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(0.37, 0.98), (0.15, 0.79), (0.12, 0.03), (0.11, 0.02)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(0.75, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	5.375	4.785
Cooling water (te/hr)	Control variable	0.0	8.0	[(0.37, 0.0), (0.15, 0.0), (0.12, 3.11), (0.11, 5.87)]
Jacketed reactor II				
Processing time (hr)	Time invariant parameter	0.75	9.0	3.78
Idle time (hr)	Time invariant parameter	0.0	20	0.0
Initial charge R_1 ($kmol$)	Time invariant parameter	0.0	30	0.77
Initial charge R_2 ($kmol$)	Time invariant parameter	0.0	30	1.74
Initial charge R_3 ($kmol$)	Time invariant parameter	0.0	20	13.38
Initial charge S ($kmol$)	Time invariant parameter	0.0	30	0.04
Initial charge Cat (dm^3)	Time invariant parameter	0.0	30	0.78
Initial charge $Int1$ ($kmol$)	Time invariant parameter	0.0	45	21.08
Addition R_1 ($kmol/hr$)	Control variable	0.0	1.0	[(3.78, 0.0)]
Addition R_2 ($kmol/hr$)	Control variable	0.0	1.0	[(3.78, 0.0)]
Addition Cat (dm^3/hr)	Control variable	0.0	500	[(3.78, 0.0)]
Volume (m^3)	Time invariant parameter	1.875	5.375	3.875
Cooling water (te/hr)	Control variable	0.0	8.0	[(3.21, 0.0), (0.57, 1.35)]

Table C.8: Reactor networks: Case 3 results

C.4. Case Studies of Chapter 8

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	9.0	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	5.28
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	4.41
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	6.81
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Addition B ($kmol/hr$)	Control variable	0.0	1.0	[(0.75, 0.0)]
Volume (m^3)	Time invariant parameter	1.50	2.75	1.50
Cooling water (te/hr)	Control variable	0.0	5.0	[(0.40, 0.0), (0.18, 2.76), (0.09, 3.67), (0.08, 4.76)]
Distillation column I				
Processing time (hr)	Time invariant parameter	0.75	9.50	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	20.28
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Reboiler volume (m^3)	Time invariant parameter	1.00	8.00	1.84
Reflux ratio	Control variable	0.70	0.99	[(0.08, 0.74), (0.32, 0.70), (0.18, 0.78), (0.09, 0.87), (0.08, 0.79)]
Reboiler load (kJ/hr)	Control variable	550	1200	[(0.75, 1200)]
Jacketed reactor II				
Processing time (hr)	Time invariant parameter	0.75	9.0	1.17
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	1.54
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	4.79
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	9.30
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Addition B ($kmol/hr$)	Control variable	0.0	1.0	[(1.17, 0.0)]
Volume (m^3)	Time invariant parameter	1.50	2.75	1.50
Cooling water (te/hr)	Control variable	0.0	5.0	[(0.92, 0.00), (0.13, 1.77), (0.12, 4.77)]
Distillation column II				
Processing time (hr)	Time invariant parameter	0.75	9.50	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	12.91
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Reboiler volume (m^3)	Time invariant parameter	1.00	8.00	1.17
Reflux ratio	Control variable	0.70	0.99	[(0.08, 0.96), (0.32, 0.70), (0.18, 0.82), (0.09, 0.95), (0.08, 0.70)]
Reboiler load (kJ/hr)	Control variable	550	1200	[(0.08, 550), (0.32, 568), (0.18, 1102), (0.09, 1127), (0.08, 550)]

Table C.9: Reactor-separator networks: Case study 1 results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	9.0	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	5.55
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	4.51
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	6.43
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Addition B ($kmol/hr$)	Control variable	0.0	1.0	[(0.08, 0.14), (0.67, 0.0)]
Volume (m^3)	Time invariant parameter	1.50	2.75	1.50
Cooling water (te/hr)	Control variable	0.0	5.0	[(0.37, 0.0), (0.19, 2.72), (0.08, 1.03), (0.11, 5.00)]
Distillation column I				
Processing time (hr)	Time invariant parameter	0.75	9.50	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	20.19
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Reboiler volume (m^3)	Time invariant parameter	1.00	8.00	1.84
Reflux ratio	Control variable	0.70	0.99	[(0.08, 0.81), (0.29, 0.70), (0.19, 0.76), (0.07, 0.84), (0.12, 0.81)]
Reboiler load (kJ/hr)	Control variable	550	1200	[(0.75, 1200)]
Jacketed reactor II				
Processing time (hr)	Time invariant parameter	0.75	9.0	1.07
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	1.63
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	5.18
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	9.68
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Addition B ($kmol/hr$)	Control variable	0.0	1.0	[(1.07, 0.0)]
Volume (m^3)	Time invariant parameter	1.50	2.75	1.50
Cooling water (te/hr)	Control variable	0.0	5.0	[(0.79, 0.0), (0.11, 0.07), (0.17, 5.0)]
Distillation column II				
Processing time (hr)	Time invariant parameter	0.75	9.50	0.75
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_3 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_4 ($kmol$)	Time invariant parameter	0.0	45	15.28
Initial charge I_5 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_6 ($kmol$)	Time invariant parameter	0.0	45	0.0
Reboiler volume (m^3)	Time invariant parameter	1.00	8.00	1.39
Reflux ratio	Control variable	0.70	0.99	[(0.08, 0.99), (0.29, 0.72), (0.19, 0.84), (0.07, 0.97), (0.12, 0.80)]
Reboiler load (kJ/hr)	Control variable	550	1200	[(0.08, 550), (0.29, 1061), (0.19, 1200), (0.07, 1022), (0.12, 550)]

Table C.10: Reactor-separator networks: Case study 2 results

Decision variable	Time invariant parameter/ Control variable	Lower bound	Upper bound	Optimal value variation [(duration (hr), value)]
Jacketed reactor I				
Processing time (hr)	Time invariant parameter	0.75	9.0	1.12
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	8.23
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	7.50
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	0.0
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	9.32
Addition B ($kmol/hr$)	Control variable	0.0	1.0	[(0.12, 0.17), (0.39, 0.04), (0.607, 0.0)]
Volume (m^3)	Time invariant parameter	1.500	2.750	2.275
Cooling water (te/hr)	Control variable	0.0	9.0	[(0.12, 0.0), (0.39, 0.0), (0.33, 1.45), (0.13, 1.13), (0.15, 9.0)]
Distillation column I				
Processing time (hr)	Time invariant parameter	0.75	9.50	1.00
Idle time (hr)	Time invariant parameter	0.0	16	0.0
Initial charge A ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge B ($kmol$)	Time invariant parameter	0.0	14	0.0
Initial charge I_1 ($kmol$)	Time invariant parameter	0.0	45	26.37
Initial charge I_2 ($kmol$)	Time invariant parameter	0.0	45	0.0
Reboiler volume (m^3)	Time invariant parameter	1.500	3.000	2.397
Reflux ratio	Control variable	0.70	0.99	[(0.10, 0.70), (0.34, 0.70), (0.30, 0.70), (0.12, 0.77), (0.14, 0.78)]
Reboiler load (kJ/hr)	Control variable	550	1200	[(1.00, 1200)]

Table C.11: Reactor-separator networks: Case study 3 results

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