Optimal Design of Hybrid Membrane Networks for Wastewater Treatment

By

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Doctor of Philosophy

in

Chemical Engineering

Waterloo, Ontario, Canada, 2008

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Yousef Ahmed Mohammed Saif

Abstract

Water consumption and wastewater generation depletes water resources and has a destructive impact on the environment. Recent attention has aimed at preserving water resources and preventing pollution through several routes. Restrictions on wastewater discharge into the environment, recycling, reuse and regeneration of wastewater streams are now common practices toward achieving these objectives. Membrane and integrated membrane processes have been shown to be effective at reducing water usage and recovering valuable compounds. This thesis focuses on topics related to the optimal synthesis of wastewater treatment networks by hybrid membrane systems.

The use of superstructures has been a useful tool to synthesize chemical engineering process flowsheets. The approach postulates all possible alternatives of a potential treatment network. Within the representation, an optimal solution is assumed to be hidden in the given superstructure. State space is a framework to process synthesis problems which involves heat and mass exchange. In this representation, unit operations, utility units and utility streams can be embedded in such a way that all the process synthesis alternatives can be realized. Such a framework can be applied for water and wastewater synthesis problems.

Several research optimization studies presented membrane and hybrid membrane process synthesis problems for wastewater treatment. Nonetheless, the problems in fact can be represented in several ways. Therefore, the mathematical programs are expected to be different for every postulated representation. Comparison between different

representations and their mathematical programs are analyzed to highlight the relationship between the superstructure representation and their mathematical programming formulations. Possible improvement of these superstructures is addressed. Also, a generic representation is provided to give a systematic and clear description for assembling hybrid membrane system superstructures via the state space approach.

The synthesis of reverse osmosis networks (RON) for water and wastewater treatment network is presented as a superstructure problem. The mathematical programming model describes the RON through a nonconvex mixed integer nonlinear program (MINLP). A mixed integer linear program (MILP) is derived based on the convex relaxation of the nonconvex terms in the MINLP to bound the global optimum. The MILP models are solved iteratively to supply different initial guesses for the nonconvex MINLP model. It is found that such a procedure is effective in finding local optimum solutions in reasonable time. Water desalination and treatment of aqueous wastes from the pulp and paper industry are considered as case studies to illustrate the solution strategy.

The RON mathematical program is a nonconvex MINLP which contains several local optima. A deterministic branch and bound (B&B) algorithm to determine the global optimum for the RON synthesis problem has also been developed. A piecewise MILP is derived based on the convex relaxation of the nonconvex terms present in the MINLP formulation to approximate the original nonconvex program and to obtain a valid lower bound on the global optimum. The MILP model is solved at every node in the branch and bound tree to verify the global optimality of the treatment network within a pre-specified gap tolerance. Several constraints are developed to simultaneously screen the treatment network alternatives during the search, tighten the variable bounds and consequently accelerate algorithm convergence. Water desalination is considered as a case study to illustrate this approach for global optimization of the RO network.

Wastewater and groundwater streams contaminated with volatile organic compounds (VOCs) require proper treatment to comply with discharge standards or drinking requirement restrictions. Air stripping and pervaporation are two common treatment technologies for water streams contaminated with VOCs. The combination of these technologies for water treatment which are representative of hybrid membrane systems may offer advantages over stand-alone treatments. Superstructure optimization uses the framework of hybridization to determine the optimal treatment network and the optimal operational requirements for the treatment units to achieve desired water qualities. Two case studies are presented to illustrate the proposed approach and sensitivity of the optimal solutions to given perturbations is analyzed.

Acknowledgments

For this thesis, I would like to express my thanks to my parents, Professor Ahmed Saif and Fatima Saif. I am lucky to have you as great parents and beautiful friends. Thank you for your time, love, encouragements, and support in my life. Lot of thanks is to my beautiful brothers and sweetheart sisters.

I am deeply indebted to Professor Mark Pritzker and Professor Ali Elkamel for being sincere advisors in research. This dissertation would never have been accomplished without their continuous discussion, encouragement, and valuable advice through my academic journey.

I would like to express my thanks to my supervisory committee members:
Professor Peter Douglas, Professor Xianshe Feng and Professor Kumaraswamy Ponnambalam.

I also would like to take this opportunity to thank my colleagues, the chemical engineering department faculty, and the chemical engineering department students at my favorite school "University of Waterloo". I also thank the Saudi higher education ministry for my graduate study and research fund.

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Nomenclature

Sets

SIN	Set of inlet wastewater streams
AS	Set of air stripper units
PV	Set of pervaporation stages
VOC	Set of volatile organic compounds
C	Set of pollutants
USI	Set of inlet utility streams
O	Set of unit operations
UO	Set of utility units
SOT	Set of wastewater-exit streams
P	Set of product streams
USO	Set of utility-exit streams
SRO	Set of RO stages
SPU	Set of pump stages
STU	Set of turbine stages
MIX	Set of mixer nodes
SSP	Set of splitter nodes
PERM	Set of final permeate product streams
SIN	Set of inlet wastewater streams
SPU	Set of pump stages in RO network
STU	Set of turbine units in RO network
SRO	Set of RO stages
SROREJ	Set of reject streams from RO stage
SROPER	Set of permeate streams from RO stage
SFPER	Set of final permeate streams in RO network
SFREJ	Set of final reject streams in RO network
DIS1	Set of intervals for a concave function
DIS2	Set of intervals for a bilinear function
DIS3	Set of intervals for a bilinear function

Parameters/Variables

$f(x,y)$	Objective function
M	Large number
y	A binary variable
Y	Vector of binary variables
x	A continuous variable
X	Vector of continuous variables

$h(x)$	Vector of functions in equality constraints
$g(x)$	Vector of functions in inequality constraints
NMd_{SRO}	Number of parallel modules at every RO stage belongs to SRO
a_{MRO}	Cost of the single RO module
PPu_{pu}	Power consumption by a pump unit belong to SPU
PTu_{tu}	Power production by a turbine unit belong to STU
$a_{pu,f}$	Fixed cost coefficient of a pump unit pu
$a_{tu,f}$	Fixed cost coefficient of a turbine unit tu
$a_{pu,o}$	Fixed cost coefficient for the operating cost of a pump unit pu
$a_{tu,o}$	Fixed cost coefficient for the operating cost of a turbine unit tu
ΔP_{SPU}	Pressure difference across a pump unit pu belong to SPU
F_{SPU}	Flowrate through a pump unit pu belong to SPU
y_{SPU}	Binary variable defines the existence of pump unit pu belong to SPU
y_{STU}	Binary variable defines the existence of pump unit tu belong to STU
ΔP_{STU}	Pressure difference across a turbine unit tu belong to STU
F_{STU}	Flowrate through a pump unit tu belong to STU
Fp_{SRO}	Permeate flowrate from a RO stage belong to SRO
ΔP_{MRO}	Pressure difference across a RO module
W	Water permeability coefficient
SA	Surface area of a RO stage belong to SRO
r_i	Inner radius of the hollow fiber membrane
r_o	Outer radius of the hollow fiber membrane
l	RO hollow fiber membrane length
l_s	RO hollow fiber membrane seal length
$xp_{c,SRO}$	Component concentration of c in any permeate stream from RO stage
$xr_{c,SRO}$	Component concentration of c in any reject stream from RO stage
$x_{c-avg,SRO}$	Average component concentration of c in any RO stage
K_c	Component permeability coefficient of c belong to C
Fp_{SRO}	Permeate flowrate of a RO stage belong to SRO
y_{SRO}	Binary variable of a RO stage belong to SRO
F_{SRO}	Inlet feed to a RO stage belong to SRO
NMd_{SRO}	Number of parallel modules in RO stage belong to SRO
P_{SRO}	Inlet feed pressure to a RO stage belong to SRO
Fr_{SRO}	Reject stream from a RO stage belong to SRO

F_{SSP}	Inlet feed to a splitter node belong to *SSP*
$F_{SSP,MIX}$	Stream assignment from a splitter node belong to *SSP* to a mixer node belong to *MIX*
F_{MIX}	Exit stream from a mixer node belong to *MIX*
$y_{SSP,MIX}$	Binary variable defines the stream match between a splitter and a mixer belong to *SSP* and *MIX*
P_{MIX}	Pressure of a stream from a mixer node belong to *MIX*
$P_{SSP,MIX}$	Pressure of a stream $F_{SSP,MIX}$
F_{SPER}	Flowrate of a final permeate product stream belong to *SPER*
$x_{c,SPER}$	Concentration of a pollutant c in the final permeate stream belong to *SPER*
χ	Bilinear function
q, w	Independent variables of a bilinear function χ
F_{in}	Inlet wastewater stream belong to *SIN*
F_{in-pu}	Stream assignment from inlet node *in* to a pump unit *pu*
$F_{in-frej}$	Stream assignment from the inlet node *in* to the final exit node *frej*
$F_{in-fper}$	Stream assignment from the inlet node *in* to the final exit node *fper*
$F_{rorej-pu}$	Stream assignment from the RO reject stream *rorej* to a pump node *pu*
$F_{roper-pu}$	Stream assignment from the RO permeate stream *roper* to a pump node *pu*
F_{pu}	Pump *pu* feed stream
F_{pu-ro}	Stream assignment from a pump node *pu* to RO stage *ro*
F_{roper}	Permeate stream from RO stage *ro*
F_{rorej}	Reject stream from RO stage *ro*
$F_{roper-fper}$	Permeate stream assignment from RO stage to the final permeate node *fper*
F_{fper}	Permeate stream at the final permeate product node *fper*
$F_{rorej-ro}$	Reject stream assignment from RO stage to another RO stage
$F_{rorej-tu}$	Reject stream assignment from RO reject stream to a turbine node *tu*
$F_{rorej-frej}$	Stream assignment from a RO reject stream to the final reject node *frej*
F_{tu}	Inlet feed stream to a turbine unit *tu*
F_{tu-ro}	Stream assignment from a turbine unit *tu* to RO stage
$F_{tu-fper}$	Stream assignment from a turbine unit *tu* to the final permeate node *fper*
$F_{tu-frej}$	Stream assignment from a turbine unit *tu* to the final reject node *frej*

z_{dis1}	Independent variable z in a concave function $\psi(z)^{\alpha}$ within subinterval *dis1* bilinear function
y_{PL}	A binary variable which defines permeate looping
$ymix_{pu}$	A binary variable define the condition by Eq. (4.21)
Gap_{node}	Gap for any node in the search tree
OUB	Overall upper bound
LB	Lower bound
a	Specific surface area of packing
a_{Ph}	Specific hydraulic surface area of packing
$SurA_{PV}$	Pervaporation stage surface area
C_L	A parameter related to the packing material
$\mathrm{Cost}_{\mathrm{Capital}}$	Capital cost of the units
$\mathrm{Cost}_{\mathrm{operating}}$	Operating cost of the treatment
C_P	A parameter related to the packing material
C_S	A parameter related to the packing material
C_V	A parameter related to the packing material
D_L	Diffusivity of a solute in the liquid phase
D_{AS}	Diameter of the air stripper tower
D_V	Diffusivity of a solute in the gas phase
F_A	Air flow rate
$\dot{F}_A$	Molar air flow rate
F_{MIX}	Exit flow stream from mixer *MIX*
$F_{SSP,MIX}$	Inlet flow from splitter *SSP* to mixer *MIX*
F_{VOC}	Molar flowrate of a VOC in a pervaporation stage
$\dot{F}_W$	Molar wastewater flow rate
F_W	Wastewater flow rate
g	Gravity acceleration
h_L	Specific liquid holdup
hn	Henry's constant
$H_{C,OL}$	Height of the transfer unit for component c
H_{AS}	Height of the air-stripping column
k_{VOC}	Mass transfer coefficient of a VOC in the concentration polarization layer
K_{VOC}	Overall mass transfer coefficient of VOC in the pervaporation stage
K_{water}	Overall mass transfer coefficient of water in a pervaporation stage
l_m	Thickness of the PV membrane

Lt_m	Length of a PV membrane
MW	Molecular weight
$N_{C,OL}$	Number of the transfer unit in the air-stripping column for component c
P_{MIX}	Pressure of mixer MIX
Pm_{VOC}	Permeability coefficient of a VOC in the membrane
Pm_{water}	Permeability coefficient of water in the membrane
P_{Perm}	Permeate pressure in a pervaporation stage PV
$PPu_{Air\ blower}$	Power consumption by a vacuum pump
PPu_{pump}	Power consumption by a pump
$PPu_{Vaccum\ pump}$	Power consumption by a vacuum pump
P_{SSP}	Pressure of splitter SSP
P_{AS}	Pressure in the column
Re_L	Reynolds number of the liquid phase
Re_V	Reynolds number of the gas phase
u_L	Superficial velocity of the liquid phase
$u_{L,S}$	Superficial velocity of the liquid phase at the loading point
u_V	Superficial velocity of the gas phase
$u_{V,S}$	Superficial velocity of the gas phase at the loading point
x	Mole fraction of a solute in the liquid phase
y_{PV}	Binary variable for pervaporation stage PV
y_{AS}	Binary variable for the air stripper tower belong to AS
$va_{VOC,Perm}$	Average molar concentration of a VOC in the permeate side of a pervaporation
va	Mole concentration of a solute in the gas phase
ρ_M	Molar density of wastewater mixture in a pervaporation stage
ρ_L	Density of the liquid phase
ρ_V	Density of the gas phase
μ_L	Viscosity of the liquid phase
μ_V	Viscosity of the gas phase
$\in$	Void fraction
ψ_S	Resistance coefficient in the liquid and gas critical velocities equations
ψ_L	Resistance coefficient of trickle packing
β_L	Mass transfer coefficient in the liquid phase
β_v	Mass transfer coefficient in the gas phase
α_{pu}	Fractional constant of in the fixed cost part of a pump unit

α_{tu}	Fractional constant of in the fixed cost part of a turbine unit
π_{MRO}	Osmotic pressure in a RO module
γ	RO module constant as defined by Eq. 3.7
η	RO module constant as defined by Eq. 3.8
μ	Viscosity of water
$\psi(z)^{\alpha}$	Concave function
$\underline{\psi}(z)$	Underestimation of a concave function $\psi(z)^{\alpha}$
$\psi(z)_{dis1}$	Concave function in subinterval *dis1*
ω_{dis1}	Binary variable of existence of subinterval *dis1*
$\tau_{dis2,dis3}$	Binary variable which determines the existence of intervals *dis2*, *dis3* for a
ε	Gap tolerance within the B&B tree

Abbreviations

AS	Air Stripper
ASB	Air Stripper Box
B&B	Branch and Bound
DB	Distribution Box
DCM	DiChloroMethane
ED	Electrodialysis
EDC	Ethylene DiChloride
EDI	Electordeionization
GAMS	General Algebraic Modeling System
GDB	Generalized Disjunctive Programming
GS	Gas Separation
HB	Heat integration Box
LB	Lower Bound
LP	Linear Program
MCP	MonoChloroPhenol
MEB	Mass Exchange Box
MF	Microfiltration
MILP	Mixed Integer Linear Program
MINLP	Mixed Integer Nonlinear Program
NF	Nanofiltration
NLP	Nonlinear Program
OUB	Overall Upper Bound
PB	Pump Box
PTB	Pump/Turbine Box
PV	Pervaporation
PVB	Pervaporation Box
PVB	Pervaporation Box
RB	Regeneration Box
RLT	Reformulation Linearization Technique
RO	Reverse Osmosis
ROB	Reverse Osmosis Box
RON	Reverse Osmosis Network
SEN	State Equipment Network
STN	State Task Network
TAC	Total Annualized Cost
TB	Turbine Box
TCE	TriChloroEthylene
TCP	TriChloroPhenol
UF	Ultrafiltration
VOC’s	Volatile Organic Compounds

Chapter 1

Introduction

1.1 Background

Water consumption and wastewater generation occur throughout the world due to both domestic and industrial activities. Due to increased attention to water conservation, pollution prevention and health concerns, much attention is being paid to water and wastewater management in modern societies. Large amounts of money are spent annually world wide for water and wastewater treatment. The global market is valued at 360 billion USD (2003), with annual growth of more than 6 percent. In Canada, water and wastewater treatment costs reached $1.8 billion USD in 2002, up 28 percent from 2000. Figure 1.1 shows the distribution of the global expenditures for water and wastewater treatment forecasted for the year 2010.

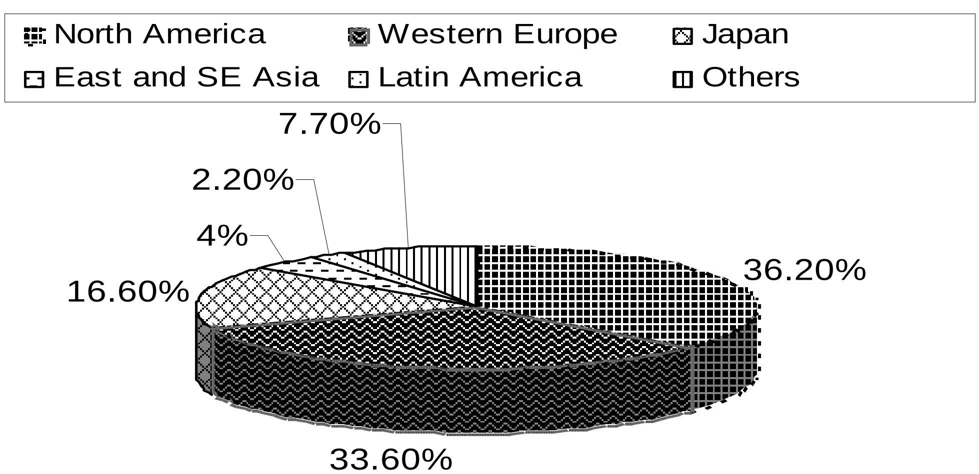


Figure 1.1. Global water and wastewater market share forecasted by region for the year 2010 (Industry Canada, 2005).

Opportunities exist for innovations in the treatment of water and wastewater. This includes the need for efficient, less expensive treatment technologies that effectively reduce the cost of daily operations and increase production capabilities. Of course, industrial processes must be improved and environmentally safe chemicals introduced to prevent pollution in the first place. Recent trends toward improvement focus on minimizing water intake through process integration, recycling, reuse and regeneration (Dunn and El-Halwagi, 2003; Dunn and Bush, 2001). In 1996, roughly 40% of total industrial wastewater was recycled with considerable variation between the industrial sectors (Schaefer et al., 2004). In addition, decentralization of wastewater treatment has resulted in pollutant source reduction replacing 'end-of-pipe' treatment approaches (Kuo and Smith, 1997).

During the last 35 years, continuous improvements of membrane processes have been achieved. Improvements in selectivity flux and operating practice of membrane processes have enabled them to become competitive with more conventional processes. In 1998, the annual sales of membrane systems reached 19 billion USD with 10% annual growth in the water and wastewater treatment sectors (Starthmann et al., 2001). Clearly, membrane technologies have become appealing for water and wastewater treatments from the point of view of pollution prevention, efficient operation and cost reduction.

1.2 Wastewater Contaminants and their Impacts

Every water and wastewater problem varies from location to location in terms of its constituents. Water and wastewater are usually characterized in terms of their organic, inorganic and biological contaminants. The organic part can contain carbohydrates, oil and grease, surfactants and priority pollutants, e.g. benzene, ethylbenzene, toluene etc. Inorganic compounds can include nonmetals such as arsenic and selenium and/or metals (for example, chromium, lead, silver etc.). In addition, microorganisms and pathogens are often present in water and wastewater (Metcalf & Eddy, 1991).

Public health and environmental concern have led to strict regulations for drinking water quality and wastewater discharge. Exposure to the previously mentioned chemicals and biological constituents can be very harmful to all life forms. Dissolved oxygen depletion is a serious threat to aquatic life through decomposition processes and the potential formation of toxic gases such as hydrogen sulfide. Discharge of high loads of nutrients, such as nitrogen and phosphorus, lead to excessive and destructive growth of algae. By law, effective water and wastewater treatment is mandatory to achieve and maintain health and safety standards and minimize pollution.

1.3 Membrane Processes: Classifications and some Applications

Membranes are selective thin layer materials that can be used to separate different species. The separation can be accomplished when a driving force is applied across a membrane. Due to membrane selectivity, water and wastewater streams can be separated into lean and concentrated products. Separation requires the application of driving forces such as pressure, electrical potential or chemical activity gradients across the membrane. The use of synthetic membranes with appropriate structure and properties can allow very efficient separation, often with substantial energy savings over more traditional separation techniques (Baker, 2004).

There are several ways to classify membranes. Based on their constituents, membranes are classified as being organic such as polymer membranes or inorganic in the case of metal and ceramic membranes. Membranes are also classified in terms of their geometry. These include flat sheet or cylindrical (tubular or hollow fiber) configurations. Another classification can be attributed to the operating driving forces such as pressure, electrical or concentration gradients. In addition, membranes can be classified according to whether their structure is porous, dense or composite. The varieties of the membrane structures and their operations give them very wide applications. Table 1.1 shows some practical applications of membranes processes in different industries (Wenten, 2002).

Table 1.1 Practical industrial applications of membrane processes.

Industrial sector	**Membrane processes**	**Industrial sector**	**Membrane processes**
Drinking Water	NF,UF,RO	**Biotechnology** Enzyme purification Concentration of fermentation broth SCP harvesting Membrane reactor Marine biotechnology	 UF MF MF,UF UF MF,UF
Deminerlaized Water	RO,ED,EDI	**Energy** Fuel cell	Proton exchange membrane
Wastewater Treatment	 MF,NF,RO,ED MF,UF	**Medical** Control release	 UF
Food Industry Dairy Meat Fruit and vegetables Grain milling Sugar Beverages Fruit juice Wine and brewery Tea factories	 UF,RO,ED UF,RO RO UF UF,RO,ED,MF,NF MF,UF,RO MF,UF,RO,PV MF,UF,NF	**Chemical industry** Hydrogen recovery CO2 separation Ethanol dehydration Organic recovery Chlor-alkali process	 GS GS PV PV Membrane electrolysis

1.4 Thesis Content

The design of wastewater and water hybrid membrane networks represents a process synthesis problem. The task is to separate pollutants present in different feed streams into lean and concentrated streams using the optimum combination of units, operating conditions and distribution of process streams from an assortment of alternatives. Although there are numerous examples from the literature and industry of case studies regarding water and wastewater treatment by membranes, there have been very few research studies to date that addresses the optimization of such networks in a general and systematic way. As an example, desalination relies on conventional distillation and membrane technologies. The effectiveness of any technology depends heavily on the raw seawater characteristics (Figure 1.2). The cost advantage of these technologies depends strongly on the inlet salt concentration. Therefore, it is an important point to give a framework for optimizing hybrid membrane systems for water and wastewater treatment. A brief discussion of the main objectives given in the thesis is summarized in the following paragraphs. Further analysis will be covered in the subsequent chapters.

Chapter 2 presents a review of previous optimization studies which deal with membrane and hybrid membrane networks. The impact of the problem representation on the mathematical programming formulations is analyzed. Drawbacks of these previous studies are explained based on the relation between the superstructure representation and the mathematical programming formulation. Possible improvement in the superstructure representation and consequently the mathematical formulation is provided. A generic representation of hybrid membrane networks is presented to assist the construction of their superstructures and formulation of their mathematical programs.

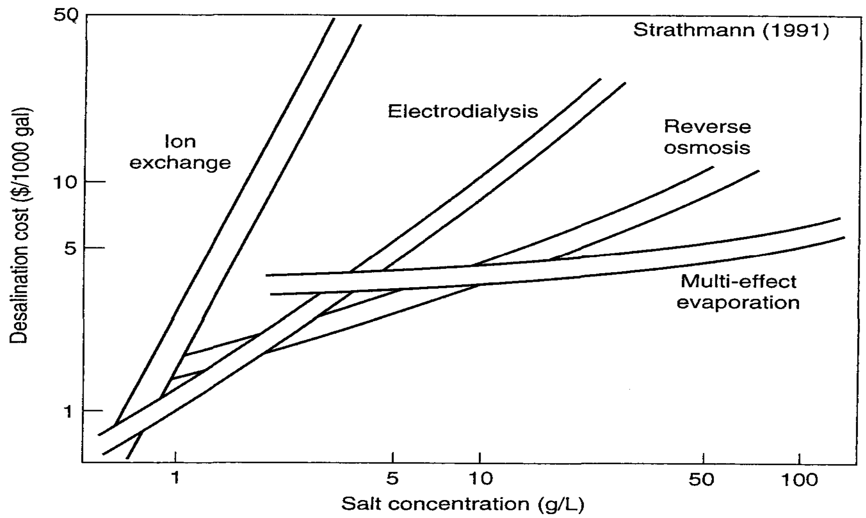


Figure 1.2 Cost comparison of desalination by different technologies as a function of salt concentration (Baker, 2004).

Reverse osmosis (RO) has been shown to be a viable technology for water and wastewater treatment. An RO network is composed mainly of multiple RO stages, pumps and turbines. Common practice focuses on continuous treatment of the reject streams through several RO stages and the direct collection of the permeate streams to the final permeate product stream. The design of RO networks differs from common wastewater network design problems addressed in the literature. These networks assume that the wastewater streams are continuously purified within the network (e.g. single input-single output for every process unit). Also, their mathematical programs do not take into account utility units (pump, heat exchangers, etc.).

These differences require a suitable representation of the RO network. Chapter 3 discusses the RO network superstructure and a heuristic search procedure to obtain local optimal solutions for the RO network. The search procedure is based on convex relaxation of the nonconvex terms present in the mathematical program. This approximation provides a lower bound on any optimal solution of the treatment network. As a result, the search procedure simplifies the initialization steps to solve the RO mathematical program.

One of the techniques for global optimization of nonconvex MINLP programs relies on convex relaxation of the nonconvex functions. The branch-and-bound (B&B) algorithm relies on rigorous elimination of the search space that does not bound global optima. The convergence of any B&B algorithm requires fathoming the nodes in the search tree according to a set of rules. The lower bound at some of the nodes may not improve down the tree. This effect normally leads to infinite branching, large number of nodes in the search tree and convergence problems. Chapter 4 presents an effective (B&B) global search-based algorithm for the RO network. The approach taken is to obtain a tighter formulation of the treatment network by developing a set of constraints in the relaxed formulation which helps to close the gap in the B&B tree. Seawater desalination is considered as a representative case study of the proposed approach.

Volatile organic compounds (VOC) constitute an important class of priority pollutants listed by the environmental protection agencies of most countries. A hybrid membrane network is illustrated by presenting the air stripper/pervaporation system for the treatment of wastewater streams contaminated by VOC's. Chapter 5 presents the superstructure representation of a hybrid air stripper/pervaporation system. Two case studies are presented as representative examples of the treatment of wastewater streams contaminated by VOC's. Sensitivity of the optimal solutions is also analyzed. The thesis concludes in Chapter 6 with a summary of the major findings of this research and recommendations for further research.

Chapter 2

Hybrid Membrane Superstructure Optimization for Wastewater Treatment *

2.1 Introduction

The scope of process synthesis has evolved over years due to the recent concerns on the effect of industrial operations on the environment (Li et al., 2004). Between the 1960s and 1980s, process synthesis was concerned with the development of unit operations and optimizing chemical processes. Later, in the 1990s, due to the high concern over environmental degradation and sustainable development, the range of possibilities considered in process synthesis has broadened (e.g. plant integration). Since 1995, process intensification has resulted in the introduction of units having multi-functional purpose. It was during this period that the idea of coupling product and process design began to be explored. Both product and process design have been positioned within the chemical supply chain, reflecting that process synthesis is influenced by a number of economical (enterprise scale), environmental and molecular constraints (Grossmann, 2004).

The common approaches for optimizing the process synthesis problems are the use of hierarchical decomposition, superstructures and targeting techniques (Grossmann and Daichendt, 1996). Despite its considerable value, hierarchical techniques cannot evaluate process alternatives simultaneously nor can they accommodate multiple objectives. On the other hand, the superstructure approach can handle wide range of practical synthesis problems. Targeting techniques apply physical knowledge to understand features of a

* This chapter is under preparation for submission: Y. Saif, A. Elkamel, M. Pritzker, Optimization and Engineering.

feasible design without explicit construction of a process network. Each of these techniques has its advantages and disadvantages. Nevertheless, there has been some agreement that the superstructure approach is the most favorable for process synthesis problems (Barnicki and Siirola, 2004; Westerberg, 2004).

Chemical processing plants typically involve reaction, separation and utility sections. The optimization of these sections can be done either individually or by integration into single flowsheet. The complexity of the process synthesis models falls in the NP-hard space. To date, there is no polynomial time method to solve these problems. As a result, the modeling stage has a critical impact on the solution time. Since the number of research studies on process synthesis problems is vast, this review will be restricted to the optimization work based on the superstructure approach, the method to be studied in this thesis. More comprehensive discussions on chemical synthesis networks can be found elsewhere (Floudas, 1995; Biegler et al., 1998).

Superstructure optimization has been applied to design single units or to retrofit existing units. Examples are the optimization of a distillation column and hybrid units (e.g. distillation column coupled with pervaporation unit). An MINLP model was developed to analyze the optimal number of trays, feed location and recycle streams for a distillation column (Viswanathan and Grossmann, 1993). Optimal synthesis of a reactive distillation column was addressed in terms of the optimal tray numbers, stream assignment between trays and the determination of the reactive and separation zones (Ciric and Gu, 1994). The separation of azeotrope mixtures requires intensive energy consumption and may require introducing separating agents to alter the concentration of chemical species. An MINLP model for the optimal integration of a distillation column and a pervaporation unit to separate propylene/propane mixture was presented to reduce energy consumption by a single distillation unit (Kookos, 2003). These examples showed that superstructure optimization were successful in improving the design of individual units.

The optimization of a process flowsheet is a rather complicated issue due to the large number of alternatives. The state space approach for process synthesis representation gives a framework for processes which involve mass and/or heat exchange (e.g. heat exchange networks, energy-integrated distillation networks, mass exchange networks) (Bagajewicz et al., 1992; 1998). This representation provides a large number of alternative process layouts and different modeling relations to assess the interaction between units and network streams. Interesting designs of integrated distillation trains have been identified due to the richness of network alternatives considered. This approach has also been applied to reverse osmosis (RO) networks, pervaporation (PV) networks and integrated mass exchange-RO networks for waste treatment and reduction (El-Halwagi 1992; Srinivas and El-Halwagi 1993; El-Halwagi 1993).

State task networks (STN) and state equipment networks (SEN) have been proposed as two different concepts to represent superstructures for process synthesis problems (Yeomans and Grossmann, 1999). The STN approach determines the quantitative (intensive and extensive) and qualitative properties of the streams and the tasks to be performed by the units. In a second step, the optimization routine assigns predefined equipment to carry out the tasks in the network. On the other hand, the first step of the SEN method determines all possible states and equipment in the network; this is followed by the optimization step to identify the different tasks that all equipment must complete. Generalized disjunctive programming (GDP) is applied to formulate these networks.

Integration of hierarchical decomposition and superstructure optimization has been proposed as a modelling tool for the synthesis of total process flowsheets (Daichendt and Grossmann 1997). The aim is to exploit the advantages of both techniques in the synthesis problem through an appropriate decomposition algorithm. The reaction, distillation and heat exchanger sections are simultaneously optimized based on aggregated models as a first step. In another level, a detailed model of every section of the flowsheet is optimized with other simplified models (e.g. black box models) for the downstream sections to account for interactions. The result of decomposition gives a base-case solution for the entire flowsheet. In a multi-level search tree, quick elimination of uneconomical solutions are accomplished early within the search tree by comparing the current solution value to the base case value helps to reduce the computation time.

Unit operations can be viewed as sets of mass and heat exchanger units where the mass and/or heat flow are limited by driving forces between concentrated (or hot) streams and other diluted (or cold) streams (El-Halwagi and Manousiouthakis, 1989). A general modular framework for process synthesis has been proposed for the purposes of process intensification rather than optimization of conventional process units (Papalexanderi and Pistikopoulos, 1996). The representation of the unconventional unit operations within a superstructure is included as mass/heat and pure heat modules that allow heat and mass transfer between phases. The solution of a superstructure, which allows for extensive connectivity between modules, determines the module duties (e.g. distillation column, absorber, reactive distillation etc.), optimal stream connectivity within the network and the optimal operation of the modules. The proposed methodology has been applied to design distillation networks for azeotropic mixtures (Ismail and Pistikopoulos, 1999), combined reaction-separation systems (Ismail and Pistikopoulos, 2001) and heat integrated distillation sequences (Proios et al., 2005; Proios and Pistikopoulos, 2006).

Another modeling approach has been presented to address integrated reaction-separation networks (Mehta and Kokossis, 2000; Linke and Kokossis, 2003). The superstructure given in this case is flexible to represent reaction networks, separation process configurations and reaction-separation systems. The flexibility in the problem representation is based on the description of generic units, namely reaction-mass exchanger units and separation task units which form the building blocks of the superstructure. The modeling approach was applied to several applications in chemical engineering which feature combined reaction-separation processes involving multiphases. Also, it was applied to wastewater treatment and natural gas sweetening applications (Linke and Kokossis, 2003).

2.2 Examples of Hybrid Membrane Systems

This section reviews several membrane and hybrid membrane superstructures for wastewater treatment. These systems include energy-integrated RO networks, energy integrated pervaporation networks and mass exchange-RO networks. The effects of the superstructure representation on the mathematical programming models are analyzed. Possible improvement in the superstructure representation of these networks is discussed with respect to better mathematical programming formulations. A unified approach of hybrid membrane superstructure representation is also provided. This representation overcomes some of the previous optimization study pitfalls and hopefully yields better mathematical programming models.

Hybrid membrane systems have been studied and shown to enhance separation capabilities (Suk and Matsuura, 2006). The optimization of membrane and hybrid membrane via superstructure optimization has been addressed for the treatment of wastewater streams (El-Halwagi, 1992; Srinivas and El-Halwagi, 1993; El-Halwagi, 1993). State space approach was the fundamental framework for building these superstructures. The mathematical programming models are formulated as MINLP models to search for an optimal treatment network. These models cover energy-integrated reverse osmosis networks, energy-integrated pervaporation networks and hybrid mass exchange-reverse osmosis networks. These earlier studies were concerned primarily with optimization problems and consequently put less emphasis on improving the optimization model formulations.

2.2.1 Reverse Osmosis Network

Energy-integrated RO networks include pumps, turbines and RO stages to treat multicomponent wastewater streams. Figure 2.1 shows an energy-integrated RO superstructure representation which has four main parts: DB1, DB2, PTB and ROB (El-Halwagi, 1992). The distribution box DB1 mixes and splits streams prior to and after the unit operations. Before entering the RO stage (ROB), the wastewater streams are passed through the pump/turbine unit box (PTB) to be pressurized or depressurized. Subsequently, the stream proceeds through another distribution box DB2 prior to the RO stage box. It should be noted that the streams from the RO units can be mixed with the inlet wastewater feed streams before the PTB to allow for possible direct bypass of some portion of the feed to the final product nodes. It can be seen that the unit operations are arranged in series in the superstructure representation. The RO network superstructure will be explained in more detail in Chapters 2 and 3.

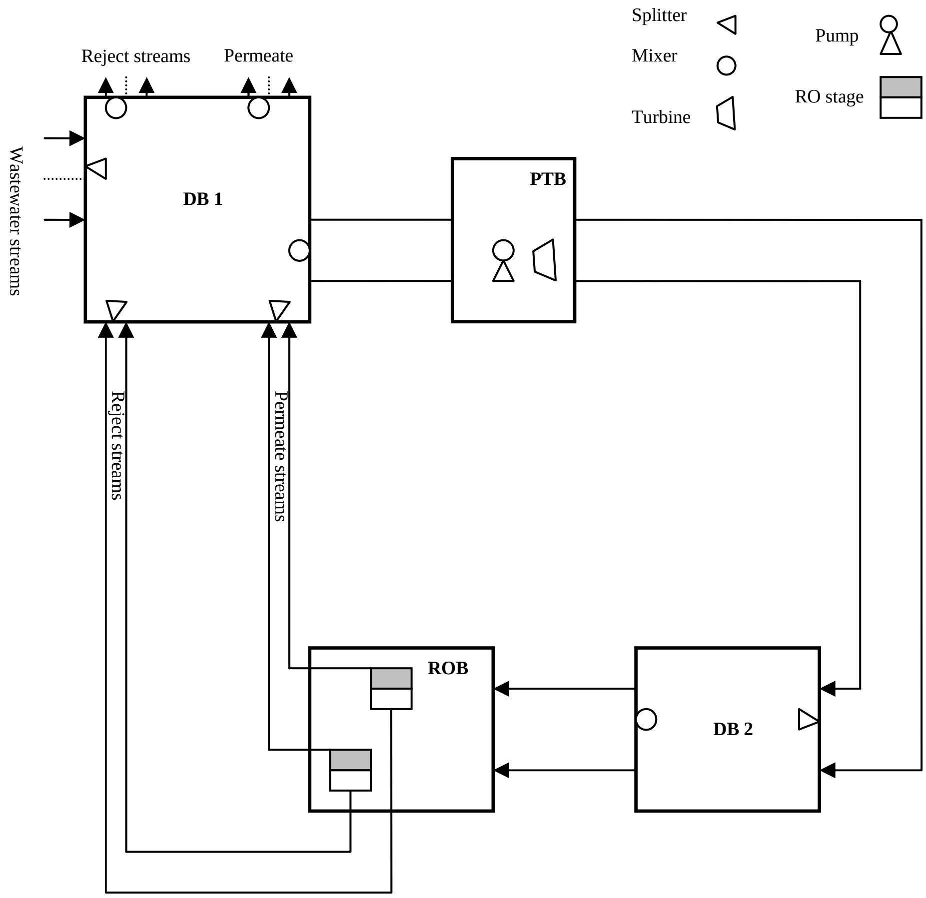


Figure 2.1. Superstructure of reverse osmosis network (El-Halwagi, 1992).

Seawater desalination is widely and successfully carried out by the use of RO systems. An example of an optimal solution for the processing of seawater by an RO system is given in Figure 2.2. The feed stream passes through a pump, two RO stages and two turbine stages to reach the final product qualities. The optimal solution projection on the original superstructure is shown in Figure 2.3. The superstructure which encompasses a broader set of alternatives requires the presence of four pump/turbine stages and four RO stages to obtain the optimal treatment network. If one assumes that the given optimal solution is a global solution of the treatment network, the mathematical program of the given superstructure should contain three nonexistent stages in order to verify global optimality of the network. This increased number of equations and variables arises from the series arrangement of units in the superstructure representation. Other disadvantages of the mathematical program formulation will be described in the following sections.

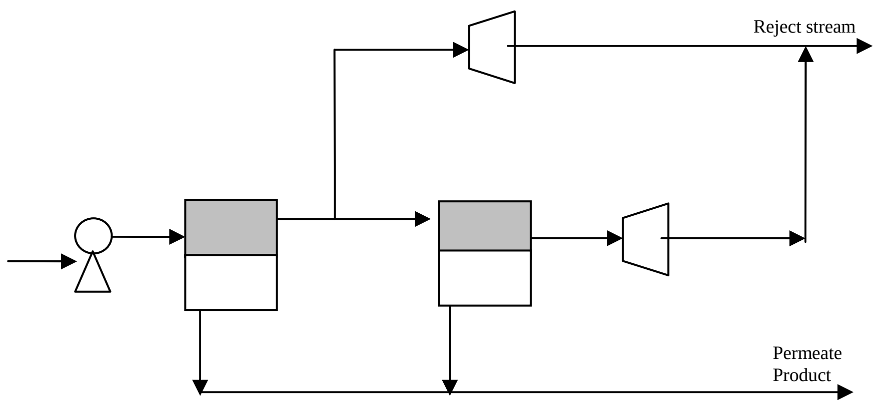


Figure 2.2. Optimal design of seawater treatment (El-Halwagi 1992).

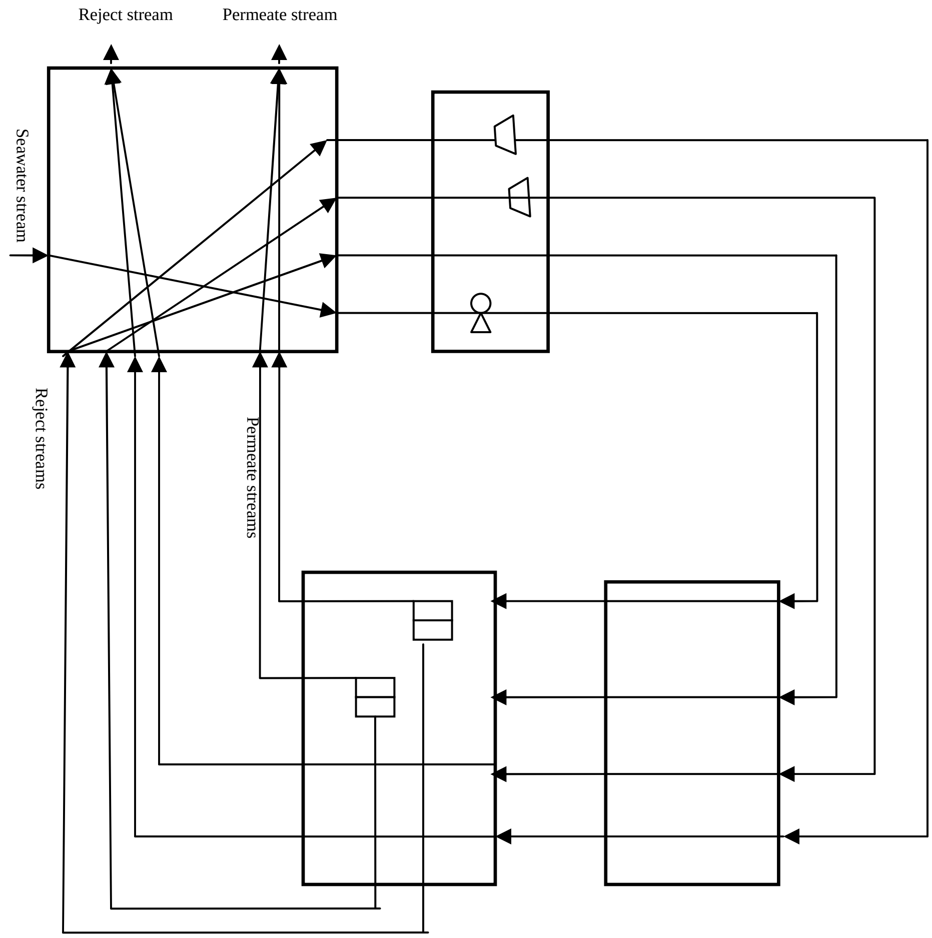


Figure 2.3. Projection of the RO optimal solution on the RO superstructure.

2.2.2 Pervaporation Network

The driving force for separation by pervaporation is the existence of a pressure difference and/or temperature gradient across the membrane. Optimization of pervaporation systems has been formulated as an MINLP with energy integration according to the superstructure shown in Figure 2.4 (Srinivas and El-Halwagi, 1993). As in the RO networks, a series arrangement of the unit operation is used. First the wastewater stream is distributed over the pump nodes followed directly by a one-to-one match between the pump and pervaporation stages. The pervaporation product streams are further distributed in a secondary distribution box where hot and cold utility streams are matched with the process hot and cold streams for energy integration.

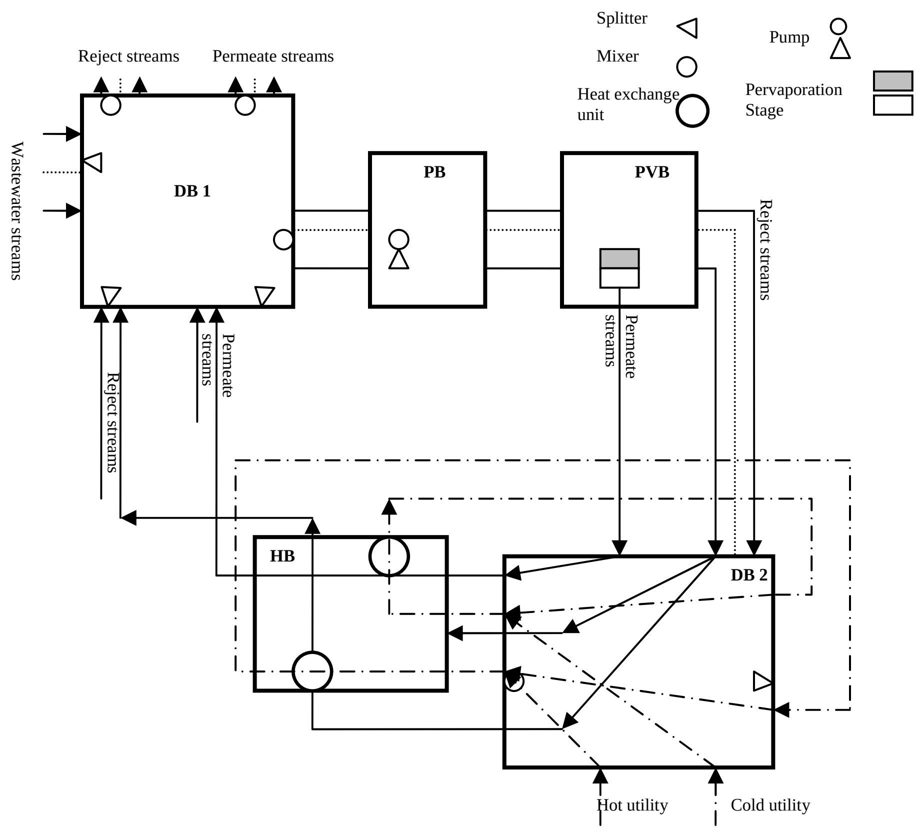


Figure 2.4. Pervaporation superstructure representation (Srinivas and El-Halwagi, 1993).

Chloroform is a priority VOC which requires proper treatment when present in wastewater streams. An optimal solution of integrated pervaporation system includes steam heating the feed stream followed by pressurizing the feed to the pervaporation stage (Figure 2.5). Afterwards, the pervaporation product streams are cooled down by utility cooling water. Once again, extra unit operations should be included in the superstructure in order to obtain an optimal solution.

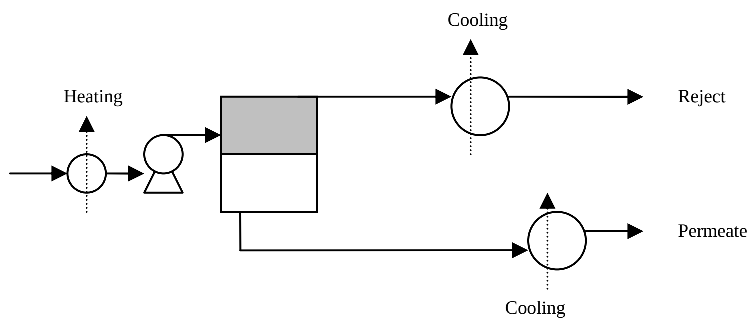


Figure 2.5. Optimal design of chloroform separation by pervaporation system.

Another observation concerning the pervaporation system is that two utility units are integrated within the pervaporation system. This may raise a question about whether to locate the utility unit boxes for energy integration before the pump-pervaporation box or after the separation, as is proposed in the design shown in Figure 2.5. In this particular case (e.g. the pervaporation system), heat integration will be more likely to be over the pervaporation product streams and therefore, the series arrangement of pump-pervaporation-heat integration is more desirable. However, in the case of a hybrid circuit where two separation techniques can be used, the question of the proper series arrangement is still valid, as analyzed in the next example.

2.2.3 Mass Exchange-RO Hybrid Network

Mass exchange is carried out in many unit operations that allow the transfer of chemical species between different phases (e.g. absorption, adsorption, extractors, etc.). Since RO has wide applications in wastewater treatment, the integration of RO with other mass exchange units can potentially provide enhanced separation performance. Figure 2.6 shows an integrated mass exchange-RO superstructure (El-Halwagi; 1993). The RO superstructure is extended to include other unit operations (e.g. mass exchange units) in two other boxes – mass exchange box (MEB) and regeneration box (RB). Possible functions of the MEB and RB boxes are assignment, superstructure, and split-match operators (Bagajewicz and Manousiouthakis; 1992, Bagajewicz et al.; 1998).

The hybrid superstructure shown in Figure 2.6 has some weaknesses:

- The series arrangement of the unit operations requires the introduction of a large number of extra unit operations above that required in the optimal solution. Since these extra units are embedded directly within the representation, these cannot be eliminated from the mathematical program.
- The arrangement sequence of unit operations is not unique. In general, different mathematical programming formulations are possible with different sequences and different degrees of complexity. It is not clear how to formulate the best series sequence arrangement of these units.

- The superstructure is limited to a hybrid system involving RO only. Therefore, other hybrid membrane systems cannot be directly assembled from the previously mentioned superstructures.
- The execution time of the optimization problem based on the superstructure shown in Figure 2.6 in general will be higher than that required for the superstructure representation to be described in the following section.

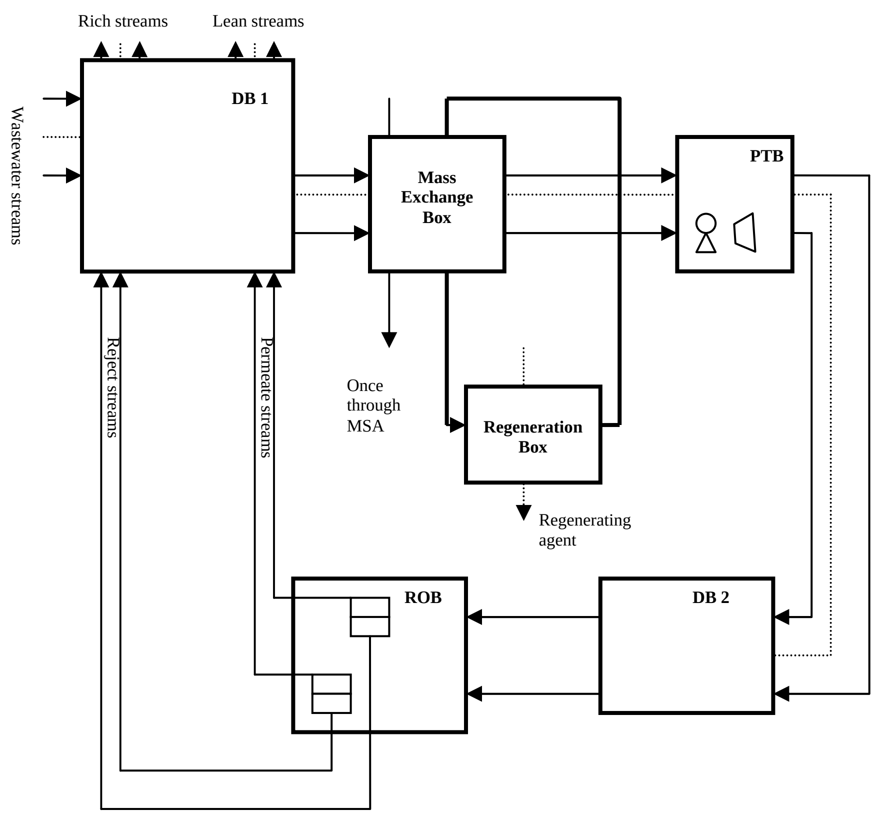


Figure 2.6. Superstructure representation of hybrid mass exchange-RO system (El-Halwagi; 1993).

2.3 Hybrid Membrane Superstructure

Chemical processing plants are a sequence of unit operations linked in a series and/or parallel way with possible recycle streams. The unit operations perform certain tasks on feed streams to alter their states in order to reach the final product states. A design engineer, however, will be given input-output information with the ultimate objective to map the best route between the input-output information while minimizing or maximizing given criteria. The design task can be visualized as a screening process among an assortment of different layouts of a treatment plant. The superstructure framework for process synthesis provides tools for building a family of process designs in a large representation. Thereafter, the mathematical formulation follows closely upon what has been framed in the superstructure representation. It is therefore important to formulate a good representation in order to minimize complicated mathematical programming.

A hybrid membrane process synthesis problem for the treatment of water or wastewater streams can be formulated from the following sets:

$$SIN = \left\{ \sin_1, \ldots\ldots\ldots, \sin_n \right\}$$

$$C = \left\{ 1, 2, \ldots\ldots\ldots\ldots, c \right\}$$

$$USI = \left\{ usi_1, \ldots\ldots, usi_n \right\}$$

$$O = \left\{ o_1, o_2, \ldots\ldots\ldots, o_n \right\}$$

$$UO = \left\{ uo_1, \ldots\ldots, uo_n \right\}$$

$$SOT = \{sot_1, ..., sot_n\}$$

$$P = \{p_1, p_2, ..., p_n\}$$

$$USO = \{uso_1, ..., uso_n\}$$

where SIN is a set of inlet wastewater streams, C is a set of pollutants in the system, USI is a set of inlet utility streams to carry out certain tasks where usi_n is a subset of utility streams of certain type (e.g. steam, air, etc.). O is a set of unit operations where o_n is a subset of unit operations of similar type. UO is a set of utility unit operations where uo_n is a subset of utility units of similar type (heat exchangers, pumps, etc.). SOT is a set of wastewater streams with acceptable qualities obtained after discharge from the treatment network. P is a set of product streams that results from the separation. USO is a set of utility streams leaving the treatment network. The design problem then requires a superstructure that embeds many design alternatives to achieve separation targets.

The state space approach for process synthesis provides tools to assemble the superstructure of a process network (Bagajewicz et al., 1992; 1998). Figure 2.7 represents a generic superstructure of a process synthesis problem. A large box (DB) accommodates several streams either entering or leaving the treatment network. Incoming flow streams (e.g. wastewater streams) are split by the mixer nodes. Utility streams can also be split by the mixer nodes. The utility and the operation units receive single or multiple feed streams and consequently the state variables of the inlet streams change to other values satisfying the unit operation models if these units exist. The exit streams from the utility and unit operations loop back to the DB mixer nodes for further processing or leave the treatment network.

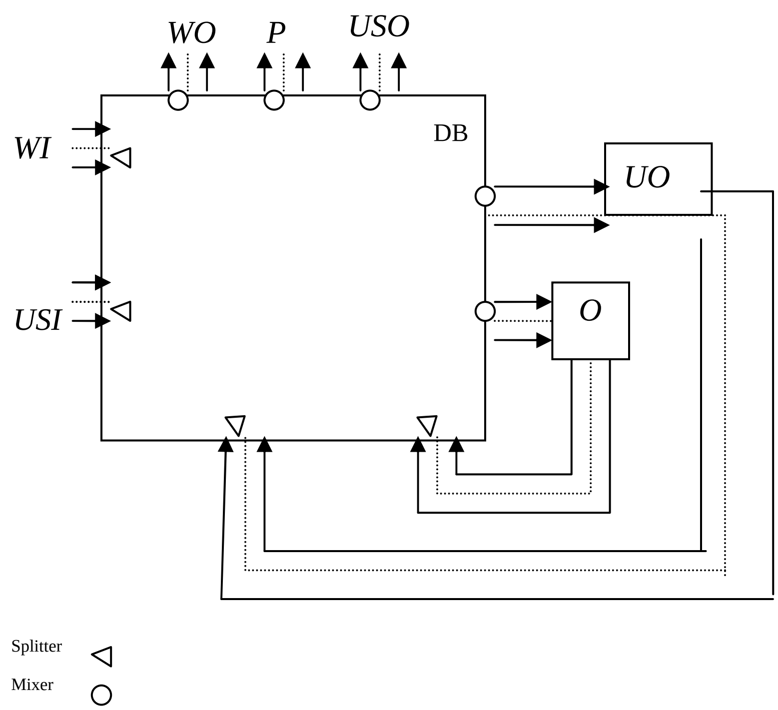


Figure 2.7. Superstructure of hybrid membrane systems.

According to the superstructure representation and the unit operation models, the mathematical programming formulation can be derived in terms of a combination of parameters, continuous variables, discrete variables (e.g. binary and/or integer variables), equality and inequality equations and an objective function to be maximized or minimized. The process synthesis optimization problem may be formulated as:

$$
\begin{aligned}
&Min/Max \qquad f(x,y) \\
&s.t. \\
&\qquad h(x) = 0 \\
&\qquad g(x) + M\ y \le 0 \\
&\qquad x \in X\ ,\ y \in Y
\end{aligned}
$$

where x is the vector of the continuous variables which may represent flow, concentration, and pressure etc., and y is the vector of binary variables which may represent the existence of units and/or streams. The equality constraints may include balances in the network (e.g. mass balance, component balance, energy balance, unit models, etc.). The inequality logical constraints show relations between the continuous variables and the binary variables (i.e. the existence of a unit requires that the value of the binary variable be set to 1). An objective function $f(x,y)$ may be defined to minimize or maximize a design criterion (e.g. total annualized cost, utility cost, unit surface area etc.).

This representation of a hybrid membrane superstructure takes into account parallel/series arrangements and recycle streams among the units that may exist in a treatment network. Such an arrangement of units is observable in chemical process layouts. However, it includes no prior knowledge about the proper arrangement of the units within the superstructure since this issue is left to be determined by the optimizer. Different possible superstructures for RO networks are presented in the next section.

2.4 Comparison for RO Network

Although this section focuses on RO networks, the conclusions can be extended to other membrane networks such as those discussed in section 2.2. The analysis considers different combinations of units that may exist in an RO network superstructure. Advantages and disadvantages of these superstructures are discussed based on qualitative insights. Also, comparisons of the parallel and the series arrangement of units are given. Finally, the relation between the network configuration and optimization problem size is analyzed.

Compact representation of the units can be assembled by series arrangement of pumps, RO stages and turbines, as shown in Figure 2.8. Prior to every RO stage, the feed can be pressurized. The kinetic energy carried by the RO reject streams can be extracted by a turbine unit which follows the RO stage. The compact representation seems to have fewer mixer nodes in the DB which may lead to fewer nonconvex terms in the mathematical program. However, the following remarks can be made concerning this representation:

- Every unit in the treatment network has a fixed installation cost. In this case, if a decision is made to install a pump, then the down-stream unit cost (RO-stage, turbine) will be affected by the pump size. Therefore, splitting the stream after the RO-stage may reduce the load to the turbine stage (Figure 2.9a).
- Figure 2.9b shows that a reduction in the treatment may be accomplished by a decision to install a single pump. The pump exit stream can be subsequently

distributed to several RO stages. In this arrangement, the fixed cost of installing multiple pumps is avoided and thus a reduced cost is realized.

These interpretations show that decoupling the units in the superstructure representation can help reduce the required number of stages.

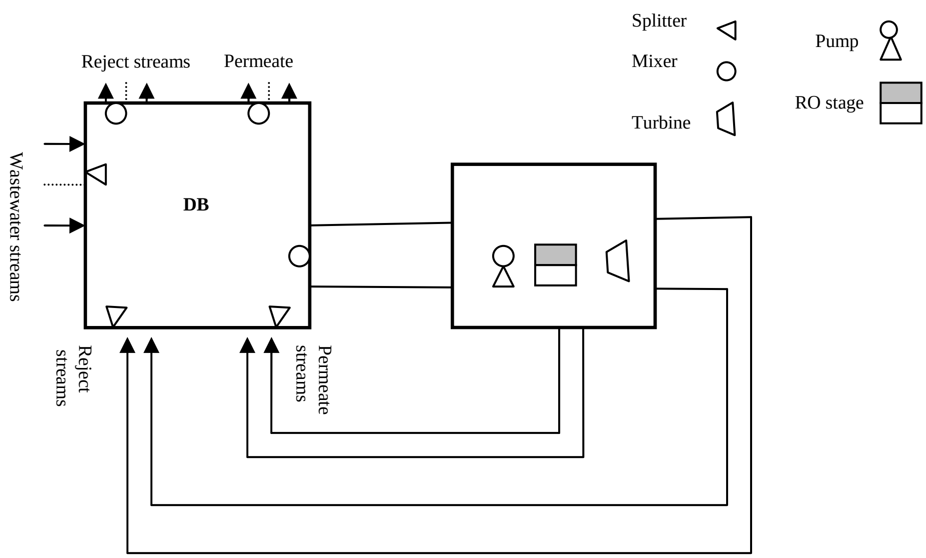


Figure 2.8. Compact representation of the RO network.

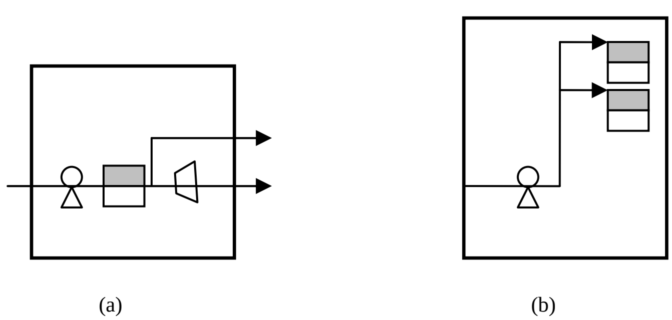


Figure 2.9. Compact representation of RO network with stream splits.

Another alternative representation of the network is to combine the pump and turbine units in a separate box while locating the RO stages in another box (Figure 2.10). In this representation, the wastewater streams are split by the PTB for pressurization. Then, the pressurized streams are distributed over the ROB, the final reject and permeate nodes. The RO product streams are looped back to the ROB, PTB and the final reject and the permeate streams. It is clear that the series arrangement in Figure 2.1 represents a subset of the more comprehensive network shown in Figure 2.10. The difference between them is mainly attributed to the inclusion of direct stream flows between the RO stages and direct stream flows between the PTB stages and the final mixer nodes.

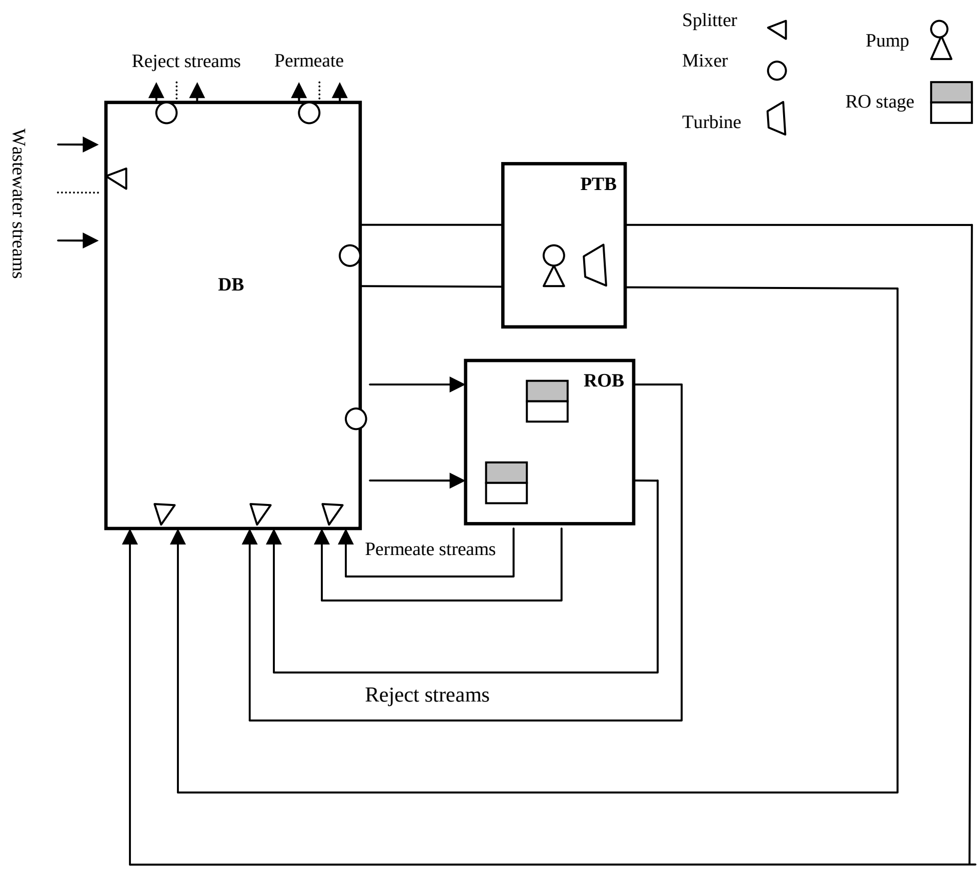


Figure 2.10. RO network under parallel arrangement of the unit operations.

To compare the superstructures given in Figures 2.1 and 2.10, an optimal solution of a RO network (e.g. Figure 2.2) is projected over these superstructures. This projection provides an idea of the required size of the mathematical programs that must be solved to obtain the optimal solution. Figure 2.11 shows the optimal solution projection over the RO network of Figure 2.10 to treat seawater stream. The optimal solution projected over the superstructure of Figure 2.1 appears in Figure 2.3.

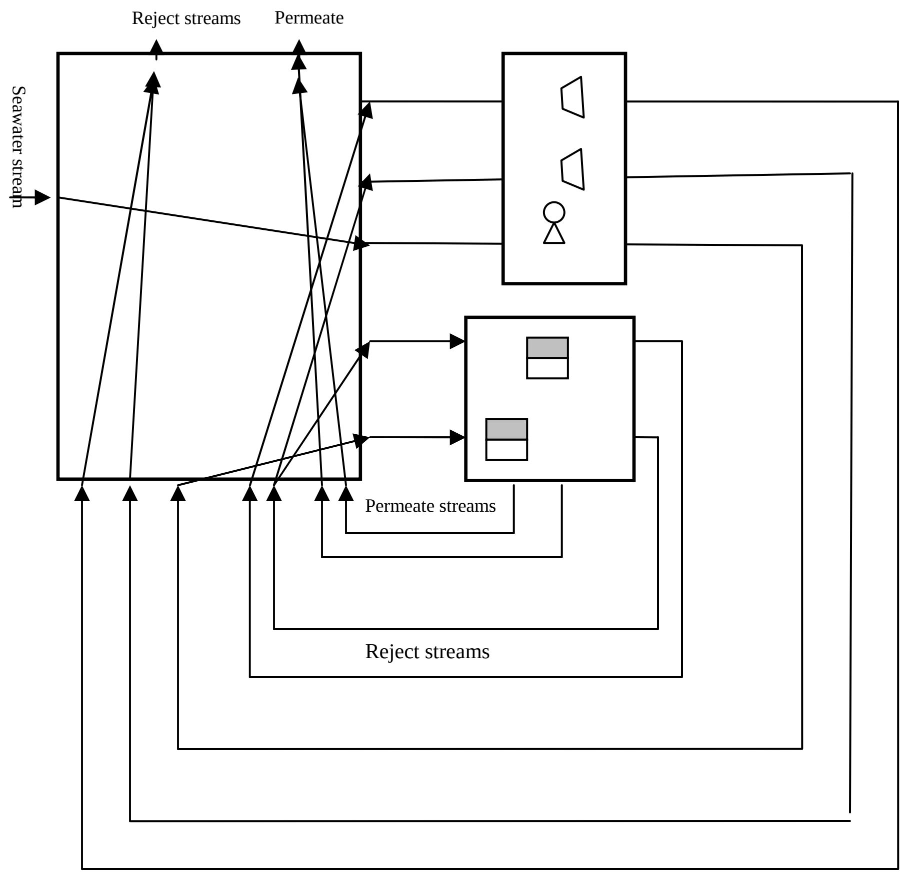


Figure 2.11. Projection of the optimal solution over the RO network for seawater treatment.

For both superstructures, the objective function aims to minimize the total annualized cost. It includes the fixed and the operating costs for the unit operations given in the superstructure. The series arrangement (Figure 2.3) requires the presence of twelve units as an initial guess, whereas the parallel arrangement (Figure 2.11) requires eight unit operations in the mathematical programming model. Thus, the parallel arrangement gives fewer terms in the objective function compared with the series arrangement. The stream assignments within the superstructures can be calculated by counting the number of splitter and mixer nodes. The number of stream assignments is 56 in the case of the parallel arrangement, whereas 110 streams are required for the series arrangement. Clearly, the computational effort for optimization of the parallel arrangement will be smaller than that for the series arrangement.

The branch-and-bound algorithm (B&B) evaluates the binary variables in successive nodes of a search tree. Within every node, NLP problem is solved to obtain an upper bound for the MINLP model. An essential property of the series arrangement of units is to allow flow of wastewater through nonexistence units, as given in Figure 2.3. Two important issues should be emphasized:

- From the previous simple calculation of the model sizes, one expects a higher number of nodes to exist within the search tree for the series arrangement compared to the parallel arrangement.
- The variable bounds of the nonexistence units remain at their limits.

The reason that the variable bounds remain at their limits is due to the requirement for flow through nonexistent units. On the other hand, the flow of wastewater through nonexistent units is not required for parallel arrangement of units. Thus, the following constraints can be added to the mathematical programming formulation in the case of parallel arrangement:

$$\left.\begin{array}{l} x \le x^{UP} \; y_{unit} \\ x \ge x^{LO} \; y_{unit} \end{array}\right\}$$

where x is a continuous variable, x^{UP} is the upper bound for x, x^{LO} is the lower bound for x and y_{unit} is a binary variable which defines the existence of a unit operation. Such constraints will force both bounds of continuous variables to be zero in the case of nonexistent units. Also, all the inlet streams to a mixer node prior to a nonexistent unit and all the streams from a splitter node after a nonexistent unit can have similar constraints. Thus, a reduced NLP problem for the nodes in the search tree is guaranteed in the case of parallel arrangement of units and reduction of the degree of nonconvexity effects is achieved (Türkay and Grossmann, 1996).

The main reason for combining a pump and a turbine in a single stage within the PTB is that these two units are never usually directly connected in a circuit. In other words, a pump in a RO network is never followed by a turbine unit since pressurization of a stream followed immediately by depressurization does not serve any physical purpose within a treatment plant. Thus, there is no loss of possible alternatives by combining a turbine and a pump within every stage in the PTB. Also, this will reduce the number of mixer nodes in the superstructure. On the other hand, the possibility of a pump followed by a turbine unit or vice versa still exists within the representation given by Figures 2.1. Consequently, these alternatives are contained within the branch-and-bound tree when the alternatives among different stages of the PTB are considered. Figure 2.12 presents this condition within the series arrangement of units.

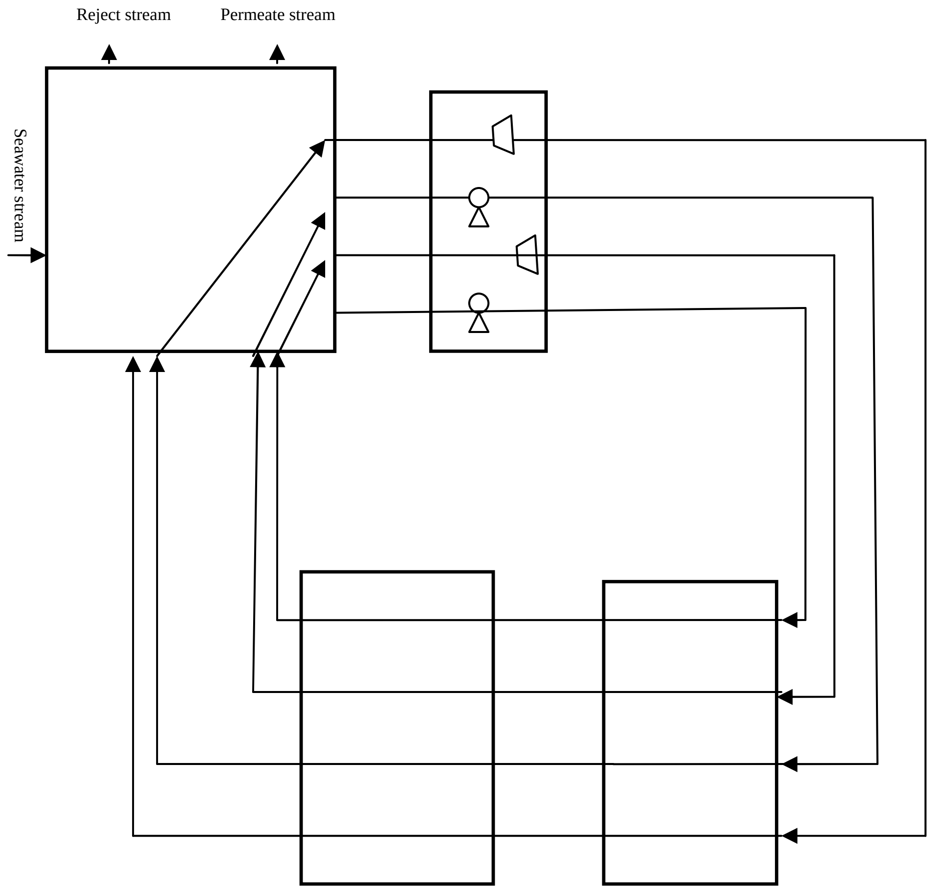


Figure 2.12. Series of pumps and turbines in the series superstructure representation.

This condition can be eliminated from enumeration in the search tree by formulating logical propositions. In fact, the previous point suggests that the superstructure in Figure 2.10 is reducible. Precisely, the direct stream assignments from one unit within the PTB to another can be dropped before the mathematical programming formulation. In this way, the logical propositions are not required at all. Also, the direct stream assignments between the inlet feed wastewater streams and the ROB can also be eliminated. It is worth pointing out that the superstructure given in 2.1 and the reduced superstructure given by Figure 2.10 will have the same number of stream assignments if both representations have the same number of unit operations.

The possibility of cyclic pressurization and depressurization among different stages of the PTB shows that the RO representation may have reduced dimensionality. Decoupling the unit operations can create conditions where some alternatives can be dropped safely from the mathematical formulation. Therefore, decoupling the pump and turbine units in separate stages may give a better representation. Such representation simplifies the distribution of streams within the DB and assists the construction of the logical propositions among the network alternatives. Further analysis of this kind of superstructure is provided in Chapters 3 and 4.

2.5 Conclusion

Superstructure optimization is presented as a tool to generate hybrid membrane process systems. The state space approach is the essential framework to build the superstructure representation. Previous hybrid membrane optimization studies were discussed and analyzed qualitatively for the treatment of water and wastewater networks. Although these research studies successfully solved the optimization problems, several drawbacks exist to the approaches used in the mathematical programming formulation. Examples of improvement of the superstructure representation and the mathematical programming formulation were presented to emphasize the use of prior knowledge of the operation to improve and simplify the superstructure representation and the mathematical programming models.

Chapter 3

Optimal Design of Reverse Osmosis Network for Wastewater Treatment *

3.1 Introduction

Reverse osmosis (RO) has been an effective technology for water and wastewater treatment. It is a pressure-driven process in which the membrane acts as a semi-permeable barrier to allow primarily water to pass through as a purified permeate stream, but retain pollutants in a concentrated stream. Due to their extremely small pore size, RO membranes have the capability of retaining molecules and ions. In addition, RO systems are modular, compact and consume only moderate energy during operation. These and other advantages have made RO systems strongly competitive against other separation processes (Lyonnaise des eaux, 1996).

RO networks are nonisobaric systems in which pumps deliver kinetic energy to wastewater streams, turbines extract energy from reject streams and RO stages carry out the separation. The state space approach has been shown to give an adequate superstructure for RO networks (El-Halwagi, 1992). Further extensions to RO networks have been proposed, such as the use of hybrid RO-mass exchange networks which combine RO units with other separation units (El-Halwagi, 1993). RO and hybrid RO networks are formulated as nonconvex MINLP. Due to the high nonconvexity of the RO network (El-Halwagi, 1992), a genetic algorithm was applied to optimize the RO network considering different RO stages in different case studies (Vyhmeister et al., 2004).

* This chapter is in print: Y. Saif, A. Elkamel, M. Pritzker, Chemical Engineering and Processing: Process Intensification, 2007.

However, the execution time for the algorithm was found to be prohibitively long when as many as ten unit operations were considered in the superstructure.

A practical problem with RO membranes that must be continually addressed is the loss of performance due to membrane fouling. Thus, the optimization of RO network operation to include scheduling for membrane cleaning is an important issue that has received attention. In one study, the RO design model accounted for fouling by considering the permeate flux to decay exponentially with time between cleaning steps (Zhu et al., 1997). Several predetermined schedules for membrane regeneration were specified. For each schedule, an optimal network was designed to meet several operation targets. The overall minimum total annualized cost of the network generated from all the schedules was chosen to be the best configuration of the RO-network.

Optimal RO network and RO module dimensions was presented as an MINLP model (Maskan et al., 2000). The choice between module types (e.g. tubular, hollow fiber) was made on the basis of decision variables to determine optimum membrane dimensions and the surface area of the module. The performance model for RO module took care of pressure losses due to friction and flow in the module manifolds. In addition, the effect of concentration polarization was included to better estimate the osmotic pressure. Their analysis yielded the optimum hollow fiber module dimensions and series arrangement for the RO network.

Another modeling approach to the RO scheduling problem was given as a multi-period optimization problem (See et. al., 1999). The optimization problem is rather more involved compared to the other approaches. This is due to the highly combinatorical nature of multiple discrete decision making for design and maintenance schedules. Simulated annealing algorithm was applied to find the optimal design and scheduling of an RO network. However, solutions based on gradient-based search algorithms performed better in terms of time execution and solution qualities compared to a stochastic-based search algorithm (See et al., 2004).

Optimal RO membrane cleaning schedules and replacement were formulated as an MINLP problem (Lu et al., 2007). The model in this case considers degradation of membrane performance due to irreversible and reversible fouling. Therefore, the optimal design determines the required membrane cleaning and replacement over a long time horizon. There was no attempt to determine the optimum RO network layout in this study. Instead, a circuit with two RO treatment trains in parallel was considered to produce permeate at a specified rate. Also, the fouling mechanism was not explicitly stated or related to the operating conditions.

Desalination by RO networks is a very well established process. The design of RO networks normally does not exceed two RO stages in series in industrial practice. The effect of product quality having to meet multiple specifications (e.g. salt content in the final product, final product flowrate) on the RO network was addressed in a sensitivity analysis (Lu et al., 2007). Their results show that the need to achieve very high product quality (e.g. low salt concentration in the product streams) may require further treatment of the RO permeate from one stage in a subsequent RO stage. In addition, the RO networks do not follow the common RO industrial layouts in terms of the RO stage number and the stream distributions within the network. The superstructure representation in this study follows the series arrangement of the unit operations (El-Halwagi, 1992).

In this chapter, a RO design network is determined on the basis of a superstructure which embeds all possible alternatives of a potential treatment network for water and wastewater streams. The superstructure contains several units of pumps, turbines, and RO stages. The mathematical programming model is formulated as a nonconvex mixed integer nonlinear program (MINLP). Bilinear terms in the constraint set and concave functions in the objective function lead to the nonconvexity of the mathematical programming model. The solution steps search for an improved optimal solution of the treatment network progressively. Section 3.2 provides the superstructure description. Section 3.3 follows up to give the mathematical programming model formulation. In section 3.4, the solution steps are described in detail. Section 3.5 presents several case studies of water desalination and wastewater treatment from the pulp and paper industry. Finally, conclusions are given in section 3.6.

3.2 Superstructure

RO network is assumed to have three different types of unit operations. Pumps are necessary to raise the pressure of different wastewater streams. RO stages separate single feeds to different concentrated and diluted streams. Every RO stage is assumed to have parallel RO modules operating under the same conditions. Turbines serve essentially as units to recover kinetic energy from high-pressure streams. The RO network also has the ability to receive multiple wastewater streams with multiple pollutants. With the view of a superstructure, one should allow all possible connections between the unit operations, the unit-operations exit streams, and the inlet wastewater streams coming to the network. Figure 3.1 depicts the proposed superstructure for RO treatment network.

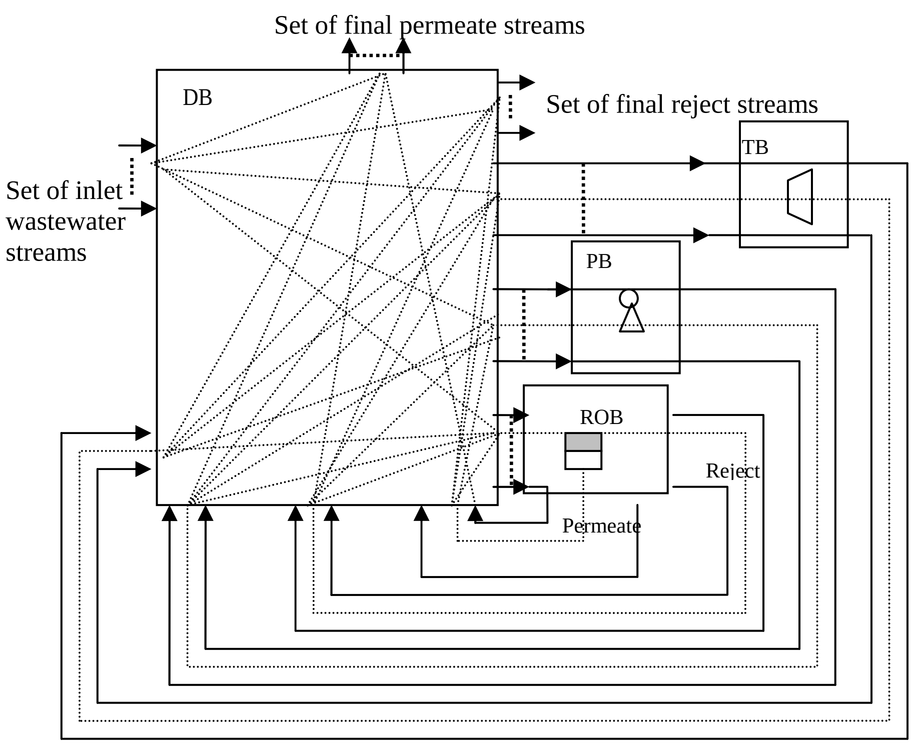


Figure 3.1. RON superstructure representation.

The superstructure is split into two parts, a distribution box (DB) where mixing/splitting of the streams occur, and another part has different boxes containing different unit operations which alter their feed stream conditions. The set of inlet wastewater streams represents different wastewater streams that need to be treated in the network. Every inlet wastewater stream is distributed over all the stages present in the unit-operation boxes, the set of final permeate nodes, and the set of final reject streams. Within every unit-operation box (e.g. TB, PB, ROB), different stages of similar units may exist and they operate under different conditions. Every stage in every box receives a single feed stream. In any RO stage, the feed stream is split into a concentrated and a dilute stream if that stage exits in the network. For every pump stage, the feed stream is pressurized. The turbine box is composed of different turbines which decrease their inlet feed pressure. All the exit streams from the unit operations are looped back to the DB for further recycle and bypass between the unit-operation stages, the set of final permeate streams, and the set of final reject streams. The stream distributions in the DB can be stated briefly as every incoming stream to the DB is distributed over all the exit streams in the DB. The abovementioned representation of RO superstructure gives all the possible alternatives for a potential treatment network.

3.3 Model Formulation

3.3.1 MINLP Model

The superstructure is composed of several unit operations (e.g. Turbines, Pumps, RO stages) which represent the total cost of the network. Mixers and splitters nodes provide mixing and splitting for the streams within the network. The objective function of the mathematical programming model can be defined as to minimize the total annual cost (TAC) of the unit operations as:

$$
\begin{aligned}
Min \qquad TAC &= \sum^{SRO} a_{MRO}\, NMd_{SRO} + \sum^{SPU} a_{pu,f}\, PPu_{pu}^{\alpha_{Pu}} \\
&+ \sum^{SPU} a_{pu,o} PPu_{pu} + \sum^{STU} a_{tu,f}\, PTu_{tu}^{\alpha_{tu}} - \sum^{STU} a_{Ttu,o} PTu_{tu}
\end{aligned}
\qquad (3.1)
$$

The total cost of the network is assumed to depend linearly on the number of modules (NMd_{SRO}) at every RO stage (SRO) through the fixed/operating cost of the single RO module (a_{MRO}). Pump and turbine fixed costs which are attributed to the power produced/recovered (PPu_{pu}, PTu_{tu}) at every pump or turbine stage belong to the sets (SPU, STU) raised to a fractional constant (α_{pu}, α_{tu}). $a_{pu,f}$, and $a_{tu,f}$ give the fixed cost coefficients for the pump and turbine stages, respectively. The pump operation cost and the turbine operation value are assumed to be a linear function with respect to the unit's power through the constants $a_{Pu,o}$, and $a_{Tu,o}$.

The power produced by any pump is the pressure difference across the unit ΔP_{SPU} multiplied by the total flow through the unit F_{SPU}, Eq. (3.2). A binary variable y_{SPU} defines the existence of any pump if the pressure difference across the unit has a nonzero value, Eq.(3.3).

$$PPu_{SPU} = F_{SPU}\ \Delta P_{SPU} \qquad \forall SPU \qquad (3.2)$$

$$\Delta P_{SPU} \leq \Delta P_{SPU}^{UP} \; y_{SPU} \qquad \forall SPU \qquad (3.3)$$

For the turbine stages, the power recovered by any turbine is given by Eq.(3.4) and the existence of any turbine within the network is related to a binary variable y_{STU}, Eq. (3.5).

$$PPu_{STU} = F_{STU} \; (-\Delta P_{STU}) \qquad \forall STU \qquad (3.4)$$

$$-\Delta P_{STU} \leq \Delta P_{STU}^{UP} \; y_{STU} \qquad \forall STU \qquad (3.5)$$

The permeate production Fp_{SRO} from an RO stage is described by a short-cut model (Evangellsta, 1985). This model relates the permeate flow with the pressure drop across the module ΔP_{MRO}, osmotic pressure of the feed stream π_{MRO}, and the total number of parallel modules present in the stage, Eq. (3.6-3.8).

$$Fp_{SRO} = NMd_{SRO} \, W \, SA \, \gamma \left(\Delta P_{MRO} - \pi_{MRO} \right) \qquad \forall SRO \qquad (3.6)$$

$$\gamma = \frac{\eta}{1 + 16 \, W \, \mu \, r_o \, l \, l_s \eta / r_i^4} \qquad (3.7)$$

$$\eta = \frac{\tanh\left[\left(16 W \, \mu \, r_o \; / r_i^2 \right)^{1/2} \left(l / r_i \right) \right]}{\left[\left(16 W \, \mu \, r_o \; / r_i^2 \right)^{1/2} \left(l / r_i \right) \right]} \qquad (3.8)$$

where W is the water permeability coefficient, SA is the RO module surface area, γ is a parameter related to the RO module dimension and water properties. The component concentration in any permeate stream ($xp_{c,SRO}$) is related to the component average concentration at the reject side of the RO module ($X_{c-avg,SRO}$), the solute permeability coefficient (K_c), the osmotic pressure (π_{MRO}), the pressure drop in RO module (ΔP_{MRO}), water permeability and the geometrical parameter of the RO module, Eq. (3.9).

$$xp_{c,SRO} = \frac{K_c \, x_{c-avg,SRO}}{W \ \gamma \left(\Delta P_{MRO} - \pi_{MRO}\right)} \qquad \forall \, c, SRO \tag{3.9}$$

The total number of modules present in every RO stage is an integer variable. To simplify the RO balance Eq. (3.10), the integrality of the parallel module, NMd_{SRO} , is relaxed to give estimate for the RO stage surface area. This assumption is reasonable to reduce the combinatory of the mathematical program.

The osmotic pressure π_{MRO} at every stage is approximated by a rule of thumb for dilute solutions (Weber, 1972) as:

$$\pi_{MRO} = OS \sum^{c} x_{c-avg,SRO} \tag{3.10}$$

where OS represents a proportionality constant between the osmotic pressure and the total concentration of the solute species in that stage.

Every RO stage may exist if the stage binary variable is true. The stage binary variable is related to the permeate production from the RO stage as given by Eq.(3.11).

$$Fp_{SRO} \leq \; Fp_{SRO}^{UP} \; y_{SRO} \qquad \forall SRO \qquad (3.11)$$

The RO module may require bounds on the operation variables to improve the system productivity. Eq.(3.12) enforces the inlet feed to any RO stage to be bounded between upper and lower limits. Also, the inlet feed pressure to any RO stage may not exceed an upper value as it is described by Eq.(3.13).

$$F_{MRO}^{LO} \; NMd_{SRO} \;\leq\; F_{SRO} \;\leq F_{MRO}^{UP} \; NMd_{SRO} \qquad \forall SRO \qquad (3.12)$$

$$P_{SRO} \;\leq\; P_{SRO}^{UP} \qquad \forall SRO \qquad (3.13)$$

Conservation of the total and component streams are described by Eqs.(3.14-3.15) over every RO stage.

$$F_{SRO} \; = Fp_{SRO} + Fr_{SRO} \qquad \forall SRO \qquad (3.14)$$

$$F_{SRO} \; x_{c,SRO} = Fp_{SRO} \; xp_{c,SRO} + Fr_{SRO} \; xr_{c,SRO} \qquad \forall c, SRO \qquad (3.15)$$

In the DB, there are several splitting nodes for the incoming streams to the DB, and mixing nodes before the unit operation stages and the final exit permeate and reject streams. Figure 3.2 shows a splitter node where a single feed stream (F_{SSP}) is split to several exit streams ($F_{SSP,MIX}$). Eq.(3.16) gives total material balance over the splitter node.

$$F_{SSP} = \sum^{MIX} F_{SSP,MIX} \quad \forall SSP \tag{3.16}$$

A mixing node is represented by Figure 3 where several streams ($F_{SSP,MIX}$) are mixed through the mixer unit to yield a single stream. Total and component balances over the mixer node are given by equations (3.17-3.18).

$$F_{MIX} = \sum^{SSP} F_{SSP,MIX} \quad \forall MIX \tag{3.17}$$

$$F_{MIX}\ X_{c,MIX} = \sum^{MIX} F_{SSP,MIXX}\ X_{c,SSP,MIX} \quad \forall\, c, MIX \tag{3.18}$$

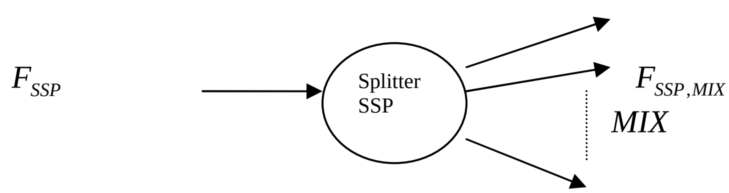


Figure 3.2. Inlet and exit streams conditions in a splitter unit.

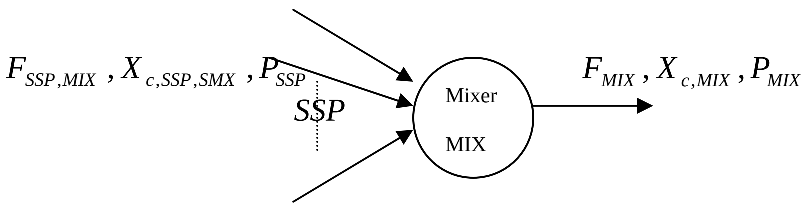


Figure 3.3. Inlet and exit conditions for a mixer unit.

Further, it is assumed here that mixing is not allowed between streams which have different pressure values. This condition is modeled through a binary variable $y_{SSP,MIX}$ which forces the flow of a stream $F_{SSP,MIX}$ to vanish if the stream pressure does not match the mixer-exit stream pressure, Eqs.(3.19-3.21).

$$P_{MIX} - P_{SSP,MIX} \leq M\ (1 - y_{SSP,MIX}\ ) \quad \forall SSP, MIX \tag{3.19}$$

$$P_{MIX} - P_{SSP,MIX} \geq -M\ (1 - y_{SSP,MIX}\ ) \quad \forall SSP, MIX \tag{3.20}$$

$$F_{SSP,MIX} \leq F^{UP}_{SSP,MIX} \quad y_{SSP,MIX} \quad \forall SSP, MIX \tag{3.21}$$

Other constraints are imposed on the final exit streams from the network. Eq.(3.22-3.23) gives limitation on the final permeate streams (F_{fper}) to have minimum flow and the concentration of the components in these streams ($x_{c,fper}$) not to exceed an upper value, respectively.

$$F_{fper} \geq F^{LO}_{fper} \qquad \forall\, FPER \tag{3.22}$$

$$x_{c,fper} \leq X_{c,fper}^{UP} \qquad \forall\, c, FPER \tag{3.23}$$

The set of equations (3.1-3.23) define a nonconvex MINLP for the RO treatment network. The mathematical program describes the unit existences and stream assignments within the network. The MINLP model can be reduced by examining the mixer nodes in the DB. Next section will explain the model constraint reductions.

3.3.2 Model Reduction

Although the superstructure given by Figure 3.1 truly represents all the alternatives for a potential treatment network, several alternatives can be excluded from the superstructure based on exploiting the mathematical programming model, and on the conceptual design of a potential RO treatment network. By inspecting the equations (3.19-3.20), it is possible to eliminate several stream assignments in the DB. Within the DB, several streams are assumed to have low-pressure values and others to have high-pressure values. In addition, the pressure of several streams in the DB is given beforehand, i.e., the pressure of the RO-permeate and the inlet feed wastewater streams is one atmosphere. Therefore, one should screen all the alternatives at every mixing point in the DB to explore possible simplification of the mathematical program. The following stream sets can be dropped from the model formulation:

1. Turbine stages should recover energy from high-pressure streams. Thus, the streams going from the inlet wastewater stream set to any turbine stage should not

have stream assignments due to their low kinetic energy. Similar reasoning applies for the RO permeate streams going to any turbine stage.

2. Any reject stream from a RO stage cannot have a recycle stream to the same stage since a pressure drop exists at every RO stage.
3. Any permeate stream from a RO stage should not have any stream assignments to every RO stage because in general they have low-pressure values.

Further alternative reductions can be achieved by examining the exit streams from the pump and the turbine stages, and the permeate streams of the RO stages. The following reduction in the stream assignments are based on the conceptual design of the network rather than exploiting the problem assumptions. The following gives reasoning for stream eliminations:

1. For any pump stage, the exit pressure from the unit can reach the inlet feed pressure upper bound of any RO stage. Therefore, the exit streams from any pump stage should only have stream assignments to all RO stages. Also, any stream assignment can be dropped from any pump-exit streams to any other pump stages, turbine stages, and the final reject and permeate streams.
2. The turbine exit streams should not have interactions between the turbine stages and the pump stages in the network. This is based on eliminating existence of series turbines and/or pump stages.

3. The permeate streams from any RO stage are considered as valued products. Consequently, these streams should not have stream assignments with the final reject stream set.
4. RO networks require the presence of at least a pump and a RO stage in the treatment network. Thus, in the mathematical program, it is safe to fix the binary variable of a pump and a RO stage. Also, the fixed pump node will only receive streams from the set of inlet wastewater streams, and the RO-permeate stream set.

Other constraint reductions can be achieved by examining the final reject and the permeate sets. Specifically, the constraints (3.19-3.20) should not be included in the mathematical program in the final reject and the permeate mixer nodes. The final reject nodes has inlet feed streams from the set of inlet wastewater streams, the turbine exit streams, the RO reject streams. Imposing the previous constraints at the final reject nodes will:

1. Either prevents flow from the set of inlet wastewater streams to the final reject nodes if the network does not have turbine stages. Consequently, higher cost of the RO treatment network is expected.
2. Or there might be flow from the set of inlet wastewater streams to the final reject nodes. This condition enforces turbine installations in the network to meet the final reject node mixing requirements.

Similar analysis can be addressed for the final permeate nodes. Therefore, the constraints (3.19-3.21) should be dropped from the mathematical program for the final reject and permeate nodes. Figure 3.4 shows the reduced superstructure.

Due to the nonconvexity of the mathematical program (MINLP), one expects several local solutions for the treatment network. The solution approach adapted to the mathematical program model is based on the convex relaxation of the bilinear terms through their convex/concave envelopes and the underestimation of the concave functions by chord lines. The convexification yields an MILP model, and its solution will provide a valid lower bound on the global optimum.

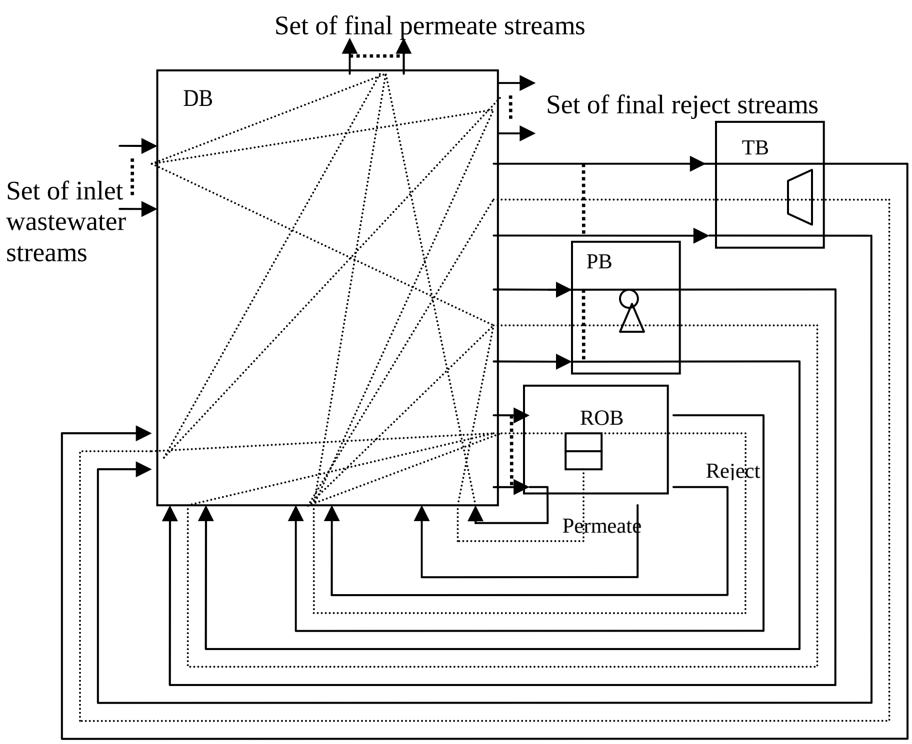


Figure 3.4. Reduced RO superstructure representation.

3.3.3 Convex Relaxation (MILP Model)

For a concave function, $\psi(z)^{\alpha}$, the underestimation function is a chord line

$$\underline{\psi}(z) \geq \left(\psi(z)^{LO}\right)^{\alpha} + \left(\frac{\left(\psi(z)^{UP}\right)^{\alpha} - \left(\psi(z)^{LO}\right)^{\alpha}}{z^{U} - z^{L}} \right) \left(z - z^{L}\right) \qquad (3.24)$$

For a bilinear function, $\chi = q\,w$, the convex/concave envelopes (McCormick, 1976):

$$\left.\begin{array}{l} \chi \geq q^{LO}w + q\;w^{LO} - q^{LO}w^{LO} \\ \chi \geq q^{UP}w + q\;w^{UP} - q^{UP}w^{UP} \\ \chi \leq q^{LO}w + q\;w^{UP} - q^{LO}w^{UP} \\ \chi \leq q^{UP}w + q\;w^{LO} - q^{UP}w^{OL} \end{array}\right\} \qquad (3.25)$$

The convex relaxed program (MILP) provides a lower bound on the global optimum. In general, the replacement of the nonconvex terms by their convex/concave envelopes gives loose relaxation. The reformulation linearization technique (RLT) is a technique which improves the relaxed MILP problem (Sherali and Alameddine, 1992). This technique generates redundant equations with respect to the nonconvex program in the relaxed problem by a multiplication process. Such technique adds large number of nonreduandant constraints in the relaxed problem which help to tighten the lower bounding problem. In this work, however, the redundant equations are generated based on the component balances between different levels in the network which have no direct balance equations in the original nonconvex program. Figure 3.5 depicts an example of deriving redundant constraints based on component balances. It shows that the network feed streams are split at early stage, then, sequentially processed by several units to reach the final product stage. In modeling the MINLP, the relation between different stages are implicitly stated through the model variables and equations. Therefore, the MILP model will not capture all the implicit relations present in the original MINLP. The dash box gives an example of deriving additional component balance equations between mixer and splitter nodes. It is clear that these equality constraints do not exist in the original model formulation of the treatment network. Thus, the generation of these equality constraints in the relaxed problem will help to tighten the lower bound. Certainly, the tightness of the relaxed problem is not stronger than the relaxed problem generated from the RLT bounding problem, though fairly good to improve the problem variable values in the relaxed problem.

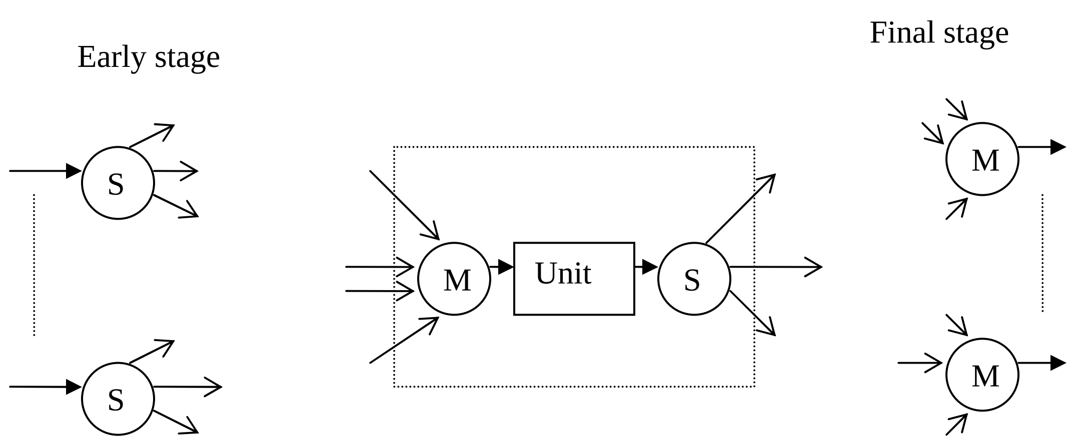


Figure 3.5. Different level representation of a superstructure.

Other redundant equations can be derived based on the energy conservation between the units in the network. An energy based redundant constraint can be stated as:

The energy produced by the pump stages =
the separation work in the RO stages + the recovered energy by the turbines +
the energy stored in the reject streams going to the final reject stream set.

Therefore, the MILP model will have the linear constraints of the original nonconvex MINLP model, the convex relaxation equations for the nonconvex terms, and the redundant equations based on the discussion in this section.

3.4 Solution Strategy

3.4.1 Substructure Generations

The first step in the solution strategy aims to reduce the nonconvexity of the MINLP model through exploring simplified substructures of the original problem. Tapered design of RO network is a series arrangement of the RO stages with possible interstage-pump existence. A turbine unit, as a final energy recovery stage, usually exists to receive high-pressure reject stream. The reject stream is continuously processed in the RO stages while the permeate streams are collected to a final product stream, Figure 3.6. This design may give the highest cost since the unit costs are function of the unit's feed-flow. Moreover, streams splitting are not allowed within the network which may increase the load on the down-stream processing units.

A second possible substructure is the tapered design with RO-reject and the set of inlet wastewater streams splitting to the final reject and permeate nodes, Figure 3.6. This design reduces the load on the down-stream processing units. Possible parallel/series arrangement of the units is the third substructure with additional splitting of the set of inlet wastewater streams over the pump nodes, and RO-reject streams over the RO-stages, pump stages, and the turbine stages, Figure 3.7. More alternatives can be added on

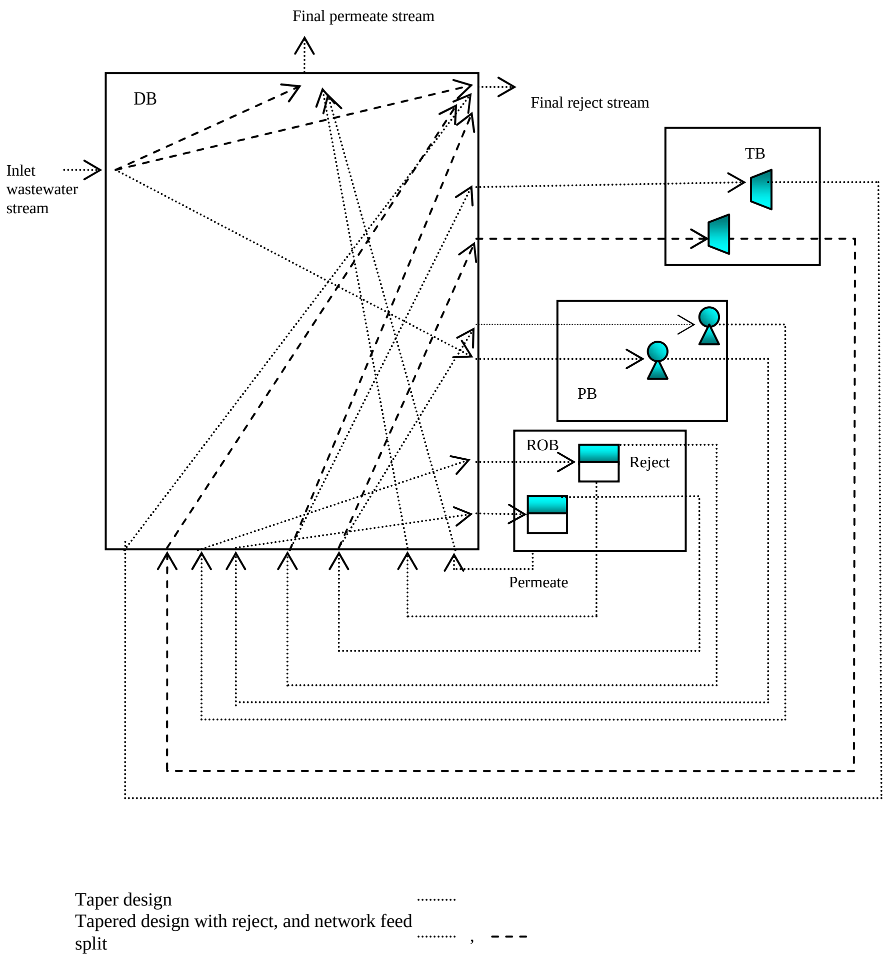


Figure 3.6. Different RO tapered design flowsheets.

top of the third substructure by exploring the benefit of RO-permeate streams split over the pump nodes, and the turbine-exit streams split over the RO-stages and the final permeate stream set. The fourth substructure is the total superstructure of the given problem where one might see that further processing of the permeate streams may reduce the total treatment cost.

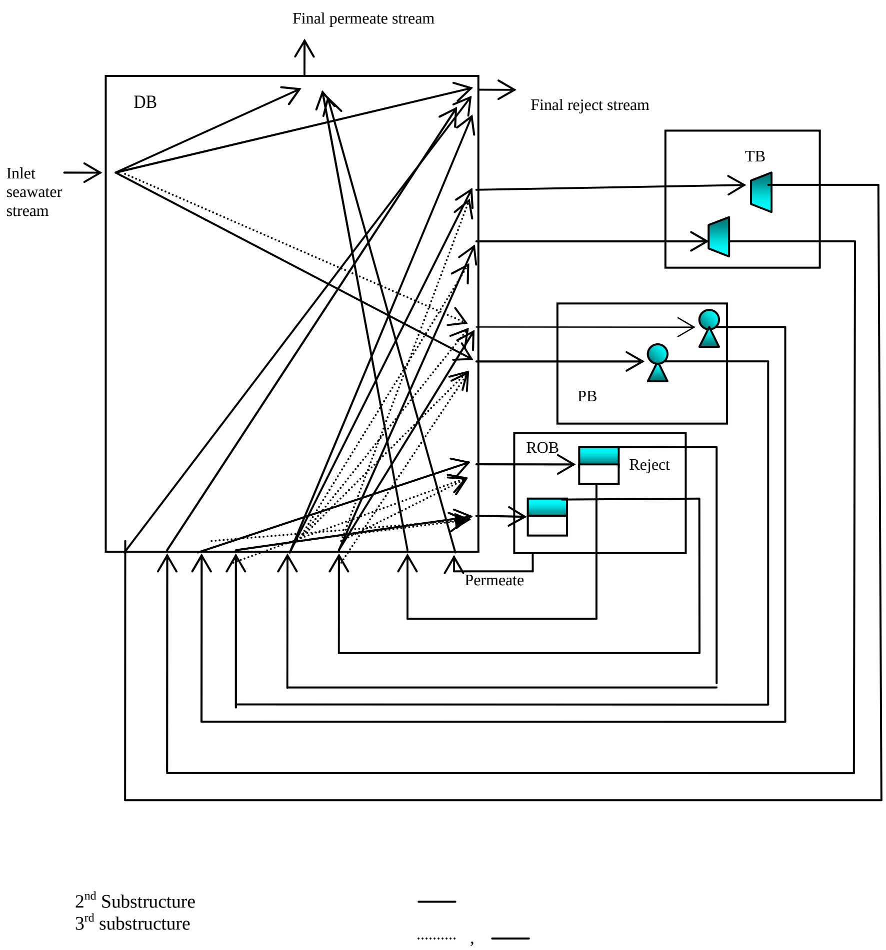


Figure 3.7. RO network under parallel/series arrangement of the unit operations.

Substructure generations, in the solution strategy, will reduce the total superstructure to the tapered design as a first option. In the tapered design, the bilinear terms rising from the component balance equations are eliminated from all the mixer nodes except for the final permeate stream set and the first pump node. Thus, the tapered design MILP formulation will have better bounds on the problem variables compared to the total superstructure. After that, additional alternatives can be added on the tapered design-substructure gradually by allowing stream splitting/mixing between the processing units until one reaches the original problem superstructure.

3.4.2 Heuristic

The solution strategy will proceed by choosing a substructure from the substructure list. Then, the MILP problem is formulated based on the given substructure alternatives, and on the substructure valid redundant equations. The heuristic solves different MILP problems and a nonconvex NLP problem for a given nonconvex MINLP (Galan and Grossmann, 1998). Fixing the binary variables in the MINLP model and solving the NLP problem may result with a local solution of the original problem. The binary variable values are obtained from solving the MILP problem and the initial starting points for the NLP problem are the MILP continuous variable values. Additional search, within the substructure space, is possible by supplying different values for the binary and the continuous variables in the original MINLP model. By minimizing the load for every unit operation (unit' cost function) in the MILP problem, other starting points for the MINLP problem are assisted. The elimination process can be repeated as many as units we have in the MILP objective function. It is worth pointing out that convergence to local solutions, for the MINLP model, depends on the feasibility of the treatment network (e.g.

the binary variable values) and the quality of the initial guesses for the continuous variables in solving the NLP problem. Figure 3.8 shows the solution strategy steps.

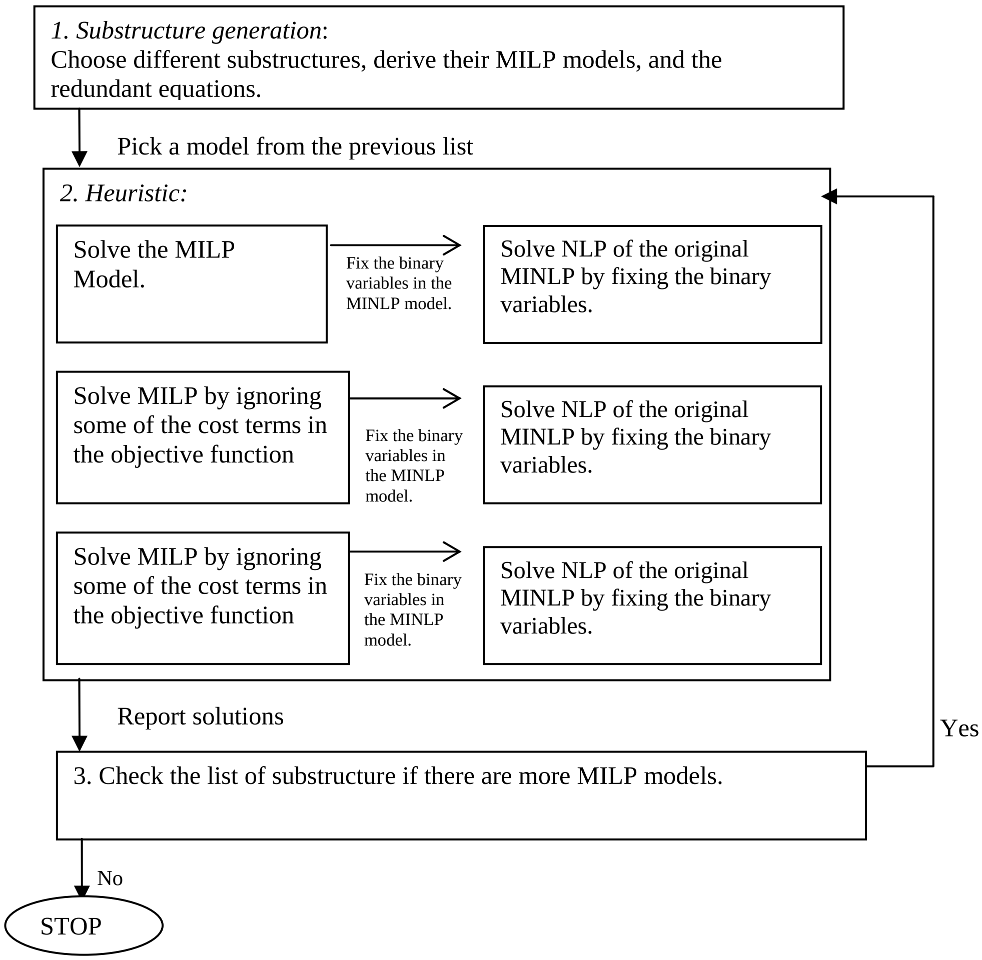


Figure 3.8. The solution strategy steps.

3.5 Case Studies

This section applies the concepts presented in the previous sections on single seawater stream desalination and the treatment of multiple wastewater streams from the pulp and paper industry by hollow fine fiber RO network. Table 3.1 gives the geometrical properties of DuPont hollow fiber RO modules and Table 3.2 lists the cost coefficients for the unit operations (El-Halwagi, 1992). The MILP and NLP solvers are CPLEX and CONOPT 2 in GAMS 20.5, respectively.

Table 3.1. Geometrical properties of DuPont RO modules and their dimensions.

Module Properties	**B-10 (Desalination case)**	**B-9 (Pulp and paper case)**
Fiber length (l) m	0.75	0.75
Fiber seal length (l_s) m	0.075	0.075
Outer radius of fiber (r_o) m	$50 * 10^{-6}$	$42 * 10^{-6}$
Inner radius of fiber (r_i) m	$21 *10^{-6}$	$21 * 10^{-6}$
Membrane area (SA) m^2	152	180

Table 3.2. Cost coefficients for the unit operations.

	Seawater desalination case	Pulp and paper case
a_{MRO}, $\frac{\$}{Module*Yr.}$, (it includes the annualized installation cost of the RO module, membrane regeneration, labor and maintenance)	1450	1140
$a_{Pu,f}$, $\frac{\$}{(kg/s*bar)^{0.79}*Yr.}$, fixed cost of the pump installation.	139.93	139.93
$a_{Pu,o}$, $\frac{\$}{(kg/s*bar)\ *Yr.}$, operating cost of the pump.	80	80
$a_{Tu,f}$, $\frac{\$}{(kg/s*bar)^{0.47}*Yr.}$, fixed cost of the turbine installation.	93.62	93.62
$a_{Tu,o}$, $\frac{\$}{(kg/s*bar)\ *Yr.}$, operating cost of the turbine.	34	34

3.5.1 Seawater Desalination

This case study presents the optimization of seawater desalination network by DuPont B-10 RO modules. Input data for the optimization problem is given in Table 3.3. The superstructure includes dual RO stages, dual pump and turbine stages. The proposed solution is applied for the entire substructures presented earlier (substructure 1-4). The MILP problems have the total objective function terms in the first iteration and the single unit cost terms in the subsequent iterations for every chosen substructure as shown in Table 3.4. The table also gives the MILP and NLP solution conditions and their execution time.

Table 3.3. Input data for the seawater desalination case.

Seawater feed flow rate, kg/s	19.29
Feed composition	0.0348
Minimum final permeate flow rate, kg/s	5.787
Maximum final permeate composition	0.00057
Minimum flow rate per module, kg/s	0.21
Maximum flow rate per module, kg/s	0.27
Maximum feed pressure, Pa	$68.88*10^5$
Pressure drop per module, Pa	$0.22*10^5$
Pure water permeability (W), kg/s.N	$1.2*10^{-10}$
Solute transport parameter (K_c), kg/m^2.s	$4.0*10^{-6}$

Generally, successful convergence to local solutions can be observed when the substructures have smaller number of alternatives compared to the total superstructure. During the search, several local solutions were obtained and the best solution (230906 $/yr.) is identified within substructure 2. Figure 3.9 presents the layout of the best local solution for the RO treatment network. The main feature of the design is the early splitting of the inlet feed to the final reject and the permeate streams. Thus, the load on the down stream units are reduced and lower treatment cost is achieved.

Table 3.4. Results for the four substructures in the case of seawater desalination.

Superstructure	**Objective function**	**MILP**	**MILP -CPU, Sec.**	**NLP**	**NLP-CPU, Sec.**	**Total CPU, Sec.**
Substructure 4	Total units	54626	0.203	Infeasible	0.029	0.232
	RO-stage # 1	0	0.125	Infeasible	0.012	0.137
	RO-stage # 2	0	0.093	Infeasible	0.02	0.113
	PUMP-stage # 1	0	0.109	Infeasible	0.031	0.14
	PUMP-stage # 2	0	0.125	Infeasible	0.01	0.135
	TURBINE-stage # 1	-42857	0.875	246398	0.1	0.975
	TURBINE-stage # 2	-42857	0.62	246398	0.061	0.681
Substructure 3	Total unit costs	73905	0.234	274766	0.1	0.334
	RO-stage # 1	0	0.14	274766	0.012	0.152
	RO-stage # 2	0	0.109	274766	0.02	0.129
	PUMP-stage # 1	0	0.14	246398	0.02	0.16
	PUMP-stage # 2	0	0.218	Infeasible	0.02	0.238
	TURBINE-stage # 1	-37936	0.796	274767	0.109	0.905
	TURBINE-stage # 2	-37936	0.75	246494	0.09	0.84
Substructure 2	Total unit costs	99445	0.14	Infeasible	0.016	0.156
	RO-stage # 1	55278	0.093	230906	0.029	0.122
	RO-stage # 2	0	0.093	Infeasible	0.031	0.124
	PUMP-stage # 1	1109	0.093	231037	0.08	0.173
	PUMP-stage # 2	0	0.125	Infeasible	0.01	0.135
	TURBINE-stage # 1	-29902	0.125	Infeasible	0.01	0.135
	TURBINE-stage # 2	-29902	0.128	230906	0.1	0.228
Substructure 1	Total unit costs	237616.2	0.109	286627	0.031	0.14
	RO-stage # 1	103594	0.109	286835	0.023	0.132
	RO-stage # 2	59519	0.125	286627	0.029	0.154
	PUMP-stage # 1	47672	0.11	286627	0.02	0.13
	PUMP-stage # 2	1109	0.07	286627	0.08	0.15
	TURBINE-stage # 1	-29753	0.09	286627	0.031	0.121
					Total CPU, Sec.	7.071

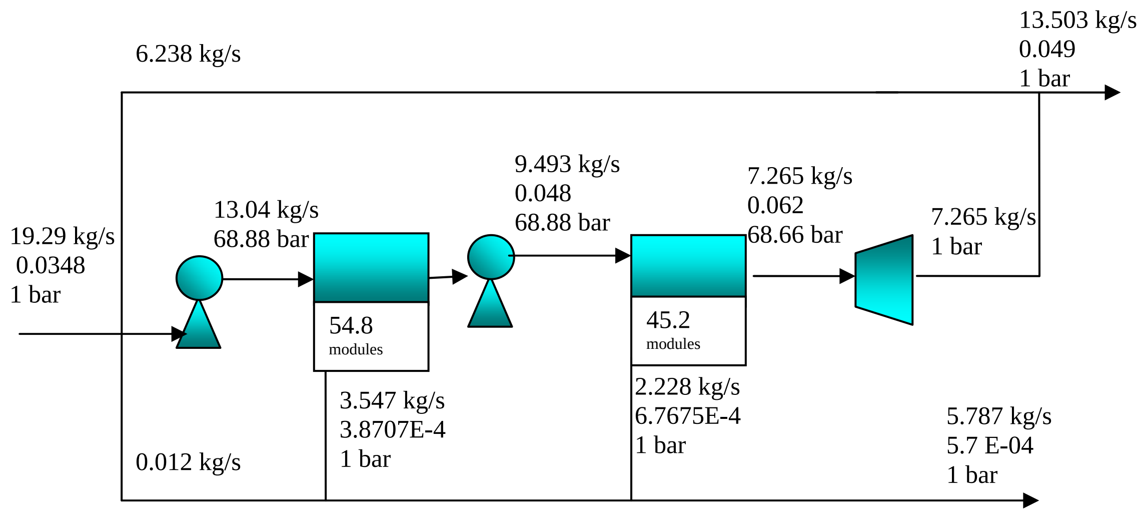


Figure 3.9. Optimal design of the RON for seawater desalination.

On the other hand, substructure 4 provides a design with total cost of 286627 \$/yr. The design shows continuous processing of the total feed in all the units present in the network and continuous collection of the permeate streams from all the RO stages. This design scheme explains the higher cost of the network compared to the solution obtained from substructure 2. Other solutions (substructures 2, 3) have similar design features of the best solution; however, the amounts of the feed stream diverted by the first splitter to the final reject and permeate streams are less than those for the best solution.

3.5.2 Pulp and Paper Wastewater Treatment

This case study presents the optimization of two-wastewater stream treatment with two organic pollutants, mono-chloro phenol (MCP) and tri-chloro phenol (TCP), from the pulp and paper industry by DuPont B-9 RO modules. Input data for the optimization problem is given in Table 3.5. The superstructure includes three RO stages, three pumps, and three turbine units. The same solution strategy is applied on the current case study and Table 3.6 summarizes the results. The best solution (152406 $/yr.) is identified within substructure 4 and Figure 3.10 depicts the RO treatment and the operating conditions in the network.

The RO treatment network shows similar observation from the pervious case study which is a partial treatment of the network-feed streams. Interesting result from the case study shows that partial mixing of the feed-wastewater streams is beneficial to attain reduced treatment cost. In fact, the first wastewater stream (6 kg/s) is partially mixed with the other stream to reduce the concentration of the pollutant prior to the RO treatment unit. This observation, within the current case study conditions, opposes the current proposal of distributed treatment network. However, routing pollutants between different streams can be observed to meet the final product stream requirements.

Table 3.5. Input data for the pulp and paper wastewater treatment network.

Stream 1 flow rate, kg/s	6
Stream 2 flow rate, kg/s	25
Feed composition of solute 1 in stream 1	$26.00*10^{-6}$
Feed composition of solute 1 in stream 2	$12.00*10^{-6}$
Feed composition of solute 2 in stream 1	$3.00*10^{-6}$
Feed composition of solute 2 in stream 2	$4.00*10^{-6}$
Minimum final permeate flow rate 1, kg/s	4.5
Minimum final permeate flow rate 2, kg/s	9
Maximum final permeate composition of solute 1 in permeate 1	$8.8*10^{-6}$
Maximum final permeate composition of solute 2 in permeate 1	$1.4*10^{-6}$
Maximum final permeate composition of solute 1 in permeate 2	$8.8*10^{-6}$
Maximum final permeate composition of solute 2 in permeate 2	$1.4*10^{-6}$
Minimum flow rate per module, kg/s	0.21
Maximum flow rate per module, kg/s	0.46
Maximum feed pressure, Pa	$28.58 *10^5$
Pressure drop per module, Pa	$0.405 *10^5$
Pure water permeability (W), kg/s.N	$1.2*10^{-10}$
Solute transport parameter (K_{c1}), kg/m^2.s	$2.43*10^{-4}$
Solute transport parameter (K_{c2}), kg/m^2.s	$2.78*10^{-4}$

Table 3.6. Summary of the solution steps for the pulp and paper-wastewater treatment.

Superstructure	Objective function	MILP	MILP-CPU, Sec.	NLP	NLP-CPU, Sec.	Total CPU, Sec.
Substructure 4	Total unit costs	25722	1.281	Infeasible	0.102	1.383
	RO-stage # 1	0	0.906	Infeasible	0.06	0.966
	RO-stage # 2	0	0.187	Infeasible	0.01	0.197
	RO-stage # 3	0	0.484	Infeasible	0.13	0.614
	PUMP-stage # 1	0	0.296	Infeasible	0.03	0.326
	PUMP-stage # 2	0	0.546	Infeasible	0.12	0.666
	PUMP-stage # 3	0	0.328	Infeasible	0.05	0.378
	TURBINE-stage # 1	-25346	0.593	152406	0.39	0.983
	TURBINE-stage # 2	-26604	0.86	155532	0.439	1.299
	TURBINE-stage # 3	-28765	1.8	Infeasible	0.289	2.089
Substructure 3	Total unit costs	46519	0.485	Infeasible	0.03	0.515
	RO-stage # 1	0	0.25	165211	0.141	0.391
	RO-stage # 2	0	0.234	Infeasible	0.029	0.263
	RO-stage # 3	0	0.171	Infeasible	0.141	0.312
	PUMP-stage # 1	0	0.375	Infeasible	0.2	0.575
	PUMP-stage # 2	0	0.484	162071	0.15	0.634
	PUMP-stage # 3	0	0.312	Infeasible	0.091	0.403
	TURBINE-stage # 1	-15242	1.89	Infeasible	0.18	2.07
	TURBINE-stage # 2	-15242	0.625	152997	0.181	0.806
	TURBINE-stage # 3	-16480	0.187	152997	0.2	0.387
Substructure 2	Total unit costs	46541	0.203	152997	0.5	0.703
	RO-stage # 1	24872	0.265	Infeasible	0.117	0.382
	RO-stage # 2	0	0.14	152997	0.44	0.58
	RO-stage # 3	0	0.171	152997	0.5	0.671
	PUMP-stage # 1	0	0.265	Infeasible	0.305	0.57
	PUMP-stage # 2	0	0.171	152997	0.54	0.711
	PUMP-stage # 3	0	0.11	152997	0.529	0.639
	TURBINE-stage # 1	-15242	0.171	152997	0.36	0.531
	TURBINE-stage # 2	-15242	0.187	152997	0.203	0.39
	TURBINE-stage # 3	-16480	0.14	Infeasible	0.29	0.43
Substructure 1	Total unit costs	184775	0.171	Infeasible	0.141	0.312
	RO-stage # 1	76826	0.078	Infeasible	0.189	0.267
	RO-stage # 2	24782	0.125	232639	0.11	0.235
	RO-stage # 3	24782	0.125	Infeasible	0.109	0.234
	PUMP-stage # 1	7434	0.171	Infeasible	0.15	0.321
	PUMP-stage # 2	113	0.187	232639	0.12	0.307
	PUMP-stage # 3	113	0.14	232639	0.09	0.23
	TURBINE-stage # 1	-15242	0.156	Infeasible	0.281	0.437
					Total CPU Sec.	23.207

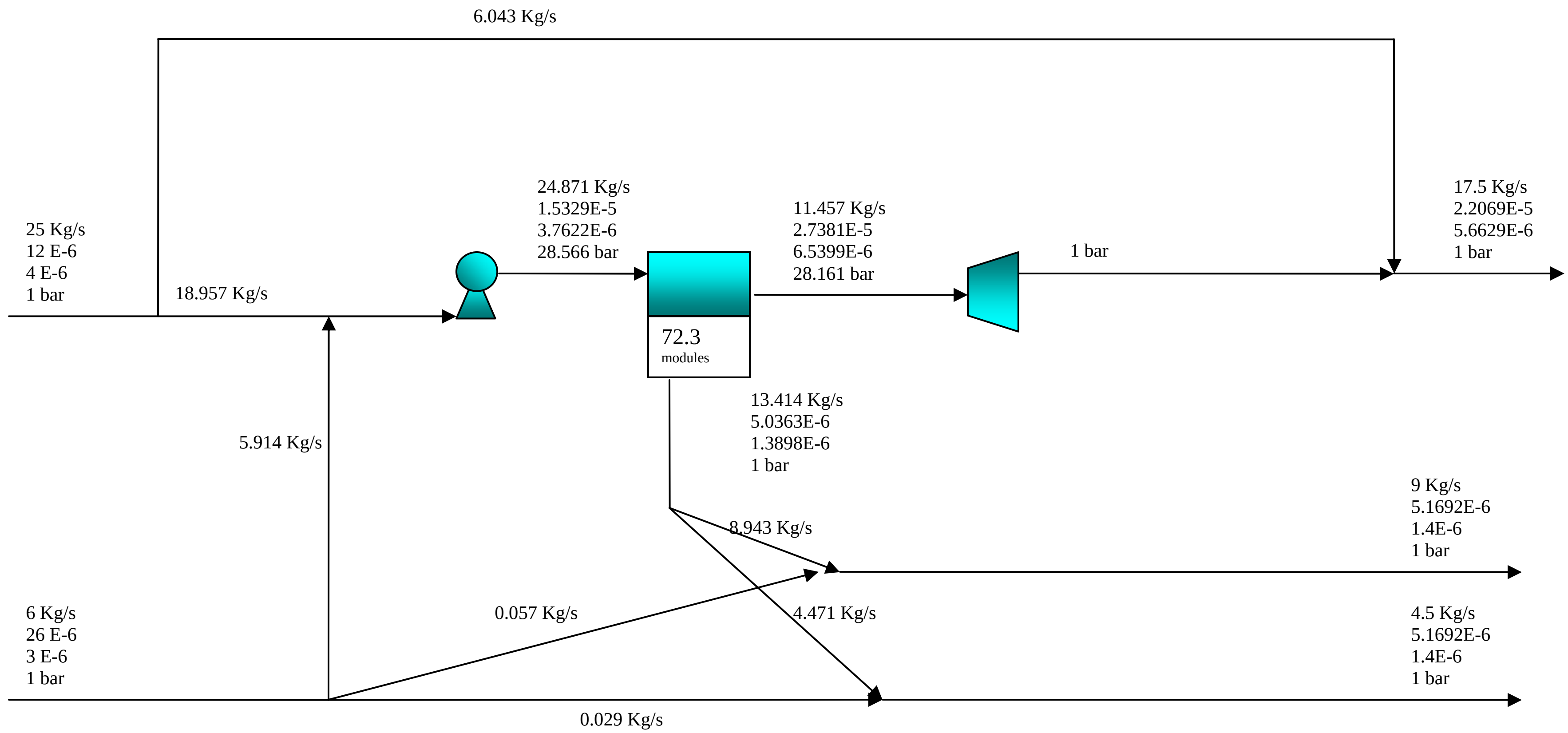


Figure 3.10. Optimal design of the RON for the pulp and paper-wastewater treatment.

3.6 Conclusion

Reverse osmosis network synthesis problem was addressed for the treatment of water and industrial wastewater streams. A superstructure is assumed to embed all possible alternatives to attain a hidden treatment network. Nonconvex mathematical programming model (MINLP) is formulated to identify the unit operation existences, stream assignments in the network, and the optimal operation of the existing units. Based on the problem assumptions and the RO conceptual design, some of the alternatives were safely dropped from the superstructure representation.

The solution strategy of the mathematical program decomposes the superstructure to several substructures where the nonconvexity of the problem is reduced. Convex relaxation of the nonconvex terms present in the substructure models yields MILP models. Upon their solutions with the original superstructure model, many local solutions are obtained. Several case studies are presented to illustrate the solution strategy steps.

Chapter 4

Global Optimization of Reverse Osmosis Network for Wastewater Treatment *

4.1 Introduction

A common practice in optimizing water/wastewater treatment has been through a centralized approach in which several wastewater streams are collected, mixed and directed to central treatment facilities. Such strategy has proven to be more costly than decentralized approaches. Decentralized treatment deals with the multiplicity of the wastewater streams as distinct streams with multiple pollutants. The treatment network is normally represented by mixing, splitting and bypass of different streams in a representation which accommodates all possible treatment alternatives (superstructure). A mathematical programming model based on this superstructure can be formulated to sort all the possible alternatives for minimizing the total wastewater treatment cost.

In the area of water and wastewater synthesis networks, the optimal allocation of water in a petroleum refinery was introduced in the form of nonlinear programming (NLP) problem (Takama et al., 1980). The superstructure gave rich connectivity for wastewater reuse between water use and wastewater treatment subsystems. The model aimed to minimize fresh water intake by water use units and reduce wastewater treatment requirements. The solution of the model was obtained using the complex method.

Other insights into integrated water usage and distributed wastewater network design have been addressed (Huang et al., 1998). The authors combined the water-use units and

* This chapter has been accepted: Y. Saif, A. Elkamel, M. Pritzker, Industrial and Engineering Chemistry Research, 2008.

distributed wastewater superstructures so that several water sources and sinks were added to a general superstructure. Water losses from these units were also included to describe conditions relevant to petroleum refineries. Extensions of this approach to the integrated water and wastewater network addressed the piping cost to the network (Alva-Argáez et al., 1998). Moreover, the operating conditions for the water-use units were bounded by inequality constraints so that these units had variable inlet-outlet conditions. The solution methodologies adopted in the previous work aims to find optimal local solution.

A heuristic-based search procedure was presented for a distributed wastewater network (Galan and Grossman, 1998). The authors developed a search procedure to find good upper bounds on the global optimum for nonconvex NLP and MINLP models of the wastewater treatment networks. The nonconvex terms present in the models were concave functions in the objective function and bilinear terms in the constraints. Multi-start heuristic rules were applied to solve the nonconvex models based on the convex relaxation of the nonconvex functions. The solution of the relaxed models (i.e. LP, MILP) provided different initial guesses for the solution to the nonconvex models.

The distributed wastewater network superstructure has also been formulated as an NLP model (Hernández-Suárez et al., 2004). Decomposition of the superstructure to several substructures was proposed by assuming straight-through flow of process streams (i.e. no backward connectivity between the units). Based on the substructures, the resulting mathematical model had fewer bilinear terms in the case of a small number of processing units. A linear programming model was obtained in the case of a single treatment unit. A heuristic approach was suggested to iteratively exchange initial starting points between the LP models and nonconvex model by fixing one of the complicated variable values in the nonconvex terms. Although global solutions were obtained in the case of a small number of units within a reasonable time, computational difficulties arose when the number of units in the superstructures was increased.

Very recently, a wastewater treatment network was considered as a case study for the pooling problem (Meyer and Floudas, 2006). The convex relaxation of the bilinear terms present in their models was carried out using the concepts of the Reformulation Linearization Technique (RLT). It was observed that the piecewise discrete intervals of the quality variables could give very tight lower bounds on the global optimum at the expense of large execution time. The integrated and wastewater treatment network was formulated as nonconvex Generalized Disjunctive Program (GDP) (Karuppiah and Grossmann, 2005). An effective branch-and-contract global optimization-based algorithm was proposed to solve the NLP and MINLP models. The main feature of the algorithm was that the flow variable was portioned into several discrete intervals and the resulting relaxed model was solved at every node in the search tree.

RO design networks are different from the circuits considered in these previous mathematical models in terms of the stream distribution and the presence of utility units. Within the RO network, the feed wastewater streams are continuously concentrated. Also, the production of dilute permeate streams is the main separation task. The pump units raise the pressure of the network streams while the turbine units reduce the energy consumption by the network. Therefore, the structure of the RO mathematical program has several differences from the previous mathematical programs which deal with wastewater network optimization.

In this chapter, the RO network superstructure from the previous chapter is considered to obtain a global optimum for the network. An effective branch-and-bound algorithm is developed to search simultaneously for the RO network global solution. Further tightening of the mathematical program is achieved by deriving additional constraints which exploit the mathematical programming structure and common knowledge concerning the operation of RO networks. These constraints significantly improve the relaxed models at every node within the search tree and improve the variable bounds. It is worth emphasizing that the proposed approach is indeed applicable for other pressure membranes or hybrid pressure membrane systems (e.g. nanofiltration with reverse osmosis).

Section 4.2 presents the superstructure description with more emphasis on the stream flow in the network. In section 4.3, the bounding problem of the mathematical program (MILP) is derived based on the convex relaxation of the mathematical program. Section 4.4 presents the mathematical program tightening constraints. In section 4.5, a water desalination case study is presented to illustrate the proposed algorithm. Finally, conclusions are given in section 4.6.

4.2 Superstructure

The superstructure of RO network is reconsidered (Saif et al., 2007). The following sets are defined to explain clearly the stream assignments within the DB and to clarify the model equation derivation (see Figure 3.4).

$SIN = \{1, 2, ..., in, ...\}$: set of inlet wastewater streams;

$SPU = \{1, 2, ..., pu, ...\}$: set of pumps in the superstructure;

$STU = \{1, 2, ..., tu, ...\}$: set of turbine units;

$SRO = \{1, 2, ..., ro, ...\}$: set of RO stages;

$SROREJ = \{1, 2, ..., rorej, ...\}$: set of reject streams from the SRO;

$SROPER = \{1, 2, ..., roper, ...\}$: set of permeate streams from the SRO;

$SFPER = \{1, 2, ..., fper, ...\}$: set of final permeate streams;

$SFREJ = \{1, 2, ..., frej, ...\}$: set of final reject streams;

$C = \{1, 2, ..., c, ...\}$: set of components present in each wastewater stream.

By definition, the number of the elements in $SROREJ$ and $SROPER$ is the same as that in SRO. Each inlet wastewater stream F_{in} is split over the sets SPU, $SFREJ$ and $SFPER$. The streams F_{in-pu} represent a stream assignment from the wastewater stream in to pump node pu. We allow for the possibility that not all of each wastewater stream be processed and so streams $F_{in-frej}$ and $F_{in-fper}$ provide the option of bypassing the network.

At every pump pu , streams F_{in-pu} , $F_{rorej-pu}$ and $F_{roper-pu}$ may mix before the pressurization process. Mixing $F_{roper-pu}$ with F_{in-pu} and $F_{rorej-pu}$ will reduce the osmotic pressure of the pump-inlet stream. However, mixing may not be economical in the case where some of the $F_{rorej-pu}$, and/or F_{in-pu} streams are highly polluted. If this situation arises, the set of $F_{roper-pu}$ will be processed separately to reduce the treatment cost.

After the pressurization process, every pump-exit stream F_{pu} is split into F_{pu-ro} streams and distributed over the RO stages SRO. Separation by each RO stage ro yields a permeate stream F_{roper} and a reject stream F_{rorej}. The permeate stream F_{roper} is split into two subset streams. $F_{roper-pu}$ loops back to all the pump nodes SPU , whereas $F_{roper-fper}$ contributes to the final permeate product streams F_{fper}. On the other hand, the reject stream F_{rorej} is split into four subset streams $F_{rorej-ro}$, $F_{rorej-pu}$, $F_{rorej-tu}$ and $F_{rorej-frej}$. $F_{rorej-ro}$ provides the option of processing reject streams in subsequent RO stages when their pressure remains high enough. $F_{rorej-pu}$ streams flow to the pumping node to raise their pressure. $F_{rorej-tu}$ represents streams that are fed to turbines STU for recovery of kinetic energy. Finally, the $F_{rorej-frej}$ streams are included to provide exit streams from the network. The discharge stream F_{tu} from the turbines is split into 3 streams: F_{tu-ro} to allow for additional processing in the RO stages and $F_{tu-fper}$ and $F_{tu-frej}$ for the option of leaving the treatment network.

4.3 Convex Relaxation of the Nonlinear Model

Branch and bound global search algorithms usually approximate nonconvex systems by functions which bound the nonconvex function values over their intervals. The approximation of the concave function and the bilinear function is given as Eqs. 3.20, and 3.21 from Chapter 3. Alternatively, a tighter MILP model can be constructed by introducing binary variables to formulate a piecewise discrete approximation of every nonconvex function through its interval (Meyer and Floudas, 2006; Karuppiah and Grossmann, 2005).

A concave function $\psi(z)^{\alpha}$ can be further approximated by partitioning its independent variable into *DIS1* subintervals and approximating the function by its underestimate over all the subintervals as (Karuppiah and Grossmann, 2005):

$$z = \sum_{dis1=1}^{DIS1} z_{dis1} \tag{4.1}$$

$$\psi(z) = \sum_{dis1=1}^{DIS1} \psi(z)_{dis1} \tag{4.2}$$

$$\underline{\psi}(z) \geq \sum_{dis1=1}^{DIS1} \left(\psi(z)_{dis1}^{LO}\right)^{\alpha} \omega_{dis1} + \left(\frac{\left(\psi(z)_{dis1}^{UP}\right)^{\alpha} - \left(\psi(z)_{dis1}^{LO}\right)^{\alpha}}{z_{dis1}^{U} - z_{dis1}^{L}} \right) \left(z_{dis1} - z_{dis1}^{L}\,\omega_{dis1}\right) \tag{4.3}$$

$$z_{dis1}^{LO}\,\omega_{dis1} \leq z_{dis1} \leq z_{dis1}^{UP}\,\omega_{dis1} \tag{4.4}$$

$$\psi(z)_{dis1}^{LO}\,\omega_{dis1} \leq \psi(z)_{dis1} \leq \psi(z)_{dis1}^{UP}\,\omega_{dis1} \tag{4.5}$$

$$\sum^{DIS1} \omega_{dis1} = 1 \tag{4.6}$$

The domains of the independent variable z and dependent variable $\psi(z)$ are split into *DIS1* subintervals (Eqs (4.1, 4.2)) where the variables z_{dis1} and $\psi(z)_{dis1}$ cover the z and $\psi(z)$ values in the subinterval *dis1*, respectively. Eq. (4.3) defines *DIS1* chord lines for the concave function in its domain. The binary variables ω_{dis1} ensure z_{dis1} and $\psi(z)_{dis1}$ lie within the appropriate intervals through Eqs. (4.4-4.6).

For a bilinear function $\chi = q\,w$, the domains of the variables q and w are divided into *DIS2* and *DIS3* subintervals, i.e., Eqs.(4.7, 4.8):

$$q = \sum_{dis2=1}^{DIS2} q_{dis2} \tag{4.7}$$

$$w = \sum_{dis3=1}^{DIS3} w_{dis3} \tag{4.8}$$

The formulation of a bilinear function after the division process is represented as:

$$\left.\begin{aligned}
\chi &\geq \sum_{dis2=1}^{DIS2} \sum_{dis3=1}^{DIS3} q_{dis2}^{LO}\, w_{dis3} + q_{dis2}\, w_{dis3}^{LO} - q_{dis2}^{LO}\, w_{dis3}^{LO}\, \tau_{dis2,dis3} \\
\chi &\geq \sum_{dis2=1}^{DIS2} \sum_{dis3=1}^{DIS3} q_{dis2}^{UP}\, w_{dis3} + q_{dis2}\, w_{dis3}^{UP} - q_{dis2}^{UP}\, w_{dis3}^{UP}\, \tau_{dis2,dis3} \\
\chi &\leq \sum_{dis2=1}^{DIS2} \sum_{dis3=1}^{DIS3} q_{dis2}^{LO}\, w_{dis3} + q_{dis2}\, w_{dis3}^{UP} - q_{dis2}^{LO}\, w_{dis3}^{UP}\, \tau_{dis2,dis3} \\
\chi &\leq \sum_{dis2=1}^{DIS2} \sum_{dis3=1}^{DIS3} q_{dis2}^{UP}\, w_{dis3} + q_{dis2}\, w_{dis3}^{LO} - q_{dis2}^{UP}\, w_{dis3}^{LO}\, \tau_{dis2,dis3}
\end{aligned}\right\} \tag{4.9}$$

$$q_{dis2,dis3}^{LO}\, \tau_{dis2,dis3} \leq q_{dis2,dis3} \leq q_{dis2,dis3}^{UP}\, \tau_{dis2,dis3} \tag{4.10}$$

$$w^{LO}_{dis2,dis3}\,\tau_{dis2,dis3} \le w_{dis2,dis3} \le w^{UP}_{dis2,dis3}\,\tau_{dis2,dis3} \tag{4.11}$$

$$\sum_{dis2=1}^{DIS2}\sum_{dis3=1}^{DIS3}\tau_{dis2,dis3} = 1 \tag{4.12}$$

The over/underestimators given in Eq. (4.9) are constructed for every subinterval (*dis2,dis3)*. Also, the binary variables $\tau_{dis2,dis3}$ ensure that the values for the continuous variables will be within the appropriate subinterval *(dis2,dis3)* through Eqs.(4.10-4.12). To avoid introducing a large number of binary variables, the intervals of the flowrate variables in the bilinear functions present in the component balance equations are partitioned. In contrast, the partitioned variables of the bilinear functions involved in the unit operation models are chosen based on the variable which has the larger interval. In the current study, the concave functions represent the fixed cost of the pumps and turbines. The bilinear functions in the mathematical program are the nonconvex terms in the component balance equations and the unit operation model equations.

4.4 Model Tightening Constraints

In this section, several tightening constraints are presented to improve the relaxed formulation. These constraints are developed for the original MINLP, relaxed MILP and piecewise discrete MILP formulations.

4.4.1 MINLP-Based Tightening Constraints

The mixing assumption between the streams at every mixing node (Eqs. (3.19)-(3.21)) can be exploited to reduce the number of possible stream assignments. The following points explain these tightening constraints:

1. Since a pressure drop exists at every RO stage, a stream discharged from an RO stage cannot be directly recycled back to the same stage. Consequently, RO-stage reject recycle streams can be dropped from the formulation.
2. Every existing RO reject stream has possible stream assignments to the turbine stages. In addition, any discharge from a turbine has may have directed streams to the RO stages. Therefore, the following constraint can be added to limit the existence of the following streams due to the pressure drop in the turbine stage:

$$y_{rorej-tu} + y_{tu-ro} \leq 1 \quad \forall\ ro, tu \tag{4.13}$$

3. During the solution of the problem, it may happen that high-pressure streams ($F_{rorej-pu}$) and low-pressure streams ($F_{in-pu}, F_{roper-pu}$) are directed to the same pump node. To eliminate this possibility, the following constraints are added:

$$y_{rorej-pu} + y_{in-pu} \leq 1 \quad \forall\ rorej, pu, in \tag{4.14}$$

$$y_{rorej-pu} + y_{roper-pu} \leq 1 \quad \forall\ rorej, roper, pu \tag{4.15}$$

4.4.2 MILP-Based Tightening Constraints

The redundant constraints, from section 3.3.3, form sets of relations to correct the component and energy balances in the network. Other tightening constraints pertain to RO-permeate looping within the network. RO-permeate looping is a definition of the $F_{roper-pu}$ streams being processed separately from other wastewater and RO-reject streams. The $F_{roper-pu}$ streams serves one of two objectives – to dilute the inlet wastewater streams F_{in-pu} or to reprocess permeate streams (RO-permeate looping) to reduce costs when treating the RO-reject streams is not economical. The proportion of mixing between $F_{roper-pu}$ and F_{in-pu} prior to any pump node determines whether the resulting stream from mixing is dilute or concentrated.

Streams $F_{rorej-fper}$ and $F_{tu-fper}$ are included in the superstructure to provide the option of mixing with the final permeate streams only when permeate looping is done. In addition, streams $F_{rorej-fper}$, and $F_{tu-fper}$ should have component concentrations close to the upper allowed value c_{fper} in the final permeate. However, due to the convexification of the component balance terms, the component balance terms corresponding to the $F_{rorej-fper}$ and $F_{tu-fper}$ streams are underestimated which satisfies the final permeate flow and concentration requirements even if no permeate looping is done. To determine whether permeate is being looped, a new binary variable y_{PL} is introduced as follows:

$$y_{PL} = \begin{cases} 1 & if \quad \sum^{roper} \sum^{pu} F_{roper-pu} \leq 0 \\ 0 & otherwise \end{cases} \tag{4.16}$$

The following inequalities are used to ensure that the condition $\sum^{roper} \sum^{pu} F_{roper-pu} \leq 0$ holds:

$$\in \; + \; y_{PL} * \left(\sum^{roper} \sum^{pu} F_{roper-pu} \right)^{LO} \leq \sum^{roper} \sum^{pu} F_{roper-pu} \tag{4.17}$$

$$\left(1 - y_{PL}\right) * \left(\sum^{roper} \sum^{pu} F_{roper-pu} \right)^{UP} \geq \sum^{roper} \sum^{pu} F_{roper-pu} \tag{4.18}$$

The absence of permeate looping implies that the RO-reject streams are processed within the network and the RO-permeate streams are collected to satisfy the final permeate flow and concentration demand. As a result, the streams $F_{rorej-fper}$ and $F_{tu-fper}$ should not be mixed with the final permeate products F_{fper} since this will significantly increase the permeate product concentration. Mathematically, these conditions are formulated as:

$$F_{tu-fper} \leq F^{UP}_{tu-fper} * \left(1 - y_{PL}\right) \qquad \forall tu,\, fper \tag{4.19}$$

$$F_{rorej-fper} \leq F^{UP}_{rorej-fper} * \left(1 - y_{PL}\right) \qquad \forall rorej,\, fper \tag{4.20}$$

On the other hand, if any permeate is recycled or reprocessed, Eqs. (4.17) and (4.18) are violated. Figure 4.1 shows the possible conditions involving the pump nodes in the network. Since conditions (a-c) do not include any permeate stream, only a reject or wastewater stream is discharged from the pump unit. Condition (d) depicts the case of permeate looping in the network, whereas condition (e) shows two mixing situations. These cases are:

1. The value of $\sum^{ROPER} F_{roper-pu}$ is smaller than $\sum^{In} F_{in-pu}$. This situation corresponds to the case of the treatment of a highly polluted wastewater stream. Therefore, mixing of the RO-permeate stream with the inlet wastewater reduces the osmotic pressure and avoids expensive continuous processing of the RO-reject streams in several RO stages.
2. The opposite condition to 1 above is less likely to take place since it represents conflict with the objectives of the treatment network.

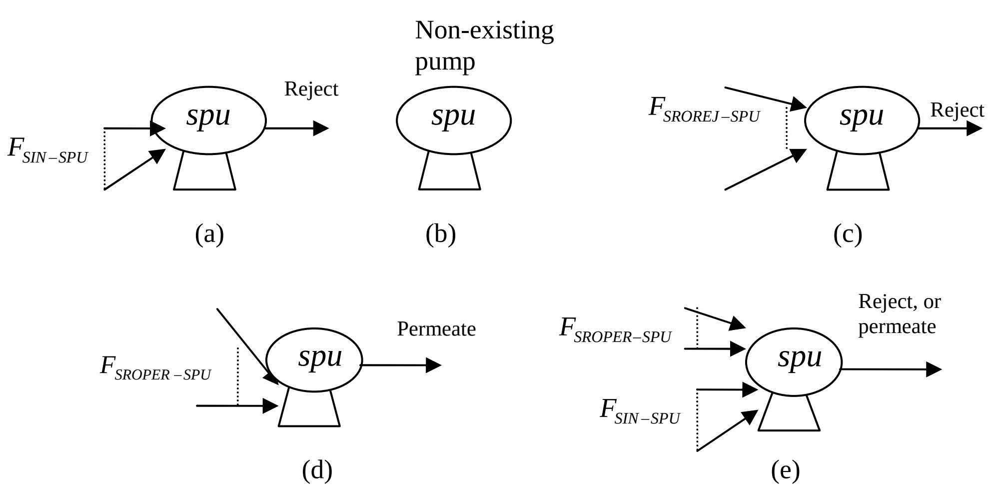


Figure 4.1. All possible conditions that may occur for streams flowing into a pump present in the treatment network.

Therefore, binary variables are introduced to assist in deciding whether mixing yields a stream that can be considered to be a concentrate or permeate at every pump node. For every pumping node, a binary variable is defined as:

$$ymix_{pu} = \begin{cases} 1 & if \quad \sum^{ROPER} F_{roper-pu} - \sum^{IN} F_{in-pu} \geq \in \\ 0 & otherwise \end{cases} \qquad \forall pu \tag{4.21}$$

If the inequality holds (i.e. $\sum^{ROPER} F_{roper-pu} - \sum^{IN} F_{in-pu} \geq \in$), the stream passing through the pumping node is taken to be a permeate. Otherwise, the pump exit stream is considered to be a concentrate. Other inequality constraints added to evaluate the previous conditions are given below in Eqs.(4.22) and (4.23):

$$\sum^{ROPER} F_{roper-pu} - \sum^{IN} F_{in-pu} - \in \geq -\left(\sum^{IN} F_{in-pu}\right)^{UP} \left(1 - ymix_{pu}\right) \quad \forall pu \tag{4.22}$$

$$\sum^{ROPER} F_{roper-pu} - \sum^{IN} F_{in-pu} - \in \leq \left(\sum^{ROPER} F_{roper-pu}\right)^{UP} ymix_{pu} - \in \quad \forall pu \tag{4.23}$$

It is also valid to state that if these conditions do not hold for all the pump nodes, then no permeate looping occurs in the network, i.e.,

$$\sum^{PU} ymix_{pu} + y_{PL} \geq 1 \tag{4.24}$$

If looping of permeate occurs at a pumping node, this requires that the stream flow be traced through all possible arrangement of the units to derive additional tightening constraints. Within these configurations, the set of streams $F_{rorej-fper}$ and $F_{tu-fper}$ may exist. On the other hand, the presence of a reject stream at a pumping node requires the elimination of the permeate streams from the RO and the turbine stages.

To achieve this objective, binary variables ($y_{rorej-fper}$, $y_{tu-fper}$) are defined for the stream set $F_{rorej-fper}$ and $F_{tu-fper}$ as follows:

$$y_{rorej-fper}, y_{tu-fper} = \begin{cases} 1 & if\ a\ reject\ or\ watewater\ stream\ passes\ through\ the\ unit \\ 0 & otherwise \end{cases} \tag{4.25}$$

Additional constraints (Eqs. 4.26 and 4.27) are necessary to eliminate the streams $F_{rorej-fper}$ and $F_{tu-fper}$ whenever the previous conditions hold. Other constraints (Eqs. 4.28 and 4.29) can be added to relate the binary variable y_{PL} to the binary variables $y_{rorej-fper}$, $y_{tu-fper}$.

$$F_{rorej-fper} \leq F^{UP}_{rorej-fper} \left(1 - y_{rorej-fper}\right) \ \forall rorej,\ fper \tag{4.26}$$

$$F_{tu-fper} \leq F^{UP}_{tu-fper} \left(1 - y_{tu-fper}\right) \ \forall tu,\ fper \tag{4.27}$$

$$y_{rorej-fper} \geq y_{PL} \quad \forall rorej, fper \tag{4.28}$$

$$y_{tu-fper} \geq y_{PL} \quad \forall tu, fper \tag{4.29}$$

Figure 4.2 shows all possible unit arrangements after a stream passes through a pumping node, assuming the existence of a total of six units in the network (e.g. two RO stages, two pumps, two turbines). Of course, these configurations are defined over the sets SRO, SPU, and STU. The formulation of the tightening constraints (Eq. 4.30) is developed as logical propositions based on conditions for the non-existence of permeate recycling at a pump, stream assignments among the unit operations and elimination of the stream sets $F_{rorej-fper}$, and $F_{tu-fper}$. y_{unit} represents the binary variables $y_{rorej-fper}$ and $y_{tu-fper}$. These logical propositions can be transformed into linear inequalities following the DeMorgan transformation. As an example, Figure 4.3 presents the constraints for configuration (c) shown in Figure 4.2 defined over the sets SRO, and SPU. It gives all their constraints assuming the final permeate stream set has a single element.

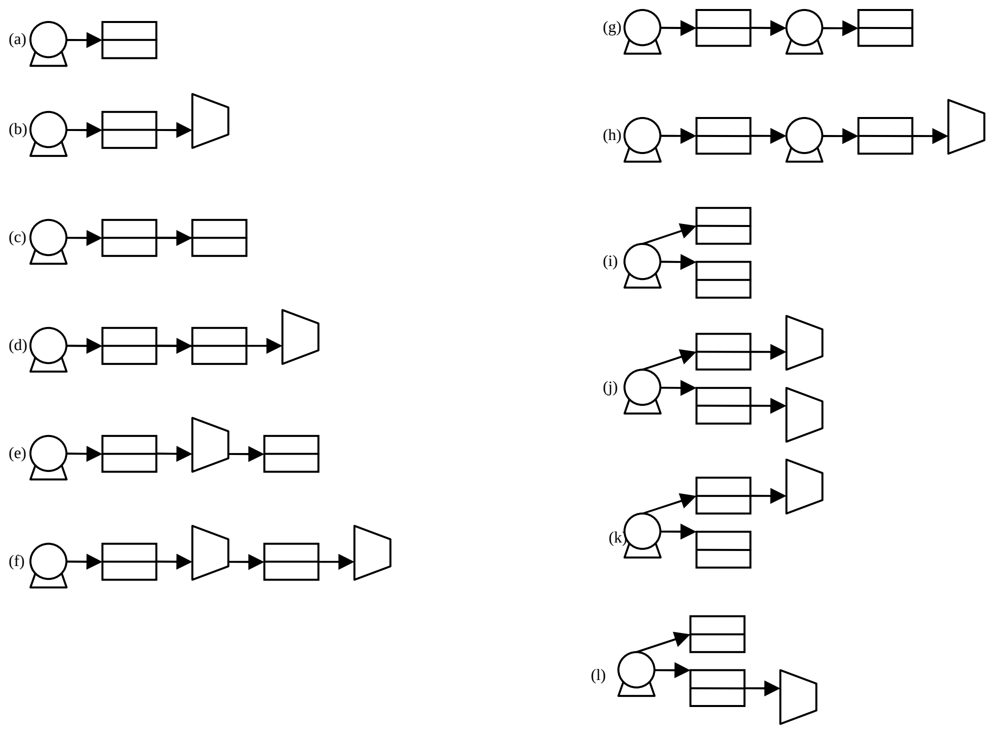
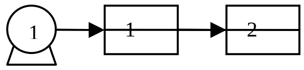
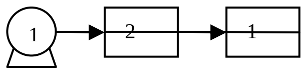


Figure 4.2. All possible configurations for the sequence of the unit operations considered in the superstructure of the treatment network.

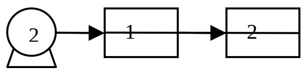
$$\left\{\begin{array}{l} \neg\, ymix_{pu} \wedge \overbrace{y_{unit\,1-unit\,2}\ .....\wedge\, y_{unit\,x-unit\,y}} \Rightarrow\ y_{unit\,1-\,fper} \\ \vdots \\ \vdots \\ \neg ymix_{pu} \wedge y_{unit\,1-unit\,2}\ .....\wedge\, y_{unit\,x-unit\,y} \Rightarrow\ y_{unit\,x-\,fper} \\ \neg ymix_{pu} \wedge y_{unit\,1-unit\,2}\ .....\wedge\, y_{unit\,x-unit\,y} \Rightarrow\ y_{unit\,y-\,fper} \end{array}\right. \qquad \forall pu \qquad (4.30)$$

(c 1)


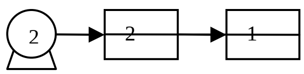
$$ymix_{pu1} + 1 + y_{ro1-fper} \ge y_{pu1-ro1} + y_{ro1-ro2}$$
$$ymix_{pu1} + 1 + y_{ro2-fper} \ge y_{pu1-ro1} + y_{ro1-ro2}$$

(c 2)


$$ymix_{pu1} + 1 + y_{ro1-fper} \ge y_{pu1-ro2} + y_{ro2-ro1}$$
$$ymix_{pu1} + 1 + y_{ro2-fper} \ge y_{pu1-ro2} + y_{ro2-ro1}$$

(c 3)


$$ymix_{pu2} + 1 + y_{ro1-fper} \ge y_{pu2-ro1} + y_{ro1-ro2}$$
$$ymix_{pu2} + 1 + y_{ro2-fper} \ge y_{pu2-ro1} + y_{ro1-ro2}$$

(c 4)


$$ymix_{pu2} + 1 + y_{ro1-fper} \ge y_{pu2-ro2} + y_{ro2-ro1}$$
$$ymix_{pu2} + 1 + y_{ro2-fper} \ge y_{pu2-ro2} + y_{ro2-ro1}$$

Figure 4.3. All possible arrangements and corresponding logical constraints associated with configuration (c) of Figure 4.2.

4.4.3 Piecewise Discrete MILP-Based Tightening Constraints

The solution of the piecewise discrete MILP model at every node in the branch and bound tree requires extensive computations. To accelerate the convergence of the branch and bound tree, other tightening equations are added to the model. These equations represent relations between the binary variables based on the discussion in section 4.3.

For non-existent unit operations and stream assignments within the DB, the optimal values for their operation conditions and flow variables must be in the first sub-divided interval. A set of relations can be established between the pump/turbine-binary variable and the binary variables appearing in Eq.(4.6) as follows:

$$y_{pu} + \omega_{dis1} \geq 1 \quad \forall pu, dis1 = 1 \tag{4.31}$$

$$y_{tu} + \omega_{dis1} \geq 1 \quad \forall tu, dis1 = 1 \tag{4.32}$$

$$y_{pu} \geq \omega_{dis1} \qquad \forall pu, dis1 \neq 1 \tag{4.33}$$

$$y_{tu} \geq \omega_{dis1} \qquad \forall pu, dis1 \neq 1 \tag{4.34}$$

Similarly, other relations can be derived for the bilinear functions representing component balance terms and energy balance equations for the unit operations. Eqs. (4.35) and (4.36) give these relations for the stream assignments in the DB as:

$$y_{stream} + \tau_{dis2,dis3} \geq 1 \quad \forall stream, dis2 = 1, dis3 = 1 \tag{4.35}$$

$$y_{stream} \geq \tau_{dis2,dis3} \qquad \forall stream, dis2 \neq 1, dis3 \neq 1 \tag{4.36}$$

Other relations can also be established for the binary variables y_{PL} , $ymix_{pu}$, $y_{rorej-fper}$ and $y_{tu-fper}$ to obtain additional constraints similar to the previous constraints.

4.5 Spatial Branch and Bound Algorithm

The branch and bound algorithm consists of the following steps:

1. Preprocessing: After screening the decision variable bounds, a heuristic search (Saif et al., 2007) is applied to obtain a valid overall upper bound (OUB) of the MINLP model. The MINLP model can also be solved locally by any MINLP commercial software.

2. Contraction: Within the branch and bound tree, the variable upper and lower bounds can be further optimized based on the following sub-optimization problems:

$$
\begin{aligned}
& min/\,max \quad \kappa \\
& s.t. \\
& relaxed\ \ problem\ constra\,int\ \ set \\
& OBJ\ \leq OUB
\end{aligned}
$$

where κ represents the independent variables involved in any nonconvex term given by the MINLP model. In this study, contraction is applied to the flowrate variables in the network and all the variables included in any nonconvex term present in the unit models.

3. Upper bounding step: The binary variable values (stream assignments, unit operations) from the discrete MILP model solution are fixed in the MINLP to generate a NLP problem. When the NLP problem is solved, a new OUB may be found.

4. Node fathoming: Any node in the branch and bound tree can be fathomed either if the node lower bound (LB) is greater than the OUB or if the node gap is less than some tolerance ε . The node gap is defined as

$$
Gap_{node} \;=\; \begin{cases} \left| \dfrac{OUB-LB}{OUB} \right| & if\ OUB \neq 0 \\ -LB & if\ \ OUB = 0 \end{cases}
$$

Examination of the branch and bound tree can be stopped whenever all the open nodes are fathomed.

5. Spatial branch and bound: Node selection in the branch and bound tree seeks a node with the lowest lower bound. Upon solution of the current node, the mother node can be divided into two other open nodes after selection of a branching variable if the node gap is greater than the tolerance. The branching variable is chosen to be in a nonconvex term where the absolute value difference between the nonconvex term and its approximation is the largest among all the model nonconvex terms. This variable will also be the one with the largest interval value in this nonconvex term. The bisection rule is picked as a division point for the branching variable.

4.6 Case Study

This section applies the concepts presented in the previous sections on a case study involving the desalination of a single seawater stream by hollow fiber DuPont B-10 RO modules. Input data of the case study were taken from the desalination problem in Chapter 3. The MILP and NLP were solved using the CPLEX and CONOPT 3 packages in GAMS 22.5, respectively (Brook et al., 1992). The program was run on a Pentium 4 personal computer with 2.8 GHz CPU and 1 Gbyte memory. The superstructure includes two RO stages, two pumps and two turbine stages.

The resulting mathematical program contains 30 binary variables, 123 continuous variables, 112 nonconvex terms and 156 constraints. In the formulation of the piecewise discrete MILP model (see section 4.3), all the nonconvex term variable intervals are divided into four equal intervals (see Eqs. (4.1) – (4.12)). For every node in the branch and bound tree, the node gap is compared to a tolerance of $\varepsilon = 0.03$. The contraction problems are solved for the first three nodes within the branch and bound tree.

By applying the proposed algorithm, the global solution was verified by exploring only seven nodes in the branch and bound tree. An execution time of 644 CPU seconds was required to obtain the global optimum for the case study. By comparison, solution of the RO model using the global solver BARON in GAMS failed to converge after more than 24 hours execution time. The effects of the tightening constraints on the efficiency of the algorithm and the solution time are worth noting. A lower bound that showed no improvement was observed during the search when the tightening constraints were dropped from the relaxed formulation. They significantly improved the contraction routine, variable bound updates and consequently the required execution time of the algorithm.

The globally optimum RO network for the desalination case study was found by the heuristic search to require a treatment cost of 230906 \$/yr. Figure 4.4 presents the layout of the global solution for this network. The optimum layout includes two RO stages in series, a pump prior to the 1^{st} RO stage, a booster pump between RO stages and a turbine following the 2^{nd} RO stage to extract energy from the 2^{nd} stage reject stream. One of the turbines included in the superstructure was not needed. The optimum layout results in a cascade configuration with 55 modules in parallel in the 1^{st} RO stage and 45 modules in the 2nd stage. The RO-permeate streams are continuously collected and combined to supply the final permeate product for the network. The most interesting feature of the design is the bypass of a significant portion of the inlet feed seawater from the treatment train directly to the final reject stream where it is combined with the portion of the inlet that was treated and rejected. This reduces the load on the downstream units and consequently the treatment cost significantly. A portion of the inlet stream is bypassed directly to the final permeate stream, but the amount is very small. For the sake of comparison, another local solution for the same case study (270868 $/yr.) shows higher number of process units in the treatment network (El-Halwagi, 1992). This realization of higher cost is due to the higher load of the seawater flow on the process units, Figure 4.5.

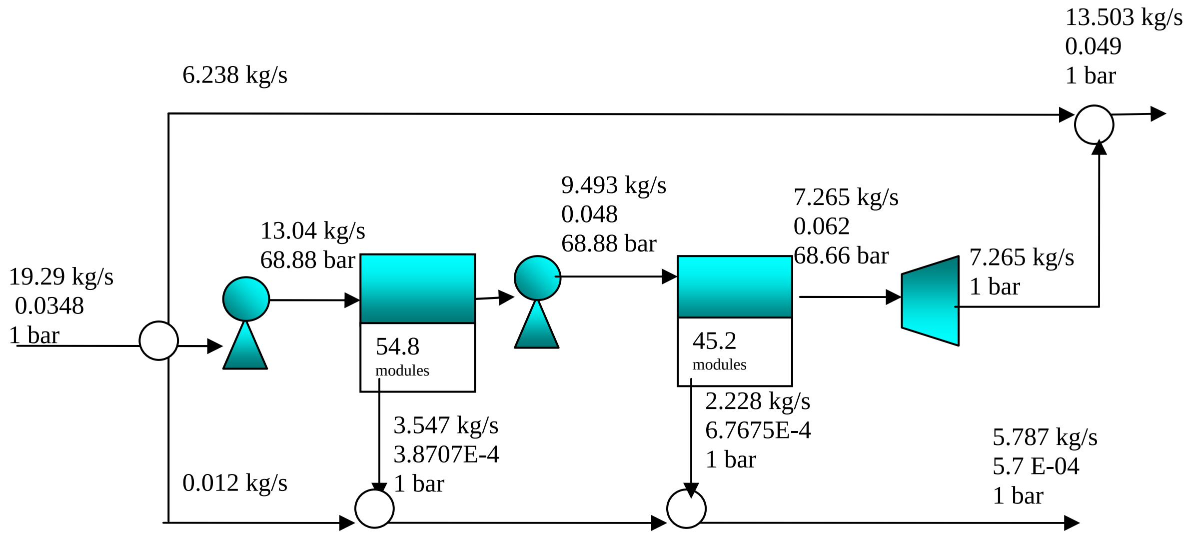


Figure 4.4. Globally optimum design and operating conditions for the RO network for the seawater desalination case study.

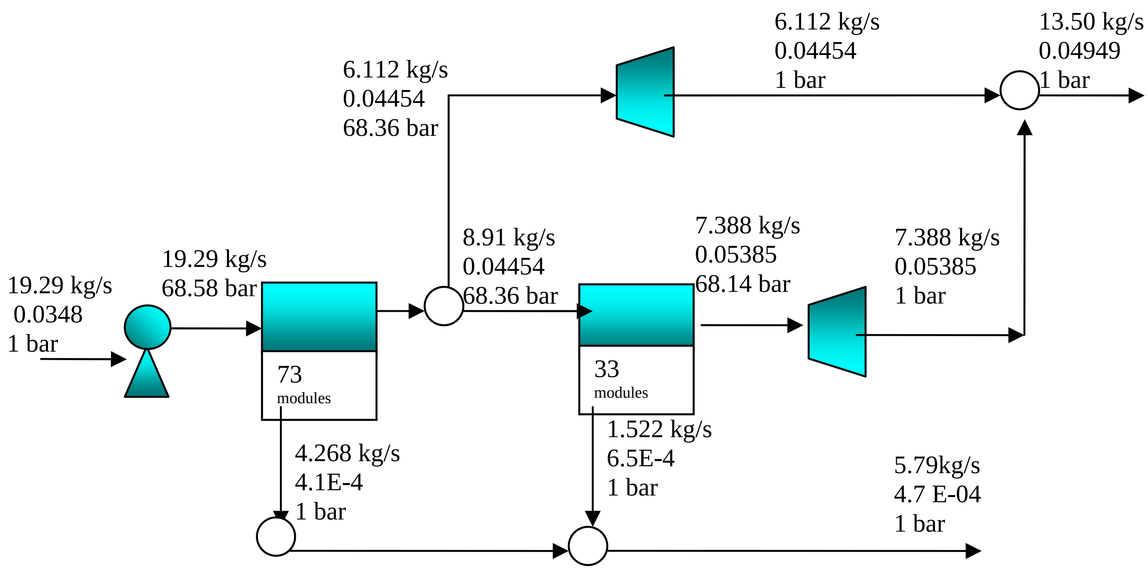


Figure 4.5. Optimal design of RO seawater desalination (El-Halwagi, 1992).

4.7 Conclusion

The search for a globally optimal design and operation of a reverse osmosis network was addressed for the treatment of water and industrial wastewater streams. A superstructure is assumed to embed all possible alternatives and encompass a hidden optimum treatment network. A nonconvex mathematical model (MINLP) is formulated to identify the layout of unit operations, stream assignments in the network and operating conditions that minimize the treatment cost objective function.

Due to the nonconvexity of the problem, a branch and bound search algorithm is applied to obtain the global solution for the treatment network. The formulation of tight lower bounds is carried out by approximating the nonconvex functions with piecewise under-and over-estimators. In addition, several tightening constraints are added to facilitate the convergence of the proposed algorithm. An example of seawater desalination is presented as a case study to illustrate the proposed solution algorithm for the RO network global optimization.

Chapter 5

Optimal Design of Hybrid Air Stripping-Pervaporation System for the Removal of Multi VOC from Water Streams *

5.1 Introduction

Groundwater and industrial wastewater streams are commonly contaminated with VOCs. VOCs are considered to be priority pollutants according to the US Environmental Protection Agency (EPA) due to their known or suspected carcinogenicity or toxicity (Metcalf and Eddy, 1991). The Henry's law constants for these compounds provides useful information concerning the behavior of VOCs in water as well as the applicability of a potential treatment technology. Air stripping has been applied for the treatment of wastewater contaminated with VOCs (Hand et al., 1986; Nirmalakhandan et al., 1987; Adams et al., 1991; Dzombak et al., 1993). However, this technology is inefficient if the VOCs have low Henry law constants. Consequently, the air stripper column height would have to be excessively high to treat such wastewater streams. Pervaporation is another option for the treatment of VOC which exhibits broader separation flexibility. In general, hybrid systems provide flexibility and enhanced performance over a single technology. In this regard, air stripper unit can remove VOCs with high volatility while pervaporation complements the system by removing the low volatile compounds (Shah et al., 2004).

Pervaporation-based hybrid systems have been shown to be efficient over single technologies to achieve hard separation targets. Besides, these systems require less

* This chapter is under preparation for submission: Y. Saif, A. Elkamel, M. Pritzker, Chemical Engineering Journal.

energy to operate and consequently reduced operational cost. Pervaporation synergistic effects basically overcome limiting conditions that may exist within chemical mixtures to enhance system throughput (i.e. altering azeotropic mixture composition, shifting reaction equilibrium toward products). Examples of such systems are hybrid pervaporation-distillation, pervaporation-reactor and pervaporation-reactor-distillation. A review of pervaporation hybrid systems can be found elsewhere (Lipnizki et al., 1999; Suk et al., 2006). Structural optimization has been applied to pervaporation hybrid systems and yielded attractive hybrid system designs (Eliceche et al., 2002).

The optimization studies related to VOCs deal with these compounds in air streams and wastewater streams. For air streams contaminated with VOCs, heat integrated condensation system has been proposed to study their recovery via superstructure optimization (Dunn and El-Halwagi, 1994). The optimization model takes into account multiple air streams with multiple pollutants to be treated in a treatment network with several optional refrigerants. The optimization model thus presents a highly combinatorial problem. A global search algorithm has also been proposed to solve the VOC condensation network (Parthasarathy and El-Halwagi, 2000). Another optimization study discussed the hybrid gas permeation-condensation system for VOC recovery (Crabtree et al., 1995).

A simulation-based optimization study for hybrid air stripper-gas permeation addressed the recovery of VOC (Wijmans et al., 1997). The air stream from the air stripper is continuously purified from the VOC in a closed loop configuration. Hybrid air stripping-pervaporation is presented to investigate the benefit of integrating an air stripper column with pervaporation unit (Shah et al., 2004). The possibility of several water withdrawals from the air stripper column to the pervaporation unit was considered to determine if pervaporation has impacts on the air stripper performance. The degree of freedom of the mathematical model is reduced to allow the simulation of the system. Nonetheless, the simulation approach does not allow economical trade-off among the problem system of equations and variables.

In this chapter, a hybrid air stripper-pervaporation system is revisited through superstructure optimization. Large alternative designs are embedded in a superstructure combined with utility units. The mathematical model is formulated as a nonconvex mixed integer nonlinear program (MINLP) which seeks an optimal treatment network for water streams with multiple VOCs. Several case studies are presented to illustrate the proposed approach and sensitivity analysis is applied to study perturbation effects on the optimal solutions.

5.2 Superstructure and Mathematical Programming Model

Hybrid air stripper-pervaporation superstructure is assisted by several utility units and air stream. The air stripper unit is coupled with an air blower to pressurize the air through the packed column. Another utility unit is a feed pump which raises the wastewater stream to the top of the packed column. The pervaporator requires a feed pump that pressurizes the wastewater feed to the required inlet pressure by the pervaporation unit. A vacuum pump is linked with the pervaporation permeate side. Figure 5.1 gives the stream distribution and the unit operations in the proposed superstructure.

The air stripper box (ASB) is assumed to have several air stripper stages in the network. Every air stripper tower is linked with air blower and water pump units. The pervaporation box (PVB) is composed of several pervaporation stages while every stage has a feed pump and a vacuum pump. Every pervaporation stage has several parallel pervaporation modules operating under the same operating conditions. The wastewater stream is first distributed over the unit operation nodes and the final reject stream nodes. Also, the air stream feed is linked only with the air stripper units. Within the network, the wastewater streams are linked directly between the unit operations and the final reject streams. The permeate streams from all pervaporation units are combined to produce the final VOC stream.

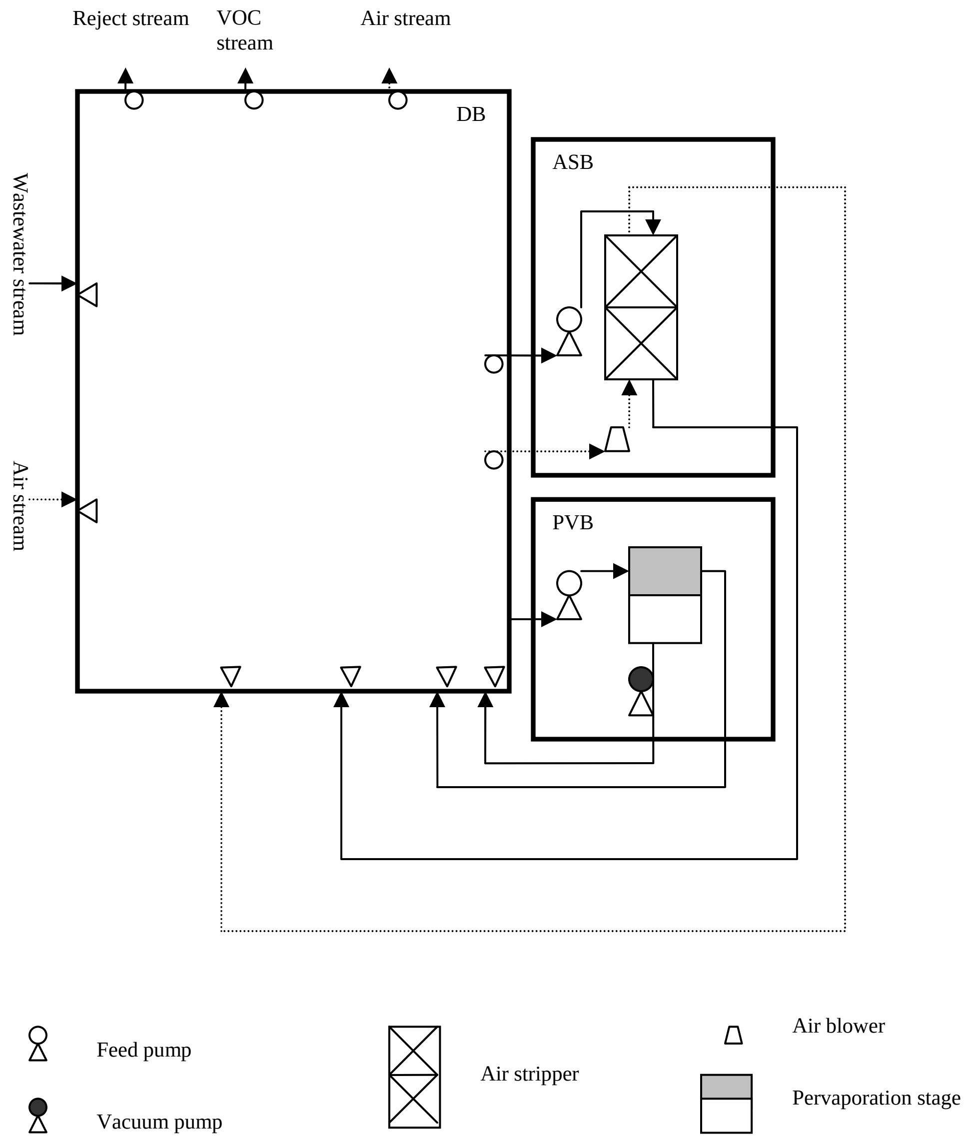


Figure 5.1. Hybrid air stripper-pervaporation superstructure.

It is worth pointing out the following remarks about the previous superstructure representation:

- The air stripper stage can represent a section of an air stripper unit or a stand-alone unit. Therefore, the decision to withdraw or inject streams from or to the unit can be left to the optimization algorithm. Coupling the pervaporation stages with the air stripper units will allow optional integration between the units and within sections of the air stripper units.
- Parallel/series arrangement between the units is given in the superstructure representation without any postulated design layout. Therefore, simultaneous evaluation of different layouts is embedded within the superstructure.
- The compact representation of the utility units within the unit operation boxes reduces the mathematical programming complexity and thus provides more emphasis on the integration between the unit operations.
- The superstructure representation is flexible to include other unit operations. Therefore, other hybrid pervaporation systems can be modeled easily through the given representation by providing their appropriate mathematical models.

The mathematical programming model describes basic material and component balances through all the mixer and splitter nodes in the superstructure. The mixing between the network streams requires that these streams have equivalent pressure values. A threshold of VOC concentrations in the reject streams is also predetermined to comply with given discharge regulations. In the case of VOC recovery, the previous inequality constraints can be reformulated over the permeate and the air streams by defining minimum recovery fractions. The air stripping model covers the operation of the unit up to the loading point. This condition is more practical and common with industrial practice (Hines and Maddox, 1985). The pervaporation model takes into account the effect of concentration polarization and pressure drop within the pervaporation module. The objective function is defined so as to minimize the total annualized cost of the unit operations. A summary of the mathematical programming model is given in Appendix A.

5.3 Case Studies

Groundwater normally contains a wide number of VOCs with broad range of Henry's law constant values. Figure 5.2 shows the effect of temperature on the Henry's constant values for trichloroethylene (TCE), dichloromethane (DCM) and ethylene dichloride (EDC) (Staudinger and Roberts, 2001). The first case study deals with the recovery of TCE from groundwater stream while the second case study covers the treatment of a multicomponent system (TCE, DCM,EDC). Sensitivity analysis is provided to observe the effect of the temperature and flow rate variations on the optimal treatment network. The case studies were implemented in GAMS and the MINLP solver used was SBB. Due to the nonconvexity of the problems, the solver is assisted by generating 1000 random starting points. These starting points initialize the solver with the unit existences, network stream assignments and the initial feed conditions for the unit operations.

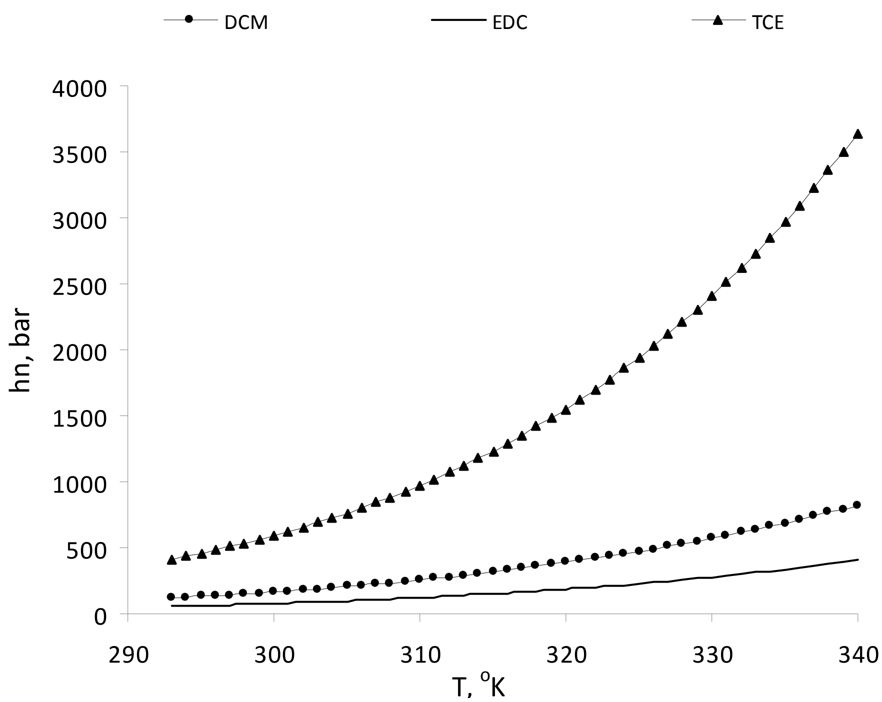


Figure 5.2. Effect of temeprature on Henry's law constant for VOC's.

5.3.1 TCE Case Study

The proposed methodology is to use a hybrid air stripper-pervaporation system for the treatment of a groundwater stream by embedding two air stripper units and two pervaporation units. Input conditions for the wastewater stream and the cost coefficients for the process units are given in Appendix A and B.1. The optimal solution of the case study requires the existence of a single air stripper tower. Figure 5.3 shows the optimal design of the air stripper which has a cost of 88495 \$/yr.

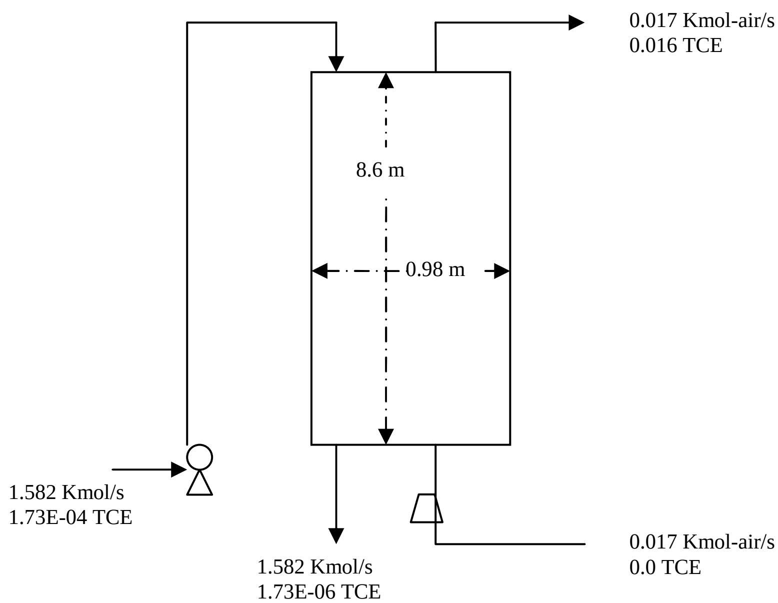


Figure 5.3. Optimal design of the TCE-wastewater stream.

The effect of increasing the wastewater feed and air temperatures on the treatment cost are given in Figure 5.4. In general, the increase of feed temperature reduces the column height and thus reduces the required treatment cost. The reduction of the column height is due to the increase in the stripping factor with increasing column operating temperature. However, this effect diminishes since the overall height of the transfer unit is less affected by temperature beyond 35 ^{o}C. Further decrease in the height of the transfer unit can be achieved either by increasing the air flow rate or decreasing the wastewater flowrate. However, such conditions are limited by the hydrodynamics in the preloading region within the air stripper column.

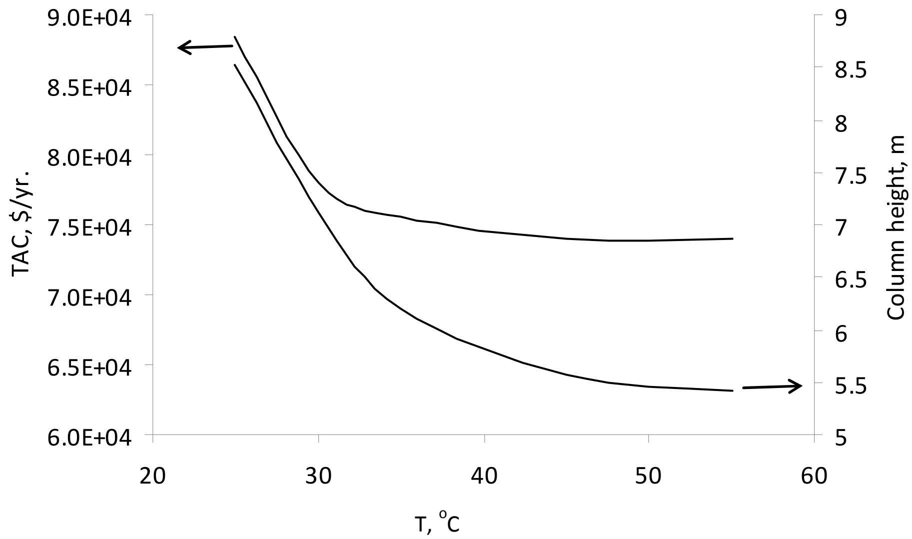


Figure 5.4. Effect of temperature on the air stripper removal efficiency.

The change of the inlet flowrate may be viewed as a change in the drinking water demand. Figures 5.5 shows the effects of the feed flowrate change on the treatment cost and the tower height, while Figure 5.6 presents the effect of the air flowrate. In general, a trade-off between the fixed and operating cost must be made to achieve a minimum treatment cost. These results are in agreement with other air stripper design problems (Kutzer et al., 1995).

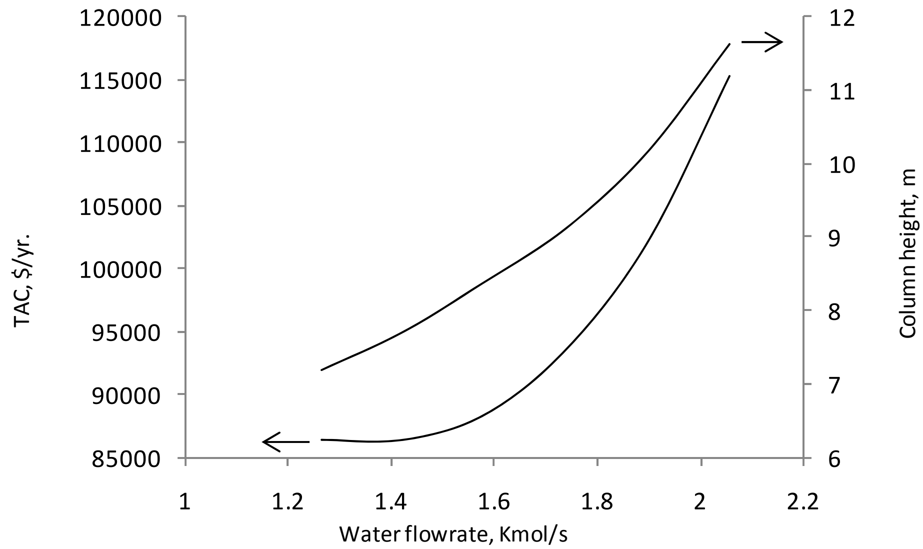


Figure 5.5. Effect of water feed change on the treatment cost and the column height.

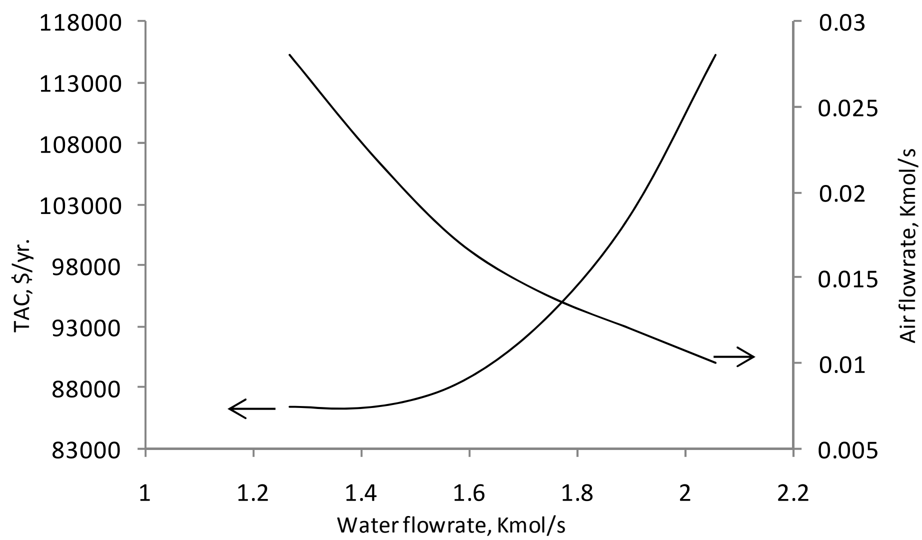


Figure 5.6. Effect of water feed change on the treatment cost and the air flowrate.

5.3.2 Multicomponent System

This system includes two volatile VOCs (TCE, DCM) and a semi-volatile component (EDC) present in a groundwater stream. Input data for the case study are given in Appendix A and B.2. The superstructure involves two air stripper units and two pervaporation stages. The optimal solution of the treatment network (376862 $/yr.)

features one air stripper and one pervaporation stage (Figure 5.7). This flowsheet follows a series arrangement where the pervaporation stage acts as a clean-up step for the air stripper effluent to meet the discharge requirements.

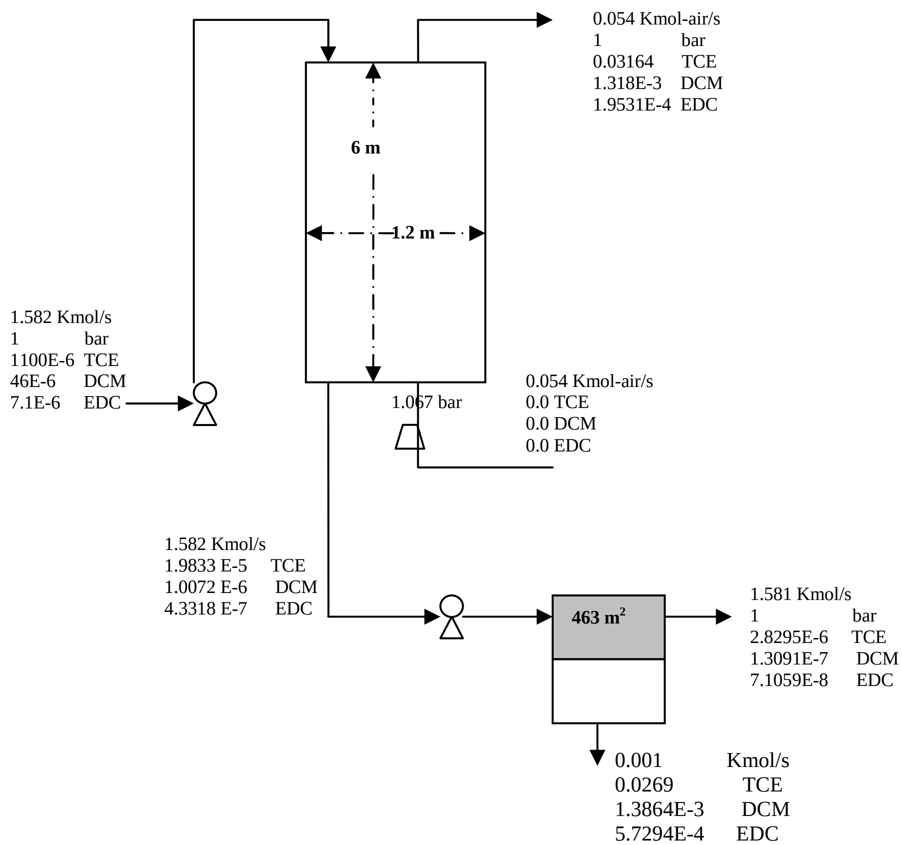


Figure 5.7. Optimal network design of multicomponent VOC's treatment.

Within the operating temperature range of 25-55 ^{o}C, the treatment network has similar structure. The changes of the pervaporation stage membrane surface area and air stripper height over this temperature range are given in Figure 5.8. An increase in temperature leads to a reduction in required pervaporation membrane surface area, while the air stripper column height remains almost constant at 6 m height. This is due to the increase of the removal efficiency in the air stripper column with increasing operating temprature. In addition, the required pervaporation feed pressure is reduced with increase of the operating temperature (Figure 5.9). In general, approximately 40% reduction of the treatment cost can be achieved by increasing the feed temperature to 55 ^{o}C.

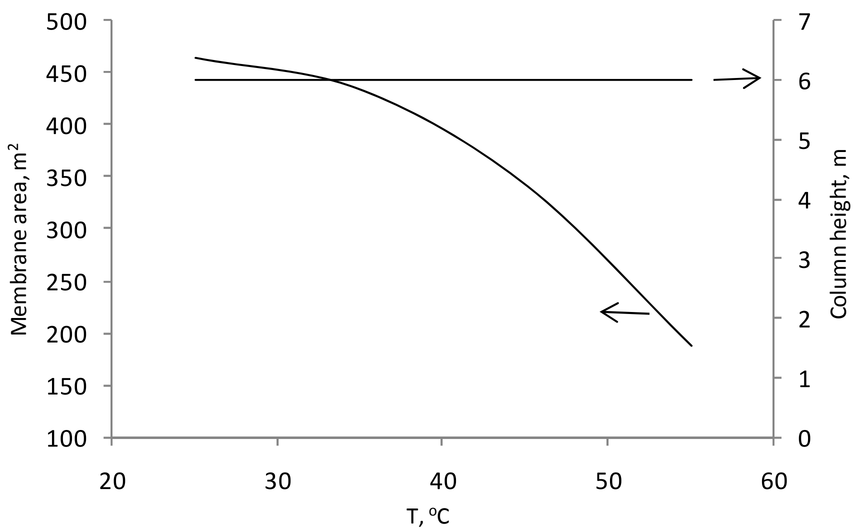


Figure 5.8. Effect of the operating temperature on the membrane area and column height.

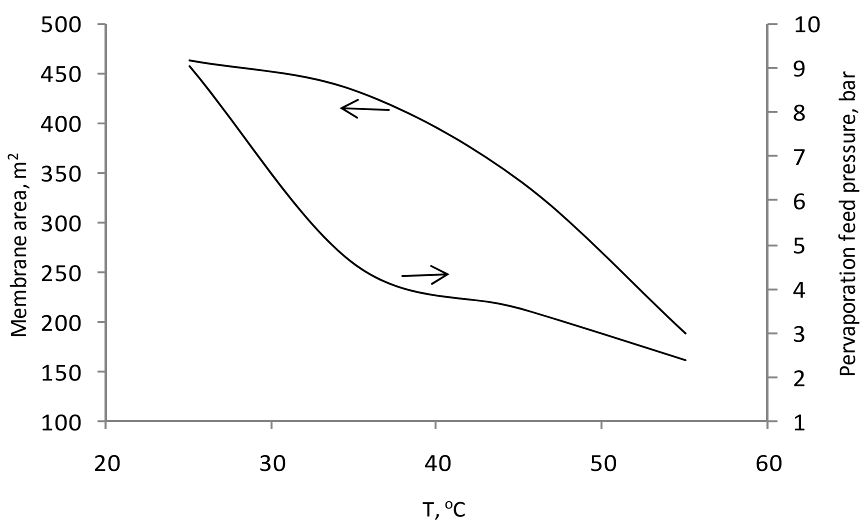


Figure 5.9. Effect of temperature on the optimal pervaporation membrane area and feed pressure.

The aforementioned analysis shows the significant effect that temperature has on the separation efficiency and thus the treatment cost. However, the cost to generate this thermal energy has not been considered in the optimization routine. Further analysis of the proposed approach would be to consider a heat-integrated hybrid air sripper pervaporation system. Henry law constant shows that a reduction in its value imposes separation limitations on the air stripper efficiency. The presence of less volatile compounds may force the selection of pervaporation as a treatment option alone. Thus, the optional treatment is problem-specific (i.e. the network depends on the type of VOCs). A direct conclusion of the series arrangment of air stripper pervaporation units may not be obvious since the optimal stream assignments within the network can only be determined from the solver optimal solution. Another important issue is how to treat the VOCs that end up in the gas streams discharged from the air stripper units. This will entail additional costs and should be included in future work.

5.4 Conclusion

Hybrid air stripper-pervaporation network for groundwater treatment is addressed to deal with multiple VOC systems. The proposed approach to the problem is given through the tools of superstructure optimization. For the given system, the MINLP model is formulated to determine optimal unit existences and their operation and the stream assignments within the network. The solution of the multiple VOC system shows the benefits of the hybridization of air stripper units with pervaporation units. Further improvements to the analysis of the problem can be made by considering the treatment of the gas stream discharged from the air stripper and heat integration within the network.

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

Membrane and hybrid membrane systems can be used as stand-alone units or integrated with other unit operations to enhance separation performance. The integration of these systems with conventional unit operations or with each other has been considered in this research using the framework of superstructure optimization. Previous research related to hybrid membrane systems had several drawbacks in the problem representation and the mathematical programming formulations. Consequently, one of the important objectives of this research was to address these problems and make improvements to the hybrid membrane superstructure and the mathematical programming formulations. This in turn would allow the development of general guidelines for assembling hybrid membrane systems for use in wastewater treatment networks. The approach can also be applied for hybrid membrane systems in other chemical engineering applications.

The RO network synthesis problem is analyzed to seek an improved superstructure representation. It is found that a parallel arrangement of the unit operations (pump box, turbine box, RO stages box) gives more realistic stream assignments in the superstructure representation and improves the mathematical programming formulation. A heuristic search procedure is developed based on concepts from global optimization to search effectively for local optimal solutions. The results show better local optimal solutions compared with reported solutions from the literature. In addition, the search heuristic requires reasonable execution time.

The global optimization of RO network is developed by construction of an effective branch-and-bound algorithm. The search algorithm is based on continuous refinement of the search space by proper contraction of the variable bounds during the branching routes. The algorithm is applied to a seawater desalination case study. The global solution of the treatment network is found to be the best solution from the search heuristic. The major contribution of this aspect of the research is through development of a set of effective tightening constraints which accelerates convergence. Without these constraints, non-improving lower bounds of set of open nodes in the search tree is found to hinder the algorithm convergence.

VOCs represent an important class of harmful pollutants in groundwater and wastewater streams. A hybrid air stripper-pervaporation system has also been optimized through the concepts of superstructure optimization to seek an optimal treatment network for VOC recovery. The superstructure representation is flexible to integrate between sections of air stripper columns and pervaporation stages. The case studies considered include the treatment of a groundwater stream containing a single VOC and a stream containing three VOCs. For a VOC with a high Henry's law constant (e.g. TCE), air stripping is found to be an efficient option for their recovery. However, when a less volatile compound is also present, integration of air stripping and pervaporation is a better option. Extension of the proposed superstructure may be to include heat integration of the system and treatment of the gas emissions from the air stripper units.

The expected contributions of this research are:

- comprehensive approach to optimize hybrid membrane systems through the concepts of superstructure optimization.
- improved RO superstructure representation and a heuristic search of the optimal RO network for wastewater treatment.
- deterministic branch and bound global search algorithm for the optimization of RO networks.
- highlighting of further extensions and research for the optimization of hybrid membrane systems.

6.2 Recommendations

Integration of design and scheduling is an important aspect to maintain reliable operation of processes over time. Many mathematical models appear in the chemical engineering literature to address this topic. In the past, the models for RO network design and maintenance scheduling have typically assumed constant RO membrane deactivation over time. This also assumes that membrane deactivation proceeds independently of the manner in which the process is operated. However, in reality, membrane does not proceed at a constant rate and is certainly affected by the operating conditions. To improve this shortcoming of the RO models, the following extensions are suggested:

- RO membrane fouling mechanism should be properly linked to the operational design variables. The assumption of constant decay over time may lead to some problems in accurately predicting optimum maintenance schedules. An optimization design study which properly links fouling to the operational design variables should give better prediction of optimum maintenance schedules.

- In the analysis of the current study, the flowrate and composition of the inlet wastewater stream and the permeate flowrate and product quality were specified beforehand. However, in real situations, disturbances or larger changes in these quantities inevitably occur, particularly when considering operation over extended periods of time. Modeling the design and scheduling problem under conditions of uncertainty concerning feed composition and flowrate, permeate flowrate and quality should provide a more robust RO design and better optimal cleaning/replacement schedules.

Hybrid membrane networks have broad applications that may extend beyond water and wastewater treatment network. Extension of the optimization of hybrid membrane networks to a wide range of optimization problems in chemical engineering will be useful. Examples of such applications are given in Table 1.1.

Utility consumption costs make up a considerable amount of the operating budget of chemical plants. The integration of air stripper towers with pervaporation units is mainly useful for the separation of less volatile VOCs. The sensitivity analysis of VOC separation by the hybrid system shows that the thermal energy has significant effects on the overall separation performance. Thus, the inclusion of heat exchange units within the network would improve the economic feasibility of heat-integrated hybrid systems. In addition, treatment of the gas emissions from the air stripper units should also be included in the network and optimization problem. This will give a better assessment of the economics of combining air strippers with pervaporation units.

References

Adams, J.Q. and Clark, R.M., 1991, Evaluating the costs of packed-tower aeration and GAC for controlling selected organics. AWWA, 1, 49-57.

Alva-Argáez A., Kokossis A.C. and Smith R., 1998, Wastewater minimization of industrial systems using an integrated approach. Supp. Comp. Chem. Eng., 22, S741-S744.

Bagajewicz M.J. and Manousiouthakis V., 1992, Mass/heat-exchange network representation of distillation networks. AIChE J., 11, 1769-1800.

Bagajewicz M.J., Pham R. and Manousiouthakis V., 1998, On the state space approach to mass/heat exchanger network design. Chem. Eng. Sci., 14, .2595-2621.

Baker R.W., 2004, Membrane technology and applications. 2nd ed., Wiley, U.K.

Barnicki S.D., Siirola J.J., 2004, Process synthesis prospective. Comp. Chem. Eng., 28, 441-446.

Biegler L.T., Grossmann I.E., Westerberg A.W., 1997, Systematic methods of chemical process design. Prentice-Hall.

Billet R. and Schultes M., 1991, Modeling of pressure drop in packed columns. Chem. Eng. Technol., 14, 89-95.

Billet R. and Schultes M., 1993, Predicting mass transfer in packed columns. Chem. Eng. Technol., 16, 1-9.

Billet R. and Schultes M., 1999, Prediction of mass transfer columns with dumped and arranged packing, updated summary of the calculation method of Billets and Schultes. Trans IChemE, 77, 498-504.

Brooke, A., Kendrik, D. and Meeraus, A., 1992, GAMS User's Guide; Boyd & Fraser Publishing Co.: Danvers, MA.

Canada Industry, 2005, WWW.stratigeis.gc.ca.

Ciric A.M., Gu D., 1994, Synthesis of nonequilibrium reactive distillation processes by MINLP optimization. AIChE J., 9, 1479-1487.

Crabtree E.W.; El-Halwagi M.M. and Dunn R.F. 1995, Synthesis of hybrid gas permeation membrane/condensation systems for pollution prevention. J Air & Waste Mang. Assoc., 7, 616-626.

Daichendt M.M. and Grossmann I.E., 1997, Integration of hierarchical decomposition and mathematical programming for the synthesis of process network. Comp. Chem. Eng., 22, 147-175.

Douglas J.M., Conceptual design of chemical processes, 1988, McGraw-Hill.

Dunn R.F. and Bush G.E., 2001, Using process integration technology for cleaner production. J. Clean Prod. , 9, 1-23.

Dunn R.F. and El-Halwagi M., 1994, Optimal design of multicomponent VOC condensation systems. J. Hazard. Mater., 38, 187-206.

Dunn R.F. and El-Halwagi M., 2003, Process integration technology review: background and applications in the chemical process industry. J. Chem. Technol. Biotechnol., 78, 1011-1021.

Dzombak, D.A.; Roy S.B. and Fang H., 1993, Air-stripper design and costing computer program. AWWA, 10, 63-72.

El-Halwagi M.M., 1992, Synthesis of reverse osmosis networks for waste reduction. AIChE J., 38, 1185-1198.

El-Halwagi M.M., 1993, Optimal design of membrane-hybrid systems for waste reduction. Sep. Sci. Techn. , 28, 283-307.

El-Halwagi M.M. and Manousiouthakis V., 1989, Synthesis of mass exchange networks. AIChE J., 8, 1233-1244.

Eliceche A.M.; Daviou M.D.; Hoch P.M. and Uribe I.O. 2002, Optimization of azeotropic distillation columns combined with pervaporation membranes. Comp. Chem. Eng., 5, 563-573.

Evangellsta F., 1985, A short cut method for the design of reverse osmosis desalination plants. Ind. Eng. Chem. Process Des. Dev.,24, 211-223.

Floudas C.A., 1995, Nonlinear and Mixed-Integer Optimization: Fundamentals and Applications. Oxford University Press.

Galan B. and Grossmann I.E., 1998, Optimal design of distributed wastewater treatment networks. Ind. Eng. Chem. Res., 37, 4036-4048.

Grossmann I.E., 2004, Challenges in the new millennium: product discovery and design, enterprise and supply chain optimization, global life cycle assessment. Comp. Chem. Eng., 29, 29-39.

Grossmann I.E., Daichendt M.M., 1996, New trends in optimization-based approaches to process synthesis. Comp. Chem. Eng., 6, 665-683.

Hand, D.W.; Crittenden, J.C.; Gehin, J.L. and Lykins, B.W., 1986, Design and evaluation of an air-stripping tower for removing VOCs from groundwater. AWWA, 9, 87-97.

Hernández-Suárez R., Castellanos-Fernández J. and Zamora J.M., 2004, Superstructure decomposition and parametric optimization approach for the synthesis of distributed wastewater treatment networks. Ind. Eng. Chem. Res., 43, 2175-2191.

Hickey P.J. and Gooding C.H., 1994, Mass transfer in spiral wound pervaporation modules. J. Membrane Sci., 92, 59-74.

Hickey P.J. and Gooding C.H., 1994, Modeling spiral wound modules for the pervaporative removal of volatile organic compounds from water. J. Membrane Sci., 88, 47-68.

Hines, A.L. and Maddox R.N., 1985, Mass transfer, Fundamentals and applications. Prentice-Hall.

Huang C.H., Chang C. T., Ling H.C. and Chang C.C., 1999, A mathematical programming model for water usage and treatment network design. Ind. Eng. Chem. Res., 38, 2666-2679.

Ismail S.R., Pistikopoulos E. N. and Papalexandri K.P., 1999, Modular representation synthesis framework for homogeneous azeotropic separation. AIChE J., 45, 1701-1720.

Ismail S.R., Proios P. and Pistikopoulos E. N., 1999, Modular synthesis framework for combined separation/reaction systems. AIChE J., 3, 629-649.

Karuppiah, R. and Grossmann, I.E, 2005, Global optimization for the synthesis of integrated water systems in chemical processes. Comp. Chem. Eng., 30, 650-673.

Kookos I.K., 2003, Optimal design of membrane/distillation column hybrid processes. Ind. Eng. Chem. Res., 8, 1731-1738.

Kuo W.J. and Smith R., 1997, Effluent treatment system design. Chem. Eng. Sci., 3, 4273-4290.

Kutzer S.; Wintrich H. and Mersmann A., 1995, Air stripping- a method for treatment of wastewater. Chem. Eng. Technol., 18, 149-155.

Li X. and Kraslawski A., 2004, Conceptual process synthesis: past and current trends. Chem. Eng. Proc., 43, 589-600.

Linke P. and Kokossis A.C., 2003, Advanced process systems design technology for pollution prevention and waste treatment. Adv. Env. Res. 8(2), 229-245.

Linke P. and Kokossis A.C., 2003, Attainable reaction and separation processes from a superstructure-based method. AICHE 49(6) 1451-1470.

Lipnizki F. and Field R.W., 2002, Hydrophobic pervaporation for environmental applications: process optimization and integration. Env. Prog., 4, 265-272.

Lipnizki F.; Field, R.W. and Ten P., 1999, Pervaporation-based hybrid process: a review of process design, applications and economics. J. Membrane Sci., 153, 183-210.

Lu Y.Y., Hu Y.D., Xu D.M. and Wu L.Y., 2006, Optimum design of reverse osmosis seawater desalination system considering membrane cleaning and replacing. J. Memb. Sci., 282, 7-13.

Lu Y.Y., Hu Y.D., Zhang X.L., Wu L.Y. and Liu Q.Z., 2007, Optimum design of reverse osmosis system under different feed concentration and product specification. J. Memb. Sci., 287, 219-229.

Lyonnaise des eaux, 1996, Water treatment membrane processes. AWWA research foundation, Water research commission of South Africa, McGraw-Hill.

Maskan F., Wiley D.E., Johnston L.P.M. and Clements D.J., 2000, Optimal design of reverse osmosis module networks. AIChE J., 46, 946-954.

McCormick G.P., 1976, Computability of global solutions to factorable nonconvex programs- Part I- convex underestimating problems. Math. Prog., 10, 146-175.

Mehta V.L., Kokossis A.C., 2000, Nonisothermal synthesis of homogeneous and multiphase reactor networks. AIChE J., 11, 2256-2273.

Metcalf & Eddy Inc., 1991, Wastewater engineering treatment, disposal, and reuse. Irwin/McGraw-Hill.

Meyer, C.A. and Floudas, C.A., 2006, Global optimization of a combinatorially complex generalized pooling problem. AIChE J., 52, 1027-1037.

Nirmalakhandan, N.; Lee, Y.H. and Speece R.E., 1987, Designing a cost-efficient air-stripping process. AWWA, 1, 56-63.

Papalexandri K.P. and Pistikopoulos E.N., 1996, Generalized modular representation framework for process synthesis. AIChE J., 4, 1010-1032.

Parthasarathy G. and El-Halwagi M.M., 2000, Optimum mass integration strategies for condensation and allocation of multicomponent VOCs. Chem. Eng. Sci., 5, 881-895.

Proios P. and Pistikopoulos E. N., 2006, Hybrid generalized modular/collocation framework for distillation column synthesis. AIChE J., 3**,** 1038-1056.

Proios P., Goula N.F. and Pistikopoulos E. N., 2005, Generalized modular framework for the synthesis of heat integrated distillation column sequences. Chem. Eng. Sci., 17, 4678-4701.

Saif, Y., Elkamel, A., Pritzker, M., 2007, Optimal design of RO network for wastewater treatment and minimization. Accepted by Chem. Eng. Proc..

Schaefer K., Exall K. and Marsalek J., 2004, Water reuse and recycling in Canada: A status and need assessment. Can. Water Resour. J., 3, 195-208.

See H.J., Vassiliadis V.S. and Wilson D.I. (1999), Optimization of membrane regeneration scheduling in reverse osmosis networks for seawater desalination. Desalination, 125, 37-54.

See H.J., Wilson D.I., Vassiliadis V.S., Parks G.T. (2004), Design of reverse osmosis (RO) water treatment networks subject to fouling. Water Sci. Technol., 49, 263-270.

Shah, M.R.; Noble R.D. and Clough D.E., 2004, Pervaporation-air-stripping hybrid process for removal of VOCs from groundwater. J. Membrane Sci., 241, 257-263.

Sherali H.D., Alameddine A., 1992, A new reformulation-linearization technique for bilinear programming problems. J. Global Opt., 2, 379-410.

Srinivas B.K. and El-Halwagi M.M., 1993, Optimal design of pervaporation systems for waste reduction. Comp. Chem. Eng., 17, 957-970.

Starthmann H., 2001, Membrane separation processes, Current relevance and future opportunities. AIChE J., 5, 1077-1087.

Staudinger J. and Roberts P.V., 2001, A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. Chemosphere, 44, 561-576.

Suk D.E. and Matsuura T., 2006, Membrane-based hybrid processes: a review. Sep. Sci. Technol., 41, 595-626.

Suk D.E., and Matsuura T. 2006, Membrane-based hybrid processes: a review. Sep. Sci. Technol., 41, 595-626.

Takama N., Kuriyama T., Shiroko K. and Umeda T., 1980, Optimal water allocation in a petroleum refinery. Comp. Chem. Eng., 4, 251-258.

Türkay M. and Grossmann I.E., 1996, Logic-based MINLP algorithms for the optimal synthesis of process networks. Comp. Chem. Eng., 20, 959-078.

Viswanathan J., Grossmann I.E., 1993, Optimal feed locations and number of trays for distillation columns with multiple feeds. Ind. Eng. Chem. Res., 32, 2942-2949.

Vyhmeister E., Saavedra A. and Cubillos F. A., 2004, Optimal synthesis of reverse osmosis systems using genetic algorithms, European symposium on computer-aided process engineering-14.

Weber W., 1972, Physiochemical processes for water quality, Wiley.

Wenten I.G., 2002, Recent development in membrane science and its industrial applications. Songklanakarin J. Sci. Technol., 24, 1009-1024.

Westerberg A.W., 2004, A retrospective on design and process synthesis. Comp. Chem. Eng., 28, 447-458.

Wijmans J.G.; Kamaruddin H.D.; Segelke S.V.; Wessling M. and Baker R.W., 1997, Removal of dissolved VOCs from water with an air stripper/membrane vapor separation system. Sep. Sci. Technol., 14, 2267-2287.

Yeomans H. and Grossmann I.E., 1999, A systematic modeling framework of superstructure optimization in process synthesis. Comp. Chem. Eng., 6,709-731.

Zhu M., El-Halwagi M.M., Al-Ahmad M., 1997, Optimal design and scheduling of flexible reverse osmosis networks. J. Memb. Sci., 129, 161-174.

Appendix

Appendix A

A.1 Air Stripper Model

The mathematical model for the air-stripping unit describes the mass transport of VOC's from the wastewater stream to the air stream, and the pressure drop along the column height (Billet and Schultes; 1991, 1993, 1999). The height of air stripper can be calculated from a material balance for every component present in the tower. This result with the following set of equations:

$$H_T = H_{C,OL} \; N_{C,OL}$$

$$H_{C,OL} = H_{C,L} + \frac{\dot{F}_W}{\dot{F}_A \, H^{/}} H_{C,v}$$

$$N_{C,OL} = \frac{1}{CO_1} \left(\frac{CO_1 \; x_{in} + CO_2}{CO_1 \, x_{out} + CO_2} \right)$$

$$CO_1 = 1 - \frac{\dot{F}_W}{\dot{F}_A \, H^{/}} \;\; ; \;\; CO_2 = -\frac{va_{out}}{H^{/}} + \frac{\dot{F}_W}{\dot{F}_A \, H^{/}} X_{in} \;\; ; \;\; H^{/} = \frac{hn}{P_T}$$

Correlation of the mass transfer coefficients in the liquid and gas phases are given as:

$$H_{C,L} = \frac{1}{C_L} \left(\frac{\mu_L}{\rho_L \; g} \right)^{\frac{1}{6}} \left(\frac{4 \in}{D_L a} \right)^{\frac{1}{2}} \left(\frac{u_L}{a} \right)^{\frac{2}{3}} \left(\frac{a}{a_{Ph}} \right)$$

$$H_{C,L} = \frac{u_L}{\beta_L a_{Ph}}$$

$$H_{C,v} = \frac{1}{C_V} \left(\in - h_L \right)^{1/2} \left(\frac{4 \in}{a} \right)^{1/2} \left(\frac{1}{a} \right)^{\frac{3}{2}} \left(\frac{\rho_V u_V}{a \, \mu_V} \right)^{-3/4} \left(\frac{\mu_V}{\rho_V D_V} \right)^{-1/3} \left(\frac{u_V a}{D_v a_{Ph}} \right)$$

$$H_{C,v} = \frac{u_v}{\beta_v a_{Ph}}$$

The correlations for the specific liquid holdup h_L and the effective interfacial area a_{Ph} / a in the preloading region are given as:

$$h_L = \left(12 \frac{\mu_L}{g \, \rho_L} \, u_L \, a^2 \right)^{1/3} \; ; \quad u_V \le u_{V,S}$$

$$\frac{a_{Ph}}{a} = 1.5 \left(4 \in \right)^{-0.5} \left(\frac{4 \in u_L \rho_L}{a \, \mu_L} \right)^{-0.2} \left(\frac{u_L^2 a}{4 \in g} \right)^{-0.45} \left(\frac{4 \; \in u_L^2 \; \rho_L}{a \; \sigma_L} \right)^{0.75}$$

The calculation for the air and the water velocities at the loading point are given as:

$$u_{V,S} = \left(\frac{g}{\psi_S} \frac{\rho_L}{\rho_V} \right)^{0.5} \left(\frac{\in}{a^{1/6}} - a^{0.5} \left(12 \frac{\mu_L}{g \, \rho_L} u_{L,S} \right)^{1/3} \right) \left(12 \frac{\mu_L}{g \, \rho_L} u_{L,S} \right)^{1/6}$$

$$\psi_S = \frac{g}{C_S^2} \left(\frac{L}{V} \left(\frac{\rho_V}{\rho_L} \right)^{0.5} \left(\frac{\mu_L}{\mu_V} \right)^{0.4} \right)^{-2 n_S}$$

$$u_{L,S} = \frac{\rho_V}{\rho_L} \frac{L}{V} \, u_{V,S}$$

For:

$$\frac{L}{V}\left(\frac{\rho_V}{\rho_L}\right)^{1/2} < 0.4:\ n_S = -0.326\ ;\ C_{S1} = 2.959$$

$$\frac{L}{V}\left(\frac{\rho_V}{\rho_L}\right)^{1/2} \geq 0.4:\ n_S = -0.723\ ;\ C_{S2} = 0.695\, C_{S1}\left(\frac{\mu_L}{\mu_V}\right)^{0.1588}$$

The pressure drop equations are given as:

$$\frac{\Delta P}{H_T} = \psi_L \frac{a}{(\in - h_L)^3}\frac{F_V^2}{2}\frac{1}{K}$$

$$\psi_L = C_P\left(\frac{64}{\mathrm{Re}_V} + \frac{1.8}{\mathrm{Re}_V^{0.08}}\right)\left(\frac{\in - h_L}{\in}\right)^{1.5} EXP\left(\frac{\mathrm{Re}_L}{200}\right)$$

$$\mathrm{Re}_L = \frac{u_L \rho_L}{a\,\mu_L}$$

$$\mathrm{Re}_v = \frac{u_v \rho_v}{a\,\mu_v}$$

The existence of an air stripper is a relation between the column height and a binary variable as:

$$H_{AS} \leq H_{AS}^{UP}\ y_{AS} \qquad \forall\ AS$$

$$H_{AS} \geq H_{AS}^{LO}\ y_{AS} \qquad \forall\ AS$$

A.2 Pervaporation Model:

The pervaporation model takes into account concentration polarization and the pressure drop in the spiral wound module (Hickey and Gooding; 1994). For every VOC, the molar flow in every pervaporation stage is given as:

$$F_{VOC} = SurA_{PV}\,\rho_M\;K_{VOC}\left(X_{VOC,ST} - \frac{va_{VOC,Perm}\,P_{Perm}}{hn}\right)$$

The overall mass transfer coefficient of a VOC and water can be estimated as:

$$\frac{1}{K_{VOC}} = \frac{l_m}{Pm_{VOC}} + \frac{1}{k_{VOC}}$$

$$\frac{1}{K_{Water}} = \frac{l_m}{Pm_{water}}$$

The mass transfer coefficient in the concentration polarization layer and the pressure drop are given as:

$$k_{VOC} = 0.5\,D_L\left(\frac{1.14\,u_L\,\rho_L}{\mu_L}\right)^{0.46}\left(\frac{\mu_L}{\rho_L\,D_L}\right)^{0.33}$$

$$\frac{\Delta P}{Lt_m} = 2.54\,u_L^{1.551}$$

The existence of a pervaporation stage is relation between the pervaporation binary variable and its surface area as:

$$SurA_{PV} \le SurA_{PV}^{UP} \; y_{PV} \qquad \forall PV$$
$$SurA_{PV} \ge SurA_{PV}^{LO} \; y_{PV} \qquad \forall PV$$

A.3 Distribution box (DB) constraints:

The DB streams have several states that may allow prior elimination of mixing streams with different properties. For example, the pervaporation permeate streams can be collected directly to the final permeate stream set. The air streams within the network are only allowed to mix between teach other (e.g. gas phase), and allowed to pass the network to the final air exit stream set. On the other hand, the wastewater steams (e.g. liquid phase) are allowed to mix at any mixing point that involve wastewater liquid stream. Therefore, every stream in the DB is characterized by flowrate, composition, pressure, and state. Mixing is only allowed between streams which have similar states (e.g. air, liquid wastewater, permeate streams). For every mixer, material and component balances hold:

$$F_{MIX} = \sum^{SSP} F_{SSP,MIX} \qquad \forall \; MIX$$

$$F_{MIX} \; x_{C,MIX} = \sum^{SSP} F_{SSP,MIX} \;\; x_{C,SSP} \qquad \forall \; C, MIX$$

In addition, mixing is only allowed between streams with equivalent pressure through definition of binary variables as:

$$P_{MIX} - P_{SSP} \le UP \;\; y_{SSP,MIX} \qquad \forall \; MIX, SSP$$

$$P_{MIX} - P_{SSP} \geq LO \quad Y_{SP,MIX} \qquad \forall \ MIX, SP$$

The splitter nodes only require material balances as:

$$F_{SSP} = \sum^{MIX} F_{SSP,MIX} \qquad \forall \ SSP$$

The demand constraints are set of inequalities which enforce discharge restrictions on the final reject streams as:

$$x_{c,SFREJ} \leq x_{c,SFREJ}^{UP} \qquad \forall \ C, SFREJ$$

A.4 Objective function:

The total annualized cost of the treatment cost is a combination of the fixed and operating cost of the process units and the utility units (Douglas, 1988; Lipnizki and Field; 2002). The cost of units was updated to 2002 following Marshall and Swift index (M&S).

Total annualized cost (TAC) of the treatment:

$$\mathrm{TAC}_{\mathrm{treatment}} = \mathrm{Cost}_{\mathrm{capital}}\ (\mathrm{amortiz.}) + \mathrm{Cost}_{\mathrm{operating}}$$

$\mathrm{amortiz.} = 0.25$

Total capital cost:

1. Membrane system

Membrane: PDMS

Membrane $= 720\,SurA$

Feed pump $= 46.6E3\left(PPu_{pump}\right)^{0.53}$

Vacuum pump $=16.6E3\left(PPu_{Vacuum\ pump}\right)^{0.53}$

$$PPu_{pump} = F_{pump}\ \Delta P_{pump}\ /\ \rho_M$$
$$PPu_{Vaccum\ pump} = F_{pump}\ \Delta P_{Vaccum\ \ pump}\ /\ \rho_M$$

2. Air Stripper

Packing material: 50 mm NORPAC®

Tower and packing cost $=33000\,D_{\mathrm{AS}}^{0.57} H_{AS} + 1105\,D_{AS}^{2} H_{AS}$

Feed pump $=12.265\left(PPu_{pump}\right)^{0.53}$

Air blower$=14.2E3\left(PPu_{Air\,blower}\right)^{0.82}$

$$PPu_{pump} = MW\ F_{pump}\ H_{AS}\ /\ g$$

$$PPu_{Air\,blower} = \left(\left(\frac{P_{out}}{P_{in}}\right)^{0.283} - 1\right)\left(\frac{F_{air}\ RT}{0.1415}\right)$$

Total operating cost:

1. Membrane

Membrane replacement cost $=169\,SurA$

2. Tower operating cost = 10% of the fixed cost.

Power cost = $=0.05\$/Kwh$

Days of operation$=300\,D/yr$.

Appendix B

B.1 Input Data for TCE Case Study:

$\dot{F}_{Water}$ = 1.582 (kmol/s)

X_{TCE} = 1.73×10^{-4}

Recovery = 99%

a = 86.8 (m^2/m^3)

C_L = 1.08

C_P = 0.35

C_S = 2.959

C_V = 0.322

$$hn = \frac{T(^o K)}{0.2194} 10^{\left(5.874 - \frac{1871}{T(^o K)}\right)} \text{ (bar)}$$

l_m = 5×10^{-6} (m)

Lt_m = 1 (m)

Pm_{TCE} = 2.822×10^{-8} (m^2/s)

Pm_{water} = 2.48×10^{-13} (m^2/s)

$\in$ = 0.947 (m^3/ m^3)

B.2 Input Data for the Multicomponent Case Study:

$\dot{F}_{Water}$ = 1.582 (kmol/s)

X_{TCE} = 1100×10^{-6}

X_{DCM} = 46×10^{-6}

X_{EDC} = 7.1×10^{-6}

Recovery = 99%

a = 86.8 (m^2/m^3)

C_L = 1.08

C_P = 0.35

C_S = 2.959

C_V = 0.322

$$hn \text{ (TCE)} = \frac{T(^o K)}{0.2194} 10^{\left(5.874 - \frac{1871}{T(^o K)}\right)} \text{ (bar)}$$

$$hn \quad \text{(DCM)} \quad = \frac{T(^{o}K)}{0.2194} 10^{\left(4.561 - \frac{1644}{T\left(^{o}K\right)}\right)} \text{ (bar)}$$

$$hn \quad \text{(EDC)} \quad = \frac{T(^{o}K)}{0.2194} 10^{\left(4.434 - \frac{1705}{T\left(^{o}K\right)}\right)} \text{ (bar)}$$

$l_m \quad = \ 5 \times 10^{-6}$ (m)

$Lt_m \quad = \ 1$ (m)

$Pm_{TCE} \ = \ 2.822 \times 10^{-8}$ (m^2/s)

$Pm_{DCM} \ = \ 5.59 \times 10^{-9}$ (m^2/s)

$Pm_{EDC} \ = \ 3.83 \times 10^{-9}$ (m^2/s)

$Pm_{water} \ = \ 2.48 \times 10^{-13}$ (m^2/s)

$\in \quad = 0.947$ (m^3/ m^3)