CHEMICAL PROCESS OPTIMIZATION AND POLLUTION PREVENTION VIA MASS AND PROPERTY INTEGRATION

A Thesis

by

ANA CAROLINA HORTUA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2007

Major Subject: Chemical Engineering

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Approved by:

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ABSTRACT

Chemical Process Optimization and Pollution Prevention via Mass and Property
Integration. (May 2007)

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The process industries such as petrochemicals, chemicals and pharmaceuticals, among others, consume large amounts of material and energy resources. These industries are also characterized by generating enormous amounts of waste that significantly contribute to the pollution of the environment. Integrated process design is a very effective technique in conserving process resources and preventing pollution. The design and environmental constraints may involve a variety of component- and property-based restrictions. To date, most techniques have been developed to handle process constraints which is either composition-based (via mass integration) or property-based. No work has been reported to handle the synthesis of resource conservation network that is governed by both constraints.

The objective of this work is to develop a systematic and cost-effective design technique that is aimed at minimizing the consumption of fresh resources and the discharge of pollutants simultaneously. Because of the nature of the component- and property-based constraints, this approach is based on mass and property integration and takes into account the process constraints and also environmental regulations.

In this research work, a new approach has been developed to simultaneously address component-based recycle constraints as well as property-based discharge constraints. The proposed optimization technique is intended to minimize the consumption of fresh resources, the pollutant content in the waste streams, and the operational and waste treatment costs. Additionally, a mixed-integer nonlinear programming (MINLP) formulation is solved for a case study of phenol production from cumene hydroperoxyde to illustrate the new problem and devised solution algorithm.

DEDICATION

This thesis is dedicated to Roberto Rodriguez, without his love, support and guidance I would not have ended up where I am today. I thank him for giving me the strength and confidence that I needed when times turned out very difficult and my spirit was feeling too weak to continue. I am very fortunate to have him by my side.

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First and Foremost, I would like to thank God for enabling me to achieve all that I have achieved and for sending me his blessings in every day of my life.

I would like to express my sincere gratitude to my advisor, Dr. Mahmoud El-Halwagi, for his kind help, guidance, support and encouragement throughout my graduate studies at Texas A&M University. Without him this research work would not have been possible.

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Last, but not least, I thank my parents and my sister for their love, support and prayers through all these years.

NOMENCLATURE

$C_{r,\mathrm{fresh}}$	cost of fresh resource r
$C_{recovery,u}$	cost of recovery component u
C_{waste}	cost of waste treatment
$\bar{C}_p$	mixture cluster for the property p
$C_{p,i}$	cluster for property p in stream i
$d_{i,,j}$	piping cost factor coefficient from source i to sink j
$d_{r,,j}$	piping cost factor coefficient from fresh resource r to sink j
$eff_{,u}$	recovery unit efficiency for component u
$f_{r,j}$	flowrate of fresh resource r fed to sink j
F_r	total fresh resource flowrate required after optimization
F_T	total mass flowrate of the mixture (lb/hr)
F_i	flowrate contribution of source i to the mixture
G_j	flowrate entering to sink j
$G_j^{\max}$	upper bound on flowrate to sink j
$G_j^{\min}$	lower bound on flowrate to sink j
G_j^{out}	flowrate leaving sink j
I	binary term
L	lower feasible value of $y_{i,u}^{in.rev}$

$M_j^{\sin k}$	load of impurities entering to sink *j*
M_i^{source}	load of impurities in source *i*
Ni	number of streams being mixed
Np	number of properties of importance for the process
$\overline{pH}$	pH value of the mixture
p_i	property value of source *i*
p_T	property value of the mixture
$p_{j,p}^{\max}$	maximum value of property *p* allowable for sink *j*
$p_{j,p}^{\min}$	minimum value of property *p* allowable for sink *j*
$P_{j,p}^{out}$	value of property *p* leaving the sink *j*
$P_{p_{(Env.\,\mathrm{Re}\,gulation)}}$	value of property p established by environmental regulations,
p_T	property value of the mixture
$ThOD_m$	theoretical oxygen demand of organic compound *m*.
$ThOD_i$	overall theoretical oxygen demand of source *i*
$\overline{ThOD}$	theoretical oxygen demand of the mixture
U	upper feasible value of $y_{i,u}^{in.rev}$
$w_{i,j}$	flow rate fraction of source *i* that is assigned to sink j
W_i	flowrate of source *i*, lb/hr
$w_{i,waste}$	flow rate fraction of source *i* send to waste

$w_{i,waste}^{in.rev}$	waste flowrate of process stream *i* sent to a recovery unit
x_i	ratio of flowrate of source *i* to the total flowrate
$y_{i,u}$	composition of component *u* in stream *i*
$y_{i,u}^{in.rev}$	concentration of component *u* in source *i*
$y_u^{\min.}$	minimum concentration of component *u* worth to recover
$\overline{Y}$	mortality percentage of the mixture
z_j^{in}	composition of impurities entering to sink *j*
$z_j^{\max}$	upper bound on admissible impurity composition to sink *j*
$z_j^{\min}$	lower bound on admissible impurity composition to sink *j*
β_i	mixing are of stream *i* on the ternary cluster diagram
$\psi(p_i)$	property-mixing operator for source *i*
$\psi(p_T)$	property-mixing operator for the mixture
$\psi_p(p_{i,p})$	mixing-operator of property *p* in stream *i*
$\psi_p(p_{j,p}^{in})$	mixing-operator of property *p* entering to sink *j*
$\psi_p^{\max}(p_{p,j})$	maximum value of mixing-operator of property *p* for sink *j*
$\psi_p^{\min}(p_{p,j})$	minimum value of mixing-operator of property *p* for sink *j*
$\psi_p^{in}(p_{p,j})$	inlet value of mixing-operator of property *p* for sink *j*

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

CHAPTER I

INTRODUCTION

Every day, tons of industrial wastes are disposed into the environment causing an accelerated and irreversible damage to the environmental surroundings and affecting the human health. Therefore, the protection of the environment has become a major priority around the world. In order to control and diminish the amount of pollutants that are discharged into the environment, stringent environmental regulations have been established. The process industries have been seriously affected from by these restrictions since they contribute in considerable ways to the technical, operational, and economic issues of the process. The goals of conserving natural resources and abating industrial pollution provide motivation to find new techniques to help optimize the process performance while reducing waste discharge.

Process engineering has played a major role in devising design modifications that address the goals of resource conservation and pollution abatement. In particular, a branch of process engineering referred to as “process integration” provides a holistic framework for optimizing the design and operation of the process. Through process integration, several optimization techniques have been developed leading to reduction in

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This thesis follows the style of *Industrial & Engineering Chemistry Research*.

the usage of material and energy resources and discharge of waste. To date, most of these techniques have been based mostly on process constraints or environmental constraints but not both. As such, it is possible that after process optimization is performed, the quantity of the resulting waste streams may decrease but the treatment cost and environmental impact may go up. Also, pollution prevention studies have been mostly based on tracking concentrations of pollutants. It is beneficial to incorporate properties of process streams and wastes. Therefore, the main objective of this work is to simultaneously address the process constraints as well as the environmental constraints. Component- and property-based constraints are incorporated. A systematic design approach is developed to provide the following benefits:

- Minimization of the total cost of fresh resources and waste treatment while satisfying process and environmental constraints
- Determination of a tradeoff between the cost of fresh resources versus the cost of environmental compliance and pollution prevention
- Development of implementation projects needed to achieve the target at minimum cost

In order to demonstrate the applicability of the developed approach, a case study is solved to address resource conservation and pollution prevention of a phenol process. The environmental regulations including chemical oxygen demand (COD), toxicity, and pH were taken into consideration in addition to process constraints.

CHAPTER II

LITERATURE REVIEW

Process integration is a holistic approach to process design, retrofitting and operation which emphasizes the unity of the process (El-Halwagi, 2006[1], El-Halwagi, 1997[2]). This approach is based on three basic concepts:

1. *Look at the big picture:* Before focusing on the details of the solution, it is important to understand the global insights of the system as a whole. This is achieved by considering the process as an integrated system of interconnected processing units, process stream, waste streams and utilities.
2. *Targeting:* Using process-engineering principles; the process performance benchmarks are identifying. This concept is one of the most important tools of process integration since it allows determining how far the process performance can be pushed without specifying how it may be reached.
3. *Detail process design:* The different alternatives that reach the identified targets are generated and analyzed in order to select the one that best suits the process requirements.

Process integration research may be categorized into three branches: Mass Integration, Heat Integration and Property Integration. Mass and Property Integration will be addressed in this chapter since both have a direct application in the development of this work. On the other hand, Heat Integration will not be discussed since this approach is out of the scope of this research work.

2.1 Mass Integration

It is a holistic and systematic methodology that provides a fundamental understanding of the global flow of mass within the process and employs this understanding in identifying performance targets and optimizing the allocation, separation, and generation of streams and species. (El-Halwagi and Spriggs, 1998[3]). Several mass integration strategies such as segregation, mixing, recycle/reuse, material substitution, reaction alteration, process modifications among others are being applied to industry processes with the purpose of reaching desired mass targets while minimizing the generation of waste discharge and the consumption of fresh resources. One of mass-integration strategies is the synthesis of pollutant-removing separation networks such as mass-exchange networks (e.g., El-Halwagi and Manousiouthakis, 1989[4]; Hallale and Fraser, 2000[5]; Foo C.Y., 2004[6]), reactive mass-exchange networks (e.g., El-Halwagi and Srinivas, 1992[7]), reverse-osmosis networks (e.g., El-Halwagi, 1992[8]). Another important strategy is material recycle/reuse via stream rerouting. In this present work, this strategy will be frequently used throughout the thesis. It includes segregation, mixing and recycle of streams. The following section summarizes key techniques for material rerouting.

2.2 Material Rerouting Network

This optimization technique is based on the rerouting of process sources (streams carrying targeted species), without the addition of new devices, to process units (units that can use this sources). This optimization strategy, also known as Direct Recycle, is used to identify the targets for minimum usage of fresh resources, maximum stream recycle and minimum waste discharged. In order to achieve this, a graphical technique called *Material Recycle Pinch Analysis* (El-Halwagi, 2003[9]) is used, which involves the following steps:

1. *Identify sources and sinks*: Identify the process streams that can be considered as sources for recycle and the process units (sinks) that are able to accept them as replacement for fresh resources.

2. *Identify sink constraints:*_ Determine the sink operation bounds that restrict the use of recycle streams in each process unit. In this approach just restrictions in flow rate ($G_j^{\min} \le G_j \le G_j^{\max}$) and inlet composition of the targeted specie ($z_j^{\min} \le z_j^{in} \le z_j^{\max}$) are considered.

3. *Developing sink composite diagram:* After identifying the operational constraints, the sinks should be ranked in ascending order from the one with least admissible inlet composition of the targeted specie to the maximum as shown in Table 2.1.

Table 2.1: Ranking of sinks

Sink	**Flowrate**	**Composition Targeted Specie**	**Load**
1	G_1	$z_1^{\min}$	$M_1^{\min}$
2	G_2	z_2	M_2
....	....	$\ldots$	$\ldots$
j	G_j	$z_j^{\max}$	$M_3^{\max}$

where, the load of the targeted specie entering the each sink is calculated by using the following equation ($M_j^{\sin k} = G_j z_j^{\max}$). Finally, the sink composite curve is generated by plotting the load, $M_j^{\sin k}$ for each sink versus their respective flow rates. As shown in Figure 2.1.

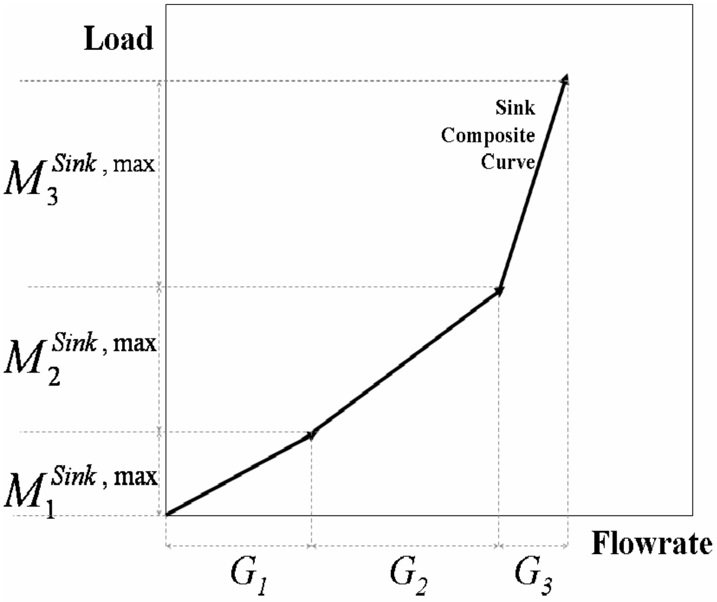

Figure 2.1: Sink Composite Diagram (El-Halwagi, 2003[9])

4. *Developing source composite diagram:* This diagram is generated using the same procedure explained for the sink composite curve but using the sources flow rate(W_i) and the load for each source ($M_i^{source} = W_i\ y_i$). Therefore, it will not be further explained. An example of a source composite diagram is shown in Figure 2.2.

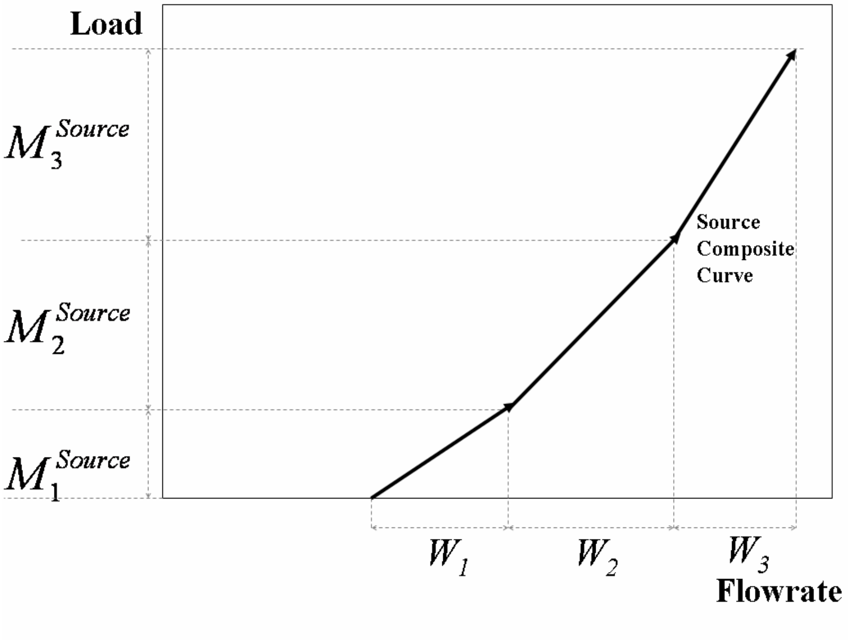

Figure 2.2: Source Composite Diagram (El-Halwagi, 2003[9])

5. *Developing a material pinch diagram:* After the source and sink composite curves are generated, both plots are placed in the same diagram (Figure 2.3). Afterwards the source composite curve is moved horizontally until it touches the sink composite curve. The point where both curves unite is called the pinch point (Figure 2.4). Figure 2.4 can be divided in three sections. The area below the

pinch point where there are no sources is the target for minimum fresh consumption. The overlapped region between the source and composite curve represents the maximum recycled flowrate. And the horizontal distance above the pinch point which there is no sink represents the minimum waste discharged.

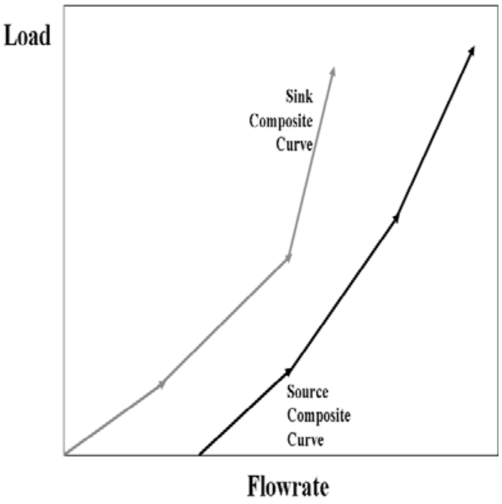

Figure 2.3: Sink and Source Composite Diagrams

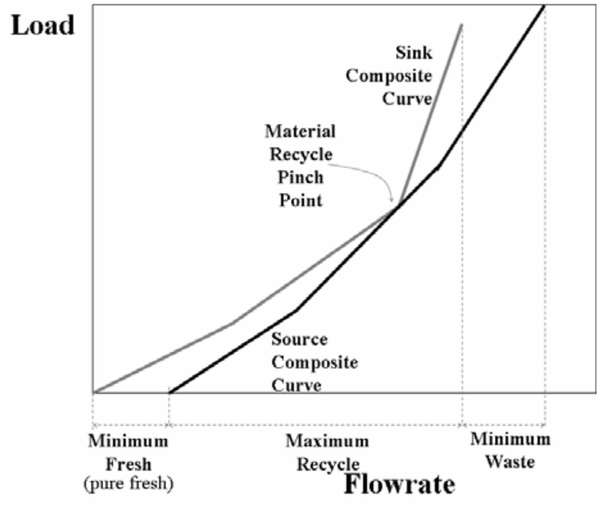

Figure 2.4: Material-Recycle Pinch Diagram (El-Halwagi, 2003[9])

2.3 Property Integration

The paradigm of *property integration* has been introduced by El-Halwagi and co-workers. Property integration is a functionality-based, holistic approach to the allocation and manipulation of streams and processing units, which is based on the tracking, adjustment, assignment, and matching of functionalities throughout the process (El-Halwagi et al., 2004[10]; Shelley and El-Halwagi, 2000[11]). Similar to *direct recycle* strategy, this holistic approach can be used for identifying the process mass targets such as the minimum use of fresh resources and waste discharge based on tracking properties instead of chemical species. Properties, unlike mass, are not conserved. As a result, concepts such as mixing rules and clusters need to be introduced.

Mixing Rules: In the case where more than one process streams are mixed, the property value of the resultant mixing stream must be evaluated as a function of the flow rate and the property of each stream. As a result, for every property a mixing rule that follows the form of equations 2.1 or 2.2 need to be established.

$$F_T \times \psi(p_T) = \sum_i F_i \times \psi(p_i) \tag{2.1}$$

Where $\psi(p_T)$ is the property-mixing operator, (p_T) is the property of the mixture, and (F_T) is the total flow rate of the mixture. The properties operators can be calculated from first principles or estimated through empirical or semi-empirical methods.

Equation 2.1 can also be rewriting as shown in equation 2.2

$$\psi(p_T) = \sum_{i=1}^{N_{sources}} x_i \psi(p_i) \qquad (2.2)$$

where x_i is the fraction contribution of the i^{th} stream into the total flowrate of the mixture.

Clusters: In order to track multiple properties simultaneously, a technique called clustering has been developed by Shelley and El-Halgawi (2000). This technique uses mixing rules to transform properties into dimensionless quantities (clusters), which allow the conserved tracking of properties throughout a process. Property Clusters are defined by two important characteristics: intra- and inter-stream conservation.

- *Intra-Stream Conservation:* Define that the summation of clusters within a stream must be equal to a constant, which is shown in the equation 2.3.

  $$\sum_{i=1}^{N_p} C_{p,i} = 1 \qquad i = 1,2\ldots, \mathrm{N_{sources}} \qquad (2.3)$$

  where $C_{p,i}$ is the cluster for property, *p* in stream *i* and *Np* is the number of properties of importance for the process. The concept intra-stream conservation for three clusters is represented graphically within a ternary diagram in figure 2.5.

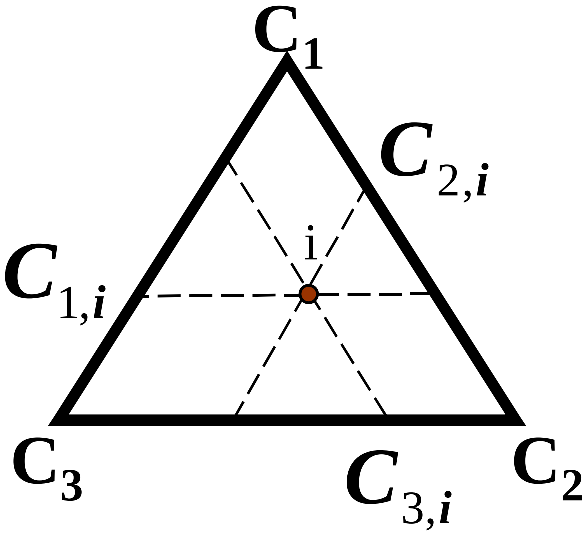

Figure 2.5: Intra-stream conservation (Shelley and El-Halwagi, 2000[11])

- *Inter-Stream Conservation:* Define that when two or more streams are mixed, the resulting individual clusters are conserved by using standard additive rules, which follow the principle of lever-arm. This lever-arm additive rule for clusters is stated mathematically in equation (2.4) and it is represented graphically in figure 2.6.

$$\bar{C}_p = \sum_{i=1}^{N_i} \beta_i C_{p,i} \tag{2.4}$$

Where $\bar{C}_p$ is the mixture cluster, for the *p* property, β_i is the fractional lever arm of cluster $C_{p,i}$, of stream *i* and *Ni* is the number of streams being mixed.

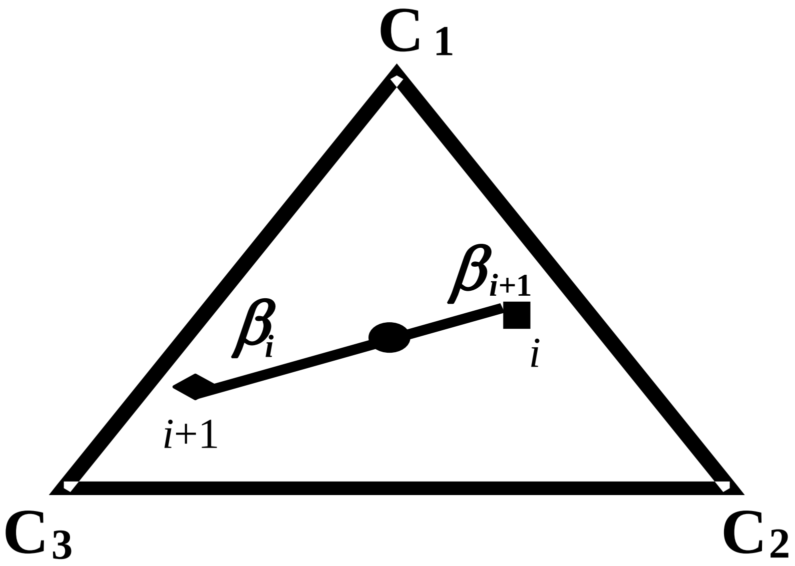

Figure 2.6: Lever arm addition for clusters of two streams (Shelley and El-Halwagi, 2000[11])

The optimization of properties using the clustering technique is used when the sinks and/or process sources constraints depends on properties instead of chemical components. This technique is used as a tool to determine the mass targets for the process and to develop recycling and allocation strategies.

2.4 Key Contributions in the Synthesis of Optimal Water Recycle Network

Table 2.2 summarizes key contributions in the area of synthesizing optimal recycle networks.

Table 2.2: Summary of Key Contributions in the Synthesis of Optimal Water Recycle Network

Category Description	Approach	Objective	Constraints	References
Wastewater minimization with mass-exchange units	Water pinch graphical analysis	Flowrate of wastewater	Units modeled as mass exchangers with constraints on transferred load and maximum inlet composition of impurities	Wang and Smith (1994)[12]
Water minimization with sources and sinks	Water pinch graphical analysis	Flowrate of fresh water and wastewater	Maximum allowable composition of impurities allowed in each sink	Dhole (1996)[13]
Water minimization with sources and sinks	Source-sink mapping diagram	Flowrate of fresh water and wastewater	Minimum and maximum allowable composition of impurities and flowrates allowed in each sink	El-Halwagi and Spriggs (1996)[14]
Wastewater minimization with mass-exchange units	Algebraic Evolutionary Table	Flowrate of fresh water and wastewater	Units modeled as mass exchangers with constraints on transferred load and maximum inlet composition of impurities	Sorin and Beddard (1999)[15]
Water minimization with sources and sinks	Optimality conditions for recycle	Flowrate of fresh water and wastewater	Maximum allowable composition of impurities allowed in each sink	Polley and Polley (2000)[16]

Table 2.2: Continued

Category Description	**Approach**	**Objective**	**Constraints**	**References**
Water minimization with global pinch	Water surplus diagram	Flowrate of fresh water and wastewater	Maximum allowable composition of impurities allowed in each sink	Hallale (2002)[17]
Water and Wastewater Minimization	Material recovery pinch diagram	Minimum fresh water, maximum recycle, and minimum wastewater	Single- and multi-component constraints on maximum allowable compositions for each sink	El-Halwagi (2003)[9]
Water and Wastewater Minimization	Mathematical programming techniques	Minimum fresh water or minimum cost	Single- and multi-component constraints on maximum allowable compositions for each sink	Alva-Argaez (1999)[18], Benko and Rev.(2000)[19] Dunn and Wenzel(2001)[20] Saveiski and Bagajewicz.(2000, 2001)[21,22]
Water network with interception	Mathematical programming	Minimum fresh and interception costs	Single- and multi-component constraints on maximum allowable compositions for each sink	Gabriel and El-Halwagi (2005)[23]
Property-based wastewater minimization	Clustering graphical technique	Minimum fresh water and wastewater	Minimum and maximum allowable properties for each sink (up to three properties)	Shelley and El-Halwagi (1999)[24] , El-Halwagi (2003)[9]

Table 2.2: Continued

Category Description	**Approach**	**Objective**	**Constraints**	**References**
Property-based wastewater minimization	Property-based algebraic technique	Minimum fresh water and wastewater	Minimum and maximum allowable properties for each sink (any number of properties)	Qin et al. (2004)[25]
Property-based wastewater minimization	Property-based material recovery pinch diagram	Minimum fresh water and wastewater	Minimum and maximum allowable properties for each sink	Kazantzi and El-Halwagi (2005)[26]
Property-based wastewater minimization	Surplus diagram cascade algebraic technique	Minimum fresh water and wastewater	Minimum and maximum allowable properties for each sink	Foo C.Y. (2006)[27]

The foregoing discussion illustrates the lack of a technique that can address all of the following aspects simultaneously:

- Composition- and property-based constraints
- Constraints on process units as well as the environment
- Waste-treatment units that adjust both compositions and properties
- Cost of fresh, recycle, and waste treatment

This work is intended to overcome this literature gap by introducing a systematic approach to tackle these limitations.

CHAPTER III

PROBLEM STATEMENT

The problem addressed in this work deals with the allocation of streams for direct reuse/recycle and waste treatment simultaneously. It has the following characteristics:

- Constraints are considered for the process units (sinks) as well as the environment.
- Composition- and property-based constraints are considered for recycle and for waste discharge
- Waste treatment units are used to adjust compositions and properties
- Cost of fresh usage, recycle, and waste treatment are all included

The problem can be formally stated as follows:

Given a process with a set of sources or streams: SOURCES = $\{i|i=1,N_{\text{Sources}}\}$. Each source, i, has a flowrate W_i, and a composition $y_{i,u}$ (where u is index for components). The stream i is characterized by a set of properties: $\text{PROP}_i = \{p_{i,p}|\ p=1,\text{N}_{\text{properties}}\}$. Given also is a set of sinks or process units: SINKS = $\{j|j=1,\text{N}_{\text{Sinks}}\}$. Each sink has constraints on the compositions and properties of its feed, i.e.,

$$z_{j,u}^{\min} \le \text{composition of component u in feed to sink j} \le z_{j,u}^{\max} \quad j=1,2,\ldots,N_{\text{Sinks}} \quad \text{and} \quad u=1,2,\ldots,N_{\text{components}} \tag{3.1}$$

$$p_{j,p}^{\min} \le \text{property p of feed to sink j} \le p_{j,p}^{\max} \quad j=1,2,\ldots,N_{\text{Sinks}} \quad \text{and} \quad p=1,2,\ldots,N_{\text{properties}} \tag{3.2}$$

External fresh resources, with different impurity content, are available F_r : FRESH = $\{r|r=1,\ldots N_{\text{Fresh}}\}$ to supplement the use of process sources in sinks. The cost of the fresh is referred as $C_{r,\text{fresh}}$ ($/lb of the fresh). In addition, source streams that did not reused/recycled are sent to waste treatment in order to comply with environmental regulations before discharged to the environment. The cost of waste treatment includes fix and operational cost. It is represented as C_{waste} ($/ pollutant or property removed). The main objective of this work is to develop a systematic procedure that optimizes the ost of the fresh resource, piping cost for reconstructed the material reuse/recycle network and waste treatment cost. A schematic representation of the stated problem is shown in Figure 3.1.

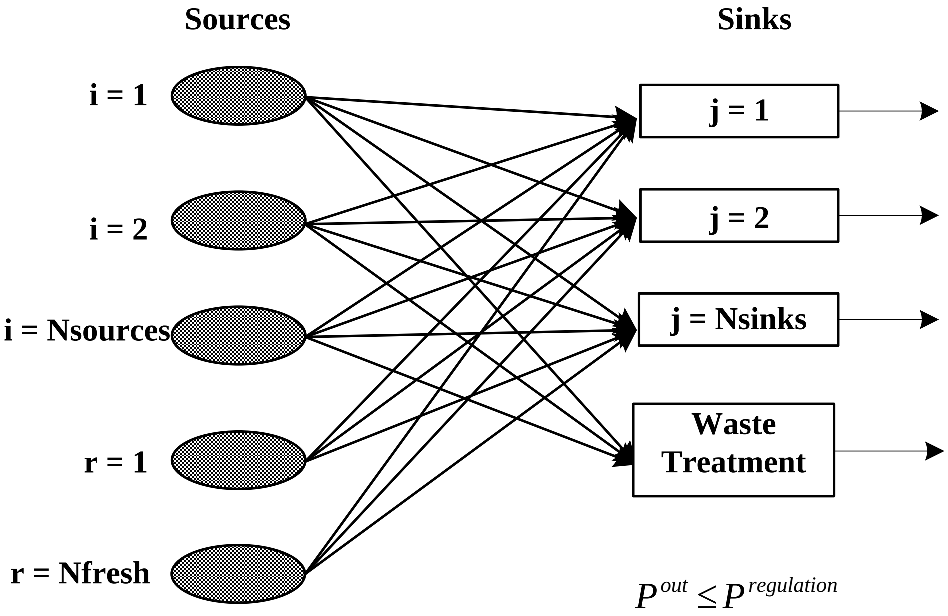

Figure 3.1: Source-sink representation

The design procedure should achieve the following:

- Determine the optimum allocation of process source to each sink that minimize the consumption of fresh resource.
- Minimize the pollutant concentration in waste streams to reduce the cost of waste treatment
- Determine the minimum total annualize cost for reconstructed the material reuse/recycle network that comply with environment regulations.

CHAPTER IV

METHODOLOGY

In order to develop an optimization technique that accomplishes all the design challenges mentioned in the problem statement, two mathematical algorithms are formulated. The first optimization program takes into consideration only process constraints while the second formulation includes environmental constraints for waste discharge. The mathematical algorithms are based on mass and property integration methodologies.

4.1 Development of Optimal Material Recycle Networks

A generalized mathematical program is formulated to design Optimal Material Recycle Networks .This formulation is based on direct material recovery pinch analysis technique and has the objectives of determining the targets for minimum consumption of fresh resources, minimum waste discharge, direct-recycle configurations and the minimum operational cost assuming that the waste produce by the process can be discharged to the environment without any restriction. To facilitate the development of the mathematical program, a graphically representation of the optimization problem is sketched. Figure 4.1 shows a source-sink representation of the problem to be solved when just process constraints are taking in consideration.

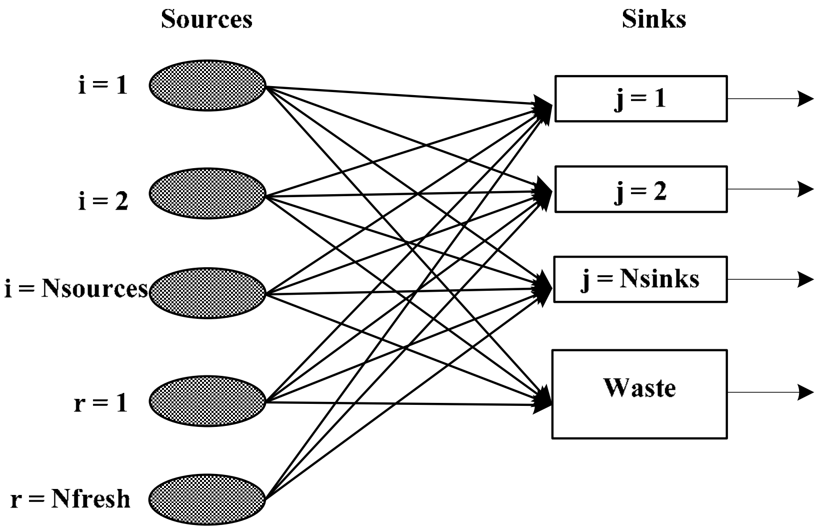

Figure 4.1: Source-sink representation (First formulation)

As seen in figure 4.1, the sources are split into unknown fractions and allocated to the different sinks. In addition, an extra sink is placed in order to account for the unrecycle material and fresh resources are always available to be split and allocated in any sink, except for the waste sink.

4.2 Mathematical Formulation Based on Process Constraints

The mathematical formulation used to represent this problem is illustrated in the following equations. The objective function of this program is to minimize the operational cost, which includes the cost for consumption of fresh resources and the cost of piping for building the recycle network after optimization. The objective function is shown in Equation 4.1.

$$Minimize\left(\sum_{r=1}^{N_{fresh}} C_{r,Fresh} \times f_{r,j} + Piping\_Cost\right) \tag{4.1}$$

where $C_{r,Fresh}$ is the cost of fresh resource *r*, and $F_{r,j}$ is the amount of fresh resource *r* fed to the j^{th} sink. The total piping cost is proportional to the flowrate going through the pipe and a factor coefficient. This is shown in Equation 4.2.

$$Piping\_Cost = \sum_{i=1}^{N_{source}} \left(w_{i,j} \times d_{i,j}\right) + \sum_{r=1}^{N_{fresh}} \left(f_{r,j} \times d_{r,j}\right) \tag{4.2}$$

where $d_{i,,j}$ and $d_{r,,j}$ are cost factor coefficients, which are function of material of construction, diameter of the pipe and manhattan distance for source *i* or fresh *r* to sink *j*. $f_{r,j}$ is flow rate fraction of fresh *r* allocated in sink *j* and $w_{i,j}$ is the flow rate fraction of source *i* that is assigned to sink j

The objective function is subjected to the following constraints:

Splitting constraint for sources:

$$W_i = \sum_{j=1}^{N_{\sin ks}} w_{i,j} + w_{i,waste} \tag{4.3}$$

where $w_{i,waste}$ represents the flow rate fraction that can not be recycle; and therefore, it is taken as waste.

Splitting constraint for fresh resources:

$$F_r = \sum_{i=1}^{N_{Sinks}} f_{r,j} \tag{4.4}$$

Waste constraint:

$$Waste = \sum_{i=1}^{N_{sources}} w_{i,waste} \qquad (4.5)$$

In order to satisfy sink constraints, split fractions that come from process sources and the fresh streams might be required to mix before entering to a process unit. Mass and component balances at the mixing point are needed to determine possible mixing alternatives and the allocation of the resultant mixing streams to sinks.

Mass Balance:

$$G_j = \sum_{i=1}^{N_{sources}} w_{i,j} + \sum_{i=1}^{N_{fresh}} f_{r,j} \qquad \forall j \qquad (4.6)$$

where G_j is the flowrate entering to sink *j*.

Component balance:

$$G_j z_{j,u}^{in} = \sum_{i=1}^{N_{sources}} w_{i,j} y_{i,u} \qquad \forall j, u \qquad (4.7)$$

where $z_{j,u}^{in}$ is the feed composition of component *u* to sink *j*. This value must lie between the lower and upper composition constraints for component u on sink *j*. And $y_{i,u}$ is the composition of component *u* in process source *i*.

All the variables in this formulation require nonnegative constraints illustrated in equation 4.8 through 4.10

$$f_{r,j} \geq 0 \qquad \{r|r=1,N_{Fresh}\},\ \{j|j=1,N_{Sinks}\} \tag{4.8}$$

$$w_{i,j} \geq 0 \qquad \{i|i=1,N_{Sources}\},\ \{j|j=1,N_{Sinks}\} \tag{4.9}$$

$$z_{j,u}^{in} \geq 0 \qquad \{j|j=1,N_{Sinks}\},\ u = \text{ index for component} \tag{4.10}$$

Using this formulation, the mass targets for the process are identified, the minimum operational cost is determined and different direct-recycle configurations are generated.

4.3 Development of Optimal Recycle Networks Based on Mass and Property Integration

Process waste must comply with environmental regulations before it can be discharged to the environment; therefore, waste streams must be sent to treatment units where the pollutants are removed up to an acceptable value for discharging. As a result, waste treatment has become an important expenditure increasing significantly the overall operational cost. The main objective of this approach is to minimize the fresh resource consumption and the waste treatment cost simultaneously. In order to solve this problem a mathematical program is developed which takes into consideration process and property constraints. Environmental regulations involve limits on properties such as pH, toxicity, color, ThOD etc. Therefore, property integration methodology is needed to track the property values within the process. The source sink representation for this problem is shown in figure 3.1 (Chapter III).

4.4 Mathematical Formulation Based on Process and Property Constraints

The mathematical formulation is illustrated in the following equations. The objective function of this program is to minimize the operational cost, which includes the cost for consumption of fresh resources, piping, recovery and waste treatment. Waste streams are sent to recovery units before going through waste treatment with the aim of recovering components that have commercial value or that can be reused within the process.

The objective function is shown in Equation 4.11.

$$Minimize\left(C_{Fresh} \times F_r + Piping\_Cost + \mathrm{Re\,cov}\,ery\_Cost \ + \sum_{j=1}^{N_{Sinks}} Waste\_Cost_j\,(G_j, G_j^{out}, P_{j,p}^{out}, P_{p_{(Env.\mathrm{Re}\,gul).}}\ \forall p) \right) \tag{4.11}$$

The waste treatment cost is a function of the property value, p^{th} leaving the sink j, $P_{j,p}^{out}$, the property value, p^{th} established by environmental regulations, $P_{p_{(Env.\mathrm{Re}\,gulation)}}$ and the flowrates entering and leaving the sink j, G_j and G_j^{out} . $\forall p$ stands for all values of p.

$\mathrm{Re\,cov}\,ery\_Cost$ is the cost associated with the technology used to recover component u and it is shown in equation 4.12

$$Recovery\_Cost = \sum_{u=1}^{N_{Component}} \left(C_{recovery,u} \left(\sum_{i=1}^{N_{Source}} \sum_{u=1}^{N_{Component}} \left(w_{i,waste}^{in.rev}, y_{i,u}^{in.rev}, eff_{u} \right) \right) \right) I \qquad (4.12)$$

where $C_{recovery,u}$ is the cost of recovery for component u, $w_{i,waste}^{in.rev}$ are the waste flowrate of process stream i , which is sent to a recovery unit , $y_{i,u}^{in.rev}$ is the concentration of component, u in waste stream i and the efficiency of the recovery unit for component, u is expressed in term $eff_{,u}$. I is a binary term that takes the value of 1 if component u is recovered or 0 (zero) if is not.

The value assign to the binary term I_u is determined using the constraint shown in Equation 4.13.

$$\left(L - y_{i,u}^{\min.}\right) * \left(1 - I\right) \le y_{i,u}^{in.rev} - y_{u}^{\min.} \le \left(U - y_{i,u}^{\min.}\right) * \left(I\right) \qquad (4.13)$$

where $y_{u}^{\min.}$ is the minimum concentration of component u that is worth to recover and L and U are the lower and upper bounds on the feasible values of $y_{i,u}^{in.rev}$. In order to satisfy the linear constraint I is forced to be 0 when $y_{i,u}^{in.rev} \le y_{u}^{\min.}$, otherwise if it is 1, the value of $\left(L - y_{i,u}^{\min.}\right) * \left(1 - I\right)$ becomes zero which violates the constraint $\left(L - y_{i,u}^{\min.}\right) * \left(1 - I\right) \le y_{i,u}^{in.rev} - y_{u}^{\min.}$. On the other hand, when $y_{i,u}^{in.rev} \ge y_{u}^{\min.}$, the term $y_{i,u}^{in.rev} - y_{u}^{\min.}$ is positive and I is forced to be 1, otherwise, if I is zero then the term $\left(U - y_{i,u}^{\min.}\right) * \left(I\right)$ becomes zero which is a violation of the statement that $y_{i,u}^{in.rev} - y_{u}^{\min.} \le \left(U - y_{i,u}^{\min.}\right) * \left(I\right)$.

The objective function is subject to the following constraints:

Splitting constraint for sources:

$$W_i = \sum_{j=1}^{N_{\sin ks}} w_{i,j} + w_{i,waste} \tag{4.14}$$

Splitting constraint for fresh resources:

$$F_r = \sum_{i=1}^{N_{Sinks}} f_{r,j} \tag{4.15}$$

Waste constraint:

$$Waste = \sum_{i=1}^{N_{sources}} w_{i,waste} \tag{4.16}$$

Mass Balance at the mixing point:

$$G_j = \sum_{i=1}^{N_{sources}} w_{i,j} + \sum_{i=1}^{N_{fresh}} f_{r,j} \tag{4.17}$$

Component balance at the mixing point:

$$G_j z_{j,u}^{in} = \sum_{i=1}^{N_{Sources}} w_{i,j} y_{i,u} \qquad \forall j,u \tag{4.18}$$

Property balance at the mixing point:

$$G_j \psi_p(p_{j,p}^{in}) = \sum_{i=1}^{N_{Sources}} w_{i,j} \psi_p(p_{i,p}) \qquad \forall j,p \tag{4.19}$$

where $\psi_p(p_{j,p}^{in})$ is the operator of property *p* going to sink *j* and $\psi_p(p_{i,p})$ is the operator of property *p* in stream *i*.

It is important to mention that this formulation applies to the class of properties that have mixing rules that follow the form of equation (4.20).

$$\psi(p_T) = \sum_{i=1}^{N_{sources}} x_i \psi(p_i) \tag{4.20}$$

where $\psi(p_T)$ is the property-mixing operator, (p_T) is the property of the mixture, and x_i is the fractional contribution of stream *i*.

Process sinks have constraints in compositions and properties, which are shown in Equations 4.21 and 4.22

$$z_{j,u}^{\min} \le z_{j,u}^{in} \le z_{j,u}^{\max} \tag{4.21}$$

where $z_{j,u}^{\min}$ and $z_{j,u}^{\max}$ are the minimum and maximum composition of component u that can be feed to sink *j*.

$$\psi_p^{\min}(p_{p,j}) \le \psi_p^{in}(p_{p,j}) \le \psi_p^{\max}(p_{p,j}) \tag{4.22}$$

where $\psi_p^{\min}(p_{p,j})$ and $\psi_p^{\max}(p_{p,j})$ are the minimum and maximum constraints on the operators of property p going to sink *j*. The property sink constraints given in equation 3.2 can be rewritten in terms of mixing operators as shown in equation 4.22.

Nonnegative constraints:

$f_{r,j} \geq 0$ {r|r=1,N_{Fresh}}, {j|j=1,N_{Sinks}} (4.23)

$w_{i,j} \geq 0$ {i|i=1,$N_{Sources}$}, {j|j=1,N_{Sinks}} (4.24)

$z_{j,u}^{in} \geq 0$ {j|j=1,N_{Sinks}}, $u =$ index for component (4.25)

$\psi_p(p_{j,p}^{in}) \geq 0$ {j|j=1,N_{Sinks}}, $p =$ index for properties (4.26)

$\psi_p(p_{i,p}) \geq 0$ {i|i=1,$N_{Sources}$}, $p =$ index for properties (4.27)

This formulation will generate a solution that determines minimum use of fresh resource, minimum waste discharged, minimum waste treatment cost and will generate different recycle configurations that achieve the identified targets.

CHAPTER V

CASE STUDY

To demonstrate the applicability of the proposed approach, a case study is addressed in this chapter. A description of the case study is firstly presented. Then, the relevant data is gathered and summarized. Next, the developed methodology is applied in the case study and the results are then further analyzed.

5.1 Case Study

Production of phenol from cumene hydroperoxide is selected as the case study in this work. Due to the phenol is considered to be an extremely hazardous and toxic substance that even in small quantities can cause severe damage in human health and/or significantly contributes to the pollution of the environment. Therefore, this process is very concerned by the public and industries. Besides, the strict environment regulations towards discharge of phenol have caused a lot of problems and high treatment cost for the industries. Thus, this process is chosen as the case study to illustrate the proposed methodology. Although, the waste generated from the phenol production process is restricted by several properties such as color, temperature, odor etc., in this study the chemical oxygen demand (COD), toxicity and pH are the parameters taken into consideration. This is because the selected properties are strongly environmentally regulated. The objective of this case study is to design an optimal network that not only reduces the consumption of fresh resources but also comply with the environmental regulations. Besides, the recovery cost, treatment cost and piping cost are also taken into consideration during the optimization.

5.2 Process Description

Figure 5.1 showed the schematic representation of the process flowsheet for the production of phenol from cumene hydroperoxide (CHP). In this process, the cumene is selected as the raw material. Firstly, the raw material (i.e. cumene) is fed in to the reactor along with air, and Na_2CO_3 which work as a buffer solution. In the reactor, the cumene is oxidized into cumene hydroperoxide (CHP) with atmospheric oxygen which is found in the air. The mixture of CHP and cumene is then sent to a wash operation to remove the excess of the buffer solution and water soluble materials. Next, the stream leaving the washer is sent to a Concentration Unit in order to increase the low concentration of CHP to 80% by weigh or higher. After that, the concentrated cumene hydroperoxide stream is fed to the cleavage units where the CHP is decomposed to form phenol and acetone with the presence of sulfuric acid. The resulting cleavage stream is neutralized with a small amount of sodium hydroxide and then it is separated into two phases (i.e. organic and water phase). The water phase is sent to wastewater treatment. Meanwhile, the organic phase, which is mainly a mixture of phenol, acetone and cumene, is treated in a water wash to remove the excess of alkali and finally sent to a section of distillation columns where it is fractioned into the pure products phenol and acetone.

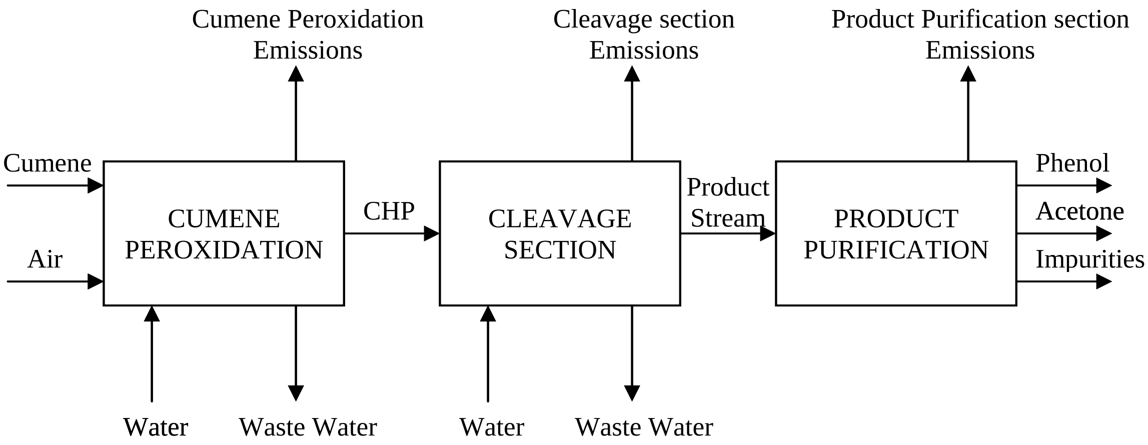

Figure 5.1: Simplified process flow diagram for the manufacture of acetone and phenol from cumene

5.3 Data Extraction

In this case study, the water is targeted as the fresh resource for process integration. Therefore, the operational data, properties values and operational costs of the process units that consume and discharge water directly are analyzed. Figure 5.2 shows a detailed process flow sheet of the cumene peroxidation and cleavage sections. According to the process description and Figure 5.2, the process units, process streams and fresh resources of interest for this case study are summarized as follows:

- Process sinks:
    1. Waterwash cumene peroxidation section (Wash101)
    2. Neutralizer (R104)
    3. Waterwash cleavage section (Wash102)

- Process sources:
    1. Stream 8 from Wash101
    2. Stream 22 from Decanter (D101)
    3. Stream 25 from Wash102

- Fresh water sources:
    1. Freshwater1: 0 impurity concentration
    2. Freshwater2 : 0.012 impurity concentration (mass fraction)

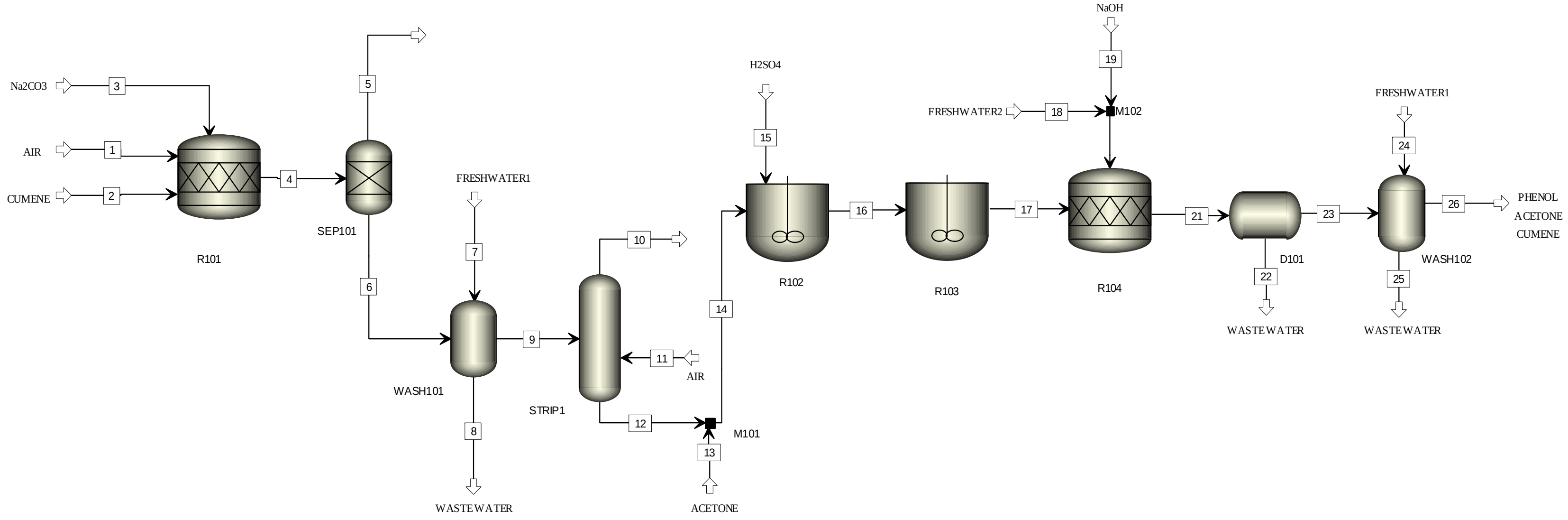

Figure 5.2: Cumene peroxidation and cleavage sections flow diagram

5.4 Operational Data

In order to obtain the operational data needed to apply the proposed optimization technique, the peroxidaxion and cleavage sections of the phenol plant are modeled using a computer-aided simulation program called Aspen Plus. The results obtained from the simulator are summarized in Table 5.1 and Table 5.2. For detail Aspen simulation results are shown in appendix A.

Table 5.1: Sink Data

Sinks	**Water Flowrate G_j (lb/hr)**	**Max. Inlet Impurity Concentration z_j^{max} (Mass Fraction)**
Wash101	6000	0.013
Wash102	4400	0.013
Neutralizer R104	2490	0.1

Due to there is not enough information to determine the maximum allowable impurity concentration accepted by each process sink, the values of z_j^{max} for each process sink were assumed by allowing a deviation from the actual impurity content on the feed stream which enter to each sink.

Table 5.2 Source Data

Source	**Flowrate G_j (lb/hr)**	**Impurity Concentration y_i (Mass Fraction)**
Washer101	8083	0.016
Decanter101	3900	0.024
Washer102	3279	0.22

The impurity concentration of each stream source was calculated following the procedure which is showed in Appendix B.

5.5 Property Data

Besides of the operational data, property values for pH, toxicity and ThOD (Theoretical Oxygen demand) for each process source are needed for the optimization process. The procedure used to determine each property is described as follows:

5.5.1 pH

The pH value, for each process source, was calculated using as a tool the simulation program Aspen Plus. The pH data are obtained from the results of the simulator and are shown in the Table 5.3.

Table 5.3: pH Source Data

Source	**pH**
Wash101	6.68
Decanter101	6.46
Wash102	5.69

5.5.2 Toxicity

Prior to describe the procedure to calculate the toxicity data, it is important to define the following terms:

Toxicity

It is a property that describes the effect of hazardous chemicals on biological organisms.

Acute Toxicity

It is the adverse effects observed, on the tested organism, during a short period of time, which is usually less than 96 hours.

Dose Response Curve

It is a graphical representation between the degree of response on a biological organism and the amount of toxicant administered. The dose response curve is usually plotted versus the logarithm of the dose in order to provide a much straight line in the middle of the curve. If the response of interest is death or lethality, the response curve is called the lethal dose curve.

LD$_{50}$ (Lethal Dose 50%)

It represents the dose at which 50% of the organisms exposed to a toxic will die.

Probit Function (Y)

It is a mathematical relationship that transforms the sigmoid shape for the normal response-dose curve into a straight line.

The probit variable Y is represented mathematically in equation 5.1

$$Y = k_1 + k_2 \log V \tag{5.1}$$

where k_1 and k_2 are the probit parameters and V is the magnitude of the exposure.

The relationship between the percentages P and the probit variable Y is provided in equation 5.2. The transformations from percentages to probits are also found tabulated as shown in Table 5.4.

$$P = 50\left[1 + \frac{Y-5}{|Y-5|}\, erf\left(\frac{|Y-5|}{\sqrt{2}}\right)\right] \tag{5.2}$$

Table 5.4: Transformation from percentages to probits. (D.J. Finney, Probit Analysis, 1971)

%	**0**	**1**	**2**	**. . .**	**9**
0	-	2.67	2.95	….	3.66
10	3.72	3.77	3.82	….	4.12
20	4.16	4.19	4.23	….	4.45
.	.	.	.	….	.
.	.	.	.	….	.
.	.	.	.	….	.
.	.	.	.	….	.
90	6.28	6.34	6.48	….	7.33

Phenol Toxicity

In this case study, two chemicals, phenol and acetone are mainly discharged to the environment. However, phenol toxicity is only evaluated since acetone is recognized for having low acute and chronic toxicity; and therefore, the release of this chemical do not represent a threat to the environment and/or human health. Phenol toxicity is calculated using the probit correlation shown in equation 5.3

$$Y = -0.22 + 5.27 \log C \qquad (5.3)$$

where Y represents the lethal response and C (ppm) is the phenol concentration.

This probit equation was determined by performing several phenol acute toxicity experiments on Daphnia Magna as tested organism (Soboslay, 1987[28]). Using equation 5.3 the Y values (mortality response) for each process source is calculated and then transform to percentage using Table 5.4. Description of this toxicity calculation are shown in Appendix C and the results are summarizes in Table 5.5.

Table 5.5 Toxicity Source Data

Source	Phenol Concentration (ppm)	Toxicity Mortality %
Wash101	17	89.6
Decanter101	13000	100
Wash102	24000	100

5.5.3 Theoretical Oxygen Demand (ThOD)

ThOD is the theoretical amount of oxygen, O_2 required to oxidize an organic compound to its final oxidation products. ThOD in wastewater streams have been strictly regulated since the discharge of high values of ThOD in public effluents would reduce significantly the oxygen available in the water causing adverse effects on fish and aquatic life in general. In this case study, the ThOD required for each process source was calculated using the following procedure:

First, the balance oxidation reaction for each organic compound contained in stream *i* is written as shown in equation 5.4.

$$aOrganicCompound + bO_2 \rightarrow cCO_2 + dH_2O \tag{5.4}$$

where *a, b, c, d* are stoichiometry coefficients.

e.g.: Stream 8 contains three organic compounds Cumene Hydroperoxide ($C_9H_{12}O_2$), Dimetylphenylcarbinol ($C_9H_{12}O$), and Phenol (C_6H_5OH). Oxidation reactions for these compounds are shown in equations 5.5 through 5.7

Cumene Hydroperoxide: $C_9H_{12}O_2 + 11\,O_2 \rightarrow 9CO_2 + 6H_2O$ (5.5)

Dimetylphenylcarbinol: $C_9H_{12}O + 11.5O_2 \rightarrow 9CO_2 + 6H_2O$ (5.6)

Phenol: $C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$ (5.7)

Second, the oxygen require to reach complete oxidation (ThOD) of each organic compound is determined by using stoichiometry relationships as shown in equation 5.8.

$$ThOD_m = \left(\frac{b\ molO_2}{a\ mol\ m.}\right)\left(\frac{MW_{O_2}}{molO_2}\right)\left(\frac{1mol\ m.}{MW_m}\right) \quad \{m|m=1,\ldots N_{\text{Organic Compound}}\} \tag{5.8}$$

where MW_{O_2} and MW_m are the molecular weights of oxygen and the organic compound respectively and $ThOD_m$ is the theoretical oxygen demand of the organic compound *m*.

e.g.: ThOD values for the organic compound in stream 8 are calculated in equations 5.9 through 5.11

$$ThOD_{cumene.} = \left(\frac{11molO_2}{mol\,cumene.}\right)\left(\frac{32\,lbO_2}{molO_2}\right)\left(\frac{1mol\ cumene.}{152\,lb\,cumene.}\right) = 2.315\,{}^{lb\,O_2}\!\big/_{lb\,cumene.} \tag{5.9}$$

$$ThOD_{\dim etyl.} = \left(\frac{11.5molO_2}{mol\,\dim etyl.}\right)\left(\frac{32\,lbO_2}{molO_2}\right)\left(\frac{1mol\ cumeneh.}{136\,lb\,\dim etyl.}\right) = 2.70\,{}^{lb\,O_2}\!\big/_{lb\,\dim etyl.} \tag{5.10}$$

$$ThOD_{phenol} = \left(\frac{7\,molO_2}{mol\ phenol}\right)\left(\frac{32\,lbO_2}{molO_2}\right)\left(\frac{1mol\ phenol}{94.11lb\ phenol}\right) = 2.38\,{}^{lb\,O_2}\!\big/_{lb\ phenol} \tag{5.11}$$

Finally, The overall ThOD of the stream *i* is calculated by using equation (5.12)

$$ThOD_i = \sum_{m=1}^{N_{Org.Compound}} x_m ThOD_m \tag{5.12}$$

where x_m is the fractional contribution (mass/volume) of the organic compound *m* in stream *i*.

e.g.: The ThOD for stream 8 is calculated in equation 5.13

$$0.00091 \frac{lb\ Cumene}{ft^3} * \frac{2.70\ lb\ O_2}{lb\ Cumene} + 0.0027 \frac{lb\ Dimetyl}{ft^3} * \frac{2.70\ lb\ O_2}{lb\ Dimetyl} + \\ + 0.00094 \frac{lb\ Phenol}{ft^3} * \frac{2.381\ lb\ O_2}{lb\ phenol} = 0.0117 \frac{lb\ O_2}{ft^3} \tag{5.13}$$

The compositions of the organic components in stream 8 were determined based on the mass balance results obtained from the simulation. The ThOD results for all process sources are summarized in Table 5.6

Table 5.6 ThOD Source Data

Source	**ThOD** lbO_2 / ft^3	**ThOD** gO_2 / l
Wash101	0.0117	0.187
Decanter101	3.05	48.85
Wash102	5.75	92.10

5.6 Environmental Regulations

The discharge of waste streams to the environment is restricted by the following environmental regulations (Nemerow, 1978[29]):

- ThOD = 75 mg O_2 /l
- $5.5< pH < 9.0$
- Maximum Phenol load discharged <= 0.054 lb/hr
- Phenol Toxicity = 0% mortality

5.7 Waste Treatment Technologies

In this case study, four water treatment technologies were used to reduce the pollution content in the wastewater streams. The descriptions of these units are given as follows:

Solvent Extraction:

Solvent extraction is one of the most important techniques used in the pretreatment of high-phenol concentrated wastewater streams. This process was used to recover phenol from waste streams that have a phenol content of more than 500 ppm. The recovery of phenol is highly recommended since it reduces the pollutant content in the waste streams and additionally brings economic benefits to the company. Solvent extraction units show an efficiency of 93% phenol removal. The phenol recovery treatment cost is given in Table 5.7.

Table 5.7: Solvent Extraction Treatment Cost. (Yang, and Qian, 2006[30])

Description	**Cost** ($/lb phenol recovered)
Operational Cost	0.186
Fixed Cost	0.015
Subtotal	0.201
Economic Return (Recovered Phenol sales)	-0.136
Total Cost	**0.065**

Air Stripping:

This technology is mainly used to remove volatile organic compounds from water streams. In this case study, this technology was used to recover acetone from waste streams with a high content of this compound; and besides, to remove phenol from wastewater streams with a very low phenol concentration for which solvent extraction is not economically recommended. The removal efficiencies for acetone and phenol air stripping units are assumed to be 97% and 95% respectively. The air stripping treatment cost is shown in Table 5.8.

Table 5.8: Air Stripping Treatment Cost

Description	**Acetone Recovery** ($/lb Acet. recovered)	**Phenol Removal** ($/lb phenol removed)
Operational Cost	0.125	0.143
Fixed Cost	0.0215	0.0215
Subtotal	0.1462	0.164
Economic Return (Recovered Acet. sales)	-0.113	----
Total Cost	**0.033**	**0.164**

Aeration:

Aeration is a well developed technology in the wastewater treatment industry that have as a main objective to reduce the high content of oxygen demand in wastewater streams. This goal is achieve by putting in contact the wastewater streams with air for a specific period of time. In this case study the Aeration treatment cost was determined to be 0.06 $/$_{\text{lb of air diffused}}$.

Neutralization:

Neutralization technique was used to adjust the pH in the wastewater streams to a value that complies with the environmental regulations. In this case study, the costs for acid-neutralizing and base-neutralizing were assumed to be 0.40 $/lt of H_2SO_4 0.5M and 0.31 $/lt of NaOH 0.5 M respectively.

With the given process information along with the operational and property data gathered, two optimization algorithms based on mass on property integration methodologies were formulated.

5.8 Mass Integration

Direct Recycle approach was applied to this case study in order to determine the targets for minimum consumption of freshwater, minimum wastewater discharge and minimum operational cost (including freshwater and piping cost). This optimization problem was solved using LINGO optimization software. The entire program formulation that was used to develop this solution as well as the program output can be seen in Appendix D. Additional information regarding Freshwater and piping cost was needed to solve the optimization problem. The costs for Freshwater1 and Freshwater2 was determined to be 0.0006$/lb and 0.0004$/lb respectively. The piping cost between process sources and process units are shown in Table 5.9.

Table 5.9: Assumed Cost Pipe Coefficients

Sources / **Sinks**	**Washer 101**	**Decanter 101**	**Washer 102**	**Freshwater1**	**Freshwater2**
Wash101	5	2	3	4.5	2.5
Neutralizer R104	3.5	1	5	3	1
Wash101	2	4	2	3.5	1.5

After solving the direct recycle problem using LINGO, the global solution obtained for this case study was 41815.89 $/year with targets for minimum consumption of freshwater of 4595.lb/hr and a minimum target for waste discharge of 6969.28 lb/hr. The optimum recycle network suggested for implementing mass integration is shown in Figure 5.3

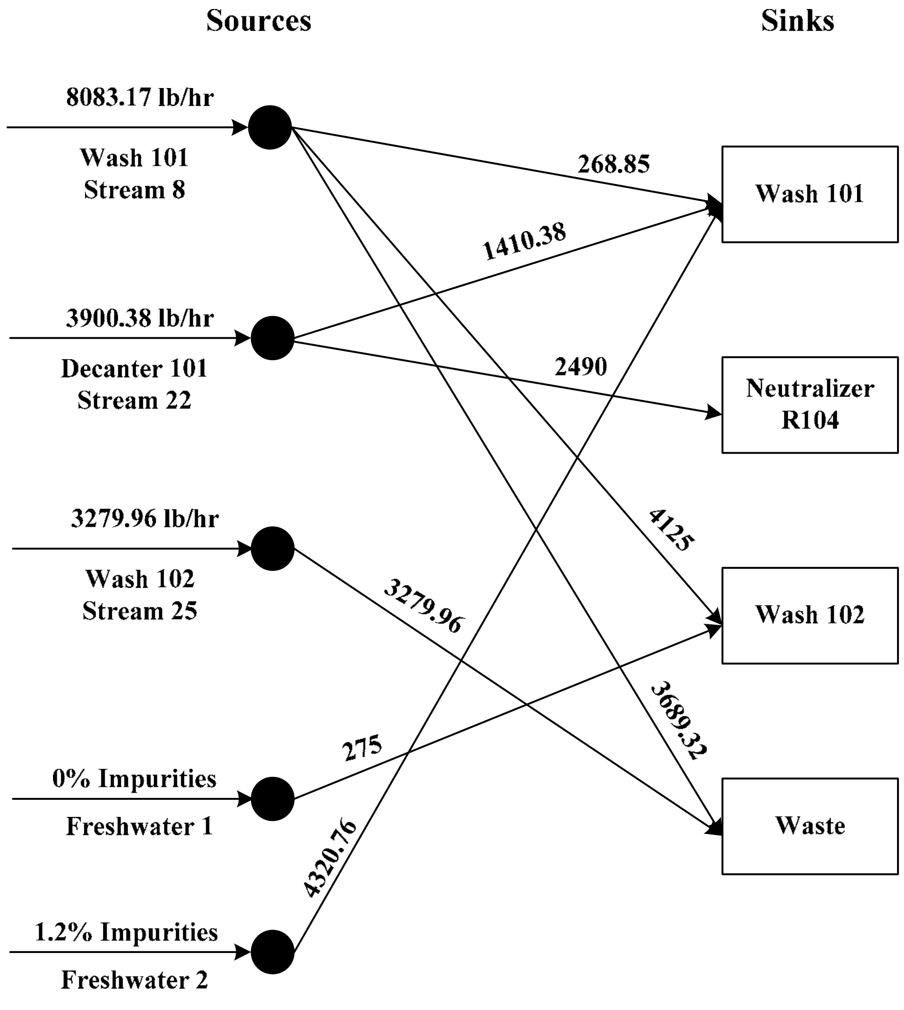

Figure 5.3: Optimized Direct Recycle Network

5.9 Property Integration

Property Integration was applied to this case study in order to minimize the pollutant content in the wastewater streams and thus the waste treatment cost for the process. The flow diagram describing the waste treatment configuration used in this case study is shown in Figure 5.4.

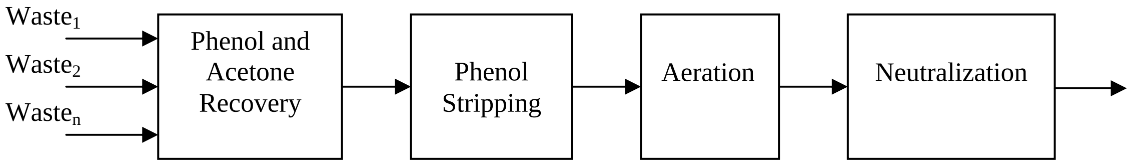

Figure 5.4: Waste Treatment Flow Diagram

Before going through the mathematical formulation developed to solve this problem, it is required to determine the mixing rules for each of the properties involve in this optimization. The mixing rules for phenol toxicity, ThOD and pH are shown in Equations 5.14 through 5.16.

- ThOD Mixing Rule

$$\overline{ThOD}\,(mg\,O_2\,/\,l\;waste) = \sum_{i=1}^{N_{Sources}} x_i ThOD_i \tag{5.14}$$

- Phenol Toxicity Mixing Rule

$$\overline{Y}(\%\,Mortality) = -0.22 + 5.27 \sum_{i=1}^{N_{Sources}} \log(c_i) \tag{5.15}$$

where c_i is the phenol concentration in stream *i*.

- pH Mixing Rule:

$$10^{\overline{pH}} = \sum_{i=1}^{N_{Sources}} x_i 10^{pH_i} \tag{5.16}$$

This second formulation, developed in this work, has the aim of minimizing the cost of fresh water, piping and waste treatment simultaneously. As a result, the waste treatment cost is included in the objective function. The waste treatment cost is a function of phenol and acetone recovery, toxicity removal, oxygen demand reduction and pH adjustment processes. The description of the waste treatment process technologies, used in this case study, are stated in the following sections.

5.9.1 Phenol Recovery

Figure 5.5 showed the schematic representation of the phenol recovery process using an extraction column.

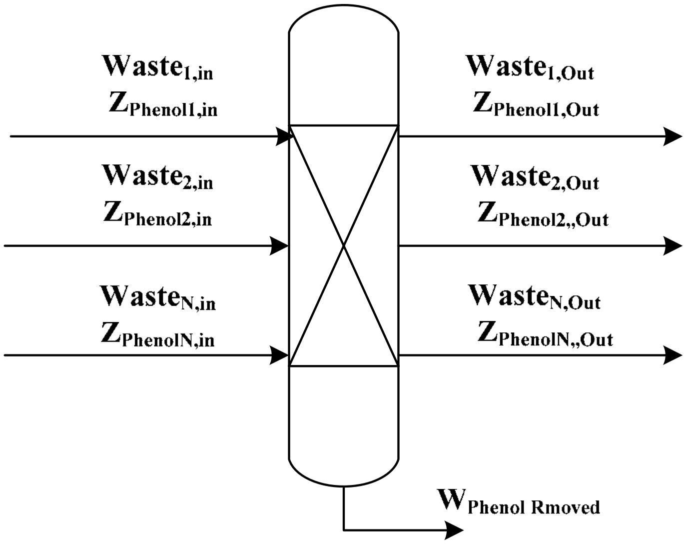

Figure 5.5: Phenol recovery process

In order to determine the total recovery cost (including phenol and acetone) for this case study, the following formulation was developed:

- *Phenol Recovered*

$$W_{i\,Phenol\,\mathrm{Re}\,\mathrm{cov}\,ered} = \left(eff_{Column,p}\, w_{i,waste}\, z^{in}_{i,Phenol}\right) I_{i,phenol} \qquad (5.17)$$

where $W_{i\,Phenol\,\mathrm{Re}\,\mathrm{cov}\,ered}$ is the flowrate of phenol removed from stream *i*, $eff_{Column,p}$ is the removal efficiency of the extraction column and $z^{in}_{i,Phenol}$ is the phenol concentration in waste stream i. $I_{i,phenol}$ is a binary term that takes the value of 1 if the waste stream has a phenol concentration $z_{i,Phenol}^{in}$ greater than 500ppm otherwise it become 0 (zero).

- *Phenol Remaining*

$$W_{Phenol\,\mathrm{Re}maining} = \sum_{i=1}^{N_{Sources}} (1 - eff_{Column}) w_{i,waste} z_{Phenol}^{in} \tag{5.18}$$

where $W_{Phenol\,\mathrm{Re}maining}$ is the total flowrate of phenol remaining in the waste streams after recovery process.

- *Waste after Phenol Recovery*

$$W_{Wastei,After\ Phenol\,\mathrm{Recov}ery} = W_{Wastei,in} - W_{Phenol\,\mathrm{Recov}ered} \tag{5.19}$$

where $W_{Wastei,After\ Phenol\,\mathrm{Recov}ery}$ is the flowrate of waste stream *i* after the phenol recovery process.

- *Phenol recovery Cost*

$$Phenol\,\mathrm{Recov}eryCost = W_{Phenol\,\mathrm{Recov}ered} C_{Phenol\,\mathrm{Recov}er} \tag{5.20}$$

where $C_{Phenol\,\mathrm{Recov}er}$ is the cost of removing phenol.

5.9.2 Acetone Recovery

Figure 5.6 showed the schematic representation of the phenol recovery process using an air stripping column.

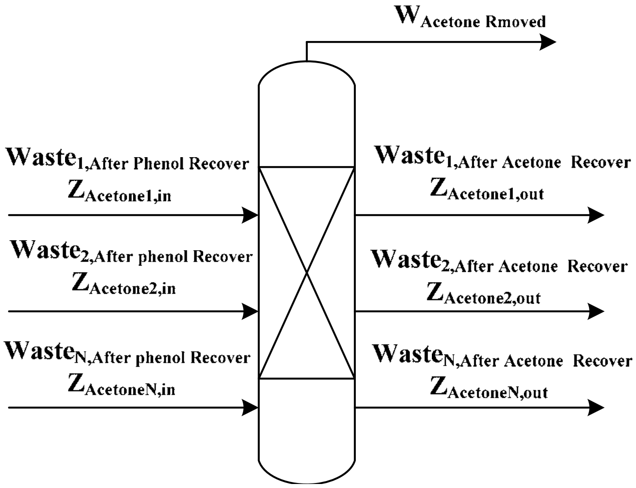

Figure 5.6: Acetone recovery process

Similarly to recovery of phenol, the following information is required:

- *Acetone Recovered*

$$W_{i\,Acetone\,Recovered} = \left(eff_{Column,A}\, w_{i,waste\,after\,Phenol\,Recovery}\, z^{in}_{i,Acetone}\right) I_{i,Acetone} \qquad (5.21)$$

- *Waste after Acetone Recovery*

$$W_{Waste\,i,After\,Acetone\,Recovery} = W_{Waste\,i,After\,Phenol\,Recovery} - W_{i,\,Acetone\,Recovered} \qquad (5.22)$$

- *Acetone Remaining*

$$W_{Acetone\,Remaining,i} = \sum_{i=1}^{N_{Sources}} (1 - eff_{Column,A})\, w_{i,waste}\, z^{in}_{Acetone} \qquad (5.23)$$

- *Acetone Recovery Cost*

$$Acetone\,\mathrm{Recov}ery\,Cost = W_{Acetone\,\mathrm{Recov}ered}\,C_{Acetone\,\mathrm{Recov}er} \tag{5.24}$$

5.9.3 Phenol Toxicity Removal

Phenol toxicity is a function of phenol concentration. Therefore, the waste streams were mixed after the acetone recovery process in order to dilute the phenol concentration, thus reducing the phenol load required to be removed. Figure 5.7 showed the schematic representation of the phenol toxicity removal treatment using an air stripping column.

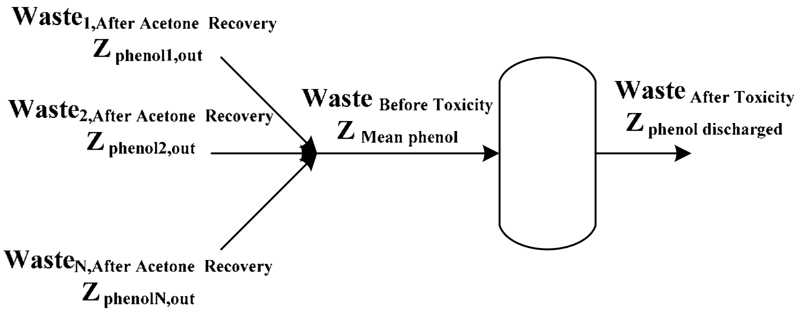

Figure 5.7: Phenol Toxicity Removal

The mathematical formulation developed to determine the cost of this process is described as follows:

- *Total Waste Entering to Toxicity Treatment*

$$Total\ Waste_{After\ Acetone\,\mathrm{Re}\,\mathrm{cov}\,ery} = \sum_{i=1}^{N_{Sources}} W_{Waste\ i,After\ Acetone\,\mathrm{Re}\,\mathrm{cov}\,ery} \tag{5.25}$$

- *Phenol Concentration Entering to Toxicity Treatment*

$$Z_{mean\ phenol} = {W_{Phenol\ \mathrm{Re}\,maining}} \Big/ {Total\ Waste_{After\ Acetone\,\mathrm{Re}\,\mathrm{cov}\,ery}} \tag{5.26}$$

- *Concentration of Phenol Removed*

$$Z_{Phenol\,\mathrm{Re}\,moved} = Z_{mean\ phenol} - Z_{disch\,\mathrm{arg}\,ed\ Phenol} \tag{5.27}$$

where $Z_{Phenol\,\mathrm{Re}\,moved}$ is the phenol concentration need to be removed and $Z_{disch\,\mathrm{arg}\,ed\ Phenol}$ is the allowed phenol concentration to be discharged to the environment.

- *Load of Phenol Removed*

$$W_{Phenol\,\mathrm{Re}\,moved} = Z_{mean\ phenol}\,Total\ Waste_{After\ Acetone\,\mathrm{Re}\,\mathrm{cov}\,ery} \tag{5.28}$$

- *Waste After Toxicity Treatment*

$$W_{Waste\ After\ Toxicity} = Total\ Waste_{After\ Acetone\,\mathrm{Re}\,\mathrm{cov}\,ery} - W_{Phenol\,\mathrm{Re}\,moved} \tag{5.29}$$

- *Phenol Remaining after Toxicity*

$$W_{Phenol\ \mathrm{Re}\,maining\ after\ Tox.} = Z_{disch\,\mathrm{arg}\,ed\ Phenol}\,W_{Waste\ After\ Toxicity} \tag{5.30}$$

- *Phenol Toxicity Cost*

$$PhenolToxicityCost = W_{Phenol\,\mathrm{Re}moved} C_{Phenol\,\mathrm{Re}moved} I_T \qquad (5.31)$$

where $C_{Phenol\,\mathrm{Re}moved}$ is the cost of removing phenol using air stripping and I_T is a binary term that takes the value of 0 (zero) when the phenol concentration after recovery $Z_{mean\,phenol}$ is equal to the phenol allowed discharge concentration $Z_{disch\mathrm{arg}ed}$; otherwise, it becomes 1.

Phenol toxicity treatment cost is constraint by the following environmental regulations:

- *Phenol Load Regulation*

$$Z_{disch\,\mathrm{arg}\,ed\ Phenol} W_{Waste\ After\ Toxicity} \le 0.054 \qquad (5.32)$$

- *Phenol Toxicity Regulation*

Using the toxicity mixing rule stated in equation 5.15, the phenol concentration at which the mortality is 0% was determine to be 1.10 mg_{phenol}/lt_{waste}.

$$Z_{disch\,\mathrm{arg}\,ed\ Phenol} \le 0.0000011\, {}^{lb_{phenol}}\!\!/_{lb_{waste}} \qquad (5.33)$$

5.9.4 ThOD Treatment

Figure 5.8 showed the schematic representation of the phenol recovery process using an aeration basin.

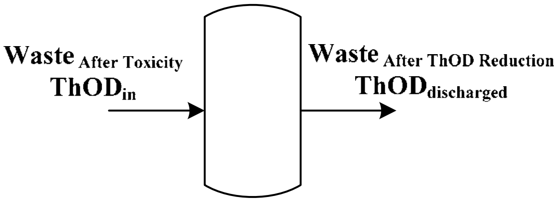

Figure 5.8: ThOD Treatment

The total ThOD value for the waste stream after toxicity treatment was calculated using the following equations.

- *Concentration of Organic Compounds in Waste Stream*

$$y_{m,WasteStream} = \sum_{i=1}^{N_{Sources}} y_{m,i} w_{i,waste} \Big/ W_{Waste\,After\,Toxicity} \tag{5.34}$$

Where $y_{m,i}$ is the composition of component *m* in stream *i* and $y_{m,WasteStream}$ is the final composition of component *m* in the waste stream after toxicity treatment.

For phenol and acetone the composition in the waste stream is calculated based on the remaining load after the toxicity treatment. This is shown in equations 5.35 and 5.36

$$y_{Phenol,WasteStream} = {W_{Phenol\ \mathrm{Re}maining\ after\ Tox.}}\Big/{W_{Waste\ After\ Toxicity}} \tag{5.35}$$

$$y_{Phenol,WasteStream} = {W_{Acetone\ \mathrm{Re}maining}}\Big/{W_{Waste\ After\ Toxicity}} \tag{5.36}$$

- *Total ThOD in Waste Stream*

$$ThOD_{Waste\ Stream} = \sum_{u=1}^{N_{Organic\ Compound}} y_{m,WasteStream} ThOD_m \tag{5.37}$$

where $ThOD_{Waste\ Stream}$ is the total Oxygen Demand of the waste stream leaving the toxicity treatment and $ThOD_m$ is the Theoretical Oxygen Demand of component *m*.

The treatment cost of reducing ThOD was determined as a function of the oxygen required to be diffused in the waste stream. Therefore, the ThOD treatment cost was calculated as follows:

- *Oxygen to be Diffused*

$$W_{Oxygen\ Diffused} = (ThOD_{Waste\ Stream} - ThOD_{\mathrm{Re}gulation})\ W_{Waste\ After\ Toxicity} \tag{5.38}$$

Where $W_{Oxygen\ Diffused}$ is the mass flowrate of oxygen diffused in the waste stream and $ThOD_{\mathrm{Re}gulation}$ is the environmental regulation for Oxygen Demand in wastewater streams. The Oxygen injected in this process is taken from the air. Therefore, the amount of air required to supply the Oxygen demand is calculated using equation 5.41.

- *Air to be Diffused*

$$n_{Oxygen\,Diffused} = \left({W_{Oxygen\,Diffused}} \big/ {MW_{O_2}} \right) \tag{5.39}$$

Where $n_{Oxygen\,Diffused}$ are the moles of oxygen to be diffused.

Since one mol of air contents 21% of oxygen, the moles of air required to supply the demand of oxygen are calculated using equation 5.40

$$n_{Air\,Diffused} = \left({n_{Oxygen\,Diffused}} \big/ {0.21} \right) \tag{5.40}$$

where $n_{Air\,Diffused}$ is the total moles of air that need to be diffused.

$$W_{Air\,Diffused} = n_{Oxygen\,Diffused}\ MW_{Air} \tag{5.41}$$

Where $W_{Air\,Diffused}$ is the mass flowrate of air diffused in the waste stream and MW_{Air} is the molecular weight of air.

- *ThOD Treatment Cost*

$$ThOD\ Treatment\ Cost = W_{Air\,Diffused}\ C_{DiffusedAir} \tag{5.42}$$

Where $C_{DiffusedAir}$ is the cost of compressing and diffusing air into the aeration basin.

ThOD treatment cost is constraint by the following environmental regulation

$$ThOD_{\mathrm{Re}\,gulation} \le 0.75\,mg\,/\,lt \tag{5.43}$$

5.9.5 Neutralization Treatment

Figure 5.9 showed the schematic representation of the pH neutralization process.

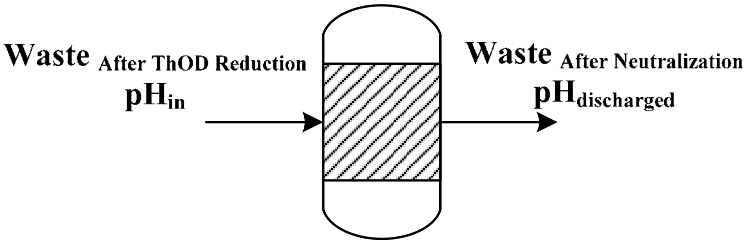

Figure 5.9: Neutralization Treatment

The treatment cost of adjusting pH was determined as a function of the amount of acid or base solution needed to neutralize the wastewater stream. Therefore, the neutralization treatment cost was calculated using the following mathematical formulation:

- *Waste Stream pH Value :*

The pH value for the waste stream after ThOD treatment is calculated by determining the fractional process stream contributions to the total waste and by applying the mixing rule stated in equation 5.16. The split stream ratio is calculated after the acetone recovery process and it is shown in equation (5.44). The stream ratio is assumed to remain constant within the process.

$$WasteRatio_i = {W_{Waste\ i, After\ Acetone\ \mathrm{Re}\,\mathrm{cov}\,ery}} \Big/ {Total\ Waste_{After\ Acetone\ \mathrm{Re}\,\mathrm{cov}\,ery}} \tag{5.44}$$

where $WasteRatio_i$ is the fractional contribution of waste stream *i* in the total waste after acetone recovery and $W_{Waste\ i, After\ Acetone\ \mathrm{Re}\,\mathrm{cov}\,ery}$ is the flowrate of waste stream *i* after the acetone recovery process.

The $\overline{pH}_{Waste}$ value for the waste stream was calculated using equation 5.45.

$$10^{\overline{pH}_{Waste}} = \sum_{i=1}^{N_{Sources}} WasteRatio_i 10^{pH_i} \tag{5.45}$$

where, pH_i is the *pH* value of process stream *i*.

Two neutralization processes are available to treat either a basic or alkaline waste stream as follows:

Base Neutralization

In this case study, the alkaline waste stream is neutralized using a sodium hydroxide (NaOH) solution 0.5 M. In order to determine the cost of this treatment process the following data is required:

- *Concentration of* $\left[OH^-\right]$ *in Base Solution*

In this case study, it is assumed that NaOH is completely ionized and is the sole source of hydroxide ion (OH^-). Therefore, the hydroxide ion concentration in the base solution is determined to be $\left[OH^-\right] = 0.5M\ (mol/lt)$.

- *Concentration of* $\left[H_3O^+\right]$ *in waste stream*

The concentration of hydronium ion $\left[H_3O^+\right]_{waste}$ in the waste stream is calculated using equation 5.46.

$$\left[H_3O^+\right]_{waste}(mol/lt) = 10\hat{}\,(-\overline{pH}_{Waste}) \tag{5.46}$$

where $\overline{pH}_{Waste}$ is the pH value of the waste stream.

- *Total amount of moles of* $H_3O^+{}_{waste}$ *to be treated*

$$Total\,H_3O^+{}_{waste}(mol) = W_{Waste\,After\,Toxicity}\,1/\rho_{waste}\left[H_3O^+\right]_{waste} \tag{5.47}$$

where $H_3O^+{}_{waste}$ are the moles of H_3O^+ required to be removed from the waste stream and ρ_{waste} is the waste stream density.

- *Total amount of moles of* OH^-

The amount of moles of OH^- used to neutralize the $H_3O^+{}_{waste}$ concentration in the waste stream is calculated using equation 5.48.

$$Total\,OH^-(mol) = Base\left[OH^-\right] \tag{5.48}$$

where *Base* is the amount of base solution used to adjust the pH in the waste stream up to a value allowed for discharging into the environment.

- *Total amount of moles of* $H_3O^+{}_{waste}$ *after Base Neutralization*

The number of moles of $H_3O^+{}_{waste,\,remaining}$ remaining after the neutralization reaction is calculated using equation 5.49

$$H_3O^+{}_{waste,\,remaining} = Total\,H_3O^+{}_{waste} - Total\,OH^- \qquad (5.49)$$

- *Total Waste after Neutralization*

$$Total\ Waste = W_{Waste\,After\,Toxicity}\,1/\rho_{waste} + Base \qquad (5.50)$$

- *Concentration of* $\left[H_3O^+\right]$ *in Waste Stream after Neutralization*

$$\left[H_3O^+\right]_{waste,\,remaining}(mol/lt) = {H_3O^+{}_{waste,\,remaining}}\Big/{Total\,Waste} \qquad (5.51)$$

- *pH Value after Neutralization*

$$10^{\wedge}(-pH_{discharged}) = \left[H_3O^+\right]_{waste,\,remaining} \qquad (5.52)$$

where $pH_{discharged}$ is the final pH value in the waste stream before discharging it to the environment.

- *Base Neutralization Cost*

$$TreatmentBaseCost = BaseC_{BaseSolution}\ I_B \qquad (5.53)$$

where $C_{BaseSolution}$ is the cost of the base solution (NaOH, 0.5M) and I_B is a binary term that takes the value of 0 (zero) if no base neutralization is needed; otherwise, it becomes one (1).

Acid Neutralization

In this case study, the base waste stream is neutralized using a sulfuric acid (H_2SO_4) solution 0.5 M. Similarly to base neutralization treatment, the following data is required:

- *Concentration of* $\left[H_3O^+\right]$ *in Acid Solution*

In this case study, it is assumed that H_2SO_4 is completely ionized and is the sole source of hydroxide ion H_3O^+. Therefore, the hydronium ion concentration in the acid solution is determined to be $\left[OH^-\right] = 0.5M\ (mol/lt)$.

- *Concentration of* $\left[OH^-\right]$ *in waste stream*

The concentration of hydroxide ion $\left[OH^-\right]_{waste}$ in the waste stream is calculated using equation 5.54.

$$\left[OH^-\right]_{waste}(mol/lt) = 10^\wedge(-\overline{pOH}_{Waste}) \tag{5.54}$$

where $\overline{pOH}_{Waste}$ is the mathematically represented in equation 5.55

$$\overline{pOH}_{Waste} = 14 - \overline{pH}_{Waste} \tag{5.55}$$

- *Total amount of moles of OH^- to be treated*

$$Total\,OH^-{}_{waste}(mol) = W_{Waste\,After\,Toxicity}\,1/\rho_{waste}\,\left[OH^-\right] \tag{5.56}$$

where $OH^-{}_{waste}$ are the moles of OH^- required to be removed from the waste stream.

- *Total amount of moles of H_3O^+*

The amount of moles of H_3O^+ used to neutralize the $OH^-{}_{waste}$ concentration in the waste stream is calculated using equation 5.57.

$$Total\,H_3O^+(mol) = 2Acid\left[H_3O^+\right] \tag{5.57}$$

where Acid is the amount of base solution used to adjust the pH in the waste stream up to a value allowed for discharging into the environment. This equation is multiplied by a factor of 2 because there are two acidic hydrogens.

- *Total amount of moles of $OH^-{}_{waste}$ after Acid Neutralization*

The number of moles of $OH^-{}_{waste,\,remaining}$ remaining after the neutralization reaction is calculated using equation 5.49

$$OH^-{}_{waste,\,remaining} = Total\,OH^- - \;Total\,H_3O^+ \tag{5.58}$$

- *Total Waste after Acid Neutralization*

$$Total\;Waste = W_{Waste\,After\,Toxicity}\,1/\rho_{waste} + Acid \tag{5.59}$$

- *Concentration of* $\left[OH^{-}\right]$ *in Waste Stream after Neutralization*

$$\left[OH^{-}\right]_{waste,\ remaining}(mol/lt) = {OH^{-}}_{waste,\ remaining} \big/ TotalWaste \qquad (5.60)$$

- *pH Value after Neutralization*

$$10^{\wedge}(-pOH_{discharged}) = \left[OH^{-}\right]_{waste,\ remaining} \qquad (5.61)$$

$$pH_{discharged} = 14 - pOH_{discharged} \qquad (5.62)$$

where $pH_{discharged}$ is the final pH value in the waste stream before discharging it to the environment.

- *Neutralization Cost*

$$AcidTreatmentBaseCost = BaseC_{AcidSolution}\ I_{A} \qquad (5.63)$$

where $C_{AcidSolution}$ is the cost of the acid solution (H_2SO_4, 0.5M) and I_A is a binary term that takes the value of 0 (zero) if no acid neutralization is needed; otherwise, it becomes one(1).

The acid and base neutralization treatments are restricted by the following environmental constraints:

$$pH_{discharged} \leq 9 \qquad (5.64)$$

$$pH_{discharged} \geq 5.5$$

(5.65)

To solve this problem that involves mass and property integration, LINGO optimization software was used to obtain the global solution. For this case study, the minimum operational cost, including waste treatment, was determined to be 111005.8 $/year with targets for minimum consumption of freshwater of 2663.72lb/hr and a minimum target for waste discharge of 5037.72 lb/hr. The penalty that the company has to pay for complying with environmental regulations is approximately 69189.9 $/year.

The optimum recycle network suggested for implementing the proposed solution is shown in Figure 5.10

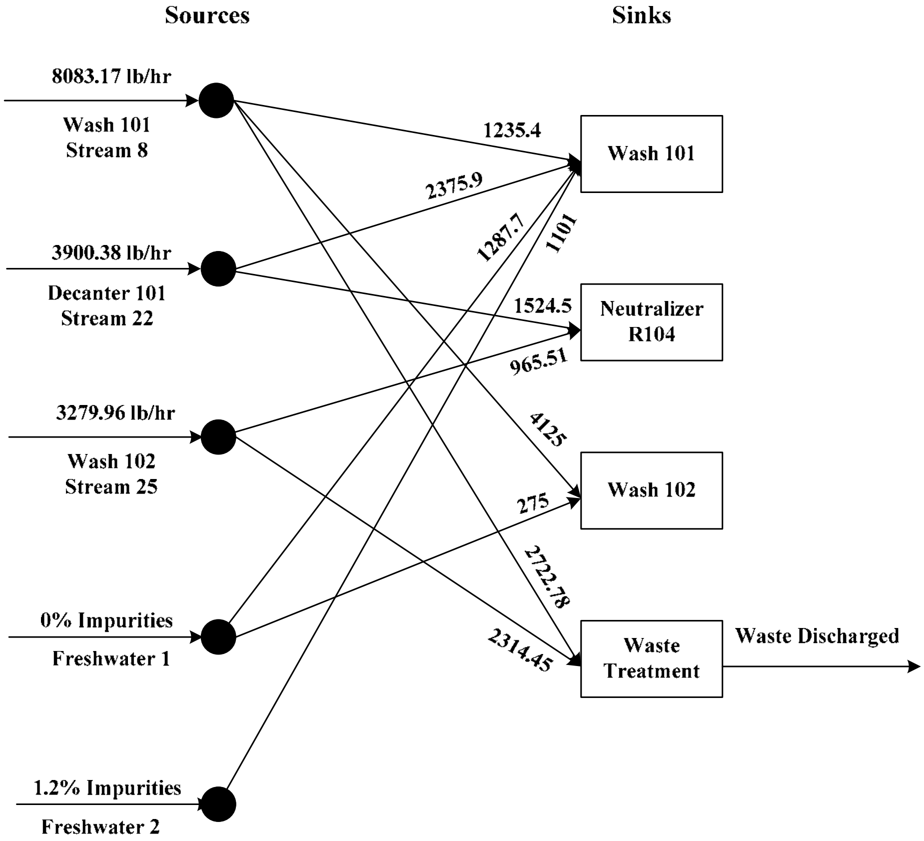

Figure 5.10: Optimized Mass-Property Direct Recycle Network

The final flowsheet diagram for the phenol process after mass and property integration is shown in figure 5.11. The description of the process sources used in this optimization is shown in Tables 5.10 and 5.11. The entire program formulation that was used to develop this solution as well as the program output can be seen in Appendix E.

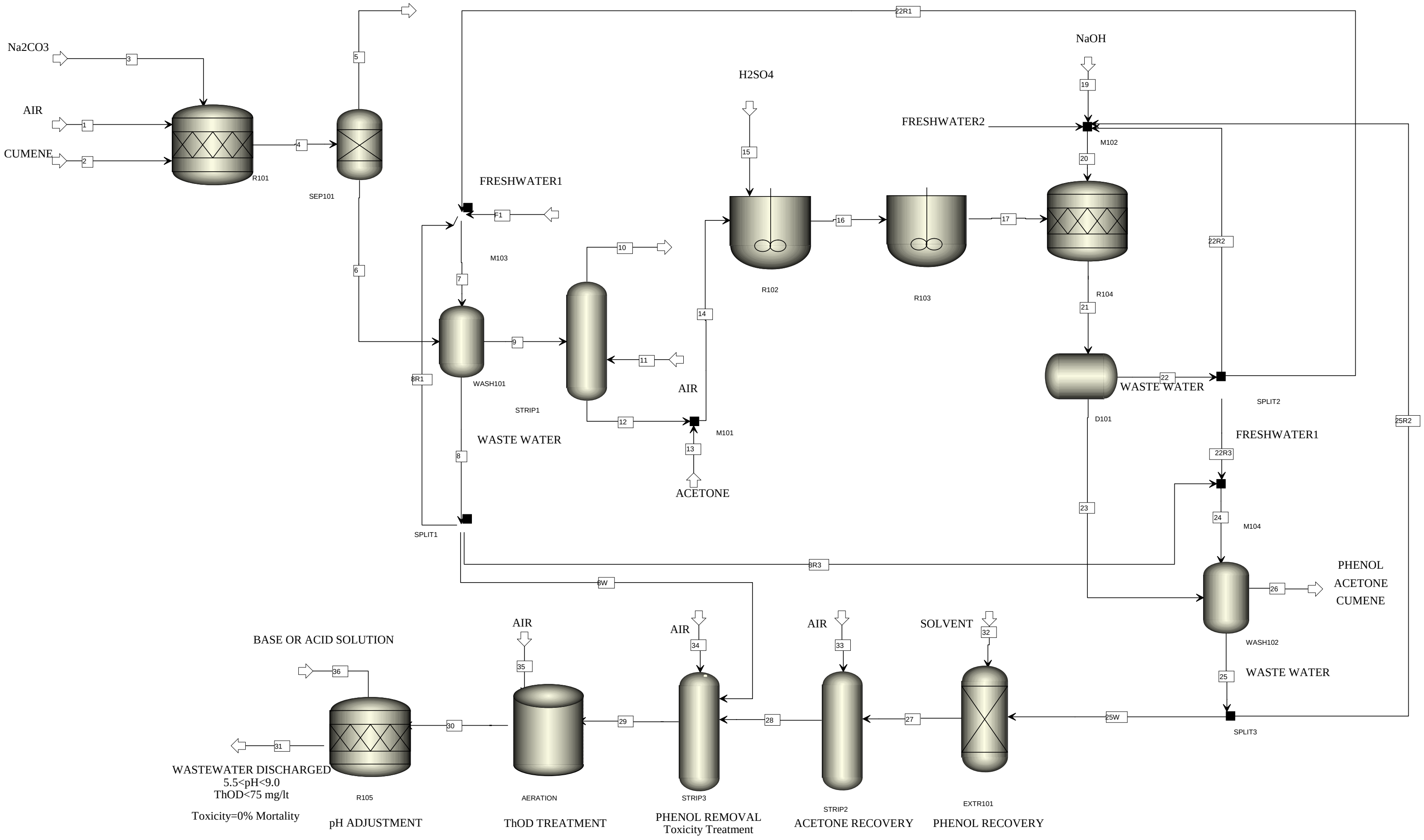

Figure 5.11: Phenol process Flowsheet Diagram after Optimization

Table 5.10: Waste Stream Data

Process Streams	**Flowrate lb/hr**	**Phenol Mass fraction ppm**	**Acetone Mass fraction ppm**	**pH**	**Toxicity % Mortality**	**ThOD gO_2/l**
Wash101 8	8083.019	17	---	6.68	89.6	0.187
Wash101 8W	2783.968	17	---	6.68	89.6	0.064
Wash102 25	3279.96	24000	28000	5.69	100	92.16
Wash102 25W	2249.94	24000	28000	5.69	100	63.21
Extr101 27	2199.73	1700	28000	5.69	100	52.65
Strip2 30	2137.99	1700	589	5.69	100	4.69
Strip3 33	4918.182	1.1	256	6.465	0	1.625
Aeration 34	4918.182	1.1	256	6.465	0	0.075
R105 35	4918.182	1.1	256	6.465	0	0.075

Table 5.11: Recycle Stream Data

Process Streams	**Flowrate lb/hr**	**Phenol Mass fraction (ppm)**	**Acetone Mass fraction (ppm)**
Wash101 (8R1)	2036.29	17	----
Wash101 (8R2)	1233.27	17	----
Wash101 (8R3)	2029.62	17	----
D101 (22R1)	2262.59	13000	10000
D101 (22R2)	240.87	13000	10000
D101 (22R3)	1396.91	13000	10000
Wash102 (25R1)	14.16	24000	28000
Wash102 (25R2)	1015.84	24000	28000

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A new approach has been developed to simultaneously address component-based recycle constraints as well as property-based discharge constraints. The problem was represented as a source-sink mapping task. Mass- and property-integration techniques were included in the approach. Two mathematical formulations were developed. In the first formulation, the objective was to minimize fresh consumption while satisfying all the process constraints for recycle. In the second formulation, cost of waste treatment was added. Also, component- and property-based discharge constraints were included to account for the environmental regulations and the waste-treatment activities. The proposed optimization technique serves as a tool to evaluate the extra cost that the company has to pay either in fresh resources or waste treatment cost in order to comply with the environmental regulations. The developed optimization technique was applied to a case study on production of phenol.

The following research activities are recommended for future work:

1. Include heat integration for process modification (In addition of mass and property integration).
2. Developing mixing rules for the different properties that regulate the discharge of wastewater into the environment such as hardness, turbidity, odor, conductivity, etc.

3. Developing a toxicity mixing rule that measures the adverse effect caused when two or more toxicants are mixed.Developing a systematic methodology to address the unsteady state operation base on mass and property integration simultaneously.
4. Include scheduling issues; it could be beneficial when the same waste treatment plant is used to treat the waste of different process.
5. Generate an alternative rerouting network for the wastewater discharged to the environment.

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APPENDIX A

ASPEN SIMULATION RESULTS FOR THE PHENOL CASE STUDY

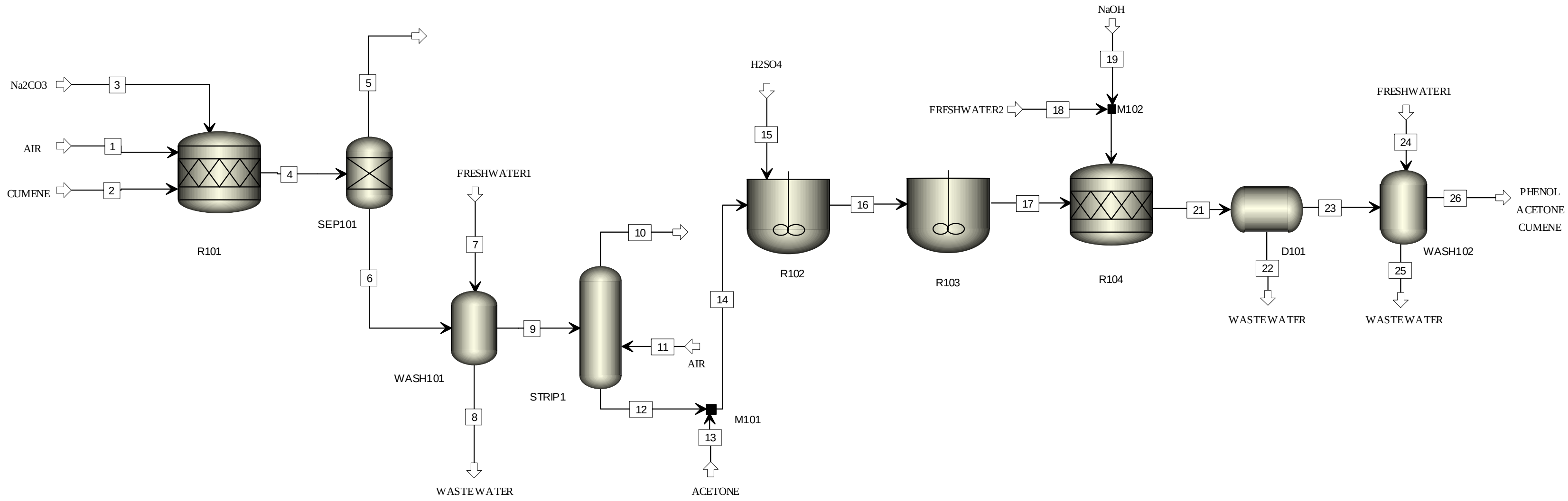

Figure A1: Aspen Process Flowsheet

Table A1: Aspen Results for Streams 1 through 9

Streams	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature F	235	221	221	228	228.5194	228.5194	217	235	235
Pressure psi	94.69595	99.69595	99.69595	94.69595	99.69595	99.69595	94.69595	80	80
Vapor Frac	0	1	0	0.490254	1	0	0	0	0
Mole Flow lbmol/hr	1525.094	1627.606	87.16476	2940.386	1297.084	1643.302	333.0506	447.8365	1528.516
Mass Flow lb/hr	183265	46608	1585	231458	36474.09	194983.9	6000	8083.169	192900.7
Volume Flow cuft/hr	3747.468	119195.1	26.07222	115588.2	96120.16	3801.957	105.093	144.5572	3782.375
Enthalpy MMBtu/hr	-16.3121	-1.71461	-10.5306	-41.4273	1.232639	-44.7226	-40.439	-53.4872	-30.7864
Mass Flow lb/hr									
WATER	30	578	1555	2168.091	21.68091	2146.41	6000	8052.509	93.90074
ISOPR-01	179978	0	0	143982.4	14.39824	143968	0	0.00E+00	143968
ACETO-01	300	0	0	300	0	300	0	8.66E-08	300
DIMET-01	2722	0	0	2722	0	2722	0	3.93E-01	2721.607
METHY-01	200	0	0	233.9514	0	233.9514	0	8.02E-09	233.9514
PHENO-01	5	0	0	5	0	5	0	0.136058	4.863942
ETHYL-01	30	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0	0
OXYGEN	0	10710	0	1118.006	1118.006	0	0	0	0
NITROGEN	0	35320	0	35320	35320	0	0	0	0
CUMEN-01	0	0	0	45578.55	0	45578.55	0	0.131605	45578.42
ACETONE	0	0	0	0	0	0	0	0	0
SULFU-01	0	0	0	0	0	0	0	0	0
SODIU-02	0	0	0	0	0	0	0	0	0
SODIU-03	0	0	0	0	0	0	0	0	0
NA+	0	0	13.01415	13.01415	0	13.01415	0	13.01414	4.44E-06
H3O+	0	0	4.52E-05	1.69E-09	0	1.96E-08	0	4.44E-09	1.51E-08
OH-	0	0	4.05E-05	1.51E-09	0	1.75E-08	0	3.97E-09	1.35E-08
CO3--	0	0	16.98585	16.98585	0	16.98585	0	16.98585	5.80E-07
SO4--	0	0	0	0	0	0	0	0	0

Table A1: Aspen Results for Streams 1 through 9 (Continuation)

Streams	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Mass Frac									
WATER	0.000164	0.012401	0.981073	0.009367	0.000594	0.011008	1	0.996207	0.000487
ISOPR-01	0.982064	0	0	0.622067	0.000395	0.738358	0	0	0.746332
ACETO-01	0.001637	0	0	0.001296	0	0.001539	0	1.07E-11	0.001555
DIMET-01	0.014853	0	0	0.01176	0	0.01396	0	4.86E-05	0.014109
METHY-01	0.001091	0	0	0.001011	0	0.0012	0	9.92E-13	0.001213
PHENO-01	2.73E-05	0	0	2.16E-05	0	2.56E-05	0	1.68E-05	2.52E-05
ETHYL-01	0.000164	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0	0
OXYGEN	0	0.229789	0	0.00483	0.030652	0	0	0	0
NITROGEN	0	0.75781	0	0.152598	0.968359	0	0	0	0
CUMEN-01	0	0	0	0.196919	0	0.233755	0	17 PPM	0.236279
ACETONE	0	0	0	0	0	0	0	0	0
SULFU-01	0	0	0	0	0	0	0	0	0
SODIU-02	0	0	0	0	0	0	0	0	0
SODIU-03	0	0	0	0	0	0	0	0	0
NA+	0	0	0.008211	5.62E-05	0	6.67E-05	0	0.00161	2.30E-11
H3O+	0	0	2.85E-08	7.28E-15	0	1.00E-13	0	5.49E-13	7.85E-14
OH-	0	0	2.55E-08	6.51E-15	0	8.98E-14	0	4.91E-13	7.02E-14
CO3--	0	0	0.010717	7.34E-05	0	8.71E-05	0	0.002101	3.01E-12
SODIU(S)	0	0	0	0	0	0	0	0	0
SO4--	0	0	0	0	0	0	0	0	0
***** LIQUID PHASE *****									
pH			6.063744	6.922084		6.421538		6.680892	10.53884

Table A1: Aspen Results for Streams 10 through 18

Streams	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Temperature F	78.54318	235	111.4509	170	204.8096	170	170	170	170
Pressure psi	0.676787	94	0.676787	15	15	15	15	15	15
Vapor Frac	1	1	0	1	0.20534	0	0.000188	0.000334	0
Mole Flow lbmol/hr	10917.04	9733.767	345.2469	289.8033	635.0502	2.755125	920.5142	935.9791	137.3966
Mass Flow lb/hr	421579.7	280000	51321.07	16387	67708.07	248	67956.07	67956.07	2490
Volume Flow cuft/hr	93155036	772091.1	815.3402	127822.7	61880.09	2.395006	1346.663	1414.736	40.44841
Enthalpy MMBtu/hr	0.959957	10.65859	-21.0877	-26.7692	-47.8569	-0.89949	-83.0049	-84.7518	-16.7031
Mass Flow lb/hr									
WATER	93.90074	0	5.90E-14	200	200	5	205	205	2459.879
ISOPR-01	140939.3	0	3028.664	0	3028.664	0	3028.664	3028.664	0
ACETO-01	236.9037	0	63.09635	0	63.09635	0	63.09635	63.09635	0
DIMET-01	209.533	0	2512.074	0	2512.074	0	2512.074	2512.074	0
METHY-01	43.53635	0	190.415	0	190.415	0	190.415	190.415	0
PHENO-01	2.196266	0	2.667675	0	2.667675	0	26609.26	28064.71	0
ETHYL-01	0	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0	0
OXYGEN	58799.73	58800	0.269867	0	0.269867	0	0.269867	0.269867	0
NITROGEN	221199.6	221200	0.391239	0	0.391239	0	0.391239	0.391239	0
CUMEN-01	54.92994	0	45523.49	0	45523.49	0	2497.149	143.5051	0
ACETONE	0	0	0	16187	16187	0	32606.75	33504.94	0
SULFU-01	0	0	0	0	0	243	243	243	0
SODIU-02	0	0	0	0	0	0	0	0	0
SODIU-03	0	0	0	0	0	0	0	0	0
NA+	0	0	4.44E-06	0	4.44E-06	0	4.44E-06	4.44E-06	13.06662
H3O+	0	0	1.51E-08	0	3.67E-10	0	3.67E-10	3.67E-10	3.58E-05
OH-	0	0	1.35E-08	0	3.28E-10	0	3.28E-10	3.28E-10	3.20E-05
CO3--	0	0	5.80E-07	0	5.80E-07	0	5.80E-07	5.80E-07	17.05434
SO4--	0	0	0	0	0	0	0	0	0

Table A2: Aspen Results for Streams 10 through 18 (Continuation)

Streams	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Mass Frac									
WATER	0.000223	0	1.15E-18	0.012205	0.002954	0.020161	0.003017	0.003017	0.987903
ISOPR-01	0.334312	0	0.059014	0	0.044731	0	0.044568	0.044568	0
ACETO-01	0.000562	0	0.001229	0	0.000932	0	0.000928	0.000928	0
DIMET-01	0.000497	0	0.048948	0	0.037102	0	0.036966	0.036966	0
METHY-01	0.000103	0	0.00371	0	0.002812	0	0.002802	0.002802	0
PHENO-01	5.21E-06	0	5.20E-05	0	3.94E-05	0	0.391566	0.412983	0
ETHYL-01	0	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0	0
OXYGEN	0.139475	0.21	5.26E-06	0	3.99E-06	0	3.97E-06	3.97E-06	0
NITROGEN	0.524692	0.79	7.62E-06	0	5.78E-06	0	5.76E-06	5.76E-06	0
CUMEN-01	0.00013	0	0.887033	0	0.67235	0	0.036747	0.002112	0
ACETONE	0	0	0	0.987795	0.23907	0	0.479821	0.493038	0
SULFU-01	0	0	0	0	0	0.979839	0.003576	0.003576	0
SODIU-02	0	0	0	0	0	0	0	0	0
SODIU-03	0	0	0	0	0	0	0	0	0
NA+	0	0	8.66E-11	0	6.56E-11	0	6.54E-11	6.54E-11	0.005248
H3O+	0	0	2.95E-13	0	5.42E-15	0	5.40E-15	5.40E-15	1.44E-08
OH-	0	0	2.64E-13	0	4.85E-15	0	4.83E-15	4.83E-15	1.29E-08
CO3--	0	0	1.13E-11	0	8.56E-12	0	8.53E-12	8.53E-12	0.006849
SODIU(S)	0	0	0	0	0	0	0	0	0
SO4--	0	0	0	0	0	0	0	0	0
***** LIQUID PHASE *****									
pH					8.109693		11.80652	11.80778	6.314194

Table A3: Aspen Results for Streams 19 through 26

Streams	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
Temperature F	170	170.0492	200	190	190	170	180	180
Pressure psi	15	15	15	15	15	15	15	15
Vapor Frac	0	0	0	0	0	0	0	0
Solid Frac	0	0	0	0	0	0	0	0
Mole Flow lbmol/hr	69.019	206.4156	1142.395	212.5777	929.817	244.2371	151.6109	1022.443
Mass Flow lb/hr	1450	3940	71896.07	3900.383	67995.69	4400	3279.965	69115.73
Volume Flow cuft/hr	29.44149	69.89029	1371.366	67.44603	1305.094	74.84027	69.78147	1299.385
Enthalpy MMBtu/hr	-8.13427	-24.8373	-107.638	-25.8115	-81.2544	-29.8968	-17.8476	-92.6247
Mass Flow lb/hr								
WATER	1074.074	3533.953	3828.222	3804.664	23.55753	4400	2549.122	1874.434
ISOPR-01	0	0	3028.664	0	3028.664	0	0.291901	3028.372
ACETO-01	0	0	63.09635	1.90E-08	63.09635	0	3.252472	59.84388
DIMET-01	0	0	2512.074	1.19E-06	2512.074	0	0.00028	2512.074
METHY-01	0	0	190.415	0	190.415	0	0.221426	190.1936
PHENO-01	0	0	28064.71	50.85386	28013.86	0	79.50387	27934.35
ETHYL-01	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0
OXYGEN	0	0	0.269867	0.269867	0	0	0	0
NITROGEN	0	0	0.391239	0.391239	0	0	0	0
CUMEN-01	0	0	143.5051	0	143.5051	0	0.211885	143.2932
ACETONE	0	0	33504.94	38.48003	33466.47	0	93.30667	33373.16
SULFU-01	0	0	0	0	0	0	0	0
SODIU-02	375.9259	375.9259	177.7336	0.11446	177.6192	0	177.6191	4.74E-09
SODIU-03	0	0	351.9236	0.004636	351.919	0	351.9188	9.39E-09
NA+	0	13.06662	13.06663	2.431449	10.63518	0	10.63517	7.17E-07
H3O+	3.38E-06	3.15E-05	0.00013	2.41E-05	0.000106	0	0.000105	7.07E-07
OH-	3.02E-06	2.82E-05	0.000116	2.16E-05	9.44E-05	0	9.37E-05	6.32E-07
CO3--	0	17.05434	17.05434	3.173486	13.88086	0	13.88085	9.36E-07
SO4--	0	0	0	0	0	0	0	0

Table A3: Aspen Results for Streams 19 through 26 (Continuation)

Streams	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
Mass Frac								
WATER	0.740741	0.896942	0.053247	0.975459	0.000346	1	0.77718	0.02712
ISOPR-01	0	0	0.042126	0	0.044542	0	8.90E-05	0.043816
ACETO-01	0	0	0.000878	4.87E-12	0.000928	0	0.000992	0.000866
DIMET-01	0	0	0.03494	3.05E-10	0.036945	0	8.53E-08	0.036346
METHY-01	0	0	0.002648	0	0.0028	0	6.75E-05	0.002752
PHENO-01	0	0	0.390351	0.013038	0.411995	0	0.024239	0.404168
ETHYL-01	0	0	0	0	0	0	0	0
SODIU-01	0	0	0	0	0	0	0	0
OXYGEN	0	0	3.75E-06	6.92E-05	0	0	0	0
NITROGEN	0	0	5.44E-06	0.0001	0	0	0	0
CUMEN-01	0	0	0.001996	0	0.002111	0	6.46E-05	0.002073
ACETONE	0	0	0.466019	0.009866	0.492185	0	0.028447	0.482859
SULFU-01	0	0	0	0	0	0	0	0
SODIU-02	0.259259	0.095413	0.002472	2.93E-05	0.002612	0	0.054153	6.86E-14
SODIU-03	0	0	0.004895	1.19E-06	0.005176	0	0.107293	1.36E-13
NA+	0	0.003316	0.000182	0.000623	0.000156	0	0.003242	1.04E-11
H3O+	2.33E-09	7.99E-09	1.80E-09	6.19E-09	1.55E-09	0	3.20E-08	1.02E-11
OH-	2.08E-09	7.15E-09	1.61E-09	5.53E-09	1.39E-09	0	2.86E-08	9.15E-12
CO3--	0	0.004329	0.000237	0.000814	0.000204	0	0.004232	1.35E-11
SODIU(S)	0	0	0	0	0	0	0	0
SO4--	0	0	0	0	0	0	0	0
***** LIQUID PHASE *****								
pH	6.396411	6.367118	6.463553	6.463553	6.479854		5.695106	8.695106

APPENDIX B

IMPURITY CONCENTRATION CALCULATIONS FOR PROCESS SOURCES

- *Wash101(stream 8*)

From Aspen:

Total Flowrate (lb/hr) = 8083.17

Impurity Flowrate (lb/hr) = 128.379

Mass Impurity Concentration:

$$y_{Wash101} = \frac{128.379}{8083.17} = 0.016$$

- *Decanter101(stream 22*)

From Aspen:

Total Flowrate (lb/hr) = 3900.383

Impurity Flowrate (lb/hr) = 95.718

Mass Impurity Concentration:

$$y_{Decanter101} = \frac{95.718}{3900.383} = 0.024$$

- *Washer102(stream 25*)

  From Aspen:

  Total Flowrate (lb/hr) = 730.842

  Impurity Flowrate (lb/hr) = 3279.96

  Mass Impurity Concentration:

  $$y_{Decanter101} = \frac{730.842}{3279.96} = 0.22$$

- *Freshwater2(stream 18*)

  From Aspen:

  Total Flowrate (lb/hr) = 2490

  Impurity Flowrate (lb/hr) = 30.121

  Mass Impurity Concentration:

  $$y_{Decanter101} = \frac{30.121}{2490} = 0.012$$

APPENDIX C

TOXICITY CALCULATIONS FOR PROCESS SOURCES

Probit Equation

$Y = -0.22 + 5.27 \log C$ (phenol concentration ppm)

Process Sources

- *Wash101(stream 8)*

  $Y_{Wash101} = -0.22 + 5.27 \log(17)$

  $Y_{Wash101} = 6.26$

  Probit value is transformed to percentage % using Table 5.4

  Mortality % = 89.6

- *Decanter101(stream 22)*

  $Y_{Wash101} = -0.22 + 5.27 \log(13000)$

  $Y_{Wash101} = 21.46$

  Probit value is transformed to percentage % using Table 5.4

  Mortality % = 100

- *Wash102(stream 25)*

  $Y_{Wash101} = -0.22 + 5.27 \log(24000)$

  $Y_{Wash101} = 22.86$

  Probit value is transformed to percentage % using Table 5.4

  Mortality % = 100

APPENDIX D

LINGO PROGRAM AND OUTPUT FOR PHENOL CASE STUDY

(PROCESS CONSTRAINTS)

```
min=TotalCost;

TotalCost=CostFreshwater+PipingCost;

!Input;

!Sources Flowrates;

Wwash101=8083.169;
WD101=3900.383;
Wwash102=3279.965;

!Sinks Flowrates;

Gwash101=6000;
GR104=2490;
Gwash102=4400;

!Sinks Max. Inlet Impurity Composition;

Zwash101<0.015;
ZR104<=0.1;
Zwash102<0.015;

!Cost of freshwater;

CostFreshwater=(0.0006*Freshwater1+0.0004*Freshwater2)*8000;

Freshwater1=F11+F12+F13;
Freshwater2=F21+F22+F23;

!Source Balance;

Wwash101=W11+W12+W13+Waste1;
WD101=W21+W22+W23+Waste2;
Wwash102=W31+W32+W33+Waste3;
```

```
!Sink Balance;

Gwash101=W11+W21+W31+F11+F21;
GR104=W12+W22+W32+F12+F22;
Gwash102=W13+W23+W33+F13+F23;
!Component Balance;

Gwash101*Zwash101=W11*0.016+W21*0.024+W31*0.22+F21*0.012;
GR104*ZR104=W12*0.016+W22*0.024+W32*0.22+F22*0.012;
Gwash102*Zwash102=W13*0.016+W23*0.024+W33*0.22+F23*0.012;

!Waste;

Waste=Waste1+Waste2+Waste3;

!Piping Cost;

PipingCost=W11*5+W12*3.5+W13*2+W21*2+W22*1+W23*4+W31*3+W32*5+W33*
2+F11*4.5+F12*3+F13*3.5+F21*2.5+F22*1+F23*1.5;

!Non-Negative Constraints;

W11>0;
W12>0;
W13>0;
W21>0;
W22>0;
W23>0;
W31>0;
W32>0;
W33>0;
Zwash101>0;
ZR104>0;
Zwash102>0;
Freshwater1>=0;
Freshwater2>=0;
F11>0;
F12>0;
F13>0;
F21>0;
F22>0;
F23>0;
end
```

Lingo Output

```
Global optimal solution found.

Objective value:                     41815.89
Total solver iterations:                   11

            Variable                    Value            Reduced Cost

            TOTALCOST                 41815.89               0.000000
            COSTFRESHWATER            15146.45               0.000000
            PIPINGCOST                26669.44               0.000000
            WWASH101                  8083.169               0.000000
            WD101                     3900.383               0.000000
            WWASH102                  3279.965               0.000000
             GWASH101                 6000.000               0.000000
             GR104                    2490.000               0.000000
             GWASH102                 4400.000               0.000000
             ZWASH101             0.1500000E-01              0.000000
             ZR104                0.2400000E-01              0.000000
             ZWASH102             0.1500000E-01              0.000000
             FRESHWATER1              275.0000               0.000000
             FRESHWATER2              4320.766               0.000000
             F11                      0.000000               1.500000
             F12                      0.000000               5.200000
             F13                      275.0000               0.000000
             F21                      4320.766               0.000000
             F22                      0.000000               1.600000
             F23                      0.000000               1.125000
             W11                      268.8510               0.000000
             W12                      0.000000              0.9000000
             W13                      4125.000               0.000000
             WASTE1                   3689.318               0.000000
             W21                      1410.383               0.000000
             W22                      2490.000               0.000000
             W23                      0.000000               6.750000
             WASTE2                   0.000000               1.600000
             W31                      0.000000               33.70000
             W32                      0.000000               2.400000
             W33                      0.000000               80.32500
             WASTE3                   3279.965               0.000000
             WASTE                    6969.283               0.000000
```

Row	Slack or Surplus	Dual Price
1	41815.89	-1.000000
2	0.000000	-1.000000
3	0.000000	0.000000
4	0.000000	1.600000
5	0.000000	0.000000
6	0.000000	-5.175000
7	0.000000	-2.600000
8	0.000000	-2.393750
9	0.000000	1050000
10	0.7600000E-01	0.000000
11	0.000000	1732500
12	0.000000	-1.000000
13	0.000000	-4.800000
14	0.000000	-3.200000
15	0.000000	0.000000
16	0.000000	-1.600000
17	0.000000	0.000000
18	0.000000	7.800000
19	0.000000	2.600000
20	0.000000	8.300000
21	0.000000	-175.0000
22	0.000000	0.000000
23	0.000000	-393.7500
24	0.000000	0.000000
25	0.000000	-1.000000
26	268.8510	0.000000
27	0.000000	0.000000
28	4125.000	0.000000
29	1410.383	0.000000
30	2490.000	0.000000
31	0.000000	0.000000
32	0.000000	0.000000
33	0.000000	0.000000
34	0.000000	0.000000
35	0.1500000E-01	0.000000
36	0.2400000E-01	0.000000
37	0.1500000E-01	0.000000
38	275.0000	0.000000
39	4320.766	0.000000
40	0.000000	0.000000
41	0.000000	0.000000
42	275.0000	0.000000

43	4320.766	0.000000
44	0.000000	0.000000
45	0.000000	0.000000

APPENDIX E

LINGO PROGRAM AND OUTPUT FOR PHENOL CASE STUDY

(PROPERTY CONSTRAINTS)

```
min=TotalCost;

TotalCost=CostFreshwater+Piping+TotalRecoveryCost+TreatmentCost;

!Input;

!Sources Flowrates;

Wwash101=8083.169;
WD101=3900.383;
Wwash102=3279.965;

!Sinks Flowrates;

Gwash101=6000;
GR104=2490;
Gwash102=4400;

!Sinks Max. Inlet Impurity Composition;

Zwash101<0.015;
ZR104<=0.1;
Zwash102<0.015;

!Cost of freshwater;

CostFreshwater=(0.0006*Freshwater1+0.0004*Freshwater2)*8000;
Freshwater1=F11+F12+F13;
Freshwater2=F21+F22+F23;

!Source Balance;

Wwash101=W11+W12+W13+Waste1;
WD101=W21+W22+W23+Waste2;
Wwash102=W31+W32+W33+Waste3;
```

```
!Sink Balance;

Gwash101=W11+W21+W31+F11+F21;
GR104=W12+W22+W32+F12+F22;
Gwash102=W13+W23+W33+F13+F23;

!Component Balance;

Gwash101*Zwash101=W11*0.016+W21*0.024+W31*0.22+F21*0.012;
GR104*ZR104=W12*0.016+W22*0.024+W32*0.22+F22*0.012;
Gwash102*Zwash102=W13*0.016+W23*0.024+W33*0.22+F23*0.012;

!Waste;

Waste=Waste1+Waste2+Waste3;

!Piping Cost;

PipingCost=W11*5+W12*3.5+W13*2+W21*2+W22*1+W23*4+W31*3+W32*5+W33*
2+F11*4.5+F12*3+F13*3.5+F21*2.5+F22*1+F23*1.5;

!Recovery Treatment;

! 93% Recovery Phenol;

!Phenol Composition in Waste Streams;

ZPhenol1 = 0.000017;
ZPhenol2 = 0.013;
ZPhenol3 = 0.024;

!<500 ppm, no recovery of Phenol;

ZPhenol1-0.0005<=(1-0.0005)*I21;
(0-0.0005)*(1-I21)<=ZPhenol1-0.0005;

ZPhenol2-0.0005<=(1-0.0005)*I22;
(0-0.0005)*(1-I22)<=ZPhenol2-0.0005;

ZPhenol3-0.0005<=(1-0.0005)*I23;
(0-0.0005)*(1-I23)<=ZPhenol3-0.0005;
```

```
!Stream 1;

WRecoveryPhenol1 = 0.93*(Waste1*ZPhenol1)*I21;
WasteafterrecoveryPh1 = Waste1 - WRecoveryPhenol1;
WPhenolafterrecovery1 = 0.07*(Waste1*ZPhenol1);
RecoveryCostPhenol1 = WRecoveryPhenol1*0.065*8000;

!Stream 2;

WRecoveryPhenol2 = 0.93*(Waste2*ZPhenol2)*I22;
WasteafterrecoveryPh2 = Waste2 - WRecoveryPhenol2;
WPhenolafterrecovery2 = 0.07*(Waste2*ZPhenol2);
RecoveryCostPhenol2 = WRecoveryPhenol2*0.065*8000;

!Stream 3;

WRecoveryPhenol3 = 0.93*(Waste3*ZPhenol3)*I23;
WasteafterrecoveryPh3 = Waste3 - WRecoveryPhenol3;
WPhenolafterrecovery3 = 0.07*(Waste3*ZPhenol3);
RecoveryCostPhenol3 = WRecoveryPhenol3*0.065*8000;

RecoveryCostPhenol = RecoveryCostPhenol1 + RecoveryCostPhenol2 +
RecoveryCostPhenol3;

! 98% Recovery Acetone;

!Acetone Composition in Waste Streams;

ZAcetone1 = 0;
ZAcetone2 = 0.01;
ZAcetone3 = 0.028;

!<500 ppm, no recovery of Acetone;

ZAcetone1-0.0005<=(1-0.0005)*I31;
(0-0.0005)*(1-I21)<=ZPhenol1-0.0005;

ZAcetone2-0.0005<=(1-0.0005)*I32;
(0-0.0005)*(1-I22)<=ZPhenol2-0.0005;

ZAcetone3-0.0005<=(1-0.0005)*I33;
(0-0.0005)*(1-I23)<=ZPhenol3-0.0005;
```

```
!Stream 1;

WRecoveryAcetone1 = 0.98*Waste1*ZAcetone1*I31;
RecoveryCostAcetone1 = WRecoveryAcetone1*0.033*8000;
WasteafterRecoveryAc1 = WasteafterrecoveryPh1 - WRecoveryAcetone1;

!Stream 2;

WRecoveryAcetone2 = 0.98*Waste2*ZAcetone2*I32;
RecoveryCostAcetone2 = WRecoveryAcetone2*0.033*8000;
WasteafterRecoveryAc2 = WasteafterrecoveryPh2 - WRecoveryAcetone2;

!Stream 3;

WRecoveryAcetone3 = 0.98*Waste3*ZAcetone3*I33;
RecoveryCostAcetone3 = WRecoveryAcetone3*0.033*8000;
WasteafterRecoveryAc3 = WasteafterrecoveryPh3 - WRecoveryAcetone3;

TotalWasteafterrecoveryAc = WasteafterRecoveryAc1 + WasteafterRecoveryAc2 +
WasteafterRecoveryAc3;

WAcetoneafterrecovery = 0.02 * (Waste1*0 + Waste2*0.013 + Waste3*0.028);

RecoveryCostAcetone = RecoveryCostAcetone1 +RecoveryCostAcetone2 +
RecoveryCostAcetone3;

ZMeanPhenolafterrecoveryAc =
(WPhenolafterrecovery1+WPhenolafterrecovery2+WPhenolafterrecovery3)/(TotalWaste
afterrecoveryAc);

!Total Recovery Cost;

TotalRecoveryCost = RecoveryCostPhenol + RecoveryCostAcetone;

!Waste Treatment;

!Toxicity Treatment;

ZremovedPhenol =(ZMeanPhenolafterrecoveryAc - Zdischargedphenol);

Wphenolremoved = ZremovedPhenol*TotalWasteafterrecoveryAc;

Wphenolremainaftertox = Zdischargedphenol* Wasteaftertoxicity;
```

```
Wasteaftertoxicity = (TotalWasteafterrecoveryAc - Wphenolremoved);

TreatmentCostToxicity = Wphenolremoved*0.164*8000*I11;

!if ZMeanPhenolafterrecoveryAc=Zdischargedphenol, no toxicity treatment;

(ZMeanPhenolafterrecoveryAc - Zdischargedphenol) <= (1-Zdischargedphenol)*I11;
(0-Zdischargedphenol)*(1- I11) <= (ZMeanPhenolafterrecoveryAc - Zdischargedphenol);

! Toxicity regulation;

Zdischargedphenol = 0.0000011;

! Mass load regulation;

Zdischargedphenol*Wasteaftertoxicity =0.00541;

! ThoD Treatment;

ywasteIsoProphil      = ((Waste1*0)+(Waste2*0)+
(Waste3*0.000089))/Wasteaftertoxicity;

ywasteHydroA          = (Waste1*0 + Waste2*0 + Waste3*0.000992)/Wasteaftertoxicity;

ywasteAcetonePhenone  = (Waste1*0 + Waste2*0 +
Waste3*0.000068)/Wasteaftertoxicity;

ywasteDimethyl        = (Waste1*0.000049 + Waste2*0 + Waste3*0)/Wasteaftertoxicity;

ywasteCumene1         = (Waste1*0.000016+ Waste2*0 +
Waste3*0.000065)/Wasteaftertoxicity;

ywastePhenol         =  Wphenolremainaftertox/Wasteaftertoxicity;

ywasteAcetone         =  WAcetoneafterrecovery/Wasteaftertoxicity;

!Total ThOD in Wastestream!

TotalThoDwaste = 2.38*10^6 * ywastePhenol + 2.2*10^6 * ywasteAcetone + 3.2*10^6 *
ywasteIsoProphil + 1.51*10^6 * ywasteHydroA + 2.53*10^6 * ywasteAcetonePhenone +
2.70 * 10^6*ywasteDimethyl + 2.315*10^6 * ywasteCumene1;
```

```
Oxygentobedifused = (TotalThoDwaste - ThODRegultion)*Wasteaftertoxicity*0.4535;

IbOxygentobedifused =  Oxygentobedifused/453592;

Ibmolofoxygen = (IbOxygentobedifused/32);

Ibmolofair = Ibmolofoxygen/0.21;

Ibofair = Ibmolofair*29;

TreatmentCostThoD = Ibofair * 0.06 *8000;

!ThoD regulation;

ThODRegultion <= 75;

!pH Treatment;

Waste1ratio = WasteafterRecoveryAc1/TotalWasteafterrecoveryAc;
Waste2ratio = WasteafterRecoveryAc2/TotalWasteafterrecoveryAc;
Waste3ratio = WasteafterRecoveryAc3/TotalWasteafterrecoveryAc;

10^pHmean = (Waste1ratio)*10^(pH1) + (Waste2ratio)*10^(pH2) +
(Waste3ratio)*10^(pH3);
pOHmean = 14 - pHmean ;

pH1 = 6.68;
pH2 = 6.46;
pH3 = 5.69;

!Base solution NaOH 0.5M;
!Concentration of OH in Base Solution (mol/l);

OH = 0.5;

!Acid solution H2SO4 0.5M
!Concentration of H30 in Base Solution (mol/l);

H3O = 0.5;

!Concentration of H30 Waste stream (mol/l);

WH3O = 10^(-pHmean);
```

```
!Concentration of 0H Waste stream (mol/l);
WOH = 10^(-pOHmean);

!Moles of H30 to be treated;
!1/waterdensity = 0.4535 l/lb;

TotalH3O = (Wasteaftertoxicity*0.4535*WH3O);

!Moles of OH to be treated;
TotalOH = (Wasteaftertoxicity*0.4535*WOH);

!Base Treatment ;

!Moles of Acid H3O remaing after Neutralization;

IB*H3Oremaining = (TotalH3O - (IB*Base*OH))*IB;

!Concentration of Acid remaining in Waste Stream (mol/l);

IB*WH3Oafterneutralization = (H3Oremaining/TotalWaste)*IB;

IB*TotalWaste = ((Wasteaftertoxicity*.4535)+(IB*Base))*IB;

!pH Discharged;

(10^(-pHdischarged))*IB = IB*WH3Oafterneutralization;

!cost of NaOH 0.5M = 0.31 $/lt;

TreatmentBaseCost = IB*Base * 0.31 * 8000;

!Acid Treatment ;

!Moles of Base OH remaing after Neutralization;

IA*OHremaining = (TotalOH - (IA*Acid*H3O*2))*IA;

!Concentration of Base remaining in Waste Stream (mol/l);

IA*WOHafterneutralization = (OHremaining/TotalWaste)*IA;

IA*TotalWaste = ((Wasteaftertoxicity*0.4535)+(IA*Acid))*IA;
```

```
!pOH Discharged;

WOHafterneutralization*IA = (10^(-pOHdischarged))*IA;

IA*pOHdischarged = (14 - pHdischarged)*IA;

!cost of H2SO 0.5M = 0.46 $/lt;

TreatmentAcidCost = Acid*IA * 0.46 * 8000;

!pH constraint;
pHdischarged <9*IA;
pHdischarged >5.5*IB;

pHmean-9 <=(10000-9)*IA;
(-10000-9)*(1-IA)<=pHmean-9;

pHmean-5.5 <=(10000-5.5)*(1-IB);
(-10000-5.5)*IB<=pHmean-5.5;

!Total Treatment Cost;
TreatmentCost = TreatmentCostToxicity + TreatmentCostThoD +TreatmentAcidCost
+TreatmentBaseCost;

!Non-Negative Constraints;

W11>0;
W12>0;
W13>0;
W21>0;
W22>0;
W23>0;
W31>0;
W32>0;
W33>0;
Zwash101>0;
ZR104>0;
Zwash102>0;
Freshwater1>=0;
Freshwater2>=0;
F11>0;
F12>0;
F13>0;
F21>0;
```

```
F22>0;
F23>0;
Acid>0;
Base>0;
Zdischargedphenol>0;

@bin(I11);

@bin(I21);
@bin(I22);
@bin(I23);
@bin(I31);
@bin(I32);
@bin(I33);
@bin(IA);
@bin(IB);

End
```

Lingo Output

```
Global optimal solution found.
Objective value:                    111005.8
Extended solver steps:                     2
Total solver iterations:                 553

        Variable                     Value            Reduced Cost

        TOTALCOST                   111005.8            0.000000
        COSTFRESHWATER              11024.20            0.000000
        PIPINGCOST                  35040.44            0.000000
        TOTALRECOVERYCOST           43628.77            0.000000
        TREATMENTCOST               21312.43            0.000000
        WWASH101                    8083.169            0.000000
        WD101                       3900.383            0.000000
        WWASH102                    3279.965            0.000000
        GWASH101                    6000.000            0.000000
        GR104                       2490.000            0.000000
        GWASH102                    4400.000            0.000000
        ZWASH101                0.1500000E-01           0.000000
        ZR104                      0.1000000            0.000000
        ZWASH102                0.1500000E-01           0.000000
        FRESHWATER1                 1562.689            0.000000
        FRESHWATER2                 1101.029            0.000000
        F11                         1287.689            0.000000
        F12                         0.000000            0.000000
        F13                         275.0000            0.000000
        F21                         1101.029            0.000000
        F22                         0.000000            0.000000
        F23                         0.000000            0.000000
        W11                         1235.389            0.000000
        W12                         0.000000            0.000000
        W13                         4125.000            0.000000
        WASTE1                      2722.780            0.000000
        W21                         2375.893            0.000000
        W22                         1524.490            0.000000
        W23                         0.000000            0.000000
        WASTE2                      0.000000            11.49690
        W31                         0.000000            0.000000
        W32                         965.5102            0.000000
        W33                         0.000000            0.000000
        WASTE                       5037.235            0.000000
```

```
ZPHENOL1                        0.1700000E-04              0.000000
ZPHENOL2                        0.1300000E-01              0.000000
ZPHENOL3                        0.2400000E-01              0.000000
I21                                0.000000                22.37816
I22                                1.000000                0.000000
I23                                1.000000                26854.86
WRECOVERYPHENOL1                   0.000000                0.000000
WASTEAFTERRECOVERYPH1              2722.780                0.000000
WPHENOLAFTERRECOVERY1     0.3240109E-02                0.000000
RECOVERYCOSTPHENOL1             0.000000                   0.000000
WRECOVERYPHENOL2                0.000000                   0.000000
WASTEAFTERRECOVERYPH2           0.000000                   0.000000
WPHENOLAFTERRECOVERY2           0.000000                   0.000000
RECOVERYCOSTPHENOL2             0.000000                   0.000000
WRECOVERYPHENOL3                51.65863                   0.000000
WASTEAFTERRECOVERYPH3           2262.796                   0.000000
WPHENOLAFTERRECOVERY3          3.888284                    0.000000
RECOVERYCOSTPHENOL3             26862.49                   0.000000
RECOVERYCOSTPHENOL              26862.49                   0.000000
ZACETONE1                       0.000000                   0.000000
ZACETONE2                     0.1000000E-01                0.000000
ZACETONE3                     0.2800000E-01                0.000000
I31                             0.000000                   0.000000
I32                             1.000000                   0.000000
I33                             1.000000                   16756.90
WRECOVERYACETONE1               0.000000                   0.000000
RECOVERYCOSTACETONE1            0.000000                   0.000000
WASTEAFTERRECOVERYAC1           2722.780                   0.000000
WRECOVERYACETONE2               0.000000                   0.000000
RECOVERYCOSTACETONE2            0.000000                   0.000000
WASTEAFTERRECOVERYAC2           0.000000                   0.000000
WRECOVERYACETONE3               63.50864                   0.000000
 RECOVERYCOSTACETONE3           16766.28                  0.000000
WASTEAFTERRECOVERYAC3           2199.288                  0.000000
TOTALWASTEAFTERRECOVERYAC  4922.068                       0.000000
WACETONEAFTERRECOVERY           1.296095                  0.000000
RECOVERYCOSTACETONE             16766.28                  0.000000
ZMEANPHENOLAFTERRECOVERYAC    0.7906279E-03               0.000000
ZREMOVEDPHENOL                0.7895279E-03               0.000000
ZDISCHARGEDPHENOL             0.1100000E-05               0.000000
WPHENOLREMOVED                  3.886110                  0.000000
WPHENOLREMAINAFTERTOX         0.5410000E-02               0.000000
WASTEAFTERTOXICITY              4918.182                  0.000000
```

```
TREATMENTCOSTTOXICITY          5098.576            0.000000
I11                            1.000000            5098.575
YWASTEISOPROPHIL             0.4188265E-04         0.000000
YWASTEHYDROA                 0.4668268E-03         0.000000
YWASTEACETONEPHENONE         0.3200023E-04         0.000000
YWASTEDIMETHYL               0.2712715E-04         0.000000
YWASTECUMENE1                0.3944629E-04         0.000000
YWASTEPHENOL                 0.1100000E-05         0.000000
YWASTEACETONE                0.2635313E-03         0.000000
TOTALTHODWASTE                 1666.842            0.000000
OXYGENTOBEDIFUSED              3550437.            0.000000
THODREGULTION                  75.00000            0.000000
IBOXYGENTOBEDIFUSED            7.827379            0.000000
IBMOLOFOXYGEN                 0.2446056            0.000000
IBMOLOFAIR                     1.164789            0.000000
IBOFAIR                        33.77887            0.000000
TREATMENTCOSTTHOD              16213.86            0.000000
WASTE1RATIO                   0.5531781            0.000000
WASTE2RATIO                    0.000000            0.000000
WASTE3RATIO                   0.4468219            0.000000
PHMEAN                         6.457355            0.000000
PH1                            6.680000            0.000000
PH2                            6.460000            0.000000
PH3                            5.690000            0.000000
POHMEAN                        7.542645            0.000000
OH                            0.5000000            0.000000
H3O                           0.5000000            0.000000
WH3O                         0.3488549E-06         0.000000
WOH                          0.2866521E-07         0.000000
TOTALH3O                     0.7780845E-03         0.000000
TOTALOH                      0.6393475E-04         0.000000
IB                             0.000000            0.000000
H3OREMAINING                   0.000000            0.000000
BASE                           0.000000            0.000000
WH3OAFTERNEUTRALIZATION        0.000000            0.000000
TOTALWASTE                     0.000000            0.000000
PHDISCHARGED                   0.000000            0.000000
TREATMENTBASECOST              0.000000            0.000000
IA                             0.000000            0.000000
OHREMAINING                    0.000000            0.000000
ACID                           0.000000            0.000000
WOHAFTERNEUTRALIZATION         0.000000            0.000000
POHDISCHARGED                  0.000000            0.000000
  TREATMENTACIDCOST            0.000000            0.000000
```

Row	**Slack or Surplus**	**Dual Price**
1	111005.89	-1.000000
2	0.000000	-1.000000
3	0.000000	2.622206
4	0.000000	1.533309
5	0.000000	-25.14467
6	0.000000	-2.758318
7	0.000000	8.811214
8	0.000000	-2.758318
9	0.000000	816672.8
10	0.000000	338919.2
11	0.000000	598893.4
12	0.000000	-1.000000
13	0.000000	-4.800000
14	0.000000	-3.166654
15	0.000000	-2.622206
16	0.000000	-1.533309
17	0.000000	25.14467
18	0.000000	4.800000
19	0.000000	4.800000
20	0.000000	4.800000
21	0.000000	-136.1121
22	0.000000	-136.1121
23	0.000000	-136.1121
24	0.000000	0.000000
25	0.000000	0.000000
26	0.000000	-256258.8
27	0.000000	0.000000
28	0.000000	-1301402
29	0.4830000E-03	0.000000
30	0.1700000E-04	0.000000
31	0.9870000	0.000000
32	0.1250000E-01	0.000000
33	0.9760000	0.000000
34	0.2350000E-01	0.000000
35	0.000000	-522.9745
36	0.000000	2.974475
37	0.000000	-1314.972
38	0.000000	-1.000000
39	0.000000	-522.9745
40	0.000000	2.974475
41	0.000000	-1314.972
42	0.000000	-1.000000

```
43        0.000000        -522.9745
44        0.000000         2.974475
45        0.000000        -1314.972
46        0.000000        -1.000000
47        0.000000        -1.000000
48        0.000000         0.000000
49        0.000000         0.000000
50        0.000000        -588665.3
51    0.5000000E-03        0.000000
52    0.1700000E-04        0.000000
53       0.9900000         0.000000
54    0.1250000E-01        0.000000
55       0.9720000         0.000000
56    0.2350000E-01        0.000000
57        0.000000        -266.9745
58        0.000000        -1.000000
59        0.000000         2.974475
60        0.000000        -266.9745
61        0.000000        -1.000000
62        0.000000         2.974475
63        0.000000        -266.9745
64        0.000000        -1.000000
65        0.000000         2.974475
66        0.000000         2.974475
67        0.000000        -4556.219
68        0.000000        -1.000000
69        0.000000         -6472238
70        0.000000        -1.000000
71        0.000000         -6472238
72        0.000000        -1314.972
73        0.000000        -4929.000
74        0.000000         2.973028
75        0.000000        -1.000000
76       0.9992314         0.000000
77    0.7675424E-03        0.000000
78        0.000000      0.1260463E+11
79        0.000000         -2566477.
80        0.000000     -0.3259391E+08
81        0.000000     -0.1538025E+08
82        0.000000     -0.2576956E+08
83        0.000000     -0.2750111E+08
84        0.000000     -0.2357965E+08
85        0.000000     -0.2424172E+08
86        0.000000     -0.2240831E+08
```

```
    87              0.000000          -10.18560
    88              0.000000          -0.4566722E-02
    89              0.000000          -2071.429
    90              0.000000          -66285.71
    91              0.000000          -13920.00
    92              0.000000          -480.0000
    93              0.000000          -1.000000
    94              0.000000           10.18560
    95              0.000000           0.000000
    96              0.000000           0.000000
    97              0.000000           0.000000
    98         -0.1795823E-04          0.000000
    99             0.000000            0.000000
   100             0.000000            0.000000
   101             0.000000            0.000000
   102             0.000000            0.000000
   103             0.000000            0.000000
   104             0.000000            0.000000
   105             0.000000            0.000000
   106             0.000000            0.000000
   107             0.000000            0.000000
   108             0.000000            0.000000
   109             0.000000            0.000000
   110             0.000000            0.000000
   111             0.000000            0.000000
   112             0.000000            0.000000
   113             0.000000           -1.000000
   114             0.000000            0.000000
   115             0.000000            0.000000
   116             0.000000            0.000000
   117             0.000000            0.000000
   118             0.000000            0.000000
   119             0.000000           -1.000000
   120             0.000000            0.000000
   121             0.000000            0.000000
   122             2.534619            0.000000
   123             10006.47            0.000000
   124             9993.535            0.000000
   125            0.9653808            0.000000
   126             0.000000           -1.000000
   127              2036.297           0.000000
   128              1233.279           0.000000
   129              2029.625           0.000000
   130              2262.593           0.000000
```

131	240.8730	0.000000
132	1396.917	0.000000
133	14.16824	0.000000
134	1015.848	0.000000
135	0.000000	0.000000
136	0.1500000E-01	0.000000
137	0.1000000	0.000000
138	0.1500000E-01	0.000000
139	2660.400	0.000000
140	0.000000	-0.3334564E-01
141	1686.942	0.000000
142	0.000000	0.000000
143	973.4585	0.000000
144	0.000000	0.000000
145	0.000000	0.000000
146	0.000000	0.000000
147	0.000000	0.000000
148	0.000000	0.000000
149	0.1100000E-05	0.000000

VITA

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