

การสร้างแบบจำลองและการเชื่อมโยงกระบวนการเรียนรู้



นายปฐมพงศ์ บัณฑิตวิวานนท์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

ภาควิชาวิศวกรรมเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2533

ISBN 974-578-249-1

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

016939

110309998

MODELING AND SIMULATION OF REFORMING PROCESS

Mr. Prathompong Panyavivanond

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering

Department of Chemical Engineering

Graduate School

Chulalongkorn University

1990

ISBN 974-578-249-1



Thesis Title Modeling and Simulation of Reforming Process
By Mr. Prathompong Panyavivanond
Department Chemical Engineering
Thesis Advisor Associate Professor Sutham Vanichseni, Ph.D.
Co Advisor Dr. Pailin Chuchottaworn

Accepted by the Graduated School, Chulalongkorn University in
Partial Fulfillment of the Requirements for the Master's Degree.

..... *Thavorn Vajrabhaya* Dean of Graduate School
(Professor Thavorn Vajrabhaya, Ph.D.)

Thesis Committee

..... *K. Sukanjanatee* Chairman
(Associate Professor Kroekchai Sukanjanatee, Ph.D.)

..... *Wiwut Tanthapanichakoon* Member
(Associate Professor Wiwut Tanthapanichakoon, Ph.D.)

..... *Pienpak Tassakorn* Member
(Pienpak Tassakorn, Ph.D.)

..... *Pailin Chuchottaworn* Member
(Pailin Chuchottaworn, Ph.D.)

..... *Sutham Vanichseni* Member
(Associate Professor Sutham Vanichseni, Ph.D.)



ประชุมพงศ์ ปัญญาวิวานนท์ : การสร้างแบบจำลองและการซิมูเลตกระบวนการรีฟอร์มมิง (MODELING AND SIMULATION OF REFORMING PROCESS)

อ.ที่ปรึกษา : รศ.ดร. สุธรรม วาณิชเสนี, ดร. ไพรินทร์ ชูโชติถาวร,
160 หน้า. ISBN 974-578-249-1

แบบจำลองของกระบวนการรีฟอร์มมิงโดยใช้คะตาลีสต์ได้ถูกพัฒนาขึ้นในระบบของปฏิกรณ์แบบเบดนิ่ง ซึ่งมีแพลทินัมบนอลูมินาเป็นตัวคะตาลีสต์ภายใต้สภาวะปฏิบัติการแบบ Isothermal และ adiabatic สารป้อนเข้าเป็นไฮโดรคาร์บอนที่มีจำนวนคาร์บอน 6 ตัว และ คาร์บอน 7 ตัว แบบจำลองใหม่ได้ตั้งสมมุติฐานที่ว่าปฏิกริยาระหว่างคาร์บอน 6 ตัว และ คาร์บอน 7 ตัวไม่ขึ้นแก่กัน ผลที่ได้จากการซิมูเลตได้เปรียบเทียบกับผลการทดลองจริงพบว่าสอดคล้องกัน แบบจำลองที่พัฒนาขึ้นนี้สามารถที่จะถูกขยายไปใช้กับคะตาลีสต์ตัวอื่น โดยการหาค่าคงที่ของปฏิกริยาจากการทดลอง โดยใช้สมการอัตราเร็วของ Houggen-Watson วิธีการของแบบจำลองนี้อาจจะนำไปใช้ในการพัฒนาแบบจำลองของกระบวนการรีฟอร์มมิงโดยใช้คะตาลีสต์สำหรับจำนวนคาร์บอน 8 ถึง 10 ตัวได้

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2533

ลายมือชื่อนิติกรประชุมพงศ์ ปัญญาวิวานนท์
ลายมือชื่ออาจารย์ที่ปรึกษา
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

PRATHOMPONG PANYAVIVANOND : MODELING AND SIMULATION OF
REFORMING PROCESS. THESIS ADVISOR : ASSO. PROF. SUTHAM
VANICHSENI, Ph.D., PAILIN CHUCHOTTAWORN, Ph.D. 160 PP.
ISBN 974-576-249-1

The modeling of a catalytic reforming process was developed for a system of a fixed-bed reactor with a commercial platinum on alumina type of catalyst under both isothermal and adiabatic mode of operation. The feedstock is limited to a mixture of C_6 and C_7 hydrocarbons. The new model is based on the assumption that the reaction of C_6 and C_7 are independent. The simulated results are in agreement with existing experimental data. The model can be extended to other catalysts by determining the rate constants from experiments using Hougen-Watson rate equations. This model approach may be applicable for the catalytic reforming model development of C_6 - C_{10} feedstock.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2533

ลายมือชื่อนิสิต ปริญญพงศ์ ปัทมวิจิตร
ลายมือชื่ออาจารย์ที่ปรึกษา สุทนต์ วนิชเสนี
ลายมือชื่ออาจารย์ที่ปรึกษาพร้อม ปริญญพงศ์ ปัทมวิจิตร

ACKNOWLEDGEMENTS

I wish to express my appreciation to Associate Professor Sutham Vanichseni and Dr. Pailin Chuchottaworn for his invaluable advice and general comments have been extremely helpful to this study. When the thesis was begun, I recieved valuable assistance from Dr. Pailin Chuchottaworn. There was the useful suggestion by Associate Professor Wiwat tanthapanichakoon and Dr. Pienpak Tassakorn. Special thanks are also due to all of my friends for their general help. Finally, the love, patience, and forbearance of my parents have been very important factors in making my thesis possible.

Prathompong Panyavivanond

Oct, 1990

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



TABLE OF CONTENTS

	page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
TABLE OF CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
NOMENCLATURE	xv
CHAPTER	
1. INTRODUCTION.....	1
1.1 The Objective of This Study.....	2
1.2 The Scope of This Study.....	3
2. REVIEWS OF CATALYTIC REFORMING.....	5
2.1 Product From Reforming.....	5
2.2 Feedstocks For Reforming.....	6
2.3 Catalytic Reforming For Aromatic.....	8
2.4 Process Design of Catalytic Reforming.....	9
2.4.1 Feed Preparation.....	11
2.4.2 Temperature Control.....	11
2.4.3 Reactor.....	12
2.4.4 Product Recovery.....	14
2.5 Reformer Classification.....	15
2.6 Commercial Processes.....	17
2.6.1 Historical Development.....	17
2.6.2 Licensed Reforming Processes.....	19

	page
3. THEORY OF REFORMING REACTION.....	33
3.1 Reforming Reaction.....	34
3.2 Reaction Rate.....	38
3.3 Rate Equations.....	39
3.4 Catalyst.....	41
4. REVIEW MODELING OF REFORMING PROCESSES.....	47
4.1 Introduction.....	47
4.2 Smith Reforming Model.....	48
4.2.1 Assumption.....	48
4.2.2 Reactor Model.....	49
4.2.3 Material Balance Equation.....	53
4.2.4 Energy Balance Equation.....	58
4.2.5 Operating Condition And Reactor Type....	60
4.2.6 Limitation.....	61
4.3 Krane et al. Reforming Model.....	61
4.3.1 Assumption.....	61
4.3.2 Rate Equation And Reaction Model.....	65
4.3.3 Limitation.....	65
4.4 Henningsen et al. Reforming Model.....	67
4.4.1 Assumption.....	67
4.4.2 Rate Equation And Reaction Model.....	67
4.4.3 Limitation.....	69
5. MODELING AND SIMULATION.....	71
5.1 Assumptions.....	72
5.2 Reactor Model.....	75
5.2 Model Development.....	80
5.4 Development of Computer Code for New Model....	87

	page
6. SIMULATION RESULTS AND DISCUSSION.....	89
6.1 Simulation Study.....	89
6.2 Comparison of Simulation and Experimental Results.....	90
7. CONCLUSIONS.....	119
REFERENCES.....	120
APPENDICES.....	123
APPENDIX A. Physical Properties.....	124
APPENDIX B. Groups in Kinetic Equations for Reaction on Solid Catalysts.....	128
APPENDIX C. Equilibrium Constant.....	130
APPENDIX D. Viscosity Gas Mixture	131
APPENDIX E. Programming.....	133

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



LIST OF TABLES

	page
Table 2-1 Catalytic Reforming Processes.....	20
Table 2-2 Commercial Catalytic Reforming Processes.....	21
Table 4-1 Feedstock Analysis and System Operating Parameters.....	62
Table 4-2 First-Order Rate Constants for Naphtha-Reforming Reactions.....	66
Table 4-3 Reaction Rate Constant.....	70
Table 5-1 Arrhenius Constants, Activation Energies and Adsorption Constant for C ₆ Hydrocarbons Obtained from Marin et al, (1982).....	78
Table 5-2 Arrhenius Constants, Activation Energies and Adsorption Constant for C ₇ Hydrocarbons Obtained from Van Trimpont et al, (1986) and (1988).....	80
Table 6-1 Input Data Used in the Simulation.....	92
Table 6-2 Input Data Used in the Simulation of Mixed C ₆ and C ₇ Hydrocarbons.....	93
Table 6-3 Input Data Used in the Simulation of East-West Texas C ₆ to C ₇ Hydrocarbons.....	94
Table 6-4 The Error of the Simulation.....	116

จุฬาลงกรณ์มหาวิทยาลัย



LIST OF FIGURES

	page
Figure 1-1 Development of the Petrochemical Complex in Thailand.....	4
Figure 2-1 Motor Fuel Refinery with Catalytic Reforming...	7
Figure 2-2 Refinery with Motor Fuel and BTX Catalytic Reforming.....	10
Figure 2-3 Process Flow Scheme of a Catalytic Reformer....	13
Figure 2-4 IFP Continuous Regenerative System.....	22
Figure 2-5 IFP Semiregenerative Reformer.....	23
Figure 2-6 Magnaforming Flow Diagram.....	26
Figure 2-7 Catalyst Regeneration Section for UOP Continuous Catalyst Regeneration Process.....	26
Figure 2-8 Platforming UOP Continuous Catalyst Regeneration Process.....	27
Figure 2-9 Powerforming Unit.....	28
Figure 2-10 Rheniforming Process with Hydrotreater.....	31
Figure 2-11 Ultraforming Process.....	32
Figure 3-1 Reactions of a Multifunction Reforming.....	43
Figure 4-1 Tubular Reactor.....	55
Figure 4-2 Schematic of Four-Reactor Reforming.....	63
Figure 4-3 Calculated Temperature Profiles in the Four Reactors.....	63
Figure 4-4 Scheme of General Reaction of Reforming Processes.....	68
Figure 5-1 Reaction Network for the Reforming of C ₆ Hydrocarbons.....	74
Figure 5-2 Lumped Reaction Network for the Reforming of C ₇ Hydrocarbons.....	74

	page
Figure 5-3 Flow Chart of the Programming.....	88
Figure 6-1 Flow Sheet of Two-Reactor Reforming for Case 23 and 24 of Table 6-3.....	91
Figure 6-2 Conversion at 460.9 °C, 16 bar, H ₂ /hydrocarbon of 9.98, and n-Hexane Feed. Experimental (Marin et al, (1982)): Points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al ₂ O ₃ Catalyst.....	98
Figure 6-3 Conversion at 419 °C, 10 bar, H ₂ /Hydrocarbon of 10.01, and 23DMB Feed. Experimental (Marin et al, (1982)): Points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al ₂ O ₃ Catalyst.....	99
Figure 6-4 Conversion at 435 °C, 10.5 bar, H ₂ /Hydrocarbon of 20, and n-Hexane, 2MP, 3MP, and 22DMB (0.4, 0, 0.3, 0.3) Feed. Experimental (Christoffel (1979)): Points. Catalyst: 0.35 %wt Pt on Al ₂ O ₃ Catalyst.....	100
Figure 6-5 Conversion at 435 °C, 10.5 bar, H ₂ /Hydrocarbon of 20, and n-Hexane, 2MP, 3MP, and 22DMB (0.1, 0.1, 0.7, 0.1) Feed. Experimental (Christoffel (1979)): Points. Catalyst: 0.35 %wt Pt on Al ₂ O ₃ Catalyst.....	101
Figure 6-6 Conversion at 454 °C, 13.7 bar, H ₂ /Hydrocarbon of 10, and MCP Feed. Experimental (Selman, (1975)): Points. Catalyst: 0.3 %pt, 0.3% Rhenium, and 0.6 %Cl on Alumina Catalyst.....	102

	page
Figure 6-7 Conversion at 420 °C, 20.5 bar, H ₂ /Hydrocarbon of 40, and n-Heptane Feed. Experimental (Van Trimont et al, (1988)): Points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al ₂ O ₃ Catalyst.....	103
Figure 6-8 Effect of Pressure on Yield of Hydrocracking. Experimental (Hettinger et al, (1955)): Points. Catalyst: 0.6 %wt Pt on Al ₂ O ₃ Catalyst.....	104
Figure 6-9 Dehydrogenation of Methylcyclohexane at Temperature 350 °C. Effect of Pressure and Hydrogen/Hydrocarbon Ratio on Yield of Toluene. Experimental (Van Trimont et al, (1986)): Points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al ₂ O ₃ Catalyst.....	105
Figure 6-10 Dehydrogenation of Methylcyclohexane at Temperature 400 °C. Effect of Pressure and Hydrogen/Hydrocarbon Ratio on Yield of Toluene. Experimental (Van Trimont et al, (1986)): Points. Catalyst: 0.59 %wt Pt, 0.67 %wt Cl on Al ₂ O ₃ Catalyst.....	106
Figure 6-11 Dehydrogenation of Methylcyclohexane at Pressure 48.2 bar and H ₂ /Hydrocarbon Ratio =6.6. Effect of Temperature and Feed Composition on Yield of Toluene. Experimental (Heinemann (1951)): Points. Catalyst: Platinum on Al ₂ O ₃ Catalyst.....	107

Figure 6-12	Dehydrogenation of Methylcyclohexane at H_2 /Hydrocarbon ratio =4. Effect of Temperature and Pressure on Yield of Toluene. Experimental (Heinemann (1951)):Points. Catalyst: Platinum on Al_2O_3 Catalyst.....	108
Figure 6-13	Comparison of Aromatic Yields Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 22 of Table 6-2.....	109
Figure 6-14	Comparison of Temperature profile in one Reactor Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 22 of Table 6-2.....	110
Figure 6-15	Comparison of Aromatic Yields Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 23 of Table 6-3.....	111
Figure 6-16	Comparison of Temperature profile in Two Reactors Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 23 of Table 6-3.....	112
Figure 6-17	Comparison of Aromatic Yields Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 24 of Table 6-3.....	113
Figure 6-18	Comparison of Temperature profile in Two Reactors Between Computed and experimental data (Meerbott, (1954)). Operating conditions are case 24 of Table 6-3.....	114
Figure 6-19	Comparison of the step size in the simulation.	115

NOMENCLATURE

A	Cross-section of reactor, m^2
ACH	Alkylcyclohexanes
ACP	Alkylcyclopentane
A_i	Frequency factor of reaction i
AR	Aromatics
BZ	Benzene
C	Carbon
C	Cracked products
C_i	Moles per mole of feed
C_j	Molar concentration of species j ($kmol/m^3$ fluid)
Cp_j	The heat capacity of species j, $kcal/kg \text{ } ^\circ C$
C_5^-	Cracked product of C_5^- hydrocarbons
C_6^-	Cracked product of C_6^- hydrocarbons
22DMB	2,2-dimethylbutane
23DMB	2,3-dimethylbutane
E	Activation energy, $kcal/kmol$
F_{HC}	Molar feed rate of hydrocarbon at initial condition, $kmol/hr$
F_j	Molar flow rate of i^{th} component, $kmol/hr$
ΔG_f°	Standard Gibbs free energy of formation, $kcal/g\text{-mol}$
H	Hydrogen
H_j	Partial molar enthalpy of species j, $kcal/kmol$
k_f	Rate constant for forward reaction
k_r	Rate constant for reverse reaction
Kp	Equilibrium constant
kc'	Rate constant for paraffins

kc''	Rate constant for naphthenes
K	Equilibrium constant, constant in the adsorption term
IP	i-Paraffins
M_A	Molecular weight of aromatic (C_nH_{2n-6})
M_F	Molecular weight of feed
M_j	Molecular weight of species j
M_P	Molecular weight of paraffin (C_nH_{2n+2})
M_N	Molecular weight of naphthene (C_nH_{2n})
MCH	Methylcyclohexane
MBP7	Multibranched isoheptane
MCP	Methylcyclopentane
2MP	2-Methylpentane
3MP	3-Methylpentane
n	Number of carbon atoms
n_i	Mole of component i per mole of feed
nHEP	n-Heptane
nHEX	n-Hexane
η_m	Viscosity of gas mixture
NP	Normal paraffins
5N7	Five-ring naphthenes with seven carbon atom
P_i	Partial pressure of component i, bar
r_i	Rate of reaction of component i
R	Ideal gas constant, kcal/kmol K
R_j	Total rate of change of the amount of component j
SBP7	Single-branched isoheptane
T	Temperature, K, °C
T_c	Critical temperature
TOL	Toluene
u	Three-dimensional mass average velocity vector
u_s	Superficial velocity, $m^3/m^2 \text{ hr}$
V_c	Critical volume, cm^3/mole

W	Weight of catalyst, kg
X_i	Fraction conversion
y_i	mole fraction of i in the mixture
Z	Axial reactor coordinate, $Z = \frac{W}{\rho_B A}$, m
Z_c	Critical compressibility factor

Greek Symbols

θ	Adsorption term for the metal function
γ	Adsorption term for the acid function
ρ_f	Fluid density, kg/m^3
ρ_B	Bulk density of the catalyst bed, kg cat./m^3
α_{ij}	Stoichiometric coefficient of component j in the i th reaction
λ	Thermal conductivity, $\text{kcal/m.hr}^\circ\text{C}$
μ	Dipole moment, debyes
μ_r	Dimensionless dipole moment
ω	Acentric factor

Subscripts

A,B	With respect to A, B,.....
A-B	Reaction $A \rightleftharpoons B$
A	Aromatics
F	Feed
N	Naphthenes
P	Paraffins

Superscripts

o	Inlet condition, standard condition
B	Bed
f	fluid