LONG-TERM SCHEDULING TECHNIQUE FOR WASTEWATER MINIMISATION IN MULTIPURPOSE BATCH PROCESSES

100
1908 - 2008

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA
Denkleiers • Leading Minds • Dikgopolo tša Dihlalefi

DONALD ROBERT NONYANE

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Long-term scheduling technique for wastewater minimisation in multipurpose batch processes

By

Donald Robert Nonyane

A dissertation submitted in partial fulfilment of the requirement for the degree

MEng: Chemical Engineering

in the

Faculty of Engineering, the Built Environment and Information Technology

Supervisor: Prof T. Majozi

University of Pretoria

February 2011

SYNOPSIS

Most of the methodologies published in literature on wastewater minimisation for batch processes are based on short-term scheduling techniques. When these methods are applied to longer time horizons, the computational time becomes intractable, hence the focus of this thesis. This thesis presents a methodology for simultaneous optimization of production schedule and wastewater minimisation in a multipurpose batch facility. The key feature of the presented methodology is the adaption of cyclic scheduling concepts to wastewater minimisation. The methodology is developed based on continuous-time formulation and the state sequence network (SSN) representation. The methodology is successfully applied to two common literature examples and an industrial case study to demonstrate its effectiveness. None of the currently published wastewater minimisation techniques could solve the case study for a time horizon of 168h. However, through the application of the presented methodology, a time horizon of 168h for the case study was reduced to 8 cycles with the cycle length of 23h, for which the CPU time for the optimum cycle is 64.53s.

Keywords: Cyclic scheduling, Central storage, Multiple contaminants

I, **Donald Robert Nonyane**, with student number **25346556**, declare that:

1. I understand what plagiarism is and am aware of the University's policy in this regard.
2. I declare that this thesis is my own original work. Where other people's work has been used (either from a printed source, internet or any other source), this has been properly acknowledged and referenced in accordance with departmental requirements.
3. I have not used work previously produced by another student or any other person to hand in as my own.
4. I have not allowed, and will not allow, anyone to copy my work with the intention of passing it off as his or her own work.

SIGNATURE________________________________

ACKNOWLEDGEMENTS

"Gratitude is the best attitude." ~Author Unknown

First and foremost, I would like to thank God almighty for my existence.

I would like to express my deepest and sincerest gratitude to my supervisor, Prof. T. Majozi for his constructive criticism and his expert guidance.

I would like to acknowledge SAPPI and Water Research Commission for their financial support.

Special thanks to my family, especially my brother Adriot Mpho Nonyane, for their motivation and patience.

To my colleagues, Bola, Esmael, Jane, Tim, Knowledge, Vhutshilo and Vincent, it was an honour working with you.

Finally, I owe my loving thanks to Dorcas "Snowy" Riba for her emotional and moral support.

CONTENT

CHAPTER 01 INTRODUCTION **1**
1.1. Background 1
1.2. Motivation of the proposed mathematical technique 3
1.3. Aim 5
1.4. Problem statement 5
1.5. Thesis scope 5
1.6. Thesis structure 6
References 6

CHAPTER 02 LITERATURE SURVEY **8**
Introduction 8
2.1. Background on batch processes 8
  2.1.1. Batch processes vs. Continuous processes 9
  2.1.2. Types of batch processes 9
2.2. Scheduling 10
  2.2.1. Overview of important scheduling concepts 11
  2.2.2. Short-term scheduling techniques 14
  2.2.3. Long-term scheduling: the concept of cyclic scheduling 15
2.3. Wastewater minimisation techniques 19
  2.3.1. Graphical techniques 22
  2.3.2. Mathematical programming techniques 27
2.4. Conclusions 41
References 42

CHAPTER 03 MATHEMATICAL MODEL **48**
Introduction 48
3.1. Mass balance constraints 48
  3.1.1. Mass balance constraints without storage 49
  3.1.2. Mass balance constraints with storage 52
3.2. Sequencing and scheduling constraints 55
  3.2.1. Scheduling constraints associated with the washing operation 55
  3.2.2. Water recycle/reuse sequencing constraints 56
  3.2.3. Sequencing and scheduling constraints associated with storage 57
3.3. Production scheduling constraints 59
  3.3.1. Capacity constraint 59
  3.3.2. Material Balance constraints 60

3.3.3. Duration constraints 60
3.3.4. Feasibility and time horizon constraints 61
3.3.5. Sequence constraint within the cycle 62
3.3.6. Mass balance between two cycles 62
3.3.7. Cycle length constraint 62
3.3.8. Sequence constraints between cycles 63
3.3.9. Objective function 63
3.4. Solution procedure 64
References 65

CHAPTER 04 ILLUSTRATIVE EXAMPLES **66**
Introduction 66
4.1. Illustrative Example 1 (Kondili *at el.* 1993) 66
4.1.1. Results and discussions 71
4.2. Illustrative Example 2 (Sundaramoorthy and Karimi, 2005) 77
4.2.1. Results and discussions 81
References 87

CHAPTER 05 INDUSTRIAL APPLICATION **88**
Introduction 88
5.1. Case study background 88
5.2. Results and discussions 89
References 93

CHAPTER 06 CONCLUSIONS AND RECOMMENDATIONS **94**
Introduction 94
6.1. Conclusions 94
6.2. Recommendations 95

APPENDIX LINEARIZATION TECHNIQUE **96**
A.1. Linearization (Majozi and Gouws, 2009) 96
References 99

LIST OF FIGURE

Figure 2.1: Multipurpose batch plant (Majozi, 2010:6)......10

Figure 2.2: Multiproduct batch plant (Majozi, 2010:6)......10

Figure 2.3: The original time horizon H is greater than the optimal cycle length T......16

Figure 2.4: a) Task 2 in unit 2 overlaps over the cycle. b) Task 2 is wrapped......16

Figure 2.5: Even time discretization for a single cycle (Castro *et al.* 2003)......17

Figure 2.6: Uneven time discretization over one cycle (Castro *et al.* 2003)......18

Figure 2.7: Cyclic scheduling in the middle period repeated N times......19

Figure 2.8: A depiction of mass transfer-based operations (Chen and Lee, 2008)......20

Figure 2.9: Direct water reuse in (a) continuous and (b) batch processes......21

Figure 2.10: Superstructure for Kim and Smith (2004)......27

Figure 2.11: Superstructure of source-tank-sink formulation (Shoaib *et al.*, 2008)......29

Figure 2.12: Superstructure for the mathematical formulation with no reusable water......34

Figure 2.13: Superstructure for the mathematical formulation with reusable water......35

Figure 2.14: Solution procedure from Gouws *et al*. (2008)......38

Figure 2.15: Solution procedure for (a) short-term and (b) periodic operations proposed by Chen *et al*. (2010)......39

Figure 3.1: Superstructure for the mathematical formulation with no reusable water storage Majozi and Gouws (2009)......49

Figure 3.2: Superstructure for the mathematical formulation with reusable water storage Majozi and Gouws (2009)......53

Figure 3.3: Solution procedure......64

Figure 4.1: Flowsheet for BATCH 1 multipurpose plant......67

Figure 4.2: (a) STN and (b) SSN for the literature example......67

Figure 4.3: Schedule for the optimum cycle length without storage......72

Figure 4.4: Schedule for the optimum cycle length without storage......73

Figure 4.5: Initial period without central storage vessel......74

Figure 4.6: Final period without storage for a time horizon of 48h..75
Figure 4.7: Initial period with storage..76
Figure 4.8: Final period with storage..76
Figure 4.9: STN representation of the second illustrative example..78
Figure 4.10: SSN representation of the second illustrative example......................................78
Figure 4.11: Schedule for the optimum cycle length without central storage 82
Figure 4.12: Initial period without storage for the time horizon of 168h 83
Figure 4.13: Final period without storage for the time horizon of 168h.................................83
Figure 4.14: Schedule for the optimum cycle length for the case with central storage...........84
Figure 4.15: Initial period with storage..85
Figure 4.16: Final period with central storage present 86

Figure 5.1: Optimum schedule for the case study without storage vessel...............................91
Figure 5.2: Optimum schedule in the presence of a central storage vessel 92

Figure A.1: Solution procedure from Majozi and Gouws (2009)...98

LIST OF TABLES

Table 1.1: Demonstration results from Wu and Ierapetritou (2004) 4
Table 1.2: Wastewater minimisation for BATCH 1 4

Table 2.1: Intermediate storage policies for batch processes 13

Table 4.1: Scheduling data for the illustrative example 68
Table 4.2: Wastewater minimisation data for the illustrative example 69
Table 4.3: Results for BATCH 1 using method by Majozi and Gouws (2009).......................70
Table 4.4: Result for BATCH 1 using the presented methodology without storage 71
Table 4.5: Result for BATCH 1 using the developed methodology with storage 72
Table 4.6: Results for initial and final period with storage for the time horizon of 48h 75
Table 4.7: Summary of freshwater savings for example 1 77
Table 4.8: Scheduling data for the second illustrative example 79
Table 4.9: Wastewater minimisation data for the second illustrative example 80
Table 4.10: Result for the example without a central storage vessel......................................81
Table 4.11: Results for initial and final period for 168h time horizon 82
Table 4.12: Result for example with a central storage vessel present 84
Table 4.13: Result for the initial and the final period in the presence of a central storage 85
Table 4.14: Summary of example 2 for 168h time horizon...86

Table 5.1: Data for the case study...89
Table 5.2: Maximum inlet concentrations for cleaning operation for the case study..............89
Table 5.3: Demonstration of computational problems 90
Table 5.4: Results for the case study without central storage...90
Table 5.5: Results for the case study with central storage present 92

NOMENCLATURE LIST

All the sets, variables and parameters used in this thesis are listed below.

Sets

P	$\{ p \mid p = \text{time point}\}$
J	$\{ j \mid j = \text{unit}\}$
C	$\{ c \mid c = \text{contaminant}\}$
S_{in}	$\{ s_{in} \mid s_{in} = \text{input state into any unit}\}$
S_{out}	$\{ s_{out} \mid s_{out} = \text{output state from any unit}\}$
S	$\{ s \mid s = \text{any state}\} = S_{in} \cup S_{out}$
$S_{in,j}$	$\{ s_{in,j} \mid s_{in,j} = \text{input state into unit } j\} \subseteq S_{in}$
$S^{*}_{in,j}$	$\{ s^{*}_{in,j} \mid s^{*}_{in,j} = \text{input state into unit}\} \subseteq S_{in}$
$S_{out,j}$	$\{ s_{out,j} \mid s_{out,j} = \text{output state from unit } j\} \subseteq S_{out}$

Variables associated with wastewater minimisation

$mw_{in}(s_{out,j}, p)$	mass of water into unit j for cleaning state s_{out} at time point p
$mw_{out}(s_{out,j}, p)$	mass of water produced at time point p from unit j
$mw_{f}(s_{out,j}, p)$	mass of freshwater into unit j at time point p
$mw_{e}(s_{out,j}, p)$	mass of effluent water from unit j at time point p
$mw_{r}(s_{out,j}, s_{out,j'}, p)$	mass of water recycled to unit j' from j at time point p
$ms_{in}(s_{out,j}, p)$	mass of water transferred from unit j to storage at time point p
$ms_{out}(s_{out,j}, p)$	mass of water transferred from storage to unit j at time point p
$c_{in}(s_{out,j}, c, p)$	inlet concentration of contaminant c, to unit j at time point p
$c_{out}(s_{out,j}, c, p)$	outlet concentration of contaminant c, from unit j at time point p
$cs_{in}(s_{out,j}, c, p)$	inlet concentration of contaminant c, to storage at time point p

$cs_{out}\left(s_{out,j}, c, p\right)$	outlet concentration of contaminant c, from storage at time point p
$qw_s(p)$	amount of water stored in storage at time point p
$ts_{in}\left(s_{out,j}, p\right)$	time at which water is transferred from unit j to storage at time point p
$ts_{out}\left(s_{out,j}, p\right)$	time at which water is transferred from storage to unit j at time point p
$tw_{in}\left(s_{out,j}, p\right)$	time that the water is used at time point p in unit j
$tw_{out}\left(s_{out,j}, p\right)$	time at which water is produced at time point p from unit j
$tw_r\left(s_{out,j}, s_{out,j'}, p\right)$	time at which water is recycled from unit j to unit j' at time point p
$yw_r\left(s_{out,j}, s_{out,j'}, p\right)$	binary variable showing usage of recycle from unit j to unit j' at time point p
$yw\left(s_{out,j}, p\right)$	binary variable showing the usage of unit j at time point p
$ys_{in}\left(s_{out,j}, p\right)$	binary variable showing transfer of water from unit j to storage at time point p
$ys_{out}\left(s_{out,j}, p\right)$	binary variable showing transfer of water from storage to unit j at time point p

Variables associated with production scheduling

$t_{out}\left(s_{out,j}, p\right)$	time at which a state is produced from unit j at time point p
$t_{in}\left(s_{in,j}, p\right)$	time at which a state is used in or enters unit j at time point p
$q_s(s, p)$	amount of state s stored at time point p
$m_{out}\left(s_{out,j}, p\right)$	amount of state produced from unit j at time point p
$m_{in}\left(s_{in,j}, p\right)$	amount of state used in or enters unit j at time point p
$y\left(s^*_{in,j}, p\right)$	binary variable associated with usage of state s at time point p
$d\left(s_{out}, p\right)$	amount of state delivered to customers at time point p
H	time horizon for a single cycle

Parameters associated with wastewater minimisation

CE	cost of effluent water treatment (c.u./kg water)
CF	cost of freshwater (c.u./kg water)
$M\left(s_{out,j}, c\right)$	mass load of contaminant c added from unit j to the water stream
$Mw^U\left(s_{out,j}\right)$	maximum inlet water mass of unit j

$C_{in}^{U}\left(s_{out,j},c\right)$	maximum inlet concentration of contaminant c in unit j
$C_{out}^{U}\left(s_{out,j},c\right)$	maximum outlet concentration of contaminant c from unit j
$\tau w\left(s_{out,j}\right)$	mean processing time of unit j
Qw_{s}^{0}	initial amount of water in storage
Qw_{s}^{U}	maximum capacity of storage

Parameters associated with production scheduling

V_{j}^{U}	maximum design capacity of a particular unit j
V_{j}^{L}	minimum design capacity of a particular unit j
H^{u}	uppper bound of the cycle time length
$\tau\left(s_{in,j}^{*}\right)$	mean processing time for a state
$Q_{s}^{0}(s)$	initial amount of state s stored
$Q_{s}^{U}(s)$	maximum amount of state s stored within the time horizon
CF	interest selling price of product s , $s =$ product

CHAPTER 01

INTRODUCTION

1.1. Background

The detrimental impact of chemical processing industries on natural resources, particularly freshwater, has become more apparent in the past few decades. This has led to an increase in freshwater and effluent treatment costs. Furthermore, environmental regulations on industrial effluent discharge have become more stringent. Traditionally, end-of-pipe treatment approach was employed to mitigate environmental offences. However, this is no longer a viable option because of the escalating wastewater disposal costs. This has stimulated processing industries to seek economical and sustainable methods to minimise wastewater generation at source rather than to rely on end-of-pipe treatment methods. Thus, a significant industrial and academic effort has been devoted to the development of wastewater minimisation techniques.

The abovementioned concern can be effectively addressed through the application of process integration. Through process integration, water recovery within the plant through reuse/recycle of less contaminated water is identified before external water sources are considered. In contrast to the conventional end-of-pipe treatment, process integration provides a more positive approach to minimise freshwater consumption and wastewater generation from an environmental sustainability point of view. Majority of the published wastewater minimisation techniques are based on this principle. These techniques can be classified into graphical and mathematical techniques. The graphical techniques are based on pinch analysis, which was originally intended for process heat integration. Wastewater minimisation using graphical techniques is achieved in two steps. In the first step, minimum freshwater consumption is targeted and the second step involves the synthesis of the water using network to satisfy the target. Mathematically based techniques are mainly based on optimization formulations. The freshwater target and the water using network to satisfy the target are obtained simultaneously in mathematical techniques.

However, majority of the early published wastewater minimisation techniques were dedicated to continuous processes operating under steady-state. Very little attention has been directed towards the development of wastewater minimisation techniques for batch processes. This can be attributed to a number of reasons, the main of which is the time dependence of batch operations. Thus, developing wastewater minimisation techniques for batch processes is generally more challenging than their continuous counterparts.

Batch processes are intrinsically more flexible than their continuous counterparts since a variety of products can be produced through the sharing of the same equipment. Batch processing mode is favourable for the production of high-value-added products such as pharmaceuticals, foods, fine chemicals, and agrochemicals. As demands of such products are highly seasonal and low in volume, the flexibility of batch processes is often preferred. However, this flexibility leads to additional complexity in developing wastewater minimisation techniques. As multiple tasks can be performed in the same equipment, optimal task scheduling becomes exceedingly crucial when developing wastewater minimisation techniques.

As aforementioned, wastewater minimisation techniques for batch processes can be divided into graphical and mathematical techniques. Some of the methods that fall under graphical techniques include the work by Wang and Smith (1995b), Majozi *et al.* (2006), Foo *et al.* (2005), Hallale (2002), Yongjian *et al.* (2007) and Chen and Lee (2008). Despite their strength of providing good insight into the synthesis problem, graphical techniques have two common major drawbacks. Firstly, the schedule must be predefined ahead of the water target. Therefore, the obtained water target is schedule specific. Secondly, they are not capable of dealing with streams characterized by multiple contaminants, due to the multiple dimensions introduced. Due to these drawbacks, graphical techniques have limited practical applications since multiple contaminants streams are common occurrence in practice.

Mathematical techniques can easily address the drawbacks of graphical techniques since they are not limited in dimensions. However, it should be mentioned that most of the mathematical techniques do not truly address the time dependence of batch processes. Therefore, mathematical techniques can be categorized into two structures, sequential and simultaneous framework. In the sequential framework, the production schedule is predetermined prior to the synthesis of the water-using network. The techniques that fall into this structure are those proposed by Li and Chang (2006), Shoaib *et al.* (2008), Majozi (2005b) and Liu *et al.* (2009). This implies that these techniques treat time as a parameter as pointed out by Gouws *et al.* (2010). However, for simultaneous frameworks both the water using network and the production schedule are determined simultaneously. Some of the methodologies under simultaneous framework include the work by Cheng and Chang (2007), Zhou *et al.* (2008), Majozi and Gouws (2009) and Li *et al.* (2010).

Besides the remarkable few contributions in mathematical techniques, they share a common major drawback. Their application is limited to wastewater minimisation in batch processes operated over a short time horizon. When applied to problems with longer time horizon as traditionally encountered in practice, they experience computational difficulties i.e. longer computational/CPU time, hence this investigation.

1.2. Motivation of the proposed mathematical technique

As aforementioned, batch processes are time dependent. Thus, a good scheduling technique must be in place to effectively address the issue of wastewater minimisation in batch processes. Published scheduling methodologies were originally dedicated to batch processes operated over a short time horizon. When these methodologies are applied to batch processes operated over a long time horizon, they experience long CPU time. The long CPU time is mainly due to the problem structure as well as large problem sizes. When the problem size increases as encountered in industrial scale problems, the CPU time becomes intractable.

Wu and Ierapetritou (2004) demonstrated the problem of longer CPU time experienced by currently published scheduling techniques by applying the short-term scheduling technique by Ierapetritou and Floudas (1998a) to a commonly encountered literature example, BATCH 1. The results from their demonstration are presented in Table 1.1. The objective value for the time horizon of 24h could not be proven optimum since further increase of event points caused computational infeasibility. It is important to note in Table 1.1 that a feasible solution for the time horizon of 168h could not be obtained regardless of the number of time points used.

Table 1.1: Demonstration results from Wu and Ierapetritou (2004)

Time horizon (*h*)	8	24 (1 day)	168 (1 week)
Constraints	374	1517	--
Continuous variables	260	546	--
Binary variables	40	156	--
CPU time (*s*)	0.28	79551.29 (~22h)	--
Objective function	1503.15	6036.491	--

When the short-term scheduling techniques are adapted to wastewater minimisation, the same problem of lengthy CPU time is observed. To substantiate this observation, the wastewater minimisation technique by Majozi and Gouws (2009) was applied to same problem, BATCH 1. The results are shown in Table 1.2.

Table 1.2: Wastewater minimisation for BATCH 1

Time horizon (*h*)	**CPU time** (*s*)
10	0.31
13	2044.44 (~0.57h)
15	56736.67 (~15.76h)
24	**--**

From the presented results, the need for the development of a methodology for wastewater minimisation in batch processes operated over a long time horizon is mandatory.

1.3. Aim

The aim of this study is to develop a mathematical technique to minimise wastewater generation in multipurpose batch processes operated over a long time horizon i.e. industrial scale problems, with significantly reduced computational difficulties.

1.4. Problem statement

The problem addressed in this thesis can be formally stated as follows: For each water using operation, *given*:

(i) the production recipe for each product, including mean processing times in each unit operation,
(ii) the available units and their capacities,
(iii) the maximum storage capacity for each material,
(iv) the mass load, maximum inlet and outlet concentration for each contaminant,
(v) water requirement and the cleaning duration for each unit to achieve the required cleanliness,
(vi) the maximum storage available for reusable water, and
(vii) time horizon of interest,

determine the optimal production schedule which will generate the minimum amount of wastewater through reuse and recycle opportunities.

1.5. Thesis scope

The scope of this thesis was to develop a mathematical technique for wastewater minimisation in multipurpose batch processes operated over a long time horizon. This was achieved through the integration of cyclic scheduling concepts originally proposed by Shah *et al.* (1993) into wastewater minimisation concepts from the work by Majozi and Gouws (2009). The concept of cyclic scheduling was developed with the intent to resolve the problem of long CPU time by determining an optimum cycle length and repeating it over a long time horizon. However, the concept of cyclic scheduling has not yet been applied in the context of wastewater minimisation, hence the focus of this thesis.

1.6. Thesis structure

The rest of the thesis is structured as follows: Chapter 2 comprises the literature survey on published wastewater minimisation techniques in batch processes. Chapter 3 presents the methodology development where the proposed mathematical technique is developed in detail. The capability of the developed methodology presented in Chapter 3 is demonstrated in Chapter 4 by solving two illustrative examples. The practical application of the developed methodology is presented in Chapter 5 by solving a real life case study. The conclusion and recommendations are presented in Chapter 6.

References

Cheng, K. and Chang, C, 2007, Integrated water network designs for batch processes, *Ind. Eng. Chem. Res.*, 46: 1241-1253.

Chen, C. and Lee, J., 2008, A graphical technique for the design of water-using networks in batch processes, *Chem. Eng. Sci.*, 63: 3740-3754

Gouws, J.F., Majozi, T., Foo, D.C.Y, Chen, C.L. and Lee, J.Y, 2010, Water minimization techniques for batch processes, *Ind. Eng. Chem. Res.,*49: 8877-8893

Ierapetritou, M.G., Floudas, C.A., 1998a, Effective continuous-time formulation for short-term scheduling. 2. Continuous and semi-continuous processes, *Ind. Eng. Chem. Res.*, 37: 4341- 4359.

Li, B. and Chang, C., 2006, A mathematical programming model for discontinuous water-reuse system design, *Ind. Eng. Chem. Res.,* 45: 5027–5036

Li, L. J., Zhou, R. and Dong, H., 2010, State-Time-Space superstructure-based MINLP formulation for batch water-allocation network design, *Ind. Eng. Chem. Res.,* 42: 236-251

Liu, Y., Li, G., Wang, L., Zhang, J and Shams, K., 2009, Optimal design of an integrated discontinuous water-using network coordinating with a central continuous regeneration unit, *Ind. Chem. Res.,* 48: 10924 - 10940.

Majozi, T., 2005b, An effective technique for wastewater minimization in batch processes, *J. Clean. Prod.*, 13: 1374-1380

Majozi, T., Brouckaert, C.J.B. and Buckley, C.A.B., 2006, A Graphical technique for wastewater minimisation in batch processes, *J. Environ. Man*., 78: 317-329

Majozi, T. and Gouws, J.F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng*. 33:1826-1840.

Shah, N., Pantelides, C.C. and Sargent, R.W.H., 1993, Optimal periodic scheduling of multipurpose batch plants, *Ann. Oper. Res*., 42:193-228

Shoaib, A.M., Aly, S.M., Awad, M.E., Foo, D.C.Y. and El-Halwagi, M.M., 2008, A hierarchical approach for the synthesis of batch water network, *Comp. Chem. Eng*, 32: 530-539

Wang, Y.P., Smith, R., 1995b, Time pinch analysis, *Trans IChemE*, 73a: 905-914.

Wu, D. and Ierapetritou, M., 2004, Cyclic short-term scheduling of multiproduct batch plants using continuous-time representation, *Comp. Chem. Eng.*, 28:2271-2286

Yongjian, L., Xigang, Y. and Yiqing, L., 2007, Synthesis of water utilization system using concentration interval analysis method (II) Discontinuous process, *Chin. J. Chem. Eng.*, 15(3), 369-375

Zhou, R., Li, L. J. and Dong, H., 2008, Simultaneous optimization of batch process schedules and water-allocation network, *Comp. Chem. Eng.*, 15(3), 369-375

CHAPTER 02

LITERATURE SURVEY

Introduction

This chapter presents the literature survey which provides the necessary background to understand the nature and purpose of the methodology proposed in this thesis. The chapter starts with the background on batch processes, Section 2.1, where all the characteristics that distinguish batch processes from other processes are highlighted. The time dependence of batch processes is the main characteristic that distinguishes them from other processes. To effectively address the time dependence of batch processes, scheduling is of importance, which is dealt with in Section 2.2. The quality and purity specifications of products produced from batch processes require that the cleaning operation of the processing units be strictly controlled. Consequently, wastewater is produced. Section 2.3 presents currently published wastewater minimization techniques for batch processes. The advantages and the disadvantages of these techniques are also discussed in Section 2.3. The final section, Section 2.4, presents conclusions which can be drawn from the literature survey.

2.1. Background on batch processes

The background on batch processes is presented in this section. The choice between continuous and batch processing mode is presented in subsection 2.1.1 and the types of batch processes are presented in subsection 2.1.2.

2.1.1. Batch processes vs. Continuous processes

The choice between continuous or batch processing mode is governed primarily by the production volume and related trade-offs between capital and operating costs. Continuous processing mode is advantageous in the production of bulk volumes of identical products or repeated processes. Petrochemical and commodity chemicals industries are largely operated under continuous mode. In contrast, batch processing mode is advantageous in the production of low-volume but high-value-added products such as speciality chemicals, pharmaceuticals, food and agrochemicals. Batch processes have proven advantageous over continuous processes even for certain large volume products, such as in the polymer industries. In the production of neoprene rubber and phenolic resins continuous alternatives were developed but failed to find wide application (Fromm *et al.*, 1988). In addition, when two or more products require similar processing steps, the same set of equipment can be used due to the inherent flexibility of batch processes. The inherent operational flexibility of batch processes give rise to considerable complexity in the design and synthesis of such plants.

Batch processes are characterized by discrete tasks i.e. time dependent task. A task has a definite start and finish time with a finite duration. The processing of raw materials to produce one or more products in batch processes follows a prescribed recipe for a finite operational time, time horizon. The processing of raw material can be achieved through various processing sequences depending on the set up of the plant. The two categories of batch processing plants are detailed in the next subsection.

2.1.2. Types of batch processes

A batch plant producing multiple products can be categorized as either a multipurpose batch plant or a multiproduct batch plant. Multipurpose batch plants are general purpose facilities where a variety of products can be produced via different recipes. Each product follows one or more distinct processing paths as depicted in Figure 2.1, by sharing the available equipments, raw materials and intermediates, utilities and production time resources. Consequently, more than one product can be produced simultaneously in such batch plants. The operational flexibility inherent in such plants is what makes them attractive in situations where product demands and formulations change rapidly (Barbosa-Povoa and Macchietto, 1994).

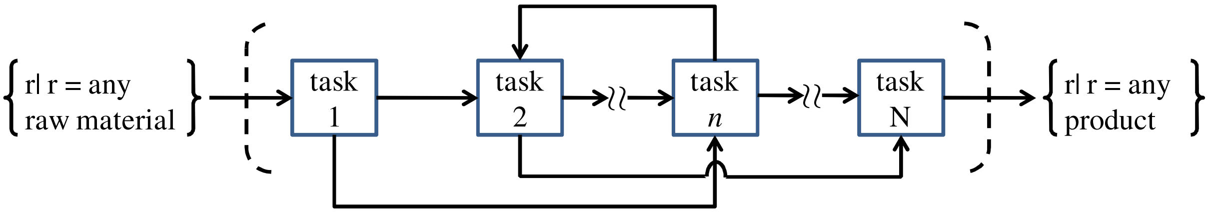


Figure 2.1: Multipurpose batch plant (Majozi, 2010:6)

In contrast, multiproduct batch plants produce variety of products following a sequential similar recipe. In such a plant, all the products follow the same path through the process and only one product is manufactured at a time, as depicted in Figure 2.2. Processing of other products is carried out using the same equipment in successive production runs or campaigns.

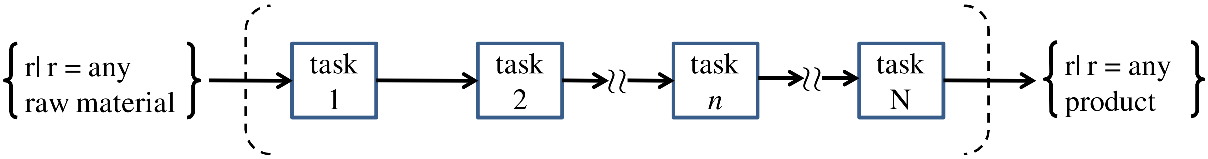


Figure 2.2: Multiproduct batch plant (Majozi, 2010:6)

As aforementioned, batch processes are time dependent. Thus, scheduling is crucial in this type of processes for economical operation. Some of the published scheduling techniques are detailed in the next section.

2.2. Scheduling

Due to the discontinuous nature of batch processes, an understanding of batch process scheduling is required to effectively address the problem of wastewater minimisation. Appropriate production scheduling is a commonly invoked method to decrease the generation of wastewater. Equipment utilization strategies and the production schedules should be derived through optimization analysis, where the objective is to meet the desired production goals with due consideration of constraints such as wastewater minimisation, which includes minimisation of equipment cleaning frequency.

Batch plants scheduling entails the determination of an optimal sequence of events utilizing the available resources given prime requirements of the final products. Furthermore, plant scheduling is also crucial for making waste management decisions; consequently, promotes environmental friendly production. An overview of some important scheduling concepts is presented first before delving into scheduling techniques.

2.2.1. Overview of important scheduling concepts

Production scheduling can generally be defined as a decision making process to determine when, where and how to produce a set of products given requirements in a specific time horizon with a set of limited resources and processing recipes (Floudas and Lin, 2004). Some of the key concepts which form the base of scheduling are briefly discussed in this subsection.

Time representation

The first and the most important key element of batch process scheduling problems is the selection of the time horizon representation. The representation of the time horizon can be classified into even time discretization or uneven time discretization representation. For the even time discretization, also known as discrete time representation, the time horizon is divided into time intervals with uniform durations. The beginning or the end of a task has to coincide with the end points of a time interval. For accurate scheduling with this class of time representation, the time intervals have to be sufficiently small i.e. the greatest common factor of the processing times. The major drawback of this time representation is that for certain problem, the size of the binary dimension turns to be big which makes it difficult to solve with available procedures. This consequently makes the computational/solution time longer, especially for large scale problems. A binary variable in batch operations is used to show the usage of a unit j, processing a task i at the beginning of time slot or time point t.

To overcome the limitation of the previous time representation uneven time discretization representation, also known as continuous time representation, was developed. For this representation, the time horizon is divided into time intervals of unknown duration. The boundaries of each time interval coincide with the start and/or finish of a particular task(s). Because of the possibility of eliminating a major fraction of the inactive time intervals, mathematical programming problems modelled using this class of time representation usually result in smaller size problem and require less computational effort (Floudas and Lin, 2004).

Recipe representation

The second element to consider when solving a scheduling problem is the recipe representation of the process. One of the most common recipe representations is the State-Task Network representation which was originally proposed by Kondili *et al* (1993). The STN representation consists of two nodes, the state and the task node. The state node represents all the material involved in the production processes i.e. raw materials, intermediates and products, and it is symbolized by a circle. The task node represents all the unit operations conducted in various equipments and it is symbolized by a rectangle. The two nodes are linked with an arc indicating the flow of states (Mėndez *et al.*, 2006).

Pantelides (1993) introduced the Resource-Task Network (RTN) representation. This was an extension of the STN representation. The RTN representation describes the processing equipment, storage, material transfer and utilities as resources. The representation of the RTN framework is similar to the STN representation except that the circle does not only represent states but also the resources required in the batch process such as processing units and storage vessels. Majozi and Zhu (2001) introduced the State-Sequence Network (SSN) representation which is very similar to the STN representation. The difference between the STN and SSN representation is that only the states node is present in the SSN representation. The task node is replaced with an arc which represents the change of a state from one state to another. Furthermore, the arc tracks the flow of states within the process network.

Intermediate storage policies

Because of the staging nature of batch processes, a finite number of intermediate storage units maybe present between processing units in the different processing stages. Intermediate storage unit installed between processing stages can help reduce idle times in these stages by freeing them to process other batches and thus increase equipment utilization and process productivity (Ku and Karimi, 1988). Intermediate storage policies are rules established to govern the transfer of intermediate products between processing stages. Some of the prominent intermediate storage policies are given in Table 2.1.

Table 2.1: Intermediate storage policies for batch processes

Storage policy	Description
Unlimited Intermediate Storage (*UIS*)	It is assumed that unlimited storage capacity between processing units is available. The intermediate material produced is removed from the processing unit and stored without limitation.
Finite Intermediate Storage (*FIS*)	Similar to UIS policy but the capacity of the storage unit is finite. The intermediate material produced is removed from the processing unit and stored provided the storage unit in not full.
No Intermediate Storage (*NIS*)	There is no storage unit for intermediate materials but the intermediate materials are allowed to be held in the processing unit they just finished processing in.
Zero Wait (*ZW*)	There is no storage unit between stages. Intermediate materials are transferred immediately to the next processing unit downstream after processing.
Common Intermediate Storage (*CIS*)	A storage unit is commonly used by various tasks within the whole process network to accomplish complete batch plant flexibility.
Mixed Intermediate Storage (*MIS*)	A batch process employing a combination of any number of the other storage policies at different stages.

Most of the batch process scheduling techniques are developed and categorized according to the concepts discussed in this subsection. An overview of some of the scheduling techniques published in literature is presented in the next subsection.

2.2.2. Short-term scheduling techniques

In the past few years, the problem of short-term scheduling of multiproduct and multipurpose batch plants has received considerable amount of attention in the academic and industrial research communities. This if due to the challenges and high economical tradeoffs involved in the operations of batch processes (Shaik *et al*. 2006). Extensive reviews on short-term scheduling techniques have been written by several researchers including Floudas and Lin (2004, 2005), Shaik *et al*. (2006) and Méndez *et al*. (2006).

Some of the short-term scheduling techniques published in literature includes the work by Kondili *et al.* (1993), Schilling and Pantelides (1996), Mockus and Reklaitis (1997), Ierapetritou and Floudas (1998a), Majozi and Zhu (2001), Sundaramoorthy and Karimi (2005). These techniques are all based on the scheduling concepts discussed in subsection 2.2.1. The integrity of the schedule obtained and computational effort to get to the schedule depends on the type of time horizon representation used, the recipe representation used and other factors such as the type of the resulting problem i.e. Linear program (LP), nonlinear program (NLP), mixed integer linear program (MILP) or mixed integer nonlinear program (MINLP). The effect of the time horizon representation on the computational time was discussed in the subsection 2.2.1. The effect of the recipe representation on the solution time is discussed below.

A general rule of thumb in mathematical modelling is that "the more binary variables a formulation has, the longer the computational time you need to solve the model". Hence, a formulation with less number of binary variables is better in terms of computational effort. For the STN representation, a single binary variable, $y(i,j,n)$, is used to describe a task (*i*) performed in a unit (*j*) at any time point or time slot, *n*. The binary dimension resulting from this recipe representation is given by $i \times j \times n$.

Ierapetritou and Floudas (1998a) decoupled the task events (*i*) from the unit events (*j*) in an effort to reduce the binary dimension resulting from STN recipe representation. Different binary variables were used to represent the beginning of task events, $wv(i,n)$ and the beginning of unit events, $yv(j,n)$. If task event *i* starts at event point *n*, then $wv(i,n)=1$ or is otherwise 0. If unit event *j* takes place at event point *n* then $yv(j,n)=1$ or is otherwise 0. The binary variables expressing the start of task *i* in unit *j* at point *n* are therefore avoided. This leads to a much smaller binary dimension, which is given by $n\times(i+j)$. The RTN representation leads to a much larger binary dimension since resources do not refer to states only.

For the SSN representation introduced by Majozi and Zhu (2001), a single binary variable, $y(s,n)$, is used when a state *s* is used at time point *n*. When more than one state is used simultaneously, only one state is assigned to the binary variable and is then termed the effective state, s^*. This recipe representation therefore leads to fewer binary variables as compared to the other recipe representation since the binary dimension is given by $s\times n$. The solution time of mathematical formulations based on SSN recipe representation will be less as compared to mathematical formulations based on the other two recipe representations.

2.2.3. Long-term scheduling: the concept of cyclic scheduling

Short-term scheduling methodologies presented in subsection 2.2.2 are appropriate for determining a production schedule for batch processes operated over a shorter time horizon. Moreover, they are appropriate for batch processes where the demands for different products are subjected to rapid changes. Although these models greatly advanced the range of scheduling approaches, the computational complexity of the resulting mathematical models is still a challenging subject when batch processes operated over a longer time horizon are considered. When determining a production schedule for batch processes operated over a long time horizon as encountered industry, the computational time becomes intractable. Consequently, short-term scheduling methodologies are not suitable for industrial scale problems.

The concept of cyclic/periodic scheduling was developed to address the issue of longer solution time when determining a schedule for batch processes operated over longer time horizons. The concept was originally introduced by Shah *et al.* (1993) and it is based on the following axiom:

> *Consider a case where the time horizon (**H**) is much longer when compared to the duration of an individual tasks, a sub-schedule exists with a much smaller time horizon (**T**), periodic execution of which achieves production very close to the optimal production of the original longer time horizon (**H**).*

The axiom is depicted in Figure 2.3, the optimal cycle length being ***T*** on the diagram.

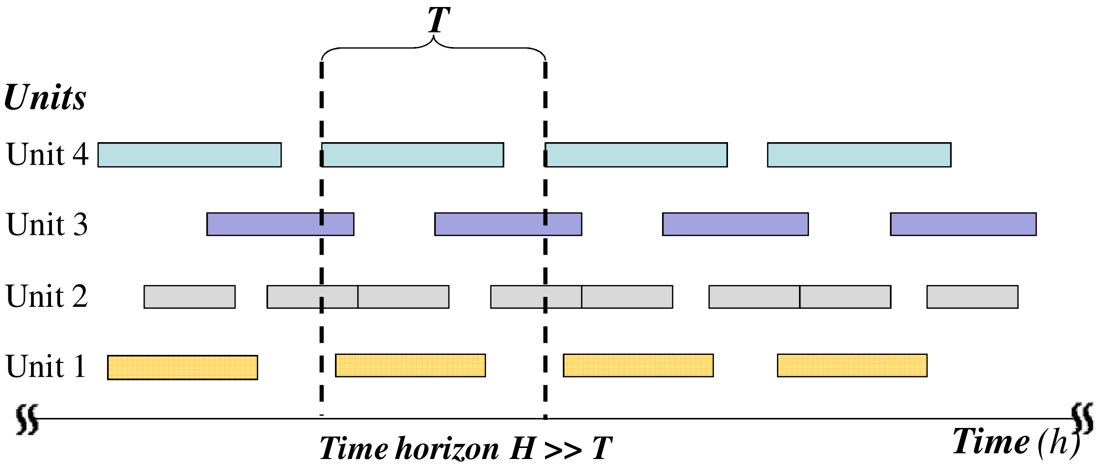


Figure 2.3: The original time horizon *H* is greater than the optimal cycle length *T*.

From Figure 2.3, it is clear that some of the tasks cross the boundary of the optimal cycle length ***T***. A task that has such an effect can be viewed as a task extended past the cycle of interest notionally *wrapping around* to the beginning of the cycle. This notion was also introduced in the work by Shah *et al.* (1993) and it is depicted in Figure 2.4 by the tasks in units 2 and 3.

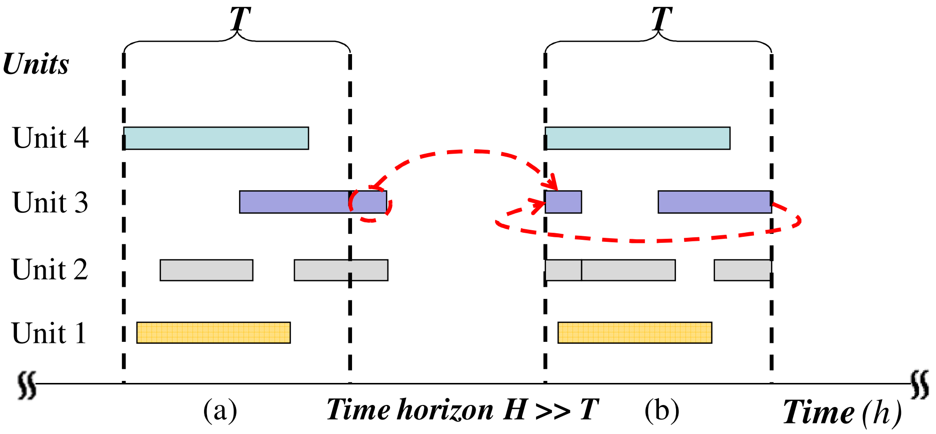


Figure 2.4: a) Task 2 in unit 2 overlaps over the cycle. b) Task 2 is wrapped around the beginning of the cycle.

Thus, by applying the concept of cyclic scheduling, the size of an industrial scale problem (***H***) can be reduced to a problem with a smaller time horizon (***T***) which can be solved with ease. The computational time associated with finding the schedule for time horizon ***T*** is much less as compared to the computational time associated with finding the schedule for time horizon ***H***.

Based on the axiom and the concept of task wrapping around, Shah *et al.* (1993) developed a cyclic scheduling technique based on the STN representation. The technique was formulated based on discrete time representation in which the cycle is discretised into *T* time intervals of equal duration (σ) as depicted in Figure 2.5. The optimum cycle length was determined by solving a sequence of fixed cycle time problems i.e. the cycle length was treated as a parameter. The cycle starts at t = 1 and ends at t = *T*+1, which coincides with the start of the next cycle. The solution time of the model resulting from this mathematical formulation was still a concern since the technique was based on discrete time formulation.

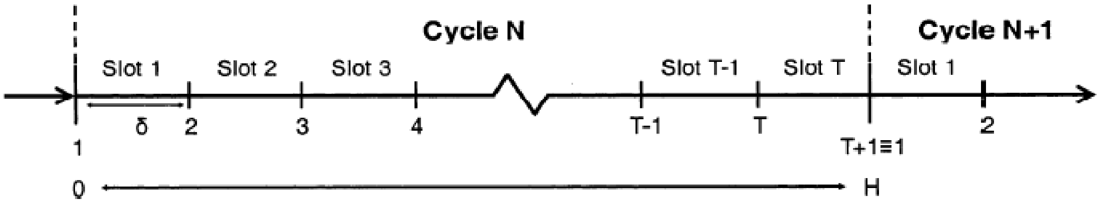


Figure 2.5: Even time discretization for a single cycle (Castro *et al.*, 2003)

Since the concept of cyclic scheduling was introduced, very few researchers took interest in exploring and exploiting this it. Amongst the few work done on cyclic scheduling, some of the published techniques were proposed by Schilling and Pantelides (1999), Castro *et al.* (2003) and Wu and Ierapetritou (2004).

Schilling and Pantelides (1999) formulated a periodic scheduling model based on RTN recipe representation for general multipurpose plant comprising of batch, semi-batch and continuous operations. The time horizon was formulated using continuous time representation. The cycle was divided into *T* time intervals of variable durations as depicted in Figure 2.6. In contrast to the technique by Shah *et al.* (1993), the cycle length was treated as an optimization variable instead of a parameter. Their mathematical formulation resulted in a MINLP problem, which could not be linearized exactly. They developed a special branch and bound algorithm for solving the problem by branching on both discrete and continuous variables.

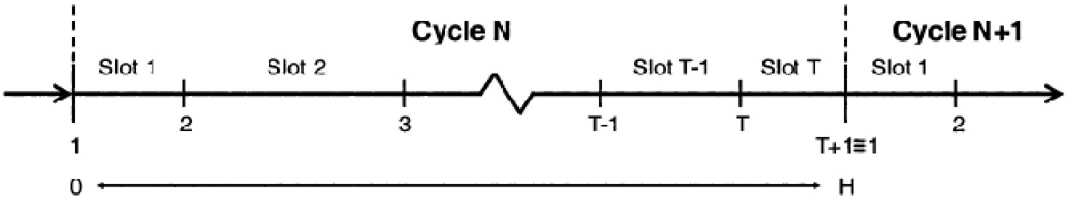


Figure 2.6: Uneven time discretization over one cycle (Castro *et al.,* 2003)

Castro *et al.* (2003) also developed a periodic scheduling technique based on the RTN recipe representation through a case study approach. They used a case study from the pulp and paper industry for the formulation which rendered their technique industry specific. They presented two methods, one based on continuous and one based on discrete time representation. For discrete time representation, the cycle length was treated as parameter and for continuous time representation the cycle length was treated as an optimization variable.

For a given cycle duration, the discrete time representation resulted in a MILP problem which was solved to optimality in a reasonable computational time, even for fine discretization on the time grid. On the other hand, the continuous time representation resulted in a MINLP problem, which under the assumption of constant throughput becomes a MILP problem. After the simplification, the continuous time representation could be solved to optimality within reasonable computational effort only for a relatively small number of event points, making it practically impossible to find the global optimum.

Wu and Ierapetritou (2004) proposed a cyclic scheduling technique, which was based on the STN recipe and continuous time representation. The proposed technique was an extension of the short-term scheduling technique by Ierapetritou and Floudas (1998a). The other presented cyclic scheduling techniques ignored the start-up and the finishing/shut-down period with the assumption that their duration is negligible as compared to the entire time horizon. The outstanding feature of the cyclic scheduling technique by Wu and Ierapetritou (2004) over the other cyclic scheduling techniques is the detailed consideration of the start-up and finishing period.

To ensure smooth operation, they divided the longer time horizon (***H***) into three periods, the initial period, the cyclic period and the final period, as depicted in Figure 2.7. In the initial period, all the necessary intermediate products needed to start the cyclic period are produced. The cyclic period is the main period where the determined optimum cycle length is executed repeatedly and the intermediates from the last cycle are consumed in the final period. The sum of all the periods must be equal to the longer time horizon (***H***).

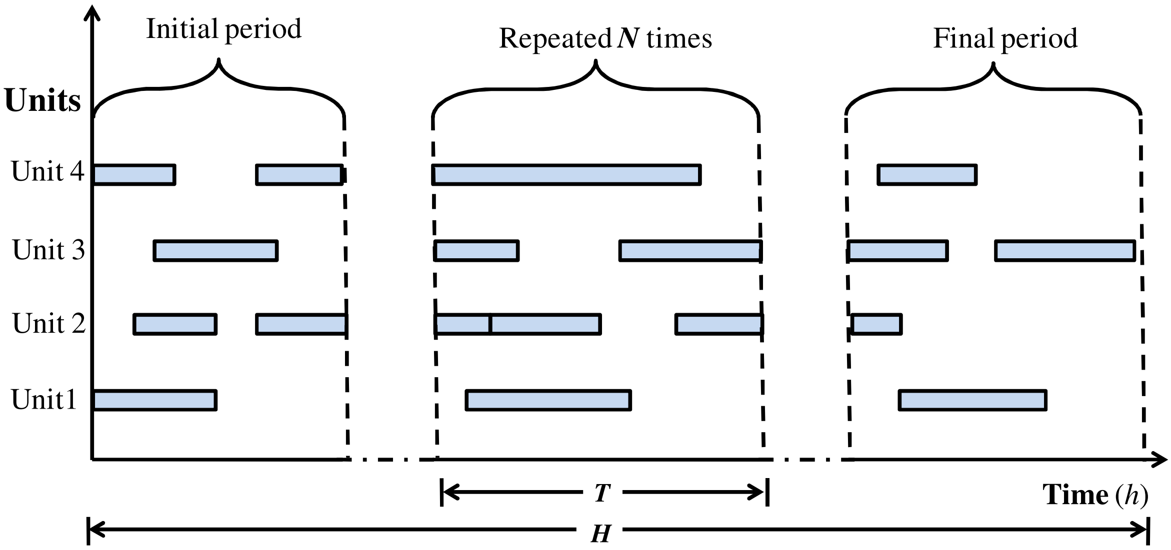


Figure 2.7: Cyclic scheduling in the middle period repeated *N* times

The aspect of sequence and scheduling of operations in batch plants was covered in this section. In the next section, some of the published wastewater minimisation techniques for batch processes are presented.

2.3. Wastewater minimisation techniques

The nature of products widely produced from batch processes are such that the effluent generated is of extreme toxicity e.g. agrochemical and pharmaceutical products. The quality and purity specifications of products from pharmaceutical industries require that the cleaning operation of the processing units be strictly controlled. Consequently, large amounts of solvents and cleaning agents are commonly used, thus leading to high volume of effluent generation. From these observations, the need for wastewater minimisation techniques is apparent. In this section, published wastewater minimisation techniques are presented. Some of the important wastewater minimisation concepts and terms are presented first.

Classification of water-using operations

Water-using operations in processing plants are generally categorized into mass transfer-based and non-mass transfer-based operations. In mass transfer-based operations, also known as fixed load operations, water is used as a mass separating agent (MSA). This category of operations is characterized by the preferential transfer of certain amount of impurity load from a rich stream to a water stream which is used as a lean stream, as shown in Figure 2.8 (Chen and Lee, 2009). For water-using operations under this category, the fixed contaminant load in the processing unit is a parameter of importance. Typical examples of these operations are washing operations, extraction, scrubbing, *etc*. It is usually assumed that the input and the output flowrates of the MSA streams are equal for this type of operations i.e. the impurity mass load collected in the unit is negligible as compared to the total flowrate.

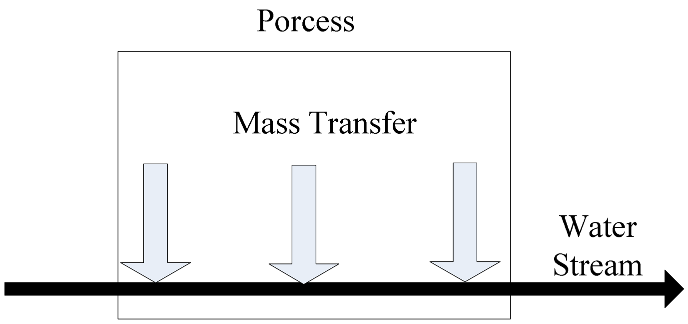


Figure 2.8: A depiction of mass transfer-based operations (Chen and Lee, 2008)

The second category of water-using operations is the non-mass transfer-based operations, also known as fixed flowrate operations. This category covers all the other functions of water in processing plants other than as a MSA. A typical example of this category includes water sink and water source operations, e.g. boilers and cooling towers. One typical characteristic of this category of operations is that the inlet and outlet flowrates of the water-using processes may not be equal, which is not the case for mass transfer-based operations (Foo *et al*., 2005; Chen and Lee, 2008).

The principle of water reuse and recycle

A well established principle for wastewater minimisation in the processing industries is the principle of water reuse and recycle. This principle can be implemented directly or indirectly. For direct water reuse/recycle, the reusable water is directly reused from one process to another. The concentration constraint must be satisfied for direct water reuse in continuous processes, as depicted in Figure 2.9(a). In batch processes, both concentration and time constraints must be satisfied for direct water reuse to take place, as depicted in Figure 2.9(b).

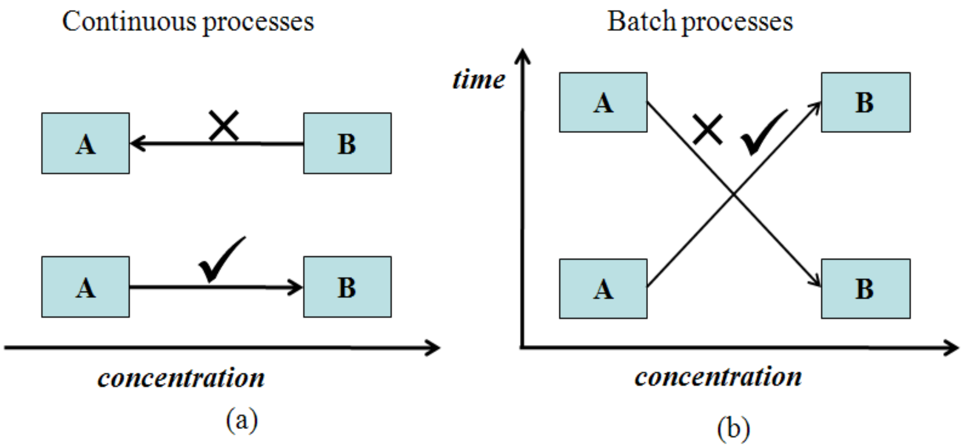


Figure 2.9: Direct water reuse in (a) continuous and (b) batch processes

Indirect water reuse involves the use of a water storage vessel to achieve water reuse between operations. The use of a water storage vessel for wastewater minimisation is commonly employed in batch processes to bypass the time constraint. To minimise the capital cost associated with wastewater minimisation exercise, direct water reuse is exploited first before any water storage vessel options are considered.

The problem of freshwater consumption minimisation in processing plants comprises of two steps. The first step involves the targeting of minimum freshwater consumption, which is equivalent to the minimisation of wastewater generation. The second step involves the synthesis of the water-using network which will satisfy the freshwater target. The two main approaches used to deal with wastewater minimisation problems are graphical and mathematical approaches. In the former approach, the two steps are performed separately and the later approach performs both steps simultaneously. Some of the published wastewater minimisation methodologies based on the two approaches are presented in the following subsections.

2.3.1. Graphical techniques

The first graphical technique for wastewater minimisation in batch processes was presented by Wang and Smith (1995b). They adopted water pinch methodology based on the limiting water profile, which was originally developed for wastewater minimisation in continuous processes. The limiting water concentration profile is based on the specified maximum inlet and outlet concentration of water being used in an operation. The water supply line is drawn against the limiting concentration curve on the same set of axis. From the constructed curves, the pinch point and the mass of contaminants that needs to be removed can be determined. Furthermore, the minimum water requirement can be determined. The available water curve from the process and the water required by the process are plotted against time on the same set of axis. From these curves, the needed storage capacity can be determined.

The technique by Wang and Smith (1995b) only addresses wastewater minimisation problems for mass transfer-based operations since the mass load is fixed by the specified flowrate, duration of the operation, maximum inlet and outlet contaminant concentration. Furthermore, their technique was applicable to semi-continuous operations since water reuse was permissible between operations with overlapping durations.

Hallale (2002) proposed a new graphical targeting technique. The technique was based on a new representation of the composite curves and the concept of water surplus. Before applying this technique, the process streams data was divided into source and demand streams. The first step of this technique was to draw the demand curve based on the demand streams and the source curve based on the source streams against the accumulative flowrate on the same set of axis. This is different from the conventional composite curve because the purity of the required water is plotted on the vertical axis rather than the streams contaminant concentration. The purity of the water required was determined based on the stream's contaminant concentration. Equation 2.1 was used to determine the purity with C in *ppm*.

$$Purity = \frac{1\ 000\ 000 - C}{1\ 000\ 000} \tag{2.1}$$

The second step is to guess the freshwater flowrate and include it in the source composite curve, and check if the assumed flowrate is feasible. This is done by checking if the flowrate of the water source is equal or greater than the demand flowrate. If the resulting source composite curve extends to the right of the demand composite curve then this criterion is met. This is done until the demand composite is completely under the source composite curve. The network corresponding to the target was synthesised using mathematical programming. The mathematical formulation resulted in a LP problem. This method has an advantage over the methods by Wang and Smith (1995b) since it can handle non-mass transfer-based operations like reactors, cooling towers and hoses. Nonetheless, the fact that this technique is based on an iterative graphical procedure is a major drawback because graphical techniques are generally time intensive.

The abovementioned techniques only address one category of operations, either mass transfer-based or non-mass transfer-based operation. Foo *et al.* (2005) developed a two-stage technique for the synthesis of a maximum water recovery (MWR) network for batch and semi-continuous processes. The technique was applicable to both mass transfer-based and non-mass transfer-based water-using operations. The first stage of the technique was to target the minimum utility requirement for the processes and the required intermediate storage capacity. This was done using the newly developed *time-dependent* water cascade analysis (TDWCA) technique. The TDWCA technique is a numerical approach, which was originally developed for mass transfer and non-mass transfer water-using operations in continuous processes by Manan *et al.* (2004). The advantage of using numerical targeting approaches is that they produce accurate targets and reduce the required time for tedious drawings and calculations involved in graphical approach.

For the first stage, the time horizon was divided into time intervals. Water demands and sources are determined in each of the time intervals. They introduced a time interval table for this purpose. In the time interval table, the streams are located in specific purity level using the same principled used by Hallale (2002), Equation 2.1. Water cascade analysis is done in each of the time intervals to find the utility requirements for each time interval. The addition of all the targets for each of the intervals gave the overall utility requirements for the whole process. The second step was to synthesis the water recovery network for the obtained target. This was achieved with the newly introduced *time-water network diagram*.

Yongjian *et al.* (2007) developed a time-dependent concentration interval analysis technique for wastewater minimisation which dealt with both steps of pinch analysis. The technique was an extension of their previously developed technique, concentration interval analysis (CIA), which was originally intended for continuous processes. In the first step of the technique, time intervals were defined, analogous to concentration intervals. The starting and the ending times for the water-using operations were defined as the intervals. The longest time interval corresponds to the shortest duration of the washing operation. Washing operations with longer durations were artificially partitioned into a series of operations operating within the defined time intervals.

Within each interval, the water-using operations were considered continuous processes, and the CIA which was originally developed for continuous processes was used to obtain freshwater targets within the time intervals. The summation of all the targets in their respective time intervals was considered the upper bound without the consideration of contaminated water reuse for the defined intervals. The second step of the technique was to target minimum freshwater requirements for each time interval taking into account water reuse between intervals. Storage vessels were introduced to keep the surplus reusable water from one interval to be reused in the next interval. Only water from the previous time interval could be used in the subsequent time intervals. The freshwater in this step correspond to the absolute minimum freshwater requirement. The last step was to synthesis the water-using network which satisfies the minimum freshwater target. The drawbacks from the technique by Yongjian *et al.* (2007) is the assumption of continuous behaviour of batch processes within the defined time intervals and the artificial partitioning of operations with longer durations into a series of continuous processes.

The common drawback of the techniques presented above is that they do not address wastewater minimisation for processes which are operated strictly under batch mode since they allow water to be reused between processes which are active over the same time interval. Similar to the work by Wang and Smith (1995b), Majozi *et al.* (2006) presented a graphical technique for wastewater minimisation in processes which are operated strictly under batch mode. To address a wastewater minimisation problem for processes operated strictly under batch mode, water reuse and recycle is only allowed to take place either at the start or at the end of an operation. The technique also took into consideration the intrinsic two-dimensionality constrained nature of batch processes by interchanging time and concentration as the primary constraint. In the first case, the time dimension was first posed as the primary constraint and the concentration constraints as the secondary constraint. In the second case, the priorities of the constraints were reversed. This was done to demonstrate the effect of the two dimensions on the final design.

Chen and Lee (2008) focused on the second step of the conventional pinch analysis, water network synthesis. The minimum freshwater target was assumed to be predetermined. The objective of the network synthesis was to determine an effective streams allocation, which minimized freshwater consumption by maximising the water recovery amongst water-using operations. This was achieved through the introduction of a new graphical representation to visualise the process streams called the quantity-time diagram. The water inlet and outlet streams were separately considered as water demand and water sources, respectively. The proposed graphical analysis was carried out by selecting suitable water sources to satisfy each water demand taking into account the time constraints.

To minimise water requirements for fixed load operations, the outlet concentration was set to its maximum allowable value which is the necessary condition of an optimal network design proven by Savelski and Bagajewicz (2000). For fixed flowrate operations the principle of “nearest neighbours with available sources” was employed by maximizing the inlet concentration. The validity of this principle was proven by Prakash and Shenoy (2005) by using a water source with the highest concentration without violating the maximum inlet concentration requirement; the cleaner sources were reserved for other operations.

Their water network synthesis methodology was similar to the synthesis methodology proposed by Foo *et al.* (2005). The time horizon was partitioned into several time intervals according to the starting and finishing times of each operation. The processes were treated as continuous sub-processes in the defined time intervals. The freshwater requirement of the synthesised network was compared to the target obtained from the conventional pinch analysis to ensure that the network correspond to the minimum water requirement possible. The complexity and the capital cost of the resulting network was simplified by reducing the number of water storage vessels. This technique is a combinatory graphical problem since there are many networks that can correspond to an optimal freshwater target. This is a major drawback for a graphical technique since graphical methods are generally time intensive, as aforementioned.

The advantage of graphical techniques is their ability to give the engineer the insight to the problem and to identify which operations are the constraining operations in terms of water reuse, bottleneck operations. However, graphical techniques have two major drawbacks. Firstly, the schedule must be predefined ahead of the freshwater target. Therefore, the obtained freshwater target is schedule specific. Secondly, graphical techniques fail to deal with streams characterized by multiple contaminants, due to the multiple dimensions introduced. Due to these drawbacks, graphical techniques have limited practical application since multiple contaminants streams are a common occurrence in practice.

Mathematical techniques are capable of dealing with the drawbacks from graphical techniques. They can effectively handle multiple contaminants operation. They have an added advantage of being able to handle practical based constraints like forbidden matches for operability, flowrate constraints, flowrate changes different mass transfer models, *etc.* Some of the mathematical techniques published in literature are discussed in the next subsection.

2.3.2. Mathematical programming techniques

Overall, mathematical techniques can be categorized into two structures, sequential and simultaneous framework. In the sequential framework, the production schedule is first determined and the results are then used to determine the optimum water-using network. However, for simultaneous framework both the water-using network and the production schedule are determined simultaneously. A true optimality can be realised if the production schedule and water-using network are optimised simultaneously. Consequently, the results obtained from the later framework are superior. Both these mathematical technique frameworks are presented in this subsection.

2.3.2.1 Sequential framework

Kim and Smith (2004) developed a mathematical technique for wastewater minimisation in batch processes. The technique was based on the modification of the work by Wang and Smith (1994a), which was originally intended for wastewater minimisation in continuous processes. The mathematical technique was formulated based on the superstructure shown in Figure 2.10. The time horizon of interest was divided into time intervals and water reuse between intervals was made possible through the use of intermediate storage vessels. Operations with longer durations than the defined time interval were artificially partitioned into a series of operations operating within the defined time intervals. The mathematical technique was applicable to both fixed mass load and fixed flowrate operations characterized by multiple contaminants.

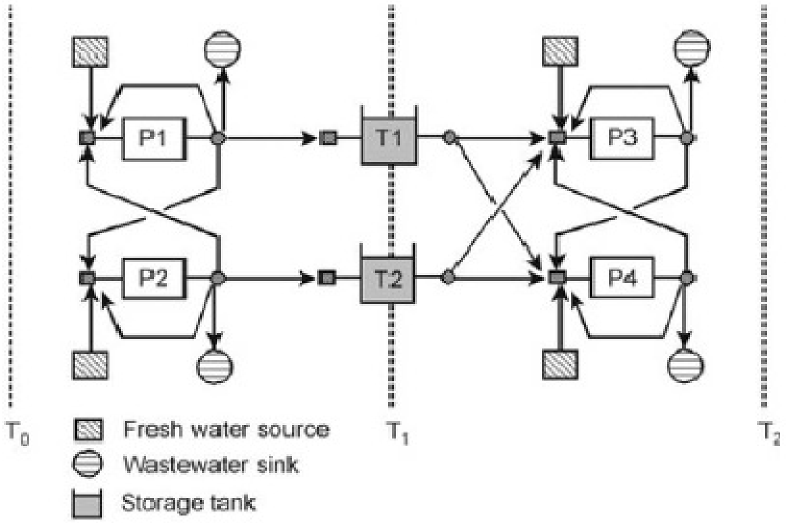


Figure 2.10: Superstructure for Kim and Smith (2004)

The mathematical formulation resulted in a MINLP problem. The authors proposed a decomposition solution strategy to deal with any computational difficulties that might arise for industrial scale problems. The original MINLP problem was decomposed into a MILP and a LP problem, which were solved iteratively. The MILP was obtained by fixing the outlet concentrations at the maximum allowable values. Positive slack variables were introduced to the MILP model to compensate for the deviation in the mass load balance constraints that might result from the decomposition of the original problem. The values of water flowrates obtained from the MILP problem were passed to the LP problem. The objective of the LP problem was to minimize the introduced slack variables, to zero if possible. The values of the outlet concentrations obtained from the LP problem were used in the next iteration. The iteration continues until the sum of the slack variables approaches zero. The output from this iterative procedure was used as the starting point for solving the original MINLP problem. It is apparent from the presented superstructure that self-recycling without the presence of an intermediate storage vessel was allowed. Water reuse was also allowed to take place between operations which were active over the same time interval. From these observations, one can conclude that their technique is more suitable for semi-continuous processes not for processes operated strictly under batch mode.

Wastewater generated in processing plants is first treated to meet the stipulated contaminant concentration levels before it is disposed off to the environment. The technique by Kim and Smith (2004) and many other published wastewater minimisation techniques do not consider the link between the water-using operations and the treatment plant. The costs of the treatment plants are generally high and there is no return on this investment. To reduce the capital investment of wastewater treatment plants, the fluctuation of both the flowrate and the concentration of wastewater need to be minimised, at best eliminate it.

Li and Chang (2006) recently developed a mathematical programming technique to synthesis an integrated water-reuse network and an equalization system for batch processes. An equalization system was incorporated to eradicate possible shock loads, sudden high concentration and flowrate, to the wastewater treatment system. The developed model was applicable to batch processes characterized by multiple contaminants; however, it is only relevant to fixed mass load operations. In developing the model it was assumed that all reuse water streams are taken directly from the intermediate storage vessels i.e. direct water reuse opportunities were not exploited. Due to this assumption, the freshwater consumption resulting from this model might be suboptimum since not all water reuse avenues were exploited. The model was formulated based on discrete time representation. Therefore, the model might encounter lengthy solution time when applied to industrial scale problems because of the large number of binary variables associated with discrete time representation. The resulting formulation was a MINLP problem, which means a global optimal solution could not be guaranteed from this model.

Shoaib *et al.* (2008) developed a three stage hierarchical approach for the synthesis of batch water-reuse network. In the first stage, the minimum freshwater consumption was determined. This was done by mapping a source to a sink via a reusable water storage vessel, as show in the superstructure depicted in Figure 2.11. This was done to avoid the time dependence of batch processes. This method of mapping limits this technique to indirect water reuse only. It is clear from the superstructure shown in Figure 2.11 that for every water reuse there must be an accompanying reusable water storage vessel. Thus, the capital cost of the resulting water-reuse network might be higher. The first stage resulted in a LP problem which guaranteed a globally optimum solution.

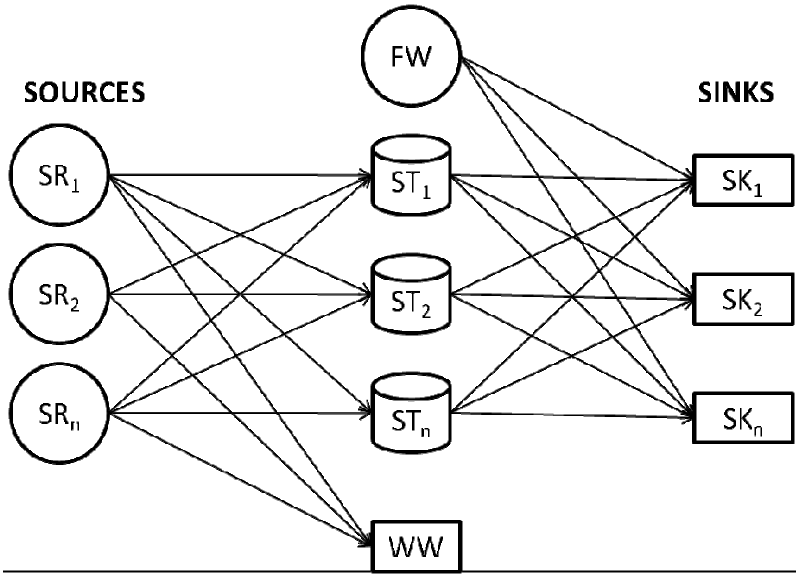


Figure 2.11: Superstructure of source-tank-sink formulation (Shoaib *et al.*, 2008)

The second stage aimed at simplifying the complexity and reducing the high capital cost of the resulting network from the first stage by reducing the number of reusable water storage vessels. The minimum freshwater target obtained from the first stage was not altered in the second stage. The formulation of the second stage resulted in a MINLP problem, which was linearized to a MILP problem using the relaxation technique proposed by McCormick (1976). For the third stage, the complexity of the network was further simplified by minimising the number of inter-connections, without compromising the results from the previous two stages. A wastewater regenerator was also considered as a standalone unit by first identifying the pinch concentration of the resulting water network. The pinch concentration of the water-reuse network was determined using the time-dependent water cascade analysis technique proposed by Foo *et al.* (2005). The formulation has limited practical application since it is only applicable to fixed mass load operations characterized by single contaminant streams.

Chen *et al.* (2008) developed a mathematical formulation for the synthesis of water-using network for batch plants based on the continuous time and RTN recipe representation. Furthermore, the developed formulation addressed practical scenarios like forbidden matches. The formulation is applicable to operations characterized by multiple contaminants. However, it is limited to fixed load operations. Four objective functions were presented to demonstrate the versatility of the formulation. The first objective function considered the determination of minimum freshwater consumption. The results from the first objective function usually correspond to multiple water-using network configurations. The second objective function aimed at narrowing down the number of possible configurations by minimising the size of the reusable water storage vessels corresponding to the first objective value. The second objective value still corresponds to numerous possible pipeline inter-connections. The third and fourth objective functions aimed at reducing the number of inter-connections in the network to give the final design. The last two objective functions resulted in a MINLP problem, which means a global optimum solution could not be guaranteed from this mathematical formulation.

Tokos and Pintarič (2009) developed mathematical formulation for minimising freshwater consumption based on a case study approach. The case study considered was from a brewery plant. The mathematical formulation was based on the modification of the technique by Kim and Smith (2004) to suite the specific needs of the brewery plant. The formulation by Kim and Smith (2004) was modified to enable efficient integration of discontinuous and semi-continuous water using processes. The original formulation was further modified by including a batch and semi-continuous treatment units in order to introduce the option of regeneration re-use.

Semi-continuous streams were treated as water sources of limited capacity and the unused water from these streams was discharged. For every water reuse from a semi-continuous stream, a storage vessel was installed. Thus, the resulting water-using network might have high capital cost. The formulation was based on a fixed schedule since the production was not allowed to be altered due to the sensitivity of the operations involved in the brewery plant. The resulting model was a MINLP problem. The objective function for the formulation consisted of the overall cost of the water network which involved the freshwater cost, annual investment costs of intermediate storage vessels, piping installation cost and wastewater treatment costs. Due to the consideration of the costs contributing to the overall cost, the resulting objective function was complex which made the model hard to solve.

Chen *et al.* (2009) also developed a mathematical technique for wastewater minimisation in batch processes. Wastewater generation was minimised through the optimum synthesis of water-using networks incorporating both direct and indirect water reuse. Indirect water reuse was achieved through the use of a central intermediate storage vessel, which was a concept originally proposed by Majozi (2005a). The mathematical formulation was extended to cover forbidden water reuse between water-using operations and water loss from operations. The mathematical technique was limited to fixed flowrate operations characterized by multiple contaminants. Two objective functions were considered in their work. The first objective function considered wastewater minimisation without any limitation to water reuse/recycle between operations. The resulting formulation for the first objective function was a NLP problem. The second objective function involved wastewater minimisation with consideration of forbidden water reuse between water-using operations. The resulting formulation was a MINLP problem. A global optimum solution could not be guaranteed for both objective functions due to the non-convexity of the resulting models.

Halim and Srinivasan (2010) proposed an integrated scheduling and wastewater minimisation optimization methodology. The scheduling sub-problem was solved using the short-term scheduling technique proposed by Sundaramoorthy and Karimi (2005). The solution from the scheduling sub-problem, the Gantt chart, is not necessary unique. Different schedules may give the same objective value. The novelty of their proposed methodology lies in that they looked into the wastewater generated from the other alternative schedules. The freshwater consumption was minimized through direct reuse only. The possibility of using an intermediate storage vessel to increase the opportunities of wastewater reuse was not explored.

Other than the composition/concentration of a stream, there may be other important properties e.g. conductivity, pH, toxicity, colour *etc,* that should be considered when determining minimum freshwater consumption. The methodologies presented above do not cater for these kinds of scenarios. To address this drawback, Ng *et al.* (2008) developed a systematic property-based technique for the synthesis of batch water-using network. The technique was applicable to fixed load operations characterized by multiple contaminants. The technique was based on the concept of property integration introduced by El-Halwagi (2004), which was originally intended for continuous processes. Using this concept, water sources were characterized by a number of properties instead of concentration and water sinks requirements were bounded by property constraints.

To enhance the reuse/recycle opportunities of the water sources, an interception device was introduced into the water network synthesis. Interception devices are units that maybe added to the process to change the properties of a water source e.g. pH adjustment, filters, dilution tanks, *etc*. The concept of source-tank-sink representation presented by Shoaib *et al.* (2008), Figure 2.11, was modified to a source-tank-interception-tank-sink representation. A source stream follows a tank-interceptor-tank sequence before sent to a sink. An imaginary interception device was added for sources which did not require any property interception to allow for bypass. An interceptor was sandwiched between two tanks. The main purpose of the tanks was to ensure that the properties of the streams achieves the desired homogeneity before they are sent to an interception device or sinks. A global optimum solution from this formulation could not be guaranteed because the formulation resulted in a MINLP problem.

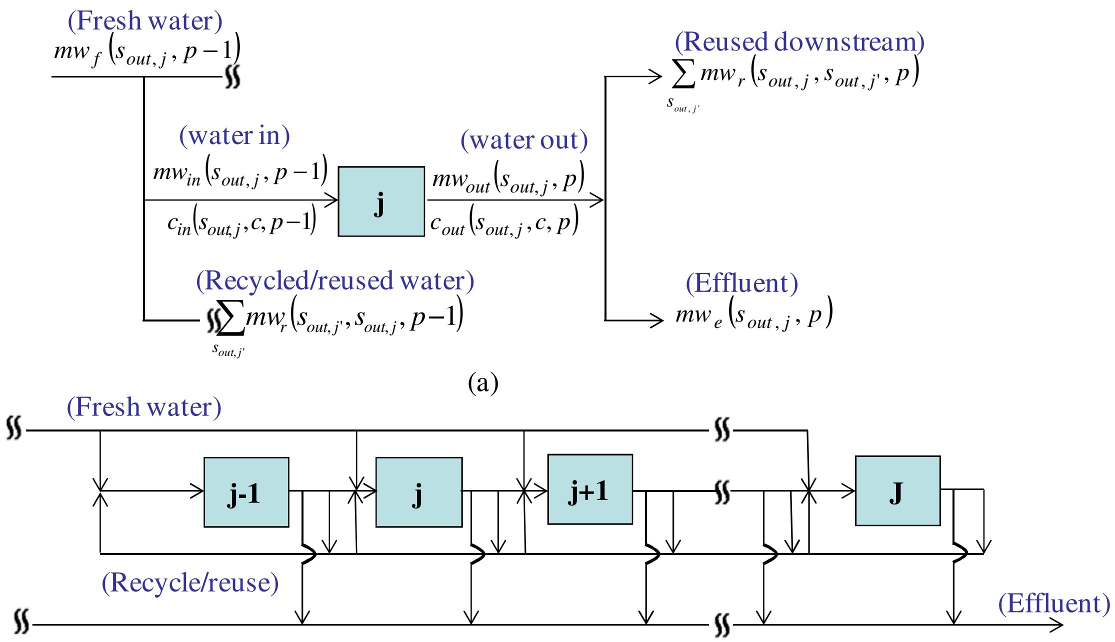
When the developed model is applied to large scale problems, the resulting network configuration might be complex with high capital cost due to the number of storage vessels and interception devices.

As aforementioned, wastewater minimisation techniques under sequential framework treat the time dimension charactering batch processes as a parameter. In the next subsection, wastewater minimisation techniques under simultaneous framework where time is treated as an optimization variable are presented.

2.3.2.2 Simultaneous framework

In batch processes, wastewater generation is closely tied to the operating procedure and the schedule of the production plan. Consequently, wastewater minimisation in batch processes is highly dependent on the schedule of the plant. In the past, enough effort has been invested into the development of rigorous scheduling techniques that are robust with low solution time. Some of the scheduling techniques were adopted into wastewater minimisation. The attractiveness of these techniques lies in their ability to simultaneously determine the optimal production schedule and minimise the generation of wastewater from the resulting production schedule. In this subsection some of the wastewater minimisation techniques under simultaneous framework are presented.

Majozi (2005a) presented a mathematical technique for wastewater minimisation in multipurpose batch plants. The mathematical formulation of the technique was based on continuous time representation. The production scheduling sub-problem was based on the scheduling technique proposed by Majozi and Zhu (2001). Wastewater generation was minimised through the exploitation of direct and indirect water reuse/recycle. Indirect water reuse/recycle was achieved through the use of a central intermediate storage vessel. The mathematical model in the absence of a central intermediate storage vessel was formulated based on the superstructure shown in Figure 2.12 and the mathematical model in the presence of a central intermediate storage vessel was formulated based on the superstructure shown on Figure 2.13.



(a)

(b)

Figure 2.12: Superstructure for the mathematical formulation with no reusable water storage Majozi (2005a)

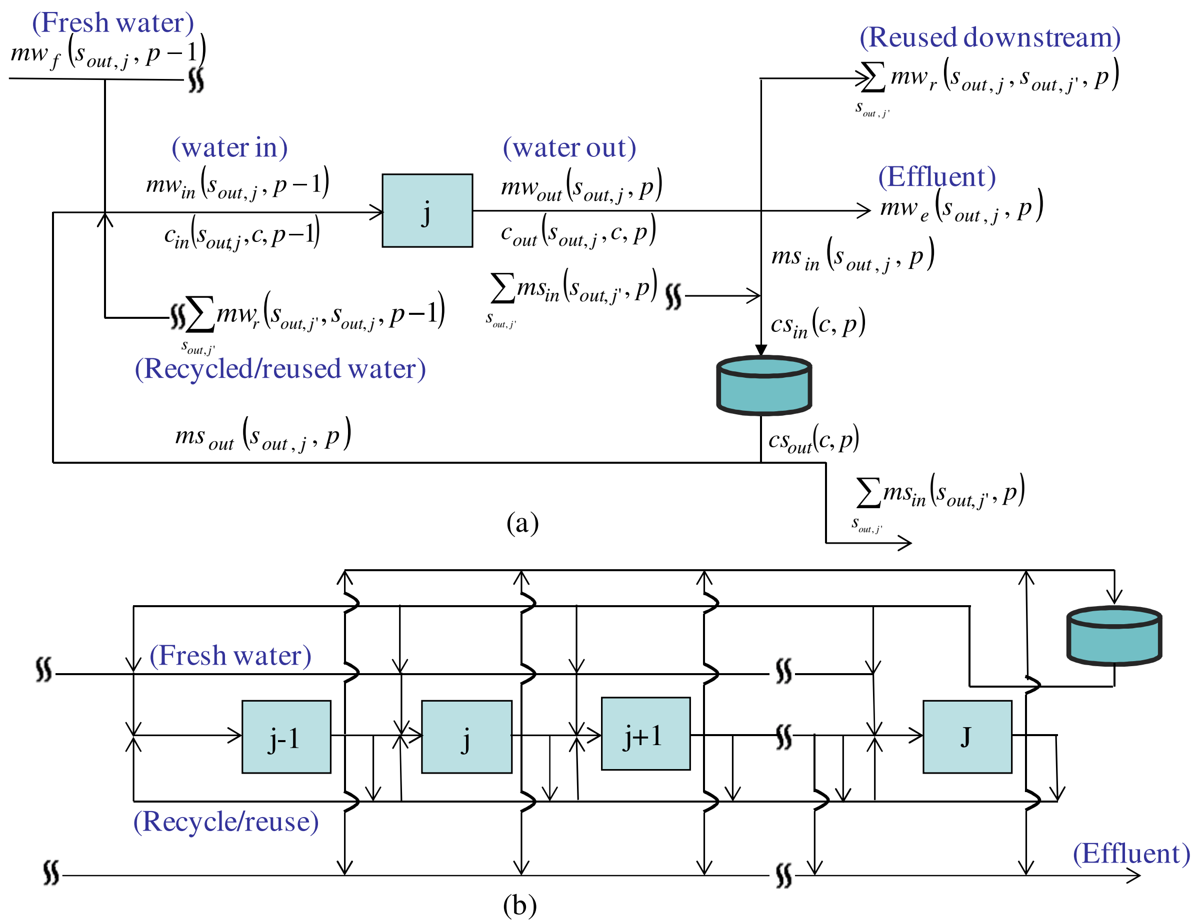


Figure 2.13: Superstructure for the mathematical formulation with reusable water storage Majozi (2005a)

The technique was derived for four scenarios. In the first scenario, the outlet concentration of each process was fixed at its maximum value in the absence of a central intermediate storage vessel. With the outlet concentration treated as a parameter, the water flowrate through each operation was treated as an optimization variable. In the second scenario the amount of water used by each process was fixed in the absence of a central intermediate storage vessel. For the second scenario, the inlet and outlet concentrations were treated as optimization variables since the flowrate was treated as parameters. The third and fourth scenarios were the same as the first two respectively, but in the presence of a central intermediate storage vessel. Thus, both direct and indirect water reuse between processes was considered for the third and fourth scenarios.

Fixing the outlet concentration for each water-using operation in the absence of central intermediate storage vessel initially rendered the formulation as a nonconvex MINLP problem which was linearized exactly using Glover (1975) transformation to a convex MILP problem. In contrast, allowing the outlet concentration to vary within predefined boundaries while fixing the water requirement of the processing unit yielded a MINLP problem for which a global optimality could not be guaranteed. The mathematical technique by Majozi (2005a) was only applicable to batch processes characterized by single contaminants.

In most published wastewater minimisation techniques, the task of optimising the production schedule, the water-using subsystems and the onsite wastewater treatment facilities are treated as three different sub-problems. Hence, they are usually optimised separately. Cheng and Chang (2007) developed a mathematical programming technique to effectively incorporate these three sub-problems into a single comprehensive model so as to determine the optimal solution for a fully integrated batch water-using network. They developed the formulation of these problems separately and integrated them through their objective functions. The formulation of the production scheduling sub-problem was based on STN recipe representation and discrete time formulation. The resulting objective function from the production scheduling sub-problem was the maximisation of revenue taking into account the price of the products and the raw material cost.

For the water-reuse network sub-problem, wastewater was minimised through direct and indirect water reuse/recycle. The number of buffer tank in the system was not limited to any upper bound. This may result in a system with a higher capital cost. The integration between the production schedule and water-reuse sub-problems was based on the assumption that the amount of water consumed and/or generated by water-using operations is proportional to the amount of material been processed in the same unit. In the presented case study, water was reused between two water-using operations active simultaneously. From this observation, one can conclude that the developed model was not suitable for processes operated strictly under batch mode. The model was only capable of handling single contaminant operations which is a serious drawback in terms of its practical application. The model might encounter longer computational time when applied to industrial scale problems since the production scheduling sub-problem was based on discrete time representation.

Zhou *et al.* (2008) developed a mathematical technique to optimize the production schedule and water-allocation network simultaneously. The methodology was based on the concept of state-space modified for batch processes. The original concept of state-space was proposed by Bagajewicz and Manousioutakis (1992) as an alternative representation of mass and heat exchange network in distillation networks. The scheduling sub-problem was based on the short-term scheduling formulation proposed by Ierapetritou and Floudas (1998a). The resulting mathematical technique had the capability of handling streams characterized by multiple contaminants.

The formulation resulted in a nonconvex MINLP problem, for which a global optimum solution could not be guaranteed. They introduced a two stage interactive iteration solution strategy to help solve the model. In the first stage, a set of feasible schedules resulting from a profit maximisation problem were determined. The results were passed to the water-allocation network model as parameters for the computation of the necessary variables for constructing a water-allocation network. This was done for each of the determined schedules. In the second stage, the most suitable initial values for solving the complete integrated scheduling and water-allocation model were selected. The selection was based only on four variables, the inlet and the outlets flowrates from a water-using operation with their corresponding concentrations. From the selection criterion of the initial values, it is implied that these four variables contribute strongly to the determination of the optimal solution, which is not entirely true.

Majozi and Gouws (2009) presented a wastewater minimisation mathematical technique for multipurpose batch processes characterized by multiple contaminant streams. The technique was based on the modification of the wastewater minimisation technique proposed by Majozi (2005a) which was limited to batch processes characterized by single contaminant streams, as aforementioned. The mathematical formulation resulted in a MINLP problem for which a global optimum solution could not be guaranteed. A solution procedure proposed by Gouws *et al.* (2008) was used to reduce the computational intensity associated with the resulting highly nonlinear formulation. The solution procedure is shown in Figure 2.14.

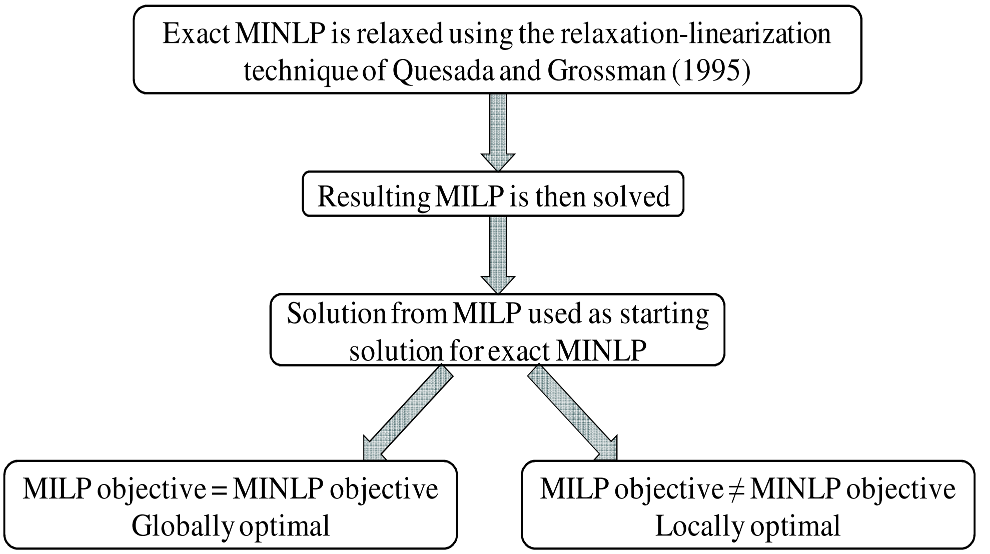


Figure 2.14: Solution procedure from Gouws *et al.* (2008)

The methodology proposed in this thesis is based on the extension of the work by Majozi and Gouws (2009). The intricate details of their methodology together with the new modifications will be presented in Chapter 3 of this thesis.

Li *et al.* (2010) developed a mathematical programming technique to synthesis a batch WAN. The WAN included water-reuse subsystem and wastewater treatment subsystem which are characterized by multiple contaminants. The technique was based on the newly proposed state-time-space (STS) superstructure, which was a modification of the state-space superstructure proposed by Zhou *et al.* (2008). The state-space superstructure was modified by incorporating the concepts of STN, state equipment network (SEN) and Gantt chart. The scheduling sub-problem was based on the formulation proposed by Ierapetritou and Floudas (1998a). However, discrete time representation was used in the formulation of the scheduling sub-problem. This is a drawback since the model might encounter longer computational time when applied to industrial scale problems because of the large number of binary variables associated with discrete time representation.

A global optimum solution could not be guaranteed from the technique because the mathematical formulation resulted in nonconvex MINLP problem. The authors proposed a two stage solution procedure to solve the model. In the first stage, the original MINLP problem was decomposed to get a MILP-MINLP formulation which was solved in a sequential manner to provide feasible solutions which were used as initial starting points for the second stage. In the second stage, the inputs from the first stage were refined by solving the original MINLP problem to get the final optimal solution.

Chen *et al.* (2010) developed a mathematical technique for simultaneous production scheduling and water-using network synthesis for multipurpose batch processes. The mathematical model involved two modules. The first module was concerned with the production scheduling for both short-term and periodic scheduling. The second module was concerned with the synthesis of the water-using network. The production scheduling sub-problems was based on the RTN representation and on continuous time formulation. The water-using network synthesis sub-problem was developed for batch processes characterized by multiple contaminates. The mathematical formulation resulted in a MINLP problem. They developed a solution strategy for both short-term and periodic scheduling models and the solution procedure is shown in Figure 2.15.

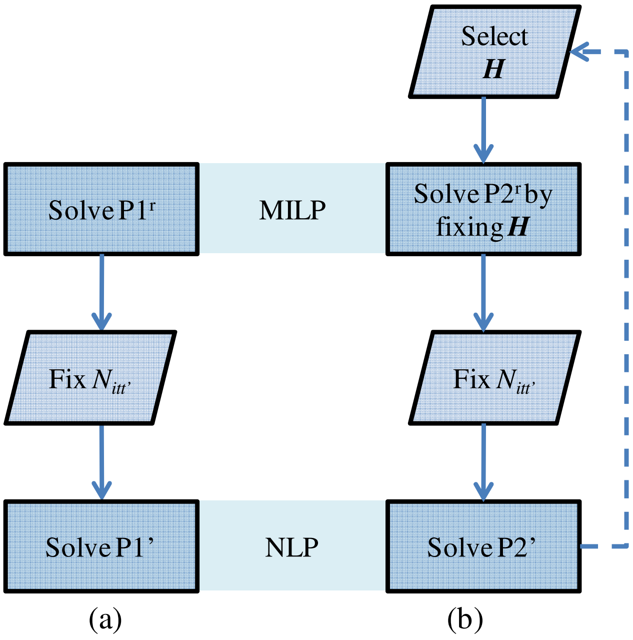


Figure 2.15: Solution procedure for (a) short-term and (b) periodic operations proposed by Chen *et al.* (2010)

For short-term scheduling problem, the model was linearized using the technique proposed by McCormick (1976), **P1^r** on Figure 2.15(a) represents the linearized model. The solution/schedule of the linearized model was fixed. With the schedule fixed, the model becomes a NLP problem which was solved to optimise the water-using network. The drawback with this strategy is that the solution from the linearized model, **P1^r**, does not necessary represent the solution of the original MINLP problem. Thus, the solution obtained from this solution procedure does not represent the solution of the original MINLP problem.

The linearization technique proposed by McCormick (1976) could not fully linearize the periodic scheduling model since it could not be applied to the objective function. To address the nonlinearity of the objective function, the periodic scheduling model was solved for a series of constant cycle length between two bounds, lower and upper bound. With the cycle length kept constant, the periodic scheduling model resembled the short-term scheduling model. The periodic scheduling model was also linearized to **P2^r**, as shown in Figure 2.15(b). The same procedure used to solve the short-term scheduling problem was followed for different constant cycle lengths. The cycle length corresponding to the maximum profit was selected as the optimum cycle length. The solution procedure for the periodic scheduling problem had two drawbacks, inclusive of the obvious drawback from the short-term scheduling problem solution procedure. The second drawback is with regards to the cycle length. The cycle length was not treated as an optimization variable. Thus, the claim of an optimum cycle length cannot be valid.

Conventional wastewater minimisation techniques only consider the quantity of waste disposed off to the environment. They do not consider the impact of individual contaminant in the waste disposed to the environment. Certain wastes have more environmental impact than others regardless of the quantity. For a true reflection of the impact of waste disposed to the environment, the impact of individual contaminants in the waste should be taken into account. Yao and Yuan (2000) developed a multi-objective mathematical formulation approach for waste minimisation taking into account the environmental impact of individual contaminants in the waste. They extended the formulation to incorporate raw material selection as an additional factor to minimise waste generation.

The authors defined a variable called the effective quantity of waste (EQW) which represented the total environmental impact of the process wastes. The approach was divided into two phases. In the first phase the equipment route for each product was determined. In the second phase, an optimum campaign was selected. A campaign consists of a set of compatible routes, which can operate at the same period of time. In their formulation, they assumed that semi-continuous processes behave in a similar fashion as batch processes, which is not true. For this assumption, their formulation did not address waste minimisation in a strict batch process. The formulation resulted in a MINLP problem for which a global optimum solution could not be guaranteed.

Closing remarks for mathematical techniques

In addition to their ability to handle the multidimensionality of batch processes, the advantage of mathematical techniques is in their adaptability of the objective function, also known as the performance index. The objective function can take the form of capital cost in a design problem or take the form of makespan minimisation, maximisation of throughput for a given time horizon. In wastewater minimisation, the objective will be to find the minimum freshwater consumption, which is similar to minimisation of wastewater generation. The disadvantage of mathematical methods is the inability to manipulate the solution procedure.

2.4. Conclusions

It is evident from the literature survey presented in this chapter that considerable amount of work has been done in the development of wastewater minimisation techniques for batch processes. The developed wastewater minimisation techniques can be categorized into graphical and mathematical techniques. It was made clear in Section 3.1 that graphical techniques have limited practical applications due to two major drawbacks. Firstly, the schedule must be predefined ahead of the freshwater target. Therefore, the obtained freshwater target is schedule specific. Secondly, graphical techniques fail to deal with streams characterized by multiple contaminants, due to the multiple dimensions introduced.

Some of the drawbacks from graphical techniques can be easily addressed through mathematical techniques. It is clear from the presented literature survey that most published mathematical techniques for wastewater minimisation have been focussed on batch processes characterized by single contaminants with the production schedule known *a priori*. Thus, these techniques treat time as a parameter rather than an optimization variable. The absolute true minimum wastewater generation can only be realised when the sequence of operations and the operating procedure are free to change. This can be achieved if the production schedule and wastewater minimisation are performed simultaneously. Once more, it is clear from the presented literature survey that very few authors, to date, managed to accomplish this.

Despite the remarkable contribution of the presented wastewater minimisation techniques, they share a common major drawback. They are limited to wastewater minimisation in batch processes operated over a short time horizon. When applied to problems with longer time horizon as traditionally encountered in practice, they experience computational difficulties i.e. longer solution time. Consequently, it is apparent that a methodology for wastewater minimisation in batch processes operated over a long time horizon is needed. In the next chapter, a methodology to address this drawback is presented.

References

Bagajewicz, M. and Manousiouthaks, V., 1992, On the mass/heat exchanger network representation of distillation networks, *AIChE J.*, 38:1769

Barbosa-Povoa, A.P. and Macchietto, S., 1994, Detailed design of multipurpose batch plants**,** *Comp. Chem. Eng*. 18:1013-1042.

Castro, P.M., Barbosa-Povoa, A.P. and Matos, H.A., 2003, Optimal periodic scheduling of batch plants using RTN-based discrete and continuous time formulations: A case study approach, *Ind. Eng. Chem. Res.*, 42: 3346-3360

Cheng, K.-F. and Chang, C.-T., 2007, Integrated water network designs for batch processes, *Ind. Eng. Chem. Res*., 46: 1241-1253.

Chen, C.-L., Chang, C.-Y. and Lee J.-Y., 2008, Continuous-time formulation for the synthesis of water-using network in batch plants, *Ind. Eng. Chem. Res*., 47: 7818-7832.

Chen, C.L., Chang, C.Y. and Lee, J.Y., 2010, Resource-Task Network approach to simultaneous scheduling and water minimisation of batch plants, *Ind. Eng Chem. Res.,* 17: 1465-1479.

Chen, C. and Lee, J., 2008, A graphical technique for the design of water-using networks in batch processes, *Chem. Eng. Sci.*, 63: 3740-3754

Chen, C. and Lee, J, 2009, On the use of graphical analysis for the design of batch water networks, *Clean. Techn. Environ. Policy*, 12:117-123

Chen, C.L., Lee, J.Y., Tang, J.W. and Ciou Y.J., 2009, Synthesis of water-using network with central reusable storage in batch processes, *Comp. Chem. Eng*., 33(1): 267-276.

El-Halwagi, M.M., Glasgow, I.M., Qin, X. and Eden, M.R., 2004, Property integration: componentless design techniques and visualization tools, *AIChE J.*, 50:1854-1869

Floudas, C.A. and Lin, X., 2004, Continuous-time versus discrete-time approaches for scheduling of chemical processes*, Comp. Chem. Eng*, 28: 2109-2129.

Floudas C.A. and Lin X., 2005, Mixed integer linear programming in process scheduling: Modeling, Algorithms, and Applications, *Ann. Oper. Res*., 139, 131-162.

Foo, D.C.Y., Manan, Z.A. and Tan, Y.L., 2005, Synthesis of maximum water recovery network for batch process systems, *J. Clean. Prod.*, 13:1381–1394.

Fromm, C.H, Budaraju, S. and Cordery, S.A, 1988 Chapter 5: Minimization of process equipment cleaning waste, *Jacobs Engineering Group, Inc. HTM Division,* Pasadena, CA 91-101.

Glover, F., 1975, Improved linear integer programming formulations of nonlinear integer problems, *Man. Sci.* 22(4): 455-460.

Gouws, J.F., Majozi, M. and Gadalla, M., 2008b, Flexible mass transfer model for water minimization in batch plants, *Chem. Eng. Process,* 47:2323-2335

Halim, I. and Srinivasan, R., 2010, Sequential methodology for simultaneous batch process scheduling and water reuse optimization, *Chem. Eng. Tran.,* 21: 727-732.

Hallale, N., 2002, A new graphical targeting method for water minimisation, *Adv. Environ. Res*, 6: 377-390

Ierapetritou, M.G. and Floudas, C.A., 1998a, Effective continuous-time formulation for short-term scheduling 2. Continuous and semi-continuous processes, *Ind. Eng. Chem. Res.*, 37:4341-4359.

Kondili, E., Pantelides, C.C. and Sargent, R.W.H., 1993, A general algorithm for short-term scheduling of batch operations-I. MILP formulation, *Comp. Chem. Eng.*, 17(2):211-227

Kim J.K. and Smith R., 2004, Automated design of discontinuous water systems, *TI Chem. Eng.-long, Part B,* 82(B3): 238-248.

Ku, H.M. and Karimi, I.A., 1988, Scheduling in serial multiproduct batch processes with finite interstage storage: A mixed integer linear program formulation, *Ind. Eng. Chem. Res.*, 27, 10

Li, B. and Chang, C., 2006, A mathematical programming model for discontinuous water-reuse system design, *Ind. Eng. Chem. Res.,* 45: 5027–5036

Li, L.-J., Zhou, R.-J. and Dong, H.-G, 2010, State-Time-Space superstructure-based MINLP formulation for batch water-allocation network design, *Ind. Eng. Chem. Res.,* 42: 236-251

Majozi, T., 2005a, Wastewater minimization using central reusable water storage in batch processes, *Comp. Chem. Eng.*, 29(7): 1631-1646

Majozi, T., 2010, Batch chemical process integration: analysis, synthesis and optimization, *Springer*, Dordrecht Heidelberg.

Majozi, T., Brouckaert, C.J.B. and Buckley, C.A.B., 2006, A Graphical technique for wastewater minimisation in batch processes, *J. Environ. Man.*, 78: 317-329

Majozi, T. and Gouws, J.F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng.* 33:1826-1840.

Majozi, T. and Zhu, X.X., 2001, A novel continuous-time MILP formulation for multipurpose batch plants-1. Short-term scheduling. *Ind. Eng. Chem. Res.*, 40(25):5935-5949.

Manan, Z.A., Foo, C.Y. and Tan, Y.L., 2004, Targeting the minimum water flowrate using water cascade analysis technique. *AIChE J.,* 50(12):3169-3183.

McCormick, G.P., 1976, Computability of global solutions to factorable nonconvex programs, part I. convex underestimating programs, *Math. Program.*, 10: 147-175

Méndez, C.A., Cerdá, J., Grossmann, I.E, Herjunkoski, I and Fahl, M., 2006, State-of-art review of optimization methods for short-term scheduling of batch processes, *Comp. Chem. Eng.*, 30:913-946.

Mockus, L. and Reklaitis, G.V., 1997, Mathematical programming formulation for scheduling of batch operations based on non-uniform time discretization, *Comp. Chem. Eng.*, 21(10), 1147-1156.

Ng, D.K.S., Foo, D.C.Y., Rabie, A. and El-Halwagi, M.M., 2008, Simultaneous synthesis of property-based water reuse/recycle and interception network for batch processes, *AIChE J*, 54: 2624-2632

Pantelides, C.C., 1994, Unified frameworks for optimal process planning and scheduling, *In Foundations of computer-aided process operations*. New York: Cache publications, pp. 253-274.

Prakash, R. and Shenoy, U.V., 2005. Targeting and design of water networks for fixed flowrate and fixed contaminant load operations, *Chem. Eng. Sci.,* 60 (1), 255-268.

Quesada, I. and Grossmann I.E., 1995, Global optimization of bilinear process networks with multicomponent Flows, *Comp. Chem. Eng.*, 19:1219.

Savelski, M.J. and Bagajewicz, M.J., 2000, On the optimality conditions of water utilization systems in process plants with single contaminants, *Chem. Eng. Sci.*, 55:5035-5048

Schilling, G., Pantelides, C.C., 1996, A simple continuous-time process scheduling formulation and a novel solution algorithm, *Comp. Chem. Eng.*, 20:S1221-1226.

Schilling, G. and Pantelides, C.C., 1999, Optimal periodic scheduling of multipurpose plants, *Comp. Chem. Eng.*, 23: 635-655

Shah, N., Pantelides, C.C. and Sargent, R.W.H., 1993, Optimal periodic scheduling of multipurpose batch plants, *Ann. Oper. Res.*, 42:193-228

Shaik, M.A., Janak, S.L. and Floudas, C.A., 2006, Continuous-time models for short-term scheduling of multipurpose batch plants: A comparative study, *Ind. Eng. Chem. Res*. 45:6190-6209

Shoaib, A.M., Aly, S.M., Awad, M.E., Foo, D.C.Y. and El-Halwagi, M.M., 2008, A hierarchical approach for the synthesis of batch water network, *Comp. Chem. Eng.*, 32:530-539

Sundaramoorthy, A. and Karimi, I.A., 2005, A simpler better slot-based continuous-time formulation for short-term scheduling in multipurpose batch plants, *Chem. Eng. Sci.* 60, 2679-2702.

Tokos, H. and Pintarič, Z.N., 2009, Synthesis of batch water network for a brewery plant, *J. clean prod.,* 17: 1465-1479.

Wang Y.P. and Smith R., 1994a, Wastewater minimization, *Chem. Eng. Sci.,* 49:981-1006.

Wang, Y.P., Smith, R., 1995a, Waste minimization with flowrate constraints, *Trans IChemE*, 73: 889-904.

Wang, Y.P., Smith, R., 1995b, Time pinch analysis, *Trans IChemE*, 73a: 905-914.

Wu, D. and Ierapetritou, M., 2004, Cyclic short-term scheduling of multiproduct batch plants using continuous-time representation, *Comp. Chem. Eng.*, 28:2271-2286

Yao, Z.L. and Yuan, X.G., 2000, An approach to optimal design of batch processes with waste minimisation, *Comp. Chem. Eng.,* 24: 1437-1444.

Liu, Y., Yuan, X. and Luo, Y., 2007, Synthesis of water utilization system using concentration interval analysis method (II) Discontinuous process, *Chin. J. Chem. Eng.*, 15(3), 369-375

Zhou, R.-J., Li, L.-J. and Dong, H.-G, 2008, Simultaneous optimization of batch process schedules and water-allocation network, *Comp. Chem. Eng.*, 15(3), 369-375

CHAPTER 03

MATHEMATICAL MODEL

Introduction

This chapter presents the proposed mathematical formulation for wastewater minimisation in multipurpose batch plants operated over a long time horizon. The batch processes considered for the formulation are characterized by multiple contaminant streams. As aforementioned in Chapter 2, the presented mathematical formulation is, in essence, an extension of the published work by Majozi and Gouws (2009). The constraints considered in the mathematical formulation are divided into three modules. The first module is presented in Section 3.1 and it deals with the water mass balance constraints, for the case where a central storage vessel for reusable water is available and a case where it is absent. The second module, presented in Section 3.2, deals with the sequencing and scheduling constraints, i.e. time, for direct and indirect reuse/recycle of water. Section 3.3 presents the third module, which is presented in detail in the work by Majozi and Zhu (2001), it deals with the necessary scheduling of production operations. More emphasis will be on the new constraints added to cater for cyclic scheduling. Section 3.4 presents the solution procedure followed when solving a long-term horizon using the proposed mathematical formulation. The application of the mathematical formulation is presented in the next chapter.

3.1. Mass balance constraints

Due to the high quality and purity specifications of products produced from batch processes, proper cleaning of the processing units is of paramount importance. The philosophy is that the processing units need to be washed after each production task in order to remove contaminants that are formed as byproducts, so as to ensure product integrity. In this subsection all the essential water and contaminant mass balances for a washing operation are presented. It is assumed throughout the formulation that none of the water using operations produce or consume water i.e. water is conserved during a washing operation.

3.1.1. Mass balance constraints without storage

The mathematical formulation for a multiple contaminant system without a central storage vessel is based on the superstructure given in Figure 3.1, adopted from the work by Majozi and Gouws (2009). For each water using operation, water into the unit is a combination of freshwater and water recycled from other units to that unit. Water leaving the unit can either be discarded as effluent or be recycled/reused in other units. It is highly imperative to realise that the water use and reuse variables shown in Figure 3.1 correspond to the washing operation that follows immediately after the production of a particular state in unit j, i.e. $s_{out,j}$.. Consequently, these variables are task-specific, which allows scheduling to be readily embedded within the water reuse and recycle framework.

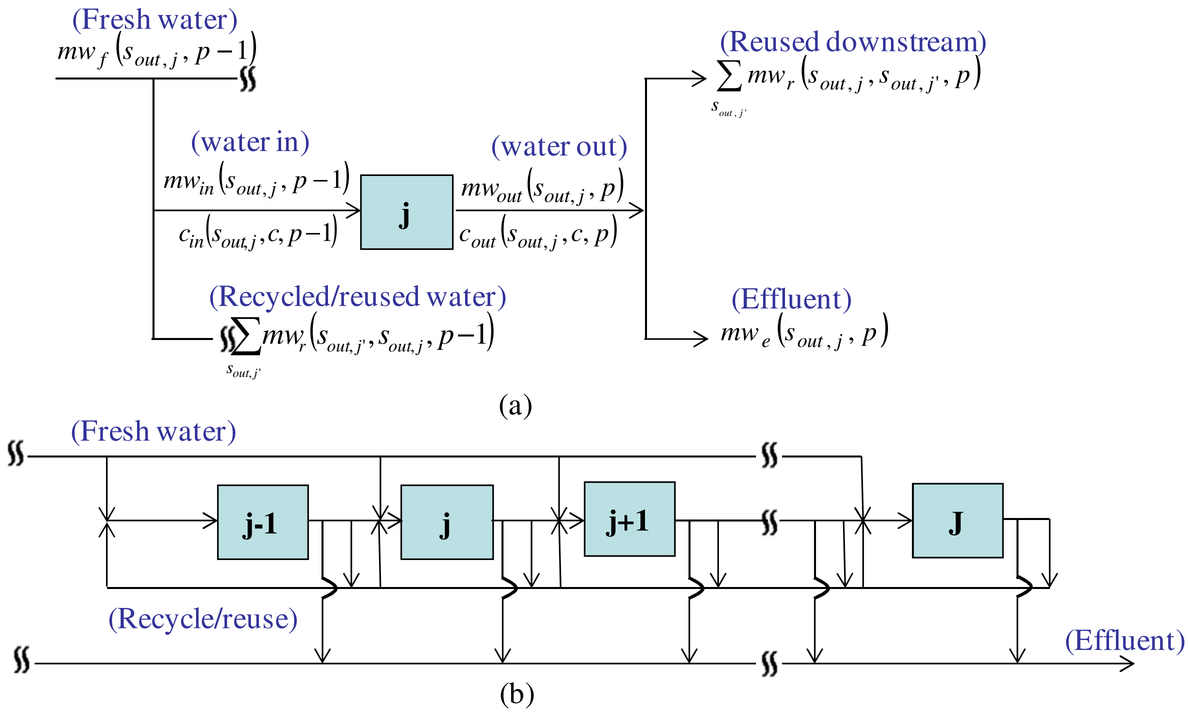


Figure 3.1: Superstructure for the mathematical formulation with no reusable water storage Majozi and Gouws (2009)

The first constraints considered are the mass balance constraints around unit *j*. Constraint (3.1) is a water mass balance over the inlet of unit *j*. The total water into a unit is the sum of all the recycles to the unit and the freshwater into the unit *j* at time point *p*. As aforementioned, it is assumed that any operation that takes place in unit *j* does not produce or consume water. Consequently, water is conserved as captured in Constraint (3.2). Constraint (3.3) is the outlet water balance from unit *j*. Here the total water out of a unit is the sum of all the recycle streams to other units and the water discarded as effluent. Constraint (3.4) is a contaminant balance over unit *j*. The mass of the contaminants out of the unit *j* is the sum of the contaminant into the unit *j* and the mass of the contaminant added during the washing operation of the unit. As there are more than one contaminants present in the system the balance has to be done for each contaminant *c*. Constraint (3.5) is the definition of the inlet concentration of contaminant *c* to unit *j*.

$$mw_{in}\left(s_{out,j}, p\right) = \sum_{s_{out,j'}} mw_r\left(s_{out,j'}, s_{out,j}, p\right) + mw_f\left(s_{out,j}, p\right), \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.1)$$

$$mw_{in}\left(s_{out,j}, p-1\right) = mw_{out}\left(s_{out,j}, p\right), \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (3.2)$$

$$mw_{out}\left(s_{out,j}, p\right) = \sum_{s_{out,j'}} mw_r\left(s_{out,j}, s_{out,j'}, p\right) + mw_e\left(s_{out,j}, p\right), \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.3)$$

$$mw_{out}\left(s_{out,j}, p\right) c_{out}\left(s_{out,j}, c, p\right) = mw_{in}\left(s_{out,j}, p-1\right) c_{in}\left(s_{out,j}, c, p-1\right) + M\left(s_{out}, c\right) yw\left(s_{out,j}, p-1\right),$$
$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1, c \in C \qquad (3.4)$$

$$c_{in}\left(s_{out,j}, c, p\right) = \frac{\sum_{s_{out,j'}} mw_r\left(s_{out,j'}, s_{out,j}, p\right) c_{out}\left(s_{out,j'}, c, p\right)}{mw_{in}\left(s_{out,j}, p\right)},$$
$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \qquad (3.5)$$

The outlet concentration of each contaminant *c* in unit *j* cannot exceed its maximum limit as stated in Constraint (3.6). Constraint (3.7) ensures that the total water into unit *j* does not exceed the maximum allowable for the operation in unit *j*. Constraint (3.8) restricts mass of water recycled into the unit *j* to the maximum allowable water for operation in unit *j*.

Constraint (3.9) stipulates that the inlet concentration for contaminant *c* into unit *j* cannot exceed its upper limit.

$$c_{out}\left(s_{out,j},c,p\right)\le C_{out}^{U}\left(s_{out,j},c\right)yw\left(s_{out,j},p-1\right),\quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P,p>p_1,c\in C \tag{3.6}$$

$$mw_{in}\left(s_{out,j},p\right)\le Mw^{U}\left(s_{out,j}\right)yw\left(s_{out,j},p\right),\qquad \forall j\in J,s_{out,j}\in S_{out,j},p\in P \tag{3.7}$$

$$mw_{r}\left(s_{out,j'},s_{out,j},p\right)\le Mw^{U}\left(s_{out,j}\right)yw_{r}\left(s_{out,j'},s_{out,j},p\right),\quad \forall j,j'\in J,s_{out,j}\in S_{out,j},p\in P \tag{3.8}$$

$$c_{in}\left(s_{out,j},c,p\right)\le C_{in}^{U}\left(s_{out,j},c\right)yw\left(s_{out,j},p\right),\quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P,p>p_1,c\in C \tag{3.9}$$

The maximum water quantity into a unit is represented by Equation (3.10). It is important to note that for multi-contaminant wastewater the outlet concentration of the individual components cannot all be set to the maximum, since the contaminants are not limiting simultaneously. The limiting contaminant(s) will always be at the maximum outlet concentration and the non-limiting contaminants will be below their respective maximum outlet concentrations.

$$Mw^{U}\left(s_{out,j}\right)=\max_{c\in C}\left\{\frac{M\left(s_{out,j},c\right)}{C_{out}^{U}\left(s_{out,j},c\right)-C_{in}^{U}\left(s_{out,j},c\right)}\right\},\qquad \forall j\in J,s_{out,j}\in S_{out,j} \tag{3.10}$$

Linearization

Constraints (3.4) and (3.5) contain bilinear terms. This makes the model thus far nonlinear. These two constraints are not the only source of non-linearity in the model, as this will be more apparent as the rest of the formulation unfolds. These nonlinear terms can be linearized according to the linearization of bilinear terms proposed by Quesada and Grossmann (1995). The detailed linearization procedure of these terms is detailed in the work by Majozi and Gouws (2009), and appears in the Appendix of this work.

3.1.2. Mass balance constraints with storage

The mathematical formulation for the case where there is reusable water storage available is based on the superstructure given in Figure 3.2. This superstructure is similar to the previous one. However, there is a central storage vessel available. The total water flowing into the unit in this case is the sum of the freshwater, the water recycled/reused from the other unit and water from the central storage vessel. The water leaving the unit is the sum of the water going to effluent, water going to storage and the water being recycled/reused.

Constraints (3.1), (3.3) and (3.5) need to be modified to cater for the reusable water from the central storage vessel, thus yielding (3.11), (3.12) and (3.13). The difference in the new constraints is that water into and out of the unit includes water from and to the central storage vessel as well. Moreover, the inlet concentration is not only affected by the concentration from the previous recycle as in the previous case, but also the concentration in the water from the central storage vessel as stated in Constraints (3.13). Constraint (3.13) contains additional nonlinear terms due to storage. These additional nonlinear terms can be linearized in the same manner as aforementioned.

$$mw_{in}\left(s_{out,j},p\right)=\sum_{s_{out,j'}} mw_r\left(s_{out,j'},s_{out,j},p\right)+mw_f\left(s_{out,j},p\right)+ms_{out}\left(s_{out,j},p\right),$$

$$\forall j,j'\in J,\ s_{out,j}\in S_{out,j},p\in P \qquad (3.11)$$

$$mw_{out}\left(s_{out,j},p\right)=\sum_{s_{out,j'}} mw_r\left(s_{out,j},s_{out,j'},p\right)+mw_e\left(s_{out,j},p\right)+ms_{in}\left(s_{out,j},p\right),$$

$$\forall j,j'\in J,\ s_{out,j}\in S_{out,j},p\in P \qquad (3.12)$$

$$c_{in}\left(s_{out,j},c,p\right)mw_{in}\left(s_{out,j},p\right)=\sum_{s_{out,j'}} mw_r\left(s_{out,j'},s_{out,j},p\right)c_{out}\left(s_{out,j'},c,p\right)$$

$$+cs_{out}\left(c,p\right)ms_{out}\left(s_{out,j},p\right),$$

$$\forall j,j'\in J,\ s_{out,j}\in S_{out,j},p\in P,c\in C \quad (3.13)$$

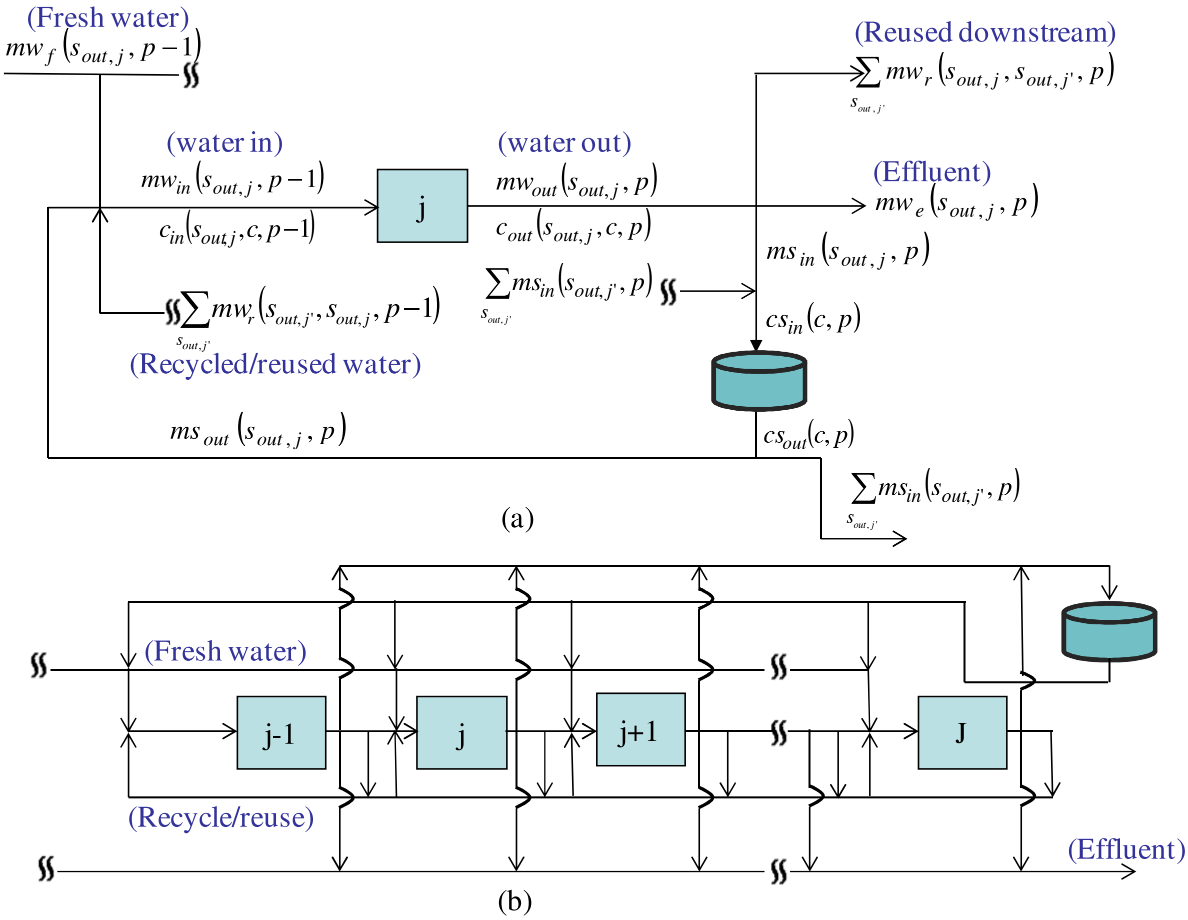


Figure 3.2: Superstructure for the mathematical formulation with reusable water storage Majozi and Gouws (2009)

Besides the mass balance over a water using operation, there also has to be mass balance over the central storage vessel. Constraint (3.14) is the mass balance over the central storage vessel. The water in the central storage vessel at a certain time point is the difference between the water flowing into and from the storage vessel and the water possibly stored from the previous time point. Constraint (3.15) is a water mass balance at the beginning of the time horizon. Constraints (3.16) and (3.17) are the definition of the inlet and outlet concentration of the storage vessel, respectively. It should be noted that Constraint (3.17) is based on the assumption that the contaminant concentration inside the storage is the same as the concentration of the exit stream. Constraint (3.18) is the initial concentration of the water in the storage vessel at the beginning of the time horizon, provided there is an initial amount of water in the storage vessel. Constraint (3.19) ensures that the water in the storage vessel does not exceed the storage vessel's capacity. Constraint (3.20) ensures that water flowing from storage to unit *j* does not exceed unit *j* capacity.

$$qw_s(p) = qw_s(p-1) + \sum_{s_{out,j}} ms_{in}\left(s_{out,j}, p\right) - \sum_{s_{out,j}} ms_{out}\left(s_{out,j}, p\right),$$

$$\forall j \in J,\ s_{out,j} \in S_{out,j},\ p \in P,\ p > p_1 \qquad (3.14)$$

$$qw_s(p_1) = Qw_s^o - \sum_{s_{out,j}} ms_{out}\left(s_{out,j}, p_1\right), \quad \forall j \in J, s_{out,j} \in S_{out,j} \qquad (3.15)$$

$$cs_{in}(c, p) = \frac{\sum\limits_{s_{out,j}} \left(ms_{in}\left(s_{out,j}, p\right) c_{out}\left(s_{out,j}, c, p\right)\right)}{\sum\limits_{s_{out,j}} ms_{in}\left(s_{out,j}, p\right)}, \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P\ c \in C \qquad (3.16)$$

$$cs_{out}(c, p) = \frac{qw_s(p-1) cs_{out}(c, p-1) + \left(\sum\limits_{s_{out,j}} ms_{in}\left(s_{out,j}, p\right)\right) cs_{in}(c, p)}{qw_s(p-1) + \sum\limits_{s_{out,j}} ms_{in}\left(s_{out,j}, p\right)},$$

$$\forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P,\ p > p_1, c \in C \qquad (3.17)$$

$$cs_{out}(c, p_1) = Cs_{out}^0(c), \qquad \forall c \in C \qquad (3.18)$$

$$qws(p) \leq Qw_s^U, \qquad \forall p \in P \qquad (3.19)$$

$$ms_{in}\left(s_{out,j}, p\right) \leq Qw_s^U\, ys_{in}\left(s_{out,j}, p\right), \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.20)$$

As one would notice there are nonlinear terms in Constraints (3.16) and (3.17). One of the nonlinear terms can be eliminated by substituting Constraints (3.16) into (3.17). The nonlinear terms in the resulting equation are then linearized in a similar fashion to that previously discussed. Due to the discontinuous nature of batch processes, the mass balances are not enough to fully describe the system. Sequencing constraints need to capture the discontinuous nature of the operation.

3.2. Sequencing and scheduling constraints

The sequencing and scheduling constraints pertaining to direct and indirect reuse/recycle are presented in this section. The constraints are presented for both cases where there is a central storage vessel and where there is none. The sequencing and scheduling constraints can be divided into three groups. The first group comprises of constraints pertaining to sequencing and scheduling of the washing operations. The second group comprises of constraints pertaining to direct recycle/reuse of reusable water, whilst the third group comprises of the constraints necessary for the scheduling of the storage vessel. These groups are discussed below.

3.2.1. Scheduling constraints associated with the washing operation

Each water using operation in the time horizon has to be scheduled accordingly, within the overall framework of operation scheduling. This is captured by Constraints (3.21)-(3.25). Constraints (3.21) and (3.22) ensure that unit *j* is washed immediately after a task that produced $s_{out,j}$. Constraint (3.23) is the duration constraint, which defines the starting and the ending times of a washing operation. Constraint (3.24) stipulates that the washing operation can only commence at time point *p* if the task producing $s_{out,j}$ was active at the previous time point. Constraint (3.25) stipulates that only one washing operation can take place at any given time point.

$$tw_{in}(s_{out,j}, p) \geq t_{out}(s_{out,j}, p) - H^U(1 - yw(s_{out,j}, p)), \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.21)$$

$$tw_{in}(s_{out,j}, p) \leq t_{out}(s_{out,j}, p) + H^U(1 - yw(s_{out,j}, p)), \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.22)$$

$$tw_{out}(s_{out,j}, p) = tw_{in}(s_{out,j}, p-1) + \tau w(s_{out,j})\, yw(s_{out,j}, p-1), \\ \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (3.23)$$

$$yw(s_{out,j}, p) = y(s^*_{in,j}, p-1), \qquad \forall j \in J, s_{out,j} \in S_{out,j}, s^*_{in,j} \in S^*_{in,j}, s^*_{in,j} \rightarrow s_{out,j}\, p \in P\ , p > p_1 \quad (3.24)$$

$$\sum_{s_{out,j}} yw\left(s_{out,j}, p\right) \le 1, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.25}$$

3.2.2. Water recycle/reuse sequencing constraints

Scheduling of the recycle/reuse streams is important because of the discontinuous nature of the streams. Reusable water can only be directly recycled/reused if the unit producing water and the unit receiving water finish operating and begin operating at the same time, respectively. Constraint (3.26) stipulates that recycle/reuse between units can only take place when the unit receiving the reusable water start operating at that time point. The unit receiving the reusable water, however, does not necessary need the recycled water to operate, i.e. it can operate independent of the recycled water. Constraints (3.27) and (3.28) ensure that the time at which recycle/reuse of water occurs coincides with the time that the water is produced. Constraints (3.29) and (3.30) ensure that the starting time of the unit receiving water coincides with the time at which that water is recycled/reused.

$$yw_r\left(s_{out,j'}, s_{out,j}, p\right) \le yw\left(s_{out,j}, p\right), \qquad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.26}$$

$$\begin{aligned} tw_r\left(s_{out,j}, s_{out,j'}, p\right) \le tw_{out}\left(s_{out,j}, p\right) + H^U\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right), \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \end{aligned} \tag{3.27}$$

$$\begin{aligned} tw_r\left(s_{out,j}, s_{out,j'}, p\right) \ge tw_{out}\left(s_{out,j}, p\right) - H^U\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right), \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \end{aligned} \tag{3.28}$$

$$\begin{aligned} tw_r\left(s_{out,j}, s_{out,j'}, p\right) \le tw_{in}\left(s_{out,j}', p\right) + H^U\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right), \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \end{aligned} \tag{3.29}$$

$$\begin{aligned} tw_r\left(s_{out,j}, s_{out,j'}, p\right) \ge tw_{in}\left(s_{out,j}', p\right) - H^U\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right), \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \end{aligned} \tag{3.30}$$

3.2.3. Sequencing and scheduling constraints associated with storage

Constraints (3.31) and (3.32) ensure that the time at which reusable water goes to storage coincides with the time at which it is produced. Furthermore, reusable water can only be sent to storage at time point *p* if unit *j* has conducted a washing operation in the previous time point. This is captured by Constraint (3.33). However, the fact that unit *j* has conducted a washing operation in the previous time point does not mean that the resulting contaminated water needs to be sent to the storage vessel.

$$ts_{in}(s_{out,j}, p) \geq tw_{out}(s_{out,j}, p) - H^U\left(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)\right), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.31)$$

$$ts_{in}(s_{out,j}, p) \leq tw_{out}(s_{out,j}, p) + H^U\left(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)\right), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.32)$$

$$ys_{in}(s_{out,j}, p) \leq yw(s_{out,j}, p-1), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (3.33)$$

Constraints (3.34) and (3.35) ensure that the time at which water is used in unit *j* coincides with the time at which water is transferred from the storage vessel to the unit. Constraint (3.36) ensures that unit *j* is indeed active when the unit is using recycled water from the storage vessel. The unit does not necessarily have to use the water from the storage vessel when it operates. A unit will not use the water in storage if there is a violation of the inlet concentration limit of the water into the unit or if there is simply no water in the storage vessel.

$$ts_{out}(s_{out,j}, p) \geq tw_{in}(s_{out,j}, p) - H^U\left(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)\right), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.34)$$

$$ts_{out}(s_{out,j}, p) \leq tw_{in}(s_{out,j}, p) + H^U\left(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)\right), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.35)$$

$$ys_{out}\left(s_{out,j}, p\right) \le yw\left(s_{out,j}, p\right), \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.36}$$

Constraint (3.37) ensures that when water is transferred to a unit at time point *p*, the time at which this happens is later in the time horizon than any previous time water was transferred to other units at previous time points. Constraints (3.38) and (3.39) ensure that the reusable water leaving the storage vessel to different units at time point *p* leaves at the same time.

$$ts_{out}\left(s_{out,j}, p\right) \ge ts_{out}\left(s_{out,j'}, p'\right) - H^U\left(2 - ys_{out}\left(s_{out,j}, p\right) - ys_{out}\left(s_{out,j'}, p'\right)\right)$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \ge p' \tag{3.37}$$

$$ts_{out}\left(s_{out,j}, p\right) \ge ts_{out}\left(s_{out,j'}, p\right) - H^U\left(2 - ys_{out}\left(s_{out,j}, p\right) - ys_{out}\left(s_{out,j'}, p\right)\right)$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.38}$$

$$ts_{out}\left(s_{out,j}, p\right) \le ts_{out}\left(s_{out,j'}, p\right) + H^U\left(2 - ys_{out}\left(s_{out,j}, p\right) - ys_{out}\left(s_{out,j'}, p\right)\right)$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.39}$$

Constraint (3.40) is similar to Constraint (3.37), but applies to inlet streams to the storage vessel. Constraints (3.41) and (3.42) ensure that the time at which reusable water going to storage vessel from unit *j* and unit *j'* corresponds to the same time at the same time point.

$$ts_{in}\left(s_{out,j}, p\right) \ge ts_{in}\left(s_{out,j'}, p'\right) - H^U\left(2 - ys_{in}\left(s_{out,j}, p\right) - ys_{in}\left(s_{out,j'}, p'\right)\right),$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \ge p' \tag{3.40}$$

$$ts_{in}\left(s_{out,j}, p\right) \ge ts_{in}\left(s_{out,j'}, p\right) - H^U\left(2 - ys_{in}\left(s_{out,j}, p\right) - ys_{in}\left(s_{out,j'}, p\right)\right),$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.41}$$

$$ts_{in}\left(s_{out,j}, p\right) \le ts_{in}\left(s_{out,j'}, p\right) + H^U\left(2 - ys_{in}\left(s_{out,j}, p\right) - ys_{in}\left(s_{out,j'}, p\right)\right),$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.42}$$

Constraint (3.43) ensures that the outlet time of water from storage vessel at a time point occurs later than the inlet time at the previous time point. Constraints (3.44) and (3.45) ensure that at time point *p* the time at which reusable water is moved to storage is the same as the time at which water leaves the storage.

$$ts_{out}\left(s_{out,j},p\right) \geq ts_{in}\left(s_{out,j'},p'\right) - H^U\left(2 - ys_{out}\left(s_{out,j},p\right) - ys_{in}\left(s_{out,j'},p'\right)\right),$$
$$\forall\ j,j' \in J, s_{out,j} \in S_{out,j}, p,p' \in P, p \geq p' \qquad (3.43)$$

$$ts_{in}\left(s_{out,j},p\right) \geq ts_{out}\left(s_{out,j'},p\right) - H^U\left(2 - ys_{in}\left(s_{out,j},p\right) - ys_{out}\left(s_{out,j'},p\right)\right),$$
$$\forall\ j,j' \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.44)$$

$$ts_{in}\left(s_{out,j},p\right) \leq ts_{out}\left(s_{out,j'},p\right) + H^U\left(2 - ys_{in}\left(s_{out,j'},p\right) - ys_{out}\left(s_{out,j'},p\right)\right),$$
$$\forall\ j,j' \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (3.45)$$

3.3. Production scheduling constraints

As aforementioned, the intricate details of this section are presented in another publication, Majozi and Zhu (2001), but it is briefly presented here for continuity purposes. Emphasis will be on the new constraints added to cater for the concept of cyclic scheduling.

3.3.1. Capacity constraint

The capacity constraint, given by Constraint (3.46), ensures that the amount of material processed in unit *j* at any time point *p* does not exceed the capacity of the unit.

$$V_j^L\, y\left(s^*_{in,j},p\right) \leq \sum_{s_{in,j}} m_{in}\left(s_{in,j},p\right) \leq V_j^U\, y\left(s^*_{in,j},p\right), \qquad \forall j \in J, s_{in,j} \in S_{in,j}, s^*_{in,j} \in S^*_{in,j}, p \in P \qquad (3.46)$$

3.3.2. Material Balance constraints

Constraints (3.47) to (3.53) are the mass balance constraints. These constraints ensure that the conservation of mass around each unit and the mass of each state involved in the production are maintained.

$$\sum_{s_{in,j}} m_{in}(s_{in,j}, p-1) = \sum_{s_{out,j}} m_{out}(s_{out,j}, p), \forall j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.47)$$

$$q_s(s, p_1) = Q_s^0(s) - m_{in}(s, p_1), \qquad s \neq product, \forall s \in S \quad (3.48)$$

$$q_s(s, p) = q_s(s, p-1) - m_{in}(s, p), \qquad s = feed, \forall s \in S, p \in P, p > p_1 \quad (3.49)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - m_{in}(s, p), \qquad s \neq product, feed, \forall s \in S, p \in P, p > p_1 \quad (3.50)$$

$$q_s(s, p_1) = Q_s^0(s) - d(s, p_1), \qquad s = product, \forall s \in S \quad (3.51)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - d(s, p), \quad s = product, byproduct, \forall s \in S, p \in P, p > p_1 \quad (3.52)$$

$$q_s(s, p) \leq Q^U, \qquad \forall s \in S, p \in P \quad (3.53)$$

3.3.3. Duration constraints

The duration constraint is one of the most crucial constraints as it addresses the intrinsic aspects of the time dimension in batch plants. Constraint (3.54) simply states that the time at which a particular state is produced is dependent on the duration of the task that produces the same state.

$$t_{out}(s_{out,j}, p) = t_{in}(s_{in,j}^*, p-1) + \tau(s_{in,j}^*) y(s_{in,j}^*, p-1),$$
$$\forall j \in J, s_{in,j}^* \in S_{in,j}^*, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.54)$$

3.3.4. Feasibility and time horizon constraints

A washing operation starts immediately after a production task, i.e. if there is a task taking place in a unit at time point *p*, a washing operation will take place at the next time point. This is captured by Constraint (3.24). Constraint (3.55) ensures that a washing operation and a processing task do not coincide at the same time point. Constraint (3.56) ensures that only one production task takes place in a given unit at a given time point.

$$yw(s_{out,j}, p) + y(s^*_{in,j}, p) \leq 1, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, s^*_{in,j} \in S^*_{in,j}, p \in P \tag{3.55}$$

$$\sum_{s^*_{in,j}} y(s^*_{in,j}, p) \leq 1, \qquad \forall j \in J, s^*_{in,j} \in S^*_{in,j}, p \in P \tag{3.56}$$

For cyclic scheduling a task is allowed to cross the boundary of the cycle, as aforementioned, but its duration must not be more than the length of two cycles (*2**H***). Constraints (3.57)-(3.63) ensure that this is the case.

$$t_{in}(s_{in,j}, p) \leq 2H, \qquad \forall j \in J, s_{in,j} \in S_{in,j}, p \in P \tag{3.57}$$

$$t_{out}(s_{out,j}, p) \leq 2H, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.58}$$

$$tw_{in}(s_{out,j}, p) \leq 2H, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.59}$$

$$tw_{out}(s_{out,j}, p) \leq 2H, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.60}$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq 2H, \qquad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.61}$$

$$ts_{in}(s_{out,j}, p) \leq 2H, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.62}$$

$$ts_{out}(s_{out,j}, p) \leq 2H, \qquad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.63}$$

3.3.5. Sequence constraint within the cycle

Before using a unit, all the tasks must be complete in the unit including their corresponding washing operations. Constraints (3.64) and (3.65) ensure that this is the case. For a unit that is suitable to conduct more than one task, Constraint (3.66) is necessary in the formulation.

$$t_{in}\left(s^{*}_{in,j}, p\right) \geq tw_{out}\left(s_{out,j}, p'\right) - H^{U}\left(2 - y\left(s^{*}_{in,j}, p\right) - yw\left(s_{out,j}, p'-1\right)\right),$$
$$\forall j \in J, s^{*}_{in,j} \in S^{*}_{in,j}, s_{out,j} \in S_{out,j}, p, p' \in p, p' > p_1, p \geq p' \qquad (3.64)$$

$$t_{in}\left(s_{in,j}, p\right) \geq t_{out}\left(s_{out,j}, p'\right) - H^{U}\left(2 - y\left(s_{in,j}, p\right) - y\left(s^{*}_{in,j}, p'-1\right)\right),$$
$$\forall j \in J, s^{*}_{in,j} \in S^{*}_{in,j}, s_{out,j} \in S_{out,j}, p, p' \in p, p' > p_1, p \geq p', s^{*}_{in,j} \rightarrow s_{out,j} \qquad (3.65)$$

$$t_{in}\left(s_{in,j}, p\right) \geq \sum_{s_{out,j}} \left\{\left(\tau\left(s^{*}_{in,j}\right) + \tau w\left(s_{out,j}\right)\right) yw\left(s_{out,j}, p'-1\right)\right\},$$
$$\forall j \in J, s_{in,j} \in S_{in,j}, s^{*}_{in,j} \in S^{*}_{in,j}, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p', p' \geq 2, s^{*}_{in,j} \rightarrow s_{out,j} \qquad (3.66)$$

3.3.6. Mass balance between two cycles

Constraint (3.67) ensures that the amount of intermediate material needed to start the current cycle is stored at the last time point of the previous cycle in order to maintain smooth operation without any accumulation or shortage of material between cycles. This is the key constraint for cyclic scheduling.

$$q_s(s, p) = Q^{0}_{s}(s), \qquad s \neq product, feed, \forall s \in S, p \in P, p = |P| \qquad (3.67)$$

3.3.7. Cycle length constraint

Constraint (3.68) stipulates that the sum of all the durations of the tasks and their corresponding washing operations in a processing unit must be less than the cycle length.

$$\sum_{s_{out,j}} \left\{\left(\tau\left(s^{*}_{in,j}\right) + \tau w\left(s_{out,j}\right)\right) yw\left(s_{out,j}, p-1\right)\right\} \leq H,$$
$$\forall j \in J, s^{*}_{in,j} \in S^{*}_{in,j} p, \in P, p > p_1, s^{*}_{in,j} \rightarrow s_{out,j} \qquad (3.68)$$

3.3.8. Sequence constraints between cycles

Constraints (3.69) and (3.70) express the relationship between the last task of the previous cycle and the first task of the current cycle in the same unit *j* to maintain continuity between cycles. Constraint (3.69) stipulates that the first task in unit *j* of the new cycle must start after the completion of the last task and its corresponding washing operation in the same unit *j* of the previous cycle. Constraint (3.70) holds for tasks which do not need washing after its completion.

$$t_{in}\left(s^*_{in,j}, p_1\right) \geq tw_{out}\left(s_{out,j}, p\right) - H^U\left(2 - y\left(s^*_{in,j}, p_1\right) - yw\left(s_{out,j}, p-1\right)\right) - H,$$
$$\forall j \in J, s^*_{in,j} \in S^*_{in,j}, s_{out,j} \in S_{out,j}, p = |P| \qquad (3.69)$$

$$t_{in}\left(s_{in,j}, p_1\right) \geq t_{out}\left(s_{out,j}, p\right) - H^U\left(2 - y\left(s_{in,j}, p_1\right) - y\left(s^*_{in,j}, p-1\right)\right) - H,$$
$$\forall j \in J, s^*_{in,j} \in S^*_{in,j}, s_{out,j}, s^*_{in,j} \rightarrow s_{out,j} \in S_{out,j}, p = |P| \qquad (3.70)$$

3.3.9. Objective function

The objective function takes the form of Equation (3.71) for cyclic scheduling, i.e. performance index per unit time. The performance index can either be the maximisation of profit or the minimisation of effluent. This is dependent on the nature of the given data for the problem.

$$Max\ Z = \frac{Performance\ Index}{H} \qquad (3.71)$$

A typical objective function for the maximisation of profit can take a form of Constraint (3.72), which is maximisation of profit while taking into account freshwater and the effluent treatment cost.

$$Max\ Z = \frac{\sum_{s}\sum_{p} CP(s)d(s,p) - CF\sum_{s_{out,j}}\sum_{p} mw_f\left(s_{out,j}, p\right) - CE\sum_{s_{out,j}}\sum_{p} mw_e\left(s_{out,j}, p\right)}{H} \qquad (3.72)$$

The resulting mathematical formulation is a MINLP problem due to the presence of bilinear terms and a fractional term in the objective function. The linearization technique presented in the Appendix cannot be applied to the objective function. It is important to mention that for the presented model, a global optimal cannot be guaranteed through the application of the linearization technique presented in the Appendix. However, the technique can be used to provide a feasible starting point prior to solving the model.

3.4. Solution procedure

The solution procedure followed is presented in Figure 3.3. This solution procedure is adopted from Wu and Ierapetritou (2004).

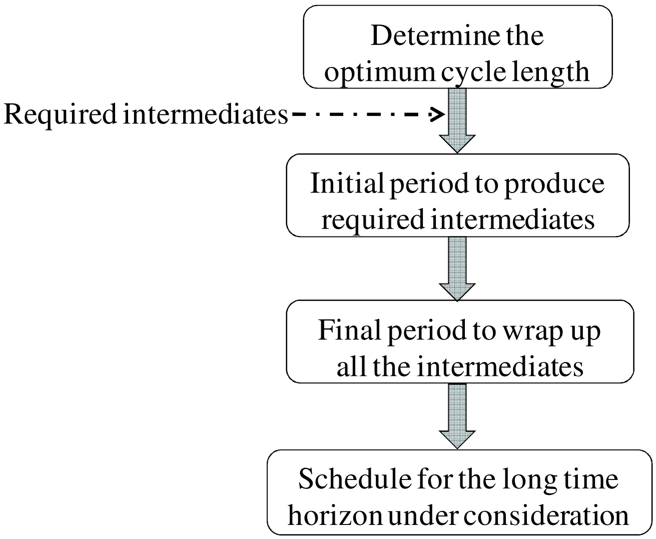


Figure 3.3: Solution procedure

The optimum cycle length is first determined from the methodology presented in this chapter with the objective function taking the form of Constraint (3.72). The results dictate the amount of intermediate products required to start the cyclic scheduling. With the data from the cyclic scheduling period, the minimum duration of the initial period is determined through makespan minimisation problem. This is done to ensure the existence of a feasible schedule to provide the required intermediate products to start the cyclic scheduling period. The same problem is then solved with the objective of profit maximisation with the time horizon obtained from the solution of the makespan minimisation problem. The intermediate products from the main period, cyclic scheduling period, are consumed in the final period with the objective function being profit maximization. With the initial, the cyclic and the final period known, a wastewater minimisation problem with a longer time horizon can be solved. Two illustrative examples are presented in the next chapter to demonstrate the effectiveness of the presented methodology.

References

Majozi, T. and Gouws, J.F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng.* 33:1826-1840.

Majozi, T. and Zhu, X.X., 2001, A novel continuous-time MILP formulation for multipurpose batch plants. 1. Short-term scheduling. *Ind. Eng. Chem. Res.*, 40(25): 5935-5949.

Quesada, I. and Grossmann I.E., 1995, Global optimization of bilinear process networks with multicompnent Flows, *Comp. Chem. Eng.*, 19:1219.

Wu, D. and Ierapetritou, M., 2004, Cyclic short-term scheduling of multiproduct batch plants using continuous-time representation, *Comp. Chem. Eng.*, 28:2271-2286

CHAPTER 04

ILLUSTRATIVE EXAMPLES

Introduction

This chapter presents the application of the mathematical formulation presented in Chapter 3. The application of the mathematical formulation is demonstrated through solving two literature examples. The first literature example is presented in Section 4.1 and it was adopted from the work by Majozi and Gouws (2009). The second literature example is presented in Section 4.2 and it is similar to the first example but considerably more complex as compared to the first example as it consists of more tasks and more units. The example was originally presented in the work by Sundaramoorthy and Karimi (2005) to demonstrate the application of their scheduling technique. However, in this thesis it is adapted to wastewater minimisation.

4.1. Illustrative Example 1 (Kondili *et al.,* 1993)

The illustrative example considered is a well published multipurpose facility which is commonly known as BATCH 1 in literature. It mainly consists of three chemical reactions which take place in two common reactors, Reactor 1 and 2 as depicted in Figure 4.1. In addition to the two common reactors, the flowsheet also entails the heater and the separator, before and after the reactors, respectively, as shown in Figure 4.1. The STN and SSN recipe representation of the flowsheet are given in Figure 4.2(a) and 4.2(b), respectively. The scheduling data for this illustrative example are given Table 4.1.

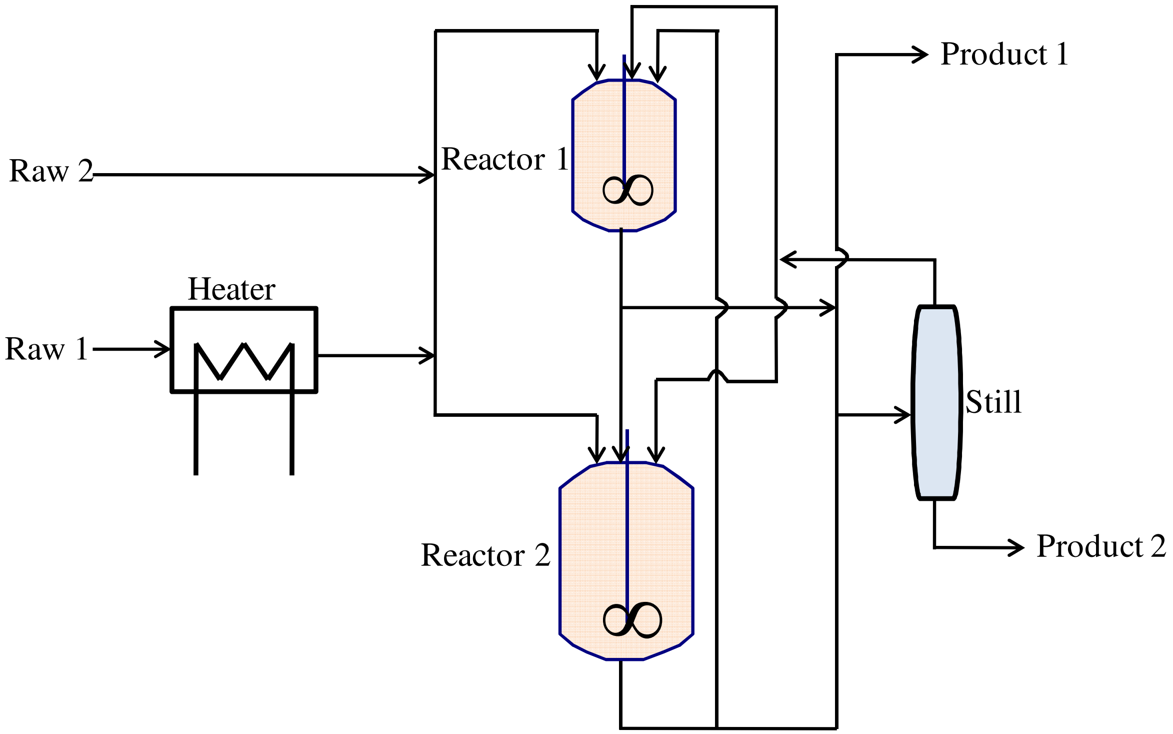


Figure 4.1: Flowsheet for BATCH 1 multipurpose plant

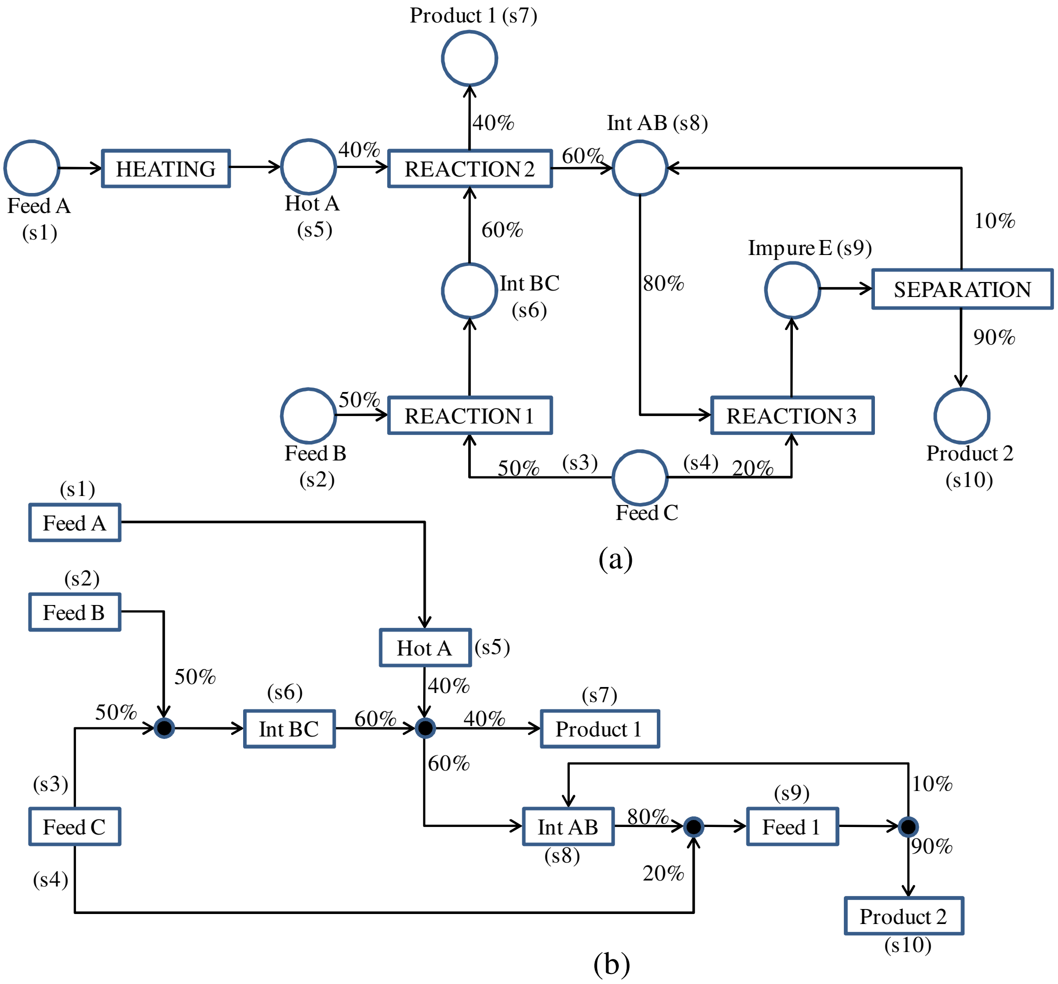


Figure 4.2: (a) STN and (b) SSN for the literature example

Table 4.1: Scheduling data for the illustrative example

Units	**Capacity**	**Suitability**	**Mean processing time** (τ)
Heater	100	Heating	1
Reactor 1	50	Reaction 1,2,3	2,2,1
Reactor 2	80	Reaction 1,2,3	2,2,1
Still	200	Separation	1 for product 2, 2 for IntAB

States	**Storage capacity**	**Initial amount**	**Price**
Feed A	Unlimited	Unlimited	0
Feed B	Unlimited	Unlimited	0
Feed C	Unlimited	Unlimited	0
Hot A	100	0	0
IntAB	200	0	0
IntBC	150	0	0
Impure E	200	0	0
Product 1	Unlimited	0	100
Product 2	Unlimited	0	100

This example was adapted to wastewater minimisation in the work by Majozi and Gouws (2009). The philosophy is that the reactors need to be cleaned after each reaction in order to remove contaminants that are formed as byproducts, so as to ensure product integrity. Data pertaining to cleaning tasks is given in Table 4.2. It is important to note that the streams are characterized by multiple contaminants, which is a common occurrence in industry. The variation in performance in the reactors could be ascribed to the different designs, which is indeed a common encounter in practice. In addition to this data, it is known that the cost of freshwater is 2 c.u./kg water (c.u.- cost units), whilst the effluent treatment cost is 3 c.u./kg.

Table 4.2: Wastewater minimisation data for the illustrative example

		Maximum concentration (g contaminant/kg water)		
		Contaminants		
		1	**2**	**3**
Reaction 1 (Reaction 1)	Max. inlet	0.5	0.5	2.3
	Max. outlet	1	0.9	3
Reaction 2 (Reaction 1)	Max. inlet	0.01	0.05	0.3
	Max. outlet	0.2	0.1	1.2
Reaction 3 (Reaction 1)	Max. inlet	0.15	0.2	0.35
	Max. outlet	0.3	1	1.2
Reaction 1 (Reaction 2)	Max. inlet	0.05	0.2	0.05
	Max. outlet	0.1	1	12
Reaction 2 (Reaction 2)	Max. inlet	0.03	0.1	0.2
	Max. outlet	0.075	0.2	1
Reaction 3 (Reaction 2)	Max. inlet	0.3	0.6	1.5
	Max. outlet	2	1.5	2.5
		Mass load (g)		
		Contaminants		
		1	**2**	**3**
Reaction 1	Reactor 1	4	80	10
	Reactor 2	15	24	358
Reaction 2	Reactor 1	28.5	7.5	135
	Reactor 2	9	2	16
Reaction 3	Reactor 1	15	80	85
	Reactor 2	22.5	45	36.5
		Duration of washing (h)		
		Reaction1	**Reaction2**	**Reaction3**
Reactor 1		0.25	0.5	0.25
Reactor 2		0.3	0.25	0.25

The wastewater minimisation method by Majozi and Gouws (2009) in the absence of a central storage vessel was applied to the illustrative example for different time horizons to demonstrate the common drawback of techniques currently available in literature and the results are given in Table 4.3. As aforementioned, when these techniques are applied to problems with a longer time horizon they present longer computational times. The model was formulated as a MINLP problem. The model was solved using GAMS 22.0, with CONOPT and CPLEX being the selected solvers for NLP and the MIP problems, respectively, in a DICOPT platform. All the results presented in this thesis were obtained using a Pentium 4, 3.2 GHz processor with a 512 MB RAM.

Table 4.3: Results for BATCH 1 using method by Majozi and Gouws (2009)

Time horizon (h)	**Objective function** (c.u.)	**CPU time** (s)
10	11537.5	0.31
13	19587.5	2044.44 (~0.57h)
15	26830.556	56736.67 (~15.76h)
48	---	Intractable

The results in Table 4.3 indicate that for a time horizon of 48h, the solution could not be obtained. From these results it is apparent that a methodology to solve scheduling problems for wastewater minimisation in batch processes for a longer time horizon is crucial, hence the methodology proposed in Chapter 3.

The proposed methodology was applied to the illustrative example. From the solution procedure presented in Chapter 3, the first step is to determine the optimal cycle length. The strategy used by Wu and Ierapetritou (2004) to determine the optimum cycle length was adopted. The time horizon range for determining the cycle length was 3-15h. Instead of considering the whole time horizon range, the time horizon was subdivided into smaller intervals as indicated in Table 4.4. The objective function for the illustrative example is the maximisation of profit per unit time, as given by Constraint (3.72), repeated below for convenience purposes.

$$Max\ \ Z = \frac{\sum_{s}\sum_{p} CP(s)d(s,p) - CF\sum_{s_{out,j}}\sum_{p} mw_f\left(s_{out,j},p\right) - CE\sum_{s_{out,j}}\sum_{p} mw_e\left(s_{out,j},p\right)}{H}$$

The objective function comprises the product revenue, the freshwater and the wastewater treatment cost. For the objective function presented above to be maximised, freshwater and effluent treatment cost must be minimised by minimising the amount of freshwater used and wastewater generated per unit time.

4.1.1. Results and discussions

Determination of the optimum cycle length without central storage

The results for the determination of the optimum cycle length are presented in Table 4.4. The results presented in Table 4.4 are for a case where there is no central storage vessel.

Table 4.4: Result for BATCH 1 using the presented methodology without storage

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
3 - 6	7	2785.507	5.75	73.792
6 - 9	8	2669.444	6	106.634
9 - 12	10	2774.517	9.25	2056.567
12 - 15	11	2154.762	12	1353.127

As shown in Table 4.4, the optimum cycle length was determined to be 5.75h corresponding to a profit per unit time of 2785.507 c.u. per cycle. The schedule for the determined optimum cycle length is given in Figure 4.3. The values on top of the blocks represent the amount of material processed in the unit for production purposes. A washing operation starts after every material processing task, represented as the shaded blocks on the diagram. The values in the curly brackets represent the amount of freshwater supplied to the unit for the washing operation and the value in the square brackets represents the amount of reused water from one operation to another. In the absence of possible reuse and recycle the amount of freshwater consumption is 527.78 kg per cycle. Applying reuse and recycle concept, the amount of effluent generated was reduced by 33.68% per cycle.

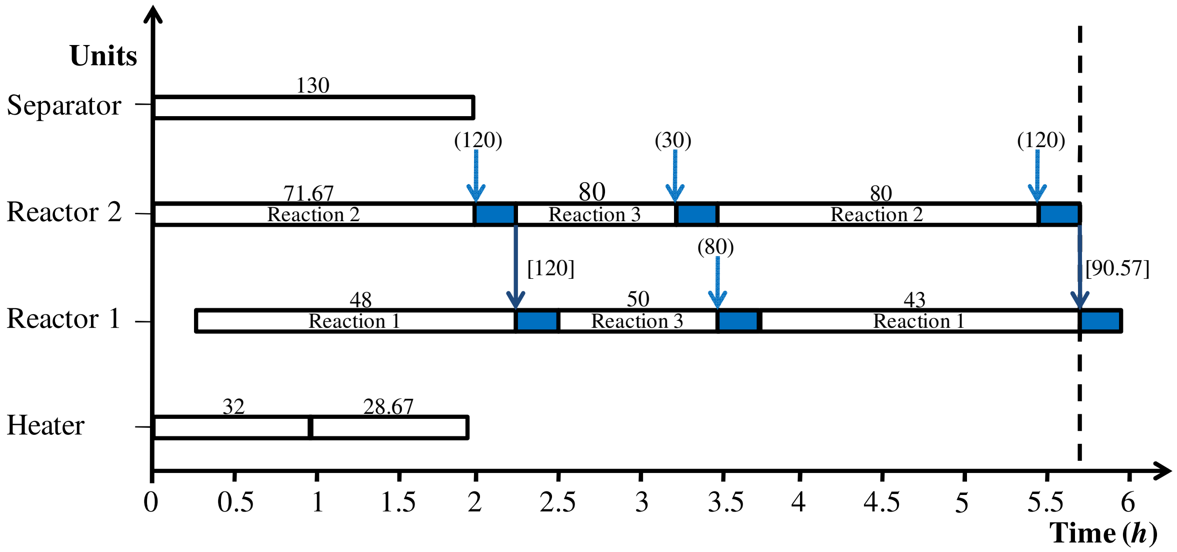


Figure 4.3: Schedule for the optimum cycle length without storage

Determination of the optimum cycle length with central storage

The cycle length for the illustrative example in the presence of a central storage vessel was also determined. It is important to note that to truly minimise wastewater generation in the presence of a storage vessel, the storage vessel must be empty at the end of every cycle. To ensure that this is the case, Constraint (4.1) was added to the model presented in Chapter 3. The results for this case are given in Table 4.5.

$$qw_s(p) = 0 \quad \forall\ p = |P| \tag{4.1}$$

Table 4.5: Result for BATCH 1 using the developed methodology with storage

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
3 - 6	7	2907.246	5.75	274.233
6 - 9	9	2669.444	8.05	345.485
9 - 12	11	2847.954	9.25	1125.784
12 - 15	12	2579.407	12	2157.469

As shown in Table 4.5, the optimum cycle length for this case is also 5.75h corresponding to an average profit of 2907.246 c.u. per cycle. The schedule for the determined cycle length in the presence of a central storage vessel is given in Figure 4.4. The values on the diagram are as described in Figure 4.3 above. In the absence of possible direct and indirect water reuse/recycle the amount of freshwater consumed is 518.89 kg per cycle. Applying reuse and recycle in the presence of a central storage vessel, the amount of effluent generated was reduced by 59.53% per cycle.

It is important to note that the margin of difference in reduction/savings for the two presented cases with and without a central storage vessel is quite significant. This is due to the flexibility in the recycling and reusing time between the units, introduced by the presence of the storage vessel. In the case where the storage vessel is absent, only direct reuse is possible which decreases the degree of flexibility in the recycling and reusing opportunities.

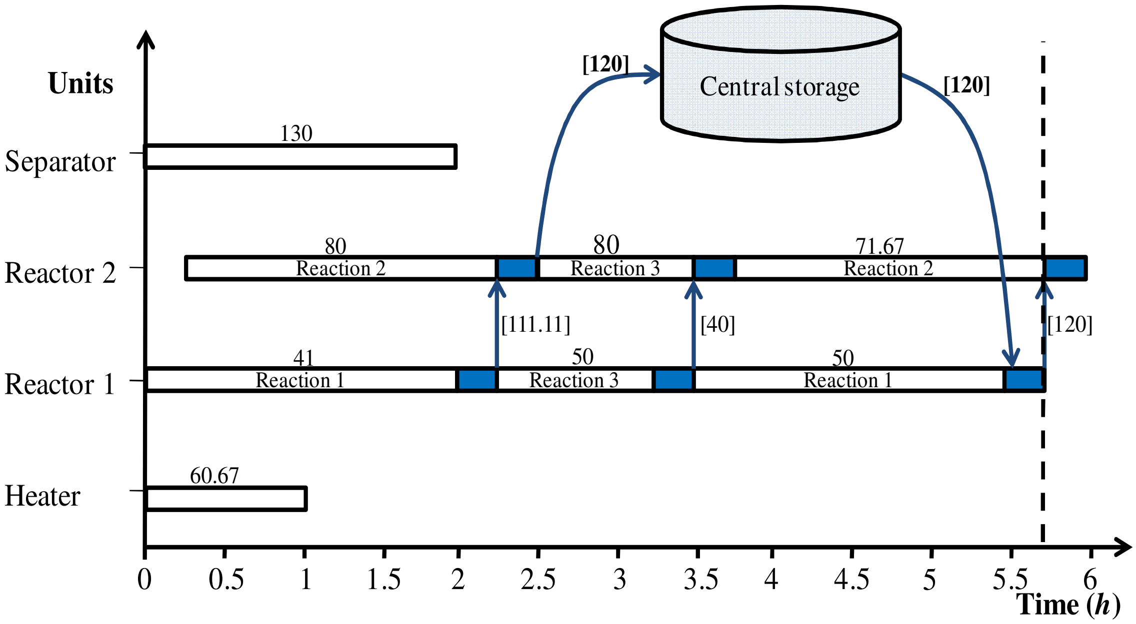


Figure 4.4: Schedule for the optimum cycle length without storage

Wastewater minimisation without central storage for 48h time horizon

The illustrative example could not be solved for a time horizon of 48h when the wastewater minimisation method by Majozi and Gouws (2009) was used, as demonstrated in Table 4.3. Therefore the proposed methodology was applied for 48h time horizon. The time horizon was divided into three periods, as aforementioned in the solution procedure in Chapter 3. The optimum cycle length in the absence of central storage is as determined above in Table 4.4, 5.75h, with the average profit of 2785.507 c.u. per cycle.

Six cycles were determined to provide enough time for the initial period to produce the necessary intermediates and the final period to wrap up the intermediates from the cyclic period. The CPU time for the initial period problem was 321.276*s*. The duration of the initial period was determined to be 10.35h with an objective value of 6201.786 c.u. using 11 time points. The schedule for the initial period is shown in Figure 4.5. The freshwater usage without exploiting reuse and recycle opportunities is 1103.889 kg. Exploiting these opportunities the freshwater consumption and wastewater generated was reduced by 9.185%.

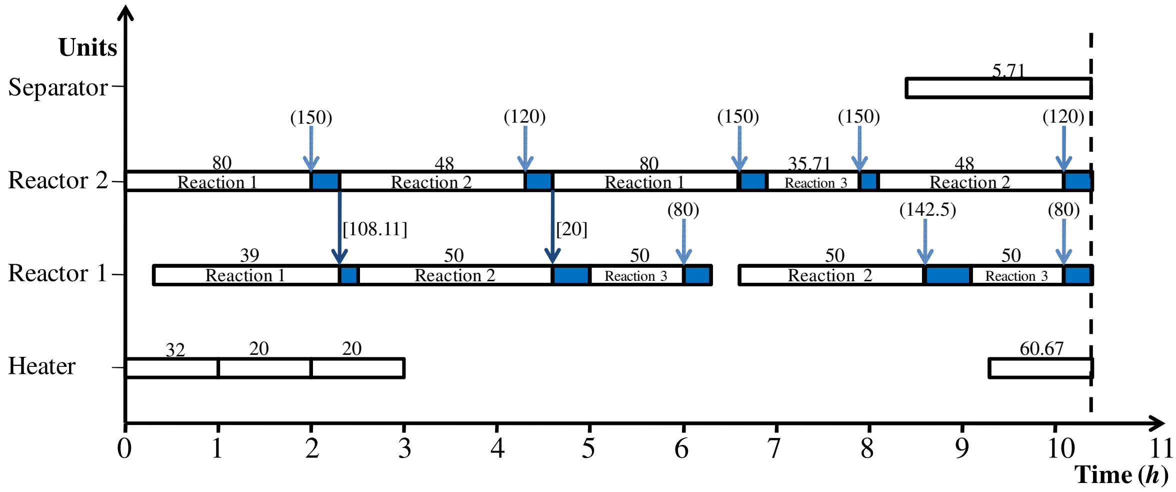


Figure 4.5: Initial period without central storage vessel

The duration of the final period was determined to be 3.15h. This duration was determined from the duration of the total time horizon and the duration of the other two periods. The CPU time for the final period problem was 65.73s. The objective value for this period is 18237.5 c.u., which was obtained using 5 time points. The schedule for the final period is shown in Figure 4.6. The freshwater consumption for this period was determined to be 172.5 kg. There were no reuse and recycle opportunities for this period as it is apparent in Figure 4.6.

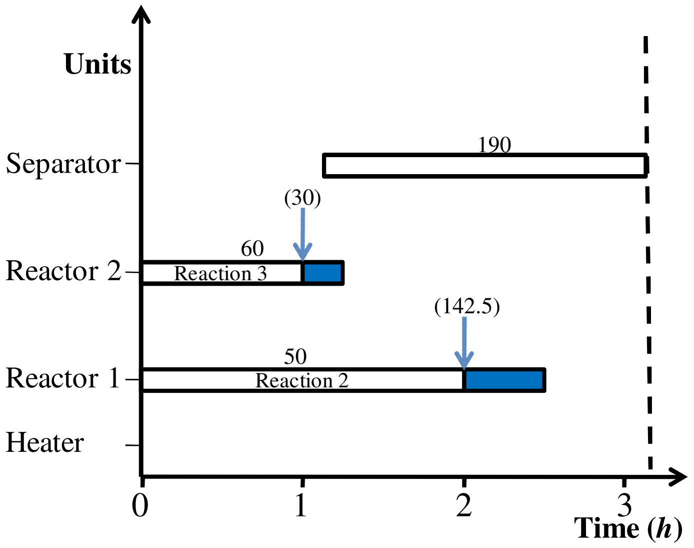


Figure 4.6: Final period without storage for a time horizon of 48h

The overall objective value representing the total profit, including the profit of the initial and the final period, for the time horizon of 48h is 41 152.33 c.u. Disregarding the principle of reuse and recycle, the total freshwater consumption is 4443.069 kg. Exploiting all the possible reuse and recycle opportunities, the total freshwater consumption was reduced by 26.287%.

Wastewater minimisation with central storage for 48h time horizon

The same problem of 48h was solved in the presence of a central storage vessel. The optimum cycle length in the presence of the storage vessel was determined to be 5.75h with an average profit of 2907.246 c.u. per cycle, as abovementioned in Table 4.5. The procedure used to determine the initial and the final period for the case without central storage vessel above was also used for the case with central storage vessel and the results are presented in Table 4.6.

Table 4.6: Results for initial and final period with storage for the time horizon of 48h

Period	**Duration** (h)	**Objective function value** (c.u.)	**Water usage without** (kg)	**CPU** (s)	**Freshwater reduction**
Initial	9.5	7197.222	866.239	254.675	8.35%
Final	4	17350	110	93.756	0%

The corresponding Gantt charts for the initial and the final periods are given Figures 4.7 and 4.8, respectively. Important to note is that for the final period in the case where a central storage vessel is present only direct reuse of water between units was possible since the central storage vessel was not used. This was due to the maximum inlet concentration limit for the units.

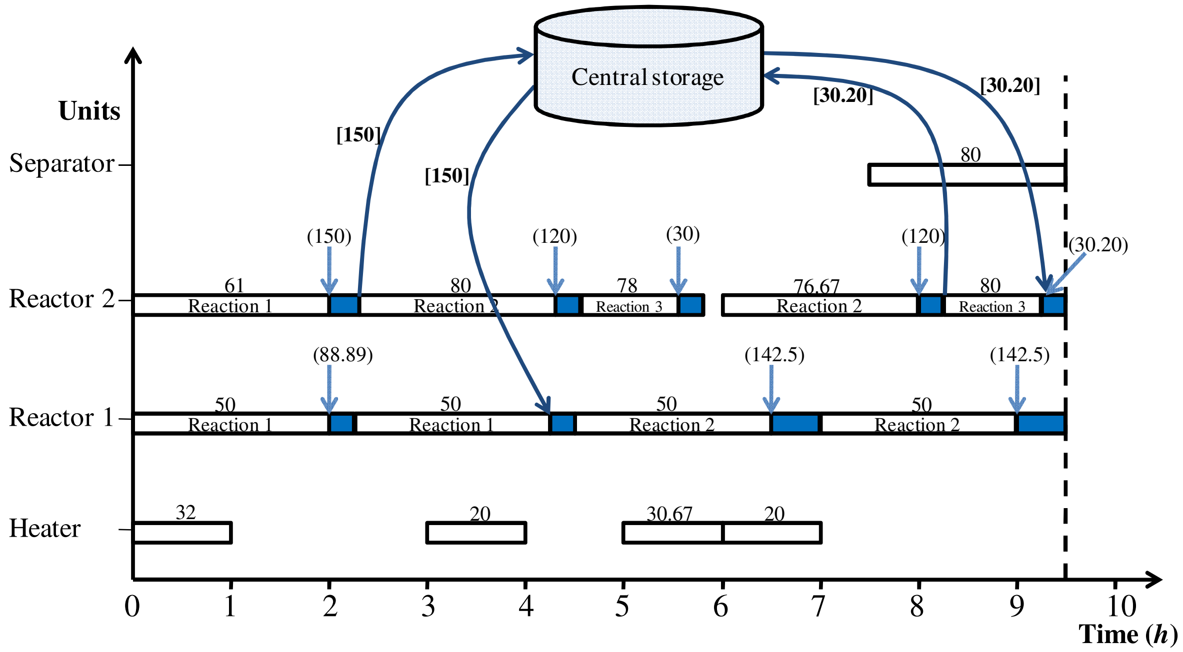


Figure 4.7: Initial period with storage

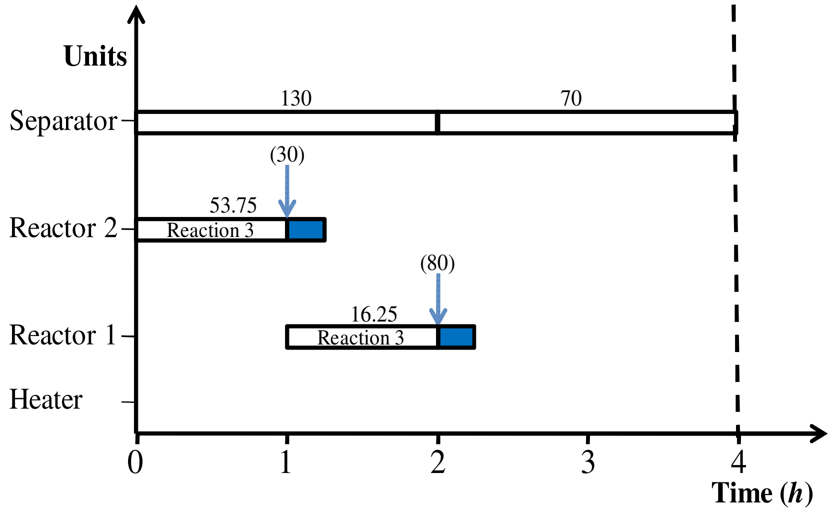


Figure 4.8: Final period with storage

The overall objective value representing the total profit for the time horizon of 48h in the presence of a central storage vessel is 41 990.7 c.u. The total freshwater consumption is 4089.579 kg in the absence of both direct and indirect water reuse/recycle. Exploiting all the available direct and indirect water reuse/recycle opportunities, the total freshwater consumption was reduced by 47.088%.

To facilitate understanding of the presented results, the freshwater savings for the time horizon of 48h in the presence and absence of a central storage vessel are given in Table 4.7. The savings for the cyclic period are given per cycle and 6 operating cycles were obtained for both cases.

Table 4.7: Summary of freshwater savings for example 1

	With storage		**Without storage**	
Period	**Duration** (h)	**Savings** (%)	**Duration** (h)	**Savings** (%)
Initial	9.5	8.35	10.35	9.185
Cyclic	5.75	59.53	5.75	33.68
Final	4	0	3.15	0
Overall	48	47.008	48	26.287

4.2. Illustrative Example 2 (Sundaramoorthy and Karimi, 2005)

This second illustrative example was presented in the work by Sundaramoorthy and Karimi (2005). It is similar to the first example but considerably more complex. In this example, two products are produced through 6 processing units and 7 processing tasks. It consists of three reactions which take place in two common reactors and two heating tasks which take place in one common heater. In addition, it involves one separation task and two mixing tasks which take place in two different mixers. The STN and SSN representation of the example are given in Figures 4.9 and 4.10, respectively. The scheduling data for this example is given in Table 4.8.

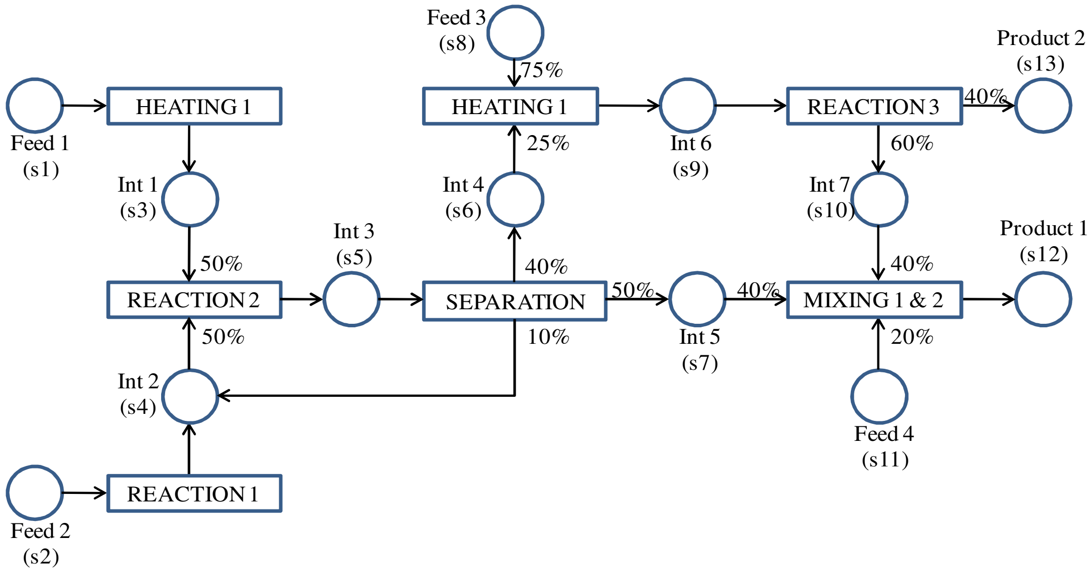


Figure 4.9: STN representation of the second illustrative example

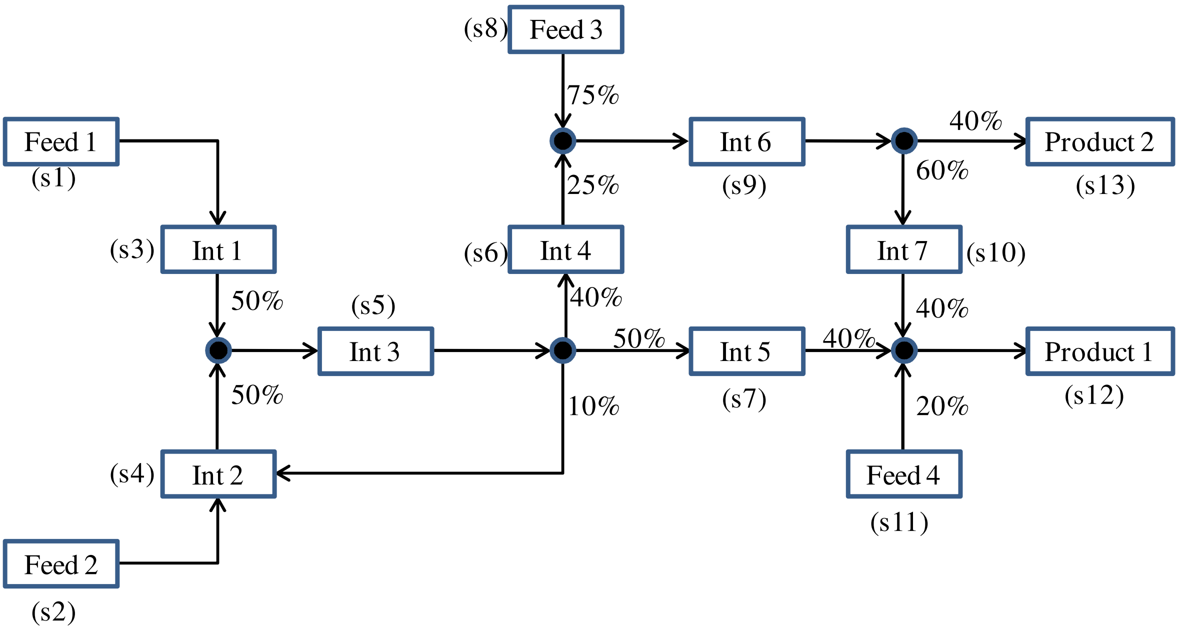


Figure 4.10: SSN representation of the second illustrative example

Table 4.8: Scheduling data for the second illustrative example

Units	**Capacity**		**Suitability**	**Mean processing time**
	Min	*Max*		
Heater	0	100	Heating 1,2	1, 1.5
Reactor 1	0	100	Reaction 1,2,3	2,1,2
Reactor 2	0	150	Reaction 1,2,4	2,1,2
Still	0	300	Separation	3
Mixer 1	20	200	Mixing	2
Mixer 2	20	200	Mixing	2
State	**Price**		**Initial amount**	**Storage capacity**
Feed 1	0		10000	Unlimited
Feed 2	0		10000	Unlimited
Feed 3	0		10000	Unlimited
Feed 4	0		10000	Unlimited
Int1	0		0	100
Int2	0		0	100
Int3	0		0	300
Int4	0		50	150
Int5	0		50	150
Int6	0		0	150
Int7	0		0	150
Product 1	100		0	Unlimited
Product 2	100		0	Unlimited

This example is adapted to wastewater minimisation in this thesis to illustrate the applicability of the presented methodology to a more complex multipurpose facility. The philosophy is that the reactors and the heater must be washed after each production operation. This is to clean contaminants that are formed as byproducts in the units, so as to ensure product integrity. Data pertaining to cleaning tasks is given in Table 4.9.

Table 4.9: Wastewater minimisation data for the second illustrative example

		Maximum concentration (g contaminant/kgwater)		
		Contaminant		
		1	**2**	**3**
Heating 1 (Heater)	Max. inlet	0.5	0.35	1
	Max. outlet	1.15	0.65	1.5
Heating 2 (Heater)	Max. inlet	0.65	0.2	1.35
	Max. outlet	1.5	0.7	2.5
Reaction 1 (Reaction 1)	Max. inlet	0.5	0.5	2.3
	Max. outlet	1	0.9	3
Reaction 2 (Reaction 1)	Max. inlet	0.01	0.05	0.3
	Max. outlet	0.2	0.1	1.2
Reaction 3 (Reaction 1)	Max. inlet	0.15	0.2	0.35
	Max. outlet	0.3	1	1.2
Reaction 1 (Reaction 2)	Max. inlet	0.05	0.2	0.05
	Max. outlet	0.1	1	12
Reaction 2 (Reaction 2)	Max. inlet	0.03	0.1	0.2
	Max. outlet	0.075	0.2	1
Reaction 3 (Reaction 2)	Max. inlet	0.3	0.6	1.5
	Max. outlet	2	1.5	2.5
		Mass load (g)		
		Contaminant		
		1	**2**	**3**
Heating 1	Heater	7.5	13	20
Heating 2	Heater	11	15	25
Reaction 1	Reactor 1	4	80	10
	Reactor 2	15	24	358
Reaction 2	Reactor 1	28.5	7.5	135
	Reactor 2	9	2	16
Reaction 3	Reactor 1	15	80	85
	Reactor 2	22.5	45	36.5
		Duration of washing (h)		
		Heating 1		**Heating 2**
Heater		0.2		0.25
		Reaction1	**Reaction2**	**Reaction3**
Reactor 1		0.25	0.5	0.25
Reactor 2		0.3	0.25	0.25

The method by Majozi and Gouws (2009) could not solve the second illustrative example when a time horizon of 168h was considered. The proposed methodology was applied to the illustrative example with the same objective function considered for the first illustrative example for a time horizon of 168h. The results are presented in the following subsection.

4.2.1. Results and discussions

Wastewater minimisation without central storage for 168h time horizon

The procedure used in the first illustrative example for determining the optimal cycle length is also used in this example. The time horizon range for determining the optimal cycle length and the results are given in Table 4.10. The results presented in Table 4.10 are for a case where a central storage vessel is absent.

Table 4.10: Result for the example without a central storage vessel

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
3 - 6	8	4720.253	4.7	2391.904
6 - 9	9	5167.557	6.45	5042.156
9 - 12	10	3880.959	9.2	3845.292
12 - 15	12	3008.294	12	29239.092

The optimum cycle length was determined to be 6.45h with an average profit of 5167.557 c.u. per cycle. The schedule for the optimum cycle length for this case is given in Figure 4.11. In the absence of possible reuse and recycle the amount of freshwater consumed is 501.675 kg per cycle. Applying the concept of reuse and recycle, the amount of freshwater consumption for the determined cycle length was reduced by 12.53%.

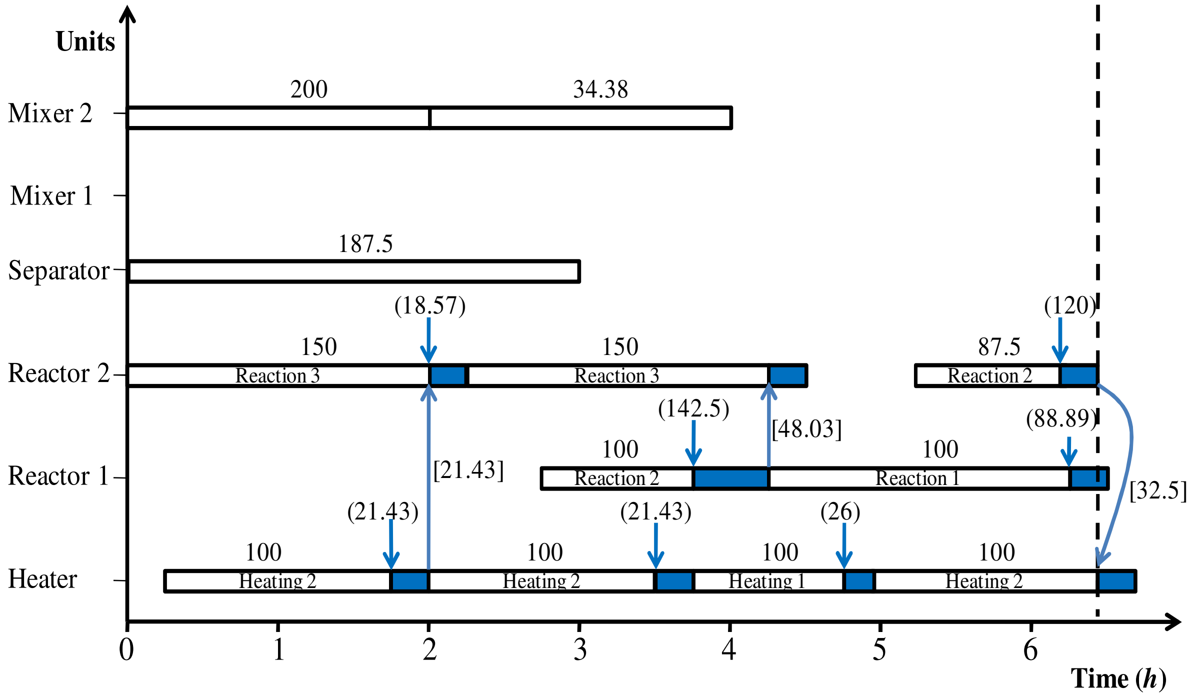


Figure 4.11: Schedule for the optimum cycle length without central storage

Considering the simultaneous production scheduling and wastewater minimisation problem for the time horizon of 168h, the proposed methodology determines 24 cycles of operation. This leaves enough time for the initial and the final period. The results for the initial and the final schedules are given in Table 4.11.

Table 4.11: Results for initial and final period for 168h time horizon

Period	**Duration** (h)	**Objective function value** (c.u.)	**Water usage without** (kg)	**CPU time** (s)	**Freshwater reduction**
Initial	6.7	12897.371	559.857	2923.03	8.00%
Final	6.5	42467.857	302.857	166.439	7.08%

The corresponding Gantt charts for the initial and final period are given in Figures 4.12 and 4.13, respectively.

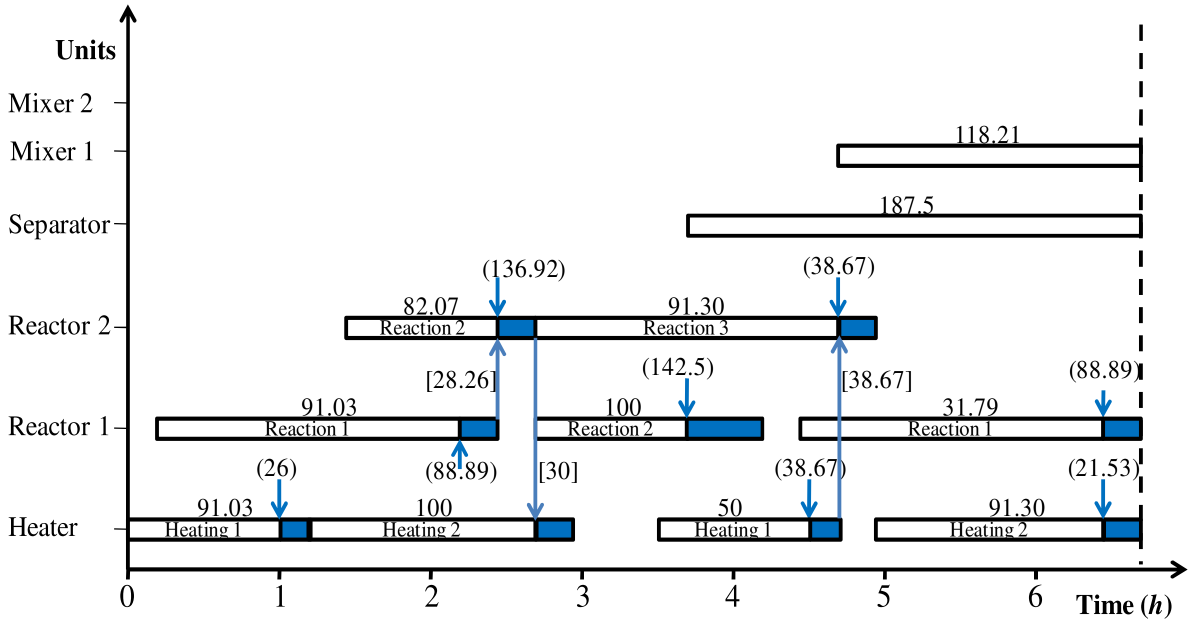


Figure 4.12: Initial period without storage for the time horizon of 168h

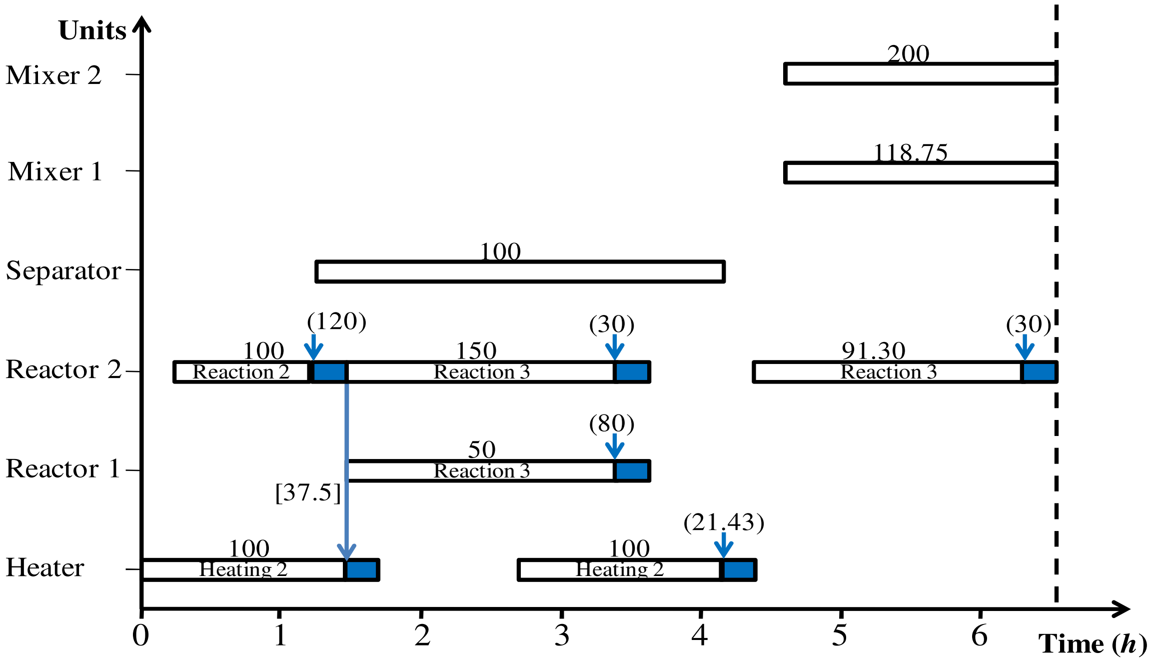


Figure 4.13: Final period without storage for the time horizon of 168h

The objective value corresponding to the total profit for the time horizon of 168h is 179 386.596 c.u. The total freshwater consumption for this time horizon is 12 902.914 kg in the absence of water reuse and recycle. Exploiting all the available reuse and recycle opportunities, the total freshwater consumption is reduced by 16.363%.

Wastewater minimisation with central storage for 168h time horizon

The illustrative example for the time horizon of 168h in the presence of central storage vessel was also considered. The optimum cycle length for the example for case where a central storage was presented was also determined and the results are shown in Table 4.12.

Table 4.12: Result for example with a central storage vessel present

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
3 - 6	7	4885.904	4.7	2019.64
6 - 9	9	5326.345	6.45	14963.811
9 - 12	10	4006.984	9	8401.495
12 - 15	11	3025.014	12	22937.718

The optimum cycle length for this case was also determined to be 6.45h, corresponding to the average production of 5326.345 c.u. per cycle as shown in Table 4.12. The schedule for the optimum cycle length for this case is given in Figure 4.14. The freshwater consumption for the determined cycle while exploiting the concept of reuse and recycle is 372.22 kg per cycle. Considering this concept, the freshwater consumption for was reduced by 41.83% per cycle.

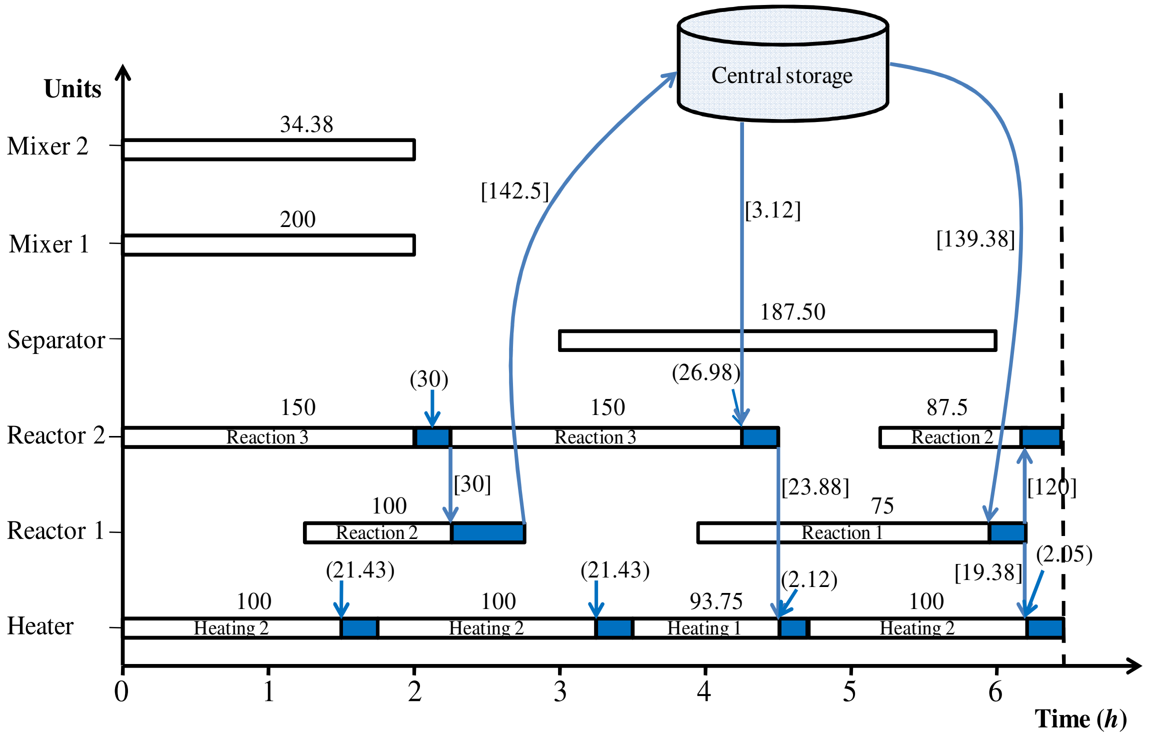


Figure 4.14: Schedule for the optimum cycle length for the case with central storage

Considering the illustrative example for the time horizon of 168h time horizon in the presence of a central storage vessel, the proposed methodology determines 24 cycles of operation which leaves enough time for the initial and the final period. The results for the initial and the final period are given in Table 4.13.

Table 4.13: Result for the initial and the final period in the presence of a central storage

Period	**Duration** (h)	**Objective function value** (c.u.)	**Water usage without** (kg)	**CPU time** (s)	**Freshwater reduction**
Initial	8.85	14111.27	592.635	2728.143	19.39%
Final	4.35	42787.5	273.93	98.235	6.94%

The corresponding Gantt charts for the initial and final period are given in Figures 4.15 and 4.16, respectively. Take note that the schedule for the initial period does not utilise the central storage vessel. This can be attributed to the inlet concentration limit constraints for the water using units.

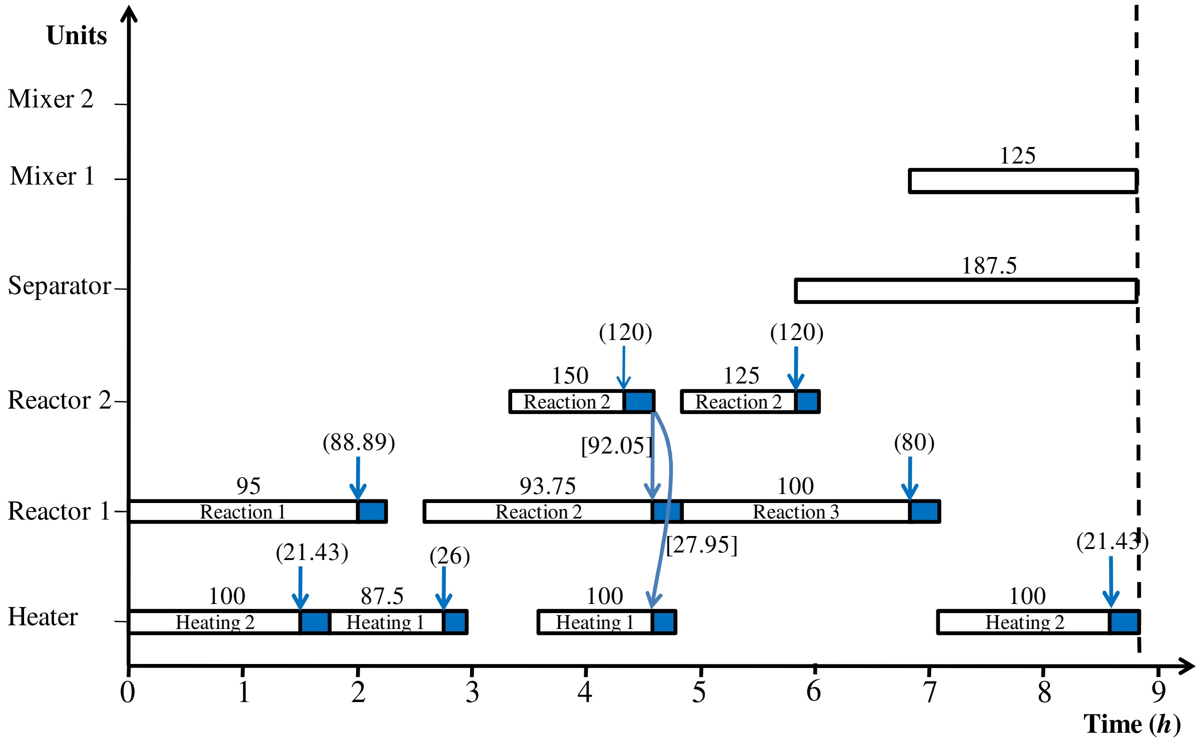


Figure 4.15: Initial period with storage

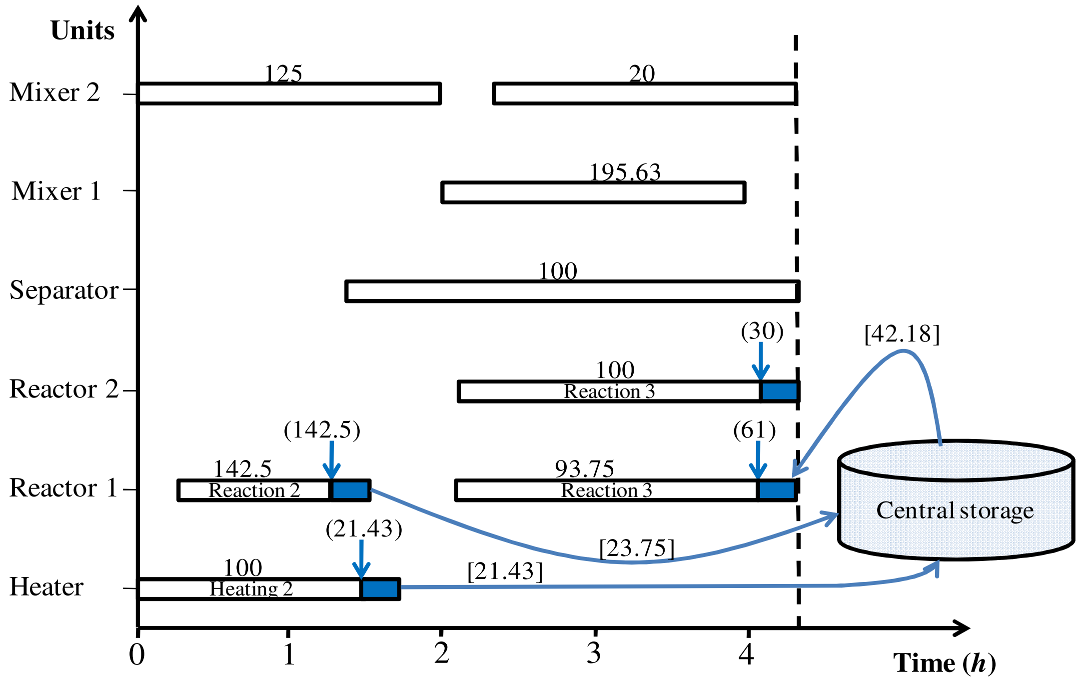


Figure 4.16: Final period with central storage present

The objective value representing the total profit for the time horizon of 168h is 184 731.05 c.u. The total freshwater consumption corresponding for this time horizon in the absence of direct and indirect water reuse/recycle is 9799.845 kg. Exploiting all possible direct and indirect water reuse/recycle, the total freshwater consumption is reduced by 39.498%.

The freshwater savings results for the time horizon of 168h in the presence and absence of a central storage vessel are given in Table 4.14. The savings for the cyclic period are given per cycle and 24 operating cycles were obtained for both cases.

Table 4.14: Summary of example 2 for 168h time horizon

	With storage		**Without storage**	
Period	**Duration** (h)	**Savings** (%)	**Duration** (h)	**Savings** (%)
Initial	8.85	19.39	6.7	8
Cyclic	6.45	41.83	6.45	16.985
Final	4.35	6.94	6.5	7.08
Overall	168	39.498	168	16.363

Remarks

From the results presented in this chapter, it is evident that the developed methodology can be used to reduce problems with longer time horizon to a smaller problem which can be solved with ease. The first illustrative example could not be solved for 48h using the common technique for wastewater minimisation for short-term time horizon. With the application of the proposed methodology, the 48h time horizon in the absence of central storage vessel was reduced to 6 cycles with a time horizon of 5.75h, initial period with a duration of 10.35h and a final period with a duration of 4h. For the second illustrative example, the time horizon of 168h was reduced to 24 cycles, each cycle with the length of 6.45h, initial period of 8.85h and final period of 6.5h in the absence of central storage vessel. The global optimality of the presented results cannot be guaranteed since the developed methodology is nonlinear. The nonlinearity of the objective function cannot be linearized with the technique presented in the Appendix but it was used to determine a starting point for solving the model. The developed technique is further applied to an industrial case study in the following chapter, to demonstrate the practical application.

References

Kondili, E., Pantelides, C.C. and Sargent, R.W.H., 1993, A general algorithm for short-term scheduling of batch operations-I. MILP formulation, *Comp. Chem. Eng.*, 17(2): 211-227

Majozi, T. and Gouws, J. F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng.* 33:1826-1840.

Sundaramoorthy, A. and Karimi, I. A., 2005, A simpler better slot-based continuous-time formulation for short-term scheduling in multipurpose batch plants, *Chem. Eng. Sci.* 60, 2679-2702.

Wu, D. and Ierapetritou, M., 2004, Cyclic short-term scheduling of multiproduct batch plants using continuous-time representation, *Comp. Chem. Eng.*, 28:2271-2286

CHAPTER 05

INDUSTRIAL APPLICATION

Introduction

The industrial application of the proposed methodology presented in Chapter 3 is presented in this chapter. The application is demonstrated through solving a simultaneous production scheduling and wastewater minimisation problem for a case study from a pharmaceuticals facility. Section 5.1 presents the case study background which includes all the necessary data to solve the problem. The results and discussion are presented Section 5.2.

5.1. Case study background

The case study is taken from a pharmaceuticals facility that produces 4 types of products, viz. shampoos, deodorants, lotions and creams. All the products involve mixing and there are four mixing units dedicated to each product i.e. one unit is suitable for mixing of one product. It is mandatory to wash the unit after every mixing task to ensure product integrity. The streams are characterized by multiple contaminants due to the multiple products found in the facility. The residue mass left in the unit after a mixing operation is given in Table 5.1. Also given in Table 5.1 is the necessary information to conduct wastewater minimisation and the duration of each mixing operation. Because of different designs of the stirrers in the mixing vessels, mixing durations vary according to the vessel used. All the mixers have a capacity of 2 tons.

Table 5.1: Data for the case study

Mixer	Product	Residue mass (kg)	Max. outlet conc (kg/kg water)	Mass water (kg)	Duration (h)
1	Shampoos	15	0.040	576.9	7
2	Deodorants	15	0.045	361.4	5.5
3	Lotions	30	0.050	697.6	11
4	Creams	70	0.060	1238.9	11

The maximum inlet concentration of each mixer is given in Table 5.2. It is important to note that the inlet concentration for the deodorant is zero in mixers 1, 3 and 4. This is due to the incompatibility of this residue with the other residues. Thus, the reuse of water contaminated with deodorant to the other units is forbidden. The duration of the washing operation is 30 min. A 10 tons central storage vessel for less contaminated water is available. In addition to the given data, the cost of freshwater is 0.2 c.u./kg of water, whilst the effluent treatment cost is 0.3 c.u./kg.

Table 5.2: Maximum inlet concentrations for cleaning operation for the case study

Mixer	Shampoos (kg / kg water)	Deodorants (kg / kg water)	Lotions (kg / kg water)	Creams (kg / kg water)
1	0.014	0	0.007	0.0035
2	0.014	0.0035	0.007	0.007
3	0.014	0	0.007	0.0035
4	0.014	0	0.007	0.0035

5.2. Results and discussions

The methodology by Majozi and Gouws (2009) was applied to the industrial case study to demonstrate the computational problems short-term scheduling techniques for wastewater minimisation have when they are applied to industrial scale problems. The same objective function used for the illustrative examples in Chapter 4 was used for the industrial case study, i.e. maximization of profit per unit time. The results are shown Table 5.3. The methodology by Majozi and Gouws (2009) encountered a computational difficulty for the time horizon of 168h and the solution time for the time horizon of 72h is quite long.

Table 5.3: Demonstration of computational problems

Time horizon (h)	**Objective function**	**CPU** (s)
24	41758.062	10.625
48	105167.217	5724.550
72	229163.475	50786.576
168	---	---

Wastewater minimisation without central storage for 168h time horizon

The methodology presented in Chapter 3 was applied to the industrial case study. The formulation of the problem in the presence and in the absence of a central storage vessel resulted in a MINLP problem. It is important to note that for the case study, the raw materials needed for the mixing process are readily available; hence the initial and the final period problems are absent. The same procedure followed for the illustrative examples to determine the optimal cycle length is followed for the case study. The time horizon range for determining the optimal cycle length for the case where a central storage vessel is not available is chosen to be 12-72h. The results for the case study without a central storage vessel are presented in Table 5.4.

Table 5.4: Results for the case study without central storage

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
12 - 24	7	1740.910	23	55.202
24 - 36	9	1730.886	24	71.538
36 - 48	11	1718.852	37.5	984.048
48 - 60	12	1663.541	48	771.453
60 - 72	14	1595.436	64	2036.576

As shown in Table 5.4, the optimum cycle length was determined to be 23h with a profit per unit time of 1740.910 c.u. per cycle. The Gantt chart corresponding to the optimum cycle length showing both the production operations and the washing operations is depicted in Figure 5.1. The values in the curly brackets represent the amount of freshwater supplied to the unit and the value in the square brackets represents the amount of water reused from one operation to another. In the absence of possible reuse and recycle the amount of freshwater used is 5658.33 kg per cycle. Applying the concept of reuse and recycle, the amount of effluent generated was reduced by 18.12% per cycle. The overall objective value which represents the total profit for the time horizon of 168h is 12 716.21 c.u. This corresponds to a total freshwater consumption of 41 330.41 kg in the absence of reuse and recycle. The reduction in the overall freshwater consumption is the same as the reduction per cycle for the case study since the initial and the final period are not present, as aforementioned.

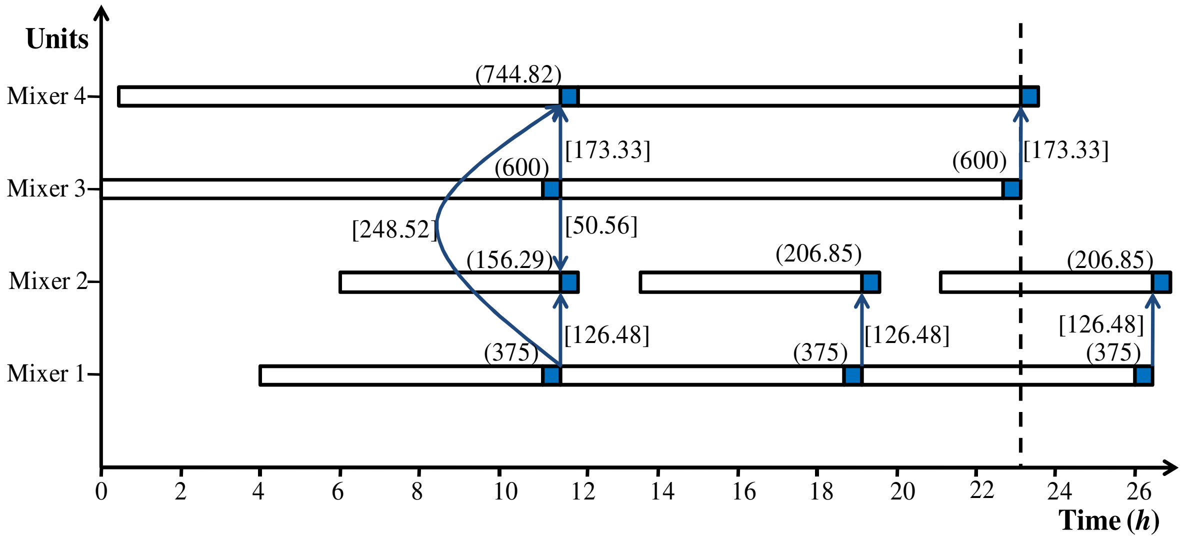


Figure 5.1: Optimum schedule for the case study without storage vessel

Wastewater minimisation with central storage for 168h time horizon

For a case where a central storage was present, the cycle length was also obtained to be 23h with the objective function of 1787.278 c.u. per cycle, as shown in Table 5.5. In the absence of possible reuse and recycle the amount of freshwater required is 5658.33 kg per cycle. Applying the concept of reuse and recycle, the amount of effluent generated was reduced by 45.40% per cycle and the Gantt chart for these results is given in Figure 5.2. The objective value for the time horizon of 168h in the presence of a central storage vessel is 13 054.9 c.u. This corresponds to a total freshwater consumption of 41 330.41 kg in the absence of direct and indirect water reuse/recycle. The reduction in the overall freshwater consumption is the same as the reduction per cycle for the case study since the initial and the final period are not present, as aforementioned.

Table 5.5: Results for the case study with central storage present

Cycle time range (h)	**Number of time points**	**Objective function value** (c.u.)	**Optimal cycle time** (h)	**CPU time** (s)
12 - 24	8	1787.278	23	64.53
24 - 36	9	1750.281	24	87.435
36 - 48	11	1734.563	37.5	882.361
48 - 60	13	1683.342	51.5	561.453
60 - 72	14	1695.436	60	1045.583

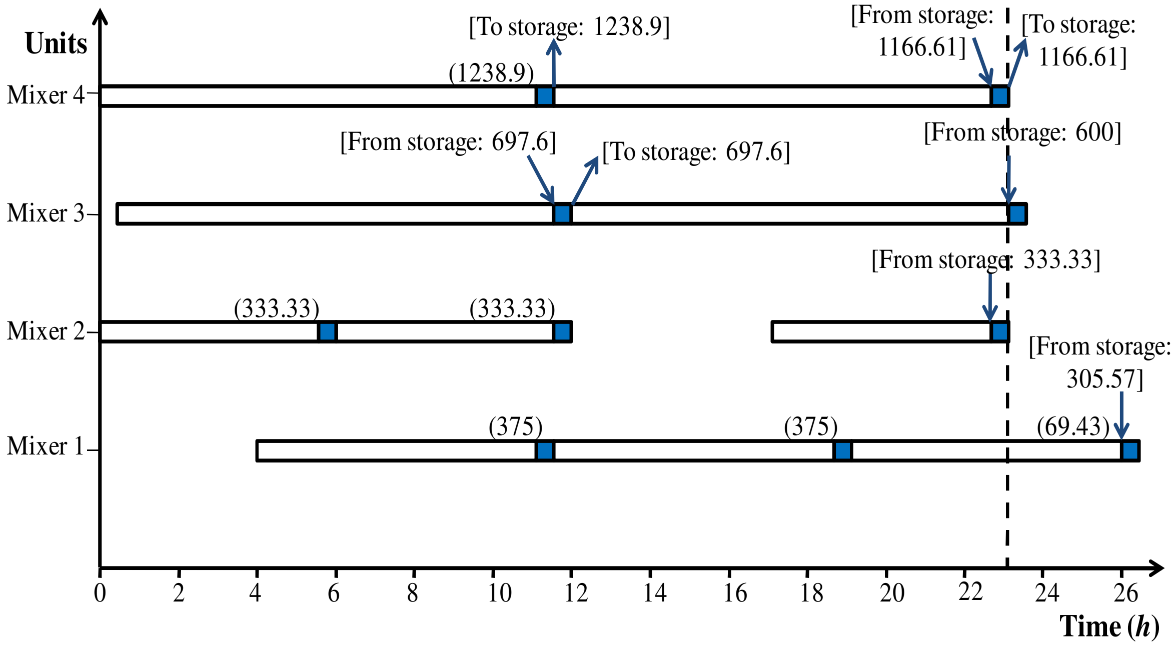


Figure 5.2: Optimum schedule in the presence of a central storage vessel

Remarks

The currently published wastewater minimisation techniques could not find a solution for the time horizon of 168h. Applying the developed methodology in this work, the time horizon of 168h was reduced to 8 cycles with the length of 23h. The CPU time for the optimum cycle length was 64.53s. The reduction in freshwater usage and wastewater generation for the determined cycle was 18.12% per cycle in the absence of central storage vessel and 45.40% per cycle in the presence of a central storage vessel.

From the results of the industrial case study, the developed methodology proves to be capable of reducing an industrial scale problem to a problem with a smaller time horizon. As mentioned for the illustrative example, the global optimality of the presented results cannot be proven due to the nonlinearities present in the formulation of the methodology, particularly in the objective function.

References

Majozi, T. and Gouws, J. F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng.* 33:1826-1840.

CHAPTER 06

CONCLUSIONS AND RECOMMENDATIONS

Introduction

This chapter presents the conclusions and recommendations drawn from the work presented in this thesis. The conclusions are presented in Section 6.1 and the recommendations are presented in Section 6.2.

6.1. Conclusions

A long-term scheduling methodology for wastewater minimisation in multipurpose batch facilities was presented in this thesis. The main advantage of the presented methodology is the ability to reduce a wastewater minimisation problem with a longer time horizon to a problem with a smaller time horizon, which can be solved within reasonable CPU time. This was achieved through the exploitation of cyclic scheduling concepts in the context of wastewater minimisation. The concept of water reuse and recycle was used to minimise wastewater generation. The proposed methodology optimises both the production schedule and wastewater minimisation simultaneously. It is applicable to operations with streams characterized by multiple contaminants, which is more prevalent in industry. The resulting mathematical formulation was a MINLP problem. Thus, global optimum solution from the presented methodology cannot be guaranteed.

The methodology was applied to two illustrative examples to demonstrate its application. For the first illustrative example, the time horizon of 48h was reduced to 6 cycles of operation with a duration of 5.75h, in the presence of a central storage vessel. The corresponding initial and final period had a duration of 9.5h and 4h, respectively. The total freshwater consumption for the time horizon of 48h was reduced by 47.01%. The methodology was also applied to an industrial case study taken from a pharmaceutical industry to prove its practical capabilities and effectiveness. A time horizon of 168h for the case study was reduced to 8 cycles of operation with a length of 23h. The total freshwater consumption for the time horizon of 168h was reduced by 18.12%, in the absence of a central storage vessel and 45.40% in the presence of a central storage vessel.

6.2. Recommendations

The following is recommended for future work:

- The linearization technique used to relax the presented model is not applicable to the objective function, as aforementioned in Chapter 3. Thus, the resulting highly nonlinear mathematical formulation could not be fully linearized. It is recommended that an alternative linearization technique be considered to linearize the model.

- The presented methodology reduces wastewater generation based on the concept of direct and indirect water reuse/recycle. It is recommended that an option of regeneration reuse/recycle be considered for future work.

- The concept of cyclic scheduling is limited to batch processes with stable operating conditions or stable product demand. Hence, the presented methodology is not suitable for production facilities with large variability of production parameters. It is recommended that future work consider the effect of unstable operating conditions on wastewater generation.

APPENDIX

LINEARIZATION TECHNIQUE

A.1. Linearization (Majozi and Gouws, 2009)

To demonstrate the linearization technique presented in the work by Majozi and Gouws (2009), Constraints (3.4) and (3.5) presented in Chapter 3 will be considered. The two constraints contain bilinear terms. These nonlinear terms can be linearized according to the linearization technique proposed by Quesada and Grossmann (1995). The linearization is as follows.

Let:

$$c_{in}\left(s_{out,j}, c, p\right) mw_{in}\left(s_{out,j}, p\right) = \Gamma_1\left(s_{out,j}, c, p\right)$$

$$c_{out}\left(s_{out,j}, c, p\right) mw_{out}\left(s_{out,j}, p\right) = \Gamma_2\left(s_{out,j}, c, p\right)$$

$$c_{out}\left(s_{out,j'}, c, p\right) mw_r\left(s_{out,j'}, s_{out,j}, p\right) = \Gamma_3\left(s_{out,j'}, s_{out,j}, p\right)$$

With each variable having the following bounds

$$0 \le c_{in}\left(s_{out,j}, c, p\right) \le C_{in}^{U}\left(s_{out,j}, c\right)$$

$$0 \le mw_{in}\left(s_{out,j}, p\right) \le Mw^{U}\left(s_{out,j}\right)$$

$$0 \le c_{out}\left(s_{out,j}, c, p\right) \le C_{out}^{U}\left(s_{out,j}, c\right)$$

$$0 \le mw_{out}\left(s_{out,j}, p\right) \le Mw^{U}\left(s_{out,j}\right)$$

$$0 \le mw_r\left(s_{out,j'}, s_{out,j}, p\right) \le Mw^{U}\left(s_{out,j}\right)$$

then the following constraints are true for Γ_1:

$$\Gamma_1\left(s_{out,j}, c, p\right) \geq 0, \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.1}$$

$$\begin{aligned}\Gamma_1\left(s_{out,j}, c, p\right) \geq Mw^U\left(s_{out,j}\right)c_{in}\left(s_{out,j}, c, p\right) + C_{in}^U\left(s_{out,j}, c\right)mw_{in}\left(s_{out,j}, p\right) \\ - Mw^U\left(s_{out,j}\right)C_{in}^U\left(s_{out,j}, c\right), \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C\end{aligned} \tag{A.2}$$

$$\Gamma_1\left(s_{out,j}, c, p\right) \leq Mw^U\left(s_{out,j}\right)c_{in}\left(s_{out,j}, c, p\right), \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.3}$$

$$\Gamma_1\left(s_{out,j}, c, p\right) \leq C_{in}^U\left(s_{out,j}, c\right)mw_{in}\left(s_{out,j}, p\right), \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.4}$$

and the following constraints are true for Γ_2:

$$\Gamma_2\left(s_{out,j}, c, p\right) \geq 0, \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.5}$$

$$\begin{aligned}\Gamma_2\left(s_{out,j}, c, p\right) \geq Mw^U\left(s_{out,j}\right)c_{out}\left(s_{out,j}, c, p\right) + C_{out}^U\left(s_{out,j}, c\right)mw_{out}\left(s_{out,j}, p\right) \\ - Mw^U\left(s_{out,j}\right)C_{out}^U\left(s_{out,j}, c\right), \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C\end{aligned} \tag{A.6}$$

$$\Gamma_2\left(s_{out,j}, c, p\right) \leq C_{out}^U\left(s_{out,j}, c\right)mw_{out}\left(s_{out,j}, p\right), \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.7}$$

and the following constraints are true for Γ_3:

$$\Gamma_3\left(s_{out,j'}, s_{out,j}, c, p\right) \geq 0, \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.8}$$

$$\begin{aligned}\Gamma_3\left(s_{out,j'}, s_{out,j}, c, p\right) \geq Mw^U\left(s_{out,j}\right)c_{out}\left(s_{out,j'}, c, p\right) + C_{out}^U\left(s_{out,j'}, c\right)mw_r\left(s_{out,j'}, s_{out,j}, p\right) \\ - Mw^U\left(s_{out,j}\right)C_{out}^U\left(s_{out,j'}, c\right), \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C\end{aligned} \tag{A.9}$$

$$\Gamma_3\left(s_{out,j'}, s_{out,j}, c, p\right) \leq Mw^U\left(s_{out,j}\right)c_{out}\left(s_{out,j}, c, p\right), \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.10}$$

$$\Gamma_3\left(s_{out,j'}, s_{out,j}, c, p\right) \leq C_{out}^U\left(s_{out,j'}, c\right)mw_r\left(s_{out,j}, p\right), \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{A.11}$$

Substituting the above linearized variables into Constraints (3.4) and (3.5) gives Constraints (A.12) and (A.13):

$$\Gamma_2(s_{out,j},c,p)=\Gamma_1(s_{out,j},c,p-1)+M(s_{out,j},c)yw(s_{out,j},p-1), \quad \forall j\in J, s_{out,j}\in S_{out,j}, p\in P, c\in C, p>p_1 \qquad (A.12)$$

$$\Gamma_1(s_{out,j},c,p)=\sum_{s_{out,j}}\Gamma_3(s_{out,j'},s_{out,j},c,p), \qquad \forall j,j'\in J, s_{out,j}\in S_{out,j}, p\in P, c\in C \qquad (A.13)$$

The same linearization procedure can be followed to linearize any source of nonlinearity in the model with the exception of the nonlinearity present in the objective function.

The solution procedure presented in Figure A.1 is followed when the nonlinear terms in the model are linearized. It is important to mention that for the presented model, global optimality cannot be guaranteed through the application of this solution procedure. However, this procedure can be used to provide a feasible starting point prior to solving the exact nonlinear model.

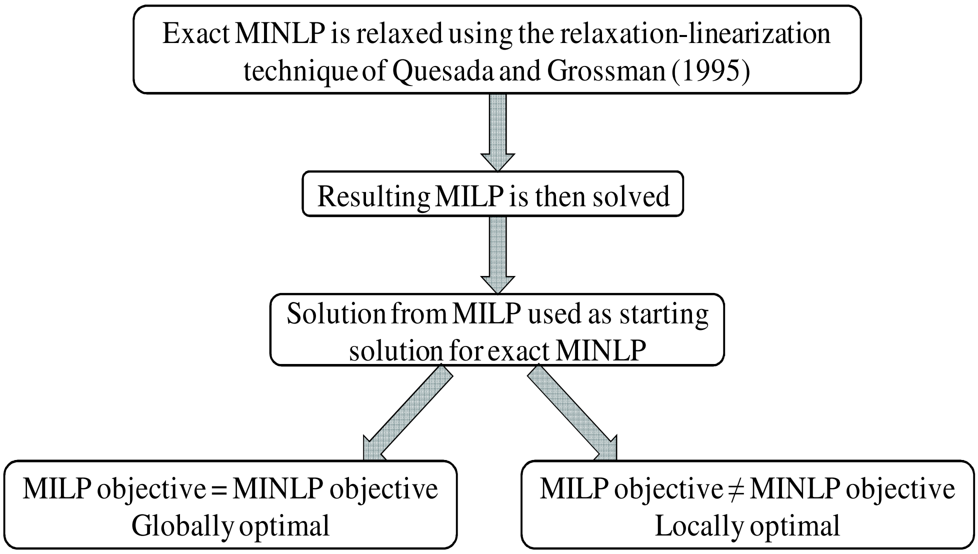


Figure A.1: Solution procedure from Majozi and Gouws (2009)

References

Majozi, T. and Gouws, J.F., 2009, A mathematical optimization approach for wastewater minimization in multiple contaminant batch plants, *Comp. Chem. Eng*. 33:1826-1840.

Quesada, I. and Grossmann I.E., 1995, Global optimization of bilinear process networks with multicomponent flows, *Comp. Chem. Eng*., 19:1219.