WATER USE OPTIMIZATION IN INDUSTRY:
Development of a Mathematical Model for Wastewater Minimization in a Multipurpose Batch Plant

Report to the
Water Research Commission

by

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Executive Summary

The nature of products widely produced from batch chemical plants is 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 liquid waste volume. From these observations, it is desirable to minimize the production of such effluent at worst and eliminate it at best.

Two unique investigations were considered in this report. The aim of the first investigation was to develop a mathematical technique to minimize wastewater generation in multipurpose batch processes operated over a long time horizon, i.e. industrial scale problems, with significantly reduced computational difficulties. The aim of the second investigation was to develop a wastewater minimization methodology that incorporates wastewater regeneration in batch plants.

Published literature abounds with wastewater minimization techniques for batch processes. However, these are only limited to short term time horizons. When these methodologies are applied to industrial scale problems with longer time horizons, computational difficulties are encountered, as characterized by impractically long CPU times. Presented in this report is a mathematical formulation that seeks to address this shortcoming. The developed technique has been applied to much longer time horizons with great success.

The other aspect that is lacking in most published techniques is the inclusion of regeneration option within the recycle and reuse framework. This report also presents a methodology to address the problem of wastewater minimization by extending the concept of water reuse to include a regeneration system. The methodology is equally applicable in situations where the batch plant schedule is known and unknown beforehand. The regenerator purifies wastewater to such a quality that it can be reused in other operations, which further increases water reuse opportunities in the plant, thereby significantly reducing freshwater demand and effluent generation.

The overall report is structured as follows. Chapter 1 gives the objectives of the investigation, followed by Chapter 2 which presents a detailed survey of relevant literature. After Chapter 2, the report is divided into Sections A and B. *Section A*, focuses on cyclic scheduling as a way of handling longer time horizon in batch processing. *Section B* on the other hand presents the incorporation of regeneration in order to increase recycle and reuse opportunities. Both sections systematically present mathematical formulations and detailed case studies where these techniques have been applied with freshwater savings in excess of 25%. Future studies could look at the development of software to ensure industries are able to use the model for their batch process water optimization steps.

It should be highlighted that the results of the mathematical optimization models in both investigations were time point specific. The number of time points quoted in the results was not proven to be the optimal number of time points. An iterative procedure is carried out until there is no change in the results for each new increment of time points. The optimal number of time points is the smallest number that gave the best result.

It was observed in the long term scheduling model that the linearization technique used to relax the presented model was not applicable to the objective function. 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. Also, the presented methodology reduced 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 in long term scheduling for future work.

The concept of cyclic scheduling is limited to batch processes with stable operating conditions or stable product demand. Hence, the long term scheduling 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.

The model for the regeneration methodology had a considerable number of bilinear terms. Upon linearization, additional variables and constraints were introduced in the model which resulted in the model being very large. It is recommended that different scheduling methods be considered in the wastewater minimization methodology to investigate the effect on computational times and wastewater minimization results.

Finally, adopting these models to real life situations would require a shift in mindset with regards to operating procedures. This could prove to be a challenge, especially in situations where it may appear that there is no urgent need for wastewater minimization.

Due to the fine contributions that have been made in the topic of wastewater minimization, the point has been reached where the commercialization of software is possible. This will be beneficial in the sense that it would not require users to understand the sometimes complex mathematical formulation but would only involve the input of data.

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NOMENCLATURE

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

Sets

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

Variables associated with wastewater minimization

$mw_{in}(s_{out,j}, p)$	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
$mreg_{in}(s_{out,j}, p)$	mass of water transferred from storage to regenerator at time point p
$mreg_{out}(s_{out,j}, p)$	mass of water transferred from regenerator to unit j at time point p
$m_{dirt}(c, p)$	mass of contaminant c removed from water by regenerator 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
$cs_{out}(s_{out,j}, c, p)$	outlet concentration of contaminant c, from storage at time point p
$cr_{out}(c, p)$	outlet concentration of contaminant c, from regenerator at time point p
$qw_s(p)$	amount of water stored in storage at time point p
$ts_{in}(s_{out,j}, p)$	time at which water is transferred from unit j to storage at time point p
$ts_{out}(s_{out,j}, p)$	time at which water is transferred from storage to unit j at time point p
$treg_{in}(s_{out,j}, p)$	time at which water is transferred from storage to regenerator at time point p
$treg_{out}(s_{out,j}, p)$	time at which water is transferred from regenerator to unit j at time point p
$tw_{in}(s_{out,j}, p)$	time that the water is used at time point p in unit j
$tw_{out}(s_{out,j}, p)$	time at which water is produced at time point p from unit j
$tw_r(s_{out,j}, s_{out,j'}, p)$	time at which water is recycled from unit j to unit j' at time point p
$yw_r(s_{out,j}, s_{out,j'}, p)$	binary variable showing usage of recycle from unit j to unit j' at time point p
$yw(s_{out,j}, p)$	binary variable showing the usage of unit j at time point p
$ys_{in}(s_{out,j}, p)$	binary variable showing transfer of water from unit j to storage at time point p
$ys_{out}(s_{out,j}, p)$	binary variable showing transfer of water from storage to unit j at time point p

Variables associated with production scheduling

$t_{out}(s_{out,j}, p)$	time at which a state is produced from unit j at time point p
$t_{in}(s_{in,j}, p)$	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
$m_{out}(s_{out,j}, p)$	amount of state produced from unit j at time point p
$m_{in}(s_{in,j}, p)$	amount of state used in or enters unit j at time point p

$y(s^*_{in,j}, p)$	binary variable associated with usage of state *s* at time point *p*
$d(s_{out}, p)$	amount of state delivered to customers at time point *p*
H	time horizon for a single cycle (Section A)

Parameters associated with wastewater minimization

CE	cost of effluent water treatment (c.u./kg water)
CF	cost of freshwater (c.u./kg water)
$M(s_{out,j}, c)$	mass load of contaminant c added from unit *j* to the water stream
$Mw^U(s_{out,j})$	maximum inlet water mass of unit *j*
$C^U_{in}(s_{out,j}, c)$	maximum inlet concentration of contaminant *c* in unit *j*
$C^U_{out}(s_{out,j}, c)$	maximum outlet concentration of contaminant *c* from unit *j*
$\tau w(s_{out,j})$	mean processing time of unit *j*
Qw^0_s	initial amount of water in storage
Qw^U_s	maximum capacity of storage

Parameters associated with production scheduling

V^U_j	maximum design capacity of a particular unit *j*
V^L_j	minimum design capacity of a particular unit *j*
H^u	upper bound of the cycle time length
H	time horizon of interest (Section B)
$\tau(s^*_{in,j})$	mean processing time for a state
$Q^0_s(s)$	initial amount of state *s* stored
$Q^U_s(s)$	maximum amount of state s stored within the time horizon
$CP(s)$	interest selling price of product s, $s =$ product

CHAPTER 1:

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 minimize 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 minimization 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 minimize freshwater consumption and wastewater generation from an environmental sustainability point of view. Majority of the published wastewater minimization 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 minimization 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. Mathematical based techniques are mainly centered on optimization formulations. The freshwater target and the water using network to satisfy the target are obtained simultaneously in mathematical techniques.

Wastewater regeneration has been widely accepted as an effective means to reduce wastewater generation further and is usually employed after the opportunities for reuse/recycle have been exhausted. Water reuse refers to the use of an outlet wastewater stream from a processing unit in another processing unit while recycle refers to the reuse of an outlet wastewater stream from a processing unit in the same unit. Wastewater regeneration refers to the purification of water to such an extent that it can be reused by water-using operations, thus reducing the requirement for freshwater

Published literature for wastewater minimization techniques for continuous processes operating under steady-state is very vast. However, very little attention has been directed towards the development of wastewater minimization techniques for batch processes. This can be attributed to a number of reasons, the main reason being the time dependence of batch operations. Thus, developing wastewater minimization 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 favorable for the production of high-value-added products such as pharmaceuticals, foods, fine chemicals, and agrochemicals. As demands of such products are seasonal and low in volume, the flexibility of batch processes is often preferred. However, this flexibility leads to additional complexity in developing wastewater minimization techniques. Due to the fact that multiple tasks can be performed in the same equipment, optimal task scheduling becomes exceedingly crucial when developing wastewater minimization techniques.

As aforementioned, wastewater minimization 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 in 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 contaminant streams are a common occurrence in practice.

Mathematical techniques can easily address the drawbacks of graphical techniques since they are not limited in dimension. 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.* (2009), Majozi and Gouws (2009) and Li *et al.* (2010).

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

1.2. Motivation for the research

Firstly, as previously stated, batch processes are time dependent. Thus, a good scheduling technique must be in place to effectively address the issue of wastewater minimization 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 size. 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 minimization, the same problem of lengthy CPU time is observed. To substantiate this observation, the wastewater minimization 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 minimization 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 minimization in batch processes operated over a long time horizon is mandatory.

Secondly, in the past, an optimal batch schedule was assumed before the minimization of wastewater, which was an oversimplification of the problem. This is because the batch schedule influences the starting and finishing times of water-using operations, hence any wastewater target obtained was specific to the schedule given. In the sequential approach, the results obtained from optimization of the batch schedule were used for the optimization of the water network equivalent to minimum wastewater production. The best model is one that simultaneously determines a cost optimal schedule that fulfills the batch production requirement as well as the minimum wastewater production. Majozi and Gouws (2009) presented a mathematical optimization methodology that optimized the batch production schedule and minimized wastewater production simultaneously. In this situation, the starting and finishing times of the batch processes were optimization variables. This work, however, did not consider regeneration to reduce the overall wastewater target further.

1.3. Aim

Two unique investigations were considered in this report. The aim of the first investigation was to develop a mathematical technique to minimize wastewater generation in multipurpose batch processes operated over a long time horizon, i.e. industrial scale problems, with significantly reduced computational difficulties. The aim of the second investigation was to develop a wastewater minimization methodology that incorporates wastewater regeneration in batch plants. Moreover, the batch production schedule and water network corresponding to the minimum water requirement were determined simultaneously within the same optimization framework.

1.4. Problem statement

1.4.1 First investigation

The problem addressed in this investigation 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.

1.4.2. Second investigation

The problem addressed in this investigation can be stated as follows:

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 necessary costs and stoichiometric data,
(iv) the contaminant mass load of each contaminant,
(v) the water requirement and cleaning duration for each unit to achieve the required cleanliness,
(vi) maximum inlet and outlet concentrations of each contaminant,
(vii) the maximum storage available for water reuse,
(viii) the performance of the regenerator and
(ix) the time horizon of interest,

determine the production schedule that achieves the minimum amount of wastewater generated by exploring recycle and reuse opportunities in the presence of a central storage vessel and a wastewater regenerator.

1.5. Report scope

The development of a mathematical technique for wastewater minimization in multipurpose batch processes operated over a long time horizon was achieved through the integration of cyclic scheduling concepts originally proposed by Shah *et al.* (1993) into wastewater minimization 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. This concept of cyclic scheduling has not yet been applied in the context of wastewater minimization, hence the first investigation of this report. Similarly for the second investigation, the work by Majozi and Gouws (2009) was extended to include regeneration.

1.6. Report structure

In Chapter 2 of this report, a literature survey on published wastewater minimization techniques in batch processes is provided. Thereafter, the report is divided into two sections, Sections A and B. Section A addresses the long term scheduling technique for wastewater minimization in batch plants. In Section A, 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. Section B addresses wastewater minimization in multipurpose batch plants with a regeneration unit. In Section B, Chapter 6 presents the proposed wastewater minimization methodology. In Chapter 7, the applicability of this methodology to two case studies is demonstrated. Finally, in Chapter 8 conclusions drawn from the two investigations in Sections A and B are discussed. Also in this chapter are limitations of the works as well as some recommendations.

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CHAPTER 2:

LITERATURE SURVEY

Introduction

This chapter presents a literature survey which provides the necessary perspective in understanding the nature and purpose of the methodologies proposed in this report. The chapter starts with a brief background of 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, the concept of scheduling becomes important. This is dealt with in Section 2.2. The quality and purity specifications of products produced from batch processes require that the cleaning of the processing units be strictly controlled. This cleaning operation generates wastewater. Section 2.3 discusses currently published wastewater minimization techniques in literature. The advantages and the disadvantages of these techniques are also discussed. Finally in Section 2.4, the conclusions drawn from the literature survey are highlighted.

2.1. Background of batch processes

A background of batch processes is presented in this section. The choice between continuous and batch processing mode is discussed in subsection 2.1.1 and the different types of batch plants 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 tasks. 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 plants

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 equipment, 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).

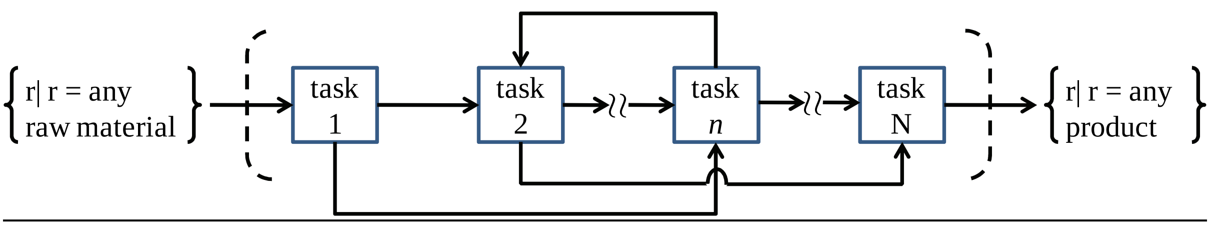

Figure 2. 1: Multipurpose batch plant (Majozi, 2010:6)

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.

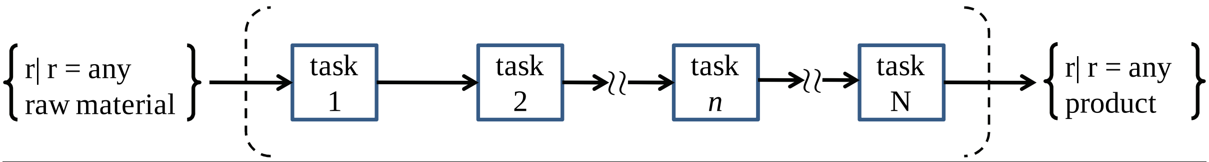

Figure 2.2: Multiproduct batch plant (Majozi, 2010:6)

As previously stated, 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

Scheduling is at the heart of any problem facing batch processes. It is a decision making process to determine the appropriate time intervals within which certain tasks occur and to which units these tasks must be allocated, in order to maximize profits. In other words, a batch process schedule determines when, where and how to produce a set of products given a set of limited resources, the processing recipes and the specific time horizon (Ierapetritou and Floudas, 1998). Hence, an understanding of batch process scheduling is required to effectively address the problem of wastewater minimization. Appropriate production scheduling will decrease the generation of wastewater by invoking strategies for equipment utilization and for equipment cleaning frequencies through optimization analysis. The objective is to meet the desired production goals with due consideration of constraints such as wastewater minimization. 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.

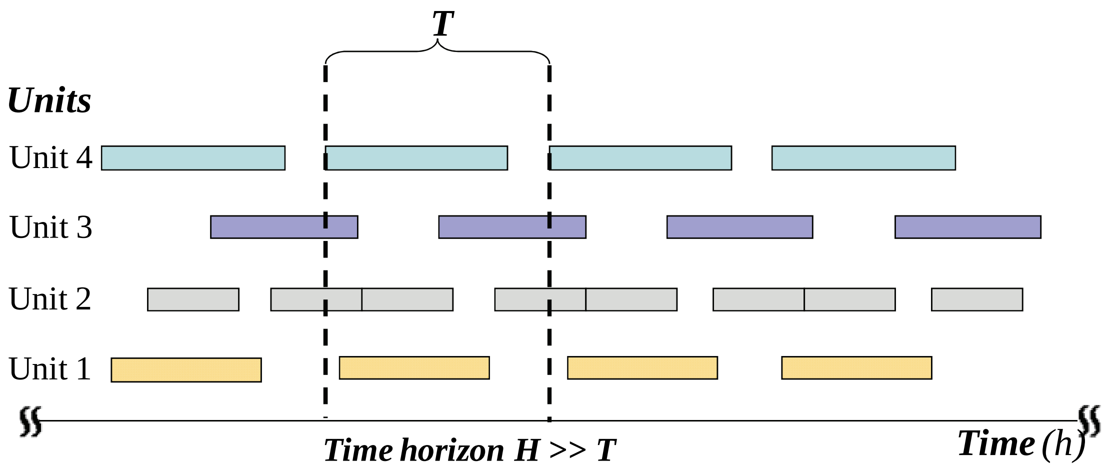

Figure 2.3: The original time horizon *H* is greater than the optimal cycle length *T*.

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.

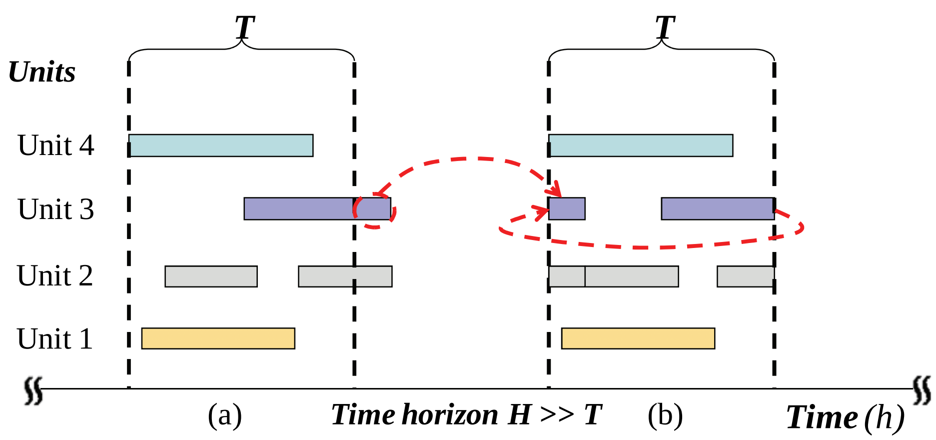

Figure 2.4: a) Task 2 in unit 2 overlaps over the cycle. b) Task 2 is wrapped around the beginning of the cycle.

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.

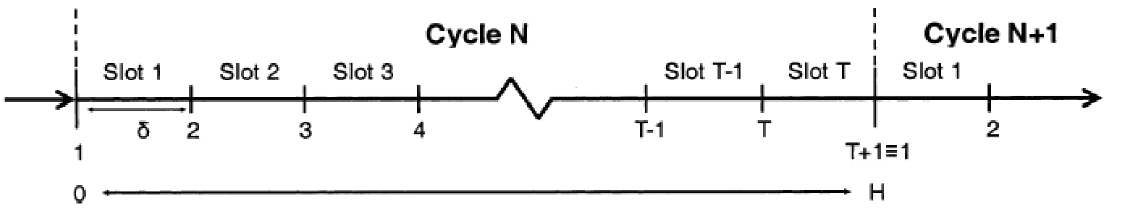

Figure 2.5: Even time discretization for a single cycle (Castro *et al.*, 2003)

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.

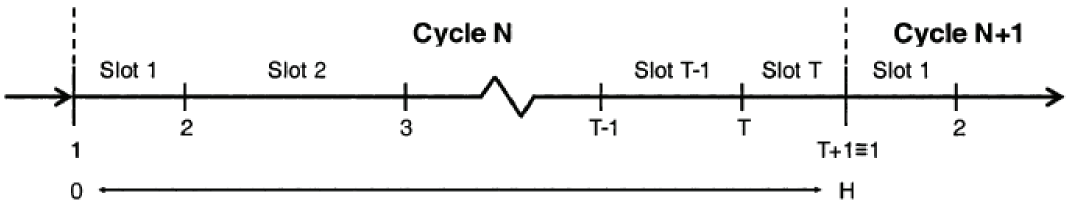

Figure 2.6: Uneven time discretization over one cycle (Castro *et al.*, 2003)

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***).

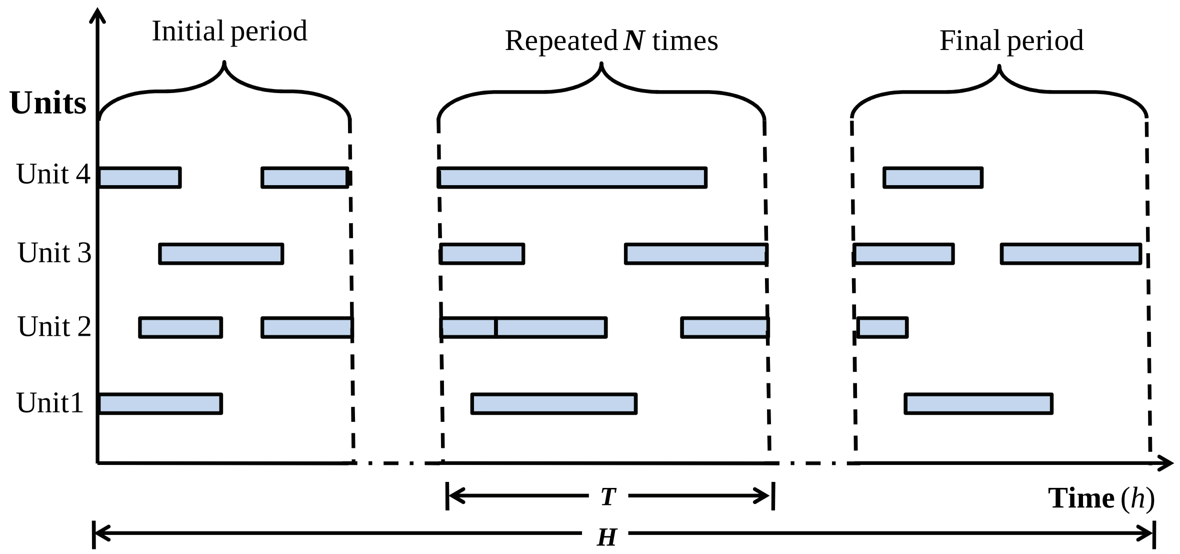

Figure 2.7: Cyclic scheduling in the middle period repeated *N* times

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 minimization techniques for batch processes are presented.

2.3. Wastewater minimization 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 minimization techniques is apparent. Wastewater minimization methodologies for continuous processes have been well documented in literature. Furthermore, these methodologies have provided many useful insights in addressing the same problem in batch processes. A good starting point therefore, is a brief discussion of methodologies for continuous processes. Some important issues that will be extracted from the survey of wastewater minimization methodologies in continuous processes are: the nature of the problem addressed, i.e. fixed load/fixed flowrate problems, the applicability of the method to single or multiple contaminant problems and whether or not a treatment or regeneration unit is considered. These issues are discussed forthwith to facilitate understanding.

Classification of water-using operations

In fixed load problems, the water-using operations are modeled as mass-transfer based operations, i.e. water is used as a mass separating agent (MSA). The contaminant concentration of the water changes due to the mass load of contaminant picked up. The maximum allowable inlet and outlet concentrations of the operations are specified. Examples are washing and extraction operations. Figure 2.8 illustrates this.

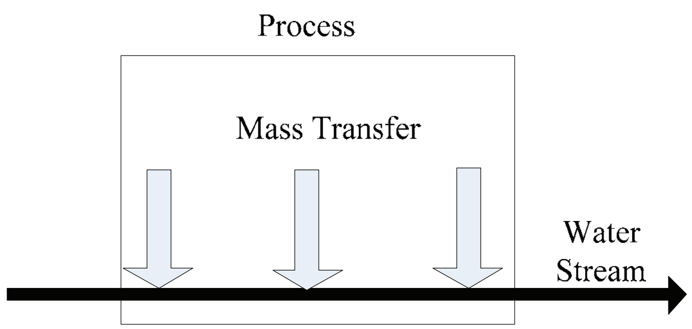

Figure 2.8: A depiction of mass transfer-based operations (Chen and Lee, 2008)

In fixed flowrate problems, the concern is not about the mass transfer of contaminants but the flowrate of water. The inlet and outlet flowrates of the operations, which may not be equal, are specified. These operations may be modeled with outlet streams leaving at a specified concentration, while the inlet streams have a maximum allowable concentration. Cooling towers, boilers and reactors can be modeled this way.

Classification of contaminants

Single contaminant streams have been assumed in problems for simplicity, though multiple contaminant systems are more readily encountered in industry. However, there are certain practical situations where the assumption of a single contaminant is applicable, e.g. the pulp and paper industry where suspended solids are modeled as a single contaminant (Bagajewicz and Savelski, 2001). Also found in literature is the grouping of contaminants with similar properties together as a single pseudo-contaminant, to distinguish them from species with different properties. Other pollutants can be ignored if their concentrations are too low (Bagajewicz, 2000).

Availability of wastewater treatment or regeneration

Wastewater treatment differs from wastewater regeneration with regard to the final destination of treated water. Wastewater treatment refers to the purification of water to a concentration level acceptable by legislation, for discharge to the environment. Regeneration refers to the purification of water to such an extent that it can be reused by water-using operations, thus reducing the requirement for freshwater.

Existing methodologies for wastewater minimization in both continuous and batch processes can be broadly divided into two groups, namely, graphical/numerical techniques based on pinch analysis and mathematical optimization techniques. The main advantage of graphical pinch analysis techniques is that, the various water network targets such as freshwater and wastewater flowrates and the pinch location can be identified beforehand. These are used as guidelines during network synthesis. A drawback however, is that these techniques are often limited to problems with a single contaminant. Mathematical optimization techniques on the other hand can handle multiple contaminant problems, are flexible in the definition of the objective function, but do not provide the same insights as the graphical techniques. Also, when the resulting mathematical formulation is in the form of a nonconvex, nonlinear program, NLP or a nonconvex, mixed integer nonlinear program, MINLP, finding the global solution may be a challenge.

2.3.1 Graphical techniques for wastewater minimization in continuous processes

Wang and Smith (1994) pioneered research in wastewater minimization using graphical pinch analysis, whereby the minimum wastewater target of a system of water-using operations, which exploited recycle and reuse, could be obtained. The method, applicable to fixed load problems, was a special case of the concept of mass exchange between rich streams and lean streams, developed by El-Halwagi and Manousiouthakis (1989). On a plot of concentration against mass load, a limiting composite curve was constructed. Against this curve, a water supply line was matched and the inverse of the slope of this line gave the freshwater and wastewater target. The freshwater and wastewater targets were equal because there was no loss or gain of water. An illustration is provided in Figure 2.1. In the figure, freshwater was used, hence the water supply line went through the coordinate (0, 0). The water pinch was located on the plot as the point that limited the slope of the water supply line.

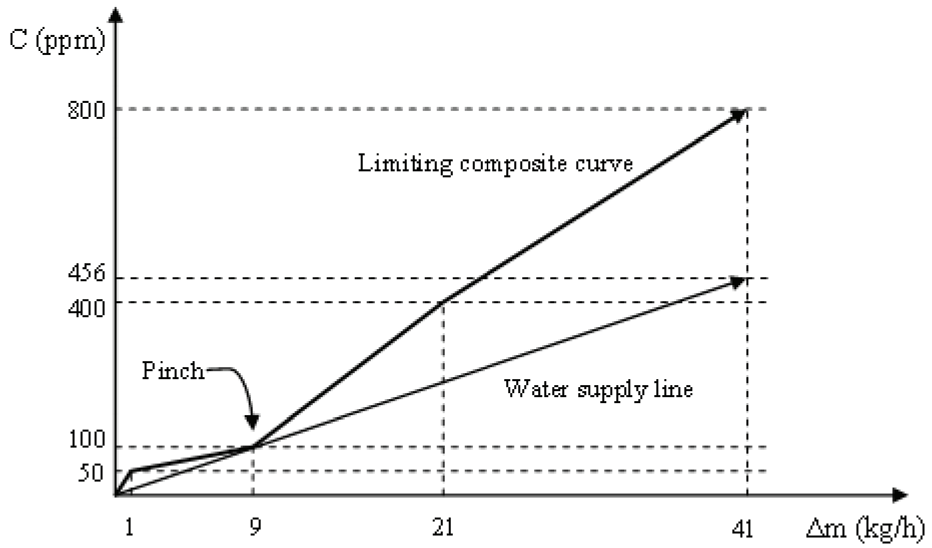

Figure 2.9: Limiting composite curve

Next, the water network corresponding to the determined target was synthesized using a method analogous to the heat exchanger network design by Linnhoff and Hindmarsh (1983). The advantage of the method by Wang and Smith (1994) was that the minimum wastewater (or freshwater) target was obtained before network synthesis. Drawbacks of this method were that more complex constructions of limiting composite curves were required to address multiple contaminants. Secondly, the method was only applicable to fixed load problems. Thirdly, as pointed out by Ulson de Souza *et al.* (2009), in some scenarios during network synthesis, operations had to be divided in order to achieve the established targets. In reality, operation divisions are impossible. These drawbacks gave rise to several modifications and advancements to the work of Wang and Smith (1994).

Dhole *et al*. (1996) proposed a method suitable for fixed flowrate problems. In this method, all inlet streams were defined as demands and all outlet and freshwater streams were defined as sources. This allowed units with multiple inlet or outlet streams to be modeled effectively. In this technique, two separate curves representing the source and demand composites were plotted on a contaminant concentration vs. flowrate graph. The water pinch was the point where the two composite curves touched. This pinch point however could be adjusted by mixing different source streams together. This meant that many local flowrate targets could be identified. Unless the correct mixing was identified, there was no guarantee that the targets obtained were minima. To obtain the minimum flowrate targets, numerous trial and error exercises were performed. As pointed out by Hallale (2002), this mixing should ideally be performed in the network synthesis stage. To address the limitations of the method, Hallale (2002) developed the water surplus diagram as a new targeting approach also applicable to fixed flowrate problems.

In the method by Hallale (2002), a plot similar to that by Dhole *et al*. (1996) was utilized. In the plot, regions where the source composite curve was above the demand composite curve (water surplus regions) and vice versa (water deficit regions) were identified. The amount of water surplus or deficit in each region could be determined by calculating the area enclosed by each rectangle representing the region. Next, cumulative values of the water surplus and water deficit were plotted on a water purity vs. flowrate graph such that the water surplus values were positive and the water deficit values were negative. This new plot was the water surplus diagram. An example is provided in Figure 2.10. The minimum freshwater target was obtained when the water surplus diagram just touched the vertical axis such that no part of the curve existed to the left of the vertical axis. This was achieved by guessing initial freshwater flowrates and thus modifying the source composite curve. In situations where some part of the surplus diagram existed to the left of the vertical axis, more freshwater had to be assumed. In situations where the surplus diagram existed too far to the right of the vertical axis, the guessed freshwater flowrate had to be reduced. Although the method gave true targets, the procedure of guessing freshwater flowrates and transferring data from one diagram to the other was cumbersome.

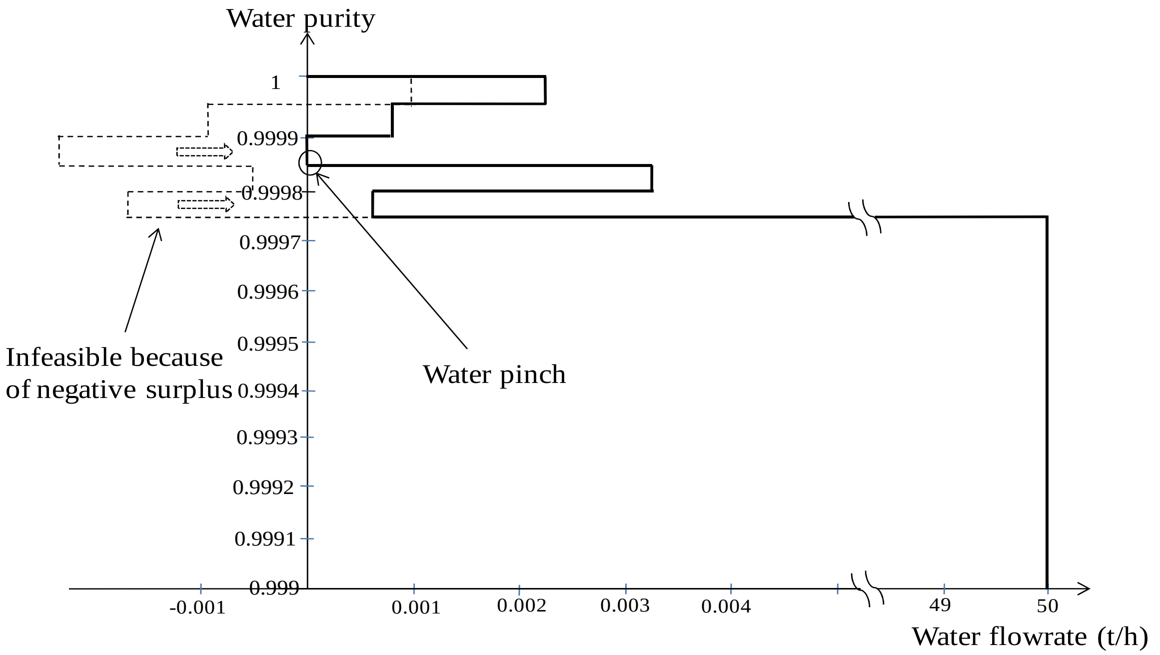

Figure 2 10: Water surplus diagram (Hallale, 2002)

To overcome the limitations of Hallale (2002), Manan *et al.* (2004) developed a numerical technique called the water cascade analysis, WCA, in which a water cascade table, WCT, was used for flowrate targeting. In summary, the table consisted of nine columns. The concentration levels in a problem (C_k) were arranged in ascending order. The intervals $(k = 1,2..n)$ were located in column 1 and the corresponding concentrations in column 2. In columns 3 and 4, the flowrates of water sinks, $(F_j)$and water sources, (F_i) were placed in their respective concentration levels. In column 5, the net flowrate, $\left(\sum_i F_i - \sum_j F_j\right)_k$ in each interval was calculated. The net water flowrate was cascaded down the concentration intervals to give the cumulative surplus/deficit flowrate, $(F_{C,k})$ in column 6, with an assumption of zero freshwater flowrate. In column 7, the impurity load, (Δm_k) was calculated from the product of cumulative flowrate and the concentration difference across subsequent intervals, $(C_{k+1} - C_k)$. The impurity load was cascaded down the concentration intervals to give the cumulative impurity load, $(\text{cum}\Delta m_k)$ in column 8, which was equivalent to the water surplus diagram (Hallale, 2002). In column 9, the freshwater flowrate was calculated from Equation (2.1), where C_{FW} was the concentration of freshwater.

$$F_{FW,k} = \left(\frac{\text{cum}\Delta m_k}{\text{C}_\text{k} - C_{FW}} \right) \tag{2.1}$$

In column 9, the earlier assumed zero freshwater flowrate in column 6 was replaced by the absolute value of the largest negative $(F_{FW,k})$. This was in order to obtain a feasible cascade. This value, was the minimum freshwater flowrate, (F_{FW}). The final row in column 6 was the wastewater flowrate, (F_{WW}). The pinch was located at the concentration where $(\text{cum}\Delta m_k)$ was zero. This method did not involve any iteration. The works by Hallale (2002) and Manan *et al.* (2004) were only focused on flowrate targeting and not network synthesis.

Agrawal and Shenoy (2006) addressed the problem of obtaining the minimum freshwater flowrate for fixed flowrate problems. In this work, the fixed flowrate problem was recast into an equivalent fixed load problem to allow a limiting composite curve to be plotted. Similar to the method by Wang and Smith (1994) for fixed load problems, a water supply line was drawn such that it touched the limiting composite curve. The reciprocal of the slope of this line was the minimum freshwater flowrate. Agrawal and Shenoy (2006) observed that the recasting of data and the subsequent graphical application could be complicated. Hence, they proposed a numerical procedure called the composite table algorithm, CTA. The method gave absolute targets, reduced computation and was non-iterative. The CTA was conceptually the same as the WCA developed by Manan *et al.* (2004). To synthesize the network equivalent to the obtained targets, an algorithm based on the principle of nearest neighbours developed by Prakash and Shenoy (2006) was employed. This principle stated that the sources selected to satisfy a particular water demand must be the nearest available neighbours with respect to contaminant concentration.

Up to this point, the water networks have been synthesized after the water targets were obtained. This is not the case with the water sources diagram, WSD, by Gomes *et al*. (2007) for fixed load problems. The WSD is a diagram where each stream is located in its appropriate concentration level from left to right. Next, the mass load of each operation is calculated in each concentration interval. Once the mass loads are obtained, the water network is synthesized by following specific rules about source to sink allocation. Herein lies the difference, the WSD is an interactive technique where the network is synthesized as the calculations are performed, the targets are not obtained beforehand. The selling point of their method was that it could be used by process engineers to calculate problems by hand. The method as presented would be difficult to apply to large scale problems as the solution would become more complex.

The methods discussed so far have employed graphical/numerical techniques for addressing wastewater minimization in continuous processes. 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 are inadequate in their ability to cater for constraints other than concentration and flowrate. In addition, these methods are usually limited to single contaminants. Consequently, mathematical techniques have been adopted. The problem with mathematical techniques is in ensuring global optimality. In situations where the mathematical model is linear, the solution obtained can be guaranteed to be the global solution. Wherever it is possible to linearize a model, this is preferred. However, nonlinearities in models are often unavoidable. The manner in which some authors address this problem is discussed.

2.3.2 Mathematical techniques for wastewater minimization in continuous processes

Bagajewicz and Savelski (2001) addressed single contaminant problems using a linear mathematical formulation. In the formulation, water and contaminant balances were performed for each water-using process. The linearity of the model was due to the fact that the inlet and outlet contaminant concentrations were assumed to be at maximum. Consequently, bilinearities that existed when concentration was multiplied with another variable, e.g. flowrate, were eliminated. This work also investigated different network alternatives associated with different objective functions, such as minimum number of connections between units, minimum fixed cost, where cost was defined in terms of piping costs and the elimination of forbidden or enforcement of compulsory matches.

The mathematical technique by Doyle and Smith (1997) addressed multiple contaminants. To address the problem of varying water requirements by different contaminants, Equation (2.2) was solved for each contaminant present in the problem. The limiting flowrate, F_{lim} was defined as the maximum flowrate across all contaminants. At this limiting flowrate, at least one of the contaminants reaches its maximum outlet concentration.

$$F_{lim} = \frac{\Delta m}{C_{out,MAX} - C_{in,MAX}} \tag{2.2}$$

The mathematical optimization was based on a superstructure, where the inlet of every operation was connected to the outlet of every operation and to each freshwater source. Three scenarios were considered in this study. In the first scenario, water-using operations that could be modeled as fixed load problems were considered. In this scenario, it could not be assumed that all the contaminants were at their maximum, like was done for the single contaminant case by Bagajewicz and Savelski (2001). The resulting model was a nonlinear program, NLP due to the bilinearities that existed in the contaminant mass balances around each operation, when concentration was multiplied with flowrate. In the second scenario, water-using operations that could be modeled by a fixed outlet concentration (contaminants were assumed to go to their maximum solubility) were addressed. Here, the resulting model was a linear problem, LP. The third scenario considered both types of water-using operations in one problem. This resulted in a NLP. To address the nonlinearity of the problem, it was proposed to use the solution from a linear model, where concentrations were assumed to be at their maximum to provide an initialization for the nonlinear optimization. The objective function was the minimization of freshwater cost, where cost was directly proportional to flowrate. The model could easily accommodate situations where there were flow losses or flow gains.

Huang *et al.* (1999) adopted a similar initialization approach to address the nonlinearities in their NLP model for minimizing the rate of freshwater consumption. The equality constraints of the NLP model were solved by fixing the extra degree of freedom with reasonable guesses of the key design variables. These guesses were obtained from the stream data of a base case flowsheet which was available. In addition, it was stated that in some cases, certain operations were better modeled as having fixed outlet concentrations instead of as fixed load or fixed flowrate operations. The review paper by Bagajewicz (2000) discusses mathematical techniques adopted for wastewater minimization in continuous processes in more detail.

In compliance with environmental legislation, wastewater must be treated before it is discharged to the environment. This is simply end of pipe treatment. On the other hand, wastewater regeneration has been widely accepted as an effective means to increase wastewater minimization and is usually employed after the opportunities for wastewater reduction via water reuse/recycle have been exhausted. Wastewater treatment/regeneration in industry usually occurs in multiple stages, however in literature, it is often modeled using one stage. Multiple treatment units have also been considered. Regardless of whether wastewater treatment or regeneration is considered, the determination of the minimum flowrate of the regenerator/treatment unit and the identification of streams to be treated, are pertinent issues:

In addition, the type of regenerator/treatment unit employed plays a role in the way the problem is addressed. Two types of regenerators/treatment units are considered in literature:

- Regenerator with a fixed outlet concentration. Here, the concentration of wastewater is reduced to this value regardless of the quality of the inlet water. Examples of this are filtration, membrane separation, centrifugal separation and biological treatment.
- Removal ratio type regenerator. In this case, a fraction of the impurity load is removed depending on the concentration of the inlet stream. Examples are scrubbing, stripping, extraction and evaporation. The mathematical expression for this is given in Equation (2.3)

$$RR = \frac{f_{in}C_{in} - f_{out}C_{out}}{f_{in}C_{in}} \tag{2.3}$$

Regenerator flowrate determination

According to McLaughlin *et al*. (1992), capital and operating costs of most wastewater treatment processes are proportional to the total flowrate of wastewater which flows through the treatment process. Hence the treatment of large volumes of wastewater is expensive.

Kuo and Smith (1997) addressed this problem with a distributed effluent treatment system as opposed to a centralized treatment unit. The distributed system utilizes multiple treatment units to segregate effluent streams for treatment and only combine them when necessary. A graphical method based on the limiting composite curve was used. To apply the method, it was required to know beforehand the flowrates and concentrations of the wastewater streams, the available treatment processes and their corresponding removal ratios and the environmental discharge limit. In this way, instead of the usual limiting composite curve, a composite effluent curve was plotted. Similarly instead of a water supply line, water treatment lines (each line corresponding to a treatment unit) were drawn against the effluent composite curve. The reciprocal of the slopes of the treatment lines gave the flowrate through the treatment units. In the presence of multiple treatment units, the determination of the best order of treatment was not a trivial task, hence Kuo and Smith (1997) proposed an approach based on exergy analysis to evaluate wastewater degradation encountered from the various treatment schemes possible. The drawbacks of the method were that the effluent treatment network was considered in isolation from the water-using operations and the composite curve method was tedious in its application to multiple contaminants. To synthesize the corresponding network, the design rules of Wang and Smith (1994) were followed. Streams starting above the pinch for the treatment system were treated fully, those starting at the pinch were treated partially and partially bypassed treatment and those starting below the pinch completely bypassed treatment.

Kuo and Smith (1998) rightly pointed out that many researchers considered on an individual basis, the water-using operations, treatment system and the regeneration system instead of investigating the interactions between all three. Figure 2.11 is an illustration of the total water network, within which the individual elements interact with each other.

Agrawal and Shenoy (2006) considered regeneration as opposed to wastewater treatment. A central regenerator based on a fixed outlet concentration was used. In their method water reuse among the water-using operations and regeneration were considered within the same framework. This is Figure 2.11(b) without effluent treatment. The method also utilized the graphical limiting composite curve. Here, the limiting composite curve was plotted as already discussed above. The difference was that the water supply line was a combination of freshwater and regenerated water to achieve the minimum freshwater target. The drawback of this method as pointed out in the review by Foo (2009) was that when the limiting composite curve had a turning point near the composite water supply line, the freshwater flowrate had to be increased.

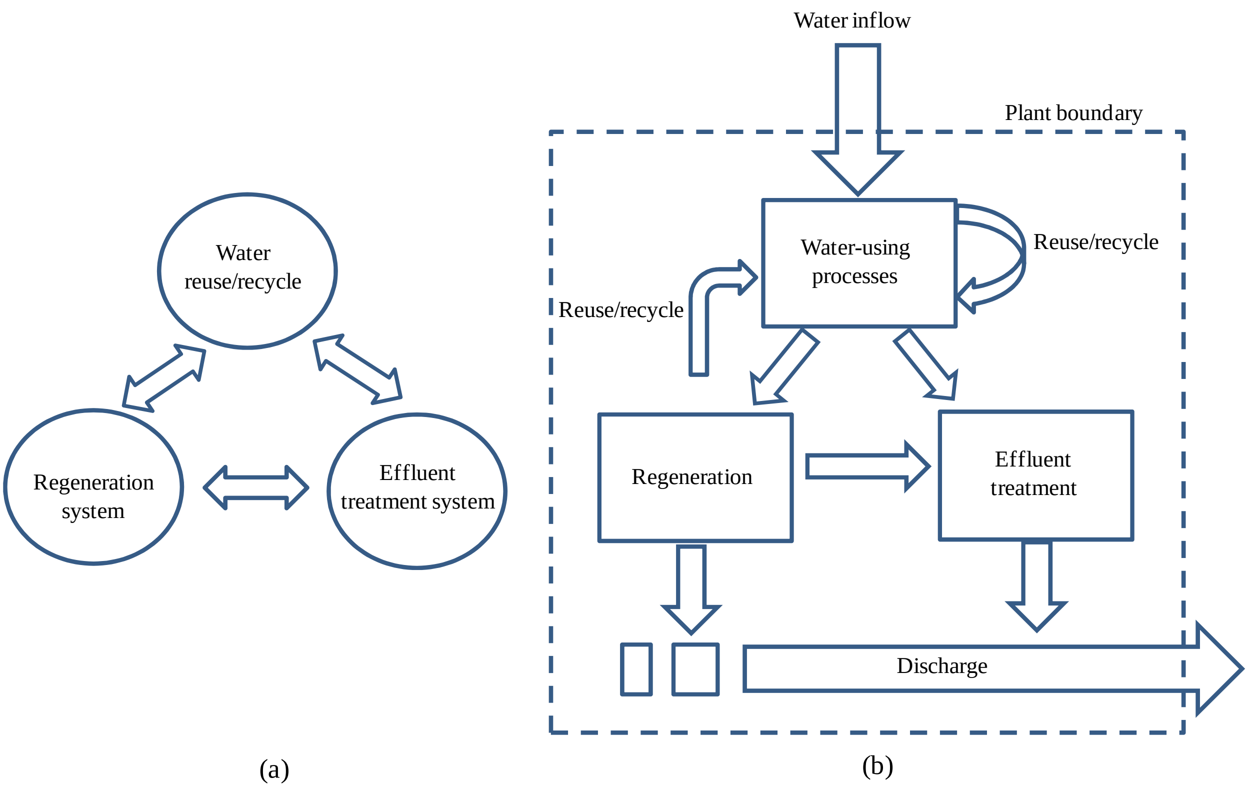

Figure 2.11: (a) Systems in isolation (b) Interactions between elements of the water system (Kuo and Smith, 1998)

None of the approaches discussed so far could guarantee the determination of the minimum regeneration flowrate along with the minimum freshwater and wastewater flowrates. Ng *et al*. (2007a) and Ng *et al*. (2008) proposed a procedure to determine the ultimate water targets for a given regeneration outlet concentration. The method was applicable to both fixed flowrate and fixed load problems. The regeneration targeting procedure was as follows. The first step was the allocation of all water sources and sinks into two regions, i.e. freshwater and regeneration regions. The freshwater region, FWR, could receive water from both freshwater and regenerated water, while the regeneration region, RWR, could only receive regenerated water. In the FWR, sources and sinks with concentrations lower than the given regenerator outlet concentration were allocated while sources and sinks with concentrations higher than the regenerator outlet concentration were allocated to the RWR. The next step, called reallocation, was to ensure that the total sink water flowrate equalled the total source water flowrate in the RWR. To do this, certain heuristics were stipulated to handle the two scenarios that could be encountered, which were a scenario where the total source flowrate was higher than the total sink flowrate and vice versa. After the reallocation was completed, a water cascade analysis was performed on both the FWR and the RWR. The freshwater and wastewater targets were obtained from the FWR, while the minimum regeneration flowrate was targeted by the RWR. These were termed the ultimate flowrate targets which were the lowest possible freshwater, wastewater and regenerator flowrates after reuse/recycle had been maximized among all the water using processes.

Huang *et al.* (1999) used a mathematical optimization method to determine the minimum wastewater treatment capacity in multiple contaminant problems. In addition to the mass and contaminant balances around each water-using operation, water and contaminant balances were performed around the treatment unit. Water loss in the treatment unit was considered, whereby the water loss was modeled as being proportional to the water flowrate into the unit. This is characteristic of filtration, membrane separation and evaporation. To address multiple contaminants, multiple treatment units were considered, one for each contaminant. The two different types of regenerators were also investigated, i.e. constant removal ratio type regenerator and fixed outlet concentration type. The objective function was the minimization of the costs associated with running the water-using operations and the water treatment units. Each cost term was roughly proportional to the flowrate through the unit. The resulting model was a NLP for which a method of initialization was proposed as aforementioned.

In the mathematical model by Bagajewicz and Savelski (2001) involving a single contaminant, one regenerator of the fixed outlet concentration type was considered to be present. This led to a linear model. In order to minimize the amount of water sent through the treatment process, they showed mathematically that this would be achieved if the outlet concentration from the regenerator was as small as possible. Firstly the mathematical model involving water-using operations and regeneration determined the minimum freshwater target, *F*. The objective function in this step was the minimization of total freshwater usage in each unit, F_j^w. This is given in Equation (2.4)

$$Min \sum_j F_j^w = F \tag{2.4}$$

Secondly, the minimum water flowrate through the regenerator was obtained by minimizing the total water flow from unit to regenerator, $F_{j,T}$ such that the total amount of freshwater used in the water-using units amounted to the target *F* obtained previously. This is given in Equation (2.5).

$$Min \sum_j F_{j,T} = \text{minimize wastewater flowrate, such that } \sum_j F_j^w = F \qquad (2.5)$$

Bandyopadhyay (2009) developed a method to target the minimum waste treatment flowrate. Only one treatment unit was considered. The method which was restricted to a single contaminant was a combination of algebraic analysis using table calculations and a graphical representation (cumulative contaminant load vs. concentration called the waste composite curve). The table calculations were similar to the water cascade table by Manan *et al.* (2004). At the end, the minimum waste flowrate to the treatment unit was determined. The method incorporated water losses in the regenerator. The flow loss was assumed proportional to the inlet flowrate to the treatment unit.

Ulson de Souza *et al*. (2009) utilized the WSD developed by Gomes *et al.* (2007) to reduce treated water consumption, where multiple contaminants were present. The performance of the regenerator was given in terms of maximum outlet concentration. Multiple treatment units were utilized for the removal of the different contaminants. The method was an algorithmic procedure based on heuristics and considered reuse/recycle, treatment and regeneration within the same framework, as illustrated in Figure 2.11(b).

Appropriate regenerator placement

The streams selected to be regenerated have an effect on the impurity load that will be removed by the regenerator. As aforementioned, this will affect the cost of the treatment system. In the work by Wang and Smith (1994), the inlet to the regenerator consisted of water streams that had reached the pinch concentration after they had been recycled/reused. This was similarly applied by Agrawal and Shenoy (2006) but for fixed flowrate problems. Foo (2009) observed that this approach of regenerating water at the pinch concentration may fail to locate the minimum water targets in cases where the pinch is reallocated to a new concentration after regeneration has taken place.

Hallale (2002) was guided by the water surplus diagram in placing regenerators with a fixed outlet concentration. In this work it was determined that regeneration units should be placed across the pinch concentration, whereby water to be regenerated is drawn from regions having concentrations higher than the pinch (with excess water) to regions having lower concentration than the pinch (with water deficit). This is due to the fact that water is taken from a region of surplus and returned to a region deficient of pure water. This led to the biggest savings in both freshwater and wastewater when compared to the placement of the regenerator above or below the water pinch.

Ng *et al.* (2007b) utilized the water cascade analysis developed by Manan *et al*. (2004) for flowrate targeting and the minimum regeneration flowrate targeting method by Ng *et al.* (2007a) to identify the water streams to be regenerated. The regeneration targeting model was based on the assumption of a fixed outlet concentration from the regenerator. Once the pinch causing source was identified from the WCA, the water sources and sinks were segregated into lower and higher concentration regions. The wastewater from the pinch source was regenerated first. This is due to the fact that it is the cleanest of all the wastewater streams. In cases where the flowrate of the pinch waste stream was lower than the minimum regeneration flowrate (the water was not sufficient), the wastewater stream(s) of the next higher concentration was/were sent for regeneration. This was continued until the regeneration flowrate target was fulfilled or until all wastewater streams were regenerated. A corresponding graphical method for waste stream identification was also demonstrated in their work.

Advancements in the wastewater minimization problem

The work by Lim and Park (2008, 2009) used mathematical optimization to address the synthesis of the most environmentally friendly wastewater treatment network. In their work, a terminal treatment plant was included in the distributed water treatment system to ensure that discharged wastewater consistently met stipulated limits. This new system was termed the total wastewater treatment network system, TWTNS. A life cycle analysis was performed to evaluate the environmental impacts of certain principal contributors. The principal contributors investigated were limited to piping in the construction stage, electricity for pumping and wastewater treatment in the operation and maintenance stage and recycling of pipelines in the disposal stage. In order to incorporate the life cycle analysis into the model mathematically, the results obtained from documented life cycle analysis, LCA, standards were fitted to generate linear regression equations of the environmental impact of the contributors. For example, the LCA results of piping were used to generate a linear regression equation which enabled the prediction of the environmental impact of a pipeline with a given cross sectional area and length. Two objective functions were considered. The first objective function was the minimization of the total environmental effects over the life cycle of the plant. The second objective function was the minimization of the total flowrate of treated wastewater. The model resulted in a MINLP problem for which the solution could not be guaranteed to be globally optimal. A model of this nature could become very large and complex, hence, a choice of what aspects of the plant to focus on had to be made. In addition, assumptions in various relationships/equations were made in order to simplify the model.

Ng *et al.* (2009) developed an automated targeting method to synthesize a total property-based network. In the past, waste streams have been identified by contaminant concentration. In property-based methods, waste streams are classified in terms of properties such as pH, turbidity, hardness, toxicity, colour, density, reflectivity, relative volatility, etc. This is due to the fact that certain processes are better described using properties rather than contaminant concentration (El-Halwagi *et al.*, 2004). The method by Ng *et al.* (2009) has the advantages of both insight based (the various network targets are obtained prior to synthesis) and mathematical optimization approaches. The aim was to synthesize simultaneously a total network that included material reuse/recycle, regeneration/interception and waste treatment (see Figure 2.11). In property-based methods, property is treated in an analogous manner to contaminant concentration. A linearized property mixing rule is adopted to define all possible mixing patterns among individual properties of streams. The mixing rule is of the form in Equation (2.6)

$$\psi\left(\overline{p}\right) = \sum_{i} x_i \psi\left(p_i\right) \qquad (2.6)$$

where $\psi\left(\overline{p}\right)$ and $\psi\left(p_i\right)$ are linearizing operators on mixture property $\overline{p}$ and stream property p_i, respectively. x_i is the fractional contribution of stream i in the total mixture flowrate. The work by Ng *et al.* (2009) was applicable to single properties. The drawbacks of the method are as follows. Firstly, it is well known that property mixing rules can be very nonlinear, linearizing of which becomes difficult. Secondly, the accuracy of such property mixing rules cannot be guaranteed. Using an incorrect property rule will lead to errors and will prevent any method based on them to be practical in their use.

The methodologies developed for wastewater minimization in continuous processes have provided many insights, namely the pinch point. However, the aforementioned techniques cannot readily be applied to batch processes without some necessary modifications. Consider the illustration in Figure 2.12, a water-using batch process is characterized not only by flowrate and concentration but also by time. This is in contrast to a continuous process which is characterized by flowrate and concentration only. As can be observed from Figure 2.12, for the continuous processes, water from process A can be reused in process B because the concentration requirement is met. Water from B cannot, however, be reused in A because it is too contaminated. On the other hand for the batch processes, water from A can be reused in B if process A ends before process B begins. This constraint is in addition to the concentration requirement. Water from B cannot be reused in A because it is too contaminated and also because it takes place after process A.

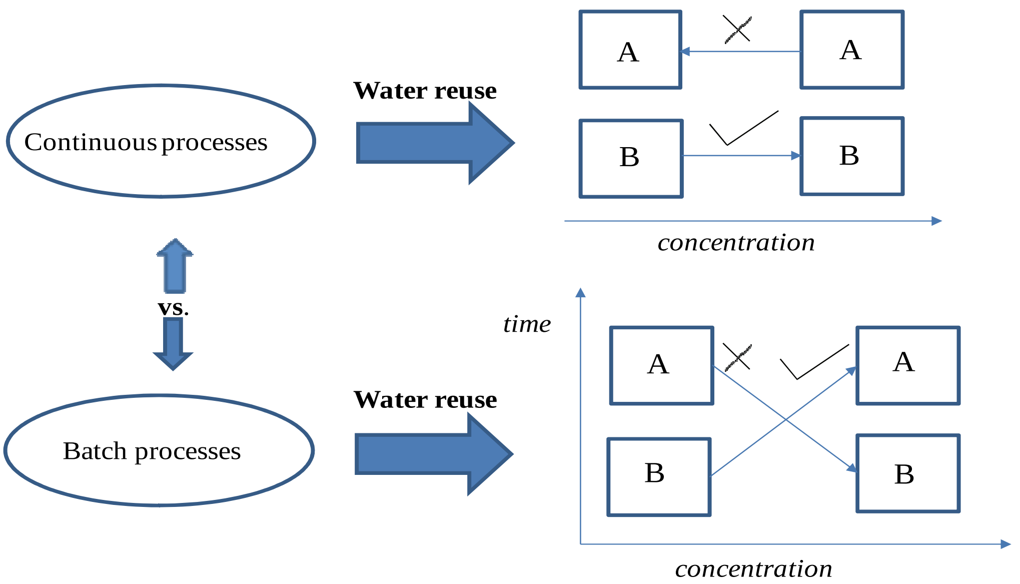

Figure 2.12: Comparison between batch and continuous processes

For this reason in batch processes, the requirement for water is time dependent, hence, time must be addressed in conjunction with the wastewater minimization problem. In order to override the time constraint and maximize water reuse even further, wastewater storage has been employed in literature, called indirect reuse. This is as opposed to direct reuse which is water transfer from process to process provided the time at which water is available coincides with the time at which water is required. Below is a discussion of wastewater minimization methodologies in batch processes.

2.3.3 Graphical/numerical techniques for wastewater minimization in batch processes

A characteristic of these methods is that information about the starting and finishing times of the water-using batch operations is essential to solve wastewater minimization problems. In general, to address both concentration and time constraints, these methods require two dimensions over which the calculations are performed. For instance, when concentration is considered as the primary constraint and time as the secondary constraint, water is cascaded in one concentration interval through all the time intervals before water is cascaded to the next concentration interval and so on. In this way, water of a lower concentration is reused in later time intervals and for operations with a higher concentration requirement. This was the procedure followed by Wang and Smith (1995b) who extended their work for continuous processes (Wang and Smith, 1994) to batch processes. The problem was divided into concentration intervals and time subintervals with the boundaries of the intervals determined by the endpoints of the individual processes. Targeting was performed in each concentration interval by reusing water which was available in its own time subinterval, where possible. Any surplus water could be reused in subsequent time intervals in the same concentration interval or could be stored for reuse in later concentration intervals. When no opportunities for recycle/reuse existed, freshwater was used. The overall freshwater target was the accumulated freshwater makeup required by the system and the eventual surplus was the total effluent of the system. This method permitted water reuse between units that were still in operation (operations with overlapping time intervals). This is possible for processes operating in a semicontinuous mode but not possible for strictly batch operations where water is available from a unit only at the end of its operation and water can be transferred to a unit only at the beginning of its operation. No systematic method was developed for the design of the corresponding batch network. Network design was done using insights drawn during targeting.

Majozi *et al.* (2006) modified the technique by Wang and Smith (1995) to address strictly batch processes. Two scenarios were considered to determine the effect of the targeting procedure on the final design. In the first scenario, time was treated as the primary constraint and concentration as the secondary constraint while in the second scenario, the primary constraint was concentration and the secondary constraint was time. The procedure for targeting in the first scenario was similar to the method by Wang and Smith (1995). In the second scenario, the problem was divided into time intervals and concentration subintervals. Targeting was performed in each time interval. Whenever possible any surplus water was transferred to higher concentration subintervals in the same time interval for reuse, or stored for reuse in later time intervals. In addition, surplus water could not be reused in lower concentration subintervals or previous time intervals. Any shortfall within any concentration subinterval could be made up from lower concentration subintervals, from previous time intervals or from freshwater. Similar to the previous case, the eventual surplus became the system effluent and the accumulated freshwater make-up constituted the system intake. At the end of their analysis, they found that reversing the priority of time and concentration constraints did not have any effect on the water target. The choice of which constraint to use could be based on the ease with which the targeting could be performed. The methods by Wang and Smith (1995) and Majozi *et al.* (2006) were applicable to fixed load problems.

Foo *et al.* (2005) presented a numerical technique based on pinch analysis that was applicable to fixed flow problems. In the context of batch processes, fixed flow corresponds to a fixed quantity of water needed or produced by water-using operations. The water cascade analysis (WCA) which was developed for continuous processes (Manan *et al.*, 2004) was utilized to determine water targets in batch processes. The method was carried out in two stages. In the first stage, the targeting stage, a method known as the time-dependent water cascade analysis was developed to identify the minimum water flows in a batch process. Typically, time was divided into time intervals where water demand and water sources could be found. The water sources and sinks were then located at their respective impurity concentration levels within the time interval in which they existed. Targeting was done in the time intervals using the water cascade analysis to obtain the minimum freshwater and wastewater flows. The overall freshwater and wastewater targets were obtained by summing the individual targets of all the time intervals. The second stage involved synthesizing the batch network that achieved the determined targets. Network synthesis was carried out independently for each time interval using the guidelines stipulated by Hallale (2002) and some feasibility constraints. Afterwards, the overall network called the time-water network diagram was developed using information from the sub-networks of each time interval. In the time-water network diagram, the interaction between the water demands/sources and time was shown. The methodology by Foo *et al.* (2005) was also applicable in the presence of a storage tank. The storage capacity, defined as the maximum amount of water that was sent to the storage tank was determined. In their method, the number of storage tanks was equal to the number of water sources at different concentration levels that were intended for reuse as a result of the fact that mixing of water sources of different concentrations was not allowed. They noted this as a potential pitfall of their method, whereby once the number of water sources for reuse increased, the complexity of the network increased.

Yongjian *et al.* (2007) developed a time-dependent concentration interval analysis technique for wastewater minimization 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.

Chen and Lee (2008) introduced a batch network design technique using a graphical representation called the quantity-time diagram, which allowed connections between sources and demands to be visualized. In this way, the utility consumption and network structure were determined simultaneously. Completely batch and semi-continuous processes modeled as fixed flowrate problems could be handled by this method. On the quantity-time diagram, the time axis guided the designer in ensuring that water sinks were satisfied with water sources that existed earlier in time, whereas the quantity axis indicated the total water flow needed or produced. To enhance water recovery, a source of lower concentration was used to fulfill flow requirements of demands. Storage was also considered to enhance water recovery. Care was taken when selecting water sources to be sent to the storage tank, this was done in such a way that the concentration of water in storage did not exceed the maximum allowable requirement of the main water users. The number of storage tanks could be reduced by sending reusable sources with similar concentrations to a storage tank. At the end of the network design, the optimality of the results was checked using any of the established targeting methods in literature. It was found that the design results by Chen and Lee (2008) agreed with the freshwater targets from pinch analysis. The drawback of their method was that it could require multiple iterations to determine the optimum design.

In general, graphical techniques are constrained to two dimensions hence; they cannot be used to solve problems with more than one contaminant effectively. It is important to note that the above graphical/numerical techniques required that the starting and finishing times of the water-using operations be defined. This means that the production schedule cannot be optimized. Once an operating schedule is given, the minimum water targets determined are unique to the schedule and so are not guaranteed to be the true minimum.

2.3.4 Mathematical optimization techniques for wastewater minimization in batch processes

Much of the research done on wastewater minimization in batch processes has been based on mathematical optimization techniques. This is due to the fact that mathematical techniques:

- afford the opportunity to optimize different objective functions,
- are useful for handling multiple contaminant systems,

- can easily accommodate special restrictions, e.g. forbidden matches, restrictions on flowrates, etc. and
- are capable of handling in a simultaneous manner, wastewater minimization and scheduling issues.

Literature on wastewater minimization using mathematical optimization followed a trend. Firstly, simple wastewater minimization problems with direct reuse were considered, followed by the introduction of storage and then the consideration of wastewater treatment or regeneration. To prevent duplicity, the methods which include regeneration or treatment will be discussed under that topic. Most mathematical formulations begin with a superstructure, whereby all water-using operations and their interactions with all other processes and equipment units are represented. According to Gouws *et al.* (2010) there are different ways of representing superstructures for batch problems. One way is to classify them based on the use of intermediate storage. Following this classification, when a storage tank is used to facilitate water reuse among water-using operations, it is referred to as indirect integration, as opposed to direct integration when no intermediate storage is present. Once the superstructure has been determined, water and contaminant mass balances are performed around every available water-using batch unit, storage tank and regenerator. Constraints associated with capacity, operation of the process and time dimension are also included. With regards to the handling of time, the methodologies for wastewater minimization in batch plants can be divided into two, namely:

- fixed schedule problems, where the starting and finishing times of the batch operations are known before optimization is performed, and
- variable schedule problems, where the starting and finishing times of the batch processes are optimization variables. The wastewater minimum and the corresponding batch schedule are determined after optimization.

The solution strategy in each methodology varies depending on how nonlinearities are addressed. These subject matters will be discussed.

Mathematical formulations based on a fixed schedule

The first batch water networks in literature were solved based on the assumption of the existence of an optimal batch schedule. These problems are simpler to solve than in the variable schedule case. Almato *et al*. (1997) developed a technique that utilized storage tanks to override the time constraint in the exploration of reuse and recycle opportunities. No direct reuse/recycle options were included in the superstructure hence, water recovery was only possible through storage vessels. The method was applicable to fixed load problems. The objective function considered was the minimization of freshwater use. The mathematical model resulted in a NLP. A two step procedure was used to obtain the solution of the model. The first step involved heuristics to find the initial tank to stream assignment and to provide the NLP with a feasible starting solution. The second step was an optimization step to solve the NLP. The optimality of the solution could not be guaranteed.

Kim & Smith (2004) developed a MINLP which exploited water reuse and a storage facility to link different time periods. The superstructure included both direct and indirect integration and is illustrated in Figure 2.13. Direct water reuse could only occur between two operations taking place within the same time interval. Reuse of water between two operations in two different time intervals took place through storage. It is also imperative to note that water flow through a unit took place during the duration of that unit's operation. This is not strictly batch mode but rather semicontinuous.

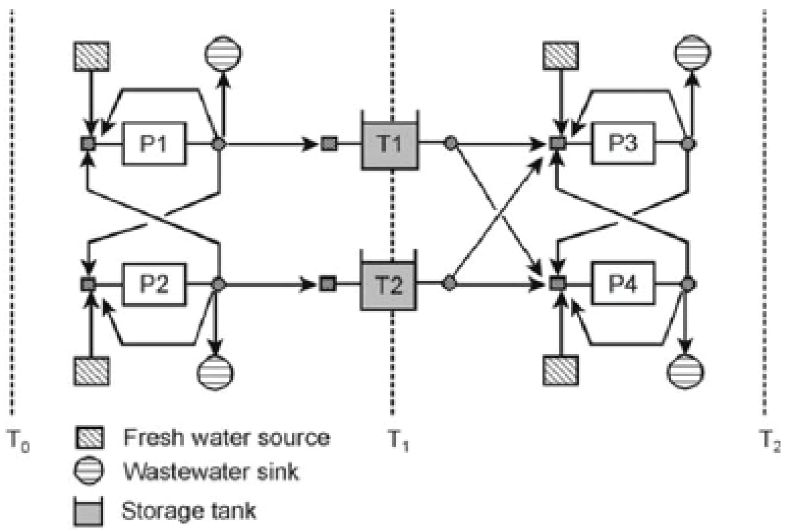

Figure 2.13: Superstructure for Kim and Smith (2004)

The method was based on the fixed load model for water-using batch processes and was applicable to multiple contaminant problems. The mass balances included water gains and losses. Water from operation to storage and vice versa was not explicitly taken into account in the mass balances. Instead a binary variable associated with the existence of a storage tank, Y_n^{ST} was defined. Similarly a binary variable associated with water reuse from operation n to operation n', both representing water-using operations was defined. An extra constraint was formulated to describe the relationship between the two binary variables. This is given in Equation (2.7).

$$Y_{n,n'}^{PP} - Y_n^{ST} \leq 0 \quad \forall n, \text{ where } T_{n'}^{S} \geq T_n^{E} \tag{2.7}$$

The constraint states that if water is transferred from n to n', i.e. $Y_{n,n'}^{PP} = 1$ where operation n' starts after operation n ends, then $Y_n^{ST} = 1$, i.e. a storage tank exists.

Constraints to limit the number of inlet and outlet streams for each operation and control compulsory or unacceptable matches were included. This was to reduce network complexity and improve its practicality. The objective function was the minimization of annual cost which consisted of the cost of freshwater, storage tank and piping. In terms of solution strategy, an MILP-LP decomposition of the original MINLP problem was proposed to find an initial solution for the MINLP. First, an MILP was obtained from the MINLP by fixing the outlet concentration, thus eliminating bilinear terms. The solution to the MILP identified connections between the various units and tanks. This information and the values of the flowrates were then substituted into the original MINLP to give an LP. The LP problem was solved and the values of the concentrations determined were then used to update the MILP. The MILP and LP were iterated until the required convergence criteria were met. The output from this was then used as an initial solution for the MINLP. Due to the solution strategy, long solution times could result.

Majozi (2005a) developed a mathematical formulation which exploited recycle and reuse opportunities. The formulation considered a single contaminant and was based on a superstructure that included direct integration only. The time horizon was represented by a number of time points and each variable was defined at each time point. The formulation catered for truly batch operations. In doing so, water was used in a unit at time point p and produced at time point p+1. Sequencing constraints were included to ensure that water reuse coincided with the time it was available from the water source and the time it was required by the water sink. Two binary variables were required: $y(s_{out,j}, p)$ associated with the usage of a state for the mass balance and $y_r(s_{out,j}, s_{out,j'}, p)$ associated with reuse for the sequencing constraints. The relationship between the two binary variables is expressed in Equation (2.8).

$$y_r(s_{out,j}, s_{out,j'}, p) \leq y(s_{out,j'}, p) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{2.8}$$

This equation simply states that for a unit j to transfer water to unit j', unit j' should require water at that time point. It does not, however, mean that unit j' must use water from unit j, it could still obtain water from the freshwater source. State as employed in this work referred to the identity of a water stream. The objective function was the minimization of freshwater or effluent. The model resulted in a MINLP problem due to the bilinearities in the contaminant mass balances. The MINLP was linearized to a MILP by fixing the outlet concentrations and using the Glover transformation (Glover, 1975).

Shoaib *et al.* (2008) utilized a mathematical optimization technique requiring three stages for batch water network synthesis. The mass balances were based on the fixed flow model, so each batch process was modeled as a source and a sink. The superstructure was based on indirect integration and is illustrated in Figure 2.14.

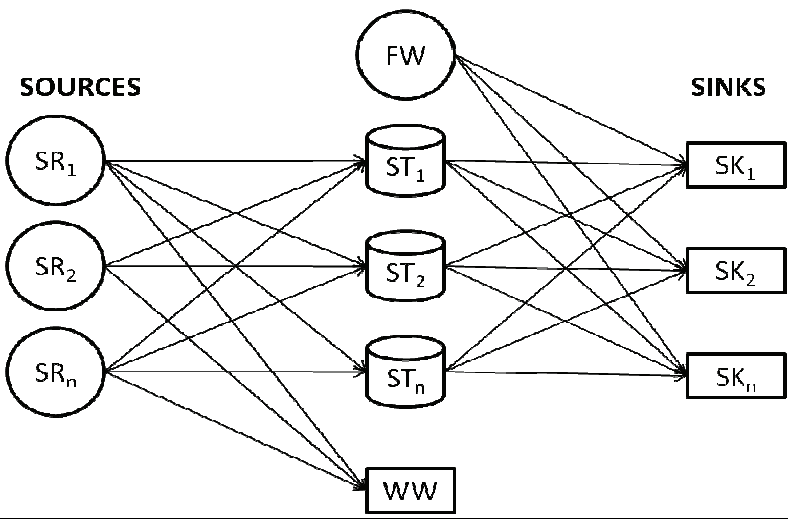

Figure 2.14: Superstructure of source-tank-sink formulation (Shoaib *et al.,* 2008)

In the first stage, the objective was to determine the minimum freshwater usage. In the second stage, the minimum freshwater usage identified in the first stage was included as an extra constraint. The objective was the minimization of storage tank capacity. The objective in the third stage was the minimization of the number of interconnections between the batch processes and the storage tanks. In this stage, the objective values from stages 1 and 2 were included as additional constraints. The overall model was an MINLP. The linear relaxation technique proposed by McCormick (1976) was adopted to relax the bilinear terms in the MINLP to form an MILP. The MILP was solved to produce an initial starting point for the exact MINLP. A key assumption made in this work was that only indirect water reuse was allowed i.e. the reuse of water between sources and sinks was done via a storage tank. This was to allow for proper mixing in the tanks so that the water reached the desired quality. The drawback of their method was that stored water could only be reused/recycled by sinks in the next batch cycle. Hence, the work was limited to cyclic operation.

Tokos and Pintarič (2009) developed mathematical formulation for minimizing 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 minimization in batch processes. Wastewater generation was minimized 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 minimization 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 minimization 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 minimization 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.

As previously stated, the limitation of these methods is that they are based on the optimal schedule being given *a priori*. In practical terms, they are suited to situations where the batch schedule seldom changes. In the next subsection, wastewater minimization techniques where time is treated as an optimization variable are presented.

Mathematical formulations based on a variable schedule

These formulations are advantageous because they can easily accommodate the situation where the schedule is known and still determine the corresponding minimum water flow/cost solution. The most attractive of these formulations are those based on scheduling methodologies which are easy to solve and do not require long solution times.

Majozi (2005b) improved on his earlier formulation (Majozi, 2005a) by including the effect of central storage in the formulation and using a flexible schedule. Mass balances over the storage vessel were included as well as the sequencing constraints involving storage. Two additional binary variables, $y_{sin}(s_{out,j}, p)$ associated with transfer of water to storage and $y_{sout}(s_{out,j}, p)$ associated with transfer of water from storage were introduced. The scheduling framework of Majozi and Zhu (2001) that utilized the SSN and continuous time representation was employed. Four scenarios were investigated in the work by Majozi (2005b). In the first scenario, which was exactly the same as the work done in Majozi (2005a), it was assumed that the outlet concentration from each unit was fixed at its maximum value. This implied that during optimization, the flowrate through each unit was free to vary below a defined upper limit. This resulted in a MILP. The second scenario assumed that the flowrate through each unit was fixed, and the inlet and outlet concentrations were free to vary within defined maximum values during optimization. The superstructure for scenarios one and two is depicted in Figure 2.15.

The third scenario was the same as scenario one but with a central reusable storage vessel included in the formulation. Likewise, the fourth scenario was the same as scenario two but with the inclusion of a central reusable storage vessel. Scenarios two, three and four resulted in MINLP problems for which global optimal solutions could not be guaranteed. The superstructures for scenarios three and four were also similar to that of Majozi (2005a), except that integration with storage was included. The superstructure for scenarios three and four is illustrated in Figure 2.16.

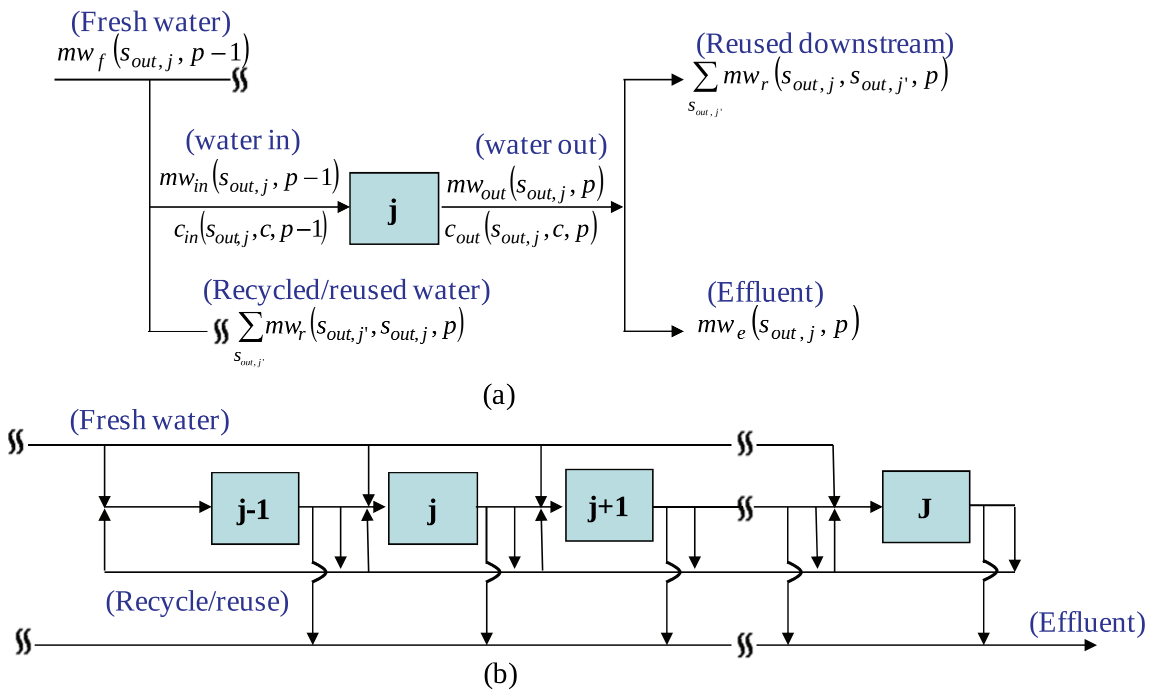

Figure 2.15: Superstructure for the mathematical formulation with no reusable water storage Majozi (2005a)

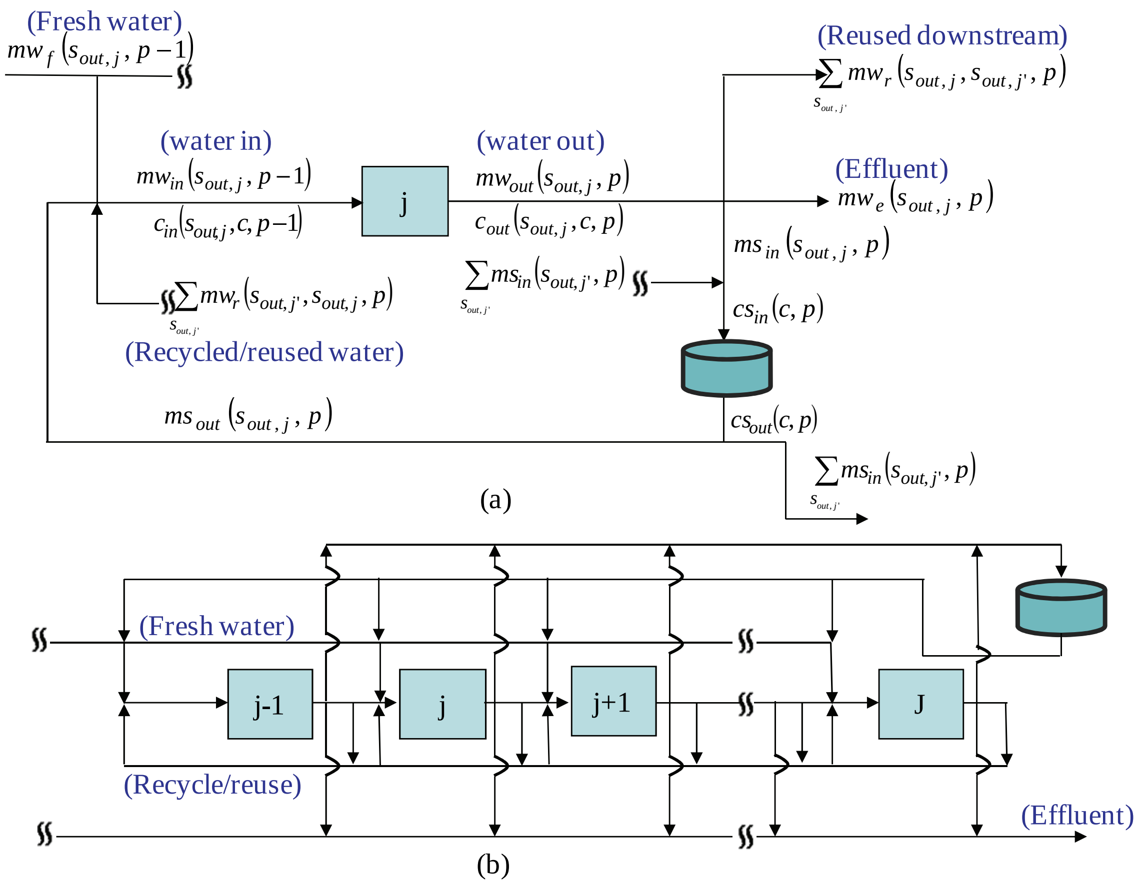

Figure 2.16: Superstructure for the mathematical formulation with reusable water storage Majozi (2005b)

The method by Majozi (2005b) differs from other methods, in that, reuse could either be direct or indirect as opposed to the methods of Almato *et al.* (1997) and Shoaib *et al.* (2008), whereby reuse could only take place through a vessel. The drawback of the work by Majozi (2005b) was that it was limited to a single contaminant.

Gouws and Majozi (2008) addressed multiple contaminants and highlighted the fact that the choice of storage option depended on the profile of contaminants present in the water streams. Different wastewater streams could contain single but different contaminants. In another situation, each wastewater stream could contain the same set of contaminants. Yet another option could be a mixture of both cases, that is, there are wastewater streams with single but different contaminants as well as wastewater streams with multiple contaminants. The effect of multiple storage vessels and multiple contaminants is shown in Equation (2.9), which is an inlet contaminant balance into a unit. In this constraint, $c_{in}(j,c,p)$ is the inlet concentration into unit j of contaminant c at time point p, $f_u(j,p)$ is the amount of water into unit j at time point p, $f_r(j',j,p)$ is the amount of water recycled between unit j' and unit j at time point p, $c_{out}(j',c,p)$ is the outlet concentration of the water from unit j' of contaminant c at time point p, $fs_{out}(u,j,p)$ is the amount of water going into unit j from storage vessel u at time point p and $cs_{out}(u,c,p)$ is the concentration of contaminant c of water inside a storage tank u at time point p.

$$c_{in}(j,c,p)f_u(j,p)=\sum_{j'} f_r(j',j,p)c_{out}(j',c,p)+\sum_{u} fs_{out}(u,j,p)cs_{out}(u,c,p) \quad \forall j,j'\in J, p\in P, c\in C \tag{2.9}$$

Due to the bilinear terms in this equation, the overall model was nonlinear and nonconvex, hence the failure to ascertain global optimality. To reduce computational intensity, some of these nonlinearities were linearized using the reformulation–linearization method proposed by Quesada and Grossmann (1995).

Majozi and Gouws (2009) presented a mathematical formulation for wastewater minimization that included multiple contaminants with one central storage tank. Equation (2.10) is an inlet contaminant balance into a unit in this work. It is very similar to Equation (2.9) except for a few differences.

$$c_{in}(j,c,p)f_u(j,p) = \sum_{j'} f_r(j',j,p)c_{out}(j',c,p) + fs_{out}(j,p)cs_{out}(c,p)$$
$$\forall j, j' \in J, p \in P, c \in C \quad (2.10)$$

In this constraint, $fs_{out}(j,p)$ is the amount of water going into unit j from the central storage vessel at time point p and $cs_{out}(c,p)$ is the concentration of contaminant c of water inside the central storage tank at time point p. 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 2.17.

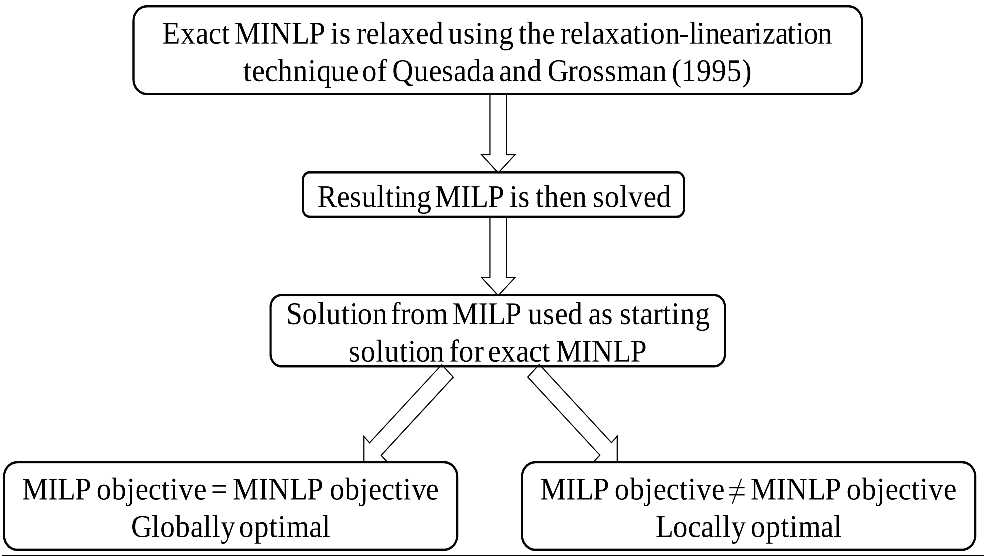

Figure 2.17: Solution procedure from Gouws *et al.* (2008)

Chen *et al*. (2010a) 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 2.18.

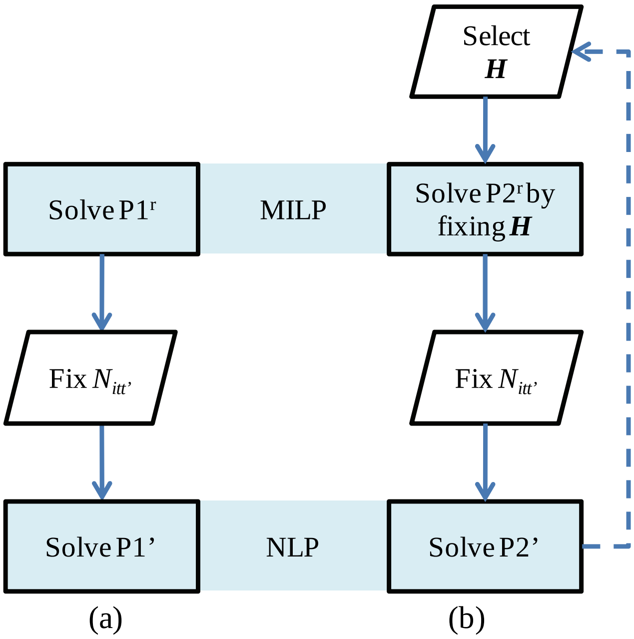

Figure 2.18: Solution procedure for (a) short-term and (b) periodic operations proposed by Chen *et al*. (2010a)

For short-term scheduling problem, the model was linearized using the technique proposed by McCormick (1976), **P1^r** on Figure 2.18(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 2.18(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 minimization 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 minimization 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 minimize 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 minimization in a strict batch process. The formulation resulted in a MINLP problem for which a global optimum solution could not be guaranteed.

Incorporating regeneration

Wastewater treatment and regeneration in batch plants have been considered in literature. The difference between treatment and regeneration was discussed under continuous processes.

Chang and Li (2006) investigated the concept of wastewater treatment, whereby buffer tanks were utilized to achieve wastewater flowrate and contaminant concentration equalization. The mathematical formulation was based on a superstructure which followed a number of rules. A splitting node was placed at the exit of each batch process and buffer tank, while a mixing node was placed at the entrance of each buffer tank and sink. Each splitting node after a batch process was connected to all mixing nodes in the superstructure, while each splitting node after each tank was connected to all mixing nodes except the one at the entrance of the same tank. In this work, the sink was a treatment unit and only batch processes that generated wastewater were considered. The treatment unit was modeled as a continuous operation, hence, the need for buffer tanks. The mathematical formulation was based on a fixed schedule. In addition, the time horizon was discretized. This was in order to express differential equations as algebraic equations which were much easier to handle. The differential equations were encountered when performing water and contaminant mass balances around the buffer tanks. A disadvantage of the discretized time horizon as already mentioned is the explosive binary dimension that could be encountered in more complex problems leading to increased computational time. The objective function was the minimization of the installed cost of buffer tanks, given in Equation (2.11).

$$obj = \sum_{t \in T} \alpha \left(V_t^{max} \right)^{0.6} \tag{2.11}$$

where α is a constant and V_t is the volume of a buffer tank. Worthy of mention is the fact that in this work the treated wastewater was not reused in the batch processes.

Li and Chang (2006) improved upon their earlier paper by considering water reuse between the batch processes. In this work, a batch process could be a source (water generating), sink (water consuming) or a water user (both water consuming and water generating). The superstructure was similar to Chang and Li (2006) but adjusted to account for the fact that a sink could consist of a treatment unit, the environment or a batch process. In addition, the mathematical formulation was based on a fixed schedule and a discretized time horizon. Their method was applicable to multiple contaminant systems. Water and contaminant mass balances were carried out at each splitting and mixing node, around each source, sink, water user and buffer tank. The contaminant mass balances at each node were carried out for each pollution index. The water balance over a buffer tank is given in Equation (2.12). In Equation (2.12), $v_{b,t}$ is the volume of water in buffer tank b at the end of time interval t, $f_{b,t}^{in}$ and $f_{b,t}^{out}$ are the inlet and outlet flowrates of buffer tank b during time interval t, respectively, and

DT is the length of the time interval. Equation (2.13) is the contaminant balance over the same buffer tank. In Equation (2.13), $c_{b,k,t}^{in}$ and $c_{b,k,t}^{out}$ are the values of pollution index k in the input and output streams of buffer tank b at the end of time interval t, respectively.

$$v_{b,t} = v_{b,t-1} + \left(f_{b,t}^{in} - f_{b,t}^{out} \right) DT \qquad b \in B, k \in K, t \in T \tag{2.12}$$

$$v_{b,t} c_{b,k,t}^{out} \cong v_{b,t-1} c_{b,k,t-1}^{out} + \left(f_{b,t}^{in} c_{b,k,t}^{in} - f_{b,t}^{out} c_{b,k,t}^{out} \right) DT \qquad b \in B, k \in K, t \in T \tag{2.13}$$

The aim of this work was to design an integrated water reuse and equalization system for batch processes. The objective function was the minimization of annualized cost which consisted of annual water costs, annualized installation costs and annual treatment costs. The mathematical formulation resulted in a MINLP. Similar to Chang and Li (2006), reuse of treated water in batch processes was not considered. The treatment unit only served as a sink for wastewater.

In the work by Cheng and Chang (2007), all three systems, i.e. optimization of batch schedules, water reuse system and wastewater treatment system were incorporated in the same model (the formulation was based on a variable schedule). This is illustrated in Figure 2.19. The model was divided into two modules, namely, the batch production module and the batch water network synthesis module. The objective function of the scheduling module, which was based on the scheduling framework by Lee *et al.* (2001), was given as the difference between the revenue from product and the cost of raw material. The scheduling formulation of Lee *et al.* (2001) was based on the discrete time formulation and the STN. The batch water network synthesis module was similar to that of Li and Chang (2006). To optimize the schedule and the batch water network simultaneously, Cheng and Chang (2007) assumed that the water consumed or generated in a batch process was proportional to the amount of material produced. The objective functions from the two modules were combined by subtracting the water recovery objective function from the scheduling objective function. Constraints associated with the network structure were also incorporated, such as, the reduction of the number of storage tanks and pipe connections. Treated wastewater was not reused in the water system but simply discharged to a water sink which in this case, was the environment.

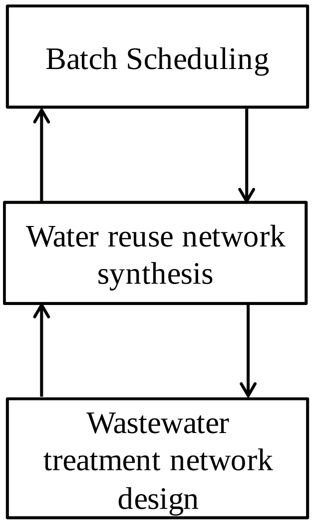

Figure 2.19: An integrated batch water network design (Cheng and Chang, 2007)

The use of a regenerator was considered in the work by Shoaib *et al.* (2008). To place the regenerator, the pinch concentration was firstly identified using the time dependent water cascade analysis TDWCA, already discussed under graphical techniques for batch processes. Once the pinch concentration had been located, the regenerator was placed across the pinch, i.e. the regenerator purified a water source at a higher concentration than the pinch concentration to a concentration lower than that of the pinch, as stipulated by Hallale (2002), this is the best option. The type of regenerator considered was the fixed outlet concentration regenerator. After the regenerator had been installed, stages 2 and 3 involving storage size and network complexity optimization respectively were carried out to synthesize the batch network. The freshwater used which is concomitant with wastewater generated, was decreased further compared to the situation where no regenerator was used.

Liu *et al*. (2009) considered the use of a central regenerator to explore more possibilities for water reuse and water recovery in batch plants. Similar to the work by Chang and Li (2006), the central regeneration unit operated continuously hence, storage tanks were installed at the inlet and outlet of the regeneration unit to act as buffers to connect the batch operations to the continuous regenerator. In their superstructure, the buffer tank at the entrance to the regenerator also served to provide indirect reuse water for the batch processes. In the mathematical formulation, the time horizon was discretized and was based on a fixed schedule. Equation (2.14) is the mass balance around the buffer tank at the entrance to the regenerator. In Equation (2.14), $Q_T^p(t)$ is the water remaining in tank T at any moment t,

$Q_T^{p-1}(t_H)$ is the residual water in tank T at the end of the preceding operating cycle $P-1$, $Q_{T,j}^{p}(t)$ is the amount of water discharged from batch process j to tank T during operating cycle P, t^R is the start moment of regeneration and $f^{R,P}$ is the flowrate of the regeneration unit during operating cycle P.

$$Q_T^p(t) = Q_T^{p-1}(t_H) + \sum_{j\in J} Q_{T,j}^p u\left(t - t_j^{out}\right) - \sum_{j\in J} Q_{T,j}^p u\left(t - t_j^{in}\right) - f^{R,P}\left(t - t^R\right) u\left(t - t^R\right) \quad (2.14)$$

where

$$u(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases}$$

Two objectives were considered in this work, the first was the minimization of freshwater consumption and effluent generation of the system. The second was to minimize the flowrate of the regeneration unit. An advantage of their method was that they considered the need for a regenerator in a problem beforehand. This is because it is the nature of some problems, though unlikely in practice, that the wastewater produced by the batch processes is sufficient for use by the other processes on the plant. The regenerator becomes necessary in problems where wastewater generated is so highly contaminated that the water cannot be reused. However, this work was limited to single contaminant problems.

The method by Zhou *et al*. (2009) and Li *et al.* (2010) took into account batch production, the water-reuse subsystem and wastewater treatment (see Figure 2.19). The formulation was based on a variable schedule. In this work, the state-time-space superstructure was introduced, which identified states, tasks, equipment and time simultaneously. An illustration is provided in Figure 2.20. In spite of the exhaustive representation of the superstructure, the authors still found it necessary to exclude some connections made in the superstructure. The mathematical model consisted of two modules, the scheduling module and the batch water network synthesis module. The production scheduling framework was based on the MILP formulation proposed by Ierapetritou and Floudas (1998) which used the continuous time representation. The mathematical formulation for the batch water network was based on the discrete time formulation similar to that by Li and Chang (2007) with the exception that wastewater regeneration was incorporated. To link the two modules together, they assumed that the water generating or consuming rate in a water-using operation was directly proportional to the processing volume of the batch unit in the batch module. Structural constraints to reduce the number of pipelines were also included in the model. The overall model was a nonconvex MINLP and was solved using a hybrid optimization strategy with iteration. The authors acknowledged the possibility of computational difficulties associated with a problem of this nature. The solution strategy decomposed the original MINLP into a MILP-MINLP formulation that was solved sequentially. The MILP model was the production formulation for scheduling. The solutions from this stage were passed unto the MINLP batch water network model. The results were then used in the original MINLP to get a final solution.

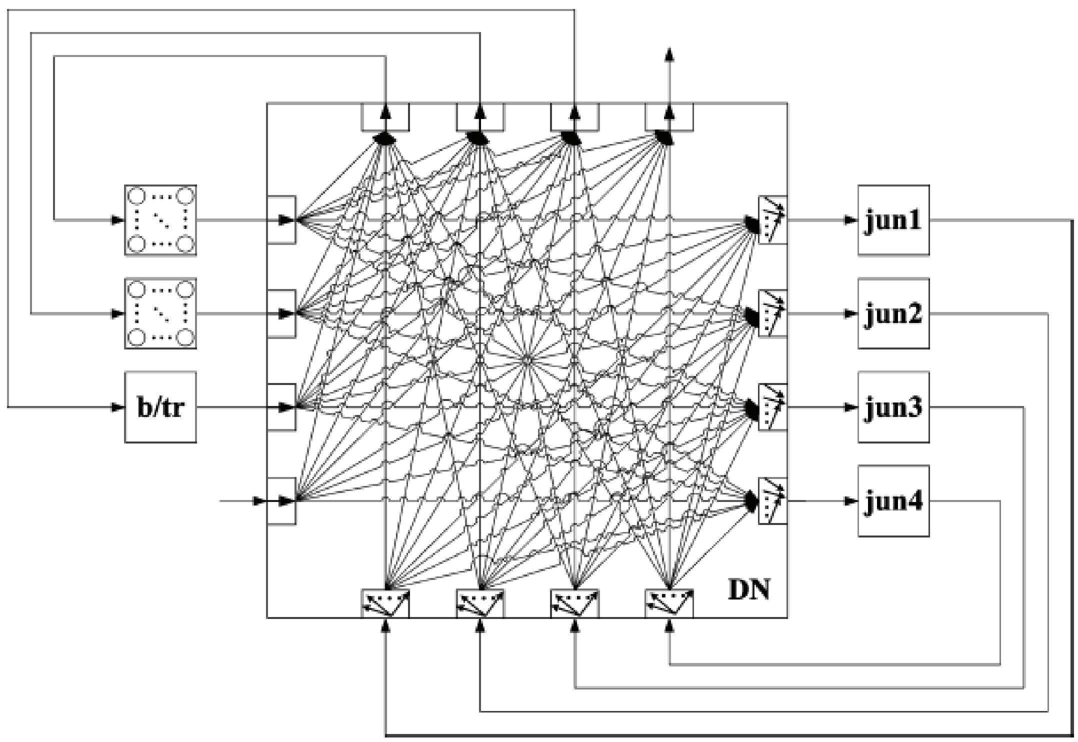

Figure 2.20: Superstructure of Li *et al.* (2010)

Ng *et al.* (2008) extended the concept of regeneration to include the purification of properties other than composition of pollutants. This was called the interception of water streams by interception devices. The aim of such devices was to adjust properties such as pH, conductivity, turbidity, theoretical oxygen demand, color, etc. before water streams were reused/recycled. Ng *et al.* (2008) utilized mathematical optimization techniques to identify the optimal allocation and interception of water sources using total annual cost as the objective function. The cost consisted of the price of freshwater, the cost associated with the interception devices and the installation of storage tanks. In addition, the procedure determined the number and assignment of storage tanks. The concept of source-tank-sink representation by Shoaib *et al.* (2008), Figure 2.14, was modified to a source-tank-interception-tank-sink representation. A source stream follows a tank-interceptor-tank sequence before sent to a sink, i.e. only indirect reuse between the batch processes was allowed. In the methodology, mass balances were performed around each mixing node and each splitting node. In addition a mixing rule was needed to define all possible mixing patterns among the individual properties. In modeling the interception device, the outlet property operator of a property leaving an interception device was a function of the inlet property operator. The time horizon was discretized into a number of time intervals. The discretization was done in order to link the continuous interception devices with the batch processes. The mathematical model was a MINLP which was solved with a commercial optimization software called extended LINGO which was used to obtain the global solution. The drawback of the method was that it was based on a fixed schedule.

Chen *et al.* (2010b) extended the work by Ng *et al.* (2008) to deal with both continuous and batch processes. A continuous process was treated as a special kind of batch process in which the process sources and sinks existed simultaneously over a time interval. Effluent treatment was incorporated to ensure compliance with environmental discharge limits. The objective function of the optimization was to synthesize a property based resource conservation network, PRCN that achieved the minimum freshwater usage for the given problem while satisfying all process and environmental constraints. Similarly, the starting and finishing times of the processes sources and sinks were known beforehand.

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 minimization techniques for batch processes. The developed wastewater minimization techniques can be categorized into graphical and mathematical techniques. It has been made clear 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 minimization 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 minimization 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 minimization techniques, they share a common major drawback. They are limited to wastewater minimization 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 minimization in batch processes operated over a long time horizon is needed. This is the first investigation addressed in this report. Similarly, the formulation by Majozi and Gouws (2009) was also adopted.

The above discussion highlights the need for a wastewater minimization methodology that incorporates wastewater regeneration. Moreover, the batch production schedule and water network that correspond to minimum water requirement ought to be determined simultaneously within the same optimization framework. The second investigation in this report presents a methodology that is aimed at addressing this particular problem. The formulation by Majozi and Gouws (2009) was adopted due to the fact that the formulation was applicable to problems with multiple contaminants and a variable schedule.

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CHAPTER 3

SECTION A: MATHEMATICAL MODEL

Introduction

This chapter presents the proposed mathematical formulation for wastewater minimization 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 by-products, 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.

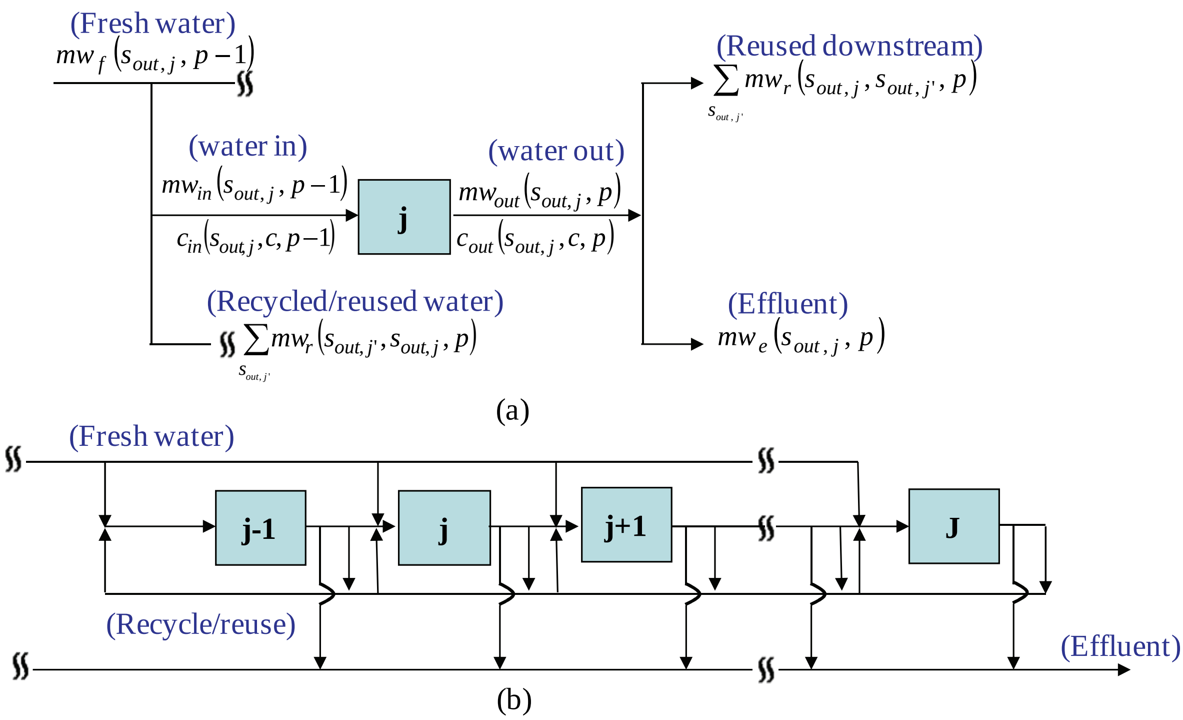

Figure 3.1: Superstructure for the mathematical formulation with no reusable water storage Majozi and Gouws (2009)

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*.

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

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

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

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

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

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.

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

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

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

$$c_{in}\left(s_{out,j},c,p\right)\leq C_{in}^{U}\left(s_{out,j},c\right)yw\left(s_{out,j},p\right),\quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P,p>p_{1},c\in C \qquad (3.9)$$

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.

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

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 report.

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.

$$mw_{in}\left(s_{out,j}, p\right) = \sum_{s_{out,j'}} mw_r\left(s_{out,j'}, s_{out,j}, p\right) + mw_f\left(s_{out,j}, p\right) + ms_{out}\left(s_{out,j}, p\right),$$
$$\forall j, j' \in J,\ s_{out,j} \in S_{out,j},\ p \in P \qquad (3.11)$$

$$mw_{out}\left(s_{out,j}, p\right) = \sum_{s_{out,j'}} mw_r\left(s_{out,j}, s_{out,j'}, p\right) + mw_e\left(s_{out,j}, p\right) + ms_{in}\left(s_{out,j}, p\right),$$
$$\forall j, j' \in J,\ s_{out,j} \in S_{out,j},\ p \in P \qquad (3.12)$$

$$c_{in}\left(s_{out,j}, c, p\right) mw_{in}\left(s_{out,j}, p\right) = \sum_{s_{out,j'}} mw_r\left(s_{out,j'}, s_{out,j}, p\right) c_{out}\left(s_{out,j'}, c, p\right)$$
$$+ cs_{out}\left(c, p\right) ms_{out}\left(s_{out,j}, p\right),$$
$$\forall j, j' \in J,\ s_{out,j} \in S_{out,j},\ p \in P, c \in C \qquad (3.13)$$

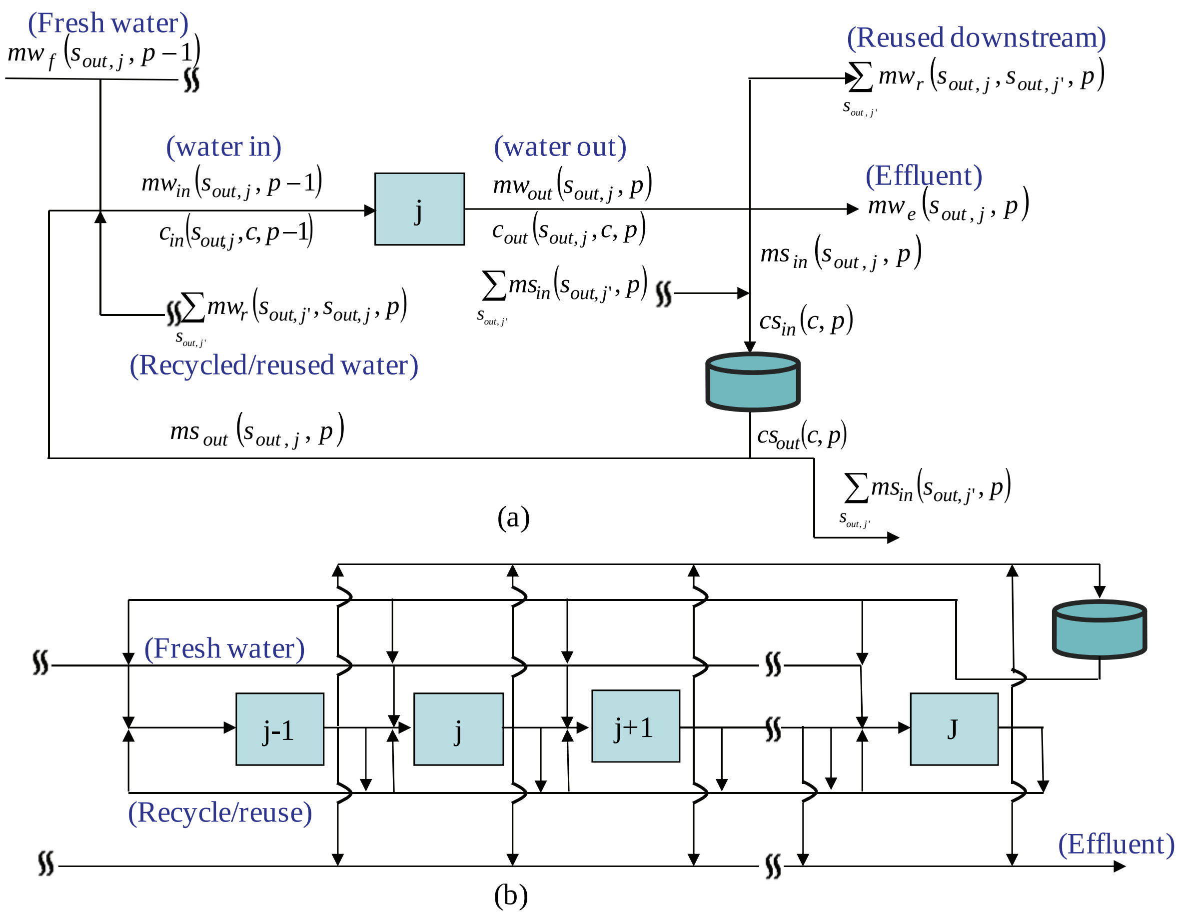

Figure 3.2: Superstructure for the mathematical formulation with reusable water storage Majozi and Gouws (2009)

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. Constraint (3.16) and (3.17) is 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.

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

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.

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

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq tw_{out}(s_{out,j}, p) + H^U(1 - yw_r(s_{out,j}, s_{out,j'}, p)), \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.27}$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \geq tw_{out}(s_{out,j}, p) - H^U(1 - yw_r(s_{out,j}, s_{out,j'}, p)), \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.28}$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq tw_{in}(s_{out,j}, p) + H^U(1 - yw_r(s_{out,j}, s_{out,j'}, p)), \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.29}$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \geq tw_{in}(s_{out,j}, p) - H^U(1 - yw_r(s_{out,j}, s_{out,j'}, p)), \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{3.30}$$

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.

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

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

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

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.

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

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

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

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.

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

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

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

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.

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

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

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

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.

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

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

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

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

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

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

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

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.

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

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 (***2H***). 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.

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

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

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

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.

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

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.

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

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 minimization 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 I 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 I. 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).

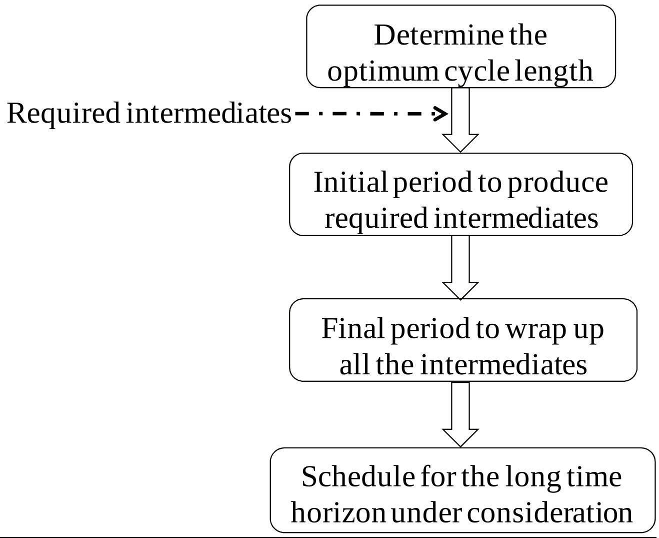

Figure 3.3: Solution procedure

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 minimization 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 minimization 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 minimization 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

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CHAPTER 4

SECTION A: 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 report it is adapted to wastewater minimization.

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.

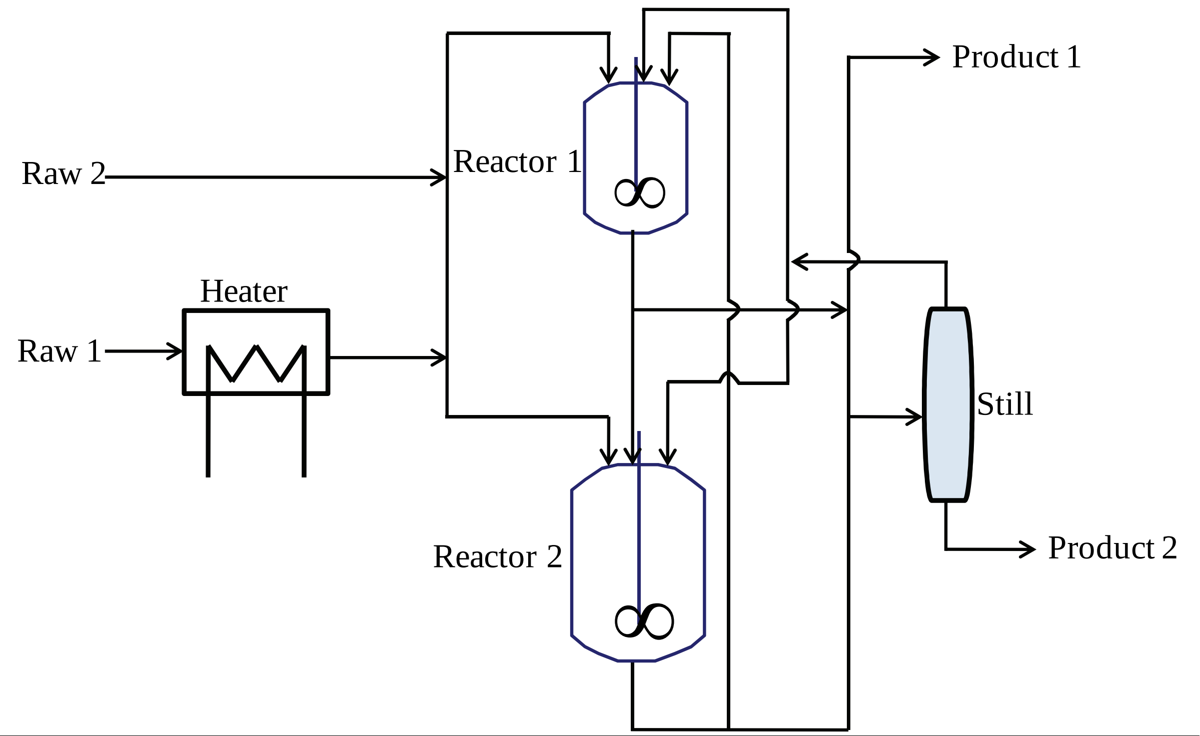

Figure 4.1: Flowsheet for BATCH 1 multipurpose plant

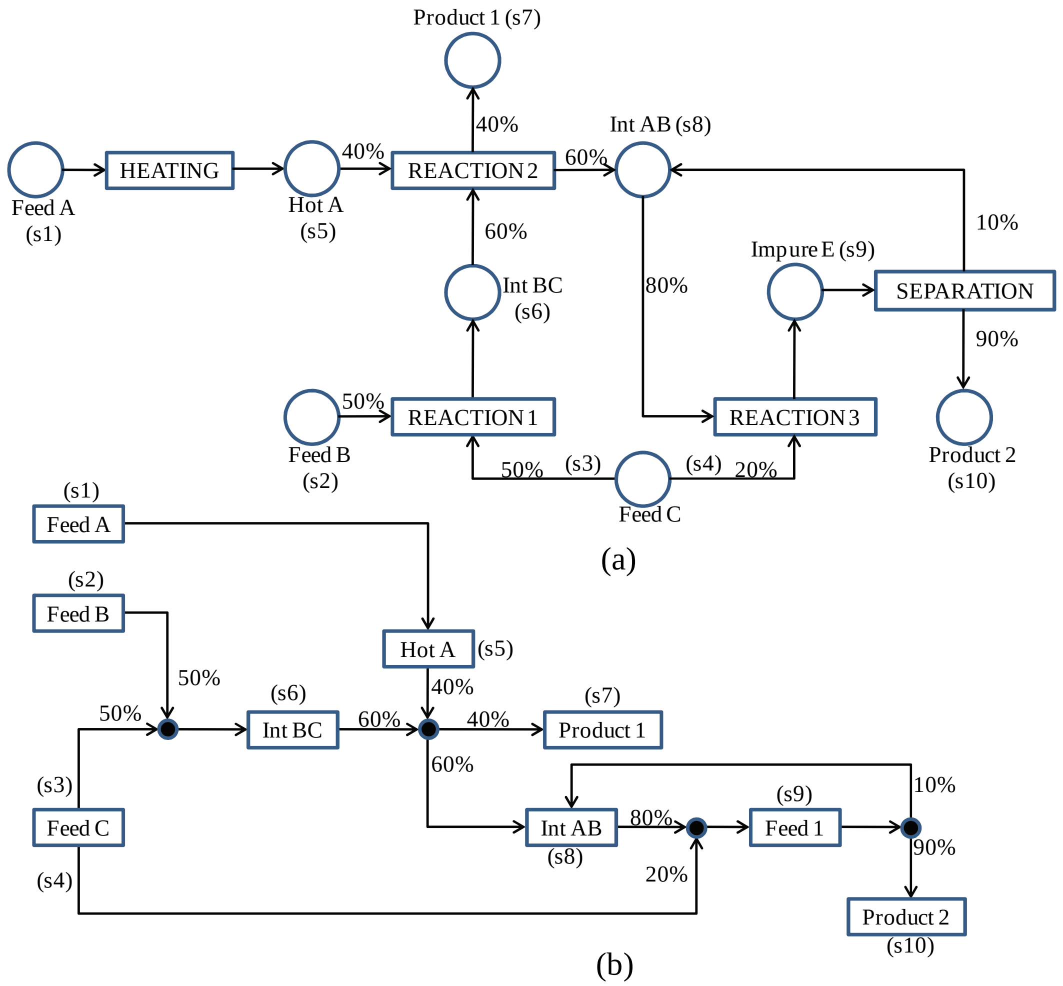

Figure 4.2: (a) STN and (b) SSN for the literature example

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 minimization 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 by-products, 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, whilst the effluent treatment cost is 3 c.u./kg.

Table 4.2: Wastewater minimization 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 minimization 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 report 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 minimization 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 minimized by minimizing 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.

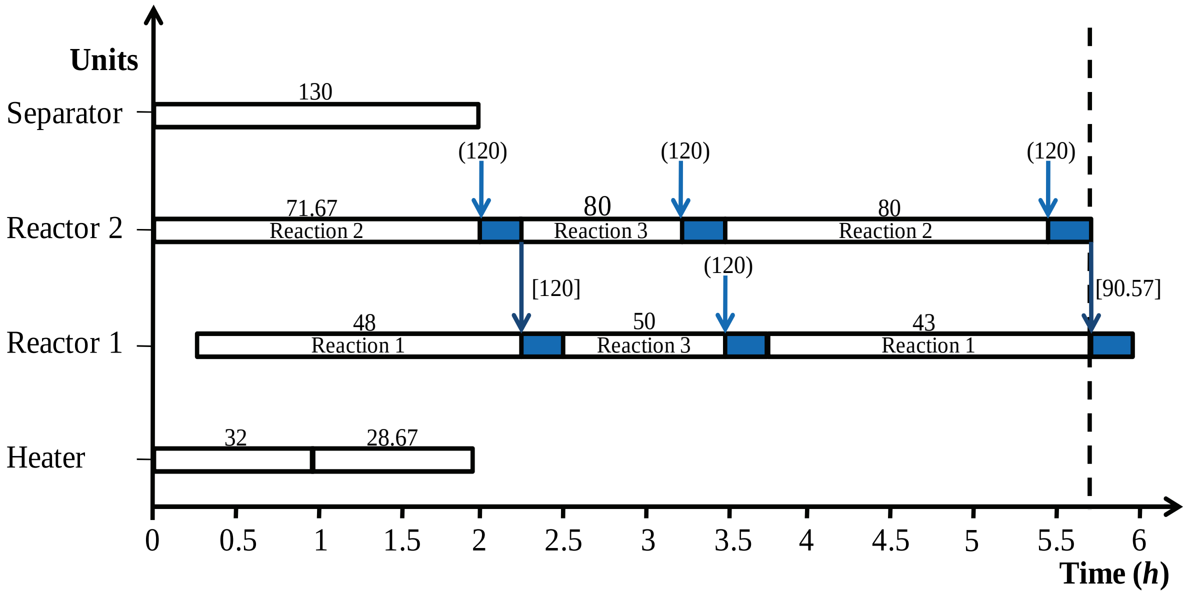

Figure 4.3: Schedule for the optimum cycle length without storage

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 minimize 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.

$$qw_s(p) = 0 \quad \forall\ p = |P| \qquad (4.1)$$

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.

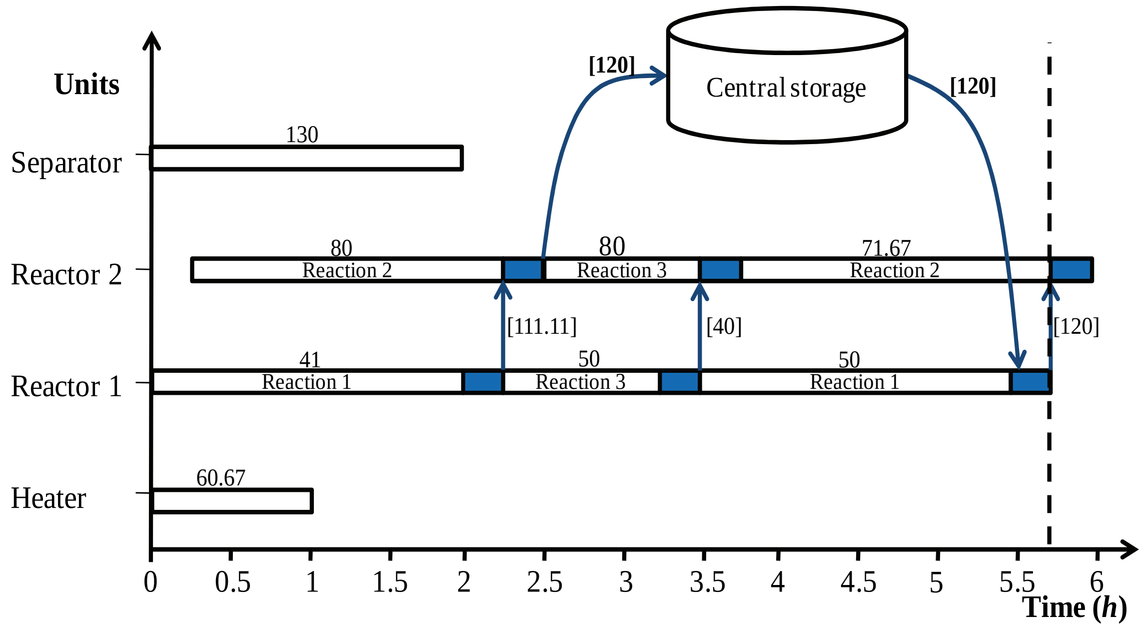

Figure 4.4: Schedule for the optimum cycle length without storage

Wastewater minimization without central storage for 48h time horizon

The illustrative example could not be solved for a time horizon of 48h when the wastewater minimization 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%.

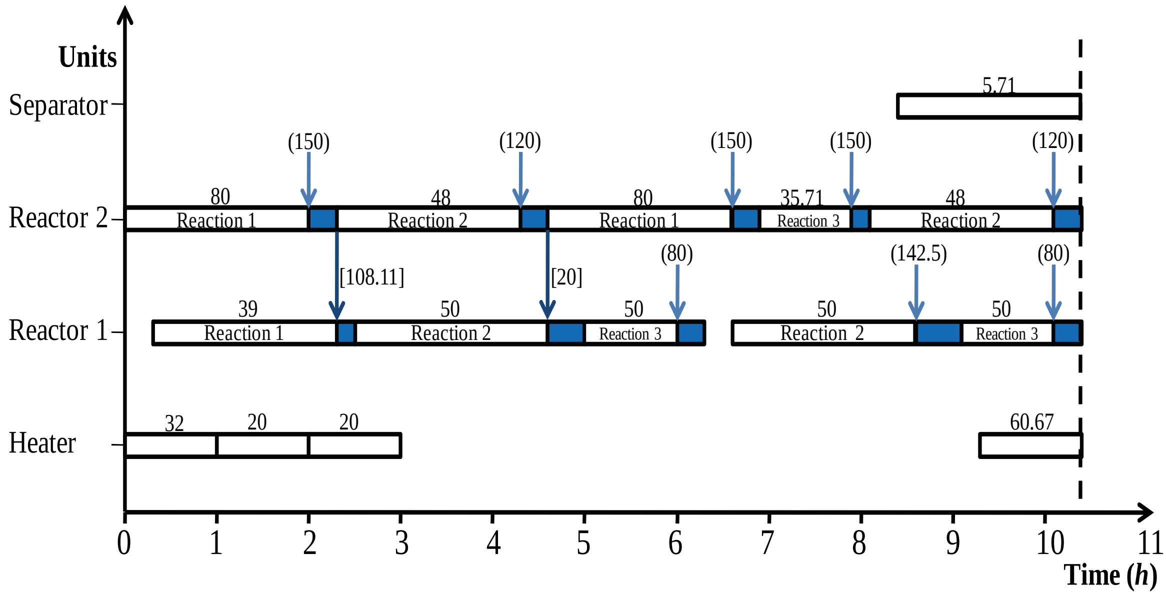

Figure 4.5: Initial period without central storage vessel

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.

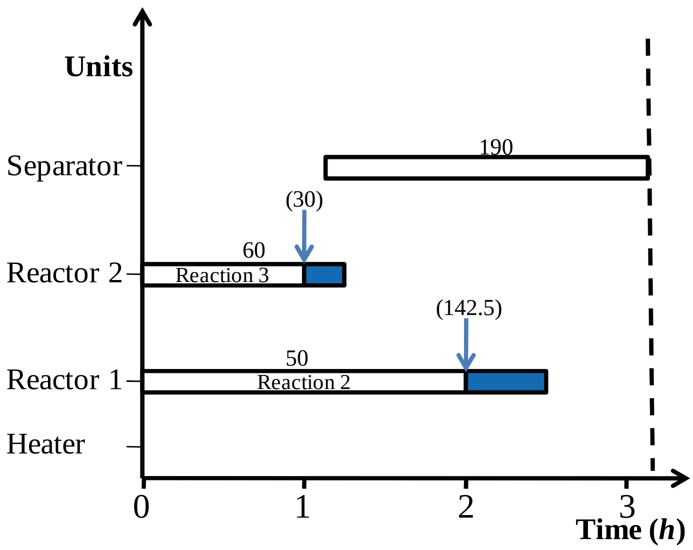

Figure 4.6: Final period without storage for a time horizon of 48h

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 minimization 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.

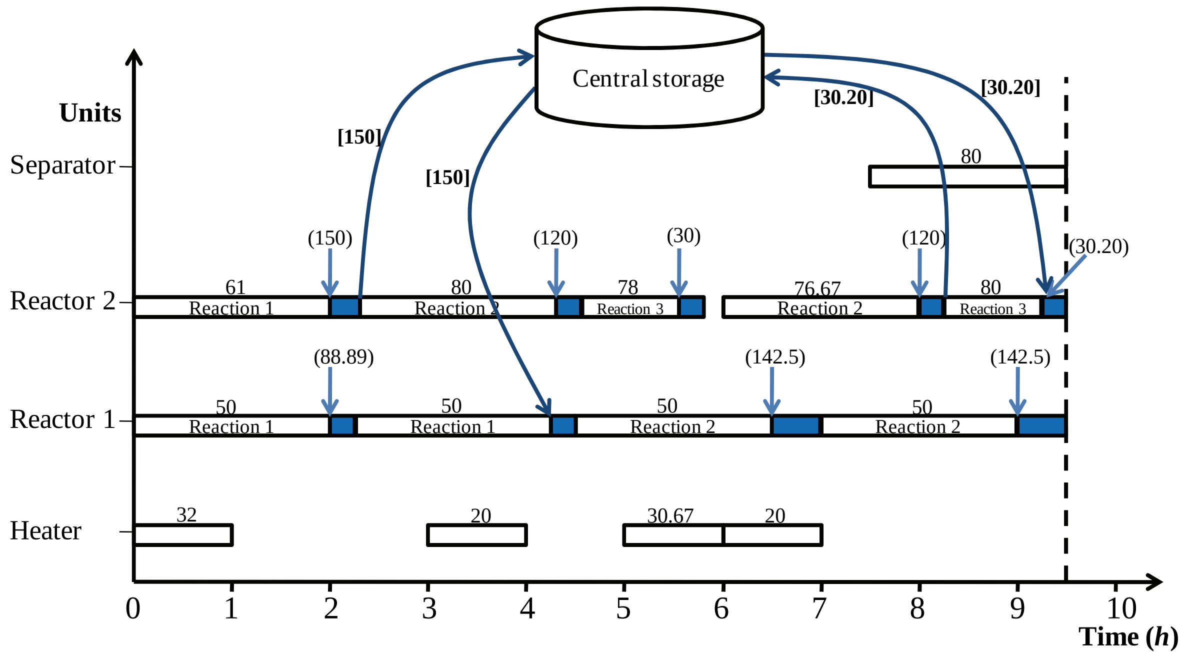

Figure 4.7: Initial period with storage

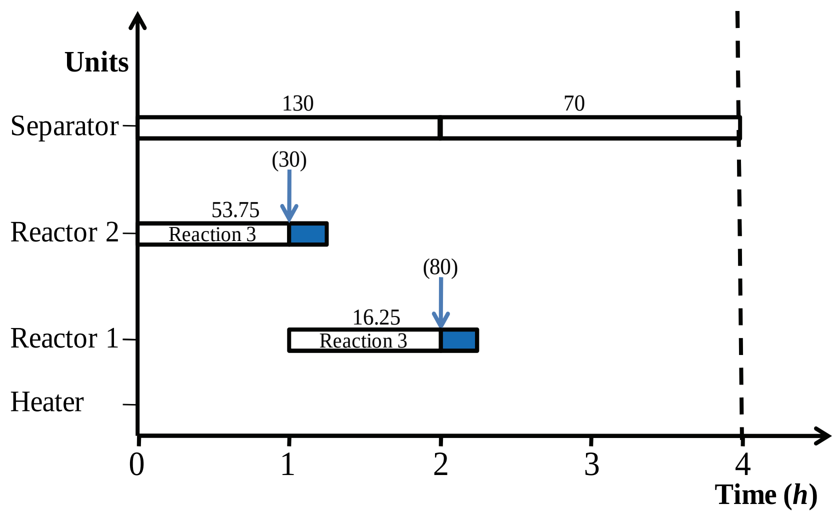

Figure 4.8: Final period with storage

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.

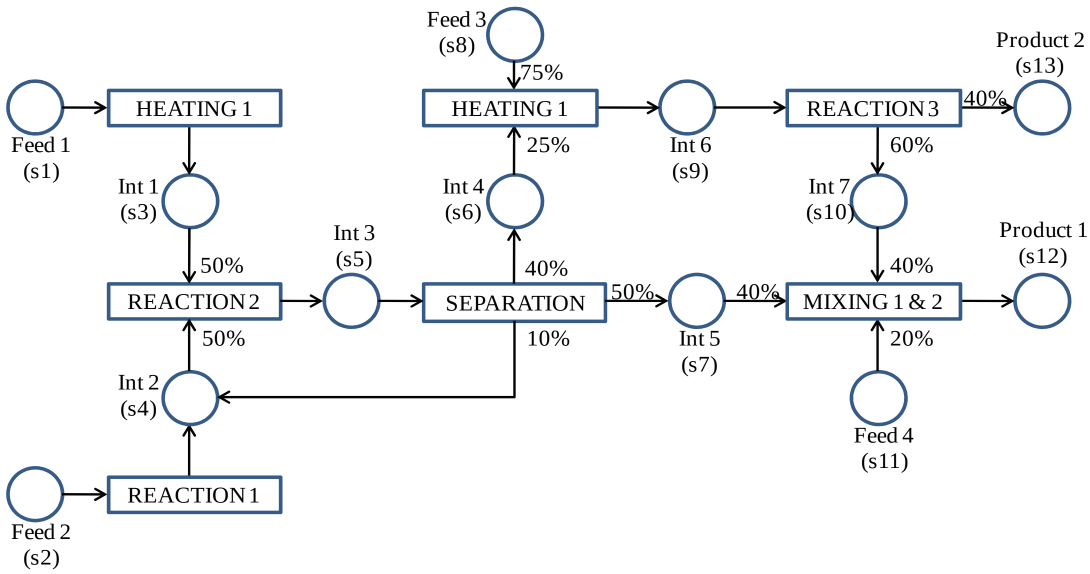

Figure 4.9: STN representation of the second illustrative example

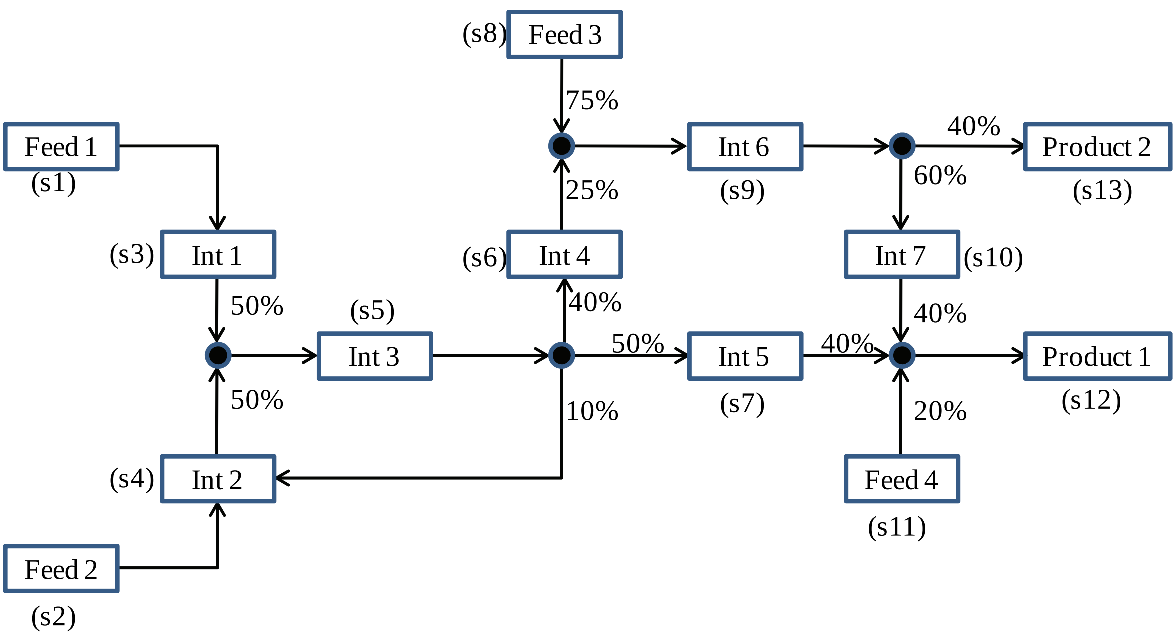

Figure 4.10: SSN representation of the second illustrative example

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 minimization in this report 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 by-products in the units, so as to ensure product integrity. Data pertaining to cleaning tasks is given in Table 4.9.

Table 4.9: Wastewater minimization data for the second illustrative example

		Maximum concentration (g contaminant/kg water)		
		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 minimization 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 16.985%.

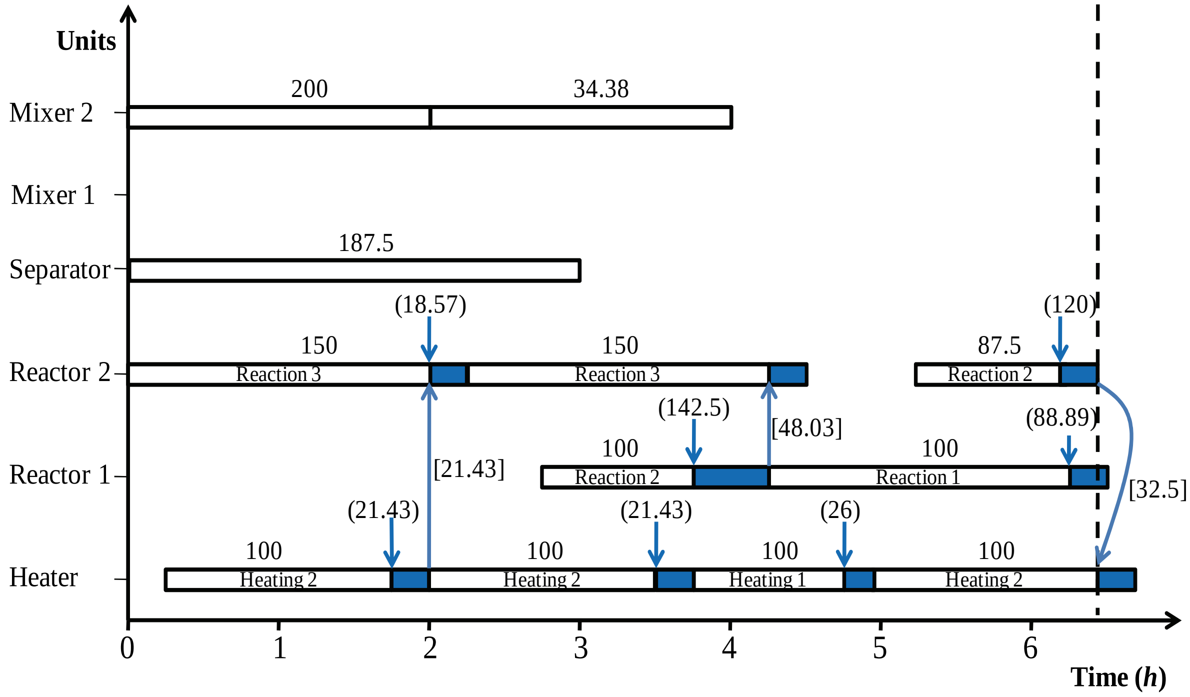

Figure 4.11: Schedule for the optimum cycle length without central storage

Considering the simultaneous production scheduling and wastewater minimization 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.

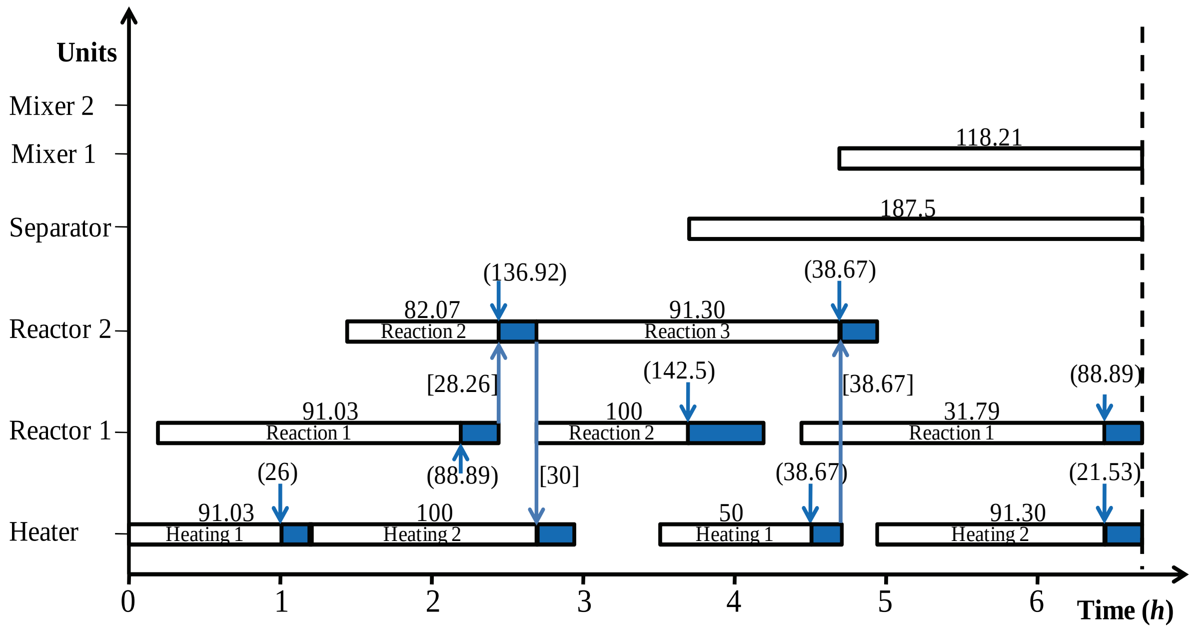

Figure 4.12: Initial period without storage for the time horizon of 168h

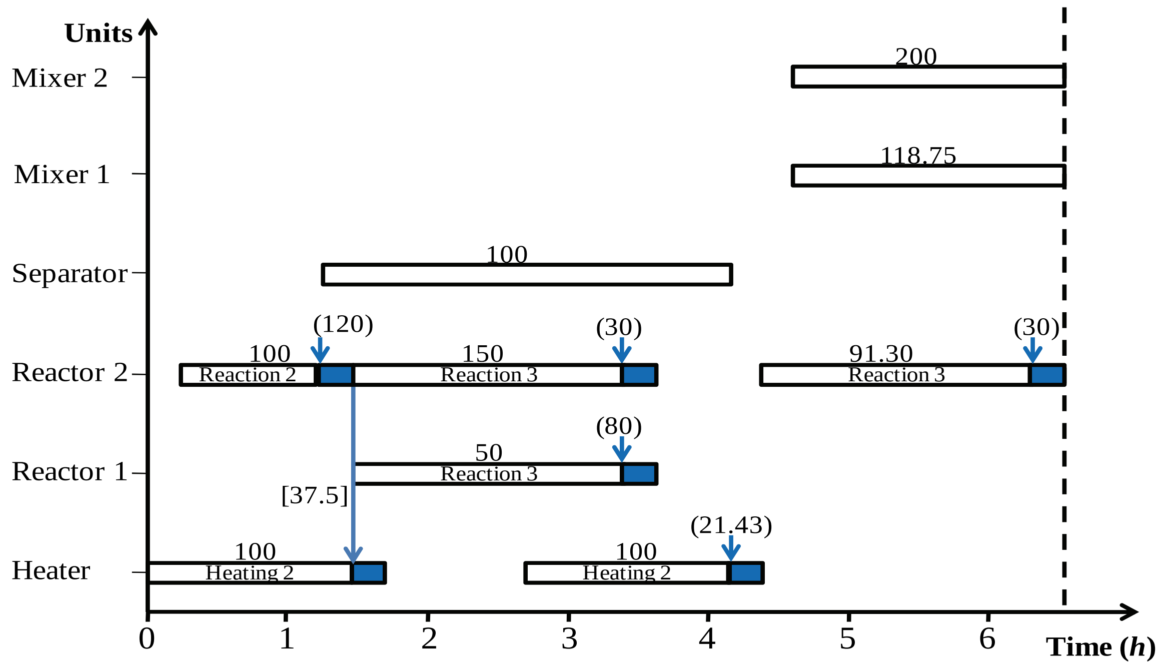

Figure 4.13: Final period without storage for the time horizon of 168h

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 minimization 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.

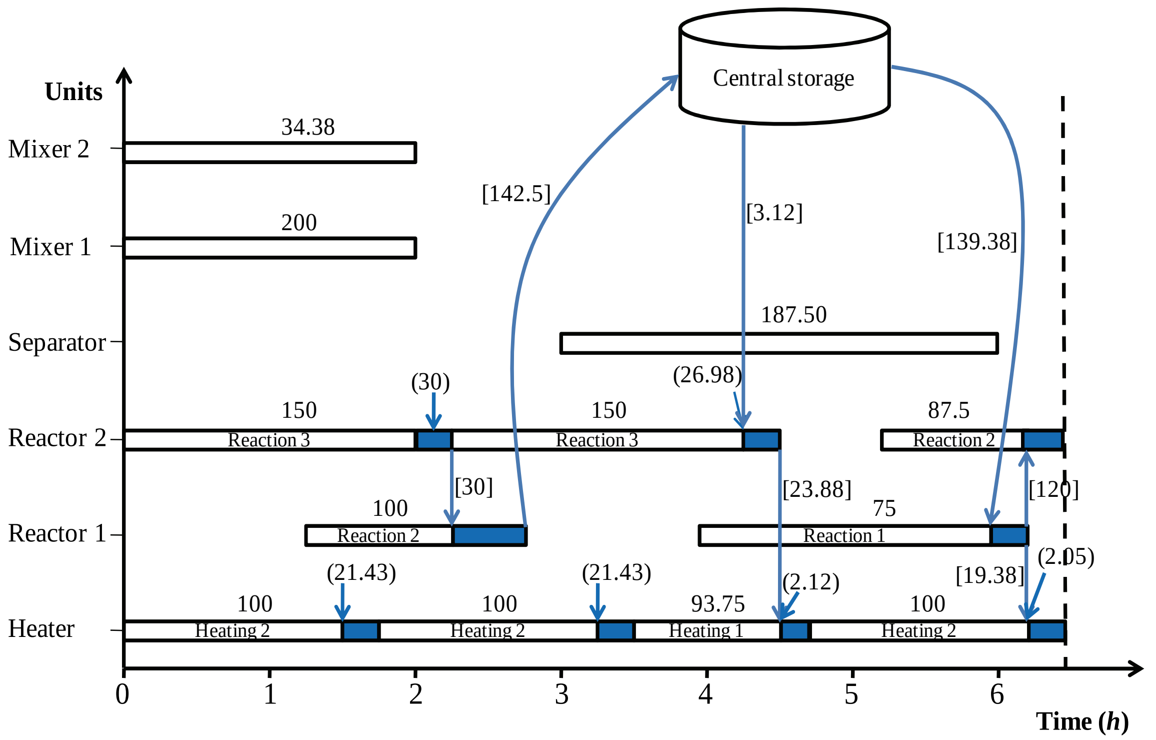

Figure 4.14: Schedule for the optimum cycle length for the case with central storage

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.

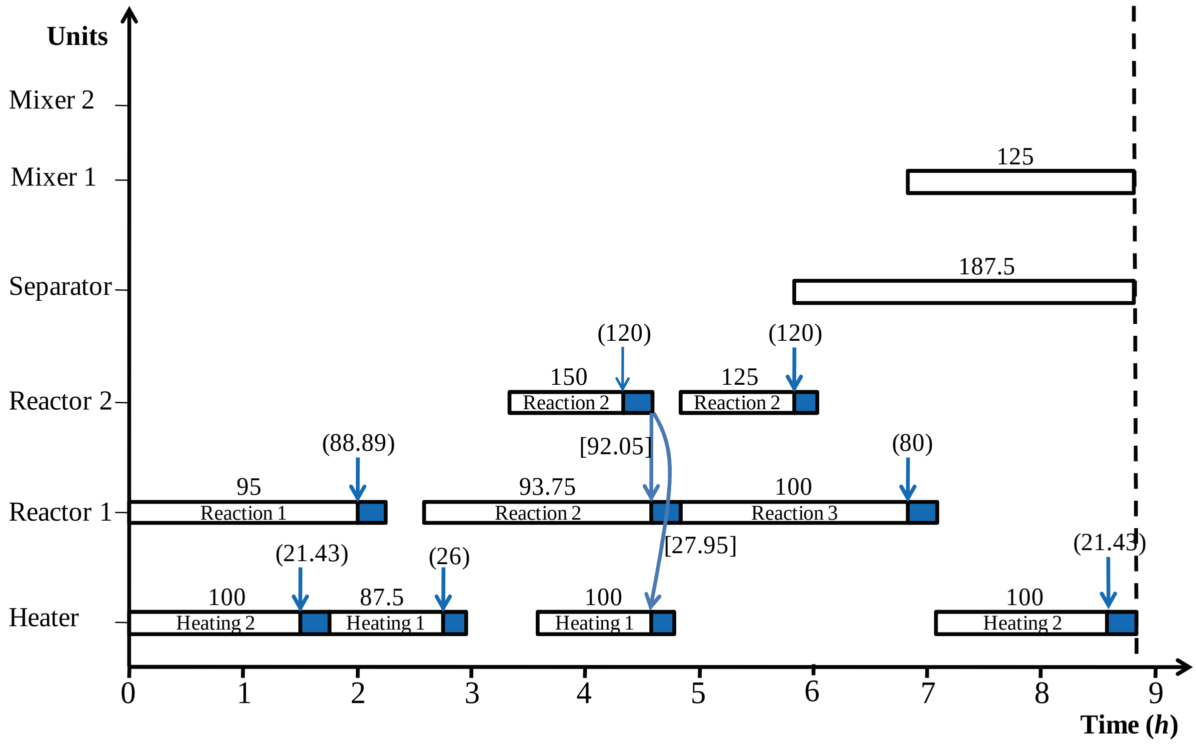

Figure 4.15: Initial period with storage

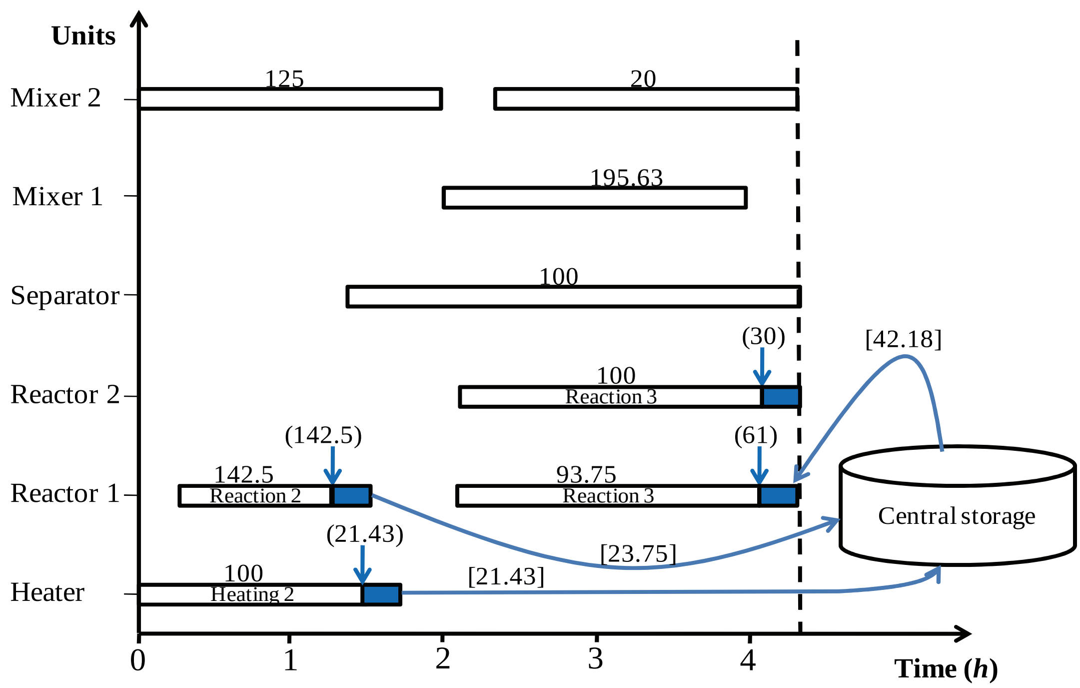

Figure 4.16: Final period with central storage present

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 minimization 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.

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CHAPTER 5

SECTION A: 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 minimization 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 was obtained from Majozi (2010) and represents 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 minimization 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 minimization 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 minimization 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.

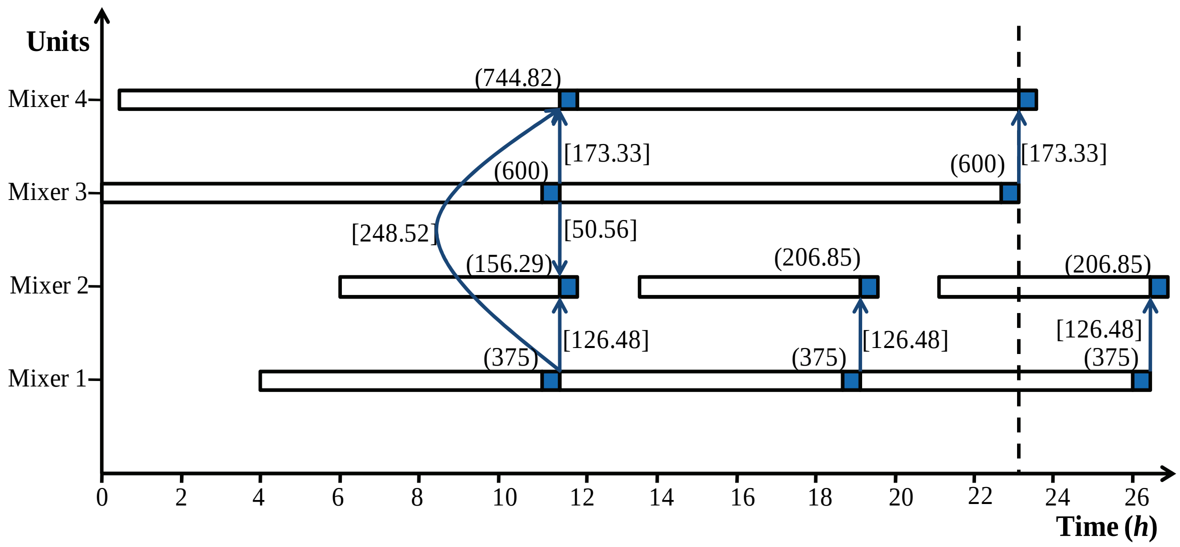


Figure 5.1: Optimum schedule for the case study without storage vessel

Wastewater minimization 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

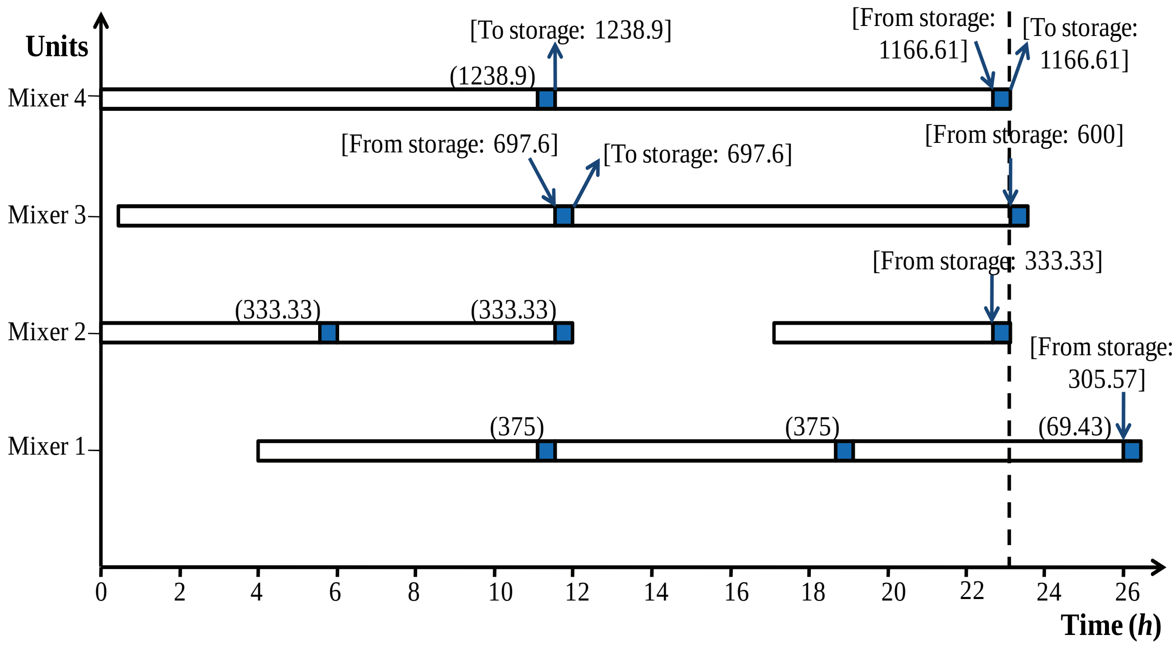


Figure 5.2: Optimum schedule in the presence of a central storage vessel

Remarks

The currently published wastewater minimization 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. (2010). *Batch chemical process integration: analysis, synthesis and optimization,* Springer, Dordrecht Heidelberg London New York.

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 6
SECTION B: METHODOLOGY DEVELOPMENT

Introduction

This chapter presents the mathematical model for wastewater minimization in batch processes that incorporates regeneration. Furthermore, the model is applicable to multiple contaminants. Majozi and Gouws (2009) developed a mathematical formulation to address wastewater minimization problems with multiple contaminants, whereby the batch production schedule and the minimum wastewater target were obtained simultaneously. Due to this advantage, the formulation is adopted and extended to include wastewater regeneration. The scheduling framework is based on the uneven discretization of the time horizon and the state sequence network, SSN representation of Majozi and Zhu (2001).

6.1 Problem statement

The problem addressed can be stated as follows:

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 necessary costs and stoichiometric data,

(iv) the contaminant mass load of each contaminant,

(v) water requirement and the cleaning duration for each unit to achieve the required cleanliness,

(vi) maximum inlet and outlet concentrations of each contaminant,

(vii) the maximum storage available for water reuse,

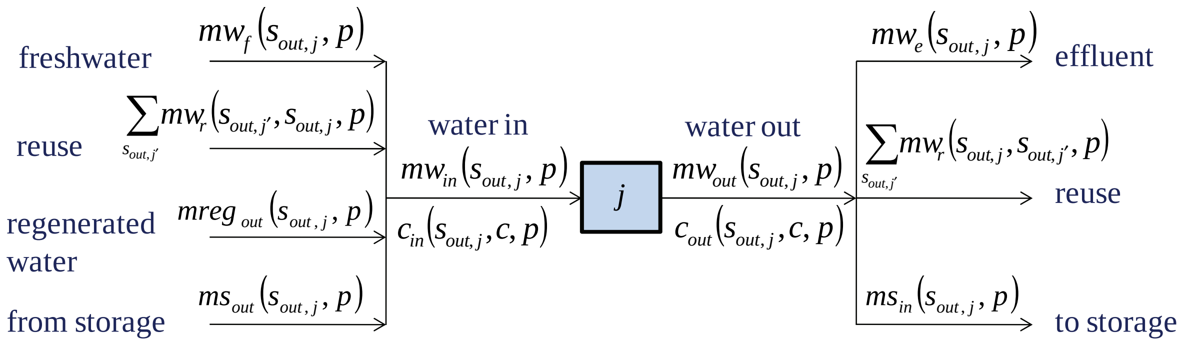
(viii) the performance of the regenerator and

(ix) the time horizon of interest.

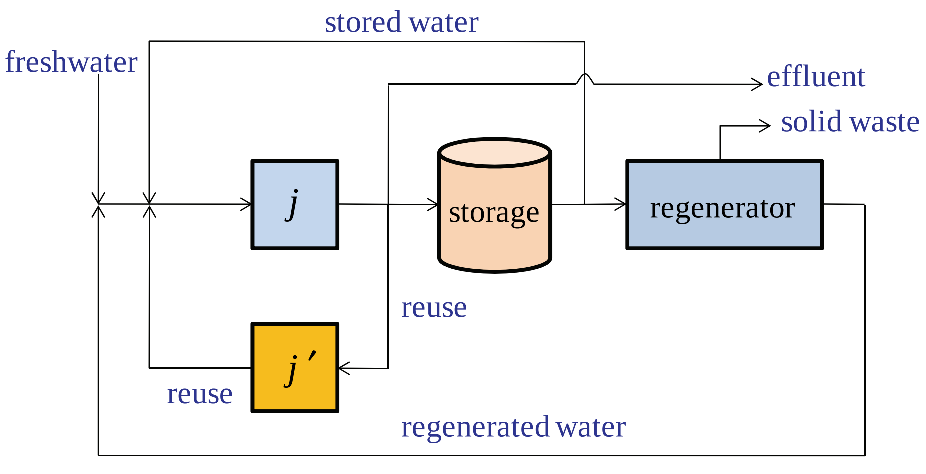
Determine the production schedule that achieves the minimum amount of wastewater generated by utilizing recycle and reuse opportunities in the presence of a central storage vessel and a wastewater regenerator.

6.2 Problem superstructure

The problem superstructure, on which the mathematical formulation is based, is illustrated in Figure 6.1. In the figure, only water-using operations which are part of a complete batch process are depicted. Unit j represents a water-using operation in which the water used consists of freshwater, regenerated water, stored water or recycle/reuse water. Water from unit j can be recycled into the same unit, reused elsewhere or sent to storage. The storage vessel can send water to a unit or to the wastewater regenerator.



(a)



(b)

Figure 6.1: Superstructure for the mathematical formulation

The philosophy of operation of the regenerator is as follows:

(i) water is sent to the regenerator provided there exists an available unit requiring that water. Whenever the regenerator is active, it operates in a continuous mode with steady inlet and outlet streams, until the sink process is satisfied,

(ii) transfer of water to the regenerator occurs to purify contaminated water because the contaminant concentration of water in storage is too high to be utilized in a unit,

(iii) the regenerator operates intermittently in the sense that it is only active if there is a unit that requires water, otherwise it remains in the passive mode and

(iv) the regenerator performance is given in terms of a constant removal ratio of contaminant.

6.3 Mathematical formulation

The constraints in the mathematical formulation are divided into three modules. The first module deals with mass balance constraints, while the second deals with sequencing and scheduling constraints. The constraints in these two modules are associated with wastewater minimization. The third module deals with scheduling of operations for production purposes. All the sets, variables and parameters used in the mathematical formulation can be found in the nomenclature.

6.3.1 Mass balance constraints

It is necessary to define the mass balances around each processing unit, the central storage vessel and the regenerator.

Mass balance around a unit j

Constraint (6.1) is the water balance over the inlet to a unit. Water entering the unit is a combination of freshwater, reuse/recycle streams from other units, j', water from storage and water from the regenerator. Constraint (6.2) states that the water leaving a unit could be recycled/reused, discarded as effluent or sent to storage. Constraint (6.3) states that the amount of water exiting a unit must equal the amount of water that entered the unit at the previous time point. This constraint captures the fact that water is not produced in the unit during the washing operation.

$$mw_{in}(s_{out,j}, p) = \sum_{s_{out,j'}} mwr(s_{out,j'}, s_{out,j}, p) + mw_f(s_{out,j}, p) + ms_{out}(s_{out,j}, p) + mreg_{out}(s_{out,j}, p) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.1}$$

$$mw_{out}(s_{out,j}, p) = \sum_{s_{out,j'}} mwr(s_{out,j}, s_{out,j'}, p) + mw_e(s_{out,j}, p) + ms_{in}(s_{out,j}, p) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.2}$$

$$mw_{in}(s_{out,j}, p-1) = mw_{out}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{6.3}$$

Constraint (6.4) defines the inlet contaminant mass balance. The contaminant mass load in the inlet stream consists of contaminant mass load in recycle/reuse water, the contaminant mass load in water from storage and the contaminant mass load in water from the regenerator. Constraint (6.5) defines the outlet contaminant mass as the mass of contaminant that entered the unit at the previous time point and the mass load of contaminant picked up in the unit during its operation.

$$mw_{in}(s_{out,j}, p) c_{in}(s_{out,j}, c, p) = \sum_{s_{out,j'}} mw_r(s_{out,j'}, s_{out,j}, p) c_{out}(s_{out,j}, c, p) + ms_{out}(s_{out,j}, p) cs_{out}(c, p) + mreg_{out}(s_{out,j}, p) cr_{out}(c, p) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \tag{6.4}$$

$$mw_{out}(s_{out,j}, p) c_{out}(s_{out,j}, c, p) = M(s_{out,j}, c) yw(s_{out,j}, p-1) + mw_{in}(s_{out,j}, p-1) c_{in}(s_{out,j}, c, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1, c \in C \tag{6.5}$$

Constraints (6.6) and (6.7) ensure that the inlet and outlet contaminant concentrations do not exceed the allowed maximum. Similarly, the maximum allowable water in a unit must not be exceeded. This is governed by Constraint (6.8). Constraints (6.9) to (6.11) restrict the mass of water entering the unit from the various sources to the maximum allowable for the unit.

Constraint (6.9) is with respect to recycle/reuse, Constraint (6.10) is with respect to water from storage while Constraint (6.11) is with respect to regenerated water.

$$c_{in}\left(s_{out,j},c,p\right)\leq C_{in}^{U}\left(s_{out,j},c\right)yw\left(s_{out,j},p\right)\forall j\in J,s_{out,j}\in S_{out,j},p\in P,c\in C \tag{6.6}$$

$$c_{out}\left(s_{out,j},c,p\right)\leq C_{out}^{U}\left(s_{out,j},c\right)yw\left(s_{out,j},p-1\right) \quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P,p>p_1,c\in C \tag{6.7}$$

$$mw_{in}\left(s_{out,j},p\right)\leq Mw^{U}\left(s_{out,j}\right)yw\left(s_{out,j},p\right)\forall j\in J,s_{out,j}\in S_{out,j},p\in P \tag{6.8}$$

$$mw_{r}\left(s_{out,j'},s_{out,j},p\right)\leq Mw^{U}\left(s_{out,j}\right)yw_{r}\left(s_{out,j'},s_{out,j},p\right) \quad \forall j,j'\in J,s_{out,j}\in S_{out,j},p\in P \tag{6.9}$$

$$ms_{out}\left(s_{out,j},p\right)\leq Mw^{U}\left(s_{out,j}\right)ys_{out}\left(s_{out,j},p\right) \quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P \tag{6.10}$$

$$mreg_{out}\left(s_{out,j},p\right)\leq Mw^{U}\left(s_{out,j}\right)yreg_{out}\left(s_{out,j},p\right) \quad \forall j\in J,s_{out,j}\in S_{out,j},p\in P \tag{6.11}$$

The maximum quantity of water into a unit is represented by Equation (6.12). It is important to note that for multiple 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.

$$Mw^{U}\left(s_{out,j}\right)=\max_{c\in C}\left\{\frac{M\left(s_{out,j},c\right)}{C_{out}^{U}\left(s_{out,j},c\right)-C_{in}^{U}\left(s_{out,j},c\right)}\right\},\forall j\in J,s_{out,j}\in S_{out,j} \tag{6.12}$$

Mass balance around central storage

Constraint (6.13) is the water mass balance around the storage tank. The amount of water stored in the storage tank consists of water stored at the previous time point and the difference between water entering the storage tank from processing unit and water leaving the storage tank either to processing unit or regenerator. Constraint (6.14) defines the initial amount of water in the tank.

$$qw_s(p) = qw_s(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j}, p) - \sum_{s_{out,j}} ms_{out}(s_{out,j}, p) - \sum_{s_{out,j}} mreg_{in}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{6.13}$$

$$qw_s(p_1) = Qw_s^o - \sum_{s_{out,j}} ms_{out}(s_{out,j}, p_1) - \sum_{s_{out,j}} mreg_{in}(s_{out,j}, p_1) \quad \forall j \in J, s_{out,j} \in S_{out,j} \tag{6.14}$$

The definition of the inlet contaminant concentration to the storage tank is given in Constraint (6.15). The concentration of water exiting the storage tank is assumed to be equal to the concentration of water in the tank as given in Constraint (6.16). This condition is true in the case of perfect mixing. The initial concentration in the storage tank is given in Constraint (6.17). Constraints (6.18) and (6.19) ensure that the maximum capacity of the tank is not exceeded.

$$cs_{in}(c, p) = \frac{\sum_{s_{out,j}} \left(ms_{in}(s_{out,j}, p) c_{out}(s_{out,j}, c, p)\right)}{\sum_{s_{out,j}} ms_{in}(s_{out,j}, p)} \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \ c \in C \tag{6.15}$$

$$cs_{out}(c, p) = \frac{qw_s(p-1) cs_{out}(c, p-1) + \left(\sum_{s_{out,j}} ms_{in}(s_{out,j}, p)\right) cs_{in}(c, p)}{qw_s(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j}, p)} \quad \forall \ j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1, c \in C \tag{6.16}$$

$$cs_{out}(c, p_1) = CS_{out}^o(c) \forall c \in C \tag{6.17}$$

$$qw_s(p) \le Qw_s^U \quad \forall \ p \in P \tag{6.18}$$

$$ms_{in}(s_{out,j}, p) \le Qw_s^U {}_s ys_{in}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.19}$$

Constraint (6.20) ensures that no water is stored in the storage vessel at the end of the time horizon. This is in order to give a true optimum, otherwise the minimum target could be misleading.

$$qw_s(p) = 0 \quad \forall\ p = |P| \tag{6.20}$$

Mass balance around the regenerator

Constraint (6.21) states that the total amount of outlet water from the regenerator at time point p consists of the total amount of inlet water to the regenerator at the previous time point. This constraint captures the assumption that during the operation of the regenerator, no water is produced or lost.

$$\sum_{s_{out,j}} mreg_{in}(s_{out,j}, p-1) = \sum_{s_{out,j}} mreg_{out}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{6.21}$$

The performance of the regenerator is given in terms of the removal ratio of contaminant, which specifies a constant ratio between the inlet and outlet mass of contaminant. This is stated in Constraint (6.22) for a constant regenerator flowrate.

$$cr_{out}(c, p) = cs_{out}(c, p-1)(1 - RR(c)) \quad \forall\ c \in C, p \in P, p > p_1 \tag{6.22}$$

The contaminant mass balance around the regenerator is expressed in Constraint (6.23). The contaminant mass load exiting the regenerator to a unit is the difference between the contaminant mass load entering the regenerator and the contaminant mass removed from the water during regeneration, $m_{dirt}(c,p)$.

$$cs_{out}(c, p-1)\sum_{s_{out,j}} mreg_{in}(s_{out,j}, p-1) = cr_{out}(c, p)\sum_{s_{out,j}} mreg_{out}(s_{out,j}, p) + m_{dirt}(c, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{6.23}$$

6.3.2 Sequencing and scheduling constraints

The scheduling constraints take care of the time dimension associated with batch processes. The scheduling aspects of the model are divided into four groups as follows:

- those related to task scheduling,
- those that cater for recycle/reuse,
- those that account for the central storage vessel and
- those that account for the regenerator.

Task scheduling

These constraints ensure that each water-using operation is integrated with production scheduling. Constraints (6.24) and (6.25) together ensure that unit j is washed immediately after the task that produced $s_{out,j}$. Constraints assuming the form of Constraints (6.24) or (6.25) are called big-M constraints. If water is used in the unit, $yw(s_{out,j}, p)$ has a value of 1 causing Constraints (6.24) and (6.25) to become active and the start time of washing is forced to coincide with the end time of production. Otherwise, when water is not used in the unit, i.e., $yw(s_{out,j}, p)$ has a value of zero, the two constraints become relaxed. Constraint (6.26) defines the duration of the washing operation performed in unit j. Constraint (6.27) 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.

$$tw_{in}(s_{out,j}, p) \geq t_{out}(s_{out,j}, p) - H(1 - yw(s_{out,j}, p)) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.24)$$

$$tw_{in}(s_{out,j}, p) \leq t_{out}(s_{out,j}, p) + H(1 - yw(s_{out,j}, p)) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.25)$$

$$tw_{out}(s_{out,j}, p) = tw_{in}(s_{out,j}, p-1) + \tau w(s_{out,j}) yw(s_{out,j}, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (6.26)$$

$$yw(s_{out,j}, p) = y(s^{*}_{in,j}, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, s^{*}_{in,j} \in S^{*}_{in.j} \rightarrow s_{out,j}, p \in P, p > p_1 \quad (6.27)$$

Recycle/reuse scheduling

Wastewater can only be directly recycled/reused if the unit producing wastewater and the unit receiving wastewater finish operating and begin operating at the same time respectively. Constraint (6.28) describes the relationship between usage of water in a unit and the opportunity for recycle and reuse. The constraint states that for a unit *j* to transfer water to unit j', unit j' should require water at that time point. It does not, however, mean that unit j' must use water from unit *j*, it could still obtain water from other sources. Constraints (6.29) and (6.30) state that the time at which water recycle/reuse takes place coincides with the time at which the water is produced. Constraints (6.31) and (6.32) ensure that the time at which water recycle/reuse takes place coincides with the starting time of the unit receiving the water.

$$yw_r\left(s_{out,j}, s_{out,j'}, p\right) \le yw\left(s_{out,j'}, p\right) \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.28}$$

$$tw_r\left(s_{out,j}, s_{out,j'}, p\right) \le tw_{out}\left(s_{out,j}, p\right) - H\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.29}$$

$$tw_r\left(s_{out,j}, s_{out,j'}, p\right) \ge tw_{out}\left(s_{out,j}, p\right) - H\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.30}$$

$$tw_r\left(s_{out,j}, s_{out,j'}, p\right) \le tw_{in}\left(s_{out,j}, p\right) + H\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.31}$$

$$tw_r\left(s_{out,j}, s_{out,j'}, p\right) \ge tw_{in}\left(s_{out,j}, p\right) - H\left(1 - yw_r\left(s_{out,j}, s_{out,j'}, p\right)\right) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.32}$$

Central storage scheduling

Constraint (6.33) relates water usage in a unit and water transfer from storage. It states that water can only be transferred to a unit if it uses water at the same time point. However it is not a prerequisite for the unit to use stored water, the water could be provided from other sources. Constraints (6.34) and (6.35) ensure that the time at which water is sent from storage to a unit coincides with the start time of washing of the same unit.

$$ys_{out}\left(s_{out,j}, p\right) \le yw\left(s_{out,j}, p\right) \quad \forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P \tag{6.33}$$

$$ts_{out}\left(s_{out,j}, p\right) \ge tw_{in}\left(s_{out,j}, p\right) - H\left(2 - ys_{out}\left(s_{out,j}, p\right) - yw\left(s_{out,j}, p\right)\right)$$
$$\forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P \tag{6.34}$$

$$ts_{out}\left(s_{out,j}, p\right) \le tw_{in}\left(s_{out,j}, p\right) + H\left(2 - ys_{out}\left(s_{out,j}, p\right) - yw\left(s_{out,j}, p\right)\right)$$
$$\forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P \tag{6.35}$$

Constraint (6.36) relates water usage in a unit and water transfer to storage. It states that water can only be transferred from a unit to storage if the unit used water at the previous time point. However, washing can take place in the unit without discharging water to the storage tank. The water could be discharged to other sinks. Constraints (6.37) and (6.38) ensure that the time at which water is sent to storage from a unit must coincide with the finishing time of washing of the same unit.

$$ys_{in}\left(s_{out,j}, p\right) \le yw\left(s_{out,j}, p-1\right) \quad \forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P, p > p_1 \tag{6.36}$$

$$ts_{in}\left(s_{out,j}, p\right) \ge tw_{out}\left(s_{out,j}, p\right) - H\left(2 - ys_{out}\left(s_{out,j}, p\right) - yw\left(s_{out,j}, p-1\right)\right)$$
$$\forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P, p > p_1 \tag{6.37}$$

$$ts_{in}\left(s_{out,j}, p\right) \le tw_{out}\left(s_{out,j}, p\right) + H\left(2 - ys_{out}\left(s_{out,j}, p\right) - y\left(s_{out,j}, p-1\right)\right)$$
$$\forall\ j \in J,\ s_{out,j} \in S_{out,j},\ p \in P, p > p_1 \tag{6.38}$$

If water is transferred from storage to a unit at a later time point, the time at which this happens must correspond to a later time in the time horizon. This is specified in Constraint (6.39). Constraint (6.40) ensures that if water is transferred from a unit to storage at a later time point, the time at which this happens corresponds to a later time in the time horizon.

$$ts_{out}(s_{out,j}, p) \ge ts_{out}(s_{out,j'}, p') - H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p'))$$
$$\forall\ j, j' \in J,\ s_{out,j} \in S_{out,j},\ p, p' \in P, p \ge p' \tag{6.39}$$

$$ts_{in}(s_{out,j}, p) \geq ts_{in}(s_{out,j'}, p') - H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p'))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (6.40)$$

Constraints (6.41) and (6.42) state that if water is transferred to storage from more than one unit at the same time point, the time at which they do so must coincide. Constraints (6.43) and (6.44) state that if water is discharged from storage to more than one unit at the same time point, the time at which the water is discharged must coincide.

$$ts_{in}(s_{out,j}, p) \geq ts_{in}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.41)$$

$$ts_{in}(s_{out,j}, p) \leq ts_{in}(s_{out,j'}, p) + H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.42)$$

$$ts_{out}(s_{out,j}, p) \geq ts_{out}(s_{out,j'}, p) - H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.43)$$

$$ts_{out}(s_{out,j}, p) \leq ts_{out}(s_{out,j'}, p) + H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.44)$$

If water is simultaneously being transferred to and discharged from storage, the time at which these happen should coincide. This is given in Constraints (6.45) and (6.46).

$$ts_{in}(s_{out,j}, p) \geq ts_{out}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.45)$$

$$ts_{in}(s_{out,j}, p) \leq ts_{out}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j'}, p) - ys_{out}(s_{out,j'}, p))$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (6.46)$$

Constraint (6.47) ensures that if water leaves storage at a later time point compared to water entering storage, the time at which water leaves storage must correspond to a later time in the time horizon.

$$ts_{out}\left(s_{out,j}, p\right) \geq ts_{in}\left(s_{out,j'}, p'\right) - H\left(2 - ys_{out}\left(s_{out,j}, p\right) - ys_{in}\left(s_{out,j'}, p'\right)\right)$$
$$\forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \qquad (6.47)$$

Regenerator scheduling

Constraint (6.48) defines the relationship between transfer of water to the regenerator and discharge of water from the regenerator. It should be reemphasised at this point that water is only transferred to the regenerator provided that there is a unit available downstream requiring that water and the concentration in the storage unit must exceed the maximum allowed inlet concentration in the receiving unit. Hence, the water transferred to the regenerator at any time is in terms of an available unit. Constraints (6.49) and (6.50) ensure that the time at which water is discharged from the regenerator to a unit coincides with the time at which the unit starts to use water. Constraint (6.51) gives the duration of regeneration.

$$yreg_{out}\left(s_{out,j}, p\right) = yreg_{in}\left(s_{out,j}, p-1\right) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (6.48)$$

$$treg_{out}\left(s_{out,j}, p\right) \leq tw_{in}\left(s_{out,j}, p\right) + H\left(2 - yreg_{out}\left(s_{out,j}, p\right) - yw\left(s_{out,j}, p\right)\right)$$
$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (6.49)$$

$$treg_{out}\left(s_{out,j}, p\right) \geq tw_{in}\left(s_{out,j}, p\right) - H\left(2 - yreg_{out}\left(s_{out,j}, p\right) - yw\left(s_{out,j}, p\right)\right)$$
$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (6.50)$$

$$treg_{out}\left(s_{out,j}, p\right) = treg_{in}\left(s_{out,j}, p-1\right) + \left[\frac{\sum_{s_{out,j}} mreg_{in}\left(s_{out,j}, p-1\right)}{freg}\right] yreg_{in}\left(s_{out,j}, p-1\right) \qquad (6.51)$$
$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1$$

Constraint (6.52) ensures that storage does not supply a unit with water through the regenerator and also supply water directly to the unit at the same time point. If the unit is directly supplied with water from storage, the need to regenerate water no longer exists. Constraint (6.53) is included to ensure that the full potential for wastewater regeneration is realised. It states that a unit does not receive water from both the storage tank and the regenerator at the same time point. This is to avoid unnecessary mixing.

$$yreg_{in}\left(s_{out,j}, p\right) + ys_{out}\left(s_{out,j}, p\right) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \qquad (6.52)$$

$$yreg_{out}\left(s_{out,j}, p\right) + ys_{out}\left(s_{out,j}, p\right) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.53}$$

Constraint (6.54) together with Constraint (6.48) defines the relationship between the usage of water in a unit and the regeneration of water for the unit. Constraint (6.54) states that for water to be charged to the regenerator from storage, the unit requiring the water should begin operation at the next time point. This however, does not mean that the unit cannot begin operation without regenerated water, since water required could be provided from other sources.

$$yw\left(s_{out,j}, p\right) \geq yreg_{in}\left(s_{out,j}, p-1\right) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{6.54}$$

Constraint (6.55) ensures that if water is charged to the regenerator at a later time point, the time at which it does so is at a later time in the time horizon. Constraint (6.56) is similar, but it applies to the time at which water is discharged from the regenerator.

$$\begin{aligned} treg_{in}\left(s_{out,j}, p\right) \geq treg_{in}\left(s_{out,j'}, p'\right) + H\left(2 - yreg_{in}\left(s_{out,j}, p\right) - yreg_{in}\left(s_{out,j'}, p'\right)\right) \\ \forall \quad j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \end{aligned} \tag{6.55}$$

$$\begin{aligned} treg_{out}\left(s_{out,j}, p\right) \leq treg_{out}\left(s_{out,j'}, p'\right) + H\left(2 - yreg_{out}\left(s_{out,j}, p\right) - yreg_{out}\left(s_{out,j'}, p'\right)\right) \\ \forall \quad j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \end{aligned} \tag{6.56}$$

6.3.3 Production scheduling constraints

The constraints in this section have been extracted from the work by Majozi and Zhu (2001). They are presented here briefly.

Capacity constraint

The capacity constraint given in Constraint (6.57) ensures that the amount of material processed in unit *j* at any time point *p* does not exceed the maximum capacity of the unit.

$$V_j^L y\left(s_{in,j}^*, p\right) \le \sum_{s_{in,j}} m_{in}\left(s_{in,j}, p\right) \le V_j^U y\left(s_{in,j}^*, p\right)$$
$$\forall j \in J, s_{in,j} \in S_{in,j}, s_{in,j}^* \in S_{in,j}^*, p \in P \qquad (6.57)$$

Material balance constraints

Constraints (6.58) to (6.64) are the mass balance constraints. These constraints ensure the conservation of mass around each unit.

$$\sum_{s_{in,j}} m_{in}\left(s_{in,j}, p-1\right) = \sum_{s_{out,j}} m_{out}\left(s_{out,j}, p\right)$$
$$\forall j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (6.58)$$

$$q_s(s, p_1) = Q_s^0(s) - m_{in}(s, p_1) \qquad s \neq product, \forall s \in S \qquad (6.59)$$

$$q_s(s, p) = q_s(s, p-1) - m_{in}(s, p) \qquad s = feed, \forall s \in S, p \in P, p > p_1 \qquad (6.60)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - m_{in}(s, p)$$
$$s \neq product, feed, \forall s \in S, p \in P, p > p_1 \qquad (6.61)$$

$$q_s(s, p_1) = Q_s^0(s) - d(s, p_1) \qquad s = product, \forall s \in S \qquad (6.62)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - d(s, p)$$
$$s = product, byproduct, \forall s \in S, p \in P, p > p_1 \qquad (6.63)$$

$$q_s(s, p) \le Q^U, \forall s \in S, p \in P \qquad (6.64)$$

Duration constraints

This constraint addresses the intrinsic aspects of time in batch plants. Constraint (6.65) states that the time at which a particular state is produced is dependent on the duration of the task that produces the same state.

$$t_{out}\left(s_{out,j}, p\right) = t_{in}\left(s_{in,j}^*, p-1\right) + \tau\left(s_{in,j}^*\right) y\left(s_{in,j}^*, p-1\right),$$
$$\forall j \in J, s_{in,j} \in S_{in,j}, s_{in,j}^* \in S_{in,j}^*, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \qquad (6.65)$$

6.3.4 Feasibility and time horizon constraints

Constraint (6.66) ensures that if a processing unit j is reusing water from unit j' at time point p, then unit j' cannot reuse water from unit j at the same time point. Constraint (6.67) ensures that at a certain time point both the charging of the regenerator and the discharging from the regenerator on behalf of a particular unit cannot take place at the same time point.

$$yw_r(s_{out,j}, s_{out,j'}, p) + yw_r(s_{out,j'}, s_{out,j}, p) \leq 1 \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.66}$$

$$yreg_{in}(s_{out,j}, p) + yreg_{out}(s_{out,j}, p) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.67}$$

Constraints (6.68) to (6.74) ensure that each event occurs within the time horizon of time of interest.

$$tw_{in}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.68}$$

$$tw_{out}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.69}$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq H \quad \forall\ j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.70}$$

$$ts_{in}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.71}$$

$$ts_{out}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.72}$$

$$treg_{in}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.73}$$

$$treg_{out}(s_{out,j}, p) \leq H \quad \forall\ j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{6.74}$$

6.3.5 Objective function

The objective of the formulation depends on whether the production is given or not. In the situation where production is not given, the objective function is expressed as Constraint (6.75). This objective here is the maximization of profit while taking into account freshwater and effluent treatment costs.

$$Max \sum_{s} \sum_{p} CP(s) d(s,p) - CF \sum_{s_{out,j}} \sum_{p} mw_f \left(s_{out,j}, p \right) - CE \sum_{s_{out,j}} \sum_{p} mw_e \left(s_{out,j}, p \right) \qquad (6.75)$$

Constraint (6.76) is the objective function when the production is given. It is the minimization of effluent.

$$Min \sum_{p} \left(\sum_{s_{out,j}} mw_e \left(s_{out,j}, p \right) \right) \qquad (6.76)$$

Due to Constraints (6.4), (6.5), (6.15), (6.16) and (6.23) which involve bilinear terms, the presented mathematical formulation is a MINLP. The method proposed by Majozi and Gouws (2009) was to solve the MINLP using a two step procedure in which the MINLP problem was linearized and solved as a MILP to provide a starting point for the exact MINLP problem. The method of linearization is discussed in the Appendix.

6.4 Practical application

Firstly, it is important to identify the section of the plant to which this methodology will be applied. To apply the presented regeneration methodology practically, information about the operation of the plant as stipulated in Section 6.1 is necessary. These values can be obtained based on thermodynamic data (inlet and outlet concentrations) or based on experience from working on the plant. The contaminants present on the plant should be identified and a careful consideration should be made about what kind of regenerator to use. The removal ratio for contaminants in the regenerator can be set from information about the purity level obtainable from the chosen regenerator.

Next, the minimum wastewater target and the corresponding batch production schedule are determined from the application of the methodology. Once these have been obtained, the plant can be set up in like manner physically.

In Chapter 7, the methodology is applied to a few case studies to strengthen and test this point.

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CHAPTER 7

SECTION B: CASE STUDIES

In this chapter the application of the regeneration methodology is demonstrated through two problems, one from literature and the other from a practical production facility.

7.1 Literature example

The example considered is a well-published multipurpose facility which is commonly known as BATCH 1 in literature. The facility consists of three different chemical reactions which can be performed in two common reactors. In addition, a heater exists for heating Feed A before reaction and a separator exists to purify product from Reaction 3. The STN and SSN representation for the literature example are given in Figure 7.1.

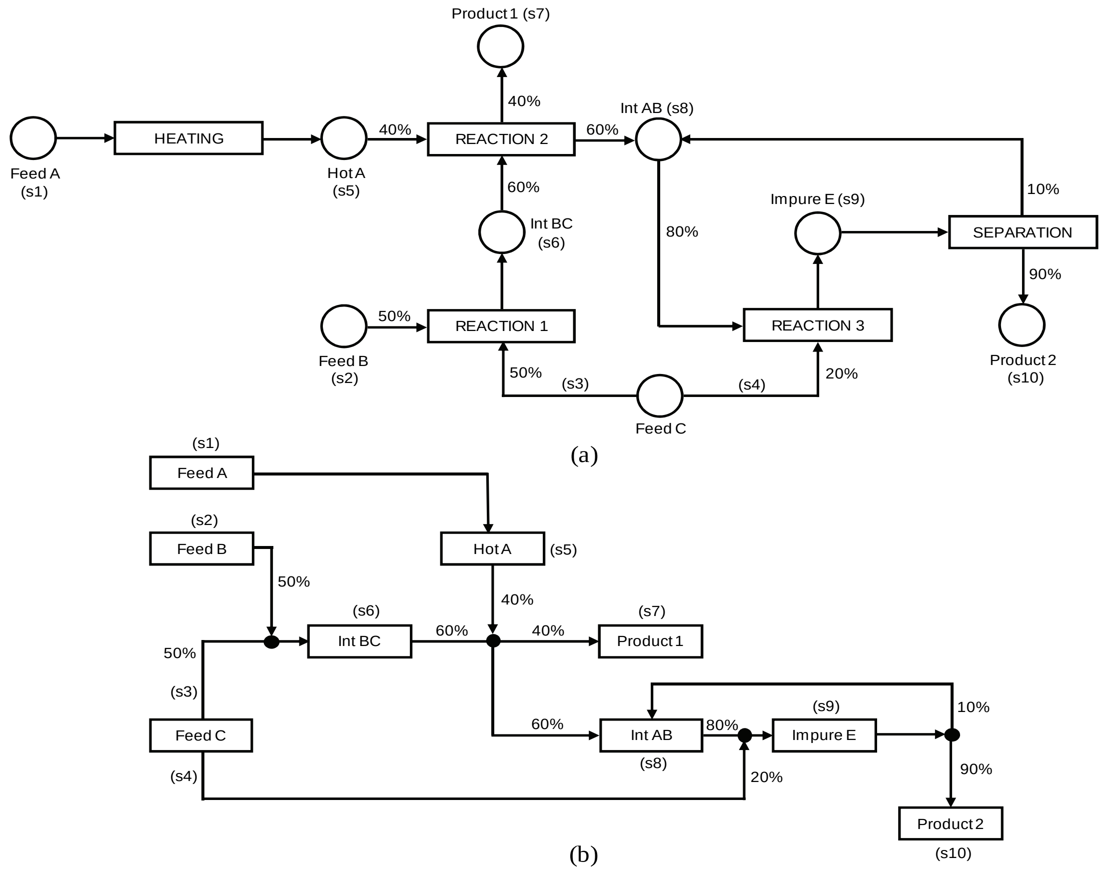

Figure 7.1: (a) STN and (b) SSN for the literature example

The data required for production scheduling are given Table 7.1.

Table 7.1: Data required for production scheduling in literature 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

Similar to the work by Majozi and Gouws (2009), the philosophy is that after a reaction has taken place in a reactor, the reactor must be washed before another reaction can take place. This ensures that any product residue is removed to ensure the integrity of subsequent product. Data pertaining to the washing operations is given in Table 7.2. In addition, the cost of freshwater is given as 2 c.u./kg water whilst the effluent treatment cost is 3 c.u./kg.

A central storage tank for wastewater is available with a capacity of 200 kg. The flowrate of the regenerator is given to be 100 kg/h. The removal ratios of the various contaminants are provided in Table 7.3. The objective function is the maximization of profit as given in Constraint (6.75). The time horizon of interest is 10 h.

Table 7.2: Wastewater minimization data for literature example

		Maximum concentration (g contaminant/kg water)		
		Contaminant 1	Contaminant 2	Contaminant 3
Reaction 1 (Reactor 1)	Max. inlet	0.5	0.5	2.3
	Max. outlet	1	0.9	3
Reaction 2 (Reactor 1)	Max. inlet	0.01	0.05	0.3
	Max. outlet	0.2	0.1	1.2
Reaction 3 (Reactor 1)	Max. inlet	0.15	0.2	0.35
	Max. outlet	0.3	1	1.2
Reaction 1 (Reactor 2)	Max. inlet	0.05	0.2	0.05
	Max. outlet	0.1	1	12
Reaction 2 (Reactor 2)	Max. inlet	0.03	0.1	0.2
	Max. outlet	0.075	0.2	1
Reaction 3 (Reactor 2)	Max. inlet	0.3	0.6	1.5
	Max. outlet	2	1.5	2.5
		Mass load (g)		
		Contaminant 1	Contaminant 2	Contaminant 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

Table 7.3: Removal ratio of contaminants

Contaminant	**Removal ratio**
Contaminant 1	0.98
Contaminant 2	0.97
Contaminant 3	0.96

7.1.1 Results and discussion

The resulting model for the literature example was formulated in GAMS 22.0 and solved using the DICOPT2 algorithm, with CPLEX 9.1.2 as the MIP solver and CONOPT3 as the NLP solver. The model had 532 binary variables. The optimum number of time points was 10. The value of the objective function, the maximization of profit in Constraint (6.75), was 21129 c.u.

The optimum amount of freshwater used was 401.7 kg. If regeneration was not considered the objective function was 20180 c.u. with an optimum freshwater usage of 479 kg. The incorporation of the regenerator resulted in a 4.7% increase in profit and a 19.24% decrease in effluent production. The solution time was 46.3 seconds using a Pentium 4, 3.4 GHz processor. The schedule corresponding to the MILP was infeasible. Hence, the resulting solution of 21129 c. u. is a local optimum. The schedule obtained from the optimization is shown in Figure. 7.2.

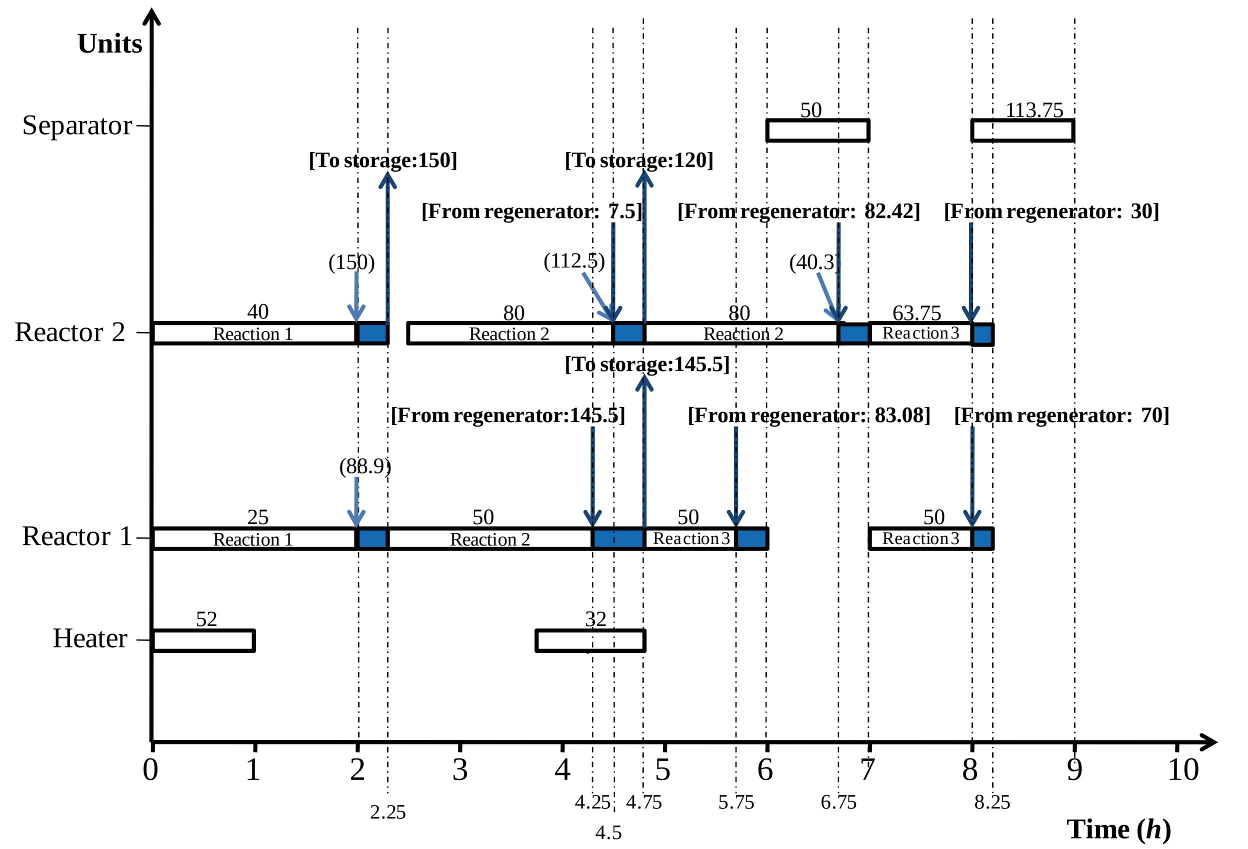

Figure 7.2: Resulting production schedule for literature example

In Figure 7.2, the clear blocks represent the production operation in the unit while the dark blocks represent the washing operation in the unit. The numbers above the clear blocks represent the amount of material used in the unit for production. The numbers in brackets represent freshwater, the sum of these amount to 401.7 kg, hence the target. Water transfer to and from storage as well as water transfer from regenerator have been clearly labelled.

From Figure 7.2, it can be seen that reaction 1 occurs twice and reactions 2 and 3 occur thrice. The water used for washing Reactors 1 and 2 (R1 and R2) consists of freshwater only. 150 kg of water produced in R2 after washing is sent to storage at 2.25h. This provides opportunity for indirect water reuse or wastewater regeneration. The storage tank discharges 145.5 kg of water to the regenerator with respect to R1 at 2.80h. Regenerated water is discharged to R1 at 4.25h for washing. The storage tank later discharges 7.5 kg of water to the regenerator with respect to R2 at 4.43h. Regenerated water is discharged to R2 at 4.5h for washing. A similar scenario is encountered with water sent to storage from R2 and R1 at 4.75h. Regenerated water is utilized in the later washing operations that follow. It can be observed from this solution that direct water reuse between units did not occur.

7.2 Industrial case study

This case study is based on a section of a pharmaceuticals production plant which produces 4 types of products, viz., shampoos, deodorants, lotions and creams (Majozi, 2010). 4 mixers for product mixing were available in this section. Each product was produced by a specific mixer. Mixer 1 was dedicated to the mixing of shampoos, mixer 2 was dedicated to the mixing of deodorants, mixer 3 was dedicated to the mixing of lotions and mixer 4 was dedicated to the mixing of creams. The general production procedure is as follows. Raw material is charged to a mixer. The raw material is then mixed until the required physical characteristics are obtained. Once a product is mixed, it is removed and stored. The mixers are then washed. There is sufficient storage available for product. The typical production requirement over a 24 hour time horizon is given in Table 7.4. In Table 7.4, the average production time for each product is also given.

The data pertaining to wastewater minimization is given in Table 7.5 together with the residue mass left in each mixer after product has been removed. These are average values taken from actual process data. The maximum outlet concentrations from each mixer are also given. It is important to note that there is maximum outlet concentration defined for only one component from each mixer. This is since each mixer will at any point only contain residue of a specific product. Also given is the maximum contaminant load that can enter with the water for a cleaning operation. In this problem, the residue left from the specific product in a mixer accounts for the contaminant mass added to water. This then makes the limiting component in each mixer the component that leaves residue in the mixer. For example mixer 1 has shampoo as the limiting contaminant, since this is the only component which leaves a residue in the mixer. The limiting amount of water for each mixer is calculated using Equation (6.12) and is given for each mixer in Table 7.5.

A central storage vessel with a capacity of 10 tons is available for storing wastewater used for washing. The washing of each mixer takes 30 minutes.

Table 7.4: Production data for industrial case study

Mixer	Product	Number of batches	Duration (h)
1	Shampoo	2	7
2	Deodorant	3	5.5
3	Lotion	1	11
4	Cream	2	11

Table 7.5: Wastewater minimization data for industrial case study

Mixer	Contaminant	Residue mass (kg)	Limiting water (kg)	C^{max} outlet (kg/kg)
	Shampoos	15	576.9	0.04
2	Deodorants	15	361.4	0.045
3	Lotions	30	697.6	0.05
4	Creams	70	1238.9	0.06

The maximum inlet concentration of each mixer is given in Table 7.6. In this case, the maximum inlet concentration of deodorant in mixers 1, 3 and 4 is set to zero. This is because the reuse of wastewater containing deodorant in a mixer with any other residue is undesirable. However, wastewater containing deodorant can be reused in a cleaning operation in mixer 2, containing another deodorant residue.

Table 7.6: Maximum inlet concentrations for cleaning operation in the industrial case study

Mixer	Shampoo (kg product/ kg water)	Deodorant (kg product/ kg water)	Lotion (kg product/ kg water)	Creams (kg product/ 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

A regenerator with a flowrate of 466 kg/h is available. The removal ratio of the various contaminants is given in Table 7.7.

Table 7.7: Removal ratio of contaminants

Contaminant	Removal ratio
Shampoo	0.95
Deodorant	0.99
Lotion	0.96
Cream	0.98

7.2.1 Results and discussion

The industrial case study was formulated using the presented methodology in GAMS 22.0 and solved using the DICOPT2 algorithm, with CPLEX 9.1.2 as the MIP and CONOPT3 as the NLP solvers. The resulting model had 576 binary variables. The optimum number of time points was 16. The value of the objective function, which was the minimization of effluent as given in Constraint (6.76), was 2653 kg of water. If regeneration was not considered the objective function was 3587 kg of water. The incorporation of the regenerator resulted in a 26% decrease in effluent production. The solution time was 464 seconds using a Pentium 4, 3.4 GHz processor. The schedule corresponding to the MILP was infeasible. Hence, the resulting solution of 2653 kg is a local optimum.

The resulting schedule of the solution is given in Figure 7.3. The clear blocks represent the production operation in the unit while the dark blocks represent the washing operation in the unit. The numbers in round brackets represent freshwater. The sum of these amount to 2653 kg, hence the target. The numbers in square brackets represent direct reuse water. Water transfer to and from storage as well as water transfer from regenerator have been clearly labelled.

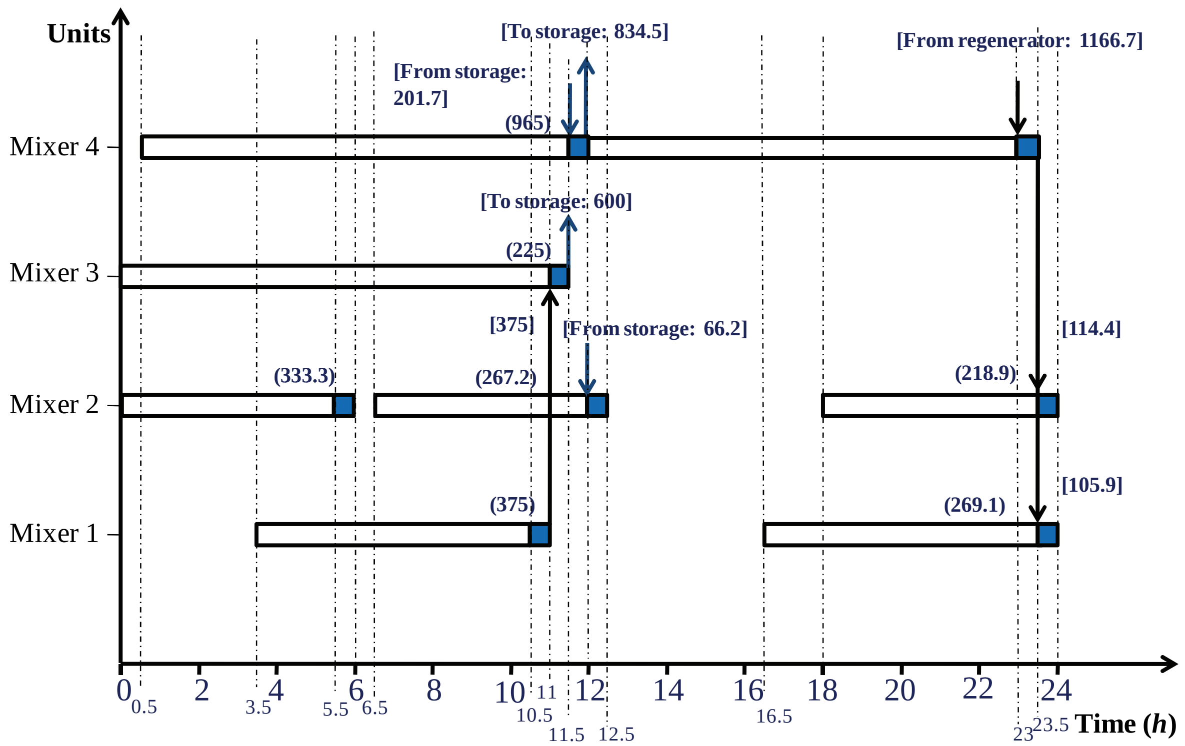

Figure 7.3: Production schedule for the industrial case study

From the Gantt chart in Figure 7.3, it can be observed that the schedule meets the production requirement, i.e. 2 batches of shampoo, 3 batches of deodorant, one batch of lotion and 2 batches of cream. Mixer 3 uses freshwater in addition to direct reuse water from mixer 1. Mixer 3 sends 600 kg of water to storage at 11.5h. Of this water, 201.7 kg is indirectly reused in mixer 4 at 11.5h. At 20.2h the storage tank discharges 1166.7 kg of water to the regenerator on behalf of mixer 4. At 23h, the regenerated water is discharged to mixer 4. The rest of the production schedule can be observed from the Figure 7.3. As mentioned earlier, it is not acceptable to use water from mixer 2 containing deodorant. This was ensured in the model by setting the binary variable associated with water transfer from mixer 2 to any other mixer to zero and also by setting the binary variable associated with mixer 2 transferring water to the storage tank to zero. These conditions were met, as can be seen from the Gantt chart.

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CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Introduction

This chapter presents the conclusions, limitations and recommendations drawn from the two investigations presented in this report. The conclusions are presented in Section 8.1 while the limitations and recommendations are presented in Section 8.2.

8.1 Conclusions

The first investigation, which involved the development of a long-term scheduling methodology for wastewater minimization in multipurpose batch facilities, was presented in this report. The main advantage of the presented methodology is the ability to reduce a wastewater minimization 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 minimization. The concept of water reuse and recycle was used to minimize wastewater generation. The proposed methodology optimizes both the production schedule and wastewater minimization 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 long-term scheduling 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.

The second investigation, which involved the development of a methodology for wastewater minimization in batch plants that incorporates a regenerator, was also presented in this report. The methodology is also applicable to multipurpose plants containing multiple contaminants. The particular advantage of this work is that it does not require the batch production schedule to be given beforehand. The resulting formulation is a MINLP for which global optimality cannot be guaranteed.

The effectiveness of the regeneration methodology was demonstrated by applying it to an illustrative example and an industrial case study. In the illustrative example, a 19.2% reduction in wastewater generation was achieved when compared to the situation that exploited only direct reuse between water-using operations and indirect reuse with storage. Similarly, in the industrial case study, a 26% reduction in wastewater was achieved. In both cases, the batch production schedule corresponding to the minimum wastewater was determined.

8.2 Limitations and Recommendations

It should be highlighted that the results of the mathematical optimization models in both investigations were time point specific. The number of time points quoted in the results was not proven to be the optimal number of time points. The procedure to determine the optimal number of time points is as follows: Firstly, an arbitrary number of time points is specified. The result of the optimization model for this specified number of time points is noted. Next, the number of time points is increased by one and the model is solved. The result obtained for this new number of time points is compared to the previous result. This iterative procedure is carried out until there is no change in the results for each new increment of time points. The optimal number of time points is the smallest number that gave the best result. It is recommended that this procedure be followed to obtain the optimal number of time points.

It was observed in the long term scheduling model that the linearization technique used to relax the presented model was not applicable to the objective function. 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. Also, the presented methodology reduced 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 in long term scheduling for future work.

The concept of cyclic scheduling is limited to batch processes with stable operating conditions or stable product demand. Hence, the long term scheduling 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.

The model for the regeneration methodology had a considerable number of bilinear terms. Upon linearization, additional variables and constraints were introduced in the model which resulted in the model being very large. It is recommended that different scheduling methods be considered in the wastewater minimization methodology to investigate the effect on computational times and wastewater minimization results.

Final remarks

Adopting these models to real life situations would require a shift in mindset with regards to operating procedures. This could prove to be a challenge, especially in situations where it may appear that there is no urgent need for wastewater minimization.

Due to the fine contributions that have been made in the topic of wastewater minimization, the point has been reached where the commercialization of software is possible. This will be beneficial in the sense that it would not require users to understand the sometimes complex mathematical formulation but would only involve the input of data.

APPENDIX I:

LINEARIZATION TECHNIQUE

A. Linearization: Section A

To demonstrate the linearization technique presented in the work by Majozi and Gouws (2009). Constraints (3.4) and (3.5) presented in Section A 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):

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

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

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.

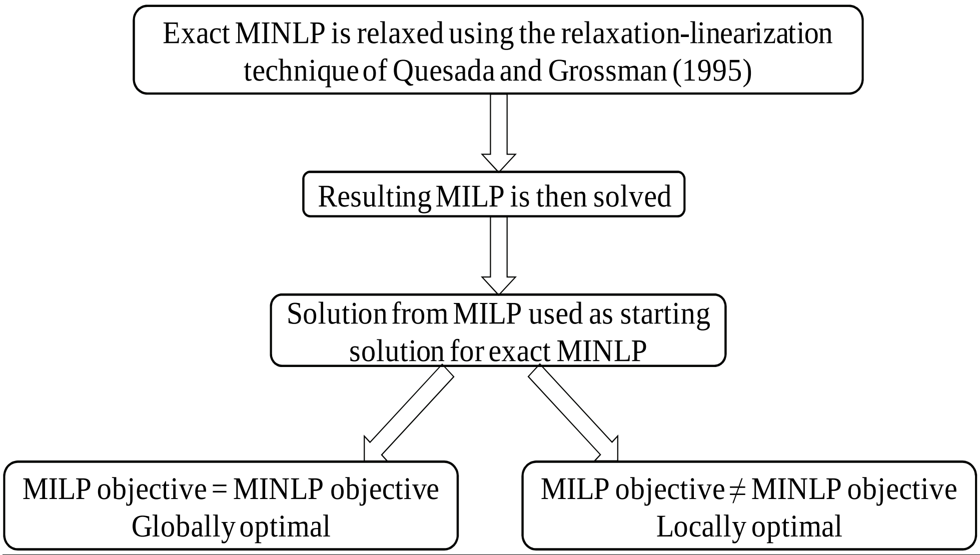

Figure A.1: Solution procedure from Majozi and Gouws (2009)

B. Linearization: Section B

This subsection is intended to give an example of how the nonlinearities of the mathematical formulation in Section B were addressed. Although the linearization technique is exactly the same as explained above, the constraint that is chosen as an example is different from that addressed in A.

The mathematical formulation in Section B is nonlinear due to the bilinear terms in Constraints (6.4), (6.5), (6.15), (6.16) and (6.23). Consider Constraint (6.4) containing the following bilinear terms:

i. $mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p)$

ii. $mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p)$

iii. $ms_{out}(s_{out,j}, p)cs_{out}(c, p)$

iv. $mreg_{out}(s_{out,j}, p)cr_{out}(c, p)$

These terms are linearized using the method discussed by Quesada and Grossmann (1995) given below:

Let:

$$mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p) = \Gamma_1(s_{out,j}, c, p)$$
$$mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p) = \Gamma_2(s_{out,j'}, s_{out,j}, c, p)$$
$$ms_{out}(s_{out,j}, p)cs_{out}(c, p) = \Gamma_3(s_{out,j}, c, p)$$
$$mreg_{out}(s_{out,j}, p)cr_{out}(c, p) = \Gamma_4(s_{out,j}, c, p)$$

With each variable having the following bounds:

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

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

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

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

$$0 \le cs_{out}(c, p) \le CS_{out}^U(c)$$

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

$$0 \le cr_{out}(c, p) \le CR_{out}^U(c)$$

The following are true for Γ_1:

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

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

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

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

The following are true for Γ_2:

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

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

$$\begin{aligned}\Gamma_2\left(s_{out,j'}, s_{out,j}, c, p\right) \le\ & Mw^U\left(s_{out,j}\right)c_{out}\left(s_{out,j'}, c, p\right) \\ & \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \tag{B.7}$$

$$\begin{aligned}\Gamma_2\left(s_{out,j'}, s_{out,j}, c, p\right) \le\ & mw_r\left(s_{out,j'}, s_{out,j}, p\right)C_{out}^U\left(s_{out,j'}, c\right), \\ & \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \tag{B.8}$$

The following are true for Γ_3

$$\Gamma_3\left(s_{out,j}, c, p\right) \ge 0, \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \tag{B.9}$$

$$\Gamma_3\left(s_{out,j},c,p\right) \geq Mw^U\left(s_{out,j}\right)cs_{out}\left(c,p\right) + ms_{out}\left(s_{out,j},p\right)CS_{out}^U\left(c\right) - Mw^U\left(s_{out,j}\right)CS_{out}^U\left(c\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.10)}$$

$$\Gamma_3\left(s_{out,j},c,p\right) \leq Mw^U\left(s_{out,j}\right)cs_{out}\left(c,p\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.11)}$$

$$\Gamma_3\left(s_{out,j},c,p\right) \leq ms_{out}\left(s_{out,j},p\right)CS_{out}^U\left(c\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.12)}$$

The following are true for Γ_4

$$\Gamma_4\left(s_{out,j},c,p\right) \geq 0,\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.13)}$$

$$\Gamma_4\left(s_{out,j},c,p\right) \geq Mw^U\left(s_{out,j}\right)cr_{out}\left(c,p\right) + mreg_{out}\left(s_{out,j},p\right)CR_{out}^U\left(c\right) - Mw^U\left(s_{out,j}\right)CR_{out}^U\left(c\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.14)}$$

$$\Gamma_4\left(s_{out,j},c,p\right) \leq Mw^U\left(s_{out,j}\right)cr_{out}\left(c,p\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.15)}$$

$$\Gamma_4\left(s_{out,j},c,p\right) \leq mreg_{out}\left(s_{out,j},p\right)CR_{out}^U\left(c\right),\ \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad \text{(B.16)}$$

Substituting the above linearized variables into Constraint (6.4) gives Constraint (B.17):

$$\Gamma_1\left(s_{out,j},c,p\right) = \sum_{s_{out,j'}} \Gamma_2\left(s_{out,j'},s_{out,j},c,p\right) + \Gamma_3\left(s_{out,j},c,p\right) + \Gamma_4\left(s_{out,j},c,p\right) \quad \forall j,j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \quad \text{(B.17)}$$

The bilinear terms in Constraints (6.5), (6.15), (6.16) and (6.23) are linearized in a similar manner and substituted in the original constraints to yield new constraints similar to Constraint (B.17).

Solution procedure

The relaxed MILP problem consists of Constraints (6.1) to (6.74), (6.75) or (6.76) with the new substituted constraints instead of Constraints (6.4), (6.5), (6.15), (6.16) and (6.23). Also included are the respective forms of Constraints (B.1) to (B.4) for each linearized variable. The relaxed MILP problem is solved to provide a starting point for the exact MINLP problem. The solution procedure is as illustrated in Figure A.1.

References

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