

**OPTIMAL DESIGN OF MEMBRANE REACTOR
COUPLING DEHYDROGENATION OF PROPANE
WITH ANILINE PRODUCTION IN AN ADIABATIC
FIXED BED MEMBRANE REACTOR**

BY

Omar Nabeel Al Deeb

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

December 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Omar Nabeel Al Deeb** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING**.



Dr. Hassan Mohammed Baaqeel
Department Chairman



Dr. Suliman Al-Homidan
Dean of Graduate Studies

27/12/2023
Date



Dr. Nabeel S. Abo-Ghander
(Advisor)



Dr. Nayef Masned Al-Saifi
(Member)



Dr. Abdallah A. Al-Shammari
(Member)



Prof. Mohammad Mozahar
Hossain
(Member)



Prof. Abdulla A. Shaikh
(Member)



© Omar Nabeel Al Deeb

2023

I dedicate this work to my supporting family and wife and my mentor, Dr. Nabeel |

ACKNOWLEDGMENTS

First and foremost, I would like to thank Allah Al Mighty for giving me the wisdom to seek knowledge and to help me use this knowledge for the betterment of myself and the society as a whole. I am grateful to him for granting me the strength, guidance, and patience to complete this master's degree thesis. Without his blessings and mercy this achievement would not have been possible.

Secondly, I would like to extend my sincere gratitude and appreciation to Dr. Nabeel Abo-Ghander for his overwhelming support throughout my thesis journey. I am deeply beholden for the time he dedicated in mentoring me. His expertise and insightful instructions played a crucial role in shaping the direction of my research and elevating the quality of my work. Dr. Nabeel has taught me a great deal and I will always cherish and appreciate the time we spent working together.

I would also like to thank the members of King Fahd University of Petroleum and Minerals and the Chemical Engineering department for their invaluable support and guidance. Their expertise and dedication to teaching have been transformative in my academic growth. I am truly grateful for the opportunity to pursue my master's degree at King Fahad University for petroleum and minerals. It is truly an honor and a pleasure to be part of such an esteemed establishment.

Finally, I would like to extend my heartfelt gratitude to my beloved wife and family for their invaluable support, encouragement and patience throughout this challenging yet rewarding period of my academic journey. Their constant support has been a source of motivation to achieve this milestone.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	VIII
LIST OF FIGURES	IX
NOMENCLATURE.....	XIII
ABSTRACT.....	XVII
ملخص الرسالة.....	XIX
CHAPTER 1 INTRODUCTION	1
1.1 Reactive systems.....	1
CHAPTER 2 LITERATURE REVIEW	4
2.1 Reactive systems.....	4
2.2 Economic aspects	14
CHAPTER 3 REACTOR CONFIGURATION AND REACTION KINETICS	15
CHAPTER 4 MATHEMATICAL MODELLING OF THE COUPLED MEMBRANE REACTOR.....	19
4.1 Model assumptions.....	19
4.2 Governing equations.....	21
4.3 Boundary conditions.....	24
4.4 Normalization of the mathematical model	25
CHAPTER 5 NUMERICAL SOLUTION OF THE MATHEMATICAL MODEL.....	31
CHAPTER 6 REACTOR PERFORMANCE AND PARAMETRIC STUDY.....	33

6.1 Comparison between the configurations of the membrane reactor and the conventional reactor	38
6.2 Parametric study	47
6.2.1 Molar fraction of helium	47
6.2.2 Number of tubes.....	52
6.2.3 Tube diameter	59
6.2.4 Dehydrogenation feed pressure	64
6.2.5 Hydrogenation feed pressure	69
6.2.6 Dehydrogenation feed temperature.....	74
6.2.7 Hydrogenation feed temperature	80
6.2.8 Steam to hydrocarbon ratio	85
CHAPTER 7 OPTIMIZATION	90
7.1 Optimization problem	90
7.2 Solution methodology	93
7.3 Results	96
CHAPTER 8 CONCLUSION AND RECOMMENDATIONS	114
APPENDICES.....	116
Appendix A – Detailed derivation of the model:.....	116
Appendix B – Detailed normalization of the model:.....	119
Appendix C – Physical properties:	143
REFERENCES.....	149
VITAE.....	153

LIST OF TABLES

Table 1: A literature review on different reaction types	8
Table 2: Organic chemical production in the USA in 2001 and 2019.....	14
Table 3: Definitions of the dimensionless groups used in the model.	26
Table 4: Parameters for the reference case	33
Table 5: Comparison between co-current and counter current configurations.....	39
Table 6: Effect of the mole fraction of Helium on the performance of the membrane reactor	48
Table 7: Effect of the number of tubes on the performance of the membrane reactor	53
Table 8: Effect of the tube's diameter on the performance of the membrane reactor	60
Table 9: Effect of the dehydrogenation feed pressure on the performance of the membrane reactor	65
Table 10: Effect of the hydrogenation feed pressure on the performance of the membrane reactor	70
Table 11: Effect of the dehydrogenation feed temperature on the performance of the membrane reactor.....	75
Table 12: Effect of the hydrogenation feed temperature on the performance of the membrane reactor.....	81
Table 13: Effect of the steam to hydrocarbon ratio on the performance of the membrane reactor	86
Table 14: Decision variables and their upper and lower limits	91
Table 15: Optimized values using the NNC and NBI multi-objective optimization methods	96
Table 16: Results for the decision variables for the multi-objective optimization of the co-current membrane reactor.....	97
Table 17: Regression coefficients for the calculation of the enthalpy of formation [41]	143
Table 18: Regression coefficients for the calculation of the heat capacity [41]	144
Table 19: Regression coefficients for the calculation of the viscosity of the gases [41].....	145
Table 20: Regression coefficients for the calculation of the thermal conductivity of the gases	146
Table 21: Regression coefficients for the calculation of the thermal conductivity of the gases	147
Table 22: Regression coefficients for the calculation of the Gibbs energy of formation of the gases [41]	148

LIST OF FIGURES

Figure 1: Cocurrent and counter-current configuration of the coupled hydrogenation and dehydrogenation reactions in a membrane reactor.....	16
Figure 2: Infinitesimal element on both sides of the coupled membrane reactor	20
Figure 3: Performance plot for the co-current reference case.....	36
Figure 4: Performance plot for the counter current reference case.....	37
Figure 5: Conversion of propane plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor, counter current membrane reactor and the conventional dehydrogenation reactor.	41
Figure 6: Yield of propene plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor, counter current membrane reactor and the conventional dehydrogenation reactor.	42
Figure 7: Conversion of nitrobenzene plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.	43
Figure 8: Hydrogen flux per tube plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.	44
Figure 9: Heat flux per tube plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.	45
Figure 10: Temperature profiles for the hydrogenation and dehydrogenation sides for both configurations plotted against the dimensionless axial distance.....	46
Figure 11: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.	49
Figure 12: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.	50
Figure 13: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.	51

Figure 14: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.	54
Figure 15: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.	55
Figure 16: Total heat flux from all tubes against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.	56
Figure 17: Total hydrogen flux from all tubes against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.....	57
Figure 18: Hydrogenation and dehydrogenation temperatures against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.....	58
Figure 19: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.....	61
Figure 20: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.....	62
Figure 21: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.....	63
Figure 22: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.	66
Figure 23: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.	67
Figure 24: Hydrogen flux per tube plotted against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.	68
Figure 25: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures.	71
Figure 26: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures	72
Figure 27: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures.	73
Figure 28: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.....	76

Figure 29: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.....	77
Figure 30: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.....	78
Figure 31: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.....	79
Figure 32: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.	82
Figure 33: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.	83
Figure 34: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.	84
Figure 35: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.....	87
Figure 36: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.....	88
Figure 37: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.....	89
Figure 38: Flowchart showing the methodology for solving the multi-objective optimization problem using the Tomlab Snopt solver to generate a Pareto solution set.	94
Figure 39: Pareto plot for maximizing the yield of propene and conversion of nitrobenzene in the co-current membrane reactor	98
Figure 40: Values of the decision variables plotted against the conversion of nitrobenzene for the multi-objective optimization using NNC and NBI	102
Figure 41: Values of the decision variables plotted against the yield of propene for the multi-objective optimization using NNC and NBI.....	103
Figure 42: Conversion of propane against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor.....	104
Figure 43: Yield of propene against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor.....	105

Figure 44: Conversion of nitrobenzene against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor.....	106
Figure 45: Hydrogenation temperature against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor.....	107
Figure 46: Temperature profile against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor.....	108
Figure 47: The optimum number of tubes for all 20 optimization cases in a co-current membrane reactor	111
Figure 48: The optimum feed flowrate of nitrobenzene for all 20 optimization cases in a co-current membrane reactor	112
Figure 49: The optimum steam-to-nitrobenzene ratio for all 20 optimization cases in a co-current membrane reactor.....	113

NOMENCLATURE

Ag	:	Silver
NNC	:	Normalized Normal Constraint method.
NBI	:	Normalized Boundary Intersection method
NB	:	Nitrobenzene
FCC	:	Fluidized Catalytic Cracking
CFD	:	Computational Fluid Dynamics
Pb	:	Palladium
Ag	:	Silver
ΔH_{298}	:	Heat of reaction (kJ mol^{-1})
$r_{C_3H_8,1}$	:	Reaction rate law for propane dehydrogenation ($\text{mol kg}^{-1} \text{min}^{-1}$)
$r_{C_3H_8,2}$	:	Reaction rate law for propane cracking ($\text{mol kg}^{-1} \text{min}^{-1}$)
$r_{C_2H_4,3}$	:	Reaction rate law for ethylene hydrogenation ($\text{mol kg}^{-1} \text{min}^{-1}$)
k_1	:	Reaction rate constant for propane dehydrogenation ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-1}$)
k_2	:	Reaction rate constant for propane cracking ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-1}$)
k_3	:	Reaction rate constant for ethylene hydrogenation ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-2}$)
k_{01}	:	Reaction rate constant at T_0 for first reaction ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-1}$)
k_{02}	:	Reaction rate constant at T_0 for second reaction ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-1}$)
k_{03}	:	Reaction rate constant at T_0 for third reaction ($\text{mol kg}^{-1} \text{min}^{-1} \text{bar}^{-2}$)
p_i	:	Partial pressure of species i on the dehydration side (bar)
K_{eq}	:	Equilibrium constant (bar)
$K_{C_3H_8}$	:	Adsorption constant of propylene (bar)

K_0	:	Adsorption constant of propylene at T_0 (bar)
E_{ai}	:	Activation energy of reaction i (kJ mol^{-1})
T, T_0	:	Dehydrogenation temperature and reference temperature (K)
r'	:	Reaction rate law for nitrobenzene hydrogenation ($\text{mol kg}^{-1} \text{s}^{-1}$)
k'	:	Reaction rate constant for nitrobenzene hydrogenation ($\text{mol kg}^{-1} \text{s}^{-1}$)
K_{NB}	:	Adsorption constant of nitrobenzene (kPa^{-1})
K_{H_2}	:	Adsorption constant of hydrogen ($\text{kPa}^{-0.5}$)
P'_i	:	Partial pressure of species i on the hydration side (kPa)
T'	:	Hydrogenation temperature (K)
n_i	:	molar flow of species i on the dehydrogenation side (mol/s)
n'_i	:	molar flow of species i on the hydrogenation side (mol/s)
z	:	Reactor length (m)
A_c	:	Cross-sectional area of the dehydrogenation side (m^2)
A'_c	:	Cross-sectional area of the hydrogenation side (m^2)
J_i	:	Flux of species i ($\text{mol m}^{-2} \text{s}^{-1}$)
U	:	Overall heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
C_{pi}	:	Heat capacity of species i in the dehydrogenation side ($\text{J mol}^{-1} \text{K}^{-1}$)
C'_{pi}	:	Heat capacity of species i in the hydrogenation side ($\text{J mol}^{-1} \text{K}^{-1}$)
R	:	Universal Gas Constant (J mol^{-1})
Q_0	:	Hydrogen membrane pre-exponential factor ($\text{mol m}^{-1} \text{min}^{-1} \text{atm}^{-0.5}$)
k_{ss}	:	Thermal conductivity of stainless steel ($\text{W m}^{-1} \text{K}^{-1}$)
k_{Pd}	:	Thermal conductivity of palladium ($\text{W m}^{-1} \text{K}^{-1}$)
x_i	:	Dimensionless fractional change in molar flow for species i (dehydrogenation)

x'_i : Dimensionless fractional change in molar flow (hydrogenation)

K' : Dimensionless equilibrium constant

K'_0 : Dimensionless pre-exponential factor

K'_{NB} : Dimensionless NB equilibrium constant (hydrogenation)

K'_{H_2} : Dimensionless H_2 equilibrium constant (hydrogenation)

R' : Dimensionless ratio of molar flow of the key components

Greek letters

σ_{ij} : Stoichiometric coefficient for species i in reaction j

σ'_i : Stoichiometric coefficient for species i in the hydrogenation reaction

ε : Bed void fraction on the dehydrogenation side

ε' : Bed void fraction on the hydrogenation side

ρ_s : Catalyst density on the dehydrogenation side (kg m^{-3})

ρ'_s : Catalyst density on the hydrogenation side (kg m^{-3})

δ_{H_2} : Membrane thickness (m)

ξ : Dimensionless fractional length

θ : Dimensionless reactor dehydrogenation temperature

θ' : Dimensionless reactor temperature on hydrogenation side (hydrogenation)

θ_0 : Dimensionless reference temperature

ϵ_i : Dimensionless activation energy for reaction i

ϵ' : Dimensionless activation energy (hydrogenation)

ϵ_k : Dimensionless ΔH_{rxn}

γ_i : Dimensionless partial pressure (dehydrogenation)

γ'_i : Dimensionless partial pressure (hydrogenation)

ϵ_{H_2}	:	Dimensionless hydrogen activation energy
Pr	:	Dimensionless feed pressures ratio (dehydrogenation / hydrogenation)
α_i	:	Dimensionless Damckholer's number (Reaction 1 and 2)
α_3	:	Dimensionless Damckholer's number (Reaction 3)
α'	:	Dimensionless Damckholer's number (hydrogenation)
α_{PER}	:	Dimensionless permeability constant for hydrogen
β_i	:	Dimensionless heat of reaction for dehydrogenation reaction i
β'	:	Dimensionless heat of reaction (hydrogenation)
ψ	:	Dimensionless reactor pressure (dehydrogenation)
ψ'	:	Dimensionless reactor pressure (hydrogenation)
β_0	:	Dimensionless pressure coefficient (dehydrogenation)
β'_0	:	Dimensionless pressure coefficient (hydrogenation)

|

ABSTRACT

Full Name : [OMAR NABEEL AL DEEB]

Thesis Title : [OPTIMAL DESIGN OF MEMBRANE REACTOR COUPLING
DEHYDROGENATION OF PROPANE WITH ANILINE
PRODUCTION IN AN ADIABATIC FIXED BED MEMBRANE
REACTOR]

Major Field : [MASTERS OF SCIENCE IN CHEMICAL ENGINEERING]

Date of Degree : [December 2023]

A novel reactor configuration where the dehydrogenation of propane to propylene and the hydrogenation of nitrobenzene to aniline occur simultaneously is proposed. This reactor configuration overcomes the thermodynamic limitations of the dehydrogenation reaction by allowing both mass (hydrogen) and heat transfer between the shell and the tubes. Hydrogen produced by the dehydrogenation reaction diffuses through the palladium-hydrogen membranes, promoting the production of propylene, to the hydrogenation side where it is consumed to form aniline. The performance boosting characteristics of the reactor were analyzed by developing a pseudo-homogeneous reactor model which was solved using the orthogonal collocation method. The model generated was used to compare the performance of the membrane reactor with that of the conventional reactor. Also, a parametric study was conducted to determine the effect of several parameters on the conversions of propylene and nitrobenzene. The model was then used to perform a multi-objective optimization procedure using the normalized normal constraint method (NNC) and the normalized boundary intersection method (NBI). The optimization was carried out by using the yield of propene and the conversion of nitrobenzene as the objective functions. The two functions were maximized by varying the number of tubes, reactor length, feed molar flowrate of nitrobenzene, steam-to-nitrobenzene ratio, and the feed hydrogenation temperature. The results

obtained show that the use of the novel membrane reactor compared to the conventional reactor led to a massive increase in the conversion of propane from 0.37 in the conventional reactor to 0.77 in the membrane reactor. Also, the co-current configuration favored the dehydrogenation side at the expense of the hydrogenation side, whereas the counter-current mode favored the hydrogenation side at the expense of the dehydrogenation reaction. The optimization showed that the maximum achievable yield of propene is 0.976 while the maximum conversion of nitrobenzene is 0.902 which is a significant improvement to the performance of the reactor.

ملخص الرسالة

الاسم الكامل: عمر نبيل الديب

عنوان الرسالة: التصميم الأمثل للمفاعل الغشائي الذي يجمع نزع الهيدروجين من البروبان مع إنتاج الأنيلين في مفاعل غشائي ذو قاعدة ثابتة ثابت الحرارة

التخصص: ماجستير العلوم في الهندسة الكيميائية

تاريخ الدرجة العلمية: ديسمبر 2023

يُقترح تكوين مفاعل جديد حيث تحدث عملية نزع الهيدروجين من البروبان إلى البروبيلين ودرجة النيتروبنزين إلى الأنيلين في وقت واحد. يتغلب تكوين المفاعل هذا على القيود الديناميكية الحرارية لتفاعل نزع الهيدروجين من خلال السماح لكل من الكتلة (الهيدروجين) ونقل الحرارة بين الغلاف والأنابيب. ينتشر الهيدروجين الناتج عن تفاعل نزع الهيدروجين عبر أغشية الهيدروجين والبلاديوم، مما يعزز إنتاج البروبيلين، إلى جانب الهدرجة حيث يتم استهلاكه لتكوين الأنيلين. تم تحليل خصائص تعزيز أداء المفاعل من خلال تطوير نموذج مفاعل شبه متجانس والذي تم حله باستخدام طريقة التجميع المتعامد. تم استخدام النموذج الناتج لمقارنة أداء المفاعل الغشائي مع أداء المفاعل التقليدي. كما أجريت دراسة حدودية لتحديد تأثير عدة عوامل على تحويلات البروبيلين والنيتروبنزين. تم بعد ذلك استخدام النموذج لتنفيذ إجراء تحسين متعدد الأهداف باستخدام طريقة القيد العادية (NNC) وطريقة تقاطع الحدود الطبيعية (NBI). تم إجراء التحسين باستخدام ناتج البروبين وتحويل النيتروبنزين كوظائف موضوعية. تم تعظيم الوظيفتين عن طريق تغيير عدد الأنابيب، وطول المفاعل، ومعدل التدفق المولي للتغذية من النيتروبنزين، ونسبة البخار إلى النيتروبنزين، ودرجة حرارة هدرجة التغذية. أظهرت النتائج التي تم الحصول عليها أن استخدام المفاعل الغشائي الجديد مقارنة بالمفاعل التقليدي أدى إلى زيادة هائلة في تحويل البروبان من 0.37 في المفاعل التقليدي إلى 0.77 في المفاعل الغشائي. أيضاً، فضل تكوين التيار المشترك جانب نزع الهيدروجين على حساب جانب الهدرجة، في حين فضل وضع التيار المعاكس جانب الهدرجة على حساب تفاعل نزع الهيدروجين. أظهر التحسين أن الحد الأقصى الذي يمكن تحقيقه من إنتاج البروبين هو 0.976 بينما الحد الأقصى لتحويل النيتروبنزين هو 0.902 وهو تحسن كبير في أداء المفاعل.

CHAPTER 1

INTRODUCTION

The chemical market has witnessed a major increase in demand for unsaturated hydrocarbons over the past decade and according to forecasts, this increase will continue until 2030. This is especially true for light alkenes such as ethylene and propylene. The propylene market is forecasted to grow at an average rate of 4-5% per year [1]. Unsaturated hydrocarbons are the building blocks of various essential chemicals. Ethylene and propylene are used as monomers to produce their corresponding polymers (polyethylene and polypropylene). Propylene is also the raw material to produce propylene oxide, acrylonitrile, cumene, butyraldehyde, and acrylic acid.

1.1 Reactive systems

A popular synthesis route to produce unsaturated hydrocarbons is the dehydrogenation of their corresponding alkanes in the presence of a catalyst. While the majority of propylene is currently being produced as a byproduct from the steam cracking of liquid naphtha and by the fluidized catalytic cracking (FCC) in refineries [2], on-purpose technologies such as propane dehydrogenation have widely spread. This increase in popularity of propane dehydrogenation is due to the higher increase in propylene's demand when compared with that of ethylene so a method that specifically produces propylene had to be adopted. Another reason for the increasing demand for dehydrogenation techniques

to produce ethylene is the construction of more ethane crackers that do not produce any propylene [2].

The dehydrogenation reaction is endothermic, reversible, and limited by equilibrium so to drive the equilibrium forward, the reaction is carried out at high temperatures and nearly atmospheric pressure [3]. To increase the efficiency of the dehydrogenation reaction used to produce propylene and other unsaturated hydrocarbons, membrane reactors were introduced. The membranes used are permeable to hydrogen, thus allowing it to escape while retaining other products and the reactants. According to Le Chatelier's principle, the reduction in the partial pressure of hydrogen would positively shift the equilibrium in the forward direction hence producing more products and enhancing the conversion of propane.

The purpose of this research is to study the design and optimization of a novel membrane reactor where the dehydrogenation of propane is carried out on one side of the membrane producing hydrogen which is utilized on the other side of the membrane in the hydrogenation of nitrobenzene to produce aniline. This research aims to provide an alternative to the conventional propane dehydrogenation reactor. The proposed alternative enhances the conversion and yield of the thermodynamically limited dehydrogenation reaction and utilizes the hydrogen produced to form a useful product that is high in demand (nitrobenzene). The membrane reactor allows mass transfer, in the form of hydrogen, between the two sides of the reactor as well as heat transfer from the exothermic hydrogenation reaction to the endothermic dehydrogenation reaction further enhancing the conversion of propane.

The heat transfer through the membrane out of the hydrogenation side of the reactor allows the reaction to take place in a fixed bed reactor without the risk of very high operating temperatures thus eliminating the need for a fluidized bed reactor. Also, the alternative reactor allows the operator to comfortably manipulate the temperature and concentrations of the species in the reactor without influencing the reactor's performance. Moreover, the proposed reactor configuration will provide significant cost reduction due to the elimination of the multiple separation units needed in the conventional process. Finally, the reactor will be optimized using a multi-objective optimization process to optimize both the yield of propene and the conversion of nitrobenzene despite their conflicting nature.

This thesis first extensively reviews the literature in Chapter 2, then presents the reactor configuration and reaction kinetics in Chapter 3. Chapter 4 shows the mathematical modelling of the coupled membrane reactor for both the tube and shell sides and the normalization of the model. Chapter 5 presents the numerical method used in solving the model. Chapter 6 shows a critical comparison between the proposed membrane reactor and a conventional propane dehydrogenation reactor. The chapter also shows the results of the parametric study carried out using the model. Relying on the previous chapters, Chapter 7 tackles the optimization of the membrane reactor in order to enhance the yield of propene and the conversion of nitrobenzene. Finally, Chapter 8 addresses the conclusion and lists the recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Reactive systems

Membrane reactors have been used to produce hydrogen from a variety of reactions; Y. Park et. al. (2020)[4] investigated the use of membrane reactors to produce pure hydrogen gas from ammonia using steam as a sweep gas. H. Lee. et al. (2020) [5] carried out a comparison between the hydrogen production from steam methane reforming in a packed-bed reactor, a membrane reactor, and a sorption enhanced membrane reactor. The results showed that the latter increased hydrogen's production in an environmentally friendly way by adsorbing the carbon dioxide produced by the reaction. Y. Hayakawa et al. (2020) [6] produced hydrogen from ammonia by a plasma membrane reactor. In an attempt to enhance the hydrogen recovery of the membrane reactor, Sharma R. et al. (2020) [7] used a multi-pass membrane reactor. Moreover, P. Tandon and M. Jain (2020) [8] studied the decomposition of hydrogen iodide in a non-isothermal packed-bed membrane reactor. Ghasemzadeh K et al. (2020) [9], studied the hydrogen production by the dehydrogenation of methylcyclohexane by carrying a CFD analysis. This study was conducted with a silica membrane reactor and a conventional fixed bed reactor. The membrane reactor outperformed its counterpart achieving complete methylcyclohexane conversion and almost 96% hydrogen recovery.

The type of membrane used is also another important aspect of a membrane reactor. There are several options available such as Silica-based membranes, or Palladium based membranes. K. Ghasemzadeh, et al. (2020) [10] studied the difference in the performance of Pd-Ag and silica-membrane reactors to produce hydrogen from methanol steam reforming. The study evaluated the reactor's performance by overserving the hydrogen yield, carbon monoxide selectivity, and methanol conversion. The conclusion was that the silica membrane reactor was the better choice when compared to both the Pd-Ag membrane reactor and the packed-bed reactor.

In the literature, several authors addressed the dehydrogenation of light alkanes to alkenes. E.V. Shelepova et al. (2011) developed a mathematical model for the dehydrogenation of propane in a membrane reactor where the outer wall of the reactor was heated, the hydrogen produced on the tube side of the reactor was oxidized in the shell side. The oxidation of hydrogen increased the yield of propylene from 65% in a packed bed reactor to 95% in the membrane reactor. The same author then investigated the effect of the reactor configuration in E.V. Shelepova and A.A. Vedyagin (2020) [11], the reactor was made of several hydrogen-permeable tubes for the dehydrogenation reaction, placed in a bigger tube. The outer tube (shell) was loaded with a catalyst to conduct the oxidation of hydrogen produced. Moreover, the outer wall was not heated, instead, the temperature inside the reactor was determined by the temperature of the feed. In this study, the dehydrogenation of ethane, propane, and ethylbenzene was carried out and it was discovered that heavier hydrocarbons led to the formation of more by-products.

In the literature, very few authors attempted the integration between a hydrogenation and dehydrogenation reaction on either side of the membrane. N.S. Abogghander et al. (2008) integrated the dehydrogenation of ethylbenzene in the tube side of a membrane reactor with the hydrogenation of nitrobenzene to aniline. Therefore, there is room for further investigating the integration between various other chemical dehydrogenation and hydrogenation reaction combinations. Table 1 shows several published areas of research on membrane dehydrogenation reactions using three main reactor configurations. The use of sweep gas in the shell side of the membrane has been thoroughly researched with only a few papers addressing the integration between hydrogenation and de-hydrogenation reactions in a membrane reactor.

When it comes to optimization, M. Dehdashtijahromi et al. (2023) [12] carried out a dynamic optimization on a membrane reactor used for olefin and pure hydrogen production to maximize the selectivity and olefin production rates of the reactor. Also, J. Liu et al. (2021) [13] obtained their preferred operating conditions for the propane dehydrogenation reactor coupled with selective hydrogen combustion using a parametric sweep method. A more refined global optimization method will be the subjective of their future work. A. Darvishi et al. (2016) [14] modeled a fixed-bed membrane reactor for oxidative dehydrogenation of propane. The model was then used to optimize the reactor by determining the length required to theoretically reach 100% conversion. A single-bed and a double-bed reactor were modelled and their optimized lengths to reach 100% conversion were calculated.

Similarly, M. Sheintuch and R. M. Dessau (1995) [15] modelled and optimized a dehydrogenation membrane reactor producing isobutane and propane using a sweeping gas on the shell side. The reactor was optimized to calculate the optimum feed and shell flow rates that gives the highest yield. D. Xiang et al. (2022) [16] simulated propane dehydrogenation with and without hydrogen production and carried out a parameter optimization process to determine the optimum reactor length, H/P ration and flash temperature.

This research models the simultaneous dehydrogenation of propane to form propylene and the synthesis of aniline by the reaction between the nitrobenzene fed to the reactor and the hydrogen produced in the dehydrogenation reaction. The tube side of the reactor contains the catalyst for the dehydrogenation reaction. The hydrogen produced then diffuses through the membrane to the shell side which is loaded with the aniline synthesis catalyst. The co-current and counter-current flow schemes will both be investigated. Moreover, using the model, a parametric study will be carried out along with the optimization of the system to maximize the yield of propylene and the conversion of nitrobenzene.

Table 1: A literature review on different reaction types

Dehydrogenation using a sweep gas							
#	Reaction Type		Type of Reactor		Type of Study	Improvement	Ref.
	Tube	Shell					
1	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	No Sweep Gas (Open)	Packed membrane reactor	bed	Experimental	21% increase in yield at 600°C	[17]
2	Dehydrogenation of ethane $C_2H_6 \leftrightarrow C_2H_4 + H_2$	Pure N ₂ and Air as sweep gas	Tubular catalytic reactor	fixed-bed membrane	Modeling + Experimental	Modeling agreed with experimental when N ₂ was used but not with air	[18]
3	Dehydrogenation of ethane $C_2H_6 \leftrightarrow C_2H_4 + H_2$	With sweep gas (N ₂) or reactive oxidation (Using air)	Fixed-bed membrane reactor	catalytic	Modeling + Experimental	Model verified using experimental data	[19]
4	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas (pure N ₂)	Packed-bed membrane reactor	catalytic	Experimental	33.8% improvement when compared to conventional packed bed reactor	[20]
5	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas (pure N ₂)	Packed-bed membrane reactor	catalytic	Experimental	34% higher than thermodynamic equilibrium conversion using a WHSV 0.16 h ⁻¹ , which can reach up to 100%	[21]

Table 1: A literature review on different reaction types (cont.)

Dehydrogenation using a sweep gas						
#	Reaction Type	Shell	Type of Reactor	Type of Study	Improvement	Ref.
	Tube					
6	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas	Packed bed catalytic membrane reactor (composite and microporous membrane reactors)	Modeling + Experimental (kinetics)	Experimental data agreed with the model.	[22]
7	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Stripping gas	Packed-bed catalytic membrane reactor	Experimental	Conversion increased by a factor of 1.6 to 2.0	[23]
8	Dehydrogenation of isobutane $C_4H_{10} \leftrightarrow C_4H_8 + H_2$	Sweep gas stream	Packed-bed catalytic membrane reactor	Modeling	10.81%	[24]
9	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas	Packed-bed catalytic membrane reactor	Modeling	N/A	[3]

Table 1: A literature review on different reaction types (cont.)

Dehydrogenation using a sweep gas						
#	Reaction Type		Type of Reactor	Type of Study	Improvement	Ref.
	Tube	Shell				
10	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas	Packed-bed catalytic membrane reactor	Experimental	N/A	[25]
11	Sweep gas	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Packed-bed catalytic membrane reactor	Modelling	25% conversion	[26]
12	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas	Packed-bed catalytic membrane reactor	Experimental	50%	[27]
13	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Sweep gas	Packed-bed catalytic membrane reactor	Modeling and Experimental	N/A	[28]

Table 1: A literature review on different reaction types (cont.)

Dehydrogenation using the oxidation of hydrogen						
#	Reaction Type		Type of Reactor	Type of Study	Improvement	Ref.
	Tube	Shell				
1	Reactive oxidation with oxygen present in the air	Dehydrogenation of n-butane $C_4H_{10} \leftrightarrow C_4H_8 + H_2$	Fixed-bed catalytic membrane reactor	Modeling	The membrane reactor outperformed the fixed bed reactor at high values of the feed air/n-butane ratios	[29]
2	Dehydrogenation of propane $C_3H_8 \leftrightarrow C_3H_6 + H_2$	Oxidation of Hydrogen using oxygen: $2H_2 + O_2 \rightarrow 2H_2O$	Packed-bed catalytic membrane reactor	Modeling	Propane conversion increased from 41% to 67%, reaching 96% with oxidation of the removed hydrogen	[30]
3	Dehydrogenation of ethane $C_2H_6 \leftrightarrow C_2H_4 + H_2$	Combustion of Hydrogen using oxygen: $2H_2 + O_2 \rightarrow 2H_2O$	Packed-bed catalytic membrane reactor	Modeling	Using a membrane reactor can increase the conversion of ethane even at lower temperatures which decreases coke formation	[31]

Table 1: A literature review on different reaction types (cont.)

Dehydrogenation using the oxidation of hydrogen					
#	Reaction Type		Type of Reactor	Type of Study	Improvement
	Tube	Shell			
4	1. Dehydrogenation of ethane		Packed-bed catalytic membrane reactor	Modeling	Increasing the molar mass of the HC increases the amount of by-product formed. Oxidation of the flux hydrogen decreases the reactor temperature which in turn decreases the amount of coke formation. And enhances the target's product yield [11]
	$C_2H_6 \leftrightarrow C_2H_4 + H_2$				
	2. Dehydrogenation of propane	Oxidation of flux			
	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	Hydrogen using oxygen:			
	3. Dehydrogenation of ethylbenzene	$2H_2 + O_2 \rightarrow 2H_2O$			
	$C_6H_5CH_2CH_3$				
	$\leftrightarrow C_6H_5CH=CH_2 + H_2$				

Table 1: A literature review on different reaction types (cont.)

Integration of hydrogenation-dehydrogenation reactions						
#	Reaction Type		Type of Reactor	Type of Study	Improvement	Ref .
	Tube	Shell				
1	Dehydrogenation of ethylbenzene $C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2$	Hydrogenation of benzene $C_6H_6 + 3H_2 \leftrightarrow C_6H_{12}$	Packed-bed catalytic membrane reactor	Modeling	The ethylbenzene conversion and styrene yield increased by 66 and 78% respectively when compared to conventional industrial reactors	[32]
2	Dehydrogenation of ethylbenzene $C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2$	Hydrogenation of benzene $C_6H_6 + 3H_2 \leftrightarrow C_6H_{12}$	Packed-bed catalytic membrane reactor	Modeling	The integrated reactor had a higher conversion, lower temperatures, and lower total reactor lengths	[33]
3	Dehydrogenation of ethane $C_2H_6 \leftrightarrow C_2H_4 + H_2$	Hydrogenation of benzene $C_6H_6 + 3H_2 \leftrightarrow C_6H_{12}$	Packed-bed catalytic membrane reactor	Modeling	The integrated reactor had a higher conversion, lower temperatures, and lower total reactor lengths	[34]
4	Hydrogenation of nitrobenzene $C_6H_5NO_2 + 3H_2 \leftrightarrow C_6H_5NH_2 + 2H_2O$	Dehydrogenation of ethylbenzene $C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2$	Fixed-bed catalytic membrane reactor	Modeling	A significant increase in the conversion of ethylbenzene and yield of styrene, compared with conventional reactors.	[35]

2.2 Economic aspects

The decision of which reactions to choose was made based on the economic study for each of the products produced. Table 2 compares the chemical production of organic chemicals in the US.

Table 2: Organic chemical production in the USA in 2001 and 2019

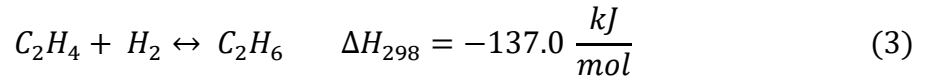
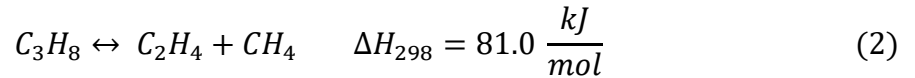
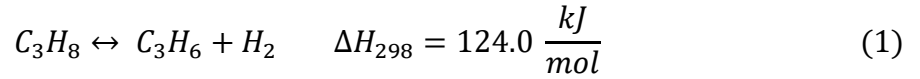
Organic Chemicals	Billion lb. in 2001	Billion lb. in 2019	Change (%)
Ethylene	49.60	69.11 [36]	39.34
Propylene	29.04	34.41 [37]	18.51
Ethylene dichloride	20.58	22.04 [37]	7.07
Urea	14.08	12.95 [38]	-8.04
Ethylbenzene	10.23	10.80 [37]	5.60
Styrene	9.29	10.32 [37]	11.06
Ethylene oxide	7.37	8.82 [37]	19.65
Cumene	6.96	5.78 [37]	-17.01
1,3 - Butadiene	3.79	3.04 [37]	-19.73
Acrylonitrile	2.96	2.38 [37]	-19.56
Benzene (in billions of gallons)	1.92	1.43 [37]	-25.36
Cyclohexane	3.06	1.89 [37]	-38.24
Aniline	1.91	1.86 [37]	-2.47
Toluene	-	11.1 [37]	-
Xylene (para)	7.92	5.885 [37]	-25.7
2- Ethyl hexanol	0.74	0.78 [37]	5.41

Table 2 shows the amount of organic chemicals produced in the USA in billion lbs. for both 2001 and 2019, the change in the production is given as a percentage in the fourth column. According to Table 2, the production of Ethylene increased the most (39.3%) over the last 18 years. The increase in production of Propylene was also significant (18.51%) which reflects the increase in the demand for Propylene and Aniline only had minor drop in production (2.47 %) thus both products are economically viable to be simultaneously produced in the membrane reactor.

CHAPTER 3

REACTOR CONFIGURATION AND REACTION KINETICS

In the reactor configuration, the dehydrogenation of propane is coupled with aniline synthesis in an adiabatic membrane reactor. The reactor configuration shown in Figure 1 is composed of two concentric tubes containing two different types of catalyst beds. The reactor's external wall is assumed to be insulated so that no heat is exchanged between the reactor and the environment. The tube walls are made up of a highly selective hydrogen membrane which is also heat conductive. On the tube side, dehydrogenation of propane to propene takes place and the reaction network is given by Eqs. (1-3):

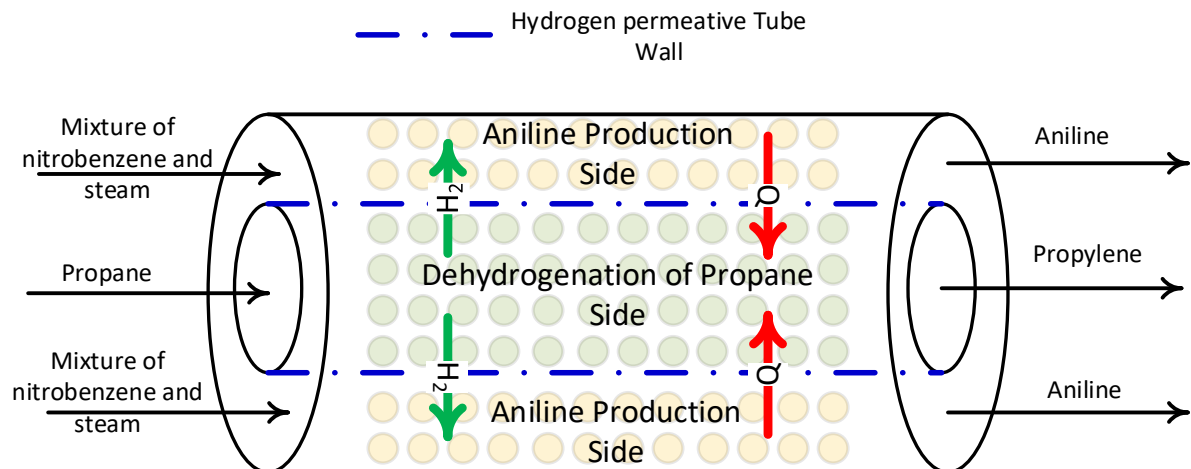


The reaction rate laws of the above reactions, expressed in mol/ (kg cat min), over Pt-Sn-K/Al₂O₃ catalyst are given by Eqs. (4-6) [39]:

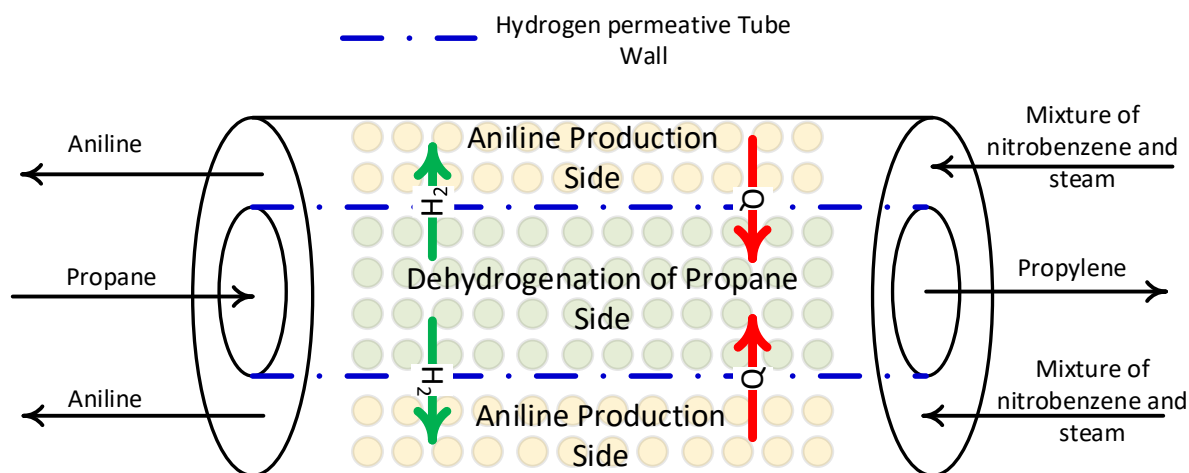
$$(-r_{C_3H_8,1}) = \frac{k_1(p_{C_3H_8} - \frac{p_{C_3H_6}p_{H_2}}{K_{eq}})}{1 + \frac{p_{C_3H_8}}{K_{C_3H_8}}} \quad (4)$$

$$(-r_{C_3H_8,2}) = k_2 p_{C_3H_8} \quad (5)$$

$$(-r_{C_2H_4,3}) = k_3 p_{C_2H_4} p_{H_2} \quad (6)$$



Cocurrent Configuration of the Coupled Membrane Reactor



Countercurrent Configuration of the Coupled Membrane Reactor

Figure 1: Cocurrent and counter-current configuration of the coupled hydrogenation and dehydrogenation reactions in a membrane reactor.

The reaction rate constants are given as functions of temperature by Eqs. (7 and 8) [39]:

$$k_i = k_{i0} \exp \left[-\frac{E_{ai}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad i \in \{1,2,3\} \quad (7)$$

$$K_{C_3H_8} = K_0 \exp \left[-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (8)$$

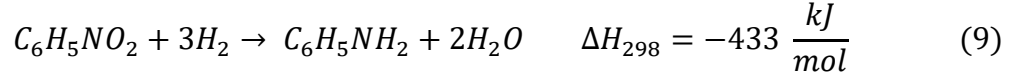
The constants in the above equations are summarized as:

$$\begin{aligned} k_{10} &= 0.5242 \frac{\text{mol}}{\text{kg} \cdot \text{bar} \cdot \text{min}}, & k_{20} &= 0.00465 \frac{\text{mol}}{\text{kg} \cdot \text{bar} \cdot \text{min}}, \\ k_{30} &= 0.000236 \frac{\text{mol}}{\text{kg} \cdot \text{bar}^2 \cdot \text{min}} \\ K_0 &= 3.46, \quad E_{a1} = 34.57 \frac{\text{kJ}}{\text{mol}}, \quad E_{a2} = 137.31 \frac{\text{kJ}}{\text{mol}}, \quad E_{a3} = 154.54 \frac{\text{kJ}}{\text{mol}} \\ \Delta H &= -85.817 \frac{\text{kJ}}{\text{mol}}, & T_0 &= 793.15 \text{ K} \end{aligned}$$

Dehydrogenation of propane is an endothermic and thermodynamically limited reaction. In a conventional fixed bed reactor, the temperature drops along the reactor due to the established endothermicity. According to *Le-Chatelier's* principle, the production of propylene can be boosted via operating at low pressure and high temperature. In the newly proposed coupled membrane reactor, however, palladium-hydrogen membranes are used to permit hydrogen produced on the tube side to diffuse to the shell side. The transportation of hydrogen from the dehydrogenation side to the shell side promotes the production of propylene.

On the shell side, a mixture of nitrobenzene and steam is introduced at a suitable feed temperature and pressure ensuring the conversion of nitrobenzene to aniline.

The hydrogenation reaction of nitrobenzene to aniline is given by the following stoichiometric equation:



The reaction rate expressed in mol/ (kg cat s), over palladium catalyst supported on α -alumina carrier, is given by [40]:

$$r' = \frac{k' K_{NB} K_{H_2} P'_{NB} \sqrt{P'_{H_2}}}{\left(1 + K_{NB} P'_{NB} + K_{H_2} \sqrt{P'_{H_2}}\right)^2} \quad (10)$$

The reaction rate constant and the adsorption constant of nitrobenzene and hydrogen are estimated by Eqs. [11-13], respectively [40]:

$$k' = 0.186 \exp \left[-\frac{10.0 \times 10^{-3}}{RT'} \right] \quad (11)$$

$$K_{NB} = 0.0151 \text{ kPa}^{-1} \quad (12)$$

$$K_{H_2} = 0.14 \text{ kPa}^{-0.5} \quad (13)$$

The hydrogenation reaction of nitrobenzene to aniline is exothermic and thermodynamically unlimited. In the proposed coupled catalytic membrane reactor, the heat produced due to the reaction will transfer to the tube side to assist in boosting the production of propylene on the tube side. This is an example of coupling reactions where both mass and heat are allowed to transfer across the boundary from one side of the reactor to the other.

CHAPTER 4

MATHEMATICAL MODELLING OF THE COUPLED MEMBRANE REACTOR

To derive the mathematical model of the coupled membrane reactor, two infinitesimal elements with thicknesses Δz on both sides of the coupled membrane reactor are considered as shown in Figure 2 with mole and energy flow across the two ends of the elements. The two elements interact via hydrogen diffusion and heat transfer between the two sides of the coupled membrane reactor.

4.1 Model assumptions

The following assumptions are considered while deriving the reactor model:

1. Steady-state operation of the coupled membrane reactor.
2. Pseudo-homogeneous reactor model.
3. Ideal gas behavior
4. Ideal Plug flow.
5. The reactor has a high surface area per unit volume which makes it adiabatically operated.
6. Catalyst deactivation is negligible.
7. The hydrogen membrane used is highly selective.
8. Hydrogen diffusion through the membrane is accounted for by Savart's law.
9. The pressure drops on both sides of the reactor are correlated by Ergun's equation.

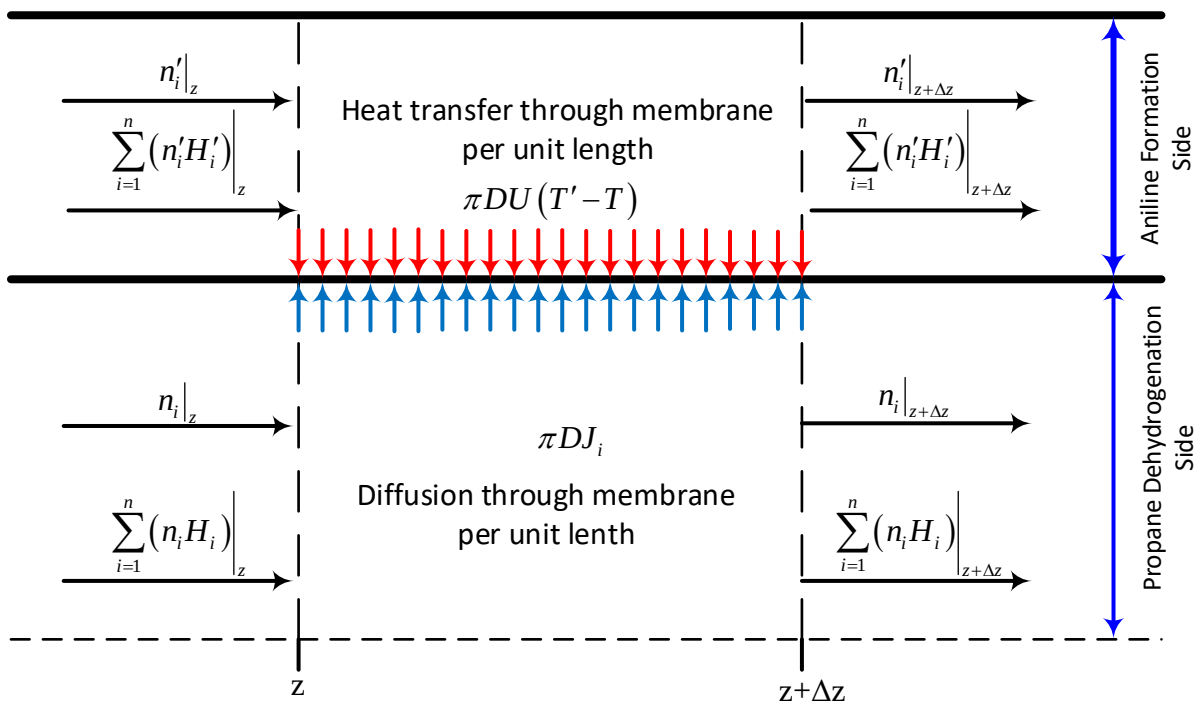


Figure 2: Infinitesimal element on both sides of the coupled membrane reactor

4.2 Governing equations

An infinitesimally small element with thickness Δz was taken in the dehydrogenation side and the mass transfer in and out of the element was considered to perform the mole balance on the dehydrogenation side of the reactor which is given by:

$$\frac{dn_i}{dz} = \sum_{j=1}^R \sigma_{ij} r_j (1 - \varepsilon) A_c \rho_s - (\pi D) J_i \quad (14)$$

The detailed derivation of the governing equation is given in Appendix A. There are six mole balances for the dehydrogenation side, one for each species on this side of the reactor. The mole balance consists of a reaction term and a diffusion term. The reaction term applies for all the species since they all take part in at least of the chemical reactions while the diffusion term only applies for hydrogen because it is the only species that can diffuse through the membrane to the hydrogenation side of the reactor.

Similarly, the infinitesimally small element with thickness Δz was used to carry out the energy balance, only this time the flow of energy in and out of the element was considered rather than the flow of mass. The energy balance on the dehydrogenation side is given by:

$$\frac{dT}{dz} = \frac{\pi D U (T' - T) + \sum_{j=1}^R [-\Delta H]_j r_j (1 - \varepsilon) A_c \rho_s}{\sum_{i=1}^n n_i C_{pi}} \quad (15)$$

The first term of the energy balance accounts for the transfer of energy between the hydrogenation and dehydrogenation sides whereas the second term accounts for the heat change due to the dehydrogenation reactions.

An infinitesimally small element with thickness Δz was then taken on the hydrogenation side of the reactor to carry out a mole balance on the hydrogenation side by taking into account the mass transfer in and out of the element. The mole balance is given by:

$$\frac{dn'_i}{dz} = (-1)^a [\sigma'_i r' \rho'_s (1 - \varepsilon') A'_c + (\pi D) J_i] \quad (16)$$

There are four species on the hydrogenation side so there are four mole balances, one for each species, on the hydrogenation side. The first term is a reaction term, and the second term is a diffusion term for hydrogen on the hydrogenation side. Moreover, the term $(-1)^a$ is used to specify the flow configuration of the coupled membrane reactor. “ a ” possesses a value of 2 for cocurrent configuration and 1 for countercurrent configuration.

Last but not least, the same infinitesimally small element on the hydrogenation side was used to derive the energy balance by taking into account the energy transfer in and out of the element. The energy balance on the hydrogenation side is given by:

$$\frac{dT'}{dz} = (-1)^a \frac{[-\Delta H(T)] r' (1 - \varepsilon') A'_c \rho'_s - \pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT}{\sum_{i=1}^n n'_i C'_{pi}} \quad (17)$$

The first term accounts for the heat change due to the hydrogenation of nitrobenzene while the second term accounts for the energy transfer between the dehydrogenation and hydrogenation sides. The third term accounts for the heat contribution

from the hydrogen flux where Ψ_i is 1 for hydrogen and 0 for all the other species. Again, the term $(-1)^a$ is used to specify the flow configuration of the coupled membrane reactor. “a” possesses a value of 2 for cocurrent configuration and 1 for countercurrent configuration.

The pressure drops on both sides of the reactor is accounted for by Ergun equation:

$$\frac{dP}{dz} = -(-1)^a \left\{ \frac{G}{\rho D_p g_c} \frac{1 - \varepsilon}{\varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \right\} \quad (18)$$

The term $(-1)^a$ is used to specify the flow configuration of the coupled membrane reactor. “a” possesses a value of 2 for cocurrent configuration and 1 for countercurrent configuration.

Hydrogen permeation rate per unit length in the coupled catalytic membrane reactor is estimated as a function of hydrogen partial pressure between the reactor side and the permeate side according to Sievert’s law (Eq. 19):

$$J'_{H_2} = \frac{Q_0}{\delta_{H_2}} \exp\left(-\frac{E_{H_2}}{RT}\right) \left(\sqrt{p_{H_2}} - \sqrt{P'_{H_2}}\right) \quad (19)$$

where:

$$Q_0 = 7.29 \times 10^{-3} \frac{\text{mol}}{\text{m} \times \text{min} \times \text{atm}^{0.5}} \quad \delta_{H_2} = 25.0 \times 10^{-6} \text{m} \quad E_{H_2} = 20.5 \times 10^3 \frac{\text{J}}{\text{mol}}$$

Heat exchanged rate per unit length between the two sides of the coupled membrane reactor is estimated by considering a series combination of heat transfer resistances including convective heat transfer resistance on the propane side, conductive heat transfer

resistance due to the hydrogen membrane, and convective heat transfer resistance on the nitrobenzene side. The mathematical formulation is given by:

$$Q' = \frac{2\pi r_1 (T' - T)}{\left[\frac{1}{h'} + \frac{r_1}{k_{ss}} \ln \left(\frac{r_2}{r_1} \right) + \frac{r_1}{k_{pd}} \ln \left(\frac{r_3}{r_2} \right) + \frac{r_1}{r_2 h} \right]} \quad (20)$$

The convective heat transfer coefficients on both sides of the reactors are given respectively by Eqs. (21 and 22):

$$\frac{hD_t}{k_g} = 0.813 \left(\frac{D_p G}{\mu_g} \right)^{0.90} \exp \left(-\frac{6D_p}{D_t} \right) \quad (21)$$

$$\frac{h'D'_t}{k'_g} = 3.50 \left(\frac{D'_p G'}{\mu'_g} \right)^{0.70} \exp \left(-\frac{4.6D'_p}{D'_t} \right) \quad (22)$$

4.3 Boundary conditions

A set of boundary conditions are required to solve the above model equations defined for both the dehydrogenation side and hydrogenation side. For the cocurrent configuration of both sides of the coupled reactor, the boundary conditions on both sides of the reactor are defined at one end only, i.e., $z = 0$. At $z = 0$, the boundary conditions on the dehydrogenation side are given as:

$$n_i = n_{i0}$$

$$T = T_0$$

$$P = P_0$$

For the hydrogenation side, it is defined at $z = 0$ as:

$$n'_i = n'_{i0}$$

$$T' = T'_0$$

$$P' = P'_0$$

For the countercurrent configuration, the boundary conditions are defined at the two ends.

For the dehydrogenation side, the boundary conditions are given at $z = 0$ as:

$$n_i = n_{i0}$$

$$T = T_0$$

$$P = P_0$$

For the hydrogenation side, however, the boundary conditions are given at $z = L$ as:

$$n'_i = n'_{i0}$$

$$T' = T'_0$$

$$P' = P'_0$$

4.4 Normalization of the mathematical model

To successfully nondimensionalize the governing equations, the following dimensionless variables shown in Table 3 were used:

Table 3: Definitions of the dimensionless groups used in the model.

Tube side (Dehydrogenation)		
Symbol	Interpretation	Definition
ξ	Dimensionless fractional length	$\xi = \frac{z}{L}$
x_i $i = \text{species number}$	Dimensionless fractional change in molar flow (tube)	$x_i = \frac{n_i - n_{i,f}}{n_{C_3H_8,f}}$
θ	Dimensionless reactor temperature on dehydrogenation side (tube)	$\theta = \frac{T - T_f}{T_f}$
θ_0	Dimensionless reference temperature	$\theta_0 = \frac{T_0 - T_f}{T_f}$
ϵ_i $i = 1, 2, 3$	Dimensionless activation energy	$\epsilon_i = \frac{E_{ia}}{RT_f}$
ϵ_k	Dimensionless ΔH_{rxn}	$\epsilon_k = \frac{\Delta H}{RT_f}$
γ_i $i = \text{species number}$	Dimensionless partial pressure	$\gamma_i = \frac{P_i}{P_f}$
K'	Dimensionless equilibrium constant	$K' = \frac{P_f}{K_{eq}}$
K'_0	Dimensionless pre-exponential factor	$K'_0 = \frac{P_f}{K_0}$
ϵ_{H_2}	Dimensionless hydrogen activation energy	$\epsilon_{H_2} = \frac{E_{H_2}}{RT_f}$
Pr	Dimensionless feed pressures ratio (shell/tube)	$Pr = \frac{P'_f}{P_f}$
α_i $i = 1, 2$	Dimensionless Damckholer's number (Reaction 1 and 2)	$\alpha_i = \frac{k_{i0} P_f (1 - \epsilon) A_c \rho_s L}{n_{C_3H_8,f}}$
α_3	Dimensionless Damckholer's number (Reaction 3)	$\alpha_3 = \frac{k_{30} P_f^2 (1 - \epsilon) A_c \rho_s L}{n_{C_3H_8,f}}$
α_{PER}	Dimensionless permeability constant for hydrogen	$\alpha_{PER} = \frac{\pi D L Q_0 \sqrt{P_f}}{\delta_{H_2} n_{C_3H_8,f}}$
β_i $i = 1, 2, 3$	Dimensionless heat of reaction	$\beta_i = \frac{n_{C_3H_8,f} (-\Delta H_i)}{T_f \sum_{i=1}^n n_i C_{p_i}}$
ψ	Dimensionless reactor pressure (tube)	$\psi = \frac{P}{P_f}$
β_0	Dimensionless pressure coefficient (tube)	$\beta_0 = \frac{GL(1 - \epsilon)}{P_f \rho_f D_p g_c \epsilon^3} \left[\frac{150(1 - \epsilon)\mu}{D_p} + 1.75G \right]$

Table 3: Definitions of the dimensionless groups used in the model.

Shell side (Hydrogenation)		
Symbol	Interpretation	Definition
γ'_i $i = \text{species number}$	Dimensionless partial pressure (shell)	$\gamma'_i = \frac{P'_i}{P'_f}$
θ'	Dimensionless reactor temperature on hydrogenation side (shell)	$\theta' = \frac{T' - T'_f}{T'_f}$
ϵ'	Dimensionless activation energy (shell)	$\epsilon' = \frac{10.0 * 10^{-3}}{RT'_f}$
α'	Dimensionless Damckholer's number (shell)	$\alpha' = \frac{0.186K'_{NB}K'_{H_2}(1 - \epsilon')A'_c\rho'_sL}{n'_{NB,f}}$
β'	Dimensionless heat of reaction (shell)	$\beta' = \frac{n'_{NB,f}(-\Delta H')}{T'_f \sum_{i=1}^n n'_i C p'_i}$
K'_{NB}	Dimensionless NB equilibrium constant (shell)	$K'_{NB} = K_{NB}P'_f$
K'_{H_2}	Dimensionless H ₂ equilibrium constant (shell)	$K'_{H_2} = K_{H_2}\sqrt{P'_f}$
R'	Dimensionless ratio of molar flow of the key components	$R' = \frac{n_{C_3H_8,f}}{n'_{NB,f}}$
ψ'	Dimensionless reactor pressure (shell)	$\psi' = \frac{P'}{P'_f}$
β'_0	Dimensionless pressure coefficient (shell)	$\beta'_0 = \frac{G'L(1 - \epsilon')}{P'_f\rho'_fD'_pg_c(\epsilon')^3} \left[\frac{150(1 - \epsilon')\mu'}{D'_p} + 1.75G' \right]$

The detailed normalization of the mathematical model is shown in Appendix B. The result of the normalization of the governing equations for the dehydrogenation side are given below by Eqs. (23-30) and that for the hydrogenation side is given by Eqs. (31-36):

Mole balance for C₃H₈:

$$\begin{aligned}
 \frac{dx_{C_3H_8}}{d\xi} = & -\alpha_1 \frac{\exp\left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp\left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right]} \\
 & - \alpha_2 \exp\left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8}
 \end{aligned} \tag{23}$$

Mole balance for C₃H₆:

$$\frac{dx_{C_3H_6}}{d\xi} = \alpha_1 \frac{\exp\left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp\left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right]} \quad (24)$$

Mole balance for H₂ (dehydrogenation side)

$$\begin{aligned} \frac{dx_{H_2}}{d\xi} = \alpha_1 & \frac{\exp\left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp\left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right]} \\ & - \alpha_3 \exp\left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4} \gamma_{H_2} \\ & - \alpha_{PER} \exp\left[\frac{-\epsilon_{H_2}}{1 + \theta}\right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}}\right] \end{aligned} \quad (25)$$

Mole balance for C₂H₄

$$\begin{aligned} \frac{dx_{C_2H_4}}{d\xi} = \alpha_2 \exp\left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \\ - \alpha_3 \exp\left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4} \gamma_{H_2} \end{aligned} \quad (26)$$

Mole balance for CH₄

$$\frac{dx_{CH_4}}{d\xi} = \alpha_2 \exp\left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \quad (27)$$

Mole balance for C₂H₆

$$\frac{dx_{C_2H_6}}{d\xi} = \alpha_3 \exp\left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4} \gamma_{H_2} \quad (28)$$

Energy balance (dehydrogenation side):

$$\begin{aligned}
\frac{d\theta}{d\xi} = & \frac{\pi DUL[T_f'(1 + \theta') - T_f(1 + \theta)]}{T_f \sum_{i=1}^n n_i C p_i} \\
& + \alpha_1 \beta_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\
& + \alpha_2 \beta_2 \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \\
& + \alpha_3 \beta_3 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2}
\end{aligned} \tag{29}$$

Pressure drop (dehydrogenation side):

$$\frac{d\psi}{d\xi} = - \frac{\beta_0(T)(1 + \theta)}{\psi} \left(\frac{n_T}{n_{T,f}} \right) \tag{30}$$

Mole balance for nitrobenzene:

$$\frac{dx'_{NB}}{d\xi} = (-1)^a \alpha' \sigma'_{NB} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \tag{31}$$

Mole balance for H₂ (hydrogenation side):

$$\begin{aligned}
\frac{dx'_{H_2}}{d\xi} = & (-1)^a \alpha' \sigma'_{H_2} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \\
& + (-1)^a \alpha_{PER} R' \exp \left[\frac{-\epsilon_{H_2}}{1 + \theta} \right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right]
\end{aligned} \tag{32}$$

Mole balance for aniline:

$$\frac{dx'_{AN}}{d\xi} = (-1)^a \alpha' \sigma'_{AN} \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}}\right)^2} \quad (33)$$

Mole balance for H₂O:

$$\frac{dx'_{H_2O}}{d\xi} = (-1)^a \alpha' \sigma'_{H_2O} \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}}\right)^2} \quad (34)$$

Energy balance (hydrogenation side):

$$\frac{d\theta'}{d\xi} = (-1)^a \alpha' \beta' \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}}\right)^2} - (-1)^a \frac{\pi DUL [T'_f(1+\theta') - T_f(1+\theta)]}{T'_f \sum_{i=1}^n n'_i C p'_i} \quad (35)$$

Pressure drop (hydrogenation side):

$$\frac{d\psi'}{d\xi} = - \frac{\beta'_0(T')(1+\theta')}{\psi'} \left(\frac{n'_T}{n'_{T,f}} \right) \quad (36)$$

CHAPTER 5

NUMERICAL SOLUTION OF THE MATHEMATICAL MODEL

The complex system of normalized differential equations presented in the previous section was solved using the *orthogonal collocation*. It is a numerical method used for the solution of differential equations in a wide variety of fields such as heat transfer, mass transfer and chemical reaction engineering. The orthogonal collocation (OD) method has been called several names such as Pseudo spectral Method (PS) and Differential Quadrature Method (DQ) [41]. It involves the approximation of the differential equation by a set of algebraic equations, which can be solved using standard linear algebra techniques. This method has been widely used in process simulation, control and optimization as it provides an efficient way to solve complex problems [41].

The method of orthogonal collocation involves dividing the domain of the differential equation into a set of spaced points, known as collocation points. An orthogonal collocation is characterized by collocation points that are roots of orthogonal polynomials. In most cases, collocation points are the roots of Chebyshev polynomials of the first or second kind, or the base points of Gaussian, Radau, or Lobatto quadrature [41]. Those methods allow the collocation points to be picked automatically thus eliminating the possibility of picking the wrong points which can occur while using other collocation methods [42].

The function to be solved is approximated by a polynomial function that passes through these collocation points. The polynomial coefficients are determined by applying the collocation conditions, which require the polynomial functions to satisfy the governing differential equation at each collocation point. The idea is to minimize the error between the differential equation and the polynomial approximation [43].

One advantage of the method of orthogonal collocation is that it allows the solution to be obtained at a set of discrete points. This is important in the context of process simulation, control, and optimization as it provides a way to find solutions quickly and efficiently. The method also allows for the direct incorporation of physical constraints and boundary conditions in the solution process. Another advantage of the method of orthogonal collocation is that it offers the ability to handle stiff differential equations. Stiff differential equations arise in chemical engineering when the differential equations have large disparities in the time scales of the different processes involved. The method of orthogonal collocation allows for the efficient solution of stiff differential equations by using high-order polynomials [41].

CHAPTER 6

REACTOR PERFORMANCE AND PARAMETRIC STUDY

In this section the performance of the reactor will be compared under several operation modes such as co-current and counter current. Moreover, the performance of the membrane reactor will be compared to that of the traditional reactor (non-membrane) for the dehydrogenation reaction. To successfully assess the differences between the modes of operation, a reference must be established using the parameters given in Table 4

Table 4: Parameters for the reference case

Variable	Numerical Value	Units
Number of tubes (N_{tubes})	1500	tubes
Tube diameter (D_h)	0.03	m
Shell diameter (D_d)	2.0	m
Reactor length (L)	5	m
Total molar flowrate of steam (n_{H_2O})	15.0	mol s ⁻¹
Mole fraction of Helium (MF_{He})	0.9	-
Dehydrogenation feed pressure (P_0)	2.5	bar
Hydrogenation feed pressure (P'_0)	1.5	bar
Dehydrogenation feed temperature (T_0)	890	K
Hydrogenation feed temperature (T'_0)	900	K
Hydrocarbon to steam ratio ($HC:H_2O$)	7.5	-

To determine the performance of the reactor, the yield of propene, conversion of propane and the conversion of nitrobenzene will be used. The yield of a product is the amount of moles formed of the product in comparison to the amount of the reactant fed [44]. The yield of propene is given by:

$$Y_{propene} = \frac{\text{Moles of propene produced}}{\text{Moles of propane fed}} = \frac{n_{C_3H_6}(L) - n_{C_3H_6,f}}{n_{C_3H_8,f}} = x_{C_3H_6} \quad (37)$$

When comparing Eq. (37) with the dimensionless fractional change in molar flow given in Table 3, it can be seen that the yield of propene is none other than the dimensionless fractional change in the molar flow of propene:

$$x_{C_3H_6} = \frac{n_{C_3H_6}(L) - n_{C_3H_6,f}}{n_{C_3H_8,f}} = Y_{propene} \quad (38)$$

The conversion of a chemical species is the fraction of the reactant that has taken part in the reaction [44]. Mathematically, the conversion of a species is the ratio of its number of moles that reacted to the number of moles fed. The conversion of propane and nitrobenzene is given below by Eqs. (39) and (40), respectively.

$$X_{propane} = \frac{\text{Moles of propane reacted}}{\text{Moles of propane fed}} = \frac{n_{C_3H_8,f} - n_{C_3H_8}}{n_{C_3H_8,f}} \quad (39)$$

$$X_{NB} = \frac{\text{Moles of nitrobenzene reacted}}{\text{Moles of nitrobenzene fed}} = \frac{n'_{NB,f} - n'_{NB}(L)}{n'_{NB,f}} \quad (40)$$

Comparing the above definitions of the conversion of the two species with their respective dimensionless fractional change in molar flow (Table 3) shows that the conversion of each species is simply the negative of their respective dimensionless fractional change in molar flows as shown below:

$$X_{propane} = \frac{n_{C_3H_8,f} - n_{C_3H_8}}{n_{C_3H_8,f}} = - \left(\frac{n_{C_3H_8} - n_{C_3H_8,f}}{n_{C_3H_8,f}} \right) = -x_{C_3H_8} \quad (41)$$

$$X_{NB} = \frac{n'_{NB,f} - n'_{NB}}{n'_{NB,f}} = - \left(\frac{n'_{NB} - n'_{NB,f}}{n'_{NB,f}} \right) = -x'_{NB} \quad (42)$$

Figure 3 shows the plots of the performance determining parameters, conversions of propane and nitrobenzene and the yield of propene, against the dimensionless axial distance for the reference case using a co-current configuration in the membrane reactor.

The membrane reactor was then operated in a counter current flow such that the dehydrogenation reactions stream was flowing in one direction while as the hydrogenation reaction stream was flowing in the opposite direction. Figure 4 shows the conversion of propane and nitrobenzene and the yield of propene against the dimensionless axial distance using the same parameters as that of the reference case.

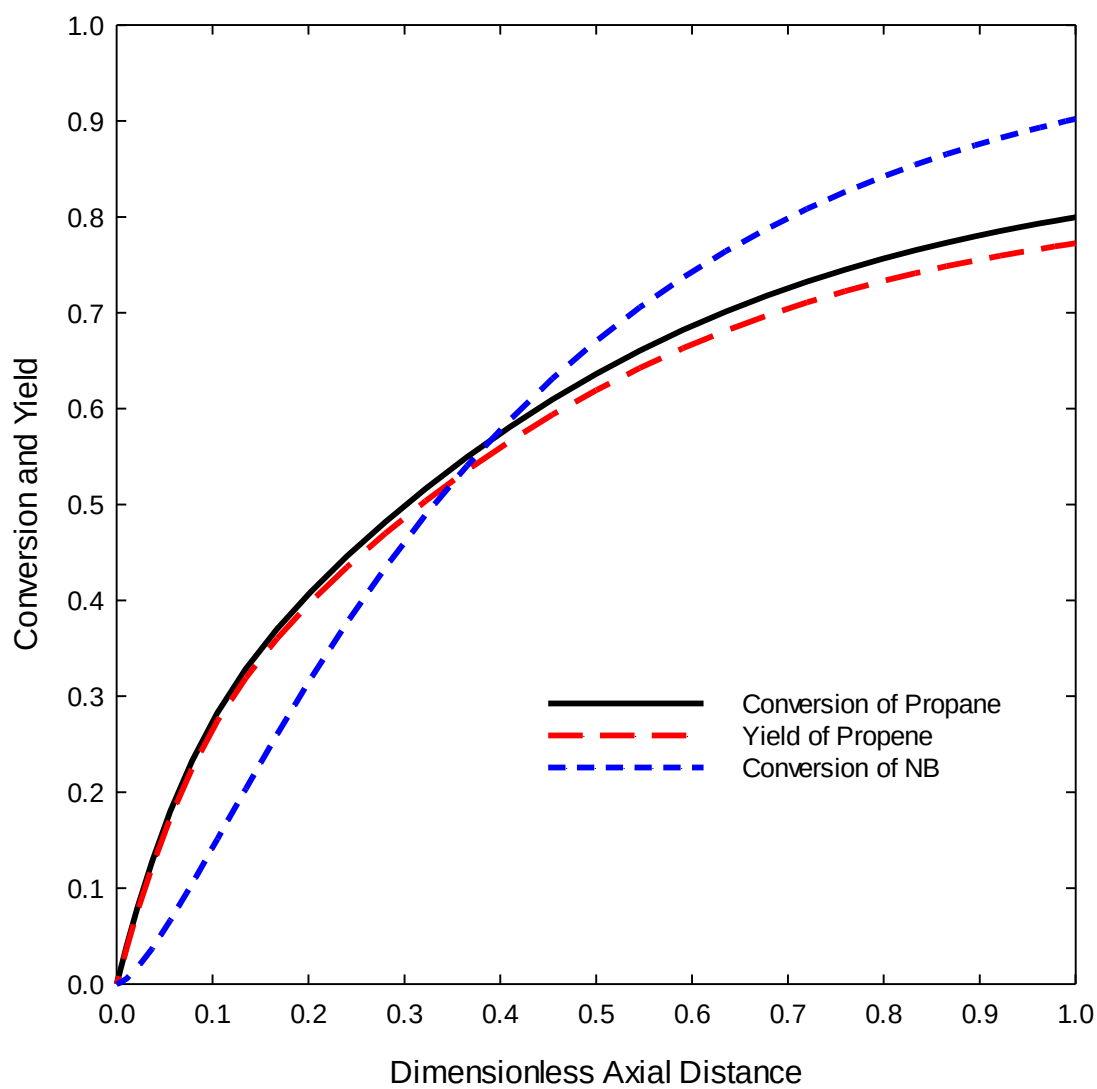


Figure 3: Performance plot for the co-current reference case

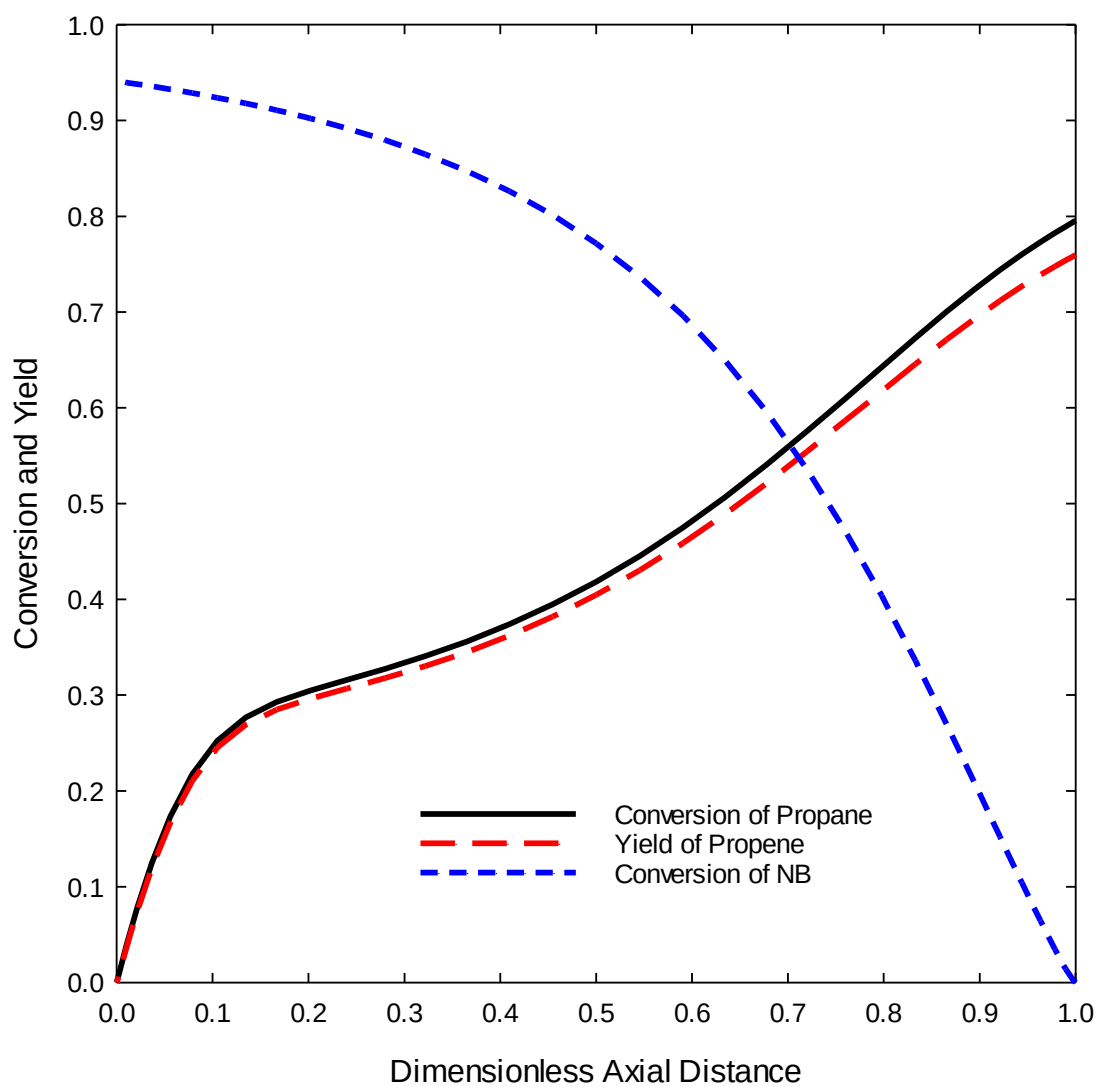


Figure 4: Performance plot for the counter current reference case

6.1 Comparison between the configurations of the membrane reactor and the conventional reactor

To compare the performance of the membrane reactors using co-current and counter current configuration, and that of the conventional reactor (non-membrane), all design and operating variables are kept the same for all three reactor models. The conventional reactor (without a membrane) was modelled by setting the hydrogen flux and the permeability of the membrane to zero. In doing so, the hydrogenation reaction is turned off and the performance of the dehydrogenation can be observed.

Figure 5 shows the conversion of propane plotted against the dimensionless axial distance along the reactor for the membrane reactor in two configurations and the conventional reactor. Similarly, Figure 6 shows the yield of propene plotted against the dimensionless axial distance along the reactor for the membrane reactor in two configurations and the conventional reactor. Figure 7 shows the conversion of nitrobenzene plotted against the dimensionless axial distance along the reactor for the membrane reactor in two configurations (cocurrent and counter current). The conventional dehydrogenation reactor does not produce any nitrobenzene.

Figures 8-10 shed light on the performance of the hydrogenation side while comparing the cocurrent and counter current modes. Figures 8 and 9 compare the hydrogen and heat fluxes, respectively, for the two reactor configurations by plotting them against the dimensionless axial distance. Figure 10 shows the temperature profiles for both sides of the reactor for each of the configurations against the dimensionless axial distance.

Moreover, the data obtained from the graphs is summarized in Table 5 which highlights the differences in the performances of the reactors.

Table 5: Comparison between co-current and counter current configurations

Performance parameter	Co-current	Counter Current	Conventional Reactor
Yield of Propene	0.82	0.79	0.35
Conversion of Propane	0.87	0.84	0.39
Conversion of Nitrobenzene	0.90	0.94	-

It can be clearly seen that transitioning from the conventional reactor to the membrane reactor in either of the configurations (co-current or counter current) more than doubled both the conversion of propane and the yield of propene. The yield of propene went from 0.35 to 0.77/0.76, while the conversion of propane significantly increased from 0.37 to 0.80 in both membrane reactors. This massive improvement in the performance of the dehydrogenation reactor is due to the heat and hydrogen flux between the shell and the tube in the membrane reactors. According to Le Chatelier's principle, the flow of the hydrogen out of the dehydrogenation segment of the reactor through the highly selective hydrogen membrane shifted the propane dehydrogenation reaction to the forward direction which increased its equilibrium conversion. Moreover, the heat flux from the hydrogenation side (exothermic) to the dehydrogenation side (endothermic) makes the reaction more thermodynamically favored thus boosting the conversion of propane.

When comparing the performance of both configurations of the membrane reactor, the co-current mode favors the dehydrogenation side at the expense of the hydrogenation side, whereas the counter-current mode favors the hydrogenation side at the expense of the dehydrogenation reaction.

The use of the counter current configuration led to a 4.3% increase in the conversion of nitrobenzene compared to the co-current. However, this increase in the performance of the hydrogenation side comes at a cost which is a decrease in the conversion of propane and the yield of propene of 1.67% and 0.52%, respectively.

As shown in Figure 9 the switch from cocurrent to counter current led to a higher peak in the heat flux, however, this peak was moved from 0.2 of the reactor length to 0.7 of the reactor length. This shift in the peak of the heat flux favored the conversion of nitrobenzene because the nitrobenzene had much higher residence time in the reactor (0.7 until 0) after the peak compared to the propane in the shell (0.7 to 1) since both reactants are moving in opposite directions. This was reflected onto the temperature profile shown in Figure 10 with the counter current hydrogenation side having a much higher temperature than its counterpart in the cocurrent configuration. The higher temperature led to a boost in the kinetics of the reaction which in turn led to a higher conversion of nitrobenzene. Also, the dehydrogenation temperature for the counter current flow experienced a lower temperature than that of the co current flow for over 60% of the reactor which led to lower kinetics and lower equilibrium conversion (endothermic reactor) which led to a decrease in the conversion of propane compared to the co-current configuration. Similarly, the peak for the Hydrogen flux has also shifted as can be seen in Figure 8 which supports the change in performance between both reactor modes.

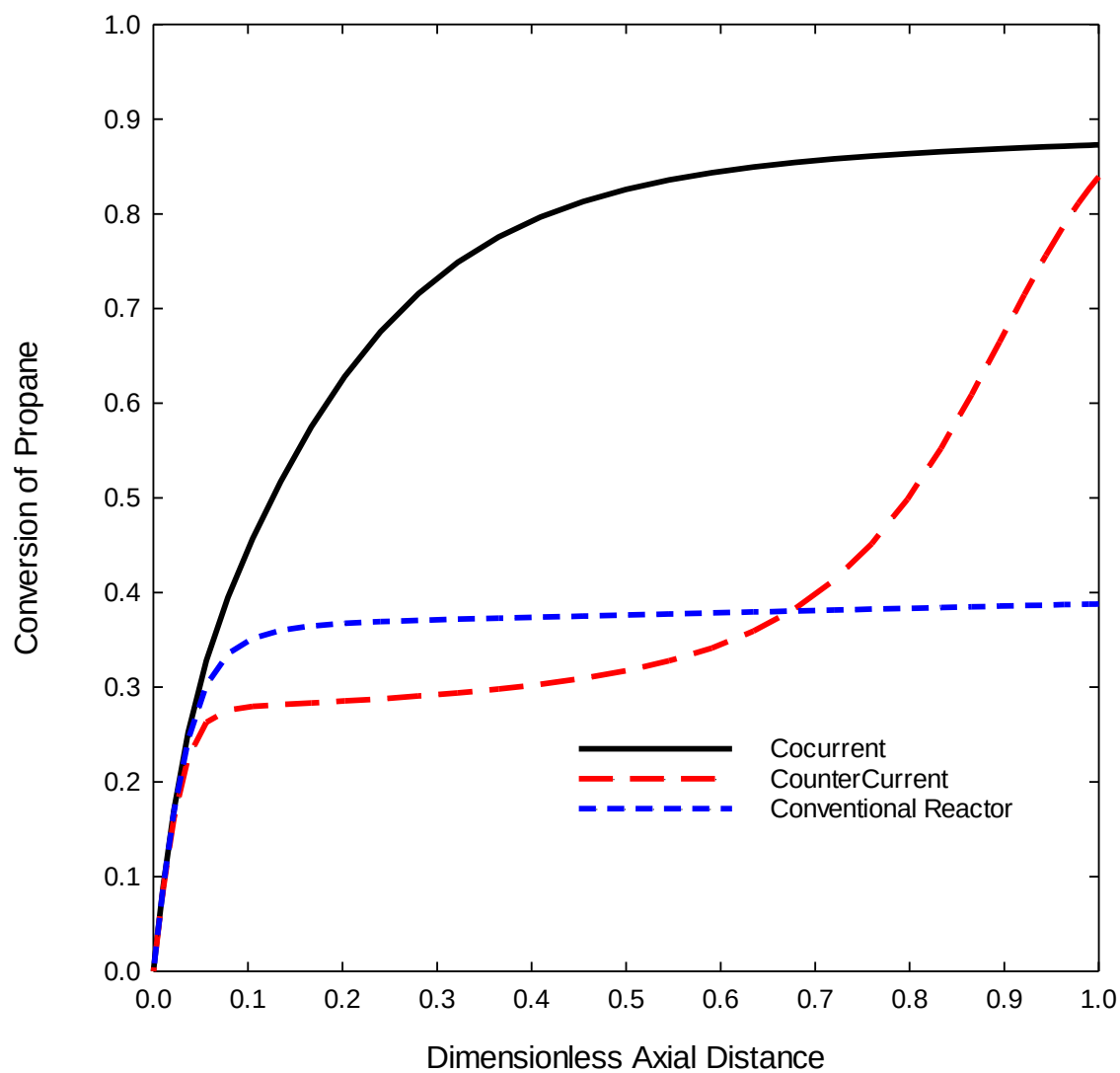


Figure 5: Conversion of propane plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor, counter current membrane reactor and the conventional dehydrogenation reactor.

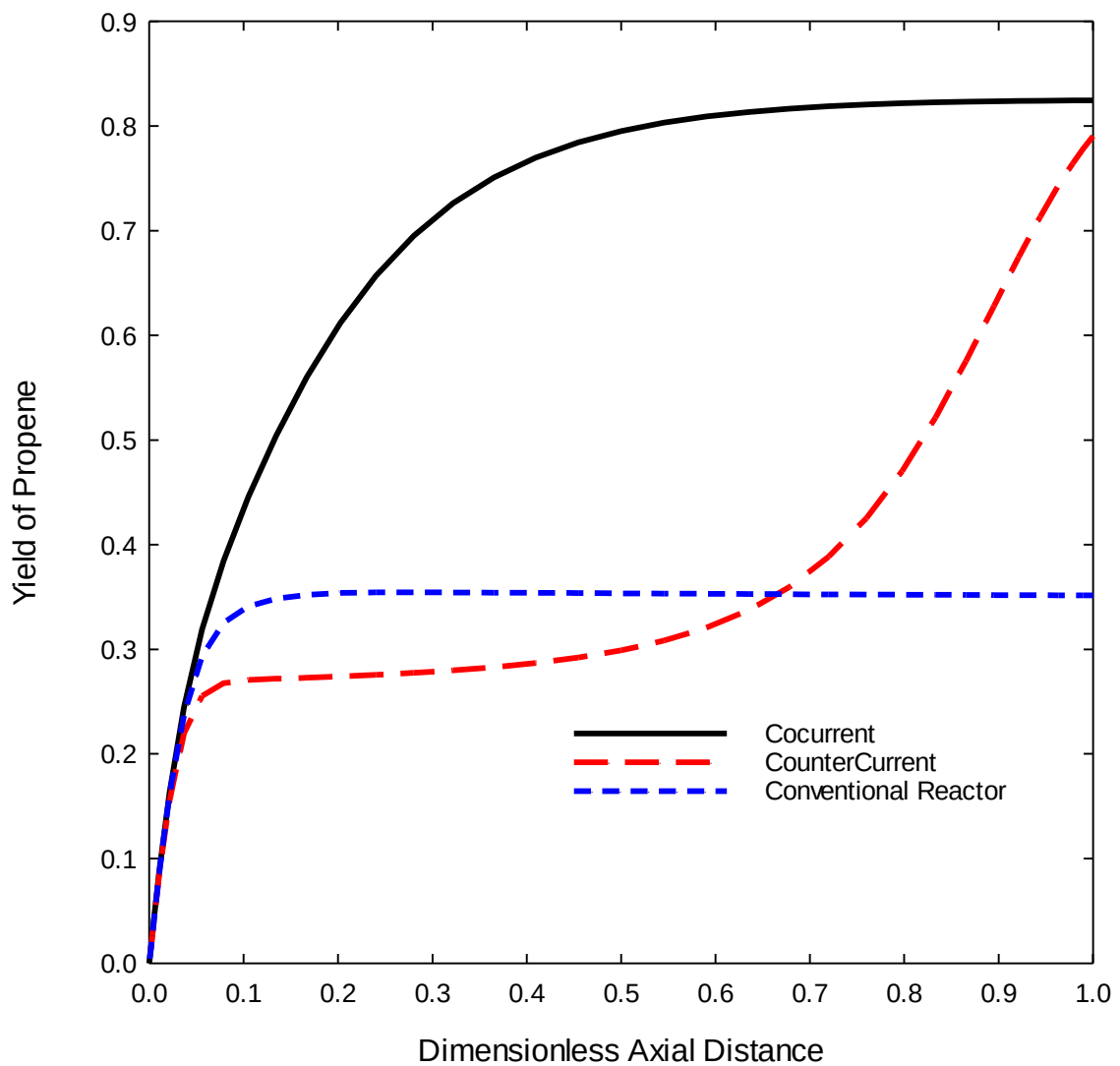


Figure 6: Yield of propene plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor, counter current membrane reactor and the conventional dehydrogenation reactor.

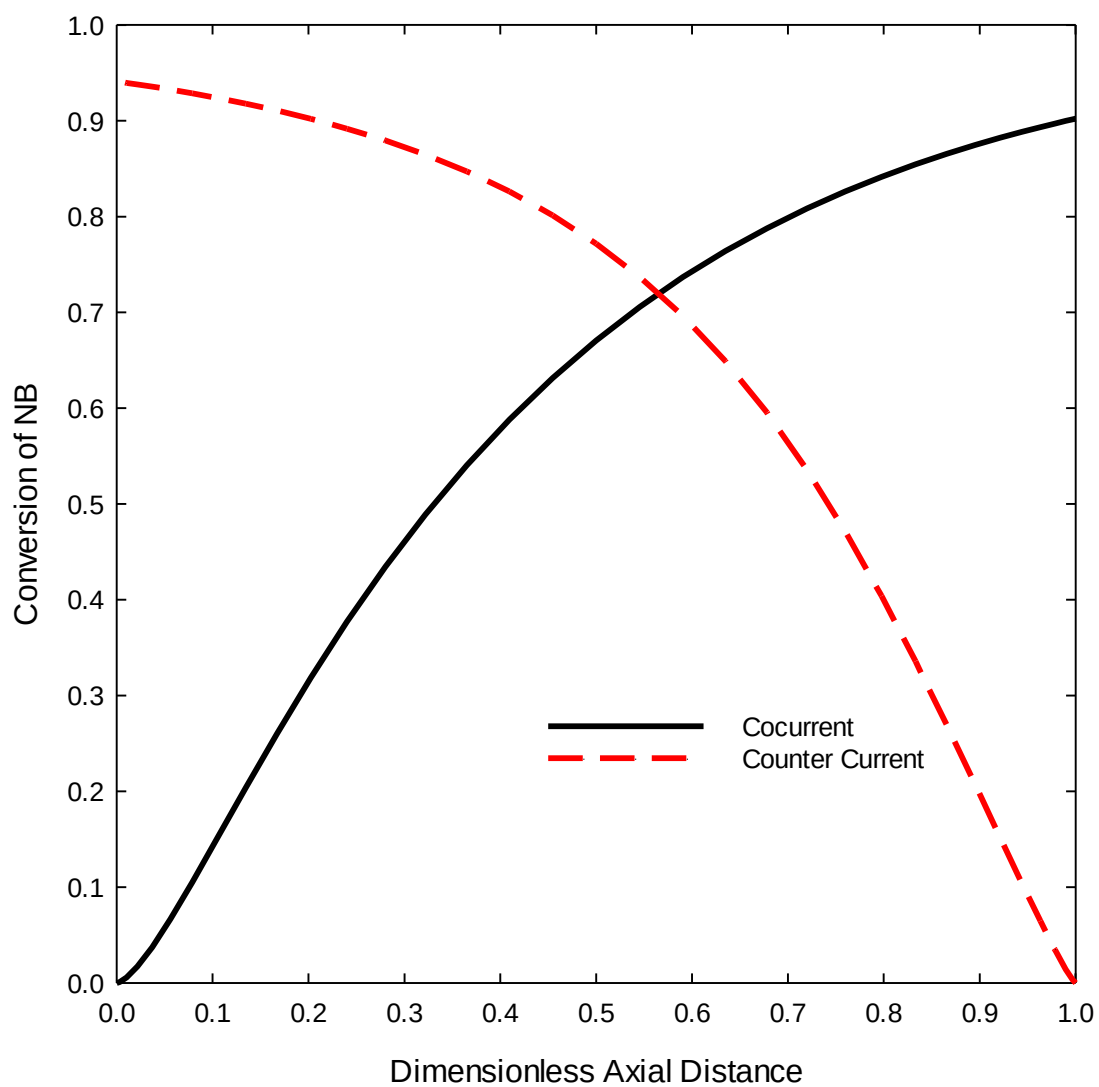


Figure 7: Conversion of nitrobenzene plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.

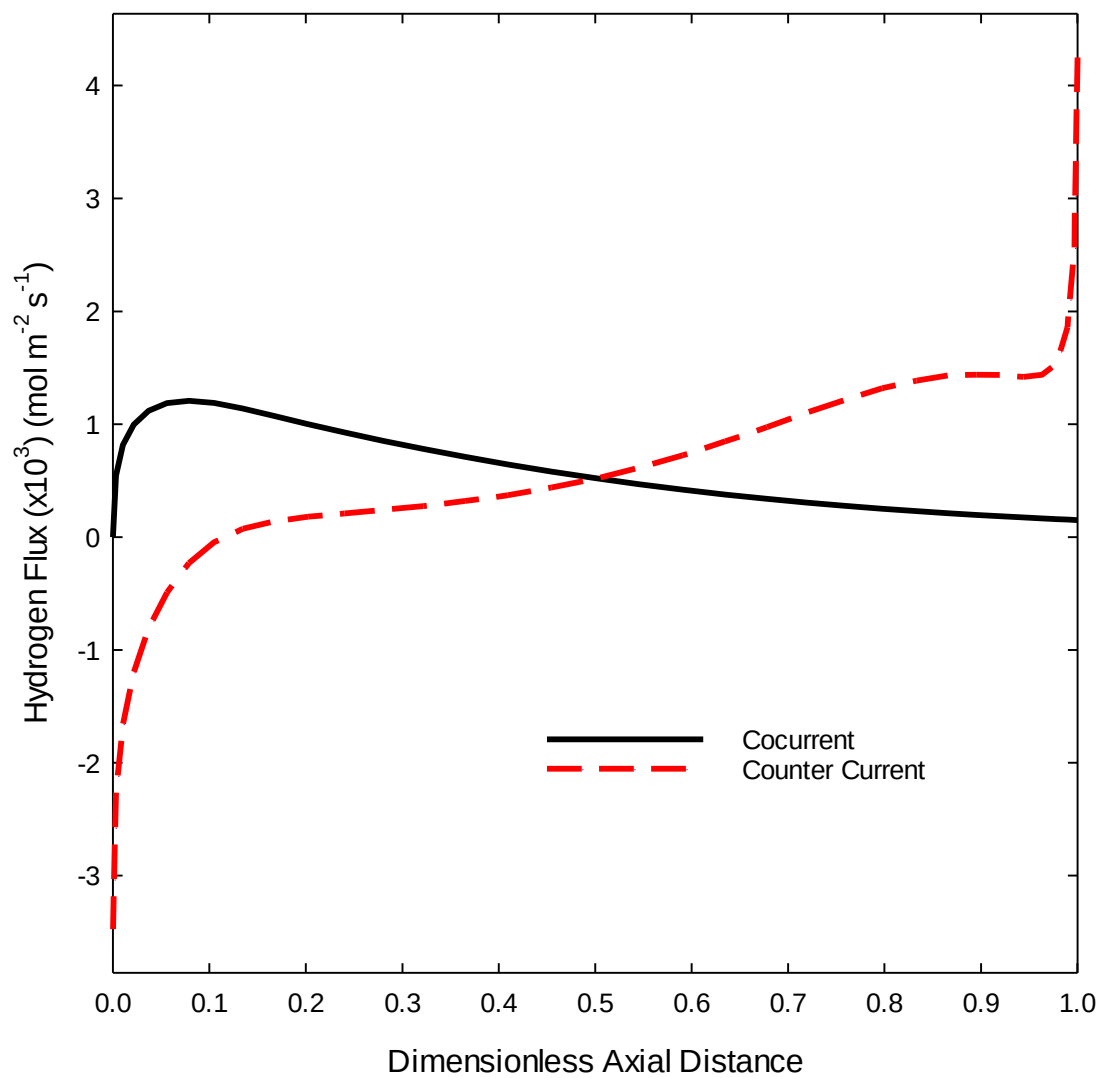


Figure 8: Hydrogen flux per tube plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.

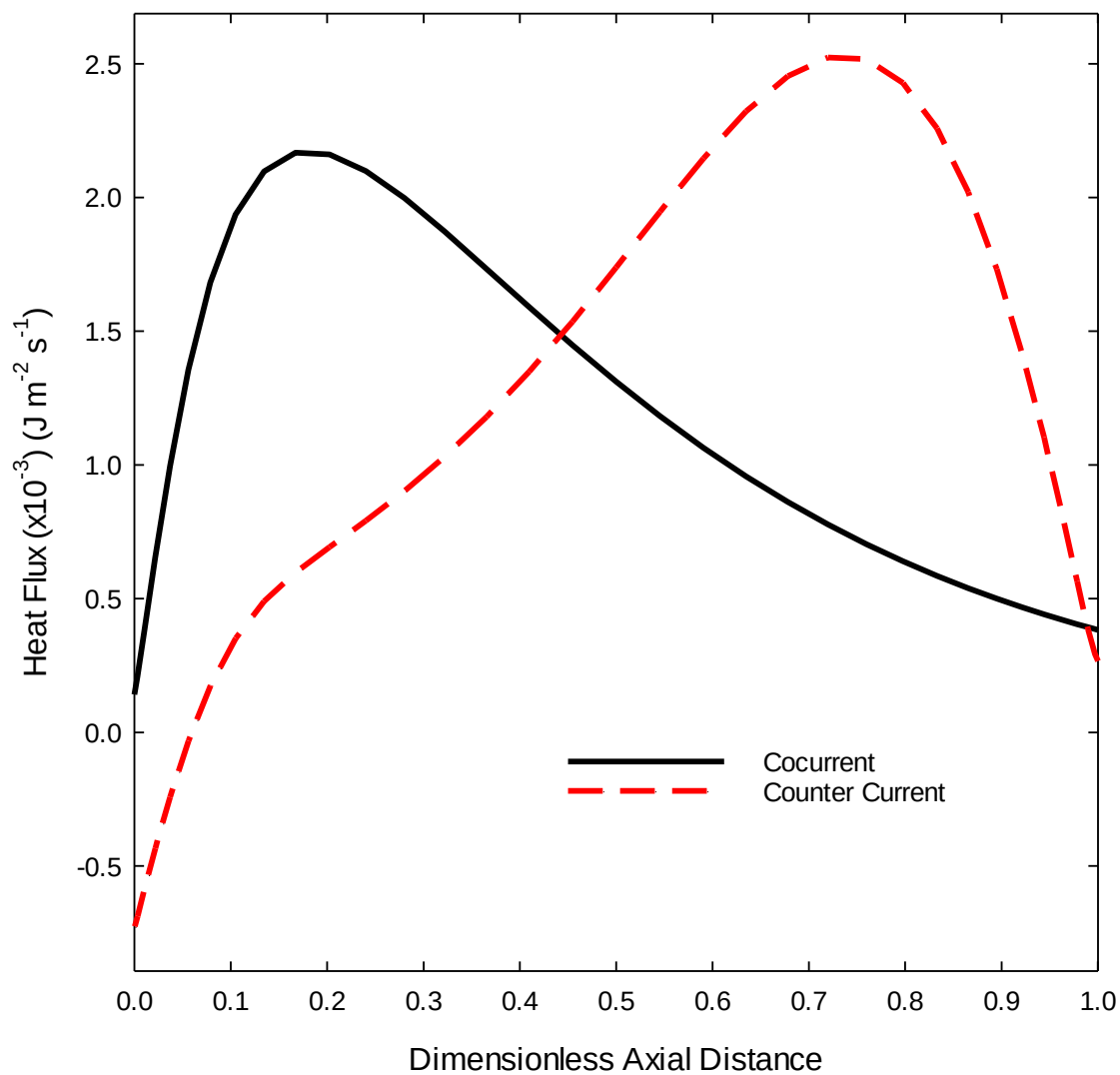


Figure 9: Heat flux per tube plotted against the dimensionless axial distance along the reactor for the cocurrent membrane reactor and the counter current membrane reactor.

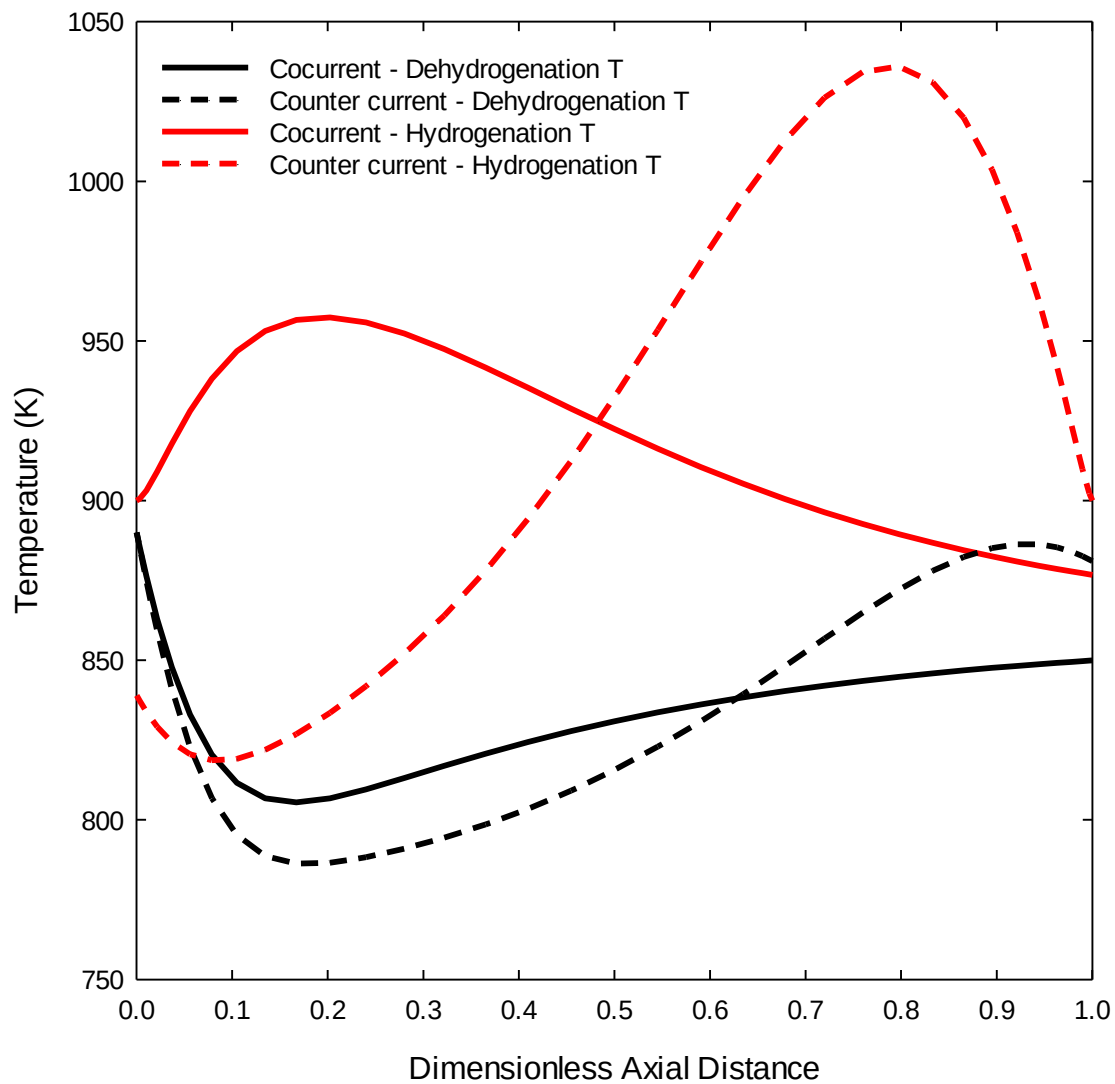


Figure 10: Temperature profiles for the hydrogenation and dehydrogenation sides for both configurations plotted against the dimensionless axial distance.

6.2 Parametric study

A parametric study for the co-current configuration was carried out to determine the effects of several parameters on the performance of the membrane reactor. To ensure a fair comparison all the parameters were kept the same as that of the reference case and the parameter being tested was varied within their physical limits. The parametric study is a crucial step to understand the reactor and will aid in the optimization phase.

6.2.1 Molar fraction of helium

The effect of the molar fraction of helium in the dehydrogenation side on the performance of the reactor was investigated by varying it from the reference value of 0.9. The molar fractions used were 0.9 (reference), 0.7, 0.5 and 0.3. Figure 11 shows the conversion of propane plotted against the dimensionless axial distance for different mole fractions of helium thus showing the effect of the mol fraction of Helium on the conversion of propane. Similarly, Figure 12 shows the conversion of nitrobenzene plotted against the dimensionless axial distance for different mole fractions of helium fed into the dehydrogenation side of the cocurrent membrane reactor. The figure shows the effect of the mole fraction of helium on the conversion of nitrobenzene. Figure 13 shows the hydrogen flux across the membrane plotted against the dimensionless axial distance for different mole fractions of helium.

The increase in the mole fraction of Helium from 0.3 to 0.9 diluted the dehydrogenation inlet and decreased the concentration of the reactants which in turn decreased the initial rate of reaction leading to a less steep increase in the conversion of propane. However, the dilution did not significantly change the conversion of propane at the reactor's outlet as shown in Figure 11.

On the other hand, the dilution of the inlet stream to the dehydrogenation side decreased the partial pressure of hydrogen formed which decreased the hydrogen flux moving to the hydrogenation side, as seen in Figure 13, which led to a decrease in the conversion of nitrobenzene as the mole fraction of Helium increased. The conversion of nitrobenzene dropped from 0.94 to 0.90 when the mole fraction of helium increased from 0.3 to 0.9. Table 6 summarizes the results obtained for the different mole fractions of Helium.

Table 6: Effect of the mole fraction of Helium on the performance of the membrane reactor

Performance parameter	Mole Fraction of Helium			
	0.9	0.7	0.5	0.3
Conversion of Propane	0.80	0.79	0.80	0.80
Yield of Propene	0.77	0.74	0.71	0.70
Conversion of Nitrobenzene	0.90	0.94	0.94	0.94

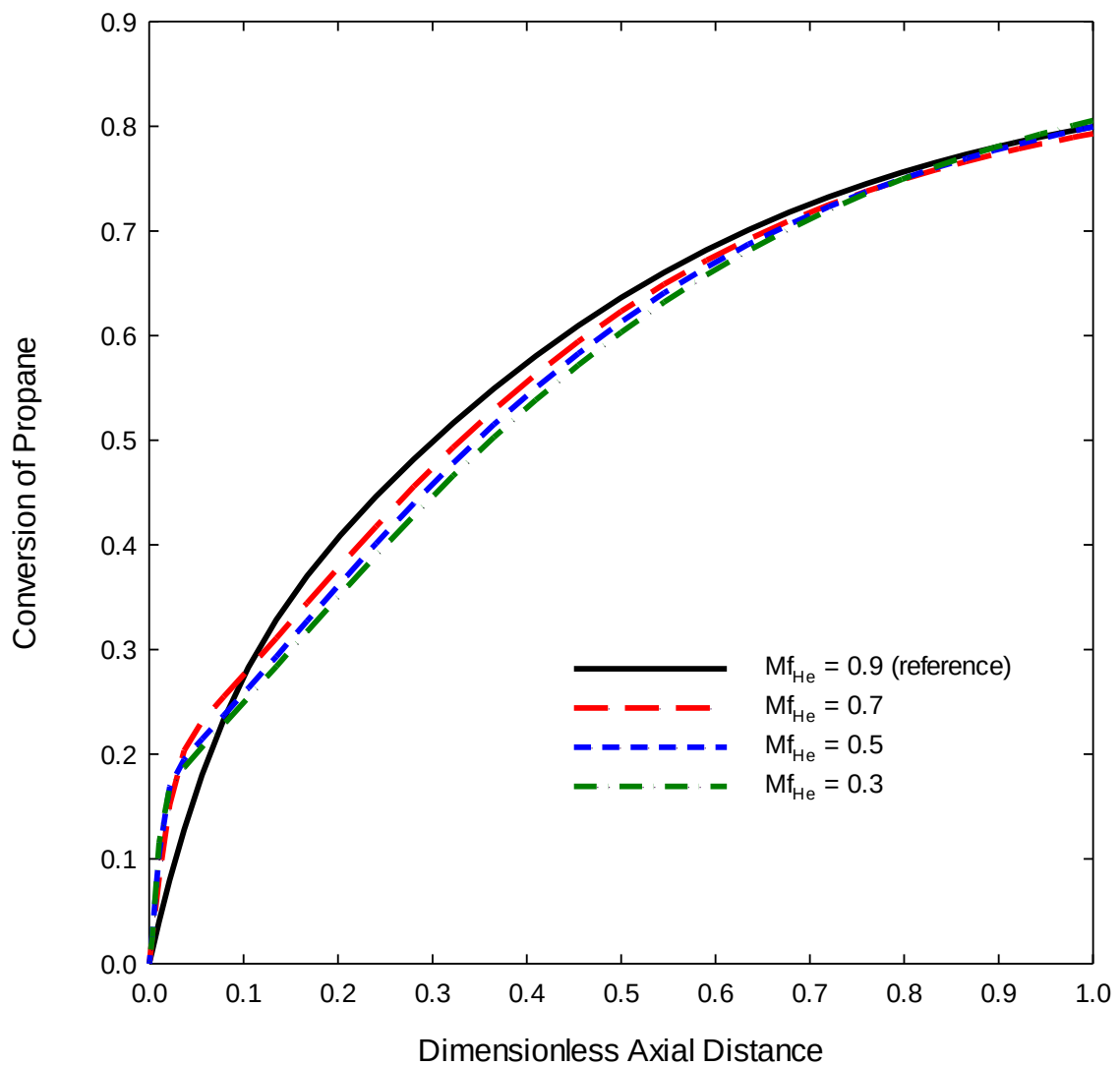


Figure 11: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.

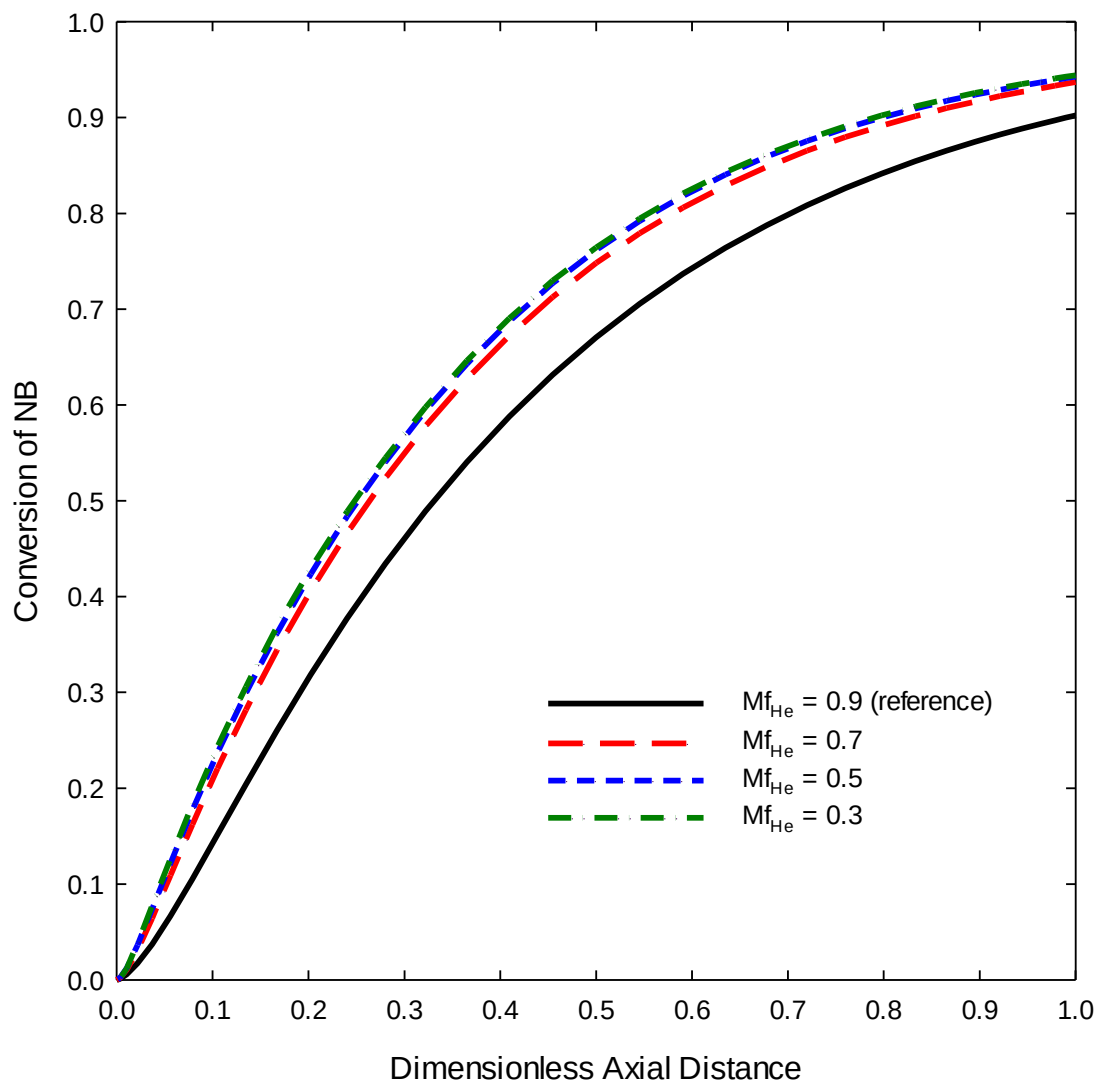


Figure 12: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.

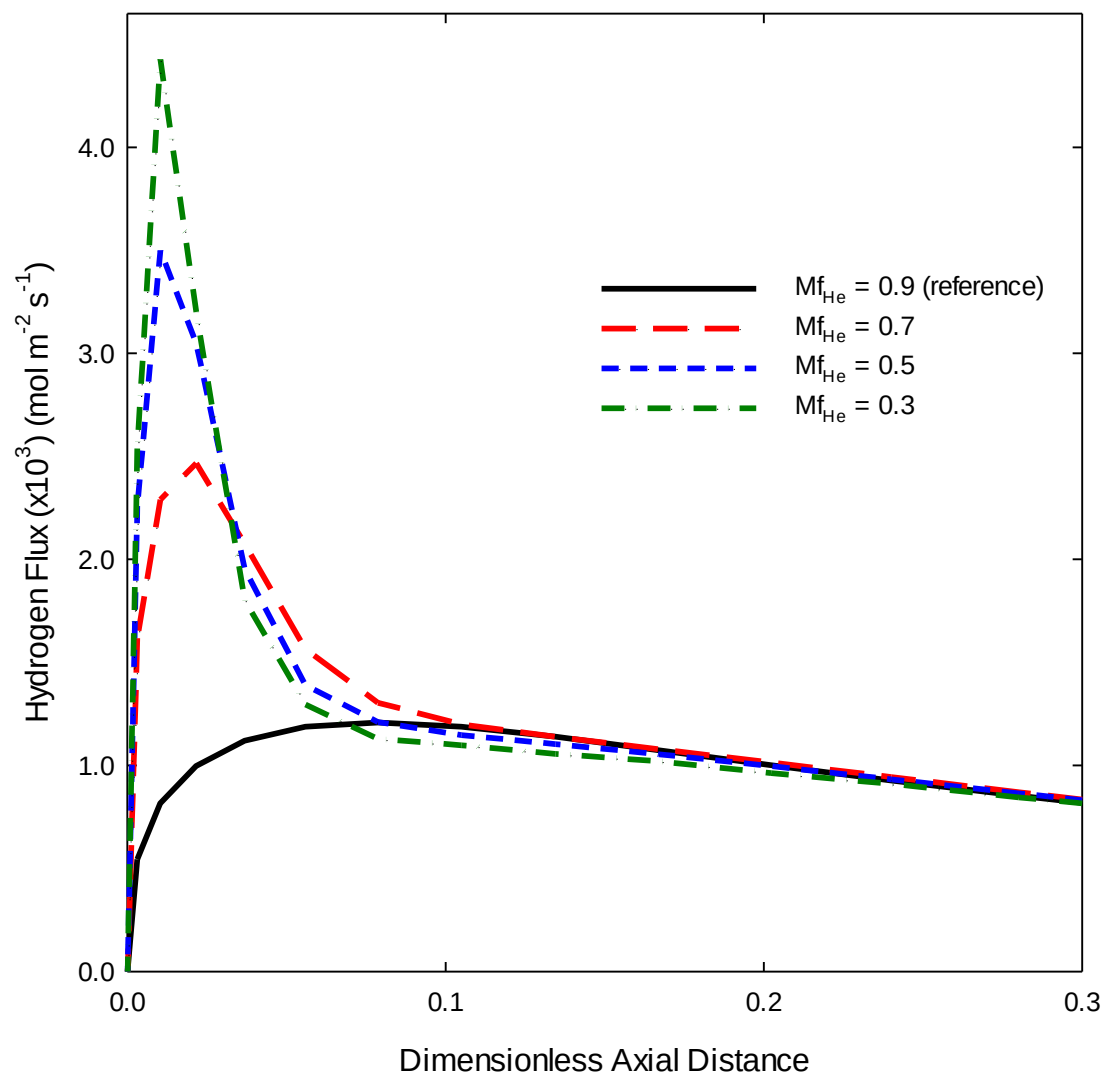


Figure 13: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor for different mole fractions of helium in the dehydrogenation side.

6.2.2 Number of tubes

To investigate the effect of the number of tubes on the performance of the membrane reactor, the molar flow rate into each tube was kept constant so as to not let the change in molar flows affect the results. This ensures a fair comparison and that only the number of tubes varied. The number of tubes used were 1200, 1500 (reference), 1800 and 2100. Figure 14 shows the conversion of propane plotted against the dimensionless axial distance for different number of tubes in the cocurrent membrane reactor. Similarly Figure 15 shows the conversion of nitrobenzene plotted against the dimensionless axial distance for different number of tubes. Figures 16 and 17 show the heat flux and hydrogen flux, respectively, plotted against the dimensionless axial distance. Both the heat and hydrogen fluxes plotted were the total fluxes from all the tubes combined. Figure 18 shows the hydrogenation and dehydrogenation temperatures plotted against the dimensionless axial distance to show the effect of the number of tubes on the temperature profiles.

Figure 14 shows that increasing the number of tubes, increased the conversion of propane that is because increasing the number of tubes increases the surface area available for the transfer of heat and hydrogen through the membrane which in turn increases the heat and hydrogen fluxes as seen in Figures 16 and 17, respectively. The increase in the hydrogen flux through the membrane, rapidly decreases the concentration of hydrogen on the dehydrogenation side which according to Le Chatelier's principle shifts the equilibrium forward and increases the equilibrium conversion of propane.

Moreover, the increase in the heat flux, due to the increase in number of tubes, from the exothermic hydrogenation side to the endothermic dehydrogenation side led to an increase in the dehydrogenation temperature as seen in the temperature profile shown in Figure 18. This increase in temperature, according to Le Chatelier's principle, pushes the endothermic dehydrogenation reaction given by Eq. (1) to the forward direction and the increase in temperature also increases the rate of the chemical reaction thus aiding the increase in the conversion of propane.

On the other hand, Figure 15 shows that increasing the number of tubes led to a slight decrease in the conversion of nitrobenzene this is due to the decrease in the peak temperature on the hydrogenation side as seen in Figure 18 which led to a decrease in the rate of the hydrogenation reaction and a decrease in the conversion of nitrobenzene.

Table 7 summarizes the results obtained and the effect of the number of tubes on the performance of the reactor. Increasing the number of tubes by 600 from 1500 to 2100, increased the conversion of propane by 14.1% from 0.80 to 0.91 at the cost of slightly decreasing the conversion of nitrobenzene from 0.90 to 0.88. Overall operating the reactor at a higher number of tubes is more favorable despite the conflicting nature of the conversion of propane and nitrobenzene because the effect of the number of tubes on the conversion of propane far outweighs its slight effect on the conversion of nitrobenzene.

Table 7: Effect of the number of tubes on the performance of the membrane reactor

Performance parameter	Number of tubes			
	1200	1500	1800	2100
Conversion of Propane	0.72	0.80	0.86	0.91
Yield of Propene	0.70	0.77	0.83	0.88
Conversion of Nitrobenzene	0.91	0.90	0.89	0.88

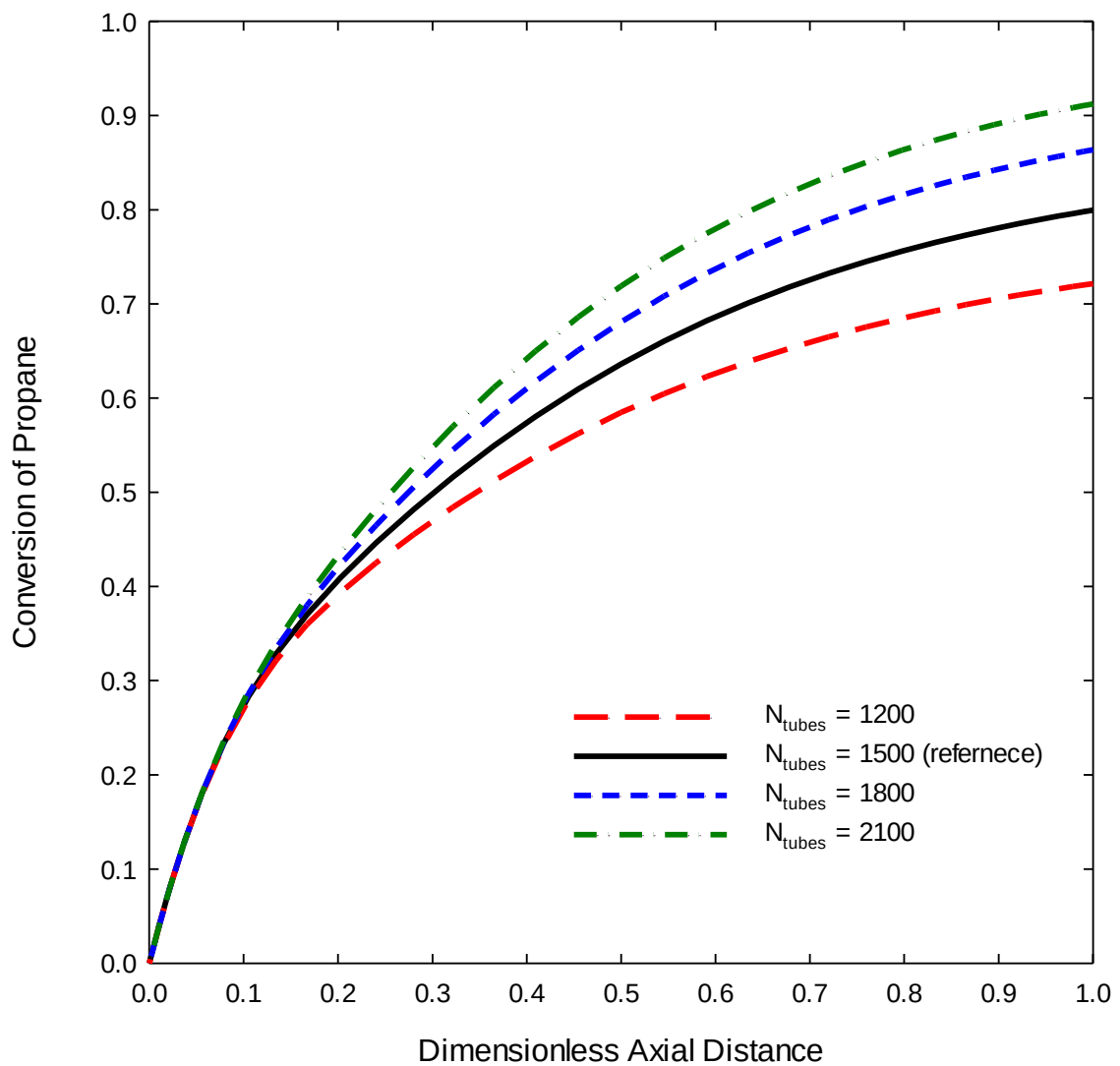


Figure 14: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.

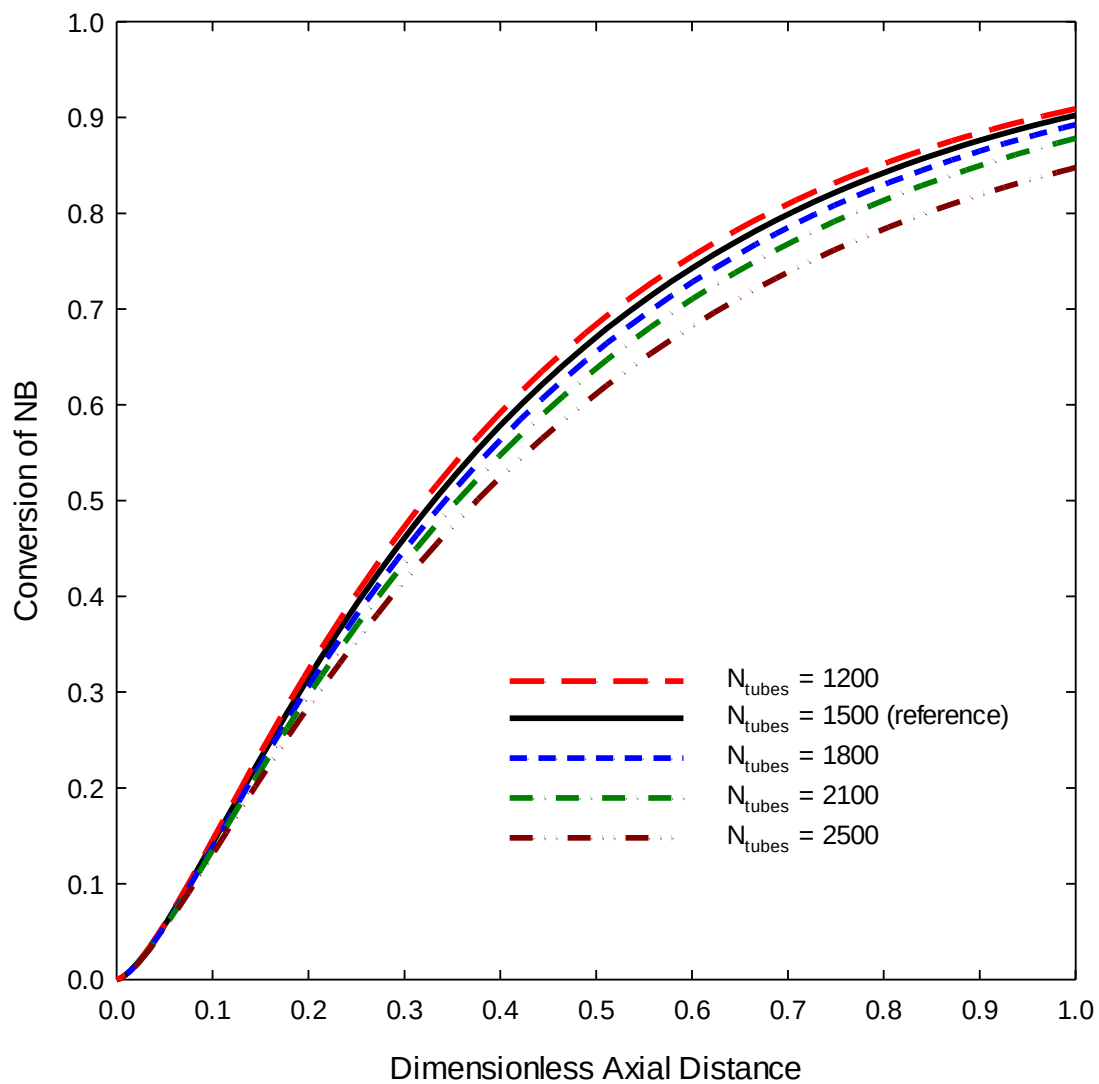


Figure 15: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.

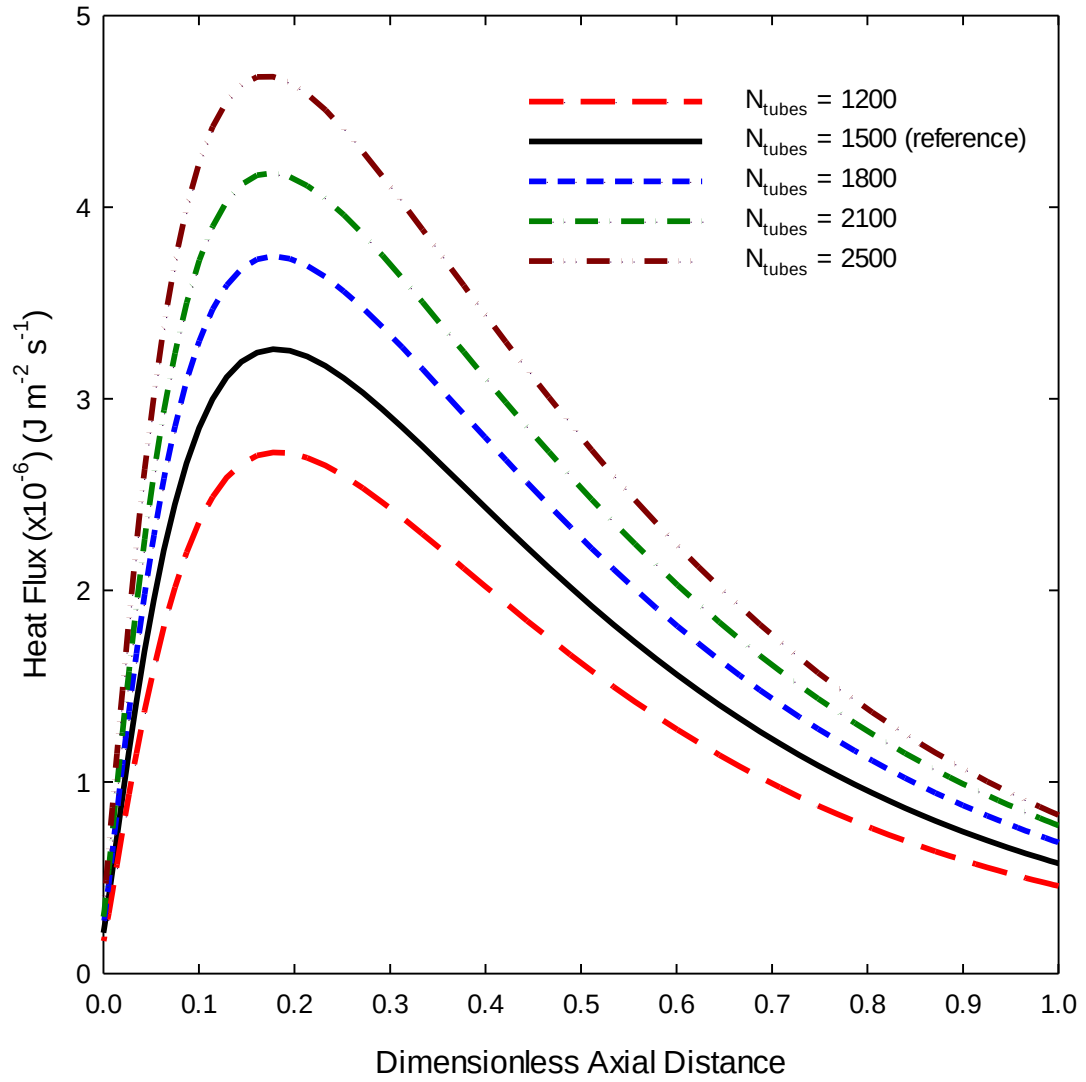


Figure 16: Total heat flux from all tubes against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.

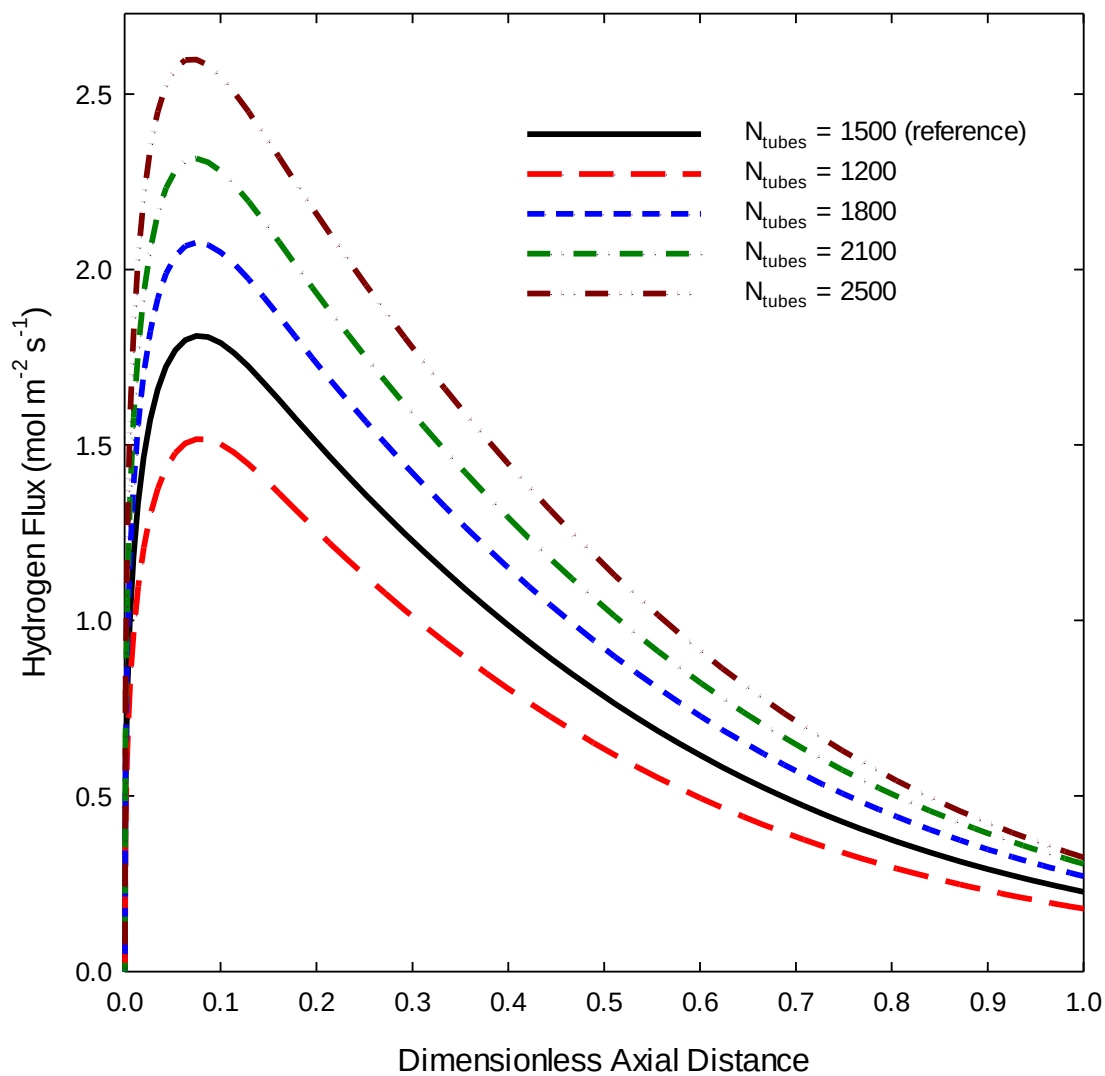


Figure 17: Total hydrogen flux from all tubes against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.

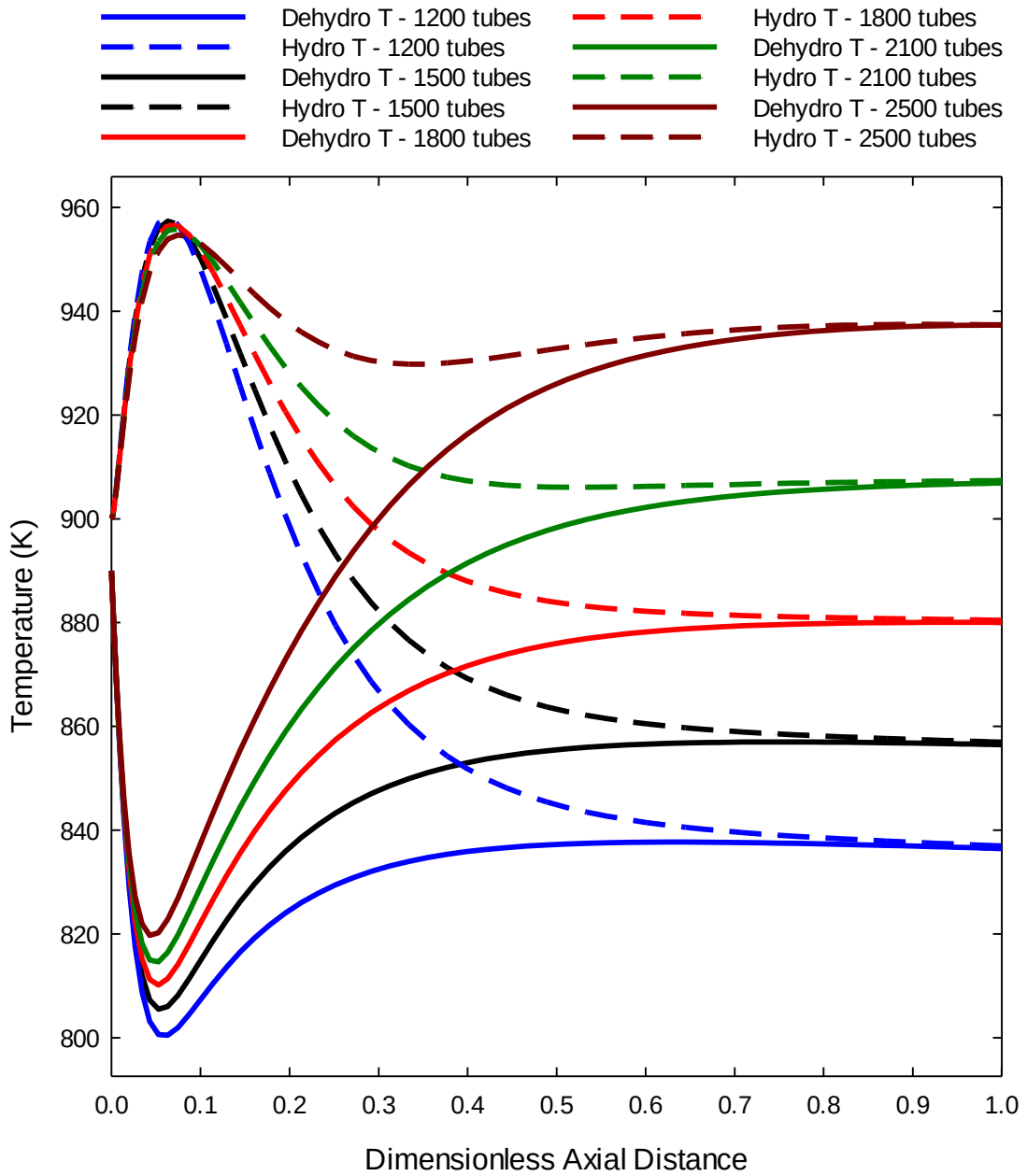


Figure 18: Hydrogenation and dehydrogenation temperatures against the dimensionless axial distance in a co-current membrane reactor using different number of tubes.

6.2.3 Tube diameter

After establishing the effect of the number of tubes, they were set back to the reference value of 1500 and the diameter of tubes were changed, to study their effect on the performance of the reactor. The reactor diameters studied were 0.02 m, 0.03 m (reference), 0.04 m and 0.05 m. Figure 19 shows the conversion of propane plotted against the dimensionless axial distance across the reactor for different tube diameters. Similarly, Figure 20 shows the conversion of nitrobenzene plotted against the dimensionless axial distance across the reactor for different tube diameters. Figure 21 shows the effect of the tube diameter on the hydrogen flux through the membrane per tube by plotting it against the dimensionless axial distance.

Figure 19 shows that as the diameter of the tubes increases, the conversion of propane also increases. Similarly, increasing the tube's diameter increases the conversion of nitrobenzene as shown in Figure 20. As the tube diameter increases, the cross-sectional area also increases, which leads to an increase in the hydrogen flux through the membrane which is seen in Figure. 21. According to Le Chatelier's principle, the increased hydrogen flux decreases the concentration of hydrogen on the dehydrogenation side which shifts the reaction to the forward direction. Consequently, the increase in the hydrogen flux increases the concentration of hydrogen on the hydrogenation side of the reactor enhances the rate of the hydrogenation reactor. Therefore, the conversions of both propane and nitrobenzene increase.

The effect of the tube diameter on the performance of the reactor is similar to the effect of the number of tubes on reactor. It is more favorable to operate the reactor at the highest possible tube diameter to benefit from the increase in the conversions of both propane and nitrobenzene.

Table 8 shows that doubling the diameter of the tube from 0.02 m to 0.04 m increases the conversion of propane 28.2% from 0.66 to 0.85 and the conversion of nitrobenzene by 66.2% from 0.59 to 0.98. Further increasing the tube diameter to 0.05 m leads to almost complete conversion of nitrobenzene and a 0.86 conversion of propane. The results obtained prove that the tube's diameter has a significant effect on the performance of the reactor boosting the conversion of both reactions.

Table 8: Effect of the tube's diameter on the performance of the membrane reactor

Performance parameter	Tube diameter (m)			
	0.02	0.03	0.04	0.05
Conversion of Propane	0.66	0.80	0.85	0.86
Yield of Propene	0.64	0.77	0.82	0.83
Conversion of Nitrobenzene	0.59	0.90	0.98	1.00

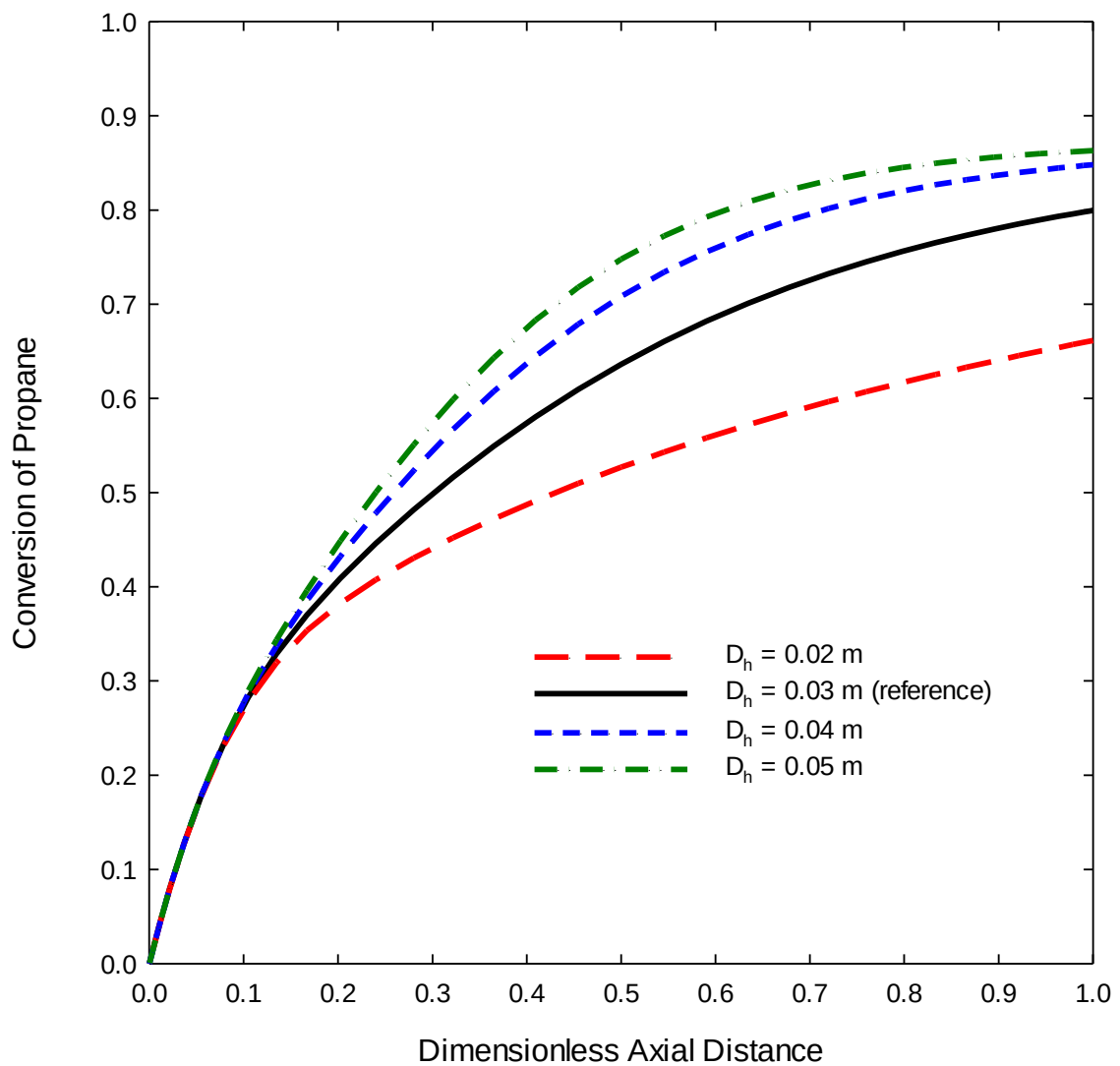


Figure 19: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.

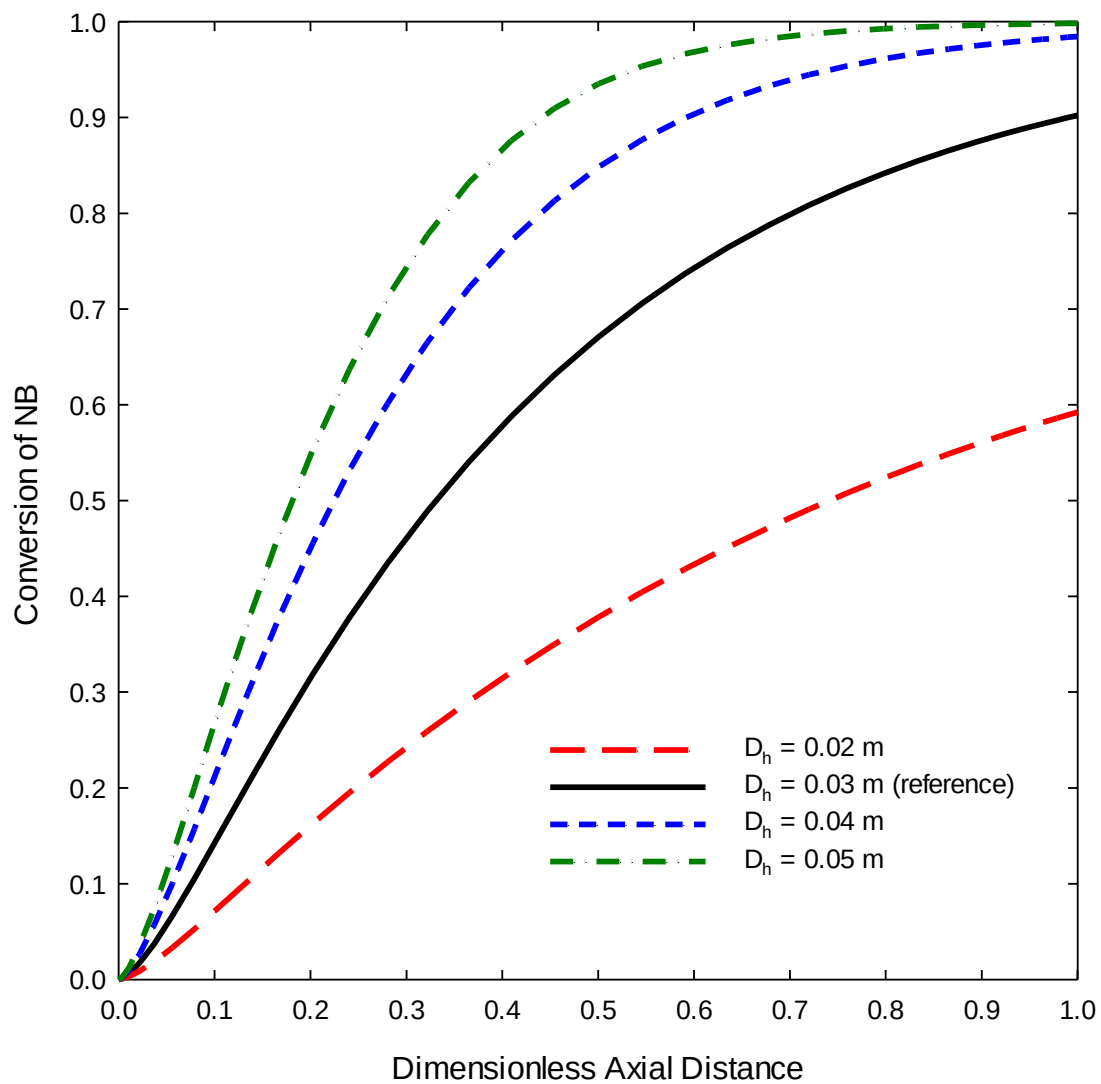


Figure 20: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.

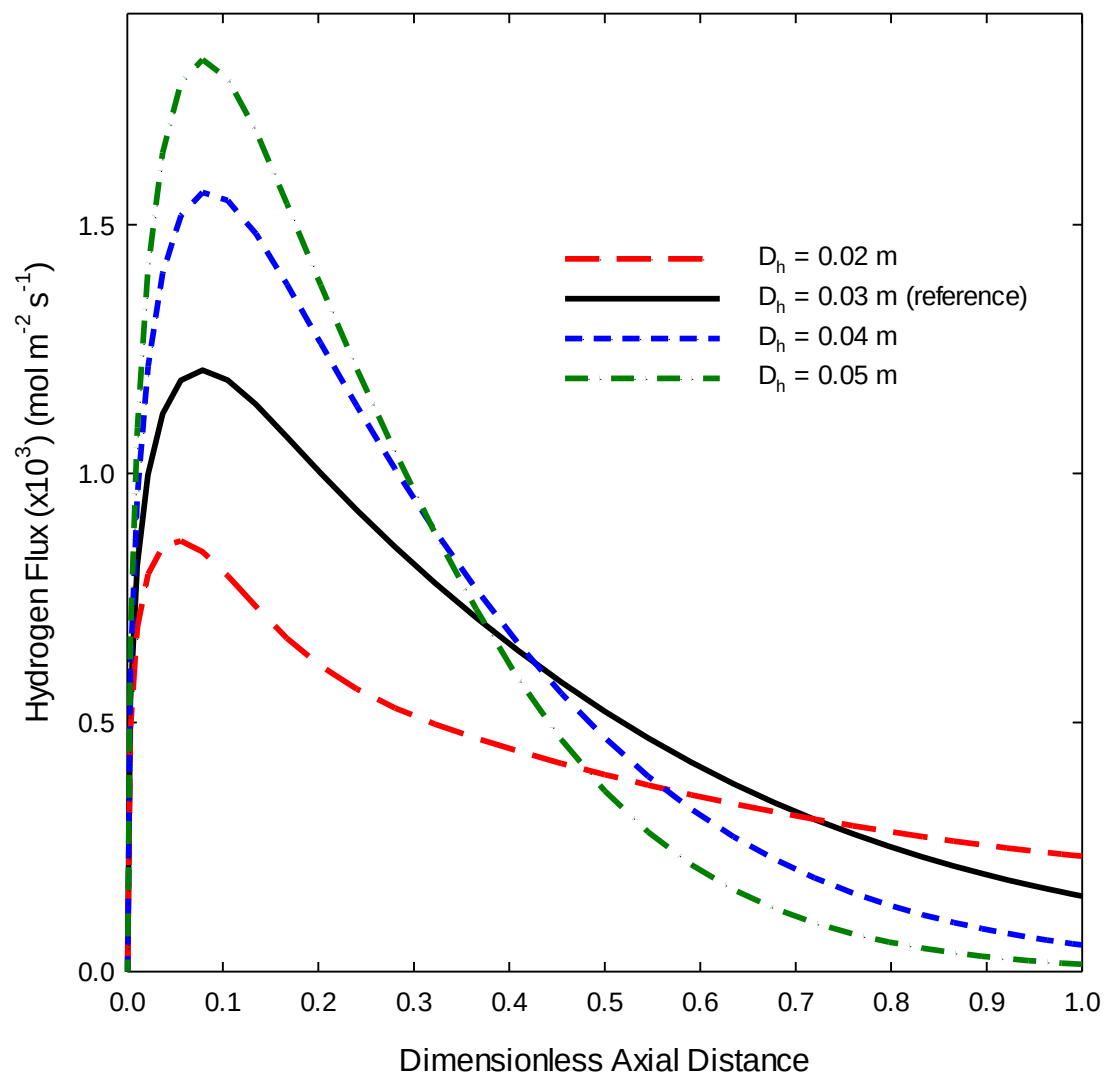


Figure 21: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different tube diameters.

6.2.4 Dehydrogenation feed pressure

In this section and the next, the effect of the hydrogenation and dehydrogenation feed pressures on the performance of the membrane reactor will be investigated. The feed pressure on the dehydrogenation side varied between 2.0 bar, 2.5 bar (reference), 3.0 bar and 3.5 bar.

Figure 22 shows the conversion of propane plotted against the dimensionless axial distance in a co-current membrane reactor using different feed dehydrogenation pressures. Similarly, Figure 23 shows the conversion of nitrobenzene plotted against the dimensionless axial distance using different feed dehydrogenation pressures. Figure 24 shows the effect of the dehydrogenation feed pressure on the hydrogen flux by plotting it against the dimensionless axial distance along the reactor.

According to Figures 22 and 23 increasing the feed pressure on the dehydrogenation side increases both the conversion of propane and nitrobenzene, respectively. However, the increase in the conversion of propane at the end of the reactor is very slight compared to the increase in the conversion of nitrobenzene. The increase in the feed pressure on the dehydrogenation side, increases the partial pressure of hydrogen produced on the dehydrogenation side which increases the differential pressure between the two opposite sides of the membrane which in turn increases the driving force for hydrogen permeation across the membrane leading to a higher hydrogen flux as the feed dehydrogenation pressure increases which is shown in Figure 24.

The higher hydrogen flux between the dehydrogenation and hydrogenation sides decreases the concentration of hydrogen (a product) on the dehydrogenation side which, according to Le Chatelier's principle shifts the equilibrium to the forward direction leading to an increase in the conversion of propane. Also, as a result of the higher hydrogen flux, the concentration of hydrogen (a reactant) is higher on the hydrogenation side which enhances the rate of the hydrogenation reaction and increases the concentration of nitrobenzene as shown in Figure 23.

As shown in Table 9, increasing the feed pressure from 2.0 bar to 3.5 bar slightly increases the conversion of propane by 1.95% from 0.79 to 0.81 and increases the conversion of nitrobenzene increased by 4.18% from 0.88 to 0.92. The increase of the dehydrogenation feed pressure has a positive effect on both conversions of propane and nitrobenzene, however, the increase in conversions is marginal and the economic cost of maintaining the higher feed pressure needs to be considered while making this decision.

Table 9: Effect of the dehydrogenation feed pressure on the performance of the membrane reactor

Performance parameter	Feed pressure - dehydrogenation (bar)			
	2.0	2.5	3.0	3.5
Conversion of Propane	0.79	0.80	0.80	0.81
Yield of Propene	0.77	0.77	0.77	0.77
Conversion of Nitrobenzene	0.88	0.90	0.91	0.92

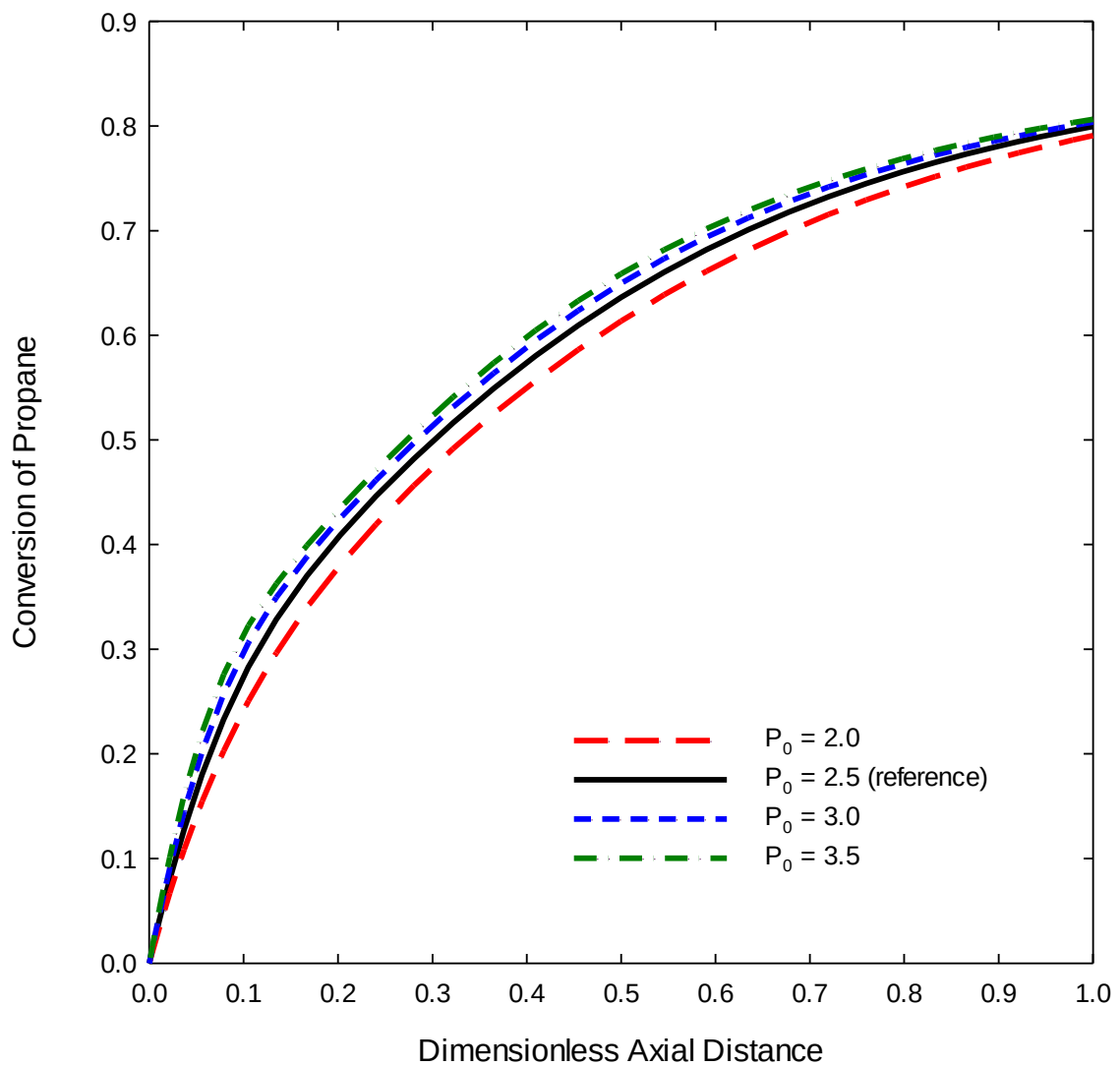


Figure 22: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.

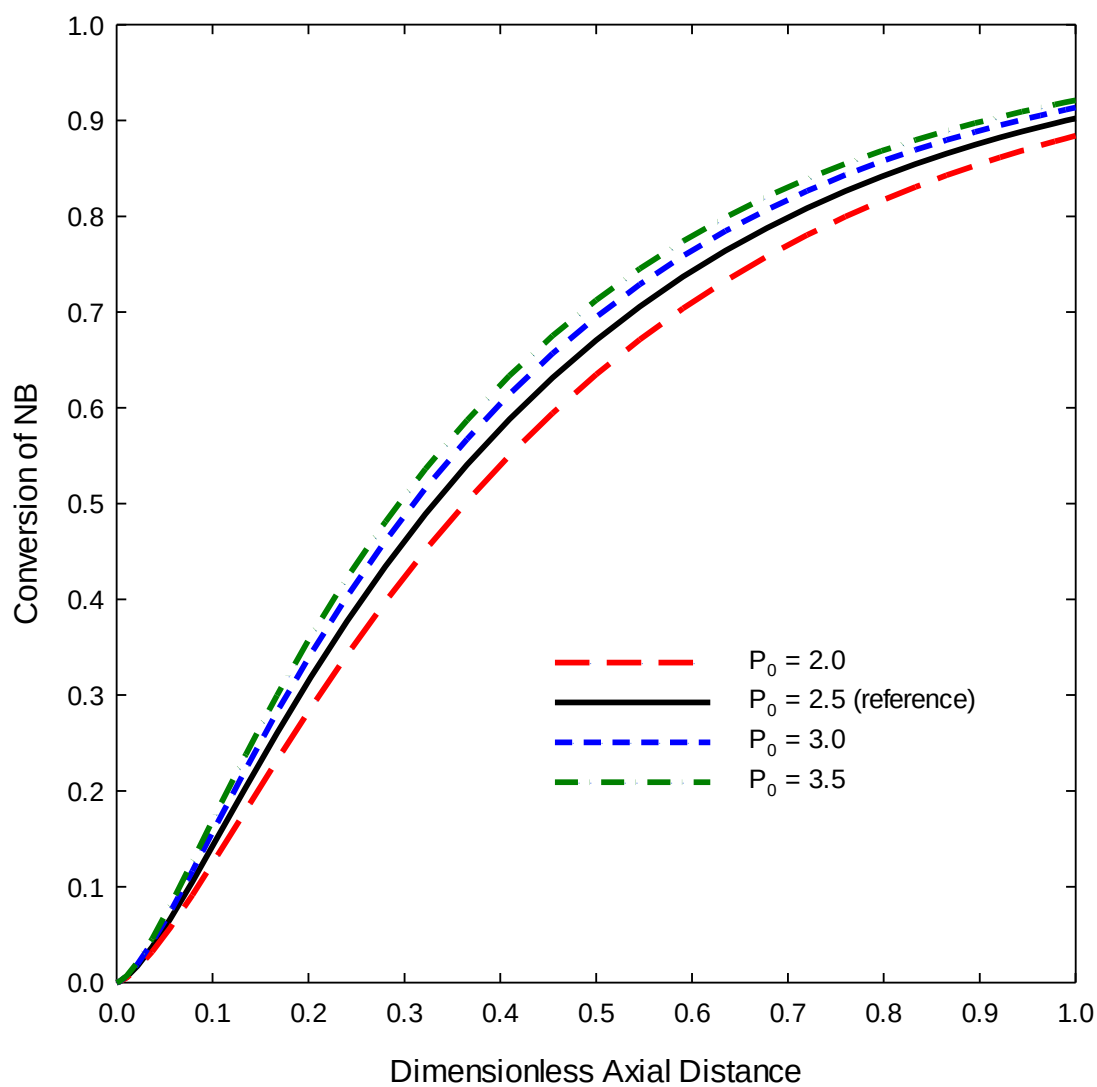


Figure 23: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.

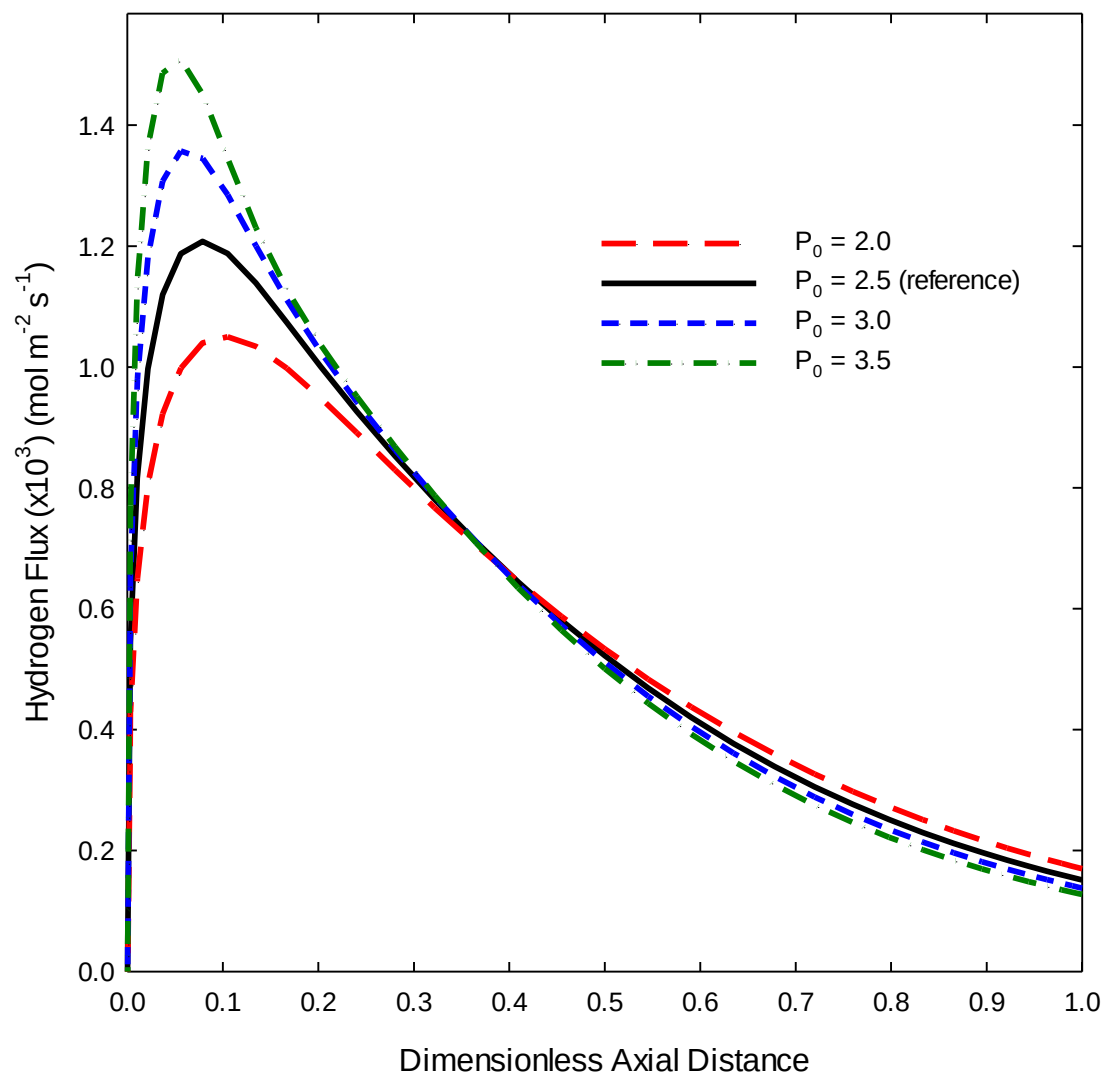


Figure 24: Hydrogen flux per tube plotted against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed pressures.

6.2.5 Hydrogenation feed pressure

Similarly, the effect of the hydrogenation feed pressure will be investigated. Before selecting the values used for the hydrogenation feed pressure it was crucial to ensure that the pressure in the dehydrogenation side was always higher than that in the hydrogenation side to maintain the flow of hydrogen in the right direction (Dehydrogenation to hydrogenation). The reference dehydrogenation feed pressure used was 2.5 bar, so the hydrogenation feed pressures used were 1.0 bar, 1.5 bar (reference) and 2.0 bar.

Figure 25 shows the conversion of propane plotted against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures. Similarly, Figure 26 shows the conversion of nitrobenzene plotted against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures. To explain the effects of the feed hydrogenation pressure on the performance of the reactor, Figure 27 was plotted showing the hydrogen flux per tube through the membrane against the dimensionless axial distance for each of the hydrogenation feed pressures.

Figures 25 and 26 show the effect of increasing the feed pressure (hydrogenation side) on the conversion of propane and nitrobenzene, respectively. Increasing the feed pressure increases both the conversions. For both propane and nitrobenzene, the increase in the conversion going from 1.0 bar to 1.5 bar was much higher than the increase in conversion going from 1.5 bar to 2.0 bar.

Moreover, Figure 27 shows that the increase in feed pressure on the hydrogenation side did not affect the driving force for the hydrogen flux and instead led to an increase in the hydrogen flux. The higher the hydrogenation feed pressure led to a higher hydrogen flux peak from the beginning of the reactor until around 0.6 of the reactor and that is when the hydrogen flux for all pressures were roughly equal. The increase in the feed pressure increased the rate of the hydrogenation reaction which increases the conversion of nitrobenzene leading to the faster consumption of hydrogen. The higher consumption of hydrogen on the hydrogenation side maintained the driving force for the hydrogen flux which in turn increased the conversion of propane on the dehydrogenation side.

Table 10 summarizes the effects of the change in the feed pressure on the hydrogenation side of the reactor. Doubling the inlet pressure from 1 bar to 2 bar increases the conversion of nitrobenzene from 0.77 to 0.96 while increasing the conversion of propane from 0.75 to 0.82.

Table 10: Effect of the hydrogenation feed pressure on the performance of the membrane reactor

Performance parameter	Feed pressure - hydrogenation (bar)		
	1.0	1.5	2.0
Conversion of Propane	0.75	0.80	0.82
Yield of Propene	0.72	0.77	0.80
Conversion of Nitrobenzene	0.77	0.90	0.96

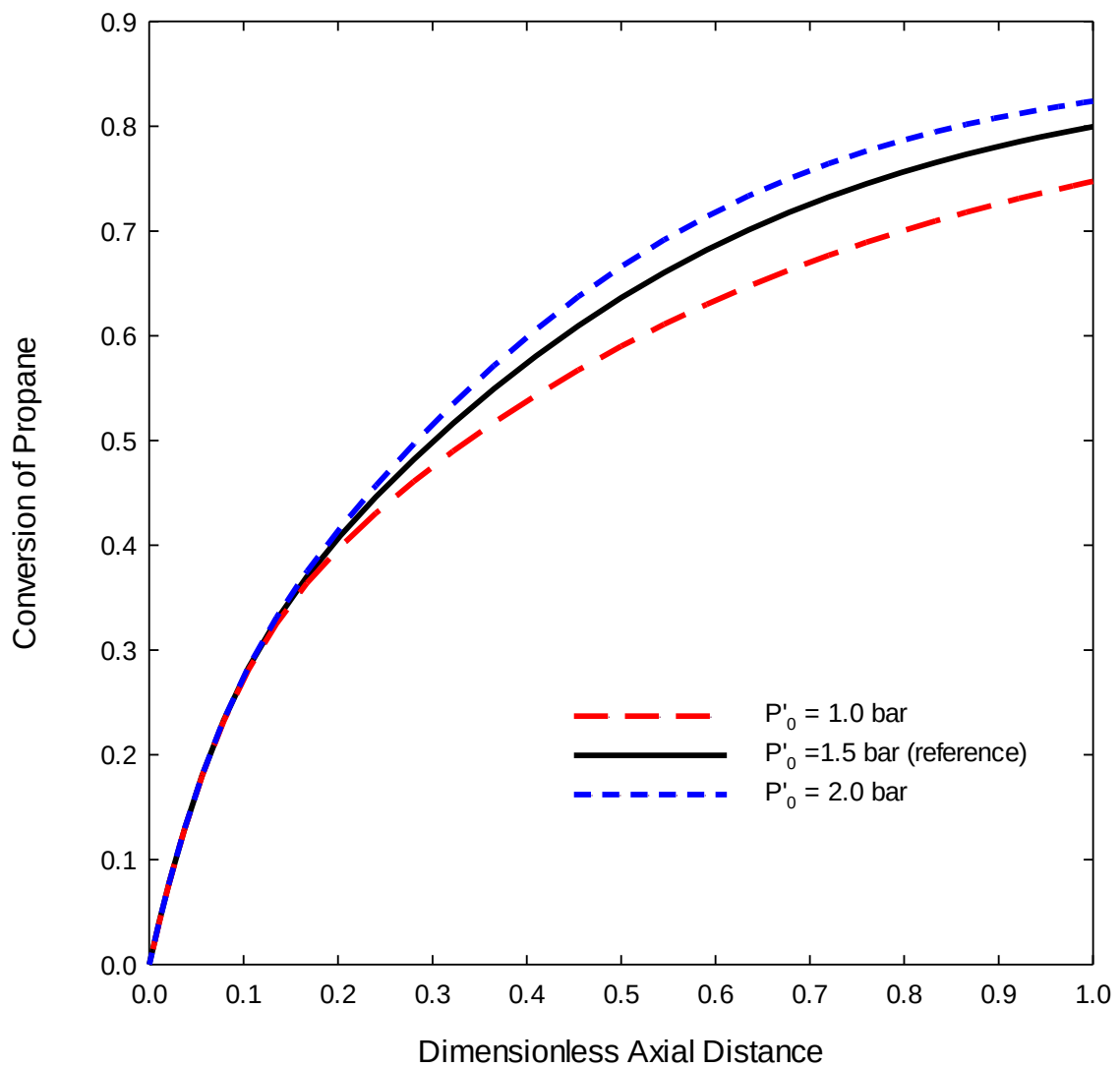


Figure 25: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures.

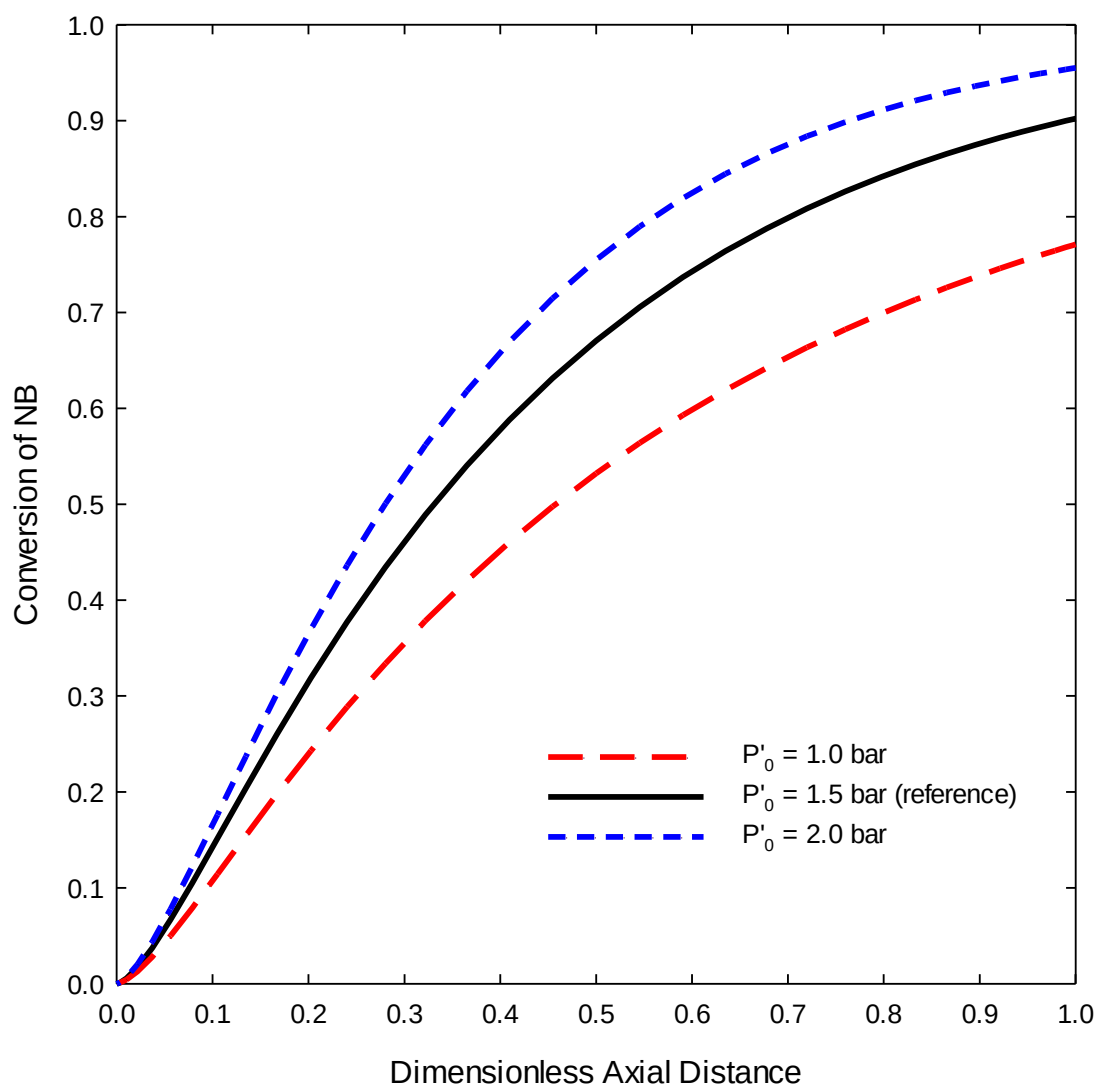


Figure 26: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures.

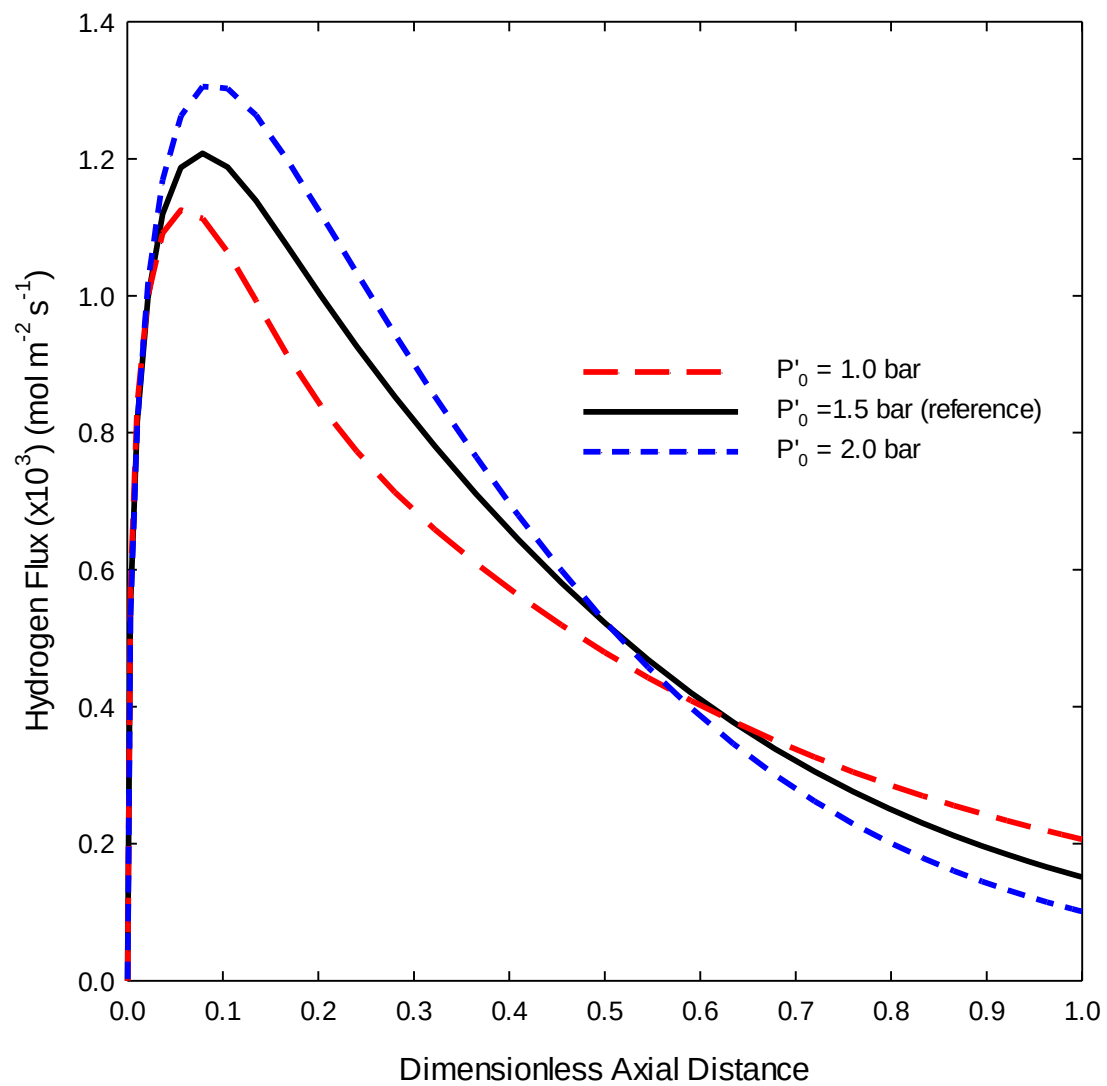


Figure 27: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed pressures.

6.2.6 Dehydrogenation feed temperature

The effect of the feed temperatures was investigated in this section and the following section. The dehydrogenation feed temperatures used were 700 K, 800 K, 890 K (reference) and 1000 K. Figure 28 shows the conversion of propane plotted against the dimensionless axial distance using a co-current membrane reactor with different dehydrogenation feed temperatures. Similarly, Figure 29 shows the conversion of nitrobenzene plotted against the dimensionless axial distance with different dehydrogenation feed temperatures. Moreover, to further explain the effect of the dehydrogenation feed temperature on the performance of the reactor, Figure 30 shows the heat flux per tube through the membrane was plotted against the dimensionless axial distance using different feed temperatures. Also, Figure 31 shows the hydrogen flux per tube against the dimensionless axial distance using the different dehydrogenation feed temperatures.

Figures 28 and 29 show the effect of the feed temperature on the conversion of propane and nitrobenzene, respectively. According to the figures, increasing the dehydrogenation feed temperature increases both the conversions of propane and nitrobenzene. The dehydrogenation reaction is endothermic and therefore, increasing the feed temperature shifts, according to Le Chatelier's principle, the equilibrium of Eq. (1) to the forward direction hence increasing the conversion of propane. Moreover, the increase in the temperature further increases the rate of reaction ensuring the effluent conversion is close to the equilibrium conversion of propane.

As the conversion of propane increases, the amount of hydrogen produced also increases, which leads to a higher hydrogen flux through the membrane to the dehydrogenation side as shown in Figure 31. The higher hydrogen flux increases the concentration of hydrogen in the hydrogenation side of the reactor which increases the rate of the hydrogenation reaction leading to an increase in the conversion of nitrobenzene. Moreover, it is worth noting that increasing the extents of both reactions lead to an increase in the heat flux through the membrane shown in Figure 30. The increase in the heat flux from the exothermic hydrogenation reaction to the endothermic dehydrogenation reaction shifts the dehydrogenation reaction to the forward direction which contributes to the increase in the conversion of propane seen in Figure 28.

Table 9 summarizes the effect of the dehydrogenation temperature on the reactor's performance. The increase in the temperature of the dehydrogenation side greatly increased the conversion of propane and slightly increased that of nitrobenzene. Increasing the temperature by 300 K from 700 K to 1000 K increases the conversion of propane from 0.47 to 0.93 and the conversion of nitrobenzene from 0.70 to 0.93.

Table 11: Effect of the dehydrogenation feed temperature on the performance of the membrane reactor

Performance parameter	Feed temperature - dehydrogenation (K)			
	700	800	890	1000
Conversion of Propane	0.48	0.66	0.80	0.93
Yield of Propene	0.48	0.65	0.77	0.84
Conversion of Nitrobenzene	0.70	0.84	0.90	0.93

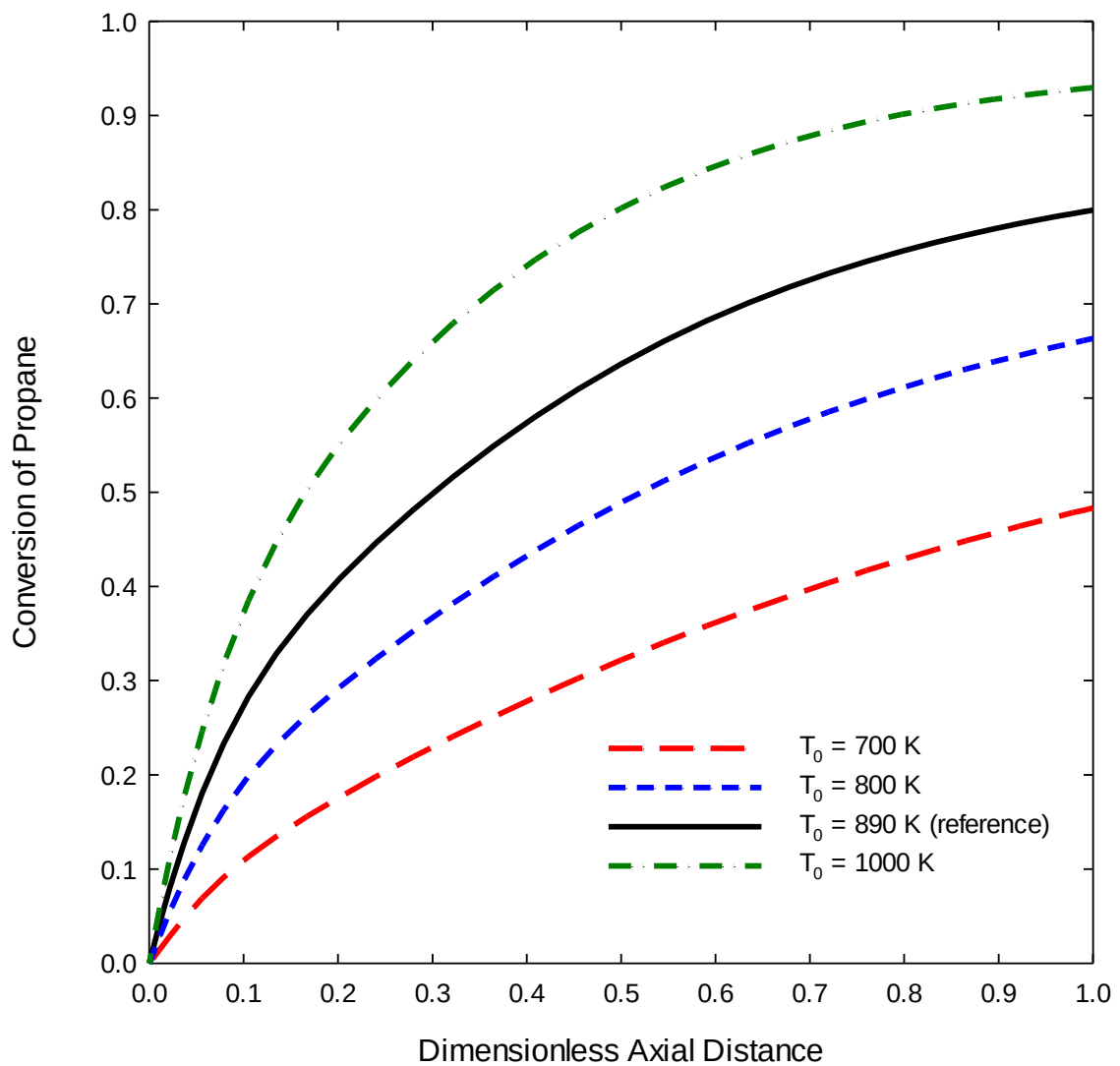


Figure 28: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.

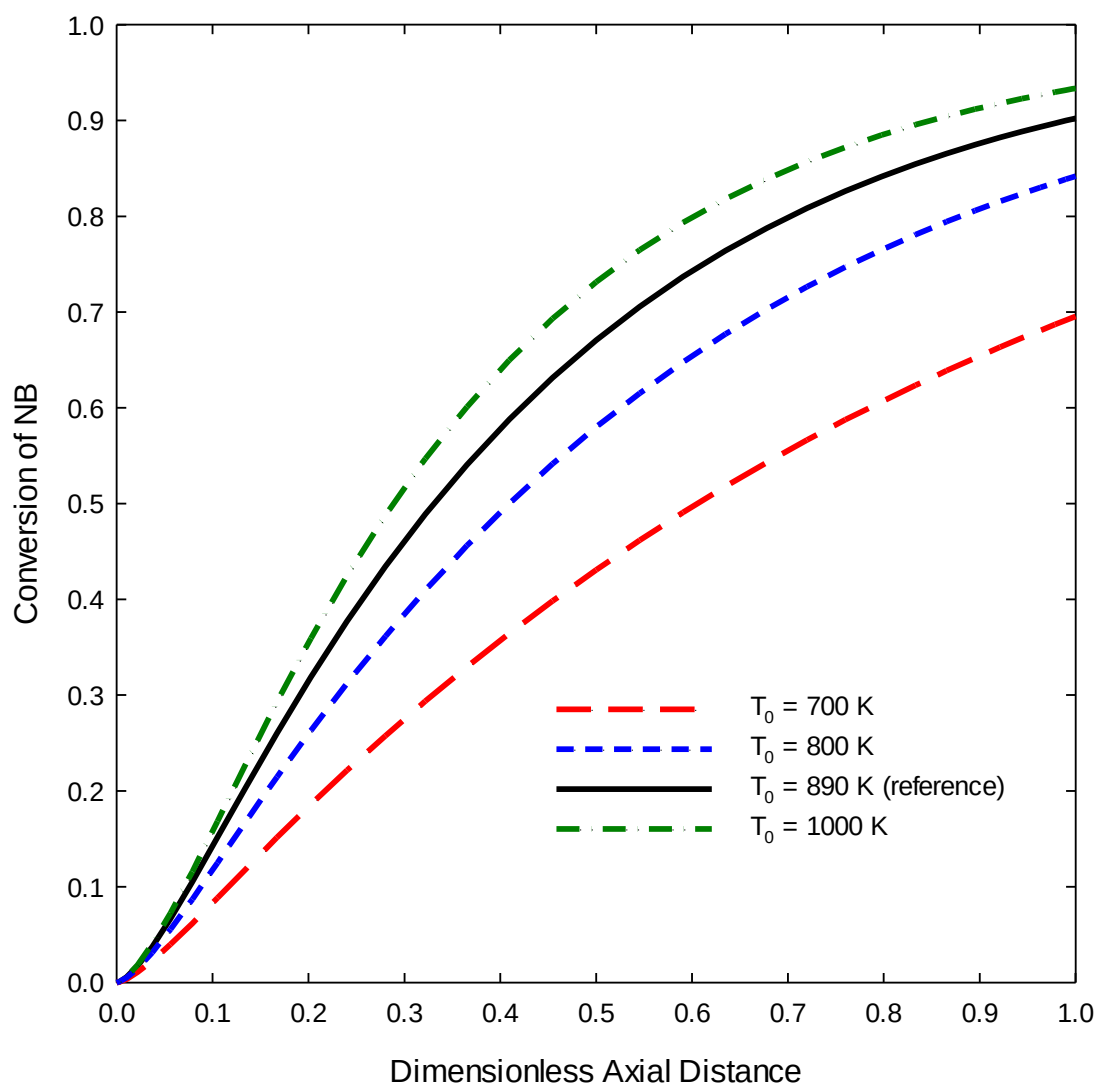


Figure 29: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.

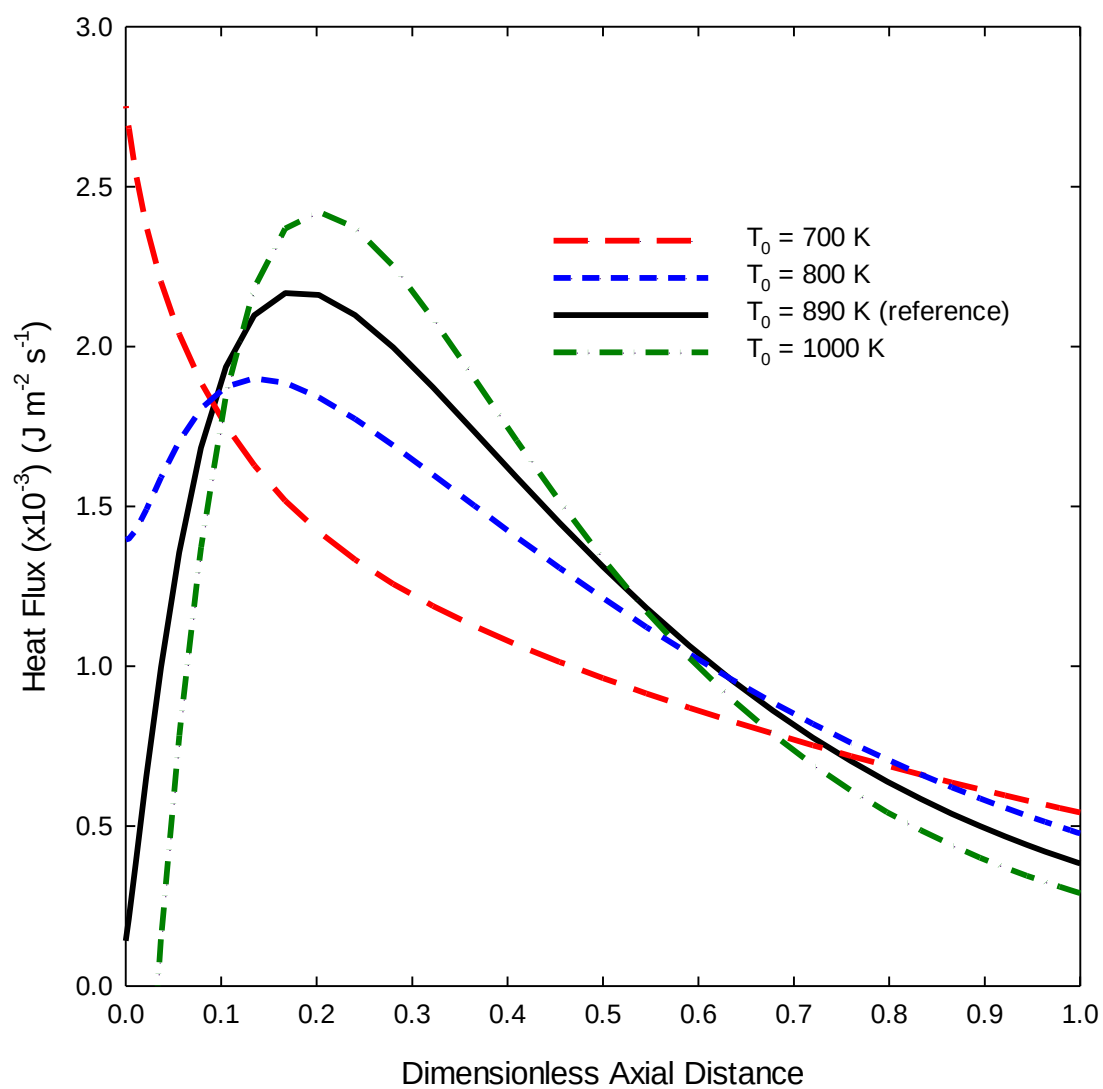


Figure 30: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.

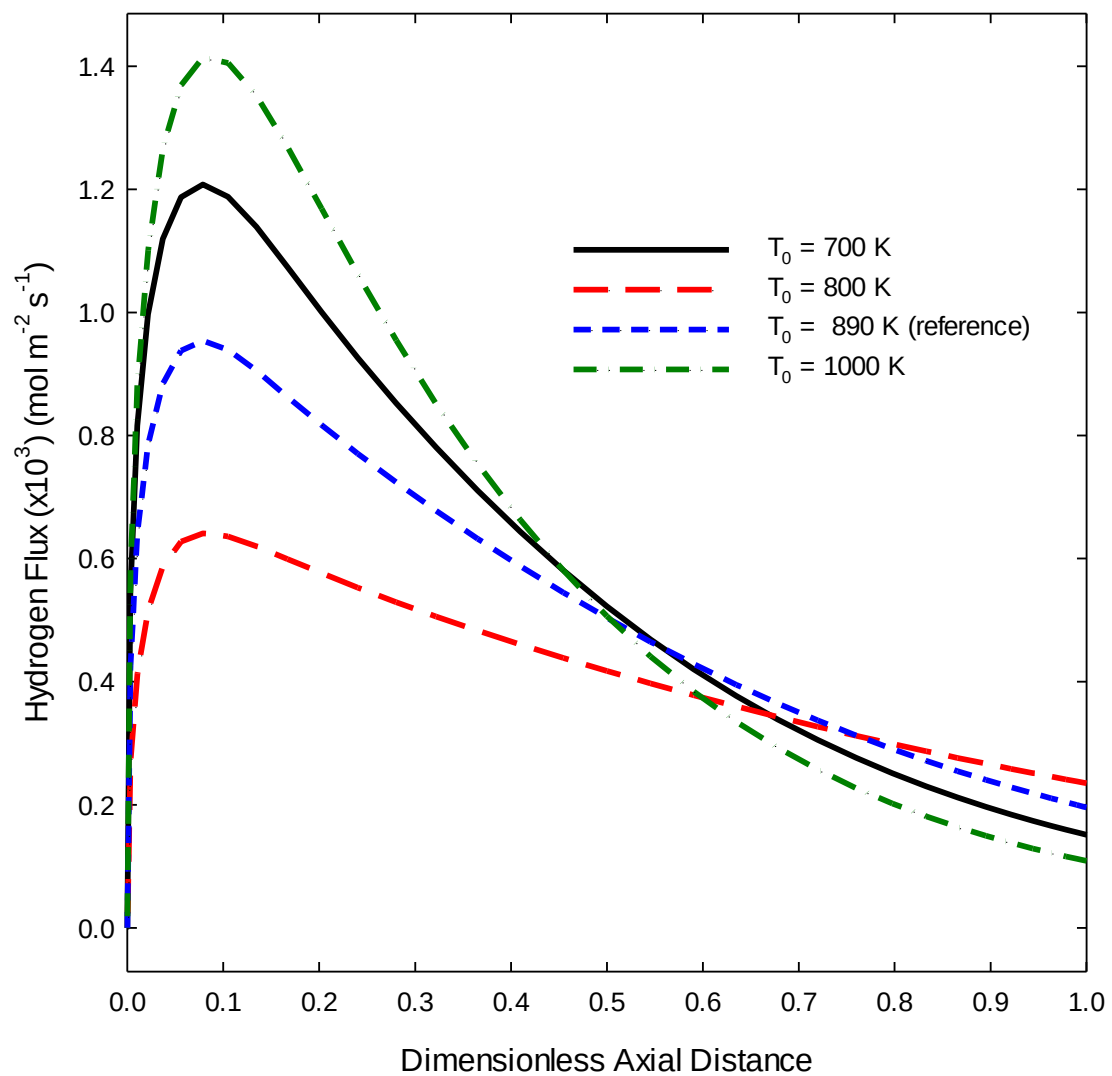


Figure 31: Hydrogen flux per tube against the dimensionless axial distance in a co-current membrane reactor using different dehydrogenation feed temperatures.

6.2.7 Hydrogenation feed temperature

Similarly, the effect of the feed temperature on the hydrogenation side was also investigated. The hydrogenation feed temperature used were 700 K, 800 K, 900 K (reference) and 1000 K. Figure 32 shows the conversion of propane plotted against the dimensionless axial distance using a co-current membrane reactor with different hydrogenation feed temperatures. Similarly, Figure 33 shows the conversion of nitrobenzene plotted against the dimensionless axial distance with different hydrogenation feed temperatures. Moreover, to further explain the effect of the hydrogenation feed temperature on the performance of the reactor, Figure 34 shows the heat flux per tube through the membrane plotted against the dimensionless axial distance using different feed temperatures.

Figures 32 and 33 show the effect of the hydrogenation feed temperature on the conversion of propane and nitrobenzene, respectively. According to the figures, increasing the hydrogenation feed temperature increases the conversion of both propane and nitrobenzene. Increasing the feed hydrogenation temperature increases the rate of the hydrogenation reaction which leads to an increase in the conversion of nitrobenzene.

The increase in the conversion of nitrobenzene increases the temperature on the exothermic hydrogenation side which increases the driving force for the heat flux leading to a higher heat flux as the feed hydrogenation temperature increases which is shown in Figure 34. The higher heat flux increases the temperature on the endothermic dehydrogenation side shifting its equilibrium to the forward direction and increasing the rate of the reaction, leading to a significant increase in the conversion of propane.

Table 12 shows the effect of the hydrogenation feed temperature on the conversion of propane, yield of propene and the conversion of nitrobenzene. The table shows that the increase in the conversion of propane was higher than the increase in the conversion of nitrobenzene. Increasing the hydrogenation feed temperature by 300 K from 700 K to 1000 K, only slightly increases the conversion of nitrobenzene from 0.86 to 0.92 while the conversion of propane goes up from 0.71 to 0.84. This difference is due to the fact that the dehydrogenation reaction had an increase in its rate and equilibrium conversion due to the increase in temperature caused by the higher heat flux whereas the hydrogenation reaction only experienced an increase in the rate of its reaction which caused a smaller increase in the conversion of nitrobenzene.

Table 12: Effect of the hydrogenation feed temperature on the performance of the membrane reactor

Performance parameter	Feed temperature - hydrogenation (K)			
	700	800	900	1000
Conversion of Propane	0.71	0.75	0.80	0.84
Yield of Propene	0.69	0.73	0.77	0.81
Conversion of Nitrobenzene	0.86	0.89	0.90	0.92

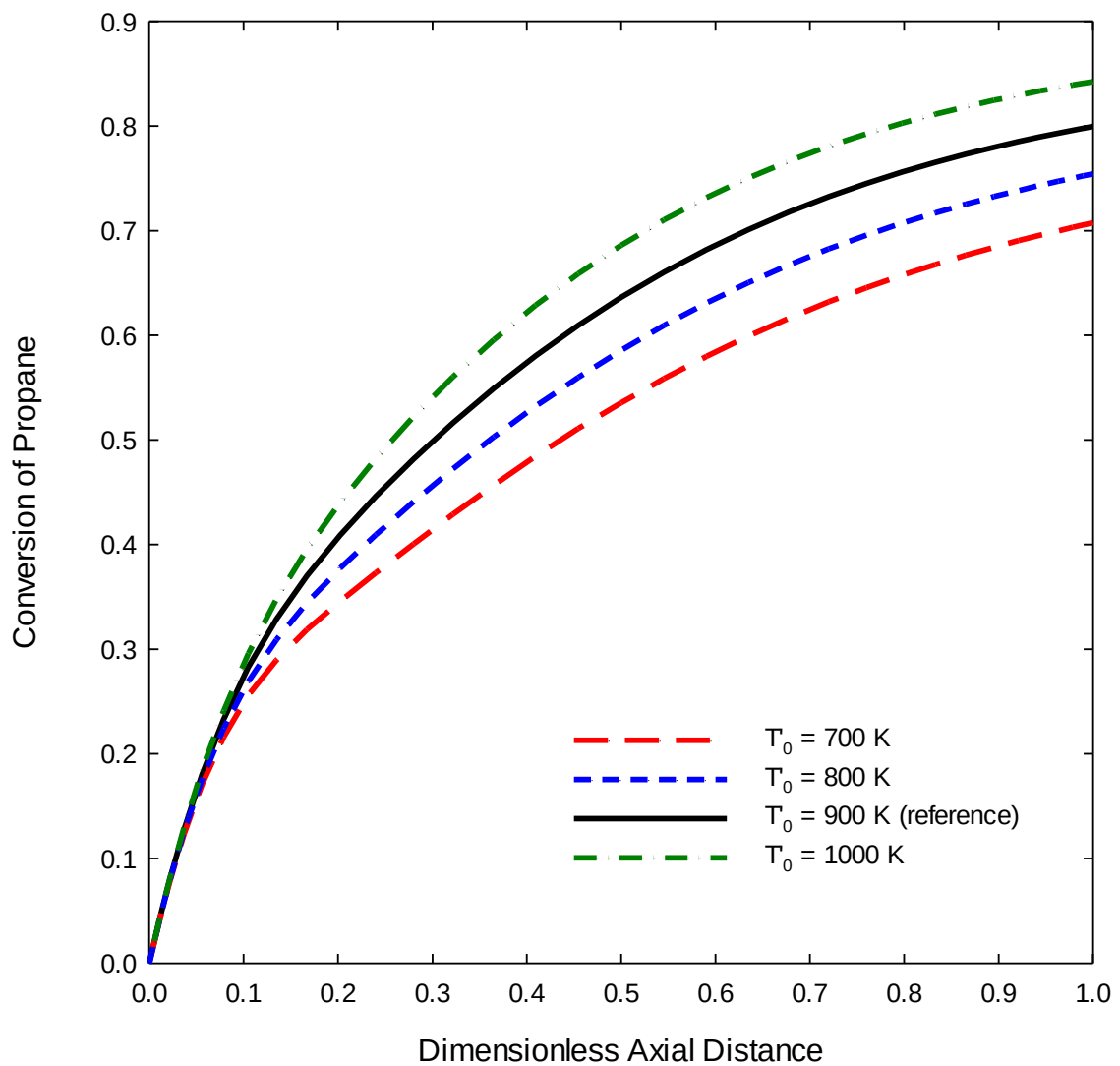


Figure 32: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.

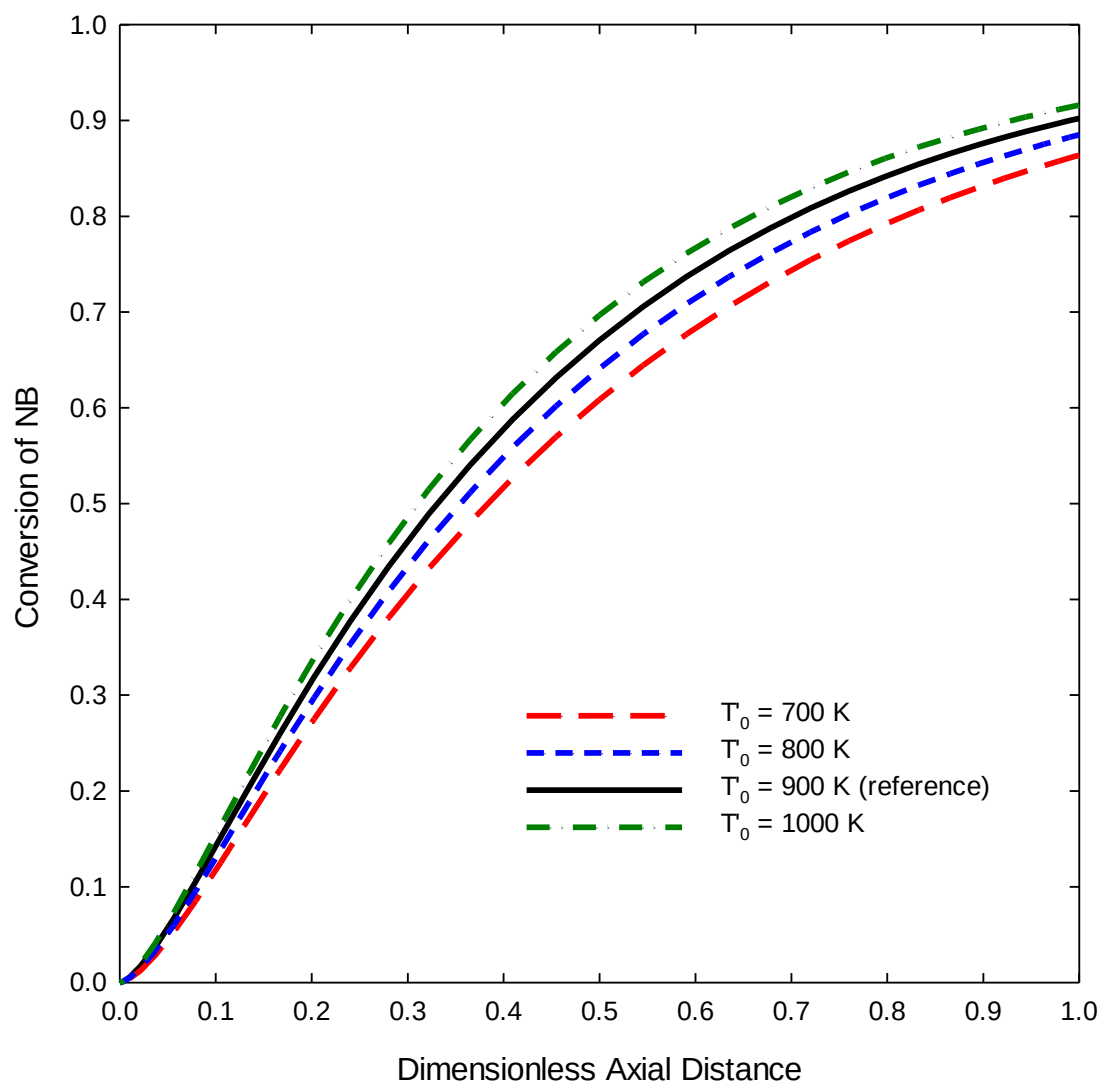


Figure 33: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.

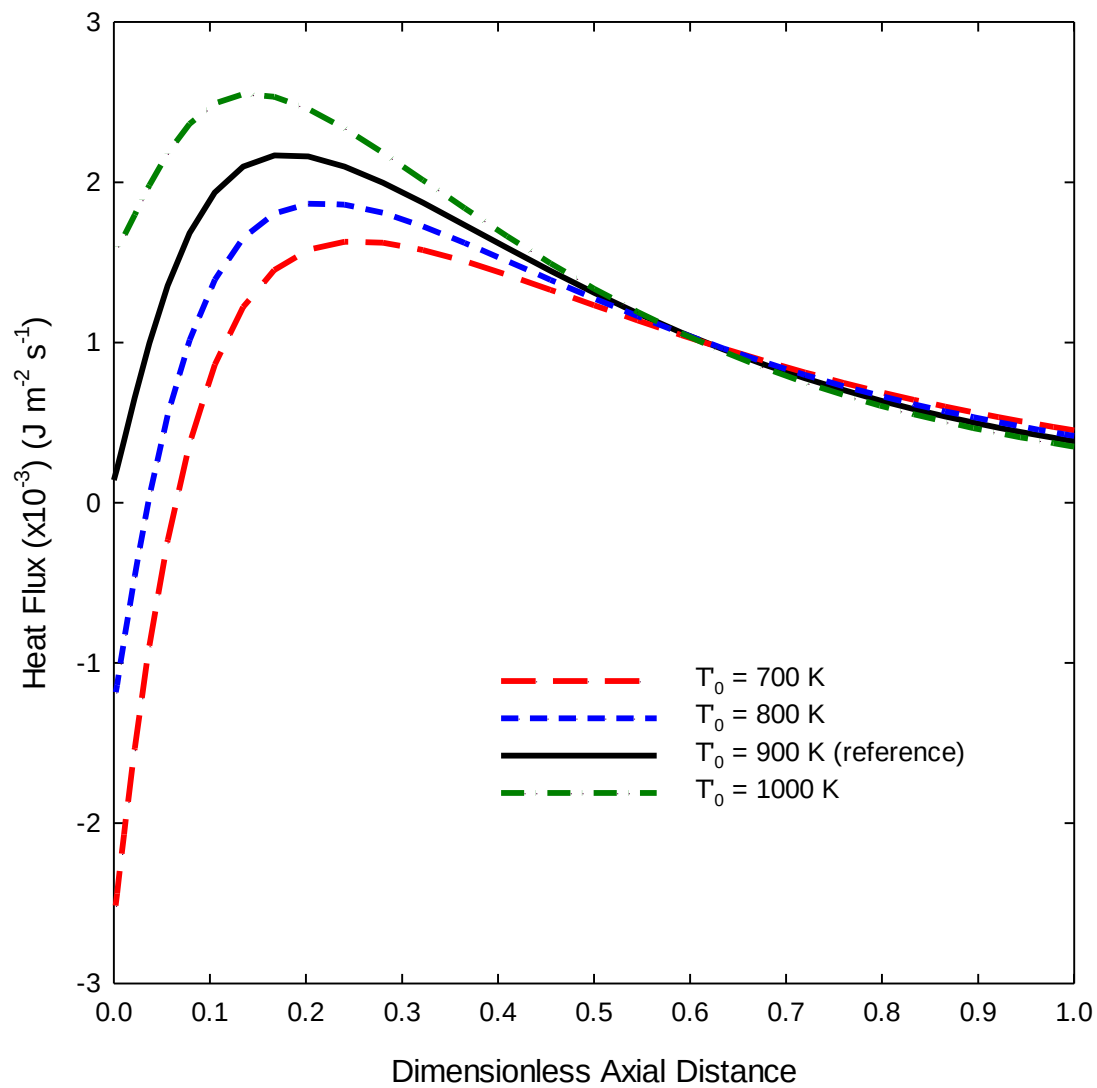


Figure 34: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different hydrogenation feed temperatures.

6.2.8 Steam to hydrocarbon ratio

On the hydrogenation side, the effect of changing the steam to hydrocarbon ratio in the feed on the reactor's performance was thoroughly investigated. The ratio of steam to hydrocarbon was changed by changing the molar flowrate of steam in the hydrogenation feed while keeping the molar flow of nitrobenzene constant to ensure a fair comparison. The steam to hydrocarbon ratios compared were 1, 3, 5, 7.5 (reference) and 9.

Figure 35 shows the conversion of propane plotted against the dimensionless axial distance using a co-current membrane reactor with different steam to hydrocarbon ratios in the feed to the hydrogenation side of the reactor. Similarly, Figure 36 shows the conversion of nitrobenzene plotted against the dimensionless axial distance with different steam to hydrocarbon ratios in the feed. Moreover, to further explain the effect of the steam to hydrocarbon ratios in the feed on the performance of the reactor, Figure 37 shows the heat flux per tube through the membrane plotted against the dimensionless axial distance using different steam to hydrocarbon feed ratios.

Figures 35 and 36 show that decreasing the steam to hydrocarbon ratio increases the conversions of both propane and nitrobenzene, respectively. Increasing the steam to hydrocarbon ratio dilutes the hydrogenation feed stream by introducing more steam which decreases the concentration of nitrobenzene which decreases the rate of the hydrogenation reaction. The reduction in the rate of the hydrogenation reaction leads to a decrease in the conversion of nitrobenzene with the increase in the steam to hydrocarbon ratio.

Moreover, it is worth noting that at a steam to hydrocarbon ratio of 1, the reaction reached the maximum possible conversion at roughly 80% of the reactor's length due to the much higher rate of reaction caused by the higher concentration of nitrobenzene in the feed.

The decrease in the conversion of nitrobenzene decreases the increase in temperature on the hydrogenation side caused by the exothermic nature of the hydrogenation reaction. The decrease in hydrogenation temperature decreases the heat flux as shown in Figure 37 and therefore decreases the heat transferred from the hydrogenation side to the dehydrogenation side which in turn decreases the dehydrogenation temperature as the steam to hydrocarbon ratio increases. According to Le Chatelier's principle, at a lower dehydrogenation temperature the endothermic dehydrogenation reaction shifts to the backward direction which causes the conversion of propane to decrease.

Table 11 shows the effect of the steam to hydrocarbon ratio on the conversion of propane, yield of propene and conversion of nitrobenzene. Increasing the steam to carbon ratio from 1 to 9 decreases the conversion of propane from 0.85 to 0.78 and decreases the conversion of nitrobenzene from almost full conversion (0.998) to 0.87.

Table 13: Effect of the steam to hydrocarbon ratio on the performance of the membrane reactor

Performance parameter	Steam to hydrocarbon (NB) ratio				
	1	3	5	7.5	9
Conversion of Propane	0.85	0.84	0.82	0.80	0.78
Yield of Propene	0.82	0.81	0.80	0.77	0.76
Conversion of Nitrobenzene	0.998	0.98	0.95	0.90	0.87

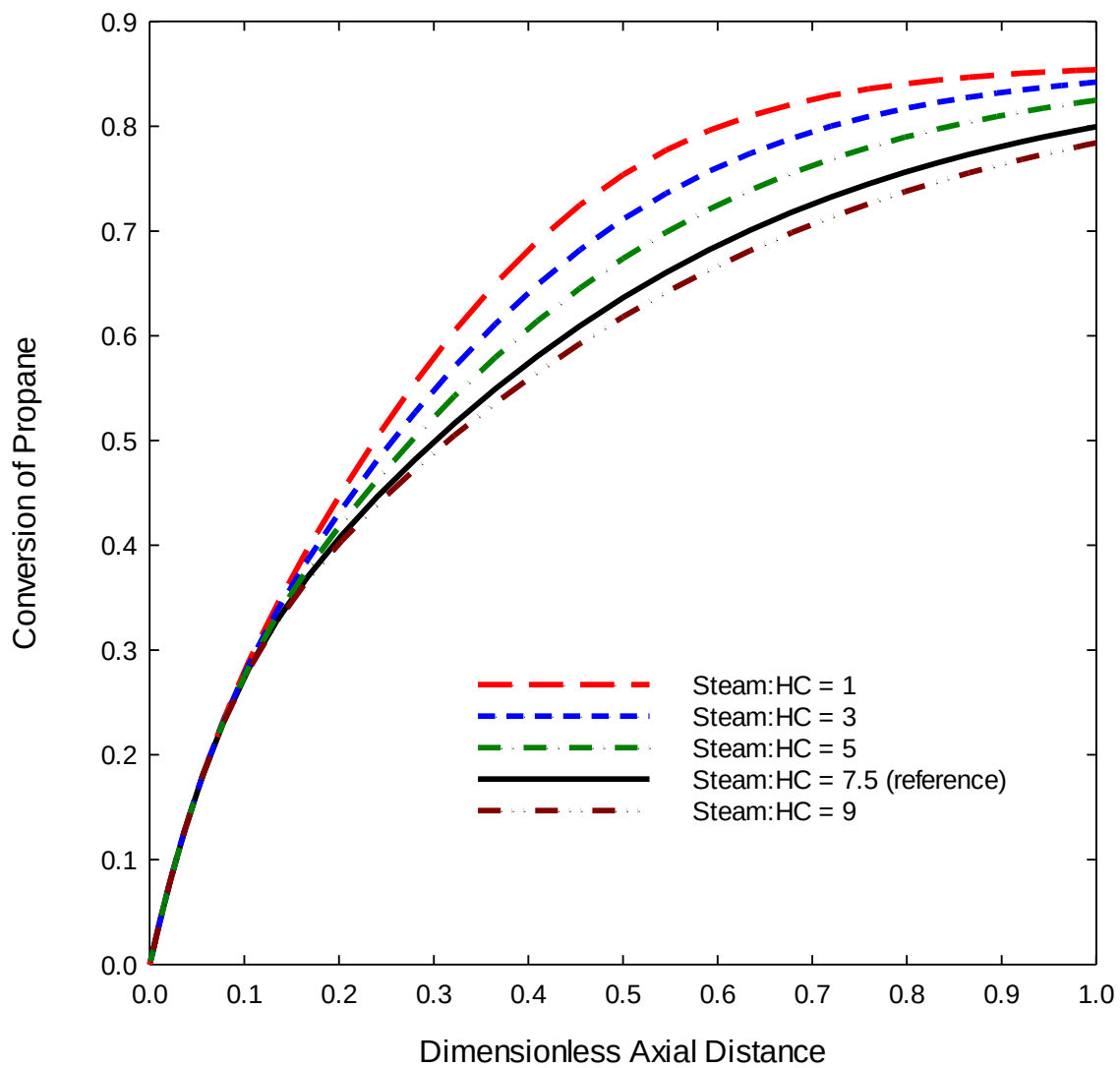


Figure 35: Conversion of propane against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.

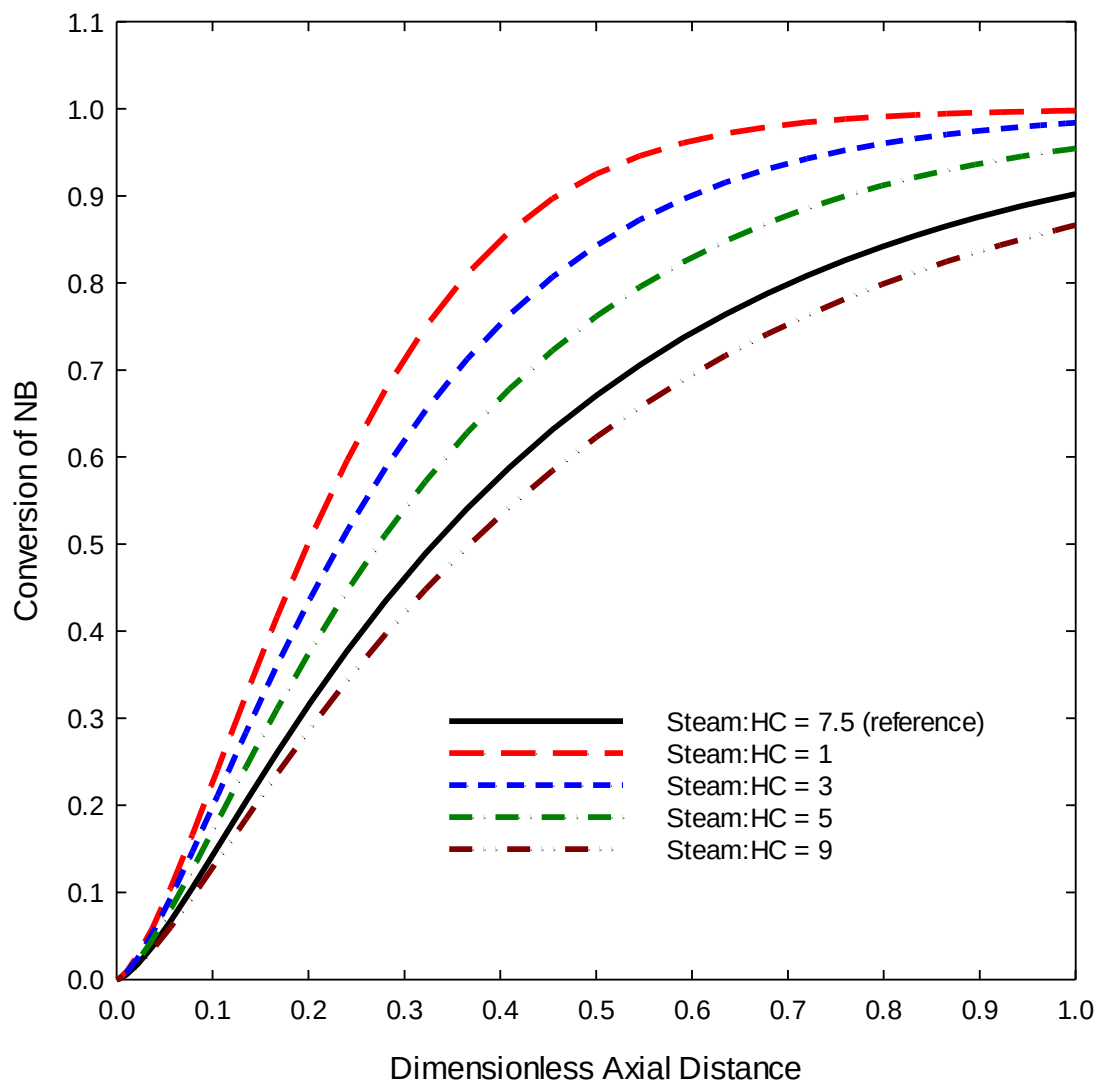


Figure 36: Conversion of nitrobenzene against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.

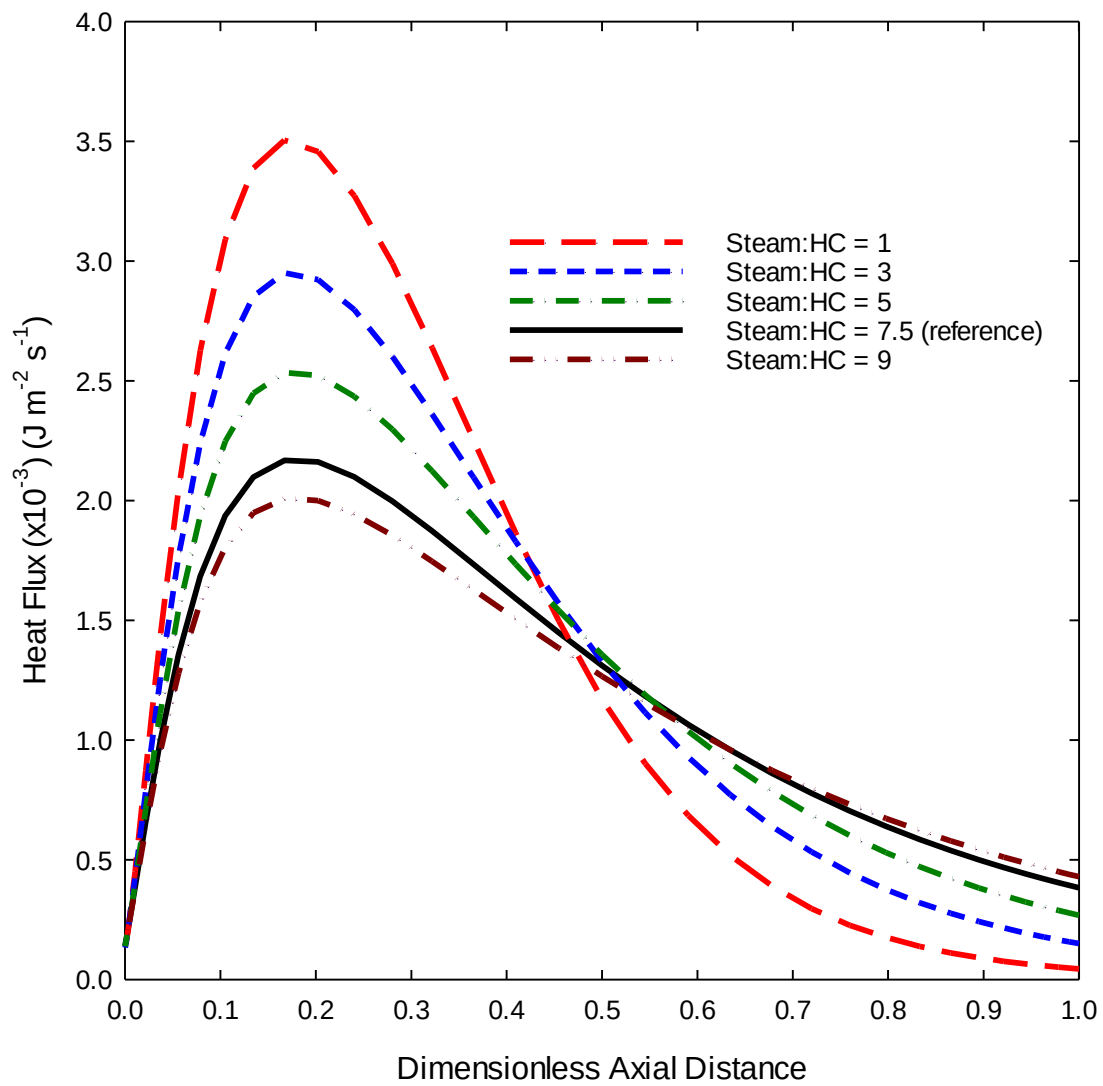


Figure 37: Heat flux per tube against the dimensionless axial distance in a co-current membrane reactor using different steam to hydrocarbon feed ratios.

CHAPTER 7

OPTIMIZATION

7.1 Optimization problem

In the adiabatically operated membrane reactor, the dehydrogenation of propane is coupled with aniline synthesis. The reactor configuration is composed of a shell where the dehydrogenation of reaction takes place and several tubes where the hydrogenation products are generated. The walls of the tubes are made from a highly selective hydrogen membrane which is also heat conductive. The reactor is operated under co-current configuration which means that the feed for both the hydrogenation and dehydrogenation reactions are fed from the same side of the reactor ($z=0$). The optimization problem was tackled by carrying out a multi-objective optimization on the co-current membrane reactor maximizing both the yield of propene and the conversion of nitrobenzene. The objective functions were selected due to their conflicting nature. For instance, as shown in section 7.2.2, the increase in the number of tubes in the reactor configuration favors the increase in the yield of propene and the decrease in the conversion of nitrobenzene (Table 5). The objective functions are given by Eqs. (43) and (44)

$$Y_{propene} = \frac{\text{Moles of propene produced}}{\text{Moles of propane fed}} = \frac{n_{C_3H_6}(L) - n_{C_3H_6,f}}{n_{C_3H_8,f}} \quad (43)$$

$$X_{NB} = \frac{\text{Moles of nitrobenzene reacted}}{\text{Moles of nitrobenzene fed}} = \frac{n'_{NB,f} - n'_{NB}(L)}{n'_{NB,f}} \quad (44)$$

The objective functions were maximized by allowing the state variables shown in Table 12 to change within their respective upper and lower limits.

Table 14: Decision variables and their upper and lower limits

Variable	Lower limit	Upper limit
Number of hydrogenation tubes (N_{tubes})	1500	2200
Reactor length (m) (L)	4.0	8.0
Feed molar flowrate of nitrobenzene (mol/s) ($n'_{NB,f}$)	3.0	6.5
Steam-to-nitrobenzene ratio (STN)	4.0	7.0
Feed hydrogenation temperature (K) (T'_f)	860	910

The solution of the governing equations is used to estimate the values of the objective functions stated above. In addition, they are forming a set of nonlinear equality constraints which should be satisfied. For the co-current configuration, the boundary conditions defined at $z = 0$ represent the linear equality constraints and the state variables shown in Table 1 represent the variable bounds of the optimization problem. Moreover, the temperature on the hydrogenation side was restricted to 915 K which, according to the literature, is the maximum temperature that both the membrane and the catalyst can withstand. This constraint is given by Eq. (45):

$$T_h(z) - 915.0 \leq 0.0 \text{ K} \quad (45)$$

To summarize, the multi-objective optimization problem can be formulated as shown in Eq. (46):

$$\begin{aligned}
 & \text{Maximize } \mathbf{J}(x) \\
 & \text{Subject to } \left. \begin{aligned}
 & \frac{dc}{dz} = f(y, x) \text{ with } y(z = 0) = y_0 \\
 & y_0 = [0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 1]^T \\
 & x^L \leq x \leq x^U \\
 & c_{ineq}(x) \leq 0
 \end{aligned} \right\} \quad (46)
 \end{aligned}$$

where,

$$x = [N_{tubes}, L, n'_{NB,f}, STN, T'_f]^T$$

$$\mathbf{J}(x) = \begin{bmatrix} Y_{propene} \\ X_{NB} \end{bmatrix}$$

$\frac{dc}{dz} = f(y, x)$ are the normalized mole, energy, and momentum balances

$$x^L = [1500, 4.0, 3.0, 4.0, 860]^T$$

$$x^U = [2200, 8.0, 6.5, 7.0, 910]^T$$

$$c_{ineq}(x) = T_h(z) - 915.0$$

7.2 Solution methodology

Multi-objective optimization involves the solution of a problem with conflicting and competing objective functions. Therefore, the result of the optimization will be a set of solutions, referred to as the Pareto set, all of which are equally valid solutions for the optimization problem [45]. Moving from one solution to another, one of the two objective functions improves while the other worsens but nevertheless all the solutions are still equally good [46].

The multi-objective optimization problem was solved using the normalized normal constraint method (NNC) and the normalized boundary intersection method (NBI) to verify the results obtained during the optimization process. Figure 38 shows a flowchart which shows the methodology for solving the multi-objective optimization problem. The problem was solved using a commercial solver called TOMLAB/SNOPT which uses successive sequential quadratic programming. The solver turns the multi-objective optimization problem into a single objective problem and solves 20 of those problems using the NBI method and 20 using the NNC method which brings the total to 40 optimization problems.

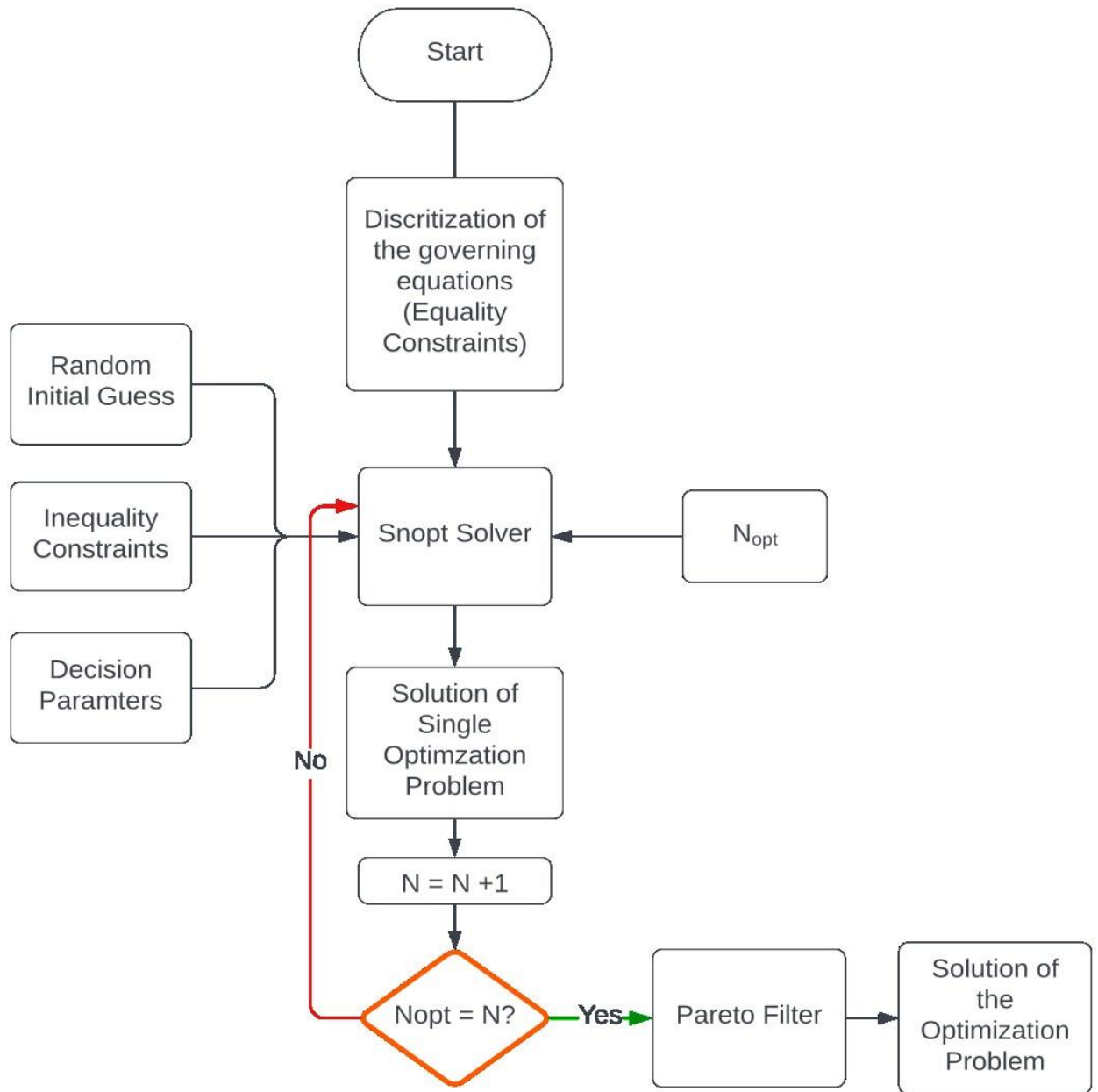


Figure 38: Flowchart showing the methodology for solving the multi-objective optimization problem using the Tomlab Snopt solver to generate a Pareto solution set.

Both the Normalized Normal Constraint (NCC) method and the Normalized Boundary Intersection (NBI) method involve the solution of the multi objective optimization problem in the normalized domain which gives important scaling properties. The NCC method involves the following steps [47]:

- 1- Solving a single objective optimization problem twice, taking turn maximizing the objective functions separately to obtain the anchor points denoted by μ^{1*} and μ^{2*}
- 2- Normalizing the anchor points to avoid scaling deficiencies. Where $\bar{\mu}$ is the normalized form of μ .
- 3- Generating the Utopia Line which is a straight line joining the two normalized anchor points. The direction of the Utopia line goes from the one normalized anchor point to the other ($\bar{\mu}^{1*}$ to $\bar{\mu}^{2*}$) such that the direction $\bar{N}_1$ is given by:

$$\bar{N}_1 = \bar{\mu}^{2*} - \bar{\mu}^{1*}$$

The number of points on the Utopia line is set (m_1) and the normalized increments donated by δ_1 is calculated using:

$$\delta_1 = \frac{1}{m_1 - 1}$$

The points on the utopia line are then generated using:

$$\bar{X}_{pj} = \alpha_{1j}\bar{\mu}^{1*} + \alpha_{2j}\bar{\mu}^{2*}$$

where, $0 \leq \alpha_{1j} \leq 1$ and $\sum_{k=1}^2 \alpha_{kj} = 1$,

α_{ij} is incremented by δ_1 which goes from 0 to 1 and j is the set of integer numbers from 1 to m_1

- 4- Generating the Normalized Pareto plot. Each point on the Utopia line is used to generate a corresponding point on the Pareto plot by adding the following constraints to the optimization problem and solving it multiple times to form the Pareto Plot:

$$\bar{N}_1(\bar{\mu} - \bar{X}_{pj})^T \leq 0 \quad \bar{\mu} = [\bar{\mu}_1(x) \ \bar{\mu}_2(x)]^T$$

- 5- Calculating the non-normalized parameters from the normalized Pareto set.

7.3 Results

The Pareto plot for the optimization is shown below in Figure 39 and the optimized values for the yield of propene and conversion of nitrobenzene are given below in Table 13. Only one set of results will be shown for the rest of this section since, according to the table and figure, both the optimization methods (NNC and NBI) are in agreement. The maximum attainable conversion of nitrobenzene was 0.9019 (case 1) while the maximum yield of propylene was 0.9764 (case 20). The values of the state variables responsible for the above results are given in Table 14.

Table 15: Optimized values using the NNC and NBI multi-objective optimization methods.

Case	Normalized Normal Constraint Method		Normalized Boundary Intersection Method	
	Yield of Propylene	Conversion of NB	Yield of Propylene	Conversion of NB
1	0.9077	0.9019	0.9077	0.9019
2	0.9149	0.9014	0.9149	0.9014
3	0.9220	0.9008	0.9220	0.9008
4	0.9291	0.8999	0.9291	0.8999
5	0.9361	0.8987	0.9361	0.8987
6	0.9430	0.8969	0.9430	0.8969
7	0.9498	0.8943	0.9498	0.8943
8	0.9546	0.8800	0.9546	0.8800
9	0.9588	0.8624	0.9588	0.8624
10	0.9625	0.8418	0.9625	0.8418
11	0.9657	0.8180	0.9657	0.8180
12	0.9682	0.7904	0.9682	0.7904
13	0.9702	0.7598	0.9702	0.7598
14	0.9717	0.7265	0.9717	0.7265
15	0.9729	0.6912	0.9729	0.6912
16	0.9738	0.6544	0.9738	0.6544
17	0.9746	0.6168	0.9746	0.6168
18	0.9753	0.5784	0.9753	0.5784
19	0.9759	0.5397	0.9759	0.5397
20	0.9764	0.5007	0.9764	0.5007

Table 16: Results for the decision variables for the multi-objective optimization of the co-current membrane reactor

Case	Optimum Values				
	Number of tubes	Reactor Length (m)	Feed flowrate of NB	Steam to NB ratio	Feed hydrogenation Temperature (K)
1	1786	8.0	3.00	7.00	860
2	1838	8.0	3.06	7.00	860
3	1894	8.0	3.11	7.00	860
4	1955	8.0	3.18	7.00	860
5	2024	8.0	3.24	7.00	860
6	2103	8.0	3.31	7.00	860
7	2193	8.0	3.39	7.00	860
8	2200	8.0	3.50	6.93	860
9	2200	8.0	3.62	6.85	860
10	2200	8.0	3.76	6.76	860
11	2200	8.0	3.90	6.66	860
12	2200	8.0	4.07	6.56	860
13	2200	8.0	4.25	6.46	860
14	2200	8.0	4.45	6.33	860
15	2200	8.0	4.69	6.19	860
16	2200	8.0	4.96	6.04	860
17	2200	8.0	5.27	5.85	860
18	2200	8.0	5.62	5.66	860
19	2200	8.0	6.03	5.42	860
20	2200	8.0	6.50	5.15	860

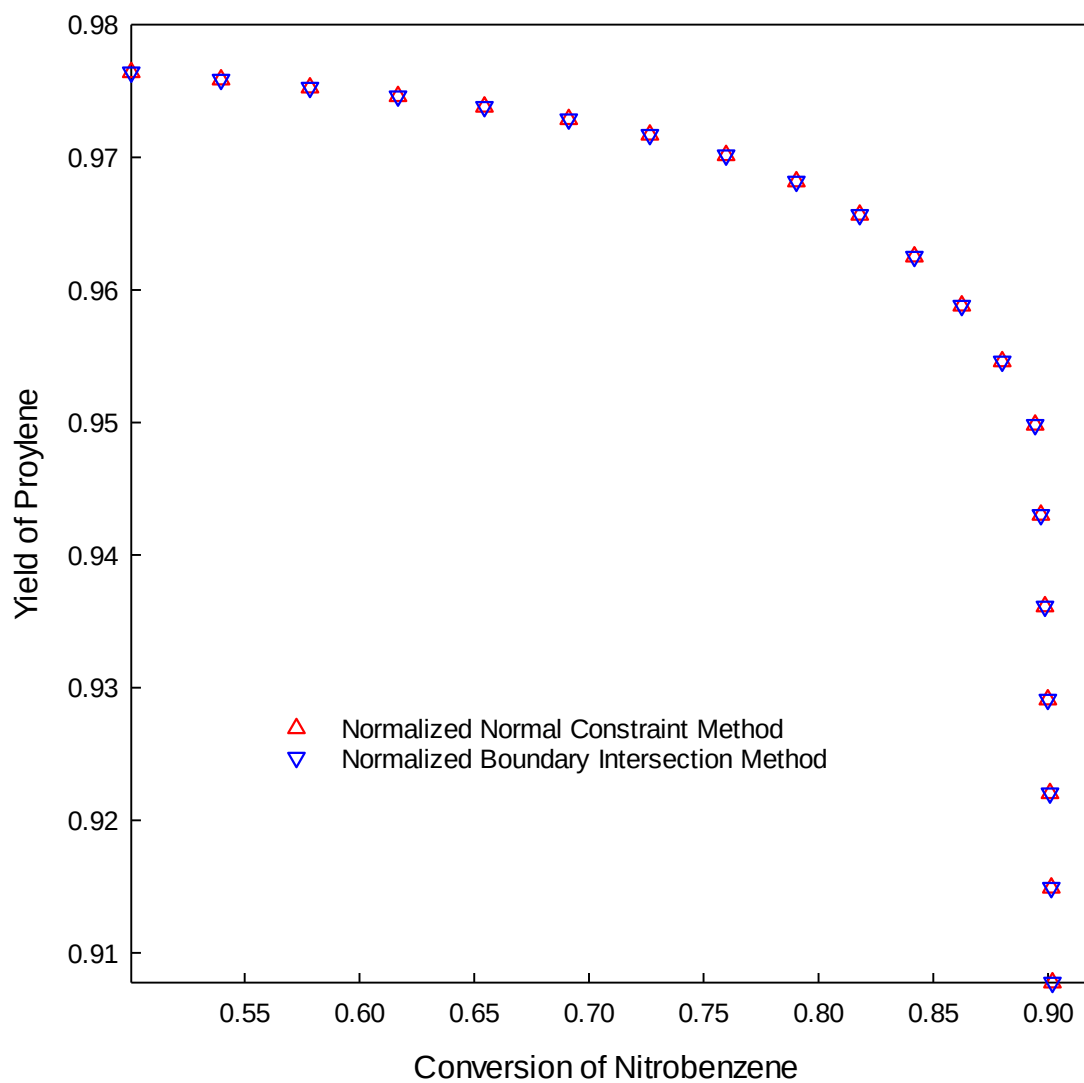


Figure 39: Pareto plot for maximizing the yield of propene and conversion of nitrobenzene in the co-current membrane reactor.

Figure 39 shows the pareto plot for the 20 optimization cases carried out to maximize the objective functions: the yield of propene and the conversion of nitrobenzene. According to the plot, case 1 prioritized maximizing the yield of propene while case 20 maximized the conversion of nitrobenzene. Going from case 1 to 20, the conversion of nitrobenzene was improving at the expense of the yield of propene and vice versa from case 20 to 1. This demonstrates the conflicting nature of the two objective functions and shows that all the twenty solutions are viable (equally good) since neither of the solutions dominates the other. To further prove this, a pareto filter was applied to the results and all the twenty solutions were dominant and therefore included in the Pareto optimal solution set. Moreover, the pareto plot shows that the solution obtained using both the NNC and NBI methods were identical which is a positive indication that the results' accuracy and dependability have been confirmed.

Figure 40 shows the decision variables plotted against the conversion of nitrobenzene whereas Figure 41 shows the same decision variables plotted against the yield of propene. The two figures give a clear understanding of the effect of the decision variables on the objective functions. Looking at Figure 40a-e and Figure 41a-e, it can be seen that the Pareto solution was a result of the conflicting nature of the feed molar flowrate of nitrobenzene and the steam-to-nitrobenzene ratio on the objective functions meanwhile, the other three decision variables were constant. An increase in the feed molar flowrate of nitrobenzene decreases the conversion on nitrobenzene (Figure 40c) and an increase in the yield of propene (Figure 41c). Also, an increase in the steam-to-nitrobenzene ratio increases the conversion of nitrobenzene (Figure 40d) and decreases the yield of propene (Figure 41d).

Out of the 20 optimization cases, cases 1, 11 and 20 will be further examined. During case 1, the conversion of NB is prioritized which leads to the highest conversion among all the twenty cases at the cost of the yield of propene due to their conflicting nature. Similarly, case 20 prioritizes the yield of propene which leads to a maximum for the yield, at the expense of the conversion of NB. Case 11 provides a middle ground where neither the objective functions are at their maximum, but both are at reasonably high values. Figure 42 shows the conversion of propane plotted against the dimensionless axial distance down the membrane reactor for the three selected optimization cases. The conversion of propane increases going from case 1 to 20 since case 20 maximizes the yield of propene which has a positive effect on the conversion of propane. Figure 43 shows the yield of propene against the dimensionless axial distance for the three selected optimization cases. Case 1 had the highest yield of propene while case 20 had the lowest. The conversion of nitrobenzene against the dimensionless axial distance is shown in Figure 44, case 1 had the highest conversion of nitrobenzene while case 20 had the lowest. Figures 42-44 shows clearly shows that case 1 prioritized the conversion of NB over the yield of propene while case 20 prioritized the yield of propene over the conversion of nitrobenzene. Also, case 11 provides a middle ground for both the objective functions.

The temperature profiles on the hydrogenation side of the co-current membrane reactor against the dimensionless axial distance for the selected optimization cases are shown in Figure 45. The hydrogenation of nitrobenzene is exothermic, so as the reaction takes place heat is being generated which increases the hydrogenation temperature. However, at the peak, the rate of heat removal through the heat-conducting tube walls overcomes the rate of heat generation which justifies the presence of the peaks in the

temperature profiles. Case 1 which had the highest conversion of nitrobenzene reached the maximum allowable temperature sooner than the other cases. This is due to the lower feed flowrate of nitrobenzene compared with other cases, also due to the lower number of tubes (1786) compared to 2200 in cases 11 and 20 which lowers the rate of heat transfer between the shell and tubes. Furthermore, it is worth noting that the hydrogenation temperature for all cases was always below the 915 K mark as per the temperature constraint applied during optimization to increase the lifetime of the membrane and catalyst. Meanwhile, Figure 46 shows the temperature profiles on both sides of the co-current membrane reactor for the selected optimization cases. The dehydrogenation temperature was lowest for case 1 which is due to the lower number of tubes in the conversion prioritizing case. The lower number of tubes provided a lower surface area for the heat exchange between the reactions therefore the endothermic dehydrogenation reaction was able to lower the temperature further in case 1 than in case 11 or 20.

Table 14 shows that for all the cases the reactor length and the feed hydrogenation temperature were set to 7.0 m and 860 K, respectively. The length of the reactor was set to the upper limits of its range (8.00 m), while the hydrogenation temperature was set to the lower limit of its range (860 K). Increasing the length of the reactor increases the residence time of the reactants which in turn leads to an increase in both the objective functions. Whereas the feed hydrogenation temperature was set to the lower limit (860 K) to comply with the maximum temperature constraint set during the optimization process.

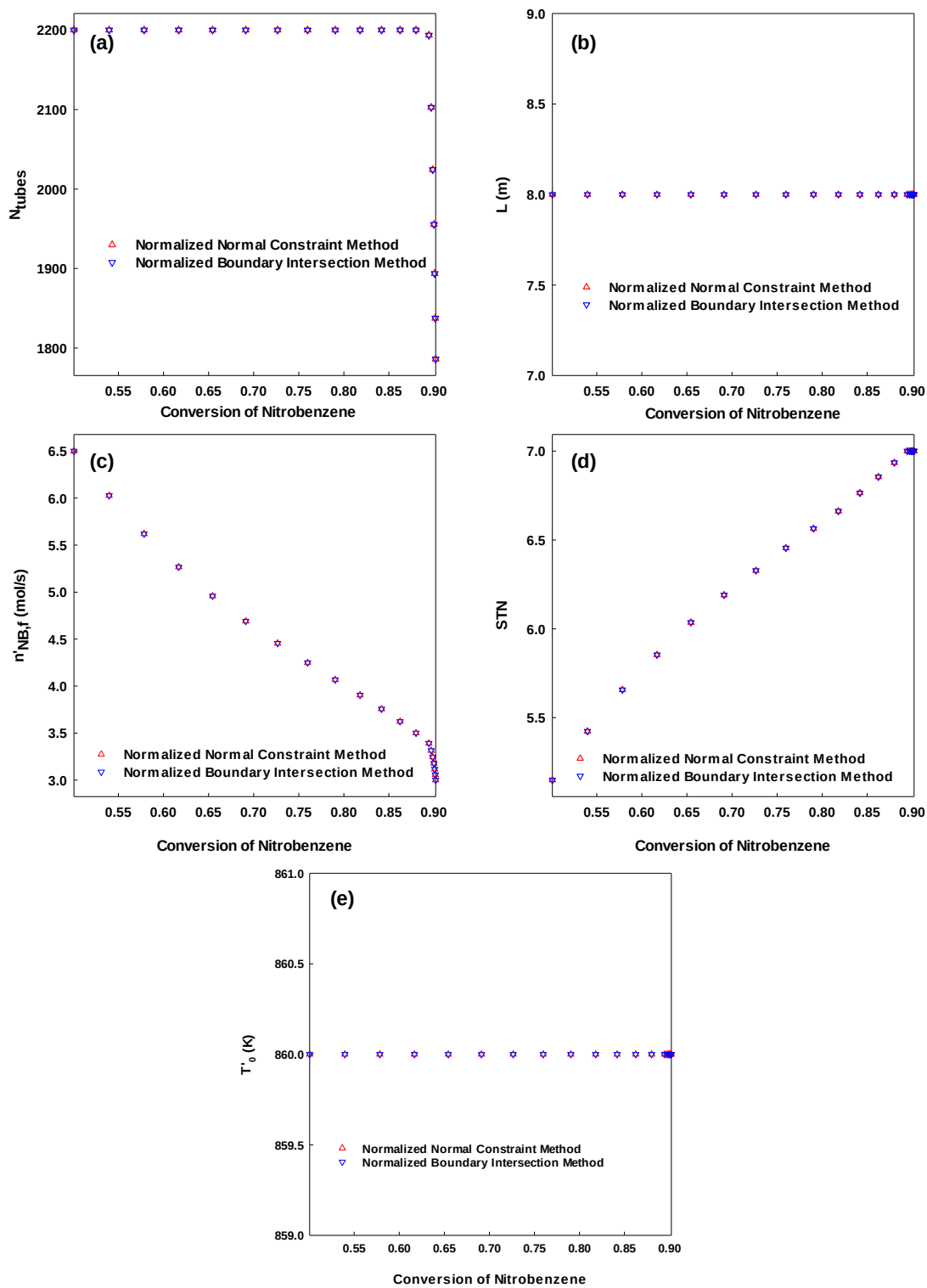


Figure 40: Values of the decision variables plotted against the conversion of nitrobenzene for the multi-objective optimization using NNC and NBI

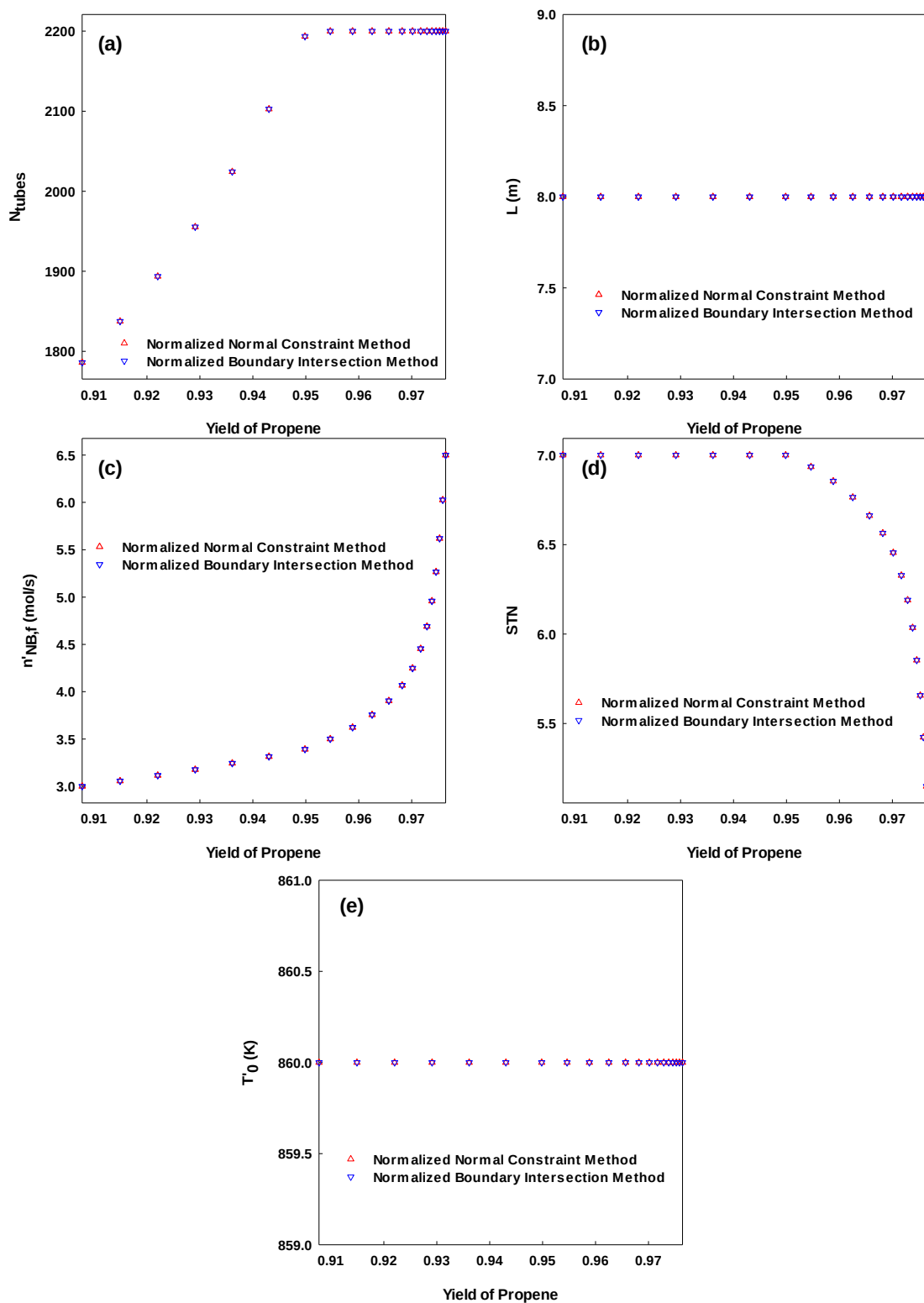


Figure 41: Values of the decision variables plotted against the yield of propene for the multi-objective optimization using NNC and NBI

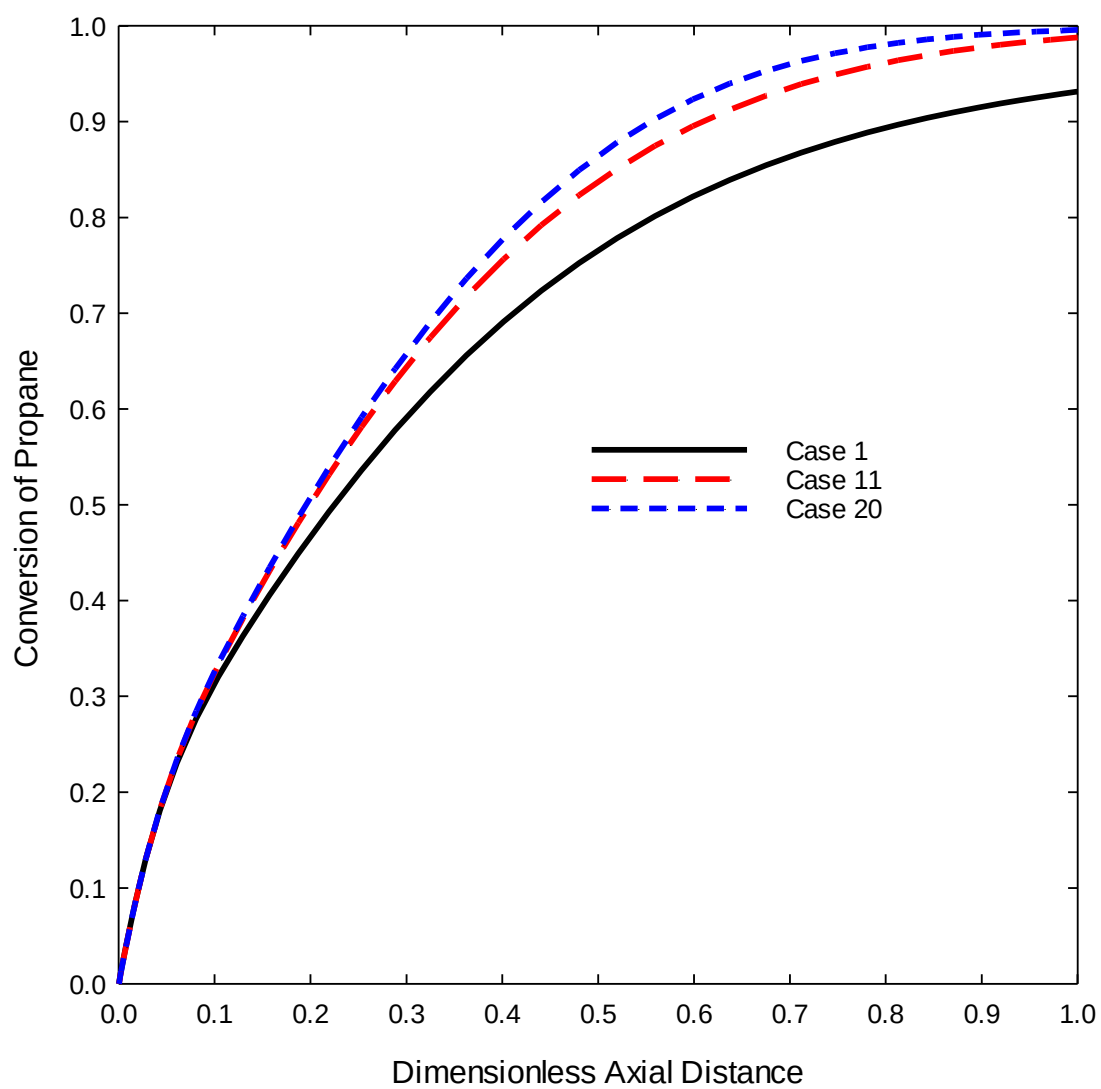


Figure 42: Conversion of propane against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor

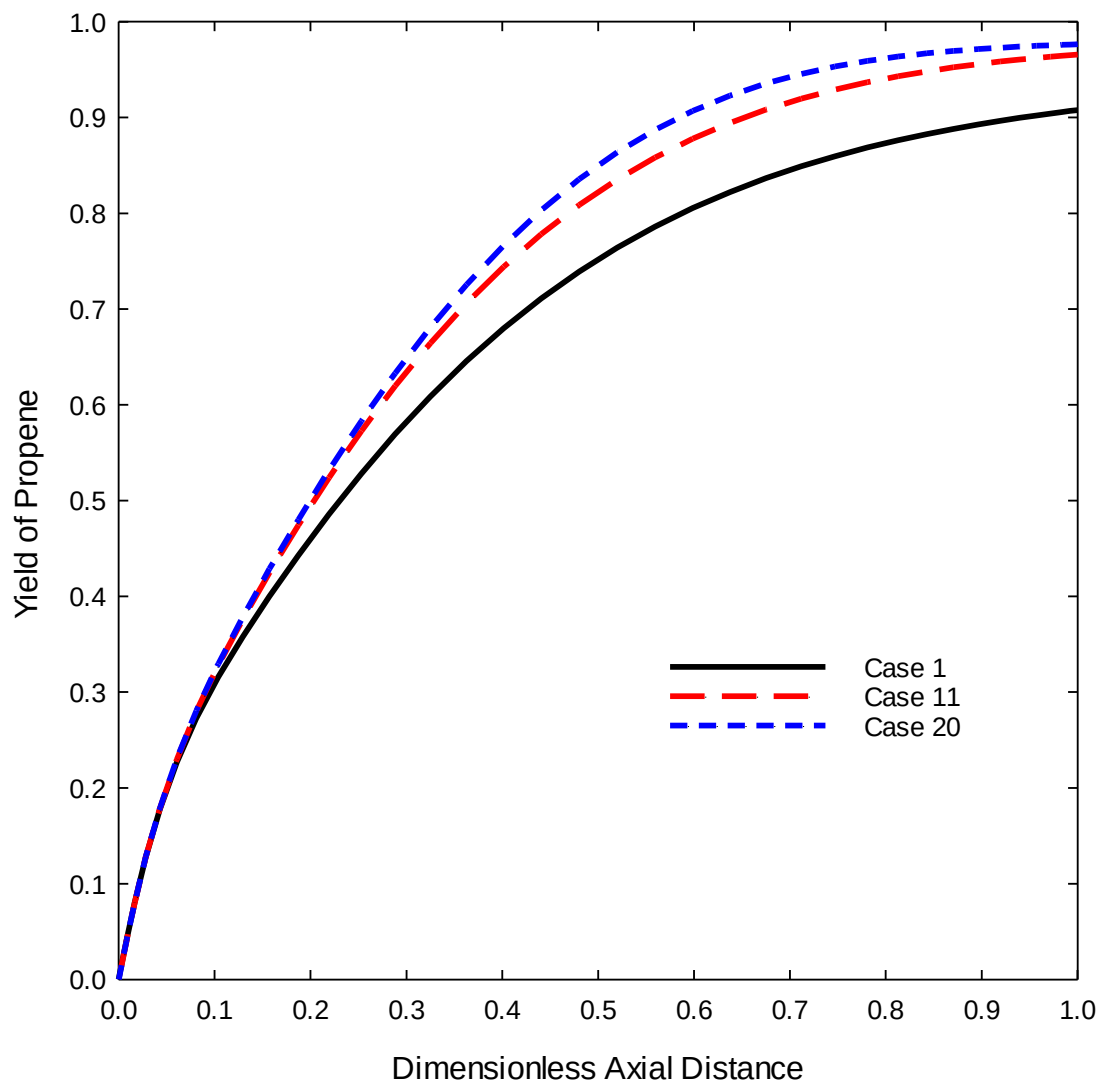


Figure 43: Yield of propene against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor

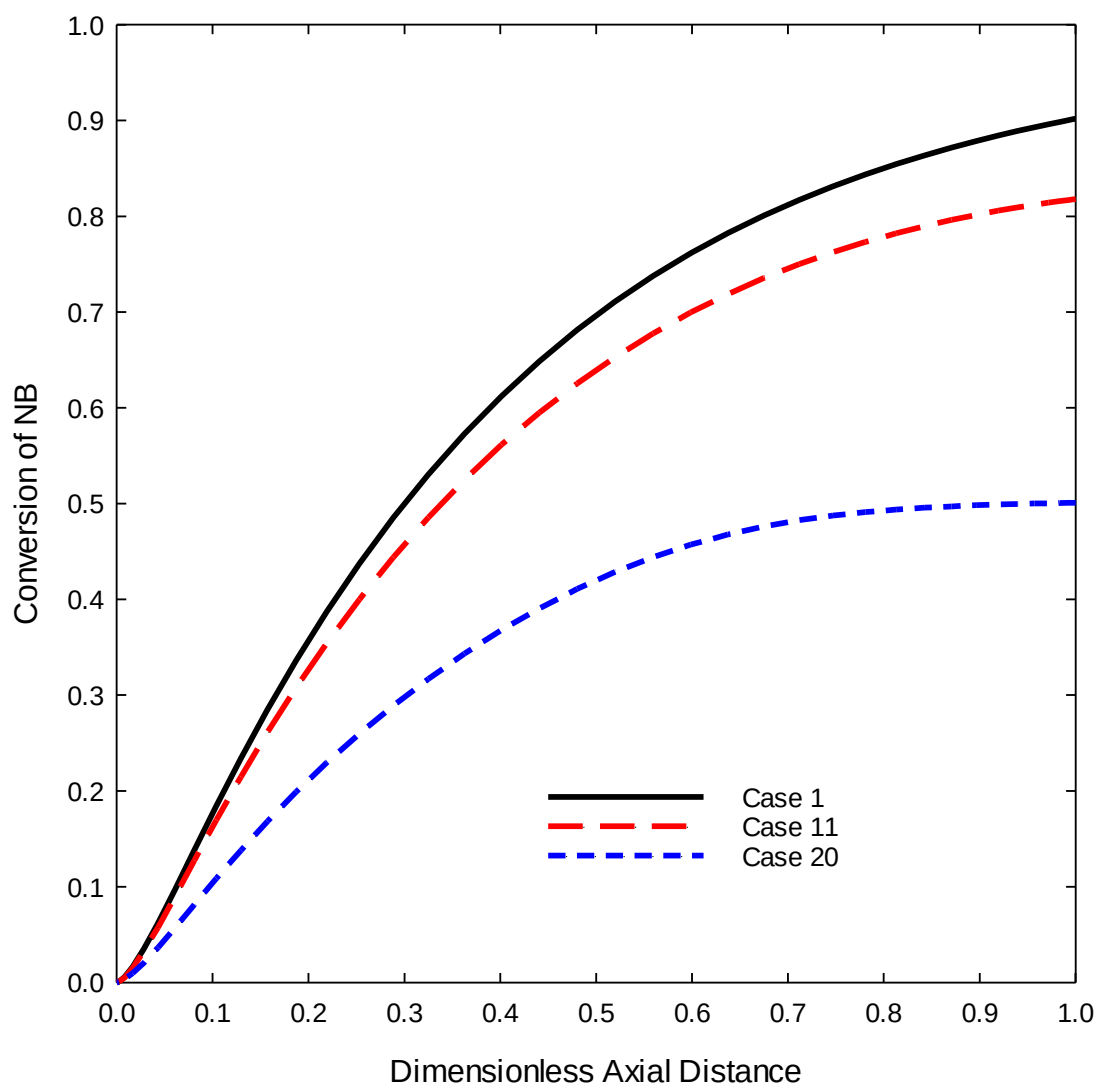


Figure 44: Conversion of nitrobenzene against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor

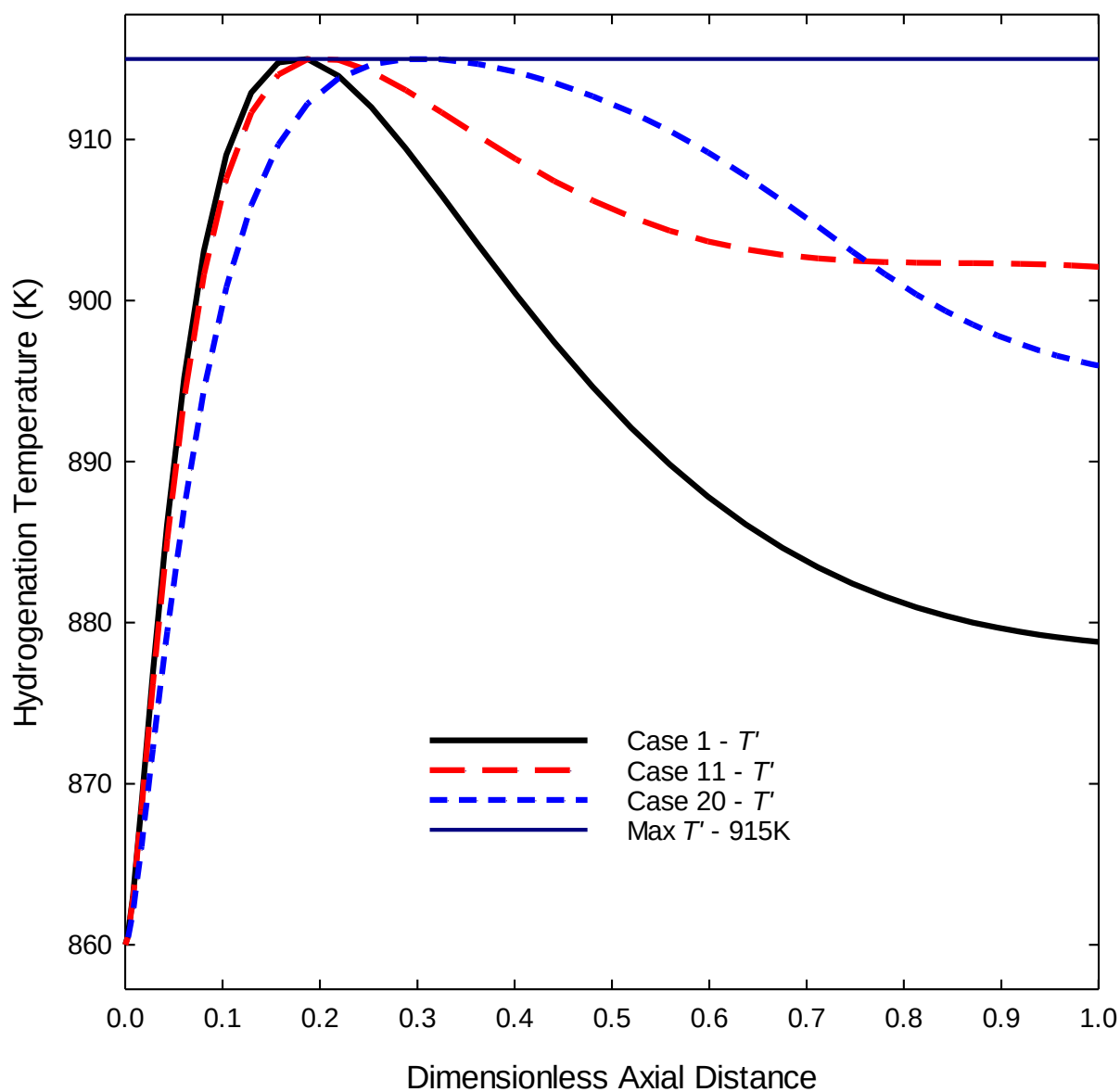


Figure 45: Hydrogenation temperature against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor

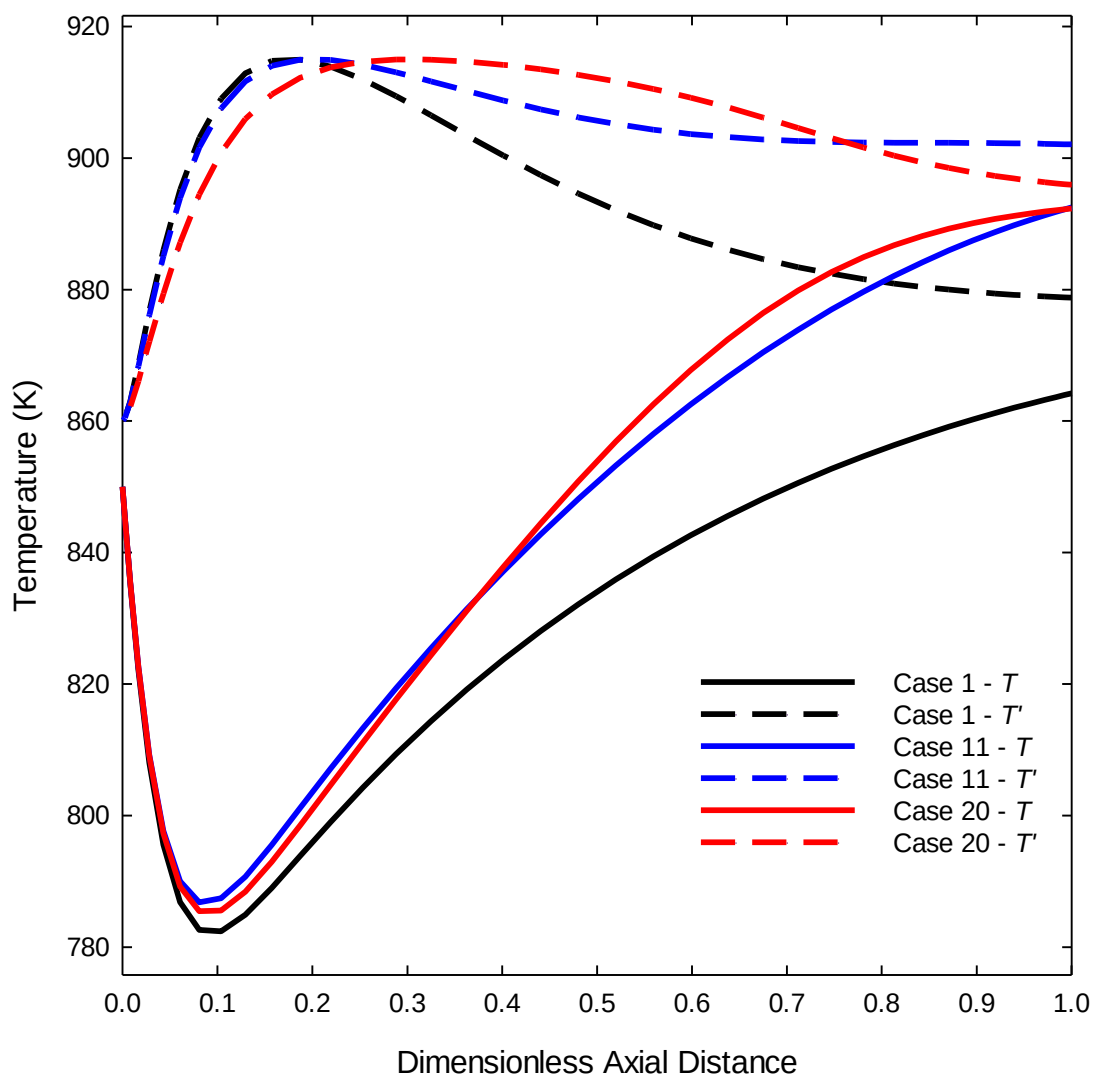


Figure 46: Temperature profile against the dimensionless axial distance for the three selected optimization cases in a co-current membrane reactor

Figure 47 shows the optimum value of the number of tubes for all the 20 optimization cases for both multi-objective optimization methods. The figure shows that the number of tubes increases going from case 1 to 8 reaching the maximum value of 2200 tubes at case 8 and the same value was used for all the remaining cases. Increasing the number of tubes enhances the heat and mass transfer between the shell and the tube thus improving the performance of both sides of the reactor.

Similarly, Figure 48 shows the optimum value of the feed flowrate of nitrobenzene to the hydrogenation side for all the 20 optimization cases for both multi-objective optimization methods. The feed flow rate of nitrobenzene increased gradually going from case 1 to 20 which led to a significant decrease in the conversion of nitrobenzene. Comparing cases 1 and 20, increasing the NB feed flow rate by a factor of 2.2, contributed to the decrease in the conversion of nitrobenzene by 44 % while contributing to the increase in the yield of propene by 7%. The increase in the feed flow rate of nitrobenzene led to a shorter residence time which decreases the conversion of nitrobenzene going from case 1 to 20. Meanwhile, the increase in the flowrate of nitrobenzene in the hydrogenation side provided a faster sweeping effect for the hydrogen which was responsible for the increase in the yield of propene on the dehydrogenation side.

Figure 49 shows the optimum steam-to-nitrobenzene ratio for all 20 optimum cases for both multi-objective optimization methods. The steam-to-nitrobenzene ratio was set at 7.0 from case 1 to 7 and decreased going from case 7 to 20, which shows that the higher ratio favored the conversion of nitrobenzene over the yield of propene and vice versa for the lower steam-to-nitrobenzene ratio which matches with the results obtained in the parametric study section.

The choice between the five cases would need to be determined based on the demand for the two main products (aniline and propene). Case 11 offers a middle ground with a propene yield of 0.9657 and a 0.8180 conversion of nitrobenzene. If the goal were to further favor the production of nitrobenzene the reactor could be operated at the parameters obtained from case 6 producing a slightly higher conversion of nitrobenzene without sacrificing a lot of the propene yield. Similarly, if a higher yield of propene was more desirable then case 14 would be ideal since it provides an increase in the yield of propene without significantly lowering the conversion of nitrobenzene.

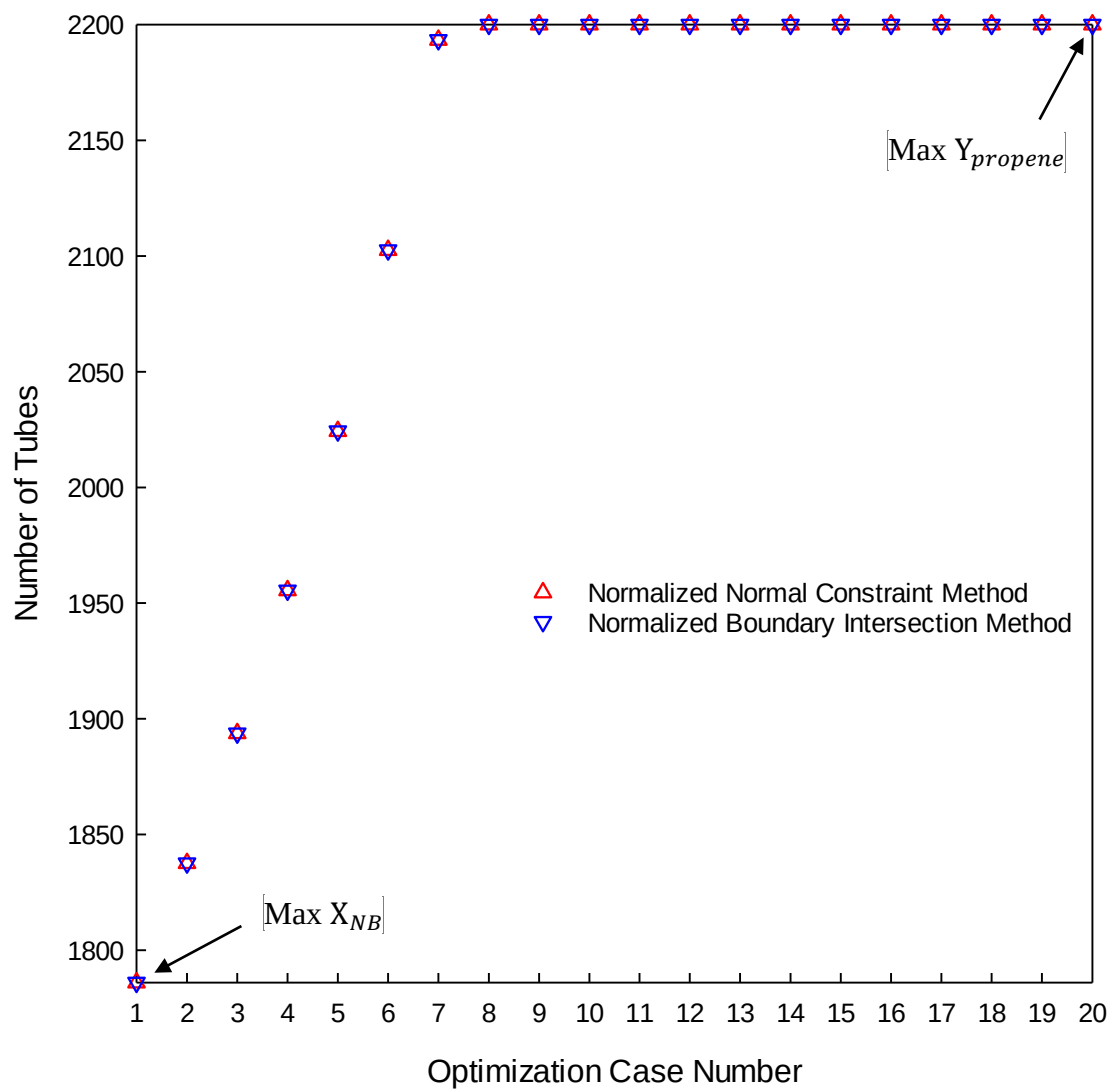


Figure 47: The optimum number of tubes for all 20 optimization cases in a co-current membrane reactor

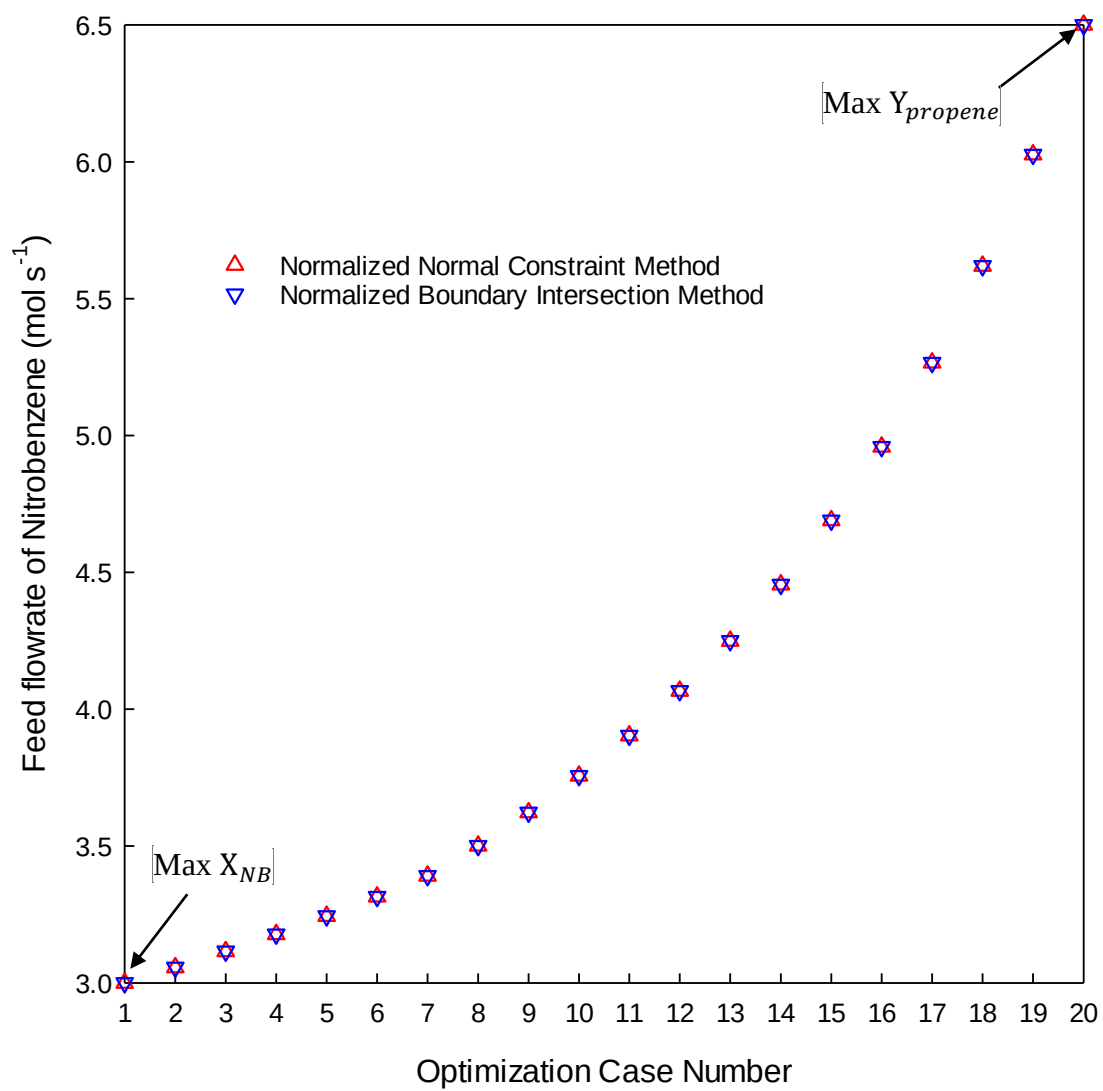


Figure 48: The optimum feed flowrate of nitrobenzene for all 20 optimization cases in a co-current membrane reactor

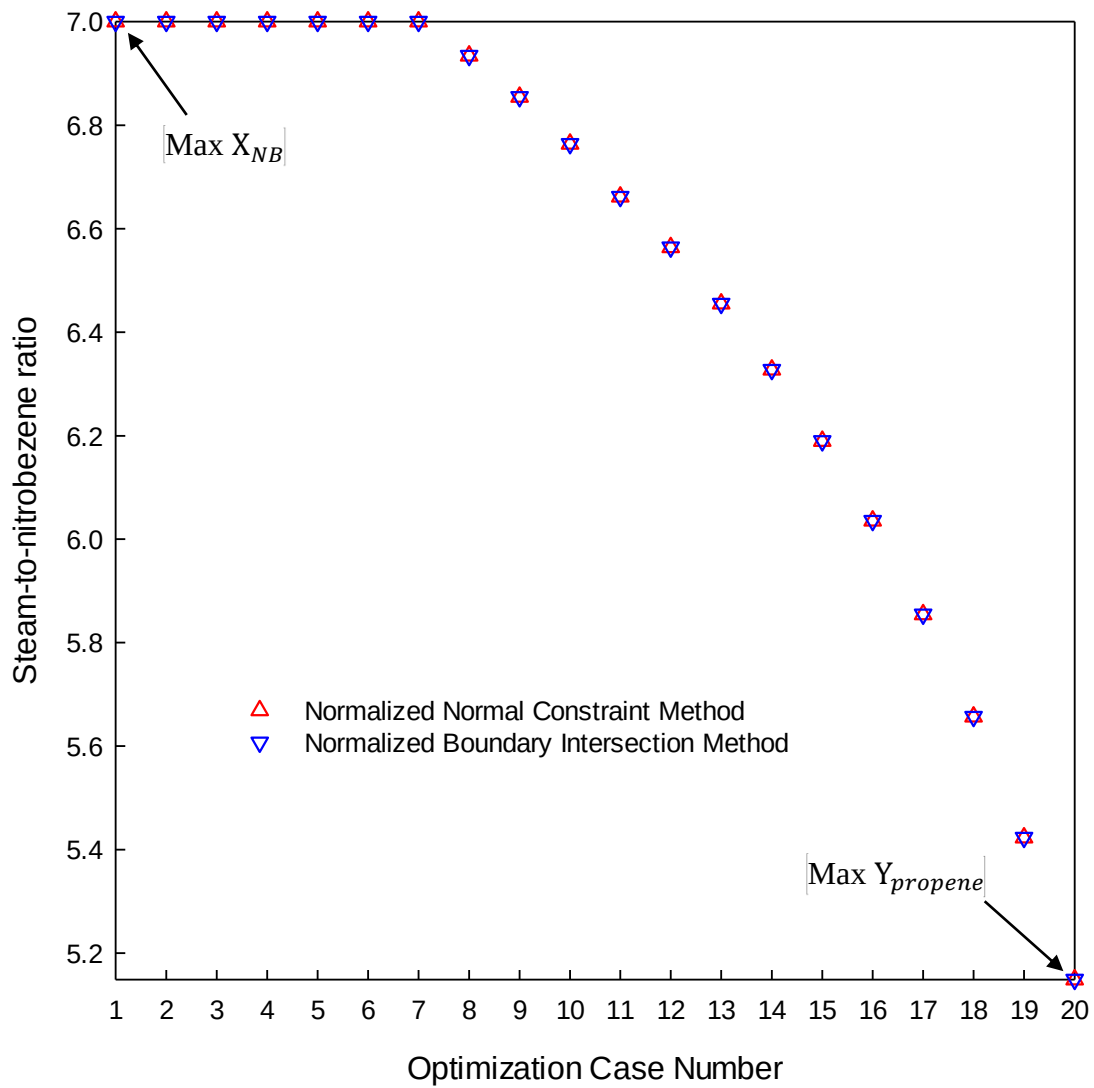


Figure 49: The optimum steam-to-nitrobenzene ratio for all 20 optimization cases in a co-current membrane reactor

CHAPTER 8

Conclusion and Recommendations

In this study, a novel membrane reactor configuration where the dehydrogenation of propane to propylene and the dehydrogenation of nitrobenzene to aniline occur simultaneously was proposed. The purpose of the reactor was to boost the thermodynamically limited dehydrogenation of propane by diffusing the hydrogen produced, through a selective membrane, to be utilized to hydrogenate nitrobenzene to aniline. A pseudo-homogeneous reactor model was developed and solved using the orthogonal collocation method. The model generated was used to compare the performance of the membrane reactor with that of the conventional reactor as well as to solve the multi-objective optimization problem to maximize the yield of propene and the conversion of nitrobenzene. Also, a parametric study was carried out to determine the effect of several parameters on the conversions of propylene and nitrobenzene.

The results obtained showed that the use of the novel membrane reactor resulted in a significant increase in the conversion of propane from 0.37 using the conventional reactor to 0.80 using either of the two configurations (co-current or counter current) of the membrane reactor. Also, the co-current configuration produced a slightly higher conversion of propane at the expense of a lower conversion of nitrobenzene when compared to the counter current configuration. The parametric analysis showed that increasing the number of tubes, tube diameter, dehydrogenation and hydrogenation feed pressures and temperatures all favored the conversion of propane. Whereas the increase in

the feed steam to hydrocarbon ratio on the hydrogenation side led to a decrease in the conversion of propane. The multistage optimization provided several optimal solutions maximizing either the yield of propene or the conversion of nitrobenzene or providing a middle ground where one is prioritized at the cost of the other. The choice between the 5 optimization cases would fall onto the operators for the plant to determine which of the two products is of higher value to prioritize.

This was an extensive study of the coupled hydrogenation/dehydrogenation membrane reactor; however, this study could further be improved by:

- I. Carrying out experimental work for a reactor with integrated hydrogenation and dehydrogenation reactions
- II. Exploring the effects of catalyst deactivation on the performance of the reactor.
- III. Modelling coke formation on the membrane's surface and investigating its effect on the reactor's performance.
- IV. Developing a heterogeneous reactor model to give a more realistic result after factoring in the diffusion of the reactants and products into and out of the catalyst.
- V. Developing a two-dimensional model to explore the changes taking place radially across the reactor.
- VI. Investigating the Optimal control of the reactor.
- VII. Exploring the optimal hydrogen flux along the length of the reactor.

Appendices

Appendix A – Detailed derivation of the model:

Dehydrogenation side:

Mole balance equation:

The derivation of the mole balance on the tube side is given below by:

$$0 = n_i|_z - n_i|_{z+\Delta z} + \sum_{j=1}^R \sigma_{ij} r_j (1-\varepsilon) A_c \rho_s \Delta z - (\pi D) J_i \Delta z \quad (\text{A-1})$$

$$\lim_{\Delta z \rightarrow 0} \frac{n_i|_{z+\Delta z} - n_i|_z}{\Delta z} = \sum_{j=1}^R \sigma_{ij} r_j (1-\varepsilon) A_c \rho_s - (\pi D) J_i \quad (\text{A-2})$$

$$\boxed{\frac{dn_i}{dz} = \sum_{j=1}^R \sigma_{ij} r_j (1-\varepsilon) A_c \rho_s - (\pi D) J_i} \quad (\text{A-3})$$

Energy balance equation:

The derivation of the energy balance on the tube side is given below:

$$0 = \sum_{i=1}^n n_i H_i|_z - \sum_{i=1}^n n_i H_i|_{z+\Delta z} + \pi D U (T' - T) \Delta z - \sum_{i=1}^n (\pi D) J_i H_i \Delta z \quad (\text{A-4})$$

$$\lim_{\Delta z \rightarrow 0} \frac{\sum_{i=1}^n n_i H_i|_{z+\Delta z} - \sum_{i=1}^n n_i H_i|_z}{\Delta z} = \pi D U (T' - T) - \sum_{i=1}^n (\pi D) J_i H_i \Delta z \quad (\text{A-5})$$

$$\frac{d}{dz} \sum_{i=1}^n n_i H_i = \pi D U (T' - T) - \sum_{i=1}^n (\pi D) J_i H_i \Delta z \quad (\text{A-6})$$

$$\sum_{i=1}^n \left[n_i \frac{dH_i}{dz} + H_i \frac{dn_i}{dz} \right] = \pi D U (T' - T) - \sum_{i=1}^n (\pi D) J_i H_i \quad (\text{A-7})$$

$$\sum_{i=1}^n n_i C_{pi} \frac{dT}{dz} + \sum_{i=1}^n H_i \left[\sum_{j=1}^R \sigma_{ij} r_j (1 - \varepsilon) A_c \rho_s - (\pi D) J_i \right] = \pi D U (T' - T) - \sum_{i=1}^n (\pi D) J_i H_i \quad (\text{A-8})$$

$$\boxed{\frac{dT}{dz} = \frac{\pi D U (T' - T) + \sum_{j=1}^R [-\Delta H]_j r_j (1 - \varepsilon) A_c \rho_s}{\sum_{i=1}^n n_i C_{pi}}} \quad (\text{A-9})$$

Hydrogenation side:

Mole balance equation:

The derivation of the mole balance on the shell side is given below by:

$$0 = n'_i \Big|_z - n'_i \Big|_{z+\Delta z} + (-1)^a \left[\sigma'_i r'_s \rho'_s (1 - \varepsilon') A'_c \Delta z + (\pi D) J_i \Delta z \right] \quad (\text{A-10})$$

$$\lim_{\Delta z \rightarrow 0} \frac{n'_i \Big|_{z+\Delta z} - n'_i \Big|_z}{\Delta z} = (-1)^a \left[\sigma'_i r'_s \rho'_s (1 - \varepsilon') A'_c + (\pi D) J_i \right] \quad (\text{A-11})$$

$$\boxed{\frac{dn'_i}{dz} = (-1)^a \left[\sigma'_i r'_s \rho'_s (1 - \varepsilon') A'_c + (\pi D) J_i \right]} \quad (\text{A-12})$$

Energy balance equation

The derivation of the energy balance on the shell side is given below by:

$$0 = \sum_{i=1}^n n'_i H'_i|_z - \sum_{i=1}^n n'_i H'_i|_{z+\Delta z} - (-1)^a \left[\pi D U (T' - T) \Delta z - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT \Delta z \right] \quad (A - 13)$$

$$\lim_{\Delta z \rightarrow 0} \frac{\sum_{i=1}^n n'_i H'_i|_{z+\Delta z} - \sum_{i=1}^n n'_i H'_i|_z}{\Delta z} = -(-1)^a \left[\pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT \right] \quad (A - 14)$$

$$\frac{d}{dz} \sum_{i=1}^n n'_i H'_i = -(-1)^a \left[\pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT \right] \quad (A - 15)$$

$$\sum_{i=1}^n \left[n'_i \frac{dH'_i}{dz} + H'_i \frac{dn'_i}{dz} \right] = -(-1)^a \left[\pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT \right] \quad (A - 16)$$

$$\sum_{i=1}^n n'_i C'_{pi} \frac{dT'}{dz} = -(-1)^a \left[\pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT \right] \quad (A - 17)$$

$$\frac{dT'}{dz} = (-1)^a \frac{[-\Delta H(T)] r'^{(1-\varepsilon') A'_c \rho'_s} - \pi D U (T' - T) - \pi D \sum_{i=1}^n \Psi_i J_i \int_{T'}^T C_{pi} dT}{\sum_{i=1}^n n'_i C'_{pi}} \quad (A - 18)$$

Appendix B – Detailed normalization of the model:

To successfully nondimensionalize the mole balance, it will be divided into several components that will be nondimensionalized separately and then grouped to form the normalized form of the model. The normalizing of the left-hand side of the mole balance will be carried out using the dimensionless fractional change in molar flow and fractional length, given by Eqs. (A-19) and (A-20), respectively, the mole balance can be nondimensionalized as follows:

$$x_i = \frac{n_i - n_{i,f}}{n_{C_3H_8,f}} \quad (A - 19)$$

$$\xi = \frac{z}{L} \quad (A - 20)$$

$$\frac{dn_i}{dz} = \frac{dx_i}{d\xi} \left(\frac{dn_i}{dx_i} \right) \left(\frac{d\xi}{dz} \right) = \frac{dx_i}{d\xi} \left(\frac{n_{C_3H_8,f}}{1} \right) \left(\frac{1}{L} \right) \quad (A - 21)$$

Giving:

$$\frac{dn_i}{dz} = \frac{dx_i}{d\xi} \left(\frac{n_{C_3H_8,f}}{L} \right) \quad (A - 22)$$

The right-hand side will be further broken down into smaller pieces that will be normalized independently:

Rate constants (k_i):

Rate constants are given by:

$$k_i = k_{i0} \exp \left[-\frac{E_{ia}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (A - 23)$$

The reactor temperature, as well as the reference temperature, are both normalized using Eqs. (A-24) and (A-25), respectively:

$$\theta = \frac{T - T_f}{T_f} \rightarrow T = T_f(1 + \theta) \quad (A - 24)$$

$$\theta_0 = \frac{T_0 - T_f}{T_f} \rightarrow T_0 = T_f(1 + \theta_0) \quad (A - 25)$$

Using the dimensionless form of the temperatures the rate constant becomes:

$$k_i = k_{i0} \exp \left[-\frac{E_{ia}}{RT_f} \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \quad (A - 26)$$

$$k_i = k_{i0} \exp \left[-\epsilon_i \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \quad (A - 27)$$

where,

$$\epsilon_i = \frac{E_{ia}}{RT_f}$$

The equilibrium constant ($K_{C_3H_6}$):

The equilibrium constant is given by:

$$K_{C_3H_8} = K_0 \exp \left[-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (A-28)$$

Using dimensionless temperatures, Eqs. (A-29 and A-30) are obtained:

$$K_{C_3H_8} = K_0 \exp \left[-\frac{\Delta H}{RT_f} \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \quad (A-29)$$

$$K_{C_3H_8} = K_0 \exp \left[-\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \quad (A-30)$$

where,

$$\epsilon_k = \frac{\Delta H}{RT_f}$$

Rate of reactions (1, 2, 3):

The rates of the reactions are given as rates of consumption of the key reactant in each reaction. **The rate of reaction 1** is given by:

$$-r_{C_3H_8,1} = \frac{k_{10} \exp \left[-\frac{E_{1a}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \left[P_{C_3H_8} - \frac{P_{C_3H_6} P_{H_2}}{K_{eq}} \right]}{1 + \frac{P_{C_3H_6}}{K_{C_3H_6}}} \quad (A-31)$$

Using the nondimensionalized forms of k_1 and $K_{C_3H_6}$ along with the dimensionless partial pressure, given by Eq. (A-32), the rate of the first reaction can be written as:

$$\gamma_i = \frac{P_i}{P_f} \quad (A - 32)$$

$$-r_{C_3H_8,1} = \frac{k_{10} \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \left[P_f \gamma_{C_3H_8} - \frac{P_f^2 \gamma_{C_3H_6} \gamma_{H_2}}{K_{eq}} \right]}{1 + \frac{P_f \gamma_{C_3H_6}}{K_0 \exp \left[-\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]}} \quad (A - 33)$$

$$-r_{C_3H_8,1} = \frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \left[\gamma_{C_3H_8} - \frac{P_f \gamma_{C_3H_6} \gamma_{H_2}}{K_{eq}} \right]}{1 + \frac{P_f \gamma_{C_3H_6}}{K_0 \exp \left[-\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]}} \quad (A - 34)$$

$$-r_{C_3H_8,1} = \frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \quad (A - 35)$$

where,

$$K' = \frac{P_f}{K_{eq}} \text{ and } K'_0 = \frac{P_f}{K_0}$$

The rate of the **second** reaction is given by Eq. (A-36):

$$-r_{C_3H_8,2} = k_{20} \exp \left[-\frac{E_{2a}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] P_{C_3H_8} \quad (A - 36)$$

Using the dimensionless form of the rate constant and the partial pressure gives:

$$-r_{C_3H_8,2} = k_{20} P_f \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \quad (A - 37)$$

Similarly, the rate of the **third** reaction is given by:

$$-r_{C_2H_4,3} = k_{30} \exp \left[-\frac{E_{3a}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] P_{C_2H_4} P_{H_2} \quad (A - 38)$$

After partially non-dimensionalizing, it gives:

$$-r_{C_2H_4,3} = k_{30} P_f^2 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \quad (A - 39)$$

The hydrogen permeation rate is given by:

$$J'_{H_2} = \frac{Q_0}{\delta_{H_2}} \exp \left[-\frac{E_{H_2}}{RT} \right] \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}} \right) \quad (A - 40)$$

Upon using the dimensionless temperature and partial pressure the above equation

becomes:

$$J'_{H_2} = \frac{Q_0}{\delta_{H_2}} \exp \left[-\frac{E_{H_2}}{RT_f} \frac{1}{1 + \theta} \right] \left(\sqrt{P_f \gamma_{H_2}} - \sqrt{P'_f \gamma'_{H_2}} \right) \quad (A - 41)$$

$$J'_{H_2} = \frac{Q_0 \sqrt{P_f}}{\delta_{H_2}} \exp \left[-\frac{E_{H_2}}{RT_f} \frac{1}{1 + \theta} \right] \left(\sqrt{\gamma_{H_2}} - \sqrt{\frac{P'_f}{P_f} \gamma'_{H_2}} \right) \quad (A - 42)$$

$$J'_{H_2} = \frac{Q_0 \sqrt{P_f}}{\delta_{H_2}} \exp \left[-\epsilon_{H_2} \frac{1}{1 + \theta} \right] \left(\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right) \quad (A - 43)$$

where,

$$\epsilon_{H_2} = \frac{E_{H_2}}{RT_f}$$

$$Pr = \frac{P'_f}{P_f}$$

Using the above, the mole balance for each component components be normalized:

I. Mole balance for C₃H₈:

$$\frac{dn_{C_3H_8}}{dz} = [r_{C_3H_8,1} + r_{C_3H_8,2}](1 - \varepsilon)A_c\rho_s \quad (A - 44)$$

After non-dimensionalizing, the mole balance becomes Eq. (65):

$$\begin{aligned} \frac{dx_{C_3H_8}}{d\xi} \left(\frac{n_{C_3H_8,f}}{L} \right) = & \left[- \frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} - \right. \\ & \left. k_{20} P_f \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \right] (1 - \varepsilon) A_c \rho_s \end{aligned} \quad (A-45)$$

$$\begin{aligned} \frac{dx_{C_3H_8}}{d\xi} = & \frac{k_{10} P_f (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & + \frac{k_{20} P_f (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \end{aligned} \quad (A - 46)$$

$$\begin{aligned} \frac{dx_{C_3H_8}}{d\xi} = & -\alpha_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & - \alpha_2 \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \end{aligned} \quad (A - 47)$$

where,

$$\alpha_1 = \frac{k_{10}P_f(1-\varepsilon)A_c\rho_s L}{n_{C_3H_8,f}} \text{ and } \alpha_2 = \frac{k_{20}P_f(1-\varepsilon)A_c\rho_s L}{n_{C_3H_8,f}}$$

II. Mole balance for C₃H₆:

$$\frac{dn_{C_3H_6}}{dz} = [-r_{C_3H_8,1}](1-\varepsilon)A_c\rho_s \quad (A-48)$$

After non-dimensionalizing, the mole balance becomes:

$$\frac{dx_{C_3H_6}}{d\xi} \left(\frac{n_{C_3H_8,f}}{L} \right) = \left[\frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right]} \right] (1-\varepsilon)A_c\rho_s \quad (A-49)$$

$$\frac{dx_{C_3H_6}}{d\xi} = \frac{k_{10}P_f(1-\varepsilon)A_c\rho_s L}{n_{C_3H_8,f}} \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right]} \quad (A-50)$$

Using the same definition of α_1 :

$$\frac{dx_{C_3H_6}}{d\xi} = \alpha_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1+\theta)(1+\theta_0)} \right) \right]} \quad (A-51)$$

III. Mole Balance for H₂

$$\frac{dn_{H_2}}{dz} = [-r_{C_3H_8,1} + r_{C_2H_4,3}](1-\varepsilon)A_c\rho_s - \pi D J_{H_2} \quad (A-52)$$

When normalized the equation becomes:

$$\begin{aligned} \frac{dx_{H_2}}{d\xi} \left(\frac{n_{C_3H_8,f}}{L} \right) = & \left[\frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \right. \\ & \left. - k_{30} P_f^2 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \right] (1 - \varepsilon) A_c \rho_s \\ & - \frac{\pi D Q_0 \sqrt{P_f}}{\delta_{H_2}} \exp \left[\frac{-\epsilon_{H_2}}{1 + \theta} \right] \left(\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right) \end{aligned} \quad (A - 53)$$

$$\begin{aligned} \frac{dx_{H_2}}{d\xi} = & \frac{k_{10} P_f (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & - \frac{k_{30} P_f^2 (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \\ & - \frac{\pi D L Q_0 \sqrt{P_f}}{\delta_{H_2} n_{C_3H_8,f}} \exp \left[\frac{-\epsilon_{H_2}}{1 + \theta} \right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right] \end{aligned} \quad (A - 54)$$

$$\begin{aligned} \frac{dx_{H_2}}{d\xi} = & \alpha_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & - \alpha_3 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \\ & - \alpha_{PER} \exp \left[\frac{-\epsilon_{H_2}}{1 + \theta} \right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right] \end{aligned} \quad (A - 55)$$

where,

$$\alpha_3 = \frac{k_{30} P_f^2 (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \text{ and } \alpha_{PER} = \frac{\pi D L Q_0 \sqrt{P_f}}{\delta_{H_2} n_{C_3H_8,f}}$$

IV. Mole balance for C₂H₄

$$\frac{dn_{C_2H_4}}{dz} = [-r_{C_3H_8,2} + r_{C_2H_4,3}](1 - \varepsilon)A_c\rho_s \quad (A - 56)$$

When normalized, the equation becomes:

$$\begin{aligned} \frac{dx_{C_2H_4}}{d\xi} = & \frac{k_{20}P_f(1 - \varepsilon)A_c\rho_s L}{n_{C_3H_8,f}} \exp\left[-\epsilon_2\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \\ & - \frac{k_{30}P_f^2(1 - \varepsilon)A_c\rho_s L}{n_{C_3H_8,f}} \exp\left[-\epsilon_3\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4}\gamma_{H_2} \end{aligned} \quad (A - 57)$$

$$\begin{aligned} \frac{dx_{C_2H_4}}{d\xi} = & \alpha_2 \exp\left[-\epsilon_2\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \\ & - \alpha_3 \exp\left[-\epsilon_3\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4}\gamma_{H_2} \end{aligned} \quad (A - 58)$$

V. Mole balance for CH₄

$$\frac{dn_{CH_4}}{dz} = [-r_{C_3H_8,2}](1 - \varepsilon)A_c\rho_s \quad (A - 59)$$

When normalized, the equation becomes:

$$\frac{dx_{CH_4}}{d\xi} \left(\frac{n_{C_3H_8,f}}{L}\right) = \left[k_{30} P_f^2 \exp\left[-\epsilon_3\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_2H_4}\gamma_{H_2}\right] (1 - \varepsilon)A_c\rho_s \quad (A - 60)$$

$$\frac{dx_{CH_4}}{d\xi} = \frac{k_{20}P_f(1 - \varepsilon)A_c\rho_s L}{n_{C_3H_8,f}} \exp\left[-\epsilon_2\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \quad (A - 61)$$

$$\frac{dx_{CH_4}}{d\xi} = \alpha_2 \exp\left[-\epsilon_2\left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)}\right)\right] \gamma_{C_3H_8} \quad (A - 62)$$

VI. Mole balance for C₂H₆

$$\frac{dn_{C_2H_6}}{dz} = [-r_{C_2H_4,3}](1 - \varepsilon)A_c\rho_s \quad (A - 63)$$

When normalized, the equation becomes:

$$\frac{dx_{C_2H_6}}{d\xi} \left(\frac{n_{C_3H_8,f}}{L} \right) = \left[k_{30} P_f^2 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \right] (1 - \varepsilon) A_c \rho_s \quad (A - 64)$$

$$\frac{dx_{C_2H_6}}{d\xi} = \frac{k_{30} P_f^2 (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \quad (A - 65)$$

$$\frac{dx_{C_2H_6}}{d\xi} = \alpha_3 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \quad (A - 66)$$

Energy balance (dehydrogenation side)

The energy balance on the tube side is given by:

$$\frac{dT}{dz} = \frac{\pi DU(T' - T) + (1 - \varepsilon)A_c \rho_s [(-\Delta H_1 r_{C_3H_8,1}) + (-\Delta H_2 r_{C_3H_8,2}) + (-\Delta H_3 r_{C_2H_4,3})]}{\sum_{i=1}^n n_i C p_i} \quad (A - 67)$$

The left-hand side of the above equation is normalized using the dimensionless temperature and length as follows, giving:

$$\frac{dT}{dz} = \frac{d\theta}{d\xi} \left(\frac{dT}{d\theta} \right) \left(\frac{d\xi}{dz} \right) = \frac{d\theta}{d\xi} \left(\frac{T_f}{1} \right) \left(\frac{1}{L} \right) \quad (A - 68)$$

$$\frac{dT}{dz} = \frac{d\theta}{d\xi} \left(\frac{T_f}{L} \right) \quad (A - 69)$$

After normalizing the left-hand side, the following equation is obtained:

$$\frac{d\theta}{d\xi} \left(\frac{T_f}{L} \right) = \frac{\pi D U (T' - T)}{\sum_{i=1}^n n_i C p_i} + \frac{(1 - \varepsilon) A_c \rho_s [(-\Delta H_1 r_{C_3 H_8, 1}) + (-\Delta H_2 r_{C_3 H_8, 2}) + (-\Delta H_3 r_{C_2 H_4, 3})]}{\sum_{i=1}^n n_i C p_i} \quad (A - 70)$$

$$\frac{d\theta}{d\xi} = \frac{\pi D L U (T' - T)}{T_f \sum_{i=1}^n n_i C p_i} + \frac{L(1 - \varepsilon) A_c \rho_s [(-\Delta H_1 r_{C_3 H_8, 1}) + (-\Delta H_2 r_{C_3 H_8, 2}) + (-\Delta H_3 r_{C_2 H_4, 3})]}{T_f \sum_{i=1}^n n_i C p_i} \quad (A - 71)$$

The right-hand side is then broken down into two terms as follows:

$$\begin{aligned} \text{Term 1: } & \frac{\pi D U L (T' - T)}{T_f \sum_{i=1}^n n_i C p_i} \\ \text{Term 2: } & \frac{L(1 - \varepsilon) A_c \rho_s [(-\Delta H_1 r_{C_3 H_8, 1}) + (-\Delta H_2 r_{C_3 H_8, 2}) + (-\Delta H_3 r_{C_2 H_4, 3})]}{T_f \sum_{i=1}^n n_i C p_i} \end{aligned}$$

Term 1 is normalized and given by:

$$\frac{\pi D U L (T'_f (1 + \theta') - T_f (1 + \theta))}{T_f \sum_{i=1}^n n_i C p_i} \quad (A - 72)$$

The second term is normalized as follows:

$$L(1 - \varepsilon)A_c\rho_s \left[\frac{\left(-\Delta H_1 \frac{k_{10} P_f \exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] [\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2}]}{1 + K'_0 \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \right)}{T_f \sum_{i=1}^n n_i C p_i} + \left(-\Delta H_2 k_{20} P_f \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \right) + \left(-\Delta H_3 k_{30} P_f^2 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \right) \right] \quad (A - 73)$$

$$\begin{aligned} & (k_{10} P_f (1 - \varepsilon) A_c \rho_s L) \left(\frac{-\Delta H_1}{T_f \sum_{i=1}^n n_i C p_i} \right) \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & + (k_{20} P_f (1 - \varepsilon) A_c \rho_s L) \left(\frac{-\Delta H_2}{T_f \sum_{i=1}^n n_i C p_i} \right) \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \\ & + (k_{30} P_f^2 (1 - \varepsilon) A_c \rho_s L) \left(\frac{-\Delta H_3}{T_f \sum_{i=1}^n n_i C p_i} \right) \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \quad (A - 74) \end{aligned}$$

The second term was then multiplied by $\frac{n_{C_3H_8,f}}{n_{C_3H_8}}$ to insert α_i into the energy balance and

Eq. (A-74) was obtained:

$$\begin{aligned} & \left(\frac{k_{10} P_f (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \right) \left(\frac{n_{C_3H_8,f} (-\Delta H_1)}{T_f \sum_{i=1}^n n_i C p_i} \right) \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\ & + \left(\frac{k_{20} P_f (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \right) \left(\frac{n_{C_3H_8,f} (-\Delta H_2)}{T_f \sum_{i=1}^n n_i C p_i} \right) \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \\ & + \left(\frac{k_{30} P_f^2 (1 - \varepsilon) A_c \rho_s L}{n_{C_3H_8,f}} \right) \left(\frac{n_{C_3H_8,f} (-\Delta H_3)}{T_f \sum_{i=1}^n n_i C p_i} \right) \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2} \quad (A - 74) \end{aligned}$$

$$\begin{aligned}
& \alpha_1 \beta_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\
& + \alpha_2 \beta_2 \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \\
& + \alpha_3 \beta_3 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2}
\end{aligned} \tag{A - 75}$$

Upon combining both terms, the energy balance for the tube side in the dimensionless form is given by:

$$\begin{aligned}
\frac{d\theta}{d\xi} &= \frac{\pi DUL [T'_f(1 + \theta') - T_f(1 + \theta)]}{T_f \sum_{i=1}^n n_i C p_i} \\
& + \alpha_1 \beta_1 \frac{\exp \left[-\epsilon_1 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] (\gamma_{C_3H_8} - K' \gamma_{C_3H_6} \gamma_{H_2})}{1 + K'_0 + \gamma_{C_3H_6} \exp \left[\epsilon_k \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right]} \\
& + \alpha_2 \beta_2 \exp \left[-\epsilon_2 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_3H_8} \\
& + \alpha_3 \beta_3 \exp \left[-\epsilon_3 \left(\frac{\theta_0 - \theta}{(1 + \theta)(1 + \theta_0)} \right) \right] \gamma_{C_2H_4} \gamma_{H_2}
\end{aligned} \tag{A - 76}$$

Pressure drop (dehydrogenation side)

$$\frac{dP}{dz} = - \left\{ \frac{G}{\rho D_p g_c} \frac{1 - \varepsilon}{\varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \right\} \tag{A - 77}$$

Using the Eq. (A-78) to define the change in density in the tube side gives Eq. (A-79)

$$\rho = \rho_f \left(\frac{P}{P_f} \right) \left(\frac{T_f}{T} \right) \left(\frac{n_{T,f}}{n_T} \right) \tag{A - 78}$$

$$\frac{dP}{dz} = - \left\{ \frac{G}{\rho_f D_p g_c} \frac{1 - \varepsilon}{\varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \right\} \left(\frac{P_f}{P} \right) \left(\frac{T}{T_f} \right) \left(\frac{n_T}{n_{T,f}} \right) \quad (A - 79)$$

Using the dimensionless reactor pressure in the tube side given by Eq. (A-80), the pressure drop can be normalized as follows to give Eq. (A-85):

$$\psi = \frac{P}{P_f} \quad (A - 80)$$

$$\frac{dP}{dz} = \frac{d\psi}{d\xi} \left(\frac{dP}{d\psi} \right) \left(\frac{d\xi}{dz} \right) = \frac{d\psi}{d\xi} \left(\frac{P_f}{1} \right) \left(\frac{1}{L} \right) \quad (A - 81)$$

$$\frac{dP}{dz} = \frac{d\psi}{d\xi} \left(\frac{P_f}{L} \right) \quad (A - 82)$$

$$\frac{d\psi}{d\xi} \left(\frac{P_f}{L} \right) = - \left\{ \frac{G}{\rho_f D_p g_c} \frac{1 - \varepsilon}{\varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \right\} \left(\frac{P_f}{P} \right) \left(\frac{T}{T_f} \right) \left(\frac{n_T}{n_{T,f}} \right) \quad (A - 83)$$

$$\frac{d\psi}{d\xi} = - \left\{ \frac{G L}{P_f \rho_f D_p g_c} \frac{1 - \varepsilon}{\varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \right\} \left(\frac{1}{\psi} \right) (1 + \theta) \left(\frac{n_T}{n_{T,f}} \right) \quad (A - 84)$$

$$\frac{d\psi}{d\xi} = - \frac{\beta_0(T)(1 + \theta)}{\psi} \left(\frac{n_T}{n_{T,f}} \right) \quad (A - 85)$$

where,

$$\beta_0 = \frac{GL(1 - \varepsilon)}{P_f \rho_f D_p g_c \varepsilon^3} \left[\frac{150(1 - \varepsilon)\mu}{D_p} + 1.75G \right] \quad (A - 86)$$

Mole balance (hydrogenation side)

Like the tube side, the mole balance will be divided into components that will be nondimensionalized separately and then combined to form the dimensionless forms of the mole balance of the components in the shell side.

The left-hand side of each mole balance will be again normalized using the dimensionless fractional change in molar flow Eq. (A-87) and the fractional length (Eq. A-88):

$$x'_i = \frac{n'_i - n'_{i,f}}{n'_{NB,f}} \quad (A - 87)$$

$$\xi = \frac{z}{L} \quad (A - 88)$$

$$\frac{dn'_i}{dz} = \frac{dx'_i}{d\xi} \left(\frac{dn'_i}{dx'_i} \right) \left(\frac{d\xi}{dz} \right) = \frac{dx'_i}{d\xi} \left(\frac{n'_{NB,f}}{1} \right) \left(\frac{1}{L} \right) \quad (A - 89)$$

Which gives:

$$\frac{dn'_i}{dz} = \frac{dx'_i}{d\xi} \left(\frac{n'_{NB,f}}{L} \right) \quad (A - 90)$$

The right-hand side will also be broken down into several components such as the rate constant, and rate of reaction.

Rate constant (k'):

Rate constant of the hydrogenation reaction is given by:

$$k' = 0.186 \exp \left[-\frac{10.0 * 10^{-3}}{RT'} \right] \quad (A - 91)$$

Using the dimensionless shell side temperature given by Eq. (A-92), Eq. (A-94) is obtained:

$$\theta' = \frac{T' - T'_f}{T'_f} \rightarrow T' = T'_f(1 + \theta') \quad (A - 92)$$

$$k' = 0.186 \exp \left[-\frac{10.0 * 10^{-3}}{RT'_f} \frac{1}{(1 + \theta')} \right] \quad (A - 93)$$

$$k' = 0.186 \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \quad (A - 94)$$

where,

$$\epsilon' = \frac{10.0 * 10^{-3}}{RT'_f} \quad (A - 95)$$

Rate of reaction (r):

$$r' = \frac{k' K_{NB} K_{H_2} P'_{NB} \sqrt{P'_{H_2}}}{\left(1 + K_{NB} P'_{NB} + K_{H_2} \sqrt{P'_{H_2}} \right)^2} \quad (A - 96)$$

Using the dimensionless partial pressure on the shell side given by:

$$\gamma'_i = \frac{P'_i}{P'_f} \quad (A - 97)$$

Gives:

$$r' = \frac{0.186 \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] K_{NB} K_{H_2} \gamma'_{NB} P'_f \sqrt{\gamma'_{H_2} P'_f}}{\left(1 + K_{NB} \gamma'_{NB} P'_f + K_{H_2} \sqrt{\gamma'_{H_2} P'_f} \right)^2} \quad (A - 98)$$

$$r' = \frac{0.186 K'_{NB} K'_{H_2} \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 99)$$

where,

$$K'_{NB} = K_{NB} P'_f \text{ and } K'_{H_2} = K_{H_2} \sqrt{P'_f}$$

I. Mole balance for nitrobenzene (dehydrogenation side)

The mole balance for NB is given by:

$$\frac{dn'_{NB}}{dz} = (-1)^a \sigma'_{NB} r' (1 - \epsilon') A'_c \rho'_s \quad (A - 100)$$

After normalization, the mole balance is given by:

$$\frac{dx'_{NB}}{d\xi} \left(\frac{n'_{NB,f}}{L} \right) = (-1)^a \sigma'_{NB} (1 - \epsilon') A'_c \rho'_s \frac{0.186 K'_{NB} K'_{H_2} \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 101)$$

$$\frac{dx'_{NB}}{d\xi} = (-1)^a \frac{0.186K'_{NB}K'_{H_2}(1 - \varepsilon')A'_c\rho'_sL}{n'_{NB,f}} \sigma'_{NB} \frac{\exp\left[\frac{-\varepsilon'}{1 + \theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB}\gamma'_{NB} + K'_{H_2}\sqrt{\gamma'_{H_2}}\right)^2} \quad (A - 102)$$

$$\frac{dx'_{NB}}{d\xi} = (-1)^a \alpha' \sigma'_{NB} \frac{\exp\left[\frac{-\varepsilon'}{1 + \theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB}\gamma'_{NB} + K'_{H_2}\sqrt{\gamma'_{H_2}}\right)^2} \quad (A - 103)$$

where,

$$\alpha' = \frac{0.186K'_{NB}K'_{H_2}(1 - \varepsilon')A'_c\rho'_sL}{n'_{NB,f}} \quad (A - 104)$$

II. Mole balance for H₂ (hydrogenation side):

The mole balance for H₂ is given by:

$$\frac{dn'_{H_2}}{dz} = (-1)^a \left[\sigma'_{H_2} r'(1 - \varepsilon')A'_c\rho'_s + \pi D J'_{H_2} \right] \quad (A - 105)$$

$$\begin{aligned} \frac{dx'_{H_2}}{d\xi} \left(\frac{n'_{NB,f}}{L} \right) &= (-1)^a \left[\sigma'_{H_2} r'(1 - \varepsilon')A'_c\rho'_s \right. \\ &\left. + \frac{\pi D Q_0 \sqrt{P_f}}{\delta_{H_2}} \exp\left[-\varepsilon_{H_2} \frac{1}{1 + \theta}\right] \left(\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}} \right) \right] \end{aligned} \quad (A - 106)$$

$$\begin{aligned} \frac{dx'_{H_2}}{d\xi} = & (-1)^a \frac{0.186K'_{NB}K'_{H_2}(1-\varepsilon')A'_c\rho'_sL}{n'_{NB,f}} \sigma'_{H_2} \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB}\gamma'_{NB} + K'_{H_2}\sqrt{\gamma'_{H_2}}\right)^2} \\ & + (-1)^a \left(\frac{\pi DLQ_0\sqrt{P_f}}{\delta_{H_2}}\right) \left(\frac{1}{n'_{NB,f}}\right) \exp\left[\frac{-\epsilon_{H_2}}{1+\theta}\right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}}\right] \quad (A-107) \end{aligned}$$

To use the dimensionless group (α_{PER}) the second term on the right-hand side of the above equation was multiplied by $\frac{n_{C_3H_8,f}}{n_{C_3H_8,f}}$ giving:

$$\begin{aligned} \frac{dx'_{H_2}}{d\xi} = & (-1)^a \frac{0.186K'_{NB}K'_{H_2}(1-\varepsilon')A'_c\rho'_sL}{n'_{NB,f}} \sigma'_{H_2} \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB}\gamma'_{NB} + K'_{H_2}\sqrt{\gamma'_{H_2}}\right)^2} \\ & + (-1)^a \left(\frac{\pi DLQ_0\sqrt{P_f}}{\delta_{H_2}n_{C_3H_8,f}}\right) \left(\frac{n_{C_3H_8,f}}{n'_{NB,f}}\right) \exp\left[\frac{-\epsilon_{H_2}}{1+\theta}\right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}}\right] \quad (A-108) \end{aligned}$$

$$\begin{aligned} \frac{dx'_{H_2}}{d\xi} = & (-1)^a \alpha' \sigma'_{H_2} \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB}\gamma'_{NB} + K'_{H_2}\sqrt{\gamma'_{H_2}}\right)^2} \\ & + (-1)^a \alpha_{PER} R' \exp\left[\frac{-\epsilon_{H_2}}{1+\theta}\right] \left[\sqrt{\gamma_{H_2}} - \sqrt{Pr \gamma'_{H_2}}\right] \quad (A-109) \end{aligned}$$

where,

$$R' = \frac{n_{C_3H_8,f}}{n'_{NB,f}} \quad (A-110)$$

III. Mole balance for aniline (hydrogenation side)

The mole balance for aniline is given by:

$$\frac{dn'_{AN}}{dz} = (-1)^a \sigma'_{AN} r' (1 - \varepsilon') A'_c \rho'_s \quad (A - 111)$$

After non-dimensionalizing, it becomes:

$$\frac{dx'_{AN}}{d\xi} \left(\frac{n'_{NB,f}}{L} \right) = (-1)^a \sigma'_{AN} (1 - \varepsilon') A'_c \rho'_s \frac{0.186 K'_{NB} K'_{H_2} \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 112)$$

$$\frac{dx'_{AN}}{d\xi} = (-1)^a \left(\frac{0.186 K'_{NB} K'_{H_2} (1 - \varepsilon') A'_c \rho'_s L}{n'_{NB,f}} \right) \sigma'_{AN} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 113)$$

$$\frac{dx'_{AN}}{d\xi} = (-1)^a \alpha' \sigma'_{AN} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 114)$$

IV. Mole balance for H₂O (hydrogenation side):

Similarly, the mole balance for H₂O is given by:

$$\frac{dn'_{H_2O}}{dz} = (-1)^a \sigma'_{H_2O} r' (1 - \varepsilon') A'_c \rho'_s \quad (A - 115)$$

Upon normalizing:

$$\frac{dx'_{H_2O}}{d\xi} \left(\frac{n'_{NB,f}}{L} \right) = (-1)^a \sigma'_{H_2O} (1 - \varepsilon') A'_c \rho'_s \frac{0.186 K'_{NB} K'_{H_2} \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 116)$$

$$\frac{dx'_{H_2O}}{d\xi} = (-1)^a \left(\frac{0.186 K'_{NB} K'_{H_2} (1 - \varepsilon') A'_c \rho'_s L}{n'_{NB,f}} \right) \sigma'_{H_2O} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 117)$$

$$\frac{dx'_{H_2O}}{d\xi} = (-1)^a \alpha' \sigma'_{H_2O} \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 118)$$

Energy balance (hydrogenation side):

The energy balance on the shell side is given by:

$$\frac{dT'}{dz} = (-1)^a \frac{(1 - \varepsilon') A'_c \rho'_s [(-\Delta H' r')] - \pi DU (T' - T)}{\sum_{i=1}^n n'_i C p'_i} \quad (A - 119)$$

The left-hand side of the above balance is normalized using the dimensionless shell temperature to give:

$$\frac{dT'}{dz} = \frac{d\theta'}{d\xi} \left(\frac{dT'}{d\theta'} \right) \left(\frac{d\xi}{dz} \right) = \frac{d\theta'}{d\xi} \left(\frac{T'_f}{1} \right) \left(\frac{1}{L} \right) \quad (A - 120)$$

$$\frac{dT'}{dz} = \frac{d\theta'}{d\xi} \left(\frac{T'_f}{L} \right) \quad (A - 121)$$

After non-dimensionalizing the left-hand side, the energy balance becomes:

$$\frac{d\theta'}{d\xi} \left(\frac{T'_f}{L} \right) = (-1)^a \frac{(1 - \varepsilon') A'_c \rho'_s [(-\Delta H' r')]}{\sum_{i=1}^n n'_i C p'_i} + (-1)^a \frac{-\pi DU (T' - T)}{\sum_{i=1}^n n_i C p_i} \quad (A - 122)$$

$$\frac{d\theta'}{d\xi} = (-1)^a \frac{-\pi DUL (T' - T)}{T'_f \sum_{i=1}^n n_i C p_i} + (-1)^a \frac{L (1 - \varepsilon') A'_c \rho'_s [(-\Delta H' r')]}{T'_f \sum_{i=1}^n n'_i C p'_i} \quad (A - 123)$$

The right-hand side is divided into two terms which will be normalized independently:

$$\text{Term 1: } (-1)^a \frac{-\pi DUL(T' - T)}{T'_f \sum_{i=1}^n n_i C p_i} \quad \text{Term 2: } (-1)^a \frac{L(1 - \varepsilon') A'_c \rho'_s [(-\Delta H' r')]}{T'_f \sum_{i=1}^n n'_i C p'_i}$$

The first term is normalized to give:

$$(-1)^a \frac{-\pi DUL [T'_f (1 + \theta') - T_f (1 + \theta)]}{T'_f \sum_{i=1}^n n_i C p_i} \quad (A - 124)$$

While the second is normalized to give:

$$(-1)^a \frac{(1 - \varepsilon') A'_c \rho'_s L \left[\left(-\Delta H' \frac{0.186 K'_{NB} K'_{H_2} \exp \left[-\frac{\epsilon'}{(1 + \theta')} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \right) \right]}{T'_f \sum_{i=1}^n n'_i C p'_i} \quad (A - 125)$$

$$(-1)^a (0.186 K'_{NB} K'_{H_2} (1 - \varepsilon') A'_c \rho'_s L) \left(\frac{-\Delta H'}{T'_f \sum_{i=1}^n n'_i C p'_i} \right) \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 126)$$

To be able to use the same Damckoler number (α') previously used in the mole balance,

the right-hand side was multiplied by $\frac{n'_{NB,f}}{n'_{NB,f}}$ to give:

$$(-1)^a \left(\frac{0.186 K'_{NB} K'_{H_2} (1 - \varepsilon') A'_c \rho'_s L}{n'_{NB,f}} \right) \left(\frac{n'_{NB,f} (-\Delta H')}{T'_f \sum_{i=1}^n n'_i C p'_i} \right) \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 127)$$

$$(-1)^a \alpha' \beta' \frac{\exp \left[\frac{-\epsilon'}{1 + \theta'} \right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}} \right)^2} \quad (A - 128)$$

where,

$$\beta' = \frac{n'_{NB,f}(-\Delta H')}{T'_f \sum_{i=1}^n n'_i C p'_i} \quad (A - 129)$$

Combining both terms gives the dimensionless energy balance for the shell side given below:

$$\frac{d\theta'}{d\xi} = (-1)^a \alpha' \beta' \frac{\exp\left[\frac{-\epsilon'}{1+\theta'}\right] \gamma'_{NB} \sqrt{\gamma'_{H_2}}}{\left(1 + K'_{NB} \gamma'_{NB} + K'_{H_2} \sqrt{\gamma'_{H_2}}\right)^2} - (-1)^a \frac{\pi D U L [T'_f(1+\theta') - T_f(1+\theta)]}{T'_f \sum_{i=1}^n n'_i C p'_i} \quad (A - 130)$$

Pressure drop (hydrogenation side):

$$\frac{dP'}{dz} = - \left\{ \frac{G'}{\rho'^{D'} p g_c} \frac{1 - \epsilon'}{(\epsilon')^3} \left[\frac{150(1 - \epsilon')\mu'}{D_{p'}} + 1.75 G' \right] \right\} \quad (A - 131)$$

Using Eq. (A-132) to define the change in density in the shell side gives:

$$\rho' = \rho'_f \left(\frac{P'}{P'_f} \right) \left(\frac{T'_f}{T'} \right) \left(\frac{n'_{T,f}}{n'_T} \right) \quad (A - 132)$$

$$\frac{dP'}{dz} = - \left\{ \frac{G'}{\rho'_f D' p g_c} \frac{1 - \epsilon'}{(\epsilon')^3} \left[\frac{150(1 - \epsilon')\mu'}{D_{p'}} + 1.75 G' \right] \right\} \left(\frac{P'_f}{P'} \right) \left(\frac{T'}{T'_f} \right) \left(\frac{n'_T}{n'_{T,f}} \right) \quad (A - 133)$$

Using the dimensionless, reactor pressure in the shell side given by Eq. (A-134), the pressure drop can be normalized as follows to give Eq. (A-139):

$$\psi' = \frac{P'}{P'_f} \quad (A - 134)$$

$$\frac{dP'}{dz} = \frac{d\psi'}{d\xi} \left(\frac{dP'}{d\psi} \right) \left(\frac{d\xi}{dz} \right) = \frac{d\psi'}{d\xi} \left(\frac{P'_f}{1} \right) \left(\frac{1}{L} \right) \quad (A - 135)$$

$$\frac{dP'}{dz} = \frac{d\psi'}{d\xi} \left(\frac{P'_f}{L} \right) \quad (A - 136)$$

$$\frac{d\psi'}{d\xi} \left(\frac{P'_f}{L} \right) = - \left\{ \frac{G'}{\rho'_f D'_p g_c} \frac{1 - \varepsilon'}{(\varepsilon')^3} \left[\frac{150(1 - \varepsilon')\mu'}{D_p'} + 1.75G' \right] \right\} \left(\frac{P'_f}{P'} \right) \left(\frac{T'}{T'_f} \right) \left(\frac{n'_T}{n'_{T,f}} \right) \quad (A - 137)$$

$$\frac{d\psi'}{d\xi} = - \left\{ \frac{G'L}{P'_f \rho'_f D'_p g_c} \frac{1 - \varepsilon'}{(\varepsilon')^3} \left[\frac{150(1 - \varepsilon')\mu'}{D_p'} + 1.75G' \right] \right\} \left(\frac{1}{\psi'} \right) (1 + \theta) \left(\frac{n'_T}{n'_{T,f}} \right) \quad (A - 138)$$

$$\frac{d\psi'}{d\xi} = - \frac{\beta'_0(T')(1 + \theta')}{\psi'} \left(\frac{n'_T}{n'_{T,f}} \right) \quad (A - 139)$$

where,

$$\beta'_0 = \frac{G'L(1 - \varepsilon')}{P'_f \rho'_f D'_p g_c (\varepsilon')^3} \left[\frac{150(1 - \varepsilon')\mu'}{D_p'} + 1.75G' \right] \quad (A - 140)$$

Appendix C – Physical properties:

1. Enthalpy of formation:

The correlation for the enthalpy of formation is given as a function of temperature by Eq. (A-141) [48]:

$$\Delta H_f = A + B T + C T^2 \quad (A - 141)$$

where, ΔH_f is the enthalpy change of formation of an ideal gas (kJ/mol), T is the temperature (K). A , B , and C are the regression coefficients for each chemical compound given in Table 17.

Table 17: Regression coefficients for the calculation of the enthalpy of formation [48]

Gas	A	B	C	T _{min} (K)	T _{max} (K)	H _f at 298 K	H _f at 500 K
Propane	-80.697	-9.0500E-02	4.2104E-05	298	1000	-103.85	-115.42
Propene	37.334	-6.5191E-02	2.8085E-05	298	1000	20.42	11.76
Ethane	-66.735	-6.9337E-02	3.0379E-05	298	1000	-84.68	-93.81
Ethylene	63.053	-4.1076E-02	1.6598E-05	298	1000	52.30	46.66
Water	-238.41	-1.2256E-02	2.7656E-06	-	-	-241.80	-
Hydrogen	-	-	-	-	-	0.00	-
Nitrogen	-	-	-	-	-	0.00	-
Oxygen	-	-	-	-	-	0.00	-
Nitrobenzene	-	-	-	-	-	67.60	
Aniline	105.261	-7.3513E-02	3.7553E-05	298	1000	86.86	77.89

2. Heat Capacity:

The correlation for the heat capacity of an ideal gas is given by Eq. (A-142) [48]:

$$C_p = A + B T + C T^2 + D T^3 + E T^4 \quad (A - 142)$$

where, C_p is the heat capacity of an ideal gas (J/mol. K), T is the temperature (K). A , B , C , D , and E are the regression coefficients for each chemical compound given in Table 18.

Table 18: Regression coefficients for the calculation of the heat capacity [48]

Gas	A	B	C	D	E	T _{min} (K)	T _{max} (K)
Propane	28.277	1.1600E-01	1.9597E-04	-2.3271E-07	6.8669E-11	100	1500
Propene	31.298	7.2449E-02	1.9481E-04	-2.1582E-07	6.2974E-11	90	1500
Ethane	28.146	4.3447E-02	1.8946E-04	-1.9082E-07	5.3349E-11	100	1500
Ethylene	32.083	-1.4831E-02	2.4774E-04	-2.3766E-07	6.8274E-11	60	1500
Methane	34.942	-3.9957E-02	1.9184E-04	-1.5303E-07	3.9321E-11	50	1500
Water	33.933	-8.4186E-03	2.9906E-05	-1.7825E-08	3.6934E-12	100	1500
Hydrogen	25.399	2.0178E-02	-3.8549E-05	3.1880E-08	-8.7585E-12	250	1500
Nitrogen	29.342	-3.5395E-03	1.0076E-05	-4.3116E-09	2.5935E-13	50	1500
Oxygen	29.526	-8.8999E-03	3.8083E-05	-3.2629E-08	8.8607E-12	50	1500
NB	-16.202	5.6182E-01	-3.9302E-04	1.0043E-07	-1.2252E-12	200	1500
Aniline	-22.062	5.7313E-01	-4.5651E-04	1.8410E-07	-2.9867E-11	200	1500

3. Viscosity of gases:

The viscosity of gases is given as a function of temperature using the correlation below (Eq. A-143)[48]:

$$\eta_{gas} = A + B T + C T^2 \quad (A - 143)$$

where, η_{gas} is the viscosity of the gas (micropoise), T is the temperature (K) and A , B , and C are the regression coefficients for each chemical compound given in Table 19.

Table 19: Regression coefficients for the calculation of the viscosity of the gases [48]

Gas	A	B	C	T _{min} (K)	T _{max} (K)	η_{gas} at 298 K	η_{gas} at T _{min}
Propane	-5.462	3.2722E-01	-1.0672E-04	193	750	82.61	53.72
Propene	-7.230	3.4180E-01	-9.4516E-05	193	1000	86.28	55.22
Ethane	0.514	3.3449E-01	-7.1071E-05	150	1000	93.92	49.09
Ethylene	-3.985	3.8726E-01	-1.1227E-04	150	1000	101.50	51.58
Methane	3.844	4.0112E-01	-1.4303E-04	91	850	110.72	39.16
Water	-36.826	4.2900E-01	-1.6200E-05	280	1073	89.68	82.07
Hydrogen	27.758	2.1200E-01	-3.2800E-05	150	1500	88.03	58.81
Nitrogen	42.606	4.7500E-01	-9.8800E-05	150	1500	175.52	111.67
Oxygen	44.224	5.6200E-01	-1.1300E-04	150	1500	201.85	126.04
Nitrobenzene	-16.569	2.9184E-01	-2.5523E-05	450	1000	-	109.59
Aniline	-6.918	2.5935E-01	-3.4348E-05	458	1000	-	104.66
Helium	71.094	4.4300E-01	-5.1800E-05	150	2000	198.63	136.41

4. Thermal conductivity of gases:

The thermal conductivity of gases is given as a function of temperature using the correlation below (Eq. A-144) [48]:

$$k_{gas} = A + B T + C T^2 \quad (A - 144)$$

where, k_{gas} is the thermal conductivity of the gas (W/(m.K)), T is the temperature (K) and A , B , and C are the regression coefficients for each chemical compound given by Table 20.

Table 20: Regression coefficients for the calculation of the thermal conductivity of the gases [48]

Gas	A	B	C	T _{min} (K)	T _{max} (K)	k_{gas} at 298 K	k_{gas} at T _{min}
Propane	-0.00869	6.6409E-05	7.8760E-08	233	773	0.01811	0.01106
Propene	-0.01116	7.5155E-05	6.5558E-08	250	1000	0.01708	0.01173
Ethane	-0.01936	1.2547E-04	3.8298E-08	225	825	0.02145	0.01081
Ethylene	-0.00123	3.6219E-05	1.2459E-07	150	750	0.02064	0.00701
Methane	-0.00935	1.4028E-04	3.3180E-08	97	1400	0.03542	0.00457
Water	0.00053	4.7093E-05	4.9551E-08	275	1073	0.01898	0.01723
Hydrogen	0.03951	4.5918E-04	-6.4933E-08	150	1500	0.17064	0.10693
Nitrogen	0.00309	7.5930E-05	-1.1014E-08	78	1500	0.02475	0.00895
Oxygen	0.00121	8.6157E-05	-1.3346E-08	80	1500	0.02571	0.00802
Nitrobenzene	-1.0283E-02	5.7531E-05	1.0851E-08	250	1000	0.0078	0.0581
Aniline	-0.01796	8.3464E-05	1.5022E-09	458	1000	-	0.02058

5. Thermal conductivity of solids:

The thermal conductivity of solids is given as a function of temperature using the correlation below (Eq. A-145) [48]:

$$k_{solid} = A + B T + C T^2 \quad (A - 145)$$

where, k_{solid} is the thermal conductivity of the solid (W/ (m.K)), T is the temperature (K) and A , B and C are the regression coefficients for each chemical compound given by Table 21.

Table 21: Regression coefficients for the calculation of the thermal conductivity of the gases [48]

Solid	A	B	C	T _{min} (K)	T _{max} (K)	k_s at 298 K	k_s at T _{max}
Palladium	62.3067	3.2174E-02	-9.5280E-07	200	1800	71.815	117.133
Stainless steel	19.00	0	0				

For stainless steel, the value of the thermal conductivity is 16.2 W/m.K at 100 °C and 21.5 W/m.K at 500 °C

6. Gibbs energy of formation:

The Gibbs energy of formation of gases is given as a function of temperature using the correlation below (Eq. A-146) [48]:

$$\Delta G_f = A + B T + C T^2 \quad (A - 146)$$

where, ΔG_f is the Gibbs energy of formation of the gas (kJ/mol), T is the temperature (K) and A , B , and C are the regression coefficients for each chemical compound given in Table 22.

Table 22: Regression coefficients for the calculation of the Gibbs energy of formation of the gases [48]

Gas	A	B	C	T _{min} (K)	T _{max} (K)	ΔG_f at 298 K	ΔG_f at 500 K
Propane	-105.603	2.6475E-01	3.2500E-05	298	1000	-23.47	34.90
Propene	19.412	1.3685E-01	2.5749E-05	298	1000	62.72	94.27
Water (gas)	-	-	-	-	-	-228.60	-
Hydrogen	-	-	-	-	-	0	0

References

- [1] A. Farshi, F. Shaiyegh, S. H. Burogerdi, and A. Dehgan, "FCC process role in propylene demands," *Pet. Sci. Technol.*, 2011, doi: 10.1080/10916460903451985.
- [2] A. Farshi, "Propylene Production Methods and FCC Process Rules in Propylene Demands," *Res. Inst. Petroeum Ind.*, 2008.
- [3] T. A. Peters, O. Liron, R. Tschentscher, M. Sheintuch, and R. Bredezen, "Investigation of Pd-based membranes in propane dehydrogenation (PDH) processes," *Chem. Eng. J.*, 2016, doi: 10.1016/j.cej.2015.09.068.
- [4] Y. Park *et al.*, "A catalytic composite membrane reactor system for hydrogen production from ammonia using steam as a sweep gas," *J. Memb. Sci.*, 2020, doi: 10.1016/j.memsci.2020.118483.
- [5] H. Lee, A. Kim, B. Lee, and H. Lim, "Comparative numerical analysis for an efficient hydrogen production via a steam methane reforming with a packed-bed reactor, a membrane reactor, and a sorption-enhanced membrane reactor," *Energy Convers. Manag.*, 2020, doi: 10.1016/j.enconman.2020.112839.
- [6] Y. Hayakawa, T. Miura, K. Shizuya, S. Wakazono, K. Tokunaga, and S. Kambara, "Hydrogen production system combined with a catalytic reactor and a plasma membrane reactor from ammonia," *Int. J. Hydrogen Energy*, 2019, doi: 10.1016/j.ijhydene.2018.12.141.
- [7] R. Sharma, A. Kumar, and R. K. Upadhyay, "Characteristics of a multi-pass membrane reactor to improve hydrogen recovery," *Int. J. Hydrogen Energy*, 2020, doi: 10.1016/j.ijhydene.2020.05.079.
- [8] P. Tandon and M. Jain, "Modeling and simulation of non-isothermal packed-bed membrane reactor for decomposition of hydrogen iodide," *Environ. Technol. Innov.*, 2020, doi: 10.1016/j.eti.2020.101162.
- [9] K. Ghasemzadeh, P. Morrone, A. Iulianelli, S. Liguori, A. A. Babaluo, and A. Basile, "H₂ production in silica membrane reactor via methanol steam reforming: Modeling and HAZOP analysis," *Int. J. Hydrogen Energy*, 2013, doi: 10.1016/j.ijhydene.2013.06.008.
- [10] K. Ghasemzadeh, J. N. Harasi, T. Y. Amiri, A. Basile, and A. Iulianelli, "Methanol steam reforming for hydrogen generation: A comparative modeling study between silica and Pd-based membrane reactors by CFD method," *Fuel Process. Technol.*, 2020, doi: 10.1016/j.fuproc.2019.106273.
- [11] E. V. Shelepova and A. A. Vedyagin, "Intensification of the dehydrogenation process of different hydrocarbons in a catalytic membrane reactor," *Chem. Eng. Process. - Process Intensif.*, 2020, doi: 10.1016/j.cep.2020.108072.

- [12] M. Dehdashtijahromi, M. Binazadeh, and M. Farsi, "Dynamic modeling, optimization and exergy analysis of novel membrane reactor for enhanced olefin and pure hydrogen production via heavy paraffin dehydrogenation," *Int. J. Hydrogen Energy*, 2023, doi: 10.1016/j.ijhydene.2023.03.454.
- [13] J. Liu *et al.*, "Modeling of propane dehydrogenation combined with chemical looping combustion of hydrogen in a fixed bed reactor," *Chinese J. Chem. Eng.*, vol. 47, 2022, doi: 10.1016/j.cjche.2021.07.032.
- [14] A. Darvishi, R. Davand, F. Khorasheh, and M. Fattahi, "Modeling-based optimization of a fixed-bed industrial reactor for oxidative dehydrogenation of propane," *Chinese J. Chem. Eng.*, vol. 24, no. 5, 2016, doi: 10.1016/j.cjche.2015.12.018.
- [15] M. Sheintuch and R. M. Dessau, "Observations, modeling and optimization of yield, selectivity and activity during dehydrogenation of isobutane and propane in a Pd membrane reactor," *Chem. Eng. Sci.*, vol. 51, no. 4, 1996, doi: 10.1016/0009-2509(95)00285-5.
- [16] D. Xiang, P. Li, and X. Yuan, "Process optimization, exergy efficiency, and life cycle energy consumption-GHG emissions of the propane-to-propylene with/without hydrogen production process," *J. Clean. Prod.*, vol. 367, 2022, doi: 10.1016/j.jclepro.2022.133024.
- [17] Z. D. Ziaka, R. G. Minet, and T. T. Tsotsis, "A high temperature catalytic membrane reactor for propane dehydrogenation," *J. Memb. Sci.*, 1993, doi: 10.1016/0376-7388(93)85071-4.
- [18] E. Gobina, K. Hou, and R. Hughes, "Equilibrium-shift in alkane dehydrogenation using a high-temperature catalytic membrane reactor," *Catal. Today*, 1995, doi: 10.1016/0920-5861(95)00115-V.
- [19] E. Gobina, K. Hou, and R. Hughes, "Ethane dehydrogenation in a catalytic membrane reactor coupled with a reactive sweep gas," *Chem. Eng. Sci.*, 1995, doi: 10.1016/0009-2509(95)00059-E.
- [20] J. P. Collins *et al.*, "Catalytic Dehydrogenation of Propane in Hydrogen Permselective Membrane Reactors," *Ind. Eng. Chem. Res.*, 1996, doi: 10.1021/ie960133m.
- [21] H. Weyten, K. Keizer, A. Kinoo, J. Luyten, and R. Leysen, "Dehydrogenation of Propane Using a Packed-Bed Catalytic Membrane Reactor," *AIChE J.*, 1997, doi: 10.1002/aic.690430717.
- [22] K. Hou and R. Hughes, "A comparative simulation analysis of propane dehydrogenation in composite and microporous membrane reactors," *J. Chem. Technol. Biotechnol.*, 2003, doi: 10.1002/jctb.737.
- [23] L. P. Didenko, V. I. Savchenko, L. A. Sementsova, P. E. Chizhov, and L. A.

- Bykov, "Dehydrogenation of propane in a combined membrane reactor with hydrogen-permeable palladium module," *Pet. Chem.*, 2013, doi: 10.1134/S0965544113010039.
- [24] M. Farsi, A. Jahanmiri, and M. R. Rahimpour, "Simultaneous isobutane dehydrogenation and hydrogen production in a hydrogen-permselective membrane fixed bed reactor," *Theor. Found. Chem. Eng.*, 2014, doi: 10.1134/S0040579514060049.
- [25] A. Ricca, V. Palma, G. Iaquaniello, E. Palo, and A. Salladini, "Highly selective propylene production in a membrane assisted catalytic propane dehydrogenation," *Chem. Eng. J.*, 2017, doi: 10.1016/j.cej.2017.08.064.
- [26] M. Sheintuch and O. Nekhamkina, "Architecture alternatives for propane dehydrogenation in a membrane reactor," *Chem. Eng. J.*, 2018, doi: 10.1016/j.cej.2018.04.137.
- [27] R. Antonio, T. Livia, I. Gaetano, P. Emma, and P. Vincenzo, "Pd-membrane Integration in a Propane Dehydrogenation Process for Highly Selective Propylene Production," *Int. J. Membr. Sci. Technol.*, 2018, doi: 10.15379/2410-1869.2018.05.01.01.
- [28] A. Ricca, F. Montella, G. Iaquaniello, E. Palo, A. Salladini, and V. Palma, "Membrane assisted propane dehydrogenation: Experimental investigation and mathematical modelling of catalytic reactions," *Catal. Today*, 2019, doi: 10.1016/j.cattod.2017.10.017.
- [29] S. Assabumrungrat, T. Rienchalanusarn, P. Praserttham, and S. Goto, "Theoretical study of the application of porous membrane reactor to oxidative dehydrogenation of n-butane," *Chem. Eng. J.*, 2002, doi: 10.1016/S1385-8947(01)00146-2.
- [30] E. V. Shelepova, A. A. Vedyagin, I. V. Mishakov, and A. S. Noskov, "Mathematical modeling of the propane dehydrogenation process in the catalytic membrane reactor," *Chem. Eng. J.*, 2011, doi: 10.1016/j.cej.2011.06.048.
- [31] E. V. Shelepova, A. A. Vedyagin, and A. S. Noskov, "Effect of catalytic combustion of hydrogen on dehydrogenation in a membrane reactor. II. Dehydrogenation of ethane. Verification of the mathematical model," *Combust. Explos. Shock Waves*, 2013, doi: 10.1134/S0010508213020019.
- [32] S. S. E. H. Elnashaie, T. Moustafa, T. Alsoudani, and S. S. Elshishini, "Modeling and basic characteristics of novel integrated dehydrogenation-hydrogenation membrane catalytic reactors," 2000, doi: 10.1016/S0098-1354(00)00335-5.
- [33] T. M. Moustafa and S. S. E. H. Elnashaie, "Simultaneous production of styrene and cyclohexane in an integrated membrane reactor," *J. Memb. Sci.*, 2000, doi: 10.1016/S0376-7388(00)00488-9.
- [34] M. E. E. Abashar and A. A. Al-Rabiah, "Production of ethylene and cyclohexane

- in a catalytic membrane reactor,” *Chem. Eng. Process. Process Intensif.*, 2005, doi: 10.1016/j.cep.2005.02.004.
- [35] N. S. Abo-Ghander, J. R. Grace, S. S. E. H. Elnashaie, and C. J. Lim, “Modeling of a novel membrane reactor to integrate dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline,” *Chem. Eng. Sci.*, 2008, doi: 10.1016/j.ces.2007.12.007.
- [36] M. Garside, “Statistics and facts on chemical industry,” 2020. <https://www.statista.com>.
- [37] M. Garside, “Statistics and facts on chemical industry,” 2020. .
- [38] “Knoema – World Data Atlas.” <https://knoema.com>.
- [39] M. P. Lobera, C. Téllez, J. Herguido, and M. Menéndez, “Transient kinetic modelling of propane dehydrogenation over a Pt-Sn-K/Al₂O₃ catalyst,” *Appl. Catal. A Gen.*, vol. 349, no. 1–2, 2008, doi: 10.1016/j.apcata.2008.07.025.
- [40] B. Amon, H. Redlingshöfer, E. Klemm, E. Dieterich, and G. Emig, “Kinetic investigations of the deactivation by coking of a noble metal catalyst in the catalytic hydrogenation of nitrobenzene using a catalytic wall reactor,” *Chem. Eng. Process. Process Intensif.*, vol. 38, no. 4–6, 1999, doi: 10.1016/S0255-2701(99)00037-9.
- [41] L. C. Young, “Orthogonal collocation revisited,” *Comput. Methods Appl. Mech. Eng.*, 2019, doi: 10.1016/j.cma.2018.10.019.
- [42] B. A. Finlayson, *Nonlinear Analysis in Chemical Engineering*. 1980.
- [43] G. F. Carey and B. A. Finlayson, “Orthogonal collocation on finite elements,” *Chem. Eng. Sci.*, 1975, doi: 10.1016/0009-2509(75)80031-5.
- [44] H. S. Fogler, *Elements of Chemical Reaction Engineering Fifth Edition*. 2016.
- [45] B. V. Babu, P. G. Chakole, and J. H. Syed Mubeen, “Multiobjective differential evolution (MODE) for optimization of adiabatic styrene reactor,” *Chem. Eng. Sci.*, 2005, doi: 10.1016/j.ces.2005.02.073.
- [46] A. K. Y. Yee, A. K. Ray, and G. P. Rangaiah, “Multiobjective optimization of an industrial styrene reactor,” *Comput. Chem. Eng.*, 2003, doi: 10.1016/S0098-1354(02)00163-1.
- [47] A. Messac, A. Ismail-Yahaya, and C. A. Mattson, “The normalized normal constraint method for generating the Pareto frontier,” *Struct. Multidiscip. Optim.*, 2003, doi: 10.1007/s00158-002-0276-1.
- [48] C. Yaws, L, “Yaws’ Handbook of Thermodynamic and Physical Properties of Chemical Compounds,” *Knovel*, vol. 3, no. c. 2003.

Vitae

Name	:Omar Nabeel Al Deeb
Nationality	:Egyptian
Date of Birth	:11/27/1994
Email	:omaraldeeb@hotmail.com
Current Address	:35 B St., Building 71, Al Rakkah Al Janubiya, Al Khobar, Saudi Arabia, 34226
Native Address	:1006/23 St., Miami, Awel Montazah, Alexandria, Egypt
Academic Background	:Holder of a BSc in Chemical Engineering from University of Bahrain (GPA: 4.0/4.0)
Work Experience	:Process Design Engineer (March 2017 – December 2021) Sr. Process & Product Engineer (December 2021-Present) Teacher Assistant (Jan 2013 – Jan 2017)
Previous Publication:	S. Haji, Omar A. Deeb and A. Hassan, "Optimizing a methanol reactor in Aspen Plus," 2019 8th International Conference on Modeling Simulation and Applied Optimization (ICMSAO), Manama, Bahrain, 2019, pp. 1-5, doi: 10.1109/ICMSAO.2019.8880381.