COUPLING DEHYDROGENATION OF ETHYLBENZENE WITH HYDROGENATION OF NITROBENZENE IN AN AUTOTHERMAL CATALYTIC MEMBRANE REACTOR

by

Nabeel Salim M. Abo-Ghander

B.Sc., King Fahd University of Petroleum & Minerals, Saudi Arabia (2000) M.Sc., King Fahd University of Petroleum & Minerals, Saudi Arabia (2003)

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

in The Faculty of Graduate Studies

(Chemical & Biological Engineering) The University of British Columbia (Vancouver) February 2011

© Nabeel Salim M. Abo-Ghander, 2011

ABSTRACT

Dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene form an interesting pair of reactions to be coupled in a catalytic membrane reactor. The former is reversible and thermodynamically limited, supplying hydrogen with a net endothermality, while the latter is irreversible and exothermic, consuming hydrogen to produce aniline. In this work, coupling of these two reactions is simulated in a catalytic fixed bed membrane reactor where hydrogen produced on the dehydrogenation side is transferred through hydrogen membranes to the hydrogenation side where it reacts to produce aniline. Heat generated on the hydrogenation side is transferred to the dehydrogenation side, where it is utilized by the endothermic dehydrogenation reaction to improve the styrene yield.

A pseudo-homogeneous model for the coupled reactor based on the concept of fixed bed reactors accounting for both the diffusion of hydrogen and transfer of heat is first developed. The effects of the operating and design parameters considered on the production of styrene and aniline show conflicting behaviour, i.e. improving the yield of styrene results in decreased production of aniline. Consequently, the cocurrent configuration of the coupled reactor was optimized within constraints so that it can be operated effectively to produce \sim 98% styrene as a one limiting option or \sim 80% aniline at the other extreme.

The intraparticle diffusion resistance, a major limitation in fixed bed reactors, is evaluated by developing a heterogeneous reactor model based on Fickian diffusion and the dusty gas model for both isothermal and non-isothermal catalyst pellets. Both heterogeneous models predict a significant reduction in yield and conversion relative to the pseudo-homogeneous model, indicating the importance of heterogeneity. This reduction is generally less severe for the dusty gas model than for Fickian diffusion. The mean square deviation and absolute deviation along the reactor are calculated for all models relative to the heterogeneous reactor model with dusty gas for non-isothermal catalyst pellets, considered to be the most rigorous model tested. Assuming isothermality causes larger deviations than assuming Fickian diffusion. The deviations in the predictions of the homogenous model and the heterogeneous models from those of the dusty gas model for non-isothermal pellets are $\sim 6\%$ and $\sim 11\%$, respectively.

PREFACE

The work in this thesis is based on modeling and simulation of a proposed catalytic membrane reactor used to couple dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene. It is the first attempt to integrate these two industrially important processes in a single reactor so that hydrogen produced on the dehydrogenation side diffuses through the membrane wall to react with nitrobenzene to produce aniline. Heat produced on the hydrogenation side is also transferred through the membrane wall to break the endothermality on the dehydrogenation side and shift the yield of styrene above its thermodynamic limit. The reactor is designed and optimized to be operated continuously to produce simultaneously styrene from the dehydrogenation side and aniline from the hydrogenation side.

This project was completed under the supervision of Profs. John Grace, Said Elnashaie, and C. Jim Lim who are also co-authors of the manuscripts. Inputs from Prof. Jan Van Impe and Dr. Filip Logist, BioTeC and OPTEC, Department of Chemical Engineering, Katholieke Universiteit, were also important in solving the optimization problem of the proposed membrane reactor described in chapter 3, and the heterogeneous model of the reactor based on Fickian diffusion and the dusty gas model discussed in chapters 4 and 5.

My role in this research work leading to this dissertation included:

- 1. Setting up the statements of all problems.
- 2. Deriving all reactor models.
- 3. proposing the numerical techniques which might be used to solve the proposed problem.
- 4. Receiving suggestions and comments from my co-authors, coordinating and incorporating these.
- 5. Writing and debugging all numerical Matlab codes to solve sets of initial and boundary value problems.
- 6. Doing the optimization computations.
- 7. Collecting the results from programs and reproducing them in the proper formats.

- 8. Preparing the manuscripts, i.e. text, tables, and figures, and correcting them after revision by the co-authors
- 9. Submitting the corrected manuscripts to the journals for publications after preparing all the necessary documents such as cover letters and lists of suggested reviewers.
- 10. Receiving the reviewers' comments from the journals, discussing them with the coauthors, and drafting detailed responses and revisions.

Slightly modified versions of chapters 2 and 3 have already been published as follows:

- Nabeel S. Abo-Ghander, John R. Grace, Said S.E.H. Elnashai, and C. Jim Lim, 2008. Modeling of a novel membrane reactor to integrate dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline, Chemical Engineering Science, 63(7), 1817-1826.
- Nabeel S. Abo-Ghander, Filip Logist, John R. Grace, Jan F.M. Van Impe, Said S.E.H. Elnashaie, and C. Jim Lim 2010. Optimal design of an autothermal membrane reactor coupling the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline, Chemical Engineering Science, 65(10), 3113-3127.

A version of chapter 5 has been already submitted for publication, and a modified version of chapter 4 will be submitted soon.

TABLE OF CONTENTS

ABSTRACT ii
PREFACEiii
TABLE OF CONTENTSv
LIST OF TABLES ix
LIST OF FIGURES xi
NOMENCLATURE xiv
ACKNOWLEDGEMENTS xviii
CHAPTER 1 INTRODUCTION
1.1. Thesis Overview1
1.2. Coupling of Chemical Reactions2
1.2.1. Thermal coupling of chemical reactions
1.2.2. Coupling of chemical reaction with in-situ separation
1.2.3. Coupling of chemical reaction via both in-situ separation and heat transfer 7
1.3. Sources of Novelty in this Thesis8
1.4. Thesis Objectives11
1.5. Challenges and Obstacles Encountered in this Thesis
1.6. Derivation of the Reactor Pseudo-homogeneous Model
1.7. References
CHAPTER 2 PSEUDO-HOMOGENEOUS MODELING OF A NOVEL
MEMBRANE REACTOR TO INTEGRATE DEHYDROGENATION OF
ETHYLBENZENE TO STYRENE WITH HYDROGENATION OF
NITROBENZENE TO ANILINE
2.1. Introduction
2.2. Theory
2.2.1. Assumptions
2.2.2. Reaction kinetics
2.2.3. Pseudo -homogeneous model of the coupled membrane reactor
2.2.4. Initial and boundary conditions

2.2.5.	Simulation conditions
2.3. R	esults and Discussion
2.3.1.	Hydrogen molar flowrate
2.3.2.	Conversion of ethylbenzene
2.3.3.	Yield of styrene
2.3.4.	Conversion of nitrobenzene
2.3.5.	Temperature profiles 38
2.3.6.	Practical considerations
2.4. C	onclusions
2.5. R	eferences
СНАРТЕ	CR 3 OPTIMAL DESIGN OF AN AUTOTHERMAL MEMBRANE
REACTO	OR COUPLING THE DEHYDROGENATION OF
ETHYLE	BENZENE TO STYRENE WITH THE HYDROGENATION OF
NITROB	ENZENE TO ANILINE BASED ON PSEUDO-HOMOGENEOUS
MODEL	
3.1. In	troduction55
3.2. Li	terature Review
3.3. R	eactor Configuration59
3.4. C	hemical Reactions and Kinetic Expressions60
3.5. M	athematical Reactor Model61
3.6. TI	he Optimization Problem62
3.7. D	etails of the Numerical Solution67
3.8. R	esults and Discussion
3.9. Se	ensitivity Analysis Based on Pseudo-Homogeneous Model:
3.10 C	anglusions 76
2 11 D	of changes and the second s
5.11. K	elerences
CHAPTE	EX 4 HETEROGENEOUS MODELING OF AUTOTHERMAL
MEMBR	ANE KEAUIUK UUUPLING DEHYDKUGENATION OF Renzene to studene with hundocenation of
NITROR	FNZENE TO STIKENE WITH HIDKUGENATION OF
LULINUD	

4.1. I	Introduction
4.2. I	Reactor Configuration97
4.3. I	Reactor Model
4.4. I	Results and Discussion105
4.4.1.	Conversion of ethylbenzene and nitrobenzene105
4.4.2.	Yield of styrene, benzene, and toluene on dehydrogenation side
4.4.3.	Hydrogen molar flow rates on dehydrogenation and hydrogenation sides 106
4.4.4	. Temperature profiles along coupled reactor 107
4.4.5.	Reaction effectiveness factors and reaction rates
4.4.6	Component effectiveness factors 110
4.4.7.	Behaviour inside catalyst pellets on both sides of coupled reactor 111
4.4.8	Effect of intraparticle diffusion resistance on optimal reactor design
4.5. (Conclusions
4.6. I	References134
СНАРТ	TER 5 COMPARISON OF DIFFUSION MODELS IN MODELLING
A CAT	FALYTIC MEMBRANE FIXED BED REACTOR COUPLING
DEHYD	PROGENATION OF ETHYLBENZENE WITH HYDROGENATION
OF NIT	ROBENZENE136
5.1. I	Introduction
5.2. 1	Reactor Configuration138
5.3. I	Reactor Model
5.3.1.	Diffusion inside catalyst pellets140
5.3.1.	Diffusion models for catalyst pellets142
5.4. I	Results and Discussion149
5.4.1.	Conversion of ethylbenzene and nitrobenzene
5.4.2.	Yield of styrene, benzene, and toluene on dehydrogenation side 150
5.4.3.	Hydrogen molar flow rates on dehydrogenation and hydrogenation sides 151
5.4.4	Temperature profiles on both sides of coupled reactor
5.4.5. react	Predictions of styrene yields and nitrobenzene conversions in the coupled or by the various models
5.5. (Conclusions

5.6.	References
СНАР	FER 6 OVERALL CONCLUSIONS AND RECOMMENDATIONS 172
6.1.	Conclusions
6.2.	Recommendations
6.3.	References

LIST OF TABLES

Table 2.1 Arrhenius equation and equilibrium constants for ethylbenzene reactions
Table 2.2 Unit conversion constants for reaction rates of dehydrogenation network
Table 2.3 Design and operating conditions for dehydrogenation (shell side) reaction of
ethylbenzene to styrene
Table 2.4 Operating conditions for hydrogenation (tube side) reaction of nitrobenzene to
aniline
Table 3.1 Summary of stoichiometric equations, heats of reactions and reaction rate
expressions
Table 3.2 Numerical values of kinetic pre-exponential constants and activation energies78
Table 3.3 Model equations for integrated catalytic membrane reactor. 79
Table 3.4 Values of constant variables in the optimization problem. 80
Table 3.5 Representative solutions for the Pareto frontier. 81
Table 3.6 Nominal values of the fixed variables used in the sensitivity analysis
Table 4.1 Stoichiometric equations, heats of reactions and reaction rate expressions for
reactions considered
Table 4.2 Frequency factors and activation energies for reactions considered. 117
Table 4.3 Heterogeneous model for the coupled reactor based on Fickian diffusion 118
Table 4.4 Dimensional and operating parameters for hybrid catalytic membrane reactor
for base case
Table 4.5 Representative solutions for Pareto frontier*. 120
Table 5.1 Stoichiometric equations, heats of reactions and reaction rate expressions for
reactions in coupled reactor
Table 5.2 Frequency factors and activation energies for reactions in the coupled reactor.
Table 5.3 Heterogeneous model equations for coupled catalytic membrane reactor
Table 5.4 Base case dimensional and operating parameters for coupled catalytic membrane
reactor
Table 5.5 Representative solutions for Pareto frontier. Constrained limits are bolded 159

Table 5.6 Deviations of the predictions inside the coupled reactor from the non-isot	hermal
dusty gas heterogeneous reactor model	160

LIST OF FIGURES

Figure 1.1 Schematic diagram of the reactor coupling dehydrogenation of ethylbenzene
with hydrogenation of nitrobenzene19
Figure 1.2 Schematic representation of a differential element inside the reactor for
cocurrent flow. Large arrows show directions of mass and heat fluxes
Figure 1.3 Schematic representation of a differential element inside the reactor for
countercurrent flow. Large arrows show directions of mass and heat fluxes
Figure 2.1 Schematic diagram showing integrated reactor configuration
Figure 2.2 Schematic diagram showing a differential element inside the membrane reactor.
Figure 2.3 Molar flow of hydrogen on uncoupled adiabatic fixed bed and coupled cocurrent
and countercurrent cases of the novel membrane reactor. For operating conditions see
Tables 2.3 and 2.4. For countercurrent case, feed is from the right for the
hydrogenation compartment; otherwise all feeds are from the left
Figure 2.4 Comparison of ethylbenzene conversions on dehydrogenation side for uncoupled
adiabatic fixed bed and for coupled cocurrent and countercurrent cases. For operating
conditions, see Tables 2.3 and 2.4 48
Figure 2.5 Comparison of styrene yields on dehydrogenation side for uncoupled adiabatic
fixed bed and for coupled cocurrent and countercurrent cases. For operating
conditions, see Tables 2.3 and 2.4 49
Figure 2.6 Conversion of nitrobenzene on hydrogenation side for cocurrent and
countercurrent membrane reactor configurations. For operating conditions, see Tables
2.3 and 2.4
Figure 2.7 Effect of number of hydrogenation tubes on temperature profiles in
dehydrogenation and hydrogenation compartments for the cocurrent case. For
operating conditions, see Tables 2.3 and 2.4
Figure 2.8 Effect of number of hydrogenation tubes on temperature profiles in the
dehydrogenation and hydrogenation compartments for coupled countercurrent case.
For operating conditions, see Tables 2.3 and 2.452

Figure 3.1 Conceptual design of integrated catalytic membrane reactor coupling
dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene
Figure 3.2 Flowchart showing how the Tomlab solvers, i.e. glbDirect and snopt, are linked
to the reactor model
Figure 3.3 Pareto optimal set obtained by simultaneous maximization of styrene yield and
nitrobenzene conversion
Figure 3.4 (a, b) Feed molar flowrate of ethylbenzene; (c, d) Steam-to-ethylbenzene molar
ratio on dehydrogenation side; (e, f) Feed temperature on dehydrogenation side
corresponding to Pareto optimal set
Figure 3.5 (a, b) Feed pressure on dehydrogenation side; (c, d) Molar feed of nitrobenzene
on hydrogenation side; (e, f) Steam-to-nitrobenzene molar ratio on hydrogenation side
corresponding to Pareto optimal set
Figure 3.6 (a, b) Feed temperature on hydrogenation side; (c, d) Feed pressure on
hydrogenation side; (e, f) Number of hydrogenation tubes corresponding to Pareto
optimal set
Figure 3.7 (a, b) Net diameter of dehydrogenation side; (c, d) Hydrogenation tube
diameter; and (e, f) Length of reactor corresponding to the Pareto optimal set
Figure 3.8 (a) Styrene yield and nitrobenzene yield along the membrane reactor at three
different optimal Pareto solutions; (b) Temperature profiles on both shell andtube
sides of the membrane reactor at three different optimal Pareto solutions
Figure 3.9: Sensitivity analysis on some key operating variables
Figure 4.1 Schematic of the coupled membrane fixed bed reactor
Figure 4.2 Infinitesimal slice inside catalyst pellets on dehydrogenation side showing terms
considered in: (a) mole balance, and (b) energy balance
Figure 4.3 Schematic sequence of computations for the catalyst and reactor models 123
Figure 4.4 Conversion of key components: (a) Ethylbenzene on dehydrogenation side, and
(b) Nitrobenzene on hydrogenation side124
Figure 4.5 Yield of: (a) Styrene, (b) Benzene, and (c) Toluene on dehydrogenation side 125
Figure 4.6 Hydrogen molar flowrates on: (a) dehydrogenation side, and (b) hydrogenation
side
Figure 4.7 Temperature profiles on: (a) dehydrogenation side, and (b) hydrogenation 127

Figure 4.8 Reaction effectiveness factor profiles versus bulk temperature for: (a, b)
dehydrogenation reactions, and (c) hydrogenation reaction128
Figure 4.9 Actual reaction rates and their values at surface conditions versus bulk
temperature for all reactions129
Figure 4.10 Component effectiveness factor profiles versus dimensionless axial distance for:
(a) ethylbenzene, styrene, hydrogen, benzene, and toluene on dehydrogenation side; (b)
nitrobenzene on hydrogenation side130
Figure 4.11 Intraparticle profiles of component mole fraction, temperature and component
effective diffusivities at fractional lengths of 0.1, 0.5, and 0.80 for both the isothermal
and non-isothermal catalyst pellet case on dehydrogenation side
Figure 4.12 Intraparticle profiles of component mole fraction, temperature and component
effective diffusivities at fractional lengths of 0.1, 0.5, and 0.80 for both the isothermal
and non-isothermal catalyst pellet case on hydrogenation side
Figure 4.13 Styrene yield, nitrobenzene conversion, and temperature profiles for the
optimal designs of the coupled membrane reactor, i.e. solution A (a, b, c), solution B (d,
e, f), solution C (g, h, i)
Figure 5.1 Schematic of coupled catalytic membrane for cocurrent configuration
Figure 5.2 Molar and heat fluxes across a small shell inside a catalyst pellet162
Figure 5.3 Computational sequence coupling dusty gas model equations with reactor model
equations
Figure 5.4 Conversion of (a) ethylbenzene on dehydrogenation side, and (b) nitrobenzene
on hydrogenation side for base case operating conditions in Table 5.4
Figure 5.5 Yield of (a) Styrene, (b) Benzene, and (c) Toluene along dehydrogenation side
for base case operating conditions in Table 5.4
Figure 5.6 Hydrogen molar flowrate variation along reactor for base case operating
conditions in Table 5.4 on: (a) dehydrogenation side, (b) hydrogenation side166
Figure 5.7 Temperature profiles along the reactor for base case operating conditions in
Table 5.4 on: (a) dehydrogenation side, and (b) hydrogenation side

NOMENCLATURE

Α	matrix of the linear constraints.
$A_{\rm cs}, A'_{\rm cs}$	cross-sectional area of shell and tube sides, [m ²].
a_i	constant, 1 for hydrogen, 0 otherwise, [-].
b	constant, 0 for cocurrent configuration, 1 for countercurrent configuration, [-].
Cp_i, Cp'_i	heat capacity of component i on shell and tube sides, [J/mole/K].
C(X)	vector of equality and inequality nonlinear constraints.
$c_{_{eq}}\left(\mathbf{p} ight)$	vector of nonlinear equality constraints, [-].
$c_{_{ineq}}\left(\mathbf{p} ight)$	vector of nonlinear inequality constraints, [-].
C_i, C'_i	concentration of <i>i</i> inside catalyst pellets on shell and tube sides, $[mole/m^3]$.
D	area-equivalent diameter on shell side, [m].
D_{ij}, D'_{ij}	binary diffusivity of <i>i</i> into <i>j</i> on shell and tube sides, $[m^2/s]$.
D_{im}	diffusivity of component <i>i</i> into the mixture on shell side, $[m^2/s]$.
D_{ik}, D'_{ik}	Knudsen diffusivity of <i>i</i> on shell and tube sides, $[m^2/s]$.
$D^e_{ij}, D^{\prime e}_{ij}$	effective binary diffusivity of <i>i</i> into <i>j</i> on shell and tube sides <i>j</i> , $[m^2/s]$.
D^e_{im}	effective diffusivity of component <i>i</i> into mixture on shell side, $[m^2/s]$.
$D^e_{ik}, D^{\prime e}_{ik}$	effective Knudsen diffusivity of i on shell and tube sides, $[m^2/s]$.
$D^e_{ie}, D^{\prime e}_{ie}$	mean diffusivity of <i>i</i> on shell and tube sides, $[m^2/s]$.
D_p, D'_p	diameter of catalyst particles on shell and tube sides, [m].
D_t	diameter of tube, [m].
$E_{j,} E'$	activation energy of reaction j on shell side and hydrogenation reaction on tube
	side, [J/mole/K].
F(X)	vector of the objective functions, [-].
J(p)	vector of objective functions, [-].

J_i	molar flux of component <i>i</i> , $[mole/m^2/s]$.
J_{NB}	nitrobenzene conversion generic function, [-].
J_{SY}	styrene yield generic function, [-].
H_i, H'_i	enthalpy of component i on shell and tube sides, [J/mole].
k, k'	thermal conductivities of catalyst on shell and tube sides, [Jm/s].
k _{io}	reaction <i>i</i> pre-exponential factor, $[mole/K^m/kg cat/s/bar^n]$,
	(for k_1 and k_2 , $m=0$, $n=1$; for k_3 and k_5 , $m=0$, $n=2$; for k_4 , $m=0$, $n=1.5$;
	for <i>k</i> ₆ , <i>m</i> =3, <i>n</i> =3).
<i>k</i> _i	reaction <i>i</i> rate constant, $[mole/K^m/kg cat/s/bar^n]$,
	(for k_1 and k_2 , $m=0$, $n=1$; for k_3 and k_5 , $m=0$, $n=2$; for k_4 , $m=0$, $n=1.5$;
	for k_6 , $m=3$, $n=3$).
K_{NB}	nitrobenzene adsorption constant, [1/Pa].
K_{H_2}	hydrogen adsorption constant, $[1/Pa^{0.5}]$.
L	total length of reactor, [m].
Ν	number of tubes in hybrid reactor, [-].
N_i, N'_i	molar flux of component i inside catalyst particles on shell and tube sides,
	$[mole/m^2/s].$
N_p	number of points at which styrene yields and nitrobenzene conversion are predicted, [-].
$n_{ m NBo}$	feed molar flowrates of nitrobenzene on tube side [mole/s].
n_i, n'_i	molar flow rate of component i on shell and tube sides, [mole/s].
n _{EBf}	feed molar flowrate of ethylbenzene on shell side, [mole/s].
<i>n_{NBf}</i>	feed molar flowrate of nitrobenzene, on tube side [mole/s].
p_i, p'_i	partial pressure of component <i>i</i> on shell and tube sides, [bar].
<i>P</i> , <i>P</i> ′	total pressure on shell side and tube side, [bar].
P_f, P'_f	feed pressure on shell side and tube side, [bar].
р	vector of decision variables, [-]
\mathbf{p}^{L}	lower bound vector of decision variables, [-]

\mathbf{p}^{U}	upper bound vector of decision variables, [-]
Q'	heat transferred from tube side to shell side per unit length, [W/m].
$Q_{ m o}$	pre-exponential constant of hydrogen membrane, [mole/m/s/bar ^{0.5}].
<i>r</i> _j	rate of reaction <i>j</i> on shell side, [mole/kg cat/s].
<i>r'</i>	rate of hydrogenation reaction on tube side, [mole/kg cat/s].
r_1, r_2	inner and outer radii of hydrogenation tube, [m].
<i>r</i> ₃ - <i>r</i> ₂	thickness of palladium membrane, [m].
SOR	steam-to-ethylbenzene ratio, [-].
SOR'	steam-to-nitrobenzene ratio, [-].
<i>T</i> , <i>T</i> '	temperature on shell and tube sides, [K].
T_f, T_f	feed temperature on shell side and tube side, [K].
T_s, T'_s	temperature at surface of catalyst pellet on shell and tube sides, [K].
$X_{ m NB}$	conversion of nitrobenzene on tube side, [-].
${ ilde X}_{\scriptscriptstyle NB}$	reference conversion of nitrobenzene, i.e. predictions by heterogeneous reactor
	model with dusty gas diffusion for non-isothermal catalyst pellets at designated
	distances along reactor, [-].
x_i, x'_i	mole fraction inside catalyst pellet on shell and tube sides, [-].
x_{is}, x'_{is}	mole fraction at surface of catalyst pellet on shell and tube sides, [-].
$Y_{\rm ST}$	yield of styrene, [-].
\tilde{Y}_{ST}	reference yield of styrene, i.e. predictions by heterogeneous reactor model with
	dusty gas diffusion for non-isothermal catalyst pellets at designated distances
	along reactor, [-].
<i>y</i> , <i>y</i> ′	radial coordinate inside catalyst pellet on shell and tube sides, [-].
Z	axial coordinate along reactor, [m].
$\left[\Delta H(T)\right]_{j}$	heat of reaction j at temperature T on shell side, [J/mole].
$\left[\Delta H'(T') ight]$	heat of hydrogenation reaction at temperature T on tube side, [J/mole].
Greek Letters	

Δz	thickness of differential element, [m].
ω, ω'	dimensionless radial distance inside catalyst pellets on shell and tube sides, [-].
$ ho_{s, ho's}$	catalyst density on shell and tube sides, $[kg/m^3]$.
ε, ε'	bed voidage on shell and tube side, [-].
σ_{ij}	stoichiometric coefficient of reactant <i>i</i> in reaction <i>j</i> , [-].
$\delta_{\rm H_2}$	thickness of hydrogen permeation membrane, [m].
η	effectiveness factor, [-].

Abbreviations

AN	aniline.
BZ	benzene
NB	nitrobenzene.
ST	steam.
ТО	toluene

ACKNOWLEDGEMENTS

Praise to Allah, the creator of the whole universe for blessing me with the strength, support and patience to complete this work after all obstacles and challenges and may His peace and blessings be upon the Messenger, his family, his companions, and all those who follow his way until the Day of Judgment.

I would like to express my deepest and honest appreciation to Canada, country of equality, and the Canadian people for the great and wonderful hospitality over the last five years in which I fully accessed all facilities as if I were Canadian. I'm very proud of this unforgotten stage of my life!

Being a student in the University of British Columbia (UBC) and especially in the Chemical and Biological Engineering Department (CHBE) is really a precious blessing that can't be offered to too many students. UBC is really a place where work can be gathered with peace of mind.

I would like also to express my thanks to the government of Saudi Arabia and King Fahd University of Petroleum & Minerals (KFUPM) for financially sponsoring my studies at UBC.

I would like to express my sincere and warm appreciation to my supervisor Prof. John R Grace for his continuous and outstanding support and patience during the course of this work. He is one of few who can positively sharpen the career as well as the character of students.

My co-supervisor Prof. Said H. S. Elnashaie deserves warm thanks for his guidance and suggestions especially in the earlier stages of the work. Without that, I would have wasted much time.

I'm also very thankful to Prof. C. Jim Lim for his contribution in the early design stage of the work. The information and suggestions he shared with us were of great importance and utilized in optimizing the reactor.

I owe sincere thanks to Prof. Jan Van Impe and Dr. Filip Logist from BioTeC *and* OPTEC, *Department of Chemical Engineering, Katholieke Universiteit Leuven,* with whom I have collaborated at some stages of the work. Their contribution and suggestions were of great importance shedding light on dark corners, especially pertaining to the challenging reactor optimization problem.

I will never forget to express my warmest regards, thanks and sincere prayers to my beloved parents who were/are the driving force in all aspects of my life. I will never forget their support, warm wishes and prayers which assisted me greatly during my work. I'm sure that they will be so proud of my achievement!

I am also very thankful to my brother Walid, professional engineer at Saudi ARAMCO, and all my brothers and sisters for their continuous encouragement and support.

My wife "Alaa" and the little beloved and sweetie son "Salim", who is now three years and seven months old, deserves my thanks and regards for being patient with me. I admit that I wasn't fair enough with them as I was totally busy with my work, but I promise to compensate them in near future.

Finally, I would like to thank all my CHBE friends who shared their knowledge and experience with me. Special thanks are to Nayef Al-Saifi, Mohammed Rakib, Saifuddin Shaikh, Andres Mahecha-Botero, and Monica N. Danon-Schaffer.

Dedicated to my Parents, brothers, sisters, wife and my little beloved son "Salim"

Not the Unbelievers see that the heavens and the earth were joined together (as one unit of creation), before we clove them asunder? We made from water every living thing. Will they not then believe?

Holy Quran, Al-Anbiyaa, Chapter 21, verse 30

CHAPTER 1 INTRODUCTION

1.1. Thesis Overview

This thesis analyses the coupling of two industrial catalytic reactions, i.e. dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene, in a membrane reactor such that hydrogen produced on the dehydrogenation side is permeated through hydrogen membranes and is utilized to produce aniline on hydrogenation side, with heat also transferred across the membrane. The manuscript is divided into six chapters covering different aspects of the research problems.

Chapter 1 discusses the concept of coupling reactions in general, dividing such cases into three categories. An extensive literature review is presented in which different reaction systems and reactor configurations are identified. The novelty in the present work and the goals of the research are also provided.

In chapter 2, the simplified homogenous reactor model for the coupled catalytic membrane reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene is derived, with assumptions identified. The advantages of the coupled reactor over conventional uncoupled fixed bed reactors on the yield of styrene for both cocurrent and countercurrent configurations are shown. In addition, the effects of key operating parameters such as the number of hydrogenation tubes are investigated.

Chapter 3 tackles the difficult problem of optimizing the design of the coupled catalytic membrane reactor for the cocurrent configuration, considering 12 operating and design parameters. Two objective functions, i.e. styrene yield on the dehydrogenation side and production of aniline on the hydrogenation side, are considered simultaneously leading to different optima depending on the relative importance of the main two products.

Chapter 4 discusses the effect of the intraparticle resistance on the performance of the cocurrent configuration of the coupled reactor using the heterogeneous model based on Fickian diffusion for isothermal and non-isothermal catalyst pellets. Effectiveness factors and overall reaction rates evaluated at the surface of the catalyst pellets are also displayed and discussed.

In chapter 5, a rigorous heterogeneous reactor model based on the dusty gas model is developed for both isothermal and non-isothermal catalyst pellets. Predictions from this new model are compared with those of the pseudo-homogenous model developed in chapter 2 and the heterogeneous reactor model based on the simplified Fickian diffusion in chapter 4.

Chapter 6 summarizes the main overall findings and gives recommendations for future work.

1.2. Coupling of Chemical Reactions

Coupling of chemical reactions with heat transfer, separation, or other chemical reactions is a promising techniques for eliminating unnecessary heat transfer and separation units such as heat exchangers and separators, better utilization of energy, minimization of fuel, improving the thermodynamic conversions and yields of thermodynamically limited reactions, and reducing reactor volumes. Coupling can be successfully achieved in fixed bed reactors as well as fluidized bed reactors in which chemical reactions are coupled with transport processes to transfer, remove or supply heat and mass. There are three categories or modes of coupling:

1.2.1. Thermal coupling of chemical reactions

Heat transfer units such as heat exchangers can be eliminated when chemical reactions are coupled with heat transfer. This coupling can occur in fixed bed reactors when the heat accompanying the effluent stream of exothermic reactions is utilized to heat the feed steam. In fluidized bed reactors, however, catalyst particles can act as *energy carriers* after being recirculated from catalyst regenerators (van Sint Annaland and Nijssen, 2002; van Sint Annaland et al., 2002a).

Exothermic and endothermic reaction can also be coupled together in a direct or indirect fashion. Combining both, i.e. endothermic and exothermic reactions, in the same chamber results in direct coupling, whereas periodically operated reactors result in indirect coupling (Kulkarni and Dudukovic, 1996). The chemical reactors used to achieve this form of coupling are normally fixed beds operated periodically in two semi-cycles: exothermic and endothermic semi-cycles. In the exothermic semi-cycles, the bed is heated with the catalyst particles acting as energy storage media, while in the endothermic semi-cycles, the reacting mixture is heated.

This concept of coupling has been used to couple a number of reactions. For example, Haynes et al. (1992) studied the coupling of dehydrogenation of ethylbenzene in a reverse flow reactor system. The reactor was divided into two beds so that when bed 1 was engaged in the reaction cycle, bed 2 was undergoing regeneration by injecting steam. It was reported (Haynes et al., 1992) that the conversion of ethylbenzene could reach 100%, compared to 51% for the simple fixed bed reactor. Kulkarni (1996) and Kulkarni and Dudukovic (1996, 1997, and 1998) studied the behaviour of an asymmetric bidirectional fixed bed reactor with both highly exothermic and endothermic reactions alternatively occurring in the gas phase. Choudhary and Mulla (1997) introduced a Sr-promoted La₂O₃ catalyst for partial oxidation of ethane to ethylene. At higher temperature or ethane-to-oxygen ratio, the rate of the exothermic ethane oxidation reaction became significant causing the process to accelerate and be more economical due to the thermal coupling of the two reactions. It was possible to achieve a conversion of more than 50% with an ethylene selectivity of more than 80% in less than 10 ms. A review by Kolios et al. (2000) discussed the underlying principle, applications of thermal coupling of chemical reactions, and the stability of the resulting dynamic systems.

Ismagilov et al. (2001) studied experimentally the coupling of steam reforming with methane combustion in a 1.5 cm long tubular catalytic reactor. A methane conversion of 65% could be achieved as a result of this coupling. In a catalytic plate reactor, the feasibility of coupling ethane dehydrogenation with methane combustion was studied by Zanfir and Gavriilidis (2001), Zanfir and Gavriilidis (2003) and Zanfir and Gavriilidi (2004) based on a two-dimensional reactor model. The reactor was operated in a continuous cocurrent and countercurrent mode, and it was found that the temperature profiles on both sides could be adjusted by varying the catalyst

loading and thermal conductivity of the metallic wall so that hot and cold spots inside the reactors were eliminated. Improving of the thermal coupling was one of the objectives.

A review by Kolios et al. (2002) discussed the concept of autothermal coupling of reactions as well as a proposed new reactor configuration. It was reported that controlling the temperature on both sides of the barriers is a key issue. The dynamics of a reverse flow reactor coupling dehydrogenation of propane with methane combustion was studied by van Sint Annaland et al. (2002a) and van Sint Annaland et al. (2002b). Two reactor configurations were considered: sequential and continuous. In the first part of this study, the dehydrogenation of propane was assumed to be irreversible, while its reversibility was considered in the second part. The sequentially reversed reactor generally showed better performance than the continuous one. The results of these two studies were verified against experimental data showing that the coupling is very effective and that the reversibility of the dehydrogenation of propane can be minimized by providing inactive zones at both ends of the reactor where the temperature is low (van Sint Annaland and Nijssen, 2002). For better heat coupling, Glöckler et al. (2003) suggested use of side-distributed fuel stream in a reverse flow reactor, coupling styrene synthesis (production cycle) with hydrogen combustion (regeneration cycle).

Kolios et al. (2004) and Kolios et al. (2005) studied the thermal coupling of steam reforming with methane combustion in a catalytic reactor operated in both cocurrent and countercurrent manners. The stability of the countercurrent configuration, as well as alternative designs and tips were given to improve the heat exchange between the two sides of the reactors. A proof of concept experiment showed the efficiency of the process. Direct and indirect coupling of exothermic and endothermic reactions was evaluated by Ramaswamy et al. (2006) and Ramaswamy et al. (2008) based on a one-dimensional fixed bed reactor model. The effects of a number of operating parameters on the reactor conversions and the temperature profiles were investigated. The thermal coupling of methanol reforming with the partial oxidation of methanol was studied experimentally on a Cu/Zn/Al₂O₃ catalyst sprayed on plated catalyst. It was shown that coupling is feasible and that operation is stable because the reactor was able to adjust itself to changing loads.

To sum up, coupling of exothermic and endothermic reactions in autothermal reactors is feasible with heat released from the exothermic reaction used to regenerate the catalyst and shift the thermodynamic limitation of endothermic reactions. Applying this idea can result in smaller reactors, as well as eliminating unnecessary heat transfer units. Effective heat transfer, stability of operation and avoiding the formation of hot and cold spots inside the reactors are major research challenges.

1.2.2. Coupling of chemical reaction with in-situ separation

Coupling of chemical reactions with in-situ separation can occur in reactors equipped with membranes or chemical sorbents such as carbon dioxide (CO_2) acceptors. Hydrogen and oxygen are removed in membrane reactors, while carbon dioxide (CO_2) is removed from reacting mixtures when a CO_2 acceptor such as dolomite particles reacts with CO_2 to produce calcium carbonate by the reaction:

$$CaO + CO_2 \Leftrightarrow CaCO_3 \qquad \Delta H_{298} = -178.8 \times 10^3 \frac{\text{kJ}}{\text{kmol}}$$
(1.1)

For membrane reactors, the production of hydrogen from steam reforming reactions can be enhanced by allowing hydrogen to permeate from the reaction side to the permeate side. When in-situ separation is coupled with chemical reactions, the conversion and yields of the thermodynamically limited reactions such as steam reforming and dehydrogenation of ethylbenzene can be significantly enhanced.

Several membrane reactors as well as reactor models have been proposed to investigate this concept. For example, Abdalla and Elnashaie (1994) studied the dehydrogenation of ethylbenzene to styrene in a membrane reactor for four different catalysts, one being the industrial one. A mathematical model based on the heterogeneous modeling of fixed bed reactors was also proposed, with diffusion inside the catalyst pellets modeled using the dusty gas model. It was found that operating the reaction in a membrane reactor could enhance the styrene yield by 20% to 30%.

A reactor model was presented by Kim et al. (1999) to predict the production of hydrogen in a cocurrently configured membrane methane steam reformer with a heated external wall. The prediction of the model was better than that derived at the assumption of constant temperature. The model was used to investigate the effect of some parameters such as steam-to-methane feed ratio, feed pressure on the reaction side, catalyst diameter and sweep gas flowrate. Dittmeyer et al. (2001) discussed the use of palladium membranes for dehydrogenation reactions and liquidphase hydrogenation reactions. The oxidative dehydrogenation of n-butane was studied by Assabumrungrat et al. (2002) in a fixed bed membrane reactor. A two-dimensional model was developed accounting for both the radial heat and mass dispersions in both reactors, with the external wall of the reactor maintained at a constant temperature. It was found that the membrane could help to avoid the hot spots in the reactor when oxygen distribution on the reaction side is controlled. Optimization of the configuration was essential to avoid a drop in methane selectivity. A comparative study was performed by Hou and Hughes (2003) involving dehydrogenation of propane in fixed and membrane reactors. Kinetic data were first obtained from the fixed bed reactor, and then used to simulate the performance of composite and porous membrane reactors. The performance of both membrane reactors was found to be better than the fixed bed. The effects of operating conditions such as contact time, flowrates of the sweep gas and pressure were also investigated. Addition of hydrogen to the feed of an n-hexane catalytic membrane reformer was studied by Itoh et al. (2003a). They found that hydrogen should be added because it participates in the initial steps of the mechanism of the reaction and prevents catalyst deactivation. In a palladium membrane reactor, Itoh et al. (2003b) was able to extract 80% of the hydrogen produced in the reaction chamber when the pressure on the permeation side was reduced to 0.1 bar. The effects of operating conditions such as temperature, reactor pressure and permeate pressure were also evaluated.

In fluidized bed reactors, installing hydrogen membranes can greatly enhance the performance compared to non-membrane reactors. For example, dehydrogenation of ethylbenzene to styrene was studied by Abdalla and Elnashaie (1995) in a fluidized bed reactor with and without membranes. Fluidization increased the conversion of ethylbenzene, but not the yield, while the presence of membranes improved both. The effects of a number of operating and design parameters were investigated. Steam reforming was studied experimentally by Mahecha-Botero

et al. (2008) in a fluidized reactor containing vertical membrane panels. The purity of hydrogen collected experimentally was >99.99% and the performance of the reactor was governed by the active membrane surface area. A comprehensive model for gas fluidized-bed reactors developed by Mahecha-Botero et al. (2006) was utilized to model the reactor, and accurate predictions were obtained. Rakib et al. (2008) studied the steam reforming of naphtha in a bubbling fluidized bed membrane reactor with n-heptane as the representative component. The use of membranes greatly enhanced both the conversion and the yield of hydrogen. A useful review was provided by Deshmukh et al. (2007) in which the application and challenges of membrane fluidized bed reactors were discussed. A theoretical study comparing performance of catalytic membranes with membrane fluidized beds performance was published by Gallucci et al. (2010), with steam reforming as the system reaction. At some operating conditions, it was found that the area of membrane required to achieve a certain conversion in catalytic membrane reactors is twice that required in fluidized bed reactors, making the fluidized bed more economical and attractive.

In summary, the use of hydrogen membranes with thermodynamically-limited reactions to remove hydrogen from the reaction side can greatly enhance conversion, as well as yield in catalytic and fluidized reactors. These reactor systems need to be optimized to achieve maximum benefit.

1.2.3. Coupling of chemical reaction via both in-situ separation and heat transfer

In membrane reactors, complementary reactions can be coupled such that hydrogen or oxygen diffuse through permeable membranes to the permeate side to react, and another useful product can be produced. In addition to diffusion, heat produced by exothermic reactions on one side can be transferred through the membrane wall to the other side where endothermic reactions take place, resulting in greater improvement and smaller reactors compared to membrane reactors with only in-situ separation.

A number of configurations and coupled reactions were proposed. For example, coupling dehydrogenation of ethylbenzene with hydrogenation of benzene was explored in a shell and tube catalytic fixed membrane reactor by Elnashaie et al. (2000) and Moustafa and Elnashaie

(2000). Both studies predicted enhanced ethylbenzene conversion (>90%), styrene yield (~90%) and benzene conversion (>80%) compared to the industrial units. Methane steam reforming (endothermic) and oxidative reforming (exothermic) were coupled in a novel circulating fast fluidized bed membrane reformer to overcome the thermodynamic and diffusion limitations of the steam reforming. Both hydrogen and oxygen permeative tubes were installed inside the reformer to remove hydrogen produced from the steam reforming reactions and supply oxygen to the oxidative reforming reaction. The reformer was operated autothermally and was able to achieve hydrogen productivity 8 times that of industrial fixed bed reactor and 118 times that of a bubbling bed membrane reformer (Chen et al., 2003). For higher hydrocarbon feed, the optimal design was obtained and the effect of catalyst deactivation was negligible in the new process (Chen et al., 2003). Combining the process with a catalyst regenerating unit made the process more efficient in terms of hydrogen production and energy utilization for higher hydrocarbons (Chen and Elnashaie, 2005a). The dynamic behavior of all proposed combinations was investigated by Chen and Elnashaie (2005a), and Chen and Elnashaie (2005b). Abashar (2004) studied also the coupling of dehydrogenation of ethylbenzene with hydrogenation of benzene in a fixed bed reactor containing intermingled dehydrogenation and hydrogenation catalyst pellets. A substantial increase in ethylbenzene conversion was observed (to ~100%) in addition to substantial energy savings.

In general, this form of coupling is more promising but more complex, than the previously mentioned ones. Careful design and optimization of the reactors can lead to smaller, energy-saving units compared to existing industrial reactors. However, safety and other practical issues must be considered to assure longevity and safe operation.

1.3. Sources of Novelty in this Thesis

In this thesis, the pair of chemical reactions coupled in a catalytic membrane fixed bed reactor must be chosen such that certain objectives are achieved. First, the thermodynamic limitation of the dehydrogenation reaction must be shifted by the permeation of hydrogen from the reaction side to the permeate side. Secondly, hydrogen diffusion through the membrane should participate in another useful reaction in which another a useful product is produced on the permeate side, rather than being combusted to produce steam and heat. Thirdly, heat produced on the permeate side should be transferred efficiently and in the proper direction to the dehydrogenation side to further assist in overcoming the equilibrium limitation of the dehydrogenation reaction and increasing overall productivity. Fourth, the process must proceed within the potential temperature limitations of membranes. Finally, the process should be operated in a continuous mode so that both sides of the reactor can produce simultaneously two different products.

After surveying a wide variety of reactions, it was found that an interesting pair to couple and meet the constraints and objectives identified in the previous paragraph is dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene. The former is composed of six reactions producing styrene as a main product and benzene, toluene, and light gases such as hydrogen, ethylene, methane, carbon monoxide and carbon dioxide as side products according to the stoichiometric equations:

$$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2 \qquad \Delta H_{298} = 117.6\frac{\text{KJ}}{\text{mole}}$$
(1.2)

1_T

. .

$$C_6H_5CH_2CH_3 \to C_6H_6 + C_2H_4$$
 $\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$ (1.3)

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_{298} = -54.6\frac{\text{kJ}}{\text{mole}}$$
 (1.4)

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$$
 $\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$ (1.5)

$$H_2O + CH_4 \rightarrow CO + 3H_2 \qquad \Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$$
(1.6)

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$$
(1.7)

The first of these reactions, which is the main reaction, is reversible and endothermic, with the forward reaction to styrene favored by operating at high temperature and low pressure. In industrial fixed bed reactors producing styrene by these reactions, temperature drops along the reactor due to the net endothermality unless heat is supplied externally.

Styrene is one of the most important monomers for the manufacture of thermoplastic and synthetic rubbers. More than 90% of total styrene is produced by the dehydrogenation of ethylbenzene at a temperature of 550-650°C and atmospheric or sub atmospheric pressure in the presence of a Fe₂O₃ catalyst. Its worldwide annual demand has grown at a rate of 5 to 6% (Hermann et al., 1997; She et al., 2001).

In the proposed coupled membrane reactor shown schematically in Figure 1.1, dehydrogenation of ethylbenzene takes place on the shell side as it is mechanically better to operate the shell side of the reactor at a higher pressure than the tube side. Hydrogen produced on the dehydrogenation side diffuses through hydrogen-selective membranes to the tube side where it reacts with nitrobenzene to produce aniline. This hydrogenation reaction is irreversible and exothermic. The production of one mole of aniline requires one mole of nitrobenzene and three moles of hydrogen in accordance with the stoichiometric equation:

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
 $\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$ (1.8)

1 1

The feed to the hydrogenation side of the coupled reactor contains no hydrogen, with all the required hydrogen permeating through the membrane from the dehydrogenation side. Commercially, aniline is a crucial raw material for synthetic dyes, rubber, chemicals, amino resins and polyurethane. It is produced by hydrogenating nitrobenzene on a palladium catalyst supported on α -alumina carrier in fixed bed reactors. Due to the high heat release, it is normally conducted in fluidized bed reactors or in small-diameter fixed bed reactors (Amon et al., 1999; Diao et al., 2005; Sun et al., 2002).

Dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene are industrially important processes due to the increasing worldwide demands for both styrene and aniline, their market prices and wide usage. They also form a promising pair of reactions to be coupled in a catalytic membrane reactor so that hydrogen and heat are exchanged between the two sides of the reactor. However, the feasibility of coupling has not been evaluated yet. This thesis is a real attempt to couple both processes, proving the concept of coupling, evaluating the benefits arising from the new process, and providing an optimized design for the coupled reactor considering both high productivities of styrene and aniline and safe operation for membranes. Theoretically, the achievement of these objectives requires linking the numerical solution of complex initial and boundary value problems representing the reactor models with efficient optimization subroutines to obtain the best values satisfying the constraints imposed and maximizing the productivity of the reactor.

1.4. Thesis Objectives

The objectives of this research project are:

- 1. To develop a novel configuration for an integrated autothermal reactor, with two reactions coupled by means of both hydrogen transfer and heat transfer.
- 2. To obtain design equations for this novel configuration based on pseudo-homogeneous modeling of fixed bed reactors for both cocurrent and countercurrent configurations
- 3. To optimize the performance of the coupled reactor based on maximizing the productivities on both sides of the reactor for the cocurrent configuration.
- 4. To obtain rigorous model design equations accounting for diffusional resistance inside the catalyst pellets based on both Fickian diffusion and the dusty gas model.
- 5. To investigate the effect of intraparticle diffusion on the optimal design of the coupled reactor obtained in (3).

The original plans for this project included other tasks such as designing and operating a labscale reactor, optimizing the countercurrent configuration of the coupled reactors, repeating the optimization of reactor, but with new developed models accounting for the diffusional resistances, and investigating the dynamics and multiplicity behaviour which may result from coupling these two processes. However, these tasks have been left for future work due to the complexity of the numerical solutions, as discussed in the next section, as well as limitations in time, funds and facilities.

1.5. Challenges and Obstacles Encountered in this Thesis

While working on this thesis project, a number of challenges were encountered. The numerical solution of pseudo-homogeneous reactor model was difficult especially for the countercurrent configuration, which turned the modeling equations into a boundary value problem. Different strategies and several numerical techniques had to be attempted to obtain the solutions, such as the simple shooting method, multiple shooting method, orthogonal collocation, and falsetransient method. The major challenge in solving the reactor model equations was to find good initial guessing profiles for 14 components, 2 temperatures and 2 pressures on both the dehydrogenation and hydrogenation sides of the membrane reactor. The continuation method with orthogonal collocation technique were finally found to perform the best, although significant time is needed to obtain the solution for each operating condition. This unfortunately made optimization of the countercurrent configuration almost impossible on normal desktop computers. Consequently, dedicated power stations are recommended for optimizing the countercurrent configuration of the coupled reactor. It was also found that calculating the Jacobian matrix by finite difference techniques makes the problem unsolvable, especially when the axial profiles of molar flowrates and temperatures becomes flat before the reactor exit. The analytical form of the Jacobian matrix was provided by performing manual differentiation and compared to the finite difference one to assure its reliability.

Solving the multiobjective optimization problem discussed in chapter 2 was also challenging in obtaining the solution set itself as well as the uniformity of the set. Significant time was spent attempting to solve the problem using the Evolutionary/and Genetic algorithms, but both failed. Several populations were created and used to initialize the optimization cycle but with no success. Finally, the multi-objective optimization problem turned out to be a single objective problem and has been solved numerically several times with a varying constraint to obtain the solution set. Unfortunately, the resulting solution set was found to suffer from the existence of local optimal solutions, so it had to be filtered to remove them. The solution of the single objective problem was challenging also due to the non-linearity. The solution couldn't be obtained without running a global solver for a number of iterations, usually >1000 iterations,

with the solution of the global solver then used as an initial guess for a local solver. For these cases, the use of commercial solvers was crucial and beneficial.

Evaluating diffusional resistances in chapters 4 and 5 using Fickian diffusion and the dusty gas model for the catalyst pellets involved numerical complexity due to the nature of the resulting boundary value problems and its linkage with the reactor model equations. As mentioned above, the analytical Jacobian matrix was of great importance. Usually, 10 points along the radial direction of the catalyst pellets and constant profiles were enough to locate the solution. Without using the analytical Jacobian matrix, around 300 points would be needed along the computational domain. The numerical solution of reactor model equations along with the catalysts pellets equations was then time consuming.

Due to the nature of the problem considered in this thesis, the whole work was turned out to be entirely theoretical and predictive. It is believed that the complexity involved until this stage is sufficient and challenging enough to fit the time requirement and facility offered.

1.6. Derivation of the Reactor Pseudo-homogeneous Model

In this work, the pseudo-homogeneous model of the coupled reactor was used extensively to prove the concept of coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene in the proposed catalytic membrane reactor, to predict the overall behavior of the reactor, and to optimize its performance. This model is simple and requires little time to solve.

The pseudo-homogeneous model for the coupled membrane reactor is based on the following assumptions:

- 1. Steady state flow on both sides of the coupled reactor.
- 2. Ideal gas law applies on both shell and tube sides.
- Plug flow on both shell and tube sides, justified because both Peclet numbers are of order 1000.

- 4. The external and intraparticle mass transfer resistances for the catalyst pellets are neglected.
- 5. Catalyst deactivation is negligible.
- 6. The external wall of the reactor is well insulated, giving rise to an adiabatic reactor.
- 7. Pressure drop is calculated using Ergun's equation.

Figure 1.2 shows cocurrent flow around a small slice inside the coupled reactor on both the shell and tube sides. The model balance equation for the cocurrent configuration on the shell side can be expressed according to:

$$Rate of Accumulation = flow In - flow Out + Generation - Consumption$$

$$0 = n_i |_z - n_i |_{z + \Delta z} - (\pi N D_i) a_i J'_i \Delta z + \Delta z A_{cs} (1 - \varepsilon)_s \rho_{ss} \sum_{j=1}^6 \sigma_{ij} r_j$$
(1.9)

Dividing by Δz and taking the limit as Δz goes to zero, leads to:

$$\frac{dn_i}{dz} = A_{cs} \left(1 - \varepsilon\right)_s \rho_{ss} \sum_{j=1}^6 \sigma_{ij} r_j - \left(\pi N D_t\right) a_i J_i'$$
(1.10)

where: σ_{ij} is the stoichiometric coefficient for component *i* in reactions *j*, positive for products and negative for reactants.

The energy balance equation on the shell side can be derived in a similar manner as:

Rate of Accumulation = In flow - Out flow + Generation - Consumption + Heat Added

$$0 = \sum_{i=1}^{c} H_{i} n_{i} |_{z} - \sum_{i=1}^{c} H_{i} n_{i} |_{z+\Delta z} - \sum_{i=1}^{c} a_{i} (\pi N D_{t}) J_{i}' H_{i} \Delta z + N Q' \Delta z$$
(1.11)

where: *Q*': is heat transferred from one hydrogenation tube across the membrane per unit length.c: is the number of components.

 $a_i = 1$ for hydrogen and $a_i = 0$ for all other components except hydrogen.

Dividing by Δz , taking the limit, and then substituting for $\frac{dn_i}{dz}$ from the mole balance, we obtain:

$$\frac{d}{dz}\left[\sum_{i=1}^{c} \left(n_{i}^{\prime}H_{i}^{\prime}\right)\right] = Q^{\prime} - \sum_{i=1}^{i} a_{i}\left(\pi ND_{t}\right)J_{i}^{\prime}H_{i}$$

$$(1.12)$$

If it is assumed that there is no phase change, equation (1.12) becomes:

$$\sum_{i=1}^{10} \left\{ n_i C p_i \frac{dT}{dz} + H_i \left[\sum_{j=1}^{j} \sigma_{ij} r_j (1-\varepsilon) \rho_s A_{cs} - a_i (\pi D_i N) J_i' \right] \right\} = NQ' - \sum_{i=1}^{c} a_i (\pi D_i N) J_i' H_i$$
(1.13)

$$\frac{dT}{dz} = \frac{A_{cs}(1-\varepsilon)\rho_s \sum_{j=1}^{6} \left[-\Delta H_R(T)\right]_j r_j + NQ'}{\sum_{i=1}^{10} n_i C_{pi}}$$
(1.14)

On the tube side, where dehydrogenation of nitrobenzene takes place, the mole balance equation can be derived for a single tube as:

$$0 = n_i'|_z - n_i'|_{z+\Delta z} + a_i \left(\pi D_t\right) J_i \Delta z + \sigma_i r' \left(1 - \varepsilon'\right) \rho_s' A_{cs}' \Delta z$$
(1.15)

Dividing by Δz and taking the limit as Δz goes to zero, leads to:

$$\frac{dn'_i}{dz} = a_i \left(\pi D_t\right) J'_i + \sigma_i r' \left(1 - \varepsilon'\right) \rho'_s A'_{cs}$$
(1.16)

The energy balance equation for a one hydrogenation tube is given by:

$$0 = \sum_{i=1}^{4} H'_{i}n'_{i}\Big|_{z} - \sum_{i=1}^{4} H'_{i}n'_{i}\Big|_{z+\Delta z} + \sum_{i=1}^{c} a_{i}(\pi D_{i})J_{i}H_{i}\Delta z - Q'\Delta z$$
(1.17)

Dividing by Δz , taking the limit as Δz goes to zero, leads to:

$$\frac{d}{dz} \sum_{i=1}^{4} \left(n_i' H_i' \right) = \sum_{i=1}^{c} a_i \left(\pi D_i \right) J_i' H_i - Q'$$
(1.18)

$$\sum_{i=1}^{4} \left[n_i \frac{dH_i}{dz} + H_i \frac{dn_i}{dz} \right] = \sum_{i=1}^{c} a_i \left(\pi D_i \right) J_i H_i + Q'$$
(1.19)

After substituting for $\frac{dn'_i}{dz}$ from the mole balance and cancelling similar terms on both side of the equation, we obtain:

$$\sum_{i=1}^{4} \left[n_i' \frac{dH_i'}{dz} + H_i' \left(a_i \pi D_i J_i' + \sigma_i' r \left(1 - \varepsilon' \right) \rho_s' A_{cs}' \right) \right] = \sum_{i=1}^{c} a_i \left(\pi D_i \right) J_i H_i - Q'$$
(1.20)

$$\sum_{i=1}^{4} n_{i}^{\prime} \frac{dH_{i}^{\prime}}{dz} = \sum_{i=1}^{c} a_{i} \left(\pi D_{i} \right) J_{i} \left(H_{i} - H_{i}^{\prime} \right) + \left[-\Delta H_{R} \left(T^{\prime} \right) \right]^{\prime} r^{\prime} \left(1 - \varepsilon^{\prime} \right) \rho_{s}^{\prime} A_{cs}^{\prime} - Q^{\prime}$$
(1.21)

$$\frac{dT'}{dz} = \frac{\sum_{i=1}^{c} a_i (\pi D_i) J_i (H_i - H'_i) + \left[-\Delta H_R (T') \right]' r' (1 - \varepsilon') \rho'_s A'_{cs} - Q'}{\sum_{i=1}^{4} n'_i C'_{pi}}$$
(1.22)
$$\frac{dT'}{dz} = \frac{\sum_{i=1}^{c} a_i (\pi D_i) J_i \times \int_{T'}^{T} Cp_i dT + \left[-\Delta H_R (T') \right]' r' (1 - \varepsilon') \rho'_s A'_{cs} - Q'}{\sum_{i=1}^{4} n'_i C'_p}$$
(1.23)

For the countercurrent configuration shown in Figure 1.3, the mole balance equation on the shell side can be written as:

$$\frac{dn_i}{dz} = A_{cs} \left(1 - \varepsilon\right) \rho_s \sum_{j=1}^5 \sigma_{ij} r_j - \left(\pi N D_t\right) a_i J_i'$$
(1.24)

while the energy balance equation is expressed as:

$$\frac{dT}{dz} = \frac{A_{cs}(1-\varepsilon)\rho_s \sum_{j=1}^{j} \left[-\Delta H_R(T)\right]_j r_j + NQ'}{\sum_{i=1}^{c} n_i C_{pi}}$$
(1.25)

On the tube side of the coupled reactor, the mole balance for each hydrogenation tube can be expressed as:

$$0 = n_i' \Big|_{z+\Delta z} - n_{iz}' \Big|_z + a_i \left(\pi D_i \right) J_i \Delta z + \sigma_i' r' \left(1 - \varepsilon' \right) \rho_s' A_{cs}' \Delta z$$
(1.26)

Dividing by Δz and taking the limit as Δz goes to zero, leads to:

$$\frac{dn'_i}{dz} = -a_i \left(\pi D_t\right) J_i - \sigma'_i r' \left(1 - \varepsilon'\right) \rho'_s A'_{cs}$$
(1.27)

The energy equation can be written for the slice as:

$$0 = \sum_{i=1}^{4} H'_{i}n'_{i}\Big|_{z+\Delta z} - \sum_{i=1}^{4} H'_{i}n'_{i}\Big|_{z} + \sum_{i=1}^{c} a_{i}(\pi D_{t})J_{i}H_{i}\Delta z - Q'\Delta z$$
(1.28)

Dividing by Δz , taking the limit as Δz goes to zero, we obtain:

$$\frac{d}{dz}\sum_{i=1}^{4} (n'_{i}H'_{i}) = -\sum_{i=1}^{c} a_{i} (\pi D_{i})J'_{i}H_{i}\Delta z + Q'$$
(1.29)

$$\sum_{i=1}^{4} \left[n'_{i} \frac{dH'_{i}}{dz} + H'_{i} \frac{dn'_{i}}{dz} \right] = -\sum_{i=1}^{c} a_{i} \left(\pi D_{i} \right) J_{i} H_{i} \Delta z + Q'$$
(1.30)

Substituting for $\frac{dn'_i}{dz}$ from the mole balance (1.27), gives:

$$\sum_{i=1}^{4} \left[n_i' \frac{dH_i'}{dz} - H_i' \left(a_i \pi D_i J_i' + \sigma_i' r' \left(1 - \varepsilon' \right) \rho_s' A_{cs}' \right) \right] = -\sum_{i=1}^{c} a_i \left(\pi D_i \right) J_i' H + Q'$$
(1.31)

$$\sum_{i=1}^{c} n_{i}^{\prime} \frac{dH_{i}^{\prime}}{dz} = -\sum_{i=1}^{c} a_{i} \left(\pi D_{i}\right) J_{i}^{\prime} \left(H_{i} - H_{i}^{\prime}\right) + \left[\Delta H_{R}\left(T^{\prime}\right)\right]^{\prime} r^{\prime} \left(1 - \varepsilon^{\prime}\right) \rho_{s}^{\prime} A_{c}^{\prime} + Q^{\prime}$$
(1.32)

$$\frac{dT'}{dz} = \frac{-\sum_{i=1}^{c} a_i (\pi D_i) J'_i (H_i - H'_i) + \left[\Delta H_R (T')\right]' r' (1 - \varepsilon') \rho'_s A'_{cs} + Q'}{\sum_{i=1}^{c} n'_i C'_p}$$
(1.33)

$$\frac{dT'}{dz} = \frac{-\sum_{i=1}^{c} a_i (\pi D_i) J'_i \times \int_{T'}^{T} Cp_i dT + \left[\Delta H_R (T') \right]' r' (1 - \varepsilon') \rho'_s A'_{cs} + Q'}{\sum_{i=1}^{c} n'_i C'_p}$$
(1.34)

These equations are solved in chapters 2 and 3 for the coupled dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene processes.



Figure 1.1 Schematic diagram of the reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene



Figure 1.2 Schematic representation of a differential element inside the reactor for cocurrent flow. Large arrows show directions of mass and heat fluxes.



Figure 1.3 Schematic representation of a differential element inside the reactor for countercurrent flow. Large arrows show directions of mass and heat fluxes.

1.7. References

- Abashar, M. E. E., 2004. Coupling of ethylbenzene dehydrogenation and benzene hydrogenation reactions in fixed bed catalytic reactors, Chemical Engineering and Processing 43(10), 1195-1202.
- Abdalla, B. K., Elnashaie, S. S. E. H., 1995. Fluidized bed reactors without and with selective membranes for the catalytic dehydrogenation of ethylbenzene to styrene, Journal of Membrane Science 101(1-2), 31-42.
- Abdalla, B. K., Elnashaie, S. S. E. H., 1994. Catalytic dehydrogenation of ethylbenzene to styrene in membrane reactors, AICHE Journal 40(12), 2055-2059.
- Amon, B., Redlingshöfer, H., Klemm, E., Dieterich, E., Emig, G., 1999. Kinetic investigations of the deactivation by coking of a noble metal catalyst in the catalytic hydrogenation of nitrobenzene using a catalytic wall reactor, Chemical Engineering and Processing 38(4-6), 395-404.
- Assabumrungrat, S., Rienchalanusarn, T., Praserthdam, P., Goto, S., 2002. Theoretical study of the application of porous membrane reactor to oxidative dehydrogenation of n-butane, Chemical Engineering Journal 85(1), 69-79.
- Chen Z., Prasad P., Yan Y., Elnashaie S., 2003. Simulation for steam reforming of natural gas with oxygen input in a novel membrane reformer, Fuel Processing Technology 83, 235-252.
- Chen, Z., Elnashaie, S. S. E. H., 2005a. Autothermal CFB Membrane Reformer for Hydrogen production from heptane, Chemical Engineering Research and Design 83(7), 893-899.
- Chen, Z., Elnashaie, S. S. E. H., 2005b. bifurcation behaviour during the hydrogen production in two compatible configurations of a novel circulating fluidized bed membrane reformer, Chemical Engineering Research and Design 83(6), 679-685.
- Chen, Z., Yan, Y., Elnashaie, S. S. E. H., 2003. Modeling and optimization of a novel membrane reformer for higher hydrocarbons, AIChE Journal 49(5), 16.
- Choudhary, V. R., Mulla, S. A. R., 1997. coupling of exothermic and endothermic reactions in oxidative conversion of natural gas into ethylene/olefins over diluted SrO/La₂O₃/SA5205 catalyst, Industrial & Engineering Chemistry Research 36(9), 3520-3527.

- Deshmukh, S. A. R. K., Heinrich, S., Mörl, L., van Sint Annaland, M., Kuipers, J. A. M., 2007. Membrane assisted fluidized bed reactors: Potentials and hurdles, Chemical Engineering Science 62(1-2), 416-436.
- Diao, S., Qian, W., Luo, G., Wei, F., Wang, Y., 2005. Gaseous catalytic hydrogenation of nitrobenzene to aniline in a two-stage fluidized bed reactor, Applied Catalysis A: General 286(1), 30-35.
- Dittmeyer, R., Höllein, V., Daub, K., 2001. Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium, Journal of Molecular Catalysis A: Chemical 173(1-2), 135-184.
- Elnashaie, S. S. E. H., Moustafa, T., Alsoudani, T., Elshishini, S. S., 2000. Modeling and basic characteristics of novel integrated dehydrogenation — hydrogenation membrane catalytic reactors, Computers & Chemical Engineering 24(2-7), 1293-1300.
- Gallucci, F., Van Sintannaland, M., Kuipers, J. A. M., 2010. Theoretical comparison of packed bed and fluidized bed membrane reactors for methane reforming, International Journal of Hydrogen Energy 35(13), 7142-7150.
- Glöckler, B., Kolios, G., Eigenberger, G., 2003. Analysis of a novel reverse-flow reactor concept for autothermal methane steam reforming, Chemical Engineering Science 58(3-6), 593-601.
- Haynes, T. N., Georgakis, C., Caram, H. S., 1992. The application of reverse flow reactors to endothermic reactions, Chemical Engineering Science 47(9-11), 2927-2932.
- Hermann, C., Quicker, P., Dittmeyer, R., 1997. Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor, Journal of Membrane Science 136(1-2), 161-172.
- Hou, K., Hughes, R., 2003. A comparative simulation analysis of propane dehydrogenation in composite and microporous membrane reactors, Journal of Chemical Technology & Biotechnology 78(1), 35-41.
- Ismagilov, Z. R., Pushkarev, V. V., Podyacheva, O. Y., Koryabkina, N. A., Veringa, H., 2001. A catalytic heat-exchanging tubular reactor for combining of high temperature exothermic and endothermic reactions, Chemical Engineering Journal 82(1-3), 355-360.

- Itoh, N., Xu, W. C., Hara, S., Kakehida, K., Kaneko, Y., Igarashi, A., 2003a. Effects of hydrogen Removal on the catalytic reforming of n-hexane in a palladium membrane reactor, Industrial & Engineering Chemistry Research 42(25), 6576-6581.
- Itoh, N., Tamura, E., Hara, S., Takahashi, T., Shono, A., Satoh, K., Namba, T., 2003b. Hydrogen recovery from cyclohexane as a chemical hydrogen carrier using a palladium membrane reactor, Catalysis Today 82(1-4), 119-125.
- Jun-Hun Kim, Byung-Seok Choi and Jongheop Yi, 1999. Modified simulation of methane steam reforming in Pd-membrane/packed-bed type reactor, Journal of Chemical Engineering of Japan 32, 760-769.
- Kolios, G., Frauhammer, J., Eigenberger, G., 2000. Autothermal fixed-bed reactor concepts, Chemical Engineering Science 55(24), 5945-5967.
- Kolios, G., Glöckler, B., Gritsch, A., Morillo, A., Eigenberger, G., 2005. Heat-integrated reactor concepts for hydrogen production by methane steam reforming, Fuel Cells 5(1), 52-65.
- Kolios, G., Gritsch, A., Glöckler, B., Sorescu, G., Frauhammer, J., 2004. Novel reactor concepts for thermally efficient methane steam reforming: a modeling and simulation, Industrial & Engineering Chemistry Research 43(16), 4796-4808.
- Kolios, G., Frauhammer, J., Eigenberger, G., 2002. Efficient reactor concepts for coupling of endothermic and exothermic reactions, Chemical Engineering Science 57(9), 1505-1510.
- Kulkarni, M. S., 1996. Dynamics of asymmetric fixed-bed reactors: Coupling of exothermic and endothermic reactions, D.Sc. Dissertation, St. Louis, MO, Washington University.
- Kulkarni, M. S., Dudukovic, M. P., 1998. Periodic operation of asymmetric bidirectional fixedbed reactors with temperature limitations, Industrial & Engineering Chemistry Research 37(3), 770-781.
- Kulkarni, M. S., Dudukovic, M. P., 1997. Periodic operation of asymmetric bidirectional fixedbed reactors: energy efficiency, Chemical Engineering Science 52(11), 1777-1788.
- Kulkarni, M. S., Dudukovic', M. P., 1996. Dynamics of gas phase and solid phase reactions in fixed bed reactors, Chemical Engineering Science 51(11), 3083-3088.
- Mahecha-Botero, A., Grace, J., Elnashaie, S. S. E. H., and Lim, C. J., 2006. Comprehensive modeling of gas fluidized-bed reactors allowing for transients, multiple flow regimes and selective removal of species, International Journal of Chemical Reactor Engineering 4, A11.

- Mahecha-Botero, A., Boyd, T., Gulamhusein, A., Comyn, N., Lim, C. J., Grace, J. R., Shirasaki,Y., Yasuda, I., 2008. Pure hydrogen generation in a fluidized-bed membrane reactor:Experimental findings, Chemical Engineering Science 63(10), 2752-2762.
- Moustafa, T. M., Elnashaie, S. S. E. H., 2000. Simultaneous production of styrene and cyclohexane in an integrated membrane reactor, Journal of Membrane Science 178(1-2), 171-184.
- Rakib, M. A., Grace, J. R., Elnashaie, S. S. E. H., Lim, C. J., Bolkan, Y. G., 2008. Kinetic simulation of a compact reactor system for hydrogen production by steam reforming of higher hydrocarbons, The Canadian Journal of Chemical Engineering 86(3), 403-412.
- Ramaswamy, R. C., Ramachandran, P. A., Duduković, M. P., 2008. Coupling exothermic and endothermic reactions in adiabatic reactors, Chemical Engineering Science 63(6), 1654-1667.
- Ramaswamy, R. C., Ramachandran, P. A., Duduković, M. P., 2006. Recuperative coupling of exothermic and endothermic reactions, Chemical Engineering Science 61(2), 459-472.
- She, Y., Han, J., Ma, Y. H., 2001. Palladium membrane reactor for the dehydrogenation of ethylbenzene to styrene, Catalysis Today 67(1-3), 43-53.
- Sun, A., Qin, Z., Wang, J., 2002. Reaction coupling of ethylbenzene dehydrogenation with nitrobenzene hydrogenation, Catalysis Letters 79(1), 33-37.
- van Sint Annaland, M., Nijssen, R. C., 2002. A novel reverse flow reactor coupling endothermic and exothermic reactions: an experimental study, Chemical Engineering Science 57(22-23), 4967-4985.
- van Sint Annaland, M., Scholts, H. A. R., Kuipers, J. A. M., van Swaaij, W. P. M., 2002a. A novel reverse flow reactor coupling endothermic and exothermic reactions. Part I: comparison of reactor configurations for irreversible endothermic reactions, Chemical Engineering Science 57(5), 833-854.
- van Sint Annaland, M., Scholts, H. A. R., Kuipers, J. A. M., van Swaaij, W. P. M., 2002b. A novel reverse flow reactor coupling endothermic and exothermic reactions: Part II: Sequential reactor configuration for reversible endothermic reactions, Chemical Engineering Science 57(5), 855-872.
- Zanfir, M., Gavriilidis, A., 2004. Influence of flow arrangement in catalytic plate reactors for methane steam reforming, Chemical Engineering Research and Design 82(2), 252-258.

- Zanfir, M., Gavriilidis, A., 2003. Catalytic combustion assisted methane steam reforming in a catalytic plate reactor, Chemical Engineering Science 58(17), 3947-3960.
- Zanfir, M., Gavriilidis, A., 2001. Modelling of a catalytic plate reactor for dehydrogenation– combustion coupling, Chemical Engineering Science 56(8), 2671-2683.

Chapter 2 PSEUDO-HOMOGENEOUS MODELING OF A NOVEL MEMBRANE REACTOR TO INTEGRATE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE WITH HYDROGENATION OF NITROBENZENE TO ANILINE[†]

2.1. Introduction

Styrene is one of the most important monomers for the manufacture of polystyrene used in thermoplastic and synthetic rubbers. Styrene is currently produced by two industrial processes: dehydrogenation of ethylbenzene and as a by-product in the epoxidation of propane with ethylbenzene hydroperoxide and Mo comple-based catalyst (Cavani, 1995). More than 90% of total styrene is produced by the catalytic dehydrogenation of ethylbenzene at operating temperatures of $550-650^{\circ}$ C and atmospheric or sub-atmospheric pressure in the presence of Fe₂O₃ catalyst. Worldwide demand is growing at 5 to 6% per year (Hermann et al., 1997; Shu et al., 2001). The catalytic dehydrogenation reaction of ethylbenzene is reversible, endothermic and severely limited by thermodynamic equilibrium, with a maximum ethylbenzene conversion of less than 50% (Abashar, 2004).

The potential for enhancement of styrene yield by catalyst improvement appears to be limited due to the fact that the main bottleneck is related to the thermodynamic equilibrium. Therefore, great efforts are needed to improve the performance through process design modification (Abashar, 2004). Moustafa and Elnashaie (2000); and Elnashaie et al. (2000) investigated the performance of a membrane catalytic reactor to couple the dehydrogenation of ethylbenzene to styrene with the hydrogenation of benzene to cyclohexane. A hybrid fixed bed reactor was

⁺ A version of this chapter was published: Nabeel S. Abo-Ghander, John R. Grace, Said S.E.H. Elnashai, and C. Jim Lim, 2008. Modeling of a novel membrane reactor to integrate dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline, Chemical Engineering Science, 63(7), 1817-1826.

modeled using a rigorous reactor model, leading to prediction of remarkable enhancement in both the conversion of ethylbenzene and yield of styrene compared to an industrial catalytic reactor operated by the Polymer Corporation in Sarnia, Canada. They reported an almost 51% conversion of ethylbenzene and 45% yield of styrene. Abashar (2004) investigated a similar configuration and obtained a substantial increase in the conversion of ethylbenzene to nearly 100%.

From these previous studies, coupling of hydrogenation and dehydrogenation reactions may enable both the concentration and temperature profiles along the reactor to be manipulated, shifting the conversion of thermodynamically limited reactions to higher values, and efficiently using the heat liberated by an exothermic reaction to provide the endothermic heat requirements of the other reaction (Amon, 1999). In the initial stage of our current work, we conducted an extensive literature review to find a pair of industrial reactions which could be coupled in such a way that hydrogen needed on one side of a membrane could be provided by dehydrogenation on the other side, while, at the same time, heat needed for an endothermic reaction could be supplied by exothermic heat release and transfer from the other side. A promising pair was found to be the dehydrogenation of ethylbenzene to styrene, coupled with the hydrogenation of nitrobenzene to aniline.

The integrated membrane reactor simulated for these two reactions is shown schematically in Figure 2.1. It consists of a shell compartment surrounding a tube compartment. Catalytic dehydrogenation of ethylbenzene to styrene is assumed to take place in the shell, whereas hydrogenation of nitrobenzene to aniline occurs inside the tubes, with fixed beds of different catalysts on both sides. Hydrogen-selective membranes separate the two compartments. Heat is transferred continuously through the membrane from the exothermic reaction inside the tubes to the endothermic reaction on the shell side. At the same time, hydrogen is transferred continuously through the hydrogen selective membrane from the dehydrogenation reaction on the shell side to the hydrogenation reaction on the tube side. The heat supplied from the tube compartment and the transfer of hydrogen from the compartment where the catalytic dehydrogenation of ethylbenzene is taking place should aid significantly in enhancing the conversion of ethylbenzene and the yield of styrene. The overall reactor requires a larger

dehydrogenation cross-sectional area than the hydrogenation cross-sectional area because of the stoichiometry of the reaction, i.e. one mole of ethylbenzene generates one mole of hydrogen, whereas one mole of nitrobenzene requires three moles of hydrogen to produce one mole of aniline. However, large surface area is also required to promote heat transfer between the two sides of the coupled reactor. In this study, both cocurrent and countercurrent configurations are investigated.

2.2. Theory

In this preliminary exploration of the performance of the coupled reactor, a pseudohomogeneous model is used. In this model, the fluid and solid catalyst are treated as one pseudohomogeneous phase. Intrapaticle gradients of temperature and concentration are ignored so that everywhere in the catalyst bed, the concentration and temperature are assumed to be the same as the corresponding local values of the bulk fluid. We will examine these assumptions, showing them to be the reasonable first approximation, in future work where a heterogeneous model is developed.

2.2.1. Assumptions

To derive the governing equations for both sides of the integrated fixed bed membrane reactor, the following assumptions are adopted:

- 1. Steady state operation.
- 2. Ideal gas behaviour on both sides.
- 3. Plug flow on both shell and tube sides, with both axial Peclet numbers of order 1000.
- 4. Pseudo-homogeneous one-dimensional models, i.e. radial Peclet number >> 1.0.
- 5. Catalyst deactivation is neglected.
- 6. The pressure drop along the reactor is calculated based on Ergun's equation.

2.2.2. Reaction kinetics

The reaction network for the dehydrogenation of ethylbenzene to styrene is (Abashar, 2004; Moustafa and. Elnashaie, 2000; Elnashaie et al., 2000; Abdulla and Elnashaie, 1993):

$$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2 \qquad \Delta H_{298} = 117.6 \frac{kJ}{mole}$$
 (2.1)

$$C_6H_5CH_2CH_3 \to C_6H_6 + C_2H_4$$
 $\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$ (2.2)

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$$
 (2.3)

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$$
 $\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$ (2.4)

$$H_2O + CH_4 \rightarrow CO + 3H_2$$
 $\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$ (2.5)

$$H_2O + CO \rightarrow CO_2 + H_2$$
 $\Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$ (2.6)

In this network, all side reactions are irreversible with the only reversible reaction being the main reaction which produces styrene. The corresponding rate equations, expressed as functions of component partial pressure in bars, are (Abashar, 2004; Moustafa and Elnashaie, 2000; Elnashaie et al., 2000; Abdulla and Elnashaie, 1993):

$$r_{1} = k_{1} \left(p_{EB} - \frac{p_{ST} p_{H_{2}}}{K_{A}} \right)$$
(2.7)

$$r_2 = k_2 p_{EB} \tag{2.8}$$

$$r_3 = k_3 p_{EB} p_{H_2} \tag{2.9}$$

$$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2}$$
(2.10)

$$r_5 = k_5 p_{H_2O} p_{CH_4} \tag{2.11}$$

$$r_6 = k_6 \left(\frac{P}{T^3}\right) p_{H_2 O} p_{CO}$$
(2.12)

with rate constants defined as:

$$k_i = \exp\left(A_i - \frac{E_i}{RT}\right) \tag{2.13}$$

The numerical values of A_i and E_i in Table 2.1 are used to calculate the rates of reactions in kmole (kg catalyst)⁻¹ s⁻¹. Tobe able to use the partial pressure in Pascals and then reaction rates in mole (kg catalyst)⁻¹ s⁻¹, the right hand side of the above rate equations (2.7-2.12) have to be multiplied by the constants in Table 2.2.

On the tube side, the hydrogenation reaction of nitrobenzene to aniline is given (Amon, 1999) by:

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
 $\Delta H_{295} = -443.0 \frac{\text{kJ}}{\text{mole}}$ (2.14)

The rate equation of this reaction is estimated (Amon, 1999) by:

$$r' = \frac{k' K_{NB} K_{H_2} p'_{NB} \sqrt{p'_{H_2}}}{\left(1 + K_{NB} p'_{NB} + K_{H_2} \sqrt{p'_{H_2}}\right)^2}$$
(2.15)

with reaction rate constant defined as:

$$k' = 10^3 \exp\left(A' - \frac{E'}{RT'}\right) \tag{2.16}$$

where:

A'=0.186, E'=10.0
$$\frac{\text{kJ}}{\text{mole}}$$
, K_{H₂} = 4.427×10⁻³ Pa^{-0.5}, K_{NB} = 1.510×10⁻⁵ Pa⁻¹

2.2.3. Pseudo -homogeneous model of the coupled membrane reactor

To obtain the mole balance equation and the energy balance equation, a differential element along the axial direction inside the membrane reactor was considered, as shown in Figure 2.2. After writing steady state balances, both sides of the resulting equations were divided by the thickness of the differential element, which was then forced to approach zero. The resulting balances equations of the shell side can be expressed as:

Mole balance:

$$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} r_j (1-\varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J_i$$
(2.17)

Energy balance:

$$\frac{dT}{dz} = \frac{\sum_{j=1}^{6} \left[-\Delta H(T) \right]_{j} r_{j} (1 - \varepsilon) A_{cs} \rho_{s} + NQ'}{\sum_{i=1}^{10} n_{i} C p_{i}}$$
(2.18)

Pressure drop:

$$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \left[\frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G\right]$$
(2.19)

The corresponding balance equations on the tube side can be expressed as: Mole balance:

$$\frac{dn'_i}{dz} = \left(-1\right)^b \left[\sigma_i r' \left(1 - \varepsilon'\right) A'_{cs} \rho'_s + 2\pi r_3 a_i J_i\right]$$
(2.20)

32

Energy balance:

$$\frac{dT'}{dz} = (-1)^{b} \left[\frac{(2\pi r_{3}) \sum_{i=1}^{i} a_{i} J_{i} \int_{T'}^{T} Cp_{i} dT + \left[-\Delta H'(T') \right] r'(1-\varepsilon') A'_{cs} \rho'_{s} - Q'}{\sum_{i=1}^{4} n'_{i} Cp'_{i}} \right]$$
(2.21)

Pressure drop:

$$\frac{dP'}{dz} = \left(-1\right)^{b} \frac{G'}{\rho'_{g} g_{c} D'_{p}} \left(\frac{1-\varepsilon'}{\varepsilon'^{3}}\right) \left[\frac{150(1-\varepsilon')\mu'_{g}}{D'_{p}} + 1.75G'\right]$$
(2.22)

where:

b = 0 for cocurrent configuration

b=1 for countercurrent configuration.

In equation (2.17) and (2.18), "N" is the number of membrane tubes. The flux term " J_i " in equations (2.17), (2.20), and (2.21) only applies to hydrogen, i.e. $a_i = 1$. This term disappears for all other components, i.e. $a_i = 0$.

The hydrogen flux across a palladium membrane surface is calculated by Sievert's law (Chen 2004; Shu, 1994), i.e.

$$J_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}}\right)$$
(2.23)

The pre-exponential constant, permeation activation energy, and the thickness of the hydrogen permeation membrane are taken to be 6.33×10^{-7} mol m⁻¹ sec⁻¹ Pa^{-0.5}, 15.7 kJ mol⁻¹, and $1 \sim 2 \times 10^{-5}$ m, respectively (Chen 2004; Shu, 1994). Heat transfer across the membrane involves convection from the gas mixture to the membrane, conduction across the membrane layer, and finally convection from the membrane to the second gas mixture. Radiation is neglected. The membrane

tube is considered to be a composite wall having a porous stainless steel layer coated by a thin layer of palladium alloy. The diffusional resistance of the porous steel is assumed to be negligible relative to that of the palladium alloy. The thermal conductivities of the porous stainless steel layer and the palladium are taken to be 24.5 W m⁻¹ K⁻¹ and 93.3 W m⁻¹ K⁻¹, respectively, average values over a temperature range of 200-1800 K (Assabumrungrat et al., 2002; Yaws, 1999). The heat transferred per unit length from each tube is obtained from:

$$Q' = \frac{2\pi r_1 (T' - T)}{\left[\frac{1}{h'} + \frac{r_1}{k_{ss}} \ln\left(\frac{r_2}{r_1}\right) + \frac{r_1}{k_{Pd}} \ln\left(\frac{r_3}{r_2}\right) + \frac{r_1}{r_2h}\right]}$$
(2.24)

The convective heat transfer coefficients in equation (2.24) are calculated using the correlation of Leva (1949) (Froment and Bischoff, 1990). For the shell side in which the reacting mixture is heated up, the convective heat transfer coefficient is calculated (Froment and Bischoff, 1990) by:

$$\frac{hD_t}{k_g} = 0.813 \left(\frac{D_p G}{\mu_g}\right)^{0.9} \exp\left(-\frac{6D_p}{D_t}\right)$$
(2.25)

The tube diameter (D_t) in the above equation was taken for the shell side to be four times the hydraulic diameter. In contrast, the reacting mixture in the tube side is cooled, and consequently the convective heat transfer coefficient is calculated (Froment and Bischoff, 1990) by:

$$\frac{h'D'_t}{k'_g} = 3.50 \left(\frac{D'_p G'}{\mu'_g}\right)^{0.7} \exp\left(-\frac{4.6D'_p}{D'_t}\right)$$
(2.26)

Physical properties such as, thermal conductivity, gas density and viscosity, and heat capacities are taken as functions of temperature (Yaws, 1999).

2.2.4. Initial and boundary conditions

In the case of the cocurrent operation (b=0), the above system of differential equations gives an initial value problem which can be solved by a Runge-Kutta Verner fifth and sixth order method with an automatic step size, double precision calculation, and a relative error of 1×10^{-12} to ensure high accuracy. The initial conditions for the cocurrent configuration are:

At:
$$z = 0$$

Shell Compartment: $n_i = n_{if}; T = T_f; P = P_f$ (2.27)
Tube Compartment: $n'_i = n'_{if}; T' = T'_f; P' = P'_f$ (2.28)

For the countercurrent operation case(b=1), the above differential equations result in a split two-point boundary value problem which can be solved by orthogonal collocation (Villadsen and Michelsen, 1978; Trefethen, 2000). The boundary conditions for the countercurrent configuration are:

At: z = 0 inlet end of dehydrogenation compartment

Shell Compartment:
$$n_i = n_{if}; T = T_f; P = P_f$$
 (2.29)

At: z = L inlet end of hydrogenation compartment

Tube Compartment:
$$n'_{i} = n'_{if}; T' = T'_{f}; P' = P'_{f}$$
 (2.39)

2.2.5. Simulation conditions

The operating conditions for both sides of the reactor are given in Tables 2.3 and 2.4. For the dehydrogenation of ethylbenzene to styrene, the feed molar flowrates are the same as those presented by (Moustafa and Elnashaie, 2000; Elnashaie et al, 2000; Abdulla and Elnashaie,

1993), whereas the molar flowrate of nitrobenzene is based on stoichiometry. More steam is provided in the feed line to prevent coke from forming on the catalyst. This leads to justifying the neglect of catalyst deactivation on the reactor model. The performance on the dehydrogenation side is compared with an adiabatic reference case without membrane having identical feed conditions. The simulation results of the novel reactor in the nitrobenzene side are not compared with any reference case because the hydrogenation is essentially irreversible (not limited by thermodynamic equilibrium) with hydrogen supplied along the length of the reactor through the hydrogen-permeative tubes, rather than via a hydrogen feed stream, making comparison with industrial data not possible.

2.3. Results and Discussion

The achievable performance as far as conversion of ethylbenzene and yield of styrene are concerned is much better than for the corresponding uncoupled industrial fixed bed reactors operated at the same conditions. The coupled membrane reactor also has the potential to give even better conversion of ethylbenzene and yield of styrene by increasing the length of the reactor, since the two profiles continue to evolve with distance. In this work, the practical life time of membranes at high temperature was taken into consideration in the specification that the membrane temperature must not exceed 900 K at any point along the membrane reactor. Although the feed temperature to the dehydrogenation side in our proposed reactor was below that used by Moustafa and Elnashaie (2000) by more than 70.0 K, a considerable enhancement could be obtained. Because of this low operating temperature, this proposed reactor is expected to operate more economically than that modelled by Moustafa and Elnashaie (2000). In addition, at the lower temperature the production of side products, in particular benzene and toluene, are expected to be reduced so that more of the fed ethylbenzene results in the production of styrene.

On the tube side, the conversion of nitrobenzene to aniline is also very favorable, providing another positive feature of the composite reactor. Autothermality is also achieved in the system because the exothermic heat generated by the hydrogenation of nitrobenzene is sufficient to provide the endothermic heat consumed by the dehydrogenation of ethylbenzene.

2.3.1. Hydrogen molar flowrate

Hydrogen molar flowrates for an uncoupled fixed bed reactor and for coupled cocurrent and countercurrent membrane reactors are shown in Figure 2.3. Hydrogen is generated and built up in the uncoupled fixed bed reactor case while producing styrene. For the coupled cocurrent case, on the other hand, hydrogen produced on the dehydrogenation side diffuses immediately through the membrane walls of the hydrogenation tubes where it meets nitrobenzene to react and produce aniline. The comparable rates of the net production of hydrogen on the dehydrogenation side and diffusion of hydrogen through the palladium membrane prevent the hydrogen from accumulating on the dehydrogenation side, where it reduces the net reaction rate. The coupled countercurrent case is of special interest due to the presence of a maximum where the flowrate of hydrogen reaches a maximum and then decreases. At the feed end of the dehydrogenation side (z = 0), the rate of production of hydrogen by reactions (2.1), (2.4), (2.5), and (2.6) surpasses both the rate of consumption of hydrogen by reaction (2.3) and the rate of diffusion of hydrogen through the palladium membrane. This leads to an increase in the number of moles of hydrogen until a point is reached where the hydrogen flowrate has achieved its maximum value, i.e. where the rate of change of molar flowrate of hydrogen at that point with respect to the length of the reactor is zero. At this point, the rate of the production of hydrogen is balanced by both the rate of consumption of hydrogen by reaction (2.3) and the rate of diffusion of hydrogen through the membrane. Beyond that point, the process is dominated by consumption of hydrogen by reaction (2.3) and diffusion of hydrogen through the membrane. Consequently, the molar flowrate of hydrogen decreases along the reactor. This trend induces similar behaviour in the hydrogenation tubes. As nitrobenzene moves from its feed point at z=3.0 m, it reacts with permeate hydrogen. Another maximum is reached where the rate of diffusion of hydrogen through the membrane is balanced by its rate of consumption by the hydrogenation reaction. This point is located to the left (on Figure 2.3) of that on the dehydrogenation side. After passing this maximum, the rate of consumption of hydrogen dominates, causing the amount of hydrogen in the hydrogenation tubes to drop quickly.

2.3.2. Conversion of ethylbenzene

The predicted conversion of ethybenzene on the dehydrogenation side is shown in Figure 2.4 for the same three cases. For the operating conditions chosen, the conversion reaches 23.4% for the uncoupled adiabatic fixed bed case, 54.6% for the cocurrent membrane reactor, and 61.7% for the membrane reactor with a countercurrent flow configuration. Coupling of the two reactions clearly has the potential to provide significant improvement in performance. Moreover, the heat generated by the exothermic hydrogenation reaction is put to good use, rather than being simply rejected to cooling water.

2.3.3. Yield of styrene

Three cases are investigated: an uncoupled fixed bed case corresponding to contemporary industial operation, a cocurrent coupled case, and a countercurrent coupled case. Results for the three cases appear in Figure 2.5. The lowest yield by a considerable margin is predicted for the uncoupled adiabatic fixed bed where the maximum yield is 18.9%. For the membrane reactor, the predicted yield increases to 52.5% for the cocurrent flow configuration and 57.7% for the countercurrent case.

2.3.4. Conversion of nitrobenzene

Figure 2.6 plots the predicted conversion of nitrobenzene as a function of distance along the reactor for the hydrogenation reaction to aniline. The countercurrent membrane reactor is seen to give higher conversion than the cocurrent case because of the large driving forces. The conversion for the cocurrent case is predicted to reach 51.1%, while 57.9% is calculated for the corresponding countercurrent case.

2.3.5. Temperature profiles

Temperature profiles for the uncoupled adiabatic fixed bed reactor and both the cocurrent and countercurrent membrane reactors are plotted in Figures 2.7 and 2.8 for different numbers of

membrane tubes. Heat is continuously supplied from the exothermic nitrobenzene-to-aniline reaction on the tube side to the endothermic dehydrogenation of ethylbenzene on the shell side. The temperature variation is larger at the inlet in the coupled countercurrent case than for coupled cocurrent flow. The fall in temperature for both cases of the coupled membrane reactor is much less than for the uncoupled fixed bed reactor. In the countercurrent case of the coupled reactor, the temperature on the dehydrogenation side drops because the heat transfer from the nitrobenzene side decreases due to the low driving force, i.e. the temperatures on both sides become similar.

Predicted temperature profiles on the hydrogenation side where the nitrobenzene-to-aniline reaction occurs are also plotted in Figures 2.7 and 2.8 for different numbers of membrane tubes. The temperature rises from 860 K at the feed point to slightly more than 920 K for the coupled cocurrent flow case, and to a little greater than 945 K for the coupled countercurrent flow configuration. The large temperature rise for the coupled countercurrent coupled case is due to the large driving force, causing more permeation of hydrogen through the membranes and consequently increasing the nitrobenzene conversion. However, the temperature reaches a peak where both heat generated on the nitrobenzene side due to the reaction and energy carried by the permeating hydrogen are balanced by heat transfer through the membrane to the ethylbenzene side. Later, the temperature decreases because of the dominance of the heat transfer through the membrane.

2.3.6. Practical considerations

Coupling the exothermic hydrogenation reaction with the endothermic dehydrogenation reaction is predicted to be capable of providing a significant improvement in reactor performance and energy integration. However, it must be noted that palladium membranes are currently limited to temperatures of ~ 900 K. The maximum temperature could be reduced by increasing the number of membrane tubes giving more surface area and permitting more heat transfer rate between the compartments. This is illustrated in Figures 2.7 and 2.8 where the axial temperature profiles in both compartments of the coupled membrane reactor are plotted, with flowrate unaltered. Note that the maximum temperature can be maintained below 880 K, with countercurrent operation

giving higher maximum temperature than the cocurrent option. Note also that the countercurrent configuration is likely to be very difficult to start up in practice and that a dynamic model is required to be solved to have an idea about the time needed until steady-state is reached. Hence, cocurrent operation process control and safety aspects are also expected to be easier to provide for the cocurrent configuration. Hence, despite the advantages of countercurrent operation, cocurrent flow is more likely to be practical for the foreseeable future. Finally, while pseudohomogeneous one-dimensional models, like that used here, provide a good initial sense of what could be achieved in coupled fixed bed reactors, more comprehensive heterogeneous models with fewer simplifying assumptions are needed prior to proof-of-concept experiments on such reactors. As noted above, more comprehensive modeling is in progress.

2.4. Conclusions

The performance of a novel tube-in-shell membrane reactor, first investigated by Moustafa and Elnashaie (2000), with two coupled reactions, an exothermic hydrogenation and an endothermic dehydrogenation reaction in parallel, has been modeled and evaluated for cocurrent and countercurrent operation. Pseudo-homogeneous models have been used to describe the behavior of the system. In the range of the parameters considered, the simulation predicts a marked increase in the conversion of ethylbenzene and yield of styrene when the dehydrogenation of ethylbenzene to styrene is coupled with the hydrogenation of nitrobenzene. The results from the countercurrent mode of operation were in all cases more favorable than those from the cocurrent mode of operation due to the large driving forces for hydrogen diffusion and heat transfer between the two sides of the coupled reactor. The simulation results suggest that coupling may be feasible. However, the performance of the reactor needs to be proven experimentally and tested over a range of parameters under practical operating conditions.

Reaction No.	Frequency Factor ^a A _i	Activation Energy ^a , (kJ/mole) E _i							
2.7	0.85	90.9							
2.8	14.00	208.1 91.5 104.0							
2.9	0.56								
2.10	0.12								
2.11	-3.21	65.7							
2.12	21.24	73.6							
Equilibrium constant $K_A = \exp\left(-\frac{\Delta F}{RT}\right)$									
$\Delta F = a + bT + cT^2$									
a = 1227251 kJ / mole									
a = -126.267 kJ / mole / K									
$c = -2.194 \times 10^{-3} kJ / mole / K^2$									

Table 2.1 Arrhenius equation and equilibrium constants for ethylbenzene reactions.

^a obtained from Abdulla and Elnashaie, (1993);Moustafa and Elnashaie (2000); Elnashaie et. al (2000); Assabumrungrat et. al(2002).

Та	ble	2.	.2	Uı	nit	conv	vers	ion	con	stan	ts	for	reac	tion	rates	of	deł	nvd	roge	enati	on	netv	vork	
	~		_	-												~-		-,	-~		~			

Reaction rate equation No.	Constant to multiply right side by
2.7	1/100
2.8	1/100
2.9	1/10 ⁷
2.10	1/10 ^{4.5}
2.11	1/10 ⁷
2.12	1/10 ¹²

Table 2.3 Design and operating conditions for dehydrogenation (shell side) reaction of ethylbenzene to styrene.

Parameter	Values and dimensions
Length of the reactor	3.0 m
Cross-sectional area of the shell side	3.0 m^2
Feed molar flow rates of ^a :	
Ethylbenzene	30.0 mole/s
Styrene	0.1861 mole/s
Hydrogen	0.0 mole/s
Benzene	0.03056 mole/s
Ethylene	0.0 mole/s
Toluene	0.2444 mole/s
Methane	0.0 mole/s
Carbon monoxide	0.0 mole/s
Carbon dioxide	0.0 mole/s
Steam	140.0 mole/s
Inlet temperature	850 K
Inlet pressure	4.5×10^5 Pa
Catalyst density ^b	1500 kg/m^3
Diameter of catalyst particle	$4.7 \times 10^3 \mathrm{m}$
Void fraction	0.48

^a obtained from Abdulla and Elnashaie, (1993); Moustafa and Elnashaie (2000); Elnashaie et. al (2000). ^b obtained from Assabumrungrat et. al (2002).

Table 2.4 Operating conditions for hydrogenation (tube side) reaction of nitrobenzene to aniline.

Parameter	Value and dimension				
No. of hydrogenation tubes	1270				
Outer radius of a hydrogenation tube	0.0318 m				
Thickness of the stainless hydrogenation tube	0.0030 m				
Total Cross-sectional area of the tube side available for flow	3.310 m ²				
Feed molar flow rates of:					
Nitrobenzene	10.0 mole/s				
Hydrogen	0.0 mole/s				
Aniline	0.0 mole/s				
Steam	100.0 mole/s				
Inlet temperature	860 K				
Inlet pressure	1.1×10 ⁵ Pa				
Catalyst density	1400 Kg/m ³				
Diameter of catalyst particle	$4.7 \times 10^3 \mathrm{m}$				
Void fraction	0.46				



Figure 2.1 Schematic diagram showing integrated reactor configuration.



Figure 2.2 Schematic diagram showing a differential element inside the membrane reactor.



Figure 2.3 Molar flow of hydrogen on uncoupled adiabatic fixed bed and coupled cocurrent and countercurrent cases of the novel membrane reactor. For operating conditions see Tables 2.3 and 2.4. For countercurrent case, feed is from the right for the hydrogenation compartment; otherwise all feeds are from the left.



Figure 2.4 Comparison of ethylbenzene conversions on dehydrogenation side for uncoupled adiabatic fixed bed and for coupled cocurrent and countercurrent cases. For operating conditions, see Tables 2.3 and 2.4.



Figure 2.5 Comparison of styrene yields on dehydrogenation side for uncoupled adiabatic fixed bed and for coupled cocurrent and countercurrent cases. For operating conditions, see Tables 2.3 and 2.4.



Figure 2.6 Conversion of nitrobenzene on hydrogenation side for cocurrent and countercurrent membrane reactor configurations. For operating conditions, see Tables 2.3 and 2.4.



Figure 2.7 Effect of number of hydrogenation tubes on temperature profiles in dehydrogenation and hydrogenation compartments for the cocurrent case. For operating conditions, see Tables 2.3 and 2.4.



Figure 2.8 Effect of number of hydrogenation tubes on temperature profiles in the dehydrogenation and hydrogenation compartments for coupled countercurrent case. For operating conditions, see Tables 2.3 and 2.4.
2.5. References

- Abdulla, B. K., Elnashaie, S.S.E.H, (1993). A membrane reactor for the production of styrene from ethylbenzene. Journal of Membrane Science, 85(3), 229-239.
- Amon B., Redlingshofer H., Klemm E., Dieterich E., Emig G., (1999). Kinetic investigation of deactivation by coking of a noble metal catalyst in the catalytic hydrogenation of nitrobenzene using a catalytic wall reactor. Chemical Engineering and Processing, 38(4), 395-404.
- Hermann Ch., Quicker P., Dittmeyer R., (1997). Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor. Journal of Membrane Science, 136 (1), 161-172.
- Yaws C. (1999). Chemical Properties Handbook: Physical, Thermodynamics, Engironmental Transport, Safety & Health Related Properties for Organic & Inorganic Chemical, McGraw-Hill, New York, 1999.
- Cavani F., Trifirò F., (1995). Alternative processes for the production of styrene. Applied Catalyst, 133 (2), 219-239.
- Froment G., Bischoff K. (1990). Chemical Reactor Analysis and Design. John Wiley and Sons: New York.
- Valladsen J., Michelsen M. L (1978). Solution of Differential Equation Models by Polynomial Approximation. New Jersey, Prentice Hall.
- Trefethen L. (2000). Spectral Methods in MATLAB. Society for Industrial and Applied Mathematics. Philadelphia.
- Abashar M.E.E., (2004). Coupling of ethylbenzene dehydrogenation and benzene hydrogenation reactions in fixed bed catalytic reactors. Chemical Engineering and Processing, 43(10), 1195-1202.
- Shu, Grandjean B.P.A., Kaliaguine S., (1994). Methane steam reforming in symmetric Pd- and Pd-Ag/porous SS membrane reactor. Applied Catalyst, A119, 305-325.
- Elnashaie S.S.E.H., Moustafa T., Alsoudani T., Elshishini S. S., (2000). Modeling and basic characteristics of novel integrated dehydrogenation-hydrogenation membrane catalytic reactors. Computer Chemical Engineering, 24(2), 1293-1300.

- Assabumrungrat S., Suksomboon K., Praserthdam P., Tagawa T., Goto Sh., (2002). Simulation of a Palladium Membrane Reactor for Dehydrogenation of Ethylbenzene. Journal of Chemical Engineering of Japan, 35(3), 263-273.
- Moustafa T. M., Elnashaie S.S.E.H., (2000). Simultaneous production of styrene and cyclohexane in an integrated membrane reactor. Journal of Membrane Science, 178(1), 171-184.
- She Y., Han J., Ma Y.H., (2001). Palladium membrane reactor for the dehydrogenation of ethylbenzene to styrene. Catalyst Today, 67(1), 43-53.
- Chen Zhongxiang, (2004). a Novel Circulating Fluidized Bed Membrane Reformer for Efficient Pure Hydrogen Production for Fuel Cells From Higher Hydrocarbons. Auburn University, PhD Thesis.

CHAPTER 3 OPTIMAL DESIGN OF AN AUTOTHERMAL MEMBRANE REACTOR COUPLING THE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE WITH THE HYDROGENATION OF NITROBENZENE TO ANILINE BASED ON PSEUDO-HOMOGENEOUS MODEL[†]

3.1. Introduction

Styrene and aniline are important intermediate products in the petrochemical industry. Styrene is used in the production of the polystyrene, acrylonitrile-butadiene-styrene resins (ABS), and a variety of other polymers. Its commercial production is performed by the dehydrogenation of ethylbenzene. This dehydrogenation reaction is reversible and thermodynamically limited with a maximum achievable conversion of about 50% (Elnashaie et al. 2000). Aniline, on the other hand, is used in, e.g. the synthesis of methylene diphenyl diisocyanate (MDI) and as an additive in rubber processing. About 85% of global aniline is produced via a catalytic process using metal-supported catalysts (Sangeetha et al. 2009). Because of their industrial importance, styrene and aniline manufacturing plants have large capacities (estimated as 100,000 tons/year for styrene). Hence, the investment cost in those plants is high, so that any small enhancement in the process could yield significant financial rewards (Babu et al. 2005, Li et al. 2003).

To overcome the thermodynamic limitation on the dehydrogenation of ethylbenzene to styrene, novel process designs involving membrane reactors have been proposed in recent years. In these

[†] A version of this chapter was published: Nabeel S. Abo-Ghander, Filip Logist, John R. Grace, Jan F.M. Van Impe, Said S.E.H. Elnashaie, and C. Jim Lim 2010. Optimal design of an autothermal membrane reactor coupling the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline, Chemical Engineering Science, 65(10), 3113-3127.

reactors, the reaction of interest is promoted by hydrogen-selective membrane walls which remove hydrogen from the reaction chamber to a separate compartment where hydrogen is either extracted by a sweep gas (Abdalla and Elnashaie, 1993, Abdalla and Elnashaie, 1994, Abdalla and Elnashaie, 1995, Hermann et al. 1997) or reacted separately to generate another useful product (Elnashaie et al. 2000, Moustafa and Elnashaie, 2000). The enhancements in conversion of ethylbenzene and yield of styrene were predicted to be considerable. Among these possible membrane reactors, the configuration proposed in chapter 2 is of special interest because it allows the coupling with a second important industrial process. To improve the production of styrene in such membrane reactors, it is crucial to seek an optimal design which considers geometry, design and operational variables, since a small improvement could provide high dividends to the petrochemical industry and consumers.

In view of this aim, mathematical models and optimization techniques are valuable tools. However, this configuration involves several key elements to model the reactor, for example heat transferred across the membrane walls by conduction, as well as diffusion of hydrogen from the dehydrogenation side to the hydrogenation side.

Therefore, this chapter addresses the model based optimization of the design of the cocurrent flow configuration of the fixed bed membrane reactor introduced by in chapter 2. A bi-objective optimization problem with twelve (12) parameters is formulated and solved to obtain a Pareto set. Afterwards, the designer will be able to select one design out of this set of equally good reactors, based on his preferences. The optimization problem solved in this paper is unique because it concerns the coupling of reactions in fixed bed membrane reactors, as well as the production of two main chemical products, namely styrene and aniline.

The structure of this chapter is as follows. Section 3.2 reviews some interesting results reported in literature with respect to model based reactor design optimization. Sections 3.3, 3.4 and 3.5 introduce for the fixed bed membrane reactor under study: the reactor configuration, the reaction kinetics and the mathematical reactor model, respectively. Sections 3.5 and 3.6 describe the optimization problem formulation and provide some details about the numerical solution

strategy. Section 3.7 discusses the obtained numerical results. Finally, Section 3.8 summarizes the main conclusions.

3.2. Literature Review

In optimization problems, feasible solutions are sought which correspond to extremes of one or more objective functions. This is important in early design stages of any chemical process where process parameters have to be within certain limits and to satisfy certain constraints imposed by, e.g. safety and environmental legislations. This type of problems has been addressed in the literature by a number of researchers. For example, Sheel and Crowe (1969) modeled an existing ethylbenzene dehydrogenation reactor and optimized its performance using a profit function defined as the difference between the gain due to the production of styrene and fuel gases, i.e. methane and ethylene, and the loss due to steam usage and by-products, i.e. toluene and benzene. In the same study, the case of a double bed reactor was also considered. The decision variables considered were the steam temperature, steam rate and reactor depth. It was concluded that the reactor would work better if the constraints on both the temperature and steam flow were relaxed. Clough and Ramirez (1976) studied the effect of injecting steam into a styrene reactor at a point downstream of the reactor inlet. Optimization was performed to find the best injection point considering a profit objective function defined as the difference between the market value of the products and the utility cost. A styrene pilot plant was constructed and the results confirmed the improvement predicted by the model.

In all of the previous studies, only a single objective was considered. However, in practice often multiple and conflicting objective functions are present (see, e.g., Bhaskar et al. (2000) for an overview until the year 2000). These optimization problems differ conceptually from the single objective optimization problems. As a result of the conflicting objectives, there is no single optimal solution, but rather a set of solutions which best satisfies all objectives. These solutions are referred to as *Pareto-optimal* solutions. Broadly speaking, a feasible point is a Pareto-optimal solution if it is impossible to improve one objective function without worsening at least one of the others. The exact mathematical description can be found in, e.g. Das and Dennis (1998), or Miettinen (1999).

For instance, Lim et al. (2001) optimized the production of methyl ethyl ketone (MEK) from the dehydration of sec-butyl alcohol considering bi-objective functions, i.e. profit and environmental functions. The problem was solved by an improved version of the normal boundary intersection (NBI) method (Das and Dennis, 1998) which combined the original NBI method with the summation of weighted objective functions. The enhanced method gave evenly-distributed Pareto points and reliable optimization results, even in a non-convex region of the Pareto curve. Li et al. (2003) treated the same problem as addressed by Clough and Ramirez (1976), but with two objective functions. Both the adiabatic and steam-injected styrene reactors were considered, while styrene production and styrene selectivity were taken as the objective functions of the optimization problem. The problem was solved using a non-dominated sorting genetic algorithm (NSGA) (Srinivas and Deb, 1995). Optimization of the reactor showed that the production and selectivity of styrene could be improved compared to the current operating conditions after obtaining reliable NSGA results. The multi-objective differential evolution algorithm was introduced by Babu et al. (2005). This algorithm was applied to the optimization of the styrene reactor, and the results were compared with those obtained from the NSGA. In the optimization problem, three objective functions were considered, i.e. styrene production, styrene yield, and styrene selectivity. The Pareto set based on the new algorithm was found to be much better than that obtained by the NSGA, as reflected in the profit function. Tarafder et al. (2005a) studied the optimization of a double-bed styrene manufacturing reactor and compared the results with those for a single bed and steam-injected reactor. Three objective functions were considered, i.e. styrene molar flowrate, styrene selectivity and total heat duty required by the process. The problem was solved using elitist NSGA-II (Deb et al. 2002), which works more efficiently and quickly than NSGA. The production of styrene in the double-bed reactor was higher than in the other two reactors. The production of ethylene in an industrial ethylene reactor was investigated by Tarafder et al. (2005b) considering two and three objective functions, i.e. conversion of ethane, selectivity of ethylene, and flow rate of ethylene. The elitist NSGA-II algorithm was used to solve the problem. 100% ethane conversion and more than 90% ethylene selectivity were reported.

For catalytic membrane reactors, a multi-objective optimization problem was studied by Cheng et al. (2008) for a methanol reactor and a hydrogen production reactor. The elitist NSGA-II

algorithm was again used to obtain an optimal solution with three objective functions, i.e. product flowrate (methanol or hydrogen), reactant flowrates (hydrogen or methane), and exergy loss of the reactor. The problem was solved to evaluate the effect of key membrane characteristics like membrane thickness and membrane area per unit length on these objective functions. More recently, Logist et al. (2009) reported the efficient generation of Pareto sets for several (bio)chemical processes described by ordinary differential equations based on a combination of (*i*) novel deterministic multiple objective optimization routines (i.e. Normal Boundary intersection and Normalized Normal Constraint (Messac and Mattson, 2004)) and (*ii*) an advanced deterministic multiple shooting optimization approach (Leineweber et al. 2003a, Leineweber et al. 2003b).

3.3. Reactor Configuration

Figure 3.1 depicts the membrane reactor, with only one hydrogenation tube portrayed for simplicity. There are two compartments separated by a hydrogen perm-selective membrane. The outer compartment is for the dehydrogenation of ethylbenzene to styrene, while the hydrogenation reaction of nitrobenzene to aniline takes place in the inner compartment. The external wall of the outer shell is assumed to be adiabatic. Although this assumption cannot be perfectly true, it is likely to be a good approximation for large industrial reactors with an excellent outer insulation.

In simple fixed bed reactors in which ethylbenzene is continuously dehydrogenated, styrene, hydrogen, and secondary products like benzene and toluene are produced, and the temperature drops along the reactor length due to the endothermic reaction. In the membrane reactor considered in Figure 3.1, hydrogen produced in the outer shell, diffuses through the hydrogen-selective membranes to the inner compartment under the influence of the difference in hydrogen partial pressures on the two sides. Inside the tubes, the diffused hydrogen encounters nitrobenzene and steam in the presence of a hydrogenation catalyst, where it reacts via an irreversible exothermic hydrogenation reaction. Heat produced by this reaction is transferred from the tube compartment through the hydrogen-selective membrane walls to the shell compartment where it provides the endothermic heat of the dehydrogenation of ethylbenzene.

The transfer of hydrogen from the shell compartment to the tube compartment, while heat flows in the opposite direction, promotes the formation of more styrene. However, the heat transferred from the tube compartment decreases the temperature and as a result lowers the rate of reaction.

3.4. Chemical Reactions and Kinetic Expressions

The main reactions taking place in the outer shell are listed below.

$$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2 \qquad \Delta H_{298} = 117.6 \frac{\text{kJ}}{\text{mole}}$$
 (3.1)

$$C_6H_5CH_2CH_3 \to C_6H_6 + C_2H_4$$
 $\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$ (3.2)

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$$
 (3.3)

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$$
 $\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$ (3.4)

. .

. .

$$H_2O + CH_4 \rightarrow CO + 3H_2 \qquad \Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$$
(3.5)

$$H_2 O + CO \rightarrow CO_2 + H_2 \qquad \qquad \Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}} \tag{3.6}$$

The first reaction is the principal reaction in the shell, producing one mole of styrene per one mole of ethylbenzene. This reaction is endothermic and reversible. It is favoured by high temperatures and low pressures (Le Chatellier's principle). In most modern designs, this process is carried out in three reactors in series, with heat supplied either by heating the reactants entering each stage or by injecting hot steam with the feed stream. By applying this procedure, the forward reaction can be boosted. In addition to producing styrene, there are two side products, benzene and toluene, resulting from thermally cracking ethylbenzene at high temperatures. These side reactions reduce the selectivity to styrene. On the other side of the integrated reactor (tube side), a single reaction takes place where the diffused hydrogen reacts with the feed steam consisting of nitrobenzene and steam in order to produce aniline.

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
 $\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$ (3.7)

This hydrogenation reaction is irreversible and exothermic, with three moles of hydrogen reacting with one mole of nitrobenzene in order to produce each mole of aniline. The heat of reaction and the kinetic expressions for the reactions on both sides of the integrated reactor are summarized in Tables 3.1 and 3.2.

3.5. Mathematical Reactor Model

To derive the model equations for the membrane reactor, a slice of infinitesimal length is considered on both sides of the coupled reactor. Mass, energy and momentum balances are then derived based on the following assumptions.

- 1. Steady state operation.
- 2. Ideal gas behavior on both sides.
- 3. Plug flow for the fixed beds on both the shell and tube sides, with axial mass Peclet numbers estimated to be of order 1000.
- 4. Negligible axial heat dispersion, with axial heat Peclet numbers >> 1.0.
- 5. Pseudo-homogeneous one-dimensional model, radial Peclet number >> 1.0.
- 6. Catalyst deactivation is neglected.
- 7. Pressures along both compartments are calculated based on Ergun's equation.

The resulting mole, energy and pressure equations for both sides of the integrated reactor are summarized in Table 3.3 where the balance equation on the hydrogenation side is for one tube. The heat transfer from each hydrogenation tube across the membrane per unit length is estimated assuming a composite circular tube with a convective heat resistance on the tube side, followed by a conductive heat resistance due to the presence of a layer of stainless steel with a thickness of 0.0012 m, followed by another conductive heat resistance due to the presence of a palladium layer with a thickness of 20×10^{-6} m, and finally a convective resistance on the shell side as illustrated in chapter 2. The convective heat transfer coefficients on both sides of the reactors are

calculated using the correlations accompanying the heat transfer equation in Table 3.3, assuming that the reacting mixture on the dehydrogenation side is always heated, while that on the hydrogenation side is always cooled (Froment and Bischoff, 1990). The total heat exchanged between the two sides of the coupled reactor, i.e. the dehydrogenation side and hydrogenation side, is estimated by multiplying the total number of hydrogenation tubes by the heat released from a single hydrogenation tube.

3.6. The Optimization Problem

In the current thesis, two objective functions are considered and split between the dehydrogenation and the hydrogenation sides. On the dehydrogenation side, the requirement is to maximize the yield of styrene, whereas that on the hydrogenation side is to maximize the conversion of nitrobenzene. The two objective functions may then be defined as:

Maximize:
$$Y_{ST} = \frac{Moles \ of \ Styrene \ Produced}{Moles \ of \ Ethylbenze \ ne \ Fed} = \frac{n_{ST}(L) - n_{ST}(0)}{n_{FB}(0)}$$
 (3.16)

Maximize:
$$X_{NB} = \frac{Moles \ of \ Nitrobenzene \ Reacted}{Moles \ of \ Nitrobenzene \ Fed} = \frac{n_{NB}(0) - n_{NB}(L)}{n_{NB}(0)}$$
 (3.17)

Maximization of the conversion of nitrobenzene on the hydrogenation side results in maximizing the production of aniline on the same side. Twelve decision variables are considered, i.e. the feed molar flowrate of ethylbenzene on the dehydrogenations side n_{EBo} , the steam-to-ethylbenzene ratio SOR, the feed temperature on the dehydrogenation side T_f , the feed pressure on the dehydrogenation side P_f , the feed molar flowrate of nitrobenzene on the hydrogenation side n_{NBo} , the steam-to-nitrobenzene ratio SOR', the feed temperature on the hydrogenation side T_f' , the feed pressure on the hydrogenation side P_f , the number of hydrogenation tubes N, the areaequivalent diameter on the dehydrogenation side D, the diameter of the membrane tube D_t , and the reactor length L. However, the solutions of the above mentioned problem are required to satisfy the several constraints: The feed molar flowrate of ethylbenzene on the dehydrogenation side is taken to be between -25% and 10% of the nominal value of 10.24 moles/s. These bounds are consistent with the industrial case since the plant can operate at a much lower capacity, but not at a much higher capacity (Yee et al. 2003).

$$7.66 \le n_{EBf} \le 11.27 \quad \text{mole/s}$$
 (3.18)

 The lower limit on the steam-to-ethylbenzene ratio is set as 7 to prevent coke formation on the catalyst surface. At the same time, too much steam cannot be used because it would make the process economically unfeasible. As for industrial practice, the upper limit is set to 20 (Yee, et al, 2003).

$$7.0 \le SOR \le 20.0$$
 (3.19)

3. The lower bound on the feed temperature on the dehydrogenation side is set at 780 K to ensure that the reacting mixture is not too cold for the reaction to occur, while the upper limit is set at 915 K to protect the membrane.

$$780 \le T_f \le 900 \,\mathrm{K}$$
 (3.20)

4. Although the dehydrogenation of ethybenzene to styrene is favoured at lower pressures, it is important to work at a relatively higher pressure to create a favorable driving force for hydrogen permeation through the membrane. The lower limit on the feed pressure is chosen as 1.0 bar while its upper limit is set at 4.0 bar to prevent violation of the ideal gas law and to avoid costly pressure vessel designs.

$$1.0 \le P_f \le 4.0 \text{ bar}$$
 (3.21)

5. The maximum amount of hydrogen which can be produced based on these bounds (3.18) is 11.27 mole/s. From the stoichiometry of the hydrogenation equation, each mole of

nitrobenzene needs to react with three mole of hydrogen arriving from the dehydrogenation side. Hence, the maximum amount of nitrobenzene that can react with the diffused hydrogen is around ~ 3.77 mole/s. The molar flowrate of nitrobenzene in a single hydrogenation tube, considering an average of 1750 tubes, is ~ 0.002 moles/s. This limit neglects the hydrogen produced from side reactions, i.e. reactions (3.4), (3.5), and (3.6). Consequently, the upper limit is set at 0.005 mole/s to allow for any additional hydrogen produced, so that:

$$0.002 \le n_{NBf} \le 0.005 \text{ mole/s}$$
 (3.22)

6. Bounds on the steam-to-nitrobenzene ratio are set so that:

$$2.0 \le SOR' \le 4.0 \tag{3.23}$$

7. Bounds on the feed temperature on the hydrogenation side are chosen as:

$$780 \le T_f' \le 900 \,\mathrm{K}$$
 (3.24)

8. Bounds on the feed pressure on the hydrogenation side are established at:

$$1.0 \le P_f' \le 4.0 \,\mathrm{bar}$$
 (3.25)

9. Hydrogen flux and rate of heat transfer from the hydrogenation side to the dehydrogenation side can be greatly enhanced by increasing the number of hydrogenation tubes (i.e. increasing the contact surface area), but an excessive number of tubes would escalate manifolding issues and cost. Hence, the number of hydrogenation tubes is bounded by:

$$1000 \le N \le 2500$$
 (3.26)

10. The area-equivalent diameter on shell side is set to be within the limits chosen by Li et al. (2003a):

$$1.95 \le D \le 3.0 \,\mathrm{m}$$
 (3.27)

11. Bounds on the diameter of the hydrogenation tube are specified as:

$$2.5 \times 10^{-2} \le D_t \le 5.5 \times 10^{-2} \,\mathrm{m} \tag{3.28}$$

12. To limit the reactor length, we require that:

$$1.5 \le L \le 4.0$$
 (3.28)

13. To ensure that heat is always transferred from the hydrogenation side to the dehydrogenation side, the following constraint is adopted:

$$T_f - T'_f \le 0.0$$
 K (3.29)

14. To ensure that hydrogen is always transferred from the dehydrogenation side to the hydrogenation side, we stipulate that:

$$P_f' - P_f \le 0.0 \text{ bar} \tag{3.30}$$

15. Palladium membranes are currently limited to temperatures lower than about 923 K. Hence, the temperature along the hydrogenation side is required to be less than or equal to 915 K in order to ensure the durability and sustainability of the membranes.

$$T'_{\max} (z) - 915.0 \le 0.0 \text{ K}$$
 (3.31)

16. It is important to achieve autothermality on the dehydrogenation side. This leads to the following nonlinear equality constraint to ensure that the outlet temperature of the dehydrogenation side is equal to the feed temperature of the dehydrogenation side:

$$T_f - T(L) = 0.0 \,\mathrm{K}$$
 (3.32)

The entire optimization problem can now be formulated as the following multiple objective dynamic optimization problem.

Maximize:
$$\mathbf{J}(\mathbf{p})$$

Subject to: $\frac{d\mathbf{x}}{dz} = \mathbf{f}(\mathbf{x}, \mathbf{p})$ with $\mathbf{x}(z = 0) = \mathbf{x}_0$
 $\mathbf{p}^{\mathrm{L}} \le \mathbf{p} \le \mathbf{p}^{\mathrm{U}}$
 $\mathbf{A}\mathbf{p} \le \mathbf{0}$
 $\mathbf{c}_{eq}(\mathbf{p}) = \mathbf{0}$
 $\mathbf{c}_{ineq}(\mathbf{p}) \le \mathbf{0}$
(3.33)

where:

$$\mathbf{p} = \begin{bmatrix} n_{EBf}, SOR, T_f, P_f, n_{NBf}, SOR', T_f', P_f', N_t, D, D_t, L \end{bmatrix}^{\mathrm{T}},$$

$$\mathbf{J}(\mathbf{p}) = \begin{bmatrix} Y_{ST} \\ X_{NB} \end{bmatrix},$$

$$\frac{d\mathbf{x}}{dz} = \mathbf{f}(\mathbf{x}, \mathbf{p}) \text{ is the reactor model described by equations (8) to (13),}$$

$$\mathbf{p}^{L} = \begin{bmatrix} 7.66, 7, 780, 1.0, 0.02, 2.0, 780, 1.0, 1000, 1.95, 2.5 \times 10^{-2}, 1.5 \end{bmatrix}^{\mathrm{T}},$$

$$\mathbf{p}^{U} = \begin{bmatrix} 11.27, 20, 900, 4.0, 0.05, 4.0, 900, 4.0, 2500, 3.0, 5.5 \times 10^{-2}, 4.0 \end{bmatrix}^{\mathrm{T}},$$

$$\mathbf{A} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix},$$

$$\mathbf{c}_{eq}(\mathbf{p}) = T_f - T(L)$$

$$\mathbf{c}_{ineq}\left(\mathbf{p}\right) = T_{\max}\left(z\right) - 915.0$$

All other variables not included in the decision variable vector \mathbf{p} are maintained at their industrial values as specified in Table 3.4.

3.7. Details of the Numerical Solution

To solve the above mentioned problem numerically, a number of approaches can be tried. The most common approach is the weighted sum (WS) method. It starts by linearly combining all objective functions of interest using weight vectors, and then solving the system considering the constraints. However, the WS fails to obtain solutions in non-convex regions of the Pareto set, and the Pareto optimal solutions generated are not necessarily evenly-distributed (even if the weight is varied evenly (Das and Dennis, 1997)).

Alternatively, multi-objective evolutionary strategies (EAs) and genetic algorithms (GAs) (Deb, 2001) have been successfully adopted by a number of researchers. GAs are based on the Darwinian theory of evolution while EAs are modified versions of GAs in which different operators are used to generate the candidate solutions, e.g. mutation, recombination, reproduction, and selection. However Messac et al. (2003) mentioned that methods from these classes may suffer from lack of producing well-distributed Pareto solutions.

Hence, the Normalized Normal Constraint (NNC) method and the Normal Boundary Intersection (NBI) method, introduced by Messac and Mattson, (2004), Messac et al. (2003) and Das and Dennis, (1998), have been used to solve the bi-objective optimization problems under study. These deterministic methods are easy to implement and able to produce evenly-distributed (local) Pareto solutions in a limited amount of time. Both methods suffer, however, from producing non-Pareto optimal solutions, but these can be removed by applying a Pareto filter.

To solve the problem at hand, both the NNC and NBI methods have been implemented in Matlab to obtain the Pareto frontier. A Pareto filter has been applied to remove all non-Pareto points.

Since optimization solvers are mostly designed for minimization problems, the problem of maximizing the objective functions defined in equations (3.16) and (3.17) has been first transformed into a minimization problem by introducing the following generic functions for both objectives:

$$J_{SY} = \frac{1}{1 + Y_{SY}}$$
(3.34)

$$J_{NB} = \frac{1}{1 + X_{NB}}$$
(3.35)

Minimization of equations (3.34) and (3.35) results in maximizing the styrene yield on the dehydrogenation side and the nitrobenzene conversion on the hydrogenation side. To evaluate the generic function defined by equations (3.34), and (3.35), model equations (3.8) to (3.13) have been solved numerically considering equations (3.14), and (3.15). For the cocurrent configuration of the catalytic reactor, these model equations form a set of initial value problems which can be solved by any integrating subroutine for given initial conditions. The Matlab integrator ode15s has been employed with a relative tolerance of 1×10^{-10} to ensure accuracy. To apply the NNC and NBI methods, it was required that anchor points be found which correspond to the best possible values for the respective individual objectives. Then, the utopia point was found which corresponds to all objectives simultaneously being at their best possible values. While the utopia point was used to normalize the system objective functions defined by (3.34) and (3.35), the anchor points have been used to construct the utopia line. This utopia line was divided into forty (40) segments, with an optimization problem solved at each segment. Two commercial solvers purchased from Tomlab have been utilized to solve the resulting optimization problems. Those solvers were linked to the reactor model equations as shown in Figure 3.2. Each solution cycle was started with the global glbDirect solver, and was finished with the local snopt solver. At the beginning, the global solver glbDirect was run for 100 iterations, and then its output was used to initiate the local solver snopt which converged to the feasible solution. It should also be noted that the solutions with both techniques, i.e. NNC and NBI, have been obtained independently, with the same problem solved assuming that no solution

was at hand, i.e. none of the solutions have been used to provide a starting guess for any other technique.

3.8. Results and Discussion

The optimization study has been carried out on an industrial scale catalytic membrane reactor integrating the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline. Catalyst properties, such as bulk densities and particle diameters for both reactions, have been assumed to be uniform on both sides of the integrated catalytic membrane reactor. The molar flowrates of other components in the dehydrogenation feed stream, i.e. styrene, benzene, and toluene, have been treated as impurities at their industrial levels, as shown in Table 3.4.

To confirm the optimization results, two numerical techniques have been implemented, namely the NNC and NBI methods. The results from both numerical techniques were filtered using a Pareto filter in order to remove all non-Pareto optimal points from the solution set.

The Pareto optimal solution set corresponding to the simultaneous maximization of styrene yield and nitrobenzene conversion is plotted in Figure 3.3. Both NNC and NBI methods gave the same Pareto optimal set which is a favorable sign of confirmation for both the reliability and correctness of the results. It can be also seen that along the Pareto set, while one objective improves, the other worsens, causing none of the solutions to dominate over the others. This makes all solutions of the Pareto set equally good. Hence, the final decision of the reactor design and operating point should be based on additional information which normally depends on either experience or site specifications. From the results, it is possible to optimally design the integrated catalytic membrane reactor to provide a 97% styrene yield and 20% nitrobenzene conversion at one extreme, and a 47% styrene yield and 80% nitrobenzene conversion at the other extreme. In between, a gradual evolution of both objectives is mostly observed, whereas a gap in the conversion of nitrobenzene is present when the yield of styrene is about 0.55. This gap appeared after filtering the results of the optimal solutions so that all local or non-Pareto design parameters were removed. The removed design parameters are dominated by the upper part of the Pareto solution in which the design parameters result in better reactor performance.

To quantify the role of the decision variables in realizing the objectives, the decision variables are plotted in Figures 3.4 to 3.7. Although the general trend is always clear, some 'scatter' may be present in some plots. Its presence reflects the fact that in certain regions, some of the decision variables have a limited influence on the cost functions, which makes the exact determination of the optimal values hard. However, it should be emphasized that, as their influence on the costs is only limited, an exact determination is not required for industrial practice.

In Figure 3.4a and 3.4b, the styrene yield and nitrobenzene conversion are plotted against the feed molar flowrate of ethylbenzene, illustrating the conflicting nature of both objectives. The styrene yield decreases sharply at a low ethylbenzene flowrate, scatters after that for a wide spectrum of ethylbenzene flowrates with a styrene yield mean value of 65%, and finally decreases sharply at higher flowrates. A qualitative explanation is that as the molar flowrate of ethylbenzene increases, the rates of the side reactions become significant because their reaction rates are directly proportional to the partial pressure of ethylbenzene flowrate has a positive effect on nitrobenzene conversion. This increase continues until a level of 50% nitrobenzene conversion is reached where the effect becomes almost insignificant. Then, at higher flowrates the nitrobenzene conversion increases sharply until an upper ceiling of about 80% nitrobenzene conversion is reached. This is because when the molar flowrate of ethylbenzene increases, the production of hydrogen is available for transfer to the hydrogenation side.

In Figures 3.4c and 3.4d, the yield of styrene and the nitrobenzene conversion are plotted against the steam-to-ethylbenzene molar ratio. High styrene yields can be favored by operating the dehydrogenation side at a low ratio of 7.0, whereas high nitrobenzene conversions are induced by operating the dehydrogenation side at a high ratio of 20.0. The styrene yield is high at low

steam-to-ethylbenzene ratios because the production of hydrogen from the steam reactions becomes insignificant, in turn suppressing the backward reaction of the main reaction producing styrene. The nitrobenzene conversion is favored by a high steam ratio on the dehydrogenation side because there will be more hydrogen produced in that reaction chamber, leading to increasing the amounts of hydrogen transferred to the hydrogenation side.

The effects of the dehydrogenation feed temperature on styrene yield and nitrobenzene conversion are plotted in Figures 3.4e and 3.4f. The feed temperature on the dehydrogenation side shows a conflicting effect on both objectives: as the feed temperature on the dehydrogenation side increases, the styrene yield increases, whereas the nitrobenzene conversion decreases. The styrene yield approaches the limit of 97% because the forward reaction producing styrene is favored by high temperatures as well as by receiving heat from the hydrogenation chamber transferred from the hydrogenation reaction. Although this phenomenon helps breaking the endothermality of the dehydrogenation side, and producing a high styrene yield, it also creates a drop in temperature inside the hydrogenation side, leading to low nitrobenzene conversions.

The feed pressure on the dehydrogenation side also shows a conflicting effect on both objectives as shown in Figures 3.5a and 3.5b: as it increases, the styrene yield increases, but the nitrobenzene decreases. This occurs because increasing the feed pressure creates a significant driving force for the transfer of hydrogen from the dehydrogenation side to the hydrogenation side leading to higher styrene yields. However, as the styrene is produced on the dehydrogenation side, the temperature drops, creating a significant temperature gradient between the two compartments and helping to transfer more heat from the hydrogenation side, which reduces the nitrobenzene conversion.

The effect of the feed molar flowrate of nitrobenzene on both objectives is plotted in Figures 3.5c and 3.5d. As the molar flowrate of nitrobenzene on the hydrogenation feed stream increases, the styrene yield increases because of a larger heat transfer between the two compartments. However, the heat transfer has a negative effect on the conversion of nitrobenzene as it reduces the temperature inside the tubes, causing the hydrogenation reaction to take place at a lower

temperature. Increasing the molar flowrate of nitrobenzene in the feed stream of the hydrogenation side leads to an unfinished reaction which reduces the nitrobenzene conversion.

The effect of steam-to-nitrobenzene ratio plotted in Figures 3.5e and 3.5f shows no effect, as this parameter mainly reduces the temperature along the hydrogenation side and maintains it below 915.0 K by diluting the reacting mixture on the hydrogenation side. Note that the optimum value corresponds to the boundary.

The effect of the feed temperature of the hydrogenation feed on both objectives is the same as that of the dehydrogenation side and is plotted in Figures 3.6a and 3.6b. As the feed temperature of the hydrogenation side increases, more heat is produced on the hydrogenation side due to the reaction. However, the heat produced transfers across the membrane to break the endothermality on the dehydrogenation side, resulting in a high styrene yield and low conversion of nitrobenzene (due to a lower production of aniline on the hydrogenation side). The similar behavior of the feed temperature of the dehydrogenation and the feed temperature of the hydrogenation side may result from applying too many constraints on the temperatures on both sides, i.e. constraints (3.29), (3.31), and (3.32). These constraints favor optimal designs in which both sides of the reactor operate at the same feed temperature.

In Figure 3.6c and 3.6d both objectives are plotted against the pressure of the hydrogenation feed. There is scatter visible with respect to both objectives. A low feed pressure on the hydrogenation side of 1.0 bar is preferred in order to increase the yield of styrene to around 75%, while a styrene yield of 97% can be achieved at a pressure of about 4.0 bar. For the nitrobenzene conversion, it is preferable to operate the reactor at a pressure as low as 1.0 bar in order to achieve a conversion of 80%. A higher pressure lowers the conversion to 20%.

The effect of the number of hydrogenation tubes with regard to both objectives is depicted in Figures 3.6e and 3.6f. The values are scattered, with an increasing trend in general for the yield of styrene as a function of the number of tubes. For the nitrobenzene conversion, the trend is also scattered but reversed, i.e. increasing the number of hydrogenation tubes decreases the nitrobenzene conversion. A qualitative explanation is that, as the number of the hydrogenation

tubes increases, the rate of the heat transfer across the membrane increases, leading to more styrene production on the dehydrogenation side. However, removal of hydrogen from the dehydrogenation side makes the effect of the endothermic dehydrogenation reaction significant, to the extent that the dehydrogenation side eventually acts as a "heat sink". Consequently, heat is transferred at a significant rate from the hydrogenation side which acts as a heat source, causing the kinetic rate to decrease and, as a result, a drop in the nitrobenzene conversion is observed.

In Figure 3.7a and 3.7b, the effect of the area-equivalent diameter on shell side is plotted against both objectives. For the yield of styrene, there is scatter, with an increasing trend in general. To increase the yield of styrene on the dehydrogenation side, a higher area-equivalent diameter on shell side is required, leading to a higher residence time. However, increasing the area-equivalent diameter on shell side leads to decreasing the conversion of nitrobenzene because more heat will be transferred to break the endothermality of the dehydrogenation side.

The effect of the hydrogenation tube diameter on both objectives is displayed in Figures 3.7c and 3.7d. The behavior is scattered with mixed trends. The yield of styrene increases in general as the diameter of the hydrogenation tubes increases, whereas the nitrobenzene conversion decreases. Increasing the diameter of the hydrogenation tube enhances both the rate of hydrogen removal from the dehydrogenation side and heat transfer across the membrane from the hydrogenation side by increasing the surface area available for both fluxes. Consequently, styrene is produced at a higher rate on the dehydrogenation side, causing the temperature to drop and the dehydrogenation side to act eventually as a heat sink. This results in decreasing the rate of hydrogen transfer to the hydrogenation side and in increasing the rate of heat transferred from the hydrogenation compartment. Consequently, a drop in nitrobenzene conversion is observed.

In Figure 3.7e and 3.7f, both objectives are plotted against the length of the catalytic reactor. Both show no trend with this variable, and the searching subroutine is limited by the variable bounds. To illustrate the differences in optimal designs of the membrane reactor, three solutions located along the Pareto set have been chosen. For these solutions, the reactor profiles for the styrene yield, the nitrobenzene conversion and the temperatures on both sides have been plotted in Figure 3.8a and 3.8b. The three solutions, whose numerical values are listed in Table 3.5, represent the case where: (*i*) styrene is the product of overriding importance (solution A), (*ii*) both styrene and aniline are equally important (solution B), and finally (*iii*) aniline is the product of overwhelming importance (solution C).

For solution A, the yield of styrene increases monotonically along the reactor on the dehydrogenation side until it reaches around 97%, while the conversion of nitrobenzene cannot achieve more than 21% on the hydrogenation side. The temperature along the dehydrogenation reaction decreases in the first part of the reactor due to the endothermality of the reactions, but it then recovers as a result of the transfer of heat from the hydrogenation side to the dehydrogenation side through the hydrogen membrane wall. The exit temperature of the dehydrogenation side is exactly the same as the feed temperature, indicating the satisfaction of the imposed nonlinear autothermality constraint. The temperature on the hydrogen, but it decreases later due to the transfer of the heat to the dehydrogenation compartment.

For solution B, the styrene yield and nitrobenzene conversion increase on both sides of the reactor compartments until a styrene yield of 56% and a nitrobenzene conversion of 55% are achieved. The temperature profiles on both sides of the reactor are similar to those in solution A.

For solution C, the production of aniline is higher than that of styrene, i.e. 80% nitrobenzene conversion and 49% styrene yield, with no structural differences observed in the temperature profiles on both sides of the reactor compared to solutions A and B. Note that the maximum temperature on both sides of the reactor does not exceed 915 K, thereby protecting the durability of the membranes.

3.9. Sensitivity Analysis Based on Pseudo-Homogeneous Model:

The effects of some key operating variables including the feed temperature and feed pressure of the dehydrogenation side, feed temperature and feed pressure of the hydrogenation side and number of hydrogenation tubes on the styrene yield and nitrobenzene conversion are plotted in Figure 3.9. In this analysis, the effect of each variable has been studied independently while keeping all other variables constant at the nominal values summarized in Table 3.6.

Increasing the feed temperature of the dehydrogenation side enhances both the styrene yield and the nitrobenzene conversion of the coupled reactor as shown in Figure 3.9a. However, it is noticed that above ~910K, the styrene yield drops due to the significance of the reverse reaction. The improvement of the nitrobenzene conversion on the hydrogenation side results from the fact that more hydrogen is available for permeation from the dehydrogenation side to the hydrogenation as the dehydrogenation feed temperature increases.

The effect of the feed pressure on the dehydrogenation on both the styrene yield and nitrobenzene conversion is shown in Figure 3.9b. As the feed pressure on the dehydrogenation side increases, the styrene yield and nitrobenzene conversion increase due to the increase in permeation rate resulting from the larger driving force between the two sides of the coupled reactor.

Figure 3.9c plots the effect of increasing the feed temperature of the hydrogenation side on the styrene yield and nitrobenzene conversion. It is seen that as the feed temperature of the hydrogenation side increases, both the styrene yield and the nitrobenzene conversion increase because the rates of hydrogen permeation and heat transfer are enhanced between the two sides, i.e. high temperature on the hydrogenation side enhances the rate of heat transfer to the dehydrogenation side so that more styrene yield and hydrogen are produced.

Increasing the feed pressure of the hydrogenation side as shown in Figure 3.9d has an insignificant effect on both the styrene yield and the nitrobenzene conversion. Increasing the feed

pressure of the hydrogenation side results in a pressure profile which can prevent hydrogen from diffusing from the dehydrogenation side to the hydrogenation side.

The effect of increasing the number of hydrogenation tubes on both styrene yield and nitrobenzene conversion is shown in Figure 3.9e. As the number of hydrogenation tubes increases, the rate of heat transfer between the two sides of the coupled reactor is enhanced due to the increase in the surface area. This causes the styrene yield on the dehydrogenation side to increase, but the nitrobenzene conversion drops due to the slower reaction.

3.10. Conclusions

In this work, an optimal design of a catalytic membrane coupling dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline has been obtained. To achieve this goal, a bi-objective optimization problem with linear and nonlinear constraints has been formulated. The focus has been on maximizing the styrene yield on the dehydrogenation side while simultaneously maximizing the nitrobenzene conversion on the hydrogenation side. Bounds and constraints with real industrial values have been imposed on both operational and design variables. Two numerical techniques, i.e. the normalized normal constraints (NNC) method and the normal boundary intersection (NBI) method, have successfully solved the problem giving evenly distributed Pareto solutions after applying a Pareto filter. Both techniques gave the same Pareto set although the optimization problems have been solved independently. From this Pareto set, it is seen that there exist two classes of reactor designs with styrene yields and nitrobenzene conversions going from values of about 50% and 80% when nitrobenzene conversion is focused on, to values of about 97% and 20% when the styrene yield is emphasized. The different optimal designs have been illustrated for the coupled catalytic fixed bed membrane reactor and the effects of different decision variables have been explained qualitatively. From the present Pareto optimal results, the designer will be able to select one design for the coupled reactor based on his personal preferences. Hence, these results are very valuable for the procedure of designing a reactor in which both reactions are integrated. Based on the sensitivity analysis, the degree of complexity of the optimization problem may be reduced by fixing some variables at limiting values and searching for optimal values for the remaining ones.

Chemical Reaction	Heat of Reaction	Kinetic Equation	Reference
1. Reactions on Dehydrogenation Side ^a			
$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2$	$\Delta H_{298} = 117.6 \frac{kJ}{mole}$	$r_1 = k_1 \left(p_{EB} - \frac{p_{ST} p_{H_2}}{K_A} \right)$	Elnashaie et al. (1993)
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	$\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$	$r_2 = k_2 p_{EB}$	Elnashaie et al. (1993)
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	$\Delta H_{298} = -54.6 \frac{kJ}{mole}$	$r_3 = k_3 p_{EB} p_{H_2}$	Elnashaie et al. (1993)
$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$	$\Delta H_{298} = 210.2 \frac{kJ}{mole}$	$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2}$	Elnashaie et al. (1993)
$H_2O + CH_4 \rightarrow CO + 3H_2$	$\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$	$r_5 = k_5 p_{H_2O} p_{CH_4}$	Elnashaie et al. (1993)
$H_2O + CO \rightarrow CO_2 + H_2$	$\Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$	$r_6 = k_6 \left(\frac{P}{T^3}\right) p_{H_2O} p_{CO}$	Elnashaie et al. (1993)
2. Reaction on Hydrogenation Side ^b			
$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$	$\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$	$r' = \frac{k' K_{NB} K_{H_2} p'_{NB} \sqrt{p'_{H_2}}}{\left(1 + K_{NB} p'_{NB} + K_{H_2} \sqrt{p'_{H_2}}\right)}$	Amon et al. (1999)

T II 31	P / • 1 • / •			1 4 4	•
Toblo 4 I Summor	v at staichiamatria	aduatione	hante at rangtiane	and reaction rate	NVNPAGGIANG
I ADIC J.I QUIIIIIIAI	• • • • • • • • • • • • • • • • • • • •	cuuations. I	licals of f callions	and i calion i alc	C CADI COMUND.
	,				

^a partial pressures are given in (bar) ^b partial pressures are given in (kPa)

Table 3.2 Numerical values of kinetic pre-exponential constants and activationenergies.

Reaction	$k_{io}{}^{\mathrm{a}}$	E_i (kJ/kmole)	Reference
3.1 ^b	8.32×10^{3}	0.909×10^{5}	
3.2	4.23×10 ⁹	2.080×10^5	
3.3	6.13×10 ³	0.915×10^{5}	Elposhoio et al. (1002)
3.4	3.95×10^{3}	1.040×10^{5}	Emasmale et al. (1995)
3.5	1.42×10^{2}	0.657×10^{5}	
3.6	5.80×10 ¹²	0.736×10^{5}	
3.7 ^c	1.86×10^{-4}	10.0×10^{3}	Amon, et al (1999)

^a $k_i = \frac{10}{36} k_{io} \exp(-\frac{E_i}{RT})$, where k_{io} is the pre-exponential factor, for $1 \le i \le 6$ $k_i = 10^3 k_{io} \exp(-\frac{E_i}{RT})$, for i = 7.

^b The equilibrium constant is calculated by: $K_A = \exp(\frac{-\Delta F}{RT})$, where: $\Delta F = a + bT + cT^2$, $a = 122725.16, b = -126.27 / K, c = -2.194 \times 10^{-3} / K^2$ ^c $K_{NB} = 1.51 \times 10^{-2} kPa$, $K_{H_2} = 0.14 kPa^{-0.5}$

Balance Equations	Mathematical Expressions	Equation			
Dehydrogenation Side					
Mole	$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} r_j (1-\varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J_i$	(3.8)			
Energy	$\frac{dT}{dz} = \frac{\sum_{j=1}^{6} \left[-\Delta H(T)\right]_{j} r_{j} (1-\varepsilon) A_{cs} \rho_{s} + NQ}{\sum_{i=1}^{10} n_{i} C p_{i}}$	(3.9)			
Pressure	$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \left[\frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G\right]$	(3.10)			
	Hydrogenation Side (per tube)				
Mole	$\frac{dn'_i}{dz} = \sigma_i r' (1 - \varepsilon') A'_{cs} \rho'_s + 2\pi r_3 a_i J_i$	(3.11)			
Energy	$\frac{dT'}{dz} = \frac{(2\pi r_3) \sum_{i=1}^{i} a_i J_i \int_{T'}^{T} Cp_i dT + [-\Delta H'(T')]r'(1-\varepsilon')A'_{cs}\rho'_s - Q}{\sum_{i=1}^{4} n'_i Cp'_i}$	(3.12)			
Pressure	$\frac{dP'}{dz} = -\frac{G'}{\rho'_g g_c D'_p} \left(\frac{1-\varepsilon'}{\varepsilon'^3}\right) \left[\frac{150(1-\varepsilon')\mu'_g}{D'_p} + 1.75G'\right]$	(3.13)			
Hydr	ogen diffusion from one hydrogenation tube per unit length				
Diffusion of Hydrogen across the Membrane	$J_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}}\right)$ where: $Q_o = 7.29 \times 10^{-03} \text{ (mole.m)/(m}^2.\text{min.atm}^{0.5}), \ \delta_{H_2} = 25 \times 10^{-6} \text{ m}$ $E_{H_2,P} = 20.5 \times 10^3 \text{ J/mole}$	(3.14)			
Heat transfer from one hydrogenation tube per unit length					
Heat Transferred across the Membrane	$Q = \frac{2\pi r_{1}(T'-T)}{\left[\frac{1}{h'} + \frac{r_{1}}{k_{ss}} \ln\left(\frac{r_{2}}{r_{1}}\right) + \frac{r_{1}}{k_{Pd}} \ln\left(\frac{r_{3}}{r_{2}}\right) + \frac{r_{1}}{r_{2}h}\right]}$ where: $k_{ss} = 22.88 \text{ W/m} \times \text{K}, \ k_{Pd} = 93.3 \text{ W/m} \times \text{K}$ $\frac{hD_{t}}{k_{g}} = 0.813 \left(\frac{D_{p}G}{\mu_{g}}\right)^{0.9} \exp\left(-\frac{6D_{p}}{D_{t}}\right)$ $\frac{h'D_{t}'}{k_{g}'} = 3.50 \left(\frac{D_{p}'G'}{\mu_{g}'}\right)^{0.7} \exp\left(-\frac{4.6D_{p}'}{D_{t}'}\right)$	(3.15)			

or.
)

Dehydrogenation Side					
Item	Value	Unit			
Styrene molar feed flowrate	0.1861	mole/s			
Benzene molar feed flowrate	0.0306	mole/s			
Toluene molar feed flowrate	0.2444	mole/s			
Catalyst density	2146.3	kg/m ³			
Catalyst particle diameter	4.7×10 ⁻³	m			
Bed voidage	0.48				
Hydrogenation Side					
Catalyst density	1400	kg/m ³			
Catalyst particle diameter	3.6×10 ⁻³	m			
Bed voidage	0.46				

Table 3.4 Values of constant variables in the optimization problem.

Parameter		Optimal Solution A		Optimal Solution B		Optimal Solution C	
		Value	Unit	Value	Unit	Value	Unit
ion	Feed Molar of Ethylbenzene	7.66	mole/s	9.36	mole/s	11.27	mole/s
genat de	Steam-to- Ethylbenzene Ratio	7.00		7.00		20.00	
ydro Sid	Feed Temperature on Shell Side	825.41	K	780.00	K	820.02	K
Deh	Feed Pressure on Shell Side	4.00	bar	2.52	bar	4.00	bar
uo	Feed Molar of Nitrobenzene	0.005	mole/s	0.002	mole/s	0.002	mole/s
enatio le Jube)	Steam-to- Nitrobenzene Ratio	4.00		4.00		4.00	
drog Sic	Feed Temperature on Tube Side	825.41	K	780.00	K	820.02	К
Hy	Feed Pressure on Tube Side	3.62	bar	1.00	bar	1.00	bar
_	No. of Hydrogenation Tubes	2500	tubes	1582	tubes	1000	tubes
nsional ables	Area-Equivalent Diameter on Dehydrogenation Side	3.00	m	2.39	m	1.95	m
)imeı Vari	Diameter of Hydrogenation Tube	0.048	m	0.035	m	0.040	m
П	Reactor Length	4.00	m	4.00	m	4.00	m
ctive tions	Yield of Styrene	0.975		0.564		0.491	
Obje funct	Conversion of Nitrobenzene	0.211		0.555		0.796	

 Table 3.5 Representative solutions for the Pareto frontier.

Parameter	Values	Units			
Dimensional Variables					
Cross-sectional area-equivalent diameter of dehydrogenation side	1.95	m			
Inside diameter of hydrogenation tubes	3.5×10 ⁻²	m			
Length of reactor	4.0	m			
Operating Conditions of Dehy	drogenation Si	de			
Feed molar flowrate of ethylbenzene	10.242	mole/s			
Feed molar flowrate of styrene	0.1861	mole/s			
Feed molar flowrate of benzene	0.0306	mole/s			
Feed molar flowrate of toluene	0.2444	mole/s			
Feed molar flowrate of steam	125.86	mole/s			
Bed voidage	0.48				
Operating Conditions per tube on Hydrogenation Side					
Feed molar flowrate of nitrobenzene	0.003	mole/s			
Feed molar flowrate of steam	0.008	mole/s			
Bed voidage	0.46				

Table 3.6 Nominal values of the fixed variables used in the sensitivity analysis



Figure 3.1 Conceptual design of integrated catalytic membrane reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene.



Figure 3.2 Flowchart showing how the Tomlab solvers, i.e. glbDirect and snopt, are linked to the reactor model.



Figure 3.3 Pareto optimal set obtained by simultaneous maximization of styrene yield and nitrobenzene conversion.



Figure 3.4 (a, b) Feed molar flowrate of ethylbenzene; (c, d) Steam-to-ethylbenzene molar ratio on dehydrogenation side; (e, f) Feed temperature on dehydrogenation side corresponding to Pareto optimal set.



Figure 3.5 (a, b) Feed pressure on dehydrogenation side; (c, d) Molar feed of nitrobenzene on hydrogenation side; (e, f) Steam-to-nitrobenzene molar ratio on hydrogenation side corresponding to Pareto optimal set.



Figure 3.6 (a, b) Feed temperature on hydrogenation side; (c, d) Feed pressure on hydrogenation side; (e, f) Number of hydrogenation tubes corresponding to Pareto optimal set.


Figure 3.7 (a, b) Net diameter of dehydrogenation side; (c, d) Hydrogenation tube diameter; and (e, f) Length of reactor corresponding to the Pareto optimal set.



Figure 3.8 (a) Styrene yield and nitrobenzene yield along the membrane reactor at three different optimal Pareto solutions; (b) Temperature profiles on both shell andtube sides of the membrane reactor at three different optimal Pareto solutions.



Figure 3.9: Sensitivity analysis on some key operating variables.

3.11. References

- Abdalla BK, Elnashaie SSEH. Fluidized bed reactors without and with selective membranes for the catalytic dehydrogenation of ethylbenzene to styrene. Journal of Membrane Science 1995; 101(1-2): 31-42.
- Abdalla BK, Elnashaie SSEH. A membrane reactor for the production of styrene from ethylbenzene. Journal of Membrane Science 1993; 85(3):229-239.
- Abdalla BK, Elnashaie SSEH. Catalytic dehydrogenation of ethylbenzene to styrene in membrane reactors. AICHE Journal 1994; 40(12):2055-2059.
- Babu BV, Chakole PG, Syed Mubeen JH. Multiobjective differential evolution (MODE) for optimization of adiabatic styrene reactor. Chemical Engineering Science 2005; 60(17):4822-4837.
- Bhaskar V, Gupta SK, Ray AK. Applications of multiobjective optimization in chemical engineering. Reviews in Chemical Engineering 2000; 16(1):1-54.
- Cheng S, Chen H, Chang H, Chang C, Chen Y. Multi-objective optimization for two catalytic membrane reactors-Methanol synthesis and hydrogen production. Chemical Engineering Science 2008; 63(6):1428-1437.
- Clough DE, Ramirez WF. Mathematical modelling and optimization of the dehydrogenation of ethylbenzene to form styrene. AICHE Journal 1976; 22(6):1097-1105.
- Das I, Dennis J. Normal-boundary intersection: A new method for generating the Pareto surface in nonlinear multicriteria optimization problems. SIAM journal on optimization 1998; 8:631-657.
- Das I, Dennis JE. Closer look at drawbacks of minimizing weighted sums of objectives for Pareto set generation in multicriteria optimization problems. Structural Optimization 1997; 14(1):63-69.
- Deb K. Multi-objective optimization using evolutionary algorithms. Chichester, England: John Wiley & Sons; 2001.
- Deb K, Pratap A, Agarwal S, Meyarivan T. A fast and elitist multiobjective genetic algorithm: NSGA-II. IEEE Transactions on Evolutionary Computation 2002; 6(2):182-197.

- Elnashaie, S.S.E.H.; Moustafa, T.; Alsoudani, T.; Elshishini, S.S. Modeling and basic characteristics of novel integrated dehydrogenation-hydrogenation membrane catalytic reactors. Computers and Chemical Engineering 2000; (24): 1293-1300.
- Froment GF, Bischoff KB. Chemical reactor analysis and design. 2nd ed. New York: Wiley; 1990.
- Hermann C, Quicker P, Dittmeyer R. Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor. Journal of Membrane Science. 1997; 136(1-2):161-172.
- Leineweber DB, Bauer I, Bock HG, Schlöder JP. An efficient multiple shooting based reduced SQP strategy for large-scale dynamic process optimization. Part I: Theoretical aspects. Computers and Chemical Engineering 2003a; 27(2):157-166.
- Leineweber DB, Schäfer A, Bock HG, Schlöder JP. An efficient multiple shooting based reduced SQP strategy for large-scale dynamic process optimization. Part II: Software aspects and applications. Computers and Chemical Engineering 2003b; 27(2):167-174.
- Li Y, Rangaiah GP, and Ray AK. Optimization of styrene reactor design for two objectives using a genetic algorithm. International Journal of Chemical Reactor Engineering 2003; 1: <u>http://www.bepress.com/ijcre/vol1/A13</u>.
- Lim Y, Floquet P, Joulia X. Efficient implementation of the normal boundary intersection (NBI) method on multiobjective optimization problems. Industrial and Engineering Chemistry Research 2001; 40(2):648-655.
- Logist F, Van Erdeghem PMM, Van Impe JF. Efficient deterministic multiple objective optimal control of (bio)chemical processes. Chemical Engineering Science 2009; 64(11):2527-38.
- Messac A, Ismail-Yahaya A, Mattson CA. The normalized normal constraint method for generating the Pareto frontier. Structural and Multidisciplinary Optimization 2003; 25(2):86-98.
- Messac A, Mattson C. Normal constraint method with guarantee of evenrepresentation of complete Pareto frontier. AIAA Journal 2004; 42(10):2101–11.
- Miettinen K. Nonlinear Multiobjective Optimization. Boston: Academic Publishers; 1999.

- Moustafa TM, Elnashaie SSEH. Simultaneous production of styrene and cyclohexane in an integrated membrane reactor. Journal of Membrane Science 2000; 178(1-2):171-184.
- Sangeetha P, Shanthi K, Rao KSR, Viswanathan B, Selvam P. Hydrogenation of nitrobenzene over palladium-supported catalysts-Effect of support. Applied Catalysis A: General 2009; 353(2):160-165.
- Sheel JGP, Crowe CM. Simulation and Optimization of an Existing Ethylbenzene Dehydrogenation Reactor. Canadian Journal of Chemical Engineering. 1969; 47(2):183-187.
- Srinivas N, Deb K. Multiobjective function optimization using nondominated sorting genetic algorithms. Evolutionary Computation Journal 1995; 2:221-248.
- Tarafder A, Rangaiah GP, Ray AK. Multiobjective optimization of an industrial styrene monomer manufacturing process. Chemical Engineering Science 2005a; 60(2):347-363.
- Tarafder A, Lee BCS, Ray AK, Rangaiah GP. Multiobjective optimization of an industrial ethylene reactor using a nondominated sorting genetic algorithm. Industrial and Engineering Chemistry Research 2005b; 44(1):124-141.
- Yee AKY, Ray AK, Rangaiah GP. Multiobjective optimization of an industrial styrene reactor. Computers and Chemical Engineering 2003; 27(1):111-130.

CHAPTER 4 HETEROGENEOUS MODELING OF AUTOTHERMAL MEMBRANE REACTOR COUPLING DEHYDROGENATION OF ETHYLBENZENE TO STYRENE WITH HYDROGENATION OF NITROBENZENE TO ANILINE: FICKIAN DIFFUSION MODEL[†]

4.1. Introduction

Coupling of reactions in a single reactor can be very beneficial, offering a number of advantages such as eliminating unnecessary heat transfer units (Stitt, 2004), reducing overall heat losses, cost savings (Fukuhara and Igarashi, 2005) and significant gains in yield and/or conversions due to shifting the thermodynamic equilibrium conversion by continuously removing one of the reaction products and supplying heat to the endothermic reactions (Abashar, 2004).

In the last two decades, a number of studies have appeared addressing the usefulness of reaction coupling. An interesting reaction for this purpose involves the dehydrogenation of ethylbenzene to styrene. Abdalla and Elnashaie (1993) developed a rigorous model to describe the behavior of a membrane reactor in which ethylbenzene was dehydrogenated to styrene. The dusty gas model was used to describe the diffusion inside the catalyst pellets. Later, this model was used to extract intrinsic kinetics from data obtained from an industrial reactor and to investigate the potential economic advantages of a hydrogenselective membrane. It was found that a membrane reactor could considerably improve the ethylbenzene conversion, and the yield and selectivity of styrene. Abdalla and Elnashaie (1994) studied the effect of the sweep gas flow rates in a catalytic membrane reactor in which dehydrogenation of ethylbenzene to styrene took place. An appreciable enhancement in ethylbenzene conversion, styrene yield and selectivity were observed in the proposed membrane reactor. Abdalla and Elnashaie (1995) proposed a fluidized bed

[†] A slightly revised version of this chapter will be submitted for publication.

with and without a selective membrane for dehydrogenating ethylbenzene to styrene. Different design and operating parameters, i.e. bubble diameter, steam-to-ethylbenzene ratio, feed temperature, and number of fluidized beds in series, were investigated. It was demonstrated that a careful choice of those parameters could improve the ethylbenzene conversion and styrene yield compared to industrial fixed bed reactors. Hermann et al. (1997) studied dehydrogenation of ethylbenzene to styrene in a composite Pd/porous stainless steel membrane fixed bed reactor. A model was presented in which different types of diffusion were considered. After adjusting the kinetics available to match the conversion and selectivity, the model predicted more than 90% ethylbenzene conversion as the pressure increased, with no observable decrease in styrene selectivity.

Elnashaie et al. (2000) mathematically coupled dehydrogenation of ethylbenzene to styrene with hydrogenation of benzene to cyclohexane in a membrane fixed bed reactor. This study replaced the sweep gas on the shell side with a second useful reaction to produce another useful product, i.e. cyclohexane. Both cocurrent and countercurrent configurations of the membrane reactor were considered with kinetics of four different catalysts, one being an industrial catalyst. With commercial membranes, the new configured reactor was predicted to give 79% ethylbenzene conversion, and 72% styrene yield, significantly higher than for the industrial fixed bed reactor. Moustafa and Elnashaie (2000) investigated coupling dehydrogenation of ethylbenzene with the hydrogenation of benzene in a membrane reactor. A rigorous mathematical model was developed in which the intraparticle diffusion on both sides was considered. In the hybrid reactor, the predicted yield of styrene was as high as 87%. Abashar (2004) studied the coupling of the same two reactions, but in a fixed bed reactor. The reactor chamber contained intermingled dehydrogenation and hydrogenation catalysts. A number of the operating parameters were examined and a substantial increase in ethylbenzene conversion was predicted in the new fixed bed reactor.

In chapter 2, coupling of dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline in a shell-and-tube autothermal reactor was modeled. The model included for the first time heat transfer across the membrane due to hydrogen diffusion, as well as due to conduction. Both cocurrent and countercurrent configurations were examined, and substantial enhancement was predicted compared to the fixed bed reactor. For the operating conditions investigated, the conversion reached 23.4% for the uncoupled adiabatic fixed bed case, 54.6% for the cocurrent membrane reactor, and 61.7% for the membrane reactor in a countercurrent flow configuration. The styrene yield predicted for the uncoupled adiabatic fixed bed was 18.9%. For the membrane reactor, the predicted yield increased to 52.5% for the cocurrent flow configuration and 57.7% for the countercurrent case. Apart from membrane reactors, other forms and concepts of reaction coupling, such as coupling endothermic reactions with exothermic ones for efficient utilization of energy, have also been considered (Czechowicz et al., 2004; Fukuhara and Igarashi, 2005; Glockler et al., 2003; van Sint Annaland and Nijssen, 2002; Van et al., 2002).

These studies indicate that component effectiveness factors can play a significant role for dehydrogenation of ethylbenzene to styrene in fixed bed reactors. As a result, the homogenous model of in chapter 2 should be adjusted to consider the catalyst intraparticle diffusion on both sides of the membrane reactor. To achieve this aim, the diffusion model based on Fick's law is extended in order to account for diffusion inside the catalyst pellets on both sides of the membrane. This new model is then used: (i) to study the molar flow rates of selected key components and temperature profiles compared with those from the pseudo-homogeneous model; (ii) to evaluate the performance of optimal reactor designs in terms of the styrene yield on the dehydrogenation side, conversion of nitrobenzene on the hydrogenation side, and temperature profiles on both sides of the reactor.

4.2. Reactor Configuration

The configuration of interest is portrayed in Figure 4.1. In the shell compartment packed with catalyst particles, ethylbenzene (EB) is dehydrogenated to produce styrene (ST) as the main product; benzene (BZ), toluene (TO), ethylene and other light gases are side products. The chemical equations representing the reactions are:

$$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2 \qquad \Delta H_{298} = 117.6\frac{\text{kJ}}{\text{mole}}$$
 (4.1)

$$C_6H_5CH_2CH_3 \to C_6H_6 + C_2H_4$$
 $\Delta H_{298} = 105.4 \frac{\text{KJ}}{\text{mole}}$ (4.2)

1 т

1 -

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$$
 (4.3)

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$$
 $\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$ (4.4)

$$H_2O + CH_4 \rightarrow CO + 3H_2$$
 $\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$ (4.5)

$$H_2O + CO \rightarrow CO_2 + H_2$$
 $\Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$ (4.6)

The first reaction in this network is the main reversible, endothermic one. From Le Chatelier's principle, the forward reaction, i.e. production of styrene, is favored by operating at low pressure and high temperature.

Hydrogen produced in this compartment diffuses through palladium hydrogen-selectivemembrane walls to the inside of cylindrical tubes extending along the reactor. The tube walls are permeable to hydrogen with a layer of stainless steel of a thickness of 1.2 mm coated with a palladium layer of thickness 20 μ m. On the tube side, the diffused hydrogen reacts with nitrobenzene (NB) to produce aniline (AN):

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
 $\Delta H_{298} = -433.0 \frac{\text{kJ}}{\text{mole}}$ (4.7)

This reaction is irreversible and highly exothermic. In chapter 2, it was shown that coupling these two reactions, i.e. dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene, could be very beneficial. Removing hydrogen from the dehydrogenation side and providing heat to the same side from the hydrogenation heat of reaction were predicted to play very important roles in increasing the styrene yield. The external wall of the coupled reactor is treated as adiabatic, a reasonable assumption due to

the small surface area-to-volume ratio. Expressions for the rate of reactions and numerical values for the pre-exponential constants and activation energies are listed in Tables 4.1 and 4.2. The shell side of this reactor is assumed to be packed with an iron oxide (Fe₂O₃) catalyst promoted with potassium carbonate (K₂CO₃) and chromium oxide (Cr₂O₃) while the tube side is packed with a palladium catalyst supported on an α -alumina carrier.

4.3. Reactor Model

The differential equations governing the behavior of the catalytic membrane reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene are based the following assumptions:

- 1. Steady-state operation.
- 2. Ideal gas behavior in both the tube and shell of the reactor.
- 3. Plug flow for the fixed beds on both shell and tube sides, with axial Peclet numbers ~1000.
- 4. Heterogeneous model, i.e. significant gradients in concentrations / temperatures inside the catalyst pellets.
- 5. The flow rate on both sides is high enough to minimize the external mass and heat transfer resistances. Hence, only intraparticle diffusion needs to be considered.
- 6. Reactor external wall well insulated leading to an adiabatic reactor.
- 7. Catalyst deactivation is neglected.
- 8. Pressure gradients in both the shell and tubes are based on Ergun's equation.
- 9. Spherical catalyst pellets.
- 10. Cocurrent flow in the shell and tube.

The reactor model differential equations are derived by considering an infinitesimal element inside the reactor through which both moles and energy flow. Hydrogen diffuses from the dehydrogenation side to the hydrogenation side, whereas heat is transferred from the hydrogenation to the dehydrogenations side. The reactor model equations (4.8) to

(4.15) and rates of both hydrogen diffusion and heat transfer per unit length and are given in Table 4.3.

The model equations describing the diffusion inside the catalyst pellets are based on the following assumptions.

- 1. Steady-state molar and energy flow.
- 2. Porous structure of all catalyst pellets is spatially ant timewise uniform.
- 3. Ideal gas law.
- 4. The concentration and temperature profiles are symmetrical around the centre of the spherical catalyst particles.
- 5. External mass and heat transfer resistances are negligible
- 6. Negligible viscous flow inside the pellets inducing isobaric diffusion.
- Convective diffusion is neglected; only ordinary molecular and Knudsen diffusion are significant.
- 8. Diffusion is represented by Fick's law with the component diffusion coefficient obtained from molecular diffusion and Knudsen diffusion coefficients.
- 9. For mathematical simplicity, the variation of the effective component diffusivity coefficient along the radial direction is negligible.
- 10. Heat flux introduced by species, i.e. Dufour effect, is negligible.
- 11. Thermal conductivities of the catalyst pellets on both the shell and tube sides of the reactor are uniform on each side.

To derive the catalyst model equations, a small spherical shell inside the catalyst pellets is considered across which both moles and heat flow as shown in Figure 4.2. Applying the balance equations, and expressing the molar flux using Fick's law leads to the following.

Catalyst mole balance equation on dehydrogenation side:

$$\frac{d^2 C_i}{dy^2} + \frac{2}{y} \frac{dC_i}{dy} = -\frac{1}{D_{ie}} \sum_{j=1}^6 \sigma_{ij} r_j \rho$$
(4.16)

Catalyst energy balance equation on dehydrogenation side:

$$\frac{d^2T}{dy^2} + \frac{2}{y}\frac{dT}{dy} = \frac{1}{k_e}\sum_{j=1}^{6} \left[\Delta H(T)\right]_j r_j \rho$$
(4.17)

Catalyst mole balance equation on hydrogenation side:

$$\frac{d^2 C'_i}{dy'^2} + \frac{2}{y'} \frac{dC'_i}{dy'} = -\frac{\sigma'_i r' \rho'}{D'_{ie}}$$
(4.18)

Catalyst energy balance equation on hydrogenation side:

$$\frac{d^2 T'}{dy'^2} + \frac{2}{y'} \frac{dT'}{dy'} = \frac{\left[\Delta H(T)\right]' r'\rho'}{k'_e}$$
(4.19)

These coupled equations form a split boundary value problem describing the molar and energy flow inside the catalyst on both the dehydrogenation and hydrogenation sides. The boundary conditions are:

• Dehydrogenation side:

$$y = 0 \Longrightarrow \begin{cases} \frac{dC_i}{dy} = 0\\ \frac{dT}{dy} = 0 \end{cases}$$
(4.20)

$$y = R_p \Longrightarrow \begin{cases} C_i = C_{is} \\ T = T_s \end{cases}$$
(4.21)

• Hydrogenation side:

$$y' = 0 \Longrightarrow \begin{cases} \frac{dC'_i}{dy'} = 0\\ \frac{dT'}{dy'} = 0 \end{cases}$$
(4.22)

$$y' = R'_p \Longrightarrow \begin{cases} C'_i = C'_{is} \\ T' = T'_s \end{cases}$$
(4.23)

The effective diffusivities, i.e. D_{ie} and D'_{ie} , of component *i* in equations (4.16) and (4.18) are calculated considering both the effective binary diffusivity of component *i* in a mixture D^e_{im} and the effective Knudsen diffusivity D^e_{ik} (Elnashaie et al., 1993; R. B. Bird, W.E. Stewart, E.N. Lightfoot, 1960):

$$\frac{1}{D_{ie}} = \frac{1}{D_{im}^{e}} + \frac{1}{D_{ik}^{e}}$$
(4.24)

The binary diffusivity of component *i* in the above equation is estimated on the dehydrogenation side from the well-known Wilke equation (Elnashaie et al., 1993; R. B. Bird, W.E. Stewart, E.N. Lightfoot, 1960):

$$\frac{1}{D_{im}} = \frac{1}{1 - x_i} \sum_{\substack{j=1\\j \neq i}}^{10} \frac{x_i}{D_{ij}}$$
(4.25)

The effective diffusivities are obtained (Elnashaie et al., 1993) from:

$$D_{im}^{e} = \frac{\varepsilon}{\tau} D_{im} \tag{4.26}$$

where ε is the internal porosity of the catalyst pellet and τ is the tortuosity, and both are assumed to be isotropic properties.

The numerical solution of model equations (4.16)-(4.19) evaluates the average reaction rates as well as the average heat released or absorbed due to reactions. Those values can be related to the reaction rates and heat released or absorbed at bulk conditions, i.e. concentrations and temperature, through the concept of *effectiveness factors*, defined for chemical reactions as the ratio of the rate of reaction with pore resistance to the rate of reaction evaluated at the surface conditions:

$$\eta_{j} = \frac{\int_{0}^{R_{p}} r_{j} \rho(4\pi y^{2}) dy}{r_{j}(C_{is}, T_{s}) \rho(\frac{4}{3}\pi R_{p}^{3})}$$
(4.27)

with $1 \le j \le 6$ for dehydrogenation side and j = 1 for hydrogenation side. When the dimensionless catalyst radius ($\omega = y/R_p$) is introduced into equation (4.27), the volume-averaged reaction rate can be formulated as:

$$\eta_{j} r_{j} (C_{is}, T_{s}) = 3 \int_{0}^{1.0} r_{j} \omega^{2} d\omega$$
(4.28)

with $1 \le j \le 6$ for the dehydrogenation side and j = 1 for the hydrogenation side. For non-isothermal catalyst pellets, a thermal effectiveness factor, relating the actual heat released or absorbed to that at the surface conditions, can be defined as:

$$\eta_{j}^{H}\left[-\Delta H\left(T_{s}\right)\right]r_{j}\left(C_{is},T_{s}\right)=3\int_{0}^{1.0}r_{j}\left[-\Delta H\left(T\right)\right]\omega^{2}d\omega$$

$$(4.29)$$

Component effectiveness factors can be defined as:

$$\eta_{i} = \frac{\sum_{j=1}^{j} \sigma_{ij} \int_{0}^{R_{p}} r_{j} \rho(4\pi y^{2}) dy}{\sum_{j=1}^{j} \sigma_{ij} r_{j} (C_{is}, T_{s}) \rho(\frac{4}{3} \pi R_{p}^{3})}$$
(4.30)

again with $1 \le j \le 6$ for the dehydrogenation side and j = 1 for the hydrogenation side. Integral terms in equations (4.27) to (4.30) are evaluated here by the *trapezoidal rule*. Equation (4.28) and (4.29) representing the actual reaction rate and heat released or absorbed are used to update reactor model equations (4.8)-(4.13) in Table 4.3.

The conversions of ethylbenzene and nitrobenzene on both sides of the membrane reactor and component yields on the dehydrogenation side are defined as:

Conversions
$$\begin{cases} X_{EB} = \frac{n_{EBo} - n_{EB}}{n_{EBo}} & \text{on Dehydrogenation Side} \\ X_{NB} = \frac{n_{NBo} - n_{NB}}{n_{NBo}} & \text{on Hydrogenation Side} \end{cases}$$
(4.31)

Yields
$$\begin{cases} Y_{ST} = \frac{n_{ST} - n_{STo}}{n_{EBo}} \\ Y_{BZ} = \frac{n_{BZ} - n_{BZo}}{n_{EBo}} \\ Y_{TO} = \frac{n_{TO} - n_{TOo}}{n_{EBo}} \end{cases}$$
(4.32)

The sequence of computations followed to link the reactor model equations with the catalyst pellets model equations is shown schematically in Figure 4.3. The sequence starts by using the bulk conditions to establish the boundary conditions to solve the catalyst model equations (4.16) and (4.17) on the dehydrogenation side and (4.18) and (4.19) on the hydrogenation side. These numerical solutions are then used to evaluate the molar and heat flux at the surface of the catalyst numerically by evaluating equations (4.28) and (4.29), substituted in the reactor model equations, i.e. (4.8) to (4.13), which can then be

integrated one step forward. This procedure is repeated until the entire length of the reactor is covered.

In this computational sequence, two Matlab[®] (The MathWorks, Natick) subroutines are invoked. The catalyst model equations based on Fickian diffusion are solved by bvp4c with a relative tolerance of 1×10^{-4} , while the reactor model equations are integrated by ode15s with a relative tolerance of 1×10^{-8} .

4.4. Results and Discussion

The effect of the intraparticle diffusion on the performance of the catalytic membrane reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene to aniline was simulated for the operating conditions listed in Table 4.4. The component molar flow rates and feed pressure on the dehydrogenation side are based on industrial fixed bed reactors. A feed temperature difference of 20 K is chosen to ensure that heat always transfers in the right direction, i.e. from the hydrogenation to the dehydrogenation side.

In the following sub-sections, the predictions of several reactor variables are compared and discussed based on three models, i.e. (*i*) pseudo-homogeneous model, (*ii*) heterogeneous model with isothermal catalyst pellets, and (*iii*) heterogeneous model with non-isothermal catalyst pellets.

4.4.1. Conversion of ethylbenzene and nitrobenzene

The conversion of (i) ethylbenzene on the dehydrogenation side and of (ii) nitrobenzene on the hydrogenation side are plotted versus the dimensionless distance along the reactor in Figures 4.4a and 4.4b for the pseudo-homogeneous and heterogeneous model with isothermal and non-isothermal catalyst pellets. In Figure 4.4a, the conversion of ethylbenzene on the dehydrogenation side of the catalytic membrane reactor increases monotonically along the catalytic membrane reactor due to the consumption of ethylbenzene. For the selected operating and design conditions, the pseudo-homogeneous model predicts an ethylbenzene conversion of ~88%. When the effect of intraparticle diffusion is included, the ethylbenzene conversion predicted by the heterogeneous model is significantly lower, ~78% for isothermal pellets and ~71% for non-isothermal pellets.

Conversion of nitrobenzene on the hydrogenation side of the catalytic membrane reactor in Figure 4.4b shows similar behavior to that of ethylbenzene, i.e. it increases monotonically along the reactor. It is predicted to reach ~68% by the homogenous model, ~59% by the heterogeneous model for isothermal catalyst pellets, and ~52% by the heterogeneous model for non-isothermal pellets.

4.4.2. Yield of styrene, benzene, and toluene on dehydrogenation side

Figures 4.5a, 4.5b, and 4.5c, plot the yields of styrene, benzene, and toluene versus the dimensionless axial distance along the reactor. All three yields increase along the reactor, with appreciable differences in prediction among the models. The pseudo-homogeneous model for the catalytic membrane reactor predicts a styrene yield of ~82%, a benzene yield of ~5.0%, and a toluene yield of ~1.0%. The heterogeneous model, on the other hand, predicts a styrene yield of ~73%, a benzene yield of ~4.6%, and a toluene yield of ~0.8% for isothermal catalyst pellets while it predicts corresponding yields of ~69%, ~3.2% and ~0.6% for non-isothermal pellets.

4.4.3. Hydrogen molar flow rates on dehydrogenation and hydrogenation sides

The molar flow rates of hydrogen on both sides of the catalytic membrane reactor are plotted versus the dimensionless axial distance in Figures 4.6a and 4.6b. As shown in Figure 4.6a, the hydrogen molar flow rate on the dehydrogenation side predicted by both homogenous and heterogeneous models increases monotonically in the first portion of the reactor fraction length until it reaches a maximum where the rate of hydrogen diffusion to the hydrogenation side is balanced by the hydrogen net production due to the reactions. After that, the hydrogen molar flow rate continues at a nearly constant level to the reactor

exit. The hydrogen flow rate predicted by the heterogeneous model for the nonisothermal catalyst pellets is significantly lower than that predicted by either the homogenous model or the heterogeneous model with isothermal catalyst pellets, due to the significant effect of temperature. This gives a strong indication of the significance of intraparticle heat resistance in retarding the chemical reactions and the diffusion through the membranes.

The molar flow rate inside the hydrogenation tubes is plotted in Figure 4.6b as a function of the dimensionless axial distance. All three models predict monotonically increasing profiles, with a significant difference for the heterogeneous model with non-isothermal catalyst pellets. At the reactor entrance, the homogenous model and the heterogeneous model for the isothermal catalyst pellets give similar predictions over 40% of the reactor length, with a somewhat higher subsequent value for the heterogeneous model with isothermal catalyst pellets resulting from a higher hydrogen diffusion rate compared to that predicted by the homogenous model. The difference in the predictions of these two models becomes more pronounced as the reactor exit is approached. The prediction of the heterogeneous model for the non-isothermal case is considerably lower than for the other two models due to the temperature gradient inside the catalyst pellets.

4.4.4. Temperature profiles along coupled reactor

Temperature profiles along the reactor on both the shell and tube sides are plotted in Figures 4.7a and 4.7b. In Figure 4.7a, the temperature on the dehydrogenation side decreases over the first 15% of the reactor length due to the net endothermic heat of the reaction. A point is then reached where the heat lost is balanced by the heat gained from the hydrogenation side. Given the large temperature difference established between the two sides of the integrated reactor, the temperature on the shell side then increases over the reminder of the reactor due to significant heat transfer from the tube side. The temperature profiles predicted by all three models are similar in shape.

In Figure 4.7b, the temperature profiles predicted by the three models, are plotted against dimensionless axial distance along the reactor. The temperature on the hydrogenation side rises due to the high exothermic heat of reaction. A clear maximum temperature is obtained from the homogenous model about 40% of the way along the reactor at which the heat transferred to the dehydrogenation side balances the endothermic requirement of the main reaction. This point is clearly observable for the pseudo-homogeneous model, while it is less observable in the profiles predicted by the heterogeneous model for isothermal catalyst pellets, and not observable for the heterogeneous model with non-isothermal catalyst pellets.

From the temperature profiles on both sides of the reactor, it should be noted that the intraparticle diffusion resistance not only retards the chemical reactions, but also the heat transfer between the two sides by reducing the driving force, i.e. the temperature difference between the dehydrogenation and hydrogenation compartments.

4.4.5. Reaction effectiveness factors and reaction rates

Intraparticle effectiveness factors, defined as the ratios of the observed rates of reaction to those evaluated if the surface conditions prevailed throughout the catalyst pellets are plotted versus the bulk temperature in Figure 4.8 for both sides of the membrane. Actual reaction rates and those evaluated at the conditions of the catalyst surface are plotted in Figure 4.9. In Figure 4.8a, effectiveness factors for both reactions (4.1) and (4.2) exhibit a strong nonlinear behavior with different turning points. The bulk temperatures at which the turns take place correspond to the axial location inside the reactor at which the net endothermic heat of reactions balances the heat transferred from the hydrogenation side. While the effectiveness factors of reactions (4.1) and (4.2) for the isothermal case are slightly lower than 1.0, those for the non-isothermal case are significantly lower, indicating the significance of the intraparticle heat resistance. Consequently, the difference between the actual reaction rates and these evaluated at the conditions of the catalyst pellet surface for reactions (4.1) and (4.2) is higher for the non-isothermal case than for the isothermal catalyst pellets, as shown in Figure 4.9. As the bulk temperature

increases, the actual reaction rates for both the isothermal and non-isothermal cases and those evaluated at the surface conditions approach each other. The actual rate of reaction (4.1) for the isothermal case coincides with that for the non-isothermal case when the bulk temperature on the dehydrogenation side exceeds 865 K.

The effectiveness factors of the other reactions, i.e. reaction (4.3), (4.4), (4.5), and (4.6), for the isothermal and non-isothermal catalyst pellets, plotted in Figure 4.8b also exhibit highly nonlinear behavior with different turning points. Their values start from infinity, decrease sharply in the first part of the reactor, then turn around and decrease as the bulk temperature increases until they fall below unity. The initial infinite values of the effectiveness factors result from the fact that the reaction rates at the surface of the catalyst start at zero due to the absence of some components in the bulk such as hydrogen. In Figure 4.8b, all four effectiveness factors of the reactions pass through a point in the reactor where the intraparticle resistances are negligible, i.e. $\eta_3 = \eta_4 = \eta_5 = \eta_6$ = 1.0. This point can be identified in Figure 4.9 by those points at which the actual reaction rates are equal to those evaluated at the surface conditions. The temperature at which this occurs varies from one reaction to another, e.g. ~860 K for reaction (4.3), ~861 K for reaction (4.4), ~875 K for reaction (4.5), and ~864 K for reaction (4.6) for isothermal pellets and ~873 K for reaction (4.3), ~874 K for reaction (4.4), ~870 K for reaction (4.5), and ~868 K for reaction (4.6) for non-isothermal pellets. The large effectiveness factor in Figure 4.8b indicates the large differences between the actual reaction rates and those evaluated at the catalyst surface, with the consequence that the homogenous model predictions must be interpreted with care, e.g. when utilized in optimization studies.

On the tube side, the hydrogenation reaction rate is zero at the entrance of the reactor as shown in Figure 4.9 due to the absence of hydrogen in the feed stream. Due to the diffusion of hydrogen from the dehydrogenation side to the hydrogenation side, the intraparticle effectiveness factor increases sharply from $\eta \ll 1.0$ to ~0.7. The hydrogenation effectiveness factors for isothermal and non-isothermal catalyst pellets in Figure 4.8c vary in a nonlinear manner with the bulk temperature. The effectiveness

factors for both isothermal and non-isothermal cases are almost identical for temperatures on the hydrogenation side lower than 970 K. Similar behavior is shown in Figure 4.9, with a constant difference between the actual reaction rates and those evaluated at the condition of the surface of the catalyst pellets. For temperatures exceeding 970 K, the effectiveness factors for both cases diverge, approaching unity as shown in Figure 4.8c and 4.9, with the actual reaction rates and those evaluated at the surface approach each other.

4.4.6. Component effectiveness factors

The component effectiveness factors defined by equation (4.30) are the ratios of the actual net production rates of component *i* to those evaluated for the surface conditions of the catalyst pellets. In Figure 4.10, they are plotted for key species i.e., ethylbenzene, styrene, hydrogen, benzene, toluene and nitrobenzene for the heterogeneous model with both isothermal and non-isothermal catalyst pellets. On the dehydrogenation side, the component effectiveness factors show a non-monotonic behavior when plotted against the dimensionless axial distance along the reactor for all components except toluene for both isothermal and non-isothermal catalyst pellets. The toluene effectiveness factor is infinite at the inlet of the reactor because components involved in the production reaction diffuse to the active sites of the catalyst and react. It then decreases with increasing distance along the reactor, passing a point where the actual rate of production reaction is equal to the reaction rate at the surface conditions ($\eta_{TO} = 1.0$) as hydrogen is produced on the dehydrogenation side and the surface reaction rate becomes significant, finally it approaches $\eta_{TO} = 0.80$. As hydrogen is produced in the bulk, the toluene effectiveness factor drops sharply. In general, the component effectiveness factors reflect the fact that the net production rates of the components from the pseudo-homogeneous model are not as accurate as from the heterogeneous models.

The nitrobenzene effectiveness factors on the hydrogenation side for both isothermal and non-isothermal catalyst pellets plotted in Figure 4.10b behave in a similar manner. They are mathematically undefined at the inlet point of the rector, due to the absence of hydrogen in the compartment making both the diffusion to the catalyst active sites as well as reaction at the surface zero. As hydrogen diffuses to the hydrogenation compartment though the membrane, a sharp increase is observed in both effectiveness factors, heading toward 1.0. Note that the differences between both factors for isothermal and nonisothermal catalyst pellets are negligible.

4.4.7. Behaviour inside catalyst pellets on both sides of coupled reactor

In Figure 4.11, the intraparticle mole fractions, temperature and component effective diffusivity profiles on the dehydrogenation side are plotted at three axial positions, i.e. z/L = 0.1, 0.5, and 0.8. The abscissa in Figure 4.11 is interpreted as the dimensionless radial distance inside the catalyst pellet, i.e. $\omega = 0.0$ represents the centre of the catalyst pellet, while $\omega = 1.0$ indicates its surface.

As can be seen, the ethylbenzene mole fraction at the pellet surface decreases as the fractional length increases from 0.1 (close to the inlet of the reactor) to 0.8 (close to the exit) due to the consumption in the bulk while the opposite is true for styrene. Production of the other selected components, i.e. hydrogen, benzene, and toluene, are limited. The mole fraction of hydrogen on the surface of the catalyst pellet is less than 0.01 due to diffusion through the membrane to the hydrogenation side.

The thermal resistance inside the catalyst pellet is detrimental as it reduces the production of all components inside the catalyst particles. The drop in temperature inside the catalyst pellet decreases from ~50 K at z/L = 0.1 to ~25 K at z/L = 0.8. This is because at the inlet of the reactor, the mole fractions of the reactants are high at the catalyst surface, while this is no longer the case when the reactor exit is approached.

Hydrogen has the highest effective diffusivities inside the catalyst pellet because of its small molecular size. As a consequence for the heat transferred from the tube side to the shell side, the diffusivities increase with the distance along the reactor. Inside the catalyst, however, hydrogen diffusivity decreases as the centre of the particle is approached due to the drop in temperature. The effect of temperature on the component effective diffusivities is greater than that of compositions when both isothermal and nonisothermal profiles are compared. The effective diffusivities of the other components, i.e. ethylbenzene, styrene, benzene and toluene, are limited within the range from 44 to 53 cm^2/h . The effective diffusivity of ethylbenzene decreases as the outlet of the reactor is approached as a result for the decrease of ethylbenzene concentration in the bulk phase. Similar behavior is also observed inside the catalyst pellet, but this decrease becomes more pronounced as the temperature inside the catalyst pellets drops. The effective diffusivities of styrene, benzene and toluene increase at the surface of the catalyst pellets as the outlet of the reactor is approached due to their production in the bulk, and the increase in temperature due to the heat transfer, whereas they decrease inside the catalyst as the centre is approached due to the drop in temperature which has a more pronounced effect than variation in mole fractions.

On the hydrogenation side, the mole fraction of nitrobenzene decreases at the surface of the catalyst as the fractional length increases from 0.1 to 0.8 and also as the centre of the catalyst pellet is approached. This drop in mole fraction is more significant for the isothermal catalyst pellets than for the non-isothermal catalyst pellets. Aniline, on the other hand, exhibits the opposite behavior, it increases at the surface of the catalyst and inside the catalyst pellets with increasing distance along the reactor and decreasing radius inside the catalyst pellet.

The temperature profile, on the other hand, decreases at the surface of the catalyst as the fraction length increases, i.e. it is ~990 K at z/L = 0.1 and ~980 K at z/L = 0.8. This decrease is due to the transfer of heat from the hydrogenation side to the dehydrogenation side. The rise in the temperature inside the catalyst pellet is ~35 K, and this is maintained as the exit of the reactor is approached.

As far as the effective component diffusivities are concerned, it is observed that hydrogen maintains the same performance due to its highest effective diffusivity. An increase in the effective diffusivities of most components is also observed as the dimensionless radial distance ω goes to 0 when the profiles of isothermal catalyst pellets are compared to those for non-isothermal pellets. For nitrobenzene, the effective diffusivities decrease slightly at the surface of the catalyst and inside the catalyst as a result of being consumed in the bulk and inside the catalyst. Aniline effective diffusivities, however, increase at the surface of the catalyst pellets as the exit of the reactor is approached and inside the catalyst pellets as the centre is approached due to its production in the bulk, as well as inside the catalyst. The temperature rise for the non-isothermal catalyst pellets also plays an important role in enhancing the diffusivities of aniline.

4.4.8. Effect of intraparticle diffusion resistance on optimal reactor design

In chapter 3, the bi-objective optimization problem of this coupled membrane reactor was addressed. The two objective functions considered were: (*i*) the *yield of styrene* on the dehydrogenation side, and (*ii*) the *conversion of nitrobenzene* on the hydrogenation side. The homogenous reactor model was used for the calculations. 12 operating and design parameters were used to optimize the objectives considering a number of linear and nonlinear constraints. The Pareto set, representing the set of optimal solutions, was obtained by similar approaches as in Filip et al. (2009) using two numerical scalarisation based multi-objective techniques: the normalized normal constrained method and the normal boundary intersection method. In this optimization problem, the production of styrene whereas the production of aniline can be increased by maximizing the yield of styrene whereas the production of nitrobenzene. Optimal solutions are summarized in Table 4.5 representing three cases where the focus is on: (*i*) production of styrene only (*solution A*), (*ii*) production of both styrene and aniline (*solution B*), and (*iii*) production of aniline only (*solution C*).

Testing the heterogeneous reactor model developed for the membrane reactor has revealed differences in the values of both objectives, i.e. styrene yield and nitrobenzene conversion, for all three optimal solutions. For instance, the homogenous model predicts a styrene yield of 0.975 on the dehydrogenation side for *solution A*, whereas the

heterogeneous predicts 0.930 for the isothermal catalyst pellets and 0.925 for the non-isothermal pellets. On the hydrogenation side, the pseudo-homogeneous model predicts a nitrobenzene conversion of 0.211, whereas the heterogeneous model predicts 0.208 for isothermal pellets and 0.202 for non-isothermal pellets. For solution B, the homogenous model predicts a styrene yield of 0.564 on the dehydrogenation side, whereas the heterogeneous model 0.518 for isothermal pellets and 0.488 for nonisothermal catalyst pellets. The nitrobenzene conversion predicted on the hydrogenation side is 0.555 by the homogenous model, 0.508 by the heterogeneous model for the isothermal catalyst pellets, and 0.477 by the heterogeneous model for the non-isothermal catalyst pellets. For solution C, the styrene yield predicted on the dehydrogenation side by the homogenous model is 0.491, 0.428 by the heterogeneous model for the isothermal pellets, and 0.396 by heterogeneous model for the non-isothermal pellets. On the hydrogenation side, the predicted nitrobenzene conversion is 0.796 from the homogenous model, 0.720 from the heterogeneous model for isothermal pellets, and 0.675 by the heterogeneous model for non-isothermal pellets. There are also significant differences in temperature profiles along both sides of the reactor. These differences may result in overestimating the design and operating parameters due to neglecting important effects caused by the intraparticle diffusion resistance. Styrene yield, nitrobenzene conversion and temperature profiles on both sides of the reactor are plotted in Figure 4.13.

In summary, the pseudo-homogeneous model systematically overestimates the conversion and yield by 5 to 15% of their actual values. However, the computation times required for one simulation of the pseudo-homogeneous model and the heterogeneous non-isothermal model are less than 4 seconds and around a day, respectively. Supplying the analytical Jacobians for the boundary value problems in the catalyst pellet models as well as using vectorization options can help significantly in reducing the execution time to around twenty minutes. Hence, as the trends are generally well-captured by the simpler pseudo-homogeneous model, this one may in practice serve for a preliminary rapid screening of different alternatives or even a first systematic optimization purpose. Nevertheless, these results must be interpreted with due care, given the model's tendency

for overestimating. Afterwards, the design and optimization can be fine-tuned based on the more complex heterogeneous (non-isothermal) model.

4.5. Conclusions

A heterogeneous model based on Fickian diffusion for the membrane reactor, integrating the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene, is developed in which the intraparticle diffusion resistance is considered, assuming both isothermal and non-isothermal conditions. It is found that intraparticle diffusion resistances are significant and should be taken into consideration as they not only retard the chemical reactions, but also the driving forces for permeation, as well as the heat transfer. The homogenous model used earlier in earlier chapters to optimize the membrane reactor of interest results in overestimation of both the styrene yield and the nitrobenzene conversion in the integrated reactor by 5 to 15% of their actual values. Hence, if possible, the full model should preferably be used in any further optimization studies. The dusty gas model, considered to be more rigorous than the Fickian diffusion model, should also be utilized to evaluate more precisely the effect of the intraparticle diffusion resistance.

Chemical Reaction	Heat of Reaction	Kinetic Equation	Reference	
Dehydrogenation Side ^a				
$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2$	$\Delta H_{298} = 117.6 \frac{kJ}{mole}$	$r_1 = k_1 \left(p_{EB} - \frac{p_{ST} p_{H_2}}{K_A} \right)$	Elnashaie et al. (1993)	
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	$\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$	$r_2 = k_2 p_{EB}$	Elnashaie et al. (1993)	
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	$\Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$	$r_3 = k_3 p_{EB} p_{H_2}$	Elnashaie et al. (1993)	
$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$	$\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$	$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2}$	Elnashaie et al. (1993)	
$H_2O + CH_4 \rightarrow CO + 3H_2$	$\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$	$r_5 = k_5 p_{H_2O} p_{CH_4}$	Elnashaie et al. (1993)	
$H_2O + CO \rightarrow CO_2 + H_2$	$\Delta H_{298} = -41.2 \frac{kJ}{mole}$	$r_6 = k_6 \left(\frac{P}{T^3}\right) p_{H_2O} p_{CO}$	Elnashaie et al. (1993)	
Hydrogenation Side ^b				
$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$	$\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$	$r' = \frac{k' K_{NB} K_{H_2} p'_{NB} \sqrt{p'_{H_2}}}{\left(1 + K_{NB} p'_{NB} + K_{H_2} \sqrt{p'_{H_2}}\right)^2}$	Amon, et al. (1999)	

|--|

^a partial pressure in (bars) ^b partial pressure in (kPa)

Reaction	$k_{io}{}^{\mathrm{a}}$	E_i (kJ/kmole)	Reference
1^{b}	8.32×10^{3}	0.909×10^{5}	
2	4.23×10^{9}	2.080×10^5	
3	6.13×10^{3}	0.915×10^{5}	Elnashaie et al.
4	3.95×10^{3}	1.040×10^{5}	(1993)
5	1.42×10^{2}	0.657×10^{5}	
6	5.80×10^{12}	0.736×10^{5}	
$7^{\rm c}$	1.86×10^{-4}	10.0×10^{3}	Amon, et al. (1999)

Table 4.2 Frequency factors and activation energies for reactions considered.

^a $k_i = \frac{10}{36} k_{io} \exp(-\frac{E_i}{RT})$, where k_{io} is the pre-exponential factor for $1 \le i \le 6$ $k_i = 10^3 k_{io} \exp(-\frac{E_i}{RT})$, for i = 7.

^b The equilibrium constant is calculated by: $K_A = \exp(\frac{-\Delta F}{RT})$, where: $\Delta F = a + bT + cT^2$, $a = 122725.16, b = -126.27 / \text{K}, c = -2.194 \times 10^{-3} / \text{K}^2$

^c $K_{_{NB}} = 1.51 \times 10^{-2} \text{ kPa}$, $K_{_{H_2}} = 0.14 \text{ kPa}^{-0.5}$

Balance Equations	Mathematical Expressions	Equation	
Dehydrogenation Side			
Mole	$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} \left(3\int_0^{1.0} r_j \omega^2 d\omega \right) (1-\varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J_i$	(4.8)	
Energy	$\frac{dT}{dz} = \frac{\sum_{j=1}^{6} \left(3\int_{0}^{1.0} \left[-\Delta H(T) \right]_{j} r_{j} \omega^{2} d\omega \right) (1-\varepsilon) A_{cs} \rho_{s} + NQ}{\sum_{i=1}^{10} n_{i} C p_{i}}$	(4.9)	
Pressure	$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \left[\frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G\right]$	(4.10)	
	Hydrogenation Side (per tube)	•	
Mole	$\frac{dn'_i}{dz} = \sigma_i \left(3 \int_0^{1.0} r' \omega'^2 d\omega' \right) (1 - \varepsilon') A'_{cs} \rho'_s + 2\pi r_3 a_i J_i$	(4.11)	
Energy	$\frac{dT'}{dz} = \frac{(2\pi r_3)\sum_{i=1}^{i} a_i J_i \int_{T'}^{T} Cp_i dT + \left(3\int_{0}^{1.0} \left[-\Delta H'(T')\right]r'\omega'^2 d\omega'\right) (1-\varepsilon')A_{cs}'\rho_s' - Q}{\sum_{i=1}^{4} n_i' Cp_i'}$	(4.12)	
Pressure	$\frac{dP'}{dz} = -\frac{G'}{\rho'_g g_c D'_p} \left(\frac{1-\varepsilon'}{\varepsilon'^3}\right) \left[\frac{150(1-\varepsilon')\mu'_g}{D'_p} + 1.75G'\right]$	(4.13)	
Hydrogen diffusion from one hydrogenation tube per unit length			
Diffusion of Hydrogen Across Membrane	of $J_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}}\right) \text{ where:}$ $Q_o = 7.29 \times 10^3 \text{ (mole} \times \text{m})/(\text{m}^2 \times \text{min} \times \text{atm}^{0.5}), \ \delta_{H_2} = 25 \times 10^{-6} \text{ m},$ $E_{H_2,P} = 20.5 \times 10^3 \text{ J/mol}$		
]	Heat transfer from one hydrogenation tube per unit length		
Heat Transfer Across Membrane	$Q = \frac{2\pi r_{1}(T'-T)}{\left[\frac{1}{h'} + \frac{r_{1}}{k_{ss}} \ln\left(\frac{r_{2}}{r_{1}}\right) + \frac{r_{1}}{k_{Pd}} \ln\left(\frac{r_{3}}{r_{2}}\right) + \frac{r_{1}}{r_{2}h}\right]}$ where: $k_{ss} = 22.88 \text{ W/m} \times \text{K}, \ k_{Pd} = 93.3 \text{ W/m} \times \text{K}$ $\frac{hD_{t}}{k_{g}} = 0.813 \left(\frac{D_{p}G}{\mu_{g}}\right)^{0.9} \exp\left(-\frac{6D_{p}}{D_{t}}\right)$ $\frac{h'D_{t}}{k_{g}'} = 3.50 \left(\frac{D_{p}'G'}{\mu_{g}'}\right)^{0.7} \exp\left(-\frac{4.6D_{p}'}{D_{t}'}\right)$	(4.15)	

Table 4.3 Heterogeneous model for the coupled reactor based on Fickian diffusion.

Table 4.4 Dimensional and operating parameters for hybrid catalytic membrane reactor for base case.

Parameter	Values	Units		
Dimensional Variables				
Net diameter of the	1.05	М		
dehydrogenation side	1.95			
Diameter of the	3.5×10^{-2}	М		
hydrogenation tube	5.5×10			
Total number of the	1500			
hydrogenation tubes				
Length of the reactor	4.0	М		
Operating Condition	s (Dehydrogenation S	Side)		
Ethylbenzene	10.242	mole/s		
Styrene	0.1861	mole/s		
Benzene	0.0306	mole/s		
Toluene	0.2444	mole/s		
Steam	125.86	mole/s		
Temperature	880.0	K		
Pressure	2.5	Bar		
Catalyst density	2146.3	kg/m ³		
Catalyst thermal	0.2	I /ree /a		
conductivity	0.5	J/m/s		
Pore diameters	4800×10 ⁻¹⁰	М		
Catalyst porosity	0.35			
Catalyst tortuosity	4.0			
Bed voidage	0.48			
Operating Conditions per	one tube (Hydrogena	tion Side)		
Nitrobenzene	0.003	mole/s		
Steam	0.008	mole/s		
Temperature	900.0	mole/s		
Pressure	1.0	Bar		
Catalyst density	1400	kg/m ³		
Catalyst thermal	0.05	J/m/s		
conductivity	0.03			
Pore diameters	5000×10^{-10}	М		
Catalyst porosity	0.40			
Catalyst tortuosity	4.0			
Bed voidage	0.46			

Parameter		Optimal Solution A	Optimal Solution B	Optimal Solution C
Side	Feed Molar of Ethylbenzene (mole/s)	7.66	9.36	11.27
nation 9	Steam-to-Ethylbenzene Ratio	7.00	7.00	20.00
/drogen	Feed Temperature on Shell Side (K)	825.41	780.00	820.02
Deh	Feed Pressure on Shell Side (bar)	4.00	2.52	4.00
ide	Feed Molar of Nitrobenzene per one tube (mole/s)	0.005	0.002	0.002
ation Si ube)	Steam-to-Nitrobenzene Ratio	4.00	4.00	4.00
drogen: (per t	Feed Temperature on Tube Side (K)	825.41	780.00	820.02
Hy	Feed Pressure on Tube Side (bar)	3.62	1.00	1.00
bles	No. of Hydrogenation Tubes	2500	1582	1000
Dimensional Varial	Equivalent-area Diameter of Dehydrogenation Side (m)	3.00	2.39	1.95
	Diameter of Hydrogenation Tube (m)	0.048	0.035	0.040
	Reactor Length (m)	4.00	4.00	4.00
ene	Pseudo-homogeneous Modeling	0.9747	0.5644	0.4909
Yield of Styre	Heterogeneous Modeling based on Fickian diffusion model (Isothermal Catalyst Pellets)	0.9300	0.5124	0.4259
	Heterogeneous Modeling based on Fickian diffusion model (Non-isothermal Catalyst Pellets)	0.9245	0.4775	0.3859
Conversion of Nitrobenzene	Pseudo-homogeneous Modeling	0.2119	0.5548	0.7957
	Heterogeneous Modeling based on Fickian diffusion model (Isothermal Catalyst Pellets)	0.2078	0.5018	0.7130
	Heterogeneous Modeling based on Fickian diffusion model (Non-isothermal Catalyst Pellets)	0.2011	0.4663	0.6594

 Table 4.5 Representative solutions for Pareto frontier*.

* Bold values are constrained limits.



Figure 4.1 Schematic of the coupled membrane fixed bed reactor.



Figure 4.2 Infinitesimal slice inside catalyst pellets on dehydrogenation side showing terms considered in: (a) mole balance, and (b) energy balance.



Figure 4.3 Schematic sequence of computations for the catalyst and reactor models.



Figure 4.4 Conversion of key components: (a) Ethylbenzene on dehydrogenation side, and (b) Nitrobenzene on hydrogenation side.


Figure 4.5 Yield of: (a) Styrene, (b) Benzene, and (c) Toluene on dehydrogenation side.



Figure 4.6 Hydrogen molar flowrates on: (a) dehydrogenation side, and (b) hydrogenation side.



Figure 4.7 Temperature profiles on: (a) dehydrogenation side, and (b) hydrogenation.



Figure 4.8 Reaction effectiveness factor profiles versus bulk temperature for: (a, b) dehydrogenation reactions, and (c) hydrogenation reaction.



Figure 4.9 Actual reaction rates and their values at surface conditions versus bulk temperature for all reactions.



Figure 4.10 Component effectiveness factor profiles versus dimensionless axial distance for: (a) ethylbenzene, styrene, hydrogen, benzene, and toluene on dehydrogenation side; (b) nitrobenzene on hydrogenation side.

Dimensionless Radial Distance, ω



Figure 4.11 Intraparticle profiles of component mole fraction, temperature and component effective diffusivities at fractional lengths of 0.1, 0.5, and 0.80 for both the isothermal and non-isothermal catalyst pellet case on dehydrogenation side.



Figure 4.12 Intraparticle profiles of component mole fraction, temperature and component effective diffusivities at fractional lengths of 0.1, 0.5, and 0.80 for both the isothermal and non-isothermal catalyst pellet case on hydrogenation side.



Figure 4.13 Styrene yield, nitrobenzene conversion, and temperature profiles for the optimal designs of the coupled membrane reactor, i.e. solution A (a, b, c), solution B (d, e, f), solution C (g, h, i).

- Abashar, M. E. E., 2004. Coupling of ethylbenzene dehydrogenation and benzene hydrogenation reactions in fixed bed catalytic reactors, Chemical Engineering and Processing 43(10), 1195-1202.
- Abdalla, B. K., Elnashaie, S. S. E. H., 1995. Fluidized bed reactors without and with selective membranes for the catalytic dehydrogenation of ethylbenzene to styrene, Journal of Membrane Science 101(1-2), 31-31.
- Abdalla, B. K., Elnashaie, S. S. E. H., 1993. A membrane reactor for the production of styrene from ethylbenzene, Journal of Membrane Science 85(3), 229-239.
- Abdalla, B. K., Elnashaie, S. S. E. H., 1994. Catalytic dehydrogenation of ethylbenzene to styrene in membrane reactors, AICHE Journal 40(12), 2055-2059.
- Czechowicz, D., Skutil, K., Torz, A., Taniewski, M., 2004. An integrated process of oxidative coupling of methane and pyrolysis of naphtha in a scaled-up unit, Journal of Chemical Technology and Biotechnology 79(2), 182-186.
- Elnashaie, S. S. E. H., Moustafa, T., Alsoudani, T., Elshishini, S. S., 2000. Modeling and basic characteristics of novel integrated dehydrogenation-hydrogenation membrane catalytic reactors, Computers & Chemical Engineering 24(2-7), 1293-1300.
- Elnashaie, S. S. E. H., Abdalla, B. K., Hughes, R., 1993. Simulation of the industrial fixed bed catalytic reactor for the dehydrogenation of ethylbenzene to styrene: Heterogeneous dusty gas model, Industrial and Engineering Chemistry Research 32(11), 2537-2541.
- Logist F, Van Erdeghem PMM, Van Impe JF. Efficient deterministic multiple objective optimal control of (bio)chemical processes. Chemical Engineering Science 2009; 64(11):2527-38.
- Fukuhara, C., Igarashi, A., 2005. Performance simulation of a wall-type reactor in which exothermic and endothermic reactions proceed simultaneously, comparing with that of a fixed-bed reactor, Chemical Engineering Science 60(24), 6824-6834.

- Glockler, B., Kolios, G., Eigenberger, G., 2003. Analysis of a novel reverse-flow reactor concept for autothermal methane steam reforming, Chemical Engineering Science 58(3-6), 593-601.
- Hermann, C., Quicker, P., Dittmeyer, R., 1997. Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor, Journal of Membrane Science 136(1-2), 161-172.
- Moustafa, T. M., Elnashaie, S. S. E. H., 2000. Simultaneous production of styrene and cyclohexane in an integrated membrane reactor, Journal of Membrane Science 178(1-2), 171-184.
- Bird R. B., Stewart W.E., Lightfoot E.N., 1960. Transport Phenomena. : Wiley: New York.
- Stitt, E. H., 2004. Multifunctional reactors? 'Up to a point Lord Copper', Chemical Engineering Research and Design 82(2), 129-139.
- van Sint Annaland, M., Nijssen, R. C., 2002. A novel reverse flow reactor coupling endothermic and exothermic reactions: an experimental study, Chemical Engineering Science 57(22-23), 4967-4985.
- Van, S. A., Scholts, H. A. R., Kuipers, J. A. M., Van Swaaij, W. P. M., 2002. A novel reverse flow reactor coupling endothermic and exothermic reactions. Part II: Sequential reactor configuration for reversible endothermic reactions, Chemical Engineering Science 57(5), 855-872.

CHAPTER 5 COMPARISON OF DIFFUSION MODELS IN MODELLING A CATALYTIC MEMBRANE FIXED BED REACTOR COUPLING DEHYDROGENATION OF ETHYLBENZENE WITH HYDROGENATION OF NITROBENZENE[†]

5.1. Introduction

Membrane reactors can significantly improve the production rates of thermodynamicallylimited reactions. Hydrogen-selective membranes permit hydrogen produced by reactions to escape under the influence of the difference in the hydrogen partial pressures to the permeate side where an inert gas such as nitrogen can be used to purge hydrogen. This type of reactor is promising for thermodynamically limited reactions such as steam reforming. A number of studies have reported that when steam reforming is operated in membrane reactors, hydrogen yields can exceed those in simple fixed bed reactors (Balasubramanian et al., 1999; Chen and Elnashaie, 2005; Chen et al., 2003; Itoh et al., 2003; Rakib et al., 2008; Tiemersma et al., 2006; Uemiya et al., 1990).

Another type of reaction suffering from thermodynamic limitations is the one involving the production of olefins from inexpensive paraffins via dehydrogenation. Shifting the equilibrium production rate of these thermodynamically-limited dehydrogenation reactions was the objective of a number of studies reported in the last decade. Several reactor configurations and models have stimulated these configurations. In general, the hydrogen membranes facilitate hydrogen transfer to the permeate side where it is collected by a sweep gas (Hermann et al., 1997; Itoh et al., 2003) or utilized as a reactant in complementary reactions (Abdalla et al., 1997; Elnashaie et al., 2000; Itoh and Wu, 1997; Moustafa and Elnashaie, 2000).

[†] A version of this chapter has been submitted for publication.

Dehydrogenation of ethylbenzene to styrene and hydrogenation of nitrobenzene to aniline complement each other and constitute a synergistic pair of reactions to couple in a catalytic membrane fixed bed reactor. Diffusion of hydrogen produced on the dehydrogenation side through hydrogen-selective membranes assists greatly in shifting forward the equilibrium conversion of ethylbenzene, while simultaneously improving the yield of styrene compared with fixed bed reactors without membranes. Combining the two reactions in this manner helps to significantly increase the production of styrene on the dehydrogenation side and to produce aniline as a second useful product on the hydrogenation side. Transferring the heat released from the hydrogenation reaction of ethylbenzene, consequently enhancing the styrene yield (see chapter 2). In this configuration, it is possible to boost the styrene yield from ~40% in catalytic industrial reactors (Moustafa and Elnashaie, 2000) to ~98% in an optimized catalytic membrane reactor (see chapter 3).

Abo-Ghander et al. (2010) briefly assessed the effect of the intraphase transport by considering diffusion inside the catalyst pellets on both sides of the coupled membrane reactor. The Fickian diffusion model was used in which the reactants are assumed to diffuse through a stagnant bulk phase with the diffusivities of components in the reacting mixture along the radial direction inside the catalyst pellets evaluated by the well-known Wilke equation. The predictions of the heterogeneous model are significantly less than that of the pseudo-homogeneous model, providing an indication of the importance of the intraparticle transport resistances.

In catalytic packed bed reactors, the components in reacting mixtures have to diffuse through tortuous complex networks of pores ranging from macropores to micropores to reach active sites, where they react. Hence, the selection of an appropriate diffusion model accounting for intraphase resistances is highly important when modeling these types of reactors. The *Fickian diffusion model* is considered to yield accurate predictions if the reacting component diffuses in a large excess of a second component and there is no appreciable change in the number of moles. In contrast, the *dusty gas model* is

considered to be more general and more rigorous, but also more complex. As the assumptions for Fickian diffusion may not always be met in the studied reactor (Elnashaie and Abashar, 1993; Elnashaie et al., 1993), the aim of this chapter is not only to rigorously evaluate the effect of intraparticle diffusion, but also to compare the Fickian diffusion and the dusty gas models. Moreover, the differences between the predictions of isothermal versus non-isothermal catalyst pellets are studied.

Section 5.2 introduces the reactor configuration, while Section 5.3 describes the reactor models and focuses especially on the incorporation of intraphase resistances based on the Fickian diffusion and the dusty gas model. Section 5.4 presents and compares the simulation results for all models. Finally, Section 5.5 summarizes the main conclusions.

5.2. Reactor Configuration

A conceptual schematic of the integrated reactor proposed in chapter 2 appears in Figure 5.1. The reactor is composed of two compartments provided by a shell containing a bundle of hydrogenation tubes. On the shell side, dehydrogenation of ethylbenzene takes place producing styrene and hydrogen. Five side reactions also occur, producing benzene, toluene, and light gases like ethylene, methane, carbon monoxide, and carbon dioxide. The stoichiometric equations on the shell side can be expressed as:

$$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2 \qquad \Delta H_{298} = 117.6\frac{\text{kJ}}{\text{mole}}$$
 (5.1)

1 т

$$C_6H_5CH_2CH_3 \to C_6H_6 + C_2H_4$$
 $\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$ (5.2)

- $C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$ (5.3)
- $2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$ $\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$ (5.4)

$$H_2O + CH_4 \rightarrow CO + 3H_2 \qquad \qquad \Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}} \tag{5.5}$$

$$H_2 O + CO \to CO_2 + H_2$$
 $\Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$ (5.6)

In industrial fixed bed reactors producing styrene, the temperature tends to drop along the reactor due to the endothermic nature of the main reaction if sufficient heat is not supplied. In the proposed membrane reactor, hydrogen produced on the shell side diffuses through a palladium hydrogen-selective-membranes to the tube side where it intermingles with a feed stream containing only nitrobenzene and steam. The membrane wall considered is made up of two layers: a layer of stainless steel of a thickness 0.0012 m, coated by a palladium layer of a thickness $20 \times 10^{-6} \text{ m}$.

Inside the membrane tubes, cocurrently flowing nitrobenzene reacts with hydrogen to produce aniline as a second major useful product from the integrated membrane reactor.

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$
 $\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$ (5.7)

1 т

This hydrogenation reaction is irreversible and highly exothermic. The heat generated by this reaction is transferred through the membrane layer and heats the reacting mixture on the dehydrogenation side.

The catalyst on the shell side is composed of iron oxide (Fe₂O₃) promoted by potassium carbonate (K₂CO₃) and chromium oxide (Cr₂O₃), whereas that on the tube side is a palladium catalyst supported on an α -alumina carrier. Tables 5.1 and 5.2 summarize the kinetics, frequency factors and activation energies (Amon et al., 1999; Elnashaie et al., 1993).

5.3. Reactor Model

The differential equations governing the behavior of different chemical species on both sides of the reactor, as well as the temperature profiles are derived considering two

infinitesimal slices across which exchanges of moles and energy take place. The following assumptions are adopted.

- 1. Steady state operation.
- 2. Ideal gas behavior on both the shell and tube compartments.
- Plug flow for the fixed beds on both the shell and tube sides, with Peclet numbers ~1000.
- 4. Heterogeneous model, i.e. there are concentration and temperature gradients within the catalyst particles.
- 5. The flow rates on both sides are large enough to minimize external mass and heat transfer resistances. Only intraparticle diffusion is considered.
- 6. The reactor external wall is insulated leading to an adiabatic reactor.
- 7. Catalyst deactivation is neglected.
- 8. Pressure gradients along both compartments are estimated based on Ergun's equation.

Along the integrated membrane reactor, hydrogen diffuses from the dehydrogenation side to the hydrogenation side while heat is transferred from the hydrogenation to the dehydrogenation side. The reactor model equations and the rates of both hydrogen diffusion and heat transfer per unit length are given in Table 5.3.

5.3.1. Diffusion inside catalyst pellets

Fixed bed reactors suffer from diffusion limitations resulting in temperature and concentration gradients between the bulk and surface of the catalysts (*external* mass and heat transfer), and between the surface of the catalyst pellets and the active sites inside the catalysts (*intraparticle* mass and heat transfer). Consequently, the concentration and temperature profiles between those phases are not flat anymore causing the pseudo-homogeneous model predictions to be not always highly accurate (Elnashaie and Elshishini, 1993).

Operating the reactor at high flow rates can greatly enhance the external mass and heat transfer coefficients, consequently minimizing the effect of external mass and heat transfer resistances. The effect of the intraparticle heat and mass transfer resistances, however, cannot be reduced due to the significant size of the catalyst pellets, ranging from 6 to 14 mm. As a result, neglecting the effect of the intraparticle resistance when modeling fixed bed reactors may result in a considerable discrepancy between the model predictions and reality (Elnashaie and Alhabdan, 1989).

Two diffusion models are commonly used to account for the intraparticle mass transfer resistance, namely the Fickian diffusion model and the dusty gas model. The *Fickian diffusion model* is in general less accurate, but is the most widely used due to its simplicity (Veldsink et al., 1995). It can be easily derived from the *dusty gas model* after neglecting the effect of the ratio of component molar fluxes. This approximation reduces the accuracy of the Fickian diffusion model especially in reactive systems subject to changes in molar flow rates.

The dusty gas model is more rigorous than the Fickian diffusion model. It is considered to be the most rigorous of the models for investigated treating diffusion in non-ideal systems and for systems influenced by external force fields (Krishna and Wesselingh, 1997). It can also be used to model diffusion in macro- and micro-porous catalysts (Veldsink et al., 1995), adsorbents (Krishna, 1990) and membranes (Beuscher and Gooding, 1999). The porous medium is treated in the dusty gas model as composed of giant fixed molecules uniformly distributed in space, and referred to as dust and treated as one component of the gas mixture. The model has been used widely in the modeling of reactive systems involving gases.

Both models have been used by a number of researchers to predict the diffusion inside catalysts. For example, the Fickian diffusion model was used by Wang et al. (2001) to model diffusion inside non-isothermal catalysts in Fischer-Tropsch synthesis. Diffusion inside the catalyst pellets has been studied for steam reforming of methane based on the Fickian diffusion model, the dusty gas model and another simplified model derived from

the dusty gas model. Because the reaction is characterized by high diffusion limitations, a deviation in the predictions of the Fickian diffusion model and a (simplified) dusty gas model was observed at high steam-to-methane ratios. The dusty gas model is recommended for rigorous predictions of the influence of intraparticle diffusion (Abashar and Elnashaie, 1993; Elnashaie et al., 1992; Elnashaie and Abashar, 1993; Soliman et al., 1988).

5.3.1. Diffusion models for catalyst pellets

The molar and energy fluxes inside the catalyst pellets are estimated based on the following assumptions:

- 1. Steady-state molar and energy flow.
- 2. Particles are spherical and their porous structure is isentropic.
- 3. Ideal gas law.
- 4. Concentration and temperature profiles within the catalyst particles are spherically symmetrical.
- 5. External mass and heat transfer resistances are negligible due to the high gas flow rates.
- 6. Negligible viscous flow inside the catalyst particles; the pellets are isobaric.
- 7. Convective diffusion is neglected, only ordinary molecular and Knudsen diffusion are significant for gas motion within the solid particles.
- 8. Convective energy transfer is negligible.
- 9. Thermal conductivities of the catalyst pellets are constant on both sides of the reactor.

To obtain the dusty gas model describing the diffusion inside the catalyst pellets, the molar and energy fluxes around a small shell inside the catalyst pellet on the dehydrogenation side are considered as shown in Figure 5.2. Applying the balance equations around the shell with no accumulation leads to:

$$\left(4\pi y^{2} N_{i}\right)_{y} - \left(4\pi y^{2} N_{i}\right)_{y+\Delta y} + \sum_{j=1}^{6} \sigma_{ij} r_{j} \rho \left(4\pi y^{2} \Delta y\right) = 0$$
(5.16)

$$(4\pi y^{2}q)\Big|_{y} - (4\pi y^{2}q)\Big|_{y+\Delta y} + \sum_{j=1}^{6} \left[-\Delta H(T)\right]r_{j}\rho(4\pi y^{2}\Delta y) = 0$$
(5.17)

When the shell thickness approaches zero, equations (5.16) and (5.17) become:

$$\frac{dN_i}{dy} + \frac{2}{y}N_i = \sum_{j=1}^6 \sigma_{ij}r_j\rho$$
(5.18)

$$\frac{dq}{dy} + \frac{2}{y}q = \sum_{j=1}^{6} \left[-\Delta H(T) \right]_j r_j \rho$$
(5.19)

Expressing the heat flux in equation (5.19) by Fourier's law leads to:

$$\frac{d^2T}{dy^2} + \frac{2}{y}\frac{dT}{dy} = \frac{1}{k_e}\sum_{j=1}^{6} \left[\Delta H\left(T\right)\right]_j r_j\rho$$
(5.20)

The molar flux in equation (5.18) is related to the component mole fractions by the Stefan-Maxwell diffusion equation. When the pressure drop is neglected, this can be written (Veldsink et al., 1995) as:

$$\frac{P}{RT}\nabla x_{i} = \sum_{\substack{j=1\\j=i}}^{10} \frac{x_{i}N_{j} - x_{j}N_{i}}{D_{ij}^{e}} - \frac{N_{i}}{D_{ik}^{e}}$$
(5.21)

For a one-dimensional problem in spherical coordinates, equation (5.21) becomes:

$$\frac{P}{RT}\frac{dx_i}{dy} = \sum_{\substack{j=1\\j\neq i}}^{10} \frac{x_i N_j - x_j N_i}{D_{ij}^e} - \frac{N_i}{D_{ik}^e}$$
(5.22)

Equations analogous to equations (5.18), (5.20) and (5.22) may be written to describe the diffusion inside the catalyst pellets on the hydrogenation side:

$$\frac{dN'_i}{dy'} + \frac{2}{y'}N'_i = \sigma'_i r' \rho'$$
(5.23)

$$\frac{d^{2}T'}{dy'^{2}} + \frac{2}{y'}\frac{dT'}{dy'} = \frac{\left[\Delta H(T)\right]'r'\rho'}{k'_{e}}$$
(5.24)

$$\frac{P'}{RT'}\frac{dx'_i}{dy'} = \sum_{\substack{j=1\\j\neq i}}^4 \frac{x'_i N'_j - x'_j N'_i}{D'_{ij}^e} - \frac{N'_i}{D'_{ik}^e}$$
(5.25)

Alternatively, diffusion inside the catalyst pellets can be described by the Fickian diffusion model. For multicomponent systems, Fick's law is expressed (Froment and Bischoff, 1990; Elnashaie and Elshishini, 1993) as:

$$N_i = -D_{ie} \frac{dC}{dy} \tag{5.26}$$

where the diffusivity of component *i* is expressed as:

$$\frac{1}{D_{ie}} = \frac{1}{D_{im}^{e}} + \frac{1}{D_{ik}^{e}}$$
(5.27)

The diffusivity of component *i* in the mixture is calculated using the Wilke equation:

$$\frac{1 - x_i}{D_{im}} = \sum_{\substack{j=1\\j \neq i}}^{10} \frac{x_j}{D_{ij}} \qquad 1 \le i \le 10$$
(5.28)

where effective diffusivities are defined (Froment and Bischoff, 1990; Elnashaie and Elshishini, 1993) as:

$$D_{im}^{e} = \frac{\varepsilon}{\tau} D_{im}$$
(5.29)

Inserting equation (5.27) into (5.18) gives the Fickian diffusion model on the dehydrogenation side (Abo-Ghander et al., 2010) as:

$$\frac{d^2 C_i}{dy^2} + \frac{2}{y} \frac{dC_i}{dy} = -\frac{1}{D_{ie}} \sum_{j=1}^6 \sigma_{ij} r_j \rho$$
(5.30)

Similarly, on the hydrogenation side, the Fickian diffusion model equation is written as:

$$\frac{d^2 C'_i}{dy'^2} + \frac{2}{y'} \frac{dC'_i}{dy'} = -\frac{\sigma'_i r' \rho'}{D'_{ie}}$$
(5.31)

In the above set of equations, the dusty gas model requires solution of the coupled equations (5.18), (5.20) and (5.22) on the dehydrogenation side and (5.23), (5.24) and (5.25) on the hydrogenation side. On the other hand, the Fickian diffusion model is given by the coupled equations (5.20) and (5.30) on the dehydrogenation side and (5.24) and (5.31) on the hydrogenation side. Each pair of these equations forms a set of split boundary value problems describing the molar and energy fluxes inside the catalyst on both sides of the reactor. These pairs must be solved at each axial position along the reactor to evaluate the volume-averaged reaction rates, as well as the volume-averaged heat of reactions. The corresponding boundary conditions for the dusty gas model are:

• Dehydrogenation side:

Centre of the catalyst pellets:
$$y = 0 \Rightarrow \begin{cases} N_i = 0 \\ \frac{dT}{dy} = 0 \end{cases}$$
 (5.32)

1

Surface of the catalyst pellets:
$$y = R_p \Longrightarrow \begin{cases} x_i = x_{is} \\ T = T_s \end{cases}$$
 (5.33)

• Hydrogenation side:

Centre of the catalyst pellets:
$$y' = 0 \Longrightarrow \begin{cases} N'_i = 0 \\ \frac{dT'}{dy'} = 0 \end{cases}$$
 (5.34)

Surface of the catalyst pellets:
$$y' = R'_p \Longrightarrow \begin{cases} x'_i = x'_{is} \\ T' = T'_{s} \end{cases}$$
 (5.35)

For the Fickian diffusion mode, the boundary conditions are:

• Dehydrogenation side:

Centre of the catalyst pellets:
$$y = 0 \Rightarrow \begin{cases} \frac{dC_i}{dy} = 0\\ \frac{dT}{dy} = 0 \end{cases}$$
 (5.36)

Surface of the catalyst pellets:
$$y = R_p \Longrightarrow \begin{cases} C_i = C_{is} \\ T = T_s \end{cases}$$
 (5.37)

• Hydrogenation side:

Centre of

the catalyst pellets:
$$y' = 0 \Longrightarrow \begin{cases} \frac{dC'_i}{dy} = 0 = 0\\ \frac{dT'}{dy'} = 0 \end{cases}$$
 (5.38)

Surface of the catalyst pellets:
$$y' = R'_p \Longrightarrow \begin{cases} C'_i = C'_{is} \\ T' = T'_s \end{cases}$$
 (5.39)

Numerical solution of the dusty gas and Fickian diffusion models on the hydrogenation side of the reactor leads to the evaluation of the volume-averaged reaction rates and the volume averaged heat released or absorbed due to reactions. These values can be related to the bulk concentrations and temperatures through *effectiveness factors*, defined as the ratio of the reaction rate with pore resistance to the reaction rate which would prevail if the concentrations and temperature throughout the particles were equal to those at the surface.

$$\eta_{j} = \frac{\int_{0}^{R_{p}} r_{j} \rho(4\pi y^{2}) dy}{r_{j}(C_{is}, T_{s}) \rho(\frac{4}{3}\pi R_{p}^{3})}$$
(5.40)

Introducing the dimensionless catalyst radius ($\omega = \frac{y}{R_p}$) into equation (5.40) leads to:

$$\eta_{j} r_{j} (C_{is}, T_{s}) = 3 \int_{0}^{1.0} r_{j} \, \omega^{2} d\omega$$
(5.41)

where:

 $1 \le j \le 6$ for the dehydrogenation side j = 1 for the hydrogenation side

For non-isothermal catalyst pellets, the volume-averaged heat of reaction is defined as:

$$\eta_{j}\left[-\Delta H\left(T_{s}\right)\right]r_{j}\left(C_{is},T_{s}\right)=3\int_{0}^{1.0}\left[-\Delta H\left(T\right)\right]_{j}r_{j}\left(C_{i},T\right)\omega^{2}d\omega$$
(5.42)

with *j* as for equation (5.41). Integral terms in equations (5.41) and (5.42) were evaluated numerically by the *trapezoidal rule*. Equations (5.41) and (5.42) represent the actual

reaction rates and actual heat of reactions, and they are used to update the reactor model, equations (5.8) to (5.13) in Table 5.3.

The conversion of ethylbenzene on the dehydrogenation side, the conversion of nitrobenzene on the hydrogenation side and component yields on the dehydrogenation side along the reactor are defined as:

$$Conversion = \begin{cases} X_{EB} = \frac{n_{EBo} - n_{EB}}{n_{EBo}} & Dehydrogenation Side \\ X_{NB} = \frac{n_{NBo} - n_{NB}}{n_{NBo}} & Hydrogenation Side \end{cases}$$
(5.43)

$$Yield = \begin{cases} Y_{ST} = \frac{n_{ST} - n_{STo}}{n_{EBo}} \\ Y_{BZ} = \frac{n_{BZ} - n_{BZo}}{n_{EBo}} \\ Y_{TO} = \frac{n_{TO} - n_{TOo}}{n_{EBo}} \end{cases}$$
(5.44)

Mean square and absolute deviations from the *rigorous* model predictions are defined for the styrene yield and nitrobenzene conversion as:

$$\text{Mean square deviation} = \begin{cases} \sqrt{\frac{1}{N_p} \sum_{i=1}^{N_p} (Y_{ST}^i - \tilde{Y}_{ST}^i)^2} & \text{for styrene yield} \\ \sqrt{\frac{1}{N_p} \sum_{i=1}^{N_p} (X_{NB}^i - \tilde{X}_{NB}^i)^2} & \text{for nitrobenzene conversion} \end{cases}$$
(5.45)

Mean absolute deviation =
$$\begin{cases} \frac{1}{N_p} \sum_{i=1}^{N_p} |Y_{ST}^i - \tilde{Y}_{ST}^i| & \text{for styrene yield} \\ \frac{1}{N_p} \sum_{i=1}^{N_p} |X_{NB}^i - \tilde{X}_{NB}^i| & \text{for nitrobenzene conversion} \end{cases}$$
(5.46)

The sequence of computations which successfully couples the diffusion models with the reactor model is depicted in Figure 5.3. At the reactor inlet, the feed conditions, i.e. feed molar flow rates, inlet temperatures and inlet pressures, provide boundary conditions for the catalyst equations (5.33), (5.35), (5.37) and (5.39). The dusty gas model and the Fickian diffusion model equations on both sides of the reactor are solved numerically using the Matlab[®] (The MathWorks, Natick) routine bvp4c with a relative tolerance of 1×10^{-4} in order to retrieve the molar flux, mole fraction and temperature profiles inside the catalyst pellets. Those profiles are used to calculate the volume-averaged reaction rates and volume-averaged heat of reactors by numerically evaluating the integrals in equations (5.41) and (5.42). The reactor model equations are then integrated one step forward and this procedure continues until the whole length is covered. For this integration the Matlab[®] routine ode15s is employed with relative and absolute tolerances of 1×10^{-8} .

5.4. **Results and Discussion**

The model of the catalytic membrane reactor was solved for the operating conditions in Table 5.4. The molar flow rate and feed pressure were set to match the industrial values given by Moustafa and Elnashaie (2000). The feed temperature on the dehydrogenation side was adjusted to ensure the sustainability of the membrane, i.e. the local temperature of the membrane must never exceed 923 K. On the hydrogenation side, the total molar feed rate is 17 mole/s composed of only nitrobenzene and steam. The feed temperature on the hydrogenation side is chosen to ensure that heat always flows from the hydrogenation to the dehydrogenation side. Three models, i.e. the pseudo-homogeneous and heterogeneous based on the Fickian diffusion and the dusty gas model, are evaluated. In addition, the influence of isothermal versus non-isothermal catalyst pellets is assessed for both heterogeneous models.

5.4.1. Conversion of ethylbenzene and nitrobenzene

The conversion of ethylbenzene on the dehydrogenation side and nitrobenzene on the hydrogenation side versus the dimensionless distance along the membrane reactor are plotted in Figures 5.4a and 5.4b for the homogenous model and heterogeneous models based on Fickian diffusion and the dusty gas model, for isothermal and non-isothermal catalyst particles. All three models predict monotonic increases on the dehydrogenation side as shown in Figure 5.4a. The predictions of the three models, however, diverge due to the different methods of assessing the intraphase transport resistances. For example, the overall ethylbenzene conversion is predicted to be ~88% by the pseudo-homogeneous model, ~78% and ~71% by the heterogeneous reactor model based on Fickian diffusion for isothermal and non-isothermal catalyst pellets, and ~79% and ~75% according to the heterogeneous reactor model incorporating the dusty gas model for isothermal and non-isothermal and non-isothermal catalyst pellets, respectively.

On the hydrogenation side, the nitrobenzene conversion is plotted versus the axial dimensionless distance in Figure 5.4b. The overall conversion is predicted to be ~68% by the pseudo-homogeneous model compared with ~59% and ~52% by the heterogeneous reactor model with Fickian diffusion for isothermal and non-isothermal catalyst pellets, and ~61% and ~57% according to the heterogeneous reactor model in conjunction with the dusty gas model for isothermal and non-isothermal catalyst pellets, respectively.

5.4.2. Yield of styrene, benzene, and toluene on dehydrogenation side

The yields of styrene, benzene, and toluene on the dehydrogenation side are plotted against the dimensionless axial distance based on all three reactor models in Figures 5.5a, 5.5b, and 5.5c, respectively. The yields of all three components from the reactor models are predicted to increase monotonically along the reactors. Predictions, on the other hand, differ from one model to another due to the alternative intraparticle resistances. For example, the homogenous model predicts an overall styrene yield of ~82%, a benzene yield of ~5.0%, and a toluene yield of ~1.0%, whereas the heterogeneous reactor model

with Fickian diffusion predicts respective overall yields of ~73%, ~4.4% and ~0.9% for isothermal pellets and a styrene yield of ~68%, a benzene yield of ~3.0%, and a toluene yield of ~0.6% for non-isothermal pellets. The heterogeneous reactor model based on the dusty gas model predicts an overall styrene yield of ~73%, a benzene yield of ~4.6%, and a toluene yield of ~0.8% for isothermal pellets and respective overall yields of ~69%, ~4.4% and ~0.9% for non-isothermal pellets.

5.4.3. Hydrogen molar flow rates on dehydrogenation and hydrogenation sides

Predicted hydrogen molar flow rates on both sides of the reactor are plotted in Figures 5.6a, and 5.6b. On the dehydrogenation side, the hydrogen molar flow rate is predicted to increase linearly in the first portion of the membrane reactor as indicated in Figure 5.6a due to the significant net production of hydrogen. However, this is then balanced by the hydrogen diffusion through the membrane, causing the molar flow rate of hydrogen to become almost constant on the dehydrogenation side. The difference in predicting hydrogen molar flow rates between the homogenous reactor model and the heterogeneous model with Fickian diffusion for non-isothermal pellets is ~0.4 mole/s, whereas it is ~0.2 mole/s for the heterogeneous reactor model based on the dusty gas model for non-isothermal pellets.

On the hydrogenation side, the hydrogen molar flow rate is predicted to increase along the membrane reactor by all three reactor models, due to the significant hydrogen diffusion rate compared to its consumption rate. The heterogeneous reactor model based on Fickian diffusion for the isothermal pellet predicts a higher hydrogen flow near the entrance on the hydrogenation side than the homogenous model. The heterogeneous reactor model based on the dusty gas model for the non-isothermal pellets predicts a hydrogen flow similar to that predicted by the pseudo-homogeneous model, whereas the other models all predict smaller hydrogen flow rates.

5.4.4. Temperature profiles on both sides of coupled reactor

Predicted temperature profiles along the dehydrogenation side are plotted in Figure 5.7a for the pseudo-homogeneous model, the heterogeneous model with the Fickian diffusion and the dusty gas model for the isothermal and the non-isothermal cases. In all five cases, the temperature is predicted to decrease at the entrance of the reactor due to the net endothermicity on the dehydrogenation side until a minimum is reached where the heat absorbed by reactions is balanced by that transferred from the hydrogenation side. Beyond this point, the temperature increases monotonically until the outlet of the reactor. The point of balance occurs at a fractional length of ~0.2, but at different temperatures. The lowest temperature at which the point of balance occurs is predicted by the pseudo-homogeneous model, while the highest is predicted by the heterogeneous reactor model with Fickian diffusion for non-isothermal pellets. The heterogeneous dusty gas model predicts intermediate values for both isothermal and non-isothermal pellets.

As shown in Figure 5.7b, the temperature on the hydrogenation side is predicted to increase along the reactor due to the high heat release from the hydrogenation reaction. Only the homogenous model predicts a clear point of balance. The temperatures predicted by the heterogeneous models become almost constant until the end of the reactor after a monotonic increase. The heterogeneous reactor model based on the dusty gas model gives intermediate temperature profiles for both isothermal and non-isothermal pellets compared to both the pseudo-homogeneous reactor model and the heterogeneous model with Fickian diffusion.

5.4.5. Predictions of styrene yields and nitrobenzene conversions in the coupled reactor by the various models

Previously, optimal trade-off curves for conflicting conversion and yield objectives were determined based on the pseudo-homogeneous reactor model in chapter 3 using multi-objective approaches similar to those ones employed by Logist et al. (2009). The calculated optimal operating and design parameters for the coupled reactor are

summarized in Table 5.5 for three cases: (i) focus on the production of only styrene, case A, (ii) equal focus on styrene and aniline as products, case B and (iii) focus on the production of only aniline, *case C*. The coupled reactor is simulated for these three cases using the heterogeneous reactor model based on dusty gas diffusion, listing the yield of styrene and the conversion of nitrobenzene in Table 5.5. The predicted styrene yields and nitrobenzene conversions differ significantly indicating the importance of intraparticle transport resistances and the sensitivity to the diffusion model inside the catalyst pellets. When Fickian diffusion is used to describe the intraparticle diffusion, the predicted styrene yields and nitrobenzene conversions are reduced more than when the dusty gas model is utilized. The pseudo-homogeneous reactor model predicts higher styrene yields and nitrobenzene conversions because the effect of the intraparticle resistance is neglected. The Fickian diffusion model underestimates both the styrene yields and nitrobenzene conversions because it can be strictly applied for dilute systems. It also cannot also account for the change of moles as dusty gas model does in reactive systems. All the previously mentioned reasons result in making the Fickian diffusion model only an approximating tool for complex reactive systems, not a well-predicting one.

The deviations of the pseudo-homogeneous model, the heterogeneous model with Fickian diffusion for isothermal and non-isothermal catalyst pellet cases and the heterogeneous model with dusty gas for the isothermal catalyst pellet case from the heterogeneous model with dusty gas for the non-isothermal catalyst pellet case are given in Table 5.6 for the base case operating conditions listed in Table 5.4 and the three optimization cases of Table 5.5. The prediction of the heterogeneous dusty gas model for the non-isothermal catalyst pellets is taken as the most accurate and sophisticated predictive model. The predictions of the styrene yield and nitrobenzene conversion by all other models are evaluated along the reactor with a dimensionless spacing of 0.1. Deviations are evaluated based on both the mean square deviation and mean absolute deviation. The highest deviation is observed for the homogenous reactor model, while the lowest is for the heterogeneous model with Fickian diffusion for the non-isothermal catalyst pellet case. The predictions of all other models are intermediate between these two models. The assumption of isothermality causes greater deviations than the Fickian diffusion

simplification for all investigated cases. Moreover, even the worst heterogeneous model yields in all cases predictions within 6% of the most accurate model, compared to deviations of up to ~11% for the pseudo-homogeneous model.

5.5. Conclusions

A catalytic membrane fixed bed reactor coupling the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene is modeled in three ways: via the previously employed pseudo-homogeneous model and with two heterogeneous models, one employing Fickian diffusion and the other the dusty gas model employing the Stefan-Maxwell equations to describe intraparticle transport. In these last two, both isothermal and non-isothermal catalyst pellets are considered. The pseudo-homogeneous model overestimates both the yield of styrene on the dehydrogenation side and the conversion of nitrobenzene on the hydrogenation side, while the heterogeneous Fickian diffusion model under-predicts these quantities. The heterogeneous dusty gas diffusion model is more rigorous than the heterogeneous Fickian diffusion model, and it generally results in predictions intermediate between the homogenous and heterogeneous Fickian models. When all three models are compared with the heterogeneous reactor model with the dusty gas diffusion model for non-isothermal pellets, the highest deviation is observed for the pseudo-homogeneous reactor model, while the lowest is provided by the heterogeneous reactor model with Fickian diffusion for non-isothermal catalyst pellets. However, even the least rigorous pseudo-heterogeneous models yield predictions within 6% of the most rigorous model, while the deviations are up to $\sim 11\%$ for the pseudo-homogeneous model.

Chemical Reaction	Chemical Reaction Heat of Reaction		Reference			
Dehydrogenation Side ^a						
$C_6H_5CH_2CH_3 \Leftrightarrow C_6H_5CHCH_2 + H_2$	$\Delta H_{298} = 117.6 \frac{kJ}{mole}$	$r_1 = k_1 \left(p_{EB} - \frac{p_{ST} p_{H_2}}{K_A} \right)$	Elnashaie, et al (1993)			
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	$\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$	$r_2 = k_2 p_{EB}$	Elnashaie, et al (1993)			
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	$\Delta H_{298} = -54.6 \frac{kJ}{mole}$	$r_3 = k_3 p_{EB} p_{H_2}$	Elnashaie, et al (1993)			
$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$	$\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$	$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2}$	Elnashaie, et al (1993)			
$H_2O + CH_4 \rightarrow CO + 3H_2$	$\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$	$r_5 = k_5 p_{H_2O} p_{CH_4}$	Elnashaie, et al (1993)			
$H_2O + CO \rightarrow CO_2 + H_2$	$\Delta H_{298} = -41.2 \frac{kJ}{mole}$	$r_6 = k_6 \left(\frac{P}{T^3}\right) p_{H_2O} p_{CO}$	Elnashaie, et al (1993)			
Hydrogenation Side ^b						
$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$	$\Delta H_{298} = -443.0 \frac{\text{kJ}}{\text{mole}}$	$r' = \frac{k' K_{NB} K_{H_2} p'_{NB} \sqrt{p'_{H_2}}}{\left(1 + K_{NB} p'_{NB} + K_{H_2} \sqrt{p'_{H_2}}\right)^2}$	Amon, et al. (1999)			

Table 5.1 Stoichiometric equations, heats of reactions and reaction rate expressions for reactions in coupled reactor.

^a partial pressure in (bars) ^b partial pressure in (kPa)

Table 5.2 Frequency factors and activation energies for reactions in the coupled reactor.

Reaction ^a	k_{io}^{b}	E_i (kJ/kmol)	Reference
1 ^b	8.32×10^{3}	0.909×10^{5}	
2	4.23×10^{9}	2.080×10^5	F1 1 ' / 1
3	6.13×10^{3}	0.915×10^{5}	Elnashale, et al
4	3.95×10^{3}	1.040×10^5	(1995)
5	1.42×10^{2}	0.657×10^{5}	
6	5.80×10^{12}	0.736×10^{5}	
$7^{\rm c}$	1.86×10^{-4}	10.0×10^{3}	Amon, et al (1999)

^a Reactions are numbered 1 to 7 in the same order as listed in Table 5.1.

^b
$$k_i = \frac{10}{36} k_{io} \exp(-\frac{E_i}{RT})$$
, where k_{io} is the pre-exponential factor for $1 \le i \le 6$
 $k_i = 10^3 k_{io} \exp(-\frac{E_i}{RT})$, for $i = 7$.

The equilibrium constant is calculated by: $K_A = \exp(\frac{-\Delta F}{RT})$, where: $\Delta F = a + bT + cT^2$,

a=122725.16, b=-126.27/K, c=-2.194 $\times 10^3$ /K 2 d K $_{\rm NB}$ =1.51 $\times 10^{-2}$ kPa , K $_{\rm H_2}$ =0.14 kPa $^{-0.5}$

Balance Equations	Mathematical Expressions				
Dehydrogenation Side					
Mole	$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} \left(3 \int_0^{1.0} r_j \omega^2 d\omega \right) (1 - \varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J_i$	(5.8)			
Energy	$\frac{dT}{dz} = \frac{\sum_{j=1}^{6} \left(3\int_{0}^{1.0} \left[-\Delta H(T) \right]_{j} r_{j} \omega^{2} d\omega \right) (1-\varepsilon) A_{cs} \rho_{s} + Q}{\sum_{i=1}^{10} n_{i} C p_{i}}$	(5.9)			
Pressure	$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \left[\frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G\right]$	(5.10)			
	Hydrogenation Side (per tube)				
Mole	$\frac{dn'_i}{dz} = \sigma_i \left(3\int_0^{1.0} r'\omega'^2 d\omega' \right) (1-\varepsilon') A'_{cs} \rho'_s + 2\pi r_3 a_i J_i$	(5.11)			
Energy	$\frac{dT'}{dz} = \frac{(2\pi r_3)\sum_{i=1}^{i} a_i J_i \int_{T'}^{T} Cp_i dT + \left(3\int_{0}^{1.0} \left[-\Delta H'(T')\right]r'\omega'^2 d\omega\right)(1-\varepsilon')A'_{cs}\rho'_s - Q}{\sum_{i=1}^{4} n'_i Cp'_i}$	(5.12)			
Pressure	$\frac{dP'}{dz} = -\frac{G'}{\rho'_g g_c D'_p} \left(\frac{1-\varepsilon'}{\varepsilon'^3}\right) \left[\frac{150(1-\varepsilon')\mu'_g}{D'_p} + 1.75G'\right]$	(5.13)			
	Additional Relations				
Diffusion of hydrogen across membrane per tube	$J_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}}\right) \text{ where:}$ $Q_o = 7.29 \times 10^{-03} \text{ (mole} \times \text{m})/(\text{m}^2 \times \text{min} \times \text{atm}^{0.5}), \ \delta_{H_2} = 25 \times 10^{-6} \text{ m},$ $E_{H_2,P} = 20.5 \times 10^3 \text{ J/mole}$	(5.14)			
Heat transfer across membrane per tube	$Q = \frac{2\pi r_{i} (T' - T)}{\left[\frac{1}{h'} + \frac{r_{i}}{k_{ss}} \ln\left(\frac{r_{2}}{r_{1}}\right) + \frac{r_{i}}{k_{pd}} \ln\left(\frac{r_{3}}{r_{2}}\right) + \frac{r_{i}}{r_{2}h}\right]}$ where: $k_{ss} = 22.88 \text{ W/m/K}, \ k_{Pd} = 93.30 \text{ W/m/K},$ $\frac{hD_{t}}{k_{g}} = 0.813 \left(\frac{D_{p}G}{\mu_{g}}\right)^{0.9} \exp\left(-\frac{6D_{p}}{D_{t}}\right)$ $\frac{h'D'_{t}}{k'_{g}} = 3.50 \left(\frac{D'_{p}G'}{\mu'_{g}}\right)^{0.7} \exp\left(-\frac{4.6D'_{p}}{D'_{t}}\right)$	(5.15)			

Table 5.3 Heterogeneous model equations for coupled catalytic membrane reactor.

Table 5.4 Base case dimensional and operating parameters for coupled catalyticmembrane reactor.

Parameter	Values	Units			
Dimensional Variables					
Cross-sectional area-equivalent	1 95	m			
diameter of dehydrogenation side	1.95				
Inside diameter of hydrogenation	3.5×10 ⁻²	m			
	1500				
l otal number of hydrogenation tubes	1500				
Length of reactor	4.0	m			
Operating Conditions of Dehy	drogenation Si	ide			
Feed molar flowrate of ethylbenzene	10.242	mole/s			
Feed molar flowrate of styrene	0.1861	mole/s			
Feed molar flowrate of benzene	0.0306	mole/s			
Feed molar flowrate of toluene	0.2444	mole/s			
Feed molar flowrate of steam	125.86	mole/s			
Feed temperature	880.0	K			
Feed pressure	2.5	bar			
Catalyst density	2146.3	kg/m ³			
Catalyst thermal conductivity	0.3	J/m/s			
Pore diameter	4800×10^{-10}	m			
Catalyst porosity	0.35				
Catalyst tortuosity	4.0				
Bed voidage	0.48				
Operating Conditions per tube on Hydrogenation Side					
Feed molar flowrate of nitrobenzene	0.003	mole/s			
Feed molar flowrate of steam	0.008	mole/s			
Inlet temperature	900.0	K			
Inlet pressure	1.0	bar			
Catalyst density	1400	kg/m ³			
Catalyst thermal conductivity	0.05	J/m/s			
Pore diameter	5000×10 ⁻¹⁰	m			
Catalyst porosity	0.40				
Catalyst tortuosity	4.0				
Bed voidage	0.46				

		Paramete	r	Optimal case A	Optimal case B	Optimal case C
tion	Feed Molar flowrate of Ethylbenzene (mole/s)			7.66	9.36	11.27
on Dehydrogenat sis) Side	Steam-to-Ethylbenzene Ratio		7.00	7.00	20.00	
	Feed	Feed Temperature on Shell Side (K)		825.41	780.00	820.02
	Feed Pressure on Shell Side (bar)			4.00	2.52	4.00
Conversion of Nitrobenzene Yield of Styrene Dimensional Hydrogenation Variables (one tube basis) Side	Feed Molar flowrate of Nitrobenzene (mol/s)		0.005	0.002	0.002	
	Steam-to-Nitrobenzene Ratio		4.00	4.00	4.00	
	Feed Temperature on Tube Side (K)		825.41	780.00	820.02	
	Feed	Feed Pressure on Tube Side (bar)		3.62	1.00	1.00
	No. c	No. of Hydrogenation Tubes		2500	1582	1000
oimensional Variables	Equivalent-area Diameter of Dehydrogenation Side (m)		3.00	2.39	1.95	
	Diameter of Hydrogenation Tube (m)		0.048	0.035	0.040	
	React	Reactor Length (m)		4.00	4.00	4.00
	Pseud	Pseudo-homogeneous Modeling		0.975	0.564	0.491
yrene		Fickian	Isothermal Catalyst Pellets	0.930	0.512	0.426
l of Sty	geneous eling	Model	Non-isothermal Catalyst Pellets	0.925	0.478	0.386
Yield	Heterog Mode	Dusty Gas	Isothermal Catalyst Pellets	0.942	0.522	0.429
;	ł	Model	Non-isothermal Catalyst Pellets	0.894	0.4864	0.3956
tene	Pseud	lo-homogeneo	ous Modeling	0.211	0.555	0.796
robenz	geneous eling	Fickian Diffusion Model Dusty Gas	Isothermal Catalyst Pellets	0.208	0.502	0.713
n of Niı			Non-isothermal Catalyst Pellets	0.201	0.467	0.6594
Conversion o	Hetero£ Mode		Isothermal Catalyst Pellets	0.210	0.514	0.727
	ł	Model	Non-isothermal Catalyst Pellets	0.204	0.479	0.681

Table 5.5 Representative solutions for Pareto frontier. Constrained limits are bolded

Table 5.6 Deviations of the predictions inside the coupled reactor from the non-isothermal dusty gas heterogeneous reactor model.

Reactor Models		Yield of Styrene		Conversion of Nitrobenzene	
		Root mean square deviation	Absolute mean deviation	Root mean square deviation	Absolute mean deviation
Operating Condition in Table 5.4	Pseudo-homogeneous	0.113	0.109	0.0848	0.0801
	Heterogeneous, Fickian, Isothermal	0.0294	0.0286	0.0167	0.0155
	Heterogeneous, Fickian, Non-isothermal	0.0214	0.0211	0.0312	0.0284
	Heterogeneous, Dusty Gas, Isothermal	0.0335	0.0321	0.0297	0.0281
Case A	Pseudo-homogeneous	0.111	0.110	0.0193	0.0187
	Heterogeneous, Fickian, Isothermal	0.0442	0.0436	0.0073	0.0071
	Heterogeneous, Fickian, Non-isothermal	0.0108	0.0095	0.0027	0.0026
	Heterogeneous, Dusty Gas, Isothermal	0.0557	0.0055	0.0094	0.0092
Case B	Pseudo-homogeneous	0.0521	0.0485	0.0530	0.0499
	Heterogeneous, Fickian, Isothermal	0.0188	0.0178	0.0160	0.0147
	Heterogeneous, Fickian, Non-isothermal	0.0087	0.0086	0.0101	0.0096
	Heterogeneous, Dusty Gas, Isothermal	0.0243	0.0225	0.0250	0.0234
Case C	Pseudo-homogeneous	0.0717	0.0674	0.0990	0.0934
	Heterogeneous, Fickian, Isothermal	0.0225	0.0211	0.0247	0.0225
	Heterogeneous, Fickian, Non-isothermal	0.0092	0.0090	0.0177	0.0164
	Heterogeneous, Dusty Gas, Isothermal	0.0242	0.0224	0.0380	0.0357


Figure 5.1 Schematic of coupled catalytic membrane for cocurrent configuration.



Figure 5.2 Molar and heat fluxes across a small shell inside a catalyst pellet.



Figure 5.3 Computational sequence coupling dusty gas model equations with reactor model equations.



Figure 5.4 Conversion of (a) ethylbenzene on dehydrogenation side, and (b) nitrobenzene on hydrogenation side for base case operating conditions in Table 5.4.



Figure 5.5 Yield of (a) Styrene, (b) Benzene, and (c) Toluene along dehydrogenation side for base case operating conditions in Table 5.4.



Dimensionless Axial Distance

Figure 5.6 Hydrogen molar flowrate variation along reactor for base case operating conditions in Table 5.4 on: (a) dehydrogenation side, (b) hydrogenation side.



Figure 5.7 Temperature profiles along the reactor for base case operating conditions in Table 5.4 on: (a) dehydrogenation side, and (b) hydrogenation side.

- Abashar, M. E., Elnashaie, S. S., 1993. Mathematical modelling of diffusion-reaction, and solution algorithm for complex reaction networks in porous catalyst pellets steam reforming of natural gas, Mathematical and Computer Modelling 18(7), 85-100.
- Abo-Ghander, N. S., Logist, F., Grace, J. R., Van Impe, J. F. M., Elnashaie, S. S. E. H., Lim, C. J., 2010. Feasibility of coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene in an autothermal catalytic membrane reactor: modeling study, Proceedings of the 9th International Symposium on Dynamics and Control of Process Systems, 365.
- Amon, B., Redlingshöfer, H., Klemm, E., Dieterich, E., Emig, G., 1999. Kinetic investigations of the deactivation by coking of a noble metal catalyst in the catalytic hydrogenation of nitrobenzene using a catalytic wall reactor, Chemical Engineering and Processing 38(4-6), 395-404.
- Abdalla B. K., Al-Khowaiter S. H., Elshishini S. S., Elnashaie S. S. E. H., October 12 -17, 1997. Maximization of styrene yield from the catalytic dehydrogenation of ethylbenzene in fixed and fluidized bed configurations with and without selective membranes, 15th World Petroleum Congress, Beijing, China.
- Balasubramanian, B., Lopez Ortiz, A., Kaytakoglu, S., Harrison, D. P., 1999. Hydrogen from methane in a single-step process, Chemical Engineering Science 54(15-16), 3543-3552.
- Beuscher, U., H. Gooding, C., 1999. The influence of the porous support layer of composite membranes on the separation of binary gas mixtures, Journal of Membrane Science 152(1), 99-116.
- Chen, Z., Elnashaie, S. S. E. H., 2005. Autothermal CFB Membrane Reformer for Hydrogen Production from Heptane, Chemical Engineering Research and Design 83(7), 893-899.
- Chen, Z., Prasad, P., Yan, Y., Elnashaie, S., 2003. Simulation for steam reforming of natural gas with oxygen input in a novel membrane reformer, Fuel Processing Technology 83(1-3), 235-252.

- Elnashaie, S. S. E. H., Alhabdan, F. M., 1989. A computer software package for the simulation and optimization of an industrial ammonia converter based on a rigorous heterogeneous model, Mathematical and Computer Modelling 12(12), 1589-1600.
- Elnashaie, S. S. E. H., Moustafa, T., Alsoudani, T., Elshishini, S. S., 2000. Modeling and basic characteristics of novel integrated dehydrogenation — hydrogenation membrane catalytic reactors, Computers & Chemical Engineering 24(2-7), 1293-1300.
- Elnashaie, S. S. E. H., Soliman, M. A., Abashar, M. E., Almuhana, S., 1992. Mathematical modelling of diffusion and reaction for gas-solid catalytic systems with complex reaction networks. Negative effectiveness factors, Mathematical and Computer Modelling 16(12), 41-53.
- Elnashaie, S. S. E. H., Abashar, M. E. E., 1993. Steam reforming and methanation effectiveness factors using the dusty gas model under industrial conditions, Chemical Engineering and Processing 32(3), 177-189.
- Elnashaie, S. S. E. H., Abdalla, B. K., Hughes, R., 1993. Simulation of the industrial fixed bed catalytic reactor for the dehydrogenation of ethylbenzene to styrene: heterogeneous dusty gas model, Industrial & Engineering Chemistry Research 32(11), 2537-2541.
- Elnashaie S.S.E.H., Elshishini S.S., 1993. Modelling, Simulation and Optimization of Industrial Fixed Bed Catalytic Reactors. Amesterdam: Gordon and Breach Science Publisher.
- Froment G. F., Bischoff K. B., 1990. Chemical Reactor Analysis and Design. USA: John Wiley & Sons, Inc.
- Hermann, C., Quicker, P., Dittmeyer, R., 1997. Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor, Journal of Membrane Science 136(1-2), 161-172.
- Itoh, N., Xu, W. C., Hara, S., Kakehida, K., Kaneko, Y., Igarashi, A., 2003. Effects of hydrogen removal on the catalytic reforming of n-hexane in a palladium membrane reactor, Industrial & Engineering Chemistry Research 42(25), 6576-6581.

- Itoh, N., Wu, T., 1997. An adiabatic type of palladium membrane reactor for coupling endothermic and exothermic reactions, Journal of Membrane Science 124(2), 213-222.
- Krishna, R., 1990. Multicomponent surface diffusion of adsorbed species: a description based on the generalized Maxwell—Stefan equations, Chemical Engineering Science 45(7), 1779-1791.
- Krishna, R., Wesselingh, J. A., 1997. The Maxwell-Stefan approach to mass transfer, Chemical Engineering Science 52(6), 861-911.
- Logist, F., Van Erdeghem, P. M. M., Van Impe, J. F., 2009. Efficient deterministic multiple objective optimal control of (bio)chemical processes, Chemical Engineering Science 64(11), 2527-2538.
- Moustafa, T. M., Elnashaie, S. S. E. H., 2000. Simultaneous production of styrene and cyclohexane in an integrated membrane reactor, Journal of Membrane Science 178(1-2), 171-184.
- Rakib, M. A., Grace, J. R., Elnashaie, S. S. E. H., Lim, C. J., Bolkan, Y. G., 2008. Kinetic simulation of a compact reactor system for hydrogen production by steam reforming of higher hydrocarbons, The Canadian Journal of Chemical Engineering 86(3), 403-412.
- Soliman, M. A., El-Nashaie, S. S. E. H., Al-Ubaid, A. S., Adris, A., 1988. Simulation of steam reformers for methane, Chemical Engineering Science 43(8), 1801-1806.
- Tiemersma, T. P., Patil, C. S., Sint Annaland, M. v., Kuipers, J. A. M., 2006. Modelling of packed bed membrane reactors for autothermal production of ultrapure hydrogen, Chemical Engineering Science 61(5), 1602-1616.
- Uemiya, S., Sato, N., Ando, H., Matsuda, T., Kikuchi, E., 1990. Steam reforming of methane in a hydrogen-permeable membrane reactor, Applied Catalysis 67(1), 223-230.
- Veldsink, J. W., Versteeg, G. F., Van Swaaij, W. P. M., Van Damme, R. M. J., 1995. The use of the dusty-gas model for the description of mass transport with chemical reaction in porous media, The Chemical Engineering Journal and the Biochemical Engineering Journal 57(2), 115-125.

Wang, Y., Xu, Y., Xiang, H., Li, Y., Zhang, B., 2001. Modeling of Catalyst Pellets for Fischer-Tropsch Synthesis, Industrial & Engineering Chemistry Research 40(20), 4324-4335.

CHAPTER 6 OVERALL CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

In this project, coupling dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline has been modeled in a catalytic membrane reactor. The proposed catalytic membrane reactor used to couple the two reactions is composed of two sides: shell and tube. On the shell side, dehydrogenation of ethylbenzene takes place and styrene is produced along the reactor. In addition to styrene, benzene, toluene, and other light gases such as ethylene, methane carbon monoxide and carbon dioxide are also produced as side products. The main reaction, i.e. the one producing styrene, is reversible with the yield of styrene thermodynamically limited to \sim 0.40 in industry. The overall ethylbenzene conversion is also thermodynamically limited to \sim 0.45. The temperature drops along industrial fixed bed reactors in which the process is carried out due to the net endothermic nature of the reactions.

On tube side, however, nitrobenzene is hydrogenated to produce aniline. This reaction is irreversible and exothermic with a relatively large heat of reaction. Stoichiometrically, three moles of hydrogen are required for each mole of nitrobenzene to produce one mole of aniline and with a heat output of 443.0 kJ/mole. Consequently, the temperature increases along the industrial reactor.

In the proposed catalytic membrane reactor, the reactions are coupled by making the walls of hydrogenation tubes permeable to hydrogen. Hydrogen and heat are then exchanged between the two sides, resulting in improved styrene yield on the dehydrogenation sides and production of aniline on the hydrogenation side.

The new proposed reactor is novel and useful because:

- 1. This pair of reactions can be coupled because they are complementary, i.e. one produces hydrogen while the other requires hydrogen.
- The reactor is able to produce two valuable products, i.e. styrene on the dehydrogenation side and aniline on the hydrogenation side with substantial improvement in conversions and yields.
- 3. Unlike the other coupling systems presented in the literature, hydrogen, diffusing through the membrane to the tube, is utilized for a useful reaction to produce another valuable product, i.e. aniline, rather than simply being burnt to produce heat only.
- 4. Heat produced due to the hydrogenation reaction is transferred through the membrane tube and used to assist in shifting the equilibrium conversion of ethylbenzene and the yield of styrene.

In this study, optimal designs for the proposed reactor are obtained for which the yield of styrene on the dehydrogenation side and production of aniline on the hydrogenation side form a pair of objective functions. The optimization problem is classified as bi-objective, with the yield of styrene and the production of aniline maximized simultaneously subject to constraints. The pseudo-homogeneous model of the proposed reactor is used to calculate both objective functions. Two numerical optimization techniques are utilized to solve the challenging numerical problem, involving the conversion of the bi-objective optimization problem into a single one and applying an extra constraint. A total of 12 operating and dimensional variables with proper bounds and a number of linear and nonlinear constraints were considered. The solution of this problem results in a set of equally good solution referred to as a *Pareto set*. It is found that the proposed reactor can be constructed to produce a *styrene yield at ~97%* and a *nitrobenzene conversion at ~20%* as one extreme case. At another extreme, the same reactor can be operated to produce a *styrene yield of ~49%* and a *nitrobenzene conversion of ~80%*.

Due to the conflicting nature of both objective functions, the effects of the decision variables are non-monotonic along the Pareto-optimal set. For example:

- 1. Increasing the feed molar flowrate of ethylbenzene decreases the styrene yield as the production of the side products increases and the residence time decreases leading to unfinished reactions, while the effect on the tube side is to enhance the nitrobenzene conversion.
- 2. Increasing the ratio of ethylbenzene-to-steam reduces the yield of styrene and enhances the conversion of nitrobenzene.
- 3. Increasing the feed temperature on the shell side assists in enhancing the yield of ethylbenzene, but reduces the conversion of nitrobenzene.
- 4. Increasing the feed pressure on the dehydrogenation side enhances the styrene yield, but decreases nitrobenzene conversion.
- 5. Increasing the feed molar flowrate nitrobenzene enhances the styrene yield, but reduces the nitrobenzene conversion.
- 6. The steam-to-nitrobenzene ratio on the hydrogenation side has little influence, as it is mainly used to maintain the temperature below 923 K.
- 7. Increasing the feed temperature of hydrogenation enhances the yield of ethylbenzene, but at the same time, reduces the conversion of nitrobenzene.
- 8. It is favorable to operate at a high hydrogenation feed pressure to enhance the yield of styrene, whereas it is preferable to maintain low pressure to increase the conversion of nitrobenzene.
- 9. As the number of hydrogenation tubes increases, the yield of styrene increases, whereas the nitrobenzene conversion decreases.
- 10. Increasing the cross-sectional area of the dehydrogenation side increases the styrene yield, but decreases the conversion of nitrobenzene.
- 11. As the diameter of the hydrogenation tubes increases, the yield of styrene increases while the conversion of nitrobenzene decreases.
- 12. Due to the low temperature range imposed as a constraint inside the reactor, i.e. below 923K, the reactor tends to operate at the upper limit of the length.

The effect of intraparticle resistance is assessed using two heterogeneous models, one based on *Fickian diffusion* while the other is based on the *dusty gas model*. Along the reactor, the catalyst pellets on both sides are solved assuming both isothermal and non-

isothermal particles. The reaction rates in the homogenous reactor model equations are altered considering diffusion at the surface of the catalyst pellets. It is found that:

- 1. The intraphase transport resistance reduces both the reaction rates and the magnitude of the transported quantities, i.e. hydrogen diffusion and heat transfer. Styrene yield and nitrobenzene conversion are therefore decreased.
- 2. Infinite values of component effectiveness factors result when the concentration of hydrogen is zero in the bulk, while the flux at the surface of the catalyst pellets is significant.
- 3. All reaction effectiveness factors on the dehydrogenation side show nonmonotonic behavior as the bulk temperature changes. The trend changes at the point of heat balance, i.e. when the heat transfer from the hydrogenation side balances the net endothermic requirement for heat on the dehydrogenation side.
- 4. Diffusion of hydrogen from the dehydrogenation side to the hydrogenation side causes a sharp increase in the effectiveness factor of the hydrogenation reaction.
- 5. The reduction in performance due to the thermal resistance inside the catalyst is more pronounced than that resulting from the mass diffusion resistance.
- 6. The predicted yields and conversions from the heterogeneous reactor model with Fickian diffusion are ~7% to ~10% less than that of pseudo-homogeneous model.
- 7. The heterogeneous reactor model with intraparticle diffusion based on the dusty gas model is ~4% to ~7% less than for the pseudo-homogeneous model. The heterogeneous reactor model based on Fickian diffusion model overestimates the effect of the intraphase resistance compared to heterogeneous reactor model based on the dusty gas model.
- 8. The heterogeneous reactor model combined with the dusty gas model is recommended to describe the diffusion inside the catalyst pellets, as it is more rigorous than the heterogeneous reactor model with Fickian diffusion.
- 9. It is recommended to supply the analytical Jacobian matrix required to solve the catalyst pellets problems on both sides of the reactor. This can help to reduce the execution time and the rounding off error that might arise from other techniques such as finite differences.

6.2. Recommendations

As future work, the following directions are proposed:

- 1. Construct a proof-of-concept experimental catalytic membrane reactor in which all the complex safety issues arising from the reactions or processes are fully addressed.
- 2. With the aid of high capacity computers, solve the optimization problem again considering diffusion inside the catalyst pellets. Two optimal Pareto sets should be obtained and compared for the heterogeneous reactor model based on Fickian diffusion and for the heterogeneous reactor model, combined with the dusty gas model.
- 3. Optimizing the performance of the reactor with the cost as the objective function to be minimized.
- 4. Perform a sensitivity analysis based on the pseudo-heterogeneous model of the coupled reactor.
- 5. Set up and solve the optimal control problem. For example, the admissible hydrogen profile can be calculated on both sides of the reactor maximizing both the yield of styrene and the conversion of nitrobenzene. Compare the feasibility of implementing this profile with the admissible profile of temperatures.
- 6. Assess the effect of catalyst deactivation and compare with the effect of intraphase diffusion to determine which one has a greater overall influence. Deactivation by coking of the palladium catalyst supported on α -alumina used on the hydrogenation side is found to be pronouncing and could be determined quantitatively (Amon, 1999).
- 7. Obtain the optimal design of the countercurrent configuration of the proposed reactor.
- 8. Evaluate the behavior of the reaction system for a fluidized bed reactor on one or both sides, and compare the results with those for the fixed bed reactor.
- 9. Compare the advantages of the optimal design of the proposed catalytic membrane reactor with the optimal design of the fluidized bed reactor.

6.3. References

Amon, B., Redlingshöfer, H., Klemm, E., Dieterich, E., Emig, G., 1999. Kinetic investigations of the deactivation by coking of a noble metal catalyst in the catalytic hydrogenation of nitrobenzene using a catalytic wall reactor, Chemical Engineering and Processing 38(4-6), 395-404.