Optimization of Material and Energy Integration in Eco-Industrial Networks

by

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This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Chapter 3 is based on the previously published work "Air quality and environmental impacts of alternative vehicle technologies in Ontario, Canada" by Kantor et al. [41] as seen in the International Journal of Hydrogen Energy 35(10):5145-5153 and is reproduced with permission from the International Association of Hydrogen Energy. The thesis author's specific contributions to this paper were to develop the model of emission reduction potentials, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M. Fowler and Dr. A Elkamel, who are co-authors on the publication. Amirhossein Hajimiragha contributed with primary modeling of the electricity grid in the province of Ontario to determine the supportable penetration of alternative-fuel vehicles. This effort is reflected in the Appendix.

Chapter 4 is based on previously published work "Optimized production of hydrogen in an eco-park network accounting for life-cycle emissions and profit" by Kantor et al. [69] as seen in the International Journal of Hydrogen Energy 37(6):5347-5359 and is reproduced with permission from the International Association of Hydrogen Energy. The thesis author's specific contributions to this paper were to develop the model, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M.W. Fowler and Dr. A. Elkamel, who are co-authors on the publication.

Chapter 5 is based on the forthcoming work "Optimization of Material and Energy Exchange in an Eco-park Network Considering Three Fuel Sources" by Kantor et al. [108], in press with the International Journal of Advanced Operations Management and is reproduced with permission from the International Journal of Advanced Operations Management. The thesis author's specific contributions to this paper were to develop the model, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M.W. Fowler and Dr. A. Elkamel, who are co-authors on the publication.

Chapter 6 is based on work submitted to the Journal of Cleaner Production entitled “Generalized MINLP Modeling of Eco-Industrial Networks”. The thesis author’s specific contributions to this paper were to develop the model, conduct the simulations, prepare the graphics and results, write the final manuscript and submit to the journal with an expectation of also responding to the comments of reviewers. Alberto Betancourt assisted with the implementation of the model in GAMS and also assisted with the modeling documentation. This work was conducted with direction from the project supervisors, Dr. M.W. Fowler and Dr. A. Elkamel, who are co-authors on the publication. An additional co-author on this publication is Dr. Ali Almansoori who assisted in the direction of the paper and provided feedback prior to journal submission.

Abstract

This work develops a generalized modeling framework using several techniques for assessing the feasibility of an eco-industrial network or 'eco-park' in order to demonstrate the environmental and economic benefits of industrial facilities with cooperative goals to conserve energy and materials. The work takes advantage of three distinct types of modeling techniques (linear programming, mixed-integer linear programming and mixed-integer non-linear programming) to incorporate increasingly complex circumstances for designing eco-industrial networks. The purpose of this research is to provide policy-makers and facility designers with an approach to optimize construction of facilities based upon economic and environmental incentives. This framework allows for optimizing the material and energy efficiency of a network of facilities to reduce emissions, waste, and input of materials and energy while maintaining production levels.

Major contributions from this thesis are to examine the potential for alternative-fuel vehicles within the concept of a hydrogen economy and exploration of eco-industrial networks, utilizing the tools of life cycle analysis and system optimization. Life-cycle assessment is utilized as a tool for decision-making throughout this thesis and is an invaluable asset in making environmentally-conscious decisions. This type of assessment evaluates the emissions of a product from virgin material extraction through to final disposition in the aquatic, terrestrial or atmospheric domain. The use of life-cycle assessment techniques shows clear impacts on society over the entire lifecycle of the products and processes considered herein. Development of a dual-objective function to account for economics and environmental performance of industrial facilities is developed and utilized to aid in the decision process for policy-makers and facility designers.

The concept of eco-industrial networks is further extended by including additional com-

ponents, such as transportation modes, within the model. To this end, preliminary work examines the practical possibility of shifting automobile propulsion technologies to alternative fuels with emphasis on the criteria air contaminants considered herein of greenhouse gases, volatile organic compounds, and oxides of sulphur and nitrogen. The scenarios presented are based on a model of the electricity system in the province of Ontario, Canada and energy pathway analysis to assess the supportable market penetration of, and emissions from, alternative vehicle technologies. The recommendation of this work is that a transition to electric vehicles in the near-term followed by a transition to hydrogen fuel-cell vehicles will yield the largest reduction in criteria air contaminants in both the urban centre of Toronto, Ontario and in the province as a whole.

The consideration of transportation and transitional technologies feeds directly into the concept of eco-industrial parks and the benefit to society of their implementation. The reduction in transportation distance between relatable chemical manufacturers has been hailed as a major benefit of implementing eco-industrial park topology. This work develops a generalized modeling framework for eco-industrial parks based on a dual objective of societal and industrial requirements. The nodes considered in this work include: energy generation via hydrocarbon gasification or reforming, carbon capture, carbon sequestration, pressure-swing adsorption in addition to the manufacture of ammonia and urea within the context of refueling a fleet of 1000 hydrogen vehicles. Life-cycle assessment is applied to form the societal benefits of operating facilities within an eco-industrial framework and the long-term economics of the processes are considered to form the economic portion of the objective. Modeling is carried out in three distinct types: linear programming, mixed-integer linear programming and mixed-integer non-linear programming. Each of these types represents a different modeling framework developed to assess various complexities in the eco-industrial network and yet they share common goals, themes and analysis methods. Using each of these approaches, a case study eco-industrial park is analyzed using the three types of modeling methodologies mentioned. The simpler LP model is unable to account for some of the complexities inherent in an eco-park network and thus the results from this model are subsequently viewed as an upper boundary on the benefits of eco-industrial integration for the case study mentioned. The subsequent efforts of mixed-integer linear and non-linear programming serve to refine the model and provide more realistic investigation of the benefits of such a network.

In order to achieve a reduction in emissions of harmful substances to the air, water and land to meet national targets, analysis of the interactions between humans and the environment must be explored to unlock new avenues of production and consumption to reduce the impact that society is having on the environment. This work is completed within the larger context of the potential hydrogen economy with the supposition that such a scenario will be enabled by increasingly effective technology. The transition of our current infrastructure to the hydrogen economy shows benefits to air quality from reduced emissions of vehicles and also from a reduced industrial contribution.

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Nomenclature associated with Chapter 3

Acronyms	Description
AFV	Alternative fuel vehicle
PHEV	Plug-in hybrid electric vehicle
FCV	Fuel cell vehicle
FCPHEV	Fuel cell plug-in hybrid electric vehicle
HEV	Hybrid electric vehicle
BEV	Battery electric vehicle
OMA	Ontario Medical Association
VOC	Volatile organic compounds
GTA	Greater Toronto area
NO_x	oxides of nitrogen
PM_{10}	particulate matter of diameter less than 10 microns
$PM_{2.5}$	particulate matter of diameter less than 2.5 microns
GHG	Greenhouse gases
CO_2	Carbon dioxide
SO_x	Oxides of sulphur
AMPL	A Mathematical Programming Language
GREET	Greenhouse gases, Regulated Emissions, and Energy use in Transportation

Variables	**Description**	**Units /Type**
γ	time period	
λ_i	zonal base-load growth rate	%
π_i	zonal peak-load growth rate	%
λ	annual base load growth rate of Ontario's total zones	%

Variables	Description	Units /Type
b_i	base load value in Zone i	MW
$Phpp_{iy}$	the total installed HPP capacity in Zone i, by Year y	MW
Ps_{ijy}	power component	MW
Ph_{iy}	required power of HPPs in Zone i by Year y	MW
$\Delta Phpp_{iy}$	newly installed HPP in Zone i and Year y	MW
Th_{ijy}	transferred hydrogen	$tonnes\, day^{-1}$
m	number of trucks,	integer
OC_y	operation costs of one compressed gas truck in Year y	$\$CAD\, km^{-1}$
Pg	zonal generation power in Zone i, Year y, and during the time periodω_1 orω_2	MW
Pim	imported power in Zone i, Year y, and during the time periodω_1 orω_2	MW
Pex	exported power in Zone i, Year y, and during the time periodω_1 orω_2	MW
CC_{cab}	capital cost of cab trailers	\$
CC_{tube}	capital cost of tube trailers	\$
LT_{cab}	lifetime of cab trailers	years
LT_{tube}	lifetime of tube trailers	years
DR	discount rate	%
ntr_y	maximum number of compressed gas trucks in route between Zones i and j in Year y	integer
g_{ij}	conductance of the line between buses i and j	S

Variables	Description	Units /Type
δ	bus voltage angle	rads
$Ploss_{i,j}$	power loss in line i,j	MW
$\alpha_i jy(l)$	slope of the l^{th} block of voltage angle	
$delta_{ijy}^{\gamma}(l)$	value of the l^{th} block of voltage angle	
b_{ijy}	susceptance of the line (i,j) in Year y	S
Pl	total load in each zone	MW
ϵ	very small positive number	none
th_{mijy}	auxiliary variable representing the transferred hydrogen	$tonnes\, day^{-1}$

Parameters	Description	Units
$\underline{Pg}_{iy}$	minimum zonal power generation	MW
$\overline{Pg}_{iy}$	maximum zonal power generation	MW
$\underline{Pim}_{iy}$	lower bound of imported power	MW
$\overline{Pim}_{iy}$	upper bound of imported power	MW
$\underline{Pex}_{iy}$	minimum exported power	MW
$\overline{Pex}_{iy}$	maximum exported power	MW
$\overline{Pd}_{ij}$	maximum capacity of the transmission corridor (i,j) in direct power flow	MW
$\overline{Pr}_{ij}$	maximum capacity of the transmission corridor (i,j) in reverse power flow	MW
$\overline{Phpp}_{iy}$	maximum size of HPP which is allowed to be installed in Zone i by Year y	MW
d_{ij}	approximate distance between Zones i and j	km

Sets, Subsets and Indices	Description
Z	set of indices of zones or buses in the simplified network
Z^*	is the set of indices of hydrogen transfer corridors
Υ_1	set of indices of planning years starting in 2009
Υ	set of indices of planning years starting from 2008
ω_1	index for the time period corresponding to 8 weekday hours (12 am-7 am);
ω_2	index for the time period corresponding to 14 weekend hours (12 am-1 pm);
Ω	set of indices of transmission lines
Ψ	set comprised of ω_1 and ω_2

Binary Variables	**Description**
K_{mijy}	binary variable which takes the value of 1 if m trucks are needed for daily hydrogen transfer between Zones i and j in Year y
$\omega^{\gamma}_{ijy}(l)$	binary variable which takes the value of 1 if the value of the l^{th} angle block for the line (i,j) is equal to its maximum value $\Delta\delta_y$

Nomenclature associated with Chapter 4

Acronym	Description
EIN	Eco-industrial network
LCA	Life-cycle assessment
LP	Linear programming
GHG	Greenhouse gases
CO_2	Carbon dioxide
GAMS	General algebraic Modeling System
G	Symbol for the gasification unit
PSA	Symbol for the pressure-swing adsorption unit
CHP	Symbol for the combined heat and power unit
CC	Symbol for the carbon capture unit
AM	Symbol for the ammonia manufacturing unit
U	Symbol for the urea manufacturing unit
ME	Symbol for the methanol manufacturing unit
GH	Symbol for greenhouses
SQ	Symbol for the sequestration unit
EC	Symbol for the energy crops
ET	Symbol for the ethanol unit

Variable	Description	Units /Type
S	Total sulphur output	tonnes
S_{G_i}	sulphur output from each gasifier	kmol
A	Total ash output	tonnes
A_{G_i}	Ash output from each gasifier	kmol

Variable	**Description**	**Units /Type**
$y_{S_{G_{ij}}}$	Fraction of sulphur present in fuel j used in gasifier i	Decimal
$y_{A_{G_{ij}}}$	Fraction of ash present in fuel j used in gasifier i	Decimal
F_{ij}	Moles of fuel j used in gasifier i	kmol
CO	Total moles of carbon monoxide produced from gasification	kmol
H_2	Total moles of hydrogen produced from gasification	kmol
N_2	Total moles of nitrogen produced from gasification	kmol
CO_2	Total moles of carbon dioxide produced from gasification	kmol
x_{ij}	binary variable expressing whether fuel j is being supplied to gasifier i	Binary
CO_2p_{out}	CO_2 output from plant p	kmol
CO_2p_{in}	CO_2 input to plant p	kmol
N_2p_{out}	N_2 output from plant p	kmol
N_2p_{in}	N_2 input to plant p	kmol
H_2p_{out}	H_2 output from plant p	kmol
H_2p_{in}	H_2 input to plant p	kmol
COp_{out}	CO output from plant p	kmol
COp_{in}	CO input to plant p	kmol
NH_3p_{in}	Ammonia input to plant p	kmol
NH_3p_{out}	Ammonia output from plant p	kmol

Variable	Description	Units /Type
Mep_{in}	Methanol input to plant p	kmol
Mep_{out}	Methanol output from plant p	kmol
Up_{in}	Urea input to plant p	kmol
Up_{out}	Urea output from plant p	kmol
Ep_{in}	electricity input to plant p	kWh
Ep_{out}	electricity input to plant p	kWh
Hp_{in}	heat input to plant p	MJ
Hp_{out}	Heat output from plant p	MJ
γ_{WGS}	Extent of water-gas shift reaction inside the gasifier	Decimal
EG	Energy converted in the CHP unit	MJ
LHVCO	Lower heating value of carbon monoxide	$MJ\,kmol^{-1}$
$LHVH_2$	Lower heating value of hydrogen	$MJ\,kmol^{-1}$
HGX	Heat generated for export	MJ
EGX	Electricity generated for export	kWh
$Heat_{Split}$	Split of energy conversion for heating	Decimal
Z	The objective value, value to society	none
J_{LCE}	Contribution of life-cycle emission reductions to the objective function	none
J_e	Contribution of economics to the ojective function	Dollars
ACC_{S_p}	Amortized capital cost of plant p in an independent operating scenario	Dollars
OC_{S_p}	Operating cost of plant p in an independent operating scenario	Dollars

Variable	Description	Units /Type
ACC_{I_p}	Amortized capital cost of plant p in an integrated operating scenario	Dollars
OC_{I_p}	Operating cost of plant p in an integrated operating scenario	Dollars

Sets, Subsets and Indices	Description
i	plant index
j	fuel index
p	set of plants
e	set of emissions
Ω	set of fuels
Ω_i	set of fuels that can be utilized in gasifier i

Parameter	**Description**	**units**
$Cost_e$	Environmental cost of emission e	Decimal
F_i^U	upper limit on supply of fuel to gasifier i	tonnes
F_j^U	Upper limit of supply of fuel j	tonnes
n,m,k	coefficients of a biomass product	none
η_{HG}	Efficiency of heat generation	Decimal
η_{EG}	Efficiency of electricity generation	Decimal
W_{LCE}	Objective function weighting for life cycle emissions	Decimal
W_e	Objective function weighting for economics	Decimal

Nomenclature associated with Chapter 5

Binary Variables

$$x_{p,m} = \begin{cases} 1 \text{ if plant } p \text{ of size } m \text{ exists} \\ 0 \text{ Otherwise} \end{cases}$$

$$y_{p,p2,k,v} = \begin{cases} 1 \text{ if material } v \text{ is transported by method } k \text{ between } p \text{ and } p2 \\ 0 \text{ Otherwise} \end{cases}$$

Acronym	Description
EIN	Eco-industrial network
LCA	Life-cycle assessment
EIP	Eco-industrial Park
GAMS	General algebraic modeling system
MILP	Mixed-integer linear program
DJSI	Dow Jones sustainability index
WAR	Waste reduction
ISO	International Standards Organization
SO_x	Oxides of sulphur
CO_2	Carbon dioxide
GHG	Greenhouse gases
NPV	Net present value
G	Symbol for the gasification unit
PSA	Symbol for the pressure-swing adsorption unit
CHP	Symbol for the combined heat and power unit
CC	Symbol for the carbon capture unit
AM	Symbol for the ammonia manufacturing unit
U	Symbol for the urea manufacturing unit
ME	Symbol for the methanol manufacturing unit
GH	Symbol for greenhouses
SQ	Symbol for the sequestration unit
SMR	Steam-methane reforming

Model Framework	**Description**
Z	Objective value
x	Design vector
c	Vector of fixed parameters
g	vector of inequality constraints
h	vector of equality constraints
x_i^L	the lower bound for x_i
x_i^U	the upper bound for x_i
q	number of objectives
x	vector of decision variables
c	vector of fixes parameters
m_1	number of inequalities; and
m_2	number of equalities

Model Setup	Description
λ_i	weighting factor for objective Z_i
F_i	scaling factors for Z_i
$\tilde{Z}$	aggregated objective value
$Z_1 = Z_{economic}$	economic portion of the objective value
$Z_2 = Z_{emissions}$	environmental portion of the objective value
n_e	number of emissions considered
λ_e	weighting factor for emission e
F_e	scaling factors for emission e
Z_e	emission differential between the integrated and stand-alone facilities
I_e	emissions of e from an integrated facility
S_e	emissions of e from a standalone facility
r_d	discount rate
n_p	number of manufacturing facilities

Sets	Description
k	set of the transportation technologies available
m	set of plant sizes
v	set of material vectors
e	set of emissions
p	set of facilities; and
$p2$	alias of p

Variables	Description	Units
$out_{v,p}$	amount of material v output from plant p	kg; mol
$in_{v,p}$	input of v to plant p	mol
$rx_{v,p}$	consumption of v in p	mol
$gen_{v,p}$	generation of v in p	mol
$M^U_{p,m}$	upper flowrate limit of from plant p of size m	m^3; kg; mol
R_p	return from sale of products from plant p	\$
I_{CC}	integrated plant capital cost	\$
S_{CC}	standalone plant capital cost	\$
I_{OC}	integrated plant operating cost \$	
S_{OC}	standalone plant capital cost \$	
t	year	
L	plant lifetime p	years
$TransportationCost_k$	Total transportation cost of type k	\$
$BaseCost_k$	Base cost of transportation mode k	\$
$ThroughputCost_k$	Throughput cost of transportation mode k	$\$m^{-3}$; $\$kg^{-1}$; $\$mol^{-1}$

Nomenclature associated with Chapter6

Acronyms	Description
AHP	Analytic hierarchy process
EIN	Eco-industrial network
GAMS	General Algebraic Modeling System
GHG	Greenhouse gases
H	total number of fuels available
LCA	Life-cycle assessment
LCE	life-cycle emission
LP	Linear Programming
MILP	Mixed-Integer Linear Programming
MINLP	Mixed-Integer Nonlinear Programming
SMR	Steam methane reforming

Continuous Variables	Description	Unit /type
$ACC_{i,s}$	annual amortized capital cost of the plant i with scheme s	$\$\,yr^{-1}$
AD_u	ammonia plant node's utility u demand	$J\,h^{-1}$; $tonne\,h^{-1}$; kW
AI_m	ammonia node's material m input	$mol\,h^{-1}$
$AO_{m,j}$	ammonia plant node's material m output to the jth node	$mol\,h^{-1}$
AP_m	ammonia plant node's material m product	$mol\,h^{-1}$
AR_u	ammonia plant node's utility u requirement per unit of NH_3 produced	$Jmol^{-1}$; $tonne\,mol^{-1}$; $kWh\,mol^{-1}$
ASF_j	ammonia plant node's split factor to node j	%

Continuous Variables	Description	Unit /type
CCD_u	carbon capture node's utility u demand	$tonne\, h^{-1}$
CCI_m	carbon capture node's material m input	$mol\, h^{-1}$
$CCO_{m,j}$	carbon capture node's material m output to the jth node	$mol\, h^{-1}$
CCS_j	carbon capture node split factor of the CO_2-deficient gas sent to the node j	%
$CCSF_j$	carbon capture node's stream splitting factor to the sink node j	%
CEC	combined heat and power node's input gas energy content	$J\, h^{-1}$
CER_u	combined heat and power node's energy ratio used to produce utility u	%
CF	problem's objective cost function	fractional
CG_u	combined heat and power node's utility u generation	$J\, h^{-1}$;kW
CI_m	combined heat and power node's material m input	$mol\, h^{-1}$
$CO_{m,j}$	combined heat and power node's material m (stack gas) sent to the node j	$mol\, h^{-1}$
CP_m	combined heat and power node's product m generation	$mol\, h^{-1}$
$EPC_{i,s,e}$	emission e related to the construction of plant i with scheme s	$tonnes\, emission\, e$

Continuous Variables	Description	Unit /type
$EPO_{i,s,e}$	emission e from the operation of plant i with scheme s	$tonnes\, emission\, e$
FM	mass flowrate of the fuel entering the gasifier	$kg\, h^{-1}$
GD_u	gasifier's utility u demands	$J\, h^{-1}$; $tonne\, h^{-1}$; kW
$GO_{m,j}$	gasifier's material m output to the production node j	$mol\, h^{-1}$
GP_m	gasifier's material m production	$mol\, h^{-1}$
GSF_j	gasifier's split factor to the sink node j	%
GW_m	gasifier's waste material m generation sent to waste /water treatment facilities	$mol\, h^{-1}$
$MAM_{m,j}$	market node's material m available to be sold to node j	$mol\, h^{-1}$
$MATER_{m,i,j}$	material m going from node i to node j	$mol\, h^{-1}$; $m^3\, h^{-1}$
$MEA_{u,j}$	market node's utility u exported to node j	Jh^{-1}; $tonne\, h^{-1}$
MEI_u	market node's utility u input (i.e., utility sold to the market)	$J\, h^{-1}; kW$
$MEO_{u,j}$	market node's utility u sold to node j	$J\, h^{-1}$; $tonne\, h^{-1}$; kW
MER_u	market node's utility u ratio input (i.e., utility ratio that can be sold to the market)	%
MI_m	market node's material m input	$mol\, h^{-1}$
$MO_{m,j}$	market node's material m outputs to the jth node	$mol\, h^{-1}$
NEC	eco-industrial network's annual lifecycle emissions comparison ratio	dimensionless

Continuous Variables	Description	Unit /type
NPC	eco-industrial network's annual production cost comparison ratio	dimensionless
NTC_k	networks transport cost for mode k	$\$yr^{-1}$
$OC_{i,s}$	operating cost of plant i following scheme s	$\$\,yr^{-1}$
$PC_{l,i,s}$	plant capital cost	$
PD_u	pressure swing adsorption nodes utility u demand	$J\,h^{-1}$; $tonne\,h^{-1}$; kW
PI_m	pressure swing adsorption nodes material m input	$mol\,h^{-1}$
$PlantCost_2$	plant scaled cost	$
$PO_{m,j}$	pressure swing adsorption nodes material m output to the jth node	$mol\,h^{-1}$
$POC_{i,s}$	plant's operating capacity	$mol\,h^{-1}$
$PPC_{l,i}$	plant's production capacity	$mol\,h^{-1}$; $m^3\,h^{-1}$
PS_j	pressure swing adsorption node's split factor of the H2-deficient syngas to the node j	%
PSF_j	pressure swing adsorption node's H2 stream splitting factor to the jth node	%
SD_u	sequestration node's utility u demand	$tonne\,h^{-1}$; kW
SI_m	sequestration node's material m input from the carbon capture node	$mol\,h^{-1}$
UD_u	urea plant node's utility u demand	$J\,h^{-1}$; $tonne\,h^{-1}$; kW
UI_m	urea plant node's material m input	$mol\,h^{-1}$

Continuous Variables	Description	Unit /type
$UO_{m,j}$	urea plant node's output material m into node j	$mol\, h^{-1}$
UP_m	urea plant node's product m	$mol\, h^{-1}$
$UR_{m,j}$	urea plant node's material m output to the jth node	$mol\, h^{-1}$
WD_u	waste/water treatment node's utility u demand	$J\, h^{-1}$; $tonne\, h^{-1}$; kW
WI_m	waste/water treatment node's material m input	$mol\, h^{-1}$

Binary Variables

$$f_h = \begin{cases} 1 \text{ if fuel } h \text{ is selected} \\ 0 \text{ Otherwise} \end{cases}$$

$$x_{i,l} = \begin{cases} 1 \text{ if plant } i \text{ of size } l \text{ is selected} \\ 0 \text{ Otherwise} \end{cases}$$

$$y_{i,j,k} = \begin{cases} 1 \text{ if transportation method } k \text{ is used between node } i \text{ and node } j \\ 0 \text{ Otherwise} \end{cases}$$

Integer Variables	Description
$TUN_{k,i,j}$	number of transport units k used to transfer materials from i to j

Sets and Subsets	Description
d	set of pipeline diameters
e	set of environmental emissions considered in the LCE analysis
h	set of feedstock fuels available in the eco-industrial network
i	set of source nodes
j	set of sink nodes
k	set of transport modes available to connect the nodes
m	set of materials (i.e., products and by-products of the EIN)
u	set of utilities associated to the EIN

Set elements	Description
ap	ammonia production node
B	biomass fuel
C	coal fuel
cc	carbon capture node
chp	combined heat and power node
g	gasification process node
GHG	Greenhouse Gases emissions expressed in CO_2 eq.
mk	market place node
M_1	carbon monoxide (CO)
M_2	carbon dioxide (CO_2)
M_3	hydrogen (H_2)
M_4	nitrogen (N_2)
M_5	ammonia (NH_3)
M_6	urea $CO(NH_2)_2$
M_7	water (H_2O)

Set elements	Description
M_8	methane (CH_4)
M_9	ash
M_10	sulfur (S)
M_11	other contaminants
NG	natural gas fuel
NO_x	oxides of nitrogen emissions
P_d	transport pipeline
psa	pressure swing adsorption node
Rd	road transport
Rl	rail transport
SO_x	sulfur oxides emissions
sq	sequestration node
SW	solid waste materials (i.e., landfill materials)
up	urea production node
U_1	heat utility
U_2	process water utility
U_3	electricity utility
wt	waste /water treatment node

Model Parameters	Description	Units /Type
ACF	ammonia plant node's reaction conversion	%
ACF_i	annual amortized capital factor associated to the plant i	%

Model Parameters	Description	Units /Type
ASF_m	ammonia plant node's stoichiometric relationship for the production of material m	decimal
CCR_u	carbon capture node's utility requirement per CO_2 product	$tonne\, mol^{-1}$
CEF_u	combined heat and power node efficiency for generating utility u	%
$d_{i,j}$	distance between nodes i and j	km
$EFPC_{l,i,s,e}$	emission e from the construction of a plant of size l	$tonnes\, emission e$
$EFPO_{i,s,e}$	emission factor related to the operation of the plants	$(tonnes\, emission\, e)(h)$ $(yr)^{-1}(mol)^{-1}$
$FC_{h,m}$	material m composition out of the gasifier per fuel type h	mol%; mass%
FC_k	fixed cost associated with transport method k	$\$\, yr^{-1}$; $\$(km)^{-1}(yr)^{-1}$
FCU_k	fixed cost per transportation unit type k	$\$\, yr^{-1}$
GR_u	gasifier's utility requirement per unit of product	$J\, mol^{-1}$; $tonne\, mol^{-1}$; $kWh\, mol^{-1}$
LHV_m	lower heating value of the gaseous components m	$J\, mol^{-1}$
MW_h	molecular weight of the feedstock fuel type h	$g\, mol^{-1}$
$OCF_{i,s}$	operating cost factor associated to the plant i following scheme s	%

Model Parameters	Description	Units /Type
$PlantCapacity_1$	reference plant installed capacity	$mol\, h^{-1}$
$PlantCapacity_2$	scaled plant installed capacity	$mol\, h^{-1}$
$PlantCost_1$	reference plant cost	$
POL_i	plant's operating life	years
PR_u	pressure swing adsorption node's energy requirement per unit of H_2 product	$J\, mol^{-1}$; $tonne\, mol^{-1}$; $kWh\, mol^{-1}$
SR_u	sequestration node's utility u requirement per unit of CO_2 input	$kWh\, mol^{-1}$
TC_k	transportation method k's capacity factor	$mol\, h^{-1}$; $m^3 h^{-1}$
UC_F	urea plant node's reaction conversion	%
UR_u	urea plant node's utility u requirement per product	$J\, mol^{-1}$; $tonne\, mol^{-1}$; $kWh\, mol^{-1}$
USF_m	urea plant node's stoichiometry for the production/consumption of material m	unitless
VC_k	variable cost of the transportation method k	$(\$)(h)\,(km)^{-1}\,(yr)^{-1}\,(mol)^{-1}$; $(\$)(h)\,(yr)^{-1}\,(mol)^{-1}$
W_E	weight assigned to the lifecycle emissions of the network	%
W_P	weight assigned to the production cost of the network	%
WR_u	waste /water treatment node's utility requirement per tonne process water	$J\, tonne^{-1}$; $kWh\, tonne^{-1}$

Chapter 1

Introduction

This work focuses on demonstrating the benefits of eco-industrial integration with respect to environmental and economic benefits while providing a holistic production of heat, electricity, industrial products and transportation fuel. Sections of this work contribute to the optimization of a network of chemical facilities considering economics and emissions from virgin material extraction to the network boundary, while another portion is focused upon the impacts of alternative transportation fuels from a complete life-cycle perspective. The scope of this work is limited to economic assessment and four environmental impact categories, namely: climate change potential, acidification, urban air quality and solid waste. This work is intended to impact the areas of facility design/construction, environmental assessments of industrial operation and to a large degree, those who create and influence policy within the industrial sector. Balance between economic viability and environmental impact for the operation of industrial facilities are balanced throughout this work; therefore, the most relevant recipients of this work are those who would influence the policy decisions for reducing environmental impact from industry without discouraging investment in construction of such facilities. The balance between economic and environmental components as part of a bi-objective optimization in eco-industrial networks (EINs) is a novel method and unique contribution to this field.

This thesis will contribute to re-invigorating the concepts of eco-industrial integration by empirical analysis of potential economic and environmental benefits. Implementation of the proposed modeling frameworks across a network of chemical facilities including syngas production, combined heat and power, carbon capture, carbon sequestration, ammonia manufacture, pressure-swing adsorption and urea production is completed to show the integration framework and possibilities for economic and environmental benefit from this set of facilities. The selection of facilities was completed with the mindset that integrated systems should have commonalities in the form of energy and material vectors utilized, endothermic/exothermic coupling to maximize the potential integration of material and energy transfers throughout the network.

Chapter 2 describes the methodologies utilized throughout this thesis with emphasis placed on life-cycle assessment (LCA) and eco-industrial network (EIN) concepts. The scope of this work is to provide the reader with the concepts necessary to comprehend the work contained in Chapters 3 - 6 and to provide context for this research. Some of the topics contained in this chapter include modeling techniques and programs used throughout this work, the hydrogen economy context for this research and the environmental and economic metrics discussed throughout this thesis.

Chapter 3 explores the positive contributions to reducing urban air pollution in the greater context of the hydrogen economy and alternative transportation options. This work examines the supportable market penetration of alternative-fuel vehicle types within the confines of the electricity grid in Ontario, Canada. ‘A Mathematical Programming Language’ (AMPL) software is utilized in the preliminary model to explore the supportable penetration of these vehicles technologies given the constraints of the electricity grid. The second part of the analysis is connecting these supportable penetrations to a reduction in emissions in both the urban setting of Toronto, Ontario and in the overall context of Ontario, Canada. GREET 1.8b software, developed by Argonne National Laboratories in the USA is utilized in order to assess the emission reductions from each of the alternative vehicle technologies. The overarching goal of this chapter is to analyze the potential impacts of adopting these alternative fuel technologies related to the air quality in the urban centres in the province of Ontario. Emissions from constructing hydrogen fuel distribution infrastructure are not included in this work as they are external to the fuel production and its use in the vehicles. Additionally, this chapter is based on current operation of the electrical grid in Ontario including planned improvements for generation, the emission calculations for electricity are based on the current mix of generation used in Ontario. This work includes 'cradle-to-grave' analysis of alternative fuels used in vehicles pertaining to the areas of climate change and urban air pollution. This chapter establishes a baseline requirement of hydrogen generation for 1000 fuel cell vehicles persisting in the eco-industrial integration scenarios in later chapters.

Chapter 4 continues the emphasis on emission reductions from Chapter 3 but applies the combined analysis of economics and emissions to an optimization framework of an eco-industrial park. This chapter attempts to connect the benefits from reduced transportation emissions to the chemical manufacturing industry in order to reduce the emissions from a group of chemical production facilities while providing the fueling needs for a limited number of fuel cell vehicles, the benefits of which were shown in Chapter 3 in terms of reduced airborne emissions. The modeling framework for this analysis is presented as a linear programming (LP) model for a group of facilities with the end goal of improving profitability while reducing life-cycle emissions for the end products. The case study of plants explored in this chapter yield hydrogen, ammonia and urea with reduced emissions when compared to conventional production. The network of facilities to be considered in this work includes syngas generation (by coal or biomass gasification or by steam-methane reforming of natural gas), carbon capture, carbon sequestration, combined heat and power production, pressure-swing adsorption as well as the manufacture of ammonia and urea. This analysis is also complete in the context of a potential hydrogen economy where hydrogen becomes a valuable product to support the transportation network. Two of the primary benefits connecting this work with the work in Chapter 3 are the reduction in emissions by operating hydrogen fuel-cell vehicles and the reduction in transportation distance for the feedstock materials used by the production facilities. The CPLEX solver within GAMS is utilized for solving this LP and utilizes a simplex-based algorithm to determine a global optimum for this model. This work is a 'cradle-to-gate' assessment for the facilities mentioned and as such, it is assumed that any usage beyond the network boundary will have an emissions profile identical to current usage, thus offering no benefit beyond this boundary. Benefits from alternative usages beyond the network boundary are described in Chapter 3 for hydrogen and electricity utilized as transportation fuels and exhibit the benefits of this application.

The work in Chapter 5 expands the modeling framework from the LP model discussed in Chapter 4 by including integer and binary constraints such as decisions for existence of facilities and connections. The mixed-integer linear programming (MILP) model that results from this expansion includes the ability to assess multiple hydrocarbon fuel sources (specifically biomass, coal and natural gas) for manufacturing the chemical exports from the eco-industrial park. The expansion of the modeling efforts to the MILP domain was considered necessary as the LP model was limited in its practicality for large industrial systems. This work contributes to the goal of assessing the economic and environmental reductions which can be experienced by operating facilities in an interconnected network of chemical plants and furthers the quantification of these benefits. By analyzing decisions with added modeling flexibility of binary and integer constraints, the model provides additional realistic constraints on the construction and operation of an eco-industrial network. The CPLEX solver within GAMS is again implemented to provide a global optimum for this model, though the CPLEX algorithm for solving MILP models is based on branch-and-bound techniques to accommodate the integer and binary portions of the model combined with the simplex method for solving the constituent linear problems.

Chapter 6 takes the analysis from Chapters 4 and 5 to the next level of modeling complexity by incorporating non-linear constraints into the MILP model. This mixed-integer non-linear programming (MINLP) model is a much more complex optimization problem and requires alternative solver algorithms and computational resources when compared to an MILP or LP model. This step toward MINLP was necessary as the additional complexity required from the constraints could not be forced into a linear form as it was previously with the LP and MILP models. The goals for this framework were to create the most comprehensive optimization model with the same case study facilities explored in Chapter 5 but utilizing a more sophisticated model in an attempt to provide additional accuracy and realism to the model. The models presented in Chapters 4 and 5 were completely redeveloped with the goal of a relativistic objective function and increased realism for constraints placed on the optimization. The framework developed for the MINLP model serves to investigate the benefits of operating chemical facilities under stringent economic and financial constraints. The model in this chapter also applies the most conservative estimates on the benefits of the eco-industrial park case study and further investigates the relationship between economics and reduction of environmental pollutants. The BARON solver in GAMS is used to solve the MINLP model in this chapter and provides a global optimum under general bounding assumptions for the model variables. The BARON algorithm implements a deterministic solution approach and draws upon additional MILP and NLP solvers making use of a branch-and-bound approach to return a global optimum.

Chapters 4, 5 and 6 assess environmental benefits from reducing ‘cradle-to-gate’ emissions with the assumption that emissions beyond the network boundary will be equivalent to those from conventional production. Chapter 3 explores the impacts of the entire life-cycle of alternative fuels in vehicle applications on both urban and gross air emissions. The environmental metrics used in this thesis are reflective of major environmental concerns such as climate change, acidification and urban air pollution. The form of the objective function utilized in Chapters 4, 5 and 6 can be used by policy-makers to influence decisions in facility siting, design, construction as well as to work with corporations to achieve a result that reduces environmental impact from operations with marginal economic impact. This allows for a collaborative relationship between industry and regulators to assure a net-benefits solution for all participants.

Chapter 7 draws upon the work completed in Chapters 3 - 6 and summarizes the conclusions of this work, the contributions and significance of the research and recommendations for implementation of the results and methods explored herein.

The progression through each of the modeling types exhibits the benefits and limitations of each methodology. These methods are assessed for their usefulness in modeling EINs and express how each methodolgy can provide specific, explicit results. The objective function is modified through each model developed for the eco-park under consideration and expresses the balanced approach between economics and emissions explored throughout this work. The specific examples shown through the model formulation are for the proposed EIN, yet the generalized modeling framework developed by this work can be applied across a broad range of integration scenarios for many types of facilities and situations. The introduction of additional modeling complexity to the formulation makes the

MINLP a complex, yet valuable tool in assessing potential benefits from operating many facilities within an eco-park network compared to stand-alone facilities.

The methodologies developed herein are powerful implementations of facility optimization that could be used by policy-makers to suggest approaches toward industrial development and setting realistic goals for reduction of virgin material usage and wasted energy. The same framework can be applied by industial entities to achieve such policy goals such as a reduction in environmental pollutants while improving on the business goals of profitability and corporate sustainability.

Chapter 2

Background

This chapter provides background on the concepts and methodologies used throughout this research. This chapter contains background information on eco-industrial networks, analysis tools such as life-cycle assessment, the hydrogen economy, modeling methods and programs used in this work and environmental and economic metrics.

2.1 Eco-park Concepts

Eco-park concepts are several decades old and rely on collaboration from progressive facility managers in order to implement a symbiotic strategy for responsible and sustainable chemical processing. Examples of these concepts are available in several European countries and are also found sparingly throughout North America and other parts of the world, although the major drivers for these collaborative efforts are typically economic.

In this work, a number of industial chemical manufacturing and energy conversion facilities are envisioned as working cooperatively to share outputs, emissions and wastes within a network in order to improve profitability and overall environmental impact. Such a network of the facilities can be termed an 'eco-park', eco-industrial park (EIP) or eco-industrial network (EIN). Generally, materials and energy are exchanged between eco-park partners such as:

- electricity;
- heat;
- fuel gases such as natural gas or hydrogen;
- base organic chemicals such as methane, methanol, DME, ethylene, benzene, organic chlorides, solvents, etc.;
- base inorganic chemicals such as sulphuric acid, inorganic chlorides, hydrogen, hydroxides, etc.; and finally,
- water and waste.

An eco-park will ultimately seek to improve profitability of the network as a whole. Key to the success of such a network is that the network profitability is apportioned appropriately among the various facilities such that each facility recognizes the benefit of participation in the EIN. Regulators, as the agent for society, can encourage the formation of an ecopark through regulation, emission costs, solid waste disposal fees, etc. Regulators can use incentives or fees (i.e., fees, taxes, fines, levies, etc.) in order to achieve the desirable outcomes. Especially in the case in which fees such as environmental levies or taxes are to be avoided, eco-park principles can be applied to reduce the number or severity of these measures.

One major focus of an eco-park should be the recovery of waste heat and allocation of heating. Practically every chemical processing plant and almost all buildings in Canada require heating, and often produce or consume significant amounts of process heat. Each chemical plant has its own reservoir to discharge waste heat, which results in massive energy waste in each facility. If locations were close enough, heat and steam supplies could be shared between facilities and would result in massive operational savings by optimizing the design of the system [1]. The operational savings of this plan are not the sole factor on which an eco-industrial system is based. In this analysis, the eco-park is assumed to be in the developmental and/or planning stage, heat/steam supply and distribution can be incorporated directly into the design of each respective plant. This is not to suggest that this type of arrangement could not be constructed as a retrofit, merely that it would reduce capital costs if done during the initial build. In fact, there have been several instances of retrofit heat/steam handling cooperation, most recently in parts of Alberta near Edmonton which is the oil-refining hub of Western Canada, including the oil sands refining processes. Heat distribution is also one of the key factors in the Kalundborg network (discussed in section 2.1.1), where a single facility provided heating and power for a number of neighbouring sites. Waste treatment and remediation is another obvious benefit of developing an eco-park. A large majority of chemical plants have waste storage facilities and remediation plans specific to the particular process. The cost of construction and remediation typically follows a 'base cost plus' pricing scheme having a fixed cost for equipment rental and design, with a comparatively smaller incremental sum depending on the size of the site to be constructed/remedied. Thus, pooling the industrial waste between several parties would significantly reduce the economic burden on each individual facility. Also, due to strict environmental regulations being enacted, remediation of these sites must be evaluated prior to any preparation of the site for construction and must be budgeted for in advance such that funds are available to recover the natural ecology of the land. Again, distributing this burden among several parties would greatly reduce the financial burden on any particular party.

Reduction of waste is a major focal point for many eco-park plans and exchanging co-products between facilities is one method, and the most intuitive, for accomplishing an overall reduction in eco-park waste [2, 3]. Reduction of industrial waste was the primary premise behind the Kalundborg cooperative [4, 5, 6]. The oil refinery acted as the central hub for the system, and its waste streams were used by neighbouring facilities that also took part in this relationship. Waste sulphur, normally a major environmental constraint in a refinery, was used to make gypsum in a nearby facility where it was processed into drywall. Waste gas and water from the refinery were used in the afore-mentioned power plant as fuel gas and cooling water. Excess steam from the refinery and power station were used for heating in all of the nearby buildings including several greenhouse installations. The waste gas from the refinery was not sufficient to fuel the entire power station, yet the coal fly ash from the adjacent power station was captured and processed into cement in a nearby facility. Each addition to the network made it more economical and more environmentally attractive for the citizens of Kalundborg. Significant cost savings were experienced by each partner in the cooperative; thus, it was feasible to implement without losing profits. Developing initiatives without incentive for industrial partners have a very small chance of being supported by large industries, as most will not sacrifice profit to improve the environment without clear benefit to the shareholders [7].

2.1.1 Examples of Eco-parks

Kalundborg, Denmark is the most recognized eco-park as it was one of the first applications of eco-park concepts that was developed and studied [4, 5, 6]. The network began almost accidentally as the business operators suggested that it might simply make sense to start conducting business in a different manner. This example of eco-park concepts invigorated the search for other potentially symbiotic sites and has served to show the potential benefits of industrial collaboration.

Kalundborg has had incredible success with its industrial operations and has increased profits dramatically among its industrial stakeholders. As wasted resources are inherently uneconomical, the Kalundborg network manages to save 1 million cubic meters of ground water each year, reduce annual oil consumption by 20 000 tonnes and has created markets and alternate uses for countless other normally wasted materials [5]. These massive reductions in waste, in addition to being incredibly beneficial for the environment, have also significantly boosted the profits of each organization involved. Economic and environmental benefits must be exhibited in order for industry to have renewed interest in the concepts of EINs. This information is available [8, 9, 10]yet the lack of published examples throughout the industrialized regions of North America are proof that the information is not known or there is some barrier to implementing these techniques. Jacobsen et al. [11] presents concepts for mobilizing industrial symbiosis and sustainability for a variety of industrial settings.

North American examples are considerably fewer than those in Europe as eco-park concepts have yet to root themselves amongst business owners and leaders. As mentioned in Section 2.1.3, most of the work in the area of North American eco-parks has been limited to the petrochemical industry as it is one of the most prolific and centralized industries available. As many of the co-products from organic chemical manufacturing can be reused or reprocessed in a refinery, applying eco-park concepts to these processes tends to be very advantageous for the industries involved. Although many of the proposed networks have yet to become fully functional, the opportunities are present and academic studies have shown that there may be great benefit in their operation [12, 9].

An additional example appears in the Brownsville/Matamoros park which is a joint project between industry in Mexico and the United States with the major products of cardboard, plastics, automotive products, oil and solvents. Examples elsewhere in the world are limited due to challenges presented by developing nations [7]. A proposal of a network in Rio de Janeiro, Brazil exhibits the fact that this type of network is possible in developing nations and that these areas may benefit the most from such an integration [13].

2.1.2 Academic Studies of Eco-parks

The concept of eco-parks has been studied in the academic setting as a practical way for industry to mimic the symbiotic effects of the natural world. Studies in this field have often concentrated on the petrochemical industry as there are many possibilities for exchanging co-products between refining facilities and manufacturers of plastics, paints, solvents, propellants and others. The theory behind eco-parks is an overall conservation of materials and energy which has proven to be of interest in many fields of study in the academic setting. While some studies have quantified economic benefits from these industrial integrations, many produce qualitative analysis of the possibilities without empirical assessment. The analysis discussed in this work serves to provide a quantitative approach to calculate the environmental and economic benefits from integrating industrial facilities to form an eco-park. This method can provide empirical evidence to support these cooperative initiatives from both a financial and environmental position. Previous academic pursuits in this area have failed to encompass all of these aspects using one technique [14, 15, 16] but do provide insight into the potential ecological and economic benefits of integration which are useful when attempting to create metrics for optimization as described in section 2.5. The academic realm of planning and evaluating the performance of eco-parks has a commonality in the fact that it is a diverse field and requires a multidisciplinary approach in order to properly assess the arrangement and operation of networked facilities [17].

Côté et al. [18] discusses, on a qualitative level, how eco-parks may be designed and give several examples of projects being considered but no mention of any quantitative evidence or optimal design to maximize profits or emission reductions. Côté et al. [19] also discusses environmental assessment of small enterprises in Canada, choosing to develop a new system of metrics but with limited results presented of the analysis.

Monteiro et al. [20] explores two routes for producing dimethyl carbonate (DMC) via ethylene oxide or urea methanolysis but acknowledges the limits of attempting to optimize a system within the constraints of HYSYS. Furthermore, the analysis does not account for exchanges between this process and others, as an eco-park optimization would. Similar ideas can be found elsewhere [21] but lack the supporting optimization complexity to fully support decision-making.

2.1.3 Industrial Examples of Eco-parks

Industrial applications of eco-park concepts can be seen to some extent in Eurasia, Oceania and, to a lesser degree, in North America [7]. Investigations into applying eco-park concepts in developing countries has not been ignored and may prove to be one of the most cost-effective methods for industrializing these nations [22]. The European eco-park concepts depend heavily on co-location and process similarities while most published eco-parks in North America are purely petrochemical. An excellent example of this is a thesis from Louisiana State University on the integration of facilities located in the Louisiana petrochemical corridor [23]. Similar concepts can be seen in areas of oil production and importation. Non-petrochemical eco-parks have been developed to a lesser extent worldwide but have the potential to conserve vast amounts of fossil fuels, raw materials and energy.

Networks of companies were formed in the late 1990s and early 2000s due to the interest in industrial cooperation for the benefits that may be realized from such symbiotic relationships. One example of this is the Canadian Eco-Industrial Network (CEIN) which was developed in 2000 but has not been active since 2005. The legal implications of commodity trading between co-located facilities is a barrier to implementation as failure to deliver products in a timely manner and in the specified quantities can lead to operational upsets within any chemical facility. Although applications of these principles can be seen, it is generally simpler for facilities to run as individual cells instead of as a network of processes for the ease of operations, legality and communications. European facilities, however, have shown that integration can lead to financial benefits which have drawn more interest in the industrial community. EIN development has drawn much more interest from the academic realm than it has in the industrial setting. In North America, one of the most major barriers to implementation is the shipping of products between facilities. Gibbs et al. [24] presents the planning of eco-parks within North America and observes some critical points about this practice. Evaluating eco-parks can also have unique issues between countries, eco-parks and facilities [12, 25].

2.1.4 Geographical Differences in the Application of Eco-parks

The North American climate for eco-parks is somewhat more limited by geography than are eco-parks in Europe due to the vast distances between producing facilities. As Canada and the United States are both very large countries with populations spread across thousands of kilometres, integration of chemical processing facilities can be financially challenging on a simple basis of shipping costs and constraints. The location of facilities is a related topic, typically with a seperate optimization to determine the location of various plants with respect to other facilities and proximity to natural resources [26]. North American rail networks are also less developed than their European counterparts, leading to increased dependence on roadway transportation with other considerations to pipelining and transportation by ocean. Marine transportation is limited to port cities while pipelining is intrusive to the land and is limited to fluid applications. The effects of each type of shipping can be assessed in terms of cost and its impact on the air, water and land. This transportation cost within an eco-park, both economic and environmental, must also be weighed with the associated costs of production.

2.2 Hydrogen Economy

The 'hydrogen economy' is considered to be the next generation in energy infrastructure, in which hydrogen is used as an energy vector for many applications which currently employ fossil fuels. Hydrogen is easily stored and can be combusted or utilized in a fuel cell to provide electricity. Hydrogen also has the benefit of flexible production using a variety of fuel sources such as hydrocarbon reforming or water electrolysis. The only product of hydrogen combustion is water as is also the case for using hydrogen in a fuel cell; thus, it is considered to be a cleaner fuel than many alternative energy vectors. For motive power, hydrogen can be employed in a combustion engine or fuel cell within a vehicle to provide power to the engine with the exhaust composed of simple water vapour. Many major vehicle manufactures will commence marketing a fuel cell vehicle in 2015. In electricity systems that desire peak-shaving, load-leveling or peak-shifting, hydrogen can be produced in off-peak times and stored to be utilized during high-demand periods to produce electricity. This method of energy storage is particularly useful in regions such as Ontario, Canada where there is a high baseline production of electricity from carbon-free nuclear plants, allowing for hydrogen production by electrolysis during low-demand periods. The concept of 'power to gas' in which hydrogen is produced and then distributed and stored within the existing natural gas infrastructure is also explored in the literature [27].The hydrogen economy also has several other benefits, one of the primary ones being to encourage energy independence in countries that currently rely on imports of fossil fuel from unstable economies to meet the demand for energy. Additional social and political reasoning for a transition to the hydrogen economy are discussed in the literature [28, 29, 30], this work is focused on operation within the current infrastructure but connects exceptionally well to a scenario of the hydrogen economy.

2.3 Analysis Tools

2.3.1 Life Cycle Assessment

Key to the evaluation of the performance of industrial facilities is the concept of life cycle assessment. Life-cycle assessment (LCA) is a methodology developed to account for the impacts of a product, process or service over its entire lifetime from the initial extraction of virgin materials to the final disposition into the air, water or land.

LCA is defined by the ISO 14040 standard in the following way: "LCA is a technique for assessing the environmental aspects and potential impacts associated with producing a product" [31]. As such, LCA can thus be seen as a tool that is to be used as a part of an environmental management system (EMS) in order to improve the quality of the practices within a company with respect to sustainable development and the environment. LCA can also be referred to as a "Cradle-to-Grave" assessment as it incorporates the environmental effects from the initial stages of extraction to its final disposition.

In this research, it is desired to apply LCA metrics and methods to optimize a system of production processes in order to optimize the materials and energy usage. One typical use for LCA is to compare alternative processes to determine which has the least life cycle impact on the environment [32, 21]; therefore, this methodology is very much in agreement with life cycle principles and applications.

2.3.1.1 History of LCA

The first recorded usage of an LCA-like methodology was by Harold Smith in 1963 for the World Energy Conference of that year. Since that time, LCA has seen large shifts in popularity due to changing economies and societal demands. One of these shifts was experienced during the economic turmoil that followed the crash of the oil markets in the 1980s at which point public and private concerns were more focused on recovering from the economic shock. When the “green shift”' began in the early 1990s, LCA again became favourable and started to be incorporated as a key tool and strategy in management systems. Standardization of LCA began in the late eighties and early nineties [33] and was mainly implemented to curb rampant misuse of the methodology leading to incorrect advertising statements and social views of companies. The first workshop on LCA was held in Smugglers Notch, Vermont and was organized by the Society of Environmental Toxicology and Chemistry (SETAC). The concepts of the life-cycle inventory, impact analysis and improvement analysis were founded during this workshop. A study on milk packaging in Europe in 1990 showed the necessity of standardizing the LCA methodology as the different methodologies led to very different results for the study [34]. The varying studies showed exhorbitant variation in pollution and solid waste production per container produced, causing LCA to be criticized as an ineffective method to account for waste. The weaknesses of the varying studies were identified and specifically addressed in order to achieve standardized methods which act as a base for past, current and future assessments.

2.3.1.2 Uses of LCA

A company may pursue life-cycle analysis and management within its operations or product management for a number of reasons. The most common reason for this is that the company is using an environmental management system and that LCA is simply a tool within this management system [4]. As such, it provides measurable metrics in order to demonstrate improvement toward objectives and targets; thus, it integrates very well with the process and policies already in place. If a company is not already using an EMS, they may choose to use LCA or a life-cycle mentality as a way of evaluating their environmental impacts on a purely altruistic basis; typically, though, there is an end goal or benefit in mind and that is to demonstrate environmental stewardship to society for the associated public and employee relations benefits [35]. One such benefit of using LCA is that the company may be able to use the results as part of a cost/benefit analysis, where the environmental impacts are weighed as benefits against the cost of a certain project, product or process. Using LCA also allows companies to advertize and interact with potential consumers by showing their commitment to life-cycle thinking and to the environment. Finally, LCA is a practical tool to measure improvement of materials and energy usage and such an improvement contributes to the profitability of the operation as a whole. Reduced costs can be realized in a number of areas such as:

- reduced material costs;
- reduced energy costs;
- reduced hazardous material management costs and hazardous waste disposal costs;
- reduced solid waste tipping fees;
- reduced waste and emission treatment costs;
- lower lost production time associated with fugitive releases and plant shutdowns;

- better regulator tracking;
- reduced fines and fees associated with environmental incidents; and,
- better relations with regulators and insurance providers.

2.3.1.3 LCA Process — Establishing a Baseline

Before implementing a change to a product or process and evaluating it from a life-cycle perspective, it is generally advised to conduct a preliminary study in which the baseline for the current process is established. This is an important step since the improvement may cause the emissions from the plant under consideration to decrease but may increase the overall impact on the environment due to upstream processing. One example of this would be to consider a new catalyst which would increase the single-pass conversion from 80% to 90% but its production requires 50% more energy and emits large amounts of toxic agents to the environment. Because LCA encompasses the impacts from all stages of manufacture, adoption of the new catalyst can be assessed based on its full impact throughout the supply chain.

2.3.1.4 Legislated Commitments

Currently, LCA is not required by specific legislation; however, emissions regulations, especially in the developed nations, are becoming increasingly stringent as the technology is developed to curb these emissions and society demands that industry consider impacts on the environment and potential impacts to the health of humans. Obeying policy is thus an atypical reason for applying LCA methodology to date and thus LCA completed to date would be by company mandate rather than regulator mandate.

2.3.2 Typical Life Cycle

The areas of interest for LCA are generally from the extraction of raw materials to the production of the intended product and the associated product disposal into the environment via air, water or land. The process or product under consideration can generally be visualized as undergoing the steps shown in Figure 2.1. This figure demonstrates that raw materials and energy are inputs into the product, these materials are processed using energy and finally are recycled or disposed of as waste. The outputs from each step are emissions to air, land and water as well as the desired product and its associated co-products. Figure 2.1 illustrates that upon extracting the raw materials from the environment, these raw materials are processed into a final product. Typically, this processing includes several steps of manufacturing before the eventual product is created. This upstream manufacturing generally includes several steps of bulk processing which produce bulk feedstock for many different applications. These bulk processors commonly produce co-products in addition to the desired material as basic feedstock for other processing facilities; therefore, allocation of emissions in these instances is extremely important and must be considered appropriately.

Once the appropriate feedstock has been created, it is processed into the finished product within the facility in question. Following its manufacture, the product is packaged and then transported to the appropriate customer as required. The product is then used, re-used and maintained until the user deems it time to retire the product and leads the product to its final disposition. The final disposition of a product should not be treated as being synonymous with land-filling, as there are many options for disposition including recycling and incineration in addition to the option of land-filling. LCA is an integral part of an environmental management system (EMS) as a tool that can be used to evaluate options and future projects in terms of environmental/sustainability metrics, can be included as part of a cost/benefit analysis and can also be used to identify bottlenecks within a

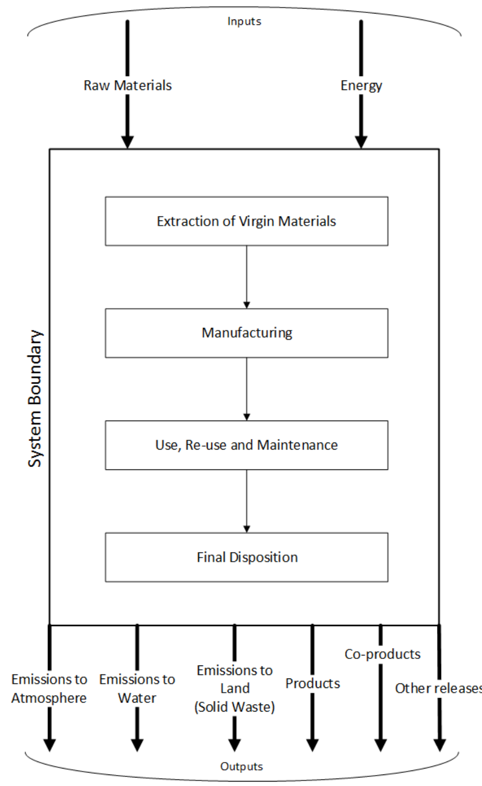

Figure 2.1: Fundamentals of a product life cycle, adapted from ISO Standards [31]

system that currently exists.

2.3.2.1 Typical LCA

Figure 2.2 shows the steps to completing an LCA. The first stage is to determine the scope of the project which includes identifying project goals, study specificity, methods of data collection and timeline. The definition and scoping steps are typically reviewed as the project progresses to ensure that the goals are being followed and that any deviations must be noted and are still in accordance with achieving the goals of the assessment.

The second step of LCA, inventory, is generally the most time-consuming portion of

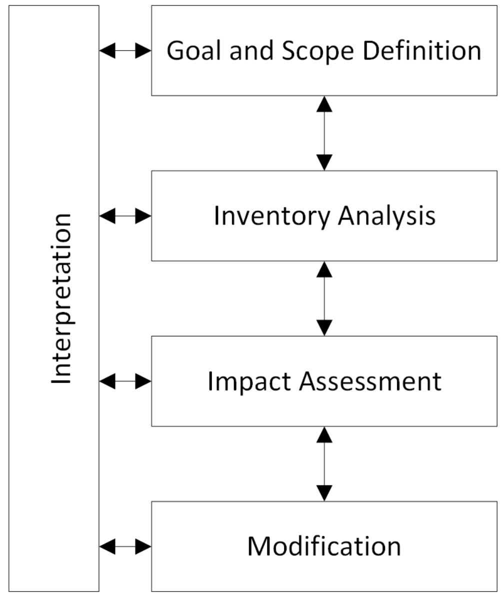

Figure 2.2: LCA Framework, adapted from [31]

an LCA and tends to also be the most difficult step in a life-cycle study. The participants need to collect all of the appropriate data in this step after revisiting the methods of data collection, boundaries, specificity and relevance.

Third, the data is analyzed under life cycle impact assessment procedures. The information collected during the inventory is evaluated systematically and it is determined how each impact category, such as climate change or ozone depletion, will be affected by the product or process emissions. These impact categories are defined in the goal definition and scoping and can reflect any of the concerns that are brought forward regarding potential impacts of a product or process. These impact categories are ranked according to their importance in the study and thus the full effects of production can be assessed according to these impacts.

The final block of the LCA framework is interpretation and monitoring. This portion of

LCA serves to provide checks for each step of the analysis in order to ensure the goals are being met and that the analysis is being conducted according to the proper procedures. The evaluation of process modifications is also carried out after the changes have been made. The modifications are evaluated based on the expected performance and the actual results achieved by collecting additional data to monitor the success of the change.

2.3.2.2 LCA in this Work

LCA is referred to as a major part of this work as the goal is to evaluate the viability of eco-parks based on life-cycle principles [4]. Process improvements that simply allocate product emissions to another processor cannot be considered as benefits for the process. The cost, energy and emissions associated with removing an impurity, for example, must be done at some point along the production pathway. If one facility in the process has observed that the impurity does not affect their operation, they may choose to simply pass the issue to the recipient of that chemical who must then remove the impurity as it can damage a critical system. By ceasing the removal of the impurity, the former company may show results that their product now uses less energy and is less harmful to the environment because of the decreased emissions from their plant. In reality, the emissions have still been produced and only the location of these emissions has changed. Evaluating the entire eco-park on LCA principles exhibits the consequences for all of the network facilities while avoiding the superficial appearance of reduced emissions where this is not the case.

2.4 Modeling Programs and Methodologies

The modeling in this work is completed using both optimization and deterministic calculation packages. Optimization approaches rely on iterative optimization algorithms to reduce and solve a system of equations with a defined objective and constraints. This approach is used when high variability exists in many decision variables but there is a defined objective that should be reached such as a least-cost or maximum-return approach. For optimization to provide meaningful results, the program must have many degrees of freedom in order to have license for altering the decision variables in order to find the best solution. Contrary to deterministic solutions to systems of equations, there must be more undefined variables in the program than there are independent equations. Excessive constraints placed on an optimization model gives rise to trivial solutions or an infeasible problem. Although there are many types of optimization problem, three of the most common are linear programming (LP), mixed-integer linear programming (MILP) and mixed-integer non-linear programming (MINLP).

Linear programming methods rely on linearization techniques to convert non-linear objectives and constraints into linear ones which can be handled by the LP solver algorithm. This type of optimization is the most widely-studied and forms the basis for other types of optimization. The solution of an LP can be computed very quickly and even very large, complex or inefficient programs can be solved using a modest amount of computing power.

MILP problems stem from the foundation of LP formulations but are allowed to include integer and binary components. This type of program is a powerful addition to the LP formulations as it allows programmers to include discrete decisions within the model. Many complex problems can be reduced to MILP formulations by applying techniques developed specifically for this purpose. The MILP can be applied to a wider array or problems than an LP and the solution algorithms are similar to those used for LP programs. Generally, the algorithms for MILP solutions consist of solving many LP sub-problems in order to find a feasible solution within the MILP super-problem.

MINLP formulations are another step in complexity from the MILP but are becoming increasingly popular with the rise of inexpensive computational power. Attempts to force non-linear constraints into linearity have been a focus of study for many years as the computational expense associated with solving MINLP problems was high. With the increase in computing power, solutions to large MINLP problems are becoming possible and more widely-used. Though still computationally-intensive, MINLP optimizations are very powerful and can be used to model even more complex systems than the MILP. Constraints that cannot be linearized can be included in an MINLP model and thus this type of optimization can be applied to increasingly complex systems. Algorithms for solving MINLP formulations are not as well-studied as those for LP or MILP problems as they are less common and considerably more complex problems to solve. The basis for finding solutions is similar in relation to the MILP algorithms as the MILP algorithms are to the LP solvers. Generally, the MINLP solver uses many linear and non-linear solutions with feasible integer solutions encompassed within the larger MINLP in order to bound the search space and use alternative methods for decisions on which sub-problem to solve in the next iteration.

Deterministic calculations involve utilizing known quantities and relations to provide the solution to a problem with known inputs. Most popular calculation packages are examples of this type. Deterministic calculations rely on known quantities and will return a solution that may not be optimal. These calculations are used in situations where more variables are specific or well-defined in order to quantify values for an unknown.

2.4.1 Software Used

The packages for optimization discussed herein are 'A Mathematical Programming Language' (AMPL) and 'General Algebraic Modeling System' (GAMS). AMPL was developed at Bell Laboratories and its development is currently under the direction of AMPL Optimization LLC. AMPL is a popular package for optimization used in both industry and academia for linear and non-linear problems with both continuous and integer variables. AMPL supports a variety of architectures common to deterministic programming packages but are omitted from many optimization softwares such as handling looping commands and case-specific declarations.

GAMS is another optimization package used in this work and is applied for the analysis of the eco-park scenarios. GAMS is created and supported by the GAMS Development Corporation and is designed for modeling and solving complex, large-scale models. Typically, GAMS is used for linear, non-linear and mixed-integer optimization problems but also includes the capability for other model types. GAMS incorporates many solvers created by research institutions around the world to create a broad-based architecture that can be applied to many realistic situations.

Deterministic calculation packages used for this work include many well-known tools such as Microsoft Excel and MATLAB but also include SimaPro, a life-cycle assessment (LCA) tool, and GREET, a tool for assessing impacts of vehicles and fuels. SimaPro is developed by PRé Consultants and includes many LCA databases from around the world in order to provide a comprehensive analysis of life-cycle impacts for many products and processes.

GREET is a calculation tool based in Microsoft Excel which is developed by the US Department of Energy at Argonne National Laboratory. GREET is a specific life-cycle assessment tool for analyzing the impacts and emissions from vehicles and vehicle fuels. There are two series' of GREET developed to date, the first series assesses the impact of vehicle fuels while the second series analyzes the impact of the physical vehicles including the materials and energy of construction etc. For the analysis herein, only the first series of GREET was utilized, specifically, version 1.8b.

2.5 Environmental Metrics

This research also contributes to society by developing a method for evaluating industrial relationships and by assisting in the planning of new facilities. This will benefit citizens as the optimization will take environmental factors into account and will attempt to minimize the overall waste from facilities that could otherwise affect living conditions in areas surrounding these facilities. The impacts on air, water and land can all be considered and the importance of the environment is taken into account in addition to the contribution to the economic performance of industrial processes. If construction of a new chemical facility can be made more economically feasible by its integration with other processes in the region, construction and factory workers would also be required to build and operate these facilities. This would contribute to the economic stability in the region in addition to causing a decline in unemployment rates. As such, a number of environmental metrics will be used to evaluate the performance of the eco-park scenarios compared to similar independently-operated facilities.

2.5.1 Climate Change

The threat of climate change from anthropogenic sources of greenhouse gases (GHGs) has been a source of environmental and political debate for many years. Public demands on policy-makers are forcing governments to consider energy supplies from more renewable sources and that regulations be placed on companies who are contributing to an increase in the CO_2 content in the atmosphere, as CO_2 emissions are the principle contributor to the enhanced greenhouse effect contributing to climate change. As such, CO_2 is used as the reference metric for greenhouse gas emissions from any source. One of the benefits of eco-parks is that efficiency in energy use leads to a reduction in GHG emissions. This reduction is one of the focal points of recent proposals for eco-parks as it is a burgeoning topic in the public realm of environmental stewardship.

2.5.2 Air Pollution

Air pollution has been a subject of concern for health officials in many major cities, including Toronto, Ontario, Canada. One estimate of the number of fatalities due to air pollution in Toronto claims that 1700 deaths per year are attributable to air pollution [36]. The combination of light, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) produces ground-level ozone (e.g., photochemical smog) which is considered to be a major contributor to air pollution and premature death. By reducing NO_x emissions and centralizing other emissions to a locale removed from urban centres, such as Toronto, eco-parks can be a factor in reducing these fatalities.

2.5.3 Ozone Depletion

Although not particularly pertinent in this study, ozone depletion became a major concern several decades ago as chloro-flouro-carbons (CFCs) were found to deplete the ozone in the atmosphere, leading to an increase in ultraviolet light striking the surface of the Earth which had potentially disastrous consequesnces for humans. Although ozone-depleting substances are not manufactured in the proposed network, this is a common impact category in life-cycle assessments to ensure that additional production of these substances is not incurred. Ammonia is also being studied as a potential refrigerant as it does not deplete ozone and is capable of operating within a refrigeration cycle which would offset the usage of CFCs.

2.5.4 Acid Rain

Oxides of sulphur and nitrogen (SO_x and NO_x, respectively) are considered to be the major culprits behind acidification and acid rain. These emissions can be produced in a number of chemical facilities but tend to be found in much larger quantities as emissions from electricity generation stations, specifically fossil fuel plants. By capturing emissions from the power generation in this network, it is expected that gases impacting acidification will be reduced; additionally, biomass can be used as a fuel source for gasification and should thus emit less SO_x than would the equivalent electricity production from coal or oil.

2.5.5 Resource Conservation

One of the major impacts that an eco-park can have is the ability of this arrangement to conserve resources. In the case of EINs, energy feedstocks are conserved by utilizing heating and cooling efficiently but also by using alternative fuel sources to replace fossil fuel energy. Other resources are conserved by appropriately using the products and co-products of other eco-park processes instead of requiring extensive production, packaging and shipping of feedstock materials.

2.5.6 Habitat Destruction and Fragmentation

Localizing many facilities in close proximity would reduce the amount of deforestation and habitat destruction to be absorbed by local wildlife. An arrangement of disparate plants and shipping routes would only endanger wildlife by fragmenting their habitats and may lead to animal management issues as can be the case in many rural climates. This can be seen as efficient land use and the economies of scale associated with land-clearing ventures would also serve to reduce the capital required for start-up operations.

2.5.7 Solid Waste

Another central idea to the vision of eco-parks is efficiency in terms of material usage and the percentage of a material that is used in final products. Although a traditional plant may only utilize 70% of a feedstock in its product, eco-park collaboration allows the unused portion to be integrated into other products or processes and may increase the material utilization of the feedstock to almost 100%. Although solid waste is typically unavoidable, the ratio of solid waste to material input can be greatly reduced by using other portions of the feedstock for other applications [3].

2.6 Financial Metrics

While environmental metrics are becoming increasingly important to business leaders, companies are still responsible to their shareholders to show solid and sustainable economic performance. The use of a dual-objective function in this work allows for profitability to also be considered in the optimization and leads to a solution that proves to be environmentally responsible as well as being economically feasible. This research is intended to reinvigorate discussions in the industrial sector regarding issues such as sustainability, process symbiosis and collaborative efforts.

The eco-park concept is synonymous with polygeneration, industrial symbiosis and the like. All of these terms are based upon the concept of a diverse group of industrial producers cooperating to achieve a common goal of cost-savings and/or reduced environmental impact. The literature has also shown that developing these eco-parks can very much be a driver for innovation and development of new technologies [37, 38]. The Dow Jones Sustainability index, DJSI, is an indicator used to manage investment funds based on sustainability metrics. The funds developed using this index have shown solid growth since the inception of the program and is an indicator that sustainability within an organization can have significant impacts on profitability. Though the index also focuses on business practices and management styles, the overarching reality is that sustainability within a company yields financial performance results [39, 40].

2.7 Summary

This chapter explains the context in which this thesis is completed. Economics and environmental concerns are assessed in terms of life-cycle impacts within the domain of eco-industrial integration. Current literature concerning eco-industrial integration is primarily focused on either economic or environmental principles while neglecting the other; however, this work is unique in its assessment of both concerns as part of the objective function in an optimization model. In addition, quantifiable assessment of eco-industrial benefits is scarce as the majority of the work to this point has been primarily qualitative and lacking empirical support whereas this research is completely focused on the quantifiable benefits of eco-industrial integration.

Chapter 3

Air quality and environmental impacts of alternative vehicle technologies in Ontario, Canada

Chapter 3 is based on the previously published work "Air quality and environmental impacts of alternative vehicle technologies in Ontario, Canada" by Kantor et al. [41] as seen in the International Journal of Hydrogen Energy 35(10):5145-5153 and is reproduced with permission from the International Association of Hydrogen Energy. The thesis author's specific contributions to this paper were to develop the model of emission reduction potentials, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M. Fowler and Dr. A Elkamel, who are co-authors on the publication. Amirhossein Hajimiragha contributed with primary modeling of the electricity grid in the province of Ontario to determine the supportable penetration of alternative-fuel vehicles.

3.1 Introduction

The economies of the developed world are increasingly expanding to include "green" technologies and processes that take into account the social, environmental and economic consequences of business decisions. Western society, as a whole, is demanding that the products and services that it uses are less harmful to human health and to the environment. The transportation industry has made significant advances in fuel efficiency of the vehicle power trains and reduction of emissions in the past decades, but more is expected from this sector. As the price of gasoline rose in combination with this societal green shift, vehicle companies have commenced production of hybrid electric vehicles and other fuel-efficient vehicle types. The impetus of this shift was to supply consumers with vehicles that would decrease their ecological footprint as well as reduce the cost associated with purchasing fuel. In recent years, energy security has also become a driving force for change in vehicle fuel types. One of the societal concerns often overlooked is the impact of alternative-fuel vehicle usage on the air quality in the urban environment. It is the purpose of this chapter to assess the impact on air quality stemming from the operation of alternative-fuel vehicles in urban environments.

While several studies have based the comparison of alternative fuel vehicles (AFVs) on least-cost comparisons or other economic metrics [42, 43, 44, 45, 46], this study is purely focused on air quality. The effects on overall air quality are considered with respect to climate change potential and acidification. The special focus of this study is on urban air quality as it can be of major concern in large centres of population.

This chapter is concentrated on the province of Ontario and specifically the city of Toronto for two major reasons. The primary reason for this focal point is that Ontario represents the most highly-populated province in Canada which naturally leads to a higher level of concern from the increased number of individuals affected. The second reason is that urban air quality in Toronto is specifically an area of concern due to the estimated fatalities in this city. Traffic volumes in smaller cities would induce less concern as the concentration of urban air pollutants is directly proportional to the emissions from vehicle traffic. In addition, the data availability for Ontario in general and Toronto specifically is more widely available due to the concerns mentioned above and to the increased government resources attributed to gathering and analyzing this data.

The AFVs considered for this analysis are fuel cell vehicles (FCVs), plug-in hybrid electric vehicles (PHEVs) and fuel cell plug-in hybrid electric vehicles (FCPHEVs). The reason that these vehicle types were chosen is that they represent the most promising technologies for partially replacing fossil fuels in conventional vehicles. The transition of vehicle drive trains will begin with electrification of the vehicle drive train which allow for hybridization with electric motors. Hybrid electric vehicles (HEVs) can make modest gains in fuel efficiency mainly through the use of regenerative braking.

Once the drive train is completely electrified, the power train can be composed of a combination of batteries and some type of range extender technology (e.g., gasoline, diesel or fuel cell) to recharge the batteries onboard or provide electricity in parallel with the batteries [47]. This differs from the methodology considered by Thomas [48] as this work includes electric vehicles with range extenders and is not a comparison between FCVs and battery-electric vehicles (BEVs) considered by Thomas [48]. FCV in this case refers to compressed gaseous hydrogen as the technology is simpler and would likely be commercialized before options that use liquefied hydrogen as the fuel.

The FCPHEV would operate as a normal plug-in vehicle except that the energy supply for the charge-sustaining mode would be supplied by hydrogen fuel cells and not by gasoline. Other AFVs could also be compared on an emissions-per-distance basis but the interest of this chapter is on the impact that could be achieved through greater utilization of base-load electricity. As such, this study focuses on the near term transition technology of the PHEV which will use electricity to recharge batteries, and the FCV which uses base-load electricity to generate hydrogen. This analysis also represents the most promising near term technology transition to PHEV and the technology with the greatest potential for emissions reduction in the long term (FCV). The transition between the near-term adoption of PHEVs to the eventual transition to FCVs is examined by Suppes [30].

Thomas [49] states that FCVs are the only vehicle technology that has potential to virtually eliminate problems relating to urban air pollution. In this study, the effects of vehicles on urban air pollution are considered in a similar fashion to the work of Thomas [49]; however, the limitations of the Ontario's electricity grid are incorporated into the calculations. As such there are some notable differences in the environment, assumptions and potentially the results. Specifically, the Ontario grid makes much less use of coal as a generation source than the system Thomas [49] assumed, and greater use of nuclear and renewable (mainly hydroelectric) sources. Also, this study assumes that only surplus, base-load power is used for the transportation sector and thus represents a more feasible transition scenario for the transportation sector, as the electricity is available and under-utilized at this time.

The emissions from manufacturing the vehicles are not included as part of this study at this time and will be considered in future analyses; however, these types of vehicles also have increased emissions resulting from the manufacturing process would likely have less impact on urban air emissions and are therefore likely to be insignificant for this study where the main focal point is urban air quality. It should be noted that preliminary estimates for the production of both types of AFV considered in this study show that current production methods of traditional vehicle manufacturing emit less pollution and consume less energy than current methods of AFV production. These preliminary results would also be affected if centralized, large-scale production of AFVs were to exist on the same level as traditional vehicle manufacturing.

Developing infrastructure has been considered by several authors for Southern California [42, 43, 50] with special focus again on the economics of its development. It is assumed for this chapter that the distribution of hydrogen is available and thus the construction of a distribution network is not included in the results of this study.

3.1.1 Health Effects

Toronto Public Health estimates that the number of annual deaths in Toronto from urban air pollution is 1700 annually [51]. Estimates from the Ontario Medical Association (OMA) [52] and Health Canada [53] estimates the number of fatalities is 5 800 throughout Ontario. These deaths attributed to air pollution are most predominantly from lung diseases but air pollution also partakes in increasing the rate of atherosclerosis which is a contributor to heart disease and stroke [51].

The life cycle of hydrogen and its impacts have been studied previously [54, 55] in an attempt to characterize the effect of hydrogen production in terms of life-cycle emissions and sustainability. The use of hydrogen as a transportation fuel has also been considered but comparisons between hydrogen and other transportation fuels are only now being developed [56, 57]. It is important to consider hydrogen as a transportation fuel relative to other fuels in order to realize the consequences related to its mainstream adoption as a transportation fuel. PHEVs have also been studied from a life-cycle perspective by several authors [58] and this study is intended to compare these different types of AFV using a realistic basis of penetration and adoption.

Overall and urban emissions from AFVs were both considered to be important since overall emissions may affect climate change, acidification and other effects related to generalized emissions into the air. Urban emissions were considered specifically for the purposes of analyzing a possible decrease in fatalities caused by poor urban air quality. Photochemical smog is particularly an issue when considering the large volumes of traffic that occur during the rush-hour times in the greater Toronto area (GTA). Due to the location and specifics of Toronto, smog formation is limited by the amount of nitrogen oxides (NO_x) present. According to the empirical kinetic modeling approach to photochemical smog, a reduction in NO_x would yield a much more pronounced effect on the reduction of photochemical smog than would an even greater reduction in VOCs.

When considering urban air emissions, four major pollutants and one additional stressor are considered. Two classifications of particulate matter, one having diameter less than 10 microns (PM_{10}) and one of diameter less than 2.5 microns ($PM_{2.5}$), are generally considered to be the most harmful to human health and are also the eventual products from some other pollutants [59]. This small particulate matter is capable of penetrating deep into the human lung, causing irritation and is too minute to be rejected by natural human mechanisms [59]. VOCs and NO_x react with sunlight to form photochemical smog which is generally the largest contributor to urban air pollution in industrialized countries. Reducing the synthesis of photochemical smog is a top priority for individuals involved with addressing urban air quality in major cities. Athens, Greece and Beijing, China among several other cities that have made similar laws, institution of bi-daily driving was initiated in an attempt to partially curb the creation of photochemical smog. Sulfur oxides are the remaining stressor and are generally viewed to be more of a significant factor with regard to acidification than urban air pollution; nevertheless, it does contribute to producing aerosols and particulate matter in the troposphere.

3.2 Modeling and Results

3.2.1 Data Gathering and usage

The current GHG emissions in Canada are shown in Figure 3.1 [36]. It is important to note that these emissions are the overall emissions for Canada and are not specific to the urban air quality which is considered to be of major concern due to the annual fatalities exhibited in the GTA from air quality issues. For analysis of the impacts of AFVs, the total emissions can be compared to the current overall emissions in Ontario. The results of these comparisons can be realized as a percentage increase or decrease in each particular emission type. For pollution that is mainly of concern in the urban setting, emission levels are significantly harder to quantify due to the number of emission sites and the varied locations of these sites as well as their relative severity.

The generation mix considered in this research is the approximate Ontario generation mix shown in Figure 3.2. While this generation mix is expected to change, the relative levels of production from each source should remain consistent. The reduction in emissions in this study are calculated using this energy mix under normal conditions whereas the base-load contribution is used in the circumstances that base-load power can be assumed to be utilized (i.e., for hydrogen production). The current base-load generation mix is shown in Figure 3.3.

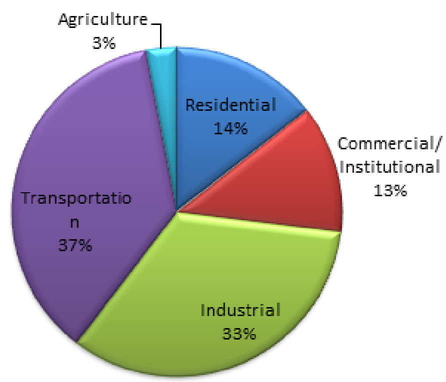

Figure 3.1: Canadian greenhouse gas emissions by sector [36]

3.2.2 Methodology

The software packages of AMPL and GREET 1.8b [60] were used to complete the analysis presented herein. The number of vehicles that can be feasibly supported by the current electricity grid in Ontario including the planned modifications was found by modeling the scenarios in AMPL. AMPL is a modeling language for mathematical programming and is especially tuned for optimization scenarios. Every effort was taken to ensure accurate results by using this model such as justifications of assumptions and sensitivity analysis, the model is presented in [61] and a summary of the model is supplied in the Appendix. The merits of this model are that it takes many factors into account such as energy import/export, electricity prices, market penetration transition, generation capacity, base-load generation mix, transmission capacity in addition to environmental credits and vehicle data. It is important to note that the AMPL model uses conservative values for predicting penetration levels based on information currently available concerning the Ontario electricity grid. Conservative values are used in order to determine the smallest possible number of AFVs that may penetrate the vehicle market in Ontario, Canada. In reality, the penetration of AFVs that may be supported using Ontario's energy grid are expected to be larger than the results of the model indicate. Similar work has been com-

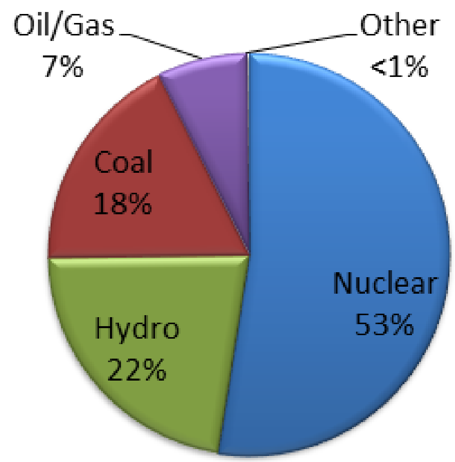

Figure 3.2: Overall electricity generation mix for Ontario [36]

pleted by Oi [44] for utilizing Japan's base-load electricity for generating hydrogen. With the resulting supportable penetration rates, GREET was used to calculate the pollution abatement resulting from the adoption schemes.

The penetration rates for both FCVs and PHEVs were assumed to follow one of two possible trajectories [61, 29]. These possible paths are shown below in Figure 3.4. The first possible transition trajectory is labeled as such and yields a slow adoption and would mimic the effects of an uncertain population who are hesitant to invest in a new technology before it is proven. This transition rate has a slower initial response than the first transition scenario but leads to a less volatile adoption scheme in which the general public steadily gains confidence in the new technology. The second transition scheme presents a rapid initial adoption of the AFVs which tapers off after the initial adoption phase before being revitalized in the final years of the simulation. This transition scheme mimics a population with environmentally and technologically oriented consumers who wish to incorporate the new technology into their lives as soon as it is available. After the target consumers

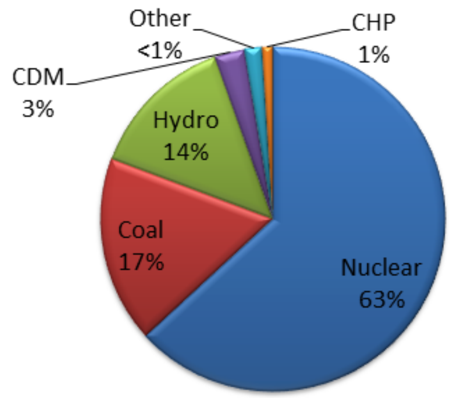

Figure 3.3: Base-load electricity generation mix for Ontario [36]

have purchased these vehicles, a downturn in sales is experienced due to uncertainty in the technology from the remainder of the general public [62]. As the technology is proven and manufacturing becomes less expensive, members of the general population who were previously hesitant are encouraged to purchase AFV technology which leads to the second period of growth for this transition scenario. Only the results for the first transition scenario are considered in this paper.

It is important to note that the scenario for the adoption of FCVs and PHEVs have been compared as being mutually exclusive to illustrate the effects on the overall and urban air pollution from adopting the individual vehicle types. This approach does not reflect a realistic scenario given that new vehicle types will likely be adopted in parallel and none of these will be sole type of AFV used, assuming that both were available. In all likelihood, a combination of these vehicle types will be adopted as individuals make decisions based on their own personal requirements. The emission changes from these reductions will then be a combination of these vehicle types in quantities which could be estimated using consumer surveys and adoption patterns of hybrid electric vehicles.

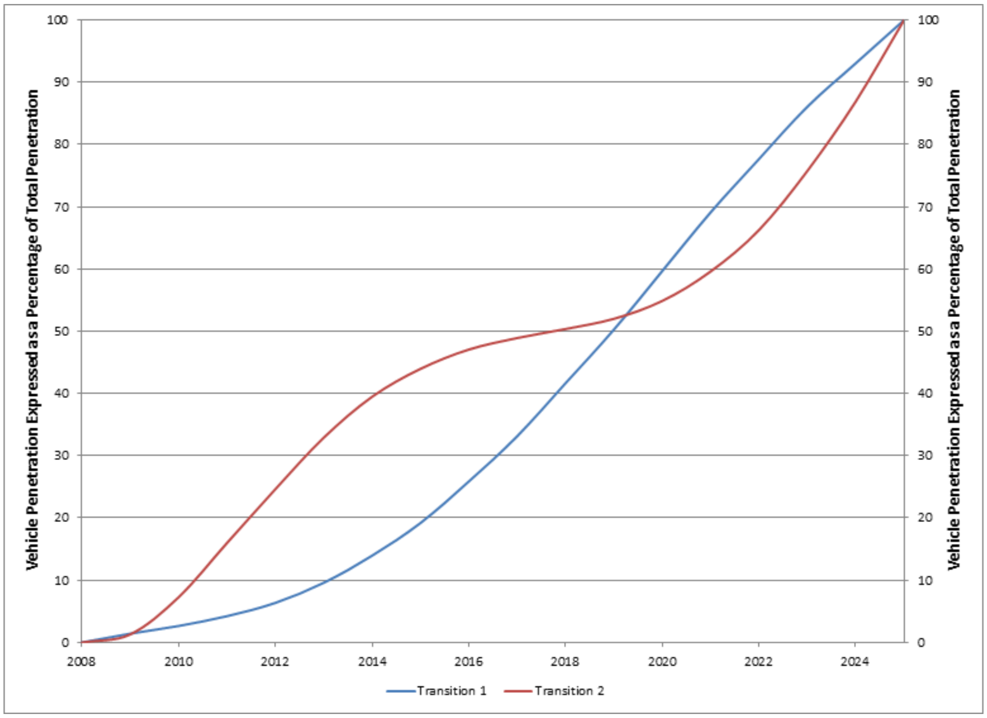

Figure 3.4: Transition scenarios for AFV penetration in Ontario

The FCPHEV has been included in this study in order to yield the maximum and minimum emission reductions that can be supported in Ontario. It is important to note that the AMPL model has not been attuned to produce the supportable penetration of FCPHEVs and that the calculations for this vehicle type are based on the maximum supportable penetrations for FCVs and PHEVs. Such analysis would be complex as not only would electrical grid transmission constraints be considered, but the location, storage and distribution of hydrogen needs to be considered as well. The potential for electrolysis to provide voltage regulation within the electrical generation system would also positively affect the use of available base-load power. The maximum achievable reduction in emissions is calculated using the supportable penetration of PHEVs while the minimum is calculated by using the penetration of FCVs. These estimates would lead to a power requirement above the feasible limits of the planned Ontario grid or an underutilization of this grid for the maximum and minimum cases, respectively. This methodology of developing a range of market penetrations has previously been demonstrated for vehicle fleets as seen in research completed by Wang, Ogden and Nicholas for the United States [63] and also by researchers in Germany [64]. The benefit from this analysis is to be able to establish lower and upper boundaries of emission reductions and not to predict actual emission reductions from the supportable adoption of FCPHEVs.

For FCPHEVs, the calculations included data from the Canadian vehicle survey showing that a daily drive for a vehicle is approximately 50 km [65] and additionally, 60% of the distance driven can be powered by electricity (i.e., from the plug-in battery capacity). FCPHEV energy usage will therefore consist of 60% grid electricity and 40% gaseous hydrogen produced by electrolysis. The penetration rates for FCPHEVs are discussed in more detail in the subsequent section 3.2.3.

3.2.3 Results of Supportable Penetration and Vehicle Growth

The population growth in Ontario and the percentage of Ontarians who currently own vehicles can be used to predict the number of vehicles that will be present in Ontario in future years. This information is found in Table 3.1. This table also shows the penetration rates of FCVs and PHEVs in Ontario for each given year based on the two transition schemes addressed previously. The analysis was completed for two final penetration rates of FCVs due to the fact that locating future generation projects in different regions have a significant impact on the final supportable penetration.

A conservative estimate of 1.2% penetration of FCVs in Ontario is based upon new nuclear generation capacity in the Bruce zone. If, instead, the location of this generation is in the Toronto zone, the supportable penetration of FCVs climbs to 2.8% [29]. This is a change which leads to further comparison of the two vehicle types. All further calculations use only the estimate of almost 2.8% because it is the most probable scenario but similar calculations have been completed for the alternative penetration rates. The corresponding penetration of PHEVs is almost 6% [66]. One assumption in the calculation of these penetration rates is that the social cost of carbon dioxide emissions is approximately $ 35 per tonne. This assumption is based on the work of Pearce [67] but was found to have an almost-negligible impact on the penetration rates calculated by the model [61].

The drivable distance for PHEVs and FCV must be compared in order to be able to compare their emissions on the same basis. The assumptions made at this stage are that the all-electric operating range for PHEVs is 30 km per day (i.e., per overnight charge) and that the annual mileage for a FCV is 20 000 km which corresponds to the approximate annual mileage for a conventional vehicle. The drivable distance for these two vehicle types can then be found and is shown in Table 3.2.

Penetration rates based on regional adoption would likely yield different results for air quality as residents in urban areas and those who commute short distances on a frequent basis may be more inclined to purchase AFVs than individuals having longer commutes or living higher distances from urban areas. These speculations are not included as definitive research is not available to confirm these market predictions.

As mentioned in the previous section, the number of FCPHEVs considered will be equivalent to the number of PHEVs for the maximum-reduction case and will be equivalent to the supportable number of FCVs for the minimum-reduction case. Though the results from this analysis are either slightly high or low based on the planned developments

Table 3.1: Calculated number of vehicles in Ontario and penetration for FCVs and PHEVs for both transition scenarios

		Transition 1		Transition 2	
Year	Total Number of Vehicles in Ontario (thousands)	Penetration of FCVs (%)	Penetration of PHEVs (%)	Penetration of FCVs (%)	Penetration of PHEVs (%)
2008	7074	0.00	0.00	0.00	0.00
2009	7155	0.04	0.09	0.04	0.08
2010	7237	0.07	0.16	0.20	0.44
2011	7321	0.12	0.25	0.45	0.96
2012	7405	0.18	0.38	0.69	1.48
2013	7491	0.27	0.58	0.92	1.97
2014	7577	0.39	0.84	1.11	2.37
2015	7665	0.54	1.15	1.23	2.64
2016	7755	0.72	1.55	1.32	2.82
2017	7845	0.93	1.99	1.37	2.93
2018	7937	1.17	2.50	1.41	3.02
2019	8030	1.41	3.02	1.46	3.12
2020	8124	1.67	3.58	1.54	3.29
2021	8219	1.93	4.15	1.67	3.58
2022	8316	2.17	4.66	1.86	3.98
2023	8414	2.41	5.16	2.12	4.55
2024	8514	2.61	5.58	2.43	5.21
2025	8615	2.80	6.00	2.80	6.00

Table 3.2: Calculated number of each type of PHEVs and FCVs in Ontario and the drivable distance

Year	Number of FCVs in Ontario	Number of PHEVs in Ontario	kms drivable by FCVs	Electric kms drivable by PHEVs
2008	0	0	0	0
2009	2840	6090	5.680×10^{7}	6.665×10^{7}
2010	5370	11500	1.074×10^{8}	1.259×10^{8}
2011	8670	18600	1.734×10^{8}	2.034×10^{8}
2012	13200	28300	2.638×10^{8}	3.095×10^{8}
2013	20100	43100	4.021×10^{8}	4.717×10^{8}
2014	29600	63400	5.919×10^{8}	6.945×10^{8}
2015	41200	88300	8.237×10^{8}	9.664×10^{8}
2016	56200	120000	1.123×10^{9}	1.318×10^{9}
2017	72800	156000	1.455×10^{9}	1.708×10^{9}
2018	92600	198000	1.852×10^{9}	2.172×10^{9}
2019	113000	242000	2.260×10^{9}	2.651×10^{9}
2020	136000	291000	2.715×10^{9}	3.185×10^{9}
2021	159000	341000	3.181×10^{9}	3.731×10^{9}
2022	181000	388000	3.617×10^{9}	4.244×10^{9}
2023	203000	435000	4.056×10^{9}	4.758×10^{9}
2024	222000	475000	4.436×10^{9}	5.204×10^{9}
2025	241000	517000	4.824×10^{9}	5.660×10^{9}

to the Ontario electricity grid, the ultimate result is to establish the maximum and minimum reduction of emissions. It should also be noted that in the case of FCPHEV there is likely to be a wide range of fuel cell and battery combinations aboard vehicles, especially during the transition phase as hydrogen distribution infrastructure is developed.

3.2.4 Pollution Abatement Results

The two scenarios presented here, which correspond to the adoption of FCVs or PHEVs, must be considered as mutually exclusive. Both penetration rate assumptions depend on maximum usage of the Ontario energy grid and thus cannot proceed in concert. As mentioned previously, other AFVs have not been considered as they could only be compared on a per-kilometre basis which would not add significant value to this work.

The two areas of concern with respect to emissions are in the overall and urban scenarios. For comparison purposes, the emission reductions resulting from the adoption of these AFVs are shown in Figures 3.5 – 3.11. Figure 3.5 represents the greenhouse gas reduction and CO_2 reduction simultaneously for consideration in the overall abatement of gases that may contribute to global warming. Because these emissions are not suspected to have appreciable effects on urban air quality, they are only analyzed from this overall perspective. The other emissions are found to have effects in both the overall setting as well as having an impact on urban air quality; therefore, the calculated reduction of a particular emission is shown as an overall reduction as well as an urban reduction. Note that these values are reductions, so a negative value is the product of an increase in that emission.

Figure 3.5 Illustrates that the majority of the greenhouse gas emissions can be at-

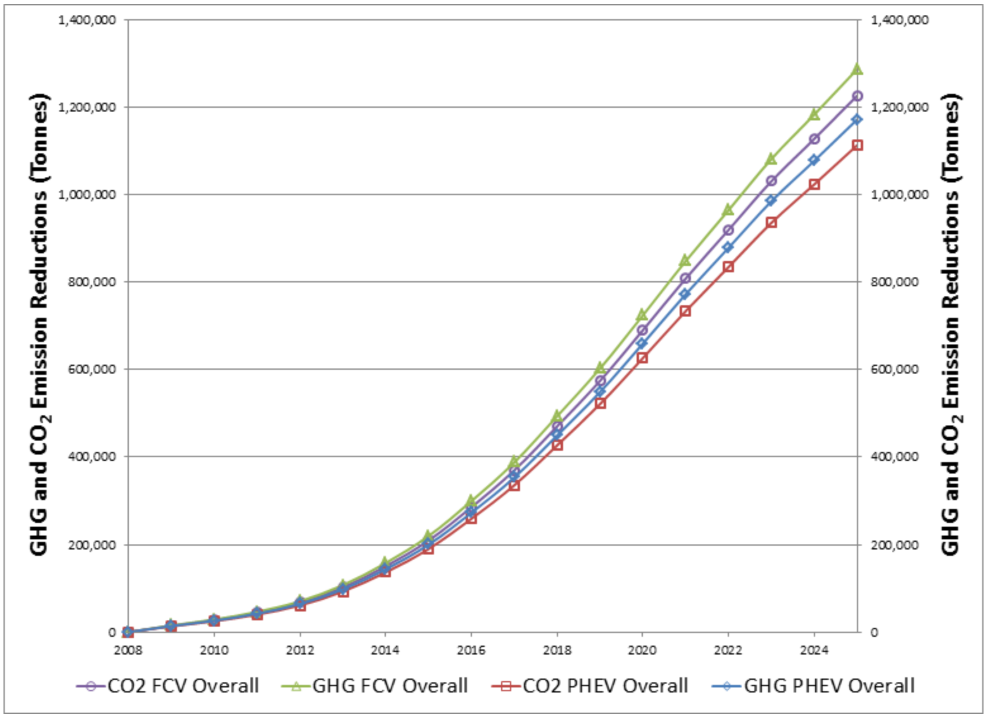

Figure 3.5: GHG and CO_2 reduction in Ontario

tributed to the release of carbon dioxide into the atmosphere which is illustrated by the fact that the GHG and CO_2 lines are almost identical. Since the transportation sector in Ontario emits approximately 3.76×10^7 tonnes of GHGs per annum based on data from 2005, the normalized reduction can also be calculated and is shown in Figure 3.6. It is observed that the reduction in the transportation GHG emissions in Ontario would reach the level of 3 to 3.5 percent by 2025. The FCPHEV predictions yield the maximum and minimum reduction from the transportation sector. It is observed that the range of reduction in GHG emissions from the transportation sector would be between 3% and 5.8%.

By analyzing the information in Figure 3.7, it is observed that PHEVs exhibit superiority in reducing VOCs in both the overall and urban scenarios when compared to the FCV. As the major concern with VOCs is related to photochemical smog production in urban

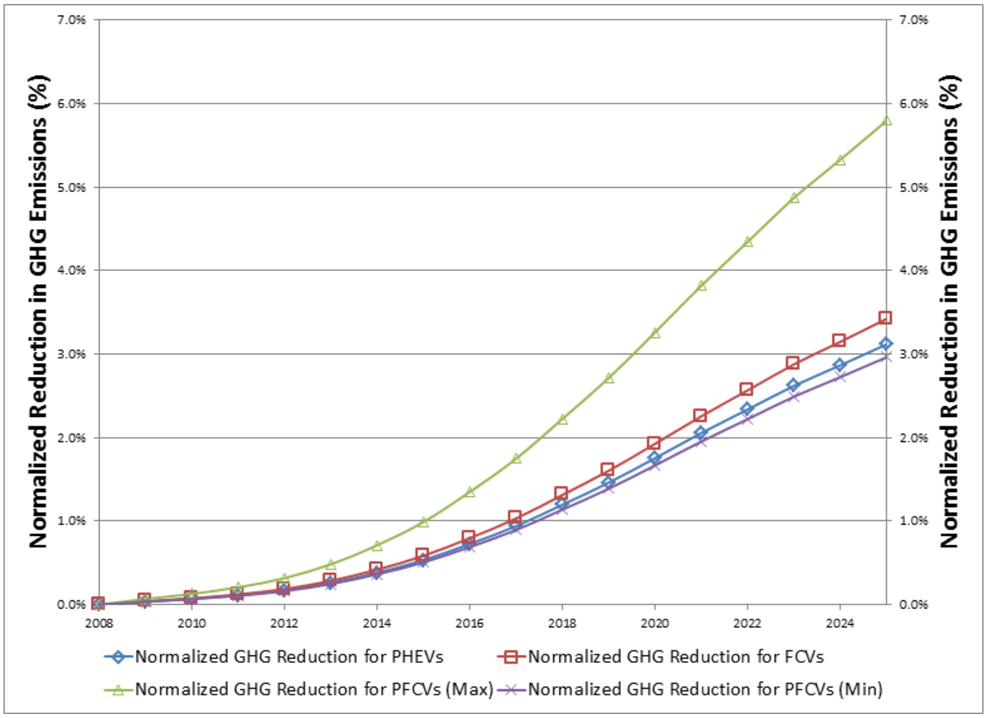

Figure 3.6: Normalized reduction in GHG emissions

areas, it is important to note that PHEVs show approximately 100 tonnes of reduction per annum above the levels that can be achieved by FCVs. The FCPHEV scenarios yield the maximum and minimum reduction of VOCs that could be achieved by adopting a fleet of FCPHEVs that would follow the high penetration rate of PHEVs or the lower penetration rate of FCVs. For the emission of VOCs, FCPHEVs could greatly exceed reductions from either FCVs or PHEVs in the overall scenario but would only show a very slight benefit in urban areas relative to PHEVs. As the most significant contribution of VOCs is urban air pollution, PHEVs and FCPHEVs are approximately equivalent in terms of emissions while they both yield a greater reduction than FCVs.

Figure 3.8 demonstrates that both PHEVs and FCVs will have similar effects on urban air quality in terms of reduced NO_x emissions. Due to the fact that the photochemical

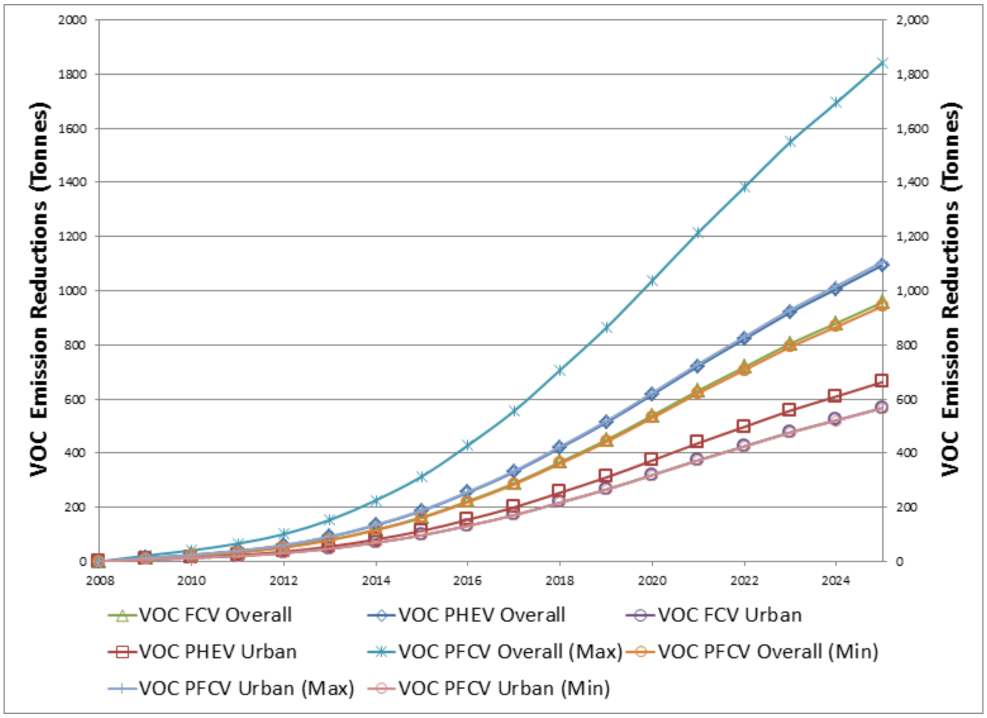

Figure 3.7: VOC emission reductions in overall and urban settings for AFVs

smog reactions in a region such as Toronto are limited by the amount of NO_x available for reaction, the urban NO_x reductions are of greater concern than similar levels of reduction in VOCs. As both PHEVs and FCVs have approximately the same reduction in NO_x, neither can be considered to be superior in terms of reducing this emission. The other pertinent information to be observed from Figure 3.8 is that the FCVs demonstrate a larger overall reduction of NO_x which would lead to a slight decrease in acidification. While this attribute is positive, this reduction in NO_x is unlikely to decrease acidification by an appreciable amount as the annual emissions of NO_x and SO_x in Ontario exceed this by over four orders of magnitude [68].

The maximum and minimum reductions in NO_x from adoption of FCPHEVs are also shown in Figure 3.8. It is observed that NO_x reduction by a maximum number of

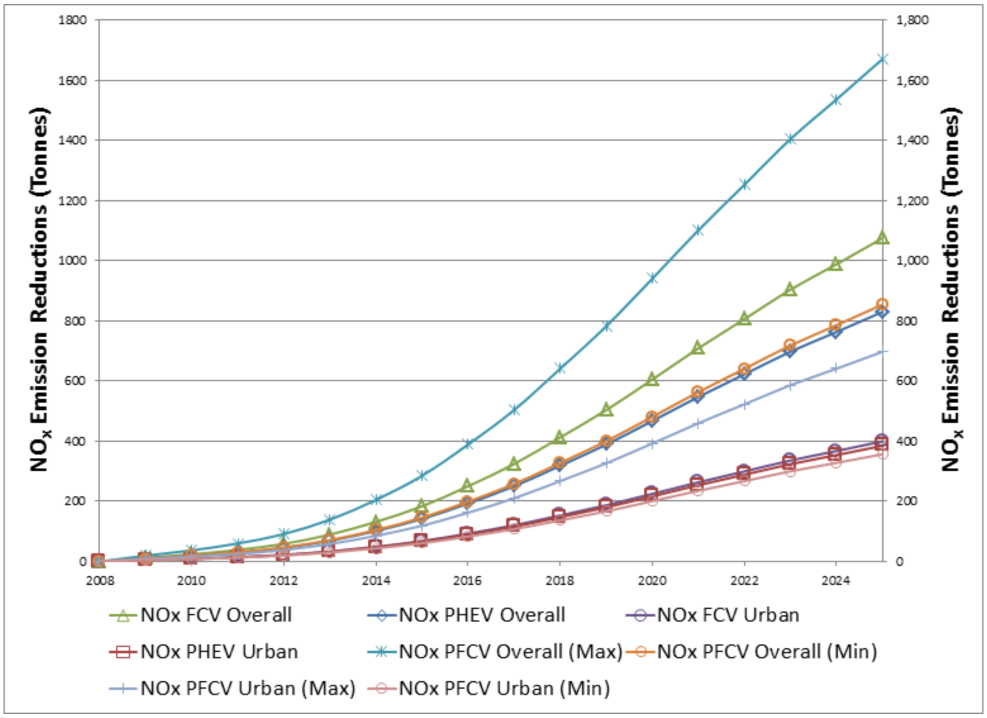

Figure 3.8: NO_x emission reductions in overall and urban settings for AFVs

FCPHEVs would reduce NO_x emissions by approximately 50% more than the supportable number of FCVs and more than double the reduction when compared to PHEVs considering overall emission levels. Since the urban emission reductions are more pertinent for NO_x, it is important to note that at a maximum level of penetration, FCPHEVs could reduce urban NO_x emissions by an additional 75% over the levels that either PHEVs or FCVs are able to achieve at their respective levels of supportable penetration. Additionally, the reduction levels for a minimum adoption of FCPHEVs show only a slight deficiency in NO_x emission reductions when compared to PHEVs and FCVs for their respective supportable penetration levels.

The reduction of particulate matter emissions with diameter less than 10 microns is shown in Figure 3.9. The dominant trend in this figure is the increase in overall PM_{10}

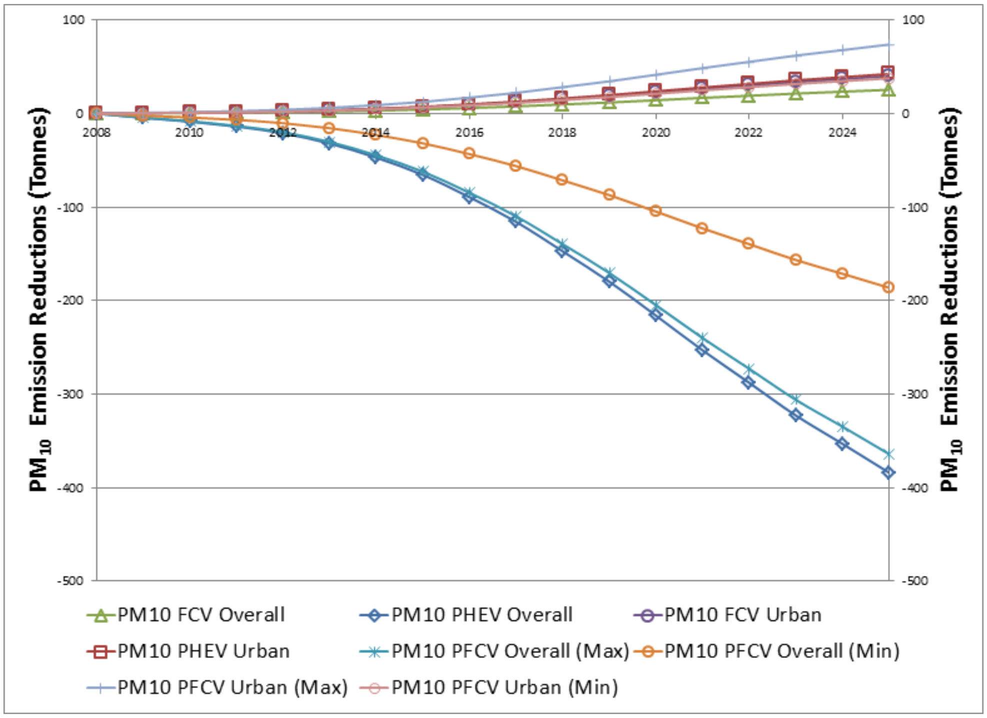

Figure 3.9: PM_{10} emission reductions in overall and urban settings for AFVs

related to the adoption of PHEVs. This increase is related to the increased particulate emissions from burning coal using the current generation mix in Ontario. The negative consequences of particulate emissions associated with coal electricity generation and PHEVs use is confirmed by other studies [49]. The PM_{10} emissions from a maximum number of FCPHEVs follow a trend similar to that shown by the PHEVs with only slightly lower increases in emissions. It is observed from the figure that the overall emission of PM_{10} will increase in a range of 190-370 tonnes per annum by adopting FCPHEVs; however, the urban reduction in this emission will be similar to the levels observed for FCVs and PHEVs. By adopting the maximum amount of FCPHEVs, the reduction in PM_{10} could achieve a reduction in PM_{10} emission of 75% greater than that achievable by PHEVs or FCVs.

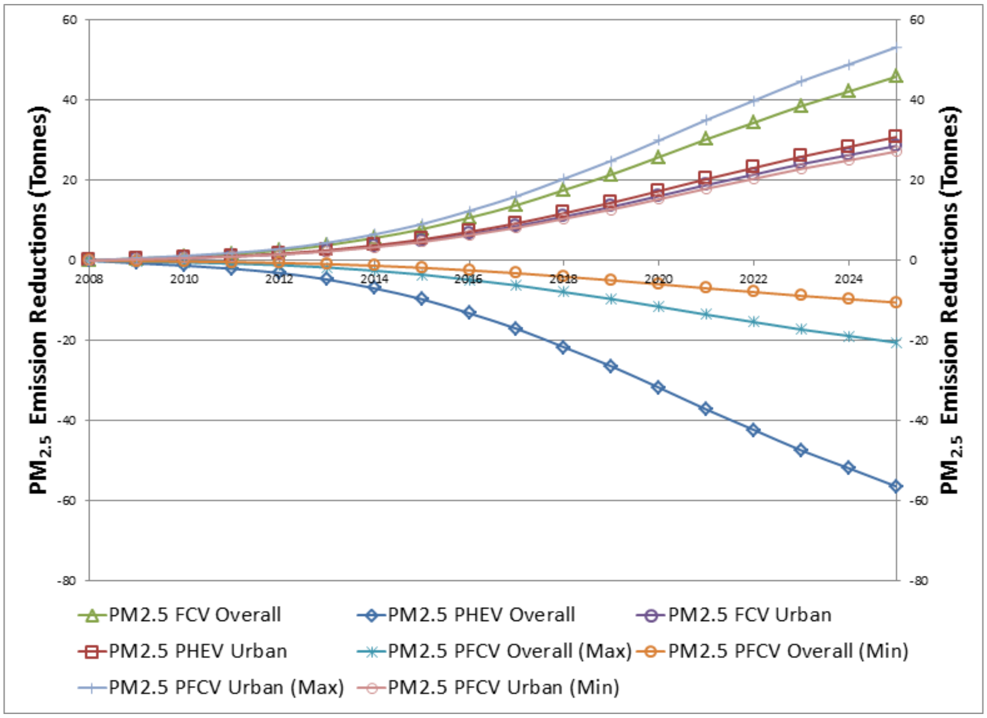

Figure 3.10: $PM_{2.5}$ emission reductions in overall and urban settings for both types of AFVs

Taking into consideration that the annual emissions of PM_{10} in Ontario exceeded 1.04 million tonnes in 1995 (including open sources) [68], an overall increase of 400 tonnes per year by 2025 is hardly significant. The reduction of particulate matter in the urban air is very similar for both FCVs and PHEVs and is 40-42 tonnes per annum in 2025.

The trends for $PM_{2.5}$ have similarities to those found for PM_{10} as is exhibited in Figure 3.10. The overall increase in emissions of $PM_{2.5}$ for PHEVs is significant as was the case in Figure 3.9 for PM_{10} with the cause again being the increased use of coal for generating the electricity for these vehicles. It is again observed that the emissions of $PM_{2.5}$ in the urban setting will decrease by approximately the same amount for both PHEV and FCV technologies with reduction reaching 29 and 31 tonnes for FCVs and PHEVs, respectively.

The upper and lower reduction limits for urban $PM_{2.5}$ by adopting FCPHEVs can be observed to bound the reductions predicted for PHEVs and FCVs; the lower limit appearing slightly below the reductions from FCVs and PHEVs while the upper reduction limit is significantly above the reduction for the other two vehicle types.

The emissions of this size of particulate matter ($PM_{2.5}$) are of most concern in the urban air as they have the greatest potential for harm to human health. It is observed from Figure 3.10 that because of the hybrid nature of the FCPHEV, the range of overall emission increases from FCPHEVs falls within a small range of approximately 10 - 20 tonnes per annum by 2025. As for PM_{10}, though, the overall emissions are again overshadowed by the province-wide emission of over 250 000 tonnes (including open sources) [68]. A minor increase in the overall emissions is thus insignificant but reductions in the urban environment could have slight positive impacts on population health.

From the two trends of particulate matter emissions, the data for SO_x in Figure 3.11 is not surprising. The increased use of coal for electricity generation has again led to an increase in emissions of SO_x. SO_x emissions are generally of concern when considering acidification and thus the overall emissions are of particular interest. The SO_x emissions in Ontario in 1995 were estimated to be over 632 000 tonnes meaning that the increase of 790 tonnes annually by 2025 would be an increase of just over 0.12%.

The adoption of FCPHEVs shows an impact on overall emissions of SO_x that encompasses a range of increasing SO_x emissions from 320 - 620 tonnes per year by 2025. These increases are slightly less than the increase attained from adoption of PHEVs yet are still significantly greater than the actual reduction achieved by adoption of FCVs. The electricity requirement for the plug-in portion of the operational time would contribute to

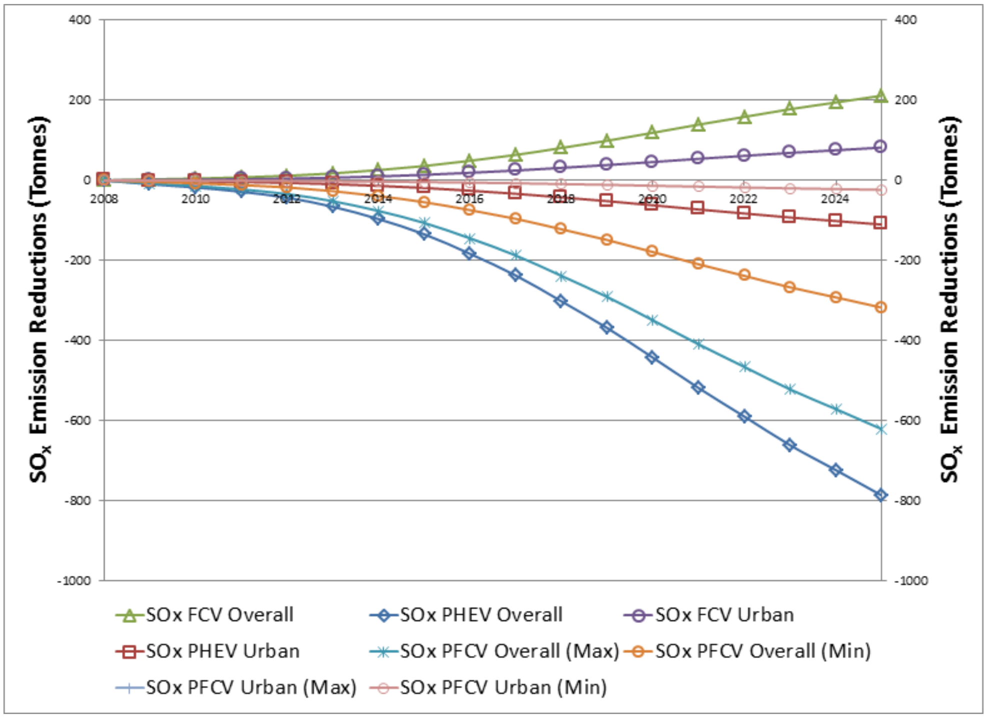

Figure 3.11: SO_x emission reductions in overall and urban settings for AFVs

increased emissions just as was the case for PHEVs.

SO_x emissions in the urban setting are of considerably less concern than precursors of photochemical smog and particulate matter and thus are not especially pertinent for discussion here.

3.3 Summary

Using the electricity grid infrastructure and planned improvements allows for calculation of the supportable penetration of PHEVs, FCVs and FCPHEVs in Ontario, Canada. From this study, it is evident that a reduction in life-cycle emissions can be achieved by transitioning a fleet of conventional vehicles to alternative fuels. For the metropolitan centre of Toronto, Ontario, alternative fuels of all types would decrease the urban emissions of small particulate matter ($PM_{2.5}$ and PM_{10}) and NO_x which are the major sources of urban air quality problems. From a provincial or national level, each alternative vehicle type is expected to decrease all emissions except for SO_x, which are expected to increase slightly in most situations.

The results show that FCVs and FCPHEVs are the most effective vehicle types for reducing life-cycle emissions during operation; however, the refueling infrastructure for these vehicles is not currently sufficient to make these vehicles practical. As such, it is recommended that PHEVs should be adopted in the near term with a transition to hydrogen as soon as the infrastructure allows.

The reduction in emissions on a national or provincial level from adoption of alternative fuel vehicles is less significant than are the reductions in the urban setting and thus the impetus for adoption of such vehicles from a policy standpoint would be to reduce health impacts from urban air pollution.

Chapter 4

Optimized production of hydrogen in an eco-park network accounting for life-cycle emissions and profit

Chapter 4 is based on previously published work "Optimized production of hydrogen in an eco-park network accounting for life-cycle emissions and profit" by Kantor et al. [69] as seen in the International Journal of Hydrogen Energy 37(6):5347-5359 and is reproduced with permission from the International Association of Hydrogen Energy. The thesis author's specific contributions to this paper were to develop the model, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M.W. Fowler and Dr. A. Elkamel, who are co-authors on the publication.

4.1 Introduction

4.1.1 Problem Definition

The purpose of this chapter is to develop a method for optimizing the material and energy usage for an existing network of industrial facilities in order to reduce emissions and waste generation, while optimizing material and energy output to maintain product output. Specifically in this case, the eco-park is used to generate hydrogen for the hydrogen economy. The overarching goals are to reduce emissions and energy use without compromising the process profitability. Through collaboration within an eco-industrial network or community of industrial facilities, chemical processors can reduce their environmental impact while still pursuing profitability to maintain favour amongst shareholders. The quantitative benefits of pursuing eco-park concepts within a network of facilities will be identified. This will help to exhibit the possibilities for industry to collaborate in order to maintain or increase profitability while reducing their individual impacts on the environment.

4.1.2 Eco-industrial Network Description

The concept of eco-industrial networks (EINs) has been discussed in detail in Section 2.1 and will not be discussed in detail here. The major principles behind EIN development are to achieve environmental and economic goals by integrating the production and usage of energy and materials from many facilities. This approach is the foundation of industrial symbiosis to mimic the behaviour of the natural world. This chapter is focused on developing a generalized linear program (LP) for optimization of these networks.

4.1.3 Analysis Methods

Economic and environmental objectives are both considered in this work in an attempt to balance the interests of society with those of industry. Economics are easily measurable based on construction and operation of chemical plants, purchase and sale of chemicals and energy and other major-cost items. The environmental objectives in this work are quantified by using llife-cycle assessment, as explained in Section 2.3.1 and are focused on emissions from each facilitiy to the air, water and land.

4.1.4 Hydrogen Economy

In the context of integrated energy and production systems, different energy infrastructures are to be studied simultaneously with the eco-park concept. In the last few years, the concept of a *hydrogen economy* has attracted attention in industry and academia [70, 71, 28]. Hydrogen as an energy carrier can be produced from multiple energy resources like fossil fuels, nuclear, and renewables for multiple end-uses; this has led to the development of the hydrogen economy concept, which concentrates on the study of the economic aspects associated with the production, distribution and utilization of hydrogen in energy systems [29, 72]. Hydrogen is a desirable energy vector because it can be stored and used to generate electricity. The use of hydrogen in transportation applications will result in decreased urban air pollution and national greenhouse gas emissions, as well as diversified energy production and security of energy supply [41]. Despite these benefits, in the present state of technological development, there remains the need for development of a production, distribution and storage network [71]. From the eco-park management point of view, the use of hydrogen as an energy carrier is appealing, given its energy storage potential and high value as an end product for the transportation sector. Hydrogen is both a product and input in a variety of potential industrial facilities in an eco-park. A hydrogen economy becomes an interesting possibility in the context of competitive electricity markets with increasing amounts of intermittent renewable sources of energy (e.g., wind and solar) and given the significant price differences between high and low demand hours for electricity, as well as in urban environments where zero-emission vehicles are highly desirable [73]. Thus, the use of hydrogen can address two key life-cycle metrics, the reduction of greenhouse gases (GHGs) and the reduction of criteria air contaminants; specifically, urban smog-generating emissions. Thus, if one considers in this market context that chemical and energy generation plants are most efficient when operating at rated production and load levels, the generation of hydrogen as a valuable end-product as well as energy storage within the eco-park becomes highly desirable [74]. When the various advantages of the use of hydrogen in transportation applications (i.e., in vehicles) are factored in, the importance of studying the production, distribution and utilization of hydrogen in association with the eco-park becomes evident. Thus, there is a need to consider hydrogen as an important part of integrated eco-park systems. This chapter studies the production of hydrogen from an eco-park perspective in association with the various hydrogen demands and uses with the eco-park itself.

4.2 Network Description

4.2.1 Chemical Processing Plants

The network is comprised of several chemical production facilities including gasification, CO_2 capture, pressure-swing absorption, combined heat and power, as well as the manufacture of ammonia and urea. Mass and energy balances can be written for each network node and are devised to maintain linearity in the model. Syngas generation can be carried out utilizing a variety of fuels, j, that can be gasified in the corresponding set of gasifiers, i. The variables are constructed of the form $SpeciesUnit_{direction}$ to be interpreted that CO_2CHP_{out} describes the amount of CO_2 output from the CHP unit.

4.2.1.1 Gasification

The process of gasification typically consists of a hydrocarbon feedstock entering the process where it is exposed to high temperatures, resulting in production of a mixture of gaseous products referred to as syngas. The gaseous products, since the fuels are generally hydrocarbons, typically consist of carbon monoxide, carbon dioxide, water, hydrogen gas and nitrogen products when air is used as the source of oxygen for the process. The resultant gaseous mixture is typically dominated by hydrogen gas and carbon monoxide; therefore, gasification utilizes hydrocarbon fuels as would standard combustion, yet the products of the process are available for further use as chemical feedstocks and to service the hydrogen economy.

Gasification is typically not practiced in the energy production sector as it adds an additional step to the traditional combustion-centric approach without yielding noticeable benefits. One benefit of gasification is in the versatility of the approach with regard to potential feedstock [75]. Combustion boilers focus on one source of fuel as the design must be catered to the normal operating parameters of the system. Gasification units can be designed to accept a wider variety of fuels so that dependence on one type of fuel is no longer a constraint on the unit. This also allows for the units to utilize biomass as a feedstock to displace the usage of fossil fuels when such biomass is available [76]. Utilizing available biomass for producing syngas can greatly reduce the overall usage of fossil fuels within the network while also reducing the emissions associated with transportation by using biomass generated in nearby agricultural facilities [77].

In this case, biomass was selected to enhance the usage of renewables within the overall EIN. Modifying reaction parameters can also allow the producer to adjust the syngas ratio depending on the downstream processes and process input [78]. The balances for this unit can be written so as to maintain the appropriate amount of syngas as feedstock to the downstream processes, as can be seen by equations 4.1 - 4.4 while the syngas is generated according to biomass gasification described by Van Der Drift et al. [79].

$$CO_2G_{out} = CO_2CHP_{in} + CO_2PSA_{in} \tag{4.1}$$

$$N_2G_{out} = N_2CHP_{in} + N_2PSA_{in} \tag{4.2}$$

$$H_2G_{out} = H_2CHP_{in} + H_2PSA_{in} \tag{4.3}$$

$$COG_{out} = COCHP_{in} + COPSA_{in} \tag{4.4}$$

Equations 4.5 and 4.6 represent the total sulphur produced from the gasification section and the sulphur produced from gasifier i, given the sulphur content of the fuel feeding the gasifier and the flowrate of this fuel, respectively. Ash is quantified in a similar way as shown in equations 4.7 and 4.8

$$S = \sum_{i=1}^{N} S_{G_i} \tag{4.5}$$

$$S_{G_i} = \sum_{j \in \Omega_i} y_{S_{G_{ij}}} F_{ij} \quad \forall i \tag{4.6}$$

where $y_{S_{G_{ij}}} F_{ij}$ represents the fraction of sulphur produced by fuel j being fed to gasifier i.

$$A = \sum_{i=1}^{N} A_{G_i} \tag{4.7}$$

$$A_{G_i} = \sum_{j \in \Omega_i} y_{A_{G_{ij}}} F_{ij} \quad \forall i \tag{4.8}$$

where $y_{A_{G_{ij}}} F_{ij}$ represents the fraction of ash produced by fuel j being fed to gasifier i.

The following four equations (4.9 - 4.12) represent the syngas product from each of the gasifiers that is fed into the syngas header.

$$CO_i = \frac{P - \gamma_{WGS}}{n} \tag{4.9}$$

where γ_{WGS} represents the extent of the water-gas shift reaction during gasification.

$$H_{2_i} = \frac{P}{\frac{n+m}{2} - k} \tag{4.10}$$

where P, n, m and k are functions of the specific biomass used as a fuel.

$$N_{2_i} \simeq 0 \ \text{for} \quad \text{biomass} \quad \text{gasification} \tag{4.11}$$

$$CO_{2_i} = \gamma_{WGS} \tag{4.12}$$

The total amount of each gas being supplied to the syngas header is then calculated as the summation of each gas from the individual gasifiers. The total mix of gas in the syngas header is then found by Equations 4.13 – 4.16.

$$CO = \sum_{i=1}^{N} CO_i \tag{4.13}$$

$$N_2 = \sum_{i=1}^{N} N_{2_i} \tag{4.14}$$

$$H_2 = \sum_{i=1}^{N} H_{2_i} \tag{4.15}$$

$$CO_2 = \sum_{i=1}^{N} CO_{2i} \tag{4.16}$$

Equation 4.17 represents the total amount of fuel that is fed into gasifier i while equation 4.18 yields the calculation of the total amount of fuel j that is used in gasification where Ω_i represents the set of fuels acceptable in gasifier i.

$$F_i = \sum_{j \in \Omega_i} F_{ij} \tag{4.17}$$

$$F_j = \sum_{i} F_{ij} \quad \forall j \in \Omega \tag{4.18}$$

Supply constraints on the operation of the gasification section are shown as equation 4.19 which limits the usage of each fuel to an upper limit of availability to the network. In this case, only biomass is used in the gasification process.

$$F_j \leq F_j^U \tag{4.19}$$

An upper limit is placed on the fuel flowrate due to possibilities of limitation in supply or desirability of a given energy feedstock. In the case of biomass, only a certain rate of agricultural waste might be available for a given time of year; therefore, it is necessary to include the availability of crop waste as a function of the season or month. For fossil fuel feedstocks, it may not be desirable to utilize the maximum amount available, and thus this constraint can also be used to fix an upper limit on usage of certain fuels.

4.2.1.2 CO_2 Capture

Historically, carbon dioxide was considered to be a necessary by-product of electricity production yet is now considered by many as a pollutant. Certainly, CO_2 is a greenhouse gas (GHG) and the principal contributor to climate change. Capturing CO_2 from a gas stream has been a focal point of research in the energy industry in an attempt to create "clean coal" plants in which the CO_2 would be captured from the stack and then disposed of in a manner that does not follow the traditional approach of releasing it to the atmosphere. The technologies developed to date generally consist of a recirculating medium used to capture the CO_2 and then a process to remove the CO_2 from the capture medium.

Captured CO_2 can be purified and used for a wide variety of processes in order to avoid emitting it to the atmosphere which would have little benefit over simply combusting the coal to produce electricity [80]. Monoethanolamine (MEA) is one of the capture media being pursued for its high capacity for capturing CO_2 from flue gas. An alternative medium is ammonia, a common chemical product that has demonstrated various advantages in its ability to capture CO_2 [81, 82]. Ammonia is being used in the proposed network as a product from the EIN and also as a precursor to the production of urea. By using ammonia as a medium for CO_2 capture, the need to import MEA is removed and the carbon capture process can be maintained by using make-up ammonia from the nearby facility.

The CO_2 generated must be sufficient to supply all of the processes requiring it while any remainder is sequestered. The balances on this unit are seen in equations 4.20 - 4.22.

$$CO_2CC_{out} = CO_2GH_{in} + CO_2EC_{in} + CO_2ME_{in} + CO_2U_{in} + CO_2SQ_{in} \tag{4.20}$$

$$N_2CC_{out} = N_2CHP_{out} \tag{4.21}$$

$$NH_3CC_{in} = 0.01\, S_{CO_2}\, CO_2CC_{in} \tag{4.22}$$

where S_{CO_2} represents the solubility of CO_2 in ammonia based on the operating parameters of the unit. 1% make-up of ammonia is used as a design rule to avoid build-up of contaminants and deactivation of the ammonia [83, 84], which is described in Eq. 4.22.

4.2.1.3 Pressure-swing Adsorption

Pressure-swing adsorption (PSA) has been used for many years and is an industrially mature process. PSA is used to separate one or more gas species from a mixture and can be applied to a wide variety of gas streams as the adsorbent material may be varied to suit the specific application. The inlet gas is passed over an adsorbent which attracts the desired gas or an impurity in the stream. The remainder of the feed thus continues to the outlet for release or further processing. This process will be used to separate hydrogen from a gaseous mixture, and as such, PSA is a key technology for implementation within the eco-park to support the development of a hydrogen economy which will demand a pure stream of hydrogen for use in fuel cells. Additionally, this process is frequently found in refineries and ammonia plants as hydrogen is required as a feed for some units in these facilities. Thus, hydrogen produced from this section of the network will supply the other facilities in the eco-park and may also provide hydrogen as a valuable co-product to the transportation market [85, 86]. Equations 4.23 - 4.25 show the balances on the PSA unit.

$$COPSA_{out} = COPSA_{in} \tag{4.23}$$

$$N_2PSA_{out} = N_2PSA_{in} \tag{4.24}$$

$$H_2PSA_{out} = H_2AM_{in} + H_2M \tag{4.25}$$

Hydrogen product gases can be exported from gasification of hydrocarbon feedstocks followed by purification of the gas streams using PSA. Alternative methods have also been proposed to utilize off-peak electricity generation to electrolyze water for the production of hydrogen. Efforts behind these initiatives to produce hydrogen gas are to stimulate low-cost hydrogen for use in vehicles and to develop the 'Hydrogen Economy', termed as such due to the concept being is that hydrogen is used as an energy carrier for powering society. Transportation of people and goods within Canada represents 27% of the total GHG emissions within the country [87]. Utilizing hydrogen as an energy carrier to power commuter transportation could reduce these emissions by 3-6% by 2025 based only upon the current infrastructure and planned improvements [41]. Thus, this reference [41] will be used to develop the target hydrogen output from the eco-park. In addition, the life cycle economic cost of hydrogen vehicles can be reduced by producing hydrogen in a more efficient manner and also by economies of scale associated with producing the vehicle itself [88, 50].

As mentioned previously, excess off-peak electrical generation can be used to electrolyze water. The hydrogen produced from this process can then be stored for later use in a fuel cell to generate electricity during peak hours. This would allow for additional peak generation capacity without constructing additional peak- or base-load plants, leading to a much more cost-effective energy system.

4.2.1.4 Ammonia Manufacture

Production of ammonia is another mature process that has been developed to produce fertilizers for the growing agricultural sector. The feedstock for this process is typically natural gas, which is processed to remove sulphur compounds and then reformed to produce syngas. Upon separating the gases and introducing air as a source of nitrogen, ammonia can be produced in large quantities. The common modern methodology for producing ammonia is the Haber-Bosch process, converting nitrogen and hydrogen directly to anhydrous ammonia in reaction 4.26.

$$3H_2 + N_2 \rightarrow 2NH_3 \tag{4.26}$$

Ammonia will be produced in the proposed eco-park using a similar methodology although the typical process will be much simpler as the feed gases are already free from sulphur compounds and other impurities. The process may also accept unreacted ammonia from the urea plant, depending on process conditions and geographical locations. LCA on ammonia processing can provide details on improvements based on the modifications [89]. The governing equation for the ammonia section is shown by equation 4.27

$$NH_3AM_{out} = NH_3CC_{in} + NH_3U_{in} + NH_3M \tag{4.27}$$

4.2.1.5 Urea Manufacture

Urea is primarily produced as a nitrogenous fertilizer for the agricultural industry but currently contributes to GHG emissions in the forms of CO_2 and oxides of nitrogen in addition to the heat and power required to operate the facilities [90]. The solid urea is broken down into two ammonia groups and one molecule of carbon dioxide. Although several small-scale methods have been developed for manufacturing urea, large-scale manufacturing methods consist of combining the afore-mentioned two molecules of ammonia with one molecule of carbon dioxide according to the Bosch-Meiser process in reaction 4.28.

$$2NH_3 + CO_2 \leftrightarrow (NH_2)_2\,CO + H_2O \tag{4.28}$$

In the proposed eco-park, carbon dioxide is readily available as a pure process stream from the carbon-capture process and ammonia is also produced as a park co-product. One advantage at this point is that the inefficiency related to compression of CO_2 into dry ice for transportation is not necessary. Since CO_2 and ammonia can both be obtained from the eco-park, the manufacture of urea may be one of the most profitable nodes of this process. Environmentally, urea acts as a convenient transportation medium for urea and carbon dioxide. The fertilizer pellets are a much easier method for applying ammonia to fields and is a convenient source of carbon dioxide immediately available to growing biomass.

The production of urea from ammonia and carbon dioxide is a two-step reaction in which the stoichiometric ratio of NH_3:CO_2 is 2:1. The reaction transpires according to equations 4.29 and 4.30, shown below.

$$CO_2 + 2NH_3 \Longleftrightarrow NH_2COONH_4 \tag{4.29}$$

$$NH_2COONH_4 \Longleftrightarrow NH_2CONH_2 + H_2O \tag{4.30}$$

Thus it can be seen that production of urea consumes ammonia and CO_2 while producing water as a co-product. Upon separation, the water can be recycled to be used in other locations in the network. Because this is an equilibrium reaction, excess CO_2 can be added to the reaction to facilitate an equilibrium shift toward the production of urea. Analyses have shown that an equilibrium conversion of 85% can be achieved by having excess CO_2 available for reaction. The remaining reactants can then be recycled within the plant or elsewhere in the network. For modeling purposes, 85% equilibrium conversion of ammonia with 50% excess CO_2 is assumed. The remaining reactants are available for recycle and use elsewhere in the network. The balances on the urea section are shown in equations 4.31 - 4.34.

$$UU_{out} = NH_3U_{in}\left(\frac{K}{SR}\right) \tag{4.31}$$

where K represents the equilibrium conversion within the reactor and SR represents the stoichiometric ratio for the reaction.

$$CO_2U_{in} = 1.5NH_3U_{in} \tag{4.32}$$

With the factor of 1.5 built in to the function so that CO_2 is supplied in 50% excess of the stoichiometric requirement.

$$NH_3U_{out} = NH_3U_{in} - 2UU_{out} \tag{4.33}$$

$$CO_2U_{out} = CO_2U_{in} - UU_{out} \tag{4.34}$$

4.2.1.6 Combined Heat and Power

Plants for generating heat and power, also termed cogeneration plants continue to receive attention as the efficiency of these plants in producing electricity and useful heat exhibits that they have potential for becoming a valuable part of the energy solution. The technology is mature yet there are relatively few of these plants that have been built due to their increased technical complexity and previously-undervalued ability to produce heat for use in facilities or as district heating. The CHP node in the proposed eco-park is an important part of the process as it provides heating for the facilities as well as an opportunity to produce the electricity for the eco-park, further reducing the operational costs. This plant will have the capability of completely oxidizing any residual carbon monoxide from the syngas as well as hydrogen gas. The flue gas is to be treated by the carbon-capture process so as to avoid emissions of CO_2 to the atmosphere. The energy generation is a function of the heating value of each of the gases fed into the unit. The heat generated for export is either the heat required by other processes or the waste heat from the CHP process that cannot be used elsewhere. The energy and heat generation are a split of the total energy generation term, given that each has a different efficiency. The overall balances on the CHP unit are shown in equations 4.35 - 4.40.

$$EG = (COCHP_{in})\,(LHVCO) + (H_2CHP_{in})\,(LHVH_2) \tag{4.35}$$

EG represents the energy generated from the fuels fed into the CHP unit and LHV for each gas is the lower heating value for each of the species.

$$HGX = EG\,(Heat_{Split})\,(\eta_{HG}) \tag{4.36}$$

$$EGX = EG\,(Elec_{Split})\,(\eta_{EG}) \tag{4.37}$$

where EGX and HGX represent the electricity and heat generated for export, respectively. Similarly $Heat_{Split}$ and $Elec_{Split}$ represent the energy split between heat and electricity generation. In addition,η_{EG} and η_{HG} from these equations represent the efficiency of electricity and heat production, respectively.

$$CO_2CHP_{out} = COCHP_{in} + COPSA_{out} + CO_2PSA_{out} \tag{4.38}$$

$$H_2OCHP_{out} = H_2CHP_{in} \tag{4.39}$$

$$N_2CHP_{out} = N_2PSA_{out}\left(\eta_{N_{2_{sep}}}\right) + N_2CHP_{in} \tag{4.40}$$

While $\eta_{N_{2_{sep}}}$ represents the efficiency at which N_2 can be separated.

4.3 Methodology

4.3.1 Introduction

The first steps to develop this model are to identify the nodes that are available to exchange quantities of material and energy. The nodes have been identified in section 4.2.1 and will be referred to by the corresponding indices for the remainder of this document:

- syngas generation G;
- pressure-swing adsorption PSA;
- combined heat and power CHP;
- carbon dioxide capture CC;
- ammonia production AM; and,
- urea production U;

With this list of facilities, it is possible to draw connections of products, co-products and energy among the facilities. The objective function of the optimization is defined by the development of the metric system shown in section 2.5. The objective function can be manipulated to fit a wide array of scenarios including environmental indices as well as profitability. The proposed network and connections is shown pictorially in Figure 4.1.

4.3.2 Definition of Environmental Metrics

Metrics for this optimization need to encompass all potential results of this collaborative effort; therefore, the objective function must be formulated with these metrics in order

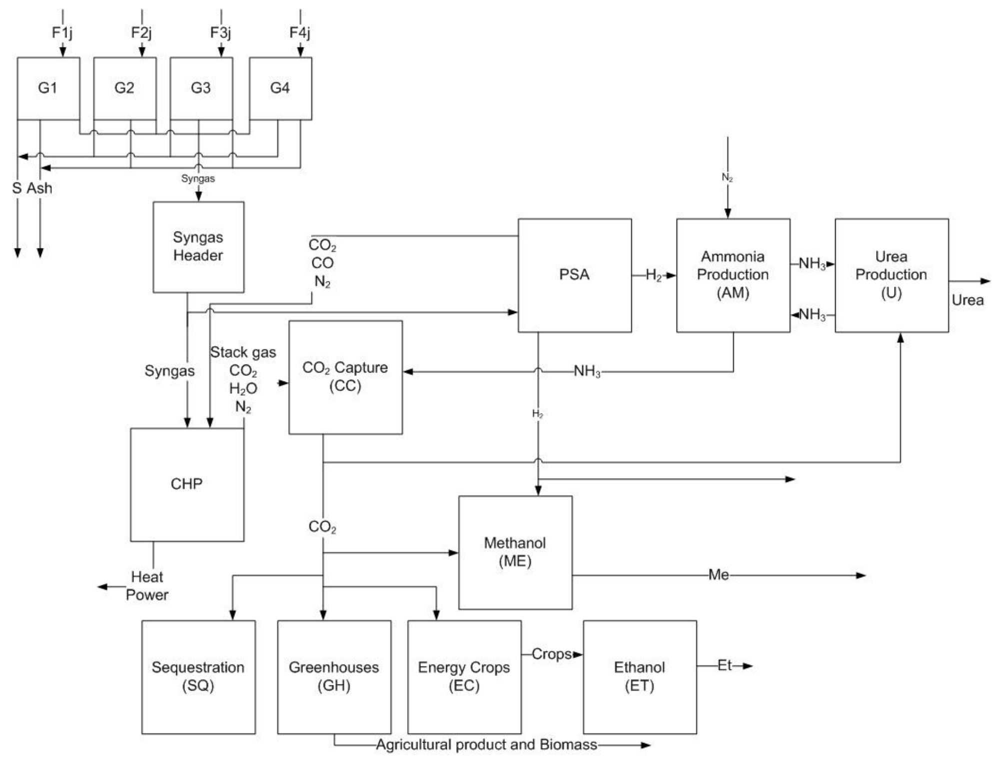

Figure 4.1: Proposed network

to achieve both goals of environmental responsibility and economic sensibility. The question of what should be included in such an index is postulated by Ziegler [91] although there are several options that already exist. An overview of different indexing systems has been completed by several authors [92, 93, 20], yet a clearly superior index has not emerged. Thus, it is important to review the applicable systems in order to develop an appropriate set of metrics, and hence, an applicable objective function for the optimization.

Methods such as the Analytic Hierarchy Process (AHP) [94, 95], developed over 30 years ago are too primitive to be applied to this type of optimization although this is one of the first standardized methods of analytical decision analysis for this type of problem. Another system, called the Sustainable Process Index (SPI) was proposed in 1995 as a universally applicable index focused on sustainability. The SPI bases the sustainability of any process on a ratio of area required for production to the area of consumption [96]. While the pursuit of a single resultant output is beneficial for building optimization routines, it is not particularly appropriate for the type of analysis considered in this work.

The Dow Jones Sustainability Index (DJSI) has been used for several years to base investment decisions on the sustainability of a company as measured using financial, environmental and social indicators [40]. This system has been used extensively in the financial community to record extensive growth in investments. Unfortunately, this system relies too heavily on qualitative information to be applicable in a numerical optimization algorithm. Other metrics such as the waste reduction (WAR) algorithm have more empirical clout but only apply to the extent that waste is reduced within a system [97, 98, 99]. This methodology can be adapted and applied to be a part of the objective function but clearly cannot be the only route pursued as it fails to include metrics traditionally important to industry. Other indexes such as the Environmental Protection Index (EPI) [100] are also somewhat applicable to this end, although it also excludes any mention of economic benefits.

Emergy, exergy and e-green analyses have also been developed as an attempt to use these systems to quantify benefits from eco-park networking [101]. These techniques are very robust in their applicability but tend to focus more on energy and the efficiency of energy usage within a process system. This type of analysis could be very effective in monitoring or optimizing an energy-based eco-park but are unwieldy for application in a material and energy exchange eco-park environment.

As none of the systems mentioned above are completely adequate for the analysis of an eco-park, it is required to produce a new index which will account for both environmental management and economic profitability. This index can then be used to formulate the objective function for an eco-park optimization. This metric basically consists of two parts, one for the calculation of cost savings and the other for assessing the reduction in waste and emissions. The caveat for this index is that there must be a comparable process so that the difference between the two options can be calculated. The mathematical formulation is shown in section 4.3.5.

4.3.3 Problem Formulation

The problem in this case is akin to a transportation/networking problem in a typical fashion yet with several additional complexities. The first of these differences is that the eco-park network includes many chemical reactions, which are atypical of a transportation problem. Generally, a transportation or networking problem may have one or several goods/signals transferred between nodes, yet the item in question remains unchanged. Chemical reactions allow for a change in the good at each node as it may be converted into another chemical and also be energetically altered.

Additionally, several types of good are being transferred and may not necessarily be permitted to utilize the same transportation pathways. For example, although water or natural gas may be transmitted through a pipeline at a capacity determined by the pipeline infrastructure, electricity cannot be transmitted in a similar fashion. Thus it is required that a minimum of two (electricity, materials) transportation pathways be implemented in order to conduct goods between the facilities. Heat integration of the network plants could potentially be transported using similar methods as the materials but at the extent that the facilities are to be integrated, it is likely that heating must also be a separate pathway.

Similarly, some materials may require different forms of transportation than others and thus the pathways for each chemical must be considered.

Simulations of eco-park concepts have been previously documented [102, 103, 104, 105] but tend to apply non-optimal algorithms or metrics which are not based on life-cycle thinking. The work presented here is an optimization model that uses a dual-objective function in order to maintain profitability while reducing environmental impact based on LCA metrics. This method is realistic as it does not compromise profitability for reduced emissions but will yield a scenario amicable to both industry and society.

4.3.4 Selection of Optimization Package

The concept of combining chemical facilities into an eco-park system in an optimized way would only be suited for an optimization package as it is desired to find the operating point at which the profits and waste reduction benefits are maximized. GAMS software was selected to complete the optimization as it is a powerful software language for optimization and is well-suited to this type of problem [106]. Deterministic, numerical packages do not provide the solution routines and are not specifically designed for optimization and thus are not considered for use here.

GAMS stands for General Algebraic Modeling System, a commercial optimization package which is used extensively in both the academic and commercial realms for solving optimization problems. The GAMS software employs a variety of strategies and solvers in order to obtain the optimal solution for a given problem. The solver that is employed for this model is CPLEX, which uses Simplex and barrier techniques for solving problems of this type.

4.3.4.1 Transportation

Transportation of materials, heat and electricity are discussed as part of the problem formulation in section 4.3.3 yet the aspects discussed were transportation associated with the number of pathways required for goods to flow through the network. The environmental impact of transportation has been studied for the consumer market and typically focuses on greenhouse gases and total energy used per kilometre travelled. The transportation options here, as the network has not yet been constructed, can be varied in order to reduce the cost and emissions from the transportation of goods between facilities. Several environmental factors have been shown to stem from altering the fuels used in vehicles [41] and vehicles powered by electricity and hydrogen would integrate very easily into the network as these two commodities are already produced.

4.3.5 Objective Function

The objective function for this optimization is a construct of two objective functions. The two factors considered in this analysis are emission deviations from stand-alone plants as well as economic incentives. It is important to consider both of these objectives so as not to bias the output to be purely profit-motivated nor purely attuned to societal benefit from reducing emissions. The portion of the objective function that governs the reduction in emissions will tend to minimize the magnitude of all facilities; therefore, relying only upon this metric, the plant sizes would be reduced to zero. In the scenario considered for this work, note that the eco-park was constrained to provide hydrogen for 1000 fuel cell vehicles, and the plants were sized accordingly as dictated by the optimal scenario. The economic portion of the objective function is then incorporated to add realism to the optimization as well as ensuring that the optimization will terminate with some plants have a size greater than zero. Equations 4.41 - 4.43 show the condensed form of the objective function.

$$Z = W_{LCE} J_{LCE} + W_e J_e \tag{4.41}$$

$$J_{LCE} = \sum_{p=1}^{n_p} EnvCost_p \left(S_p - I_p\right) \tag{4.42}$$

$$J_e = \sum_{p=1}^{n_p} \left[(ACC + OC)_S - (ACC + OC)_I\right]_p \tag{4.43}$$

Where:

- J_{LCE} = portion of the objective function attributed to the reduction in life cycle emissions;
- J_e = portion of the objective function attributed to the economics of the network;
- $EnvCost$ = the environmental cost associated with a particular emission;
- p = representative of the particular chemical plant;
- n_p = the total number of plants;
- W = weighting factor for the economics (W_e) or life cycle emissions (W_{LCE});
- S=stand-alone facilities;
- I=integrated scheme;
- ACC=annualized capital cost; and,
- OC=operating Cost.

4.4 Results of Reduced Case

4.4.1 Reduced Case Model

In order to test the eco-park optimization theory and the objective function, five nodes were extracted from the large case and the model was simplified to the one shown in Figure 4.2.

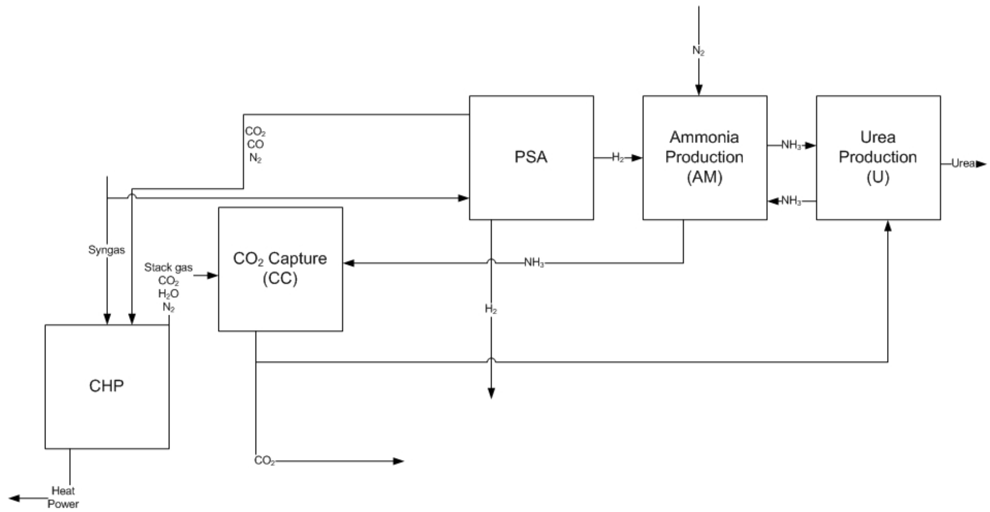

Figure 4.2: Reduced network configuration representative of the reduced case

The facilities accepted into the reduced case were carbon capture (CC), combined heat and power (CHP), ammonia production (AM), urea production (U) and pressure-swing adsorption (PSA). Transportation distances and types were removed from the model along with their associated costs for simplicity, which basically assumes that the facilities will be co-located within an eco-park complex. Additionally, the plants were able to scale linearly instead of by discretized advances. These simplifications would result in a model of these five nodes as if they shared a small geographical area with equipment that is custom-built without incurring additional costs for such equipment.

4.4.2 Results

Simulating the five nodes mentioned above yields a result that can be shown in Figure 4.2.

Testing the case with the parameters presented in Table 4.1 yields the results shown in Figure 4.3. The results from this trial represent a base case from which to experiment to ensure that the model behaves logically in accordance with the constraints.

Table 4.1: Table of input parameters for basic case in reduced model

Parameter	Description	Value
W_e	Optimization weight associated with economic performance	0.5
W_{LCE}	Optimization weight associated with life-cycle emissions	0.5
Environmental Costs	**Description**	**Value**
$Cost_{CO_2}$	Environmental cost/weight of CO_2	0.6
$Cost_{SO_x}$	Environmental cost/weight of SO_x emissions	0.05
$Cost_{NO_x}$	Environmental cost/weight of NO_x emissions	0.2
$Cost_{SW}$	Environmental cost/weight of Solid waste	0.15

4.4.3 Hydrogen Optimization

The network is comprised of several chemical production facilities including gasification, CO_2 capture, pressure-swing absorption, combined heat and power, as well as manufacturing of ammonia and urea. The amount of hydrogen produced from the network is fixed to supply hydrogen 1000 vehicles in Ontario and the remaining plants are fixed in order to accommodate the hydrogen production while maintaining an optimum value for the objective function. Assuming a 70 km kg^{-1} fuel efficiency for a hydrogen vehicle and 20 000 km

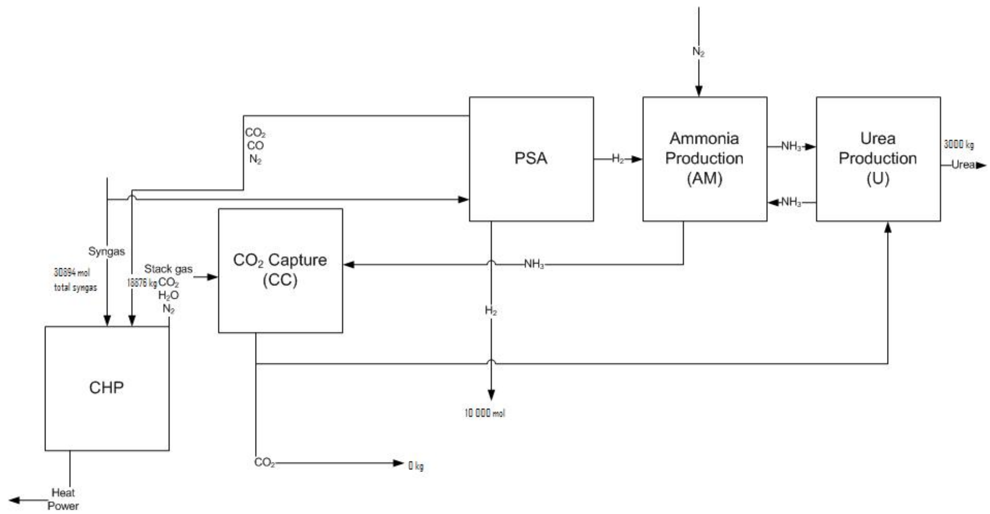

Figure 4.3: Reduced configuration representative of the reduced eco-park

a^{-1}, the resulting mass of hydrogen for 1000 vehicles for one year of driving is 285 700 kg H_2.

Varying the economic weighting between 0 and 1 by increments of 0.1 allows for the stability of the optimization to be seen in Figure 4.4.

Although the overall reduction in emissions changes only slightly in the range of W_e between 0 and 0.6, the plant sizes vary to accommodate the changes in the economic weighting of the objective function. In the range between 0 and 0.3, carbon sequestration is utilized in order to reduce emissions by a maximum amount, as the economic weighting is relatively low and sequestering the CO_2 would thus have little impact on the objective function. In addition, production of urea during this stage is minimal as the economic weighting is not at a level which would dictate that this production is necessary. When the economic weighting reaches 0.4, it is sufficient to force the urea plant to increase in size as a destination for the captured CO_2 as the scenario is more profitable than sequestering the CO_2 resulting from gasification.

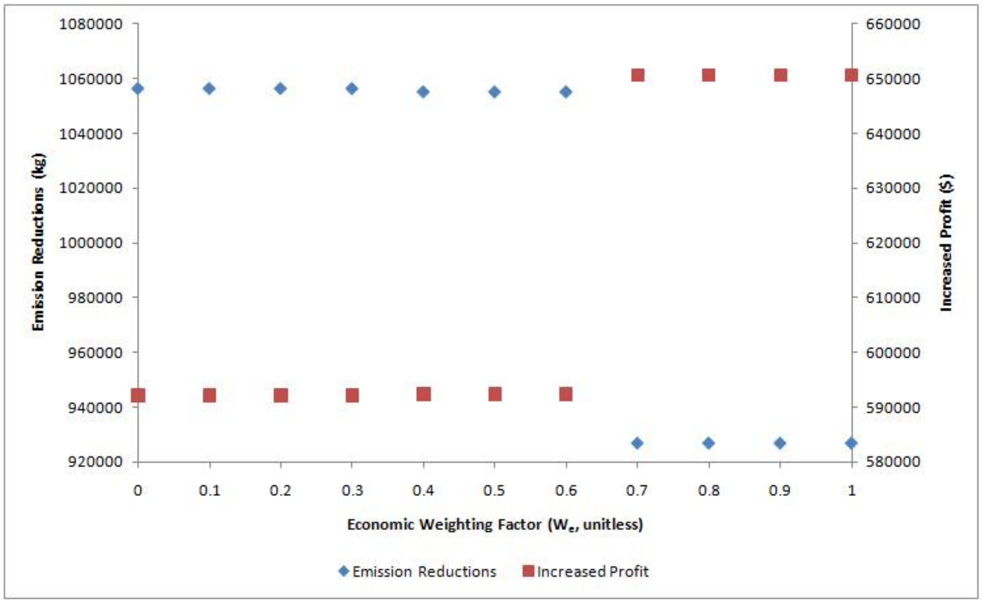

Figure 4.4: Results of producing hydrogen for 1000 fuel cell vehicles from [41]

At an economic weighting of 0.7, the optimization again reaches a new optimum value for the objective function as the profitability is increasingly important. The optimization dictates that the optimal solution for a high value of economic weighting includes reducing the size of the carbon capture and urea manufacturing plants in addition to the combined heat and power facility. In this case, the objective function is maximized by importing the required electricity as it will reduce emissions less but is more profitable for the operation of the remainder of the facilities.

The feasible region of the optimization is contained by several constraints and the limiting constraint changes at the points mentioned above, i.e., when W_e=0.4, 0.7. The differences take place in the size of the producing facilities for electricity, carbon sequestration and urea production. The hydrogen production is fixed at a level to power 1000 average hydrogen vehicles in Ontario, Canada, so the size of this overall eco-park facility

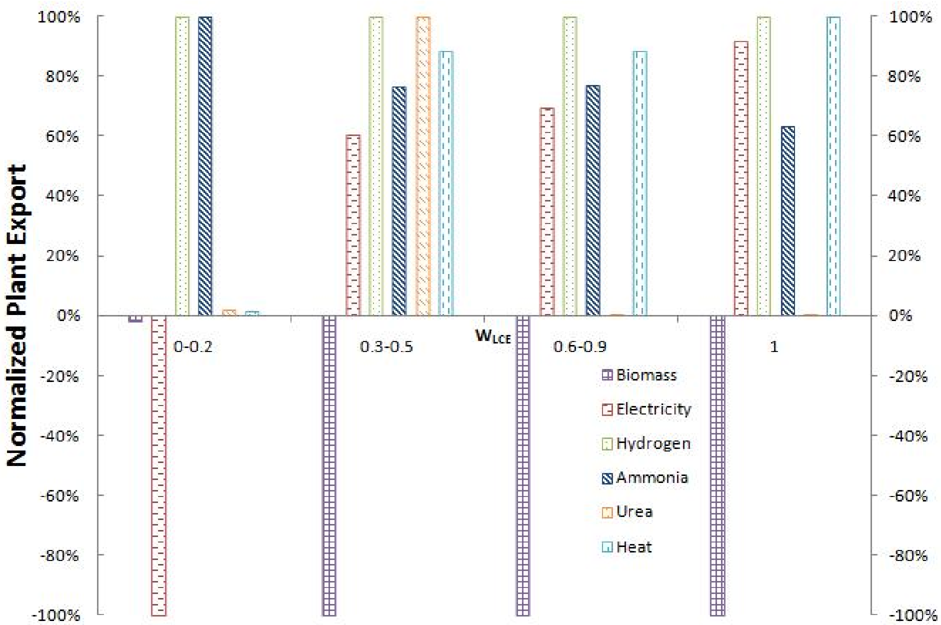

Figure 4.5: Normalized plant exports with hydrogen production for 1000 cars for various values life-cycle emissions weighting

is variable yet the net hydrogen output is fixed.

Analyzing the plant sizes for a variety of values of W_{LCE} yields the results in Figure 4.5. Positive values indicate an export of that product from the boundaries of the eco-park while negative values indicate an import into these boundaries.

This figure shows the changing plant sizes for a variety of values of W_{LCE}. The values for each plant are normalized to their respective maxima to exhibit the sensitivity of the model to the environmental and economic weighting factors. When W_e takes large values, simulating a case in which profitability is the major concern, a large amount of electricity is imported to produce the required hydrogen. Ammonia is also produced in large quantities as it is a profitable product in this network. For scenarios of moderate W_e

values, environmental impact having a larger weighting relative to profit, a greater amount of biomass is imported in order to manufacture the network products. The advantage in emission reductions provokes the optimization to produce electricity, ammonia, urea and heat in addition to the requirement for hydrogen. At $W_{LCE} = 1$, ammonia production is reduced to order to increase the production of heat and electricity while maintaining the required amount of hydrogen. Although ammonia is a profitable product, the economics of the scenario are unimportant as the weighting is entirely placed on the reduction in life-cycle emissions from the network.

4.4.4 Greenhouse Gas Emissions Compared to Criteria Air Contaminants

Criteria air contaminants are defined by Environment Canada as pollutants that "cause to air issues such as smog and acid rain. They are produced in varying quantities by a number of sources, including the burning of fossil fuels" [107]. Varying the relative importance of greenhouse gas emissions and criteria air contaminants leads to a result showing some interesting results. Figure 4.6 shows that with a reduced weighting of GHG emissions, the overall emissions from the network actual increase, as does the output of urea and ammonia. Economics, in this case, drive the size of the plants and the emission reductions follow as a result. As the network was developed for producing useful products while focusing on reducing GHG emissions, it is not surprising that emissions may increase with a very low GHG emission weighting. Until a GHG weighting of 0.3 is utilized, the overall emissions from the network increase over the baseline case of no integration among facilities. This is a reflection of the design complexities associated with the network plants compared to traditional plants. These additional complexities contribute to an increase in emissions as reducing GHG emissions yield no benefit to the objective value.

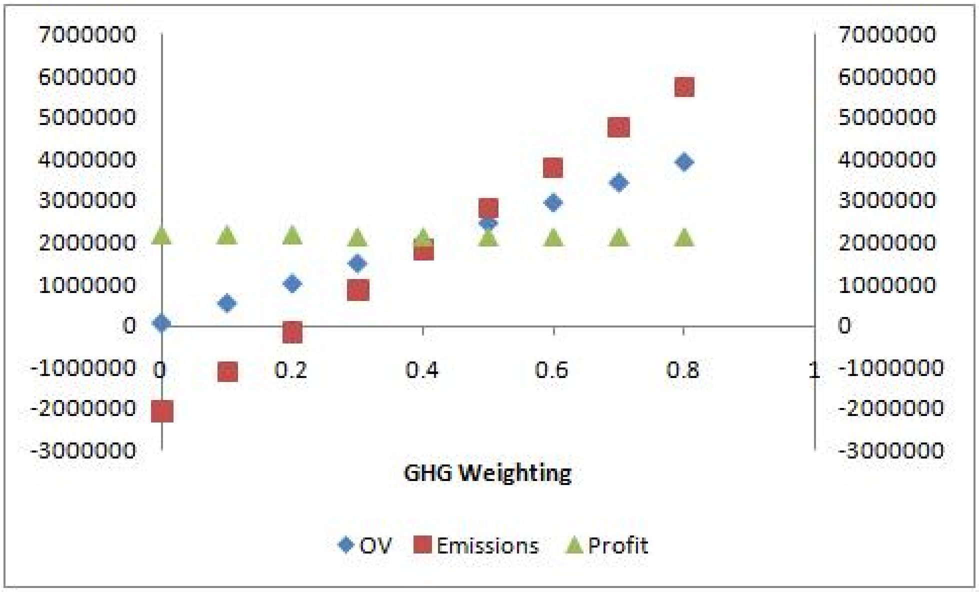

Figure 4.6: Analysis of the impact of varying the weighting of greenhouse gas emissions and criteria air contaminants with life-cycle emissions weighting of 0.5 and profit weighting of 0.5

At this time, the analysis does not account for the added benefit of avoiding the criteria contaminants being generated in the urban environment from the burning of gasoline (which is now offset by zero-emissions hydrogen), which would have a strong impact on urban health. Note the trends shown in Figure 4.4 would remain the same, only the amounts would decrease as the number of vehicles in this scenario analysis is fixed.

Figure 4.6 also shows linear relations in each of these results which is to be expected from the linear nature of the optimization program. As the relative importance of GHG emissions is increased, the overall emissions are reduced as the network is designed for this purpose. The LP model indicates that profit remains relatively unaffected compared to the reduction in emissions and the objective value also corresponds to show the optimum value changing with the reduction in emissions.

4.5 Summary

This chapter summarizes a method for constructing an optimization model to quantitatively assess the economic and environmental performance of a set of chemical facilities utilizing a dual-objective function. It is evident from the results of this work that integration of chemical facilities into an EIN format yields both economic and environmental benefits.

The products exported from each participant in the EIN varies with the weighting placed on the two parts of the objective function and leads to four stable, optimal solutions from a weighting of purely economic to purely environmental. The balance between these objectives is important for policy-makers in communication with facility owners to negotiate for the best option for profitability and also for reduced environmental impact. The framework developed in this research allows for additional applications of the methodology for policy-makers across a variety of industries.

The sensitivity of the model through a range of economic and environmental weighting factors shows that there are four optimal solutions in which the export of products from each facility varies according to these two factors. The sensitivity of each of the individual emission weighting factors is also considered and the results show that the objective value and the emissions portion of the objective function vary linearly with changes in these individual weighting factors.

The results show that emissions from the proposed network can be reduced and that the profitability of the network is also maintained. Biomass gasification is used as a feedstock to the network and an upper limit is placed on its availability in order to maintain the sustainability of the EIN. The optimization also operates under a minimum constraint of hydrogen production for 1000 fuel cell vehicles. This chapter is representative of the 'cradle-to-gate' emissions from the participating industries whereas the work in the previous chapter exhibits the benefits from the entire 'cradle-to-grave' utilization of hydrogen as a transportation fuel.

Chapter 5

Optimization of Material and Energy Exchange in an Eco-park Network Considering Three Fuel Sources

Chapter 5 is based on the forthcoming work "Optimization of Material and Energy Exchange in an Eco-park Network Considering Three Fuel Sources" by Kantor et al. [108], in press with the International Journal of Advanced Operations Management and is reproduced with permission from the International Journal of Advanced Operations Management. The thesis author's specific contributions to this paper were to develop the model, conduct the simulations, prepare the graphics and results, write the final manuscript and respond to the comments of reviewers. This work was conducted with direction from the project supervisors, Dr. M.W. Fowler and Dr. A. Elkamel, who are co-authors on the publication.

5.1 Introduction

The goal of this research is to further the efforts made in exploring eco-industrial networks (EINs) as a form of increased material and energy efficiency for manufacturing a given set of products. The benefits of operating a facility within an EIN where inputs and outputs are exchanged must be quantified in order to encourage development of these networks. As such, this work contributes to empirically modeling an EIN with emphasis on reducing environmental impacts while maintaining or improving profitability of each facility within the network. Life-cycle assessment (LCA) has been utilized in order to assess the environmental impact of the network facilities while profitability is computed using market pricing for the exports from the eco-park network. The baseline production for the network is to provide hydrogen for 1000 fuel cell vehicles which are intended to also decrease the emissions burden from the transportation sector as shown by Kantor et al. to be beneficial for urban air pollution and overall emissions [41]. Commercialization of hydrogen fuel cell vehicles is expected from most major vehicle manufacturers in 2015, and thus this research also contributes to the consideration of the transition to the 'hydrogen economy' [109].

The concepts of operating facilities within an EIP arrangement are documented in the literature. The benefits most often touted are increased efficiencies in the form of:

- reduced energy intensity through energy exchange and heat integration;
- reduction in transportation costs/impacts;
- reduced material waste;
- increased profits;
- reduced water use intensity and capital requirements through centralized water and waste-water processing; and,

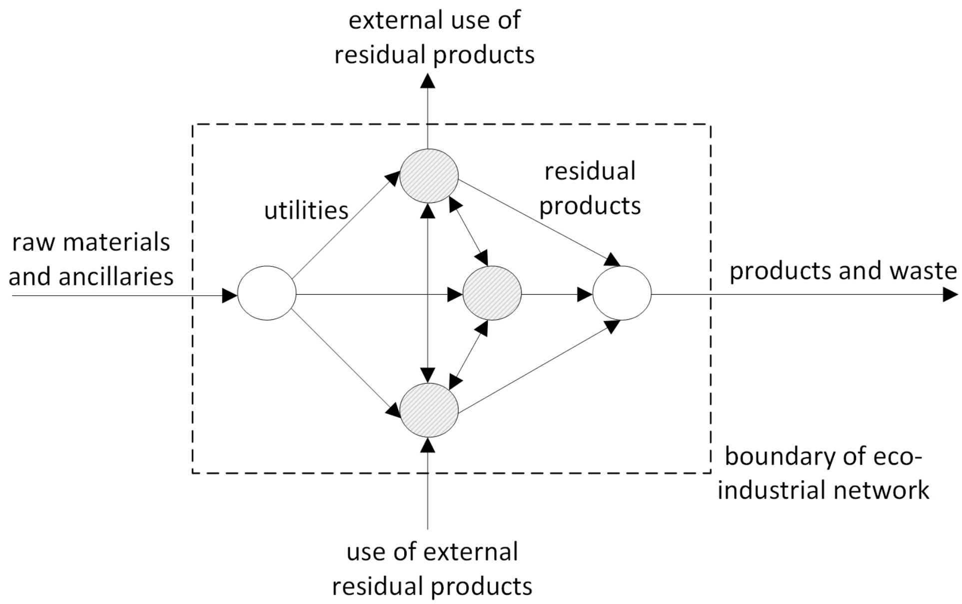

Figure 5.1: Visualization of an EIN as described by Lambert and Boons (modified) [1]

- reduced raw material use intensity though the multi-facility exchange of co-products, by-products or residual materials.

These are key factors in all eco-industrial park development and are documented as such by a number of authors [1, 10, 110, 8, 7]. A visualization of these concepts is shown in Figure 5.1 as presented by Lambert and Boons [1].

Life cycle assessment (LCA) is a technique typically used as part of an environmental management system for analyzing the performance of a process based on the emissions attributable to that process. Generally, a study conducted at a facility is compared to a baseline of emissions established for a generic plant in the same industry. In this work, LCA is used as part of the objective function in a mixed integer linear program (MILP) simulation of an EIN to optimize it for reduced emissions. Another portion of the objective function is attributed to financial gain from operating in an EIN compared to each plant operating as a stand-alone facility. GAMS is used in this work to construct and solve the

MILP simulation to determine plant capacity considering the dual objective of reducing emissions and maintaining or increasing profitability.

In recent years, several groups have attempted to apply LCA concepts to EIN arrangements. A study on the Finnish forest industry revealed a potential benefit of 5-20% in most impact categories considered by the LCA, and the authors state that "LCA seems a very useful, albeit labor-intensive, tool for this kind of assessment. It can also help in detecting those flows whose utilization could provide the greatest environmental benefits." [111]. In another study conducted by Mattila et al. in 2012, the authors address the methodology of LCA applied to industrial symbioses, i.e., EINs [112]. The conclusion of the study is that, to date, LCA has been applied in very few cases and also that "Expansion of current EIPs and implementation of new ones may result in changes in the economic structure. This change has not yet been analyzed in the IS [industrial symbiosis] literature, even though LCA provides tools for such analysis." [112]. To be clear, the work herein does not attempt to analyze a change in economic structure or overall product outputs, but to consider that reducing emissions and increased profits from industrial plants is a desirable outcome.

The eco-park considered in this work is shown in Figure 5.2 and is representative of the material flow from each facility in the eco-park. The figure is not a traditional representation of a network within an optimization context and instead represents the flow of materials within the eco-park.

Previous work has been completed on a similar arrangement of processes and can be found in a previous paper by Kantor et al. [69] which focused on a basic, preliminary development of an optimization model in GAMS to optimize the network with a requirement of hydrogen production to meet the demand of 1000 hydrogen fuel cell vehicles operating

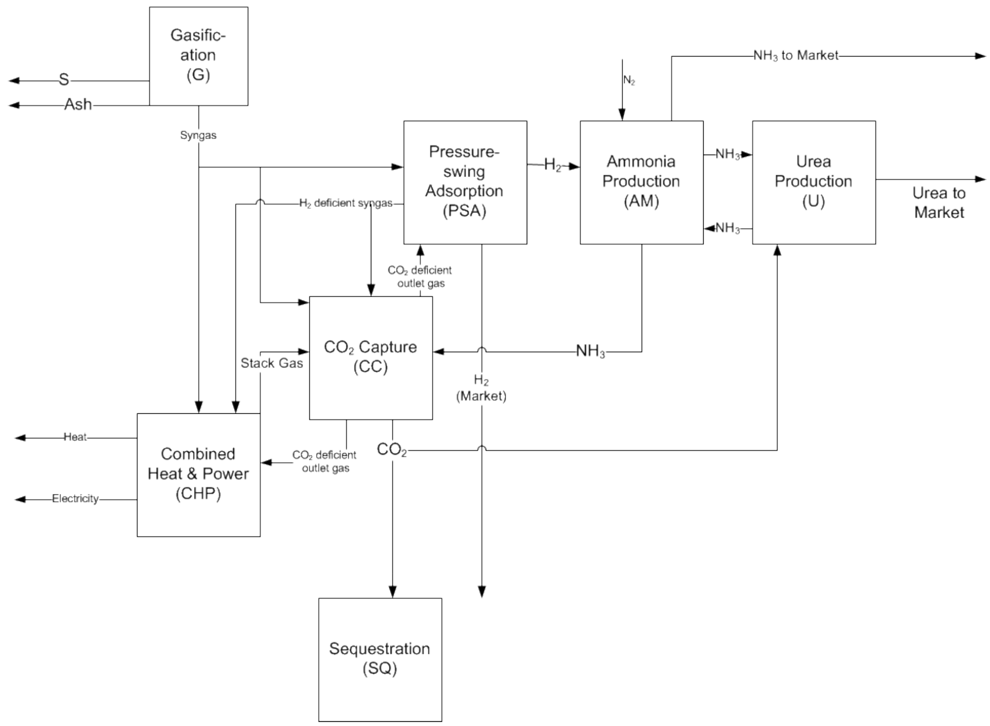

Figure 5.2: EIN considered in this work [69]

within Ontario, Canada. The work presented in this chapter expands on the previous model, introducing a more complex modeling technique of mixed-integer elements for additional realistic consideration of production. This work uses the same baseline hydrogen production as in the previous chapter but also furthers the analysis with the consideration of the benefits of industrial integration using three different feedstocks for energy and reaction components. The three fuels considered here are biomass, coal and natural gas. Each fuel is considered separately, meaning that co-gasification of a mixture of biomass and coal is not considered at this stage.

The decision variables for the optimization are:

- existence of each facility;

- existence of a connection between one facility and another;
- capacity of each facility; and,
- the division or 'split' of products from one facilities to others.

Also in this work, life-cycle assessment databases such as ecoInvent and the US LCA database are used as a primary source for life-cycle data to improve upon the reliability of the input data. These databases prescribe specific methodologies for obtaining and publishing data and thus they are assumed to be more consistent over the broad range of products considered. Additionally, each dataset is vetted for quality in the areas of reliability, completeness, temporal correlation and geographical correlation as described by Weidema and Wesnæs [113].

This work represents a growing part of the field of analyzing eco-parks and quantifying their benefits. Several authors have expressed that an EIN has many benefits [9, 16, 110, 8, 35] but empirical analysis of these benefits remains relatively unexplored [112, 111]. Karlsson and Wolf utilize an optimization model to explore the benefits from integrating a system comprised of a sawmill, pulp mill, district heating and biofuel upgrading [9]. Their method compares the baseline case of no integration with several cases of integration between the different parts of the network. Additionally, the authors use the terms industrial symbiosis and polygeneration synonymously with industrial integration, as is common practice in the field of industrial ecology.

5.1.1 Eco-park concepts

The concept of an eco-park is described in several publications [9, 8, 10, 7] and is described again briefly here to illustrate the idea. Eco-parks are a method of industrial cooperation in which products, co-products and large centralized utilities can be operated to maximize the efficiency of producing a wide array of outputs within a fixed geographical area [1]. Major improvements by operating in an EIN structure can be found in:

- large plants for water/waste treatment, heat exchange and electricity production;
- exchange of products and co-products between facilities [114, 2];
- waste reduction through facility intergration [114, 2]; and,
- increased optimized operation for higher profit or environmental performance [1].

It is the goal of this research to quantitatively exhibit the benefits of EINs in both the economic realm as well as for reducing overall environmental impact of manufacturing chemical products.

This research contributes to society by developing a method for evaluating industrial relationships and by assisting in the planning of new facilities. This will benefit citizens as the optimization will take environmental factors into account and will attempt to minimize the overall waste and air emissions from facilities that could otherwise affect living conditions in areas surrounding these facilities. The impacts on air, water and land can all be considered and the importance of the environment is taken into account in addition to the economic performance of industrial processes. If construction of a new chemical facility, or more specifically a collection of facilities, can be made more economically feasible by its integration with other processes in the region, construction and factory workers would also be required to build and operate these facilities. This would contribute to the economic stability in the region in addition to causing a decline in unemployment rates.

While environmental metrics are becoming increasingly important to business leaders, companies are still responsible to their shareholders to show solid and sustainable economic performance. The use of a dual-objective function allows for profitability to also be considered in the optimization and this will lead to a solution that proves to be environmentally responsible as well as being economically feasible. This research is intended to reinvigorate discussions in the industrial sector regarding issues such as sustainability, process symbiosis and collaborative efforts. The EIN concept is synonymous with polygeneration, industrial symbiosis and the like. All of these terms are based upon the concept of a diverse group of industrial producers cooperating to achieve a common goal of cost-savings and/or reduced environmental impact. Research has also shown that developing these eco-parks can very much be a driver for innovation and development of new technologies [37, 38]. The Dow Jones Sustainability Index (DJSI) is an indicator used to manage investment funds based on sustainability metrics. The funds developed using this index showed solid growth since the inception of the program and is an indicator that sustainability within an organization can have significant impacts on profitability. Though the index also focuses on business practices and management styles, the overarching reality is that sustainability within a company yields financial performance results [39, 40]. The DJSI was considered as a potential metric system for measuring the economic and environmental sustainability for the eco-park network scenarios but was ultimately rejected due to qualitative parameters that were not considered as part of the optimization model. The WAR algorithm, proposed by Cabezas [99], was predominantly used in the construction of the metrics for optimization. The premise of this system is utilized by researchers and government in order to assess the amount of waste reduced from a process or process alternative [98, 97]. This approach was used in combination with life-cycle assessment to construct the metric indices in the objective function for reducing the overall waste reaching final disposition within the air, water and land.

The approach for this optimization is to calculate the life-cycle impact of each product or process in the proposed network and to compare the eco-park scenario with a plant of comparable size operating as an independent facility. The eco-park concepts rely on collaboration from progressive facility managers in order to implement a symbiotic strategy for responsible and sustainable chemical processing.

5.1.2 Life-cycle Assessment

Life cycle assessment can be used as part of an environmental management strategy to assess and manage the life cycle inventory of emissions from a product or process. In this work, LCA efforts are used in the construction of the objective function and for assessing the reductions in environmental waste from operating in an integrated scenario. The life-cycle inventory is taken from LCA studies and from SimaPro software databases. Life-cycle impact assessment methods are used to relate emissions to potential impacts on people and the environment as is described in the ISO 14040 series of standards [31].

SimaPro databases are region-specific but can be used as an estimate for emissions from manufacturing a variety of products. Data quality considerations are monitored within SimaPro according to the framework set out by Weidema and Wesnæs [113] and the goal for this chapter was to obtain reliable, complete and temporally relevant data sets. Although the life cycle inventories can respond to regional electricity generation and other geographical considerations, less weight was applied to obtaining data specific to Canada. For the figures below, cut-off values between one and six percent of total emissions are applied so that only the major contributors to emissions are shown. If the figures were not truncated as such, they would be unreadable as they would contain several thousand elements contributing to the final emissions burden for the final product. As the cut-off values are very small, the omitted elements are minor overall contributors to the life-cycle emissions burden.

Figure 5.3 shows the life-cycle greenhouse gas (GHG) contributions from various sources required to produce 1 kg of ammonia. This is a representation of the GHG emission contribution from different aspects of ammonia production using steam-methane reforming which is a standard practice for producing ammonia. The cut-off applied in this instance for representing the major emission contributors is 1%. In this typical production of ammonia, it can be observed that natural gas production and use, in several stages, is responsible for the majority of GHG gas emissions. It must be noted, however, that the emission landscape changes depending on the emission being considered. For example, when considering the emission of sulphur oxides, the emissions from the natural gas streams and fuel oil streams are similar as shown in Figure 5.4 with an applied cut-off value of 3% in order to properly view the network of life-cycle contributions. This is logically sound as there is typically more sulphur contained in, and released from, crude oil when compared with natural gas [115].

The complexities involved with assessing the emission burden from each product /process requires an objective function that will take each emission into account and its relative importance to society. The scope of this work covers the emissions of GHGs, pre-cursors to photochemical smog, oxides of sulphur and solid waste.

Figure 5.3 and Figure 5.4 are examples of the life-cycle assessment where the CO_2 and SO_x emissions associated with producing ammonia in a traditional facility which is not part of an EIN are evaluated. The purpose of these examples is to show the areas in which the production of ammonia can be improved in order to decrease life-cycle emissions. The thickness of arrows exhibits the contribution from one area of the life cycle production process to the overall emissions burden associated with a product, in this case, ammonia. For

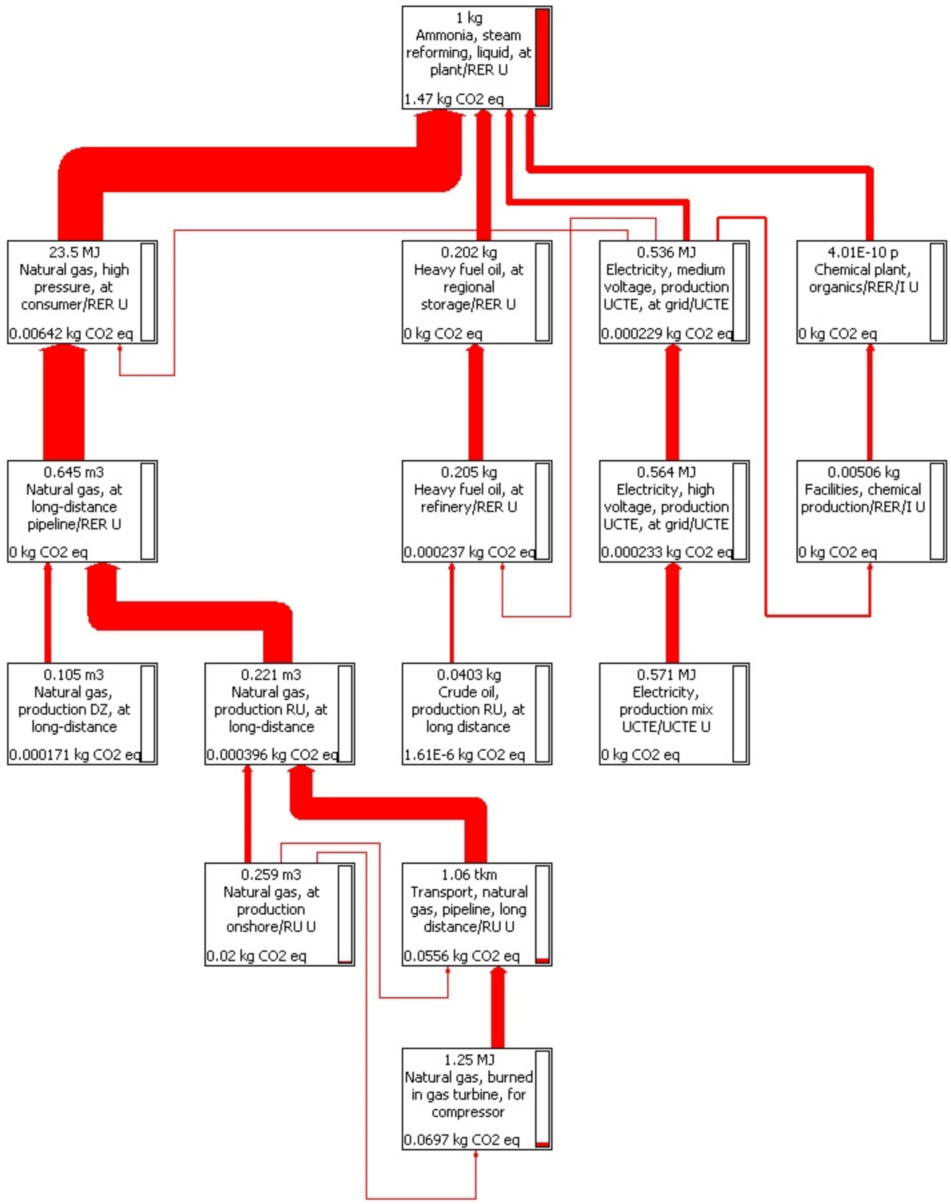

Figure 5.3: Life-cycle GHG contributions for producing Ammonia via a traditional (non-EIN) process from EcoInvent Database of SimaPro software

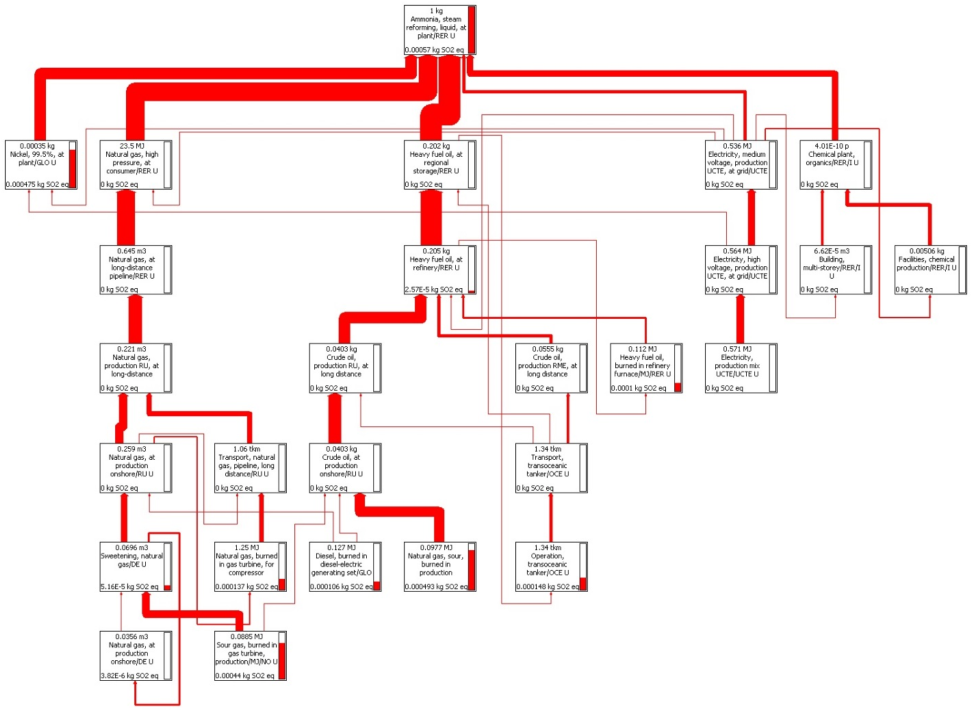

Figure 5.4: Life-cycle SO_x contributions for producing ammonia via a traditional (non-EIN) process from EcoInvent Database of SimaPro software

example, it can be seen in Figure 5.3 that the greatest contribution to GHG emissions in the ammonia production process is the steam reforming of natural gas. Minor contributors in this case are generation of electricity and fuel oil for heating and transportation. Figure 5.4 shows the life-cycle emissions of SO_x and shows a much more even split of the processes contributing to SO_x emissions stemming from ammonia production; furthermore, it exhibits that the requirements of fuel oil, natural gas and nickel are the primary areas contributing to these emissions. It is important to understand life-cycle concepts when attempting to integrate processes into an eco-park network as the major contributors to emissions of a particular type are the best candidates for improving the environmental performance of that process.

For both instances, the network layer previous to the finished product represents the sum of the process production flow charts to create the product or process used by the final manufacturing. Discrepancies between the sum of the penultimate layer and the final life cycle emission contribution are attributed to the processing within the plant, defined as gate-to-gate emissions for the facility. Figure 5.3 shows high gate-to-gate GHG emissions and thus represents a large opportunity for reducing the life-cycle GHG emissions within the plant. Figure 5.4; however, shows most of the life-cycle SO_x emissions are accounted for prior to entering the manufacturing facility. The opportunity for reducing the life-cycle SO_x emissions is thus bound with the process feedstock.

Researchers have only begun investigating the possibilities of evaluating EINs using LCA concepts, this work not only shows that this is a valuable undertaking but also proceeds to utilize optimization in order to assess the best way of constructing these facilities based on the LCA concepts.

5.2 Manufacturing Facilities

The model is formulated as an MILP with chemical reactions, conversions, product removal and recycling. Supply and demand are modeled as in a classical transportation problem but varies significantly due to reaction and/or separation at each facility or 'node'. The mass and energy balances must be written for each node to account for the flows of energy and material through the network. Following this, the technical constraints must be quantified in a mathematical format in order to implement them within the model.

The nodes of this network were chosen in order to process the streams of a fuel source into products. Gasification processes (G) can be constructed to accept input of coal or biomass and produce syngas of varying $H_2 : CO$, and $CO : CO_2$ ratios. The alternative fuel source considered is natural gas, with the syngas mixture achieved by steam-methane reforming. Some of the syngas can be used directly in a combined heat and power plant (CHP) to produce heating and electricity for the network processes.

For the remaining nodes in the network, the hydrogen in the syngas must be separated from the other gases in order to utilize them in further processing stages. The separation of these gases is completed by the pressure-swing adsorption process (PSA). To ensure that the network operates with the least possible emissions, a carbon capture process (CC) using a recirculating ammonia loop is added to the network to capture CO_2 emissions which would otherwise be emitted to the atmosphere. A CO_2 sequestration process (SQ) is added as a possibility for the network to reduce its emissions to the environment. This node relies on injection of CO_2 into a deep saline aquifer as is the most feasible form of geological storage in Ontario as explored by Shafeen et al. [116]. It is estimated in the same work that the storage capacity via geological sequestration is approximately sufficient for 730 million tonnes of CO_2. For the scale of processing considered in this work, the storage capacity is much larger than the amount produced; however, the constraint is placed within the model in the event that the scale of facilities considered is increased significantly.

Ammonia production (AM) in the network is sufficient to supply the carbon-capture process with make-up ammonia while also producing excess as a market product which is used as a chemical building block for other processes or as an agricultural fertilizer. Urea processing is naturally synergistic to the ammonia process as urea requires two molecules of ammonia and one molecule of CO_2. The ammonia can be produced at the proper conditions for urea production, negating additional processing considerations for conventional ammonia destined for use in manufacturing urea. The remainder of the ammonia is sent to market.

A urea node is included in the network as it is efficient to produce ammonia in close proximity to ammonia manufacture [117]. Urea is also a chemical fertilizer which can be used to temporarily sequester CO_2 as part of a solid fertilizer. This CO_2 is later released to the atmosphere when urea is applied as a fertilizer but the emission of CO_2 in close proximity to the vegetation can increase probability of its utilization for respiration. Urea manufacturing (U) in this network is entirely for export to external markets. A summary of the network nodes is shown in Table 5.1. Table 5.2 shows a summary of the inputs and outputs for each facility.

Table 5.1: Legend of Nodes

Process	**Node Abbreviation**
Gasification	G
Combined Heat and Power	CHP
Carbon Sequestration	SQ
CO_2 Capture	CC
Pressure-swing Adsorption	PSA
Ammonia Production	AM
Urea Manufacture	U

5.3 Objective Function

As mentioned previously, the complex nature of the life-cycle emission considerations must be included in an objective function that will lead to the optimization of the network of

Table 5.2: Summary of inputs and outputs

Process	Inputs	Outputs
Gasification	Biomass/Coal/Natural gas Heat Electricity Air	CO CO_2 N_2 H_2 H_2O
Combined Heat and Power	CO CO_2 N_2 H_2 Heat Electricity	Heat Electricity N_2 H_2O CO_2
Carbon Sequestration	CO_2 (purified stream) Heat Electricity	CO_2 (purified stream)
CO_2 Capture	CO_2 N_2 H_2O Heat Electricity	CO_2 (purified stream) N_2 H_2O
Pressure-swing Adsorption	CO CO_2 N_2 H_2 Heat Electricity	H_2 (purified stream) CO CO_2 N_2 H_2
Ammonia Production	N_2 H_2 Heat Electricity	NH_3
Urea Manufacture	NH_3 CO_2 Heat Electricity	$(NH_3)_2CO_2$

plants yielding the most beneficial emission reductions. A purely environmental objective function is impractical for two reasons; primarily, a purely environmental objective is unlikely to be undertaken by industrial interests as the manufacturers must show positive financial results. Additionally, it is impractical to consider a purely environmental objective as the optimization algorithm would naturally decrease the plant sizes to the least allowable value. This assessment does not include the emissions offset associated with reforestation. For these reasons, an economic term is included to offset the environmental term to present a balanced, applicable, practical approach to optimizing the network. The bi-objective optimization is structured as described by Kim and Weck [118] and the formulation for the program is shown below.

For an optimization program to minimize Z subject to a design vector x and a vector of fixed parameters, c, the objective function can be written as equation 5.1.

$$min\,Z(x,c) \tag{5.1}$$

The entire problem can be structured as follows:

$$\begin{aligned} min\,Z(x,c) \\ s.t.\ \ g(x,c) &\leq 0 \\ h(x,c) &= 0 \\ x_i^L &\leq x_i \leq x_i^U (i = 1, \ldots, n) \\ Z &= [Z_1(x) \ldots Z_q(x)]^T \\ x &= [x_1 \ldots x_i \ldots x_n]^T \\ g &= [g_1(x) \ldots g_{m_1}(x)]^T \\ h &= [h_1(x) \ldots h_{m_2}(x)]^T \end{aligned} \tag{5.2}$$

Where:

- g is the vector of inequality constraints;
- h is the vector of equality constraints;
- x_i^L is the lower bound for x_i;
- x_i^U is the upper bound for x_i;
- q is the number of objectives;
- x is the vector of decision variables;
- c is the vector of fixes parameters;
- m_1 is the number of inequalities; and,
- m_2 is the number of equalities;

and with these definitions, 5.2 can be reduced to a scalar problem of the form shown in 5.3

$$min\,\tilde{Z} = \sum_{i=1}^{q} \frac{\lambda_i}{F_i} Z_i \tag{5.3}$$

Where λ_i and F_i are the weighting and scaling factors for each Z_i. $\tilde{Z}$ is considered to be the aggregated objective value, being a summation of each weighted element Z_i as shown by Kim and Weck [118]. Generally, the sum of the weighting/scaling ratios is equal to unity. Kim and Weck explored this structure in the case of a bi-objective function which is applicable in this work, as the two objectives being considered are the economic objective and the environmental objective which is written in terms of reduced emissions.

Splitting the objective function into the economic portion and an environmental portion yields $Z_1 = Z_{economic}$ and $Z_2 = Z_{emissions}$, respectively. Though this form would then appear as a bi-objective function, $Z_{emissions}$ is constructed inherently as a multi-objective function to include the emissions of multiple environmental contaminants. $Z_{emissions}$ is constructed as a summation of the reduced emissions between an independently-operated facility when compared to the integrated facility such that:

$$\tilde{Z}_{emissions} = \sum_{e}^{n_e} \frac{\lambda_e}{F_e} Z_e \tag{5.4}$$

Where:

- e is representative of a considered emission;
- n_e is the number of emissions considered;
- λ_e and F_e are the weighting and scaling factors as mentioned previously; and,
- Z_e is the emission differential between the integrated and stand-alone facilities. The difference is defined in Equation 5.5 below:

$$Z_e = I_e - S_e \tag{5.5}$$

Where:

- I_e is the emissions of e from an integrated facility;
- S_e is the emissions of e from a standalone facility.

Constructing the economic portion of the objective does not require further manipulation, as it is a difference between the net present value (NPV) of the integrated and independent plants assessed at a set discount rate, r_d, and plant lifetime and is constructed as shown in Equation 5.6.

$$Z_{economic} = I_{CC} - S_{CC} + \sum_{t=1}^{L} \sum_{p}^{n_p} \frac{R_p - [I_{OC} - S_{OC}]_p}{(1 + r_d)^t} \tag{5.6}$$

Where:

- p is a manufacturing facility;
- n_p is the number of manufacturing facilities;
- R_p is the return from sale of products from plant p (\$);
- I_{CC} and S_{CC} represent the integrated and standalone capital costs, respectively(\$);
- I_{OC} and S_{OC} represent the integrated and standalone operating costs, respectively(\$);
- t represents the year; and,
- L represents the lifetime of plant p.

The numerator in equation 5.6 does not require the subscript t, as it is assumed that production is maintained at the same level for the lifetime of the plant. For this analysis, the network lifetime, L, is considered to be 30 years during which time, the discount rate, r_d, is also fixed. The full bi-objective function, based on these equations can then be seen in equation 5.7.

$$min\, \tilde{Z} = \frac{\lambda_{emissions}}{F_{emissions}} \tilde{Z}_{emissions} + \left[1 - \frac{\lambda_{emissions}}{F_{emissions}}\right] Z_{economic} \tag{5.7}$$

5.4 Modeling

The modeling is explained in detail in a previous chapter. The explanation here is presented to summarize the main differences in the model which are added in order to create a more realistic scenario with mixed-integer programming. A schematic of the network under consideration was shown previously as Figure 5.2.

The sets used in this formulation are as follows:

- k is a set of the transportation technologies available;
- m is a set of plant sizes;
- v is a set of material vectors;
- e is a set of emissions;
- p is a set of facilities; and,
- $p2$ is an alias of p.

The mass balances between units are formulated as inequalities as described by the vector g in Equation 5.2, whereas the mass balances within a unit are formulated as equalities as described by vector h in Equation 5.2. The format of some inequalities in the following equations is altered from the general format for the sake of clarity. The generalized form of the mass balances between units are described by Equation 5.9, while the mass balances within a unit are described by Equation 5.8.

$$out_{v,p} = \sum_{p} in_{v,p} - rx_{v,p} + gen_{v,p} \quad \forall v, p \tag{5.8}$$

Where $out_{v,p}$ is the amount of material v output from plant p and $in_{v,p}$ is the input of v to plant p. This equation is a mass balance based on equilibrium conditions within a unit such that the amount output from a given plant p is equal to the inputs from all other plants $p2$ with a decrease due to consumption at a rate of $rx_{v,p}$ or an increase from generation encompassed by $gen_{v,p}$. $rx_{v,p}$ and $gen_{v,p}$ are functions of conversion and stoichiometry.

$$out_{v,p} \geq \sum_{p2 \neq p} in_{v,p2} \quad \forall v, p \tag{5.9}$$

This mass balance between units forces the production of material v from plant p to exceed the requirements of input for all other plants, $p2$, that accept material v from p. At this point, the binary variable x is defined for selection of plant sizing.

$$x_{p,m} = \begin{cases} 1 \, \text{if plant } p \text{ of size } m \text{ exists} \\ 0 \, \text{Otherwise} \end{cases} \tag{5.10}$$

To force the selection of only one plant, Equation 5.11 is included:

$$\sum_{m} x_{p,m} \leq 1 \quad \forall p \tag{5.11}$$

Additionally, the flow of material v from plant p must be less than the capacity expressed by $x_{p,m}$. This constraint is applied by utilizing Equation 5.12.

$$out_{v,p} \leq M^U_{p,m} x_{p,m} \quad \forall v, p, m \tag{5.12}$$

Where $M^U_{p,m}$ is the upper limit of from plant p of size m. Each value of $M^U_{p,m}$ is defined in a table within the optimization program.

At which point I_{CC} and SA_{CC} from Equation 5.6 are calculated for plant p of size m from existing plant data for the stand-alone and integrated facilities. The economy of scale plant construction theory with an exponential scaling factor of 0.6 is used to calculate the costs for sizes lying between defined points. The costs are amortized and included in the economic portion of the objective function. The existence of a transportation connection between two plants is represented by variable y as described by equation 5.13.

$$y_{p,p2,k,v} = \begin{cases} 1 \text{ if material } v \text{ is transported by method } k \text{ between } p \text{ and } p2 \\ 0 \text{ Otherwise} \end{cases} \tag{5.13}$$

Several integer equations must be applied at this time. The first, Equation 5.14, prevents the existence of transportation connections to plant p if plant p does not exist in any size (i.e., $\sum_m x_{p,m} = 0$).

$$\sum_m x_{p,m} \geq y_{p,p2,k,v} \quad \forall p, p2, k, v \tag{5.14}$$

Equation 5.15 yields the result that only one method of transportation should be chosen to transport material v between plants p and $p2$.

$$\sum_k y_{p,p2,k,v} \leq 1 \quad \forall p, p2, v \tag{5.15}$$

The transportation cost can thus be assessed by applying the base-plus-throughput method. This is shown here in Equation 5.16.

$$TransportationCost_k = \sum_{p} \sum_{p2} \sum_{v} y_{p,p2,k,v} BaseCost_k + \sum_{v} \sum_{p} out_{v,p} ThroughputCost_k \quad \forall k \tag{5.16}$$

The transportation cost, in turn, is also included in the economic portion of the objective function. More details on the interactions of each unit and the associated reagents can be found in Chapter 4.

The structure of the environmental portion of the program is constructed in a similar manner to the economic portion shown above, yet is increasingly complex as each emission type (set e, noted above) requires its own correlations. These correlations are parallel to the economic portion of the objective function, yet they yield the differences in emissions produced from a standalone facility and an integrated facility instead of the economic differences.

5.5 Results

The EIN considered here is to support production of hydrogen for export, in anticipation of the potential 'hydrogen economy' where there is some demand to refuel fuel cell vehicles [41]. The target for hydrogen production in the EIN is enough to fuel 1000 vehicles within Ontario, Canada. As presented in a previous chapter, the results of the model show that to produce the requirement for 1000 vehicles fuelled by hydrogen, the export of products from facilities will vary based on the weighting factor of life cycle emissions in the objective function [69]. By varying the life-cycle emissions weighting in the range of 0, representing no impact of emissions on the objective function, to 1, representing no impact of profitability on the objective function yields the result shown by Figure 5.5. The x-axis in Figure

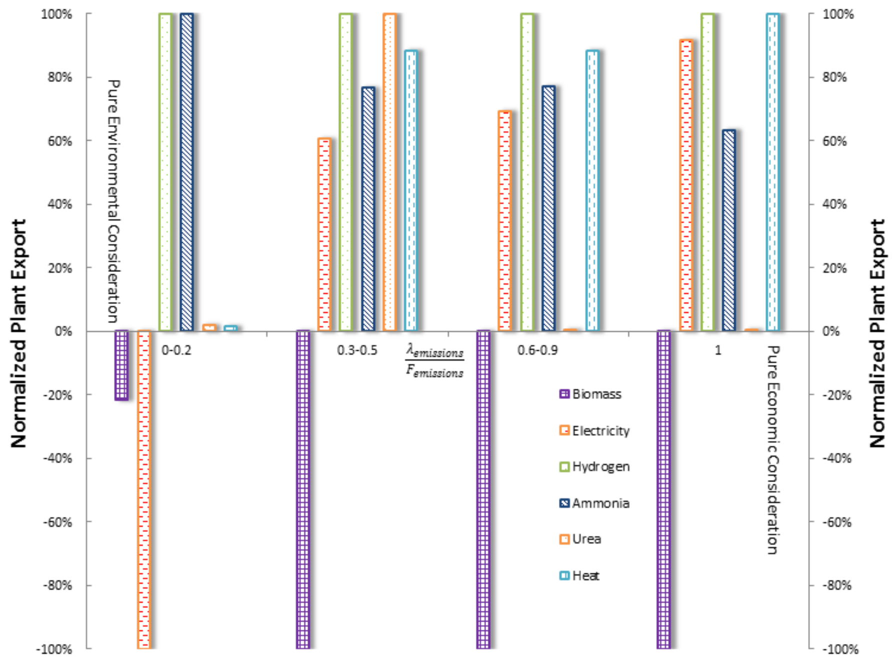

Figure 5.5: Normalized plant exports as a function of life-cycle emissions weighting

5.5 refers to the ratio $\frac{\lambda_{emissions}}{F_{emissions}}$ as mentioned in equation 5.7 and refers to the weighting of the life-cycle emissions relative to the economic weighting. As it is a bi-objective function, the two sides of the figure are noted as being the side of high environmental bias or high economic bias.

Normalized plant export, used on the y-axis of Figure 5.5- 5.7 is representative of the output from each facility in the EIP. The values are normalized to the maximum value seen over the trials for the purposes of observing changes in production from each facility. As the level of production varies largely between plants, a figure of the normalized values is best for observing variations in the level for each facility.

As suggested by previous work, the possibilities of alternative fuel sources should be considered [69]. For this work, coal and natural gas have been considered as possible alternatives to biomass as the primary fuel source for gasification. Modifying the model to accept a variety of fuel sources as inputs to the eco-park shows any potential benefits which may arise from utilizing a traditional fossil fuel as a gasification or steam-methane reforming (SMR) fuel, providing that the network still provide an adequate level of hydrogen for 1000 fuel cell vehicles. Figure 5.6 and Figure 5.7 show the same analysis but using coal or natural gas as fuels. Figure 5.6 shows that importing electricity is required for emission weighting between 0 and 0.8 in order to produce the required products. This is likely due to a balancing of emissions from using coal generation and the grid mix in order to supply the necessary electricity to the network. High volumes of coal are required at a high value of emissions weighting as coal can be utilized within the network in a more emission-efficient manner than the electricity production that would be imported into the network in the low-emission-weighting scenarios. The highest production for most industrial chemicals is at an emissions weighting of 0.9 at which point, emissions have a large impact but economics also plays a role. At higher emissions weighting, the economic portion of the objective is no longer used and thus the production drops off significantly in order to reduce the amount of emissions while maintaining the level of hydrogen production for the fuel cell vehicles as stipulated previously.

Figure 5.7 represents the same information as in the previous two figures but utilizing natural gas as the feedstock. There are three distinct regions, the first when the life-cycle weighting is between 0 and 0.4, the second between 0.5-0.9 and the final region when the life-cycle emissions are weighted as 1, representing a purely environmental objective. Similar trends are seen as with the coal except that electricity import is only occurring in the scenario in which life-cycle emissions weighting is set to 1. At this point, the optimization again reduces the amount of chemical production as economics are no longer a factor. In the intermediate to high range of emissions weighting, 0.5-0.9, large product volumes are man-

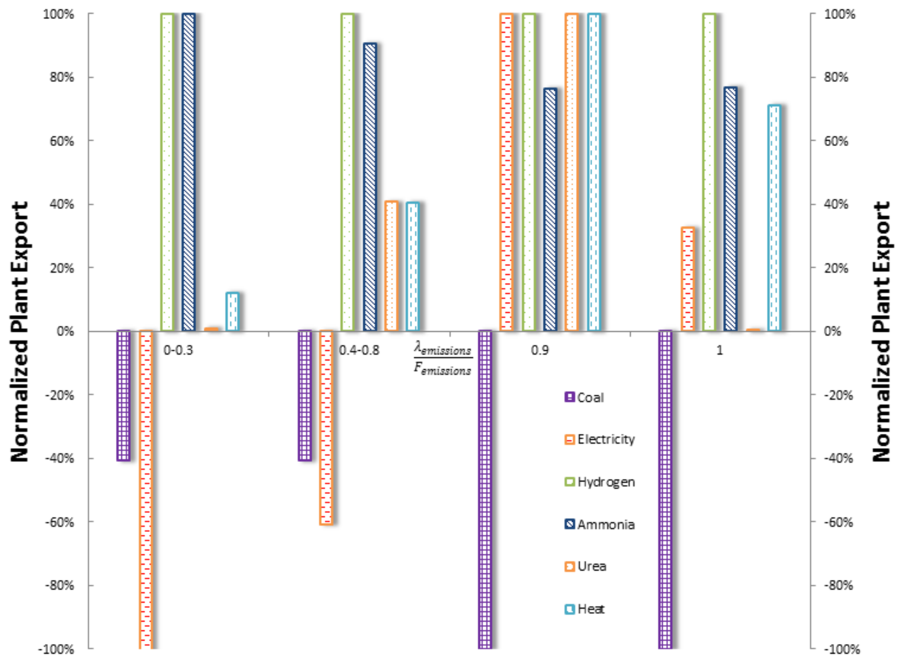

Figure 5.6: Normalized network plant export using coal as gasification feedstock

ufactured in the EIN as there is an economic incentive in addition to the reduced emissions.

Also, the analysis points to the processing of urea being most economically viable when balancing emissions and economics. Urea is a value-added product and is easier to produce using a natural gas feedstock than other potential sources. The CO_2 that is bound in the urea is also beneficial economically as the carbon sequestration facility would experience reduced loading and thus would require lower capital and operating costs.

The weighting for life-cycle emissions and profitability were set to the baseline level of 0.5 for each factor. Figure 5.8 and Figure 5.9 show the results of the updated modeling in terms of production amounts, profits and emissions for the three fuels.

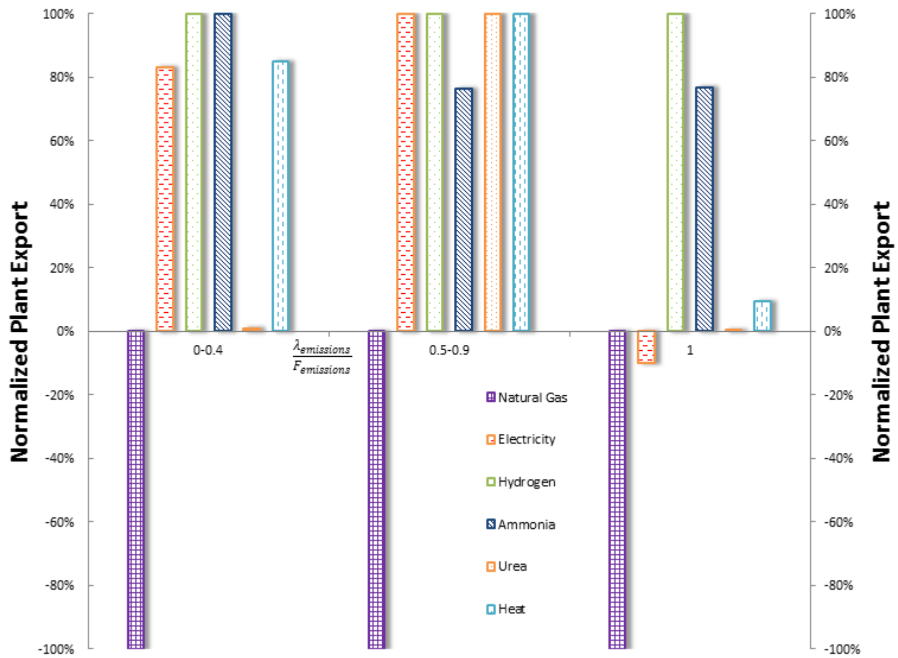

Figure 5.7: Normalized network plant export using natural gas as feedstock

In terms of profitability, the model results shown in Figure 5.8 yields that biomass is the least profitable fuel to use and that natural gas yields slightly higher profit than coal. The reasoning for a slight but marginal difference using the various fuels is due to a differing network price structure considering SMR instead of gasification of coal or biomass. The biomass yields a lower net profit due to a lower energy density and increased processing complexities associated with utilizing biomass in the system. The total emissions, surprisingly, are similar for all three fuels. Any potential emission reduction from utilizing biomass as a feed is offset by the increased transportation emissions of the biomass and the fact that reforestation has not been considered as it is not part of the EIN operations. It is assumed that inclusion of reforestation to re-sequester carbon through the growth of new biomass over the EIN lifetime would reduce the total emissions produced by utilizing biomass as a fuel. The hydrogen, as mentioned, has a fixed level in order to produce the

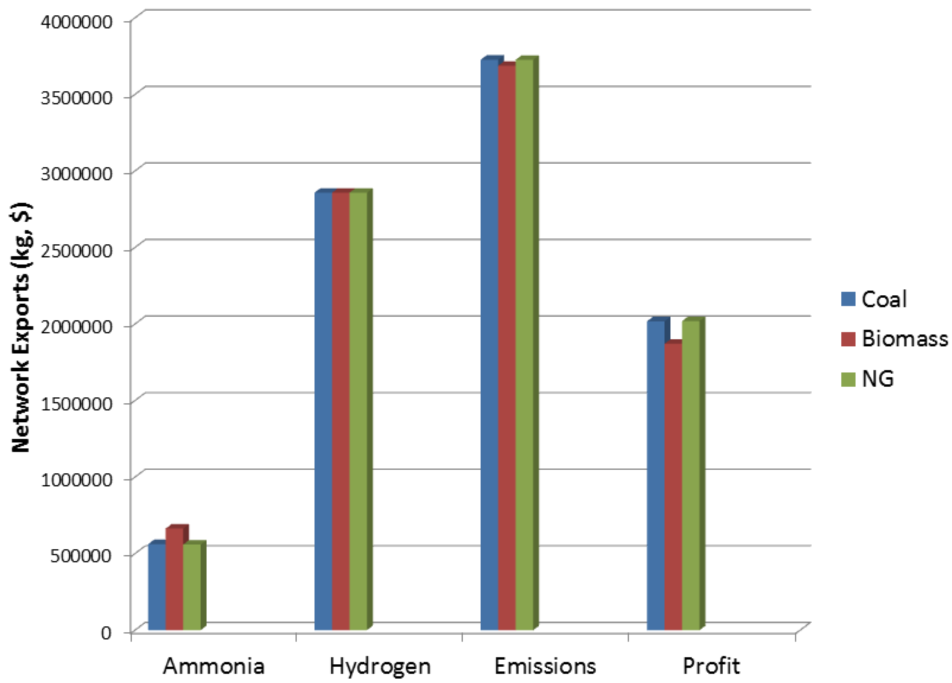

Figure 5.8: Network product exports and profit for three different fuels

required fuel for 1000 vehicles and thus it is constant across the three fuels considered. The production level of ammonia varied slightly for the three fuels, with the largest amount being produced while utilizing biomass as gasification feed.

Figure 5.9 shows the heat, power and urea output for the three fuels. Immediately, it can be seen that the net power export for using biomass is a negative value, indicating that power import is required. Both fossil fuels show a net export of power, although the level is very low. Clearly the low energy content of the biomass requires electrical input to the EIN. Heat output is also dramatically lower for biomass than for coal or natural gas, although this was expected due to the lower energy content in the fuel. The only fuel which showed a meaningful production of urea is natural gas. Due to the inclusion of life-cycle emissions as part of the objective function, ammonia is typically produced in higher quan-

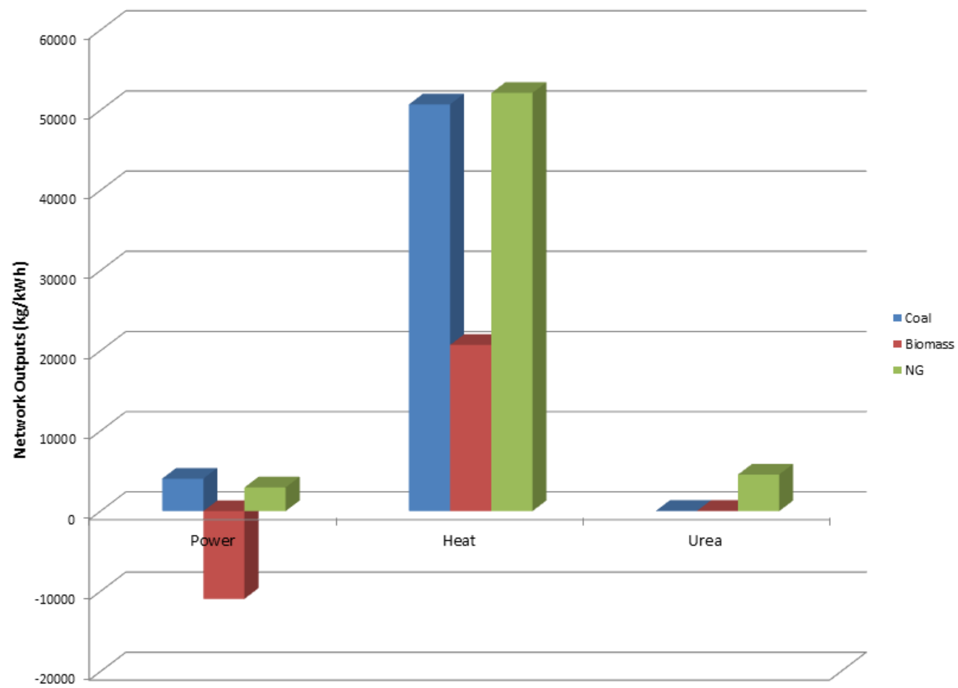

Figure 5.9: Network exports of power, heat and urea for three different fuels

tity than urea as the additional processing of ammonia to produce urea generally does not produce a favourable cost/benefit transaction in terms of the objective function. With the case of natural gas, the cost of erecting the urea facility is only slightly overcome by the profitability associated with the product. For the other fuels, this barrier is not exceeded and thus urea is not produced in any significant quantity.

Calculating the mass-specific contributions of ammonia production between the traditional process shown in Figure 5.3 for GHG emissions and Figure 5.4 for SO_x emissions yields the comparative tables shown in Table 5.3 and Table 5.4. While the differences in Table 5.3 seem minute, Table 5.4 is shown for comparison at a level representing a very small, considering typical industrial operations, production of ammonia. The reduction in significant figures for Table 5.4 belies some of the differences due to rounding; whereas, the benefits in terms of GHG emissions are very clear. Some issues, such as allocation of emissions to the appropriate facility, are sometimes difficult to address and thus it is generally a better approach to look at the emissions from the network perspective instead of each individual product. Regardless of the possible allocation issues, the EIN shows large reductions in GHG emissions using any of the three fuels and mixed results for SO_x, smog precursors and solid waste. Part of this reduction is due to the incorporation of carbon capture and sequestration within the network but reductions in transportation-related emissions and fugitive releases also contribute.

Table 5.3: Comparison of life cycle emissions per kg of ammonia based on three fuels

Basis: 1 kg Ammonia	Traditional	EIN with Natural Gas	EIN with Coal	EIN with Biomass
GHG (kg CO_2 equivalent)	1.91	1.1469	1.14125	1.00464
SO_x (kg SO_2 equivalent)	0.00333	0.00293	0.00405	0.00146
Smog Precursors (kg VOC equivalent)	0.00309	0.00329	0.00308	0.00437
Solid Waste (kg)	0.0033	0.00326	0.00386	0.00396
Total	1.91972	1.15637	1.15224	1.01443

5.6 Summary

This chapter focused on the expansion of the model from the previous chapter to include integer and binary variables for options of plant size/existence and connections between the facilities. In addition, the gasification node was implemented in the model and three fuel sources were considered. Natural gas, coal and biomass showed similar results for

Table 5.4: Life-cycle emissions of ammonia based on three fuels at a reference level of 730 tonnes

Basis: 730000 kg Ammonia	Traditional	EIN with Natural Gas	EIN with Coal	EIN with Biomass
GHG (kg CO_2 equivalent)	1400000	840000	840000	740000
SO_x (kg SO_2 equivalent)	2400	2400	3000	1100
Smog Precursors (kg VOC equivalent)	2300	2400	2300	3200
Solid Waste (kg)	2400	2400	2800	2900
Total	1410000	850000	840000	740000

many of the plant exports although the lower heat content from biomass coupled with additional impurities led to reduced profitability and less generation of heat and electricity when compared to the other two fuel options.

The sensitivity analysis on the weighting of each portion of the objective function was carried out for each fuel and result in four distinct optimal scenarios with varying levels of production from each of the facilities.

Compared to the previous chapter, the overall economic and environmental benefits are slightly lower which is attributable to the increasing constraints imposed in the model such as discrete plant sizes and inclusion of transportation costs. The MILP approach presented in this chapter allows for increasingly detailed modeling of the EIN than the LP presented in Chapter 4 and is a more realistic representation of facility construction.

Chapter 6

Generalized MINLP Modeling of Eco-Industrial Networks

6.1 Introduction

Symbiotic relationships between chemical network producers have been demonstrated effectively in both academic and industrial domains. The integration of material and energy exchange between producers typically offers economic and environmental advantages over stand-alone facilities. However, the high level of interactions between participants in an eco-industrial network (EIN) requires the application of a system integration method for the design of a common optimal infrastructure. One of the crucial factors for the success of any EIN is that the sum of the benefits achieved working together must be greater than working as many stand-alone facilities [119]. For example, the industrial symbiotic network of Kalundborg, created in the 1970s, is considered a prototype of an EIN. This network consists of an oil refinery, a pharmaceutical company, an electric power plant, a gypsum plate factory, a cement factory, a fish nursery and city heating. These facilities use surplus energy and waste materials from each other, obtaining annual savings of more than $12 million [120]. Currently, the government of South Korea is implementing a three-phase, 15-year EIN initiative to promote the balance between the economy, society and environment [121, 8, 122]. The first phase of the project (2005-2009) aimed at converting five existing industrial complexes into EIN based on the optimization of energy consumption, raw materials, and other resources. This is part of the South Korean "low-carbon green growth" strategy, which has become the core paradigm of development since 2008 [123].

Accordingly, the focus of these networks has been analyzed qualitatively by a number of authors and quantitative examples have now been presented in a number of instances. Lovelady et al. [119] developed an optimization model for the design and integration of EINs. The model focuses on the management of water among multiple processes in a common industrial network. The recycle, reuse, and separation of waste-water using interception devices are considered as management strategies. The model is based on a source-interception-sink structure to determine the best potential configuration. Fernandez et al. [124] proposed a model to determine the optimal location for a sustainable EIN. The model is based on the analytical hierarchy process (AHP) that applies multicriteria evaluation to analyze different suitable locations. The model consists of three different levels: selection of the geographic area, evaluation and selection of suitable areas, and evaluation of specific zones. The evaluation is performed according to the importance assigned to the goal variables (i.e., social, economic, environment, planning, and infrastructure). Therefore, weights are applied to the different factors considered in the model, which leads to the identification of the suitable locations.

Sendra et al. [125] adapted a material flow analysis tool to consider material flow into and out of an EIN. The model determines the amount of material and energy that are used in the network to plan the development of an eco-park. The model also takes into account environmental metrics for the analysis. Zhao et al. [126] used system dynamics and grey clusters approaches to redesign an EIN in China. Four different scenarios were considered in the analysis: base case, economic development as key priority, impact on the environment, and economic impact (subject to science, technology, and environmental improvements). Spriggs et al. [127] described the challenges involved in the development of eco-parks. The authors classified these challenges into two groups: technical/economic and organizational/commercial/political. The technical/economic challenge means that the success of an eco-park greatly depends on the feasible exchange of materials and energy among the companies involved in the network. The organizational/commercial/political challenge means that deep cooperation/integration amongst the companies in the EIN are needed to set common rules that lead to the optimal flow of information in the network. Additionally, Chertow [4] proposed taxonomy for EINs based on the type of material exchange. He studied 18 potential networks and suggested the following classification: waste exchange within a facility/organization, among facilities co-located in a defined eco-park, among facilities at some distance (e.g., Kalundborg) and among facilities structured across a broader region. Another approach presented by Baldwin et al. [128] who studied various EIN models (Kalundborg, Styria and Massachusetts) based on an evolutionary framework.

This work represents a novel approach to the construction of such networks that includes optimization of material and energy streams and uses a purely quantitative methodology for evaluating these eco-park scenarios. This work expands on the eco-park principles to include additional mathematical complexity in the model formulation as well as analytical insight into the network's design. Kantor et al. [69] developed a linear program (LP) that models an EIN to demonstrate its economic and environmental feasibility and the approach used to solve this type of problem. The model considered a dual-objective function to account for economic and environmental factors existing in processing facilities.

In this chapter, the base models presented in the previous chapters have been reformulated to add additional complexity and express the life-cycle effects of a transportation network for materials and energy between the production nodes. The extension of this model has required a shift into the realm of mixed integer non-linear programming (MINLP). This type of model allows for increased flexibility in constraint construction and improved accuracy of the model. Shifting to MINLP methods also has consequences, which include: increased computational time, less well-defined algorithms for providing solutions and concerns regarding the globality of a solution, once found.

Life cycle concepts are particularly useful in determining environmental benefits of alternatives as the methodology is capable of capturing emissions produced from resource extraction to final disposition [129, 130]. Accordingly, for further development in terms of transportation analysis and improvements, the model was reformulated as an MINLP model to design this EIN. Additionally, the objective function of the model has been reformulated in such a way to prevent either of its two terms from overshadowing the other.

6.2 Multi-Objective Optimization Model

This section presents the main features of the multi-objective optimization model proposed in this work to determine the annual production costs (accounting for environmental metrics) associated with the EIN. The model has been constructed using GAMS, as discussed previously, as it has been used extensively for multi-objective optimization as well as MINLP modeling.

6.2.1 Problem Statement

The multi-objective model proposed in this work aims to minimize the life-cycle emissions while attaining economic profits in an EIN design. Figure 6.1 shows the general layout of the present network design model. The model consists of nodes defined by different industrial processes designed to operate as a network. These nodes exchange material and/or energy, thus minimizing waste (by reutilizing process products and co-products from other EIN facilities) and maximizing profit (by generating higher added-value products) under operational constraints. As a result, the integrated relationship between nodes has been considered in the present mathematical formulation. The model's key inputs are: maximum output capacities of the production nodes, fuel composition and distances between the nodes. To meet the expected production levels of energy carriers and chemical products, the present EIN simultaneously minimizes the environmental impacts (in terms of life cycle emissions) and production costs by selecting the most suitable type of feedstock fuel, nodes in the production network and transportation modes subject to operational constraints. The model's key outputs are (see Figure 6.1): annualized network production costs, type and amount of products, plants and systems with corresponding capacities, and overall economic and environmental performance relative to non-integrated facilities.

The present EIN model includes the selection of continuous, binary and integer variables. In addition to these variable types, there are non-linearities present in the model from various constraints and calculations; thus, the resulting mathematical model is formulated as an MINLP optimization problem. Each of the processes (i.e., production nodes) considered in the present model (see Figure 6.1) are described in detail in the present section.

A formulation of this network was initially constructed as an LP model which relies on continuous variables without complex interactions between variables. This type of

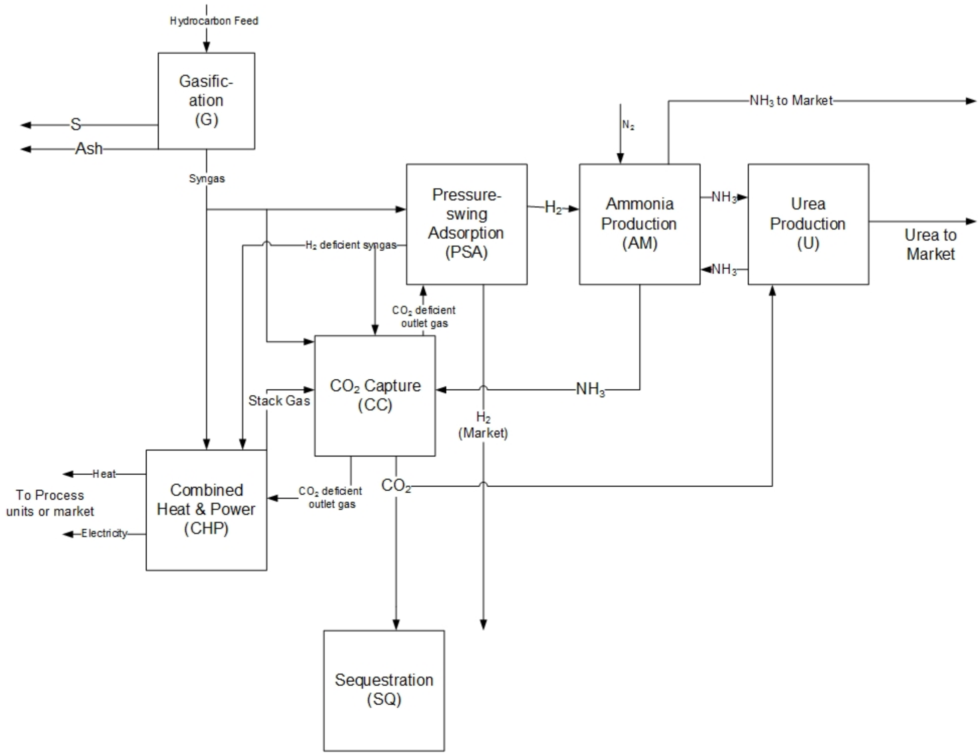

Figure 6.1: Eco-industrial network flow diagram

model is the most rigorously studied and most easily solved type of optimization. For this reason, large bodies of research have been published on this type of model and for linearizing complex constraints to take advantage of well-known algorithms for solving LP models.

Typically, LP models are incapable of capturing the full extent of a complex optimization and thus the MILP type of optimization is used. This type of model allows for binary and integer constraints to be used in the model which permits discrete decisions and discontinuous variables to be used in the model. This type of model is used for more extensive optimization problems as it allows the user to construct a more realistic model of the system. As with LP models, MILP models often rely on linearization techniques applied to more complicated constraints in order to maintain the MILP structure to comply with the solution methods. LP and MILP methods are well-studied and require relatively little computational time and power when compared to an MINLP formulation. The solvers which are included in many standard optimization packages have been refined to solve LP and MILP problems efficiently and effectively. MINLP modeling, however, introduces non-linear constraints to an MILP model and is typically considered when the constraints can no longer be linearized. The consequences of delving into this realm are less well-defined solution algorithms and a large increase in computational power and time. In this work, the nature of the constraints and the objective function would not allow for a definite linearization and thus the model was necessarily constructed as an MINLP. The benefits of utilizing this framework are that the model can be presented in a more realistic and comprehensive fashion without compromising on the specificity of constraints or the objective function.

As outlined in the previous chapters, this network of facilities was selected because of natural integration that is experienced between these facilities. The network contains products and co-products which act synergistically with other facilities in the network; thus, locating such industries and collaborating toward an end goal of increased profits and reduced emissions can be realized.

The base scenario for the optimization models is that each facility operates independently of each other, i.e., no integration between the nodes. The integrated case is always compared to this base case in order to derive a benefit of reduced emissions or improved economics compared to the case without integration.

6.2.2 Problem Representation

To simplify the terminology, key indices have been introduced into the problems formulation to represent the main properties of the model. A source-sink structural representation is used to embed potential configurations of interest. Accordingly, the indices i and j have been included to represent the source and sink nodes, respectively. The sets i and j are defined as follows:

$$i \in I = \{g,\ chp,\ cc,\ psa,\ sq,\ ap,\ up,\ mk,\ wt\} \tag{6.1}$$

$$j \in J = \{g,\ chp,\ cc,\ psa,\ sq,\ ap,\ up,\ mk,\ wt\} \tag{6.2}$$

where g represents gasification processes, chp combined heat and power plants, cc carbon capture, psa pressure swing adsorption, sq sequestration, ap ammonia production, up urea production, mk the market place, and wt water and waste treatment facilities. Also, a constraint has been included in the model to avoid material back-feeding in the nodes (i.e., $i \neq j$). The set of alternative feedstock hydrocarbon fuels, h, used in the network is given as:

$$h \in H = \{C,\ B,\ NG\} \tag{6.3}$$

where h denotes the set of feedstock fuels available in the eco-industrial network, C represents coal, B biomass and NG natural gas. Furthermore, the index m is used to denote the set of materials, which includes products and co-products involved in the eco-industrial network. The set of materials, M, is defined as follows:

$$m \in M = \{M_1, ..., M_{11}\} \tag{6.4}$$

where M_1 represents carbon monoxide (CO), M_2 carbon dioxide (CO_2), M_3 hydrogen (H_2), M_4 nitrogen (N_2), M_5 ammonia (NH_3), M_6 urea, M_7 water (H_2O), M_8 methane (CH_4), M_9 ash, M_{10} sulfur (S), and M_{11} other contaminants. On the other hand, the set of utilities, u, associated to the eco-industrial network are heat, process water and electricity. This utility set is denoted as follows:

$$u \in U = \{U_1,\, U_2,\, U_3\} \tag{6.5}$$

where U_1 represents heat, U_2 process water and U_3 electricity. Additionally, the set of transport modes, k, available to connect the nodes is given as:

$$k \in K = \{Rd, Rl, P_d\} \tag{6.6}$$

where Rd represents roadway transportation, Rl rail and P_d pipeline of diameter d. Six different pipeline sizes are considered in the formulation of the model, ranging from a minimum of two inches (2") to a maximum of twelve inches (12") with a difference of two inches between each other (i.e., $P_{2"}, P_{4"}, ..., P_{12"}$). The environmental emissions, e, considered for the life-cycle emission assessment of this study are given by the following set:

$$e \in E = \{GHG, NO_x, SO_x, SW\} \tag{6.7}$$

where index e denotes the set of emissions, GHG represents the greenhouse gases measured in CO_2 equivalent units, NO_x are the nitrogen oxides, SO_x are the sulfur oxides, and SW represent the solid waste materials (landfill materials).

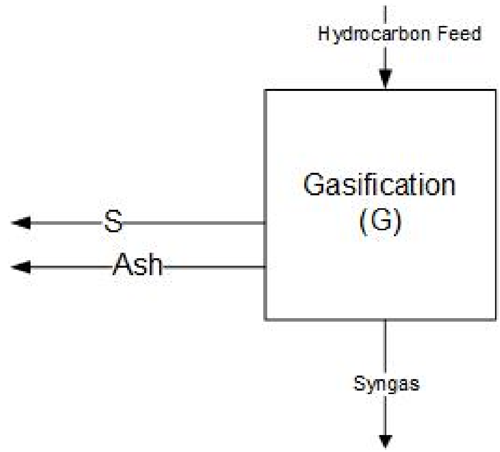

Figure 6.2: Gasification process

6.2.3 Model Formulation

As previously mentioned, the optimization model presented in this work consists of different production nodes that can be linked to each other depending on material needs and operational constraints. These nodes i and j are linked by different available transport modes k depending on economic factors and the nature of the transported materials. The EIN nodes considered in the model are described next.

6.2.3.1 Gasification node (g)

The model's first stage consists of a gasification process, where the feedstock hydrocarbon fuel, h, reacts at high temperatures generating a mixture of gaseous products. The gaseous products are typically carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), hydrogen gas (H_2) and nitrogen products (e.g., when air is used as the oxygen source of the process). The diagram of this process is shown in Figure 6.2.

Hydrogen gas and carbon monoxide are the main outputs of the process and they are available, as well as the rest of the products, for further use as chemical feedstocks in downstream nodes j [69] . The type of feedstock fuel and corresponding product composition in the gasifier are calculated as follows:

$$GP_m = \frac{f_h FC_{h,m} FM}{MW_h} \tag{6.8}$$

$$f_h = \begin{cases} 1 \text{ if fuel } h \text{ is selected} \\ 0 \text{ Otherwise} \end{cases} \tag{6.9}$$

where GP_m represents the total amount of material m produced in the gasifier, $FC_{h,m}$ is a parameter that represents the material composition of the gaseous product formed in the gasification process as a function of the type of fuel h based on the literature [131, 132, 133, 78, 134], FM is the mass flowrate of the fuel entering the gasifier, and MW_h is the molecular weight of the feedstock fuel. The selection of only one type of fuel for the gasifier is constrained as follows:

$$\sum_h f_h = 1 \tag{6.10}$$

where the index h represents the type of feedstock hydrocarbon fuel and f_h is a binary variable indicating the type of fuel h. The waste products (i.e., $M_9 - M_{11}$) obtained from the gasification process are sent to waste/water treatment facilities (wt). These waste products are given as follows:

$$GW_m = GP_m \, \forall m \in \{9, 10, 11\} \tag{6.11}$$

where GW_m represents the amount of waste materials generated in the gasifier (source node) and sent to waste/water treatment facilities (sink node) for environmental treatment and later disposal/commercialization. The rest of the materials generated in the gasifier are co-products that can be used in the remaining production nodes for further processing, these materials can be calculated as follows:

$$GO_{m,j} = GSF_j GP_m \, \forall m \in \{1, 2, 3, 4\}\,,\; j \in \{cc, chp, psa\} \tag{6.12}$$

where $GO_{m,j}$ represents the material m output from the gasifier to the production nodes j, and GSF_j is the gasifiers split factor to the sink nodes j. Furthermore, the gasification process demands certain types of energy such as heat, water and electricity. These utility demands (GD_u) associated to the gasifier can be estimated as follows:

$$GD_u = GR_u \sum_{m=1}^{4} GP_m \tag{6.13}$$

where GR_u is a parameter that denotes the amount of utility u required in the gasifier per unit of total gaseous product generated in the plant as defined by the requirements of the facility operations as found in the literature [131, 132, 133, 78, 134, 135, 136, 137, 138, 79].

6.2.3.2 Combined heat and power node (chp)

This node represents a type of cogeneration plant where the main outputs are heat and power. This node provides heat to the facilities in the EIN as well as potential power supply. This node oxidizes carbon monoxide and hydrogen gases coming from the pressure swing adsorption (psa), gasification (g) and carbon capture (cc) nodes. The overall interactions of this node are shown in Figure 6.3.

The total amount of materials entering this node can be estimated as follows:

$$CI_m = PO_{m,j} + GO_{m,j} + CCO_{m,j} + MO_{m,j}\,;\; j = chp \tag{6.14}$$

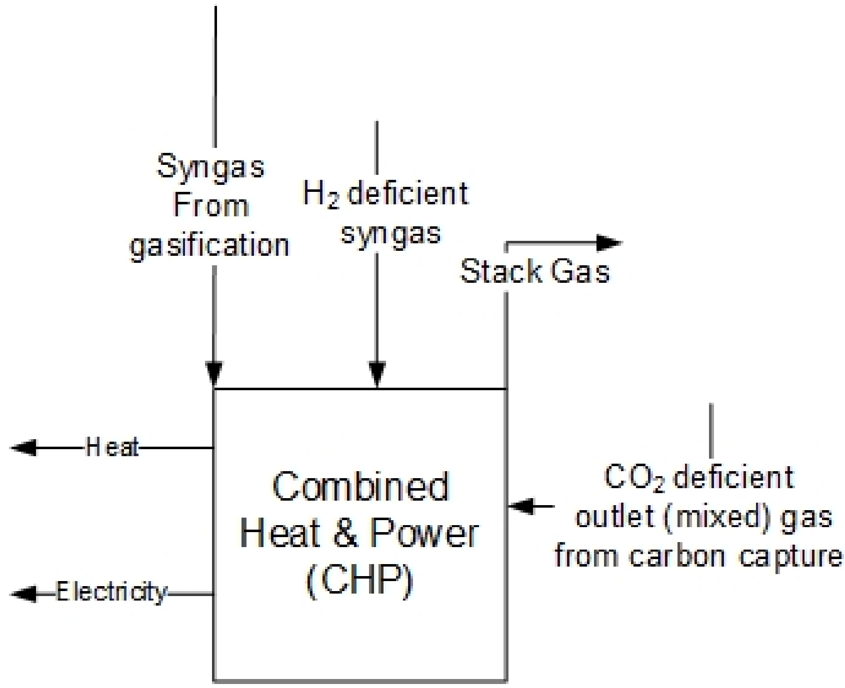

Figure 6.3: Combined heat and power process

where CI_m represents the total amount of material m entering the combined heat and power unit whereas PO_{mj}, $CCO_{m,j}$ and $MO_{m,j}$ are the material outputs from pressure swing adsorption, carbon capture and an outside source, the market, going into the *chp* node, respectively (i.e., the market can provide H_2 if needed). Moreover, only carbon dioxide and water are generated in this process. The amount of carbon dioxide produced in this node is calculated as follows:

$$CP_{M_2} = \sum_{m \in \{M_1, M_8\}} CI_m \tag{6.15}$$

where CP_m is the total amount of carbon dioxide ($m = M_2$) produced in this facility. The carbon monoxide and methane entering this node participate in a series of reactions producing carbon dioxide on a 1:1 mole ratio according to standard combustion stoichiometry. Additionally, water is generated in this process as follows:

$$CP_{M_7} = CI_{M_3} + 2CI_{M_8} \tag{6.16}$$

where CP_m is the total amount of water ($m = M_7$) produced in the combined heat and power node, which results from reactions involving hydrogen and methane. Accordingly, for each mole of hydrogen and methane that react in this process, one and two moles of water are produced, respectively, according to standard combustion stoichiometry for diatomic hydrogen (H_2) and methane (CH_4).

The main material outputs associated with this process are carbon dioxide and water. Nevertheless, nitrogen may enter and exit this node unchanged or may react to produce NO_x under some conditions. The rest of the materials that enter this node are consumed in the internal process reactions. The materials from this node (stack gas) are sent to carbon capture; these output materials can be estimated as follows:

$$CO_{m,j} = CI_m + CP_m \ \forall m \in \{M_2, M_4, M_7\} \ \ , j = cc \tag{6.17}$$

where $CO_{m,j}$ is the amount of material m sent to the carbon capture node; this product is mainly composed of CO_2. The total energy content within the gas fed to this node can be calculated as follows:

$$CEC = \sum_{m \in \{M_1, M_2, M_3, M_4\}} CI_m LHV_m \tag{6.18}$$

where CEC is the total energy content of the gas entering the combined heat and power unit, and LHV_m is the lower heating value of the gaseous components, which are widely published values and are included in the appendix. Furthermore, the total amount of electricity and heat generated can be estimated as shown in Eq. 6.19 below:

$$CG_u = CER_u CEC\, CEF_u\, \forall u \in \{U_1, U_3\} \tag{6.19}$$

where CG_u is the total amount of utility u generated in the process, CER_u is the ratio of the total energy content used to produce utility type u, CEF_u is a parameter that represents the efficiency of generating utility type u. The process modeling in this section is drawn from several major publications [131, 139, 136, 140, 141].

6.2.3.3 Carbon capture node (cc)

Captured CO_2 can be purified and used for a wide variety of processes in order to avoid emitting it to the atmosphere. Presently, monoethanolamine (MEA) is the most common CO_2 capture media used in the industrial sector. However, ammonia represents an alternative medium and has demonstrated various advantages in its ability to capture carbon dioxide [81, 82]. Therefore, ammonia is included as the CO_2 capture media in the proposed network to avoid the need of importing MEA. The diagram of this process is shown here as Figure 6.4.

The total amount of materials entering carbon capture can be calculated as follows:

$$CCI_m = GO_{m,j} + CO_{m,j} + PO_{m,j} + AO_{m,j}\,;\, j = cc \tag{6.20}$$

where CCI_m is the total amount of material m entering carbon capture, $PO_{m,j}$ is the outlet material from the pressure swing adsorption node into carbon capture, and $AO_{m,j}$ is the output from the ammonia production node used as make-up material to maintain the carbon capture process. The carbon capture process does not involve any chemical reaction, in this process the CO_2 product is purified for its use in other nodes, especially the urea plant. Accordingly, the amount of CO_2 product can be estimated as follows:

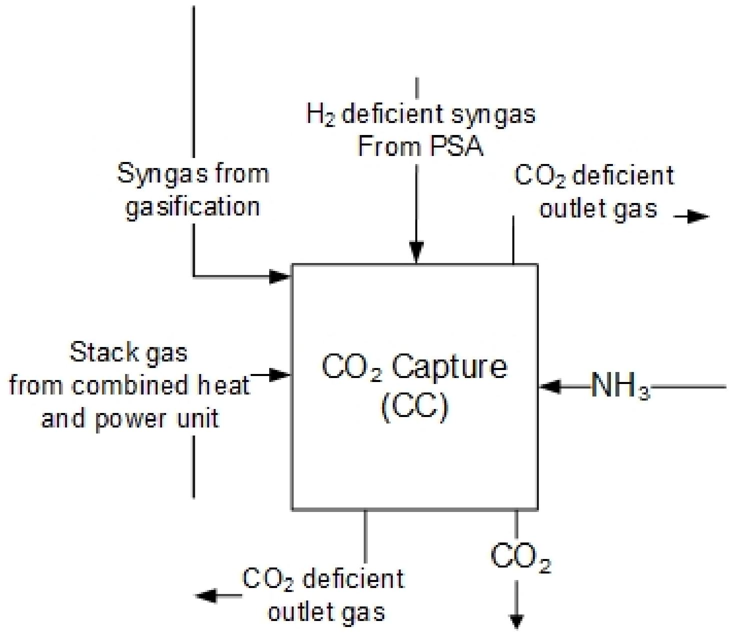

Figure 6.4: Carbon capture process

$$CCO_{m,j} = CCSF_jCCI_m\,; m = M_2, j = up, sq \tag{6.21}$$

where $CCO_{m,j}$ $(m = M_2)$ represents the output of CO_2 from the unit, $CCSF_j$ is the fractional splitting of the CO_2 stream at the outlet of this unit to the sink nodes j. Note that most of the purified carbon dioxide is sent to the urea production process whereas the remaining CO_2 is sent to the outlet node *sq* (i.e., carbon sequestration). Nevertheless, small amounts of CO_2 are also sent to the *chp* and *psa* nodes. The amount of the remaining carbon capture outlet materials can be estimated as follows:

$$CCO_{m,j} = CCSF_jCCI_m \,\forall m \in \{M_1, M_2, M_3, M_4\}\,, j = chp, psa \tag{6.22}$$

where $CCSF_j$ is the split factor of the CO_2 deficient outlet gas sent to the sink nodes j. Furthermore, the utility demands associated to the carbon capture node are electricity, water and heat. The utility demands of the carbon capture facility can be estimated as follows:

$$CCD_u = CCR_u CCO_{m,j}\,; m = M_2, j = up \tag{6.23}$$

where CCD_u represents the demand of utility type u in the carbon capture node, and CCR_u is a parameter denoting the utility requirements per unit of CO_2 product sent to the urea plant obtained from the literature [142, 143, 144, 145, 110, 146, 147, 148, 81, 139, 149, 150, 151, 138, 152, 82, 153]. Moreover, the minimum amount of CO_2 sent to the urea plant, which depends on the urea plant reactions, is constrained as follows:

$$CCO_{M_2,up} \geq 1.4\,(0.5\,AO_{M_5,up}) \tag{6.24}$$

where $CCO_{M_2,up}$ represents the amount of CO_2 sent to the urea plant and $AO_{M_5,up}$ is the amount of ammonia sent from the ammonia to the urea plant. This constraint specifies the minimum amount of CO_2 required for the main reaction in the urea plant. The design flowrate of CO_2 is set to be 40% greater than the stoichiometric requirement as recommended by Riegel and Kent [117].

6.2.3.4 Pressure Swing Adsorption node (psa)

This process is typically used to separate one or more gas species from a mixture, the inlet gas is passed over an adsorbent which attracts the desired gas or impurity in the stream, whereas the remainder of the feed continues to the outlet for release or further processing. This process will be used in the EIN to separate hydrogen from a gaseous mixture [86, 85]. The schematic of this process is shown in Figure 6.5.

The total amount of materials entering the pressure swing adsorption node can be calculated as follows:

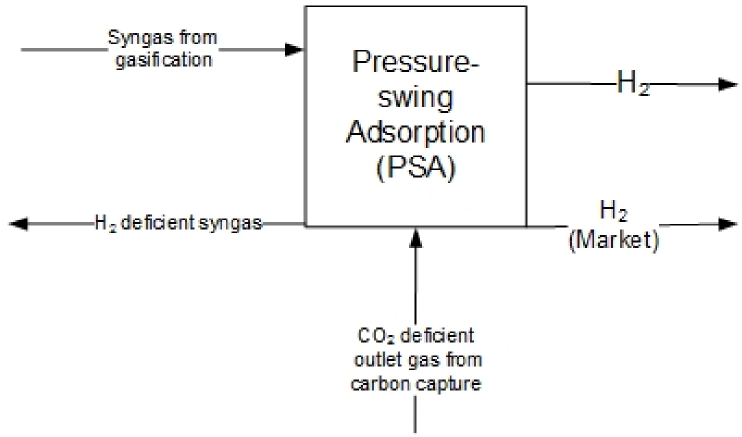

Figure 6.5: Pressure swing adsorption process

$$PI_m = GO_{m,j} + CCO_{m,j} + AO_{m,j}\,; j = psa \tag{6.25}$$

where PI_m is the total amount of material m entering the pressure swing adsorption unit, and $AO_{m,j}$ $(j = psa)$ represents the outlet materials from the ammonia plant into the psa node. The amount of hydrogen produced in this unit can be estimated as follows:

$$PO_{m,j} = PSF_j PI_m\,; m = M_3, j \in \{ap, mk\} \tag{6.26}$$

where $PO_{m,j}$ represents the amount of hydrogen product obtained in this node, PSF_j is the H_2 stream splitting factor from this unit to the ammonia plant (ap) and market (mk). However, traces of H_2 products are also sent to the chp and cc nodes. Accordingly, the remaining material outputs can be calculated as follows:

$$PO_{m,j} = PS_j PI_m\, \forall m \in \{M_1, M_2, M_3, M_4\}\,, j = chp, cc \tag{6.27}$$

where PS_j is the split factor associated with the H_2 deficient syngas sent to the production nodes j. The PSA process is well-defined in the literature [154, 155, 138, 156] and is used throughout industry for separating hydrogen from mixed gas streams.

The utility demands of the pressure swing adsorption node are electricity, water and heat. The utility demands consider in this production node can be calculated as follows:

$$PD_u = PR_u \sum_{j \in \{ap,mk\}} \sum_{m=M_3} PO_{m,j} \tag{6.28}$$

where PD_u is the total amount of utility u required in the pressure swing adsorption node, and PR_u is a parameter that defines the energy requirements per unit of H_2 product sent to the ammonia plant and the market.

6.2.3.5 Sequestration node (sq)

Part of the objective of this model consists of minimizing waste production. This is achieved using waste as a co-product in as many applications as possible. However, waste can only be utilized to a certain extent, after which sequestration plays a key role in balancing the excess of CO_2 produced in the network; thus, venting gas to the atmosphere (which would contradict part of the models objective) can be avoided.

The total amount of materials entering the sequestration (SI_m) node can be estimated as follows:

$$SI_m = CCO_{m,j}\,; m = M_2,\ j = sq \tag{6.29}$$

where SI_m ($molh^{-1}$) represents the total amount of CO_2 entering the sequestration node from the carbon capture facility. The carbon dioxide sent to this node is stored in suitable sites, e.g., deep saline aquifers. Therefore, this production node does not contain any outlet stream.

The utility demands associated to the sequestration node can be defined as follows:

$$SD_u = SR_u SI_m \tag{6.30}$$

where SD_u is the total amount of the utility type u required in the sequestration process, and SR_u is a models parameter that represents the energy requirements per unit of CO_2 entering the sequestration node as found in the literature [157, 145, 86].

The addition of carbon capture and storage represents a benefit to society in terms of reduced emissions, yet there is an economic cost of this addition. Nevertheless, this benefit will be more clearly quantifiable to plant operators in the conceivable circumstance that a carbon cap and trade system or carbon taxes are implemented in order to mitigate climate change. The literature discusses many economic and environmental aspects of carbon sequestration in conjunction with the technical specifications of such facilities [158, 159, 150, 145, 160, 144, 157, 138].

6.2.3.6 Ammonia node (ap)

The production of ammonia in the eco-park is considered to be similar to the commonly used Haber-Bosch process, where three molecules of hydrogen react with one molecule of nitrogen over a catalyst to produce two molecules of anhydrous ammonia (NH_3) as described by Riegel and Kent [117]. The diagram of this process is shown as Figure 6.6.

However, the production of ammonia in this network is simpler since the feed gases are already free of sulfur compounds and other impurities. Furthermore, this production node may also take in unreacted ammonia from the urea plant, depending on process conditions and geographical locations [89]. The total amount of materials entering this node can be estimated as follows:

$$AI_m = PO_{m,j} + MO_{m,j}\,; j = ap \tag{6.31}$$

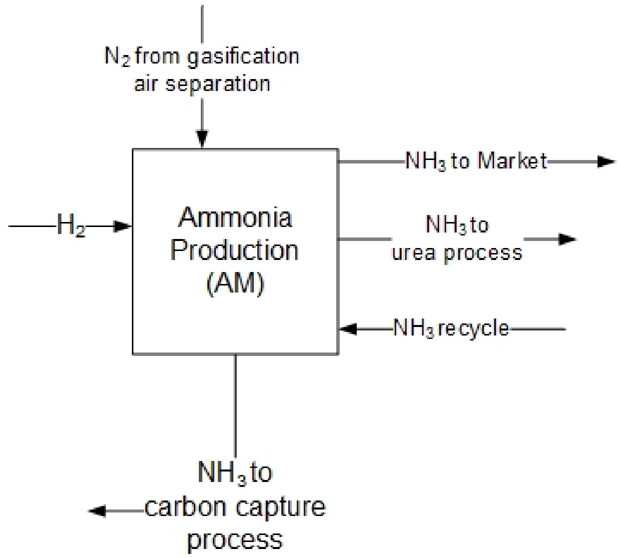

Figure 6.6: Ammonia process

where AI_m is the total amount of material m entering the ammonia production node, whereas $PO_{m,j}$, $UR_{m,j}$ and $MO_{m,j}$ ($j = ap$) are the output materials from the pressure swing adsorption plant, urea plant and market into the *ap* node, respectively. The amount of ammonia produced in this facility can be calculated as follows:

$$AP_{M_5} = ACF\left(\frac{2}{3}AI_{M_3}\right) \tag{6.32}$$

where AP_m ($m = M_5$) is the total amount of ammonia produced in this node, ACF is a parameter of the model that defines the total conversion of the reaction (e.g., 94%). The amount of NH_3 product out of this node can be calculated as follows:

$$AO_{m,j} = ASF_j\left(AI_m + ASF_m AP_m\right)\ ; m = M_5, j \in \{up, mk, cc\} \tag{6.33}$$

where $AO_{m,j}$ represents the amount of product m in the outlet streams transported to node j, ASF_j is the ammonia plant splitting factor to nodes j, ASF_m is a parameter of the model that specifies the stoichiometric relationship for the production of ammonia in this node (i.e., $ASF_{M_5} = 1.0$). The output of the reactants and remaining materials can be estimated as follows:

$$AO_{m,j} = AI_m + ASF_m AP_{M_5} \ \forall m \in \{M_3, M_4\}, j = psa \tag{6.34}$$

where ASF_m denotes the stoichiometric relationship between the amount of reactant m consumed and the amount of ammonia produced (i.e., $ASF_{M_5} = -1.5$, $ASF_{M_4} = -0.5$). The utility demands considered in the ammonia process are as follows:

$$AD_u = AR_u \sum_{j \in \{up,mk,cc\}} AO_{m,j} \ ; m = M_5 \tag{6.35}$$

where AD_u is the total amount of the utility type u required in the ammonia process, and AR_u represents the parameter that denotes the utility requirements per unit of NH_3 produced in this node. Ammonia manufacturing is a mature process with the current technology and is well-documented in the literature [84, 81, 89, 117, 161, 138, 141, 152, 82, 162].

6.2.3.7 Urea node (up)

The urea production in the eco-park network is considered through the Bosch-Meiser process where two molecules of ammonia are combined with one molecule of carbon dioxide over a catalyst as described in the literature [84, 117]. The ammonia is readily available as a co-product of the network and the carbon dioxide is obtained from the carbon capture process. The process is shown pictorially in Figure 6.7.

One of the main network advantages is the energy savings due to avoiding CO_2 compression inefficiencies for transport since CO_2 and NH_3 can both be obtained from inside

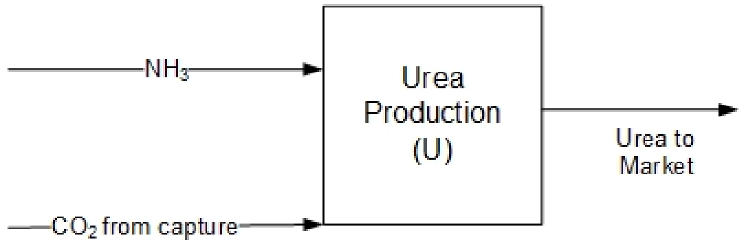

Figure 6.7: Urea process

the EIN boundaries. The total amount of materials entering the urea production process can be calculated as follows:

$$UI_m = CCO_{m,j} + AO_{m,j} \,; j = up \tag{6.36}$$

where UI_m is the total amount of material m entering the urea production process. The amount of urea produced in this node can be calculated as follows:

$$UP_{M_6} = UCF \left(\frac{1}{2} UI_{M_5} \right) \tag{6.37}$$

where UP_m ($m = M_6$) is the total amount of urea produced in the process, UCF is a models parameter that defines the assumed total conversion of the reaction (e.g., 85% as described by Riegel and Kent [117]). The full process of urea manufacturing by the Bosch-Meiser process is presented in numerous sources [84, 163, 117, 164, 138]. The amount of urea products and any remaining co-products obtained from this node can be calculated as follows:

$$UO_{m,j} = UI_m + USF_m UP_{M_6} \; \forall m \in \{M_2, M_6\} \,, j = mk \tag{6.38}$$

where $UO_{m,j}$ represents the amount of product m sent to the market node, USF_m is a parameter that determines the stoichiometric relationship for the production/consumption of material m in this node (i.e., $USF_{M_2} = -1.0$, $USF_{M_6} = 1.0$). Furthermore, the amount of unreacted ammonia recycled within the urea node ($UR_{m,j}$) can be estimated as follows:

$$UR_{m,j} = UI_m + USF_m\, UP_{M_6} \;; m = M_5, j = up \tag{6.39}$$

where USF_m denotes the stoichiometric relationship between the amount of reactant m consumed and urea produced (i.e., $USF_{M_5} = -2.0$). The utility demands associated with the urea node are as follows:

$$UD_u = UR_u UO_{m,j} \;; m = M_6\,, j = mk \tag{6.40}$$

where UD_u is the total amount of the utility type u required by the urea production process, and UR_u is a parameter that denotes the energy requirements in the process per unit of urea produced in this node.

6.2.3.8 Market node (mk)

The market node is not present in the network schematic presented as Figure 6.1 as it is assumed to be connected to every node and serves a dual function in the network. Firstly, it is the end node where the network's products are sold to generate profits; however, it can also act as an external supplier to help meet the material and energy needs associated to the network when required. Accordingly, the total amount of materials entering the market node can be calculated as follows:

$$MI_m = UO_{m,j} + AO_{m,j} + PO_{m,j} \;; j = mk \tag{6.41}$$

where MI_m is the total amount of material m entering the market node. The type and amount of utility sold to the market can be estimated as:

$$MEI_u = MER_u \, CG_u \, \forall u \in \{U_1, U_3\} \tag{6.42}$$

where MEI_u is the total amount of utility type u sold to the market from the *chp* node and MER_u represents the ratio of utility u that can be sold to the market. The amount and type of materials sent from the market to the EIN nodes are as follows:

$$MO_{m,j} = MAM_{m,j} \tag{6.43}$$

where $MO_{m,j}$ is the total amount of material m out of the market to node j, and $MAM_{m,j}$ represents the type and amount of material m available in the market to be sold to the networks node j. The type and amount of utility sold to the networks nodes can be estimated as:

$$MEO_{u,j} = MEA_{u,j} \tag{6.44}$$

where $MEO_{u,j}$ is the total amount of utility type u sold to the networks node and $MEA_{u,j}$ represents the amount of utility u that can be exported from the market to supply the eco-park nodes.

6.2.3.9 Waste and Water Treatment node (wt)

The water treatment plant is used to process the water consumed in the EIN. The total amount of water demanded by the network can be calculated as follows:

$$WD_u = GD_u + CCD_u + PD_u + SD_u + AD_u + UD_u - CP_{M_7} \; ; u = U_2 \tag{6.45}$$

where WD_u ($u = U_2$) is the total amount of process water demanded by the eco-industrial network and treated in the plant. Moreover, heat and electricity are also demanded for the operation of the water treatment plant. Accordingly, the amount of utility u required to treat the process water consumed in the EIN can be calculated as follows:

$$WD_u = WR_u WD_{u_2} \ \forall u \in \{U_1, U_3\} \tag{6.46}$$

where WD_u represents the amount of utility type u consumed in the water treatment plant and WR_u denotes the energy requirements per unit of process water produced.
On the other hand, the amount of materials treated in the waste treatment facility of this node can be calculated as follows:

$$WI_m = GW_m \tag{6.47}$$

where WI_m represents the amount of materials m entering the waste treatment unit, whereas, GW_m is the amount of waste materials (i.e., ash, sulfur and other contaminants) sent from the gasification node to waste treatment. Industrial water and water treatment is discussed in detail within industrial literature and is implemented here based on several sources [165, 166, 167, 168, 169, 170, 138, 171, 172, 173].

6.2.3.10 Transportation system

The transportation system enables the carriage of materials from node i to j; thus, linking the facilities located inside the EIN. These materials can be solid, liquid or gaseous depending on the operating or storage conditions. As a result, different transportation options, k, are included in the model to meet the specifications of the transported materials inside the network. The transportation system is constrained to select only one option between nodes; this can be formulated as follows:

$$y_{i,j,k} = \begin{cases} 1 \text{ if transportation method } k \text{ is used between node } i \text{ and node } j \\ 0 \text{ Otherwise} \end{cases} \tag{6.48}$$

$$\sum_k y_{i,j,k} \leq 1 \tag{6.49}$$

Eq. 6.49 determines the transportation option selected to transfer materials between nodes i and j and stipulates that only one of these methods can be used. The material supply constraint from node i to j can be expressed as follows:

$$\sum_k TUN_{i,j,k} TC_k \geq \sum_m MATERIAL_{m,i,j} \tag{6.50}$$

where $TUN_{i,j,k}$ is an integer variable that represents the number of transport units of type k are required to transfer materials from i to j, TC_k is the capacity of the transportation method k, and $MATERIAL_{m,i,j}$ is a variable that represents the network nodes sending material to node j.

6.2.3.11 Network Costs

This section describes the different costs involved in the operation of the EIN such as the transportation system cost, capital cost of the plants (nodes), the plant operating costs and life-cycle emissions costs. Accordingly, the costs of the transportation systems are presented forthwith. The cost associated to the pipelines transportation system can be calculated as follows:

$$NTC_k = \sum_i \sum_j \left(TUN_{i,j,k} FC_k + y_{i,j,k} d_{i,j} VC_k \sum_m MATERIAL_{m,i,j} \right) \forall k \in P \tag{6.51}$$

where NTC_k represents the networks transport cost, FC_k is the fixed cost associated to transportation method k, $d_{i,j}$ is the distance between nodes i and j, and VC_k is the variable cost of the transportation method k. Similarly, the transportation costs associated to the rail and road infrastructures can be estimated as follows:

$$NTC_k = \sum_i \sum_j \left(y_{i,j,k} d_{i,j} FC_k + TUN_{i,j,k} \left(FCU_k + TC_k VC_k \right) \right) \forall k \in Rd \cup Rl \tag{6.52}$$

where FCU_k represents the systems fixed cost per transportation unit type k. Costing for transportation options can be found in the literature [29, 174, 175, 176].

The present model compares the economics of using integrated production plants instead of stand-alone plants. Consequently, the capital costs of the plants are calculated as follows:

$$x_{i,l} = \begin{cases} 1 \text{ if plant } i \text{ of size } l \text{ is selected} \\ 0 \text{ Otherwise} \end{cases} \tag{6.53}$$

$$ACC_{i,s} = ACF_i \left(\sum_l x_{i,l} PC_{i,l,s} + \sum_k NTC_k \right) \tag{6.54}$$

where the index s, as in $s \in S = \{a, b\}$ represents the production scheme of the plant, which can be either stand-alone (a) or integrated (b), $ACC_{i,s}$ is the annual amortized capital cost of the plant i with scheme s, ACF_i is the amortized capital factor of plant i, and $PC_{l,i,s}$ is the capital cost of the plant. Also, the operating costs of the plants can be calculated as follows:

$$OC_{i,s} = \frac{OCF_{i,s} ACC_{i,s}}{ACF_i} \tag{6.55}$$

where $OC_{i,s}$ represents the total operating cost of plant i following scheme s, and $OCF_{i,s}$ is the operating cost factor associated to the plant as calculated from the literature.
The supply constraints for the production plants can be expressed as follows:

$$\sum_{l} x_{i,l} PIC_{i,l} \geq \sum_{m} \sum_{j} MATERIAL_{m,i,j} \tag{6.56}$$

$$\sum_{l} x_{i,l} \leq 1 \tag{6.57}$$

where $PPC_{l,i}$ represents the plants production capacity.

6.2.3.12 Network Emissions

An analysis regarding the lifecycle emissions of the production nodes considered in the EIN is included in the present model. Accordingly, the emissions associated to the construction of the production plants included in the network can be estimated as follows:

$$EPC_{i,s,e} = \sum_{l} x_{i,l} EFPC_{i,l,s,e} \tag{6.58}$$

where $EPC_{i,s,e}$ represents the emission e related to the construction of plant i of scheme s, and $EFPC_{l,i,s,e}$ is a factor denoting the emission e from the construction of a plant of size l as found in the literature for each node. Similarly, the emissions associated to the operation of the production nodes can be calculated as follows:

$$EPO_{i,s,e} = (EFPO_{i,s,e} POC_{i,s})\, POL_{i} \tag{6.59}$$

where $EPO_{i,s,e}$ represents the emission e from the operation of plant i of scheme s, $EFPO_{i,s,e}$ denotes the emission factor related to the operation of the plants which are found in the literature for each node, $POC_{i,s}$ is the plants operating capacity, and POL_i is the plants operating life (e.g., 30 years).

6.2.3.13 Objective Function

The model's objective function is formulated in terms of two ratios: The first ratio denotes the relation between construction and operating costs (i.e., production costs) of the integrated scheme and stand-alone plants; whereas, the second ratio indicates their relative lifecycle emissions. Accordingly, the total production cost of the network can be calculated as follows:

$$NPC = \frac{\sum\limits_{s=b}\sum\limits_{i} ACC_{i,s} + OC_{i,s}}{\sum\limits_{s=a}\sum\limits_{i} ACC_{i,s} + OC_{i,s}} \tag{6.60}$$

where NPC represents the EIN annual production cost, while the numerator and denominator terms of the equation denote the production costs related to the integrated and stand-alone schemes, respectively. Similarly, the life-cycle emissions can be calculated as follows:

$$NEC = \frac{1}{N_e}\frac{\sum\limits_{i}\sum\limits_{s=b}\sum\limits_{e} EPC_{i,s,e} + EPO_{i,s,e}}{\sum\limits_{i}\sum\limits_{s=a}\sum\limits_{e} EPC_{i,s,e} + EPO_{i,s,e}} \tag{6.61}$$

where NEC represents the annual lifecycle emission associated to the network. The reciprocal Ne factor in this equation is representative of the number of emissions considered in the analysis so as to reduce the weight of the environmental objective to align with the economic portion. Consequently, the objective function can be formulated as follows:

$$CF = W_P\,(NPC) + W_E\,(NEC) \tag{6.62}$$

where CF represents the objective cost function of the problem, W_P is the weight assigned to the profitability of the network, whereas W_E is the weight considered for the lifecycle emissions of the eco-park. The objective function takes into account the costs related to the operation of the network as well as associated life-cycle emissions (i.e., environmental and social impacts). This work clearly shows that emission reductions for society and improved profits for operators can be achieved through the implementation of eco-industrial networks.

The fractional output shows a relativistic result with reference to the base case. Accordingly, if the ratio is greater than unity, the integrated scenario costs more than the stand-alone, whereas for a ratio less than unity, it is less costly. Likewise, if the emissions ratio is greater than unity, the integrated scenario emissions are higher than the stand-alone scenario. On the other hand, for emissions ratio less than unity, the integrated scenario emissions are lower than the stand-alone. The model's objective function has been formulated in terms of these ratios to assign relevance to the environmental impacts caused by the network operations. This prevents the economic term of the objective function from becoming very large compared to the life-cycle emission term, which could negate the life-cycle emissions effect on the design of the network (as occurs in many cases). As a result, both terms of the objective function play a key role in model formulation. Accordingly, when one separates and normalizes the life-cycle emissions from the economics, one of the terms would have to be significantly larger in order to overshadow the effect of the other term, since they are normalized to the stand-alone emissions/economics.

6.3 Results and Discussion

The model was constructed with the basis of a minimum production of hydrogen to meet demand for 1000 fuel cell vehicles in the province of Ontario, Canada as was the requirement the previous LP and MILP formulations of this case study presented in previous chapters.

Previous work using LP and MILP models calculated a reduction in emissions for the base scenario of 50% weighting on each portion of the objective to be approximately 40% for the LP model and 35% for the MILP model [69, 108]. The work herein is updated to reflect current pricing, introduces additional accuracy of the model and a more consistent data set for calculating the life-cycle emissions. In addition, the model is expanded into the MINLP domain to allow for additional constraints to be placed on the model which were not possible using linear programming methods.

For this work, an upper limit on the input biomass feedstock was set to 2 million tonnes per year as a sustainable rate for harvesting from forest residues and other undesirable biomass co-products [177]. No limits were placed on coal or natural gas availability. The plant lifetimes were assumed to be 30 years as is a standard assumption in chemical engineering and the capital charge rate for amortization was set to be 15%. The following scenarios discussed are based on varying the weighting factors for the environmental and economic portions of the objective function from 0 to 1 by increments of 0.1. The purpose of this increment is to explore the different network configurations and outputs with varying priorities of the network management. The complexity of the network demands significant computing resources and it was determined that a smaller increment would require excessive computing resources and that scoping on the coarser level would exhibit the variation of the network outputs with respect to the economic and environmental weighting factors.

The reference sizing of each facility is shown in Table 6.1. The scaling for each facility was completed using the capacity scaling equation used by many chemical plant design texts and is shown as Eq. 6.63.

$$PlantCost_2 = PlantCost_1 \left(\frac{PlantCapacity_2}{PlantCapacity_1}\right)^q \tag{6.63}$$

The scaling factor, q, was assumed to be 0.6 for these facilities as is a generally accepted practice in the industry. Chemical process equipment is typically subject to sizing options given by the manufacturer and thus the plant sizes available were chosen as even multiples of the reference plant size (up to a multiple of five) or even fractions such as $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ of the reference condition.

The values of the weighting factors in the bi-objective function are varied from 0 to 1 in an attempt to analyze the difference in facility construction with emphasis placed on economics, reduction in emissions or a combination of the two. With a purely economic objective function, the resulting network is shown in Figure 6.8 with the major mass flowrates shown in Table 6.2 which is designated by the number above each flow stream. It can be seen from this that ammonia production in the network is foregone completely in favour of purchasing ammonia from outside of the eco-park. Since a price premium is not applied to importing ammonia, it is reasonable that ammonia would be imported to the network under a purely economic scenario. In addition to this, carbon sequestration is also not included in the network. Since the objective in this case is completely economic, and viable products are not produced from carbon sequestration, it is again reasonable that this facility would not be constructed. The material exports from the network under the purely economic case are then limited to hydrogen and urea. Urea is a value-added product compared to the inlet ammonia and CO_2 streams; thus, it is maintained in the network where ammonia production is excluded. The air separation for gasification would also lead to a saleable nitrogen product in this case, although this was not considered as part of the economic analysis as the nitrogen is simply used as a reagent in ammonia production.

Table 6.1: Capacities and reference costs of eco-park facilities

Unit	Reference Capacity	Reference cost ($millions)	Literature Reference
Gasifier - Coal (TPD coal feed)	3 390	269	[134]
Gasifier - Biomass TPD biomass feed	1 130	134	[136]
Gasification (Steam Methane Reforming) (TPD natural gas)	3 120	255	[178]
Carbon Capture (TPD captured CO_2)	11 000	547	[126]
Combined Heat and Power (MWe)	335	208	[179, 134]
Pressure Swing Adsorption (TPD H_2)	229	10	[180]
Sequestration (TPD CO_2 sequestered)	2 690	114	[158]
Ammonia Production (TPD ammonia produced)	1 800	678	[181]
Urea Production (TPD urea produced)	2 350	189	[182]
Water Treatment (TPD treated water)	9 450	3.16	[183]

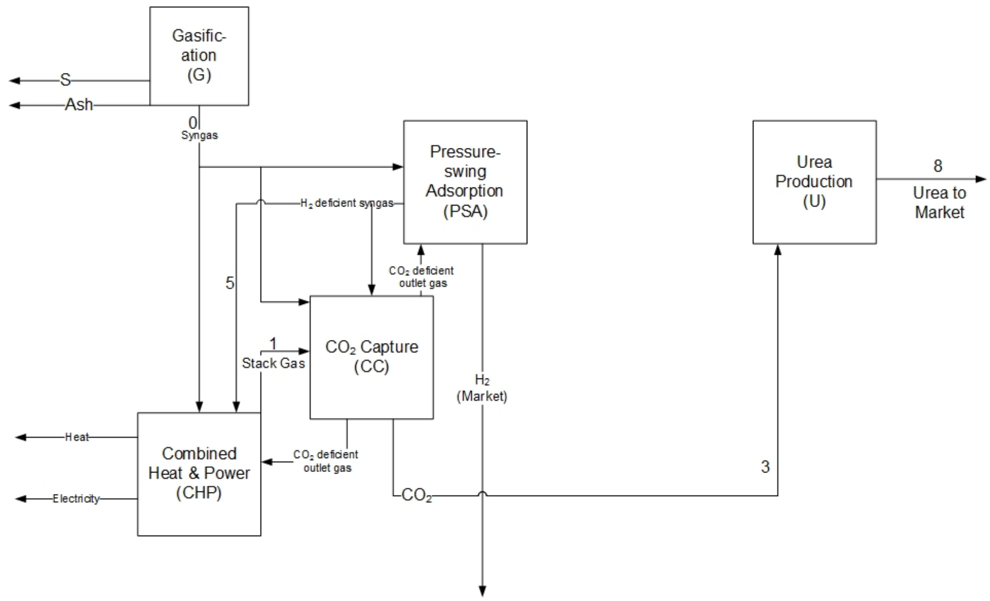

Figure 6.8: Optimal network schematic under purely economic consideration

The same analysis has been conducted over a range of values for the objective function weights, the case in which the environmental objective term dominates the objective function, $W_E = 1$, is shown in Figure 6.9 with the accompanying flowrates shown in Table 6.3. The purely environmental objective shown here includes smaller facilities, yet indicates that the facilities are all included in the network, despite the environmental burden associated with their construction. The level of production at each facility is less than shown in alternative scenarios and it was necessary to include a positive production constraint from the gasification unit in order for the optimization to solve without a trivial solution for this particular scenario. CO_2 is sequestered in this scenario, though at a lower rate than observed in other scenarios during this ten-scenario scoping analysis. This is due to the large energy burden required for CO_2 sequestration and the already-reduced plant sizing. Consequently, the additional energy required to sequester additional CO_2 would be provided by the external electricity grid (i.e., adding energy costs). Hydrogen in

Table 6.2: Summary of flowrates under pure economic consideration

Line number	Description	Million Tonnes per annum
0	Gasifier Outlet	2.77
1	CHP Outlet	2.61
2	CO_2 Sequestered	N/A
3	CO_2 to Urea production	0.429
4	Hydrogen to ammonia manufacturing	N/A
5	Hydrogen to combustion	0.0547
6	Ammonia to Urea production	N/A
7	Ammonia exported	N/A
8	Urea exported	0.363

this scenario's network is not used for combustion as was observed in some other scenarios; however, the hydrogen is utilized for producing ammonia which in turn is used as a reagent for producing the urea, sequestering CO_2 by proxy.

Figure 6.10 shows the variation in the objective value varying the weights of the two parts of the bi-objective function described by Eq. 6.62. This figure shows the balance between the objectives for a range of solutions to the problem at set parameters. In the case of a bi-objective function in which the sum of the weighing factors is equal to unity, the objective value can be shown as a correlation with only one of the weighting factors; this two-dimensional view is shown as Figure 6.11.

Figure 6.10 and Figure 6.11 show the variation in the objective value based on a variation of the two terms of the objective function. The objective function is based on environmental and economic benefits obtained from operating in an integrated EIN com-

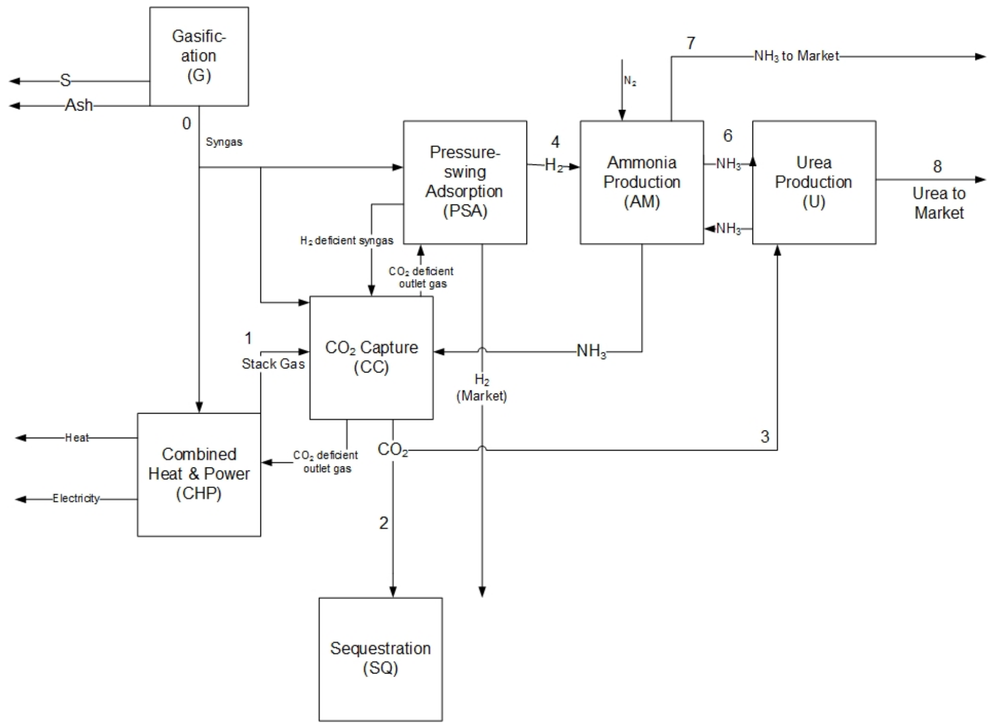

Figure 6.9: Optimal network schematic under purely environmental consideration

Table 6.3: Summary of flowrates under purely environmental consideration

Line	Description	Million Tonnes per annum
0	Gasifier Outlet	0.264
1	CHP Outlet	3.39
2	CO_2 Sequestered	0.764
3	CO_2 to Urea production	0.109
4	Hydrogen to ammonia manufacturing	0.030
5	Hydrogen to combustion	N/A
6	Ammonia to Urea production	0.132
7	Ammonia exported	0.129
8	Urea exported	0.282

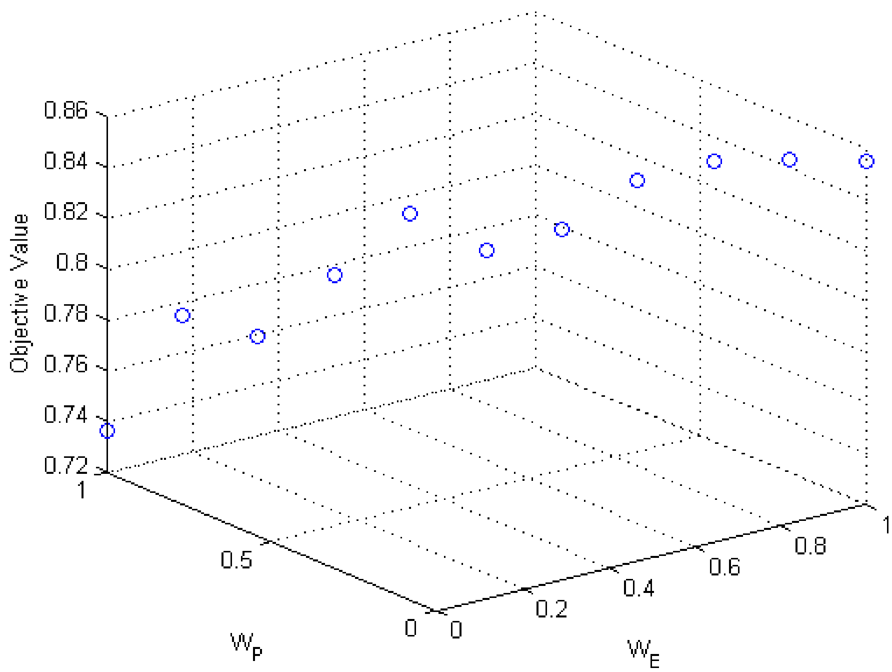

Figure 6.10: Results of the objective value for eco-park optimization varying objective function weights

pared to facilities operating independently. These results show that the best objective value is reached when the life-cycle emissions weighting is set to zero. The optimization at this point is essentially an economic optimization and shows that there are significant economic incentives to be considered for operating as part of an integrated network of facilities. Each of the scenarios presented in the figures are independent and should not be compared in order to determine which scenario is ultimately the best. In this case, however, it is notable that the weighting of the two objectives is highly influential upon the objective value found by the optimization. The optimization results show that the economic term is more favourable to a minimum objective than is an increased weighting upon the life-cycle emissions.

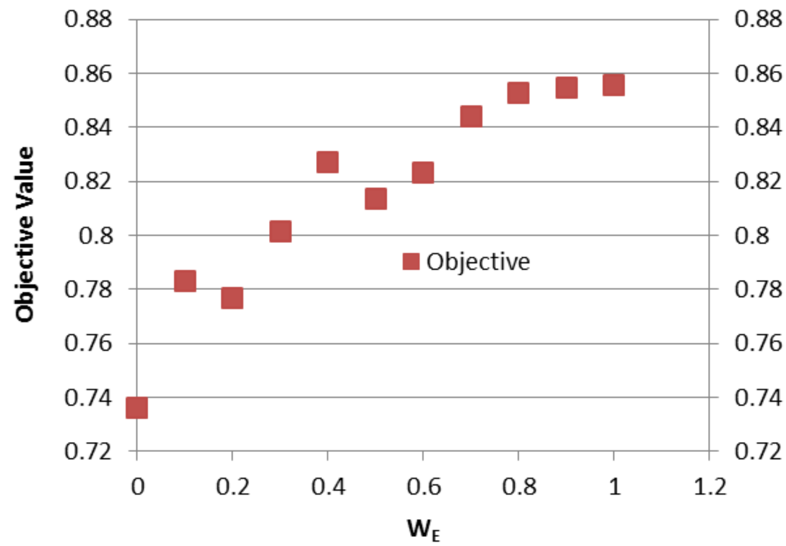

Figure 6.11: Results of variation in the objective value weights in two dimensions related to weighting for life-cycle emissions

The size of each facility in the network is allowed to vary in order to obtain the optimal objective value within the simulation and thus it is interesting to include the normalized capacity of the facilities for each of the scenarios for which the objective function weights were varied. The result is essentially a sensitivity analysis on the weighting parameters in the bi-objective function. The solution time for the MINLP is typically 7 - 10 days and thus additional sensitivity analysis on other parameters was not completed. The normalized plant capacities from varying the weighting factors in the objective function are shown in Figure 6.12.

The gasification node shows a maximum production for the economic mono-objective. A sharp decline in gasifier usage is shown with the introduction of the emissions portion of the objective function. Since the gasifier is a relatively large contributor to the emissions of all contaminants considered in this work, it becomes obvious that its size would be reduced

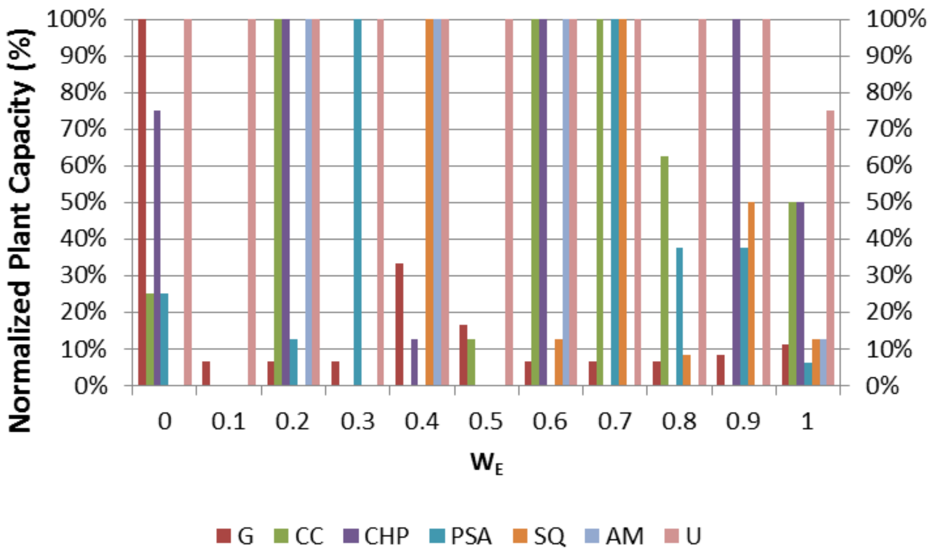

Figure 6.12: Normalized plant capacities under varying weighting of life-cycle emissions. G is descriptive of gasification, CC of carbon capture, CHP for combined heat and power, PSA for pressure-swing adsorption, SQ for sequestration, AM for ammonia manufacture and U for urea production

to a much lower level once the network emissions become incorporated into the objective function via the life-cycle emissions weighting factor.

Carbon capture processing within the network is intended to extract CO_2 from exhaust gases for purposes of sequestration or utilization in further reactions. For most of the scenarios, carbon capture processes remain at a relatively low level relative to the maximum available plant capacity. In many cases, it is favourable to purchase CO_2 from the market to avoid the contaminants associated with producing the CO_2 onsite. The exception to this is during the instances in which the combined heat and power unit operates at a high level, requiring the carbon capture capacity to increase to balance the loading from this unit. Indeed, the maximum carbon capture capacity occurs in conjunction with the maximum output from the CHP unit and also in the case of a maximum CO_2 sequestration.

The combined heat and power unit supplies heat and/or electricity to the processes within the network and excess of either product is exported through the market node. The variability in CHP output is directly related to the increased ammonia production and is favourable under only two of the simulations considered. Accordingly, a higher production of ammonia demands more heat and electricity, which causes an increase in the CHP unit size to accommodate the production of ammonia.

Hydrogen is separated in the PSA unit and utilized as a feed to the other network nodes but can also be exported as a market product. The level of production for the PSA has a lower limit set to produce hydrogen for a minimum of 1000 fuel cell vehicles in the province of Ontario, as in the previous analysis, but there is additional incentive under the objective function herein to produce additional hydrogen. This level of hydrogen production was selected as a likely entry point when dedicated facilities will be required to enable the hydrogen economy. The benefits of producing hydrogen using the proposed network of facilities are both economic and environmental; therefore, hydrogen production is a necessity to reduce the emissions burden from further processes but can also be produced as a reduced-emissions export.

Carbon sequestration is applied when the economic and environmental objective would be better served by its inclusion than its exclusion. The economics of sequestration are undesirable as it lacks a market value under the current pricing regime; therefore, the inclusion of carbon sequestration processing in the network is related solely to the environmental benefits. In the majority of simulations, sequestration is excluded or constructed on a very small scale. The anomalous occurrences are found when the life-cycle emissions weighting factor is at 0.4 or 0.7 and complement a larger burden from the gasification unit.

Ammonia production, contrary to the results of previous work, is maintained at a relatively low level in most simulations presented here. The juxtaposition of ammonia and urea production is a direct correlate to the price of these two products which was not the case in the previous published work [69, 108]. This exhibits the leverage of product cost on the simulation as urea is a more profitable product in this analysis and as the urea node approaches the maximum processing capacity, ammonia is sold to the market as an additional method for increasing the economics of the EIN.

Urea production remains relatively constant throughout the simulations, having only a slight decline to 75% of its maximum value for the environmental mono-objective. The difference between the production of urea under these simulations compared to the results presented in previous chapters is the increment in the urea price. Additionally, the overall objective function differs in the environmental objective term, which compares release of GHG emissions in an integrated and stand-alone facility concurrently. In previous publications using LP and MILP modeling, urea production was generally low which could be attributed to its relatively low reduction in absolute GHG emissions. With the objective function as implemented in this work, the relative reduction of GHG emissions relative to a stand-alone urea facility are much higher, corresponding to relatively stable levels of urea production.

Another consideration of the model solution is which part of the bi-objective dominates the result. In Figure 6.13 and Figure 6.14, the results of this question are addressed. The scalar weighting factor of each portion of the objective function is applied to the objective value resulting from the optimization to evaluate the impact of each portion of the objective

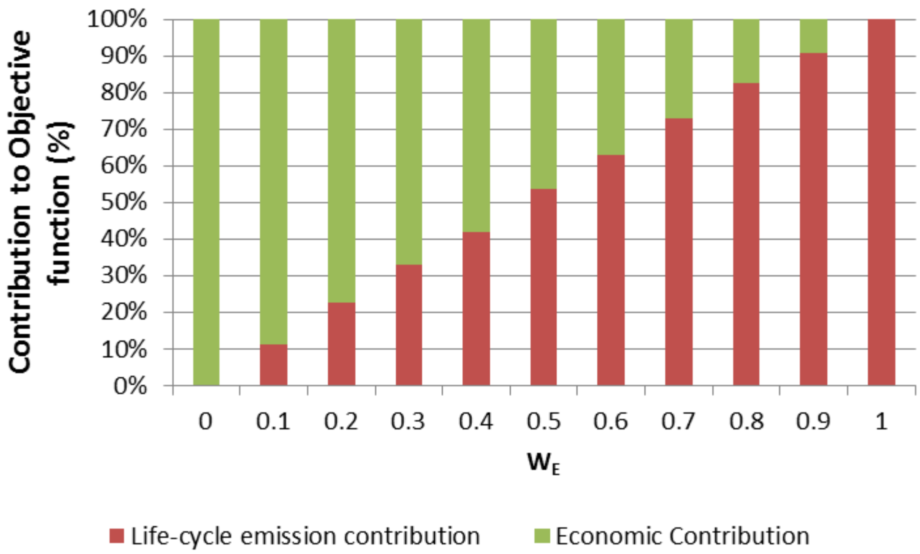

Figure 6.13: Relative contributions of emission reduction objective and economic objective to the overall objective value considering weighting factors

function on its final value. The contribution from each portion of the objective function is comparable to the weighting applied, though the emissions term in the objective function contributes a marginal surplus above the specified weighting factor for all cases except the mono-objective considerations of $W_E = 0, 1$. Figure 6.13 includes the weighting factors for each part of the bi-objective function while Figure 6.14 shows the relative weight of each part of the objective function irrespective of the weighting applied during the optimization.

This result is also shown by the contribution of each portion of the objective function excluding the weighting factors as shown in Figure 6.14. This figure exhibits the relative strength of the two components of the objective function in each of the scenarios considered. This reinforces the finding that the objective value for the life-cycle emissions is slightly more influential on the final objective value than is the impact of the economic portion of the objective function.

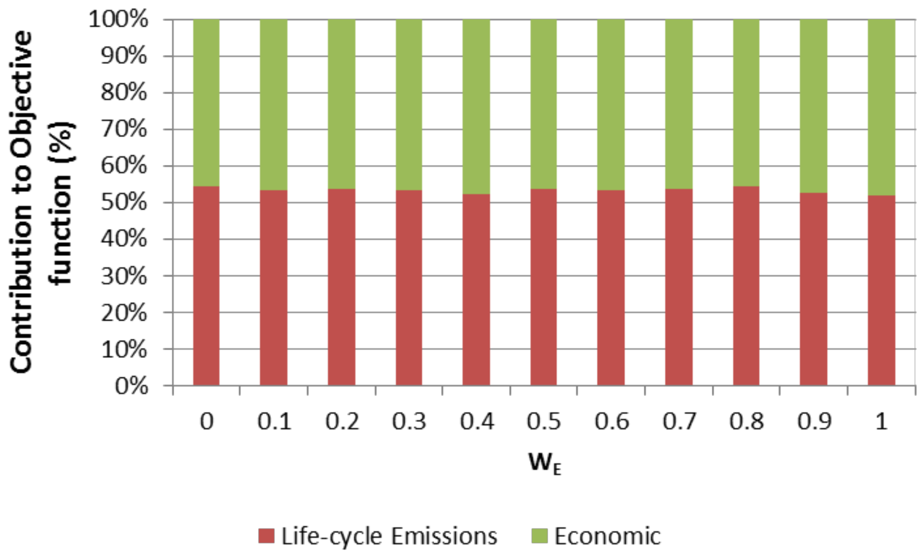

Figure 6.14: Relative strength of emission reduction and cost reduction factors on the objective function

This work and the previous chapters differ in terms of the reduction in cost and emissions. For the same base case as in previous models, the emissions are reduced by 12.7% and the cost savings amount to 24.6% which are more reasonable and conservative estimates compared with the previous model results. The LP and MILP formulations of this case study presented in earlier publications should be considered as an upper boundary for the reduction in cost or emissions from operating in an integrated network of facilities as the full complexity of the system cannot be captured comprehensively by these methods. The MINLP model is a more realistic assessment of the actual cost and emission reductions from such operating an EIN.

6.4 Summary

This chapter presents an MINLP modeling framework for assessing new construction of an EIN with many integrated nodes. One major difference between the model in this chapter and those in the previous two chapters is the relativistic bi-objective function which optmizes the configuration of the network based on percentage reduction in each emission and percentage of improvement in overall economics. This relationship is non-linear and thus cannot be applied in either the LP or MILP formulations in Chapters 4 and 5. This novel approach to EIN design is a powerful tool for policy-makers to understand the implications of regulation and pollution abatement relative to the *status quo*. This framework allows for quantitative discussions between policy-makers and industry with the intention of improving the environmental performance of chemical processes and introducing cost savings potential for improved profitability.

The solution to the MINLP shows high variability in the capacity of various facilities in the EIN relative to the weighting of the two parts of the bi-objective function. Contrasting the previous two chapters, each combination of weighting factors yields different plant capacities and configurations of the network. The model is highly sensitive to these weighting factors and it is likely that parameters such as product pricing would also have an impact on the optimal solution /network configuration.

The opportunity for collaboration between chemical processors and with regulators negates the thinking that reducing emissions and improving profitability are mutually exclusive. The framework developed here with the bi-objective function comprised of an economic term and environmental term relative to existing operations shows that both can be improved without compromising the other. While some scenarios show greater profitability or a greater reduction in emissions, policy-makers can participate in a realistic discussion with industry to find a compromise.

Chapter 7

Summary and Conclusions

7.1 Summary of Work

This work developed several models of an eco-park in order to demonstrate the environmental and economic benefits of industrial facilities working cooperatively to share energy and materials, including the production of hydrogen to support a future hydrogen economy. The EIN models constructed in this work focus on cradle-to-gate emissions from energy conversion and the production of industrial chemicals. This work utilizes three distinct modeling techniques in order to demonstrate their respective benefits, specifically: linear programming, mixed-integer linear programming and mixed-integer non-linear programming. Chapter 3 in this thesis addresses life-cycle emissions of criteria air contaminants from vehicle operations and potential reductions that could be experienced by shifting to alternative vehicle fuels. The work presented in Chapter 3 is focused on the province-wide emissions in Ontario, Canada and urban air pollution in the city of Toronto.

Chapter 4 expands on the utilization of life-cycle concepts but is focused in the application of the methodology to an EIN. An optimization method is developed in order to balance the frequently-conflicting goals of reduced cost and reduced emissions of contaminants to the air, water and land. This chapter explored eco-industrial integration using an LP model and revealed some preliminary conclusions. From this analysis, it was found that hydrogen can feasibly be produced to fuel 1000 hydrogen vehicles in Ontario within the proposed EIN. Policy-makers are the intended audience for this approach in addition to forward-thinking facility designers and environmental organizations. Utilizing this modeling framework to negotiate an acceptable plan for facility construction based on non-zero weighting factors for economic and environmental decisions allows for a quantitative discussion of benefits for policy-makers and industry. The focus on production in an EIN complements the vehicle-centric work from Chapter 3 which exhibits benefits beyond the facility gate for utilization of a potential chemical fuel produced in an EIN.

Chapter 5 attempts to address these recommendations by expanding the model to an MILP formulation and also exploring three feedstock fuels for the analysis. Chapter 5 continues the work from Chapter 4 with added complexity and realism which required adding binary/integer decisions. This work builds on the previous work to represent a quantitative assessment of the eco-park theory and its application to a case involving the production and export of several chemical products in addition to heat and electricity from an EIN comprised of a number of facilities. The network is assessed in terms of environmental impact and profitability relative to existing facilities that do not interact directly with the exchange of material and energy streams amongst the nodes. GAMS software was again employed to create the optimization program with decision variables describing which of the network nodes should be constructed and what their associated production capacities should be in order to optimize a similar dual-objective function including profit and environmental impact. Again, the focus is to provide a balance between cost-savings and reduced environmental impact to influence policy and the design of facilities.

Chapter 6 builds further on the previous modeling attempts and migrates the model to a mixed-integer non-linear program (MINLP). This is the most detailed model of the system constructed to date and implements a relativistic objective function to normalize the outputs in relation to independent facilities. This objective function is a valuable tool for policy-makers as it exhibits the increase or decrease of process profitability and emissions in an integrated scenario relative to the base case of no integration. This is capable of influencing policy decisions on facility construction in order to achieve net benefits for producers as well as society.

7.2 Conclusions

The life-cycle impacts of utilizing alternative fuels for transportation purposes is considered in terms of six major stressors for climate change, acidification and urban air quality. The vehicles considered are plug-in hybrid electric vehicles (PHEVs), fuel cell vehicles (FCVs) and fuel cell plug-in hybrid electric vehicles (FCPHEVs). Modeling of the penetration rates for these types of vehicles has been completed based on the maximum base-load capacity of Ontario's electricity grid to accommodate the generation of hydrogen and charging of vehicles using grid electricity. Results show that the reduction in greenhouse gas emissions from adoption of PHEVs or FCVs will exceed 3% of the current emissions from the transportation sector in Ontario while FCPHEVs may achieve almost twice this reduction. All vehicles exhibit similar impacts on the precursors for photochemical smog although the province-wide effects differ significantly.

Also from chapter 3, it is observed that the location of new generation in Ontario greatly affects the supportable penetration of AFVs as both vehicle types depend on electricity to generate their fuel. This study focused on near term evaluation of the potential penetration of likely PHEV and FCV technologies, and as such considered only the currently planned upgrades to the electrical generation system. The only scenario considered for this study was that new generation will be located in the Toronto region. Locating generation in the Bruce zone will decrease the supportable penetration of PHEVs mainly due to the proximity to the urban population. Clearly if greater emission reductions in GHGs and urban air pollutants from vehicles are desired, further large scale expansion of the CO_2-free generation sources such as nuclear will be required and this will dramatically change the available base-load power profile.

Comparing FCVs and PHEVs in an urban-emissions scenario shows that FCVs tend to present an advantage over or near-equality with PHEVs in almost every aspect of their emissions. The range of FCPHEV emissions for the pertinent urban air pollutants suggest that a minimum number of FCPHEVs would exhibit reductions close to those attained by PHEVs or FCVs and the potential for the reduction of these emissions could greatly exceed that achievable by either vehicle.

One of the major emissions impacts from adopting either PHEVs or FCVs is a 3-3.5% decrease in greenhouse gas emissions within the transportation sector. Since transportation accounts for approximately 37% of all emissions of these gases in Canada, it is a significant impact to reduce transportation GHG emissions in Ontario by 3-3.5%. Adoption of FCPHEVs could attain a reduction as high as 5.8% of the transportation emissions in Ontario.

The effects on emissions of particulate matter are drastically different for the adoption of the different vehicle types. The overall emissions of particulate matter are of comparatively less concern because this matter is easily dispersed in the atmosphere instead of being heavily concentrated in a densely-populated area where it can affect the health of the population. Adoption of PHEVs shows an insignificant increase in overall particulate matter whereas adoption of FCVs and PHEVs will achieve approximately the same reduction in urban particulate matter emissions. FCPHEVs perform similarly to PHEVs for increased emissions of overall particulate matter but show a potential for larger decreases in the urban environment.

Overall emissions of SO_x, a contributor to acid rain, are expected to increase from the adoption of PHEVs and FCPHEVs which corresponds to an increase in the burning of coal in order to produce electricity for powering the vehicles.

When observing the emissions and technological readiness of each vehicle type, it should be noted that PHEVs are nearer to mass production and distribution but should be coupled with fuel cells as soon as production is technologically and economically feasible in order to achieve the maximum reduction in emissions.

The work from Chapter 4 focuses on analyzing possiblities for reduced life-cycle emissions from industrial operations producing industrial chemicals including hydrogen for fuel cell vehicles. The model developed is specifically for assessing the economics and emission reductions from EINs but the environmental benefits are limited to the boundaries of the EIN. Reduced emissions from the production of industrial chemicals and fuels can also have impacts throughout the remainder of the life cycle as shown by the emission reductions from AFVs.

Applying this model for a scenario of hydrogen production for 1000 consumer vehicles shows two independent stable solutions. Both of these solutions show profitability while reducing life-cycle emissions and maintaining the appropriate production of hydrogen for these vehicles. The LP model developed in this chapter is powerful but lacking in the complexity required to fully capture the interactions between networked production facilities. This assessment emphasizes the need for further efforts in network modeling, leading to an MILP or MINLP model which will also allow for consideration of alternative gasification feedstocks.

Chapter 5 shows that life cycle analysis and eco-park network optimization provide an excellent pairing for assessing EINs. The emissions from producing typical chemical exports are reduced when operating within the construct of an EIN and the profitability of the network is also improved. The optimization of this network with three different fuels shows that biomass usage has slightly less effect on the environment but with reduced profit and a net import of electricity from an outside source. A mixed integer modeling technique has been applied to improve potential application of the simulation results. Comparisons of three fuel types showed that biomass yielded the least profitable scenario, required a net import of electricity and produced significantly less heat for use in surrounding applications as would be suggested to improve the environmental performance of the region.

Additionally, utilization of three different fuels as the primary source of chemical reagents and energy are considered in various scenarios. These fuels are coal and biomass for gasification or a steam-methane reforming process using natural gas as the feedstock. The eco-park with interacting production nodes is shown to be more profitable than the comparable non-integrated set of facilities and the outputs are produced with lower environmental impact in terms of criteria air contaminants.

The model in Chapter 6 is a reconstruction and expansion from the MILP model in

Chapter 5 to reduce approximations and expand the capabilities of the model to handle a broader range of considerations. The MINLP includes a more detailed assessment of transportation considerations in addition to a more rigorous and complex set of contraints governing the interactions between plants.

This model builds on previous iterations and lends itself to future development as a tool to assess environmental and economic feasibility of applying eco-industrial integration concepts to new construction projects. In addition, the model is formulated to assess feasible transportation distances, transportation technologies and may be modified to include stochastic import/export pricing. The results of this analysis show that the estimated cost and emission reductions are less significant than with an LP or MILP model but represent a more realistic case. Cost for the integrated set of facilities is shown to be reduced by 24% while the emission reduction is observed at 12.7% for the base scenario represented by the earlier LP and MILP models.

The work from this chapter further expresses the usefulness of MINLP modeling to assess the potential benefits of eco-industrial integration. The MINLP model is the most comprehensive of the three considered in this work for assessing eco-park scenarios though it requires significantly more computational power.

7.3 Summary Statement of Contributions

This work has focused on providing a model for the analysis of the improvement of the environmental performance of transportation technologies and industrial manufacture of base chemicals in the context of emissions to the aquatic, terrestrial and atmospheric domains.

This work has developed a novel method for analyzing the potential and impacts of alternative-fuel vehicles and a generalized modeling framework for eco-industrial network integration using linear programming, mixed-integer linear programming and mixed-integer non-linear programming. These modeling frameworks have been applied to a potential eco-park integration scenario in order to assess the realistic potential for decreased environmental emissions and improved process profitability. This analysis has been completed in the broader context of the hydrogen economy and a social desire to improve the quality of the environment. As such, the work has also demonstrated the benefits and differences of the modeling techniques explored herein.

Life-cycle assessment has been applied to construct a dual-objective function capable of balancing environmental concerns with industrial profitability. The objective functions for these analyses relate the emissions and economics of independent facilities with those operating within an eco-industrial network arrangment. The objective function in each framework is of particular interest to policy-makers who can utilize such methods to find a compromise with industrial entities to reduce emissions while implementing cost-saving measures.

The bi-objective optimization framework in this thesis is a novel approach to facility design and includes environmental and economic considerations. Emissions are considered independently of economics in each model to avoid large economic incentives from overshadowing environmental objectives.

This work also serves to re-invigorate the notion of eco-industrial integration in light of increasing corporate social responsibility and the societal shift to provide increasing environmental awareness in industry. The economic needs of industry are balanced with the societal desire for reducing emissions to achieve mutual benefits.

7.4 Recommendations

7.4.1 Recommendations for Future Work

Recommendations for further work on this topic include reformulation strategies of the MINLP to reduce the solution time which remains one of the limitations for this type of model. MINLP modeling is well-suited to optimization of industrial eco-parks, yet the solution time is such that large numbers of simulations cannot be completed in a rapid fashion.

Stochastic simulation of networks which rely heavily on static costs of base chemicals should be conducted. Prices of both the feedstock and products of these networks may be highly sensitive to these costs and thus it is important to explore predicted values for commodities and chemicals.

In order to expand the list of contaminants considered for an optimization of this structure, a more comprehensive database of contaminants must be available for use. Research and data for less widely-studied contaminants are difficult to locate and contain many uncertainties as many aspects of production are not considered. Further work into developing a comprehensive database of life-cycle emissions must be available and be backed by high-quality research and methods.

7.4.2 Recommendations for Implementation

This work exhibits the impact of adoption of alternative fuel vehicles on the air quality in the urban centre of Toronto, Canada as well as the impact on air pollution in the province of Ontario. It is recommended that policy-makers create incentives for transitioning from convential fossil-fuel powered vehicles to those powered by electricity or hydrogen. The short-term benefits can be realized immediately by transitioning the existing vehicle fleet to operate on electricity with greater improvements seen in the long-term adaptation to hydrogen-powered vehicles. These recommendations are within the broader context of the hydrogen economy in an attempt to curb urban air pollution and smog in addition to global concerns of climate change. The transitions mentioned in this work are within the scope of electricity production in Ontario, Canada as forecast to 2025.

Based on the EIN case studies, it is recommended that industrial entities strongly consider the use of eco-industrial design optimization in order to realize the benefits of eco-industrial integration. Such tools would improve the economics and environmental performance of operations, proactively making improvements to processing in the eventual scenario of greater legislation on emissions of contaminants to air, water and land. In addition, this work serves to instruct policy-makers to consider stricter environmental legislation with the goal of encouraging corporations to apply eco-industrial integration possibilities into new facility constuction.

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Appendix: Additional detail with respect to primary modeling in Chapter 3

The following is a summary of the AMPL model which was primarily constructed by Amirhossein Hajimiragha as presented in [29, 61] which yielded the supportable penetration of alternative fuel vehicles used in Chapter 3. These estimates were then used to calculate the emission reductions from these vehicles using GREET 1.8b as described in Chapter 3. A summary of the model, as published by Hajimiragha et al. is shown below with permission from the International Association of Hydrogen Energy.

$$\Omega = \frac{\lambda_i}{\pi_i} = \frac{\lambda \sum_i b_i}{\sum_i \pi_i b_i}$$

Describes the ratio of base-load growth rate (λ_i) to peak-load growth rate (π_i) under the assumption that this ratio is constant across all zones. Thus λ is the annual baseload growth rate in all zones and b_i is the base load value in Zone i. The growth rate in each zone can then be calculated:

$$\lambda_i = \lambda \frac{\pi_i \sum_i b_i}{\sum_i \pi_i b_i}$$

$Phpp_{iy}$ is the total installed HPP capacity in Zone i, by Year y which can by utilized for producing hydrogen locally and also in other zones. This total capacity is composed of smaller power components, Ps_{ijy}, which represents the contribution of zone i to the total power required in zone j to be transported by compressed gas truck transportation. Other zones can share in part of the required power in zone i based on the complementary power component Ps_{jiy}. Accordingly, the required power of HPPs in Zone i by Year y (Ph_{iy}) can be expressed as follows:

$$Ph_{iy} = Phpp_{iy} - \sum_{j \neq i} Ps_{ijy} + \sum_{j \neq i} Ps_{jiy} \;\; \forall i, j \in Z \wedge y \in \Upsilon_1$$
$$Phpp_{iy} = Phpp_{iy-1} + \Delta Phpp_{iy}$$

where:

- $\Delta Phpp_{iy}$ is the newly installed HPP in Zone i and Year y;
- Z = {1,...,10} is the set of indices of zones or buses in the simplified network; and,
- Υ_1 = {2009,...,2025} is the set of indices of planning years starting in 2009.

Operational hours or capacity factors for the HPPs must be considered to link the power component to the amount of hydrogen transferred between zones. The HHV of hydrogen coupled with assumptions of 68 hours of operation per week with 70 % plant efficiency yields the power component, Ps_{ijy}, is capable of producing 0.1724 Ps_{ijy} tonnes of hydrogen per day for transfer to zone j by compressed gas tube trailers. This transfer is represented by Th_{ijy}.

$$Th_{ijy} = 0.1724 Ps_{ijy} \ \ \forall (i,j) \in Z^{*} \wedge y \in \Upsilon$$

where $Z^{*} = \{(i,j) : i,j \in Z, i \neq j\}$ is the set of indices of hydrogen transfer corridors and $\Upsilon = \{2008, ..., 2025\}$ is the set of indices of planning years starting from 2008.

The total cost of transporting hydrogen between zone i and j, TOC_{ijy} , follows a step function depending on the total transfer of hydrogen:

$$TOC_{ijy} = m \cdot OC_{y} \cdot d_{ij}$$

where m stands for the number of trucks, OC_{y} is operational cost in year y per compressed gas truck [$\$CADkm^{-1}$] and d_{ij} is the distance between zones i and j in km.

The objective function in this optimization is to minimize costs for electricity and hydrogen transportation. The cost function is composed of the costs and revenues from electricity import/export in addition to generation costs for segments of 8 weekday hours (0:00 - 07:00) and 14 weekend hours (0:00-13:00) with an additional consideration of hydrogen tranportation costs.

$$\begin{aligned} &\sum_{y \in \Upsilon_1} \sum_{i \in Z} \big\{ \big(Pg_{iy}^{\omega_1} + Pim_{iy}^{\omega_1} - Pex_{iy}^{\omega_1}\big) \cdot HOEP_{y}^{\omega_1} \times 8 \times 261 \\ &\qquad \big(PG_{iy}^{\omega_2} + Pim_{iy}^{\omega_2} - Pex_{iy}^{\omega_2}\big) \cdot HOEP_{y}^{\omega_2} \times 14 \times 104 \big\} \\ &\qquad + \sum_{y \in \Upsilon_1} \sum_{(i,j) \in Z^{*}} \left(\sum_{m=1}^{ntr_y} m \cdot K_{mijy} \right) \left\{ 2OC_{y} \cdot d_{ij} \times 365 + \frac{DR \cdot CC_{cab}}{[1 - (1+DR)^{-LT_{cab}}]} \right. \\ &\qquad \left. + \frac{DR \cdot CC_{tube}}{[1 - (1+DR)^{-LT_{tube}}]} \right\} \end{aligned}$$

where:

- ω_1 is an index for the time period corresponding to 8 weekday hours (12 am-7 am);
- ω_2 is an index for the time period corresponding to 14 weekend hours (12 am-1 pm);
- Pg, Pim and Pex are zonal generation power, imported power, and exported power, respectively, in Zone i, Year y, and during the time periodω_1 orω_2;
- K_{mijy} is a binary variable which takes the value of 1 if m trucks are needed for daily hydrogen transfer between Zones i and j in Year y;
- CC_{cab} and CC_{tube} are the capital cost of cab and tube trailers, respectively;
- LT_{cab} and LT_{tube} are the life time of cab and tube trailers, respectively;
- DR is the discount rate; and,
- ntr_y is the maximum number of compressed gas trucks in route between Zones i and j in Year y.

The power losses in line (i,j) of the electricity network can be approximately calculated as:

$$Ploss_{ij} \cong g_{ij}\left(\delta_i - \delta_j\right)^2$$

where g_{ij} is the conductance of the line between buses i and j, and δ denotes the corresponding bus voltage angles according to the following equation:

$$\delta_{ijy}^{\gamma} = |\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma}|$$

Which can be approximated in linear terms by the following equations:

$$\begin{aligned}
\delta_{ijy}^{\gamma} &= \delta_{ijy}^{\gamma+} + \delta_{ijy}^{\gamma-} \\
\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma} &= \delta_{ijy}^{\gamma+} + \delta_{ijy}^{\gamma-} \\
\delta_{ijy}^{\gamma+} &\geq 0 \\
\delta_{ijy}^{\gamma-} &\geq 0 \\
&\forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi
\end{aligned}$$

where Ω is the set of indices of transmission lines and $\Psi = \{\omega_1, \omega_2\}$. A linear approximation of power losses in Year y and during the time period γ can be obtained using L piecewise linear blocks as follows:

$$\delta_{ijy}^{\gamma} = \sum_{l=1}^{L} \delta_{ijy}^{\gamma}(l)$$

$$Ploss_{ijy}^{\gamma} = g_{ijy} \sum_{l=1}^{L} \alpha_{ijy}(l) \delta_{ijy}^{\gamma}(l)$$

where $\alpha_i jy(l)$ and $\delta_{ijy}^{\gamma}(l)$ represent the slope and value of the l^{th} block of voltage angle, respectively. Assuming that each angle block has a constant length $\Delta\delta_y$, the slope of the blocks of angles for all lines (i,j) can be calculated as:

$$\alpha_{ijy}(l) = (2l-1)\Delta\delta_y \;\; \forall (i,j) \in \Omega \wedge y \in \Upsilon$$

Enforcing the adjacency of the angle blocks requires the following:

$$\delta_{ijy}^{\gamma}(l) \geq 0 \;\; \forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi \wedge l \in L_1$$

$$\omega_{ijy}^{\gamma}(l) \cdot \Delta\delta_y \leq \delta_{ijy}^{\gamma}(l) \;\; \forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi \wedge l \in L_2$$

$$\delta_{ijy}^{\gamma}(l) \leq \omega_{ijy}^{\gamma}(l-1) \cdot \Delta\delta_y \;\; \forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi \wedge l \in L_3$$

$$\omega_{ijy}^{\gamma}(l) \leq \omega_{ijy}^{\gamma}(l-1) \;\; \forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi \wedge l \in L_4$$

where $\omega_{ijy}^{\gamma}(l)$ is a binary variable which takes the value of 1 if the value of the l^{th} angle block for the line (i,j) is equal to its maximum value $\Delta\delta_y$; $\{L_1 = 1, \ldots, L\}$; $\{L_2 = 1, \ldots, L-1\}$; $\{L_3 = 2, \ldots, L\}$; and $\{L_4 = 2, \ldots, L-1\}$.

Considering the line losses model just described, the net power injected at Zone i can be represented as:

$$P_{iy} = \sum_{(i,j)\in\Omega} \left[\frac{1}{2} g_{ijy} \sum_{l=1}^{L} \alpha_{ijy}(l) \delta_{ijy}^{\gamma}(l) - b_{ijy}(\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma}) \right]$$

where b_{ijy} is the susceptance of the line (i,j) in Year y. Consequently, in general terms, the zonal power balance constraints can be formulated as follows:

$$Pg_{iy}^{\gamma} - Pl_{iy}^{\gamma} + Pim_{iy}^{\gamma} - Pex_{iy}^{\gamma} - \sum_{(i,j)\in\Omega} \left[\frac{1}{2} g_{ijy} \sum_{l=1}^{L} \alpha_{ijy}(l) \delta_{ijy}^{\gamma}(l) - b_{ijy}(\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma}) \right] = 0$$

$$\forall i \in Z \wedge y \in \Upsilon \wedge \gamma \in \Psi$$

where Pl is the total load in each zone and is comprised of zonal electricity demand (Pe) and total installed HPPs as follows:

$$Pl_{iy}^{\gamma} - Phpp_{iy} - Pe_{iy}^{\gamma} = 0 \;\; \forall i \in Z \wedge y \in \Upsilon \wedge \gamma \in \Psi$$

The power generation in each year and zone is bounded by minimum and maximum limits $\underline{Pg}_{iy}$ and $\overline{Pg}_{iy}$, respectively. These limits are the minimum and maximum effective generation capacities which are available in each zone during the planning years, resulting in the following inequality constraint:

$$\underline{Pg}_{iy} \leq Pg_{iy}^{\gamma} \leq \overline{Pg}_{iy} \forall i \in Z \wedge y \in \Upsilon \wedge \gamma \in \Psi$$

These limits are stated as:

$$\underline{Pim}_{iy} \leq Pim_{iy}^{\gamma} \leq \overline{Pim}_{iy} \ \forall i \in Z \wedge y \in \Upsilon \wedge \gamma \in \Psi$$
$$\underline{Pex}_{iy} \leq Pex_{iy}^{\gamma} \leq \overline{Pex}_{iy} \ \forall i \in Z \wedge y \in \Upsilon \wedge \gamma \in \Psi$$

where $\underline{Pim}_{iy}$ and $\overline{Pim}_{iy}$ are lower and upper bounds of imported power, respectively; additionally, $\underline{Pex}_{iy}$ and $\overline{Pex}_{iy}$ are exported power minimum and maximum limits, respectively.

These constraints are defined as:

$$\begin{aligned} b_{ij}(\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma}) + \frac{1}{2} g_{ij} \sum_{l=1}^{L} \alpha_{ijy}(l) \delta_{ijy}^{\gamma}(l) \leq \overline{Pd}_{ij} - b_{ij}(\delta_{iy}^{\gamma} - \delta_{jy}^{\gamma}) \\ + \frac{1}{2} g_{ij} \sum_{l=1}^{L} \alpha_{ijy}(l) \delta_{ijy}^{\gamma}(l) \leq \overline{Pr}_{ij} \\ \forall (i,j) \in \Omega \wedge y \in \Upsilon \wedge \gamma \in \Psi \end{aligned}$$

where $\overline{Pd}_{ij}$ and $\overline{Pr}_{ij}$ are maximum capacity of the transmission corridor (i,j) in direct and reverse power flow, respectively.

In order to effectively model the hydrogen transportation costs, the following constraints are also needed:

$$
\begin{aligned}
&[C(m-1)+\epsilon]K_{mijy} \leq th_{mijy} \leq C \cdot m \cdot K_{mijy} \\
&\sum_{m=1}^{ntr_y} K_{mijy} \leq 1 \\
&Th_{ijy} = \sum_{m=1}^{ntr_y} th_{mijy} \\
&\forall m \in M \wedge (i,j) \in Z^* \wedge y \in \Upsilon_1
\end{aligned}
$$

where ϵ is a very small positive number; th_{mijy} is an auxiliary variable representing the transferred hydrogen, since $Th_{ijy} = th_{mijy}$ if $K_{mijy} = 1$; and $M = \{1, \ldots, n_{try}\}$.

These limits are represented by:

$$0 \leq Phpp_{iy} \leq \overline{Phpp}_{iy} \;\; \forall i \in Z \wedge y \in \Upsilon$$

where $\overline{Phpp}_{iy}$ is the maximum size of HPP which is allowed to be installed in zone i by Year y. Since HPP is not installed for 2008, $\overline{Phpp}_{iy}$ is equal to zero for y = 2008.