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Development of a methodology for batch process waste minimisation

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Development of a Methodology for Batch Process Waste Minimisation

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Summary

The current UK regulations require the operator of a new chemical process to demonstrate that the chosen design is the Best Practicable Environmental Option (BPEO) and to implement the Best Available Techniques Not Entailing Excess Cost (BATNEEC). Therefore, the designer not only needs to provide a process design that is economically viable but that also complies with environmental regulations.

This thesis presents the development of a structured design methodology that combines process design, pollution prevention and environmental assessment specifically for batch processes. The Douglas design methodology is used as a basis of this methodology. New design questions are introduced for designing batch processes and considering environmental effects. Additionally, a new design level is required to consider the design of cleaning systems.

In addition to formulating the process design questions the work described in this thesis has extended the cost estimation techniques. In extending the methodology new factors that are particularly important to batch process design are introduced to estimate the flowsheet costs. The designer must also assess whether the design is BPEO. Therefore, the environmental impact of the releases from the process must be assessed. In the revised methodology this is accomplished by using an environmental process performance tool (EPPT) to determine an EPPT score as described by Aubrey [1].

In order to assess whether the design methodology developed in this thesis can be successfully applied to batch processes it is tested using two operating processes. This is achieved using simulations and models of two operating batch processes. The first is a process manufacturing Pepton operated by Thomas Swan and the second case study is a process manufacturing Polyvinyl Chloride operated by European Vinyls Corporation.

The resulting revised methodology provides a structured design methodology for designing inherently clean and economic batch processes by implementing waste minimisation.

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Glossary

4NDPA	4 nitrodiphenylamine
BATNEEC	Best Available Technologies Not Entailing Excessive Cost
BDK	Batch Design Kit
BPEO	Best Practicable Environmental Option
BUS	Build-Up Suppressant
BT	Benzothiazole
CFC	Chlorofluorocarbon
CIP	Cleaning In Place
DEA	Diethyl amine
EA	Environment Agency
EC	European Community
EI	Economic Instruments
EMAS	Eco Management Audit Scheme
ENVOP	Environmental Optimisation
EP	Economic Potential
EPA	US Environmental Protection Agency
EPA (90)	UK Environmental Protection Act (1990)
EPPT	Environmental Process Performance Tool
EU	European Union
EVC	European Vinyls Corporation
GMB	Graphical Mass Balance
HAZOP	Hazard and operability
HEN	Heat Exchange Network
HMIP	Her Majesties Inspectorate of Pollution
HP	High pressure
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
LCA	Life Cycle Assessment
LP	Low pressure
MEIM	Methodology for Environmental Impact Minimisation
MEN	Mass Exchange Network
MINLP	Multi Integer Non-Linear Programming
NRA	National Rivers Authority

NRTL	Non Random Two Liquid equation of state
Pepton	2,2' dibenzamino diphenyl disulphite
PHRED	Process Heuristic Review for Environmental Design
PR	Peng Robinson equation of state
PRSV	Peng Robinson Stryjek Vera equation of state
PVC	Poly Vinyl Chloride
S1 product	Stage 1 product, sodium 2-amino thiophenate
S2 product	Stage 2 product, 2,2' diamino diphenyl disulphite
SRK	Soave Redlich Kwong
TAM	Time Average Model
TSM	Time Slice Model
UNIFAC	Uniquac Functional Group Activity Coefficients Method
UNIQUAC	Universal Quasi Chemical
US	United States
VCM	Vinyl Chloride Monomer
VOC	Volatile Organic Compound
WAR	Waste Reduction computer algorithm

Table of nomenclature

ρ	density of PVC deposit
ρ_g	density of vapour stream
a	rate of deposit build-up
A	surface area of vessel
b	effectiveness of cleaning
c	change in effectiveness of cleaning
C_1	cost of standard heat exchanger
C_2	cost of required heat exchanger
C_d	value of lost product per year
C_{ej}	total cost of energy used for jet cleaning
C_{er}	total cost of energy used for intermediate cleaning
c_{jc}	cost of one jet cleaning operation
C_j	total cost jet cleaning
C_{jc}	total cost jet cleaning contractors
c_r	cost of rinsing water
C_r	total cost intermediate rinsing
C_t	total cost of cleaning operations
c_{vcm}	estimated cost of recovering VCM per jet clean
C_{vcm}	total cost of removing VCM from the vessel
c_w	cost of water
C_{wj}	total cost of water used for jetting
C_{wr}	total cost of water used for intermediate cleaning
e_{hp}	cost of the energy used for high pressure cleaning cycle for one reactor
e_j	cost of the energy used for jet cleaning one reactor
e_{lp}	cost of the energy used for low pressure cleaning cycle for one reactor
F_j	volumetric flowrate of water used during jet cleaning
F_r	volumetric flowrate of water used for intermediate cleaning
L_R	actual level/maximum level
m_g	mass flow of vented material
m_R	actual mass flow/maximum mass flow
M	total mass of material vented
n	number of batches completed
n_f	number of batches in one campaign
n_{nc}	number of batches in one campaign with no intermediate cleaning.
N	number of campaigns in a year
p	amount of product per batch
p_A^{ϕ}	vapour pressure of material A
P	total amount of product per year

P_R	actual pressure/maximum pressure
P_T	Total pressure in vessel
q_1	surface area of standard heat exchanger
q_2	surface area of required heat exchanger
R	number of reactors
t_c	total batch cycle time; sum of operating and cleaning times
t_d	time for deposit build-up i.e. batch operating time
t_j	time for jet cleaning
t_R	actual time/maximum time
t_r	time for deposit removal i.e. intermediate cleaning time
T_R	actual temperature/maximum temperature
T_r	total cleaning time per campaign
t_{sd}	total time shutdown for maintenance in each campaign
T_{sd}	time for annual shutdown
v_g	vapour volume flow from vessel
v_l	liquid volume flow into vessel
V	value of product
V_p	total value of product produced
v_R	actual vapour flow /maximum vapour flow
V_t	volume of liquid required in vessel
w_j	volume of water used for jetting per year
w_r	volume of water used for intermediate rinsing per year
W	total volume of water used per year
x_{d1}	deposit thickness after 1 batch
x_{dn}	deposit thickness after n batches
x_i	liquid composition
x_{r1}	deposit remaining after 1 batch
x_{rn}	deposit remaining after n batches
X_t	final deposit thickness at shutdown for jetting
X_{ta}	actual deposit thickness at shutdown for jetting
y_i	vapour composition
z	cost exponent for type of heat exchanger

Chapter One

Introduction

1.1 Historical background

1.1.1 Legislation

In the UK the history of environmental regulation of major process industries started in 1874 with the Alkali Works Act which addressed the problems of hydrochloric acid manufacture. Since then the ranges and types of industry have increased substantially and so has their potential to pollute the environment. As a result there has been an increase in the amount of environmental legislation to control the emissions from these industries. A detailed discussion of the development of environmental regulation can be found in Croner's Environmental Management [2].

Recently the UK has entered a new regulatory framework with the Environmental Protection Act 1990 (EPA 90). This has moved from an entirely prescriptive framework towards a consultative procedure between industry, the government and local people to achieve environmental improvements. As part of this Act the Integrated Pollution Control (IPC) system was introduced which applies to the release of pollutants to air, water and land [3]. There are two principles that are encompassed by the Act: BPEO (Best Practicable Environmental Option) and BATNEEC (Best Available Techniques Not Entailing Excessive Cost). The aim is to achieve BPEO by implementing BATNEEC in the design and operation of the process. Environmental improvements are timetabled and industry's waste production is continually reappraised. A technical guidance note has been published by the Environment Agency detailing the assessment of BPEO and BATNEEC [4]. It has been suggested that this approach is more likely to generate novel and alternative processes than the historically prescriptive approach [5]. However, the regulations still encourage "end-of-pipe" solutions because companies are only fined if their emissions are above a certified level and reducing wastes below this level is not rewarded.

An alternative approach to encourage the development of cleaner technologies is the use of economic instruments (EIs), whereby charges such as landfill taxation are introduced to encourage recycling. Tradable pollution permits can also be introduced to enable companies to sell their pollution rights, thereby providing an incentive for reducing pollution. However, in reality EIs are still found to be leading to the use of "end-of-pipe" solutions and have not increased the implementation of cleaner technologies [5].

There has been a shift from single medium legislation such as the UK Clean Air Act (1956) to multimedia approaches as in EPA 90 which covers emissions to air, water and land. In 1996 the UK moved closer towards the multimedia approach by the implementation of the Environment Act (1995). In this Act Her Majesty's Inspectorate of Pollution (HMIP), the National Rivers Authority (NRA) and local authority waste regulators were merged to form the Environmental Agency (EA) that deals with all aspects of pollution except radioactive wastes.

There has also been a realisation that environmental problems do not recognise national boundaries and international agreements are required to attack many environmental problems. The UK signed the Convention on Long Range Transboundary Air Pollution in 1979 [6], which has so far agreed on two sulphur and one nitrogen protocols. In order to protect the ozone layer, the use of chlorofluorocarbons (CFC's) has been limited by the Montreal Protocol, agreed at the Vienna Convention in 1985 [7, 8]. The Framework Convention for Climate Change signed by 150 countries at the Rio Earth Summit in 1992 has attempted to introduce global limits on the amount of carbon dioxide produced [9]. However, the recent Earth +5 Summit in New York, June 1997, showed that little advance towards this goal has been achieved due to political and cultural barriers.

Finally, there is a move towards sustainable development starting with the United Nations' Brundtland Commission, 1987, which introduced the concept [10]. More recently, the Rio Earth Summit in 1992 provided a forum for nations to discuss sustainability and global action for the environment. The Earth Summit +5 showed that success has been limited and political and cultural barriers are still preventing agreements on sustainability from being reached.

Future regulation in the UK is likely to be directed increasingly by the European Union. The proposed Integrated Pollution Prevention and Control Directive (IPPC) has recently passed its second reading in the European Parliament [11]. It is an extended form of IPC and encompasses much of the UK philosophy. However, it is likely to cover 5000 more processes than IPC presently does, including intensive food farming, food and drink, sewage works, landfill sites, mineral processes and chemical industries using more than 150 kg/hr or 200 te/yr of solvents [12]. The Directive also introduces the idea of sustainability and broadens pollution prevention to include resource conservation, energy efficiency, waste minimisation and the environment as a whole [13]. The scope of pollution is also to be widened to include noise, vibration and heat. In addition there is the proposed introduction of a statutory chemical release inventory.

1.1.2 Environmental issues

Public knowledge and concern about environmental issues has increased substantially in the past few decades. Often extreme occurrences have prompted a surge in media interest and a rise in the profile of the issue. This has long been a driving force for government regulation. In 1952 the death of 4000 people in London due to smog prompted the government to introduce the Clean Air Act. In 1971 the effects of acid rain were widely publicised and subsequently, became high on the environmental agenda. Also in the 1970's scientists detected the developing hole in the ozone layer and indicated the direct effect this would have on people. During the hot summer of 1976 the effect of high concentrations of ozone at ground level on breathing difficulties became apparent [5]. Recently, the increase in so called green house gas emissions has raised concern over the rise in the earth's temperature. In all these areas research is being carried out and it is still not certain whether anthropogenic activities are responsible for these effects and whether the results will be as disastrous as predicted. However, the current thinking is precautionary and as discussed in the previous section actions are being taken to counteract these effects. It is considered that action can not be delayed until the actual causes are defined because then it may be too late to reverse the effects.

Government regulation has followed public and media concern for the environment. Consideration of public opinion is likely to allow companies to pre-empt new regulations and allow them to achieve licences to operate more easily.

1.1.3 The chemical industry

The chemical industry is perceived by the public to be one of the major culprits for pollution generation and it is imperative that public confidence is retained to obtain the "licence to operate". Publication of IPC applications and emissions data has meant that there is more public scrutiny of industry's operations than in previous years. Therefore, the pressures on industry to reduce pollution are large and are likely to increase in the future.

1.2 Aims and objectives

As a result of the Integrated Pollution Control (IPC) regulations and increased public concern described in Section 1.1 waste minimisation and environmental considerations have become more important to the designer of chemical processes and plant. The waste minimisation philosophy has a hierarchy of techniques, starting with the most attractive, source reduction. Therefore, waste minimisation needs to be considered during the design of a process to identify and solve potential environmental and waste problems at source.

The aim of this thesis is to present a methodology to enable a process designer to generate and assess a range of design options taking into account both environmental impact and cost criteria. The methodology focuses on batch operations which tend to produce more waste per unit product than continuous processes [14] and for which few formal design methodologies exist for examining the effect of the process on the environment.

The following objectives will be accomplished:

- To develop a design methodology that takes a structured approach to process design, that can be applied easily to batch processes and that can be used to produce economically and environmentally viable plants. The aspects identified as important to batch process design will need to be included in the design methodology to enable batch processes and waste production to be considered effectively.
- To test the methodology in order to assess whether it can be successfully applied to batch processes. This will be performed using simulations and models of two operating batch processes.
- To identify areas where future work is required to enhance the proposed design methodology.

1.3 Overview of the thesis structure

The overall structure of this thesis and the interaction between the chapters is shown in Figure 1.1. This section outlines the contents of each chapter.

In order to ensure that inherently clean process plants are developed process design, pollution prevention and the environment need to be considered. A review of the current techniques and research in these areas is presented in Chapter 2. This review focuses on combining the three aspects.

The aim of this thesis is to develop a design methodology that encompasses pollution prevention and consideration for the environment specifically for batch processes. Therefore, Chapter 3 presents a review of the existing design methodologies to assess whether they could used for batch process design and waste minimisation. As a result of this review the Douglas design methodology is selected as the basis for the design methodology. The Douglas methodology, which comprises a series of levels each dealing with increasingly more detailed design, is described in detail in Chapter 3.

The design methodology developed in this thesis is to be tested using two operating processes. The first is a process manufacturing Pepton operated by Thomas Swan and the description of the plant operations are provided in Chapter 4. The second case study is a process manufacturing Poly Vinyl Chloride operated by European Vinyls Corporation and the plant operations are described in Chapter 5.

Chapter 6 presents a discussion of general batch process characteristics and describes how batch operations differ from continuous processes. Potential waste production and environmental problems associated with batch processes are also discussed. A revised Douglas design methodology is subsequently presented and incorporates the areas highlighted as important to batch process design.

The next five chapters detail the alterations that have been made to several of the existing Douglas design levels. In the Douglas methodology questions are asked of the design at each level to guide the designer and to develop alternative flowsheets. Therefore, in revising the Douglas methodology new design questions will need be introduced to the existing levels. Additionally, a new design level is required to consider the design of cleaning systems. Thus the next five chapters are as follows:

- Chapter 7: Flowsheet input and output considerations.

- Chapter 8: Consideration of the reactor design and definition of the recycle streams. Several of the new questions are to be tested using the Thomas Swan case study detailed in Chapter 4.
- Chapter 9: Design of the separation system. The Thomas Swan case study is to be used to examine a batch distillation operation.
- Chapter 10: A new design level considering the design of the cleaning system. The EVC case study detailed in Chapter 5 is to be used to examine a cleaning operation.
- Chapter 11: Consideration of process integration and the design of the process schedule.

The final chapter, Chapter 12, presents the conclusions of this thesis and discusses areas where further work would enhance the methodology.

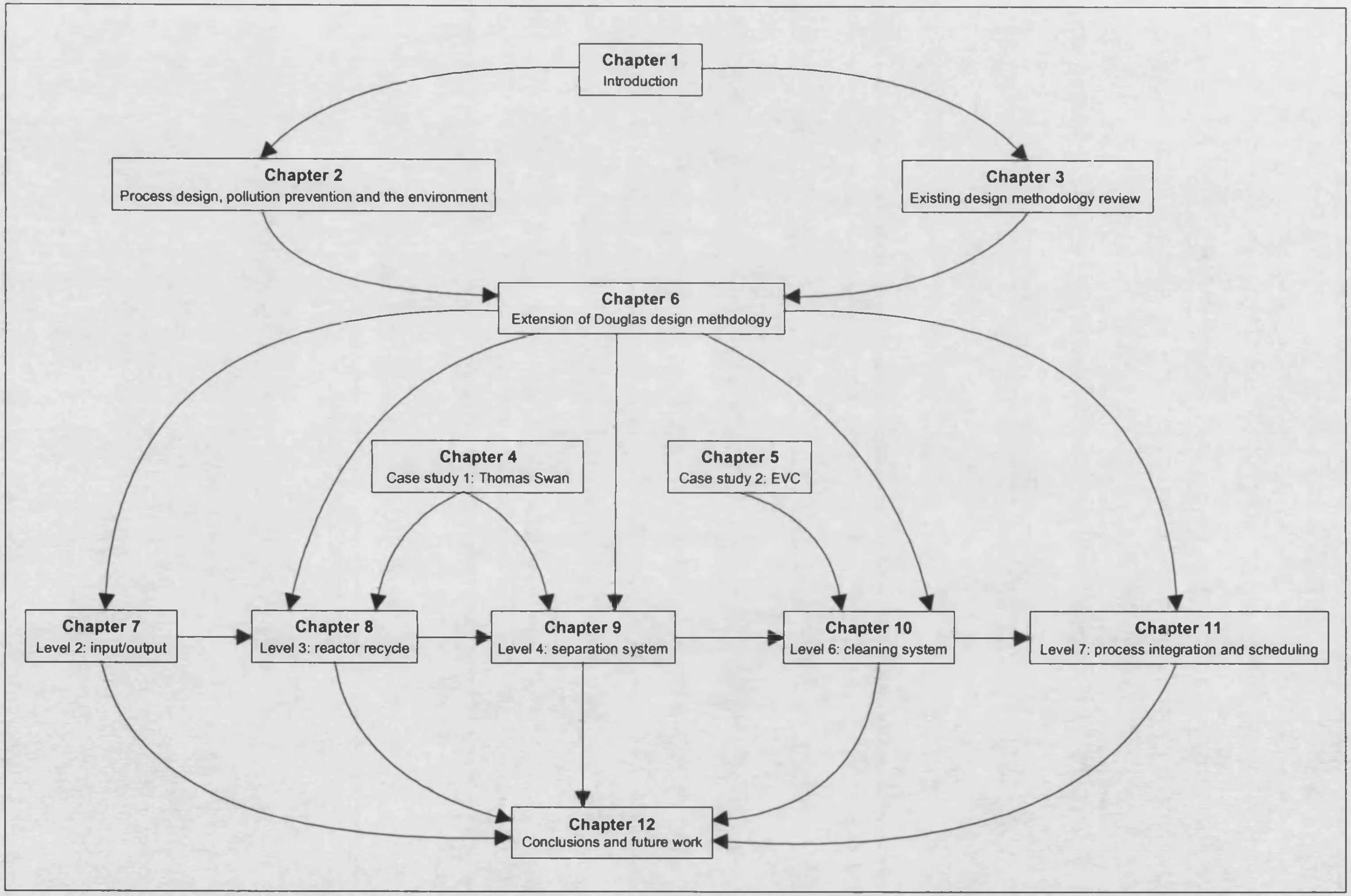


Figure 1.1: Overview of thesis structure

Chapter Two

Process Design, Pollution Prevention and the Environment

2.1 Introduction

Pollution prevention, waste minimisation and environmental considerations have become increasingly important in the design of new chemical plants. This has arisen due to increased regulation by government, increased pressure from the stakeholders and increased concern about the impact of industry on the environment. Consequently, the interest in process design, pollution prevention and the environment has progressed from the consideration of individual issues to overlapping and combining techniques and ideas. These relationships are shown Figure 2.1.

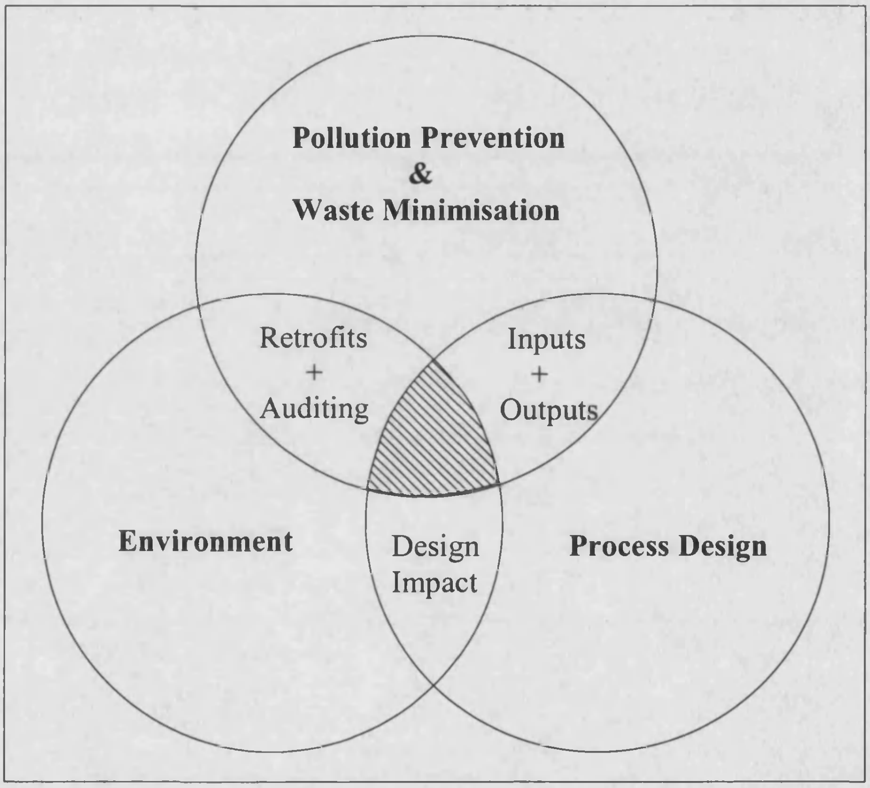


Figure 2.1: Relationship between process design, pollution prevention and the environment

Firstly, there is the task of designing the chemical process, wherein the engineer specifies the equipment requirements, defines the properties and quantities of the material and energy streams and outlines the plant operating procedures. The design is then assessed for cost and operability to ensure an appropriate and economic plant is built.

Secondly, as the issue of waste production has become more important to engineers, techniques have been developed to prevent pollution and minimise process wastes.

These have been shown to save companies money as well as benefiting the environment.

When waste production is considered during the design of the process potential problem wastes can be identified. The design can then be modified and the waste eliminated or reduced. This prevents pollution and can avoid the need for expensive end of pipe technologies. However, without consideration of the environment it is not possible to assess whether the environmental impact of the process is acceptable or whether more waste reduction measures are necessary. Also it is difficult to prioritise the waste minimisation options in terms of the most beneficial to the environment.

Therefore, the third issue considers the effect of the process on the environment. When included in the design stage it is possible to identify the potential environmental impact of the process. For existing plants waste minimisation can be used to identify retrofits that could improve the environmental performance of the process.

The area of most interest is the shaded area in Figure 2.1 where the three aspects overlap. At this point the process design is developed by considering the environmental impact as well as the plant economics and operability. Waste minimisation and pollution prevention techniques can be used to modify the process design to ensure the best practicable environmental option (BPEO) is selected.

This chapter briefly examines the work being performed in the three areas; process design in Section 2.2, pollution prevention and waste minimisation in Section 2.3 and the environment in Section 2.4. The last section discusses the work being done to combine the three issues. This highlights areas which have not been fully explored and hence provides the focus for this thesis. The aim is to give an overview of each subject rather than providing a comprehensive examination to place this thesis in context.

2.2 Process design

The first step in developing a new chemical process design is to identify a need for a new product or market. The engineer proceeds through a series of steps to design a plant that will fulfil this need often utilising computers to aid with the calculation load. To simplify the design procedure several structured design methodologies are available. Whilst designing a batch process there are factors that need to be accounted for to reflect the batch operating philosophy. Each of these points is discussed in the following sections.

2.2.1 The purpose of design

Chemical process design involves upgrading the value of materials by chemical or biological transformations. It is necessary for the designer, usually a chemical engineer, to create a design to fulfil a particular need. The needs may be those of the customer, the consumer or the market. The following reasons can fuel the need for a new plant design [15]:

- to produce a purchased raw material,
- to convert a waste by-product to a valuable material,
- to create a completely new material,
- to find an alternative way of producing a new product,
- to exploit a new technology,
- to exploit a new material of construction.

The growth of demand for new products has meant that over 50% of the products sold by most chemical companies were developed in the past two decades [15].

The actual development of a chemical plant design is a creative task. It is necessary to synthesise ideas to achieve the final goal i.e. the production of a particular material. There are likely to be a large number of possible designs and operations. Douglas [15] estimates that between 10^4 and 10^9 process alternatives exist to accomplish the same goal. Therefore, the design options must be reduced by applying design constraints. These come from both internal and external sources. The external constraints are those beyond the designer's control, whereas internal constraints are more flexible and can be varied [16]. Figure 2.2 shows some of the design constraints which the designer must work within.

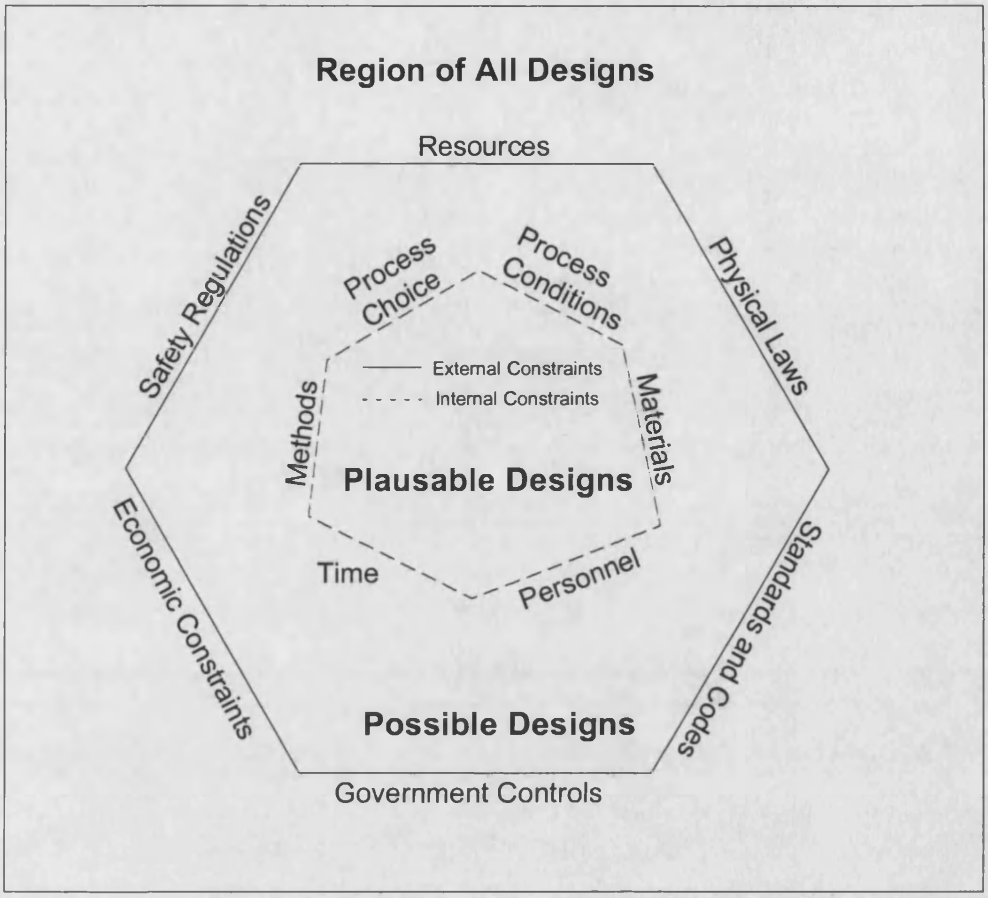


Figure 2.2: Design constraints [16]

By the end of the design procedure a designer should have considered many of the *possible* design options. *Plausible* design options which are within the project constraints will have been identified, evaluated and *probable* process designs decided upon. The development of the detailed design can then be performed and the optimum design selected. Hence the most profitable plant can be built and operated within the external and internal project constraints.

2.2.2 The main components of design

The development of a process progresses through a series of stages [17]:

- inception,
- preliminary evaluation and market,
- development of the data necessary for final design,
- final economic evaluation,
- detailed engineering design,
- procurement,
- construction,
- start-up and trial runs,
- production.

The design begins with a rough concept to fulfil the general objectives and ends up as a detailed, implementable plant. The early stage is usually screening of alternatives to decide which path the design will follow. It is necessary to carry out these first screening studies quickly and with limited information. However it is essential that they are reliable enough to screen out the unattractive options and retain the promising ones [18]. After the initial concept has been decided and the necessary data gathered, then detailed engineering can be started. Figure 2.3 shows the stages of a detailed design. It is important to note that the task is iterative and a design decision may have to be revised due to changes in the economics or operability of the plant. The designer needs to be aware of new data and ideas to evaluate the developing design.

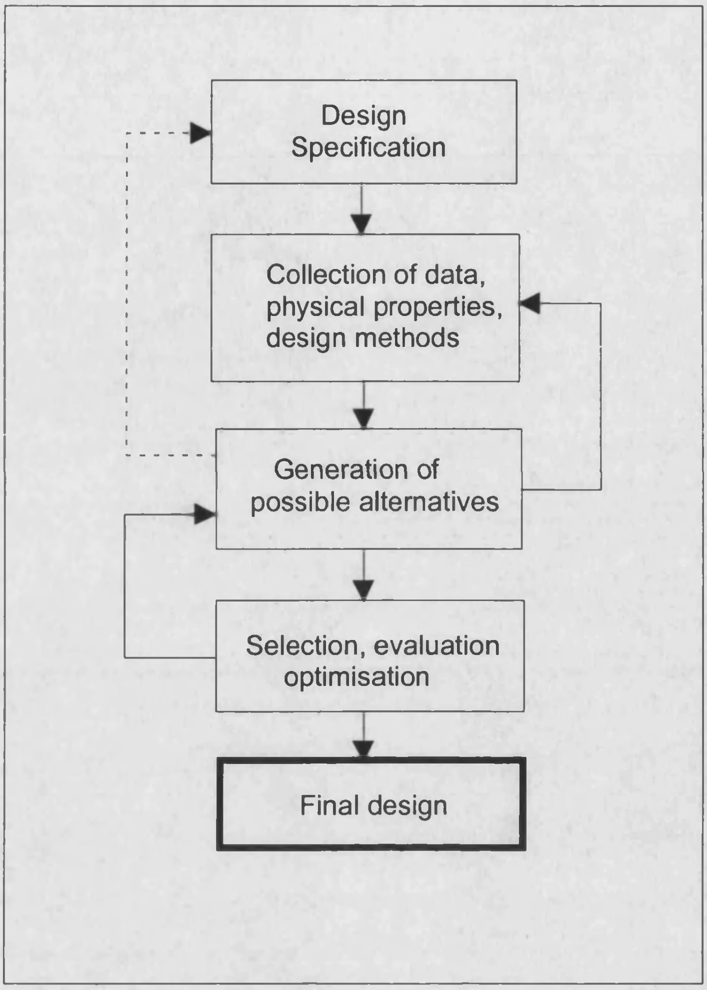


Figure 2.3: The detailed design process [16]

The basic components of a typical chemical process are shown in Figure 2.4. The actual content of the blocks will depend on the process. The designer needs to select and specify the equipment required to perform the stage functions.

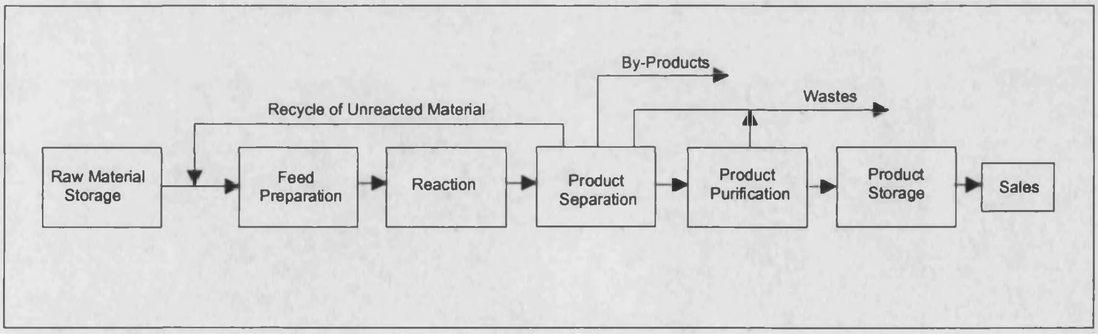


Figure 2.4: Anatomy of a chemical process [16]

The raw materials for the plant may have to be stored and transferred to the operations. In some cases the feed may need to be treated before being used to remove impurities that could cause problems in the reaction stages. For gas phase reactors liquid feeds would need to be vaporised. Solids may need to be crushed or ground.

The reaction stage is the central unit. The raw materials are converted into the required products and often by-products. After the reaction it is usually necessary to separate the valuable product from the unreacted materials and by-products. The unreacted material can be recycled and fed back into the reactor. The by-products can be sold, used in another process or may need to be disposed of.

The final product may need to go through further purification stages before being held in storage and sold.

As well as the major equipment items it is necessary to specify the utility requirements such as process water, cooling water, electricity and steam. The location of the plant, plant layout, auxiliary buildings, safety and waste disposal are also important factors to consider and may affect the economic viability of a design.

2.2.3 The use of computers for design

Designing a process plant is highly complex and calculation intensive. The development of computer programs to perform much of the calculation work has enabled more detailed analysis of processes to be carried out. The three main areas where computers have had a significant impact in process design are in process flowsheeting synthesis, performing flowsheeting calculations and the rigorous mathematical optimisation of a process design.

Process synthesis involves generating a flowsheet for a particular process, that is, to identify the unit operations required, their sequence and the material and energy streams. Process synthesis software is usually a system that defines the whole flowsheet and this type of software began to emerge in the late 1980's [17]. A review of some of these approaches is given in Kaunde [19] and Nishda [20].

The use of computers to perform flowsheeting calculations are more widespread and development started in the late 1950's [17]. These programs leave the design decisions to the engineer but perform the mass and energy balances, sizing of equipment and often costing calculations. The aim is to simulate the behaviour of the process by predicting the physical and chemical properties of materials and their interactions.

Process simulation packages can be divided into two different types: sequential modular and equation based. The sequential modular programs solve each process unit module by module. Iterative techniques are used to solve recycle streams. These are simpler to develop than the equation based systems but difficulties can occur with solving recycle loops. Also the conditions of the flowsheet are fixed in time and cannot be used to simulate a dynamic system. The equation based systems describe the process using a set of algebraic differential equations which are solved simultaneously. These can be used to simulate dynamic systems but require more computing power and time. Hybrid programs are also available that combine both these approaches by using the steady state calculations to define the starting point for solving the dynamic equations. Table 2.1 gives a selection of the major simulation packages available. Up to date information on developments in computer simulation packages can be found in the Chemputers section of the journal, Chemical Engineering.

Table 2.1: A selection of simulation packages [16, 21]

Program Name	Type of solution	Source
ASPEN/Plus Batch Plus SPEEDUP DynaPlus	S-M E-B	Aspen Technology Inc., USA
ChemCad REACTS	S-M	Coade/Chemstations, USA
Design II	S-M	WinSim Inc. USA
ESP [22]	E-B	OLI Systems Inc. USA
FLOWPACK	Hybrid	ICI, UK
HYSYS	Hybrid	AEA Technology
PROTISS [23]	Hybrid	Simulation Sciences, USA
*g*Proms [24]	E-B	Imperial College, UK
ProSim	S-M	Bryan Research, USA
Reaction	E-B	BatchCAD Ltd, UK

E-B = Equation Based, S-M = Sequential Modular

Once an accurate model of the process flowsheet has been developed it is then possible for the engineer to perform optimisation studies on the process parameters. The task of formal optimisation involving hundreds of variables is greatly simplified by the use of computers. However, it is still necessary to identify key process parameters for the program to work with. There are numerous researchers working on optimising both batch and continuous processes [25, 26, 27].

Another recent development is the use of computers to record the design history and the design rationale of a process so that it can be retrieved and examined at a later date [28, 29].

Future developments in computerised process design are likely to include using neural networks for optimisation [30] and movement towards distributed chemical manufacturing sites where the customers demands are met instantaneously [31].

2.2.4 Design of batch processes

Batch processing was probably the original form of chemical processing [32]. However, today most chemical plants are built to operate continuously on a large scale. Batch processing is used in the manufacture of small scale, value added products such as food, pharmaceuticals, polymers, agriculture additives and speciality chemicals.

Batch operations are usually chosen for low volume processes with complex reaction steps because there is little merit in designing, building and operating a dedicated plant. It is usually considered that a batch plant would be used to produce less than 500,000 tons/year [33]. As the plant is not designed for one purpose it is flexible and different products can be made in the same vessels. Therefore, batch processing is suitable for products with a short product life or changeable demand. Production can be started rapidly and a satisfactory product can be made with large uncertainties in design. Operational reasons may also lead to a batch design being the most appropriate. For example, a batch reactor is more suitable for a very slow reaction as the residence time can be easily extended. If the reaction is difficult to control then a batch process allows manual intervention and only one batch of material will be spoilt if the reaction becomes irregular. If fouling is a particular problem or regular inspection is required then the equipment may have to be shut-down regularly and easily accessed so a batch vessel is preferable.

Batch processes are designed to be started and stopped frequently. Therefore the operations are unsteady-state and process parameters will vary during the production cycle, whereas continuous processes operate at almost steady state conditions, twenty four hours a day, seven days a week, for most of the year. Therefore the main difference between designing a batch and a continuous process is the need to consider time variations and the dynamics of the process. The flexibility of batch process units introduces an added complication to the design as more than one operational step can be carried out in one vessel. In continuous operations the processing steps are attributed to a specific equipment item. Therefore, an additional design decision is required to allocate tasks to equipment items over specific intervals of time [32]. This involves plant scheduling which must be imbedded in the process design as decisions on the size and number of units will affect the schedule and vice-versa. An excellent review of scheduling operations is given in Reklaitis [34]. In designing a batch plant some of the issues to consider are the length of the cycle time and the capacity of the vessels. It may also be possible to merge or split tasks [35] or to install storage to smooth out the production cycle [36]. In conjunction with the scheduling the design of cleaning systems must also be considered.

The use of computers for the design and scheduling of batch processes is a developing area. Some general areas are vessel sizing [37], the design and optimisation of control systems [38], scheduling [34] and production optimisation [26, 27]. However, it is noted by Friedrich and Perne [39] that in industrial practice empirical methodologies are more often used due to a "lack of knowledge about reaction mechanisms and kinetics, availability of efficient software tools and restrictions that cannot be easily formalised".

2.2.5 Structured design methods

The complex design task is too large to be considered as a whole. It is necessary to break it down into smaller more manageable sections to allow the design to be built-up gradually. A method of doing this is a hierarchical system [15] which initially considers the simplest design level and adds successive layers of detail until the whole design is complete. This structured approach allows the engineer to have a full picture of the design and also the economics as these are calculated at each stage. Various structured design methodologies and their application are discussed in Section 3.1. However, it is important to note here that most of the techniques have been developed for continuous systems and that the methods for batch processing are limited [35].

2.3 Pollution prevention and waste minimisation

2.3.1 The reason for pollution prevention

"No new creation or destruction of matter is within the reach of any chemical agency" [40]. Therefore once waste is created it is only possible to move it between different media by treatment. Hence it is better to prevent or reduce waste at source. The importance of minimising waste is highlighted in the waste management hierarchy defined by the US Environmental Protection Agency (EPA) [41]. Here source reduction appears at the top of the list of current waste minimisation techniques as follows:

1. source reduction,
2. recycling,
3. waste separation,
4. energy and material recovery,
5. waste treatment and disposal,

6. waste treatment,
7. disposal.

The European Community have developed a similar framework as shown in Figure 2.5.

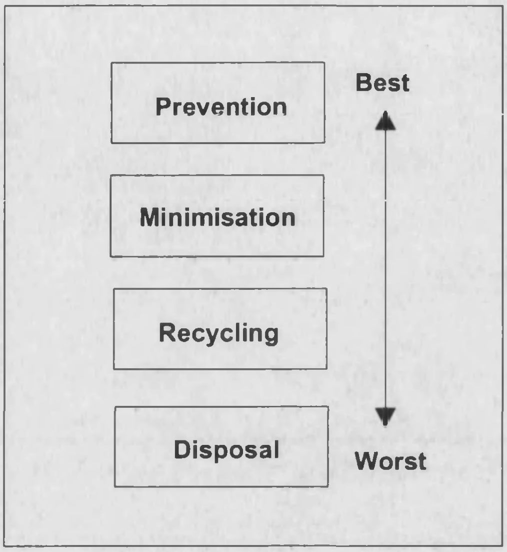


Figure 2.5: EC council hierarchy of waste management options [42]

Therefore the emphasis has shifted from "end of pipe" solutions, such as scrubbing systems and effluent treatment plants, which deal with waste treatment and disposal respectively, to methods of waste reduction at source.

Government regulation has been a major driving force for the acceptance of pollution prevention. Between 1985 and 1986 there was a 20% increase in the number of pages in the US Federal environmental regulations [43]. This was the largest increase in history resulting in the pressure on companies to minimise waste to increase. More stringent regulations requiring more effective effluent treatment have caused operating costs in the UK textiles industry to rise, in some cases, by a factor of ten [44]. The increasing threat of liability has also caused companies to become aware of site pollution [43].

Public knowledge and concern over environmental issues such as the greenhouse effect and ozone depletion, has increased greatly over the years. This is fuelled by media coverage and pressure from lobbying groups such as Greenpeace. The result has been to increase the pressure on industry to be clean. When proposing to build a new plant it is necessary to demonstrate that the emissions to the surrounding environment are minimised, otherwise the public backlash can be severe. Additionally, the competitiveness of a product or process can be affected by the perception of the environmental risk it represents.

For a company minimising wastes can also represent a reduction in operating costs in three ways;

- The wastes are produced from the raw materials requiring more to be purchased.
- The additional material has to be processed in the plant increasing the plant throughput and raising the demand for utilities. The size of the processing units will be larger requiring larger capital investment.
- The wastes have to be treated or disposed of.

So by reducing waste less money need be spent on raw materials, energy, utilities and disposal. It is also notable that the costs associated with controlling pollution are large and expected to rise due to more stringent regulations [45]. If wastes are minimised these costs could be reduced and the need for additional remediation equipment and technologies may be eliminated [46]. Money is also saved by a reduction in the costs of waste storage, waste transport and administrative paper work [47].

The scope for reducing wastes from the process industries is substantial as a review of the present UK waste production shows [48]. It is estimated that approximately 15% of the 400 million to 500 million tonnes a year of total waste are attributable to industry. The special wastes account for 2.5 million tonnes per year. Of these wastes 70% are sent to landfill and 5% are incinerated. Additionally, industrial liquid effluent is estimated to amount to 2000 million tonnes a year and the release of volatile organic compounds (VOC) to air is predicted to be 2.7 million tonnes each year.

2.3.2 Method of achieving pollution prevention and waste minimisation.

There are numerous techniques that have been developed to implement waste minimisation. These fit into three main categories [49]: macro-, meso-, and micro-scale solutions. In the macro-scale the interaction between industries is assessed. It may be possible to integrate different processes and industries so the waste from one is used by another [50, 51]. Ideally this results in a form of "industrial ecology" where the efficiency of the entire industrial system is improved. However, this technique is limited by the location of processes. Also the downstream process would be dependant on the flows from another company and the quantity and quality of the raw materials may fluctuate. At the second level, meso-scale problems are considered to improve the efficiency of the individual process and unit operations. Most of the techniques available today come under this category as a company has control over its operations and can benefit directly from the resulting waste minimisation. The design of chemicals and the choice of process routes is examined at the micro-scale. Here waste can be reduced by studying the reactions and the raw materials required. For example, improving the conversion or selectivity of a reaction by designing a specific catalyst.

Meso-scale and micro-scale methods for minimising the wastes from process operations are shown in Figure 2.6.

Waste reduction at source can be divided into four categories; good-housekeeping, technological changes, input material changes and product changes. Good-housekeeping involves improving the plant operating practices and procedures. These measures can usually be easily implemented with minimal cost and large effectiveness. The technological changes are retrofitting old processes to improve performance or designing new cleaner processes. Replacing raw materials, solvents, fuels or catalysts come under input material changes. It may also be possible to change the product or the intermediates to reduce the wastes or to allow recycling. Changing the product specification may enable wastes to be sold with the product or less raw material to be used.

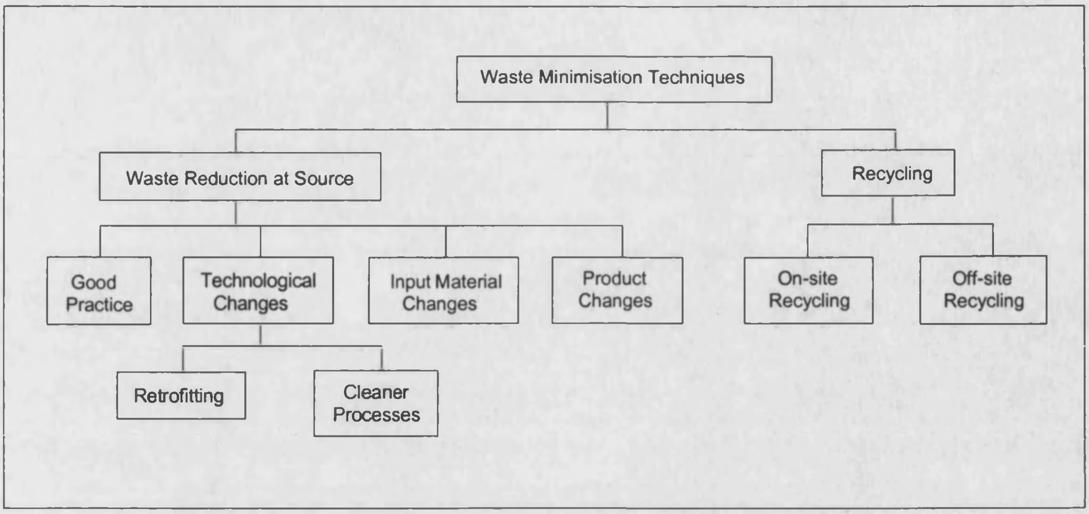


Figure 2.6: Practical waste minimisation techniques [47]

The use of recycling is less attractive than waste minimisation as energy and other raw materials are usually required. However, it can be used to recover resources and potentially reduce the overall environmental impact.

Figure 2.7 shows the relative cost and effectiveness of introducing different waste reduction measures. Good housekeeping is likely to be at the point where the graph is steepest i.e. a small investment will result in a large amount of waste being eliminated. For existing plants this is likely to be the first step in a waste minimisation project. After the initial high benefits the techniques generally become more expensive and the reductions in waste become less apparent. This may not be true for new plant designs where the design can be altered to be inherently clean and hence expensive waste minimisation techniques may not be required.

To perform a waste minimisation study it is necessary to form a team who will analyse the plant or design. Plant data must be gathered and assessed to identify potential pollution problems. The source of these problems, the hazards and magnitudes can be determined at this stage. Waste minimisation options can then be suggested to address these problems. The options can be ranked in terms of effectiveness of reducing waste, feasibility and implementation cost. The most attractive options may be implemented whilst others may prove non-viable. Examples of successful waste minimisation projects are discussed in Section 2.3.3.

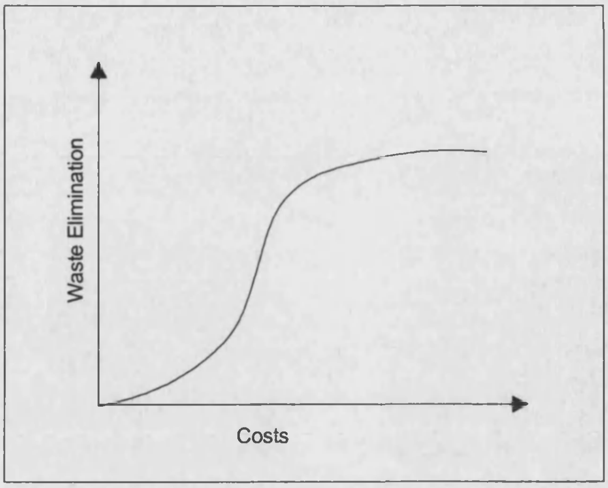


Figure 2.7: Relationship between waste reduction and implementation costs [52]

As discussed previously, it is beneficial to design plants to be inherently clean. Therefore, waste minimisation techniques must be incorporated into the design procedure. It is possible to perform a waste minimisation study on the detailed design but at this point the design is fixed and a large number of design options will have been discarded. It would be better to identify waste problems early to allow changes to be made as waste problems are identified. Process simulation can be used to simulate processes to identify the effects of process changes on waste production [53]. Methods for designing chemical plants for pollution prevention are discussed in Section 2.3.4 and Section 3.1.

Micro-scale waste minimisation techniques look in detail at the physical and chemical processes taking place at the molecular level. For example, it is possible to examine the characteristics of a solvent to identify which material would be the most suitable for a particular task [54, 55]. Analysis of chemical reaction routes may allow the chemist to identify pathways that minimise the production of unwanted by-products [56, 57].

In all waste minimisation studies it is important to consider the time scale for achieving a goal. It may not be possible to operate in the short term as the benefits may take longer to materialise. It is also important to embrace the entire company operations and not to focus on individual problems [44].

Future research in this area is likely to encompass methods to identify and quantify waste streams, life-cycle analysis for the assessment of processes and products, improved understanding of the areas of economics and politics, cleaner production and processes and improving the materials and energy recovery of a system [47].

2.3.3 Waste minimisation case studies

There are many cases that demonstrate the success of waste minimisation in operating plants. In the UK the largest study is the Aire and Calder Project [45, 58]. This was initiated in 1992 to assess and minimise the wastes discharged to the Aire and Calder river system. A consortium of companies which used the rivers was formed encompassing a variety of different industries including, chemicals manufacture, the soft drinks industry, printing plates manufacture and a commercial laundry. Their processes were examined to identify the areas for potential waste reduction. The economics and technical feasibility of each of the waste reduction options were assessed to determine which of the options would be carried out. The findings indicated a total cost saving of £3 million/annum for the 11 companies and an extra £1 million in future opportunities. The reduction in the amount of water released was 27% with the potential to increase to 40%. The payback period for 63% of the changes was less than one year and many only required a small investment [58].

In the US another large study was carried out on an oil refinery [59]. The Amoco refinery was used to demonstrate how pollution prevention could be used in planning improvements to a plant. The project identified four objectives:

i) to provide an inventory of the chemical type, the quantity, the source and the media, of all refinery releases,
ii) to develop and rank the options for reducing these emissions,
iii) to evaluate the factors such as technical, regulatory or economic barriers to implementing each option,
iv) to enhance participants' knowledge of the refinery and regulatory systems.

It was found that over 90% of the releases were to air. A monitoring programme was initiated to gain emissions data. This involved taking 1000 samples around the refinery and testing them for 15-20 chemicals. The sampling took 12 months to complete and involved an overall cost of $1 million. It was found that source reduction could reduce 20% of these releases. However, the other 80% had to be tackled using recycling, disposal or treatment options. The source reduction options were low cost, on average \$650/ton pollutant removed, whilst the other options costs averaged \$3,200/ton pollutant removed. The top five ranked options included improving the marine loading operations, installing secondary seals on tanks, installing leak detection systems, reducing soil breakthrough into sewers and upgrading blowdown stacks. These measures were estimated to prevent or capture 7,500 tons of releases, 48% of the total emissions, at a cost of \$500/ ton.

It is not only large projects that have achieved improvements using waste minimisation strategies. The Sandos plant in the Republic of Ireland looked at minimising waste at the design stage [60]. By installing systems for recycling solvents only 5% is lost during operations. The automation of the batch operations allowed the plant to be operated effectively and for environmental releases to be minimised. A successful project in the textile industry [44] showed that reductions in the costs of dyes, chemicals, energy, water and effluent treatment were of the order of 30% simply by redressing the current practices and procedures. Another company manufacturing fine chemicals instigated a £3 million investment in source reduction and recycling that reduced the raw material costs by 50% [61].

Therefore, the methodology of waste minimisation and pollution prevention has become integrated into main stream plant operations, planning and also design. The resulting savings and benefits to the environment have been shown to be substantial in many cases.

2.3.4 Design for pollution prevention

The need to consider waste and pollution at source has led engineers to adopt waste minimisation techniques during the design of both the process and the product. The design of products will not be discussed in detail but should lead to products that are "less toxic, less mobile, less persistent, more suitable for recycling or more amenable to treatment" [62].

The wastes from a process can be broken down into the following categories [62]:

- unreacted materials,
- impurities in the reactants,
- undesirable by-products,
- spent auxiliary materials (i.e. catalysts, solvents),
- off-specification products,
- maintenance waste and materials,
- material generated during start-up and shutdown,
- material generated during product and waste handling, sampling, treatment or storage,
- fugitive sources.

At the top of this list the wastes are classified as "intrinsic" to the process. That is they are part of the process and are fixed during the design of the plant. Towards the bottom of the list the wastes become "extrinsic". These are more functional properties of the operations and are not necessarily inherent to the process. To minimise intrinsic wastes it is necessary to make major equipment changes, improve the reaction, or change the separation techniques. The extrinsic wastes tend to be reduced by improving the administrative controls, improved maintenance, operator training, or changes to auxiliary aspects of the process [62].

Tackling the reduction of these wastes during design has traditionally been on an ad-hoc basis. However, more systematic approaches have been developed that allow more rapid development of inherently clean designs. These methods include both qualitative and quantitative methodologies.

Qualitative methods consider waste in a subjective but informed way. Under this heading there are two types of waste minimisation methodology, namely ENVOP (Environmental Optimisation) [63] and hierarchical or "onion diagram" methods [64, 65, 66]. Databases of environmental technology and solutions have been developed that provide access to current environmental technologies allowing solutions to environmental problems to be found by searching through the database [67, 68, 69, 70].

Simple quantitative methodologies consider the behaviour of the process using simple mathematical relations. However, they do not extend to complicated mathematical interactions or optimisations [71, 72].

Complex quantitative methodologies try to take full account of the chemical and physical behaviour of a process. The main development in this area are the Mass/Heat exchange networks (MEN/HEN) and the complete optimisation of a design. For batch processes the use of Multi Integer Non-Linear Programming (MINLP) techniques to optimise schedules has been proposed [73, 74, 75, 76, 77].

The use of these design methodologies, their benefits and disadvantages are discussed in more detail in Section 3.1.

2.4 The environment

The environmental legislation, outlined in Section 1.1.1 has moved towards controlling emissions to air, water and land. In addition, public knowledge and concern over environmental issues such as global warming and ozone layer depletion has increased together with media interest in such issues as detailed in Section 1.1.2. As a result industry has come under increased pressure to reduce their affect on the environment and reduce wastes.

The previous two sections have introduced the concepts of process design and waste minimisation. Industry is now considering the environment early in process design to reduce the costs of environmental compliance. The IPC regulations require all new chemical facilities to achieve compliance to be able to operate and this includes performing an environmental assessment. An extension of the BPEO approach is the 3Es methodology [78] that emphasises the emissions, the efficiencies and the economies of the process. Combining the improvement in environmental performance with improvements in yields and profits of the plant has helped companies realise the benefits of implementing BPEO.

An important development is using waste minimisation techniques to reduce the impact of industry on the environment. If areas of environmental concern can be identified then waste minimisation options can be prioritised to achieve the best improvements in performance. For existing plants the identification of problems can be found during an environmental review and the measures implemented will be retrofits or changes in operating philosophy. Many companies are now adopting EMAS (Eco-Managment and Audit Schemes). EMAS is a voluntary EU regulation which aims to improve industry's environmental performance by introducing an environmental management system. Part of the environmental management system is likely to be a periodic environmental audit that will identify potential waste problems and introduce reduction measures.

For new plants there is a possibility to combine all the three areas by developing waste minimisation options during plant design and assessing these for improvements in environmental performance. There is still some way to go before all three issues are successfully combined and this is discussed in the next section.

2.5 Combining the three issues

The integration of waste minimisation, process design and environmental assessment will allow inherently clean and economic plants to be built in the future. A number of researchers and industries are working on individual issues but only a small number have attempted to combine all three areas into one methodology. Amongst those doing so are the US Environment Protection Agency. They have developed WAR (WAste Reduction), a computer algorithm that considers the material balances of a process flowsheet and calculates the equivalent environmental impacts of the process options [79]. This is likely to be a powerful tool once linked to a process simulator. However, it does not attempt to create novel process designs or consider the problems of developing the flowsheet in a systematic way. At present the algorithm does not include the implementation cost of the options but this is proposed for the future.

Another field is the use of life cycle assessment (LCA) in process and product design [80, 81]. LCA is a method of determining the environmental burden of all aspects of the process. This includes factors such as raw material extraction and transport, energy usage and fate of the product. Nitric acid production has been used as a case study to demonstrate how process options could be optimised with respect to environmental performance and economics using multi objective function optimisation [82]. This appears to be a very promising tool although the amount of data required to perform an LCA is very large and can be difficult to obtain. The problem of the generation of process options is not addressed and the options presented are taken from published literature.

A similar approach is taken by Stefanis et al [83] who present a methodology for environmental impact minimisation (MEIM). Again LCA is used to produce an environmental index for the process options. The process flowsheet is then optimised with respect to the index or operating costs and the trade-off is examined. The design conditions are produced by the optimisation procedure to minimise the objective function and they vary with the objective function chosen. Therefore, in their vinyl chloride monomer (VCM) manufacture case study the unit operations are fixed and are not challenged by the environmental assessment.

The above procedures have tended to concentrate on continuous large scale processes. The design, operational and environmental issues associated with batch processes differ from continuous processes, as discussed in Section 2.2.4. A group in the US has been considering the design of batch processes with environmental considerations [84]. The result is a computer program, BatchDesign Kit (BDK), for the development of batch process design. The BDK aims to:

i) generate relevant reaction schemes and select the most appropriate,
ii) synthesise the flowsheet for batch processes,
iii) select the solvents and the other process materials so they meet design specifications,
iv) assess the ecological (health safety, and environmental) impact of the chemicals,
v) select the best treatment for the unavoidable wastes and carry out a systematic analysis to identify the optimal trade-off amongst the objective functions.

Recently the BDK has been taken up by AEA Technology to be developed into a commercial package [21]. The program is in three parts. The first generates flowsheets using a systematic hierarchical approach. The second part simulates the process at the most basic level and advises the designer on handling the wastes. The third studies the process, identifies which solvents are available to perform the required task and searches through these to find the best option. The materials are screened using a rule based expert system based on US regulations.

Although this an excellent piece of work there are a couple of areas that still require further development. Firstly, the generation of the flowsheets is not described but it is suggested that it will be done within the computer which does not allow flexibility or control over the design. This can lead to the selection of traditional unit operations that may compound problems of waste generation.

Secondly, no account is taken of the time varying nature of the process. This can prove crucial to the environmental behaviour of a release and to the company's compliance to the consent limits.

Lastly, the assessment of the environmental impact of the process is inadequate especially when considering the time varying releases from batch plants. The use of regulatory information about the chemicals does not account for their actual behaviour in the environment.

2.6 Summary

The three areas of process design, waste minimisation and the environment all need to be considered to ensure that inherently clean processes are developed and operated. Structured design methodologies exist that combine process design and waste minimisation. However, a review of these methodologies has shown that there is a need for a structured design methodology specifically for batch processes to aid with minimising environmental impact whilst developing an economically viable plant. This thesis describes an extension of the Douglas hierarchical design methodology to fulfil this need.

Chapter Three

Design Methodology

3.1 Existing design methodologies

The previous chapter indicated a need for a structured design methodology to aid in the design of inherently clean batch processes. Specific tools are required to combine process design, waste minimisation and environmental assessment. A number of structured design methodologies exist and several have been adapted to consider waste minimisation and pollution prevention. These can be categorised as qualitative, simple quantitative and complex quantitative and are summarised in Figure 3.1. The following sections describe these design methodologies and discuss their applicability to waste minimisation and batch operations.

3.1.1 Qualitative methods

Qualitative methods consider process wastes in a subjective but informed way. Under this heading there are three techniques; ENVOP (environmental optimisation), hierarchical methods and heuristic methods.

ENVOP is conceptually similar to the HAZOP (hazard and operability) technique but it focuses on the environmental effect of releases rather than the safety implications. In this type of study each segment of the process is evaluated using guidewords. For example, if the temperature was lowered would the wastes be reduced [85], or could the waste be reused [86]? This technique is currently being used by a number of companies including Zeneca [63], Knoll, Smith Kline & Beecham and BP [87]. The technique is usually applied either at the initial design phase to screen the material inputs and the expected outputs, or at the detailed design stage once the process flow diagrams are fully developed and a rigorous analysis can be performed. ENVOP is a flexible tool and is often applied to batch operations. However, no formal account is taken of the different issues that arise during the different batch operating phases. The HAZOP technique has been applied to batch operations by considering the temporal nature of the process [88] as different problems are likely to occur at different times in the batch cycle. The ENVOP technique could be developed along similar lines to become more applicable to batch design problems. However, this would not provide a structured design tool as the technique assesses the design rather than developing it.

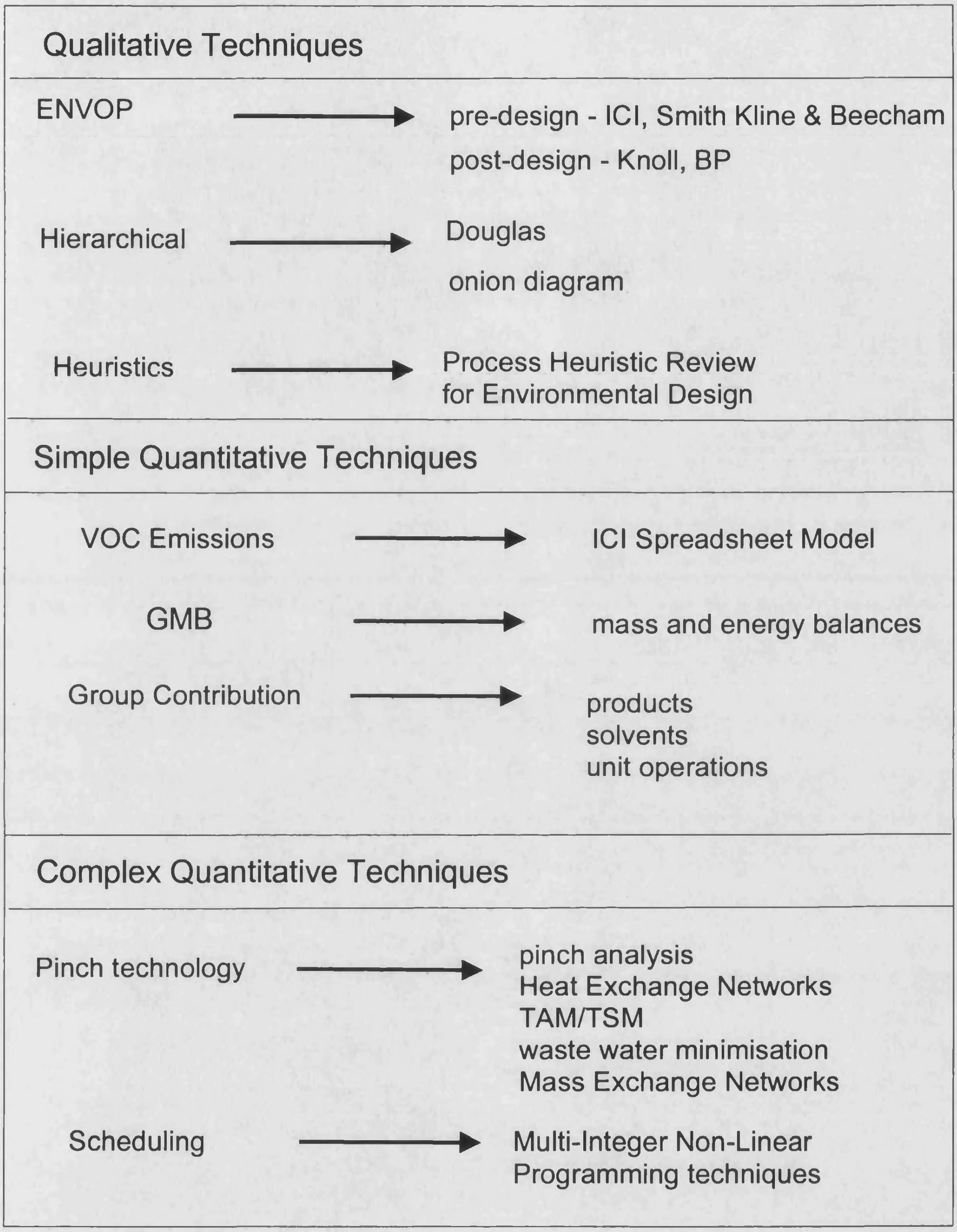


Figure 3.1: Existing design methodologies

Hierarchical methods break down the complex design problem into smaller more manageable sections and deal with each in a strict order. Using these methods the design is built up logically, moving from the simplest level to the most complex. At each stage various options are considered and discarded if unfeasible in terms of operation or cost. This approach has several positive aspects:

- it helps the designer to quickly understand the process,
- it provides a current picture of the design economics,
- it generates a list of process alternatives, and
- it estimates optimal values of the most significant design variables to minimise the cost.

Douglas [64] proposed such a method and decomposed the process synthesis problem into the following levels:

Level 1: Batch vs continuous.
Level 2: Input-output structure of the flowsheet.
Level 3: Recycle structure of the flowsheet and reactor considerations.
Level 4: Separation system specifications.
    Level 4a: Vapour recovery system.
    Level 4b: Liquid recovery system.
Level 5: Heat exchanger network.

Subsequently, Douglas adapted his methodology for waste minimisation [65]. The potential pollution problems that could occur during the first four levels were highlighted but Level 5 was not included. The Douglas methodology is discussed further in Section 3.2.

Another structured approach, proposed by Linhoff et al [66], introduced an "onion" diagram to represent the sequential or hierarchical nature of design as shown in Figure 3.2. At the centre of the onion is the reactor design followed by the separation system, heat exchange network and utility system in a similar sequence to Douglas. Smith and Petela [89] used the onion diagram for waste minimisation by adding waste considerations to each ring of the design. This approach allowed utility wastes such as water and energy usage to be included.

The design of batch operations has been considered using the Douglas methodology and the onion diagram. The approach taken by Malone [90] was to initially design a continuous plant using the Douglas methodology and then systematically replace the units with batch operations. This is discussed in more detail in Section 3.2.8.

The onion diagram has been annotated for batch process design as shown in Figure 3.3 [91]. The batch process schedule is considered central to the design and is inter-linked with the arrangement and design of equipment. The next layer considers energy integration of batch operations. The design is then analysed using dynamic simulation to optimise the units and operations. Finally the control system and utility requirements are specified. The application of the onion diagram to batch operations introduces some useful concepts but does not lead to a simplification of the process design as the equipment items are considered together in the central ring. The focus is on energy integration reducing the process energy demand. This will result in a reduction of the environmental impact of the process, however, the other environmental aspects of batch operations are not explicitly examined.

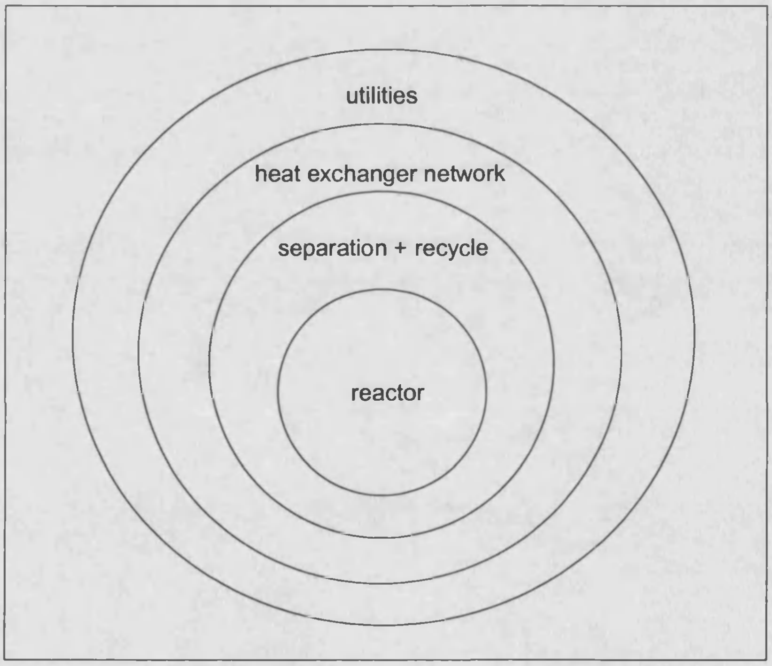


Figure 3.2: The generic "onion" diagram.

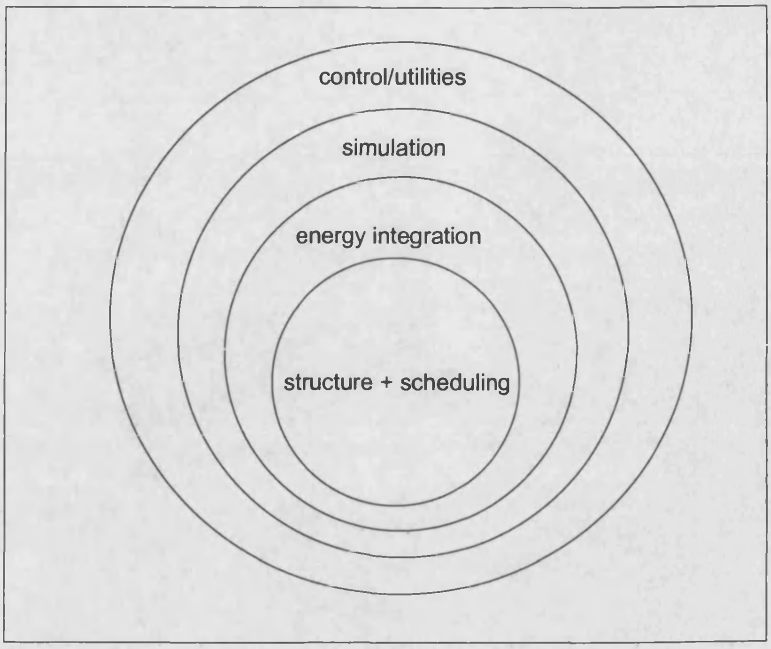


Figure 3.3: Batch design onion diagram

Heuristic methods use guidelines or “rules of thumb” to direct the design. These are often used in conjunction with other design methodologies to make preliminary design decisions with incomplete information. The “rules of thumb” are based on the fundamental properties of the process and engineering experience. A heuristic methodology for the consideration of pollution prevention named PHRED (process heuristic review for environmental design) has been developed [92]. PHRED is a knowledge based system that identifies and prioritises different environmental design strategies. It has been applied to reducing maintenance wastes, improving the selectivity of reactions, reducing mechanical losses and reducing transient wastes during start-up or shut-down operations. The technique is useful because it can be used without detailed knowledge of the process. However, it is not possible to produce a complete detailed design purely using heuristic techniques.

3.1.2 Simple quantitative methods

The simple quantitative design methodologies model the behaviour of a process using simple mathematical relations. However, the methods do not extend to complicated mathematical interactions or optimisations. The aim is to represent process behaviour in a simple but accurate way to allow quick and easy analysis. There are three important techniques under development: (i) the Graphical Mass Balance approach (GMB) [71], (ii) a spreadsheet model developed by ICI Paints for assessing the potential for releases from a process [72] and (iii) group contribution approaches [55, 93, 94].

The GMB model displays the mass balance for a system graphically and allows various parameters to be manipulated to assess different options. The technique analyses the trade-offs between different process wastes and the "optimum" operation can be selected. This approach allows the engineer to analyse the behaviour of a complex system in a simplified manner and to assess the effect of process changes. This methodology could be applied to batch processes with the variation of release mass or concentration plotted against time. Hence, any release exceeding the regulatory consent limit could be identified. The GMB has great potential for quick screening of processes. However, the simplified simulations would not be adequate for detailed design. There is no assessment of the environmental impact of the release as the method relies on the regulations to set the correct limits.

The spreadsheet model developed by ICI Paints uses simple thermodynamic relationships to predict the release profiles of volatile organic compounds (VOCs) from a paint blending process. The aim is to reduce the emission profile by considering a range of engineering and process options. This method concentrates on batch operations and therefore includes time as a variable. However, it only considers releases of VOCs and not the range of materials that are required to be analysed by IPC regulations. The releases modelled are from blending operations and do not include complex operations such as reactions, heating or separation.

Group contribution techniques use the properties of materials and molecular groups to identify appropriate process options. There are three areas that are presently being developed. Firstly, the properties of solvents are examined to assess which would have the most suitable characteristics to match the production, environmental and safety specifications of the process [55]. Secondly, active pharmaceutical ingredients can be selected by analysing the chemical functional groups of materials [93]. Lastly, the selection of the most appropriate unit operations can be predicted from examining the properties of materials to be treated [94]. For example, the most appropriate method of separating a mixture will depend on the properties such as the relative volatility or absorbency of the materials present.

3.1.3 Complex quantitative methods

Complex quantitative methods attempt to take full account of the chemical and physical behaviour of the process.

Pinch analysis is the basis for most of these techniques [95, 66]. Pinch analysis deals with energy integration of the process by introducing heat exchange networks (HEN) to reduce the energy demand. Pinch techniques are routinely used to analyse continuous processes however, they are still not widely used for batch processes. Energy integration for batch processes needs to consider time as a variable and has been carried out using Time Averaged Models (TAM) and Time Slice Models (TSM) [96, 97, 98]. Pinch analysis has been used for waste water minimisation [99].

The HEN techniques have been extended to examine mass exchange networks (MEN). Mass exchange considers mathematically the transfer of materials between streams or conversion of species to different materials. Various researchers have worked on the mathematical formulation of MEN problems. For waste minimisation Manousiouthakis and El-Halwagi [73, 74, 75, 76, 77] have worked extensively on analysing the transfer of mass between streams to allow the maximum transfer to be realised. Papalexandri et al have also worked on the development of optimising MEN networks using multi-integer non-linear programming MINLP [100, 101].

For batch processes there is also the use of Multi Integer Non-Linear Programming (MINLP) for designing schedules. Schedule planning has been used to reduce the need for additional cleaning and product change over and also to improve the recovery of heat [102, 103].

These potentially powerful methods have two limitations. Firstly, the problems are difficult to set-up and solve and are not routinely used by design engineers especially at the conceptual design stage. Secondly, it is difficult to incorporate the engineer's insight, creativity and preferences in the design the methods involve often black box type calculations which can only be understood by experts [104]. In addition their application to batch processes is complicated by having to consider time as a variable.

3.1.4 Summary of existing design methodologies

The application of existing design methodologies to the clean design of batch processes has been limited. Further development is needed to produce a more applicable methodology.

The ENVOP technique has been used for batch processes but does not consider the specific characteristics of batch operations. It could be developed further to include these considerations. However, the technique is used for analysing process flowsheets rather than providing a structured approach for developing the design. Hierarchical methods provide such a structure and can aid with waste minimisation during plant design. The Douglas design methodology and the "onion" diagram have been applied to batch processes. However, the issue of waste production from specific batch operations remains unresolved. Heuristics are best used in conjunction with these structured methodologies and can be used to generate preliminary deigns.

Batch operations could be analysed using the GMB models by including time as a variable. The use of simple spreadsheets enables specific batch operations to be considered but would be complicated to extend to the overall process. Group contribution methods are limited to considering the generic nature of the materials and cannot be applied to problems such as energy usage or optimising the operations of the process units.

The complex quantitative methods, such as mass exchange networks and pinch technologies, are extremely powerful techniques and allow the designer to develop an understanding of the process behaviour. However, their extension to batch processes would be complicated as time has to be incorporated. The amount of detailed information, the time and effort needed to set up these models means they are more likely to be used for detailed process analysis than for deciding between preliminary process options. Detailed knowledge of the operations and process units is required before the mathematical optimisation of process schedules can be carried out.

From this review it was decided that the Douglas design methodology should be the one adapted for the clean design of batch processes. The main reason for choosing the Douglas methodology is that:

- it is a highly structured but flexible method for design that encompasses the entire process,

- it provides a clear picture of the design economics,
- it has already been successfully extended to waste minimisation, and,
- it has the flexibility to be extended to batch processes.

A detailed description of the Douglas design methodology, its application to different areas and the additional requirements for batch processes are provided in the following sections.

3.2 Douglas design methodology

The decomposition of the design problem proposed by Douglas, as outlined in Section 3.1.1, originally comprised five separate design levels. At each of these levels the entire process is considered and details are added to the flowsheet. The design decisions taken at each level are guided by heuristics. It should be noted that heuristics only act as guidelines and can lead to contradictory advise. If no heuristics exist the designer can develop a list of process alternatives which can be analysed. The design decisions are focused on the parameters which directly affect the cost of the design at the level being considered. The methodology provides a series of questions to focus on these design variables. As the design evolves it may be necessary to go back to a previous level due to decisions made at a subsequent level generating other process alternatives.

At the end of each decision level an economic analysis is carried out. The accuracy of the cost estimates increases as the design develops starting with a rough estimate of the major cost items to a full scale economic assessment. The economics are presented as economic potentials (EP) which combine all the relevant costs for the level being considered.

The following sections provide a summary of the issues considered at each of the decision levels. Detailed information concerning the Douglas procedure can be found in [15].

3.2.1 Level 1: batch vs continuous operation

The first decision to be made is whether the process is to be batch or continuous. The reasons for choosing a batch process are indicated in Section 2.2.4 and are summarised as follows:

- Production rate: under 500,000 te/year batch processing would be preferred, between 500,000 and 5,000,000 te/year batch processing is common and at higher rates a continuous process is usually chosen.
- Product life: batch plants are used for products that have a short life span where a rapid product turn-around is required to respond to the market requirements.
- Multi-products: a batch plant will usually be used for a process that produces many similar products as the units can be used for more than one purpose without significant changes to the operations.
- Process reasons: processes where regular shut-downs for cleaning or maintenance are required, operations with scale-up problems or with complicated product recipes are best suited to batch operations.

Douglas' original methodology concentrated on continuous processes only. An extension to batch processes has been developed and is discussed in Section 3.2.8.

3.2.2 Level 2: input-output structure

At this level, the process is represented by an overall mass balance indicating the flows in to and out of the process as shown in Figure 3.4. The raw material costs are highlighted as the major cost item at the first stage of design.

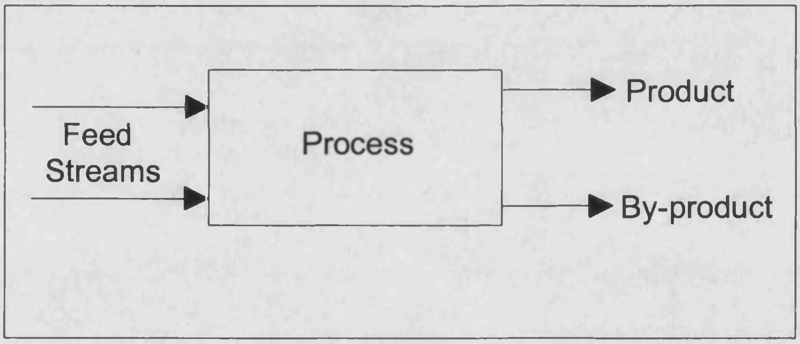


Figure 3.4: Input/output flowsheet

The decisions to be taken at this level are:

- should the feed be purified?
- should a by-product of a reversible reaction be removed or recycled?
- should a gas purge or recycle stream be used?
- should the unreacted materials be recovered and recycled?

- how many product streams should there be?
- what are the costs associated with selectivity losses?

Heuristics are presented for each of these questions and the economic trade-offs are highlighted. For example, the feed should be purified if the impurities react in the process or if there is a large amount of easily separated inert material. In this case, the economic trade-offs are between providing a purer feed, i.e. building a pre-processing plant or buying a purer feedstock, versus increased operating costs of the process. There is no simple heuristic to decide between these two options so both the process alternatives would be considered.

At the end of Level 2 the economic analysis is as follows:

$$EP_2 = (\text{product value}) + (\text{by-product value}) - (\text{raw material costs}) \ (\text{£/year}) \quad (3.1)$$

If the economic potential is negative then the option is unprofitable and other sources of raw materials or a different process route will need to be examined. The EP for the different process options can be compared to select the "best" values of the design parameters at this level.

3.2.3 Level 3: reactor and recycle structure

The major task of this level is to determine the size of the recycle streams for the process. A schematic of a typical flowsheet is given in Figure 3.5.

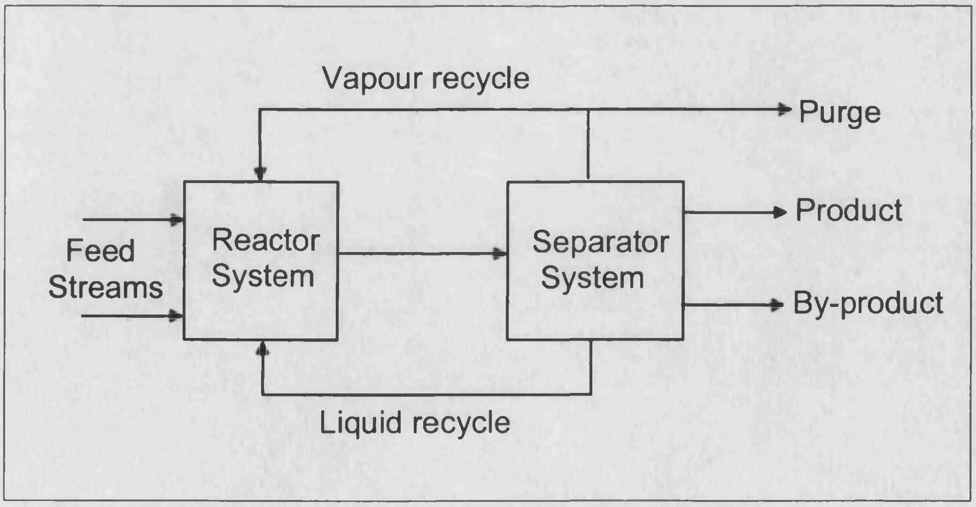


Figure 3.5: Reactor/recycle flowsheet

The decisions to be taken are:

- how many reactors are required and is separation required between the reactors?
- how many recycle streams are required?
- is an excess of reactants beneficial?
- is gas recompression and recycle required?
- should the reactor be operated adiabatically, with direct heating or cooling or should a diluent or heat carrier be used?
- if the reaction equilibrium is limited, can it be shifted forwards?
- how do the reactor costs affect the economic potential?

The initial stage is to identify the reaction steps. If the reaction conditions vary greatly between steps it will be necessary to use separate reactors. The materials requiring recycle to each reactor can be grouped and the number of these groups will decide the number of recycle streams. The definition of the recycle mass balances can then be completed by defining the amount of conversion to be achieved. The economic trade-off for a single limiting reactant is between the conversion and the cost of recycling. For large conversions the size, and therefore the cost of the reactor is greater, whereas for low conversions the amount and the cost of the recycle is greater but the reactor is smaller. If a gas recycle is to be used then a gas compressor is required and will have an effect on the economic trade-off. For reactions with equilibrium limitations it may be possible to shift the equilibrium i.e. by introducing an excess reactant, changing the reactor temperature or reactor pressure. An excellent summary of these techniques for different reaction systems is given in Smith and Petela [105].

Once the reaction mass balance is fixed and the reactor heating effects have been assessed, decisions can be made to deal with any excessive heat rise.

The last task is to design and cost the reactor. It is important to note that the design is a preliminary one as the separation system may change the recycle flows. It is necessary to obtain an estimate of the size and cost of the reactor to calculate the economic potential as follows:

$$EP_3 = EP_2 - \text{annualised compressor cost} - \text{compressor operating cost} - \text{annualised reactor cost (£/year)} \tag{3.2}$$

3.2.4 Level 4: separation system

The design of the separation system was originally divided into vapour and liquid. Flash separation is likely to be used to separate these two phases because it is considered to be the cheapest phase separation technique. A typical flowsheet for a two phase reactor exit stream is shown in Figure 3.6.

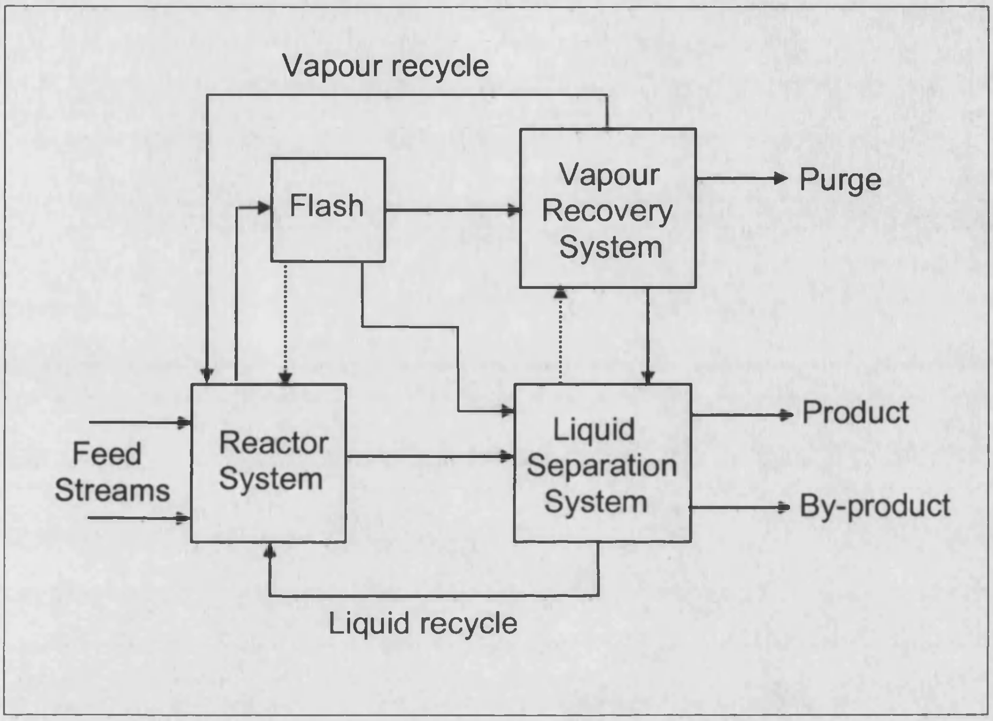


Figure 3.6: Separation flowsheet for a two phase stream

The decisions concerning the vapour separation system are; where the separation should take place and what is the most appropriate vapour recovery system? The vapour recovery systems should be positioned before the gas purge if a large amount of valuable material is lost in the purge. It should be placed on the vapour recycle stream if materials are present that will poison the catalyst or cause problems in the reactor. If both of these conditions exist then the vapour recovery system should be placed on the flash exit vapour stream. In the case where neither of these factors is important there is no need for a vapour recovery system.

The methods of vapour recovery depend on the materials to be separated and include condensation, absorption, adsorption and membranes.

For the liquid separation system the following decisions need to be considered:

- what separations can be made with distillation?

- what sequence of distillation columns should be used?
- how should light ends be removed?
- should light ends be vented to atmosphere, burnt as fuel or recycled to the vapour recovery systems?
- how can other separations be accomplished?

The components present in the liquid stream are put in order of boiling point. The relative volatility of the components are then calculated and potential splits can be identified. The remaining materials can be separated using azeotropic distillation, extractive distillation, reactive distillation, extraction or crystallisation. The original Douglas methodology did not include solvent extraction or adsorption. There are numerous heuristics for deciding the sequence of the distillation columns [106, 107]. The most commonly used are:

- remove the lightest components first,
- recover the most plentiful component first,
- make the most difficult splits last, and,
- favour equimolar splits.

The generalised economic potential becomes:

$$EP_4 = EP_3 - \text{purge losses} - \text{annualised distillation costs (£/year)} \qquad (3.3)$$

The EP calculation may vary depending on the design options considered i.e. the cost of vapour recovery systems or other separation techniques.

3.2.5 Level 5: heat exchanger networks

The analysis of the heat integration of a process can be performed once the major equipment items have been defined. The minimum heating and cooling requirements and potential stream matches can be identified using well established pinch techniques [66]. Procedures are also available to calculate the minimum number of heat exchangers and estimate their surface areas [15]. The trade-offs are between the reduction in the operating cost in terms of heating and cooling duties and the increase in capital cost of installing heat exchangers.

3.2.6 Applications

The Douglas hierarchical system has been extended as a result of numerous industrial applications. As a result, additional design levels and heuristics have been suggested.

The analysis of solids processes such as crystallisation, filtration and drying was considered by Rajagopal et al [108]. This work led to the addition of solids separation at Level 4. Also additional levels have been introduced to analyse drying operations, dealing with safety and also piping and layout [109]. Studies of polymer production have developed heuristics for parameters that affect the reaction and separation of several polymers [110]. The additional parameters included product degradation, polymer fouling and viscosity effects. In conjunction with this was the development of computer simulations to perform sensitivity analyses on the design and to identify critical process parameters [111]. Similarly work has been carried out to apply the hierarchical methodology to the design of a reverse osmosis desalination plant resulting in a new set of heuristics relevant to this system [112].

Consideration of the build-up of impurities in the process has been discussed by Joshi and Douglas [113]. New exit points from the process may have to be considered or new separation units installed.

An interesting application is in the design of control systems. The control system is examined at each design level and increased in sophistication as the design was developed [114].

Figure 3.7 shows the current Douglas hierarchical design methodology including the modifications discussed in this section.

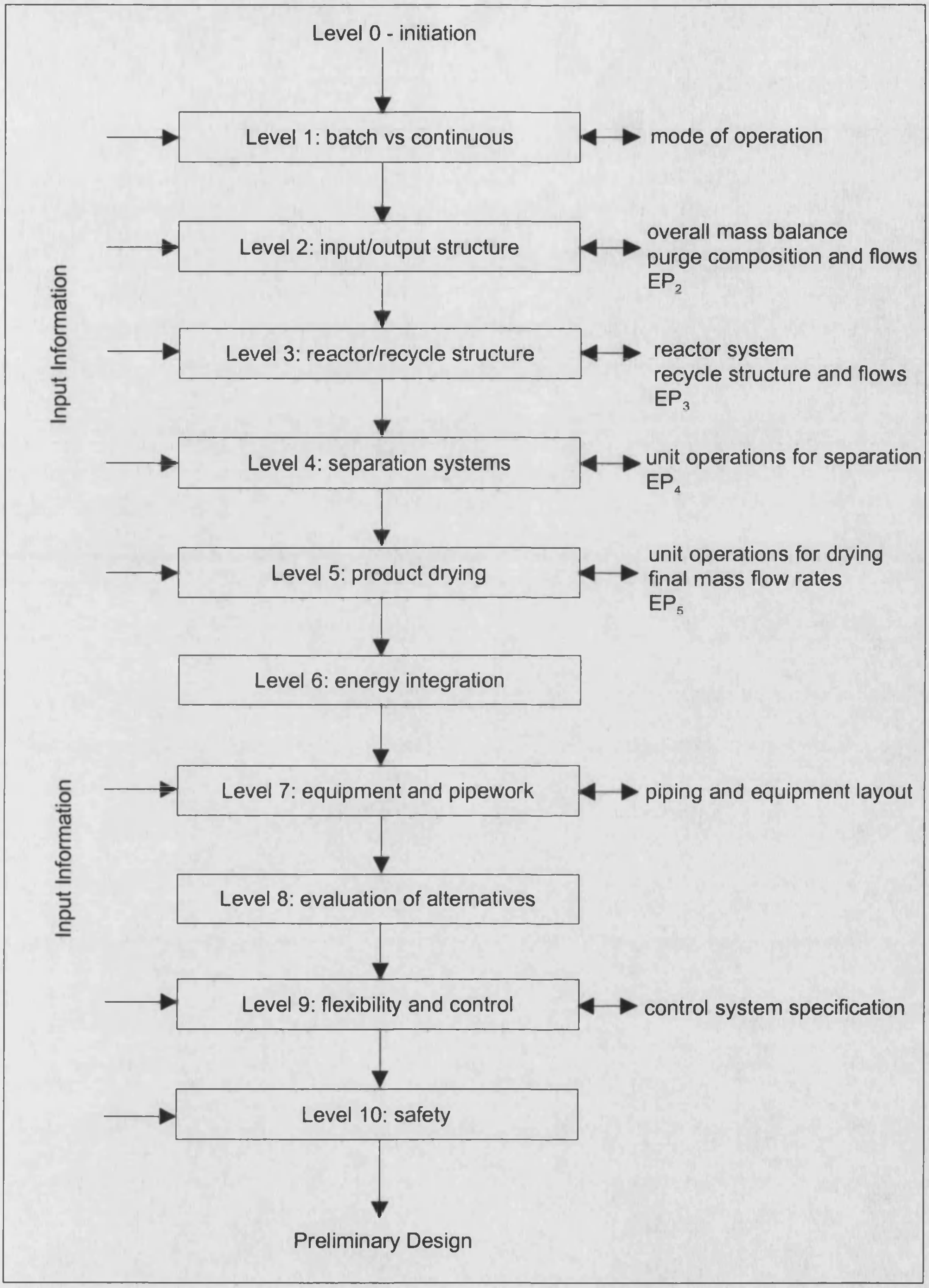


Figure 3.7: Current Douglas design methodology

3.2.7 Waste minimisation

The Douglas methodology has been adapted to address waste minimisation issues [65] by including consideration of wastes produced at each level. Initially, only the first four levels were considered but Rossiter extended this further to include the other levels [33, 109]. Process retrofits for minimising wastes were considered by Fonyo et al [115] and Fisher et al [116].

At Level 1, the choice between batch and continuous operations, the indication is that batch processes produce more waste per tonne of product than continuous processes. Therefore, it is advised that continuous processes should be chosen to avoid unnecessary waste production. However, as discussed previously, there are many situations where batch processes are preferred over continuous processes. Batch processes are widely used in the production of value added products such as food, pharmaceuticals, polymers, agriculture additives and speciality chemicals.

The waste produced by batch processes occurs mainly due to the frequent unstable start-up and shut-down operations and also the requirements for cleaning. However, there are several areas where batch processes have an advantage over continuous operations. The flexibility of the batch system means that if the operations begin to deviate from normal, manual intervention can correct the problem. As the batch size is usually small only a small amount of material will be off-grade if the operational problems cannot be rectified. In continuous operations a large amount of material can be lost due to irregular operation as changes made in parameters are slow to affect the process whilst material is flowing continuously through the plant. In batch reaction vessels the residence time is often extended to increase the reaction conversion. In continuous processes for reactions with a low residence time and low conversion high levels of recycling are often required which will involve extra energy demand due to separation and pumping requirements. Therefore, choosing a continuous process may not be operationally viable and may not result in cleaner production.

Level 2 considers the input-output structure of the process. Focusing on waste minimisation can affect the decisions taken. For example, a feed impurity may react within the reactor to produce a waste stream that is particularly difficult to dispose of. From an initial cost assessment it may not be viable to purify the feed but if the costs associated with the wastes are included it may prove to be a better option. Additional decisions include:

- can any "waste" output stream be used in the plant or by an external user?
- can any input streams, such as additives or solvents, be eliminated or replaced?
- are there any problems caused by reaction chemistry?
- are there any feed impurities that could cause waste problems?
- is spent catalyst a problem?

Douglas considered the nature of the reaction chemistry and identified areas where the process chemistry would need to be altered to solve the waste problem.

Level 3, the reactor and recycle consideration, extends several of the existing questions and introduces some additional ones as follows:

- do the waste output streams contain feed or product material that could be recycled?
- can reaction conditions be altered to minimise the formation of waste by-products?
- can waste by-products be recycled to extinction?
- can additional materials be eliminated from the process?
- do any of the added materials such as heat carriers, diluents and solvents cause a problem? If so they should be replaced.

The design of the separation system is considered in Level 4 and the impact of the separation technology on waste production is assessed. The possibility of reducing emissions by using different separation techniques should be considered. The additional decisions include:

- are any waste streams the result of poor or inappropriate separations?
- can any wastes be removed from the process by adding new separations?
- are there alternative separation technologies that could replace or supplement existing separations?
- do absorber solvents or stripping agents cause a waste problem?
- does regeneration of adsorber beds or disposal of spent material cause a problem?
- are there problems caused by release of purge streams?
- does solid cake washing cause a waste problem?

If any of the auxiliary materials such as adsorbents, stripping fluids etc. cause a waste problem a replacement should be sought.

Level 5 focuses on the waste problems associated with drying operations. The additional questions are:

- are there dryer technologies available that cause less product degradation and less dust?
- can waste materials be removed from the dryer off-gases before being released?
- can the dryer wastes be recycled?

The selection of the most appropriate dryer is a complex task. A recent development has been an expert tool which matches the types of materials and operations to specific drying equipment [117].

The next task is to consider heat integration. Energy production releases materials to the environment and therefore, minimising the energy demand of a process reduces the overall environmental burden. Additional questions include:

- how far can the energy consumption of the process be economically reduced?
- can the temperature levels at which heat is supplied be reduced?
- what fuels are used to provide heat?
- can alternative fuels be used and what are the additional costs?

The last level to be considered for waste minimisation is equipment and piping layout. The aim is to minimise the equipment inventory so less material will be released if an unplanned event occurs. Fugitive releases can be minimised by reducing the number of pipework connections and measurement points. The decisions to be made are:

- can the total number of equipment items and connections be reduced?
- which type or make of equipment shows the most favourable emission characteristics?
- can an incremental cost increase be justified by the relative decrease in emissions?
- can welded pipes be used instead of flanged connections?

The cost analysis at each level is adjusted to take account of the cost of disposal of the waste material. This method allows the cost of implementing waste reduction measures to be weighed against the cost of treating the wastes or installing end-of-pipe equipment. However, this approach does not take account of the environmental impacts of the releases. The cost of disposal may not represent the true cost of the release to the environment. A number of approaches for combining the assessment of the environment have been detailed in Section 2.5. More discussion on this will be given in Chapter 6 with the further extension of the Douglas methodology.

3.2.8 Batch processes

The Douglas methodology for batch processes concentrates on Level 1, the choice of batch or continuous units coupled with merging batch tasks. The aim of the methodology is to provide initial screening based on short-cut designs. A small number of potential flowsheets go on to be analysed further using batch scheduling optimisations and dynamic simulations.

For a single product batch plant Malone et al [90] suggest a continuous design should be configured. The process units are then replaced by batch units and the minimum amount of intermediate storage is introduced to eliminate the batch idle time. Each unit is optimised with the cycle time and batch size unconstrained. This is an unattainable operation but provides a base case to compare with the alternative operations. The addition of intermediate storage to enable scheduling will add cost to the process. If the unconstrained optimum cost is greater than the continuous option it should not be taken further. However, if the cost comparison is favourable the schedule can be recalculated with the cycle times of each unit constrained to the same value and the costs compared again.

Alternative designs are developed by replacing each batch unit with continuous units and merging batch units. For merging it is attractive to merge units that would combine units of a similar size and would smooth out the process. Parallel units can also be used. Intermediate storage may be introduced to improve the flexibility of the process. The methodology has been applied to multi-product plants where similar production targets can be identified [90].

An extension of this methodology was proposed by Iribarren et al [118]. The generation of process alternatives is performed using a computer routine that systematically replaces the batch units with continuous units and merges appropriate batch units. Heuristics are used to simplify the number of combinations.

The application of this approach to batch operations is useful in deciding which units should be batch or continuous and in getting an initial idea of the batch sizes and cycle times from short-cut calculations. However, the individual batch operations are not considered and continuous operations are the preferred option. The extended methodology needs to consider waste minimisation specifically for batch processes to ensure inherently clean processes are developed for cases where continuous operation is not a viable alternative.

3.3 Summary

Existing design methodologies have been developed mainly for continuous processes and batch process applications are limited. There is a requirement for a design methodology to aid with waste minimisation during the design of batch processes and to assess the process environmental impact.

The Douglas methodology is a hierarchical system that decomposes the design problem into several levels. The process design is built-up gradually from the simple to the detailed level. This provides a structured framework for the designer and gives a picture of the process economics as the design develops. An application for the design of batch processes has been proposed but concentrates on the choice between batch and continuous operations at the initial design level. Waste minimisation considerations have been included in the Douglas methodology but do not consider specific batch operations or the environmental impact of emissions. Therefore, a revised approach is required. An extension of the Douglas methodology for designing inherently clean batch processes has been developed and is discussed in Chapters 6 to 11.

Chapter Four

Case Study Description One: Thomas Swan

4.1 Introduction

The existing Douglas design methodology has been found to have two main weaknesses. Firstly, the methodology does not apply specifically to batch processes. In particular there is no consideration of the different batch process operations such as cleaning and no account is taken of the time varying nature of the operations. Secondly, the approach to waste minimisation does not compare the environmental impact of alternative design options or highlight potential environmental problems. Therefore, the Douglas methodology has been extended to include these areas by introducing additional questions to the procedure as detailed in Chapter 6. These additional process questions have been tested using two case studies and the effect of changing the process operations on the environmental performance of the process design has been assessed.

This chapter details the first case study, which is based on a process that manufactures Pepton and is operated by Thomas Swan Ltd. Several of the process operations have been simulated using HYSYS. These represent base case models that have been validated against plant data. In Chapter 8 and 9, these base case models are used to test the process design questions that have been introduced into the Douglas methodology. The design questions alter the process operations and the simulations are used to assess the effect of these changes. The aim was to produce a model that responded to process changes in a realistic manner. For assessing process options the absolute values of the emissions were less important than the relative differences between the values.

The initial sections of this chapter describe the Pepton process as operated by Thomas Swan. The development of the base case simulations for various operations are then detailed, including a discussion of the modelling problems encountered and how these were overcome. Several of the chemical materials are presented as contaminant A, B, C, D, E and F for confidentiality reasons.

4.2 Process description

The Thomas Swan plant, based in Consett, County Durham, produces an organosulphur compound, Pepton [119], which is used as a peptiser in the manufacture of car tyres.

The five main process stages are:

1. pressure hydrolysis of benzothiazole using a caustic soda solution,
2. oxidation of the stage 1 product using hydrogen peroxide,
3. benzoylation of the stage 2 product using benzoyl chloride,
4. distillation of toluene for recycle leaving stage 3 product (Pepton),
5. filtration, drying, milling, sieving of Pepton and packing into bags for sale.

Figure 4.1 shows the proportion of the total cycle time taken up by each operation. Due to confidentiality the batch times can not be given.

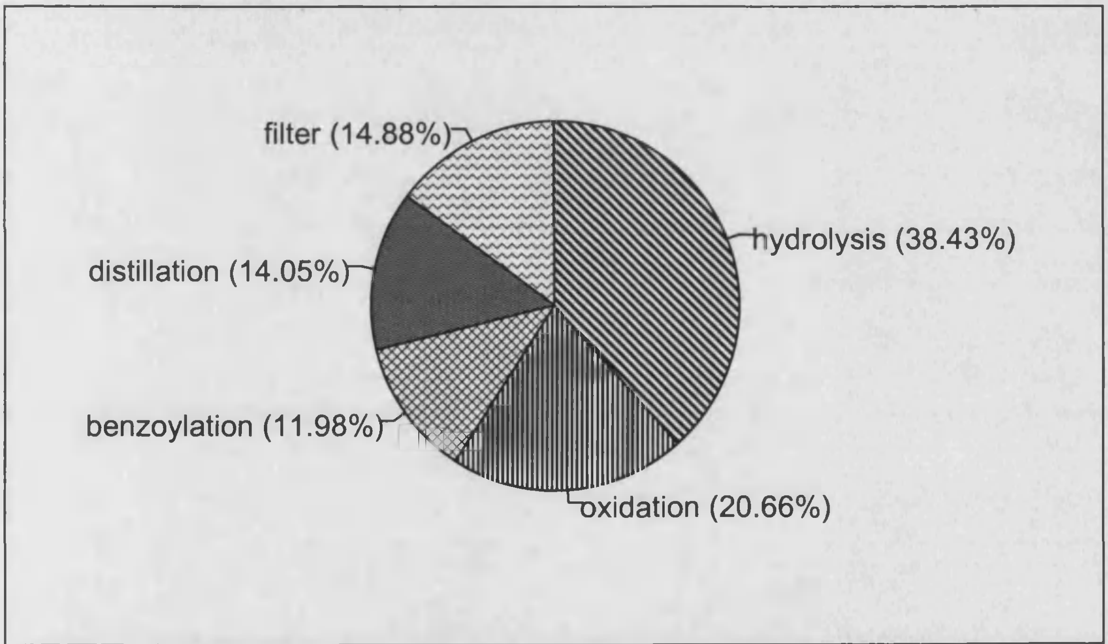
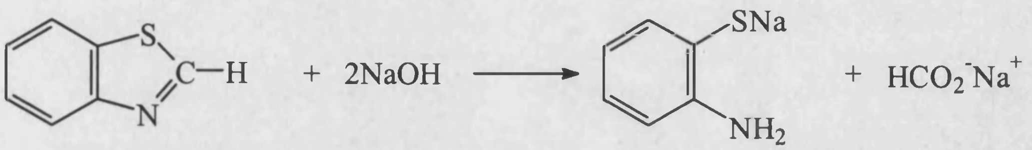


Figure 4.1: Percentage of the total cycle time for each operation

Several of the materials present in the vent streams would cause odour problems if released directly to the atmosphere. Consequently, a scrubber is used to remove these materials. The residual vapours are released and the saturated scrubbing fluid is disposed of to effluent treatment.

4.2.1 Hydrolysis

The hydrolysis reaction is as follows:



Benzothiazole [$C_6H_4(SN)(CH)$] reacts with sodium hydroxide to form sodium 2-amino thiophenate [$(C_6H_4(SNa)(NH_2)$] and sodium formate. Sodium 2-amino thiophenate is denoted by stage 1 or S1 product throughout this chapter. The benzothiazole feed contains contaminants by weight percent:

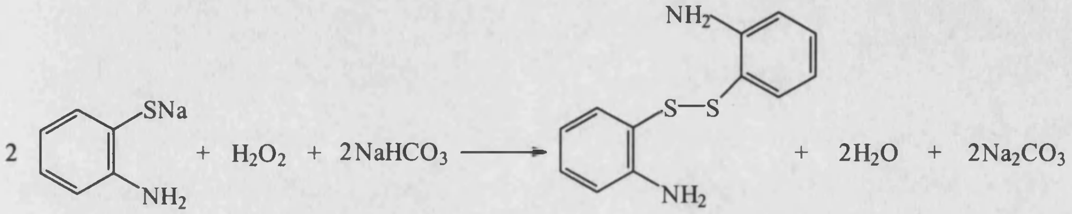
contaminant A = 2 %
contaminant B = 0.8 %
contaminant C = 0.3 %
contaminant D = 0.07 %

The main organic contaminant, contaminant A, reacts similarly to benzothiazole but produces sodium acetate instead of sodium formate. The other main contaminant, contaminant B, remains unreacted during hydrolysis.

When the reaction is complete the vessel contents are sampled and the vessel is vented to atmosphere. The vent stream passes through a condenser, thereby removing condensate for offsite disposal. Any residual vapours are sent to the scrubber. The vessel contents are then left to cool.

4.2.2 Oxidation

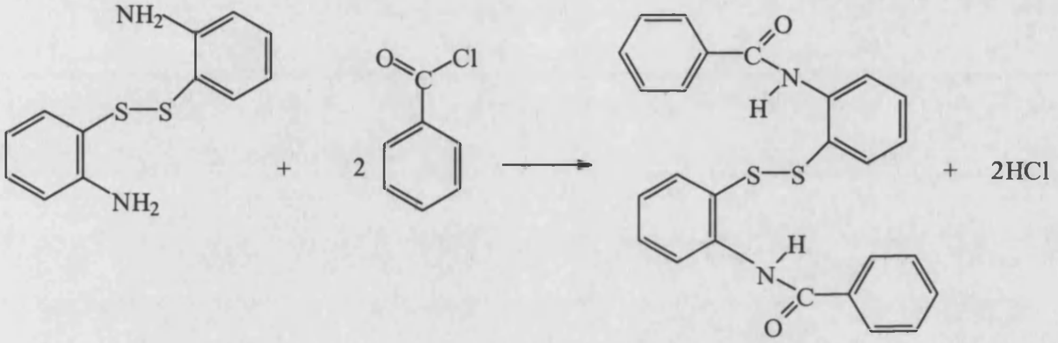
During oxidation, stage 1 product is oxidised to form 2,2'-diaminodiphenyl disulphide [$(C_6H_4(NH_2)S)_2$] in the presence of sodium bicarbonate. Stage 2 or S2 product has been used to represent 2,2'-diaminodiphenyl disulphide in this chapter. The reaction is as follows:



During the reaction the vessel pressure is kept constant by continuous venting. Owing to the fact that the oxidation product degrades if it is allowed to stand for an extended period of time, excess hydrogen peroxide is added to ensure that the reaction goes to completion rapidly.

4.2.3 Benzoylation

During benzoylation, stage 2 product is reacted with benzoyl chloride to produce 2,2'-dibenzaminodiphenyl disulphide [$(C_6H_3S(NH)C)C_6H_5)_2$] and hydrogen chloride. 2,2'-dibenzaminodiphenyl disulphide is known as Pepton and is the saleable product. The reaction is as follows:



Additional reactions occur between benzoyl chloride and the hydrolysis feed contaminants, contaminant B and contaminant C, to form contaminant E and F respectively.

After the reaction is complete, the vessel contents are heated to improve the solution of the product in the toluene phase. Additional toluene is introduced to ensure sufficient phase separation occurs. The resulting aqueous layer containing the sodium salts, soluble by-products and a trace amount of toluene is removed and transferred to waste tanks. The toluene containing Pepton and residual water is passed to the next stage.

4.2.4 Distillation

A batch distillation is carried out to remove the toluene from the product mixture. The distilled vapours produced during distillation contain both toluene and water. These are condensed and the water and toluene phases decanted in a separator tank. The recovered toluene is reused and the water is used to reslurry the product in the distillation vessel.

During the distillation the concentration of toluene in the vessel decreases causing the solid Pepton product to precipitate out in the water phase. Once the majority of the toluene has been removed the material in the vessel is slurried with water from the separation tank and subsequently, transferred to the filter beds.

4.2.5 Filtration, drying and product preparation

The aqueous stream from the distillation stage contains the Pepton product and is passed to the filter beds where water is removed. After filtering any residual water is removed in a vacuum dryer. The product is then milled and prepared for sale. The present study does not consider these stages in detail.

4.2.6 Scrubber

Several of the materials present in the manufacture of Pepton may cause odour problems if released directly to atmosphere. Hence, the major vapour flows from the process vents pass through a counter-current recirculation scrubber to remove these materials.

4.2.7 Overall mass balance

An overall mass balance for the Pepton process has been taken from the IPC application and is shown in Figure 4.2. The figures differ by less than 1% of the total flow and therefore, the values are considered acceptable for a preliminary assessment of the operations.

There are three main waste outputs from the process: aqueous wastes, vapours released to the atmosphere and solid wastes. The aqueous effluent is the largest source of waste, with the majority originating from the benzoylation stage. Aqueous emissions during hydrolysis and oxidation result from the condensers. The aqueous stream contains various contaminants and is disposed of offsite. Water that is collected from the phase separation vessel during distillation is reused to slurry the product and is removed during the product drying stage.

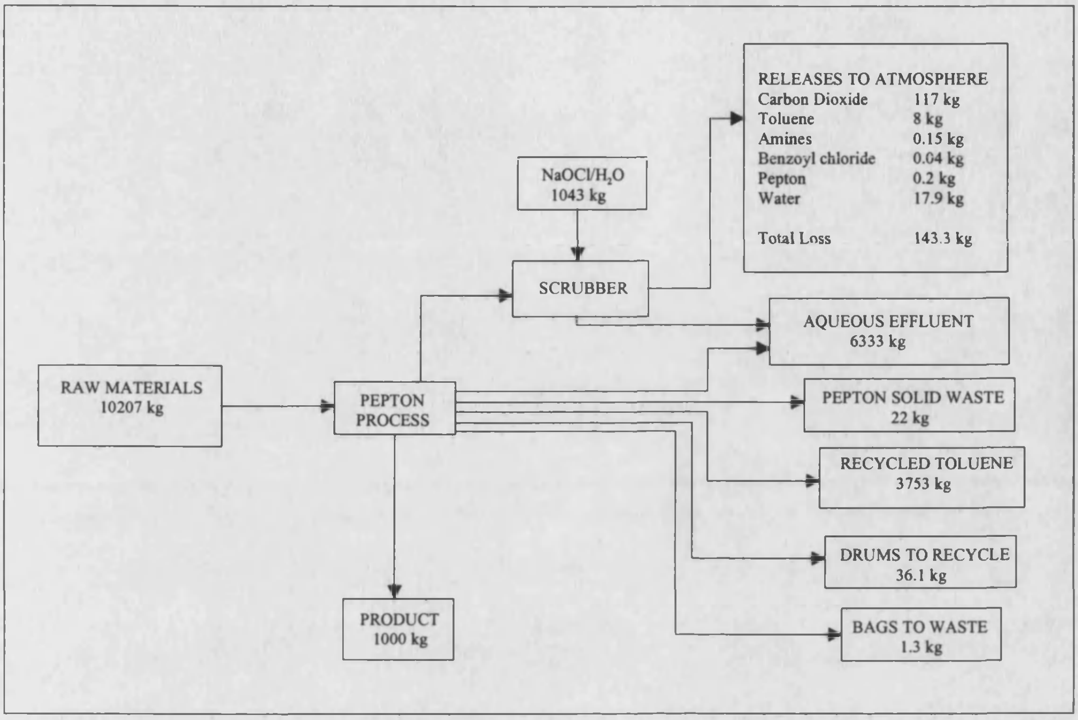


Figure 4.2: Pepton process mass balance

The emissions to air are dominated by carbon dioxide which is a by-product of the benzoylation reaction. The benzoylation stage contributes 88% of the releases to the scrubber, oxidation 9% and hydrolysis 3%. Amines are removed from the vapour streams by the scrubber so only small amounts are released.

A large proportion of the toluene is recovered by the distillation and recycled. Only a small amount of toluene is lost in the aqueous waste and the amount released to atmosphere is reduced by the operation of coolers and condensers on the vessel vents.

4.3 Modelling

HYSYS has been used to simulate several of the Thomas Swan operations. HYSYS, developed by AEA Technology (formerly Hyprotech), is a state-of-the-art hybrid package that combines steady state and dynamic modelling. HYSYS was chosen rather than any of the other available packages for three main reasons:

- The models produced were robust and used accurate physical property data and thermodynamic packages. Because HYSYS is a commercial package it utilises extensive property data that has been widely validated;
- It was easy to use and the models of the operations could be developed quickly and accurately. The HYSYS package is an object orientated program, whereby the flowsheet is built up from standard process blocks. The equations describing the units are contained within the program and therefore do not have to be developed for each operation. Other simulators such as Speedup, require the development of equations to describe the process units. This was considered to be time consuming and would require in-depth knowledge of the process. Ultimately, the aim of the study was to examine waste minimisation options and assess environmental impact rather than develop complex computer models. Additionally, the level of data available from the plant was limited due to lack of monitoring. Therefore, detailed models could not have been adequately validated against plant data;
- Process parameters could be changed quickly and their affect on the process emissions were easy to identify. HYSYS simulates the operations dynamically and produces real time strip charts. Any parameter could be changed during the simulation and the effects examined on the strip charts.

Base case models have been developed for the following operations:

- hydrolysis charging, heating and venting,
- oxidation charging, reaction and purging,
- benzoylation charging, reaction, heating, and additional toluene charging,
- batch distillation.

The hydrolysis reaction has not been modelled because the vessel is sealed and therefore, there are no emissions. As will be shown in Section 4.3.6 the base case models match well with the plant data and there is generally good agreement between the plant and model mass balances. However, there were several areas where the models needed to be manipulated to allow batch processes to be modelled. These areas are discussed below:

- The HYSYS database contains a large selection of materials applicable to a wide range of industries. However, several of the complex organic materials used in the Pepton process such as benzothiazole (BT), stage 1 product, stage 2 product and Pepton were not available in the software. Sodium compounds such as sodium bicarbonate and sodium chloride were also unavailable in the materials database.

- Modelling purely organic streams was straight-forward. However, aqueous streams proved more difficult to model, especially during charging and heating operations. In the simulation, the vessel conditions during charging are predicted from the feed stream temperature and pressure as it enters the vessel. However, the predicted properties of water were incorrect causing the initial dynamic water flash calculation to fail. As a result the vessel temperature and pressure passed out of the allowable range for the HYSYS models.

- The HYSYS program has been developed from a steady state program, HYSIM, that was used mainly in the petrochemicals industry for analysing continuous operations. Consequently, the HYSYS program is also biased towards these applications. The simulation of operations similar to those usually carried out on continuous plants, such as reaction modelling or heating, worked well. However, when individual batch operations were modelled sometimes the expected process response did not occur. For example, a vent flow was not predicted whilst charging a vessel. Also some of the operations such as convective cooling were not available in the HYSYS units operations library.

- During steady state a flow of a material passes through the process units, whilst in batch operations material is often kept in the vessel and reactants are added. However, in the HYSYS models when a reactant was kept in a vessel it was not recognised and therefore no reaction occurred when the other reactants were added.

- Either Euler or Runge-Kutta algorithms are used by HYSYS to solve the dynamic flowsheets. These worked well for most applications but during several complex combinations of operations the calculations failed to converge and no stable solution could be achieved.
- HYSYS has the capability to model reactions in detail. However, owing to the lack of kinetic data for any of the Pepton reactions the reaction modelling had to be simplified. Collecting data from the plant was limited due to the complexity of the reactions, the varying nature of each batch and the lack of online monitoring on the plant.

To simulate a process the properties of the materials are required and these are calculated within HYSYS using a property package. There is a wide range of property packages available in the HYSYS program and those selected for the current models are detailed in the next section. The prediction of the properties for materials that did not appear in the materials database is also discussed in the next section.

In the following sections the process conditions and emission flowrates have been made dimensionless as the operating conditions of the plant are confidential. The total mass released is given per batch.

4.3.1 Prediction of material properties

Within HYSYS the thermophysical properties of a chemical compound are calculated using a property package selected from a large choice of such packages available in the program. The Peng Robinson Stryjek Vera (PRSV) equation of state has been selected for use in the majority of the simulations. PRSV is a modification of the Peng Robinson (PR) equation of state and extends the original method to highly non-ideal systems [120]. The Wilson activity model was chosen for the distillation simulations as it contained an empirical relationship for the equilibrium between water and toluene that produced the best model of the distillation operations [121].

Table 4.1 shows the predicted vapour pressure of BT as determined by several thermodynamic packages using HYSYS. PRSV provided the best predictions when compared with the literature data, despite being three times too high. The activity models, UNIQUAC and Wilson, gave the same figures in each case since the ideal gas equation was used to predict the properties of the vapour phase.

Table 4.1: Vapour pressure of BT using different property packages

	BT vapour pressure (kPa)		
Property package	10°C	20°C	50°C
Literature data [122]	-	0.013	0.095
UNIQUAC [123]	0.0443	0.0879	0.5316
Wilson [121]	0.0443	0.0879	0.5316
SRK [124]	0.0163	0.0374	0.3173
PR [125]	0.0207	0.0463	0.3678
PRSV [120]	0.153	0.0353	0.3055

The complex organic molecules, such as BT, were not available in the HYSYS materials database and therefore their properties were predicted using a UNIFAC model. The UNIFAC model uses a group contribution concept [126], whereby the thermophysical properties of a material are assumed to be the sum of the contributions made by the molecules' functional groups. The HYSYS UNIFAC model enables standard molecular building blocks to be pieced together to form the required molecular structure. Predictions of the material properties are based on the type and order of the molecular blocks chosen. For example, the benzothiazole molecule was represented as $(ACH)_6NS(CH)$. The resulting property predictions from any group contribution method are only approximate as the contribution of a given functional group is not necessarily the same in different molecules. In reality a functional group may affect the behaviour of neighbouring groups so changing the expected properties of the material.

The accuracy of the UNIFAC property predictions has been compared with available published literature [122]. For example, the boiling point of BT was predicted to be 187°C by UNIFAC compared with 227°C from the literature. Consequently the vapour pressure of BT in the simulations was higher and more material was predicted to appear in the vapour stream than would be expected. The density of BT was predicted to be 801 kg/m^3 by UNIFAC, whereas the literature value is 1246 kg/m^3. This resulted in the volume of a given mass of BT being greater in the simulations than in practice and therefore, vapour displacement was over-estimated. Because both of these errors would over-predict the amount of organic material released in the vapour the emissions would also be over-estimated by the simulations. Therefore, it was decided that the predicted material properties, albeit inaccurate, could be used for the simulations.

Unfortunately no published experimental data was available for the other chemical materials whose properties were predicted using UNIFAC. Table 4.2 shows the trend in the density and boiling point predicted for these materials. As expected the density and boiling point of the materials increased with increasing molecular weight. Because the molecular structures of these materials are similar to BT, similar errors in the material property predictions, as detailed previously, are likely to occur.

Table 4.2: Comparison of the material properties predicted by UNIFAC

Molecule	Molecular weight	Density (kg/m^3)	Boiling point (°C)
benzothiazole	135	801	188
stage 1 product	149	810	204
stage 2 product	248	942	530
Pepton	454	943	899

Several of the materials (stage 1 product, stage 2 product and Pepton) contain sodium. However, sodium was not available in the UNIFAC package. Therefore, the resulting material properties may not accurately predict the interaction of the materials with water or their behaviour in the organic liquid phase. These interactions are important for calculating the composition of the liquid phases and predicting product precipitation. The two operations where the effect of interactions would be most apparent are the phase separation after the batch distillation and product precipitation during distillation. It was considered unnecessary to model the phase separation to predict the composition of the aqueous split as this was obtained from a laboratory analysis provided by Thomas Swan. The product precipitation was not modelled because it was considered that the amount of process wastes would not be altered by changing the process parameters of this operation.

A number of the inorganic sodium compounds were also not available in the HYSYS materials database. However, sodium hydroxide was available and the physical properties of the other sodium compounds were generally taken to be the same as sodium hydroxide. In order to improve the property predictions the boiling point and the density of the compounds were changed to the data listed in the literature for the relevant materials [127]. These parameters were considered to significantly affect the behaviour of the materials at the process conditions.

Aqueous streams could not be explicitly modelled within HYSYS. Consequently, the volume of organic material in the vessel was scaled up to the actual volume of contents used in the plant. To account for the absence of the aqueous solution the mole fractions of the organic materials were adjusted. Hence, the predicted composition of the organic liquid phase was higher than in the plant resulting in a larger concentration of organic material in the vapour. Consequently, the release of organic material was over-predicted by the HYSYS models and represents a 'worst case' scenario.

4.3.2 Modelling the hydrolysis operations

4.3.2.1 Charging

Schematics of the plant hydrolysis charging operations and the corresponding simulation model are shown in Figure 4.3.

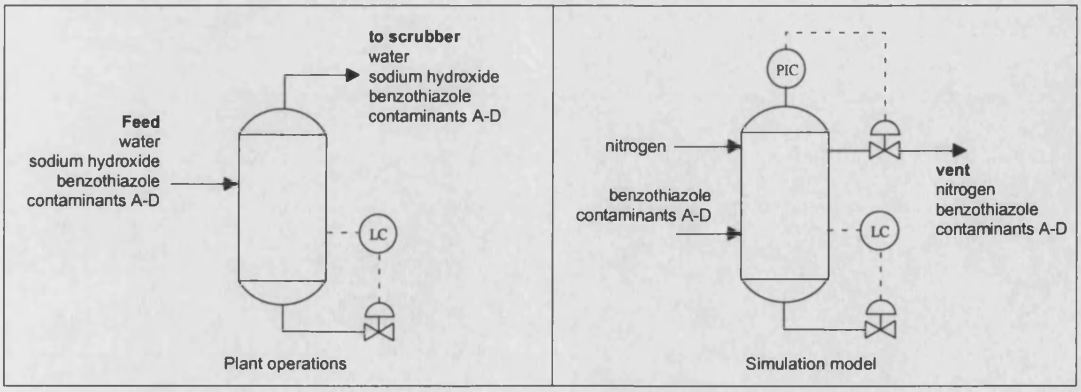


Figure 4.3: Hydrolysis charging operations

For the simulation it has been assumed that insignificant amounts of material were left in the vessel after discharging the previous batch. Consequently, the vapours displaced from the vessel would contain mainly air because no organic material would be present. Therefore, the initial charging was not modelled.

A model has been developed for charging benzothiazole (BT), including the feed contaminants A, B, C and D. In order to simulate vapour displacement during charging a flow of nitrogen, controlled by the vessel pressure, was introduced. The nitrogen enabled the model to stabilise and to ensure a steady vapour flow from the vessel was predicted. Once this was achieved the nitrogen flow was discontinued. As BT was added to the model the vessel pressure rose slightly above the controller set-point, the pressure control valve opened and vapour was displaced via the vent.

Simulation of charging aqueous sodium hydroxide could not be achieved for the reasons indicated in Section 4.3.1. Therefore, an equivalent flow rate of BT was used, thus ensuring that the correct amount of vapour displacement was predicted. In reality, the presence of water in the sodium hydroxide solution may affect the amount of BT in the displaced vapour stream. However, Table 4.3 presents the predictions of the vapour composition and this indicates that the case with no water represents the largest release of BT. The amount of BT in the vapour is likely to be over-predicted as the plant liquid phase consists of BT, water and sodium hydroxide. Both of these factors lead to an over-prediction of the organic releases from the simulated vessel and the actual plant emissions are likely to be lower. Despite the inaccuracies the simulations were used because the level of emissions predicted represented a 'worst case'.

Table 4.3: The effect of water on the amount of BT in the vent stream

Mole fraction water in feed stream	BT in vent stream (kmol)
0	1.50×10^{-4}
0.01	1.31×10^{-4}
0.02	1.31×10^{-4}
0.03	1.21×10^{-4}
0.04	1.21×10^{-4}
0.1	1.21×10^{-4}
0.2	1.21×10^{-4}
0.3	1.20×10^{-4}

The mass of each component released to the scrubber during hydrolysis charging operations has been predicted using the simulation and the results are shown in Table 4.4.

Table 4.4: Predicted releases from the hydrolysis charging simulation

Component	Mass released (kg/batch)	wt %
benzothiazole	4.60×10^{-3}	91.3
contaminant D	4.30×10^{-4}	8.5
contaminant B	8.70×10^{-6}	0.2
contaminant C	-	-
contaminant A	-	-
Total	5.04×10^{-3}	100

4.3.2.2 Hydrolysis heating

The next stage of hydrolysis is heating the vessel contents. Figure 4.4 shows schematics of this operation and the corresponding simulation model.

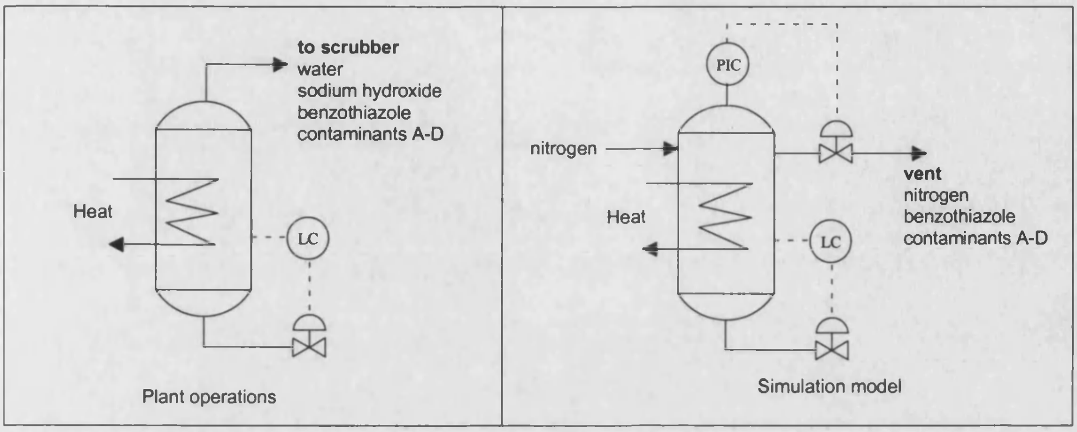


Figure 4.4: Hydrolysis heating operations

The simulation behaved in the same way as the plant operations. However, no water or sodium hydroxide was introduced due to the problems previously highlighted. Similarly to the hydrolysis charging model a nitrogen vapour flow and a pressure controller were required, as discussed in Section 4.3.2.1.

The simulation has been used to predict the amount of each material released to the scrubber during hydrolysis heating operations and the results are shown in Table 4.5.

Table 4.5: Predicted releases from the hydrolysis heating simulation

Component	Mass released (kg/batch)	%
benzothiazole	8.4×10^{-1}	96.4
contaminant D	1.4×10^{-2}	1.5
contaminant B	9.2×10^{-3}	1.1
contaminant C	2.6×10^{-3}	0.3
contaminant A	6.4×10^{-3}	0.7
Total	8.7×10^{-1}	100

4.3.2.3 Hydrolysis venting and cooling

During the plant operations the vessel is vented to atmosphere through a condenser once the reaction is complete. The temperature of the condenser outlet is controlled by the vapour flow from the vessel. The condensate is taken offsite for disposal and the remaining vapour goes to a scrubber where the residual organic materials are removed. After the vessel has been vented it is left to cool. Figure 4.5 shows a schematic of the plant operations and the corresponding simulation model.

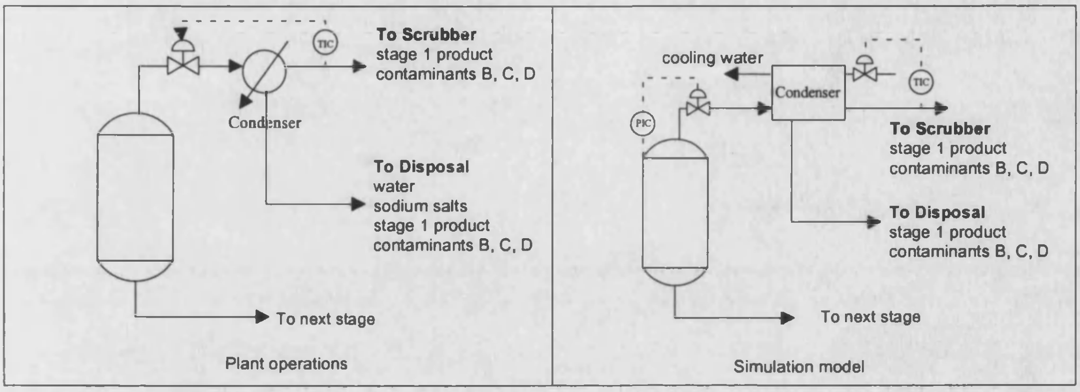


Figure 4.5: Hydrolysis venting operations

Venting has been simulated by reducing the vessel pressure gradually over the venting period at the rate indicated by the plant data. The resulting vapour stream was passed through a condenser and the temperature controlled by the flowrate of the cooling water. In the simulation, the vent flowrate could not be used to control the condenser temperature as it was not an independent variable but was calculated from the vessel conditions. An alternative control system would be to use a cascade control from the condenser temperature to the vessel pressure controller. However, the pressure controller was used to gradually reduce the vessel pressure and could not respond to two separate control actions. Aqueous materials were not included in this model due to the problems discussed in Section 4.3.1.

Table 4.6 shows the predicted amount of each material released to the scrubber and to condensate using the simulation. 1.3% of the total stage 1 product is predicted to be lost through the vent, which is a large amount when compared with the amounts of the other materials released. However, on plant the loss was estimated to be 5.3% and therefore, the simulation was under-predicting the amount of stage 1 product released. The simulation was considered to represent the 'worst case' in terms of releases to atmosphere. However, a lower loss than observed on the plant may have been predicted due to two phenomena that are not accounted for in the HYSYS program. Firstly, it is possible that stage 1 product becomes entrained in the vapour flow during the plant venting operations. Secondly, inadequate mixing may leave areas of boiling material that are released when the vent is opened, stripping out stage 1 product.

Table 4.6: Predicted releases from the hydrolysis venting simulation

Component	Mass of material (kg/batch)	
	to scrubber	to condensate
contaminant B	$2.7\text{x}10^{-3}$	$2.1\text{x}10^{-1}$
contaminant D	$6.2\text{x}10^{-2}$	$9.6\text{x}10^{-2}$
contaminant C	$5.2\text{x}10^{-4}$	$3.8\text{x}10^{-2}$
stage 1 product	$4.7\text{x}10^{-2}$	14.15
Total	$1.1\text{x}10^{-1}$	14.50

To simulate the subsequent cooling operations a constant cooling duty was applied to the vessel, resulting in a linear temperature reduction of the contents. In order to maintain the vessel pressure a small flow of nitrogen was introduced to the simulated vessel. Without nitrogen the vessel pressure was predicted to drop as the vessel cooled and no vapour flow was predicted. During the simulation the nitrogen flowing through the vessel became saturated with organic material and this was used to predict the amount of material released during the cooling operation. Therefore, the amount of BT predicted to be released by the simulation depended directly on the nitrogen flowrate used in the modelling. Because in the plant, the flowrate of air over the surface was unknown, the predictions were considered inaccurate and therefore, have not been included in the predicted emissions from the hydrolysis operations.

4.3.2.4 Summary of hydrolysis modelling

Table 4.7 provides a summary of the releases predicted from the hydrolysis process simulations using the above models. These cannot be compared with plant data as there is no monitoring of the individual streams. Figure 4.6a and 4.6b show the temperature and pressure strip charts plotted from plant data and the simulated results. There is reasonably good agreement between the two sets of data for the charging operations. During heating there is a slight difference between the heating times because a constant heat rate was used in the simulation. In the actual plant there was a short period where no heating occurred, thereby extending the heating period. There are no simulated results for the reaction exotherm because the operation was not modelled as no emissions occur. The simulated pressure curve for the venting operations compares well with the plant data. However, the temperature drop during venting was not predicted by the HYSYS model. Cooling was modelled using a constant cooling duty which does not match well with the plant data. Nevertheless because the vessel is left to cool under convective cooling over a long period of time it was considered that the emissions from cooling will be insignificant.

The predicted material release profiles resulting from the hydrolysis simulations are shown in Figure 4.7. The profile for BT reaches a peak during the heating operations. The profiles for the feed contaminants are of similar shapes to the BT profile but the overall amounts released are smaller. There is no BT or contaminant A released during venting as these materials were assumed to be completely reacted. The stage 1 product appears only during venting as the vessel is sealed during the reaction.

Table 4.7: Predicted releases from the hydrolysis simulations

Component	Mass of material (kg/batch)			
	to scrubber			to condensate
	charging	heating	venting	venting
benzothiazole	4.6×10^{-3}	8.4×10^{-1}	0	0
contaminant B	8.7×10^{-6}	9.2×10^{-3}	2.7×10^{-3}	2.1×10^{-1}
contaminant D	4.3×10^{-4}	1.4×10^{-2}	6.2×10^{-2}	9.6×10^{-2}
contaminant C	0	2.6×10^{-3}	5.2×10^{-4}	3.8×10^{-2}
contaminant A	0	6.4×10^{-3}	0	0
stage 1 product	0	0	4.7×10^{-2}	14.15
Total	5.0×10^{-3}	8.7×10^{-1}	1.1×10^{-1}	14.50

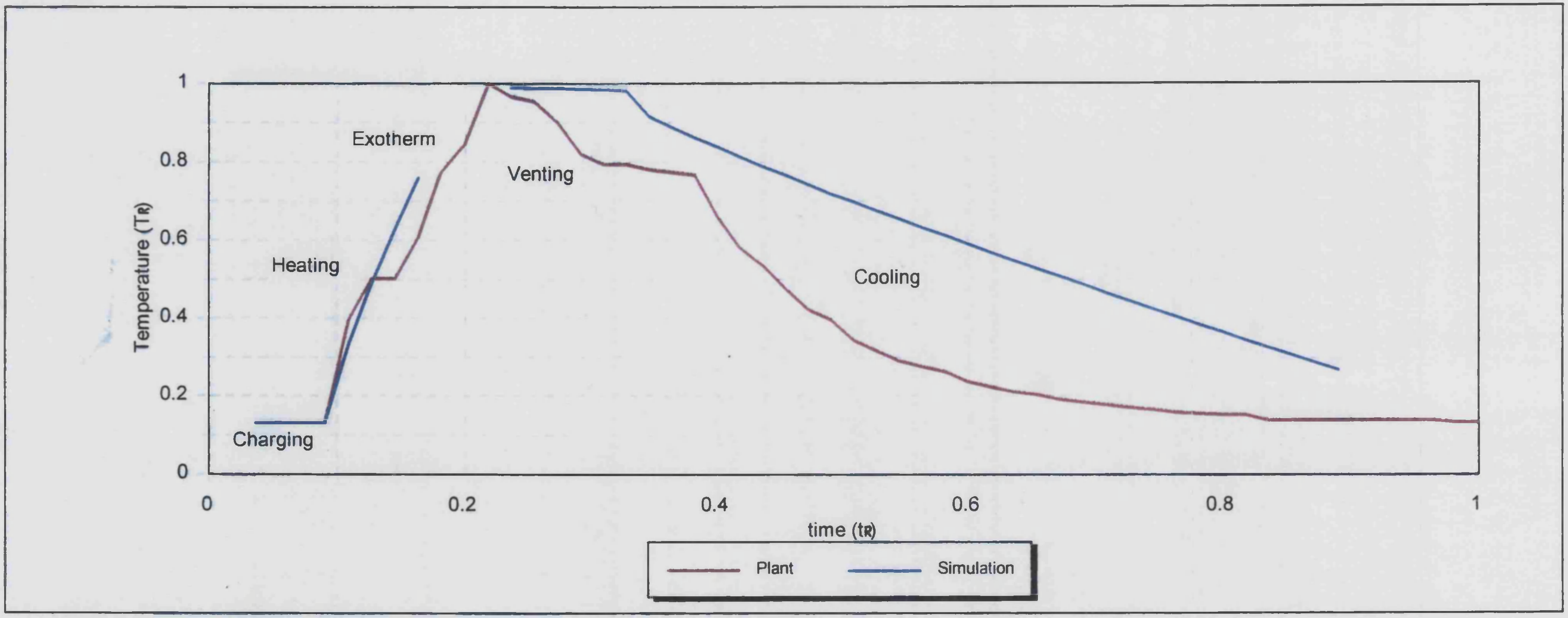


Figure 4.6a: Hydrolysis strip chart: temperature.

T_R = (actual temperature)/(maximum temperature)

t_R = (actual time)/(maximum time)

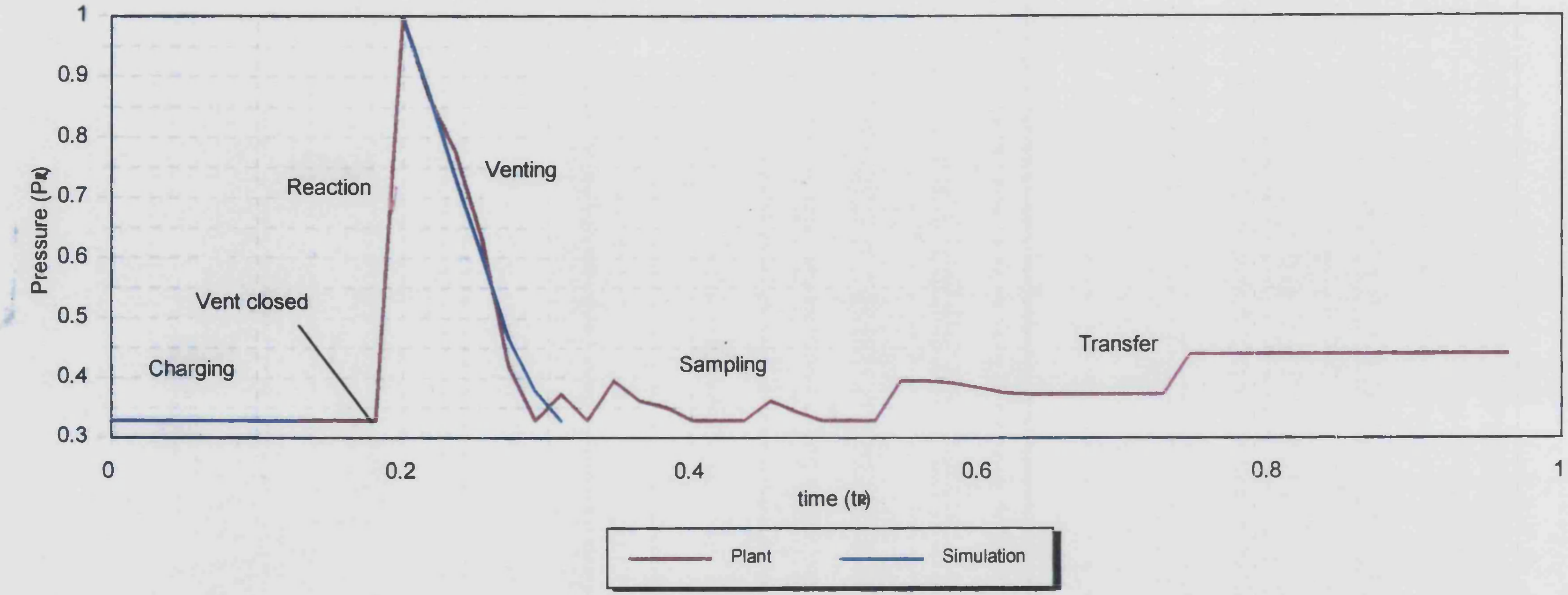


Figure 4.6b: Hydrolysis strip chart: pressure

P_R = (actual pressure)/(maximum pressure)

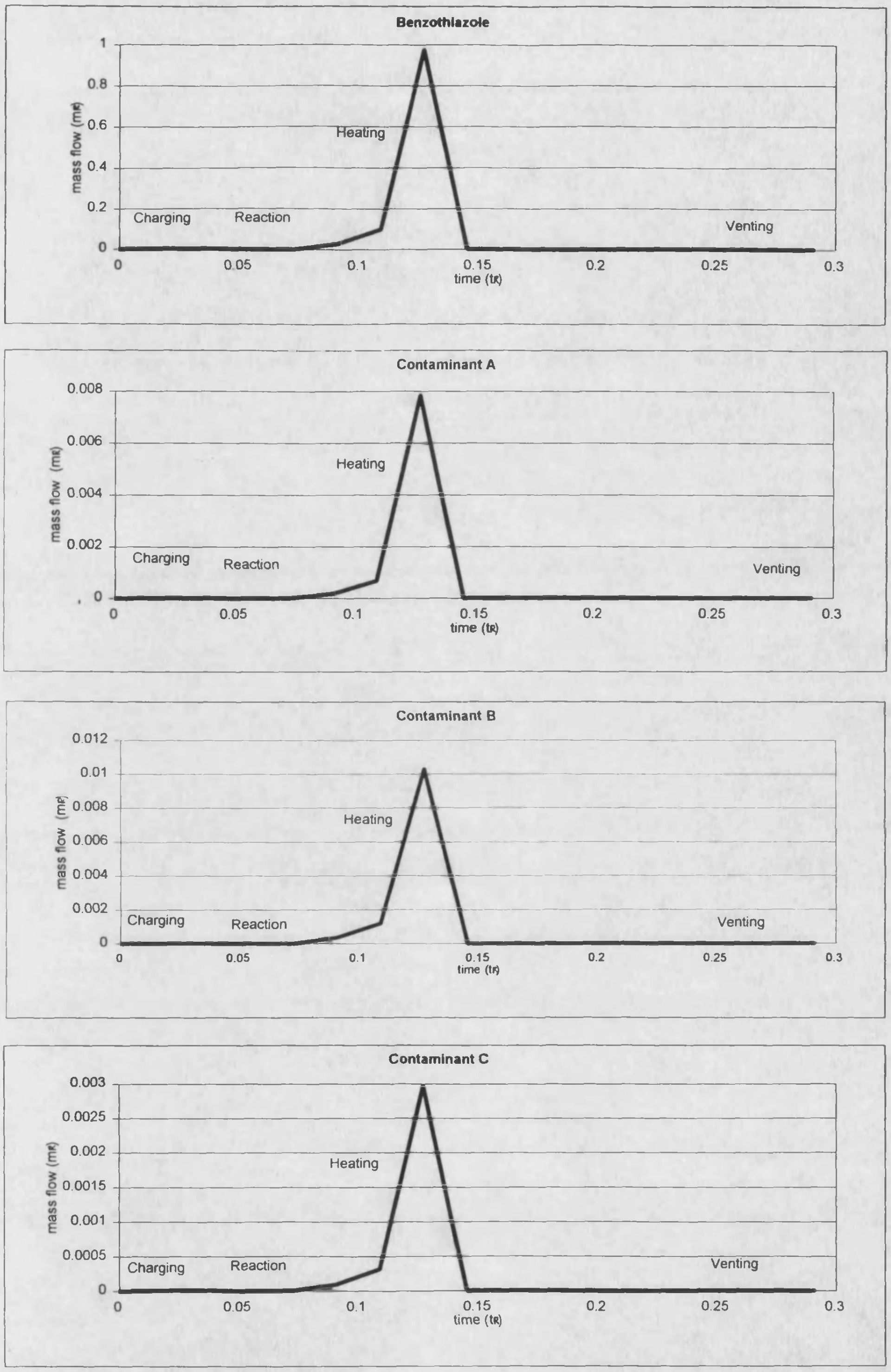


Figure 4.7: Predicted hydrolysis mass release profiles

m_R = (actual mass flowrate)/(maximum flowrate)

t_R = (actual time)/(maximum time)

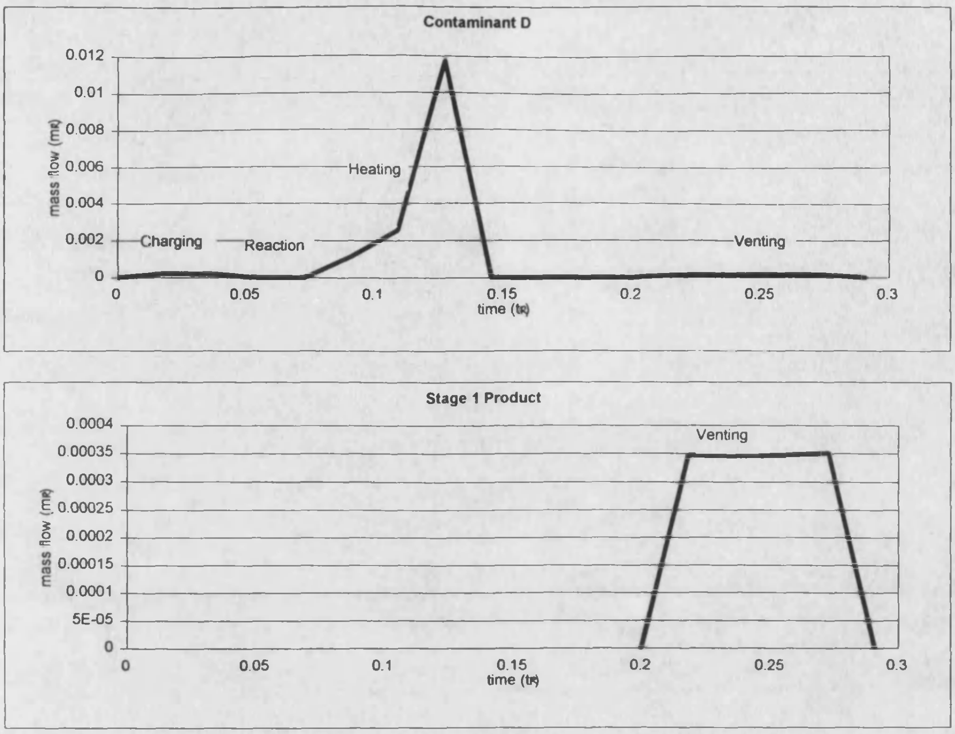


Figure 4.7 (continued): Predicted hydrolysis mass release profiles

m_R = (actual mass flowrate)/(maximum flowrate)

t_R = (actual time)/(maximum time)

4.3.3 Modelling the oxidation operations

4.3.3.1 Charging

Figure 4.8 shows a schematic of the plant operations and the model used for simulating the charging the oxidation vessel. The model has been based on the hydrolysis charging model, presented in Section 4.3.2.1.

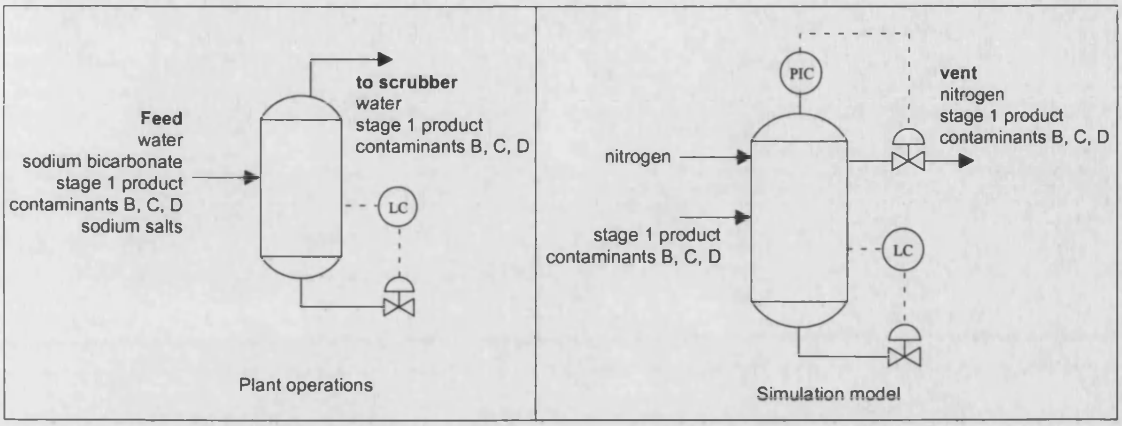


Figure 4.8: Oxidation charging operations

It has been assumed that only small amounts of material are left in the vessel after the final slurrying with water. As a result the initial charge was not modelled as the displaced vapour would only contain air and no organic material would be released.

Charging the vessel with the hydrolysis products was simulated. However, sodium formate and sodium acetate were not included in the simulation due to the problems encountered with predicting the material properties.

The simulation has been used to predict the amount of material released to the scrubber during oxidation charging operations and the results are shown in Table 4.8.

Table 4.8: Releases predicted from the oxidation charging simulation

Component	Mass released (kg/batch)	wt %
stage 1 product	$1.1\text{x}10^{-2}$	81.2
contaminant D	$2.1\text{x}10^{-3}$	15.5
contaminant B	$2.8\text{x}10^{-4}$	2.1
contaminant C	$1.6\text{x}10^{-4}$	1.2
Total	$1.4\text{x}10^{-2}$	100

4.3.3.2 Oxidation reaction

Oxidation is achieved on plant by adding hydrogen peroxide to the vessel which reacts with stage 1 product to form stage 2 product, water and sodium carbonate.

The diagrams shown in Figure 4.9 indicate the oxidation reaction plant operations and the corresponding simulation model.

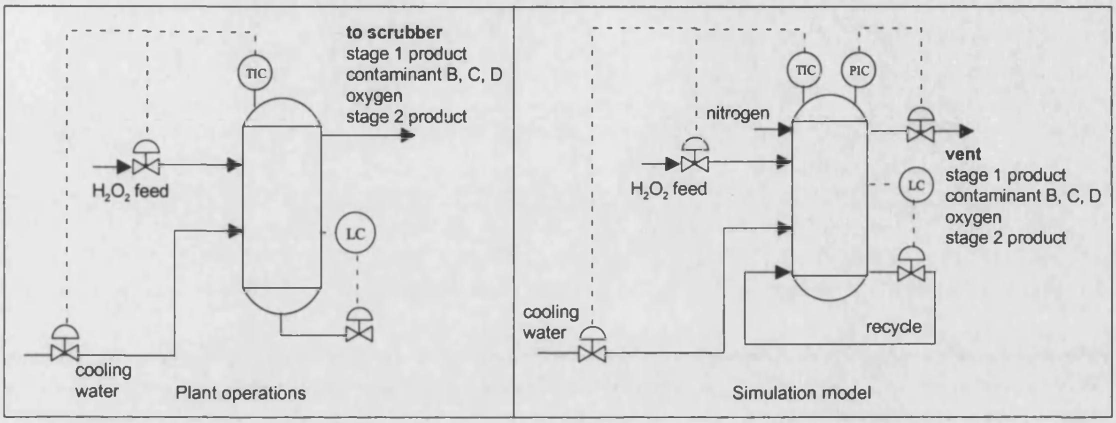


Figure 4.9: Oxidation reaction operations

During the simulation the model did not recognise the presence of the material in the vessel. Hence, when hydrogen peroxide was added no reaction took place unless there was also a flow of reactants to the vessel. To overcome this a liquid recycle was introduced to the simulation to provide a flow of stage 1 product through the vessel as indicated in Figure 4.9.

The oxidation reaction rate used in the simulations was based on the addition rate of hydrogen peroxide. It has been assumed that the hydrogen peroxide was immediately reacted as it entered the vessel. The addition rate of the hydrogen peroxide was the same as that used on the plant and a digital controller was used to control the hydrogen peroxide flowrate.

The cooling duty used for the simulation was 75% lower than that used on the plant, because when the plant cooling duty was used the temperature drop predicted was much larger than measured in reality. The reasons for the plant cooling duty being higher than the duty required in the simulation to produce the same temperature reduction may be because of ambient heat losses on the plant or because the heat of reaction predicted by the UNIFAC material properties package was too low.

The amount of material released to the scrubber during the oxidation reaction has been predicted using the simulation and the results are shown in Table 4.9.

Table 4.9: Releases predicted from the oxidation reaction simulation

Component	Mass released (kg/batch)
stage 1 product	3.4×10^{-1}
stage 2 product	1.1×10^{-7}
H_2O_2 (as oxygen)	2.7×10^{-2}
contaminant D	8.4×10^{-3}
contaminant B	1.5×10^{-2}
contaminant C	1.4×10^{-3}
Total	3.9×10^{-1}

4.3.3.3 Nitrogen purge

Purging, using nitrogen, is undertaken once the reaction is complete. Nitrogen is passed into the closed vessel containing the oxidation reaction products. When the set-point pressure is reached the vessel is depressurised. The simulation developed reflects the plant operations. The major release from the vessel was predicted to be oxygen, a by-product of the decomposition of hydrogen peroxide.

Figure 4.10 shows the schematic for the plant operations and the simulation model for the oxidation purging stage.

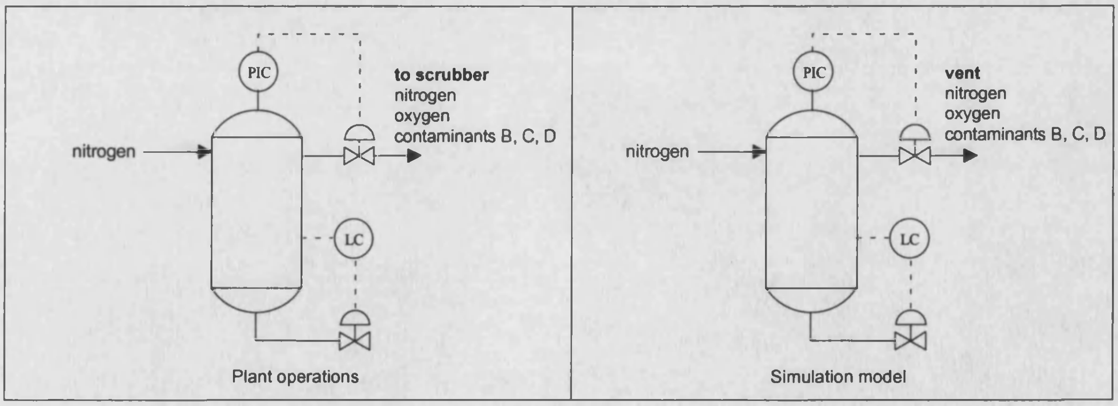


Figure 4.10: Oxidation purging operations

The amount of material released during purging was predicted using the simulation and the results are shown in Table 4.10.

Table 4.10: Releases predicted from the oxidation purging simulation

Component	Mass released (kg/batch)
stage 2 product	8.6×10^{-9}
H_2O_2 (as oxygen)	1.5×10^{-1}
contaminant D	1.5×10^{-5}
contaminant B	5.9×10^{-5}
contaminant C	8.3×10^{-6}
Total	1.5×10^{-1}

4.3.3.4 Summary of oxidation modelling

The emissions predicted from the oxidation stage simulations are summarised in Table 4.11.

Table 4.11: Releases predicted using the oxidation simulations

Component	Mass of material to scrubber (kg/batch)		
	charging	reaction	purging
stage 1 product	1.1×10^{-2}	3.4×10^{-1}	0
contaminant B	2.8×10^{-4}	1.5×10^{-2}	5.9×10^{-5}
contaminant D	2.1×10^{-3}	8.4×10^{-3}	1.5×10^{-5}
contaminant C	1.6×10^{-4}	1.4×10^{-3}	8.3×10^{-6}
H_2O_2 (as oxygen)	0	2.7×10^{-2}	1.5×10^{-1}
stage 2 product	0	1.1×10^{-7}	8.6×10^{-9}

The plant strip charts of pressure and temperature for the reaction vessel were provided by Thomas Swan. These are plotted in Figures 4.11a and 4.11b, together with the values predicted by the simulations. The plant and predicted temperature traces agree well and remain relatively constant due to the temperature control action, although the plant data is slightly more erratic than the simulated results. During the reaction the pressure of both the plant and the simulated cases is constant because the vessel is continuously vented. The plant pressure sensor is off-line during purging to protect the equipment, therefore, there is no pressure reading on the strip chart for this part of the operation.

The mass release profiles predicted from the simulations are shown in Figure 4.12. Initially, the emissions of stage 1 product increase as the temperature increases. As the reaction proceeds the amount of stage 1 product in the vessel reduces and the emissions begin to decrease. There is a build-up of excess hydrogen peroxide in the vessel towards the end of the reaction period as the stage 1 product becomes depleted resulting in a release of hydrogen peroxide to the vent. Hydrogen peroxide is released as oxygen due to decomposition in the vessel and this is released during purging. The releases of the feed contaminants B, C and D correspond directly to the variation in temperature and pressure of the simulations. Emissions of stage 2 product increase as it becomes produced as the reaction proceeds.

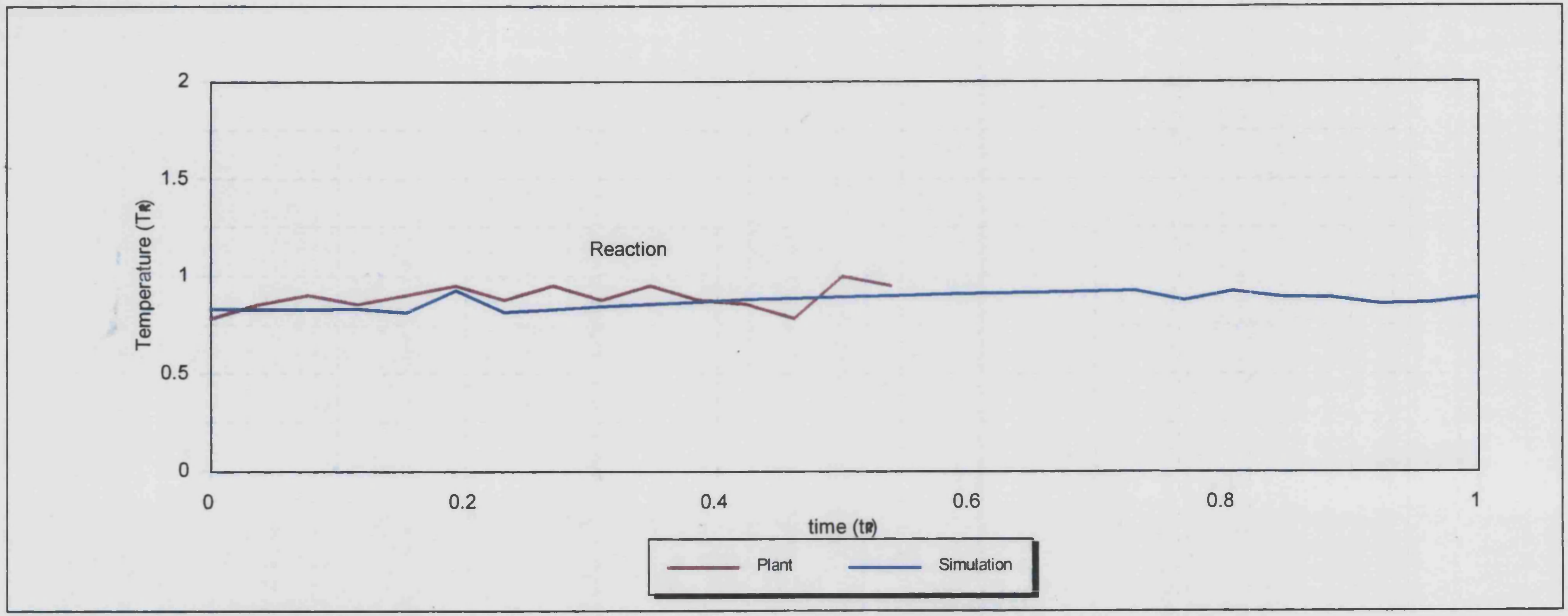


Figure 4.11a: Oxidation strip chart: temperature

T_R = (actual temperature)/(maximum temperature)

t_R = (actual time)/(maximum time)

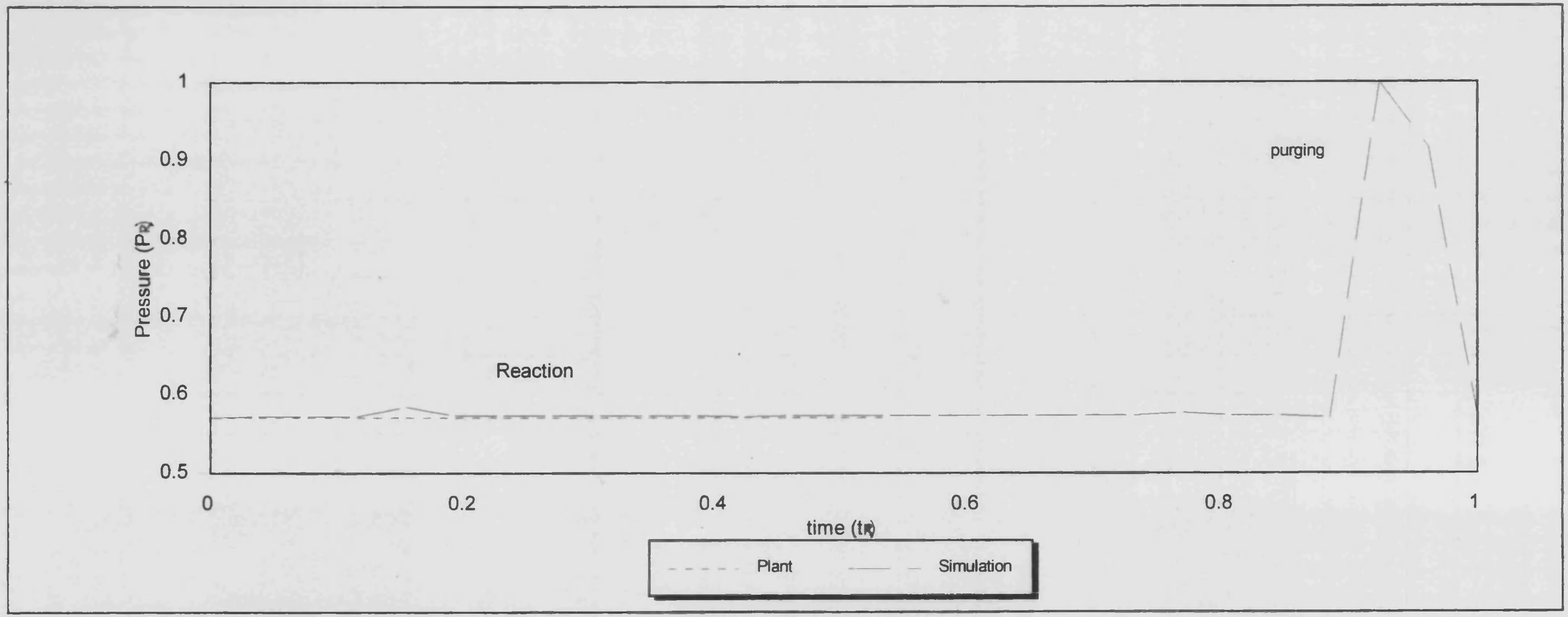


Figure 4.11b: Oxidation strip chart: pressure

P_R = (actual pressure)/(maximum pressure)

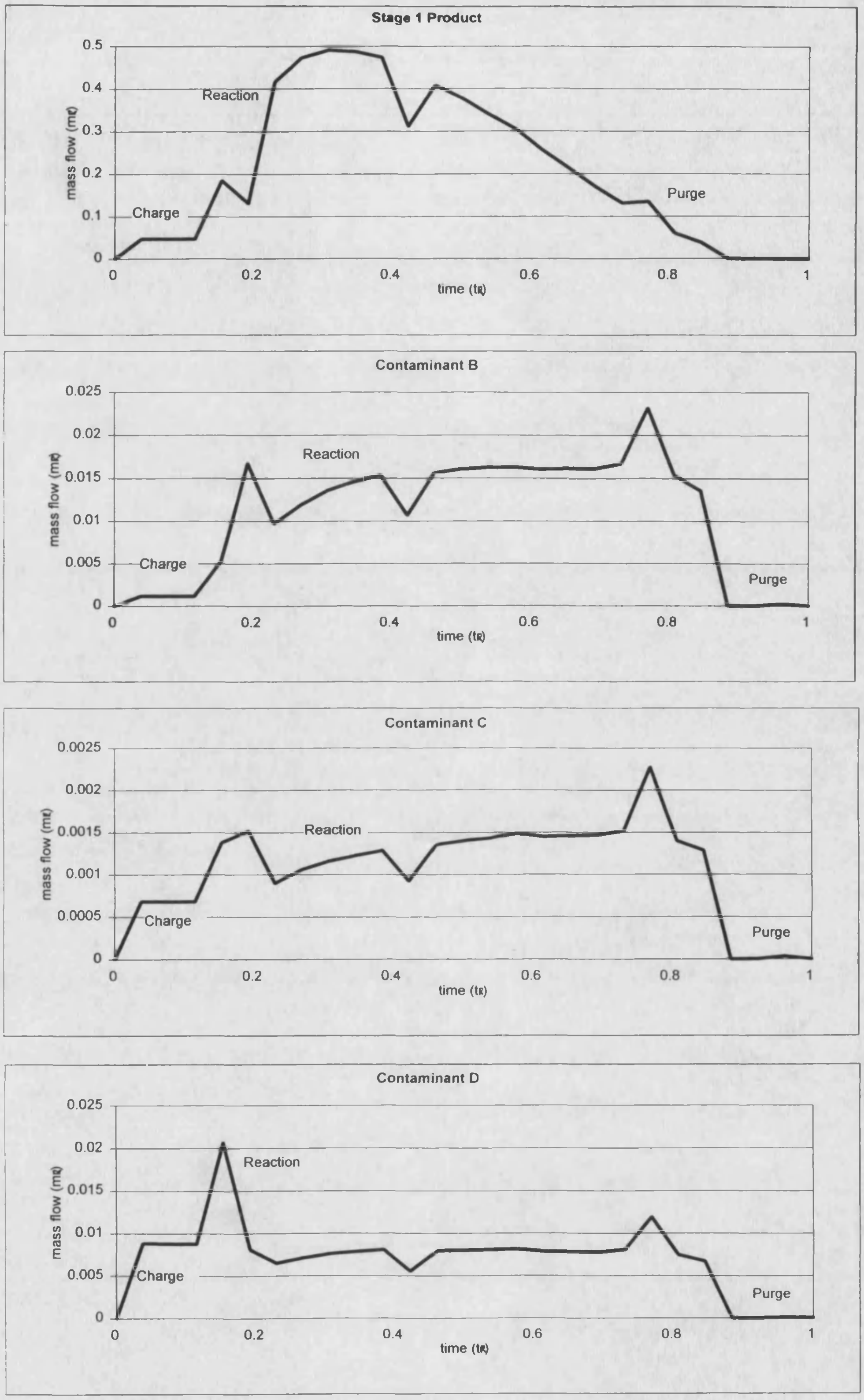


Figure 4.12: Predicted oxidation operations mass release profiles

m_R = (actual mass flowrate)/(maximum flowrate)

t_R = (actual time)/(maximum time)

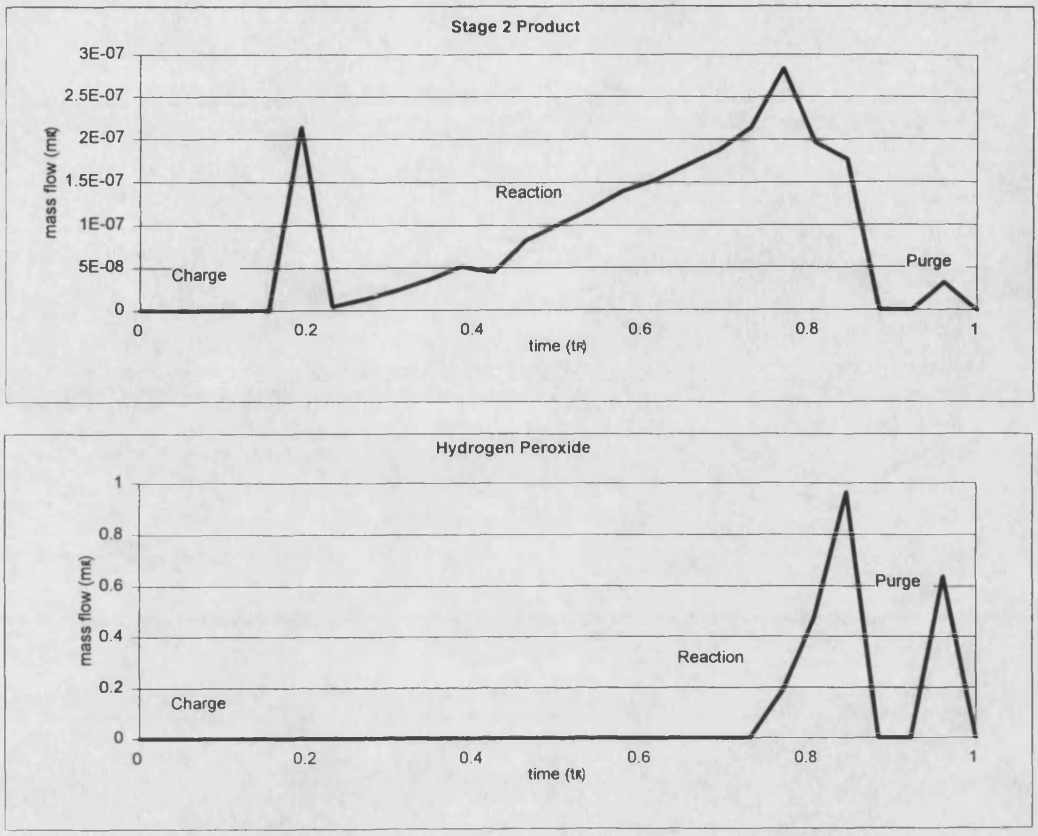


Figure 4.12 (continued): Predicted oxidation operations mass release profiles

m_R = (actual mass flowrate)/(maximum flowrate)

t_R = (actual time)/(maximum time)

4.3.4 Modelling the benzoylation operations

4.3.4.1 Charging

After the oxidation stage is completed toluene is added. In the plant operations the vapour stream displaced by the toluene is cooled in a water cooled cooler and a glycol condenser before passing to the scrubber.

The simulation has been carried out using the hydrolysis model developed in Section 4.3.2. Figure 4.13 shows a schematic of the plant operations and the simulation model developed for the benzoylation charging. In the simulation the condenser and cooler were modelled as a single unit.

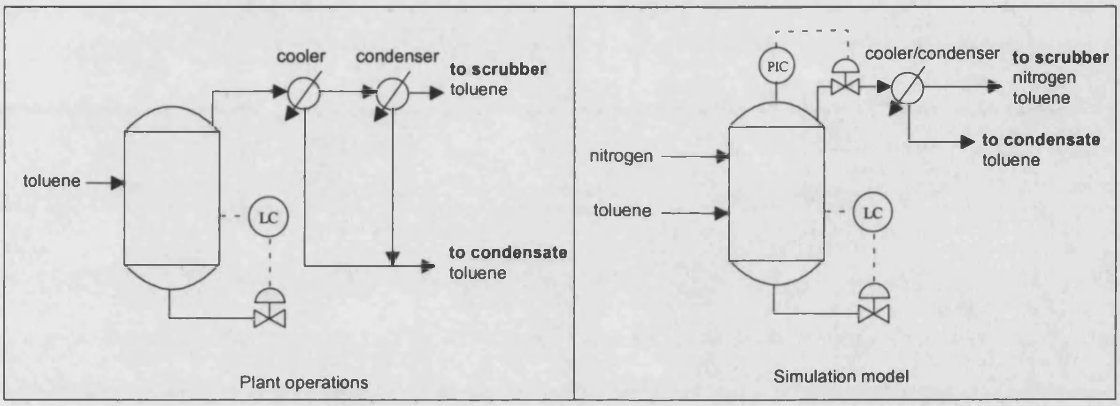


Figure 4.13: Benzoylation charging operations

The amount of toluene vapour released from the vessel and sent to the cooler/condenser unit was predicted to be 1.028 kg using the simulation. After passing through the cooler 0.134 kg of toluene remained in the vapour, whilst 0.894 kg was predicted to be removed in the condensate. To achieve this cooling 611 kJ of energy was predicted to be needed, requiring 0.5 kg of water and 12.4 kg of glycol. The following assumptions have been made:

- 42% of the temperature drop was achieved across the water cooler and 57% across the glycol condenser,
- the temperature change of both of the coolants was assumed to be 15°C, and,
- all the condensation was assumed to occur in the glycol condenser.

4.3.4.2 Reaction

Figure 4.14 shows schematics of the benzoylation reaction plant operations and the corresponding simulation model.

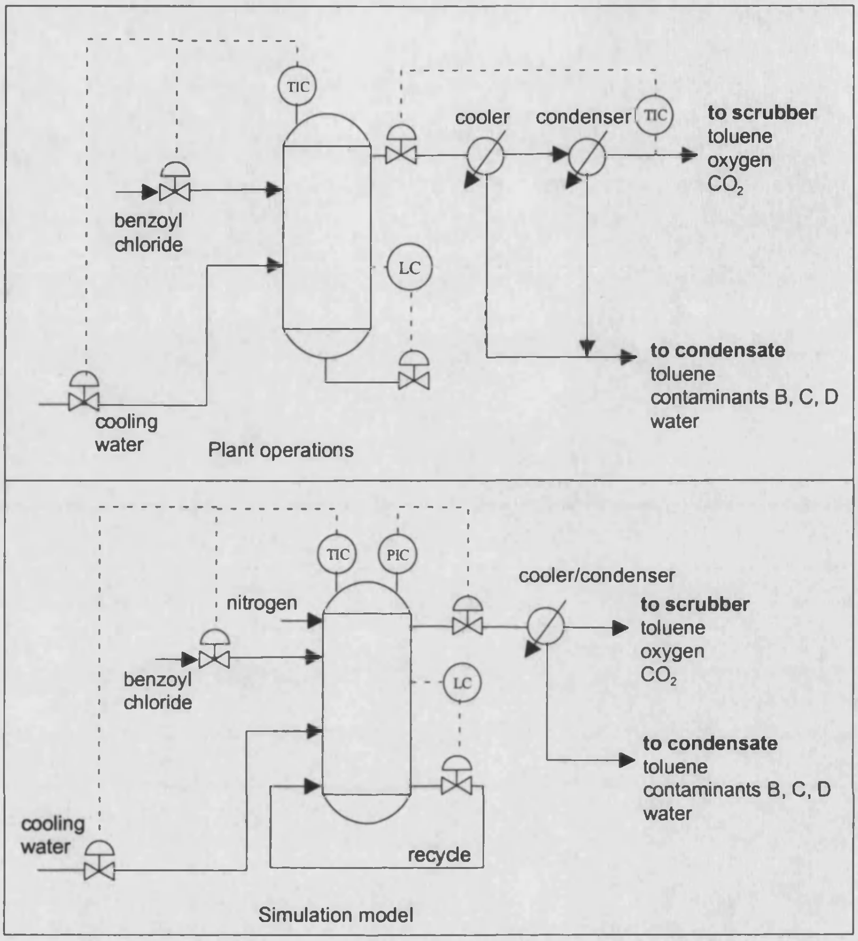


Figure 4.14: Benzoylation reaction operations

In the plant operations benzoyl chloride is added to the reaction vessel at a controlled rate because the reaction is exothermic. During the reaction, cooling is also required to maintain the temperature below the set-point. The main emission from the reaction is carbon dioxide saturated with toluene, which passes through the cooler and the condenser before being sent to the scrubber.

The simulation of the reaction was performed using a model similar to that developed for the oxidation reaction. The reaction rate was based on the addition rate of benzoyl chloride. Therefore, benzoyl chloride was assumed to react completely as it entered the vessel. The feed rate of benzoyl chloride used in the simulation was equivalent to the total amount used in the plant data, averaged over the reaction time. As with the oxidation reaction simulation a recycle stream was set up to introduce a flow of reactants to the vessel.

Sodium salts were required for the simulation and the modelling of these materials is discussed in Section 4.3.1. Water is a by-product of the reaction and the simulation delivered no errors when predicting the properties of water within the vessel.

It proved difficult to produce converged dynamic models of the entire benzoylation reaction flowsheet due to the complexity of the calculations. Therefore the composition and flows of material from the cooler and condenser were calculated using a steady state calculation within HYSYS at several time intervals.

The predicted amounts of material released from the benzoylation reaction simulation are shown in Table 4.12.

Table 4.12: Releases predicted from the benzoylation reaction simulation

Component	Mass released (kg/batch)	
	to cooler	to scrubber
carbon dioxide	155	155
H_2O_2 (as oxygen)	0	0.23
toluene	42.13	2.94
contaminant B	5.0×10^{-3}	0
contaminant C	6.8×10^{-4}	0
water	15.57	0
Pepton	1.3×10^{-9}	0
Total	212.71	158.17

4.3.4.3 Heating

In the plant operations the vessel is heated and the resulting vent stream passes through the condenser and cooler before passing to the scrubber. The simulation was performed using the model developed for hydrolysis heating, detailed in Section 4.3.2.2, with the vent stream passing through a cooler. Figure 4.15 shows a schematic of the plant operations and the simulation model.

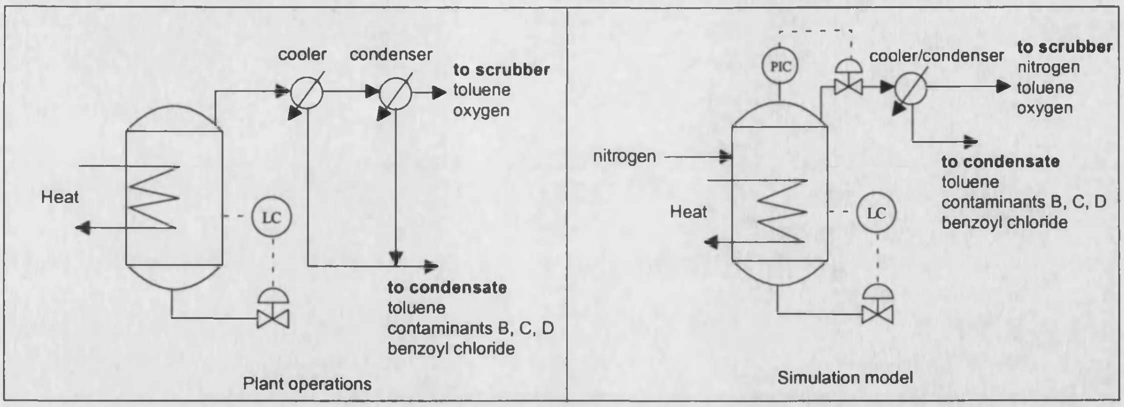


Figure 4.15: Benzoylation heating operations

The simulation has been used to predict the amount of materials released to the scrubber during the benzoylation heating operations. The results are shown in Table 4.13.

Table 4.13: Releases predicted from the benzoylation heating simulation

Component	Mass released (kg/batch)	
	To cooler	To scrubber
H_2O_2 (as oxygen)	$2.3\text{x}10^{-3}$	$2.3\text{x}10^{-3}$
toluene	$2.1\text{x}10^{-1}$	$7.0\text{x}10^{-3}$
benzoyl chloride	$2.0\text{x}10^{-4}$	0
Pepton	$1.8\text{x}10^{-18}$	0
Total	$2.1\text{x}10^{-1}$	$9.3\text{x}10^{-3}$

4.3.4.4 Second charge of toluene

The next stage in the plant operations is the addition of toluene to ensure the product is in the organic phase. This is performed at a higher temperature than the initial toluene charge. The simulation was carried out using the benzoylation charging model detailed in Section 4.3.4.1.

The simulation predicted that a total of 2.461 kg of toluene was released during this charging operation, with 2.405 kg removed in the condenser and the remaining 0.056 kg sent to the scrubber. The amount of toluene predicted to be released during the two toluene charges is shown in Table 4.14.

The amount of toluene released was dependant of the temperature of the stream and the duration of the release. The temperature of the first charge was lower than the second charge. Therefore, less material was released to the cooler. However, after the cooler, both the streams were at the same temperature, but the second charge released less toluene because the charge time was shorter.

Table 4.14: Comparison of predicted releases from the toluene charging operations

Operation	Toluene released (kg/batch)		Mass coolant used (kg/batch)	
	to condensate	to scrubber	water	glycol
1st charge	0.90	0.14	0.5	12.4
2nd charge	2.41	0.06	3.8	32.4
Total	3.31	0.20	4.3	44.8

4.3.4.5 Aqueous discharge

On plant the aqueous layer in the vessel is removed before the distillation stage begins, leaving the product in the toluene phase. The aqueous waste contains feed contaminants, salts from the process and a small amount of toluene. If this material remained in the process the sodium bicarbonate would decompose to carbon dioxide causing foaming during distillation. An equivalent aqueous stream was removed from the simulation before the batch distillation was modelled.

The composition of the aqueous phase, shown in Table 4.15, was taken from laboratory tests provided by Thomas Swan and the total mass of material was calculated from a mass balance over the previous operations. Additional materials (sodium benzoate, benzothiazole and contaminant B) have been added due to the composition of the laboratory tests. Contaminants E and F are products of a side reaction.

Table 4.15: Predicted masses released in the aqueous layer, the composition of which was taken from laboratory analysis provided by Thomas Swan

Component	Mass released (kg/batch)
benzoyl chloride	138.42
sodium salts	1983.45
hydrogen peroxide	19.10
toluene	3.53
water	7048.30
Pepton	1.01
contaminant E	7.50
contaminant F	21.14
benzothiazole	1.01
contaminant B	1.01
Total	9224.47

4.3.4.6 Summary of benzoylation operations

Table 4.16 shows a summary of the predicted releases from the simulation of the benzoylation operations. The aqueous waste is shown in Table 4.15.

Table 4.16: Releases predicted from the benzoylation simulations

Component	Mass of material released (kg/batch)			
	to scrubber			
	charging 1	reaction	heating	charging 2
H_2O_2 (as oxygen)	0	0.23	2.3x10^{-3}	0
toluene	0.14	2.94	7.0x10^{-3}	5.6x10^{-2}
carbon dioxide	0	155.02	0	0
	to condensate			
	charging 1	reaction	heating	charging 2
contaminant B	0	5.0x10^{-3}	0	0
contaminant C	0	6.8x10^{-4}	0	0
benzoyl chloride	0	0	2.0x10^{-4}	0
toluene	0.90	39.19	0.21	2.41
water	0	15.57	0	0
Pepton	0	1.3x10^{-9}	0	0

The strip charts of the plant and simulation data for the benzoylation operations are plotted in Figures 4.16a and 4.16b and there is general agreement between the two. Continuous venting means that the pressure is constant during the operations. During heating the plant temperature data are more irregular than the simulated data. However, the simulation reaches the correct final temperature at the same time as the plant data. The predicted mass release profiles of materials to the scrubber are shown in Figure 4.16. Toluene and carbon dioxide are the major releases and oxygen is produced from the decomposition of hydrogen peroxide.

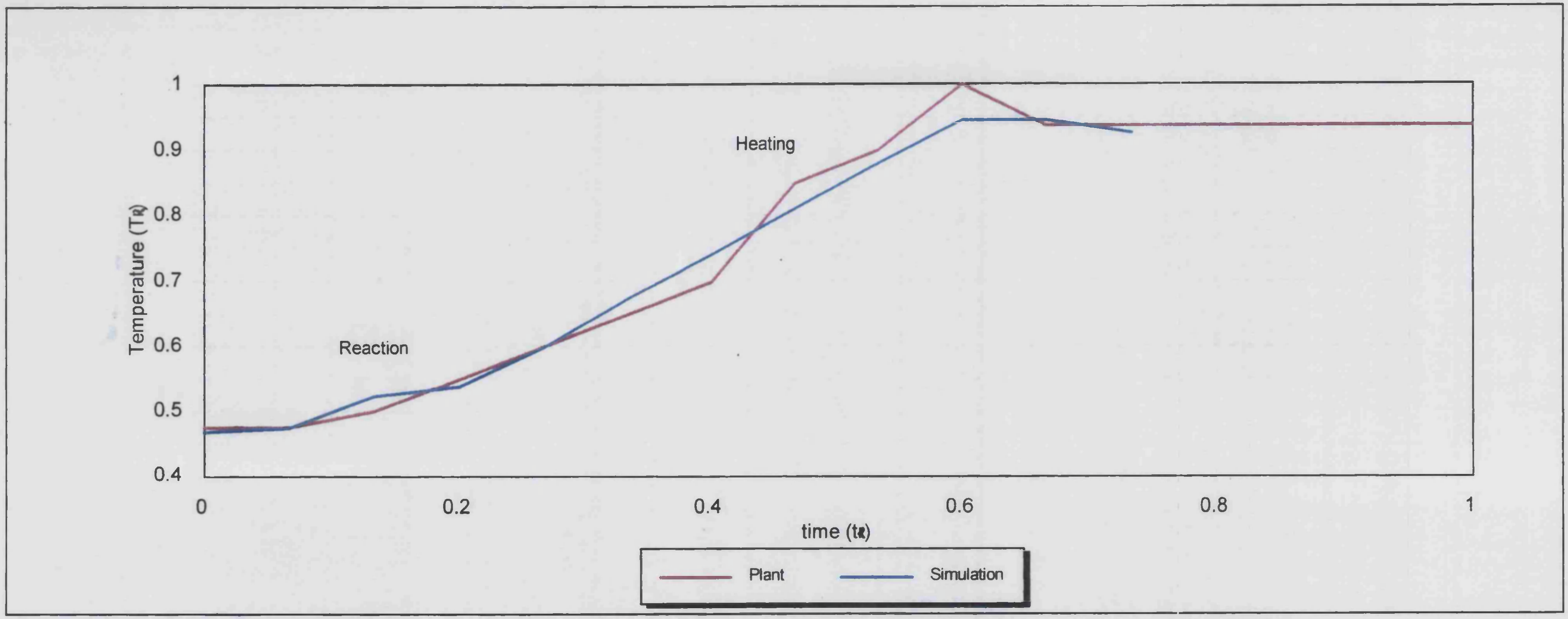


Figure 4.16a: Benzoylation strip chart: temperature

T_R = (actual temperature)/(maximum temperature)

t_R = (actual time)/(maximum time)

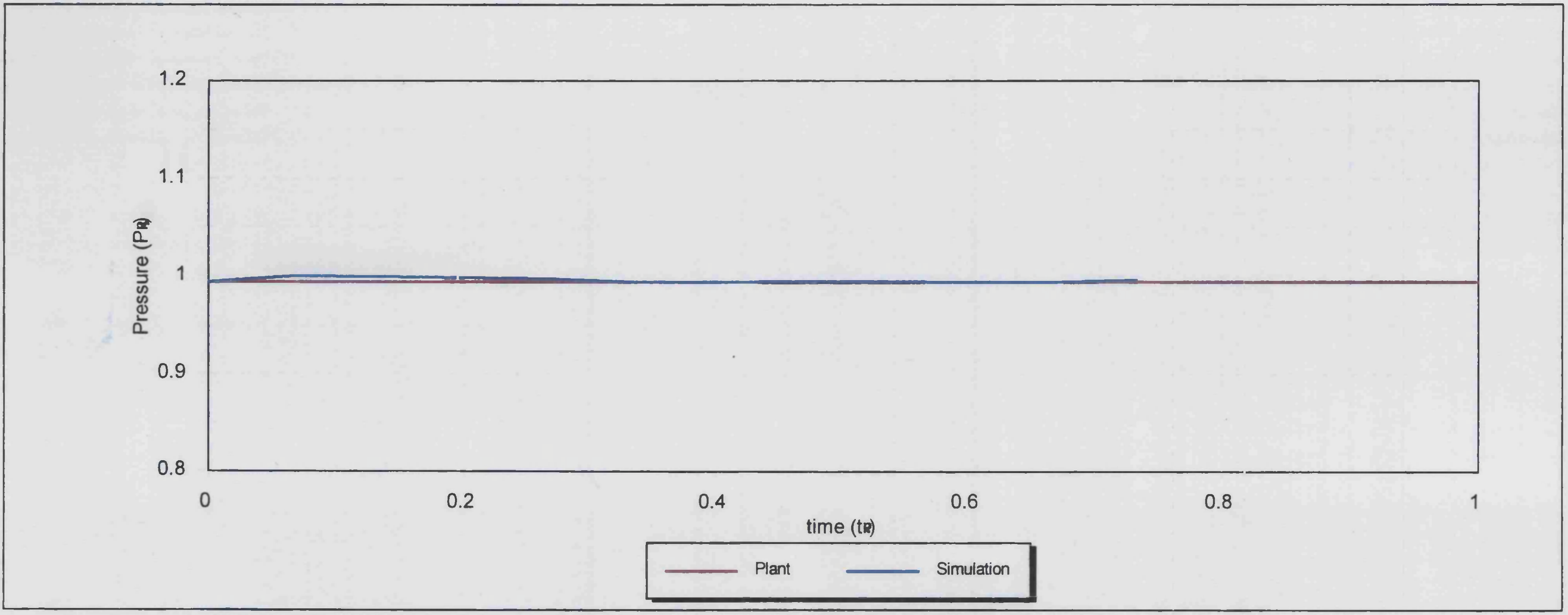


Figure 4.16b: Benzoylation strip chart: pressure

P_R = (actual pressure)/(maximum pressure)

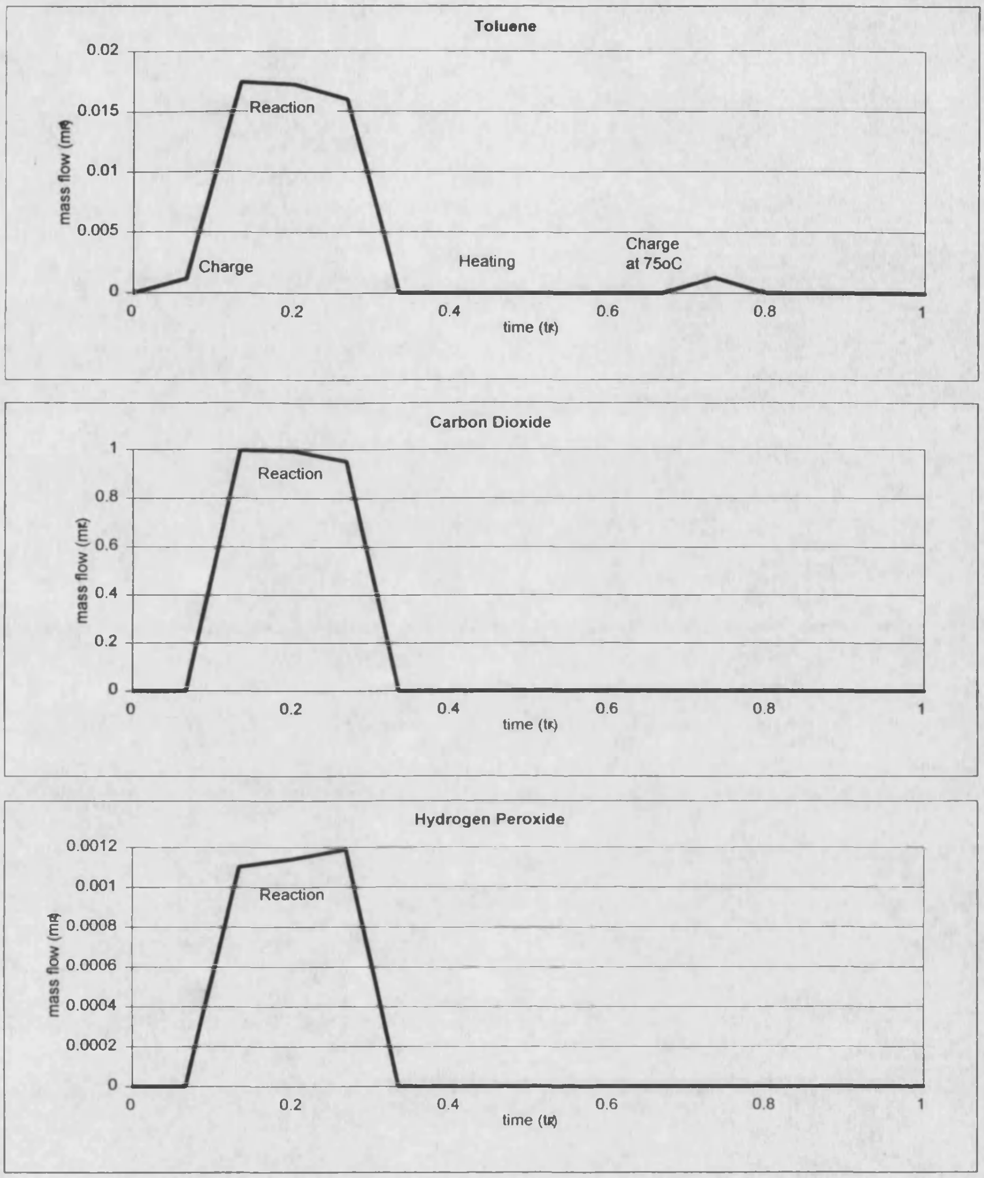


Figure 4.17: Predicted benzoylation operations mass release profile

m_R = (actual mass flowrate)/(maximum flowrate)

t_R = (actual time)/(maximum time)

4.3.5 Modelling the batch distillation operations

During distillation the distilled vapour contains both toluene and water. The vapour is condensed and the phases decanted in a separator tank.

For the simulation the distillation vessel and the condenser were modelled using a two phase separator. All the vapour was assumed to be condensed and subsequently, was passed to the toluene/water separation vessel. It was found that the toluene/water phase separation could not be modelled dynamically because the three phase separator was not available in the dynamic stage of the HYSYS programme. The three phases present in the vessel were an aqueous phase, an organic phase and a vapour phase. Hence, the phase separation has been modelled in steady state.

Figure 4.18 shows a schematic of the distillation operations and the corresponding simulation model.

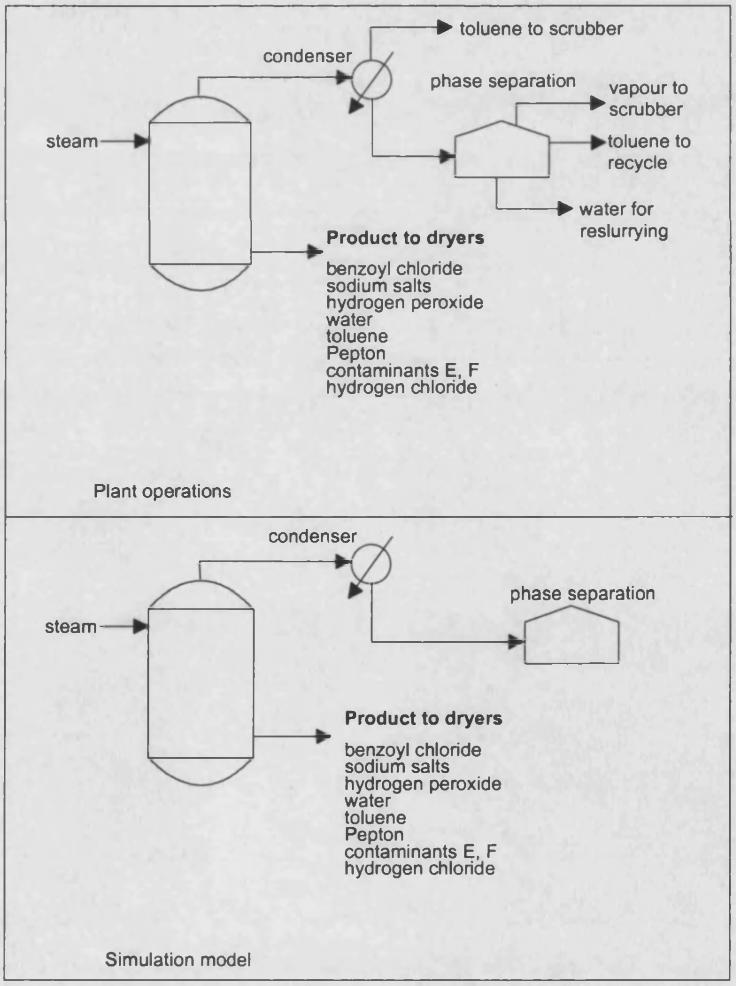


Figure 4.18: Distillation operations

The Wilson activity model was the only property estimation package that produced an accurate dynamic simulation for the batch distillation. The packages that are not based on activity models were unable to handle the complex calculations and gave meaningless results. Several limitations have been identified:

- The steam consumption in the simulation was approximately 40% less than that of an average plant batch of the same run time. Therefore, the model predicts that steam is used more efficiently than in the process. The inefficiencies in the process could be due to ambient heat loss, by-passing of steam and separation mass transfer limitations. The extra steam used on the plant causes the mole fraction of water in the vapour to be artificially high and also increases the amount of water in the final product stream.
- The model assumed that the vessel operated at equilibrium. However, in reality the plant is unlikely to reach equilibrium immediately, if at all.
- A perfectly mixed model was assumed. In the actual distillation vessel there will be areas that are not well mixed despite the use of a stirrer. Thus the simulation heat and mass transfer is likely to be over-estimated.
- It was not possible to model solids dynamically. Therefore, the Pepton was not considered in the distillation simulation and the product precipitation could not be modelled. However, the boiling point of the Pepton, water and toluene mixture in the plant is close to that of a pure toluene and water mixture. Therefore, the Pepton does not significantly affect the vapour liquid equilibrium of toluene and water.

The simulation used the average process and feed conditions for the batch. The steam flow was chosen to give a similar batch time as the plant. The predicted temperatures compared well with those recorded on the plant as shown in Figure 4.19. Figure 4.20 shows the traces of various parameters predicted during the distillation simulation. Each section of this graph is now described:

- From A to B, the distillation vessel was filled with the toluene and water mixture.
- From B to C, the steam flow started causing the temperature to increase. The mole fraction of water in the liquid phase increased because of condensing steam.

- From C to D, the boiling point of the mixture was reached and vapour started to flow from the distillation vessel. The temperature in the still stayed constant and the mole fraction of toluene in the vapour remained at the azeotropic concentration. The mole fraction of water in the liquid phase started to rise as the toluene was gradually removed throughout the course of the distillation. The level in the distillation vessel dropped as toluene and water were distilled off and the level of the product tank rose as the condensed vapours were collected.

- From D to E, the mole fraction of water in the liquid phase started to approach 1 and the mole fraction of toluene in the vapour approached 0. The boiling point of the mixture increased towards that of pure water and as a result the vapour flow dropped as nearly all the steam condensed.

- From E to F, as in the plant operations, the steam continued to flow through the system to ensure the distillation was complete. The level in the distillation vessel remained constant and both the vapour and liquid phases were pure water. The steam flow was then stopped and the distillation was complete.

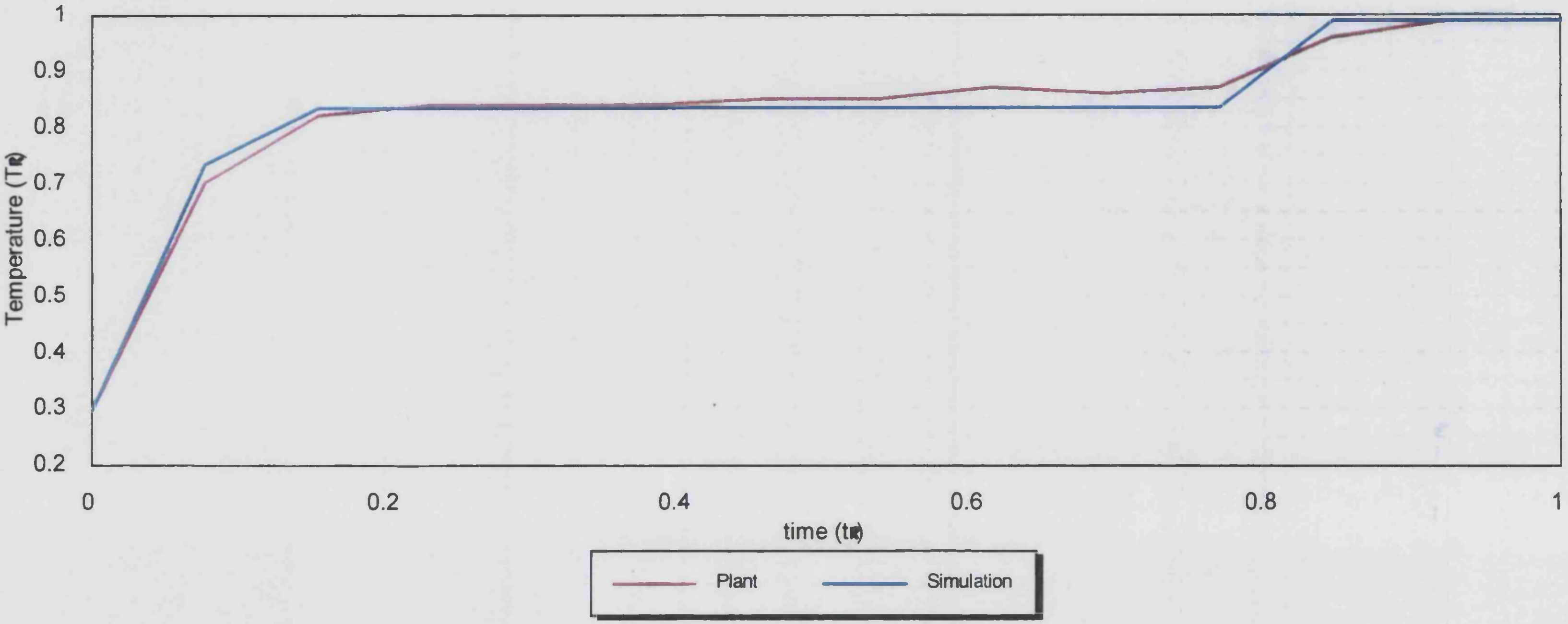


Figure 4.19: Batch distillation strip chart: temperature

T_R = (actual temperature)/(maximum temperature)

t_R = (actual time)/(maximum time)

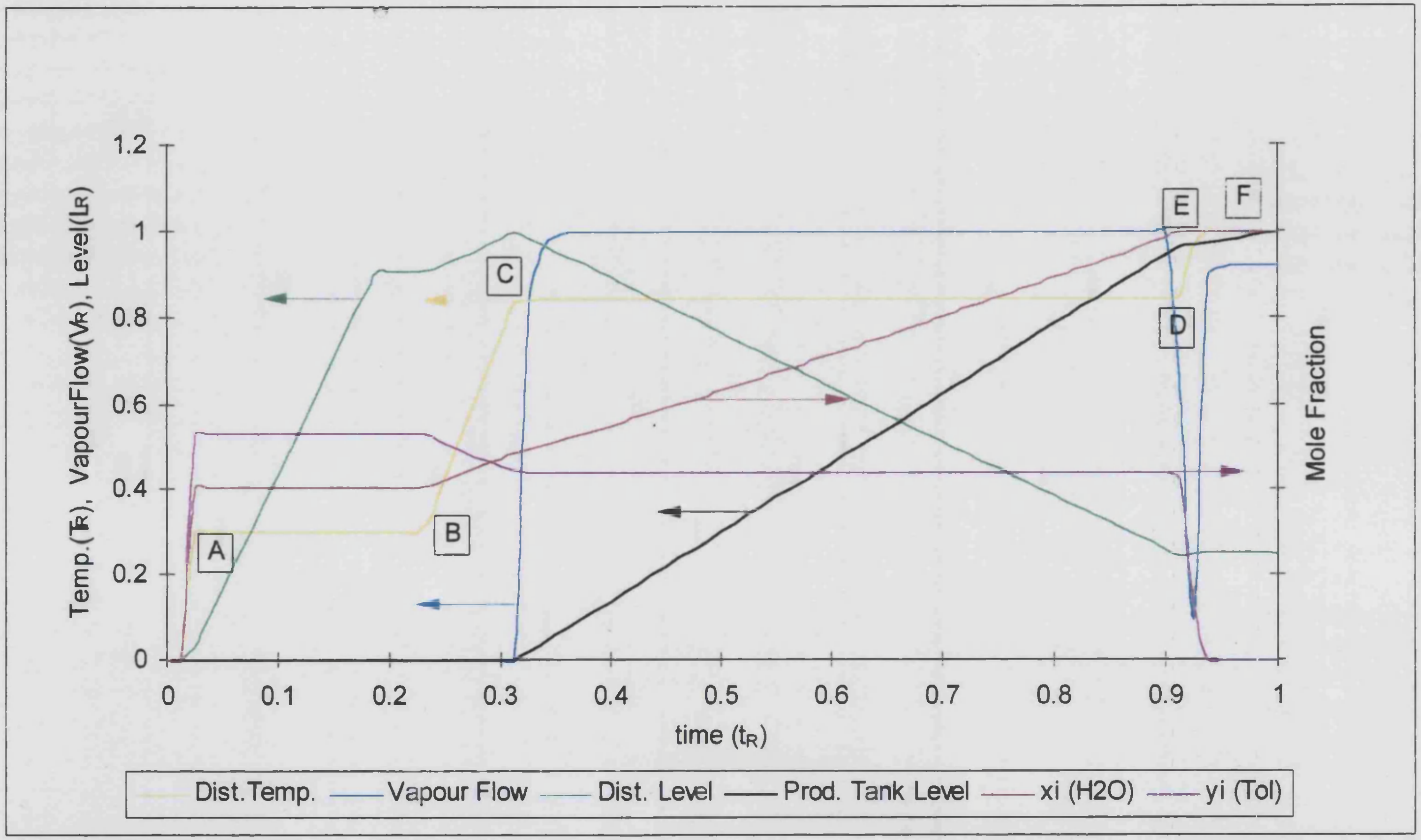


Figure 4.20: Batch distillation trace

L_R = (actual level)/(maximum level) v_R = (actual flowrate)/(maximum flowrate) x_i = composition in liquid phase y_i = composition in vapour phase

4.3.6 Scrubber

On the plant the major flows from the process vents pass through a counter-current recirculation scrubber where the trace organics are removed using a sodium hypochlorite solution. Table 4.17 shows the predictions of the flows to the scrubber taken from the simulation of each operation. However, these flows do not occur at the same time. Therefore, the scrubber has not been modelled because the amount of material passing through the scrubber at any one time was not known.

Table 4.17: Predicted material flows to scrubber

Material	Mass released(kg/batch)												
	Hydrolysis				Oxidation				Benzoylation				
	charging	heating	venting	total	charging	reaction	purging	total	charging 1	reaction	heating	charging 2	total
benzothiazole	4.6x10^{-3}	8.4x10^{-1}	-	8.5x10^{-1}	-	-	-	-	-	-	-	-	-
contaminant B	8.7x10^{-6}	9.2x10^{-3}	2.7x10^{-3}	1.2x10^{-2}	2.8x10^{-4}	1.5x10^{-2}	5.9x10^{-5}	1.6x10^{-2}	-	-	-	-	-
contaminant D	4.3x10^{-4}	1.4x10^{-2}	6.2x10^{-2}	7.7x10^{-2}	2.1x10^{-3}	8.4x10^{-3}	1.5x10^{-5}	1.1x10^{-2}	-	-	-	-	-
contaminant C	-	2.6x10^{-3}	5.2x10^{-4}	3.1x10^{-3}	1.6x10^{-4}	1.4x10^{-3}	8.3x10^{-6}	1.6x10^{-3}	-	-	-	-	-
contaminant A	-	6.4x10^{-3}	-	6.4x10^{-4}	-	-	-	-	-	-	-	-	-
stage 1 product	-	-	4.7x10^{-2}	4.7x10^{-2}	1.1x10^{-2}	3.4x10^{-1}	-	3.5x10^{-1}	-	-	-	-	-
oxygen	-	-	-	-	-	2.7x10^{-2}	1.5x10^{-1}	1.8x10^{-1}	-	2.3x10^{-1}	2.3x10^{-3}	-	2.3x10^{-1}
toluene	-	-	-	-	-	-	-	-	1.3x10^{-1}	2.94	7.0x10^{-3}	5.6x10^{-2}	3.13
stage 2 product	-	-	-	-	-	1.1x10^{-7}	-	1.1x10^{-7}	-	-	-	-	
carbon dioxide	-	-	-	-	-	-	-	-	-	155.02	-	-	155.02

4.3.7 Comparison of the overall mass balances

Figure 4.21 shows a mass balance for the Pepton process comparing the IPC application figures with the values predicted by the simulations. The difference between the amounts of raw materials used are a result of recycled water which was not included in the IPC application mass balance.

The releases to air predicted by the simulations agree well with the estimated releases of toluene, carbon dioxide and amines from the plant. Water was not predicted to be released to air by the simulations as it was either removed in the condensers or could not be modelled during operations such as charging. The simulations did not predict a release of benzoyl chloride to atmosphere because it was assumed to be completely removed in the condenser. Pepton only entered the vapour stream in very small amounts during the simulations. Consequently, it did not appear in the simulation mass balance.

Differences are seen between the aqueous discharge figures due to several reasons. Firstly, the amount of water used varies for each batch depending on the particular characteristics of that batch. Secondly, less water was predicted to be used for batch distillation due to the inefficient use of steam on plant. Lastly, the scrubber fluid was not included in the simulations because the operation was not modelled in detail and the amount of material released could not be estimated. The toluene recovered is predicted accurately by the simulation.

The Pepton solid waste was not able to be predicted using the simulations because the models would not predict off-grade product from the reactions.

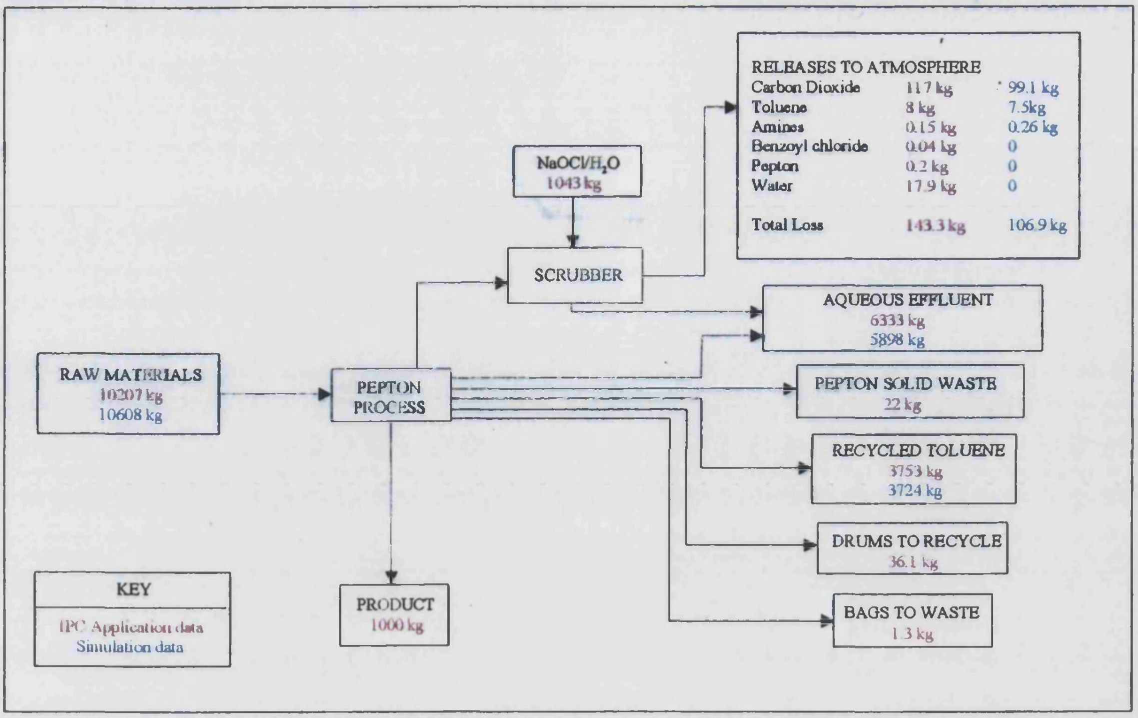


Figure 4.21: Pepton overall mass balance

4.4 Summary

The current batch operations of the Thomas Swan Pepton process have been modelled dynamically using HYSYS. Base case models have been developed for the following operations:

- hydrolysis charging, heating and venting,
- oxidation charging, reaction and purging,
- benzoylation charging, reaction, heating, and additional toluene charging,
- batch distillation.

The scrubber was not modelled because the flows through it varied with time and streams from more than one operation were treated at the same time.

The HYSYS models have been validated and agree reasonably well with the available plant data. In Chapter 8 these models are used to predict the emissions from various different process options which have been designed to reduce the amounts of waste generated by the process. Process parameters are changed and the affect on the plant emissions are assessed.

Chapter Five

Case Study Description Two: EVC

5.1 Introduction

This chapter describes the second case study that has been used to examine batch cleaning operations. The process studied manufactures Poly Vinyl Chloride (PVC) and is operated by European Vinyls Corporation (EVC (UK) Ltd.). An outline of the operations is provided, together with the development of simple spreadsheet models that have been used to examine the cleaning operations in detail. As a result of this case study, questions applicable to cleaning operations have been added to the Douglas design methodology. These questions are presented in Chapter 10.

5.2 Process description [128]

The plant operated by EVC produces PVC by batch polymerisation of Vinyl Chloride Monomer (VCM). A block diagram of the process operations is shown in Figure 5.1.

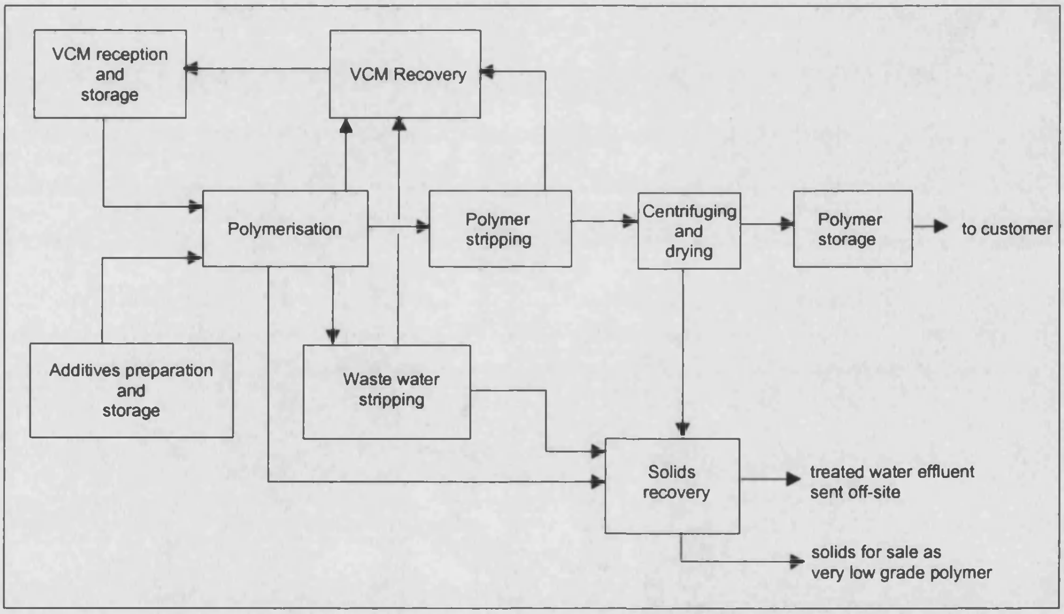


Figure 5.1: EVC process operations

The process is carried out in the following stages:

- polymerisation reaction; this is performed in four parallel reaction vessels,
- polymer stripping; VCM levels are reduced to 10-15 ppm,
- product formulation; blending, centrifuging and drying.

And secondary processing comprising;

- VCM recovery for recycle,

- waste water stripping, and,
- solids recovery.

Polymerisation is carried out in the water phase, with VCM droplets maintained in suspension using granulating agents. Monomer-soluble initiators are added to initiate a free radical polymerisation reaction. During the reaction the monomer droplets are allowed to coalesce in a controlled manner to give solid particles with the required size and structure. Typically, the reaction is stopped by adding a stabiliser, thereby removing free radicals. The quality of the PVC produced is determined from density, porosity and size distribution measurements. Different grades of product are manufactured by carrying out the reaction under slightly different conditions.

The conversion of VCM to PVC is between 85% and 92% depending on the required product grade. It is difficult to achieve a greater conversion of VCM present in the vapour phase without significantly increasing the reaction time due to mass transfer limitations.

After the reaction stage is complete the reactor contents are pumped to a blowdown vessel where the majority of the unreacted VCM is flashed off. The materials are then passed to a continuous sieve-tray steam stripping tower, where the VCM level is reduced to 10-15ppm. The VCM recovered from these operations is sent to the VCM recovery unit.

The PVC slurry from the stripper is sent to ventilated slurry tanks where different batches are blended and centrifuged. The wet cake from the centrifuges is dried using hot air. Any polymer entrained in the air is separated using cyclones. Finally, to ensure that water is removed from the polymer pores the PVC particles are dried at low temperatures in a fluid bed dryer using a long residence time.

Unreacted VCM from the process is compressed and liquefied at -20°C in the VCM recovery unit. The majority of the VCM is recycled to the process. Residual uncondensed gases, such as nitrogen and air, and trace VCM are released to atmosphere.

Water used in the process becomes contaminated with PVC particles and VCM. Treatment is therefore required before the water can be released. VCM is separated in the waste water stripper using a steam heated sieve tray column and is passed to the VCM recovery unit. Solid wastes are settled in the solids recovery unit, filtered and removed for offsite recycling. The remaining aqueous waste is sent to another site where it is mixed with other process effluent streams before being discharged into the Bristol Channel.

After each batch the reactors are emptied and a water wash sequence is initiated. Washing consists of a low pressure rinse at the scum level of the vessel and a high pressure rinse in either 3 or 4 locations depending on the vessel shape. The waste water from the low pressure rinse is sent to the blowdown filters whilst the high pressure rinse water goes to the waste water stripper.

Intermediate rinsing does not completely clean the vessel surface so PVC build-up occurs during the production campaign. A Build-Up Suppressant (BUS) is used after each batch to reduce this build-up and prevent frequent shutdowns. However, if a significant deposit is observed during the regular safety inspections, external contractors are hired to remove the deposit using high pressure water jets. Jet cleaning is also required if the measurement probes within the vessel become unreliable during normal operations. The solid waste removed from the vessel is sent offsite for disposal. Before jetting, the vessel is purged of VCM and opened. However, a small amount of VCM remains and can pose a potential health and safety risk to the personnel opening the vessel. During jet cleaning the plant is shutdown and revenue is lost due to the lack of production. For these reasons, jet cleaning is kept to a minimum.

5.2.1 Waste problems

Three types of wastes are released from the process: air emissions, releases to water and solid wastes. Air emissions mainly result from the drier area where PVC dusts are released. During normal operations the reaction vessels are totally enclosed and the possibility of a release to air is limited to a bursting disc failure.

There are no major by-products from the reaction. However, a very small quantity of hydrogen chloride is produced by hydrolysis in the reactor. This is treated with the VCM vapour on the recovery plant. An impurity in the VCM feed, ethylene dichloride, passes through the process unchanged and exits with the waste water effluent stream. Solid wastes are sold for recycle whilst reactor deposit build-up is sent to landfill.

Contaminated water is the major process waste. It is not possible to use recycled water in the reaction because any residual PVC particles would become double polymerised. These particles would become large and glassy, often causing the final PVC product to be off specification. Therefore, demineralised water is used and disposed of to effluent treatment after one pass through the process. Fresh towns water is also used for washing the vessels and this represents 4% of the total water used annually. Simple models of the EVC cleaning operations have been developed and are discussed in the following sections.

5.3 Cleaning models

There are three important aspects to consider when designing a cleaning system:

- choice of solvent or water for cleaning,
- definition of the batch process schedule, and
- the method of cleaning.

The cleaning requirements will dictate the most applicable choice of solvent or water. The fluid chosen may affect the wastes produced by a process. For example, a volatile solvent may be very effective at cleaning a surface but may result in vapour emissions. Other researchers have used group contribution techniques to match the solvent with the required cleaning characteristics of the process in order to reduce the environmental impact as discussed in Section 3.1.2.

The process schedule defines the order in which the units operate and this may affect the amount of waste produced by a process. It may be possible to arrange the tasks to reduce the number of cleaning operations required. For example, in a multi-product plant similar products can be manufactured in consecutive batches, thereby reducing the number of production changes and hence cleaning requirements [129]. The optimum process schedule and arrangement of tasks can be calculated using multi-integer non-linear optimisation techniques [34, 130, 131]. This is to be discussed further in Chapter 11. By studying the cleaning operations at the design stage it may be possible to improve the effectiveness of cleaning, thereby reducing the amount of fouling and reduce the environmental impact of the process.

Some cleaning methods may be more efficient than others and this may result in different wastes being produced. For example, a comparison has been made between the fill and dump method of cleaning and the use of spray nozzles [132]. It was shown that for a particular vessel spray nozzles used less water and needed shorter cleaning times than successively filling the vessel with water and emptying it. Reflux cleaning has also been studied. However, this work failed to compare the effectiveness and efficiency of reflux cleaning with any other cleaning systems [133].

Cleaning-in-place (CIP) systems have become common in some sectors and involve the automation of the cleaning process inside the equipment [134]. However, analysing the effect of key process parameters on CIP operations is rare except in the food and dairy industries.

In this thesis simple models have been developed to represent conceptual cleaning operations. Subsequently, these are used to gain an insight into the design of cleaning operations and to highlight parameters that may be important for optimisation in Chapter 10. The detail in the models has been limited by the amount of data available from the plant.

5.3.1 Deposit build-up

The build-up of deposits on a vessel wall generally depends on the following factors:

- fluid velocity - deposit build-up is likely to occur more readily in areas of flow stagnation rather than in areas where the fluid moves rapidly across the surface,
- surface temperature - the deposition rate may be increased by an increase in the vessel wall temperature depending on the deposition kinetics,
- fluid temperature and properties - the deposition rate will depend on the material deposited and the "stickability" at different temperatures, and,
- surface material, structure and configuration - in some cases vessels are designed to limit the amount of build-up by using materials such as stainless steel or by ensuring the internal surface is smooth to limit the attachment of particles.

Three deposition characteristics have been observed [135]: linear, falling rate and asymptotic. These are indicated in Figure 5.2. A linear rate is one where the deposit grows at a constant rate over time, whereas with a falling rate less material is deposited as the operating time increases. During asymptotic fouling the deposit rate falls until a steady state thickness is reached and there is no net increase in the deposit on the surface. The causes of these different deposition curves are numerous and are discussed in numerous texts. A good overview is provided in [135, 136].

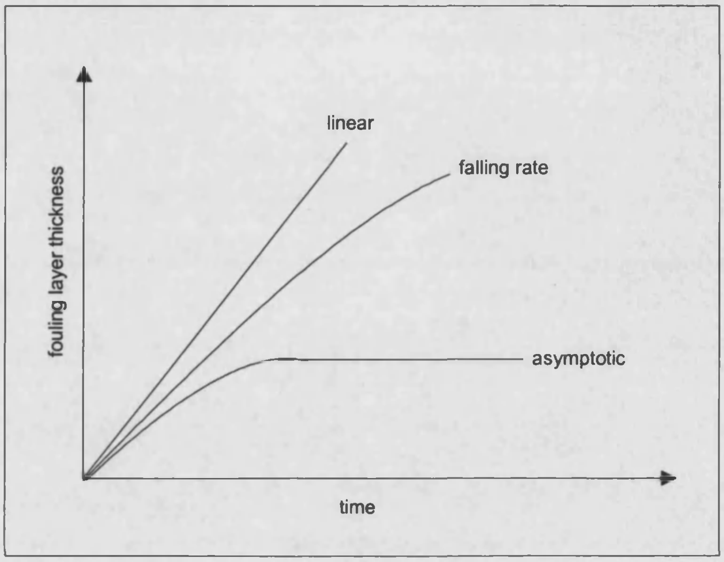


Figure 5.2: Typical fouling layer growth profiles

A linear deposit build-up with time has been assumed for the cleaning models developed in this thesis. Therefore, factors that are likely to affect the build-up such as temperature or fluid flow have not been taken into account. However, work presented in the literature on the growth of fouling layers has indicated that the deposition of polystyrene from kerosene was linear [137]. Therefore, a linear model was assumed to be an accurate representation of PVC deposition.

The PVC build-up during production is limited by the intermediate cleaning. However, complete cleaning is not achieved after each batch and a layer of deposit is formed over the production campaign. Consequently, the growth of deposit depends on the effectiveness of the intermediate cleaning. This is demonstrated in the individual models described in Section 5.4.

5.3.2 Deposit removal

The removal rate of the deposit reflects the effectiveness of the cleaning and depends on the following factors:

- strength and nature of deposit,
- nature of cleaning fluid,
- shear force exerted by the cleaning medium,
- temperature, and,
- deposit thickness.

This study assumes a linear removal rate of deposit and hence does not explicitly take into account the above factors.

Two models of deposit removal have been considered: one where the cleaning effectiveness remains constant over the production campaign and the other where the cleaning becomes less effective as the campaign progresses. In the second model, intermediate cleaning was assumed to be completely ineffective at the end of the production campaign so jet cleaning was required. These cases are discussed in detail in Section 5.4.

Jet cleaning was assumed to remove completely the deposit at a constant rate. In order to allow comparisons to be made between different operations the jet cleaning time was assumed to be the same for each jet cleaning operation. However, in reality this is unlikely as the jetting requirements will vary due to different deposit strengths and thicknesses. This is discussed further in Section 5.5.

5.4 Development of cleaning models

Two conceptual cleaning models are now considered. The first, model 1, is a simple model based on constant parameters and cleaning times. In the second model, model 2, the effectiveness of cleaning is assumed to decrease as the cycle continues and eventually becomes ineffective. Two cases, 2a, keeping the cleaning time constant and 2b, keeping the deposit removed constant, have been analysed using the second model. The models are depicted in Figure 5.3.

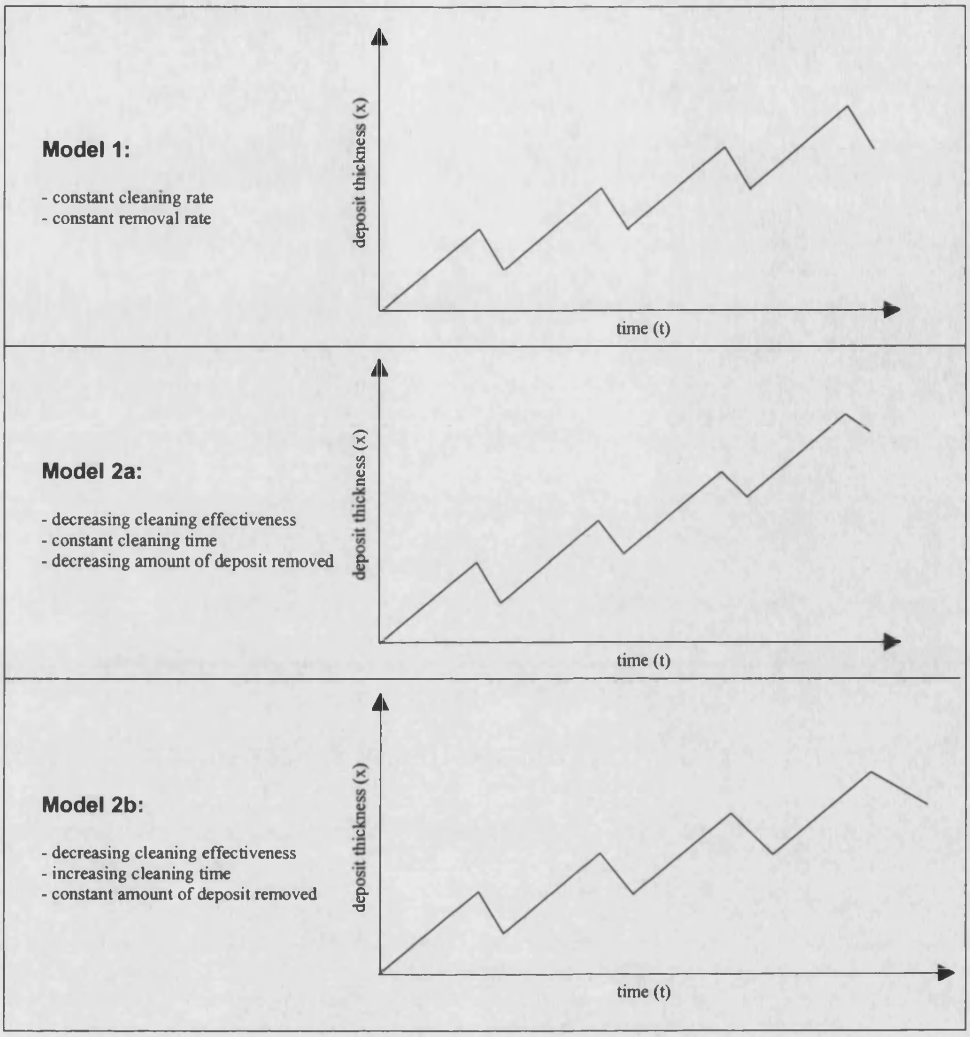


Figure 5.3: Conceptual cleaning models

In model 2a the cleaning time was assumed constant, see Section 5.4.2.1. Therefore, less material was removed as the cleaning became less effective. In model 2b, the cleaning time was extended to enable the same amount of deposit to be removed despite the cleaning becoming less effective, see Section 5.4.2.2. The final section, Section 5.4.2.3, presents the application of these models using data available from EVC.

Mathematical expressions have been developed for both models. The derivation of the equations and a complete definition of parameters are provided in Appendix B. In the models a campaign has been defined as the time to reach the point where jet cleaning is required. A cycle has been defined as the operation of one batch and the cycle time is the sum of one reaction and one cleaning times.

5.4.1 Model 1: Linear build-up and linear removal

In model 1 linear relationships have been assumed for the deposition rate and removal rate of PVC. The reaction and cleaning times have been assumed to be constant and the same amount of cleaning was achieved during each cycle. When the deposit thickness reaches X_t the vessel is assumed to be shutdown for cleaning. Figure 5.4 shows the profile of the deposit thickness with time using these assumptions. Table 5.1 defines the terms used in the mathematical expressions developed for this model.

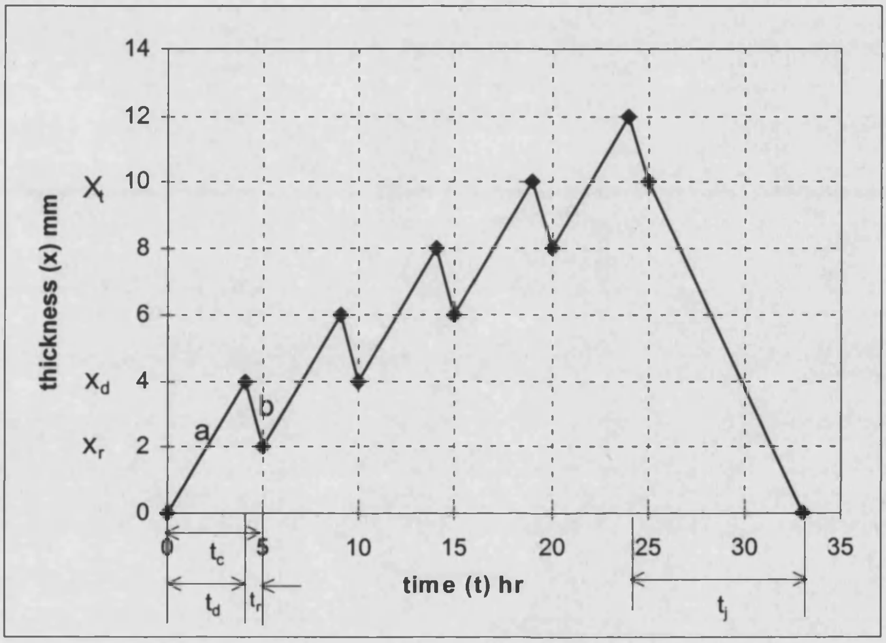


Figure 5.4: Thickness vs time with linear deposition and removal rates

The slope of the deposition line, a, is equivalent to the rate of deposit build-up and was assumed constant during the campaign. The slope of the cleaning line, b, represented the effectiveness of cleaning and was also assumed constant for the present model. From the profile shown in Figure 5.4, the gradients of the lines are expressed as:

$$a = x_d / t_d \tag{5.1}$$

$$b = (x_d - x_r) / t_r \tag{5.2}$$

Where:

x_d = deposit thickness after 1 batch, mm

x_r = deposit thickness after intermediate cleaning, mm

t_d = time for deposit build-up ie batch cycle time, hr

t_r = time for intermediate cleaning, hr

The number of cycles (n_f) in a campaign is given by the final thickness (X_t) divided by the deposit thickness remaining after intermediate cleaning at each cycle as follows:

$$n_f = X_t/x_r \tag{5.3}$$

As shown by Equation 5.4, the number of campaigns (N) in a year is the time available for production divided by the total campaign time. The production time is the number of hours in a year minus the annual shutdown time (T_{sd}). A campaign consists of production cycles, cleaning cycles, jetting and maintenance. Therefore, the campaign time is the sum of the cycle times ($n_f\, t_c$), where the cycle time is the sum of the production and cleaning times, the jet cleaning time (t_j) and the shut-down time for maintenance (t_{sd}). Thus the expression for the number of campaigns (N) per reactor in a year is as follows:

$$N = (8760 - T_{sd})/(n_f t_c + t_j + t_{sd}) \tag{5.4}$$

When calculating the total amount of water used per year (W), the number of campaigns is multiplied by the water used in each campaign. The water used in a campaign is the sum of the water used for intermediate cleaning and jet cleaning. Assuming that a constant flowrate of water is used for each clean and that the cleaning times are equal for each cycle, the expression for the total water used is:

$$W = NR(n_f F_r t_r + F_j t_j) \tag{5.5}$$

The total product is the amount produced per cycle (p) multiplied by the number of cycles (n_f), the number of campaigns (N) and the number of reactors (R) as follows:

$$P = NpRn_f \tag{5.6}$$

The results of an example calculation are shown in Table 5.1. The values have been used for illustration purposes only and have been either assumed constant or have been calculated using the relevant equations. The results show that 5 batches are completed per campaign with 105.6 campaigns in a year. The ratio of the amount of water used per tonne product was calculated as 6.24 m^3/te.

Table 5.1: Case 1; example calculation using model 1

Definition	Parameter	Value	Notes
deposit thickness after 1 batch	x_d	4 mm	constant
deposit remaining after 1 batch	x_r	2 mm	constant
final deposit thickness at shutdown for jetting	X_t	10 mm	constant
time for deposit build-up ie batch operating time	t_d	4 hr	constant
time for deposit removal ie intermediate cleaning time	t_r	1 hr	constant
total batch cycle time; sum of operating and cleaning times	t_c	5 hr	$t_d + t_r$
time for jet cleaning	t_j	8 hr	constant
total time shutdown for maintenance	t_{sd}	48 hr/shutdown	constant
time for annual shutdown	T_{sd}	204 hr/yr	constant
flowrate of water used for intermediate cleaning operations	F_r	24 m^3/hr	constant
flowrate of water used during jet cleaning	F_j	24 m^3/hr	constant
amount of product per batch	p	10 te/batch	constant
number of reactors	R	4	constant
rate of deposit build-up; assumed linear and constant	a	1	calculated from equation 5.1
effectiveness of cleaning; assumed linear and constant	b	2	calculated from equation 5.2
number of batches in one campaign ie before shutdown for jet cleaning	n_f	5 batches/campaign	calculated from equation 5.3
number of campaigns in a year	N	105.6 campaigns/yr	calculated from equation 5.4
total volume of water used per campaign	W/campaign	1248 m^3/campaign	$(n_f F_r t_r + F_j t_j)R$
total volume of water used per year	W	131800 m^3/yr	calculated from equation 5.5
total amount of product per campaign	P/campaign	200 te/campaign	pRn_f
total amount of product per year	P	21130 te/yr	calculated from equation 5.6
ratio of water used to amount of product	W/P	6.24 m^3/te	

5.4.2 Model 2: Decreasing cleaning effectiveness

In the second model the effectiveness of the cleaning was assumed to decrease as the thickness of the deposit increased. Therefore, b, the slope of the cleaning line, was assumed to decrease linearly with the number of cycles completed until it reached zero. At the final thickness, X_t, cleaning was assumed to be ineffective and jet cleaning was required. Two cases have been considered:

a) the time for cleaning was constant and the deposit remaining after the intermediate cleaning increased for each cycle,

b) the cleaning time was increased as the cleaning became less effective. In this way the amount of deposit removed remained constant.

5.4.2.1 Model 2a: Decreasing cleaning effectiveness with constant cleaning time

In the first case the effectiveness of cleaning was assumed to decrease but the cleaning time was kept constant. As the cleaning became less effective, less material was removed so the thickness X_t was reached sooner. As a result less cycles were completed in one campaign than for model 1. The resulting deposition profile for a campaign is shown in Figure 5.5.

Similarly to model 1, the deposition rate, a, was assumed constant and is expressed by Equation (5.1). However, as the cleaning becomes less effective the value of b decreases. It was assumed that b decreases linearly by a factor c in each cycle completed as follows:

$$b_n = b_1 - (n - 1)c \qquad (5.7)$$

Where:
b_n = cleaning effectiveness after n cycles
b_1 = initial cleaning effectiveness
n = number of cycles completed

The change in the slope of the cleaning line (c) has been estimated from model 1 by dividing the initial slope of the cleaning line by the number of cycles:

$$c = [b/(n_f - 1)]_{\text{model 1}} \qquad (5.8)$$

This ensured that b became zero at X_t using the model 1 expressions. However, in model 2 the value X_t was reached sooner due to the reduction in cleaning effectiveness. Hence, less cycles were completed and b did not reach zero when the final thickness (X_t) was reached, as indicated in Figure 5.5. Table 5.2 defines the terms used for the modelling.

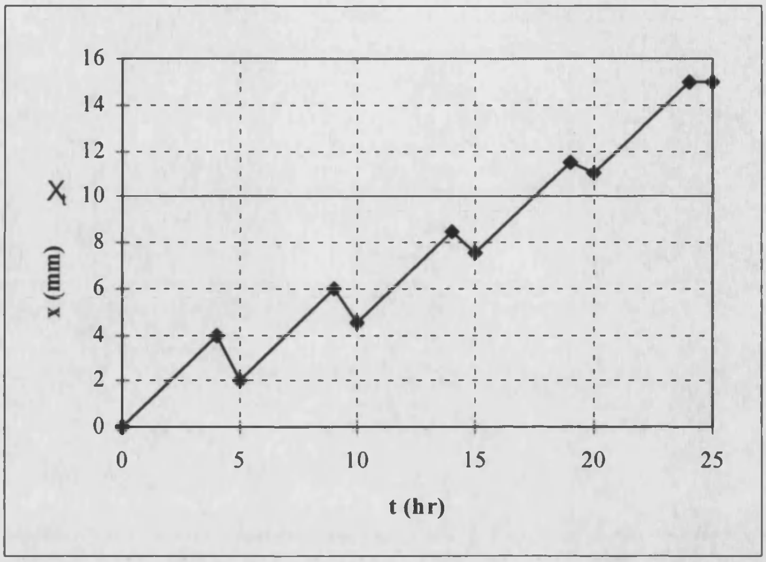


Figure 5.5: Deposit build-up for model 2a with constant clean time

The thickness of the deposit (x_{dn}) for n cycles is:

$$x_{dn} = nx_{d1} - (n-1)b_1 t_r + \frac{c(n-1)(n-2)t_r}{2} \qquad (5.9)$$

The remaining deposit (x_m) after n cycles is:

$$x_m = nx_{d1} - nb_1 t_r + \frac{cn(n-1)t_r}{2} \qquad (5.10)$$

The total number of cycles (n_f) is:

$$n_f = \frac{-B \pm \sqrt{(B^2 - 4AC)}}{2A} \qquad (5.11)$$

Where A, B and C are the roots of the quadratic equation:

$$A = ct_r/2 \qquad (5.12)$$

$$B = (-ct_r/2 - b_1 t_r + x_{d1}) \qquad (5.13)$$

$$C = - X_t \qquad (5.14)$$

The expressions for the number of campaigns in a year (N), the amount of product produced (P) and the total volume of water used (W) are the same as for model 1 and are given in Section 5.4.1.

The results of an example calculation are shown in Table 5.2. The values used are for illustration purposes and have been assumed to be constant or have been calculated using the relevant equations. It should be noted that a batch cannot be stopped mid-cycle for cleaning. Thus, the number of cycles in a campaign has been rounded up to the nearest whole number. The actual thickness reached after the full number of cycles has been completed is represented by X_{ta}. Substituting n_f into Equation (5.10) gives:

$$X_{ta} = n_f x_{d1} - n_f b_1 t_r + \frac{c n_f (n_f - 1) t_r}{2} \qquad (5.15)$$

The resulting number of batches is calculated to be 4 per campaign with 112.6 campaigns completed per year. The ratio of the water used per tonne of product was calculated to be 7.2 m^3/te.

Table 5.2: Model 2a: sample calcuation using model 2 with constant cleaning rate

Definition	Parameter	Value	Data
deposit thickness after 1 batch	x_{d1}	4 mm	constant
deposit remaining after 1 batch	x_r	2 mm	constant
final deposit thickness at shutdown for jetting	X_t	10 mm	constant
time for deposit build-up ie batch operating time	t_d	4 hr	constant
time for deposit removal ie intermediate cleaning time	t_r	1 hr	constant
total batch cycle time; sum of operating and cleaning times	t_c	5 hr	$t_d + t_r$
time for jet cleaning	t_j	8 hr	constant
total time shutdown for maintenance in each campaign	t_{sd}	48 hr	constant
time for annual shutdown	T_{sd}	204 hr	constant
flowrate of water used for intermediate cleaning operations	F_r	24 m^3/hr	constant
volumetric flowrate of water used during jet cleaning	F_j	24 m^3/hr	constant
amount of product per batch	p	10 te/batch	constant
number of reactors	R	4	constant
rate of deposit build-up; assumed linear and constant for this model	a	1	x_d/ t_d
initial cleaning effectiveness	b_1	2	$(x_d - x_r)/ t_r$
change in effectiveness of cleaning; assumed linear	c	0.5	calculated from 5.8
roots of quadratic equation	A	0.25	calculated from 5.12
roots of quadratic equation	B	1.75	calculated from 5.13
roots of quadratic equation	C	-10	calculated from 5.14
number of batches completed	n	3.73 batches/campaign	calculated from 5.11
number of batches in one campaign ie before shutdown for jet cleaning	n_f	4 total batches/campaign	n rounded up
actual thickness at end of campaign	X_{ta}	11 mm	calculated from 5.15
number of campaigns in a year	N	112.6 campaigns/yr	$(8760 - T_{sd})/(n_f t_c + t_j + t_{sd})$
total volume of water used per campaign	W/campaign	1152 m^3/campaign	$(n_f F_r t_r + F_j t_j)R$
total volume of water used per year	W	129700 m^3/yr	$NR(n_f F_r t_r + F_j t_j)$
total amount of product per campaign	P/campaign	160 te/campaign	pRn_f
total amount of product per year	P	18000 te/yr	$NpRn_f$
ratio of water used to amount of product	W/P	7.2 m^3/te	

Table 5.3 provides a comparison between the key parameters calculated using model 1 and model 2a. Because the cleaning becomes less efficient in model 2a, less batch cycles were completed in a campaign than for model 1. As a result the campaigns were shorter for model 2a, less PVC was produced per campaign and more campaigns were completed per year. However, the lost production time due to additional jet cleaning caused less PVC to be produced annually for model 2a. The amount of water used for model 2a was less than model 1, because although more jet cleans were required there were less intermediate cleans. The water for the additional intermediate cleaning in model 1 outweighed the requirement for more jet cleaning in model 2a. The findings would change if the amount of water used for jetting was significantly higher than for intermediate washing. The ratio of the water used per unit product was higher for model 2a, even though less water was used because less PVC was produced.

Table 5.3: Summary of key parameters from model 1 and model 2a

Definition	Parameter	Model 1	Model 2a
number of batches in a campaign	n_f	5 total batches/campaign	4 total batches/campaign
number of campaigns in a year	N	105.6 campaigns/yr	112.6 campaigns/yr
total volume of water used per campaign	W/campaign	1248 m^3/campaign	1152 m^3/campaign
total volume of water used per year	W	131800 m^3/yr	129900 m^3/yr
total amount of product per campaign	P/campaign	200 te/campaign	160 te/campaign
total amount of product per year	P	21100 te/yr	18000 te/yr
ratio of water used to amount of product	W/P	6.24 m^3/te	7.2 m^3/te

5.4.2.2 Model 2b: Decreasing cleaning effectiveness with constant amount of deposit removed and varying cleaning time

In this model it was assumed that the cleaning efficiency decreased but the same amount of deposit was removed after each batch by increasing the cleaning time. Figure 5.6 shows the deposit build-up profile for one campaign. Table 5.4 defines the terms used for the modelling.

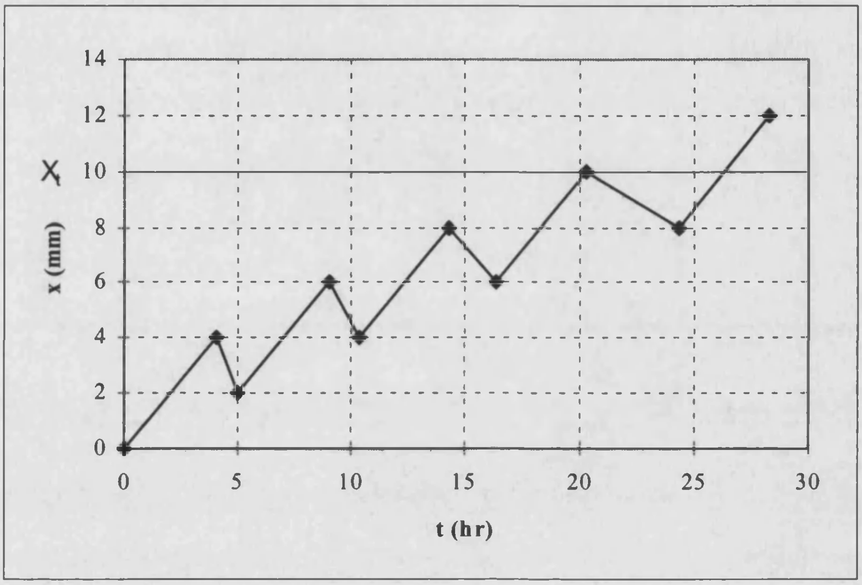


Figure 5.6: Deposit build-up for model 2b; constant deposit removed at each cycle

From model 1 the number of cycles (n_f) in a campaign is:

$$n_f = X_t / x_{r1} \tag{5.16}$$

Where: Xt = final thickness reached, mm.

x_{r1} = deposit thickness after intermediate cleaning, cycle 1, mm

As previously, the deposition rate, a, was assumed constant and is expressed by Equation (5.1). In addition, the value of b decreases linearly by factor c in each cycle completed as defined by Equation (5.7). The change in the slope of the cleaning line (c) was estimated from model 1 by dividing the initial slope of the cleaning line by the number of cycles as in Equation (5.8).

However, for this case the time required for cleaning varies for each cycle and is defined as:

$$t_{rn} = \frac{(x_{d1} - x_{r1})}{[b_1-(n-1)c]} \tag{5.17}$$

Where:
x_{d1} = deposit thickness after 1 batch, mm
x_{r1} = deposit thickness after intermediate cleaning, cycle 1, mm

The total cleaning time (T_r) in a campaign is, therefore, the sum of the cycle cleaning times:

$$T_r = t_{r1} + t_{r2} + t_{r3} \ldots\ldots\ldots + t_{r(n-1)} \tag{5.18}$$

Substituting the individual cleaning times calculated from Equation (5.17):

$$T_r = \frac{(x_{d1} - x_{r1})}{b_1} + \frac{(x_{d1} - x_{r1})}{(b_1-c)} + \frac{(x_{d1} - x_{r1})}{(b_1-2c)} \ldots\ldots\ldots \frac{(x_{d1} - x_{r1})}{(b_1-(n-1)c)} \tag{5.19}$$

As a result the campaign time is the sum of the operating time ($n_f t_d$), the intermediate cleaning time (T_r), the jet cleaning time (t_j) and the maintenance shutdown time (t_{sd}). The number of campaigns in a year (N) is as follows:

$$N = (8760 - T_{sd})/(n_f t_d + T_r + t_j + t_{sd}) \tag{5.20}$$

The expressions for the amount of product per year (P) and the amount of water used per year (W) are the same as for model 1 and are given in Section 5.4.1.

The results of an example calculation are shown in Table 5.4. The values used are for illustration purposes and have been assumed constant or have been calculated using the relevant equations. The resulting number of batches was calculated to be 5 per campaign with 101.5 campaigns completed per year. The ratio of the water used per tonne of product was calculated to be 7.84 m^3/te.

Table 5.4 : Model 2b; sample calculation with decreasign clenaing effectiveness and a constant amount of deposit removed in each cycle

Definition	Parameter	Value	Data
deposit thickness after 1 batch	x_{d1}	4 mm	constant
deposit remaining after 1 batch	x_{r1}	2 mm	constant
final deposit thickness at shutdown for jetting	X_t	10 mm	constant
time for deposit build-up ie batch operating time	t_d	4 hr	constant
time for deposit removal ie intermediate cleaning time	t_r	1 hr	constant
total batch cycle time; sum of operating and cleaning times	t_c	5 hr	$t_d + t_r$
time for jet cleaning	t_j	8 hr	constant
total time shutdown for maintenance in each campaign	t_{sd}	48 hr	constant
time for annual shutdown	T_{sd}	204 hr	constant
volumetric flowrate of water used for intermediate cleaning operations	F_r	24 m^3/hr	constant
volumetric flowrate of water used during jet cleaning	F_j	24 m^3/hr	constant
amount of product per batch	p	10 te/batch	constant
number of reactors	R	4	constant
rate of deposit build-up; assumed linear and constant	a	1	x_d/ t_d
initial cleaning effectiveness	b_1	2	$(x_d - x_r)/ t_r$
change in effectiveness of cleaning	c	0.5	$[b/(n_f - 1)]_{model\ 1}$
number of batches in one campaign ie before shutdown for jet cleaning	n_f	5 cycles/campaign	calculated from 5.16
total cleaning time per campaign	T_r	8.33 hr	calculated from 5.19
number of campaigns in a year	N	101.5 campaigns/yr	calculated from 5.20
total volume of water used per campaign	W/campaign	1568 m^3/campaign	$(n_fF_rt_r + F_jt_j)R$
total volume of water used per year	W	159000 m^3/yr	$NR(n_fF_rt_r + F_jt_j)$
total amount of product per campaign	P/campaign	200 te/campaign	pRn_f
total amount of product per year	P	20300 te/yr	$NpRn_f$
ratio of water used to amount of product	W/P	7.84	

Table 5.5 presents a summary of the key parameters produced using models 2a and 2b. In model 2a the cleaning rate was kept constant and the amount of material remaining after cleaning increased, whereas in model 2b the amount of cleaning achieved was kept constant and the cleaning time was increased. Comparing these two cases there are more cycles per campaign for model 2b than for model 2a. This was because the deposit removed during model 2a was less than in model 2b so the final thickness was reached sooner. As a result more product per campaign was produced for model 2b because more cycles were completed. However, less campaigns were completed because the cleaning time increased the total campaign time. The amount of PVC produced per year was greater for model 2b than model 2a, despite less campaigns being completed because more PVC was produced per campaign. Extending the cleaning time also resulted in more water being used for model 2b. The predicted ratio of water used to the amount of product was greater using model 2b than that predicted using model 2a because the increased water usage outweighed the increase in production.

Table 5.5: Summary of key parameters from models 2a and 2b; with constant and varying cleaning rate respectively

Definition	Parameter	Model 2a; constant cleaning rate	Model 2b; varying cleaning rate
number of batches in a campaign	n_f	4 total batches/campaign	5 total batches/campaign
number of campaigns in a year	N	112.6 campaigns/yr	101.5 campaigns/yr
total volume of water used per campaign	W/campaign	1152 m^3/campaign	1568 m^3/campaign
total volume of water used per year	W	129700 m^3/yr	159000 m^3/yr
total amount of product per campaign	P/campaign	160 te/campaign	200 te/campaign
total amount of product per year	P	18000 te/yr	20300 te/yr
ratio of water used to amount of product	W/P	7.2 m^3/te	7.84 m^3/te

5.4.2.3 Application to EVC operations

Data from the EVC cleaning operations has been used to develop a more realistic cleaning model. The parameters used in this model are defined in Table 5.6. Some of the parameter values were known from the plant data and others had to be estimated. The number of cycles, the batch times and cleaning times were known from the plant data. However, the thickness of the deposits and hence the slopes of deposit and cleaning lines were unknown.

The thickness after intermediate cleaning (x_{r1}) was estimated to be 1 mm as the plant operators indicated that only a thin film of material was likely to be left in the vessel. The thickness of the deposit before cleaning was predicted by comparing the operations with and without intermediate cleaning. If the vessel is not cleaned then build-up would occur faster and jetting would be required more often. From analysis of the plant data, presented in Appendix B, the number of batches that can be completed with no intermediate cleaning is between 105 and 140. The number of batches per campaign without intermediate cleaning (n_{nc}) was assumed to be 122.5, half way between the two limits. If intermediate cleaning is performed the plant can operate for 210 batches (n_f) before being shutdown for jet cleaning. From this the deposit thickness after one batch (x_{d1}) is calculated to be:

$$x_{d1} = \frac{n_f x_{r1}}{2(n_{nc} - n_f/2)} \qquad (5.21)$$

$$x_{d1} = 6x_{r1} \qquad (5.22)$$

The final thickness reached (X_t) is estimated from the number of cycles completed without cleaning, n_{nc}:

$$X_t = n_{nc}\, x_{d1} \qquad (5.23)$$

Therefore, using the data from the plant presented in Table 5.6 X_t is 735 mm. Assuming the deposit evenly covers 80% of the vessel area and the density of the deposit is the same as that of an average PVC grade, this deposit results in a loss of 36.5 te per campaign. This represents a 0.1% loss of product per campaign.

The operating, cleaning and shutdown times have been taken from average plant data. The slopes of the deposition and cleaning lines are calculated from the values of x and t:

$$a = x_d / t_d \tag{5.24}$$

$$b_1 = (x_d - x_r) / t_r \tag{5.25}$$

In model 2b the slope of the cleaning line (b) was taken to vary by a constant amount c which was based on the number of cycles completed in model 1. This was to ensure that b was zero at X_t. However, the decrease in b during the campaign resulted in less cycles being completed. Therefore, b did not equal zero at the same value of X_t as model 1. For the EVC model, b was therefore taken to vary linearly with the number of cycles completed. The expression is:

$$b_n = \frac{b_1 n}{(1 - n_f)} - \frac{b_1 n_f}{(1 - n_f)} \tag{5.26}$$

The cleaning time (t_r) was kept constant as for the plant operations.

The thickness of the deposit after n cycles is:

$$x_m = n x_{d1} - \frac{(n+1) n b_1 t_{r1}}{2(1 - n_f)} + \frac{n b_1 n_f t_{r1}}{(1 - n_f)} \tag{5.27}$$

The number of cycles in a campaign is:

$$n_f = \frac{-B \pm \sqrt{(B^2 - 4AC)}}{2A} \tag{5.28}$$

Where A, B and C are the roots of the quadratic equation:

$$A = x_{d1} + b_1 t_{r1}/2 \tag{5.29}$$

$$B = b_1 t_{r1}/2 - X_t - x_{d1} \tag{5.30}$$

$$C = X_t \tag{5.31}$$

The expressions for the number of campaigns a year (N), the total amount of product (P) and the total volume of water used (W) are the same as for model 1 and are given in Section 5.4.1.

Table 5.6 provides a summary of the calculations performed using the EVC cleaning data.

Table 5.6: EVC cleaning model

Definition	Parameter	Value	Data source
deposit remaining after 1 batch	x_r	1 mm	estimated
time for deposit build-up ie batch operating time	t_d	8.85 hr	plant
time for deposit removal ie intermediate cleaning time	t_r	0.75 hr	plant
total batch cycle time; sum of operating and cleaning times	t_c	9.6 hr	$t_d + t_r$
time for jet cleaning	t_j	0.38 hr	plant
time shutdown for maintenance in each campaign	t_{sd}	48 hr	plant
time for annual shutdown	T_{sd}	204 hr	plant
flowrate of water used for intermediate cleaning operations	F_r	24 m^3/hr	plant
flowrate of water used during jet cleaning	F_j	6 m^3/hr	plant
amount of product per batch	p	42 te/batch	plant
number of reactors.	R	4	plant
deposit thickness after 1 batch	x_d	6 mm	from equation 5.22
final deposit thickness at shutdown for jetting	X_t	735 mm	from equation 5.23
rate of deposit build-up; assumed linear and constant	a	0.68	from equation 5.24
effectiveness of cleaning after 1 cycle	b	6.67	from equation 5.25
root of quadratic equation	A	3.5	from equation 5.29
root of quadratic equation	B	-738.5	from equation 5.30
root of quadratic equation	C	735	from equation 5.31
number of batches in one campaign	n_f	210 batches/campaign	from equation 5.28
number of campaigns in a year	N	4.15 campaigns/yr	$(8760 - T_{sd})/(n_f t_c + t_j + t_{sd})$
total volume of water used per campaign	W/campaign	15100 m^3/campaign	$(n_f F_r t_r + F_j t_j)R$
total volume of water used per year	W	62800 m^3/yr	$NR(n_f F_r t_r + F_j t_j)$
total amount of product per campaign	P/campaign	35300 te/campaign	pRn_f
total amount of product per year	P	146500 te/yr	$NpRn_f$
ratio of water used to amount of product	W/P	0.43 m^3/te	

Costs have also been included in the calculations and comprise the following:

- cost of water (c_w) - the cost of water includes purchasing towns water and paying for disposal of the contaminated water to effluent treatment. The costs have been split into water costs for intermediate cleaning (C_{wr}) and water costs for jetting (C_{wj});

- cost of jetting operations (c_{jc}) - this is based on employing contractors to clean the vessels;
- cost of recovering VCM (c_{vcm}) - each time the reactor is opened for jet cleaning VCM is released to the recovery unit, thereby increasing the load and operating costs. Therefore, the cost of recovering VCM has been based on the cost of refrigeration and compression of the amount released;
- cost of energy used (C_{er}, C_{ej}) - energy is required to pressurise water during each of the cleaning cycles. The costs have been estimated for the low pressure rinse (e_{lp}) , the high pressure rinse (e_{hp}) and the high pressure water jetting (e_j). C_{er} is the total cost of energy used for intermediate rinsing and is the combination of the energy used for the high pressure and low pressure rinses. C_{ej} is the total cost of energy used for jet cleaning;
- loss of product - the PVC that forms the deposit is considered an additional cost (C_d). The mass of the deposit is estimated by multiplying the deposit thickness (X_t), the average density of PVC (ρ) and a proportion of the vessel surface area (A). It was assumed that the deposit covers 80% of the inside of the vessel. Multiplying the deposit mass by the value of PVC (V) results in the cost of the lost product.

The total cost of the cleaning cycles is shown in Table 5.7. For intermediate cleaning, 52% of the overall costs result from the water costs, with energy costs contributing the rest. The intermediate cleaning was predicted to be 1.6 times more expensive per year than jetting due to larger water and energy costs. The increased man power and VCM recovery costs associated with jetting did not outweigh the lower energy and water costs. However, despite purging before the vessels are opened for jetting, an additional release of VCM occurs to the atmosphere. This has not been considered in the calculations. Such a release is likely to be a health and safety risk to employees cleaning the reactor and also an environmental risk. Therefore, although the jetting operations may be cheaper, other issues may not allow the vessel to be opened on a regular basis.

Table 5.7: Calculations of costs using the EVC data

Definitions	Parameter	Value	Data source
cost of water	c_w	£ 0.55 /m^3	water company
cost of one jet cleaning operation	c_{jc}	£ 2281.56 /clean	contracting company
estimated cost of recovering VCM that is purged from the vessel before opening for jet cleaning	c_{vcm}	£ 6.74 /opening	refrigeration and compression costs
cost of the energy used for low pressure cleaning cycle for one reactor	e_{lp}	£ 0.35 /clean	amount used for operation x cost
cost of the energy used for high pressure cleaning cycle for one reactor	e_{hp}	£ 7.44 /clean	amount used for operation x cost
cost of the energy used for jet cleaning one reactor	e_j	£ 26.09 /clean	amount used for operation x cost
water used for rinsing	w_r	62748 m^3/yr	$n_f NRF_r t_r$
water used for jetting	w_j	37.85 m^3/yr	$NRF_j t_r$
total cost of water used for intermediate cleaning	C_{wr}	£ 34540 /yr	$c_w w_r$
total cost of energy used for intermediate cleaning	C_{er}	£ 27135 /yr	$(e_{lp} + e_{hp})n_f NR$
Total cost of Rinsing	C_r	£ 61675 /yr	$C_{wr} + C_{er}$
total cost of water used for jetting	C_{wj}	£ 20.82 /yr	$c_w w_j$
total cost jet cleaning contractors	C_{jc}	£ 37825 /yr	$c_{jc}NR$
total cost of energy used for jet cleaning	C_{ej}	£ 432.48 /yr	$e_j NR$
total cost of removing VCM from the vessel	C_{vcm}	£ 111.88 /yr	$c_{vcm}NR$
Total cost of jetting	C_j	£ 38389 /yr	$C_{wj} + C_{jc} + C_{ej} + C_{vcm}$
value of product	V	£ 500 /te	plant data
surface area of vessel	A	111 m^2	plant data
density of PVC deposit	ρ	0.56	average plant data
value of lost product per year.	C_d	£ 18275 /yr	$X_t A \rho V$
Total costs	C_t	£ 118342 /yr	$C_d + C_j + C_r$
total product value	V_p	£ 7.32 x 10^7 /yr	PV
ratio of water used to amount of product	C_t / V_p	1.24 x 10^{-3}	

5.5 Summary

Water has been highlighted as a waste problem for the EVC process. Cleaning is a source of waste water and therefore has been considered in detail.

Simple cleaning models have been developed due to the lack of detailed knowledge of the deposit build-up and removal. However, these simple models are adequate for the broad study that has been carried out. The three models developed were:

1. a simple model based on constant parameters and cleaning schedules,
2. a model where the effectiveness of cleaning decreased as the cycle progressed, eventually becoming ineffective at the final deposit thickness. Two cases have been considered. Firstly the cleaning time was kept constant so the deposit remaining after the intermediate cleaning increased for each cycle. Secondly the cleaning time was increased as the cleaning became less effective and the deposit removed remained constant, and,
3. the data available from the EVC plant operations has been used to develop a more realistic cleaning model.

In Chapter 10 these models are used to assess the effect of process changes on the performance of the cleaning operations.

Chapter Six

Extension of the Douglas Design Methodology

6.1 Introduction

In Chapter 2, a need was identified for a structured design methodology that combines three important aspects: process design, pollution prevention and environmental assessment. In Chapter 3, the methodologies that have been developed to date by academic researchers and companies were reviewed. This review showed that none of the methodologies have adequately taken into account all three aspects. In Chapter 3, it was also shown that the methodologies, in their present state, could not be used effectively for waste minimisation during batch process design. After reviewing existing design methodologies it was decided that the Douglas design methodology, which is detailed in Chapter 3, could be adapted and applied to batch operations waste minimisation. In order to achieve this adaptation additional process questions and design levels have been added to the existing Douglas methodology.

In this chapter the characteristics of batch processes are discussed, highlighting the areas of environmental concern and the potential for producing wastes. The Douglas design methodology is then examined in order to pinpoint its weaknesses regarding waste minimisation and batch process design. The subsequent chapters focus on each of these weaknesses in turn and new design questions are added. The value of the additional process questions are analysed using the results of the two case studies that were presented in Chapters 4 and 5.

6.2 Characteristics of batch processes

As discussed previously in Section 2.2.4, wastes produced from batch processes can differ significantly from continuous processes. As a result of these differences the impact on the environment of releases from a batch process may also differ from continuous releases. In some cases it may be necessary to deal with wastes from batch processes differently, thus requiring alternative operational approaches and waste minimisation techniques. In spite of this there are some common problems a designer will encounter during the design of both continuous and batch processes. A detailed review of waste minimisation issues specific to batch processes has already been carried out by the author [138] and the main points are summarised in this section. The major areas of environmental concern are indicated in Figure 6.1.

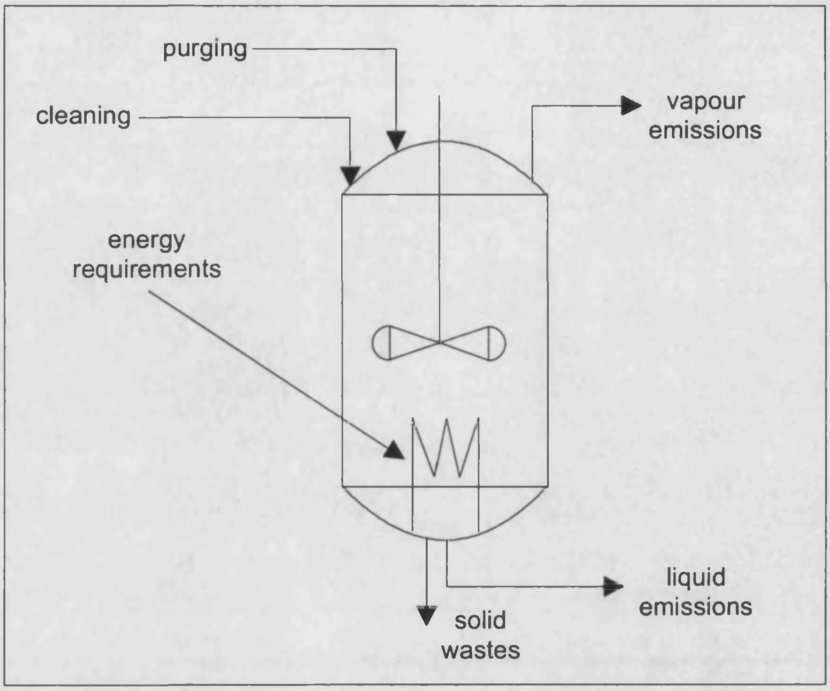


Figure 6.1: Major environmental issues associated with batch processes

In general, batch plants produce smaller amounts of product than continuous plants. However, the amount of waste produced per kilogram of product can be large [14] depending on the nature of the product and the process. For example, a pharmaceutical active ingredient or fine chemical will be often be present in small concentrations and hence, large amounts of excess material would need to be removed to obtain a saleable product.

The wastes produced from a process are vapour, liquid or solid. Vapour emissions from a batch can be caused by vapour displacement during vessel charging, during a reaction where gaseous materials are released or during purging operations. These vapour streams may contain gaseous pollutants, volatile organics or dusts. Liquid emissions can either be unwanted products, unconverted reactants or carrier materials. Once the unwanted materials have been removed they may need treatment before being released or recycled. The sources of solid waste include deposit build-up in the vessel, off-grade product or deactivated catalyst. It might be possible to recycle or regenerate such materials. If these are not viable options then the materials can be disposed of in landfill sites, incinerated or traded with another company via a waste exchange network.

Batch processes involve a number of tasks being completed in a specified way to produce the required product. It is often possible for more than one operation to be carried out in the same vessel which requires more operational change-overs and associated start-up and shut-down periods. During start-up and shut-down, plant operations are often unstable and it can be difficult to control the behaviour of the process. Thus, there is a greater potential for emissions or unwanted materials to be produced.

In a batch cycle the operations taking place vary with time. For example, a vessel may first be filled with material, a reactant is then added, the reaction takes place and the contents are emptied out. Thus, the flows from the process will vary depending on the task taking place. As a result, the flow of waste from the process are usually intermittent and variations in flowrate, composition and condition may occur. This scenario may be compared with a continuous process, where the flows are relatively constant except at infrequent start-up and shut-down operations. In batch processes, because the waste produced may vary over a period of time, end-of-pipe equipment such as scrubbers or effluent treatment units need to be designed for the peak process flows and may have to treat a combination of flows from more than one part of the plant.

Due to the varying nature of operations in batch processes, the release of materials to the environment may also vary depending on the operation taking place. These releases may result in peak level concentrations that exceed the regulatory limits at certain times. However, if release concentrations were averaged over time then the average concentration could well be below the required statutory level.

The reaction stage is central to both continuous and batch processes. The reactions performed in batch plants are often complex and may involve several stages. Environmental problems can be caused by the production of unwanted by-products or unreacted materials. The process conditions can greatly affect the performance of the reactor.

Another factor that has to be included when considering wastes from any process is energy usage. Energy generated either onsite or offsite in turn results in emissions to the environment, such as carbon dioxide, sulphur dioxide and nitrogen dioxide. Therefore, the energy demand of a process needs to be minimised. For continuous processes the energy demand can often be reduced by heat integration. However, in batch processing this is a non-trivial task as the hot and cold streams will often not occur at the same time in the batch cycle.

Cleaning of batch equipment is often required between batches to ensure no residual material is present to contaminate the next batch. This is particularly important during certain pharmaceutical production where contamination could cause the product to be rejected. For a multi-product plant it may be necessary to clean the vessels between different product campaigns, again to prevent contamination of the products. Cleaning uses solvents, water or detergents that leave the process as potential wastes.

6.3 Extension of the Douglas design methodology

The levels of the existing Douglas methodology are presented in Figure 6.2. To extend the methodology, new process questions have been included that refer directly to individual batch operations. The areas where questions have been added are shown alongside the existing levels in Figure 6.2 and are as follows:

- Level 2: input output considerations. These are presented in Chapter 7;
- Level 3: reactor and recycle considerations. This extension is presented in Chapter 8. The base case models of the Thomas Swan process, detailed in Chapter 4, have been used to examine several of the reactor operational questions in more detail;
- Level 4: the extension of the separation system is presented in Chapter 9. The Thomas Swan models have been used to examine a batch distillation operation;
- Level 7: aspects relating to heat exchanger networks, process integration and scheduling are combined into one level and are detailed in Chapter 11.

A new level has been added to the existing Douglas methodology and this is discussed in Chapter 10. This new level introduces the design of cleaning operations. The EVC case study presented in Chapter 5 has been used to examine several cleaning options.

Level 1 has not been altered in this work because it deals with the choice between batch and continuous operations and did not need updating. Level 5, product drying has also not been changed because the design choices would be similar for both batch and continuous processes. Details of Level 7, piping and equipment layout has been included in the scheduling considerations. The other levels have not been considered in detail.

In addition to formulating the new design questions the work described in this thesis has extended the cost estimation techniques. To assess the costs of a process flowsheet, Douglas uses an economic potential (EP). The EP consists of the major flowsheet cost items and for waste minimisation includes estimations of waste disposal costs, i.e. landfill costs for solid wastes or sewage treatment costs for liquids. The extended methodology introduces additional factors that are particularly important to batch processes, such as the cost of intermediate storage for recycling or the cost of combining batch vessels.

In the revised methodology for batch processes an environmental process performance tool has been used to determine an environmental score (EPPT score) and the development and application of this tool is described by Aubrey [1]. This enables the effect of the process emissions on the environment to be quantified. Hence, the environmental effects of materials released can be assessed and compared. Appendix C provides a brief summary of the environmental process performance tool.

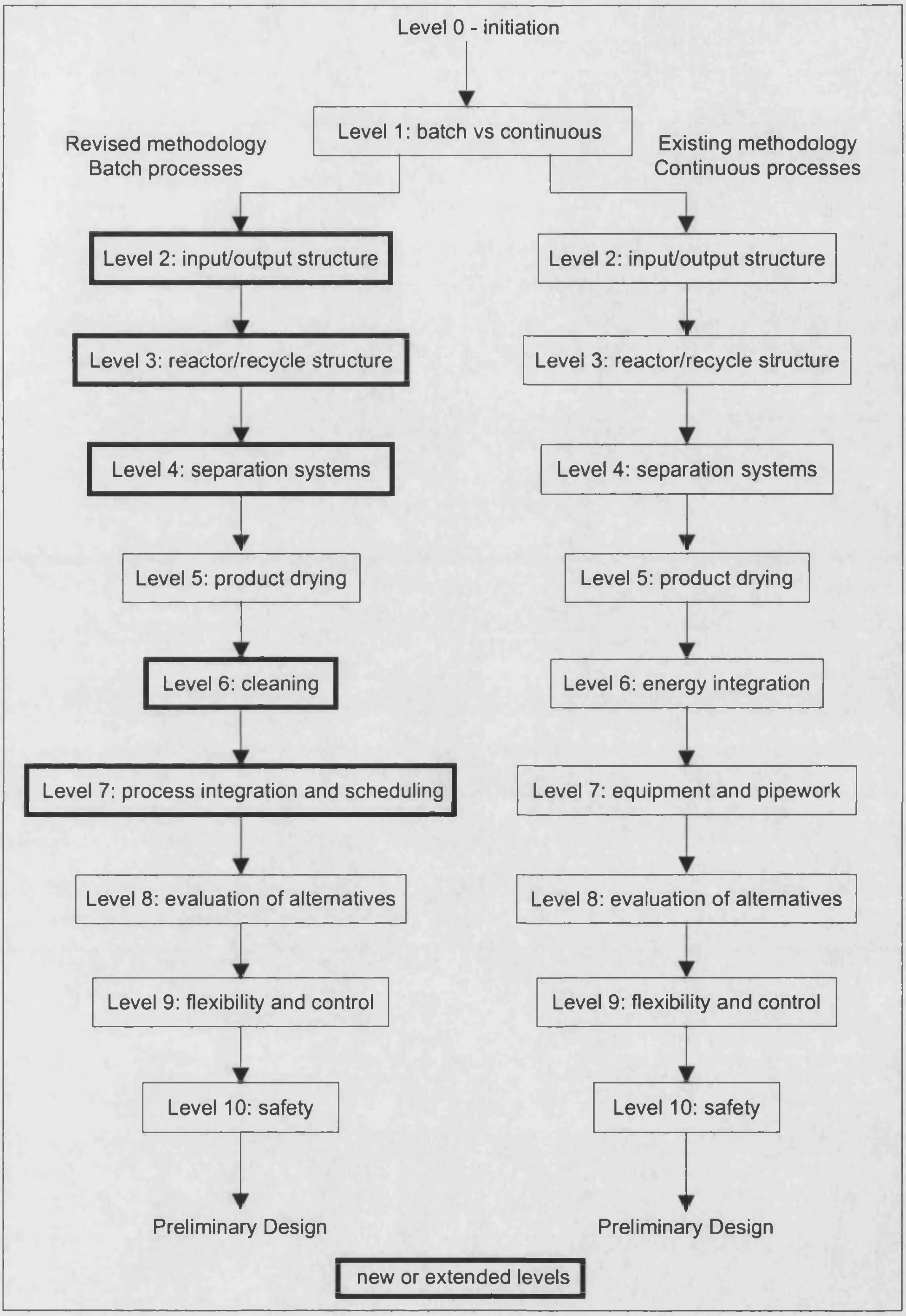


Figure 6.2: Douglas design methodology levels

6.4 Summary

At present there is no structured design methodology that aids the design of clean batch processes. The Douglas methodology has been used as the basis for developing such a methodology and has been updated to include the important batch process issues. There are some areas where the design of batch and continuous processes are similar and the Douglas design questions for continuous processes can be directly applied to batch systems. However, considering the individual batch operations it was found to be necessary to extend the Douglas methodology to include factors such as time varying releases, individual batch operations, task allocation and cleaning. It was also necessary to update the cost estimation procedures so that they apply to batch processes. Assessment of the environmental impact is performed using an environmental assessment tool and is combined into each of the design levels. The result is a methodology for designing inherently clean and economic batch plants [139, 140, 141, 142].

Chapter Seven

Level 2 Considerations: Input-Output

7.1 Introduction

Level 2 of the Douglas methodology enables the designer to gain an overview of the process using the overall mass balance. The information required is similar for both continuous and batch operations as the total inputs and outputs are considered. Therefore the questions developed for continuous processes, detailed in Section 3.2.2, can also be applied to batch processes. However, there are additional factors relevant to batch processes.

In this chapter the existing Douglas design questions have been applied to batch process design. New questions have been added to the Douglas design methodology to include factors that are specific to batch operations and these are presented in Section 7.4. As indicated in Figure 7.1 a batch plant can either produce a single product or a number of products ie a single product or multi-product plant. The type of operation required has been considered at Level 2 and the relevant process design questions are presented in Section 7.4. However, the subsequent design levels focus purely on single product plants. Therefore, the development of design questions and levels for multi-product plants would need to be considered in future work.

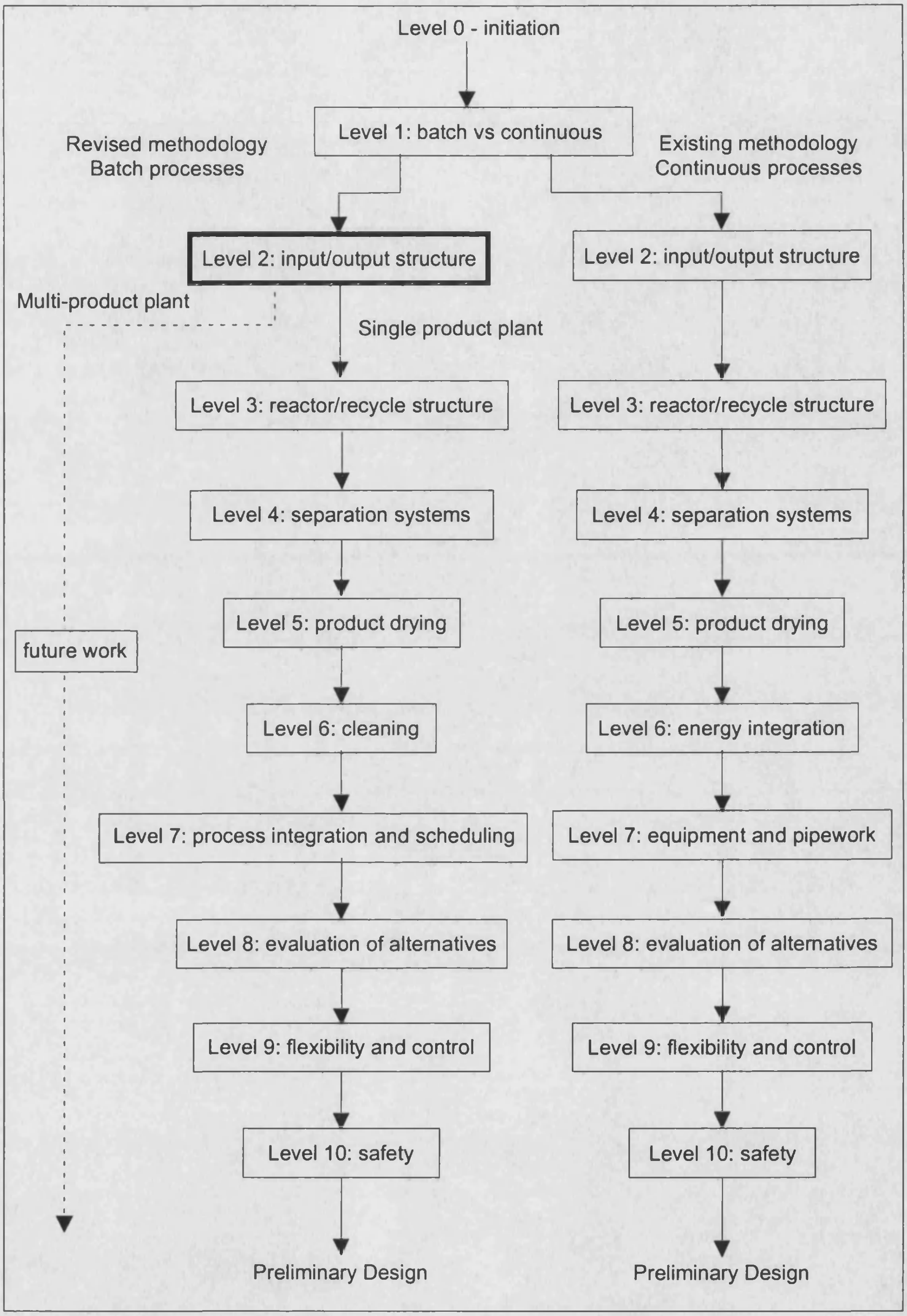


Figure 7.1: Extension of the Douglas design methodology

7.2 Application of existing Level 2 design questions

Table 7.1 details the application of several of the existing Douglas methodology questions to batch processes and waste minimisation. A full list is provided in Section 7.6. A number of examples have been obtained from IPC applications to illustrate some of the operations that would be highlighted using the Douglas design questions and these are detailed in the following sections.

7.2.1 Should a by-product of a reaction be removed or recycled?

The manufacture of sodium phenyl acetate and potassium phenyl acetate produces 351 te of ammonia by-product per batch. In the original operation the by-product stream was passed through a condenser, a water absorber and a water scrubber to remove the ammonia which then was disposed of. The company is now investigating the possibility of recovering and purifying the ammonia stream to enable it to be sold [143].

7.2.2 Should the unreacted materials be recovered and recycled?

During the production of PVC (described in Chapter 5) large amounts of fresh water are used. This water cannot be recycled to the next batch as it contains trace polymer granules. These granules would become double polymerised if they were to be passed through the reactor a second time and would cause the polymer product to become off-grade.

7.2.3 Can any "waste" output stream be used in the plant or by an external user?

An example is a company manufacturing a mixture of silicon tetrachloride and trichlorosilane for a neighbouring company [144]. The waste hydrogen gas stream is also piped to the neighbouring site, where it is used as a raw material.

7.2.4 Can any input streams, such as additives or solvents, be eliminated or replaced?

Inputs such as solvents or additives often exit the process as waste. Replacing the material could reduce the wastes and reduce the environmental impact of the process. For example, during the manufacture of PVC a methanol based suppressant was used in the reaction vessel. On examining the emissions from the plant the operators noticed that the methanol emissions could be an environmental problem. Therefore, the methanol suppressant was replaced with a water based material and the release of methanol from the process was completed eliminated [128].

7.2.5 Are there any problems caused by reaction chemistry?

The traditional method of manufacturing benzoyl chloride uses sodium cyanide as a raw material and methanol as a solvent. This route has been discontinued by one company because:

- the methanol, being highly explosive, represented a safety risk,
- sodium cyanide, being a solid material, required manual handling. The transfer of material was difficult and resulted in an increased exposure risk to the employees and the environment.

A new route was introduced that utilises benzyl chloride and an aqueous cyanide solution, reacted in the presence of a catalyst. Therefore, methanol is avoided and the raw materials are liquid so they can be pumped automatically into the vessel [143].

7.2.6 Is spent catalyst a problem?

Example 1 [145]

The manufacture of sodium chromolate uses a catalyst, known as TDA-1. After the reaction phase the aqueous phase containing the catalyst is decanted to the onsite biotreatment plant with the effluent water. Sludge from the treatment plant, which contains the spent catalyst, is sent offsite and disposed of in a licensed landfill site.

Total sludge sent to landfill = 2340 te/annum
Total amount of catalyst used = 318 kg/annum

The amount of spent catalyst therefore is only a small fraction of the waste sent to landfill.

Example 2 [146]

A platinum catalyst is used in the manufacture of 4NDPA (4-nitrodiphenylamine). Up to 0.05 kg of catalyst is used daily with only small amounts being lost to the water effluent. After the reaction the products are filtered and the catalyst removed. The catalyst is put in drums and sent to the suppliers for regeneration. The filter bags and materials contaminated by the catalyst are also sent to the suppliers for treatment and catalyst removal. Regeneration of the catalyst may cause additional pollution problems caused by burnt off material or disposal of contaminated solvents.

These two examples illustrate two different methods of dealing with catalysts. Using the extended Douglas design methodology it should be possible to compare the options in terms of environmental impact and cost. For example, if the first example was considered during the conceptual design stage it may have been shown that purchasing new catalyst represents an additional cost to the process. The disposal of the material to landfill may represent an environmental impact. Regeneration may be possible but would still have an environmental effect as materials are released to the environment. Therefore, it could be investigated whether a catalyst with a longer life could be used or whether the life of the catalyst could be prolonged by altering the reactor conditions.

Table 7.1: Application of existing Level 2 Douglas design questions to batch processes

Question	Operational options	Positive points	Negative points	Notes
Should a by-product of a reaction be recovered or recycled?	Leave in waste streams.	No separation operations required.	Materials released to the environment.	See Section 7.2.1
	Separate from waste streams.	Materials may be able to be sold or used in another batch.	Separation required that may use energy or chemicals. Additional storage requirements.	
Should the unreacted materials be recovered or recycled?	Recycle unreacted material.	Reduce waste from the process and improves the conversion to product.	May require additional storage capacity incurring additional capital and operating costs. Also may be restrictions on recycling due to potential for contamination.	See Section 7.2.2
	Recycle water or solvents.	Reduce need for fresh materials.		
Can any “waste” output stream be used in the plant or by an external user?	Exit process as waste steams.	May be operationally more straight forward.	Materials released to the environment.	See Section 7.2.3
	Use in another batch, process or plant.	Would reduce waste from the process.	Opportunities for using materials may not be obvious as batches may be operated at different times.	
Can any input stream, such as additives or solvents, be eliminated or replaced?	Use such materials in the process.	Additives may be required to inhibit, initiate or catalyse reactions. Water and solvents are often used as carrier fluids or heat transfer media.	Operational problems would occur if these materials were not present.	See Section 7.2.4
	Replace problem materials.	May be able to solve an environmental problem by replacing a material e.g. avoid volatile solvents that contribute significantly to air emissions.	A specific material characteristic may be required for operational reasons.	
	Alter operations to avoid the need for the additional materials.	For example, air blowers could be used to transfer material rather than slurrying, thereby eliminating	May be more costly options, have higher maintenance costs or alter the process	

Table 7.1: Application of existing Level 2 Douglas design questions to batch processes

Question	Operational options	Positive points	Negative points	Notes
		a potential waste stream.	schedule.	
Are there any problems caused by reaction chemistry?	Use alternative reaction route.	May be avoid the problem materials.	May not be a viable alternative.	See Section 7.2.5
Are there any feed impurities that could cause waste problems?	Pass through process.	No extra separation required.	Impurities may contaminate product, denature catalysts or poison the main reaction.	See Section 7.3.
	Remove impurities onsite.	Control the purity of the feed and remove unwanted substances.	May require additional energy input, chemical inputs and separation units.	
	Purchase purer feed stocks.	No problems with feed impurities.	Usually more costly.	
Is spent catalyst a problem?	Dispose of spent catalyst.	May be operational reasons for disposing of catalyst.	Materials released to the environment.	See Section 7.2.6
	Regenerate spent catalyst.	May be less costly than buying new catalyst and may have less environmental impact than disposing of catalyst.	Materials still released to the environment such as burnt off deposits or contaminated solvents.	
	Use catalyst with long life and safeguard it in the reactor.	Less emissions to the environment.	Catalyst may be more expensive and the reactor conditions would need to be tightly controlled.	

7.3 Level 2 considerations highlighted using the Thomas Swan case study

Thomas Swan manufactures a rubber peptiser (Pepton) and details of the operations are provided in Chapter 4. The overall mass balance for the Pepton process is shown in Figure 7.2. The data has been taken from the IPC application and it was found that the input and output figures did not balance exactly.

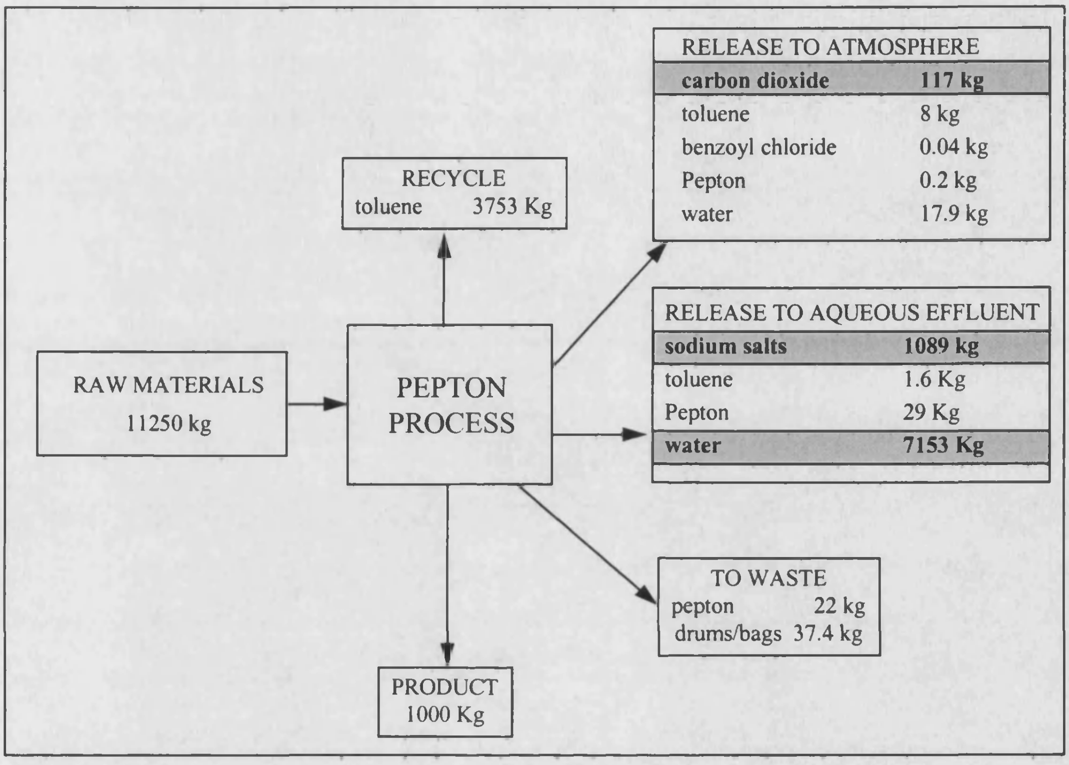


Figure 7.2: Overall mass balance for the Pepton process

By studying the inputs and outputs of the process and with a knowledge of the major reactions, several areas of concern have been identified using the Level 2 questions described in Table 7.1. These are:

- *Are there any problems caused by reaction chemistry?* - A by-product of the benzoylation reaction, carbon dioxide, is a major release to air. If this were identified as an environmental problem the specified reaction route would have to be altered.
- *Should the unreacted materials be recovered and recycled?* - The aqueous effluent consists of water contaminated with organics and sodium salts and is sent offsite for disposal. The amount of water used is crucial as it represents both a financial cost and an environmental impact. Water usage has been reduced by the

company from 30 te/te product to less than 9 te/te product by improved monitoring and recycling.

- *Are there any feed impurities that could cause waste problems?* - One of sodium salts present in the aqueous waste is the result of a feed contaminant reaction. The environmental assessment performed by Aubrey [1] of the process outputs highlighted this material as a potential environmental problem. Two options that could be investigated are to purify the feed onsite or to purchase purer feed from the supplier. Both of these options would involve additional costs but the removal of sodium salt may prevent the aqueous waste from needing treatment. A cost-benefit analysis would need to be considered in more detail at the design of the separation stage as discussed in Chapter 9.

7.4 New process design questions added to Level 2

The following eight questions are now added to the Douglas design methodology. Most of the questions aim to enhance the batch process design methodology. The questions have been adapted from various publications [147, 148, 89]. A number of these considerations are also applicable to continuous process design and therefore, should also be included in the Douglas design methodology for continuous processes.

7.4.1 How many products are required?

In multi-product plants the number of products needs to be defined. The mass balances for all products (including their wastes) will have to be performed. It may be possible to identify materials found in one batch that could be used in other batches.

7.4.2 What mode of operation will be used?

Multi-product batch plants can be operated in cyclic or acyclic mode. In cyclic mode the tasks assigned to each process unit are fixed and products are made in campaigns, one after another. This is generally inefficient and may leave some units lying idle. In an acyclic operation any vessel can be used for any task enabling some of the idle time to be eliminated. However, if cross contamination is a problem then acyclic operation may require excessive cleaning. There are four general batch operations modes [148]:

- single product plants producing the same material,
- multi-product plants where similar materials are made in campaign form e.g. paint manufacture,
- multi-purpose plants where dissimilar materials are made in the same equipment on a campaign basis e.g. manufacturing different pharmaceutical active ingredients, and,
- general multi-purpose plants where the products are made acyclically.

7.4.3 Which tasks will be assigned to which vessels?

At this level only very basic decisions need to be considered. For example, cross contamination may restrict operations being carried out in the same vessel. Process steps occurring at significantly different operating conditions are likely to be carried out in different vessels. The aim at Level 2 is to gain an initial estimate of the number of vessels and processing steps required. The tasks required can be identified and can be associated with equipment items. This will help in the design of the unit operations at the subsequent design levels.

For the initial design each operation is assumed to be assigned one vessel. The number of vessels and the operations are likely to change as the equipment items are designed and the task assignments may change as the design evolves. The final level of design is the scheduling of the plant which finalises the number of vessels and the assignment of tasks.

7.4.4 How much flexibility is required?

Batch plants are usually designed to be flexible because the units may be required to produce different amounts of material or different products. In assessing the waste production from the plant this flexibility should be considered *ab initio*, i.e. what will the plant be used for in the future? Ignoring this at the design level may result in the waste treatment units being either over or under-specified. Often the design is over-estimated and this may cause the equipment to be operated inefficiently at the normal operating levels resulting in more resources such as energy being used. If the emissions are under-estimated the treatment equipment will not be effective and additional end-of-pipe equipment may be required.

7.4.5 Is there an operation or material that is not required?

Often in batch processes, stages are introduced that may not be absolutely necessary. It may be traditional to perform specific tasks but analysis may show that the operation is not contributing to the success of the process. Two examples are: (i) the addition of excess washing operations and (ii) heating vessel contents above the required temperature to ensure the materials are in solution or have reacted.

The manufacture of Pepton, described in Chapter 4, was purchased from another company. When analysing the process Thomas Swan, the new owners, found that several unnecessary washing operations were undertaken. These consisted of washing the dryer every day, washing the product sieve screen and washing the production floor during every shift. The revised operations reduced these washings substantially, thereby reducing the aqueous waste production.

7.4.6 Are any materials used that have restricted use?

If a material is used that is restricted by law or that has strict disposal criteria then it would be beneficial to replace it with another material. Examples in the UK are red listed substances such as benzene and lead. This question is also applicable to continuous processes.

7.4.7 Are there any materials that may cause offsite problems?

For both continuous and batch processes the release of odorous chemicals, coloured smoke, plumes or dusts in residential areas may cause problems. It may be necessary to avoid these materials or be prepared to significantly mitigate their release.

7.4.8 Do any materials cause fouling problems?

The products, by-products or reactants involved in a process may cause fouling problems that require the equipment to be cleaned. The problem may be reduced by minimising by-product formation or by avoiding specific reactants. However, if the materials cannot be eliminated and fouling is considered a problem the design engineer will be aware of this when designing the reactor. The consideration is then cascaded to the next design level and the equipment can be designed to minimise the deposit of material as discussed in Chapter 8.

7.5 Cost estimation and environmental assessment

In the original Douglas methodology the stream costs were represented by:

$$EP_2 = \text{(product value)} + \text{(by-product value)} - \text{(raw material costs)} \ (\text{£/year}) \qquad (7.1)$$

In order to include waste minimisation in the cost analysis, Douglas estimated the waste disposal costs, i.e. landfill costs for solid wastes or sewage treatment costs for fluids and the EP is as follows:

$$EP_2 = \text{(product value)} + \text{(by product value)} - \text{(raw material costs)} - \text{(disposal costs)} \ (\text{£/year}) \qquad (7.2)$$

This has not been altered because it is applicable to both batch and continuous processes.

In the revised methodology an environmental assessment tool has been developed to examine the environmental effects of materials released as discussed in Chapter 6, Section 6.3. The EPPT score for Level 2 is:

$$(\text{EPPT score})_2 = \text{environmental impact of process outputs} \qquad (7.3)$$

7.6 Summary

Level 2 of the Douglas design methodology has been extended to cover waste minimisation of batch processes. The existing questions used in the Douglas design methodology have been applied to batch processes. Where necessary additional questions have been developed to extend the methodology to consider individual batch operations. Table 7.2 provides a summary of the existing and new questions for Level 2. The assessments of the cost and environmental impact of the options have also been updated.

In the next chapter the design of the reactor and recycle system are discussed in more detail.

Table 7.2: Summary of the questions used at Level 2

Existing questions
Should the feed be purified? Should a by-product of a reaction be removed or recycled? Should a gas purge or recycle stream be used? Should the unreacted materials be recovered and recycled? How many product streams should there be? What are the costs associated with selectivity losses? Can any "waste" output stream be used in the plant or by an external user? Can any input streams, such as additives or solvents, be eliminated or replaced? Are there any problems caused by reaction chemistry? Are there any feed impurities that could cause waste problems? Is spent catalyst a problem?
New questions
How many products are required? What mode of operation will be used? Which tasks will be assigned to which vessels? How much flexibility is required? Is there an operation or material that is not required? Are any materials used that have restricted use? Are there any materials that may cause offsite problems? Do any materials cause fouling problems?

Chapter Eight

Level 3 Considerations: Reactor - Recycle Design

8.1 Introduction

In this chapter, Level 3 of the Douglas design method is extended to apply to batch process design as indicated in Figure 8.1. Level 3 considers the design of the reactor-recycle with the aim to defining the amount of recycle required and to size and cost the reactor vessels. The existing Douglas design questions for designing continuous units have been applied to waste minimisation and batch process design and are detailed in Section 3.2.3. Details of the existing Douglas methodology are provided in Chapter 3.

New questions have been introduced to the methodology to consider the characteristics of the individual batch operations. A number of the new questions presented have been tested using the simulations of the Thomas Swan operations described in Chapter 4. The results of these studies are presented in Section 8.7.

The design of a batch reactor system needs to consider the specification of the individual operations as well as the design of the units. The different operations, such as charging, heating, performing a reaction etc., are likely to result in emissions of different materials, different release amounts and varying durations. For this reason, Level 3 considerations for batch processes have been divided into several sections each dealing with a different batch operation as shown in Table 8.1. The initial design is assumed to use one vessel for each reaction. The merging and splitting of tasks is dealt with at a later level during plant scheduling.

Table 8.1: Operational phases for batch processes (adapted from [84])

Operational group	Name of operation	Relevant section
Material transfer	vessel charging transfer discharge	Section 8.2.1 Section 8.2.2 Section 8.2.3
Heat transfer	cooling heating	Section 8.3.1 Section 8.3.2
Reaction	reaction fouling	Section 8.4 Section 8.4
Gaseous operations	pressurising vacuum purging venting	Section 8.5.1 Section 8.5.2 Section 8.5.3 Section 8.5.4

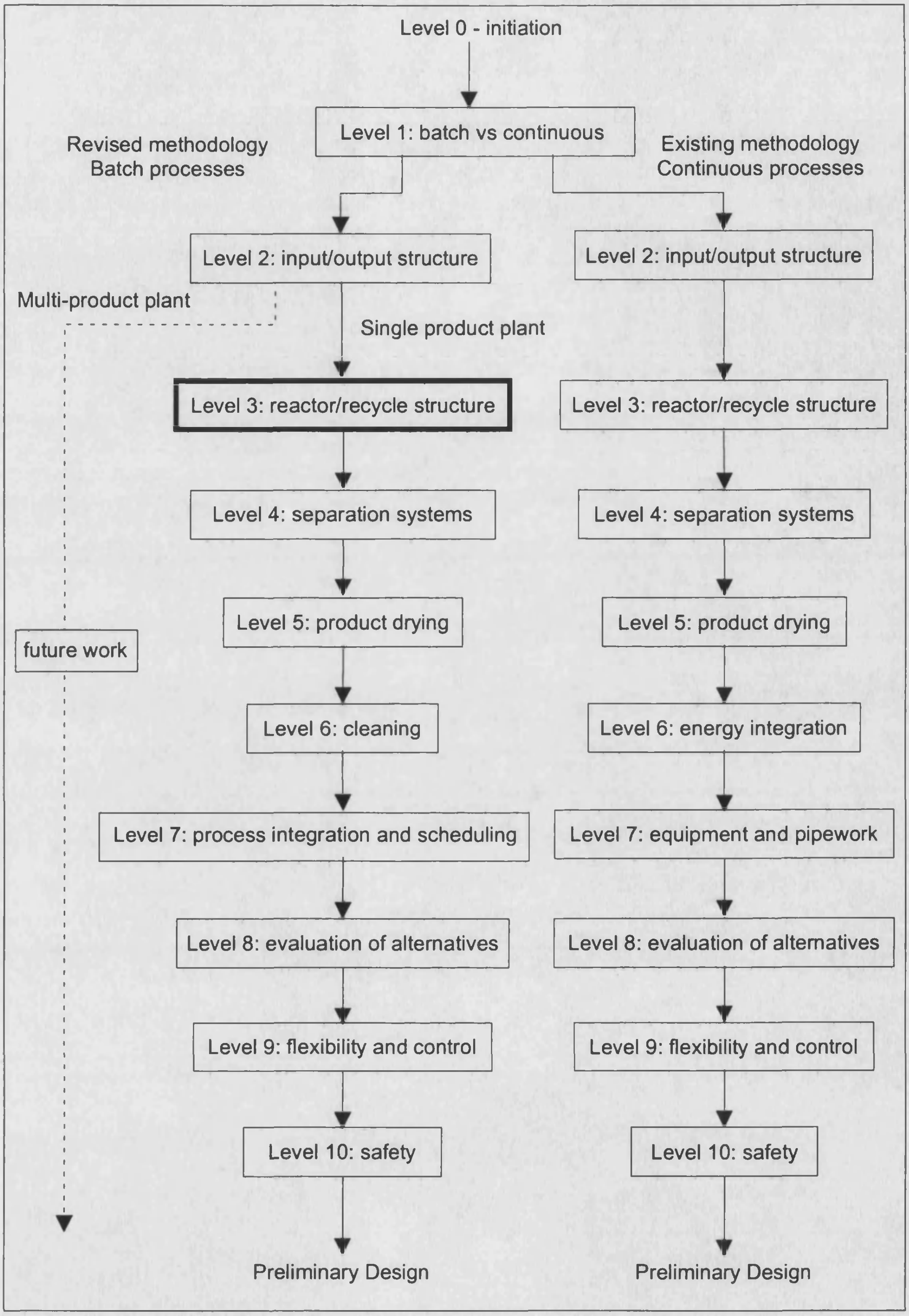


Figure 8.1: Douglas design methodology

In this chapter each of the operations in Table 8.1 is considered. Where available, the existing questions in the Douglas methodology have been included and waste minimisation issues for batch processes have been highlighted. Douglas' questions focus mainly on problems associated with the reaction which was considered to be the main concern when designing continuous plants.

It should be noted that whilst designing a batch process there is likely to be a large amount of interaction between the design levels. For example, the design of the reactors, the cleaning system, heat integration and process scheduling are all interlinked. Consequently, the decisions made at each level may affect the previous or subsequent design levels. Therefore, at the initial design stage the aim is to identify the parameters that are key to the process performance and to highlight potential environmental problems. The effect of altering factors, such as changing the number of reactors, altering the cleaning system design or varying the scheduling requirements, can be examined at the simplest level. However, assessment of the complex interactions and process optimisation will be undertaken at the final design stage.

8.2 Material transfer

Because the operations change during a batch production cycle materials are often transferred from one unit to another. Materials may be added to a vessel, transferred between equipment, discharged to treatment units or released to the environment. The new questions that have been added to the Douglas methodology are discussed in the following sections.

8.2.1 Vessel charging

The initial stage of a batch process is usually filling or charging vessels with materials. Douglas did not consider this operation, because charging was not considered relevant to normal continuous operations. During charging the liquid entering the vessel will displace vapour. This vapour may contain volatile materials from the previous batch, from residual cleaning fluids or from the feed stream. If the vessel is open during charging these vapours will be emitted to the atmosphere or be sent to treatment. Therefore, the aim is to reduce these emissions. Table 8.2 presents a summary of the questions introduced for this operation.

Table 8.2: New questions added to the Douglas methodology for charging operations

Question	Operational options	Positive points	Negative points	Notes
What is the effect of charging the vessel with the vent open or closed?	Vent open whilst charging Close the vessel whilst charging.	No rise in vessel pressure. No emissions through vent.	Materials released through vent. Pressure rise in vessel may require feeds to be pumped in, thereby increasing energy demand and operating costs.	See Section 8.7.1
Does the order of addition affect the potential for releases?	Add material with lowest boiling point first. Add materials that will react or cause a temperature rise last.	Dilution of other more volatile materials. Duration of releases as a result of the reaction or temperature rise is minimised.	- -	See Section 8.7.2
Does the method of addition affect the releases?	Use a high charge flowrate. Use a low charge flowrate.	Reduced emission duration. Easier to control heat production and ensure materials are well mixed.	Materials may not enter solution adequately or may result in an excessive heat rise. Longer release duration.	See Section 8.7.3
Can the temperature of the vessel be lowered during charging operations?	Cool the vessel contents or stream.	Less volatile material present in vapour.	Energy required for cooling.	See Section 8.7.4
What affect does the material vapour pressure have on emissions during charging?	-	-	-	See Section 8.7.5

8.2.2 Vessel transfer

There are a wide range of methods available for transferring material from one unit to another. These include mechanical conveyer belts, air blowers and slurrying solids with water. There are no existing questions in the Douglas methodology for this operation. The new questions that have been added here are:

- *What are the characteristics and conditions of the materials to be transferred?* The nature of the material i.e. either liquid, solid or vapour will affect the most appropriate choice. It may be possible to alter the process conditions, such as temperature, in order to improve the transferability of material.
- *Which methods of transfer are appropriate and what are their environmental consequences?* For example, if another agent, such as water or air, is added to the system, when does it exit the process and does it become contaminated? Using mechanical conveying may avoid adding materials but may use more energy increasing the running costs. The increased energy demand will result in greater emissions to air resulting from the production of the energy.

8.2.3 Vessel discharge

After the required reaction operations have been completed vapour, liquid or solid materials will need to be discharged from the vessel. The best way to deal with each output will depend on the material, phase and destination of the stream. Streams containing products may need to be sent for further purification, whilst waste streams may either be released or sent for treatment. At this level of design, treatment options do not need to be considered in detail but certain problem materials should be identified and if necessary avoided. The designer will become aware of the potential waste problems and can deal with them in the subsequent design levels such as separation. The new questions concerning vessel discharging are presented in Table 8.3.

Table 8.3: New questions introduced to the Douglas methodology for material discharge operations

Question	Operational options	Positive points	Negative points	Notes
What is the most appropriate method of dealing with a vapour discharge?	Send to atmosphere.	No extra equipment or operating costs.	Increased environmental impact.	Releases will be limited by statutory limits.
	Send to treatment unit.	Shift material from vapour to another media.	Increased capital and operating costs. Will still have an environmental impact as materials are released to the environment.	
	Recycle.	Lower emissions to environment.	High costs associated with gas storage and recompression.	
What is the most appropriate method of dealing with a liquid discharge?	Send to drain.	No extra equipment or operating costs.	Increased environmental impact.	Releases will be limited by statutory limits.
	Send to treatment.	Shift material from liquid to another media.	Increased capital and operating costs. Will still have an environmental impact as materials are still released to the environment.	
	Recycle.	Lower emissions to environment.	Additional costs associated with intermediate storage but unlikely to be as high as for gas recycle.	
What is the most appropriate method of dealing with a solid discharge?	Leave to accumulate.	Less additional fluids used.	May cause operational problems.	-
	Remove with water or solvent.	May need to be removed for operational reasons	May produce contaminated water or solvent streams.	
What is the duration of the discharge?	-	-	-	-

8.3 Heat transfer

Level 3 of the existing Douglas methodology for the design of continuous processes does not consider heat transfer operations. Unlike continuous processes, heat integration of batch plants can be complicated and is unlikely to significantly reduce the process energy demand. New questions that consider heat transfer operations have been developed and are presented in the following sections.

8.3.1 Cooling

Cooling is often required to either reduce the temperature of the vessel contents or to cool condensers. The new questions that should be asked are:

- *What methods of cooling are available?* Several different materials can be used for cooling i.e. water for temperatures to approximately 15°C, chilled water down to 5°C and glycol to -20°C. Other commercial refrigerants can be used or gases such as nitrogen or ammonia. The effect of the cooling system on the environment should be considered in terms of energy usage or materials released to the environment.

- *How much energy is required to operate the cooling system?* The cooling fluids are usually recycled by removing heat and the efficiency of this process should be considered. For example, water cooled in cooling towers releases steam to the atmosphere that may represent an environmental burden. Areas of high heat production or demand can be identified and considered as potential matches during heat integration in Level 7.

- *What cooling temperature is required?* This question is examined in detail in Section 8.7.8 using the simulations of the Thomas Swan operations.

8.3.2 Vessel heating

Heating is often required during the production cycle. The new questions that should be asked are presented in Table 8.4.

Table 8.4: New questions introduced to the Douglas methodology for heating operations

Question	Operational options	Positive points	Negative points	Notes
How much heat is required to initiate the reaction?	If an excessive amount of heat is required a catalyst could be introduced, or	Less energy required for heating.	Need to dispose of or regenerate catalyst.	-
	the reaction path could be altered.	As above.	May not be an economically viable alternative route.	
What method of heating is required?	Direct steam injection.	Ease of controlling temperature and quick response time. Steam may be required as a heat transfer medium.	Condensed steam may become contaminated and require treatment.	-
	Heating via vessel jacket or steam coils.	No steam added to the vessel, therefore no contaminated water stream produced.	Slow response and controllability.	
Where is the energy obtained from to achieve the heat rise?	From process streams using heat integration techniques.	Reduces demand for energy production.	Difficult because hot and cold streams may not occur at the same time in batch cycle. Heat storage could be used but may be expensive and inefficient.	See Chapter 11
At what rate should the vessel be heated?	Fast.	Lower release time.	Uneven heating.	See Section 8.7.6
	Slow.	Even heating and control of temperature rise.	Longer release time.	
What is the effect of heating the vessel with the vent open or closed?	Close vent.	No emissions from vent.	Results in a pressure rise in the vessel.	See Section 8.7.7

8.4 Reaction

The majority of the existing Douglas design questions consider the reaction stage. The application of several of the existing questions to waste minimisation of batch processes is presented in Table 8.5. A full list is provided in Section 8.8. However, new questions have been introduced to address specific batch operation issues and these are shown in Table 8.6.

Table 8.5: Application of existing questions for reaction operations

Question	Operational options	Positive points	Negative points	Notes
Should an excess of reactant be used?	-	High reactant concentration in vessel to ensure high reaction rate and improve conversion to product.	Separation of unreacted material for recycle may require additional units and energy input.	-
Can the reaction equilibrium be shifted favourably?	Various methods available depending on reaction equilibrium as detailed in Smith et al [105].	-	-	See Section 8.4.1
Is complete conversion realistic?	-	Eliminate need to separate unreacted materials and improve yield per batch.	May require excessive residence time or energy input.	-
Can by-products be minimised?	Alter reaction conditions.	Reduce the need to separate unwanted materials and improve conversion to reactants.	Changes may also affect the main reaction.	See Section 8.4.2
Should streams be recycled?	-	Reduce wastes from process.	May require extra separation units and energy input.	-

8.4.1 Can the reaction equilibrium be shifted favourably?

This example, taken from an IPC application [129], illustrates shifting the reaction equilibrium to increase the reaction yield.

Alkyds can be produced by the following esterification reaction:

organic acid,	+	glycol	⇔	polyester, alkyd	+	water
vegetable oil or		or				
fatty acid derivative		polyol				

Conversion can be increased by the removal of the polyester, alkyd or water.

Industrially alkyds are manufactured using a solvent cooking process, whereby a small amount of Class B solvent is added and refluxed. As the reaction proceeds the water is removed from the vessel by distillation. Solvent is also removed and the stream is condensed into a separator. The water, contaminated with low levels of raw materials and solvent, is removed and disposed of offsite. Whilst the solvent is recycled to the reactor.

Solvent is vented to atmosphere during the resin production and can reach a maximum flowrate of 0.0361 kg/hr. However the presence of the solvent allows the temperature of the reaction to be decreased and reduces the oxidation of the products in air so reducing the amount of nitrogen blanketing required as well as improving the yield.

8.4.2 Can by-products be minimised?

Tetraethyl lead is manufactured industrially by reacting a lead-sodium alloy with ethyl chloride at high temperatures and pressures [149]. The reaction is:

$4PbNa + 4C_2H_5Cl \rightarrow (C_2H_5)4Pb + NaCl + 3Pb$

A side reaction also occurs to produce butane as follows:

$4C_2H_5Cl + 2Na \rightarrow C_4H_{10} + 2NaCl$

Minimising the amount of side reaction would result in a better product yield. However, the company found that both the reaction mechanisms involved similar free radicals. Therefore, the side reaction rate could not be reduced without seriously affecting the main reaction.

Table 8.6: New questions added to the Douglas methodology for reaction-recycle operations

Question	Operational options	Positive points	Negative points	Notes
What is the optimum reaction temperature?	-	Improve reaction conversion.	Study of reaction kinetics required which may be time consuming.	See Section 8.7.8
What is the optimum addition rate of the reactants?	Increased addition rate.	Reduces the duration of emissions and may reduce the amount of material released.	As above.	See Section 8.7.9
Are any vapours likely to be released during the reaction?	Keep within vessel. Release via vent.	No releases to environment. No pressurisation and volatile material removed from vessel.	Pressurisation may require more expensive equipment. Vents may need treatment and material released to the environment.	-
At what point should the recycle be returned to the system?	Possibilities include; between different batch, different campaigns, different processes or the same batch.	Reduce wastes from process.	In some cases backwards recycling maybe restricted due to contamination problems.	-
Should vapour recirculation be used?	Place a condenser after the reactor and return the condensate stream.	Control pressure and temperature of the reactor.	Additional unit and possibility of contamination.	-
What is the potential for fouling?	Eliminate dead space in reactor, use stainless steel or glass vessels, use non-stick coatings or add build-up suppressants.	Reduce the need for cleaning and shut-down periods.	Specially built vessels are likely to be expensive.	-

8.5 Operations involving gases

These operations involve the specific production, removal or use of vapours in a batch process and include pressurising the vessel, vacuum operation, purging and venting. The Douglas methodology contains no questions that apply specifically to gaseous operations. Therefore, new questions have been added to the Douglas methodology and these are discussed in the following sections.

8.5.1 Pressurising

The vessel pressure will increase when the volume of the vapour phase increases in a closed vessel. The vapour phase volume will increase if additional gas is produced, the temperature rises or if materials are added. Elevated operating pressures may be required to activate a reaction or to improve the reaction conversion. The new questions that have been added to the Douglas methodology are:

- *What pressure is required and for what reasons?*
- *How much energy is required for pressurising?*
- *What are the additional vessel costs associated with pressurised operation?*

8.5.2 Vacuum

Operating under vacuum conditions is energy intensive and can require expensive equipment. Similar new questions to those introduced for pressurised operations have been added and are:

- *Why is vacuum required?*
- *Are there any benefits of operating under vacuum?*
- *How much energy is required for maintaining the vacuum?*
- *What are the additional costs associated with vacuum operation?*

As a result of operating at a low pressures less volatile material should appear in the vapour phase. Additionally, the negative pressure difference between the vessel and the atmosphere should prevent fugitive gaseous releases.

8.5.3 Purging

Purging is often used to remove materials from the vapour space in a vessel. An inert gas such as nitrogen is usually used to flush out unwanted materials. The new questions that should be asked are:

- *What materials will be present in the purged stream?*
- *How long is the required purge time?* A study of purging operations is provided in Section 8.7.10 using the simulations of the Thomas Swan operations.

8.5.4 Venting

Venting is required in order to relieve the pressure within a vessel. The excess vapours are removed from the vessel through a valve and passed to the atmosphere or to a treatment unit. The new questions that should be asked are:

- *Is further treatment required before the vapour stream can be released to the atmosphere?* In the Thomas Swan operations condensers are used to reduce the emissions of organics to the atmosphere. The simulation of this operation has been used to examine alternative process options and the results are presented in Section 8.7.11.
- *What temperature should the venting be carried out at?* The effect of varying the condenser temperature during the Thomas Swan venting operations has been assessed using the simulations and the results are presented in Section 8.7.12.

8.6 Cost estimation and environmental assessment

Douglas represented cost of the Level 3 flowsheet as:

$$EP_3 = EP_2 - \text{annualised compressor cost} - \text{compressor operating cost} - \text{annualised reactor cost (£/year)} \quad (8.1)$$

For batch processes recycling vapour between batches is unlikely to be a viable option because the costs associated with storing and recompressing gases are usually high. As a result the cost of compression has been removed from Equation (8.1). Recycling liquids is more likely and requires additional intermediate storage capacity. Therefore, the cost of additional storage has been included in the cost estimation of a batch process flowsheet. In addition, the annualised cost of each reaction vessel has been added to Equation (8.1). The cost of reactor units may alter at a later design stage, if the tasks are merged or split during scheduling. It may be necessary to include the operating cost of the individual operations to present an accurate picture of the major process costs. The waste disposal costs are also included in the cost estimation as for Level 2. The new economic potential is:

$$EP_3 = EP_2 - \text{annualised storage cost} - \text{storage operating cost} - \text{annualised reactor cost for each stage} - \text{waste disposal costs} - \text{operating cost of significant batch operations (£/year)} \qquad (8.2)$$

In the revised methodology an EPPT score has been developed to compare the environmental impact of different design options [1]. The EPPT score includes the assessment of the emissions associated with producing energy to be used in the process. As the magnitude and duration of the releases becomes more clearly defined the environmental impact assessment of the outputs becomes more detailed. The EPPT score is given as:

$$(\text{EPPT score})_3 = \text{environmental impact of process outputs and energy usage} \qquad (8.3)$$

8.7 Thomas Swan case study

Several of the new questions proposed in this chapter have been tested using the simulations of the Thomas Swan operations. The Thomas Swan operations and the associated simulations have been described in Chapter 4. The base case simulations were validated against the plant data and represent the normal plant operations. Applying the process design questions results in an alteration of these normal operations. Consequently, the process simulations have been used to assess the effect on the process emissions of changing the base case operations. The temperatures, pressures and vent flow rates presented in this chapter have been made dimensionless because the process information is confidential. The total mass of material released is given per batch. The validity of the following new questions has been tested:

Charging (from Table 8.2)

- What is the effect of charging the vessel with the vent open or closed?
- Does the order of addition affect the potential for releases?
- Does the method of addition affect the releases?
- Can the temperature be lowered during charging operations?

- What affect does the material vapour pressure have on emissions during charging?

Heating (from Table 8.4)

- At what rate should the vessel be heated?
- What is the effect of heating the vessel with the vent open or closed?

Cooling (from Section 8.3.1)

- What cooling temperature is required?

Reaction (from Table 8.6)

- What is the optimum reaction temperature?
- What is the optimum addition rate of the reactants?

Purging (from Section 8.5.3)

- How long is the required purge time?

Venting (from Section 8.5.4)

- Is further treatment required before the vapour stream can be released to the atmosphere?
- What temperature should the venting be carried out at?

The results of the simulations are presented in the following sections.

8.7.1 What is the effect of charging the vessel with the vent open or closed?

During the Thomas Swan operations vessels are charged with the vessel vents open. Therefore, vapours containing organic material are displaced and have to be treated in a scrubber. Although the scrubber removes the organic materials from the vapour phase these materials are still released to the environment via the water phase. Therefore, it is attractive to reduce the emissions to the scrubber.

The simulation of the hydrolysis charging operation has been used to study the effect of charging a vessel with the vent closed. The material charged to the vessel is benzothiazole (BT). A complete description of the operations and the base case simulation is given in Chapter 4, Sections 4.2.1 and 4.3.2. Performing the simulation with the vent closed resulted in the vessel gradually pressurising as the liquid level rises. This is shown in Figure 8.2. Because the vent was shut no emissions to the scrubber were predicted. However, energy was required to pump the material into the vessel as the pressure increased. Assuming a pump efficiency of 80% the total energy demand was calculated to be 354 kJ.

If this process option was considered during the conceptual design of a new plant the economic potential (EP) would probably decrease due to the increased cost of providing a pressurised reactor. Unless a significant pressure rise occurred the increase in the operating costs as a result of the pumping would probably be negligible compared with the overall operating costs. The reduction in the scrubber loading would be small due to the small vapour flows and amounts of organic materials. However, in some processes reducing the vapour emissions significantly may prevent the need for a scrubber, thus increasing the EP.

The EPPT score for this process option would be reduced because less organic material is released to the environment but the increased energy usage would result in an increase. There is a trade-off between the two values.

For the Thomas Swan hydrolysis operations the vessel is already pressure rated to contain the pressure rise during the reaction. Hence, there would be no additional cost associated with the vessel. It was predicted that 0.0046 kg per batch of BT would be prevented from being released to the scrubber if the vessel was closed during charging. However, the additional energy demand was calculated to be 354 kJ. The decreased cost of operating the scrubber is very small and has been estimated to be a reduction of £1.20 per charging operation. The EPPT score for this option has been calculated as 3.4 for the base case and 0.6 when the vent is closed during charging. Details of the calculation can be found in Aubrey [1].

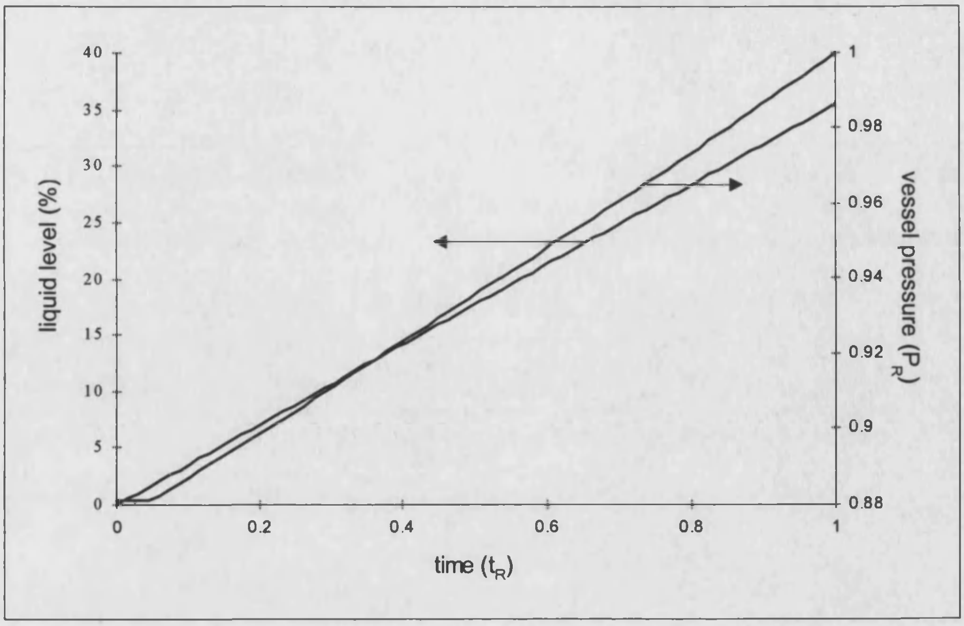


Figure 8.2: Pump energy and vessel pressure vs charge time

t_R = (time/ maximum time)
P_R = (pressure / maximum pressure)

8.7.2 Does the order of addition affect the potential for releases?

In the Thomas Swan benzoylation operation, two charges of toluene are carried out. The first is performed at a lower temperature than the second. Vapour is displaced from the vessel and the vented stream is passed through a water cooled cooler and a glycol condenser to reduce the amount of toluene passed to the scrubber.

A simulation of the toluene charging has been performed. The description of the operations and base case model are provided in Sections 4.2.3 and 4.3.4. This simulation has been used to assess the effect of charging all of the toluene in the first charging period i.e. at the lower temperature.

Table 8.7 provides a comparison between the predicted amount of toluene released using the base case simulation and the simulation at the lower temperature.

Table 8.7: Comparison of predicted releases

Operation	Toluene released (kg)		Mass coolant used (kg)	
	To condensate	To scrubber	Water	Glycol
1st Charge, $T_R = 0.47$	0.90	0.134	0.5	14.8
2nd Charge, $T_R = 1$	2.41	5.6×10^{-2}	3.8	32.4
Base Case: Total	3.31	0.190	4.3	47.14
Option: Both at $T_R = 0.47$	1.21	0.110	0.66	16.38

T_R = (temperature/ maximum temperature)

In the simulations the amount of toluene released was dependent on the temperature of the stream and the duration of the release. In the base case the temperature of the first charge was lower than the second charge. Therefore, less material was released to the cooler. However, after the cooler, both the streams are at the same temperature and less toluene was released during the second charge because the charge time is shorter.

In the simulation charging all the toluene at the lower temperature resulted in a 62% reduction in the amount of toluene predicted to be released. As a result, the amount of energy required for cooling was predicted to be 53% less than for the base case. The amount of cooling water required reduced from 4.3 kg to 0.7 kg and glycol from 47.2 kg to 16.4 kg. This assumed that the temperature drop across the water cooler and the glycol condenser was 0.2 and 0.27 T_R respectively. The temperature change of both of the coolants was assumed to be 15°C and all the condensation was assumed to occur in the glycol condenser.

When designing a new plant this option would result in a slight increase in the EP due to the reduced cooling requirements. The EPPT score would decrease because the amount of material released to the environment is reduced. The lower cooling requirements would also reduce the EPPT score because less energy would be required to operate the cooling system.

However, in the Thomas Swan plant the toluene cannot be completely charged before the benzoylation reaction occurs because the dilution of the reactants causes problems with the product formation.

8.7.3 Does the method of addition affect the releases?

The effect of altering the charge rate of material has been examined using the simulation of the Thomas Swan hydrolysis charging operations. The details of the base case simulation and description of the operations are given in Sections 4.2.1 and 4.3.2.

Figure 8.3 shows the predicted mass flow rate of BT from the vent. The flow rate increased as the charge rate increased, whilst the predicted charging time decreased. The mole fraction of BT in the vent stream was predicted to remain constant as the pressure, temperature and liquid phase composition were unchanged during charging.

Figure 8.4 shows the total mass released versus the charge rate. A slight variation in the results occurred due to fluctuations in the predicted vent flow, temperature and composition of the stream. These fluctuations were probably due to variations in the solution of the dynamic equations rather than physical behaviour of the system.

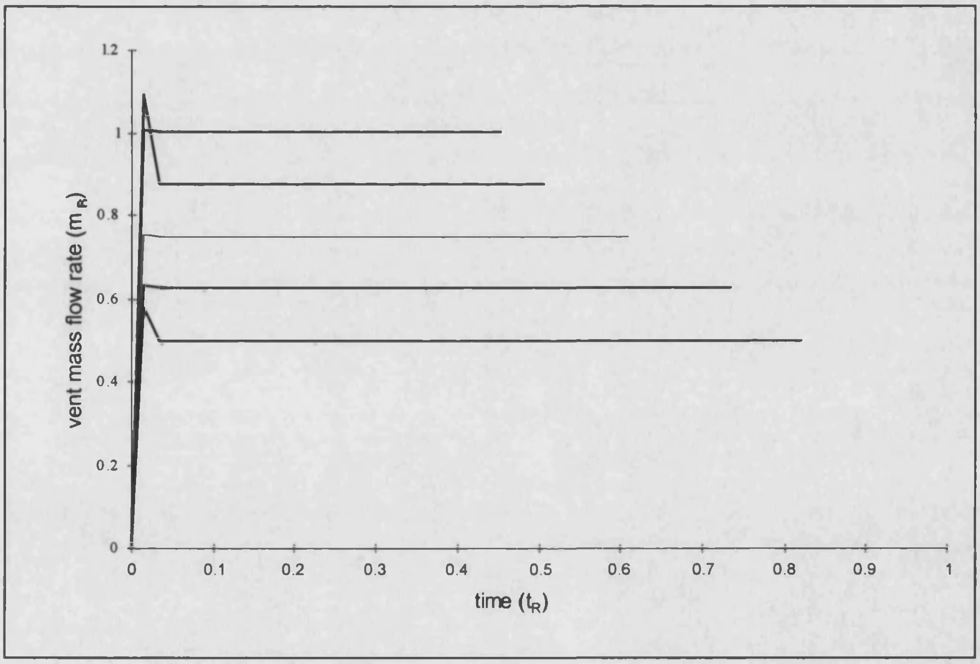


Figure 8.3: Vent mass flowrate vs charge time for varying charge rates.

t_R = (time/maximum time)
m_R = (mass flow rate/maximum mass flowrate)

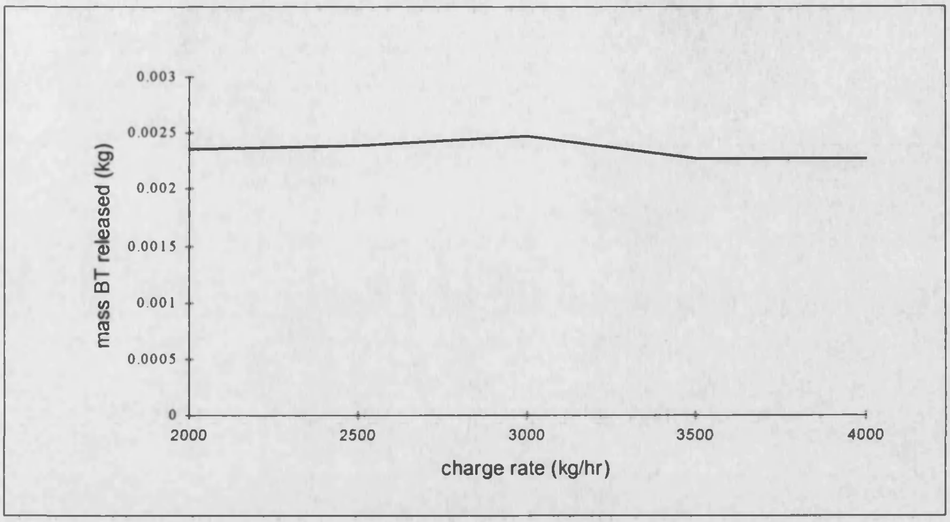


Figure 8.4: Total mass BT released vs charge rate.

The mass of material released during charging can be predicted by performing a mass balance over the vessel. Assuming that the liquid lost to the vapour is negligible compared with the flow of liquid into the vessel, the mass released is as follows:

Mass material A in vent; $m_g = v_g \rho_g y_A$ (8.4)

Total mass A released; $M = m_g t = v_g \rho_g y_A t$ (8.5)

$t = V_t / v_l$ (8.6)

Therefore; $M = v_g \rho_g y_A V_t / v_l$ (8.7)

Assuming no gas compression occurs the volume of gas displaced is equal to the volume of liquid charged into the vessel;

$v_l = v_g$ (8.8)

$M = \rho_g y_A V_t$ (8.9)

where;
m_g = mass flow of material in vent (kg/hr)
M = total mass of material released (kg)
v_g = volume flow of vapour from vessel (m^3/hr)
v_l = volume flow of liquid into vessel (m^3/hr)
V_t = volume of liquid required in vessel (m^3)
ρ_g = density of the vapour stream (kg/m^3)
y_A = mole fraction of A in vapour stream
t = charge time (hr)

Considering Equation (8.6) the volume of liquid (V_t) required in the vessel remains the same, independent of the charging rate used. In the simulation a pure liquid is charged at constant temperature and pressure. Therefore, the composition (y_A) and density (ρ_g) of the vented vapour are independent of the charging rate. Hence, the total mass released through the vent (M) is independent of the charge rate used.

If the feed stream was not the same material as the vessel contents the composition of the liquid phase would vary during charging. The composition of the vapour phase depends on the composition of the materials in the liquid phase and vapour pressures of the components. Therefore, a change in the liquid composition could alter the vapour composition causing the vapour density to vary during charging. As a result the total mass released (M) may also vary. The temperature and pressure within the vessel will also affect the amount of material in the vapour phase. Therefore, if the temperature or pressure vary during charging the amount of material in the vapour phase would change, affecting the total mass released. However, in the charging simulation the predicted temperature and pressure remained constant, equilibrium was reached immediately and pure BT was charged to the vessel. Therefore, the total mass released remained constant when the charge rate altered.

From this analysis is has been shown that varying the charge rate to a vessel will not significantly affect the mass of pollutant released through a vent as long as the vent is sized properly, one material is in excess in the vessel and no flashing occurs as the feed enters the vessel.

In the Thomas Swan operations equilibrium is unlikely to be achieved instantaneously if at all. Additionally, two materials are charged to the vessel, BT and sodium hydroxide. Therefore, the mass of material released through the vent may vary if the charge rate was changed. However, varying the charge rate would affect the cycle time and the production schedule. For a new design it would be possible to investigate this option further if the releases were shown to be significant.

8.7.4 Can the temperature be lowered during charging operations?

The simulation of the Thomas Swan hydrolysis charging operations has been used to assess the effect of reducing the temperature during charging. A description of the operations and the base case simulation is given in Sections 4.2.1 and 4.3.2. In the base case simulation the vessel was charged with benzothiazole (BT) at temperature, $T_R = 1$. Five additional feed temperatures have been modelled and Figure 8.5 shows the variation of predicted BT mass flow rate (m_R) with feed temperature (T_R).

The predicted mole fraction of BT decreased as the temperature was lowered, due to the decrease in the material vapour pressure. The predicted total mass of BT released has been shown to be proportional to the change in vapour pressure as shown below and in Figure 8.6.

From Equation (8.9): $M = \rho_g y_A V_t$

For vapour; $y_A = p_A^{\phi} x_a / P_T$ (8.10)

Therefore; $M = \rho_g V_t p_A^{\phi} x_a / P_T$ (8.11)

where;

p_A^{ϕ} = vapour pressure of material A (kPa)
x_A = mole fraction of material A in liquid phase
P_T = Total pressure in vessel (kPa)
M = total mass of material released (kg)
V_t = volume of liquid required in vessel (m^3)
ρ_g = density of the vapour stream (kg/m^3)
y_A = mole fraction of A in vapour stream

The expression used to calculate the vapour pressure in HYSYS is:

$$\ln(P^{\phi}) = a + b/(c+T) + d\ln(T) + eT^{f} \qquad (8.12)$$

T = Temperature (°C)
a,b,c,d,e = equation of state coefficients

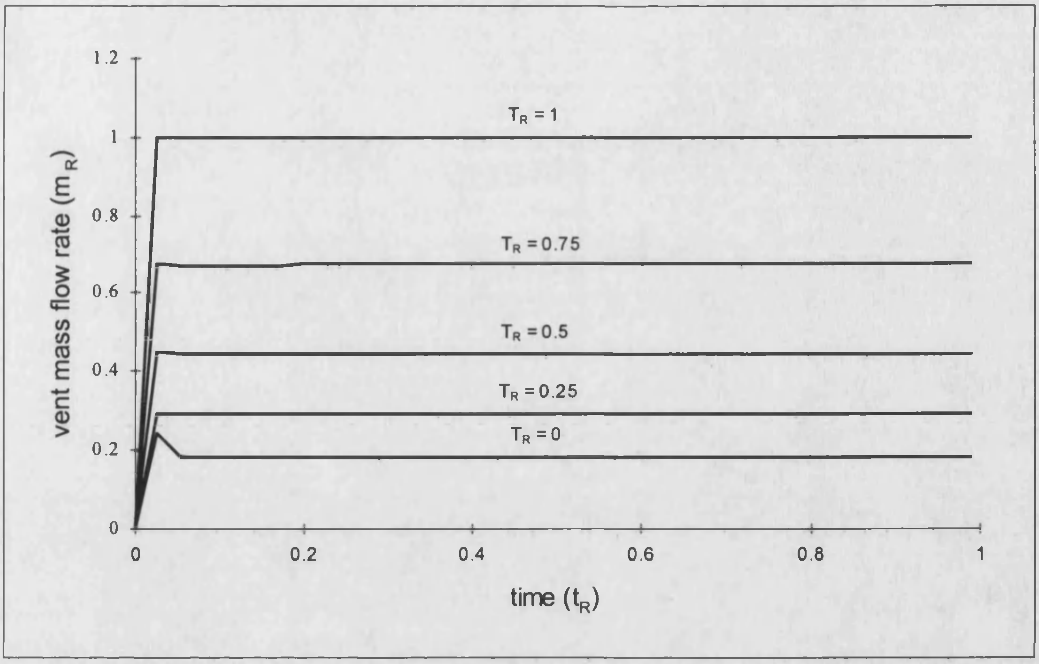


Figure 8.5: Vent mass flowrate vs charge time for various feed temperatures

T_R = (temperature/ maximum temperature)
t_R = (time/ maximum time)
m_R = (mass flow rate/ maximum mass flow rate)

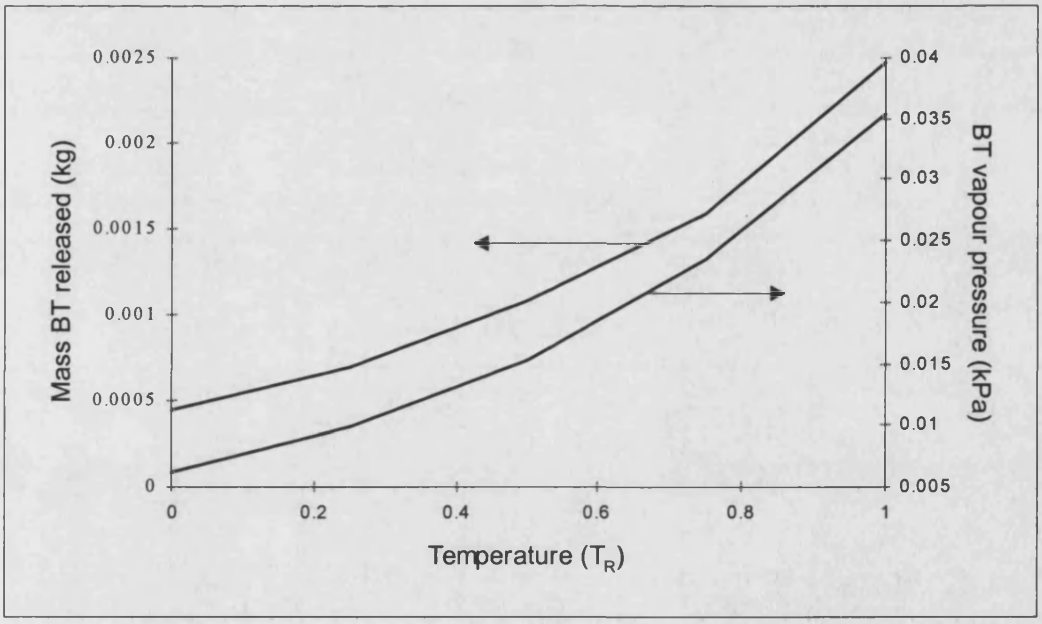


Figure 8.6: Total mass of BT released and BT vapour pressure vs feed temperature

T_R = (temperature/ maximum temperature)

The normal operating temperature is represented by $T_R = 1$. Therefore, reducing the feed temperature reduces the BT emissions. However, energy is required to operate the cooling system. Table 8.8 shows the predicted energy required to cool the stream from $T_R = 1$ using refrigeration.

Table 8.8: Predicted energy required for cooling vent stream from $T_R = 1$

Temperature (T_R)	Energy required (kJ/s)
0.75	5.92
0.5	11.77
0.25	17.55
0	23.24

When considering a new design there will be costs associated with the installation and operation of a refrigeration unit and the installation of a heat exchanger to provide cooling to the stream. The cost of a refrigeration unit depends on the operating temperatures required. Refrigeration installation costs have been calculated for -6.5°C, -29°C and -40°C [17] and the operating costs have been calculated assuming that 1 ton of refrigeration is required to remove 3.517 kW [127]. The purchased cost of a heat exchanger has been based on the following exponential expression [127]:

$$C_2 = C_1(q_2/q_1)^z \qquad (8.13)$$

where:
C_2 = cost of required heat exchanger
C_1 = cost of standard heat exchanger taken from tables [127]
q_1 = surface area of standard heat exchanger (m^2) [127]
q_2 = surface area of required heat exchanger (m^2)
z = exponent for type of heat exchanger

The installed cost of a heat exchanger was assumed to be 15% of the purchased cost.

The installation and operating costs for each of the feed temperatures and refrigeration operating temperatures are shown in Table 8.9 and Figure 8.7. The installation costs are the combined values for the refrigeration unit and the heat exchanger.

Table 8.9: Estimated refrigeration installation and operating costs

Feed Temperature (T_R)	Refrigeration temp./ £ (1994)			Operating Cost (£/batch)
	-6.5°C	-29°C	-40°C	
0.75	14578	26156	41683	814
0.5	18508	29748	45005	1620
0.25	26769	42696	60966	2419
0	37946	45167	72277	3197

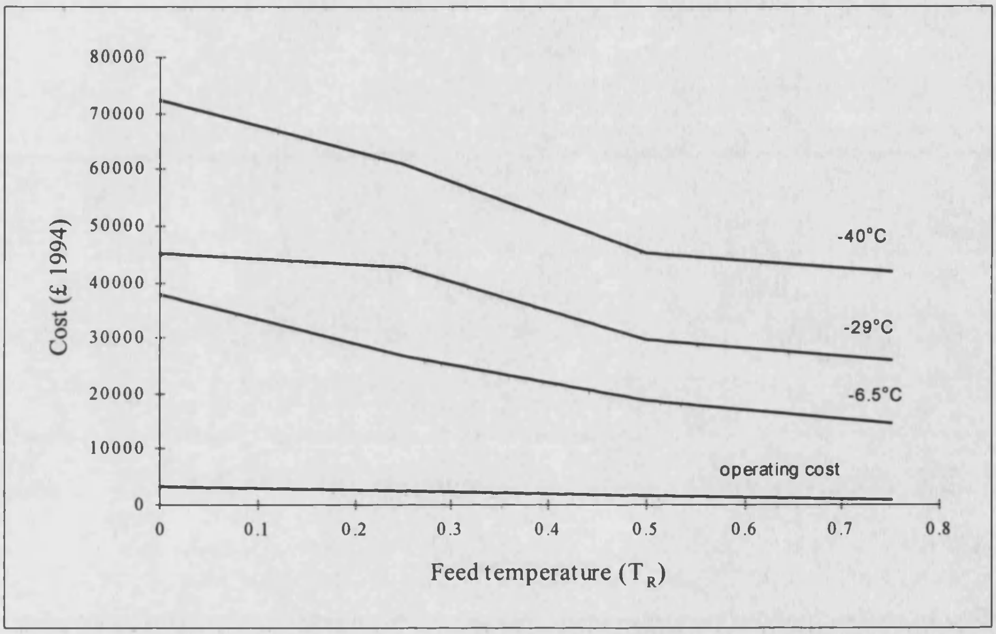


Figure 8.7: Refrigeration costs vs feed temperature for different refrigerant temperatures

T_R = (temperature/ maximum temperature)

To operate the refrigeration system energy is required for gas compression. Therefore, the environmental effect of reducing the feed temperature is a trade-off between the reduced mass of material released and the increased energy demand. The equivalent energy needed to run the compressor has been calculated assuming refrigerant 12 is used and the compressor has an efficiency of 75%. The resulting refrigeration energy requirements are given in Table 8.10 and Figure 8.8.

Table 8.10: Refrigeration energy requirements

Feed Temperature (T_R)	Refrigeration temp./Energy Requirement (kJ/s)		
	-6.5°C	-29°C	-40°C
0.75	2.04	2.88	4.11
0.5	4.06	5.61	8.18
0.25	6.06	8.37	12.19
0	8.02	11.1	16.12

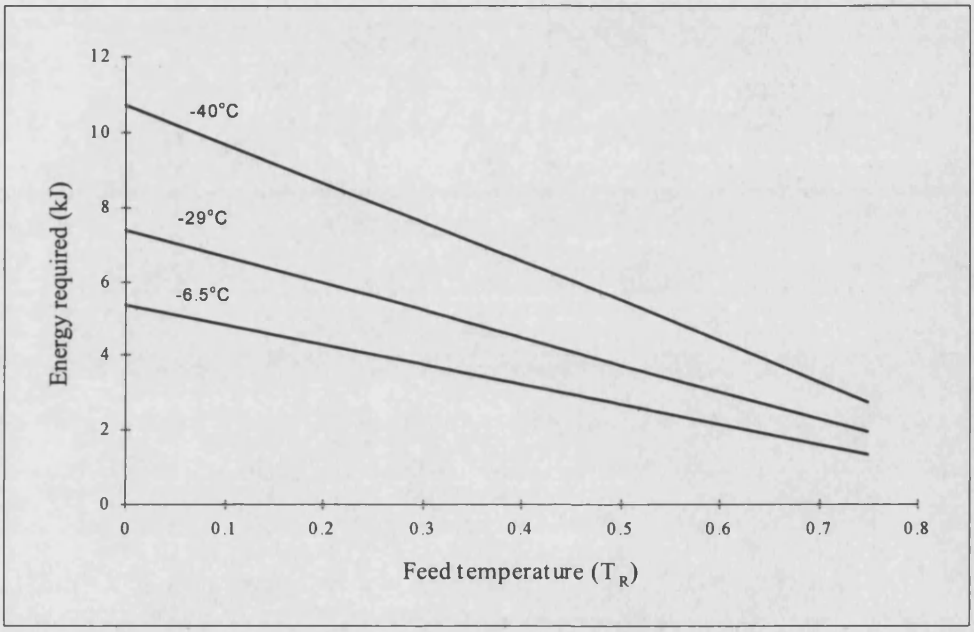


Figure 8.8: Refrigeration energy required for different refrigerant temperatures

T_R = (temperature/ maximum temperature)

Table 8.11 shows the predicted amount of material released to the scrubber for the various feed temperatures.

Table 8.11: Predicted amount of material released to scrubber

Temperature (T_R)	Mass released (kg/batch)		
	contaminant C	contaminant B	BT
1	4.30×10^{-4}	8.70×10^{-6}	4.60×10^{-3}
0.75	3.45×10^{-4}	8.70×10^{-6}	2.80×10^{-3}
0.5	2.70×10^{-4}	0	2.03×10^{-3}
0.25	2.04×10^{-4}	0	1.30×10^{-3}
0	1.47×10^{-4}	0	8.34×10^{-4}

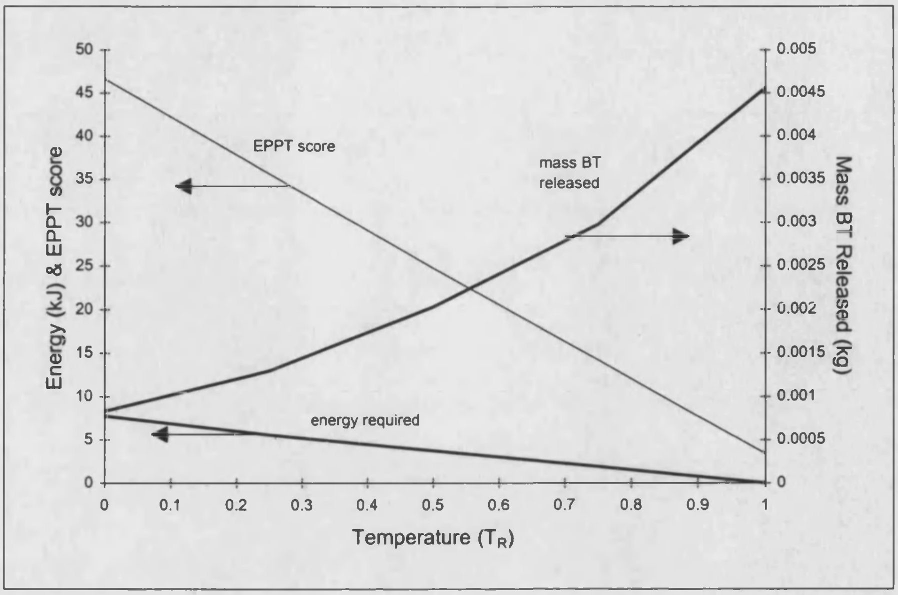
For a new design this option would decrease the EP as a result of the cost of installing a refrigeration system and a heat exchanger. However, it is unlikely that a refrigeration system would be installed for one operation and would only be included if it was required for a number of operations. The heat exchanger to cool the stream would still represent an additional cost and the operating costs would increase due to the increased load on the refrigeration unit.

Operating at lower temperatures reduces the amount of volatile material released to air, thereby reducing the EPPT score. However, the increase in energy use would result in an increase in the EPPT score. There is a trade-off between these two factors. The assessment of the EPPT score for this option has been presented by Aubrey [1].

A summary of the costs, the energy requirements and the EPPT score for the case of refrigeration to -29°C is shown is Table 8.12 and Figure 8.9. This shows that although less organic material is released at lower temperatures the energy used outweighs the benefits to the environment and the EPPT score increases. The costs also rise as the temperature decreases. Therefore, this analysis suggests that the best option would be to release the organic material.

Table 8.12: Summary of costs, energy requirements and EPPT score for the case of refrigeration to -29°C

Temperature (T_R)	Installation Costs (£ 1994)	Refrigeration operating costs (£/batch)	Energy requirement (kJ)	EPPT score
1	0	0	0	3.42
0.75	26156	814	2.88	14.24
0.5	29748	1620	5.61	24.74
0.25	42696	2419	8.37	35.67
0	45167	3197	11.1	46.63



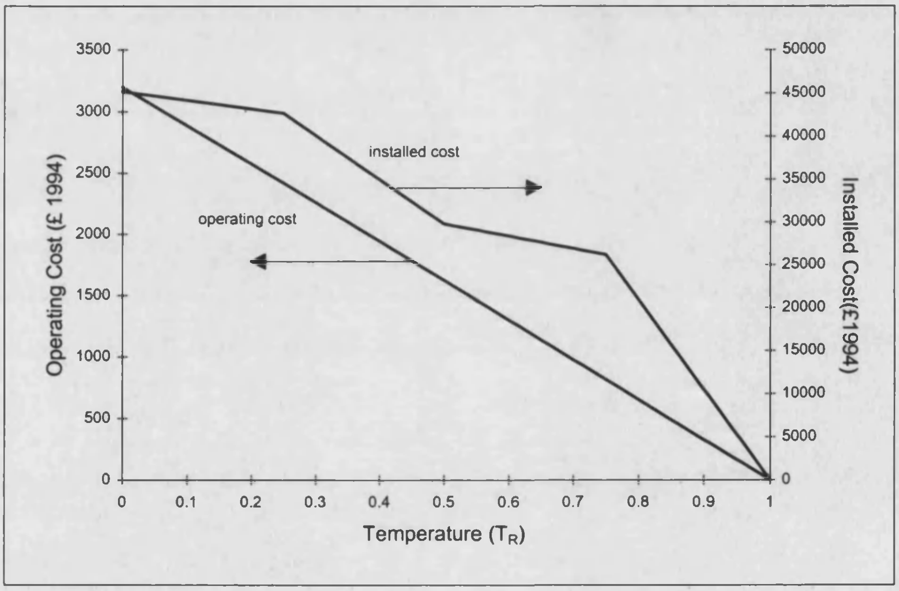


Figure 8.9: Comparison of refrigeration energy, installation cost, operating cost and mass BT released for different feed temperatures

T_R = (temperature/ maximum temperature)

8.7.5 What affect does the material vapour pressure have on emissions during charging?

The Thomas Swan hydrolysis charging simulation has been used to model the effect of charging different materials to a vessel. Descriptions of the base case simulation and operations are given in Sections 4.2.1 and 4.3.2. It has been shown previously, in Equation (8.8), that the higher the material vapour pressure the more material appears in the vapour stream;

$$M = \rho_g V_t p_A^{\phi} x_a / P_T \qquad (8.14)$$

where;
M = total mass of material released (kg)
V_t = volume of liquid required in vessel (m^3)
ρ_g = density of the vapour stream (kg/m^3)
p_A^{ϕ} = vapour pressure of A (kPa)
x_A = mole fraction of A in liquid phase
P_T = Total pressure in vessel (kPa)

The simulation was carried out with a range of materials and these are presented in Table 8.13 along with their corresponding vapour pressures and densities. These materials were chosen to represent a range of vapour pressures. The simulation was performed assuming that the same mass of each material was required.

Table 8.13: Material vapour pressure and density [127]

Material	Vapour pressure (kPa)	Density (kg/m^3)
xylene	0.41	866
epichlorohydrin	1.04	1175
pyridine	1.22	985
toluene	1.67	869
benzene	6.14	878
hexane	9.67	662
acetone	15.54	785
diethyl amine	15.96	703

Figure 8.10 shows the predicted mass of material released versus material vapour pressure. This could be used to predict loads on scrubbers or releases from vents expected when charging different materials to a vessel.

The simulations were repeated with the vessel vent closed resulting in an increase in the vessel pressure. The predicted energy required to pump the feed stream into the vessel is dependent on the density and molecular weight of the material, as well as the pressure difference. Therefore, a direct correlation was not observed between vapour pressure of the material and the energy required for pumping of different materials. If the material has a high vapour pressure more material appears in the vapour phase and a larger pressure rise is predicted. If the material has a high density then the volume of liquid charged is lower than for a low density material because the same mass of material is charged in each case. As a result, less gas compression occurs. Consequently, a material with a high vapour pressure and low density, such as diethyl amine (DEA) required a relatively large amount of energy to fill the vessel with the required mass of material. A material with a high density but low vapour pressure, such as epichlorohydrin, required a lower amount of energy. This is indicated in Figure 8.11.

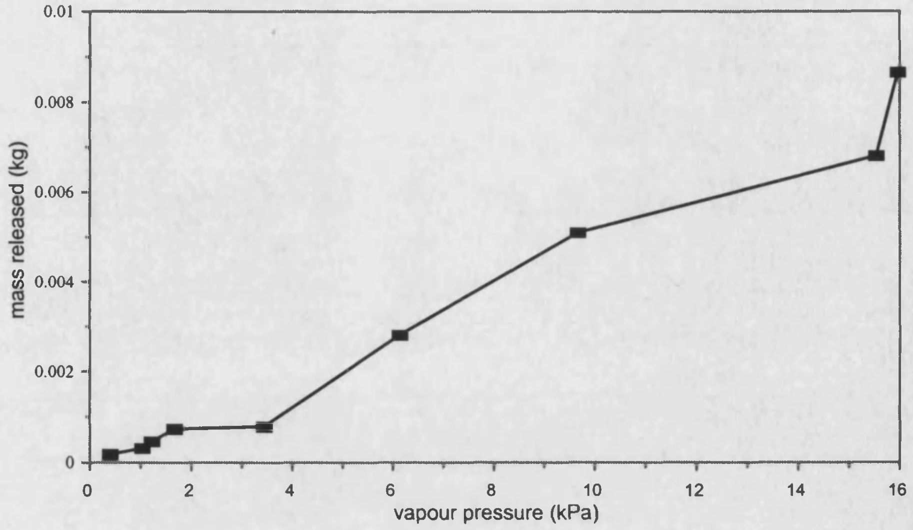


Figure 8.10: Mass of material released vs vapour pressure

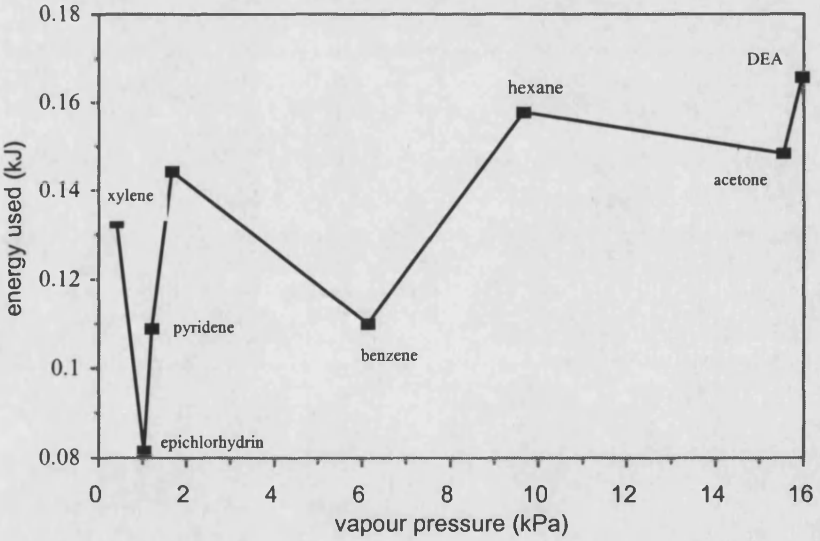


Figure 8.11: Energy required if the vent is closed vs vapour pressure.

8.7.6 At what rate should the vessel be heated?

During the Thomas Swan hydrolysis operations the vessel is heated with the vent open. As a result, BT is released through the vent as the vapour in the vessel expands. The simulation of the Thomas Swan hydrolysis heating operations has been used to assess the effect of altering the vessel heating rate. Descriptions of the plant operation and the base case simulation are given in Sections 4.2.1 and 4.3.2.

Five heating rates have been examined and Figure 8.12 shows the increase in vent flow rate with increasing heating rate. As the heating rate is increased the time for heating decreases.

The predicted mass of BT released is the product of the vent flow rate and the heating duration. The vent flow rate increases proportionally with the heating rate. However, as shown in Figure 8.13, the heating duration does not reduce linearly but approaches zero exponentially as the heating time cannot be zero. Therefore, as shown in Figure 8.13, the overall effect of increasing the heating rate is an increase in the mass of BT released.

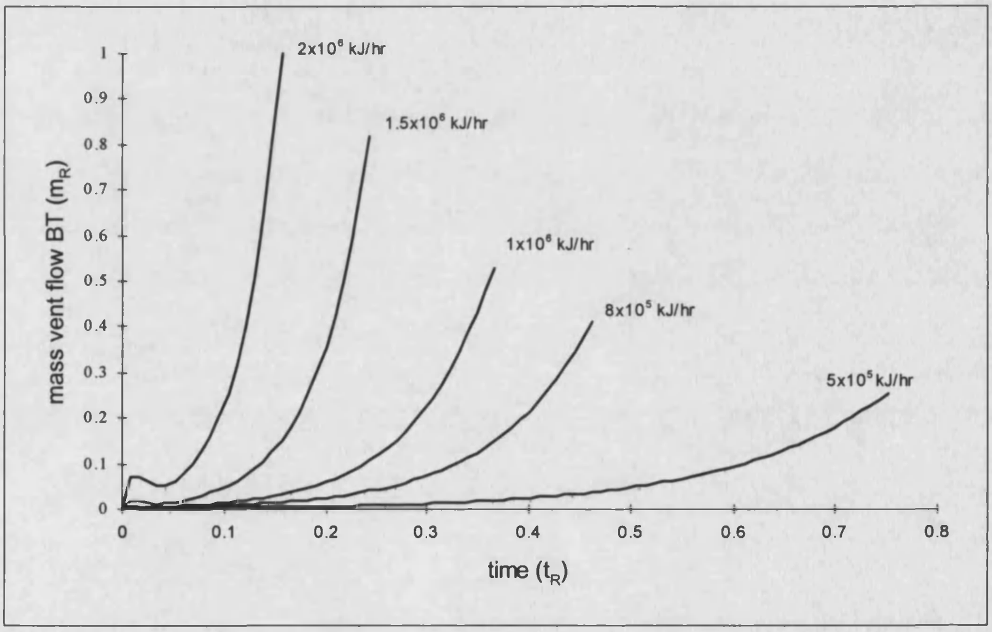


Figure 8.12: Vent BT mass flow rate vs heating time for various heating rates.

t_R = (time/ maximum time)
m_R = (mass flow rate/ maximum mass flowrate)

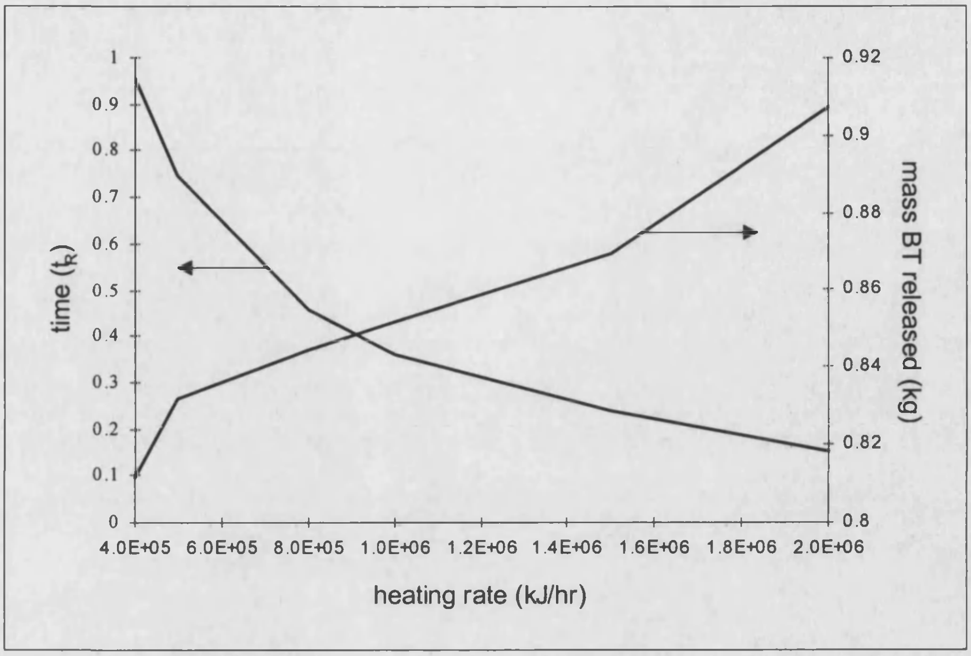


Figure 8.13: Mass of BT released vs heating rate

t_R = (time/ maximum time)

For a new design it should be possible to select the most appropriate heating rate. However, this decision will also affect the process scheduling. For example, using a very low heating rate would decrease the amount of material released but would also reduce the time available for production. Also, operational factors such as product degradation or materials settling may restrict the heating duration. The EP would be unaffected by a decrease in the heating rate unless less product per cycle was produced, whereas the EPPT score would be reduced due to the decrease in material released to the atmosphere.

8.7.7 What is the effect of heating the vessel with the vent open or closed?

Closing the vessel during the heating operations prevents material from being released. The simulation of the Thomas Swan hydrolysis heating operation has been used to model heating the vessel with the vent closed.

When the vent was closed during the heating simulation, the vessel pressure was predicted to rise by 34%. However, no additional energy was predicted to be required and the vessel heated slightly quicker due to the rise in pressure. As the vent was closed no materials were released to the scrubber. Table 8.14 summarises the materials that would be released if the vent was open.

During the conceptual design of a new plant this option would have a lower EPPT score than the base case because less materials were released to the environment. The EP would remain unchanged unless the pressurised operations resulted in an increased reactor cost.

In the Thomas Swan operations the hydrolysis heating operation is used to remove unwanted volatile materials from the reaction vessel before the reaction takes place. Therefore, closing the vent during heating would not be viable for the present Thomas Swan operations.

Table 8.14: Predicted amount of material prevented from being released

Component	Mass Released (kg)
benzothiazole	8.4×10^{-1}
contaminant D	1.4×10^{-2}
contaminant B	9.2×10^{-3}
contaminant C	2.6×10^{-3}
contaminant A	6.4×10^{-3}

8.7.8 What is the optimum reaction temperature?

The effect of reducing the reaction temperature on the amount of material released from the process has been examined using the simulation of the Thomas Swan oxidation reaction. The Thomas Swan operations and simulations are detailed in Sections 4.2.2 and 4.3.3. During the reaction, vapours are removed through the vent and passed to the scrubber.

For the simulation of the process option the temperature of the vessel was reduced to $0.5T_R$, where $T_R = 1$ is the normal operating temperature. In the simulation the oxidation reaction has been based on the addition rate of one reactant. Therefore, the production of stage 2 product was unaffected by the change in the reaction temperature. However, in reality reducing the temperature would affect the chemical kinetics and most likely reduce the reaction rate. As a result the reaction time would need to be increased to achieve the same conversion. Consequently, the emission duration would be increased and the production schedule would need to be altered.

Table 8.15: Predicted amount of material released at different reactor temperatures

Component	Mass released (kg/batch)	
	Base case T_R	Temperature $0.5T_R$
Stage 1 product	$3.4\text{x}10^{-1}$	$2.0\text{x}10^{-1}$
Stage 2 product	$1.1\text{x}10^{-7}$	$4.9\text{x}10^{-8}$
H_2O_2 (as O_2)	$2.7\text{x}10^{-2}$	$1.9\text{x}10^{-2}$
contaminant D	$8.4\text{x}10^{-3}$	$6.0\text{x}10^{-3}$
contaminant B	$1.5\text{x}10^{-2}$	$1.1\text{x}10^{-2}$
contaminant C	$1.4\text{x}10^{-3}$	$9.0\text{x}10^{-3}$

T_R = (temperature/ maximum temperature)

As expected less material was predicted to be released at the lower reaction temperature. The amount of energy required to cool the contents to $0.5T_R$ was calculated to be $3.2\text{x}10^5$ kJ which equates to 7555 kg cooling water, assuming a cooling water temperature rise of 10°C. The maximum flow through the jacket during the plant operation is 18 kg/s and therefore the cooling would take at least 7 minutes.

The EP for a new design would decrease due to the increased operating costs associated with cooling. The EPPT score would be reduced because less material would be released to the environment. However, the reaction rates would be unlikely to be independent of temperature and hence, viable operating temperatures would probably be limited. It would be necessary to examine the reaction kinetics in more detail to obtain a more realistic value for the optimum reaction temperature.

8.7.9 What is the optimum addition rate of the reactants?

The simulation of the Thomas Swan oxidation reaction has been used to assess the effect of altering the feed rate of reactants to the vessel. In the plant operations hydrogen peroxide is added to the reactor and the vessel in continuously vented whereby, the vapours are sent to the scrubber for treatment.

For simulating this process option the rate of addition of hydrogen peroxide fed into the vessel was doubled. In the simulation the reaction rate was based on the addition rate of hydrogen peroxide. Therefore, as the addition rate of hydrogen peroxide was doubled, the reaction rate also doubled. To maintain the same reaction temperature in the simulation the cooling rate also had to be increased.

Table 8.16 shows the comparison between the predicted amount of material released for the base case and for the process option. Comparing the two cases:

- The amount of stage 1 product released was less for the process option than the base case. This is because the reaction occurred faster, thereby reacting stage 1 product more quickly.
- The amount hydrogen peroxide released was larger for the process option because it was added to the vessel more quickly than in the base case. Therefore, once the reaction started to tail-off the composition of hydrogen peroxide in the vessel increased faster and more appeared in the vapour stream.
- The amounts of the feed contaminants (contaminant D, contaminant B and contaminant C) and stage 2 product released were reduced because the reaction time was shorter for the process option than for the base case.

Figure 8.13 shows the release profile of stage 1 product for both the cases. In the base case, stage 1 product appears in the vent stream over a longer period of time, but the average flows of the two cases are the same.

In theory the overall emissions could be altered by using a higher hydrogen peroxide rate. The EPPT score may vary due to the different amounts of various materials being released. However, the plant operators consider the oxidation reaction to be optimal in terms of the conversion achieved and by-product formation. Additionally, in the present plant there are likely to be restrictions in the pumping duty and the surface area available for heat transfer. The reaction kinetics would need to be examined to assess this option in more detail.

Table 8.16: Predicted amount of material released to scrubber

Component	Mass released (kg/batch)	
	Base case	2x H_2O_2 Rate
Stage 1 product	3.4×10^{-1}	1.8×10^{-1}
Stage 2 product	1.1×10^{-7}	7.4×10^{-8}
H_2O_2 (as O_2)	2.7×10^{-2}	1.4×10^{-1}
contaminant D	8.4×10^{-3}	4.7×10^{-3}
contaminant B	1.5×10^{-2}	9.0×10^{-3}
contaminant C	1.4×10^{-3}	8.1×10^{-4}

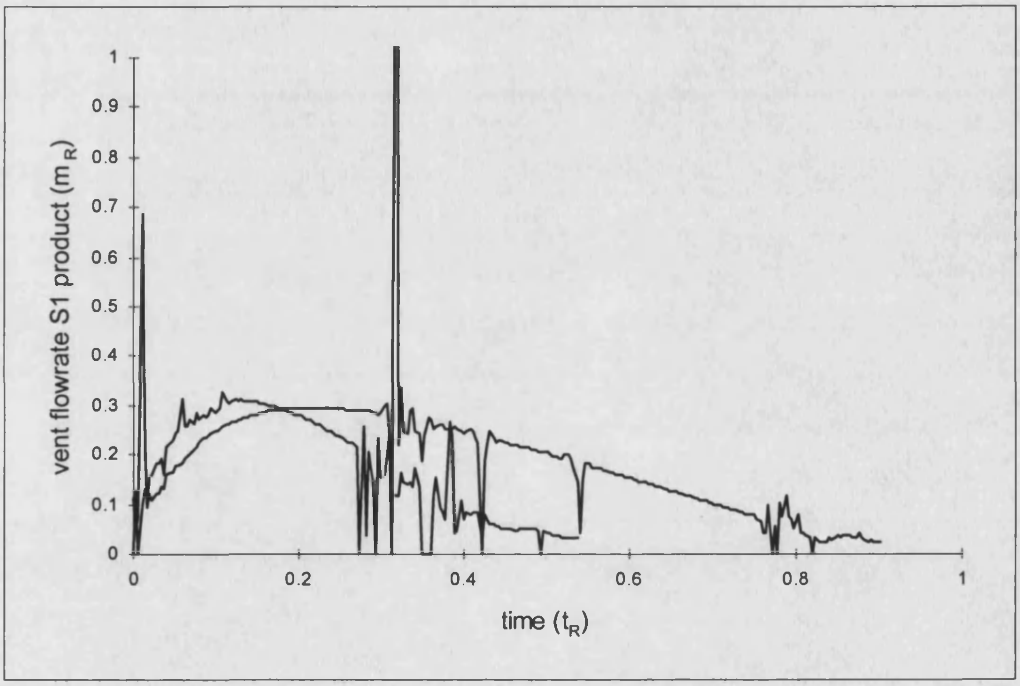


Figure 8.14: Flowrate of S1 product from the vent

m_R = (mass flow rate/ maximum mass flow rate)
t_R = (time/ maximum time)

8.7.10 How long is the required purge time?

On the plant the vessel vapour space is purged with nitrogen after the oxidation reaction has been completed. The simulation of the Thomas Swan purging operations has been used to predict the changes in the emissions resulting from a change in the purge time. Four purge times have been modelled and the normal operations are represented by $t_R = 1$. The predicted release amounts increased as the purge time increased as shown in Table 8.17 and Figure 8.15.

Table 8.17: Predicted material released for different purge times

Component	Mass released (kg/batch)			
	$t_R = 1$	$t_R = 0.5$	$t_R = 0.33$	$t_R = 0.17$
Stage 2 product	1.6×10^{-8}	8.6×10^{-9}	8.4×10^{-9}	6.1×10^{-9}
H_2O_2 (as O_2)	2.2×10^{-1}	1.5×10^{-1}	1.2×10^{-1}	1.1×10^{-1}
contaminant D	2.5×10^{-5}	1.5×10^{-5}	1.4×10^{-5}	1.1×10^{-5}
contaminant B	9.7×10^{-5}	5.9×10^{-5}	5.2×10^{-5}	4.1×10^{-5}
contaminant C	1.4×10^{-5}	8.3×10^{-6}	7.4×10^{-6}	5.7×10^{-6}

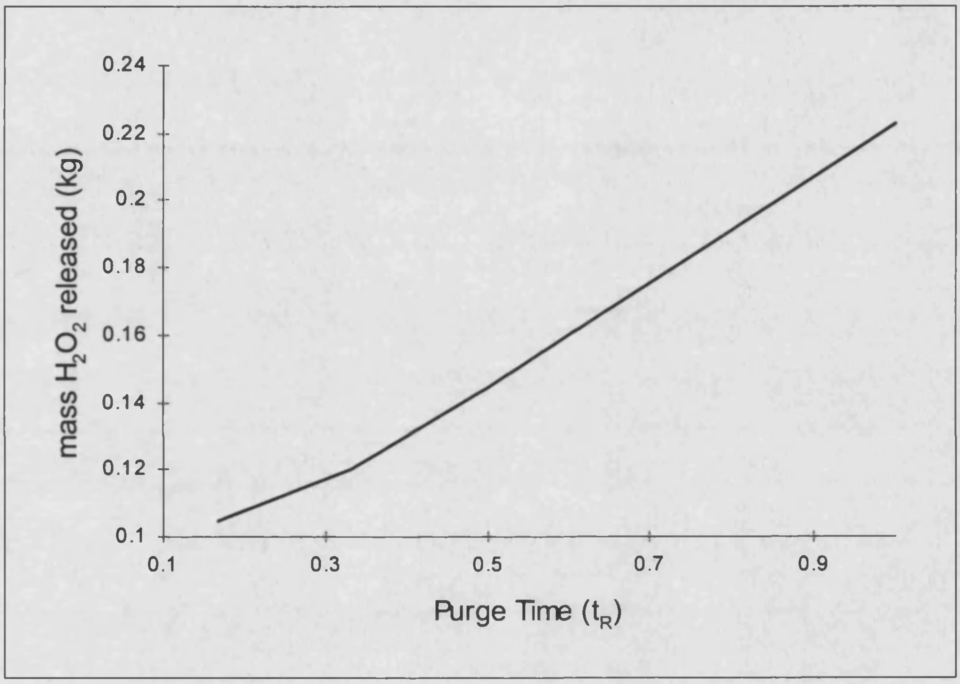


Figure 8.15: Mass released vs purge time

t_R = (time/ maximum time)

The most appropriate purge time could be selected that reduced the emissions but the required removal of material from the vapour space must be achieved. It would also be necessary to consider the process schedule when selecting a purge time.

8.7.11 Is treatment required before the vent stream can be released?

In the Thomas Swan hydrolysis operations, after the reaction is complete, the pressure in the reactor is relieved by releasing vapour through a vent. This vent stream is passed to the scrubber via a condenser and the vessel contents are left to cool. The operations and simulations are detailed in Sections 4.2.1 and 4.3.2.

If the vessel were to be cooled before venting, the temperature of the vent stream will be lower. Therefore, less volatile material will be present in the vapour and there would be no need to install a condenser. Cooling the vessel before venting has been simulated to examine the effect this has on the process emissions. The simulated vessel was cooled to the required temperature before being vented, thereby no material was released as condensate. Table 8.18 and Figure 8.16 show the difference in the amount of material released to the vent for the base case and for this process option. The predicted amount sent to the condensate in the base case is also detailed.

Table 8.18: Comparison between predicted mass of material released for venting before and after cooling

Component	Mass released (kg/batch)		
	Cooled after venting Base case		Cooled before venting Option
	to condensate	to scrubber	to scrubber
stage 1 product	14.2	4.7×10^{-2}	2.7×10^{-2}
contaminant D	9.6×10^{-2}	6.2×10^{-2}	5.6×10^{-3}
contaminant B	2.0×10^{-1}	2.7×10^{-3}	1.1×10^{-3}
contaminant C	3.8×10^{-2}	5.2×10^{-4}	2.8×10^{-4}
Total	14.5	1.1×10^{-1}	3.4×10^{-2}

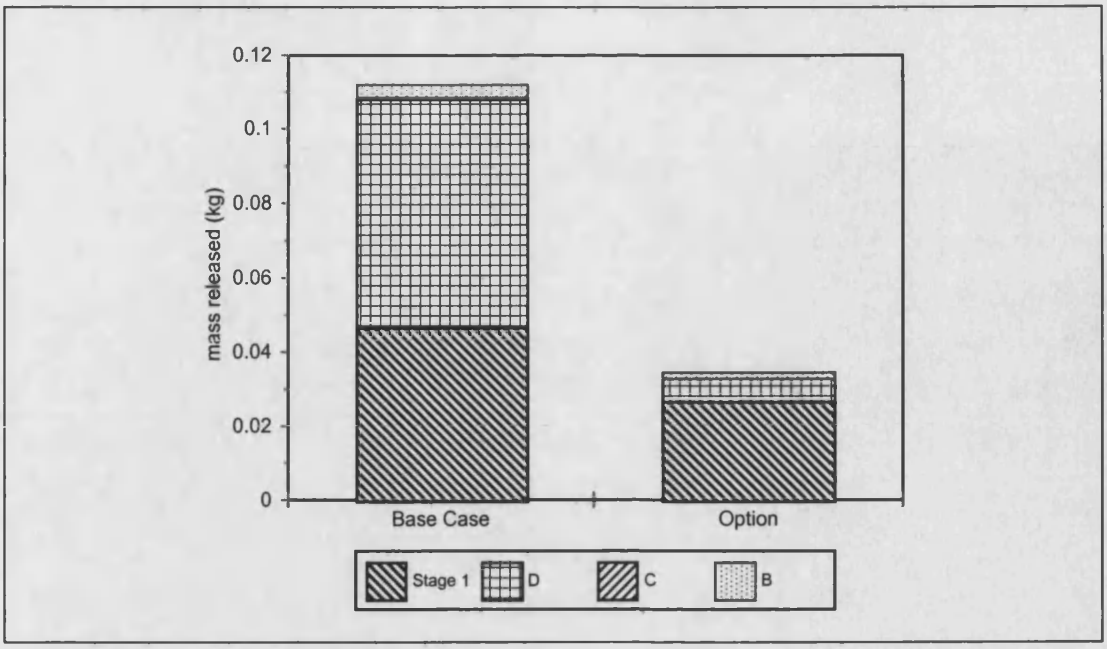


Figure 8.16: Comparison between the amounts released to scrubber during venting for the base case and the cooled option

The energy required to cool the vessel was predicted to be 3.02×10^6 kJ. Assuming a 10°C temperature rise for the cooling water this equates to 75m^3 of water. The cost of water was taken to be 0.04 £/m^3 for recycled cooling water [150], thus the cost of the cooling water used was £3/batch. The predicted amount of water required to operate the condenser in the base case was 285 kg. The cost of this water is considered negligible.

In general, for a new design this option would increase the EP by reducing the capital cost because a condenser need not be installed. In the option studied the condenser was estimated to cost £8900, using Equation (8.13). The vessel cooling could be provided by a cooling water jacket which, as in the Thomas Swan case, may be required for safety purposes. The reduction in the cooling time for this option may enable the production schedule to be tightened. However, the operating costs would increase because the entire vessel contents are cooled and not just a small vent stream, resulting in a greater cooling water demand.

The EPPT score for the base case has been predicted to be 1873.84. Cooling the vessel before venting is predicted to reduce the EPPT score to 878.73 as less material is sent to the vent and there is no condensate stream. Therefore, in this case the increase in the cooling water used does not outweigh the benefits of reducing the vent and condensate flows. Details of the calculation of the EPPT score can be found in Aubrey [1].

In the Thomas Swan operations venting is required to remove volatile contaminants from the reaction mixture. Therefore, in the present operations reducing the vessel temperature before venting would affect the plant performance.

8.7.12 What temperature should the venting be carried out?

During the Thomas Swan hydrolysis operations the vessel is vented through a condenser. The simulation of this operation has been used to examine the effect on the releases and energy requirements if a lower condenser temperature was used. This analysis is also relevant to the design question; what temperature is required for cooling?

Three condenser temperatures have been simulated. The predicted mass of material released decreased with decreasing temperature as shown in Figure 8.17. In order to reduce the temperature, more cooling water was required. Less material was released to the scrubber but was shifted to the condensate.

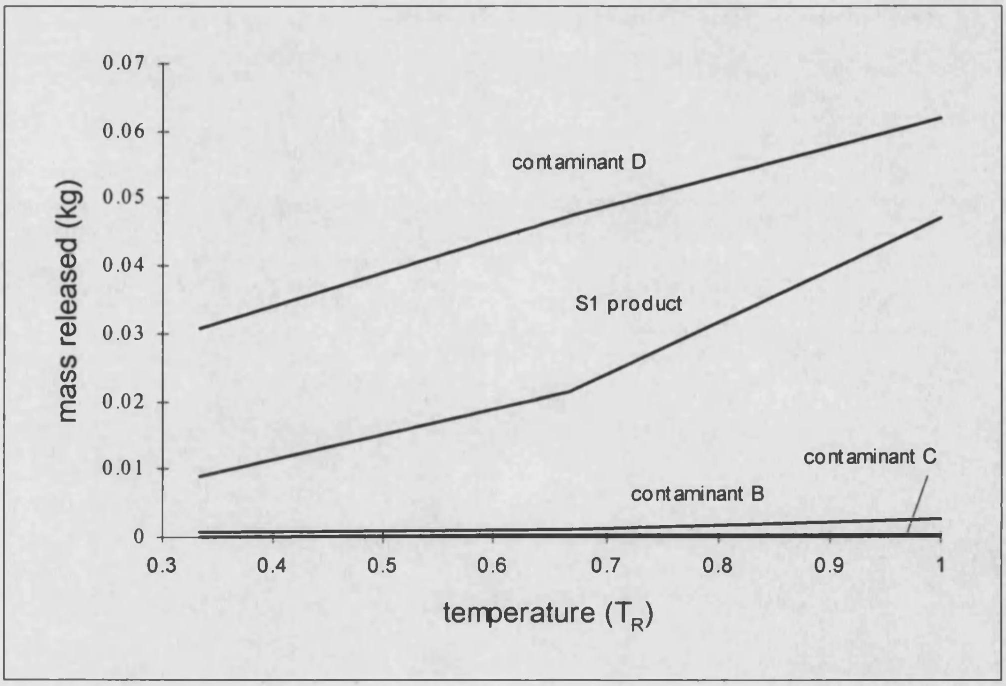


Figure 8.17: Mass released vs time for different condenser temperatures

T_R = (temperature/ maximum temperature)

Table 8.19 shows the predicted amount of materials released to the scrubber. Due to the small flows involved the calculated energy required for cooling was low and the differences between the operating temperatures did not result in a significant change in the amount of water used. Therefore, there is no change in the operating costs. The material removed from the vapour entered the condensate stream and Table 8.20 shows the predicted increase in the condensate flows. The changes in the flows are small. Refrigeration may be needed to reduce the temperature further. However, this would be limited if water was present in the stream. Due to the small vapour flows produced the knock-on effect to the scrubber was likely to be small.

For a conceptual design this option would not significantly alter the EP of the process because the cost of increasing the cooling water and the reduction in the cost of operating the scrubber are very low. The EPPT scores are shown in Table 8.21 and are predicted to decrease because material is released to the water phase rather than the vapour phase. Details of the EPPT score calculations are provided in Aubrey [1].

Table 8.19: Predicted amount of material released to scrubber

Component	Mass released to scrubber (kg)		
	$T_R = 1$	$T_R = 0.67$	$T_R = 0.33$
stage 1 product	4.7×10^{-2}	2.4×10^{-2}	9.8×10^{-3}
contaminant D	6.2×10^{-2}	5.2×10^{-2}	3.5×10^{-2}
contaminant B	2.7×10^{-3}	1.5×10^{-3}	6.9×10^{-4}
contaminant C	5.2×10^{-4}	2.8×10^{-4}	1.3×10^{-4}
Total	1.1×10^{-1}	7.8×10^{-2}	4.6×10^{-2}

Table 8.20: Predicted amount of material released to condensate

Component	Mass Released to Condensate (kg)		
	$T_R = 1$	$T_R = 0.67$	$T_R = 0.33$
stage 1 product	14.15	14.18	14.19
contaminant D	$9.6\text{x}10^{-2}$	$1.1\text{x}10^{-1}$	$1.2\text{x}10^{-1}$
contaminant B	$2.1\text{x}10^{-1}$	$2.1\text{x}10^{-1}$	$2.1\text{x}10^{-1}$
contaminant C	$3.8\text{x}10^{-2}$	$3.8\text{x}10^{-2}$	$3.9\text{x}10^{-2}$
Total	14.49	14.53	14.56

Table 8.21: EPPT score predicted for different condenser temperatures

T_R	EPPT score
1	1873.84
0.67	1848.23
0.33	1832.05

8.8 Summary

Level 3 considers the design of the reactor system and the definition of the recycle streams. New process design questions have been introduced for the individual batch operations in order to extend the existing Douglas methodology to apply to waste minimisation of batch processes. These questions are summarised in Table 8.22. The validity of several of these new questions has been tested using the simulations of the Thomas Swan operations. It has been shown that applying these questions to the Thomas Swan operations enabled the emissions to be reduced and aided the understanding of the behaviour of the process under differing conditions. The next stage is to consider the separation system and this is detailed in the next chapter, Chapter 9.

Table 8.22: New questions for Level 3 of the Douglas design methodology

Operation	Question
Vessel charging	What is the effect of charging the vessel with the vent open or closed?* Does the order of addition affect the potential for releases?* Does the method of addition affect the releases?* Can the temperature of the vessel be lowered during charging operations?* What affect does the material vapour pressure have on the emissions during charging?*
Vessel transfer	What are the characteristics and conditions of the materials to be transferred? Which methods of transfer are appropriate and what are their environmental consequences?
Vessel discharge	What is the most appropriate method of dealing with vapour, liquid and solid discharges? What is the duration of the discharge?
Cooling	What methods of cooling are available? How much energy is required to operate the cooling system? What cooling temperature is required?
Vessel heating	How much energy is required to initiate the reaction? What method of heating is required? Where is the energy obtained from to achieve the heat rise? At what rate should the vessel be heated?* What is the effect of heating the vessel with the vent open or closed?*

Table 8.23 (contd): New questions for Level 3 of the Douglas design methodology

Operation	Question
Reaction	What is the optimum reaction temperature? * What is the optimum addition rate of the reactants? * At what point should the recycle be returned to the system? Should vapour recirculation be used? Are any vapours likely to be released during the reaction? What is the potential for fouling?
Pressurising	What pressure is required and for what reason? How much energy is required for pressurising? What are the additional vessels costs associated with pressurised operation?
Vacuum	Why is a vacuum required? Are there any benefits of operating under vacuum? How much energy is required for maintaining the vacuum? What are the additional costs associated with vacuum operation?
Purging	What materials will be present in the purged stream? How long is the required purge time? *
Venting	Is further treatment required before the vapour stream can be released to the atmosphere? * What temperature should the venting be carried out at? *

* questions tested using the simulations of the Thomas Swan operations

Chapter Nine

Level 4 Considerations: Separation System

9.1 Introduction

Level 4 of the Douglas design methodology focuses on the design of the separation system as indicated in Figure 9.1. In this chapter the existing Level 4 design questions have been applied to waste minimisation and batch process design. Several new questions have been added and these are applicable to both continuous and batch operations. Details of the existing Douglas methodology are provided in Chapter 3.

Two separation systems have been examined using the Thomas Swan case study that was presented in Chapter 4. These are as follows:

1. Batch distillation - various process options have been assessed using simulation and the results are presented in Section 9.4.
2. By-product elimination - the Level 2 analysis of the Thomas Swan process, (presented in Section 7.3) identified a material in one of the output streams that could pose a potential environmental problem. The elimination of this material has been considered and the results are presented in Section 9.5. This particular operation illustrates how problems can be cascaded down through the design levels, to a point where they can be solved.

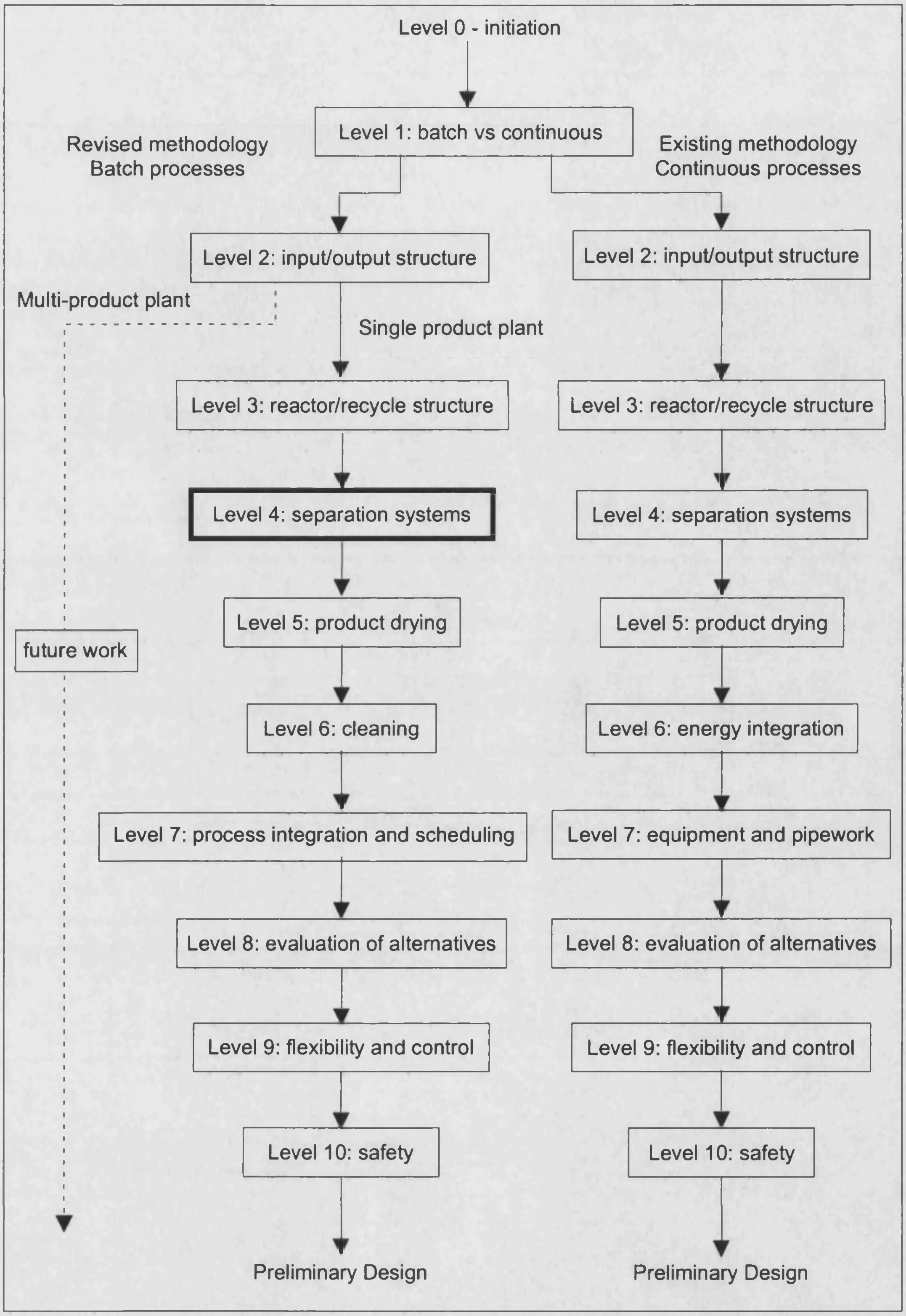


Figure 9.1: Douglas design methodology

9.2 Separation considerations for waste minimisation and batch process design

Table 9.1 shows the existing and new questions for Level 4 of the Douglas design methodology. These can be applied to both batch and continuous operations.

Table 9.1: Douglas design questions for separation system design

Existing questions for waste minimisation
Are any waste streams the result of poor or inappropriate separations? Can any wastes be removed from the process by adding new separations? Are there alternative separation technologies that could replace or supplement existing separations? Do absorber solvents or stripping agents cause a waste problem? Does regeneration of adsorber beds or disposal of materials cause a problem? Are there any problems caused by the release of purge streams? Does solid cake washing cause a waste problem?
Additional considerations
Should the separation system be batch or continuous? What are the physical properties of the components to be separated and how would these affect the system choice? Is extra energy input required? Can newly developed technologies be implemented?

The new questions that have been added to the Douglas design methodology are discussed below:

- *Should the separation system be batch or continuous?* The separation system can be operated batchwise directly from the batch process or continuously by storing material in a holding tank and feeding material at a steady rate. A comparison between the two types of separation systems would identify the effect on the process emissions. As an example of the application of this question, a UK company recently switched its separation operations from seven batch stripping units to one continuous unit in order to reduce emissions [129].

- *What are the physical properties of the components to be separated?* The properties of the components to be separated will dictate which separation system will be the most effective. For example, vapours with different dew points can be separated by condensation whilst gas adsorption or absorption can be used for removing materials from vapour streams. Components can be removed from a liquid stream by distillation, stripping or extractive crystallisation. Also, immiscible liquid materials differing in density can be separated by gravity. Recently, group contribution techniques have been used to identify the most appropriate separation systems [94].

- *Is extra energy input required?* The amount of energy used in a process has an additional effect on the environment as emissions of carbon dioxide, sulphur dioxide and nitrogen dioxides result from the combustion of fossil fuels. Therefore, in the revised methodology, energy has been included in the assessment of environmental impact [1]. Thus energy intensive techniques such as distillation can be compared with other separation technologies such as adsorption. For distillation systems the energy demand will be determined by the difficulty of the separation, the throughput and the purity of product required. For a conceptual design it may be beneficial to relax the required purity of the product, with the agreement of the customer, in order to achieve a lower level of energy usage.

- *Can newly developed technologies be implemented?* This question may overlap with the question concerning the application of alternative technologies in the existing Douglas design methodology. However, it has been introduced to encourage the designer to consider newer separation techniques, for example membranes or molecular sieves. Some companies may be unwilling to install a novel separation system because it may be expensive to build and there may be initial operating problems that are often associated with "unproven" technologies.

9.3 Cost estimation

Douglas represented the economic potential (EP) of the Level 4 flowsheet as:

$$EP_4 = EP_3 - \text{purge losses} - \text{annualised distillation costs (£/year)} \quad (9.1)$$

In batch operations, it is often possible to carry out the separation in the same vessel as the previous operations. Therefore, in the revised methodology the annualised separation costs include the operating costs of each of the separation operations as well as the costs of individual units. In Equation (9.1) the costs of separation were restricted to distillation, whereas in the revised methodology the costs of any chosen separation technology are included. Waste disposal costs have also been included in the revised cost estimation, as for Level 2. The revised economic potential (EP) therefore is:

$$EP_4 = EP_3 - \text{purge losses} - \text{annualised separation unit costs} - \text{separation operating costs} - \text{waste disposal costs (£/year)} \tag{9.2}$$

An environmental process performance tool (EPPT) has been developed for the revised methodology and is used to compare the environmental impact of different design options. The EPPT score includes the assessment of the emissions associated with energy production. As mentioned previously this allows different separation technologies to be compared more fairly. The EPPT score is as follows:

$$(\text{EPPT score})_4 = \text{environmental impact of process outputs and energy usage} \tag{9.3}$$

9.4 Batch distillation

In the Thomas Swan process toluene is removed from the product mixture by batch distillation. The distillation is performed in a vessel and heating is provided by direct stream injection. A simulation of this operation has been performed and the details have already been provided in Section 4.3.5.

The main waste stream from the distillation is contaminated water, resulting from the steam condensing in the vessel. A number of design options have been simulated to assess whether the amount of aqueous waste could be reduced. Two opportunities have been identified that would reduce the steam usage and hence reduce the condensed water waste: (i) to improve the separation efficiency and (ii) to use indirect heating. The results of this study have shown that the current Thomas Swan operations are carried out at optimal conditions and the separation can not be improved substantially by altering the process conditions. However, the generalised application of the design questions to the conceptual design of a batch system has been discussed in each section.

For a conceptual design the engineer would optimise the operating parameters to achieve the most efficient separation within the required specifications of cost, product purity and emissions. The study of the optimum separation parameters would enable the designer to improve the performance of the process, thereby addressing the Douglas question: "Are any waste stream the result of inappropriate or poor separations?" The separation design options which have been simulated are:

- to change the distillation pressure; this is described in Section 9.4.1.1, and,
- to use a two stage separation; this is described in Section 9.4.1.2.

The Douglas question: "Are there any alternative separation technologies that could replace or supplement the existing separation?" focuses on changing the method of separation to improve the environmental performance of the process. The process options studied for the Thomas Swan batch distillation are:

- to use nitrogen injection rather than steam, as described in Section 9.4.2.1.
- to replace the direct steam injection with indirect heating using steam coils. The results from this study are described in Section 9.4.2.2.

9.4.1 Are any waste stream the result of inappropriate or poor separations?

9.4.1.1 Effect of pressure on distillation

Using the simulation of the batch distillation, detailed in Section 4.3.5, the effect of reducing the pressure of the distillation vessel has been studied. Figure 9.2 shows the percentage change of several parameters from their values at the normal operating conditions.

The following points can be noted:

- As the pressure is reduced the temperature at which the required distillation occurs is decreased.
- Reducing the distillation pressure reduces the vapour pressure of water more than toluene. Consequently, the mole fraction of toluene in the vapour phase increases. As a result more toluene is removed from the vessel and the distillation time is reduced.

- The steam consumption is reduced due to the reduced distillation time and the lower temperature requirements.

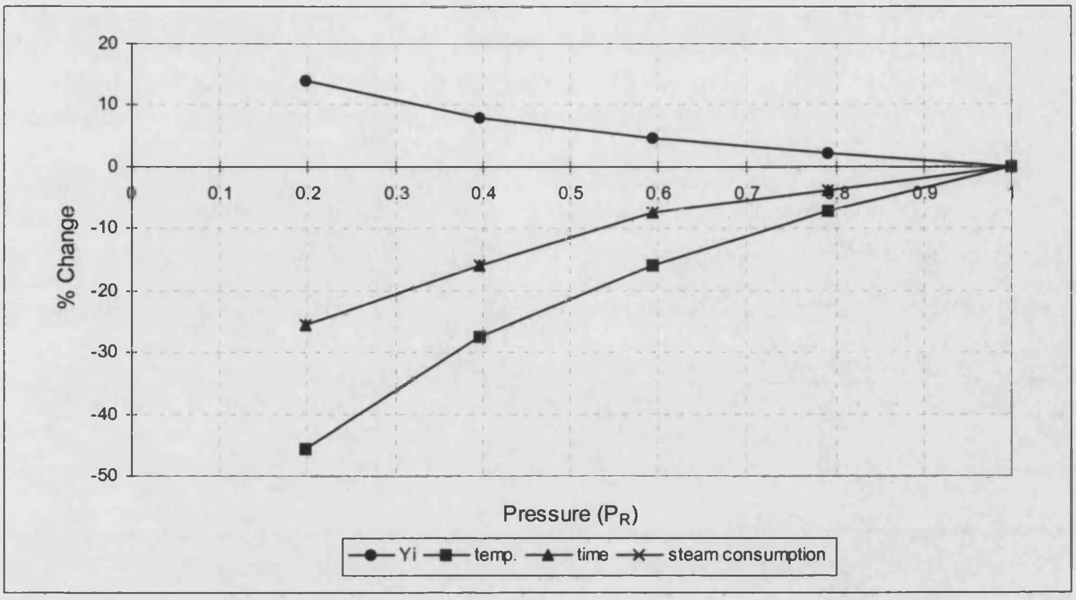


Figure 9.2: Percentage change in toluene vapour phase mole fraction (y_i), distillation temperature, distillation time and steam consumption.

P_R = (pressure/ base case pressure)

However, Figure 9.2 shows that decreasing the operating pressure to $0.2P_R$ only decreases the steam consumption by 25%. For the current Thomas Swan operations the capital costs and energy requirements to operate at a reduced pressure would not be outweighed by the reduced steam consumption.

In general, considering this option for a conceptual design the effect of distillation pressure on the degree of separation would be studied in detail in order to optimise the operations. The capital cost of a high or low pressure unit will probably be higher than that for operating at atmospheric pressure. However, if the separation efficiency can be improved, the operating costs may be reduced. The EP will therefore reflect a trade-off between the increased capital costs and the decreased operating costs. A more efficient separation should require less energy input and therefore, the effect would be to reduce the EPPT score.

9.4.1.2 Two stage separation

The current Thomas Swan operation operates with a single stage distillation. Increasing the number of stages should improve the separation achieved. A simulation incorporating two stages has been developed by joining two flash separators and returning half of the condensed vapours as reflux. However, because the toluene and water form an azeotropic mixture the composition of the vapour remains unchanged. As a result, the mole fraction of toluene in the vapour from the second stage is exactly the same as that from the first stage. Therefore, there is no advantage to be gained from having two stages. The only effect is to increase steam consumption and capital cost.

With a non-azeotropic mixture, using more stages would normally improve the separation. However, the costs of a distillation column would increase with the increasing number of stages. An infinite number of stages would be required to achieve a perfect separation. Therefore, there is a trade-off between the column size and the purity required. Improving the separation may mean less waste is produced, thereby reducing the EPPT score, but additional energy would be required as the number of stages increases and the EPPT score may increase. Therefore, the process choice would have to be trade-off between these values.

9.4.2 Are there any alternative separation technologies that could replace or supplement the existing separation?

9.4.2.1 Nitrogen injection

A simulation was carried out that replaced the steam injection with nitrogen. The high vapour pressure of nitrogen resulted in a very low toluene mole fraction in the vapour phase. Consequently, the predicted time to remove the required amount of toluene from the mixture was greatly increased. In order to remove the toluene from the nitrogen after the distillation a very low temperature was required resulting in a large cooling demand. In addition, because the nitrogen contained no latent heat a high flowrate (>300 kmol/hr) was needed to raise the temperature in a reasonable time. As a result, the capital and running costs of such a system would be excessive.

9.4.2.2 Indirect heating

An alternative to using direct steam injection is to use indirect heating via a jacket or heating coils, enabling the condensed steam to be recycled. In the simulation the same quantity and composition of toluene was recovered as predicted in the base case. However, because the steam did not condense inside the vessel the predicted mass of water remaining after the distillation was reduced. The water level was also reduced as it boiled off during the distillation. Figure 9.3 shows the product vessel and the distillation vessel levels for the two options.

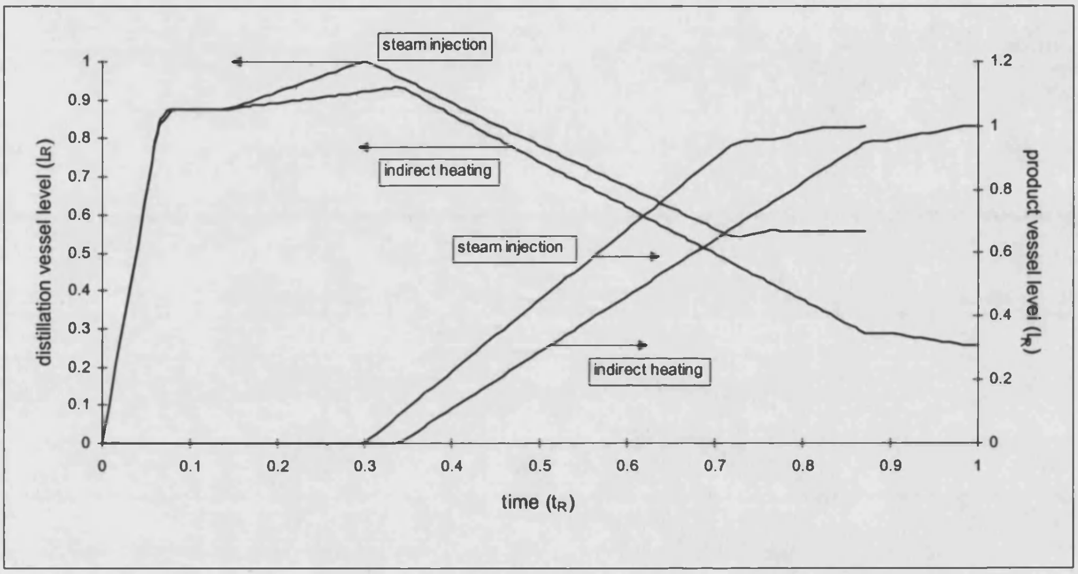


Figure 9.3: Product level and distillation vessel level for the process options

In the Thomas Swan process there is no advantage of using indirect heating because water is added to the distillation vessel to slurry the solid products after the toluene has been removed. Therefore, reducing the water present during distillation would just require more water to be added for slurrying. Additionally, considerable fouling would be expected to occur if the product concentration rose above a certain level causing precipitation to occur. The water resulting from the steam injection also maintains the composition of the distillation mixture above the azeotropic concentration at which point the separation would become limited.

Separation of a non-azeotropic mixture, where water is not required in the vessel, could utilise indirect heating. Consequently, the EPPT score of the separation process would be reduced because less contaminated water would be released from the process. The capital costs may increase if substantially more equipment is required for recycling the steam. However, the operating costs would be reduced.

9.5 Can any wastes be removed from the process by adding new separations?

In Section 7.3 a by-product of a side reaction, contaminant F, was highlighted as a potential environmental problem. Contaminant F results from the reaction of feed contaminant B in the benzoylation operation. Although only a very small amount of contaminant F was predicted to be present in the aqueous waste, the predicted EPPT score associated with it was high due to its potential environmental effects. There are three options that could be considered:

1. Remove contaminant F from the aqueous waste for separate disposal or treatment. The contaminant would still be released to the environment after separation and would remain a contributor to the EPPT score. Therefore, this has not been considered as a waste minimisation option.
2. Remove the feed contaminant B before the benzoylation reaction. If contaminant B were removed, contaminant F would not be produced. The EPPT score would be reduced as the feed contaminant B has a lower contribution than does contaminant F. This option is considered in Section 9.5.1.
3. Remove contaminant B from the original benzothiazole feed stream. This would enable contaminant B to be removed before it becomes diluted in the process. This option is detailed in Section 9.5.2.

9.5.1 Removal of contaminant before benzoylation

Two methods of removing the feed contaminant B from the oxidation products have been examined using the batch distillation simulation:

- direct steam injection, and,
- indirect heating via steam coils.

In both cases boiling water stripped the contaminant from the vessel. It was also predicted that a proportion of the stage 2 (S2) product would be removed with the water. Figure 9.4 shows the percentage of contaminant B removed and the S2 product lost for both of the cases as the separation time increases. For the case using direct steam heating, the condensed steam adds to the aqueous waste from the process, whereas for indirect heating the condensate could be recycled. For indirect heating the water in the vessel is boiled off and the vessel contents become more concentrated. In the case of the Thomas Swan process this would cause operational problems at the benzoylation stage because the product precipitates out of solution if it is not kept dilute.

The separation time for any given level of contaminant removal using direct steam injection was predicted to be greater than for steam coils because the condensed steam adds to the heating load. Contaminant B also becomes more dilute and hence more difficult to remove. As a result the separation is slower, more steam is required and more S2 product is lost to the vent. The amount of steam/water used for the separation for both the options is shown in Figure 9.5. The water removed for indirect heating is also shown.

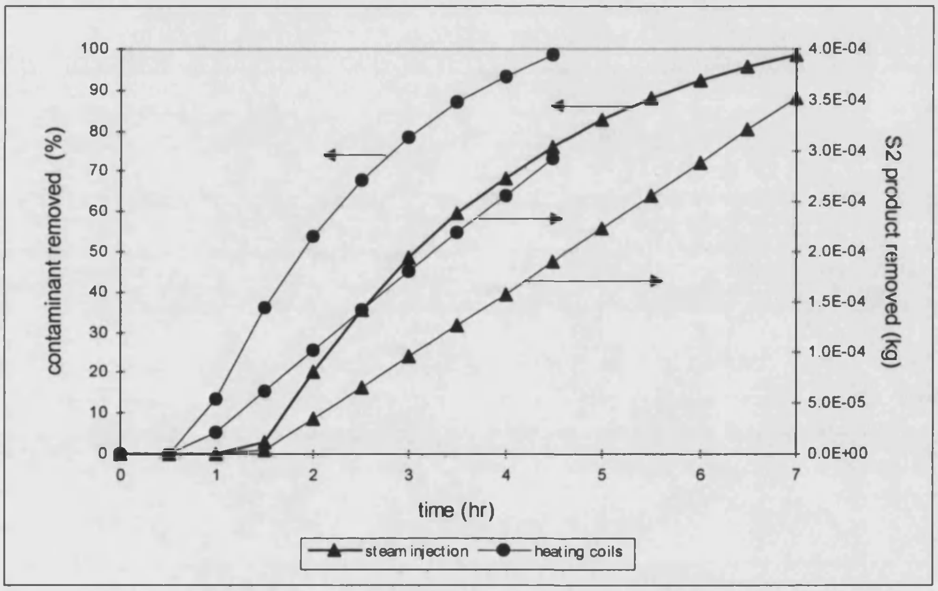


Figure 9.4: Percentage contaminant B removed and amount S2 product lost

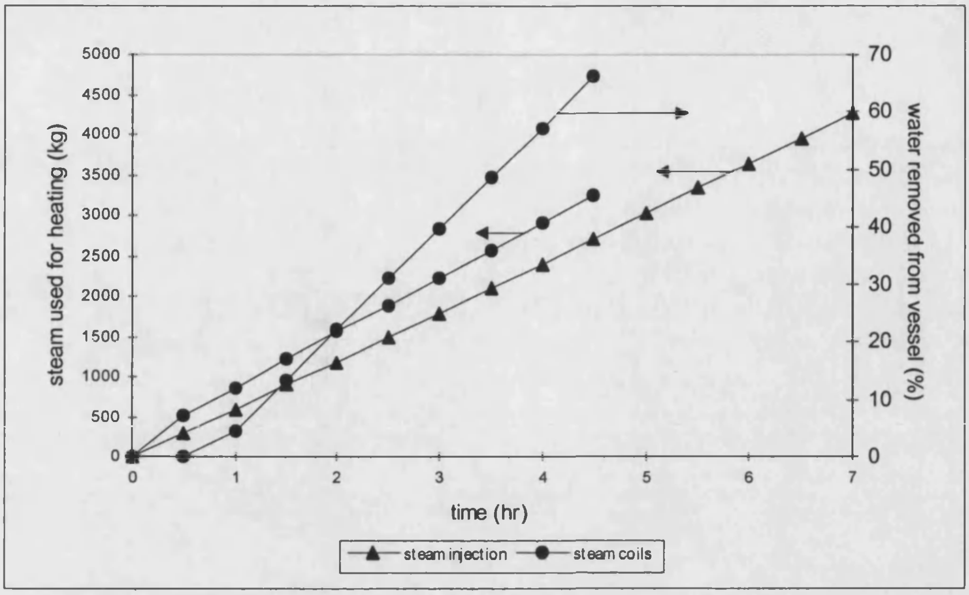


Figure 9.5: Steam used for heating and water removed from vessel

For a conceptual design using this option would decrease the EP due to the increased operating costs. The process schedule might need to be altered to accommodate the additional operation. Because less contaminant F is released the EPPT score would be reduced. Figure 9.6 provides a comparison of the EPPT score and the cost to remove contaminant B using direct steam injection. The EPPT score decreases as contaminant B is removed whilst the cost rises as more steam is used. A cost-benefit analysis would need to be carried out to find the trade-off between these factors.

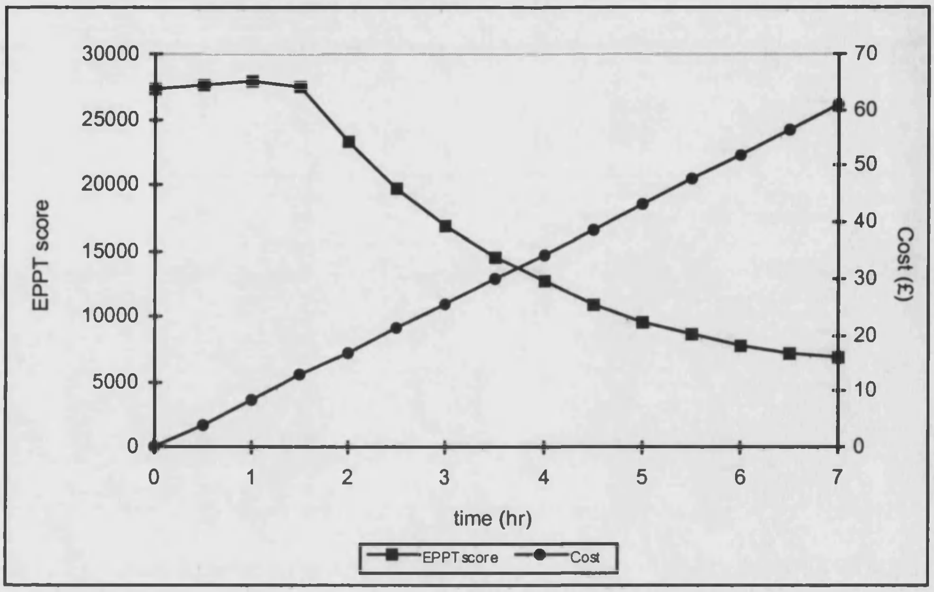


Figure 9.6: EPPT score and cost of separating contaminant B using steam injection

9.5.2 Removal of feed contaminant from the BT feed

The boiling points of contaminant B and BT are 185°C and 227°C [122], so distillation should be a viable option. However, in the HYSYS simulation the boiling point of BT was predicted to be 187°C and therefore a realistic simulation of distillation was not feasible.

This provided an opportunity to investigate a novel method of separation that could be used as an alternative to distillation. Using computational techniques [151], it was found that the BT molecule and the contaminant B molecule have the dimensions shown in Figure 9.7. The structures of the molecules cannot be revealed for confidentiality reasons.

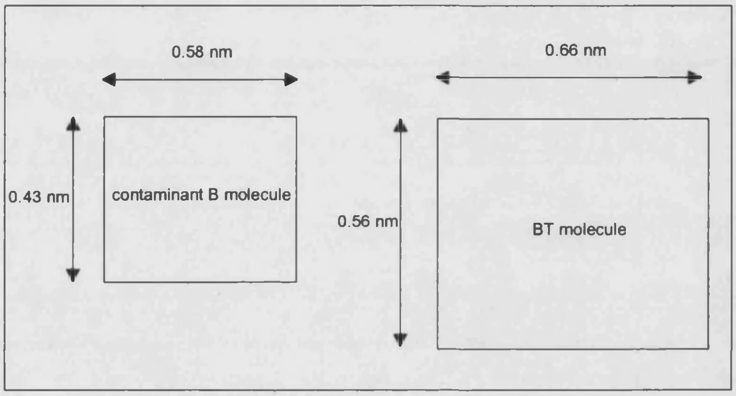


Figure 9.7: Relative sizes of the BT and contaminant B molecules

Because of the difference in the size it may be possible to use a 5A molecular sieve to separate these two molecules. The average pore size of a 5A sieve is 0.44 nm, so the contaminant B molecule should be able to pass through whilst the BT molecule would be too large.

This option has not been investigated further but illustrates that different separation techniques exist and may provide viable alternatives to the traditional separation techniques.

9.6 Summary

Level 4 considers the design of the separation system. The existing Douglas methodology has been extended to apply to waste minimisation of batch processes. New process design questions have been introduced and these are relevant to both batch and continuous operations. Several of the Thomas Swan separation processes have been analysed using the simulations developed in Chapter 4. These have provided an insight into the parameters that are important for separation system design. The next level to consider is the cleaning system design. This is described in the next chapter, Chapter 10.

Chapter Ten

Level 6 Considerations: Cleaning System Design

10.1 Introduction

A new level that considers the design of the cleaning system has been added to the revised Douglas design methodology for batch processes, as shown in Figure 10.1. The reasons for including cleaning considerations at the conceptual design phase of a batch process are as follows:

- The substances used for cleaning will usually exit the process as contaminated waste streams requiring treatment or disposal, thereby contributing to the environmental impact of the process. Therefore, the type of cleaning fluid used, the flowrate required and the cleaning times will affect the wastes resulting from the process.
- It may be possible to design equipment to minimise fouling and to optimise the effectiveness of cleaning, thereby minimising the amount of cleaning fluids required.
- The mechanisms of cleaning need to be examined and understood to enable the cleaning cycles to be optimised.
- The cleaning equipment capital and operating costs need to be included in the estimation of the flowsheet costs.
- There is interaction between the design of the cleaning system and the other design levels, such as the effect of cleaning time on the process scheduling.

In this chapter the new design questions developed for cleaning system design are presented. The EVC case study, described in Chapter 5, has been used to examine a cleaning system in more detail and the results are presented in Section 10.4.

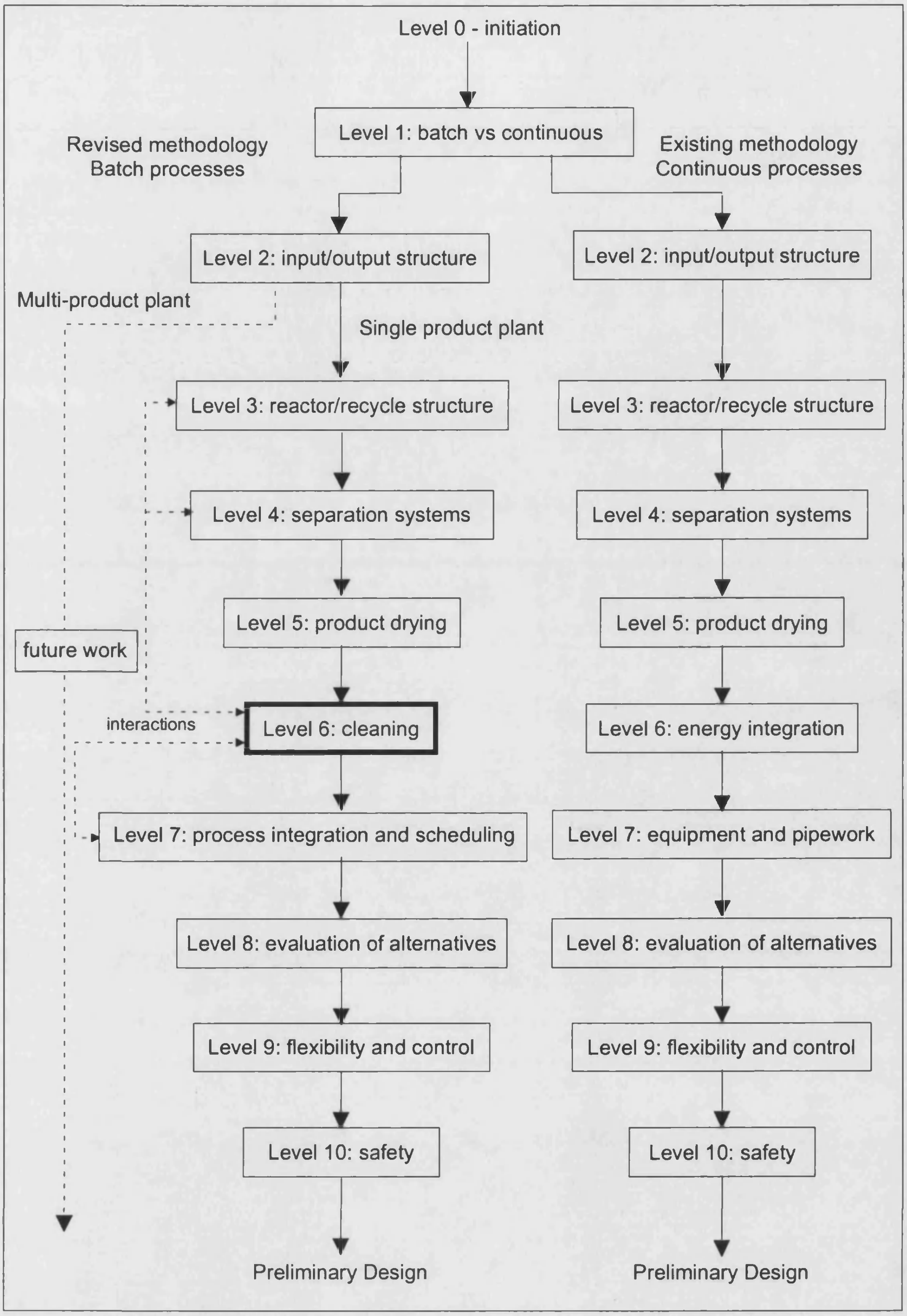


Figure 10.1: Douglas design methodology

10.2 Level 6, cleaning system design questions.

Table 10.1 presents the new questions that need to be considered for cleaning operations at Level 6. A number of the questions have been adapted from literature as indicated in the table and three of the questions are discussed in more detail in the following sections.

Table 10.1: New questions for Level 6, cleaning system design

Question	Notes	Interaction with other design levels
What solvents are required?	See Section 10.2.1.	-
What happens to the spent cleaning fluid? Can the solvents be recycled or regenerated?	Recycling may be possible if the fluid does not become too contaminated. Treatment may be required and regeneration of cleaning fluids may be possible. The treatment and recycling of cleaning fluids may require additional separation units to be designed.	This will interact with Level 4, the design of the separation system.
Can materials from the process be used for cleaning?	See Section 10.2.2.	-
How many washes are required and what is the optimum cleaning time?	The mechanism of cleaning would need to be investigated to enable the optimum number of washes and cleaning times to be selected. The performance of the process may be affected if the equipment is not cleaned regularly and this would have to be considered when fixing the cleaning cycle time and frequency. For example, heat transfer may become restricted or flow through equipment become limited by excessive deposits.	Changing the cleaning times will affect the process schedule, Level 7.
Is the minimum amount of solvent used? [152]	This may overlap with the above question as the amount of solvent used depends on the cleaning time. However, the flowrate of solvent is also a variable and should be minimised.	-
Can the length of the production schedule be increased to reduce the number of equipment washings needed? [152]	The length of the production cycle will depend on many factors including the customer demand, the maintenance requirements and also the operability of the plant if cleaning is not carried out.	Changing the cleaning times will affect the process schedule, Level 7.
Can additives be used to improve the cleaning effectiveness or inhibit fouling?	Pre-washing equipment with a detergent may help to minimise or eliminate the need for washing [152]. However, the detergents may have an effect on the environment.	-
What method of cleaning should be used?	See Section 10.2.3.	-

Table 10.1 (Continued): New questions for Level 6, cleaning system design

Question	Notes	Interaction with other design levels
Is the equipment designed to minimise cleaning? [46]	If the amount of fouling can be minimised then the cleaning requirements will be reduced. An example of designing to reduce fouling is to use an antistick coating on equipment walls [152]. Fouling can be also be minimised by reshaping the tank to prevent dead space [153].	Interaction with Level 3, the design of the reactor system and maybe Level 4, the design of the separation equipment.
Is the in-process inventory small to minimise the loss of material from cleaning? [46]	Equipment should be drained between production cycles to reduce the amount of material left on the vessel walls. This could be achieved by increasing the time between the end of the production cycle and the beginning of the cleaning cycle [152]. Also, equipment with sloping bottoms or low drain points would allow better drainage [152]. In addition pipes should be sloped and be sufficiently supported to prevent sagging [154].	Changing the cycle time will affect the process schedule and designing better drainage would need to be considered at Level 4 during the reactor design.
Does the deposit solidify on standing? [152]	If so the equipment should be washed immediately as solid deposits are usually more difficult to remove.	-
Which cleaning cycle has the least effect on the environment?	Assessing the wastes produced by the cleaning operations and also the energy requirements enables the designer to select an environmentally acceptable cleaning operation.	This question overlaps with some of those above.

10.2.1 What solvent is required?

A choice of solvents may be available and each will have different characteristics and costs. At the conceptual design stage it is necessary to define how much of each fluid would be required to perform the cleaning and also to assess whether any emissions would result from its use, e.g. vapour emissions from a volatile solvent. There may be regulations that limit or prohibit the use of a particular solvent. For example, the use of methyl chloroform is prohibited by international treaties [155]. Disposal limitations and costs will also affect the choice. An additional consideration is the provision of employee training that may be required for certain solvents, thereby adding to the costs [155]. To select an appropriate solvent it may be possible to use group contribution techniques that match the solvent with the cleaning and environmental requirements of the process [55].

Water may be used as a cleaning fluid because, at present, it is relatively cheap, readily available, usually easy to dispose of once any contaminants have been removed and produces no harmful emissions to the air. However, the two cases described below indicate situations where water cannot be used for cleaning:

1. If a dry surface is required then solvent cleaning is preferred. Using water will require additional drying equipment, a longer process time and incur higher energy costs [155].

2. In the manufacture of a pharmaceutical ingredient 204219, water washing is not possible as the materials coating the equipment are not soluble in water. Therefore, the reactors are boiled out with methanol until the contaminant concentration is less than 25 ppm. It was estimated by the company that five boil outs would be required per clean. The methanol is sent offsite for recovery [156].

10.2.2 Can materials from the process be used for cleaning?

Cleaning operations usually introduce new materials to the process and these often exit as contaminated waste streams requiring treatment or disposal. Instead of using a new material for cleaning, it may prove possible to use a waste stream from another part of the plant or from a previous batch. This will reduce the number of wastes streams emitted from the process as a whole and reduce the costs of purchasing fresh cleaning fluids.

If no suitable waste stream is available it might be beneficial to use a material that is already present in the process, such as a reactant, product or solvent. This would avoid additional treatment or separation stages being required to deal with a new cleaning fluid. For example, the vessel could be flushed with a small amount of the product which is then returned to the next batch [152]. Further, it may be possible to incorporate the contaminated cleaning fluid into the process as shown in the following two examples:

1. In the production of a synthetic resin for the paint and printing industry, the solvent washes using materials such as white spirit, xylene and acetone, are incorporated into subsequent batches [129];
2. During the manufacture of arsenic acid (H_3AsO_4) the liquors generated by washing the empty arsenic trioxide containers are fed into the arsenic acid reactors, whereby the arsenic trioxide is recovered. Additionally, wash liquors from cleaning vessels in another part of the plant are retained and incorporated in the arsenic acid process [157].

10.2.3 What method of cleaning should be used?

Various cleaning methods exist ranging from manual operations to sophisticated automated *in-situ* systems. Different methods will often use different amounts of cleaning fluid depending on the cleaning efficiency achieved. Additionally, energy may be required to operate the cleaning system and to heat or pressurise the cleaning fluids. The amount of cleaning fluid and energy used will have an effect on the emissions from the process. Therefore, the environmental impact and costs of the available techniques should be compared. For example, a waste minimisation study performed by Dupont showed that manual cleaning equipment was more efficient than an automated system [152]. This was because in this particular case the operator could stop the cleaning once he saw the vessel was clean. In contrast, an automated system would carry out the whole cleaning cycle regardless of whether the vessel was still dirty or not. In addition, the amount of solvent could be varied by the operator depending on the cleanliness of the equipment. However, in some cases manual cleaning may actually create more releases of material, especially if the vessel needs to be opened and vapours released.

Methods of cleaning include:

- using high pressure water jets inserted through a flange at the bottom of the vessel [152],
- using a rotating head spray inside the vessel which would achieve better cleaning effectiveness than a static head system [152],
- pipe cleaning pigs sent through equipment to remove deposits [152],
- wiping or brushing after each batch to prevent build-up on the walls but this method should not be used for viscous materials [152], and,
- spray cleaning achieved a reduction in cleaning chemical, water and energy consumptions compared with using a fill and dump cycle [132].

10.3 Cost estimation and environmental assessment

As cleaning is a new consideration no cost estimation for cleaning operations exists in the Douglas methodology. The economic potential (EP) proposed for the cleaning operations in Level 6 is:

$$EP_6 = EP_5 - \text{annualised costs of cleaning system} - \text{cleaning fluid costs} - \text{operating costs} - \text{lost product costs} - \text{waste disposal costs} \tag{10.1}$$

The costs that have been included are the capital cost of the cleaning equipment, the cost of the cleaning fluid and the associated running costs. An additional cost is the value of the product that is lost in the deposit layer. This can represent a major cost especially if the product is valuable. Two examples are: firstly, a company manufacturing resins that loses 1.2×10^{-2} m^3 of material at a cost of \$10,500 per year [154] and secondly, for the PVC case study described in Chapter 5, it was estimated that if 1mm of deposit remained in the vessel after every batch, the value of lost product would be £18,275 per year. The cost of waste disposal has also been included as for the previous design levels. If a number of cleaning operations are required it is necessary to separate the costs to highlight which are the major contributors to the overall flowsheet costs.

It has been assumed that the amount of product produced in the plant is fixed to fulfil a specified demand. Increasing the cleaning time would reduce the amount of production time available and therefore, additional vessels are needed to fulfil the demand. At the design stage the optimum cleaning time should be selected by studying the effectiveness of cleaning. Consideration of the cycle times and how these interrelate with the design of the equipment is dealt within Chapter 11 during process scheduling.

The EPPT score described in Chapter 6 enables different cleaning techniques and different cleaning fluids to be compared. The EPPT score for Level 6 is:

$$(\text{EPPT score})_6 = (\text{EPPT score})_5 + (\text{EPPT score associated with cleaning process emissions and energy usage}) \qquad (10.2)$$

10.4 Cleaning case study

Chapter 5 described the cleaning operations that are employed during the manufacture of PVC. The cleaning operations comprise intermediate cleaning between each batch and jet cleaning to remove more stubborn deposits during the quarterly shutdown. Fresh towns water is used as the cleaning fluid for both these operations. The intermediate cleaning operates on two cycles; one low pressure and one high pressure.

A simple model has been applied to these cleaning operations and the results have been provided in Section 5.4.2.3. In this model a cycle has been defined as the time to complete one batch, i.e. the sum of the production time and the cleaning time, and a campaign was defined as the number of cycles completed before jet cleaning is required.

This section uses the cleaning model to examine the effect of varying the following process parameters:

- intermediate cleaning time,
- water flowrate used for intermediate cleaning,
- water costs,
- jetting costs, and,
- changing the proportion of high pressure and low pressure cycles for intermediate cleaning.

As described earlier, the level of detail of this study was limited by the lack of experimental data regarding the cleaning operations. As a result, it was necessary to assume simple relationships between the deposit build-up with time and the effectiveness of cleaning. Consequently, no account could be taken of parameters such as fluid shear or temperature on the cleaning effectiveness. If more information were available it should be possible to optimise the cleaning cycles by minimising the cleaning time and water flowrates and to investigate the use of other cleaning techniques or fluids.

10.4.1 Changing intermediate cleaning time

In the base case the vessel is cleaned between every batch. If no intermediate cleaning were to be carried out then the deposit would build up more quickly and the process would need to be shut down for jet cleaning more frequently. Modelling this option predicted that less cycles would be completed per campaign as indicated in Table 10.2. Because less cycles were carried out more campaigns were completed per year. Figure 10.2 shows the ratio of the cost of cleaning to the value of the product. It is clear that the model predicts that the base case is actually worse than the option wherein no intermediate cleaning is carried out. Figure 10.3 presents the percentage change in the total cleaning costs and the product value as the intermediate cleaning time is reduced. The value of material produced per year is three times higher than the cleaning costs per year. Therefore, the ratio of the two values is dominated by the product value.

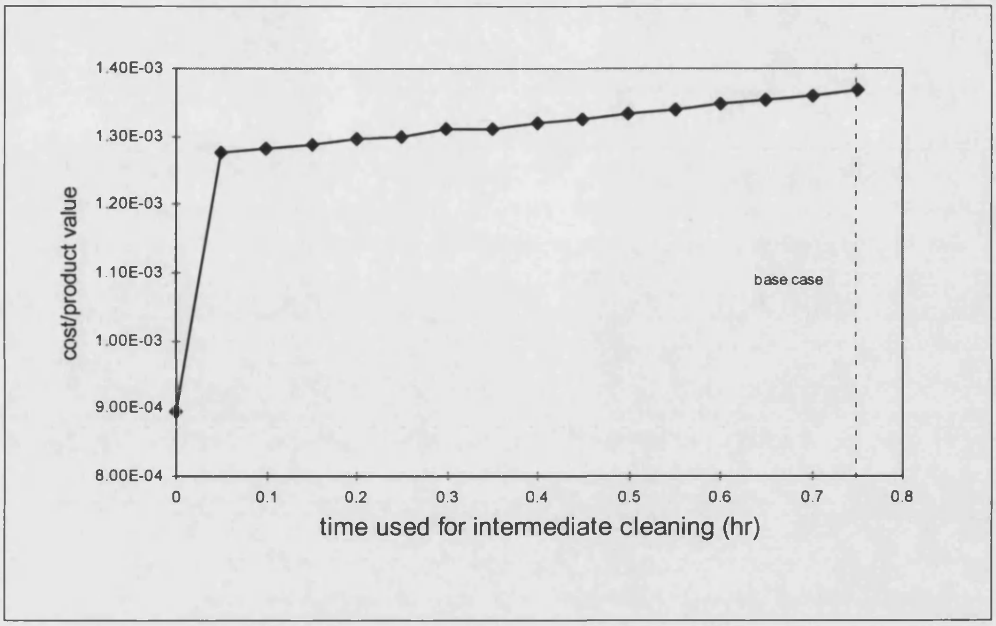


Figure 10.2: Cost to product value ratio using different intermediate cleaning times

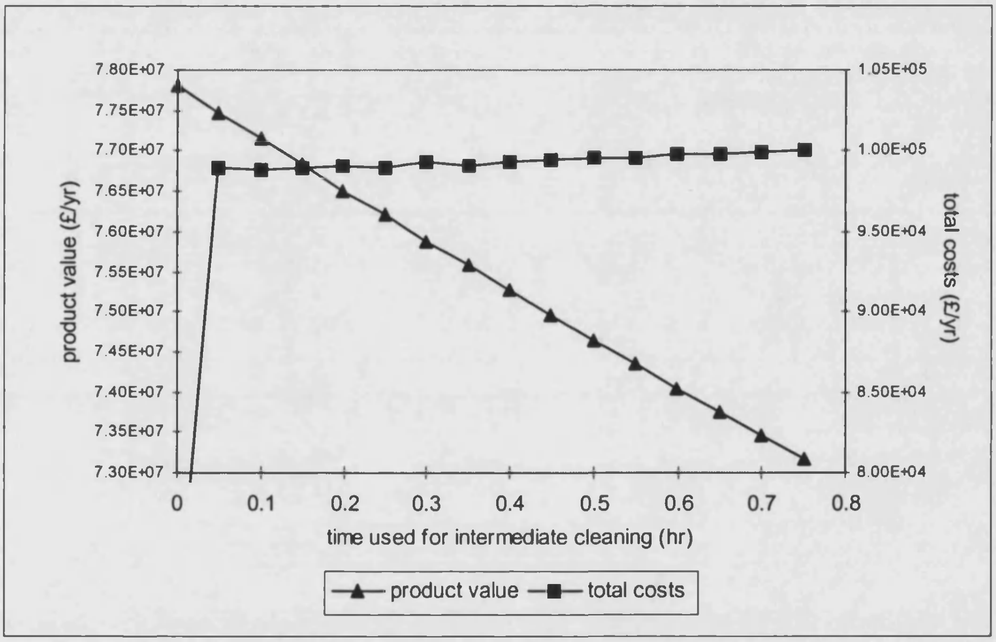


Figure 10.3: Percentage change of the total cleaning costs and the product value for different intermediate cleaning times

Table 10.2 shows that the production time for the base case is less than for the case in which no intermediate cleaning is carried out. This is because the shutdown time per year associated with intermediate cleaning in the base case is greater as shown in Table 10.3. As a result, less product is produced for the base case.

The total cost of cleaning, shown in Table 10.2, is greater for the base case than for the option. The reason can be identified from Table 10.3 where the costs are broken down into the costs of the intermediate cleaning and jetting for both the cases. Although the cost of jetting is estimated to be greater for the case without intermediate cleaning, this increase is outweighed by the magnitude of the intermediate cleaning costs required for the base case. The costs for intermediate cleaning are high because of the large volume of water consumed and the large amount of energy used. The volume of water used for one rinsing operation is $18m^3$ per reactor compared with $6m^3$ for one jetting operation. Because 926 intermediate cleaning operations are carried out per year compared with 8 jetting operations when no intermediate cleaning is carried out, the overall volume is much greater. The same is true of the energy used where 362 kJ/s is used for one rinsing operation and 740 kJ/s for one jetting operation.

Table 10.2: Summary of key parameters for the base case model and the case where no intermediate cleaning is performed

Parameter	Base case	No intermediate cleaning
Number of cycles per campaign	210	123
Number of campaigns per year	4.15	7.53
Number of jet cleans per year	4.15	7.53
Number of intermediate cleaning per year	872	0
Total cleaning costs (£/yr)	$1.00x10^5$	$6.97x10^4$
Production time (hr/yr)	7703	8195
Value of product (£/yr)	$7.32x10^7$	$7.78x10^7$
Cost to value of product ratio	$1.37x10^{-3}$	$8.96x10^{-4}$

Table 10.3: Breakdown of the costs and lost production time for the two cases

Parameter	Base case			No intermediate cleaning
	Intermediate cleaning	Jet cleaning	Total	Jet cleaning
Volume of water (m^3)	6.27×10^4	37.3	6.27×10^4	67.75
Water costs (£)	3.46×10^4	20.56	3.46×10^4	37.35
Energy costs (£)	2.71×10^4	432.45	2.75×10^4	785.22
Jetting costs (£)	-	3.78×10^4	3.78×10^4	6.87×10^4
Shutdown time (hr/yr)	653	199	852	568

From this analysis the case wherein no intermediate cleaning is carried out is the most favourable option. However, there may be other factors to consider. For example, in the PVC case a small amount of VCM maybe released to the atmosphere when the vessel is opened for jet cleaning. This presents a potential health and safety hazard to the operators opening the vessels and may also create an adverse environmental impact. For this reason EVC keep the jetting operations to a minimum and ensure that they coincide with the quarterly safety inspections which require the vessel to be opened.

In the general case a cleaning system design would be assessed at the conceptual stage in terms of the capital costs and operating costs. For the specific EVC case the capital costs would be incurred by installing the *in-situ* cleaning system for intermediate cleaning, whereas the capital costs of a jetting operation are likely to be borne by external contractors. As discussed earlier in this section, the estimated operating costs of the intermediate cleaning are larger than the jet cleaning costs and would therefore dominate the flowsheet cost.

The EPPT score for the EVC process will include the release of VCM to the atmosphere, the release of the used cleaning water and the use of energy in the operation. Although the water is treated before disposal, trace contaminants still remain and are released to the environment. There is likely to be a balance between using jet cleaning and intermediate cleaning as less water is used for the jet cleaning, whilst more VCM is released and more energy is used. The assessment of the EPPT score has been carried out but has only been based on water and energy usage as the release of VCM to the atmosphere has not been assessed at present.

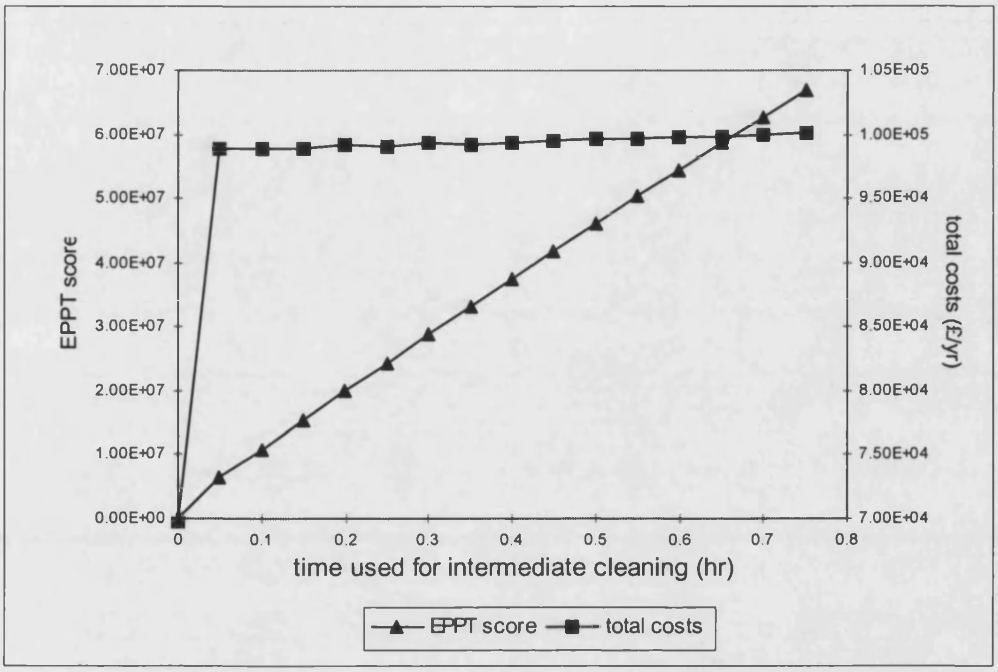


Figure 10.4: EPPT score and total costs for different intermediate cleaning times

10.4.2 Varying the water flowrate used for intermediate cleaning

A study is now made of reducing the flowrate of water used for intermediate cleaning using the model. It would be possible to use less water if the deposit were less "sticky" and hence could be removed more easily from the vessel wall. The jet cleaning flowrate has been kept constant in the model because the same amount of deposit is assumed to be removed by intermediate cleaning and the deposit thickness at the point of jetting is taken to be the same as for the base case.

Figure 10.5 displays two lines, one (the horizontal line) representing the cleaning cost to product value (C/V_p) ratio when no intermediate cleaning is performed and the other showing the reduction in the C/V_p ratio as the intermediate cleaning water flowrate is reduced. In the limiting case of zero water flowrate, the values of the C/V_p ratio are not the same for the two cases as more jet cleans are required for the case with no intermediate cleaning. This is because in modelling the option the effectiveness of cleaning is assumed to be the same as the base case but it is achieved using a lower water flowrate. Therefore the number of jet cleans is the same as for the base case and is less than with no intermediate cleaning. When the flowrate is

11.5 m^3/hr the cost to product ratio is predicted to be the same for both cases. Below this flowrate the use of intermediate cleaning is cheaper than performing jet cleaning alone. However, the base case flowrate is above this level and therefore, from this analysis, the most profitable option is the one with no intermediate cleaning.

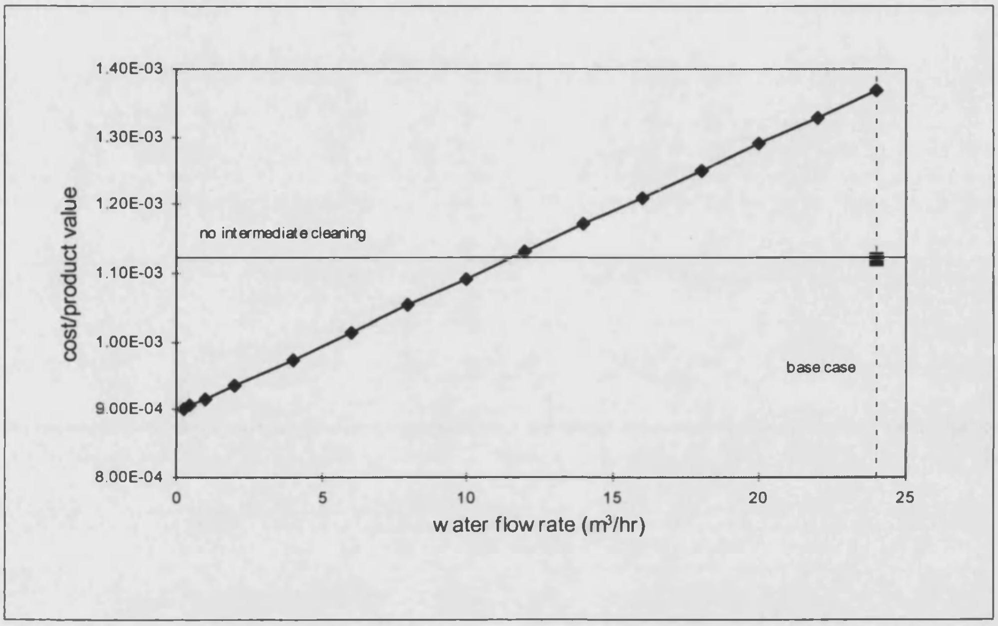


Figure 10.5: Cost to product value ratio versus water flowrate used for intermediate cleaning

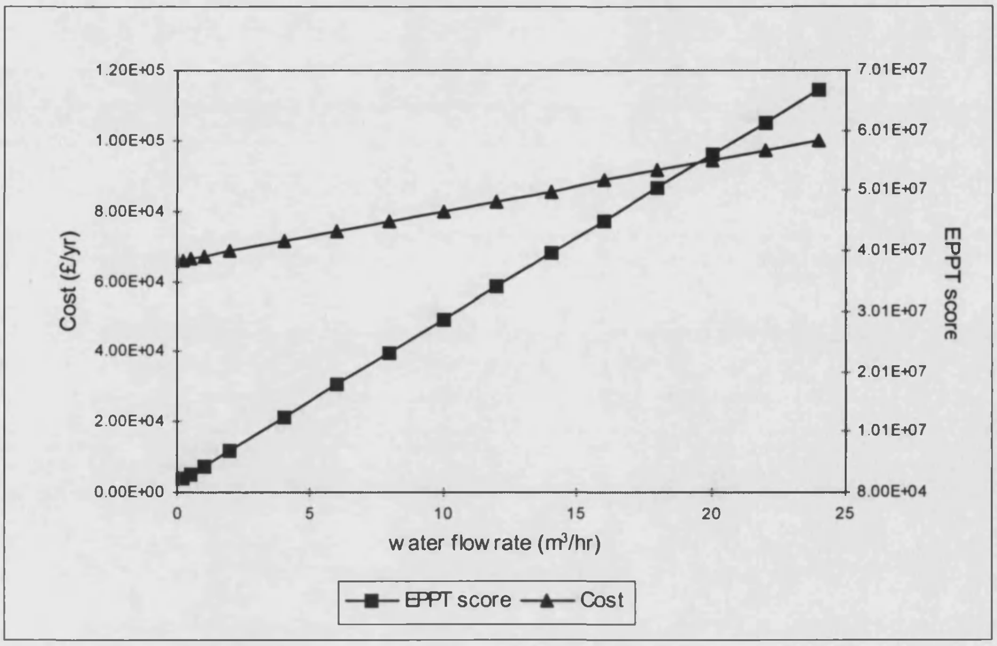


Figure 10.6: Cost and EPPT score versus water flowrate used for intermediate cleaning

In the general case, the cost of the process would decrease as less water is used for intermediate rinsing. In the specific PVC case the costs would be reduced by 5.8% if the water flowrate were to be reduced by 16.7% and the EPPT score would decrease by 16.3% as less water would require treatment, thereby less material would be released from the process. Unfortunately, it has not been possible to examine whether the amount of cleaning achieved would be reduced if the flowrate were to be reduced. To do this further understanding of the cleaning mechanisms would need to be investigated experimentally. If carried out, it would enable the "best" cleaning fluid flowrate to be selected, thereby minimising the operating costs and also the environmental impact of the cleaning operation.

10.4.3 Changing water costs

Over the past few years the cost of water has increased substantially and future increases can be foreseen. If water costs are increased then the intermediate rinsing would become more expensive as indicated in Figure 10.7. The cost of water would have to be reduced to less than 50% of the present cost for intermediate cleaning to become viable. However, this could be achieved if a water recycling system were to be used as less fresh towns water would be required. Figure 10.8 shows the predicted reduction in cleaning costs if the cleaning water were to be recycled. It has been assumed here that no extra costs would be incurred by recycling the water. As an example, the cost of purchasing towns water would be halved if the water were to used twice. In reality some treatment may be required to reduce contamination. In the EVC case the water is treated substantially before it is released to the sewage treatment plant.

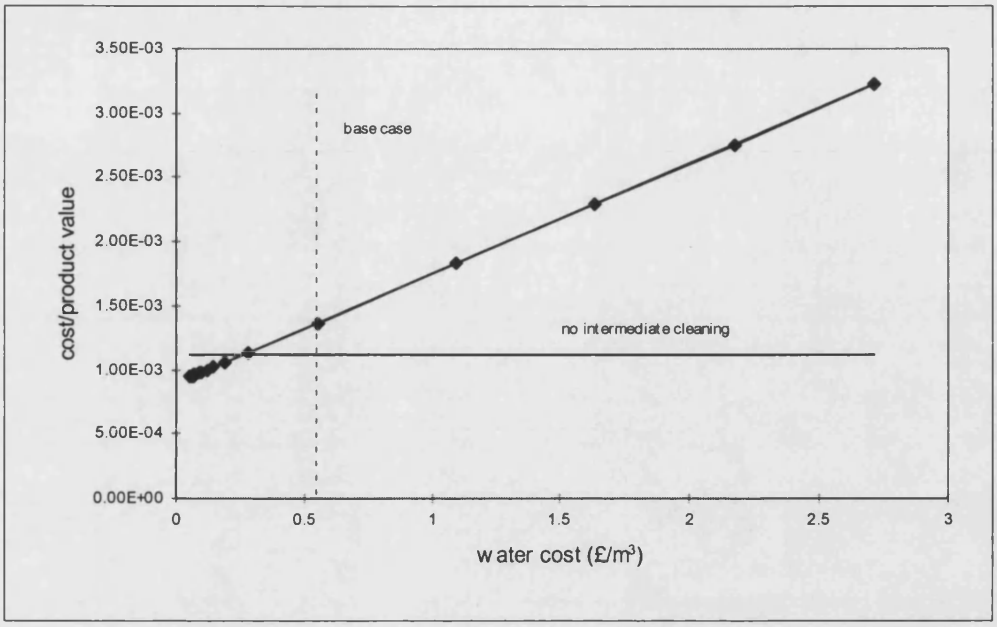


Figure 10.7: Cost to product value for varying water costs

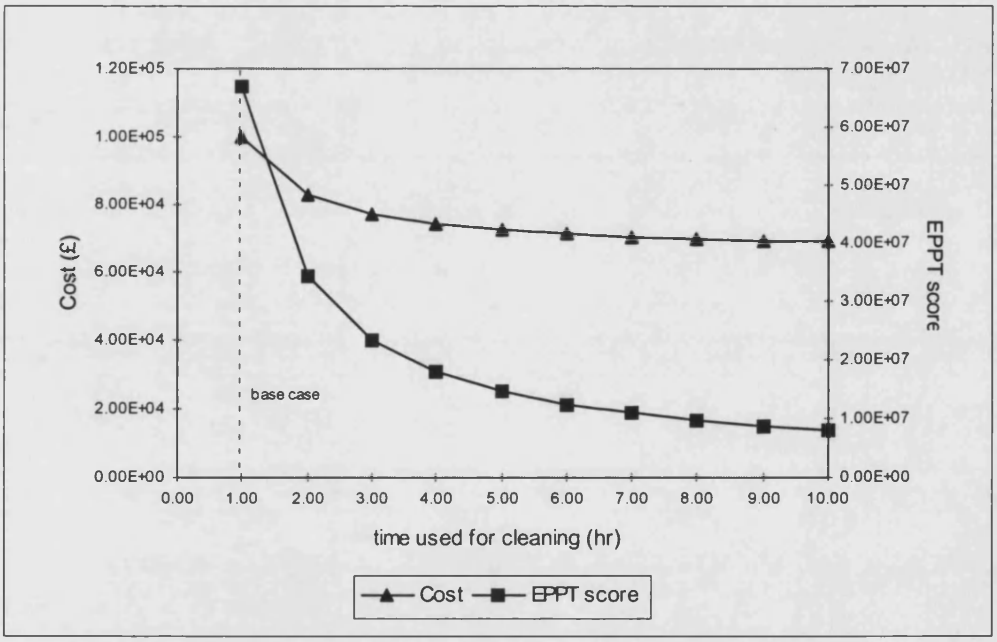


Figure 10.8: Reduction of cleaning costs and EPPT score as the cleaning water is reused

For a general case the costs could be reduced by recycling the water. For the specific case studied reusing the water once reduces the operating costs by 17.3% and the EPPT score would be reduced by 48.7% as less fresh water would be used and overall less water would be released to the environment.

10.4.4 Changing jet cleaning costs.

As shown in Figure 10.9 the jetting costs would have to increase to above £4,500 for intermediate cleaning to become more attractive than just jet cleaning. The costs of the individual operations for the base case are shown in Table 10.4.

Table 10.4: Costs of base case cleaning operations

Parameter	Cost (£)
Cost of one jetting operation	2315.6
Cost of one rinsing operation	17.71
Cost of jetting per campaign	2315.6
Cost of rinsing per campaign	3719.1
Cost of jetting per year per reactor	9609.8
Cost of rinsing per year per reactor	15419.0

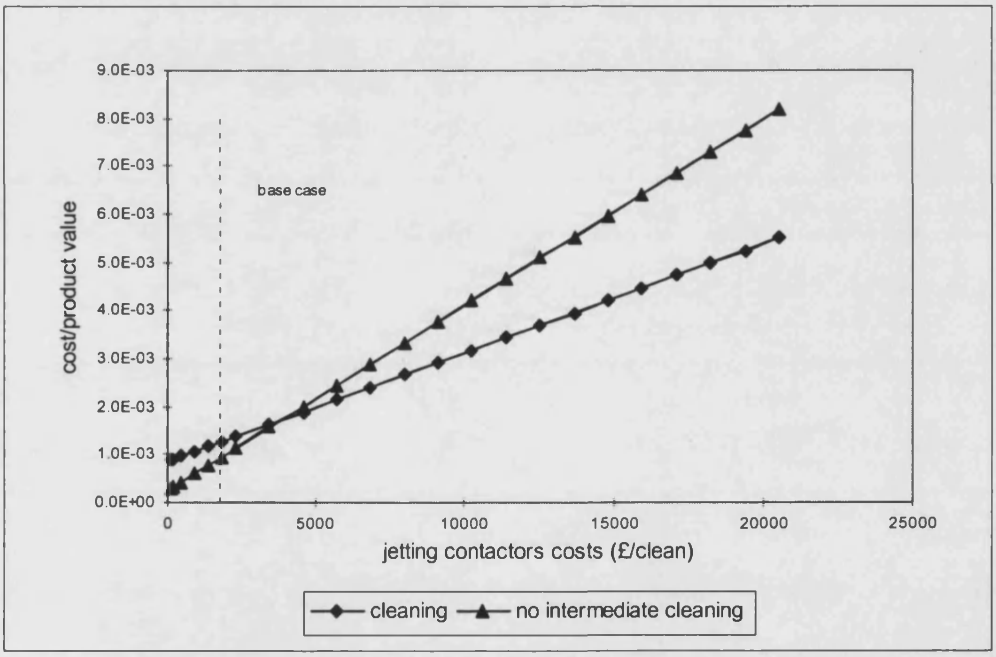


Figure 10.9: Cost to product value ratio for varying jetting contractor costs

Using the base case information suggests that use of only jet cleaning operations would be the most economical option. However, it has been shown that an increase in the contractors' costs would alter this conclusion and intermediate cleaning might become attractive. If the vessel had been designed without the provision for intermediate cleaning, this option would clearly not be viable. Therefore, the effect of future price changes should be considered when calculating the EP in those cases where the EP is sensitive to changes in the costs and major design changes are needed.

10.4.5 Changing the proportion of high pressure and low pressure intermediate cleaning cycles

During intermediate cleaning high pressure and low pressure cycles are used. In total, the rinsing is performed at four positions in the reactor and only one uses the low pressure cycle. Figure 10.10 shows that if low pressure cleaning were to be used for the whole rinsing operation the cleaning costs would be less than if high pressure cleaning alone were to be used. This is because although more water would be used, less energy would be required to pressurise the water. However, this study has not taken into account the fact that low pressure cleaning may not clean the vessel adequately and hence more jet cleaning might be required. It is not known whether this would be the case because no experiments have been carried out and in the plant operations the high pressure cleaning is used to ensure that the vessel is as clean as possible.

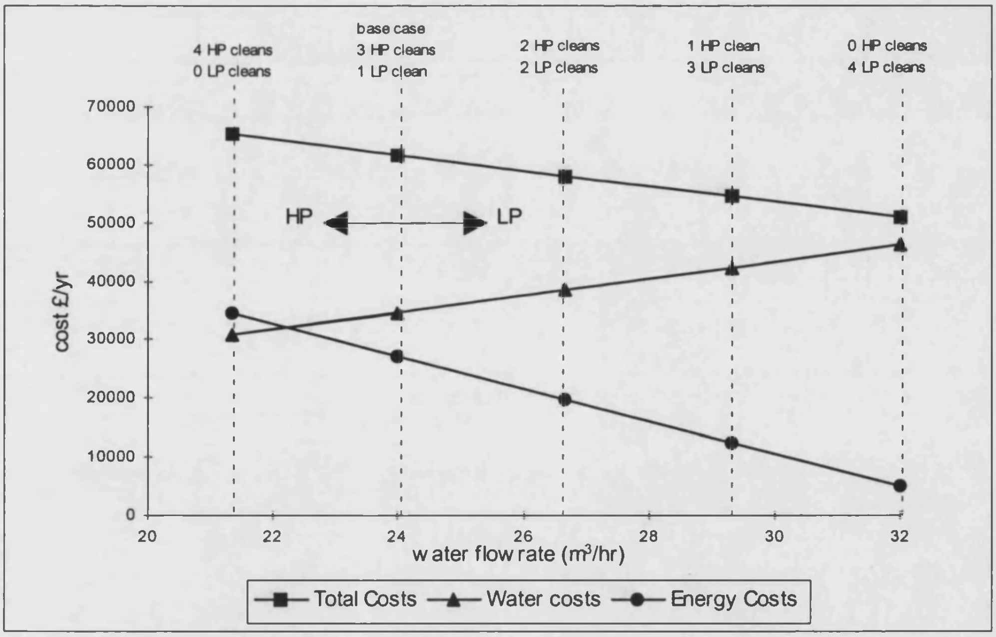


Figure 10.10: Cleanings costs with different proportions of high pressure and low pressure cleaning cycles for intermediate cleaning

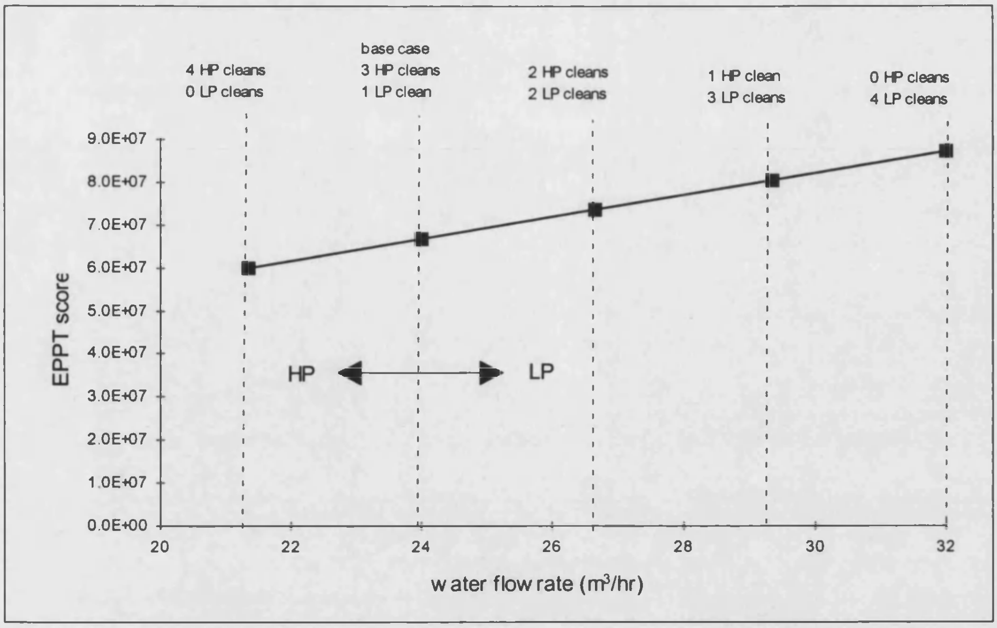


Figure 10.11: EPPT score for different proportions of high pressure and low pressure cleaning cycles for intermediate cleaning

In the general case the process costs would be reduced if a low pressure cycle were to be used for intermediate cleaning. However, experiments may show that low pressure cleaning does not achieve enough deposit removal and additional jet cleaning therefore might be required. The EPPT score is shown in Figure 10.11 and increases as more low pressure rinsing is used. This is because the EPPT score is dominated by the water used which increases for low pressure rinsing. The extra energy used during high pressure rinsing does not outweigh the effect of using less water.

10.5 Summary

A new level has been added to the Douglas design methodology that deals with the design of the cleaning system for a batch process. Cleaning is an important consideration for a batch process because it is often required between each batch, between batches of different material, or if operational problems occur due to fouling. Cleaning contributes to the overall costs of the process design in terms of the capital costs for the cleaning equipment and the operating costs of buying in solvents or water, using energy to operate the system and hiring external cleaning contractors. In addition, cleaning may have an adverse impact on the environment due to the release of materials such as volatile solvents or contaminated fluids. The design questions that have been developed for this level are shown in Table 10.5.

Table 10.5: Design questions for Level 6, cleaning system design

Question
What solvents are required?
What happens to the spent cleaning fluid?
Can the solvents be recycled or regenerated?
Can materials from the process be used for cleaning?
How many washes are required and what is the optimum cleaning time?
Is the minimum amount of solvent used?
Can the length of the production schedule be increased to reduce the number of equipment washes needed?
Can additives be used to improve the cleaning effectiveness or inhibit fouling?
What method of cleaning should be used?
Is the equipment designed to minimise cleaning?
Is the in-process inventory small to minimise the loss of material from cleaning?
Does the deposit solidify on standing?
Which cleaning cycle has the least effect on the environment?

A cleaning operation used in the manufacture of PVC has been studied in order to identify some parameters that are important in designing a cleaning system. For a conceptual cleaning study experimental details of the deposit build-up and cleaning mechanisms would enable a more detailed study to be performed and optimisation of the cleaning time and fluid flowrate would become possible.

Chapter Eleven

Level 7 Considerations: Process Integration and Scheduling

11.1 Introduction

This chapter describes Level 7 of the revised methodology. As indicated in Figure 11.1, Level 6 in the original Douglas methodology considered the heat integration of a continuous process. In the revised methodology, also shown in Figure 11.1, Level 6 deals with the design of the cleaning system. Heat integration has been moved to Level 7 and has been extended to include process integration. Process integration encompasses not only heat integration but also factors such as using streams from one part of the batch in another, reusing waste water and recycling solvents. Section 11.2 presents batch process integration, wherein the existing Douglas design questions regarding heat integration have been applied to batch processes and new design questions have been added.

During the design of batch processes the operational schedule needs to be defined, whereby the operations are assigned to vessels, tasks can be merged or split and the cycle times are determined. Scheduling can also be used to increase the process integration opportunities by ensuring that certain process streams arise at the same point in time. Therefore, scheduling has been included in Level 7 of the revised design methodology. Section 11.3 discusses process scheduling and presents the new questions that have been added to the methodology.

This revision of the Douglas design methodology only considers single product plants. Questions considering multi-product plants have not been developed and would need to be the subject of future work.

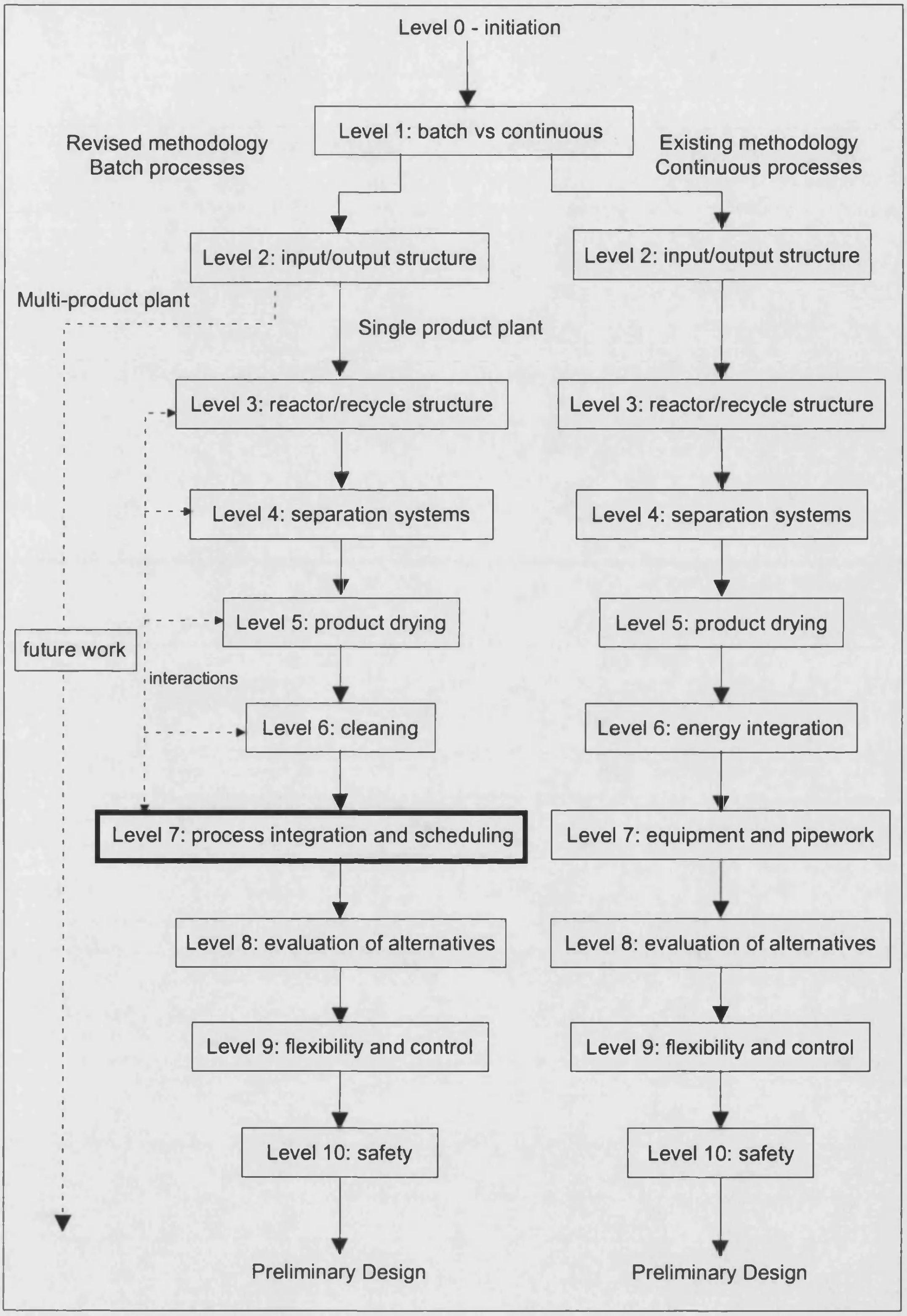


Figure 11.1: Douglas design methodology

11.2 Process integration

Pinch technology is the main technique used for achieving heat integration in continuous plants and the major developments in this area have been detailed in Chapter 3. Pinch techniques have been extended into process integration, for example by considering the transfer of material between operations and streams again detailed in Chapter 3. The application of pinch technology to batch processes is complicated by the variation of the operations with time and the process streams normally do not arise at the same time. Whilst, it may be possible to alter the process schedule to enable integration to take place, this may have other effects on the process, such as changing the number of vessels, increasing the storage requirements or altering the production times. Consequently, pinch technology and heat integration for batch processes has not yet found general acceptance in industry and clearly, is an area for further research. There are three main techniques currently being used for batch process integration; time average models, time slice models and time event models. These techniques have been summarised in a paper by Ashton [91].

In order to avoid rescheduling, heat storage could be installed to save energy from one operation for use in a subsequent operation [158]. However, the heat storage facility will add cost to the flowsheet and is likely to be less efficient than transferring the heat directly between streams.

Application of the existing Douglas design methodology heat integration questions to batch processes is shown in Table 11.1. Several new questions have been introduced to consider integration at a simple level because, at present, formal heat integration of batch processes is difficult. These questions are presented in Table 11.2.

The existing questions concerning the design of piping and equipment layout are also included in this level as the decisions concerning the scheduling will have an effect on the number of equipment items and the requirements for transferring materials between equipment, thereby affecting the piping and equipment layout. These questions have not been altered and are summarised in Chapter 3.

Table 11.1: Application of the existing Douglas design heat integration questions to batch processes

Questions	Operation options	Positive points	Negative points	Notes
How far can the energy consumption of the process be economically reduced?	Exchange heat between hot and cold process streams.	Reduce demand for external energy production.	May be complicated for batch processes and incur increased capital costs for additional heat exchangers. May compromise the flexibility of the plant.	The available pinch techniques are discussed in Section 11.2 and Chapter 3.
Can the temperatures at which the heat is supplied be reduced?	Reduce utility stream temperatures.	Reduce energy demand for heating utility streams.	May limit the efficiency of heat transfer due to low temperature driving forces and subsequently limit heat integration.	-
What fuels are used to provide heat? Can alternative fuels be used and what are the additional costs?	Offsite energy production.	No onsite emissions.	Overall energy efficiency is often low due to losses in central generating plant and distribution [159].	-
	Onsite energy production.	Control own emissions and can introduce combined heat and power units.	Will add to the overall onsite process emissions.	-
	Use low emission fuels e.g.. Low sulphur or low nitrogen fuels.	Would reduce emissions of sulphur dioxide or nitrous oxides.	Fuels may be more expensive.	-
	Use incineration of process wastes as a heat source.	Reduce fresh fuel consumption and waste treatment costs.	Combustion of some wastes may be restricted by regulation. Emissions would still result and fuel may be needed to initiate combustion.	-

Table 11.2: New questions for Level 6 of the revised Douglas design methodology

Questions	Operation options	Positive points	Negative points	Notes
Can the heat transfer coefficient be improved?	Overhaul old equipment. Regular cleaning of equipment.	Ensure the walls are clean before start-up. Reduce the build-up of material and subsequently maintain the heat transfer coefficient .	Would require cleaning operation that may introduce additional waste streams. As above.	Interlinks with Chapter 10, design of cleaning system. There will be a balance between the operability of the plant, the cleaning costs and waste production.
Do any hot and cold streams occur at the same time in a batch cycle?	Match streams.	Reduce demand for external energy production.	May compromise flexibility of production. Additional costs associated with heat exchangers.	-
Are there operations where there is a high energy use and production?	Perform energy integration between these operations.	As above.	May require rescheduling or heat storage.	-
Could heat storage be used to improve the heat integration?	Use heat storage instead of rescheduling.	Allow heat exchange between streams that exist at different times.	Increased flowsheet cost and less efficient than direct heat transfer.	Interacts with the design of the process schedule.
Can new energy production techniques be used?	Techniques such as fuel cells or catalytic combustion are newly developing energy production techniques.	Reduced emissions.	At present unproven techniques but may prove useful in future applications.	-
Can process integration reduce the amount of materials such as water or solvents used?	Use pinch techniques [99].	Reduced water or solvent usage thereby reducing operating costs and emissions.	Would be more difficult to achieve for batch processes and additional storage would be required [160].	Interacts with cleaning system design.

11.3 Process scheduling

The batch process flowsheet provides the following information [161]:

- the extent to which the task is performed,
- the time requirement, and,
- the capacity requirement.

Scheduling the operations involves defining the order of the tasks and assigning tasks to vessels. The amount of material produced by the process is fixed by the expected production demand. For each task the extent, e.g. the amount of conversion or separation achieved, determines how much material results from the task per unit of raw material used and fixes the time required for the task. The limiting cycle time is the operation that takes the longest time, whereby the equipment cannot be used until the task is finished. Therefore, dividing the total available time for production by the limiting cycle time gives the total number of batches per year.

The amount of product required per batch is given by dividing the required total production amount by the number of batches per year. Consequently, the capacity of the equipment is defined by multiplying the batch size by the size factor of the equipment. The size factor is defined as the volume (or other capacity) required to process enough material to produce one unit of the final product. Hence, the size of the batch vessels is defined and the cycle times are fixed.

The inclusion of cleaning operations would be dealt with in a similar way. The extent of cleaning required is defined and this in turn defines the cost of the cleaning operations.

The new questions that have been introduced to the revised Douglas design methodology for process scheduling are presented in Table 11.3. These questions systematically follow through a scheduling procedure for a single product plant. Further details are presented in the following sections.

Table 11.3: New questions for Level 6 concerning scheduling

Question	Notes
Is there a set order of tasks or can these be altered?	Section 11.3.1
What are the task to equipment allocations?	Section 11.3.2
Are there any cycle time constraints?	Section 11.3.3
Are there any capacity limitations?	Section 11.3.4
Can any tasks be split?	Section 11.3.5
Can any tasks be merged?	Section 11.3.6
Would intermediate storage enable the schedule to be optimised?	Section 11.3.7
Can the production chain be broken down to simplify the flowsheet?	Section 11.3.8
Can the extent of the task be altered?	Section 11.3.9
Are there other factors to consider when scheduling?	Section 11.3.10

11.3.1 Is there a set order of tasks or can these be altered?

The order of the tasks would normally be defined at the previous levels in the design hierarchy. However, there may be a possibility to alter the order in some instances. For example, the material from an operation may be held until several batches have been completed and then the separation may be performed. This would limit the number of start-ups and shutdowns of the separation unit. However, the integrity of the batch would not be maintained which could be a problem in some industries such as pharmaceutical product manufacture.

11.3.2 What are the task to equipment allocations?

Once the tasks have been defined they can be allocated to equipment items. In the initial design each operation is assigned to one vessel. At this stage a diagram of the system will help the designer to visualise the flowsheet. A simple example, adapted from Rippin [162], is shown in Figure 11.2. This includes a Gantt chart that defines the length of tasks (TA) assigned to each vessel (V). The first task (TA_1) takes place in vessel (V_1) and this vessel is only partially filled as shown in Figure 11.2. After TA_1 has been completed the contents of V_1 are passed to V_2 where the second task (TA_2) is carried out. Therefore, task TA_2 cannot take place until task TA_1 has been completed. When in use vessel V2 is full to capacity. The next task (TA_3) cannot be started until TA_2 has been completed and the contents from V_2 have been transferred to V_3.

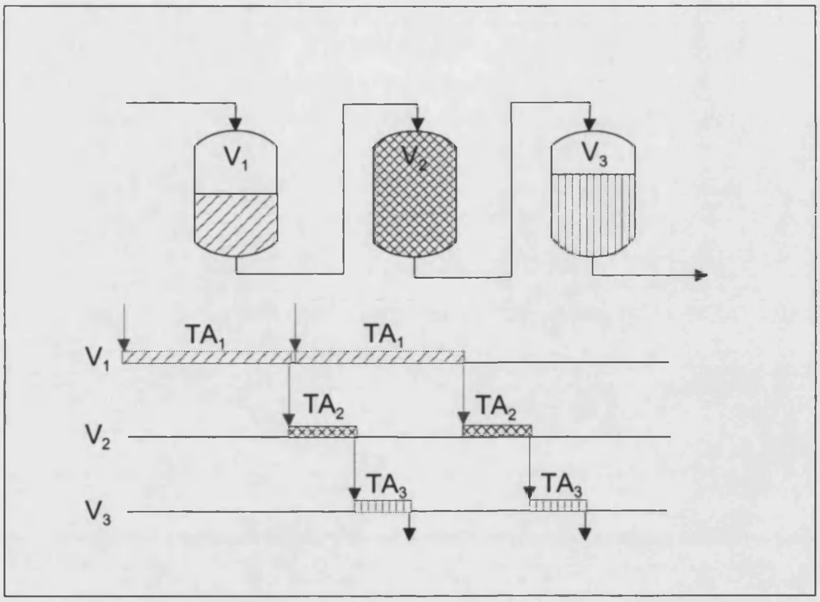


Figure 11.2: Gantt chart for a hypothetical flowsheet (adapted from Rippin [162])

11.3.3 Are there any cycle time constraints?

From Figure 11.2 it is possible to identify whether any of the operations inflict a cycle time constraint on the process. The operation taking the longest time will be the limiting task. This is task TA_1 in Figure 11.2.

11.3.4 Are there any capacity limitations?

In Figure 11.2 vessel V_2 is full and therefore represents the capacity limiting step. However, as the design fulfils the required production demand then the capacity limitations would not pose a problem. A problem may be encountered if in future the production capacity was to be increased, whereby vessel V_2 would become limiting. Consequently, the designer should consider future product demand and the required plant flexibility when calculating the size of the equipment.

11.3.5 Can any tasks be split?

Reducing the cycle time constraint identified in Section 11.3.3 could be achieved by installing a second piece of equipment and operating it out of phase with the first vessel [162]. As a result vessel V_2 could be filled from both the vessels sequentially, thereby reducing its idle time, as shown in Figure 11.3.

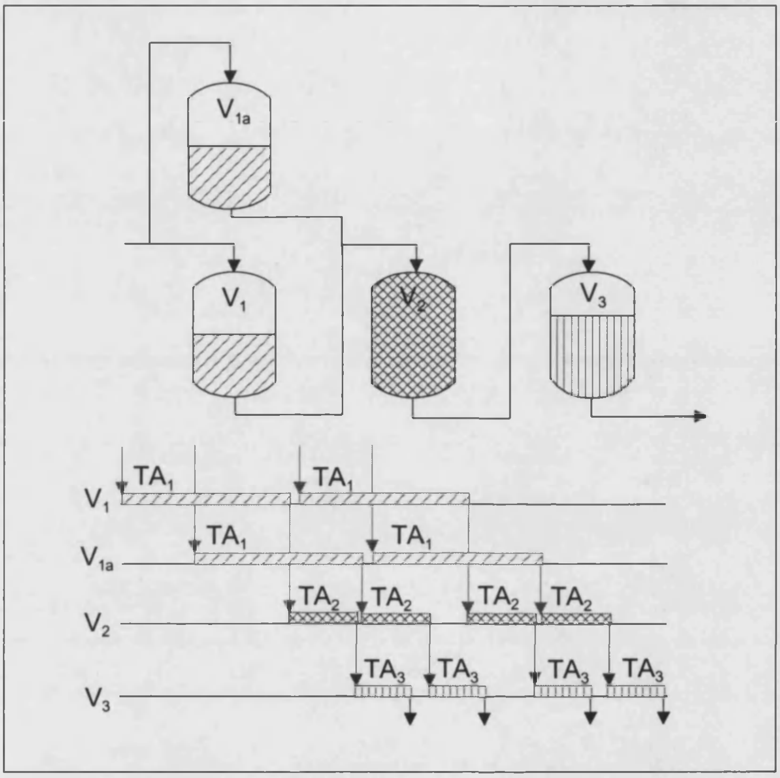


Figure 11.3: Splitting tasks to reduce the cycle time constraint (adapted from Rippin [162])

Following on from the question in Section 11.3.4, if a capacity limitation were to be identified and the equipment could not be debottlenecked then the task could be split by operating a second piece of equipment in parallel. Consequently, the product would be produced simultaneously in the two vessels, combined and passed to the next stage.

11.3.6 Can any tasks be merged?

It may be possible to merge tasks so less equipment is required [162]. For example, heating, reaction, cooling and venting operations could be performed in the same vessel sequentially. It may also be possible to merge tasks that are not sequential. For example, several vent streams could be cooled in a single heat exchanger although they may arise at different times in the production cycle. Merging tasks will not *affect* the process cycle time as long as the tasks do not *limit* the cycle time and the resulting merged cycle time does not exceed the limiting cycle time. As tasks are merged less equipment is required and subsequently the capital cost of the flowsheet is lowered.

11.3.7 Would intermediate storage enable the schedule to be optimised?

Installing intermediate storage would enable operations involving different batch sizes and frequencies to be performed in a given series of vessels [162]. For example, in Figure 11.4 installing additional storage to feed V_2 increases the number of batches that can be completed in a given time. Additionally, larger batches can be made in vessel V_1 and stored. Thus V_1 can be used to full capacity. However, installing additional storage incurs extra costs. In addition, the batch identity is lost as different batches are mixed with each other. This may not be allowed in industries where the batches need to be independent and traceable, such as in some pharmaceutical manufacturing processes.

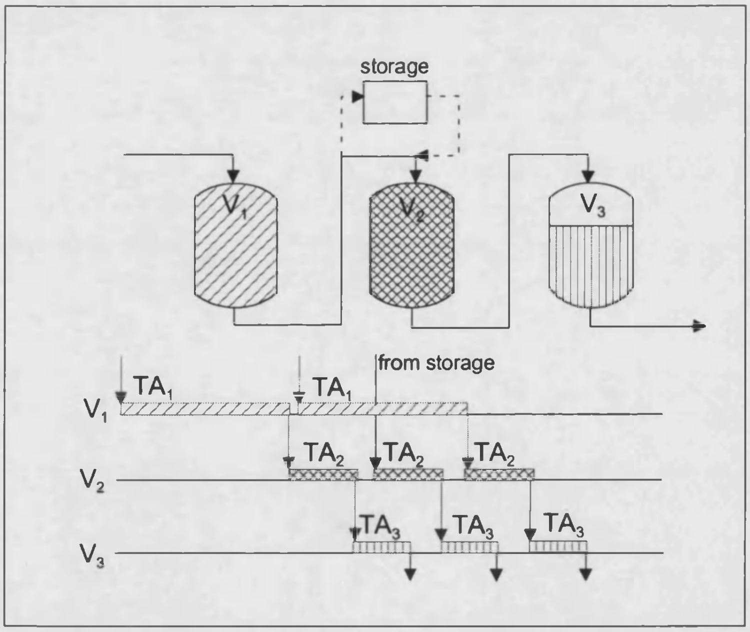


Figure 11.4: Installing intermediate storage to tighten the process schedule (adapted from Rippin [162])

11.3.8 Can the production chain be broken down to simplify the flowsheet?

For some batch processes a large number of steps are required to produce the final product [161]. The entire process may then become limited by one cycle time and this may restrict the operations. It may be beneficial to split the process into separate production lines, each operating independently with their own limiting cycle times. The intermediates from the production lines can then be stored and used as raw materials for the subsequent production steps. For example, a company manufacturing sodium chromolate has split the production chain into eight independent production lines [145].

11.3.9 Can the extent of the task be altered?

The extent of the task defines the performance of an individual process unit [161]. For example, the extent could be the amount of conversion achieved in a reactor or the degree of separation achieved in a distillation column. The extent achieved could be increased by increasing the residence time in the equipment. If the increased time was less than the limiting cycle time of the process then the amount produced per batch would be greater for that unit and therefore less capacity would be required, thereby reducing the equipment costs. There is no point in reducing the residence time if it is not limiting the process. Increasing the extent of cleaning and maintenance would usually increase the time required for these operations, thereby reducing the available production time. Consequently, the capacity of the batches would need to be increased to fulfil the production requirements, thereby increasing the equipment costs. It should be possible to trade-off the extent of performance with the required time and capacity of the units.

11.3.10 Are there other factors to consider when scheduling?

Scheduling of the operations may be required to facilitate heat integration between streams. It may be possible to arrange the operations so that hot and cold streams occur at the same time within the production cycle. If the heat integration opportunities are significant then two parallel operations could be installed and operated out of step, thereby allowing heat to be exchanged between the hot and cold streams. There will be a trade-off between additional equipment costs and the reduction in utility costs due to increased heat integration. A similar case might be identified for reusing material streams such as water or solvents.

11.4 Cost and environmental assessment

As in the previous design levels the flowsheet costs are represented by an economic potential (EP). The analysis of process integration and scheduling may alter the number of equipment units, the heating requirements and the equipment sizes. Therefore, there is close interaction between the design of the process schedule and the previous design levels. Hence, the flowsheet costs may change if changes are made to the process schedule and/or the equipment design. For example, if several tasks, such as heating the reactants, performing the reaction and product cooling, were to be merged into one unit the reactor design may need to be reconsidered. The amount of material produced would remain fixed and hence the value of the product would be unchanged. However, the EP will change due to the change in the flowsheet costs resulting from process integration and scheduling. Therefore the economic potential has been defined as EP_6 minus any additional costs, plus any cost savings as follows:

$$EP_7 = EP_6 - \text{additional costs} + \text{cost savings (£/yr)} \tag{11.1}$$

A useful tool at this stage would be a cost diagram of the units and operations of the entire flowsheet. This would allow the high cost units and operations to be easily identified.

In the revised methodology the EPPT score is also assessed for the process. At the scheduling stage the wastes released may be altered by changing the extent to which each of the tasks is performed or by improving the process integration so reducing the need for energy production or fresh materials. The EPPT score for Level 7 of the revised process is as follows:

$$(\text{EPPT score})_6 = (\text{EPPT score})_5 + \text{additional environmental impact} - \text{reduced environmental impact} \tag{11.2}$$

11.5 Summary

Level 7 of the revised Douglas design methodology considers process integration and the design of the process schedule. New questions applying specifically to single product batch processes have been added to the methodology. The complete set of questions is summarised in Table 11.4.

Table 11.4: Summary of questions for Level 7 of the revised Douglas methodology

Existing questions for waste minimisation
How far can the energy consumption of the process be economically reduced? Can the temperature levels at which heat is supplied be reduced? What fuels are used to provide heat? Are alternative fuels available and if so at what costs?
New questions for process integration
Can the heat transfer coefficient be improved? Do any hot and cold streams occur at the same time in the batch cycle? Are there operations where there is a high energy use or production? Could heat storage be used to improve the heat integration? Can new energy production techniques be used? Can process integration reduce the amount of materials such as water or solvents used?
New questions for scheduling
Is there a set order of tasks or can these be altered? What are the task to equipment allocations? Are there any cycle time constraints? Are there any capacity limitations? Can any tasks be split? Can any tasks be merged? Would intermediate storage enable the schedule to be optimised? Can the production chain be broken down to simplify the flowsheet? Can the extent of the task be altered? Are there other factors to consider when scheduling?

Chapter Twelve

Conclusions and Future Work

12.1 Conclusions

The current UK regulations require the operator of a new chemical process to demonstrate that the chosen design is the Best Practicable Environmental Option (BPEO) and to implement the Best Available Techniques Not Entailing Excess Cost (BATNEEC). Therefore, the designer not only needs to provide a process design that is economically viable but that also complies with environmental regulations. In order to ensure that a design is economical and fulfils the regulatory requirements the process design task must include consideration of pollution prevention and the environment at an early stage. As a result potential environmental or waste problems can be identified at a stage where alternative process designs can be proposed to avoid or mitigate the problem, thereby reducing the need for "end-of-pipe" technologies. "End-of-pipe" technologies such as scrubbers or incinerators are often expensive, increasing both the capital and operating costs of the plant and often fail to solve the environmental problem because emissions are shifted from one medium to another.

The interaction between the three areas of process design, pollution prevention and the environment are shown in Figure 12.1. The main area of interest of this work is the shaded overlap between the three.

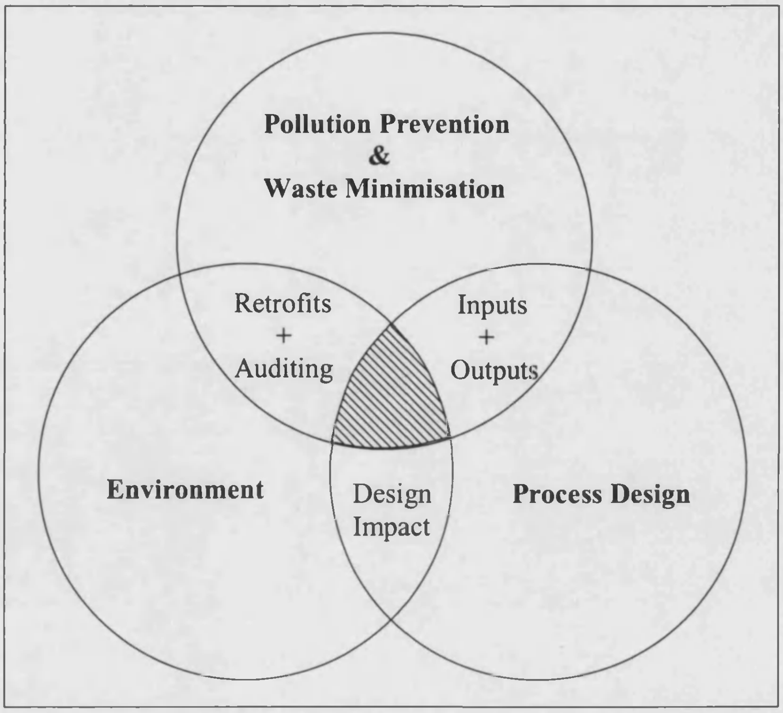


Figure 12.1: Relationship between process design, pollution prevention and the environment

A review of existing design techniques and methodologies has shown that none adequately combine the three areas. It was also found that there was a need for a structured design methodology specifically for batch processes. This thesis has described the development of a design methodology for batch processes to fulfil this need, combining environmental assessment, process design and waste minimisation. The methodology developed is an extension of the Douglas hierarchical design methodology and it will aid with the development of inherently clean and economically viable, batch process plants.

There were several reasons for choosing the Douglas hierarchical design methodology as the basis for the methodology presented in this thesis. These are as follows:

- it is a highly structured but flexible method for design that encompasses the entire process,
- it provides a clear picture of the design economics,
- it has already been successfully extended to waste minimisation, and,
- it has the flexibility to be extended to batch processes.

The Douglas methodology has previously been used for batch process design [90]. However, the approach was based heavily on the continuous process design methodology and requires a continuous process to be designed initially. Each continuous unit is systematically replaced with a batch unit. If the flowsheet cost is reduced then the batch unit is selected, otherwise the continuous unit remains. Consequently, it was found that a number of areas crucial to batch process design are not considered and the designer would not be able to consider all the waste problems associated with individual batch operations. As a result a new extension has been developed and this has been presented in this thesis.

Figure 12.2 shows the design levels for the existing version of the Douglas methodology alongside the revised methodology for batch process design. The design levels that have been extended or added are highlighted.

A summary of the alterations that have been made to each of the design levels is presented in the following sections.

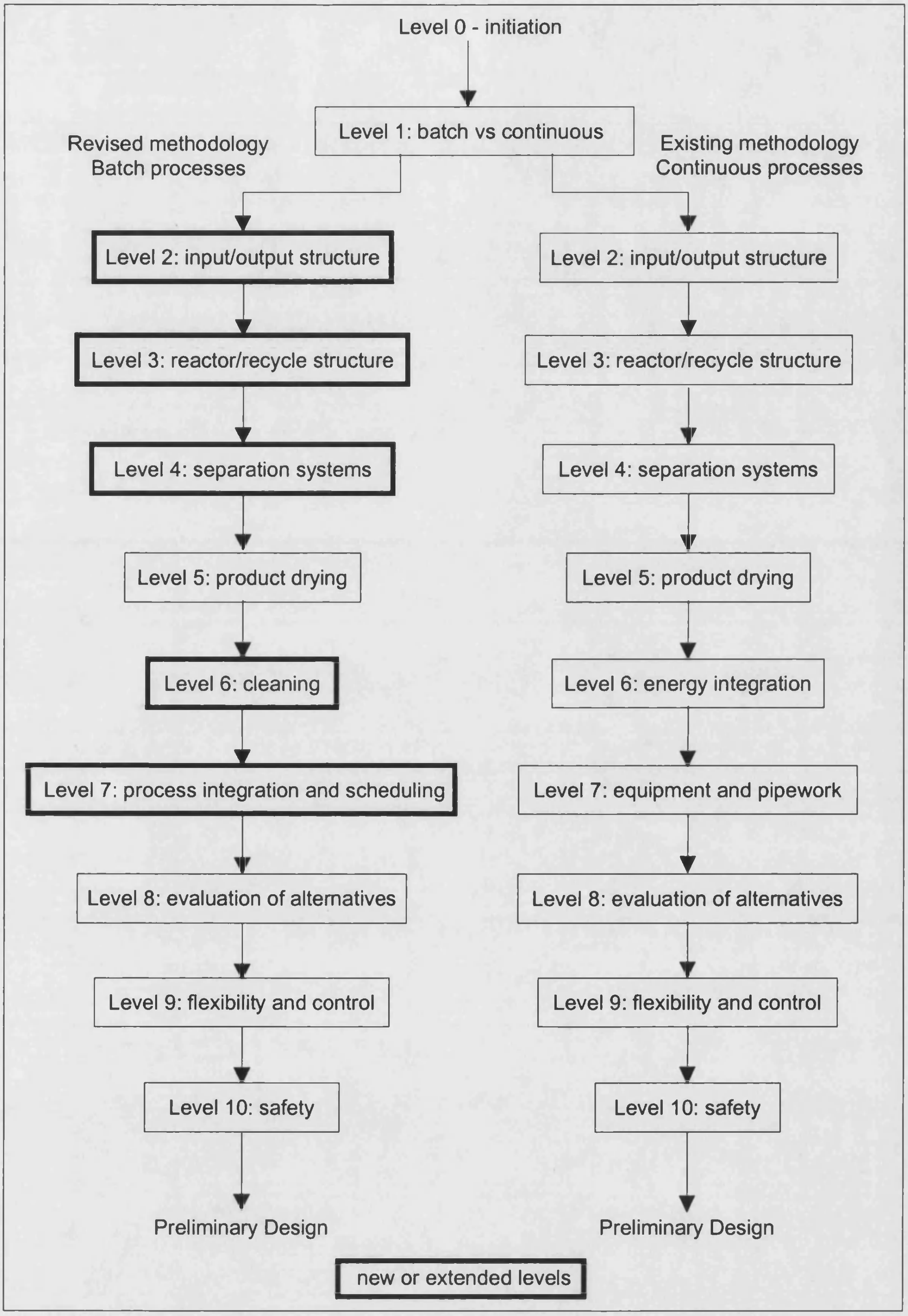


Figure 12.2: Existing and revised Douglas design methodology

Level 1 has not been altered in this work because it deals with the choice between batch and continuous operations and did not need updating. Level 5, product drying has also not been altered as the overall design choices would be similar for both batch and continuous processes. Piping design and the definition of the equipment layout have been included in Level 7, the scheduling considerations. The other levels have not been considered in detail.

It should be recognised that the Douglas design methodology is not a static activity and design levels will normally need to be revisited if problems are highlighted at a subsequent design level. Therefore, there is likely to be a large amount of interaction between the design levels. For example, when the process schedule is designed it may be possible to merge operations into one vessel, thereby requiring the redesign of equipment.

12.1.1 Level 2: Input/output

Level 2 provides a general overview of the process and helps to identify any waste streams that will be generated.

New questions have been added to this level in order to include considerations such as the mode of operation, the number of products required and the operational flexibility required. Questions have also been added concerning waste production and these could be applied to continuous process design as well as batch processes. For example, do any of the materials have restricted use or cause fouling problems?

The existing Douglas design questions have been retained in the revised methodology. However, in some cases the application of these questions to batch processes differs from continuous processes. For example, in a batch process recycling materials can be achieved between different batches, different product lines or different processes and therefore all combinations need to be considered.

12.1.2 Level 3: Reactor/recycle

Level 3 considers the design of the reactor with the aim of defining the amount of recycle required and of sizing and costing the reactor vessels.

The design of a batch reactor needs to consider the specification of the individual operations as well as the design of the units. The different operations, such as charging, heating, performing a reaction etc., are likely to result in emissions of different materials, different release amounts and varying durations. In order to consider each operation separately the reactor design has been divided into the following operational groups:

- material transfer,
- heat transfer,
- reaction, and,
- gaseous operations.

The existing Level 3 Douglas design questions have been retained in the revised methodology. These existing questions deal exclusively with the reaction because this was considered by Douglas the major operation in a continuous process.

New questions have been added to consider each of the operational groups. A number of these new questions have been tested using a simulation of a process manufacturing Pepton. It was found that the new questions enabled the environmental and economic viability of the process design to be examined and would aid the designer in reducing process wastes.

12.1.3 Level 4: Separation system

Level 4 of the Douglas design methodology focuses on the design of the separation system. Consideration of the separation system was found to be similar for both continuous and batch processes. Therefore, the existing Douglas design questions for continuous processes have been retained in the revised methodology. New questions have been introduced to consider the following points:

- whether the separation system should be operated batchwise, directly from the process, or continuously from a holding tank,
- how much energy is required for the separation, and,
- whether any novel technologies could be utilised to reduce the environmental impact.

A batch separation system used during the manufacture of Pepton has been simulated within HYSYS (a commercial simulation package). The simulation has been used to identify the process parameters that are important to the production of waste from the separation process. These process parameters were then altered to assess the effect this would have on the emissions from the process. It was found that the present batch separation was being operated in the most appropriate way within the limits imposed by the nature of the product and the existing equipment.

A second case study examining the introduction of an additional separation stage to remove a waste by-product was also performed using a simulation of the Pepton process. It was found that the by-product resulted from a feed impurity reacting during the final reaction phase. Therefore, removing the impurity before this final phase would eliminate the by-product. Two methods of separation were examined: (i) steam stripping before the final reaction phase, and, (ii) separation of the feed impurity before entering the process.

12.1.4 Level 6: Cleaning system

Cleaning is an important operation to consider whilst designing a batch process because it is often required between each batch, between batches of different material or if operational problems occur due to fouling. Cleaning contributes to the overall costs of the process design in terms of the capital costs for the cleaning equipment, the operating costs of buying in solvents or water and the cost of using energy to operate the system. In addition, cleaning may have an impact on the environment due to the release of materials such as volatile solvents or contaminated fluids.

Therefore, an additional level has been introduced to the revised methodology regarding the design of the cleaning system. The questions that have been developed focus on minimising the amount of cleaning fluid used, reducing the possibility of releasing material to the atmosphere and reducing the energy required for cleaning.

During the manufacture of PVC cleaning is required after every batch. The PVC cleaning operation has been used to assess the effect changes in the operation would have on the cost and environmental impact of the process.

12.1.5 Level 7: Process integration and scheduling

Consideration of heat integration has been extended to include process integration, whereby process streams can be used in different operations as well as being used for exchanging heat. Scheduling has been included at Level 7 because it is usually the last stage required for designing a batch process and it could be used to increase the opportunities for process integration. Piping and equipment layout has also been included at Level 7.

The existing Douglas design methodology heat integration questions have been retained for batch processes. Several new questions have been introduced that consider integration at a simple level, because, at present formal heat integration of batch processes is difficult.

The questions that have been added to the revised Douglas design methodology for process scheduling systematically consider scheduling for a single product plant. Questions relating to multi-product plants have not been developed and would be the subject of future work.

12.1.6 Cost estimation and environmental assessment

During the design of a new process it is necessary for the designer to ensure that the selected flowsheet will be economically viable. To assess the costs of a process flowsheet, Douglas devised an economic potential (EP). The EP consists of the major flowsheet cost items and for waste minimisation includes estimations of waste disposal costs, i.e. landfill costs for solid wastes or sewage treatment costs for liquids. In extending the methodology Douglas' EPs have been used. However, new factors have been introduced that are particularly important to batch processes, such as the cost of intermediate storage for recycling or the cost of combining batch vessels.

As discussed previously, the designer must also assess whether the design is BPEO. Therefore, the environmental impact of the releases from the process must be assessed. In the revised methodology this has been accomplished by using an environmental process performance tool to determine an EPPT score as described by Aubrey [1].

The revised methodology provides a structured design methodology for designing inherently clean and economic batch processes by implementing waste minimisation. However, there are areas where further work would enhance the methodology and these are discussed in the next section.

12.2 Future work

Three areas of future work have been identified . These are as follows:

- further extension of the revised methodology,
- implementation of the methodology, and,
- using the methodology to develop a process design.

12.2.1 Extension of revised methodology

12.2.1.1 Multi-product plants

The revision and extension of the Douglas design methodology presented in this thesis has been developed for single product batch processes. The next stage would be to extend the methodology to multi-product plants, wherein numerous products are produced sometimes in the same equipment and the product demand may fluctuate with time. Therefore, the design and flexibility of both the equipment and the schedule must be able to accommodate these characteristics.

In order to adapt the design to multi-product plants several of the design levels would require alteration. In particular, Level 7, the consideration of process integration and the design of the process schedule would need to be extended and additional design questions would be required. Several researchers are working on the optimisation of multi-product plant schedules by minimising energy usage and the amount of cleaning fluid used [163, 164, 103, 130]. These techniques could be used to develop further questions for the revised Douglas methodology. An excellent summary of the different approaches to multi-product batch process scheduling is given by Reklaitis [34].

12.2.1.2 Analysis of the cleaning system design

In this thesis the analysis of the PVC cleaning operations has been limited by the lack of experimental data available. If more data were known a more detailed cleaning study could have been carried out enabling the cleaning operations to be optimised. Additionally, it would have been possible to examine the trade-off, in terms of cost and environmental impact, between parameters such as increasing the cleaning efficiency versus increasing the energy used. New design questions may result from such a study and these could be used to further extend the revised methodology.

12.2.1.3 Inclusion of safety considerations

Figure 12.2 shows that the consideration of safety is the last design level in both the existing and the revised Douglas design methodologies. However, recently attention has been directed towards designing inherently safe plants, whereby the safety issues associated with the design or operation of the plant are considered at the design stage. Consequently, the potential hazards could be identified and either avoided or mitigated at source by altering the design. Therefore, a further extension of the Douglas design methodology would be to include questions regarding the safety of the design. In the revised methodology an EPPT score has been added to assess the flowsheet viability. A similar factor could be added to quantify safety such as the Mond Fire and Explosion Index or more detailed risk indices.

The resulting methodology would enable the designer to assess the environmental impact, the hazard potential, as well as the economic performance of the design. Hence, the trade-offs between the three factors could be considered and the "best" design selected.

12.2.1.4 Developing additional design questions

In this thesis several Integrated Pollution Control (IPC) applications have been examined to provide an insight into the methods that are being used by operators to reduce the environmental impact of their processes. A more detailed investigation of the batch process IPC applications would identify further examples of how process changes are being implemented in order to reduce process emissions. The data gathered from this review could be compared with the revised methodology. If the revised methodology has been formulated correctly it should cover the same areas as highlighted in the IPC review, thereby providing evidence that the revised methodology is complete or conversely, that further design questions are required. The design methodology could also be used to compare any updated operations with the original plant operations to assess whether the environmental impact of the process has actually been reduced.

12.2.1.5 Extending the dryer system design

The existing drying system design questions could be extended. A tool has been proposed by Kemp [117], whereby a computer selection procedure is used to select the most appropriate dryer depending on the material properties, the drying media, the energy requirements and the cost. Using this tool it would be possible to generate a set of standard rules for the selection of dryers that could be included in the revised design methodology. Additionally, the assessment of the environmental effects of choosing dryers could be included. If the revised methodology were to be integrated into a computer package it should be possible to include the dryer selection tool.

12.2.2 Implementation of the methodology

12.2.2.1 Development of a computer toolkit

The revised Douglas design methodology has been developed as a manual tool. However, the implementation of the methodology into a computerised toolkit would enable easy access to data, allow alternative flowsheets to be recorded, simulate process changes and also calculate the flowsheet costs, thereby expanding the usefulness and accessibility of the methodology. There are three different areas that could be developed and these are as follows:

1. Research is being performed by Han et al [165] into implementing the Douglas design methodology for continuous processes in a computerised form. As a result a computer package has been proposed that aims to provide a design support system for generating a selection of flowsheets by interaction with the process designer. In future research a similar package for the revised methodology should be developed or the Han program could be adapted to apply to batch processes.

2. As discussed in Chapter 2, a Batch Design Kit (BDK) has been developed for the design of batch processes [84]. Recently, the BDK has been bought by AEA Technology to be developed into a commercial package [21]. It is expected that the BDK will be included in the HYSYS process simulator to allow process changes to be analysed during the design development. However, at present the BDK contains no guidance to the designer as to which design areas are important to consider and does not provide a structured design methodology. Additionally, the assessment of the environmental impact of emissions is inadequate. The revised Douglas methodology presented in this thesis has concentrated on overcoming such inadequacies in the existing methodologies. It is considered that the revised Douglas design methodology and the BDK are complementary and combining the two would enhance both methodologies. In addition, the simulation package would require better standardised models to simulate batch process operations including cleaning models and scheduling tools because at present the EA Technology package (HYSYS) does not contain such models.

3. The revised design methodology could be integrated with a design tool such as the Knowledge Based Design Support tool (KBDS) [28]. Presently, KBDS is a decision recording tool, whereby the design rationale is stored and the reasons for selecting one design over another are recorded. In future KBDS could be used as a learning tool. For example, a problem may occur at a late stage in the process development that is the result of a decision taken at an earlier stage. KBDS could trace the decision back to its source allowing the designer to learn from this mistake. The Douglas design methodology could be integrated with KBDS and the design questions would be enhanced by the lessons learnt, resulting in the evolution of a specific structured design methodology and design recording tool.

12.2.2.2 Integration of the methodology and the environmental impact assessment

As described previously the revised methodology includes an assessment of the environmental impact of the process. This has made it possible to compare different designs and select the BPEO. However, at present the combination of the environmental impact assessment with the design methodology is manual and each release is assessed separately using the Environmental Process Performance Tool (EPPT) [1]. It would be useful to integrate these two methodologies and this could be done using the computer toolkit approaches described in the previous section.

A further development would be to apply the EPPT to each of the Douglas design levels. For example, at the lower levels, where the information on the emissions is sparse only a course environmental assessment is required, whereas at the later levels more details are known and the environmental assessment would need to become more detailed.

12.2.3 Applying the methodology

The most interesting area for future work would be to utilise the revised methodology to produce a process design. The development of the revised Douglas design methodology for batch processes has been based on literature and case studies rather than on operational experience. Therefore, there may be areas that have not been adequately covered. Using the methodology to develop a process design may identify the areas where additional design questions are required.

The testing could be performed by an operating company making alterations to a present design or by an engineering contractor developing a new plant design. However, it would also be beneficial to compare the designs created with and without the methodology to assess whether the methodology creates “better” designs and improves the effectiveness of the design effort. This could be achieved using either of the following two methods:

1. The methodology could be introduced to undergraduates for use during their design projects. It would then be possible to compare the resulting designs to those created in previous years. Additionally, feed back could be obtained from the students as to the usefulness of the methodology.
2. An existing process could be redesigned using the methodology and the resulting design could be compared with the existing design, in terms of cost, operability and environmental impact.

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Appendix A

Definition of terms

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A.1 Waste

Section 75 of the Environmental Protection Act (1990) defines waste as:

- any substance which constitutes a scrap material or other unwanted surplus substance arising from the application of a process; and,
- any substance or article which requires to be disposed of as being broken, worn out, contaminated or otherwise spoiled.

This definition includes [47]:

- liquids or solid wastes from a process,
- contaminated materials,
- off-specification products,
- accidental spillages and associated cleaning material,
- machine/finishing residues,
- fugitive emissions,
- gaseous discharges.

A.2 End-of-pipe technologies

End-of-pipe technologies are those that are used to treat or mitigate releases from process. The techniques include the following:

- incineration,
- detoxification,
- decomposition,
- solidification,
- dilution.

End-of-pipe technologies involve moving waste from one media to another and therefore are not considered as waste minimisation techniques.

A.3 Waste minimisation

Waste minimisation involves any technique, process or activity which either avoids, eliminates or reduces a waste at its source, usually within the confines of the production unit, or allows reuse or recycling of the waste for benign purposes [47]. Other terms that are used are:

- waste reduction,
- clean or cleaner technologies,
- pollution prevention/reduction,
- environmental technologies,
- low and non-waste technologies.

A.4 Inherently clean processes

An inherently clean process is one that has been designed to reduce its environmental impact. The potential environmental problems have been identified early in the design phase and an alternative has been developed to avoid the problem. If a process is inherently clean the environmental impact and the amount of wastes should have been reduced and the requirement of end-of-pipe technologies will be reduced.

A.5 Sustainable development

Sustainable development is defined as development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs [10].

A.6 The environment

The word environment prompts wide interpretations. Two adequate definitions are as follows:

1) EC Directive 85/337 [166]

  - human beings, flora and fauna,
  - soil, water, air, climate and the landscape,
  - the interaction of the above,
  - material assets and cultural heritage

2) BS 7750

The surroundings and conditions in which an organisation operates including living systems (human and other) therein. As the environmental effects of the organisation may reach all parts of the world, the environment in this context, extends from the workplace to the global system.

A.7 Pollution

"Pollution means the introduction by man, directly or indirectly, of substances or energy into the environment resulting in deleterious effects of such a nature as to endanger human health, harming living resources and ecosystems, and impair or interfere with amenities and other legitimate uses of the environment." [167]

A.8 BATNEEC

Best Available Techniques Not Entailing Excessive Cost required under the Environmental Protection Act 1990. BATNEEC seeks to balance the requirement to use state of the art technology and processes to minimise, reduce or render harmless emissions with the cost of doing so.

A.9 BPEO

The Best Practicable Environmental Option must be demonstrated under Integrated Pollution Control requirements. BPEO includes the assessment of discharges to air, water and land, to minimise damage or provide the best benefit to the environment as a whole, in the long-term and short-term.

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B.1 Definition of terms

Table B.1 defines the terms used for the modelling. The relationship between the parameters is indicated. A campaign is the time to reach the point where jet cleaning is required. A cycle is the operation of one full batch and is the sum of the reaction and cleaning times. The development of these relationships is detailed in the following sections.

Table B.1: Definition of parameters used in the cleaning models

Definition	Parameter	Relationship	Units
deposit thickness after n batches	x_{dn}	-	mm
deposit thickness after 1 batch	x_{d1}	-	mm
deposit remaining after n batches	x_{rn}	-	mm
deposit remaining after 1 batch	x_{r1}	-	mm
final deposit thickness at shutdown for jetting	X_t	-	mm
actual deposit thickness at shutdown for jetting	X_{ta}	-	mm
time for deposit build-up ie batch operating time	t_d	-	hr
time for deposit removal ie intermediate cleaning time	t_r	-	hr
total batch cycle time; sum of operating and cleaning times	t_c	$t_d + t_r$	hr
time for jet cleaning	t_j	-	hr
total time shutdown for maintenance in each campaign	t_{sd}	-	hr
time for annual shutdown	T_{sd}	-	hr
total cleaning time per campaign	T_r	-	hr
rate of deposit build-up, assumed linear and constant	a	x_{d1}/ t_d	mm/hr
effectiveness of cleaning, assumed linear. Two cases examined; b constant and b varying with deposit thickness	b	$(x_{dn} - x_{rn})/ t_r$	mm/hr
change in effectiveness of cleaning	c	$c = [b/(n_f - 1)]_{\text{model 1}}$	-
number of batches completed	n	-	batches completed
number of batches in one campaign ie before shutdown for jet cleaning.	n_f	expressions developed in following sections	batches/campaign
number of batches in one campaign with no intermediate cleaning.	n_{nc}	-	batches/campaign
number of campaigns in a year	N	expressions developed in following sections	campaigns/yr
amount of product per batch	p	-	te/batch

Definition	Parameter	Relationship	Units
number of reactors	R	-	-
total amount of product per year	P	$pNRn_f$	te/yr
volumetric flowrate of water used for intermediate cleaning operations	F_r	-	m^3/hr
volumetric flowrate of water used during jet cleaning	F_j	-	m^3/hr
total volume of water used per year	W	$NR(n_f F_r t_r + F_j t_j)$	m^3/yr
volume of water used for intermediate rinsing per year	w_r	$NRn_f F_r t_r$	m^3/yr
volume of water used for jetting per year	w_j	$NRF_j t_j$	m^3/yr
value of product	V	-	£/te
total value of product produced	V_p	PV	£/yr
cost of water	c_w	-	$£/m^3$
cost of rinsing water	c_r	-	£/clean
cost of one jet cleaning operation	c_{jc}	-	£/clean
estimated cost of recovering VCM that is purged from the vessel before opening for jet cleaning	c_{vcm}	-	£/opening
cost of the energy used for low pressure cleaning cycle for one reactor	e_{lp}	-	£/clean
cost of the energy used for high pressure cleaning cycle for one reactor	e_{hp}	-	£/clean
cost of the energy used for jet cleaning one reactor	e_j	-	£/operation
total cost of water used for intermediate cleaning	C_{wr}	$c_w w_r$	£/yr
total cost of water used for jetting	C_{wj}	$c_w w_j$	£/yr
total cost jet cleaning contractors	C_{jc}	$c_{jc} NR$	£/yr
total cost of energy used for intermediate cleaning	C_{er}	$NRn_f(e_{lp} + e_{hp})$	£/yr
total cost of energy used for jet cleaning	C_{ej}	NRe_j	£/yr
total cost of removing VCM from the vessel	C_{vcm}	NRc_{vcm}	£/yr
surface area of vessel	A	-	m^2
density of PVC deposit	ρ	-	kg/m^3
value of lost product per year.	C_d	$AX_t \rho RV$	£/yr
total cost intermediate rinsing	C_r	$C_{wr} + C_{er}$	£/yr
total cost jet cleaning	C_j	$C_{wj} + C_{ej} + C_{jc} + C_{vcm}$	£/yr
total cost of cleaning operations	C_t	$C_r + C_j + C_d$	£/yr

B.2 Model 1: linear build-up and linear removal

The following assumptions have been made in developing model 1:

- the deposit build-up is linear with time,
- the removal rate of deposit is linear with time and does not vary during production campaign,
- the operating and cleaning times remain constant during the production campaign.

A graph of a hypothetical deposition profile for 1 campaign is shown in Figure B.1.

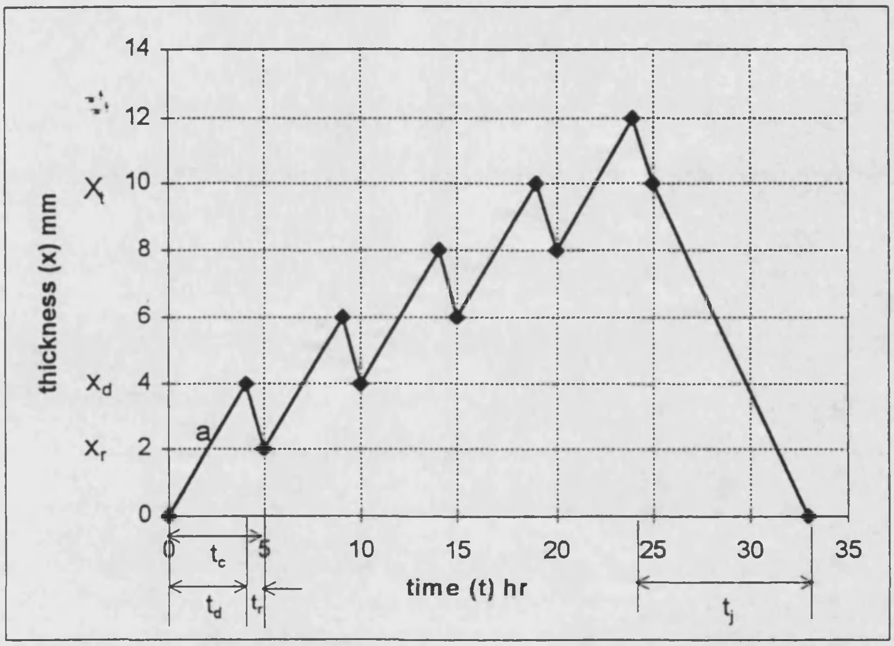

Figure B.1: Hypothetical profile for model 1

For the build-up of deposit:

$$\frac{dx}{dt} = a \tag{B.2.1}$$

For removal of deposit:

$$\frac{dx}{dt} = -b \tag{B.2.2}$$

Integrating both these expressions:

$$\int_0^{xd} dx = \int_0^{td} a dt \tag{B.2.3}$$

$$x_d = at_d \tag{B.2.4}$$

and:

$$\int_{xd}^{xr} dx = -\int_{td}^{tc} bdt \tag{B.2.5}$$

$$x_r - x_d = -b(t_c - t_d) \tag{B.2.6}$$

$$x_r - x_d = -bt_c + bt_d \tag{B.2.7}$$

$$x_r = x_d - b(t_c - t_d) \tag{B.2.8}$$

But:

$$(t_c - t_d) = t_r \tag{B.2.9}$$

Therefore:

$$x_r = x_d - bt_r \tag{B.2.10}$$

For the first cycle the build-up and removal of deposit can be expressed as:

$$x_{d1} = at_d \tag{B.2.11}$$

$$x_{r1} = x_{d1} - bt_r \tag{B.2.12}$$

With constant build-up and cleaning time for each cycle the thicknesses for the second cycle are:

$$x_{d2} = x_{r1} + x_{d1} = x_{d1} - bt_r + x_{d1} = 2x_{d1} - bt_r \tag{B.2.13}$$

$$x_{r2} = x_{d2} - bt_r = 2x_{d1} - 2bt_r \tag{B.2.14}$$

For the thickness after n cycles the expressions become:

$$x_{dn} = nx_{d1} - (n-1)bt_r \tag{B.2.15}$$

$$x_{rn} = nx_{d1} - nbt_r \tag{B.2.16}$$

$$x_{rn} = n(x_{d1} - bt_{r1}) \tag{B.2.17}$$

The parameters x_{d1}, t_d and t_r are constant for model 1 and substituting from Equation (2.1.11):

$$x_{rn} = nx_{r1} \tag{B.2.18}$$

The final thickness of the deposit at the end of the campaign is X_t. The total number of cycle completed is n_f. Assuming the last rinse is carried out before jetting the final thickness is:

$$x_{rnf} = X_t \tag{B.2.19}$$

Substituting X_t into Equation (B.2.18) gives:

$$X_t = n_f x_{r1} \tag{B.2.20}$$

$$n_f = X_t / x_{r1} \tag{B.2.21}$$

The number of campaigns (N) in a year is the time available for production divided by the total time for a campaign. The production time is the number of hours in a year minus the annual shutdown time. The total time for a campaign is the sum of the cycle times, the jet cleaning time and the shut-down time for maintenance. The expression is as follows:

$$N = (8760 - T_{sd})/(n_f t_c + t_j + t_{sd}) \tag{B.2.22}$$

The total amount of water used for cleaning per year (W) is the number of campaigns multiplied by the water used in each campaign. The water used in a campaign is the sum of the amounts for intermediate cleaning and jet cleaning. Assuming that a constant flowrate of water is used for each clean and that the cleaning times are equal for each cycle, the expression for the total water used is:

$$W = NR(n_f F_r t_r + F_j t_j) \tag{B.2.23}$$

The total product (P) is the amount produced per cycle (p) multiplied by the number of cycles (n_f), the number of campaigns (N) and the number of reactors (R) as follows:

$$P = NpRn_f \tag{B.2.24}$$

B.3 Model 2: Decreasing cleaning effectiveness

In this case the effectiveness of the intermediate cleaning, b, decreases as the cycle continues and the deposit builds-up. The change in b, factor c, is assumed to be linear with the number of cycles. Therefore:

$$b_n = b_1 - (n-1)c \tag{B.3.1}$$

At the final thickness (X_t) cleaning is ineffective and b equals zero:

$$0 = b_1 - (n_f - 1)c \tag{B.3.2}$$

$$c = b_1/(n_f - 1) \tag{B.3.3}$$

Two cases have been considered:

a) the time for cleaning was constant and the deposit remaining after the intermediate cleaning increased for each cycle,

b) the cleaning time was increased as the cleaning became less effective. In this way the amount of deposit removed remained constant.

These two cases are detailed in the following sections.

B.3.1 Model 2a: Decreasing cleaning effectiveness with constant cleaning time

In this first case the effectiveness of cleaning was assumed to decrease but the cleaning time remained constant. Figure B.2 shows the deposit build-up for one campaign. As the cleaning became less effective less material was removed. Therefore, the final thickness (X_t) was reached sooner and less cycles were completed in one campaign than for model 1. The change in the slope of the cleaning line (c) was estimated from model 1 using Equation (B.3.1). This ensured that b became zero at X_t using model 1 data. However, as b decreased during the campaign less cycles were completed and b did not equal zero at the same value of X_t as model 1.

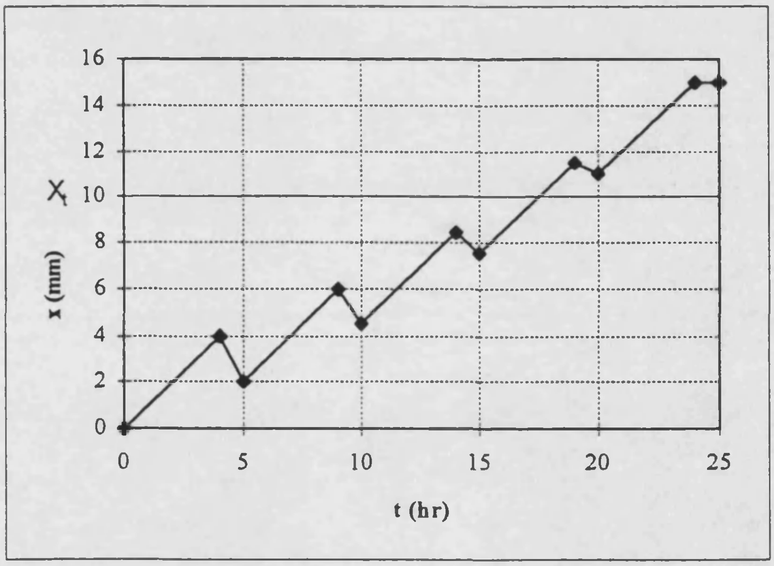

Figure B.2: Deposit build-up for Model 2a with constant clean time

For the deposit build-up in the first cycle:

$$x_{d1} = at_d \quad (B.3.4)$$

$$x_{r1} = x_{d1} - b_1 t_r \quad (B.3.5)$$

Assuming the deposition rate is constant the thickness of deposit for the second cycle is:

$$x_{d2} = x_{r1} + x_{d1} \tag{B.3.6}$$

$$x_{d2} = x_{d1} - b_1 t_r + x_d \tag{B.3.7}$$

$$x_{d2} = 2x_d - b_1 t_r \tag{B.3.8}$$

For the second cycle (n=2) the removal rate changes to b_2 but the cleaning time, t_r remains constant:

$$x_{r2} = x_{d2} - b_2 t_r \tag{B.3.9}$$

Substituting for x_{d2} from Equation (B.3.8):

$$\therefore \quad x_{r2} = 2x_{d1} - b_1 t_r - b_2 t_r \tag{B.3.10}$$

However from Equation (B.3.1) for n=2:

$$b_2 = (b_1 - c) \tag{B.3.11}$$

Substituting b_2 into Equation (B.3.10):

$$x_{r2} = 2x_{d1} - b_1 t_r - (b_1 - c)t_r \tag{B.3.12}$$

$$x_{r2} = 2x_{d1} - b_1 t_r - b_1 t_r + ct_r \tag{B.3.13}$$

$$x_{r2} = 2x_{d1} - 2b_1 t_r + ct_r \tag{B.3.14}$$

Continuing similarly for the third cycle (n=3):

$$x_{d3} = x_{r2} + x_d \tag{B.3.15}$$

$$x_{d3} = 3x_{d1} - 2b_1 t_r + ct_r \tag{B.3.16}$$

and:

$$x_{r3} = x_{d3} - b_3 t_r \tag{B.3.17}$$

$$x_{r3} = 3x_{d1} - 2b_1 t_r + ct_r - b_3 t_r \tag{B.3.18}$$

From Equation (B.3.1):

$$b_3 = (b_1 - 2c) \tag{B.3.19}$$

$$x_{r3} = 3x_{d1} - 2b_1 t_r + ct_r - (b_1 - 2c)t_r \tag{B.3.20}$$

$$x_{r3} = 3x_{d1} - 3b_1 t_r + 3ct_r \tag{B.3.21}$$

For subsequent cycles:

$$x_{d4} = 4x_{d1} - 3b_1 t_r + 3ct_r \tag{B.3.22}$$

$$x_{r4} = 4x_{d1} - 4b_1 t_r + 6ct_r \tag{B.3.23}$$

$$x_{d5} = 5x_{d1} - 4b_1 t_r + 6ct_r \qquad (B.3.24)$$

$$x_{r5} = 5x_{d1} - 5b_1 t_r + 10ct_r \qquad (B.3.25)$$

Therefore expanding the series for c, the generalised form of these expressions is:

$$x_{dn} = nx_{d1} - (n-1)b_1 t_r + \frac{c(n-1)(n-2)t_r}{2} \qquad (B.3.26)$$

$$x_{rn} = nx_{d1} - nb_1 t_r + \frac{cn(n-1)t_r}{2} \qquad (B.3.27)$$

For the final cycle $n = n_f$ and $x_{r1} = X_t$:

$$n_f^2 ct_r/2 + n_f(x_{d1} - b_1 t_r - ct_r/2) - X_t = 0 \qquad (B.3.28)$$

Solving for n_f:

$$n_f = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \qquad (B.3.29)$$

Where A, B and C are the roots of the quadratic equation:

$$A = ct_r/2 \qquad (B.3.30)$$

$$B = (-ct_r/2 - b_1 t_r + x_{d1}) \qquad (B.3.31)$$

$$C = -X_t \qquad (B.3.32)$$

The expressions for N, P and W are the same as for model 1 and are given in Section B.2.

B.3.2 Model 2b: Decreasing cleaning effectiveness with constant amount of deposit removed and varying cleaning time

For the previous model the deposit removed from the vessel decreased as effectiveness of cleaning decreased. In order to remove the same amount of deposit for each cycle the cleaning time must be increased. Figure B.3 shows the profile for such a case.

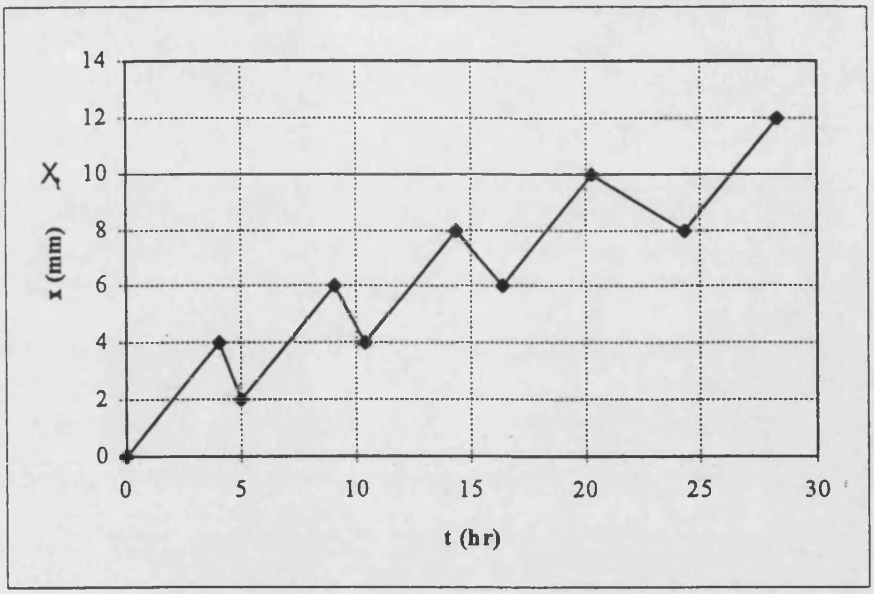

Figure B.3: Model 2b for decreasing cleaning effectiveness and varying clean time

The final rinse was not included as the cleaning had zero effectiveness and therefore infinite time would be required to remove the deposit. At this point jetting was assumed to be required.

The number of cycles in a campaign is simply:

$$n_f = X_t/x_{r1} \qquad \text{(B.3.33)}$$

The time required for cleaning needs to be calculated and the following expressions have been developed for the cleaning times of each cycle.

From previous case:

$$x_{d1} = at_d \qquad \text{(B.3.34)}$$

$$x_{r1} = x_{d1} - b_1 t_{r1} \qquad \text{(B.3.35)}$$

$$x_{d2} = 2x_{d1} - b_1 t_{r1} \qquad \text{(B.3.36)}$$

From Equation (B.3.35):

$$t_{r1} = (x_{d1} - x_{r1})/b_1 \qquad \text{(B.3.37)}$$

For the second cycle, the cleaning time (t_{r1}) varies and the thickness after cleaning (x_m) remains constant. Therefore:

$$x_{r2} = 2x_{d1} - b_1 t_{r1} - b_2 t_{r2} \qquad \text{(B.3.38)}$$

and:

$$x_{r2} = 2x_{r1} \qquad \text{(B.3.39)}$$

Substituting x_{r2} into Equation (B.3.38):

$$2x_{r1} = 2x_{d1} - b_1 t_{r1} - b_2 t_{r2} \quad \text{(B.3.40)}$$

Replacing x_{r1} from Equation (B.3.5):

$$2(x_{d1} - b_1 t_{r1}) = 2x_{d1} - b_1 t_{r1} - b_2 t_{r2} \quad \text{(B.3.41)}$$

$$2x_{d1} - 2b_1 t_{r1} = 2x_{d1} - b_1 t_{r1} - b_2 t_{r2} \quad \text{(B.3.42)}$$

$$b_2 t_{r2} = 2b_1 t_{r1} - b_1 t_{r1} \quad \text{(B.3.43)}$$

$$b_2 t_{r2} = b_1 t_{r1} \quad \text{(B.3.44)}$$

$$t_{r2} = \frac{b_1 t_{r1}}{b_2} \quad \text{(B.3.45)}$$

Substituting for t_{r1} from Equation (B.3.37):

$$t_{r2} = \frac{b_1 (x_{d1} - x_{r1})/b_1}{b_2} \quad \text{(B.3.46)}$$

$$t_{r2} = \frac{(x_{d1} - x_{r1})}{b_2} \quad \text{(B.3.47)}$$

For the next cycle (n=3):

$$x_{d3} = x_{r2} + x_{d1} \quad \text{(B.3.48)}$$

$$x_{d3} = 3x_{d1} - b_1 t_{r1} - b_2 t_{r2} \quad \text{(B.3.49)}$$

and:

$$x_{r3} = x_{d3} - b_3 t_{r3} \quad \text{(B.3.50)}$$

$$x_{r3} = 3x_{d1} - b_1 t_{r1} - b_2 t_{r2} - b_3 t_{r3} \quad \text{(B.3.51)}$$

$$x_{r3} = 3x_{r1} \quad \text{(B.3.52)}$$

$$3x_{r1} = 3x_{d1} - b_1 t_{r1} - b_2 t_{r2} - b_3 t_{r3} \quad \text{(B.3.53)}$$

Substitute for x_{r1}:

$$3(x_{d1} - b_1 t_{r1}) = 3x_{d1} - b_1 t_{r1} - b_2 t_{r2} - b_3 t_{r3} \quad \text{(B.3.54)}$$

$$3x_{d1} - 3b_1 t_{r1} = 3x_{d1} - b_1 t_{r1} - b_2 t_{r2} - b_3 t_{r3} \quad \text{(B.3.55)}$$

$$b_3 t_{r3} = 2b_1 t_{r1} - b_2 t_{r2} \quad \text{(B.3.56)}$$

$$t_{r3} = \frac{2b_1 t_{r1} - b_2 t_{r2}}{b_3} \quad \text{(B.3.57)}$$

Substituting for t_{r1}, t_{r2}:

$$t_{r3} = \frac{2b_1 (x_{d1} - x_{r1})}{b_1 b_3} - \frac{b_2 (x_{d1} - x_{r1})}{b_2 b_3} \quad \text{(B.3.58)}$$

$$t_{r3} = \frac{2(x_{d1} - x_{r1})}{b_3} - \frac{(x_{d1} - x_{r1})}{b_3} \quad \text{(B.3.59)}$$

$$t_{r3} = (x_{d1} - x_{r1})/b_3 \quad \text{(B.3.60)}$$

$$b_3 = (b_1 - 2c) \quad \text{(B.3.61)}$$

$$t_{r3} = (x_{d1} - x_{r1})/(b_1 - 2c) \quad \text{(B.3.62)}$$

For the subsequent cycle:

$$t_{r3} = (x_{d1} - x_{r1})/(b_1 - 3c) \quad \text{(B.3.63)}$$

The general expression is:

$$t_{rn} = (x_{d1} - x_{r1})/[b_1 - (n - 1)c] \quad \text{(B.3.64)}$$

The total cleaning time T_r is the sum of the cycle cleaning times:

$$T_r = t_{r1} + t_{r2} + t_{r3} \ldots\ldots + t_{c(n-1)} \quad \text{(B.3.65)}$$

$$T_r = (x_{d1}-x_{r1})/b_1 + (x_{d1}-x_{r1})/(b_1-c) + (x_{d1}-x_{r1})/(b_1-2c)\ldots\ldots(x_{d1}-x_{r1})/(b_1-(n-1)c) \quad \text{(B.3.66)}$$

This is a harmonic series and cannot be simplified.

The campaign time is the sum of the operating time, the intermediate cleaning time, the jet cleaning time and the maintenance shutdown time. The number of campaigns in a year is as follows:

$$N = (8760 - T_{sd})/(n_f t_d + T_r + t_j + t_{sd}) \quad \text{(B.3.67)}$$

The expressions for P and W are the same as for model 1 and are given in Section B.2.

B.3.3 Application to EVC Operations

Data from the EVC cleaning operations has been used to develop a more realistic cleaning model. Some parameter values were known from the plant data and others had to be estimated. The number of cycles, the batch times and cleaning times were known from the plant data. However, the thickness of the deposits and hence the slopes of deposit and cleaning lines were unknown.

In the previous case, b was taken to vary by a constant amount c which was based on the number of cycles completed. This was to ensure that b was zero at X_t. However, as b decreased during the campaign less cycles were completed and b did not equal zero at the same value of X_t as model 1. Therefore, in this case, b was taken to vary linearly with the number of cycles completed as shown in Figure B.4. The cleaning time was kept constant as for plant operations.

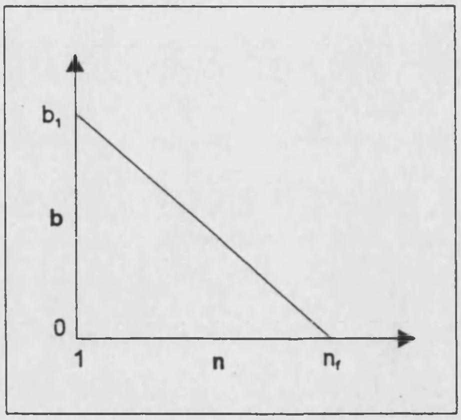

Figure B.4: b varying with n

The expression for b is:

$$b = yn + z \qquad (B.3.68)$$

When: $n = 1 \quad b = b_1$

$n = n_f \quad b = 0$

Therefore:

$$b_1 = y + z \qquad (B.3.69)$$

$$0 = n_f y + z \qquad (B.3.70)$$

From this:

$$b_1 = y(1-n_f) \qquad (B.3.71)$$

$$y = b_1/(1-n_f) \qquad (B.3.72)$$

Substituting back into Equation (B.3.69):

$$b_1 = \frac{b_1}{(1-n_f)} + z \qquad (B.3.73)$$

$$z = b_1 - \frac{b_1}{(1-n_f)} \qquad (B.3.74)$$

$$z = \frac{b_1(1-n_f) - b_1}{(1-n_f)} \qquad (B.3.75)$$

$$z = -b_1 n_f/(1-n_f) \qquad (B.3.76)$$

Substitute for y and z in Equation (B.3.68):

$$b_n = \frac{b_1 n}{(1-n_f)} - \frac{b_1 n_f}{(1-n_f)} \qquad (B.3.77)$$

Considering the build-up of deposit as in the previous cases:

$$x_{d1} = at_{d1} \qquad (B.3.78)$$

$$x_{r1} = x_{d1} - b_1 t_r \qquad (B.3.79)$$

Substituting for b_1 with n=1 from Equation (B.3.77):

$$x_{r1} = x_{d1} - \frac{b_1 t_r}{(1-n_f)} - \frac{b_1 n_f t_r}{(1-n_f)} \qquad (B.3.80)$$

For second cycle (n=2):

$$x_{d2} = 2x_{d1} - b_1 t_r \qquad (B.3.81)$$

$$x_{d2} = 2x_{d1} - \frac{b_1 t_r}{(1-n_f)} - \frac{b_1 n_f t_r}{(1-n_f)} \qquad (B.3.82)$$

As the cleaning time (t_r) is constant:

$$x_{r2} = x_{d2} - b_2 t_r \qquad (B.3.83)$$

$$x_{r2} = 2x_{d1} - \frac{b_1 t_r - b_1 n_f t_r}{(1-n_f)} - \frac{2b_1 t_r - b_1 n_f t_r}{(1-n_f)} \qquad (B.3.84)$$

$$x_{r2} = 2x_{d1} - \frac{3b_1 t_r}{(1-n_f)} + \frac{2b_1 t_r n_f}{(1-n_f)} \qquad (B.3.85)$$

For third cycle (n=3):

$$x_{r3} = 3x_{d1} - \frac{3b_1 t_r}{(1-n_f)} + \frac{2b_1 t_r n_f}{(1-n_f)} \qquad (B.3.86)$$

$$x_{r3} = x_{d3} - b_3 t_r \qquad (B.3.87)$$

$$x_{r3} = 3x_{d1} - \frac{3b_1 t_r}{(1-n_f)} + \frac{2b_1 n_f t_r}{(1-n_f)} - b_3 t_r \qquad (B.3.88)$$

Substitute for b_3:

$$x_{r3} = 3x_{d1} - \frac{3b_1 t_r}{(1-n_f)} + \frac{2b_1 n_f t_r}{(1-n_f)} - \frac{3b_1 t_r}{(1-n_f)} - \frac{b_1 n_f t_r}{(1-n_f)} \qquad (B.3.89)$$

$$x_{r3} = 3x_{d1} - \frac{6b_1 t_r}{(1-n_f)} + \frac{3b_1 n_f t_r}{(1-n_f)} \qquad (B.3.90)$$

For fourth cycle:

$$x_{d4} = 4x_{d1} - \frac{6b_1 t_r}{(1-n_f)} + \frac{3b_1 n_f t_r}{(1-n_f)} \qquad (B.3.91)$$

$$x_{r4} = 4x_{d1} - \frac{10b_1 t_r}{(1-n_f)} + \frac{4b_1 n_f t_r}{(1-n_f)} \qquad (B.3.92)$$

The general expression is:

$$x_{rn} = nx_{d1} - \frac{(n+1)nb_1 t_r}{2(1-n_f)} + \frac{nb_1 n_f t_r}{(1-n_f)} \qquad (B.3.93)$$

For the final cycle, $n = n_f$ and $x_n = X_t$:

$$X_t = n_f x_{d1} - \frac{(n_f+1)n_f b_1 t_r}{2(1-n_f)} + \frac{n_f b_1 n_f t_r}{(1-n_f)} \qquad (B.3.94)$$

$$X_t = n_f x_{d1} - \frac{n_f^2 b_1 t_{r1}}{2(1-n_f)} - \frac{n_f b_1 t_{r1}}{2(1-n_f)} + \frac{b_1 n_f^2 t_{r1}}{(1-n_f)} \qquad (B.3.95)$$

$$X_t(1-n_f) = n_f x_{d1}(1-n_f) - n_f^2 b_1 t_{r1}/2 - n_f b_1 t_{r1}/2 + b_1 n_f^2 t_{r1} \qquad (B.3.96)$$

$$X_t - X_t n_f = n_f x_{d1} - n_f^2 x_{d1} - n_f^2 b_1 t_{r1}/2 - n_f b_1 t_{r1}/2 + b_1 n_f^2 t_{r1} \qquad (B.3.97)$$

$$n_f^2(x_{d1} + b_1 t_{r1}/2) + n_f(b_1 t_{r1}/2 - X_t - x_{d1}) + X_t = 0 \qquad (B.3.98)$$

Solving for n:

$$n = \frac{-B \pm \sqrt{(B^2 - 4AC)}}{2A} \qquad (B.3.99)$$

Where A, B and C are the roots of the quadratic equation:

$$A = x_{d1} + b_1 t_{r1}/2 \qquad (B.3.100)$$

$$B = b_1 t_{r1}/2 - X_t - x_{d1} \qquad (B.3.101)$$

$$C = X_t \qquad (B.3.102)$$

The expressions for N, P and W are the same as for model 1 and are given in Section B.2.

The number of cycles, the batch times and cleaning times were known from the plant data. However, the thickness of the deposits and hence the slopes of deposit and cleaning lines were unknown. If the vessel is not cleaned between batches build-up would occur faster and jetting would be required more often. By comparing the cases with and without intermediate cleaning the efficiency of the cleaning was estimated. This was used to predict the thickness of the deposits. This is developed below.

For no intermediate cleaning the expression for the final thickness is:

$$X_t = n_{nc}\, x_{d1} \qquad \text{(B.3.103)}$$

From Equation (B.3.95) the expression with intermediate cleaning is:

$$X_t = n_f x_{d1} - n_f^2 \frac{b_1 t_{r1}}{2(1-n_f)} - \frac{n_f b_1 t_{r1}}{2(1-n_f)} + \frac{b_1 n_f^2 t_{r1}}{(1-n_f)} \qquad \text{(B.3.104)}$$

Assuming that the final thickness, X_t, which causes the vessel to be shutdown to be equal for both cases then the expressions can be equated:

$$n_{nc}\, x_{d1} = n_f x_{d1} - \frac{(n_f+1) n_f b_1 t_{r1}}{2(1-n_f)} + n_f^2 \frac{b_1 t_{r1}}{(1-n_f)} \qquad \text{(B.3.105)}$$

$$x_{d1}(n_{nc} - n_f) = n_f^2 \frac{b_1 t_{r1}}{(1-n_f)} - \frac{(n_f+1) n_f b_1 t_{r1}}{2(1-n_f)} \qquad \text{(B.3.106)}$$

$$\frac{x_{d1}(n_{nc} - n_f)}{b_1 t_{r1}} = \frac{n_f^2}{(1-n_f)} - \frac{n_f^2}{2(1-n_f)} - \frac{n_f}{2(1-n_f)} \qquad \text{(B.3.107)}$$

$$\frac{x_{d1}(n_{nc} - n_f)}{b_1 t_{r1}} = \frac{n_f^2}{2(1-n_f)} - \frac{n_f}{2(1-n_f)} \qquad \text{(B.3.108)}$$

$$\frac{x_{d1}(n_{nc} - n_f)}{b_1 t_{r1}} = \frac{n_f(n_f - 1)}{2(1-n_f)} \qquad \text{(B.3.109)}$$

$$\frac{x_{d1}(n_{nc} - n_f)}{b_1 t_{r1}} = \frac{-n_f(1 - n_f)}{2(1-n_f)} \qquad \text{(B.3.110)}$$

$$x_{d1}(n_{nc} - n_f) = -b_1 t_{r1} n_f/2 \qquad \text{(B.3.111)}$$

From Equation (B.3.79):

$$b_1 t_r = x_{d1} - x_{r1} \qquad \text{(B.3.112)}$$

Substituting into Equation (B.3.111):

$$x_{d1}(n_{nc} - n_f) = -(x_{d1} - x_{r1}) n_f/2 \qquad \text{(B.3.113)}$$

$$x_{d1}(n_{nc} - n_f) + x_{d1} n_f/2 = x_{r1} n_f/2 \qquad \text{(B.3.114)}$$

$$2x_{d1}(n_{nc} - n_f) + x_{d1} n_f = x_{r1} n_f \qquad \text{(B.3.115)}$$

$$2x_{d1}(n_{nc} - n_f + n_f/2) = x_{r1} n_f \qquad \text{(B.3.116)}$$

$$2x_{d1}(n_{nc} - n_f/2) = x_{r1} n_f \qquad \text{(B.3.117)}$$

$$x_{d1} = \frac{x_{r1} n_f}{2(n_{nc} - n_f/2)} \qquad \text{(B.3.118)}$$

For the solution of this equation to be a positive, real number:

$$n_{nc} - n_f/2 > 0 \qquad \text{(B.3.119)}$$

$$n_{nc} > n_f/2 \qquad \text{(B.3.120)}$$

For the EVC operations $n_f = 210$ therefore, $n_{nc} > 105$. This represents the lower bound. If n_{nc} is less than 105, the ratio of x_{d1} to x_{r1} is negative. The cleaning is too effective, causing more deposit to removed than is actually present.

The upper bound for the number of batches without cleaning is estimated from the case where b is constant. The following expressions were developed in Section B.2:

$$x_n = nx_{d1} - nbt_{r1} \qquad \text{(B.3.121)}$$

From first cycle:

$$b = (x_{d1} - x_{r1})/t_{r1} \qquad \text{(B.3.122)}$$

Substituting for b:

$$x_n = nx_{d1} - n(x_{d1} - x_{r1}) \qquad \text{(B.3.123)}$$

$$x_n = nx_{r1} \qquad \text{(B.3.124)}$$

$$X_t = n_f x_{r1} \qquad \text{(B.3.125)}$$

Equating this to the case where no cleaning occurs:

$$n_{nc} x_{d1} = n_f x_{r1} \qquad \text{(B.3.126)}$$

$$x_{r1}/x_{d1} = n_{nc}/n_f \qquad \text{(B.3.127)}$$

The plant operators estimated that 70 cycles, n_{nc}, could be carried out if no intermediate cleaning took place was. However, this is less than the lower bound 105 and could not be used for the case where b varied. With cleaning $n_f = 210$. Therefore using the values for the case were the cleaning achieved is constant:

$$x_{r1}/x_{d1} = 70/210 = 0.33 \qquad \text{(B.3.128)}$$

Putting this back into Equation (B.3.118):

$$0.333 = 2(n_{nc} - n_f/2)/n_f \qquad \text{(B.3.129)}$$

$$0.333n_f = 2(n_{nc} - n_f/2) \qquad \text{(B.3.130)}$$

$$0.333n_f = 2n_{nc} - n_f \qquad \text{(B.3.131)}$$

$$1.333n_f = 2n_{nc} \qquad \text{(B.3.132)}$$

$$n_{nc} = 0.667n_f \qquad \text{(B.3.133)}$$

Using $n_f = 210$, the upper bound for n_{nc} is 140.

Therefore the number of batches for not cleaning must be between 105 and 140 batches.

Appendix C

The Environmental Process Performance Tool

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C.1 Introduction

The Environmental Process Performance Tool (EPPT) has been used to assess several of the process options developed in this thesis and this Appendix provides a brief overview of the EPPT and the scoring systems used. Full details of the EPPT are given in Aubrey [1].

The EPPT is a tool to assess the inputs and outputs of chemicals to a process including the use of utilities such as energy and cooling water. It can be used as a decision making aid by ranking processes in terms of their environmental impact. Newly designed, existing and retrofitted processes can also be compared.

C.2 Chemical Assessment

The chemicals used and manufactured are the most significant factor when assessing the environmental impact of a process. It is these chemicals which may have environmental effects and cause damage to the environment. Therefore, it is essential to carry out a comprehensive evaluation of these chemicals.

The evaluation used in the EPPT comprises the chemical toxicity, persistence and effect to all three media; air, water and land, and the determination of the fate of these chemicals. A range of parameters are used in the chemical assessment. For example, toxicity to man and fish, global warming potential and bioconcentration factors. Extensive data surveys of these parameters have been undertaken for a number of chemicals to provide an assessment of their environmental effects. The data gathered are then scored on a scale of 1 to 10, 1 representing low toxicity, 10 being high. The scores, data, information and data sources are then stored in a database that can be used in future assessments.

Considering one of three parameters used to assess the toxicity of a chemical in water, the Microtox™ test. This test uses the luminescence bacterium *Photobacerium phosporeum* to assess toxicity and correlates very well with many other bioassays. Hence the reason for its selection. This test is carried out over a specific time period, usually 30 minutes. Initially, the luminescence of the *Photobacerium phosporeum* is measured. This measurement is then repeated 30 minutes after the introduction of the chemical to the culture. The decrease in luminescence can then be used to calculate the EC_{50} (concentration to reduce luminescence by 50%) in ppm (parts per million).

This is a measure of the toxicity of the chemical. Once this data had been found it was scored in the EPPT using the system shown in Table C.1. The system has been determined by assessing Microtox™ EC_{50}'s for 1300 chemicals [168] and also by comparing it with qualitative assessments [169].

Table C.1: EPPT scores assigned for Microtox™ EC_{50}'s

EPPT score	Croner's [169] assessment	Microtox™ score EC_{50} ppm
10	very high toxicity	<1
9	high toxicity	≥1<5
8	high toxicity	≥5<10
7	moderate toxicity	≥10<25
6	moderate toxicity	≥25<50
5	moderate toxicity	≥50<100
4	low toxicity	≥100<500
3	low toxicity	≥500<1000
2	low toxicity	≥1000<2500
1	low toxicity	≥2500
0	no toxicity	no effect

Thus the Microtox™ score for toluene with an EC_{50} of 23.1 based on the 30 minute test would have an EPPT score of 7. Therefore it is classed as moderately toxic. The chemical summary form for toluene is shown in Table C.2.

Table C.2: Chemical summary form for toluene

Chemical summary form		Media Fraction	
		Air:	0.74
CAS number	108-88-3	Water:	0.15
Chemical Name	Toluene	Land:	0.11

	Toxicity	Score	Persistence	Score	Effect	Score
Air	Mammal OEL	5	Degradation	3	Global warming potential	0
	Rat inhalation	4			Acidification	0
	Carcinogicity	0			Ozone depletion potential	0
					Photochemical ozone creation potential	9
					Vegetation damage potential	0
					Aesthetics	0
					Odour	6
Water	Microtox™	7	Degradation	4	Acidification	0
	Crustacean	7	Bioconcentration factor	1	Aesthetics	0
	Fish	5			Odour	6
	Carcinogicity	0				
Land	Microtox™	7	Degradation	4	Acidification	0
	Worms	7	Bioconcentration factor	1	Vegetation damage potential	0
	Deposition rate	5				
	Carcinogicity	0				

The scores assigned for each parameter are then combined into a single score for that chemical. This is determined by calculating the short term and long term effect of the chemical in the environment.

The short term or immediate effect of the release is assessed for the media into which the material is released initially i.e. if toluene were released to air the short term score would combine the toxicity and effect parameters for the chemical in air, likewise for water and land, as shown in Equation C.1.

$$\text{immediate effect} = \sum(\text{toxicity parameter scores}) + \sum(\text{effect parameter scores}) \qquad \text{C.1}$$

The long term effect is calculated by determining the long term fate of the chemical in the environment. For organic materials this is achieved using Elliott's distribution model [170] that is based on Henry's constants and soil adsorption coefficients. For inorganic materials the long term distribution is predicted using Elliott's distribution model based on solubility and vapour pressure. These media fractions are multiplied with the combined toxicity and effects scores which have been multiplied by the square root of the sum of the persistence scores squared for each separate media, as indicated in Equation C.2. The total long term effect of the chemical is the sum of the long term effects over all three media.

$$\text{long term effect} = \{\sum(\text{toxicity parameter scores}) + \sum(\text{effect parameter scores})\} \times \sqrt{(\sum\text{persistence parameters})^2} \times \text{media fraction} \qquad \text{C.2}$$

Both the short term and long term effects are normalised to a value between 0 and 100. The chemical score is the sum of the short and long term effects.

The EPPT score is calculated as follows:

$$\text{EPPT score} = \text{mass} \times 10^{(\text{chemical score}/10)} \qquad \text{C.3}$$

The chemical evaluation has been used to determine a score for the production of 1 kWh of electricity. The emissions per unit of electricity have been calculated by considering the total energy produced in the UK (excluding nuclear) and estimating the total emissions associated with that production [171]. Table C.3 summarises the emissions per kWh produced. The overall score for 1 kWh of electricity production is found by combining the emissions with the scores for these chemical emissions and the results summed, as shown in Table C.3.

Table C.3: Determination of electricity score per kWh

Chemical	Mass released (kg/kWh produced)	Chemical score for release to air	Mass (kg/kWh) x $10^{(score/10)}$
nitrogen dioxide	2.325x10^{-3}	29.3	2.0
VOCs*	4.021x10^{-5}	10.5	4.5x10^{-4}
carbon monoxide	1.508x10^{-4}	9.9	1.5x10^{-3}
carbon dioxide	1.709x10^{-1}	7.7	1.0
methane	1.005x10^{-5}	11.2	1.3x10^{-}4
particulates	8.376x10^{-5}	15.7	3.1x10^{-3}
sulphur dioxide	8.131x10^{-3}	24.3	2.2
steam	5.900x10^{-4}	0.2	6.2x10^{-4}
EPPT electricity score/kWh			5.2

* VOCs are a range of aliphatic and aromatic hydrocarbons. These have been scored as toluene as a worse case scenario.