

Table of Contents

Chapter 1	Introduction.....	1
1.1	Motivation.....	1
1.2	Background.....	2
1.3	Modeling Approaches.....	4
1.4	Molecule-based Kinetic Modeling Strategy.....	5
1.5	The Premise.....	6
	References.....	7

Part I **Methods**

Chapter 2	Molecular Structure and Composition Modeling of Complex Feedstocks.....	11
2.1	Introduction.....	11
2.2	Analytical Characterization of Complex Feedstocks.....	13
2.3	Molecular Structure Modeling: A Stochastic Approach.....	14
2.3.1	Probability Density Functions (PDFs).....	15
2.3.1.1	PDFs Used to Describe Complex Mixtures.....	16
2.3.1.2	Molecular Structural Attributes.....	17
2.3.1.3	Appropriate PDF Forms.....	18
2.3.1.4	Discretization, Truncation, and Renormalization.....	19
2.3.1.5	Conditional Probability.....	21
2.3.2	Monte Carlo Construction.....	21
2.3.2.1	Monte Carlo Sampling Protocol.....	21
2.3.2.2	Optimal Representation of a Complex Feedstock.....	22
2.3.2.3	Sample Size.....	24
2.3.3	Quadrature Molecular Sampling.....	25
2.3.3.1	Quadrature Sampling Protocol.....	25
2.3.3.2	Fine-Tuning the Quadrature Molecular Representation.....	27
2.4	A Case Study: Light Gas Oil.....	27
2.5	Discussions and Summary.....	31
	References.....	32

Chapter 3	Automated Reaction Network Construction of Complex Process Chemistries	35
3.1	Introduction.....	35
3.2	Reaction Network Building and Control Techniques	39
3.2.1	Preprocessing Methodologies.....	39
3.2.1.1	Rule-Based Model Building	39
3.2.1.2	Seeding and Deseeding.....	42
3.2.2	<i>In Situ</i> Processing Methodologies.....	45
3.2.2.1	Generalized Isomorphism Algorithm as an On-the-Fly Lumping Tool.....	45
3.2.2.2	Stochastic Rules for Reaction Site Sampling.....	47
3.2.3	Postprocessing Methodologies	48
3.2.3.1	Generalized Isomorphism-Based Late Lumping	48
3.2.3.2	Species-Based and Reaction-Based Model Reduction.....	48
3.3	Properties of Reaction Networks	51
3.3.1	Properties of Species	51
3.3.2	Properties of Reactions	53
3.3.3	Characterization of the Reaction Network	54
3.4	Summary and Conclusions	54
	References	55
Chapter 4	Organizing Kinetic Model Parameters	57
4.1	Introduction.....	57
4.2	Rate Laws For Complex Reaction Networks	58
4.2.1	Kinetic Rate Laws at the Pathways Level	59
4.2.2	Kinetic Rate Laws at the Mechanistic Level.....	63
4.3	Overview of Linear Free Energy Relationships.....	65
4.4	Representative Results and Summary of LFERS for Catalytic Hydrocracking.....	70
4.5	Summary and Conclusions	75
	References	75
Chapter 5	Matching the Equation Solver to the Kinetic Model Type	79
5.1	Introduction.....	79
5.2	Mathematical Background.....	80
5.2.1	Underlying Numerical Methods for Solving DKM Systems	80
5.2.2	Stiffness in DKM Systems.....	81
5.2.3	Sparseness in DKM Systems	82

5.3	Experiments	83
5.3.1	Candidate DKMs	83
5.3.2	Candidate Solvers	83
5.3.3	Experiment Setup	85
5.4	Results and Discussion	85
5.4.1	Pathways-Level DKM	86
5.4.2	Mechanistic-Level DKM	87
5.4.3	DKM Model Solving Guidelines	88
5.5	Summary and Conclusions	89
	References	89

Chapter 6 Integration of Detailed Kinetic Modeling Tools and Model Delivery Technology 91

6.1	Introduction	91
6.2	Integration of Detailed Kinetic Modeling Tools	92
6.2.1	The Integrated Kinetic Modeler's Toolbox	92
6.2.1.1	The Molecule Generator (MolGen)	92
6.2.1.2	The Reaction Network Generator (NetGen)	94
6.2.1.3	The Model Equation Generator (EqnGen)	95
6.2.1.4	The Model Solution Generator (SolGen)	95
6.2.2	Parameter Optimization and Property Estimation	96
6.2.2.1	The Parameter Optimization (ParOpt) Framework	96
6.2.2.2	Optimization Algorithms	96
6.2.2.3	The Objective Function	98
6.2.2.4	Property Estimation of Mixtures	98
6.2.2.5	The End-to-End Optimization Strategy	99
6.2.3	Conclusions	99
6.3	KMT Development and Model Delivery	100
6.3.1	Platform and Porting	100
6.3.2	Data Issues	102
6.3.3	User Interface Issues	102
6.3.4	Documentation Issues	103
6.3.5	Lessons Learned	103
6.4	Summary	103
	References	104

Part II **Applications**

Chapter 7 Molecule-Based Kinetic Modeling of Naphtha Reforming 109

7.1	Introduction	109
-----	--------------------	-----

7.2	Modeling Approach	110
7.3	Model Development	111
7.3.1	Dehydrocyclization.....	112
7.3.2	Hydrocracking	114
7.3.3	Hydrogenolysis.....	115
7.3.4	Paraffin Isomerization.....	115
7.3.5	Naphthene Isomerization.....	116
7.3.6	Dehydrogenation (Aromatization).....	116
7.3.7	Dealkylation.....	116
7.3.8	Coking	117
7.4	Automated Model Building.....	117
7.5	The Model For C14 Naphtha Reforming.....	118
7.6	Model Validation.....	119
7.7	Summary and Conclusions.....	121
	References	121

Chapter 8 Mechanistic Kinetic Modeling of Heavy Paraffin Hydrocracking..... 123

8.1	Introduction.....	123
8.2	Mechanistic Modeling Approach	123
8.3	Model Development	126
8.3.1	Reaction Mechanism	126
8.3.2	Reaction Families	127
8.3.2.1	Dehydrogenation and Hydrogenation.....	127
8.3.2.2	Protonation and Deprotonation.....	127
8.3.2.3	Hydride and Methyl Shift.....	128
8.3.2.4	PCP Isomerization.....	129
8.3.2.5	β -Scission	130
8.3.2.6	Inhibition Reaction.....	130
8.3.3	Automated Model Building.....	131
8.3.4	Kinetics: Quantitative Structure Reactivity Correlations.....	133
8.3.5	The C16 Paraffin Hydrocracking Model at the Mechanistic Level.....	134
8.4	Model Results and Validation.....	135
8.5	Extension to C80 Model.....	137
8.6	Summary and Conclusions.....	138
	References	139

Chapter 9 Molecule-Based Kinetic Modeling of Naphtha Hydrotreating 141

9.1	Introduction.....	141
9.2	Modeling Approach.....	142

9.3	Model Development	144
9.3.1	Reaction Families	144
9.3.1.1	Reactions of Sulfur Compounds: Desulfurization and Saturation	145
9.3.1.2	Olefin Hydrogenation.....	151
9.3.1.3	Aromatic Saturation	151
9.3.1.4	Denitrogenation	151
9.3.2	Reaction Kinetics	152
9.3.3	Automated Model Building.....	153
9.4	Results and Discussion	154
9.4.1	The Naphtha Hydrotreating Model.....	154
9.4.2	Model Optimization and Validation	154
9.5	Summary and Conclusions	155
	References	157

Chapter 10 Automated Kinetic Modeling of Gas Oil
Hydroprocessing

		159
10.1	Introduction.....	159
10.2	Modeling Approach	160
10.3	Model Development	166
10.3.1	Feedstock Characterization and Construction	166
10.3.2	Reaction Families	167
10.3.2.1	Reactions of Aromatics and Hydroaromatics	168
10.3.2.2	Reactions of Naphthenes	172
10.3.2.3	Reactions of Paraffins	173
10.3.2.4	Reactions of Olefins	173
10.3.2.5	Reactions of Sulfur Compounds	173
10.3.2.6	Reactions of Nitrogen Compounds	174
10.3.3	Kinetics: LHHW Formalism.....	175
10.3.4	Automated Model Building	177
10.4	Results and Discussion.....	178
10.5	Summary and Conclusions.....	179
	References	181

Chapter 11 Molecular Modeling of Fluid Catalytic Cracking

		183
11.1	Introduction.....	183
11.2	Model Pruning Strategies For Mechanistic Modeling.....	184
11.2.1	Mechanistic Modeling.....	184
11.2.2	Rules Based Reaction Modeling.....	184
11.2.2.1	Reaction Rules	184
11.2.2.2	Stochastic Rules	186

11.3	Kinetics	191
11.3.1	Intrinsic Kinetics	191
11.3.2	Coking Kinetics.....	192
11.4	Model Diagnostics and Results.....	193
11.5	Mechanistic Model Learning as a Basis for Pathways Level Modeling	194
11.6	Pathways Modeling	194
11.6.1	Pathways Model Development Approach.....	195
11.6.2	Pathways Level Reaction Rules.....	196
11.6.2.1	Cracking Reactions	196
11.6.2.2	Isomerization Reactions	197
11.6.2.3	Methyl Shift Reactions	198
11.6.2.4	Hydrogenation and Dehydrogenation Reactions	198
11.6.2.5	Aromatization.....	198
11.6.3	Coking Kinetics.....	198
11.6.4	Gas Oil Composition.....	199
11.6.5	Model Diagnostics and Results.....	199
11.7	Summary and Conclusions	203
	References	203

Chapter 12 Automated Kinetic Modeling of Naphtha Pyrolysis..... 205

12.1	Introduction.....	205
12.2	Current Approach to Model Building	206
12.3	Pyrolysis Model Development	207
12.3.1	Reaction Rules.....	208
12.3.1.1	Initiation	208
12.3.1.2	Hydrogen Abstraction	208
12.3.1.3	β -Scission.....	209
12.3.1.4	Radical Addition to Olefins	210
12.3.1.5	Diels–Alder Reaction.....	210
12.3.1.6	Termination Reactions	211
12.4	Contribution of Reaction Families	211
12.5	Reaction Network Diagnostics	214
12.6	Parameter Estimation.....	215
12.7	Summary and Conclusions	216
	References	218

Chapter 13 Summary and Conclusions..... 221

13.1	Summary.....	221
13.1.1	Molecular Structure and Composition Modeling of Complex Feedstocks	222

13.1.2	Automated Reaction Network Building of Complex Process Chemistries	223
13.1.3	Kinetic Rate Organization and Evaluation of Complex Process Chemistries	224
13.1.4	Model Solving Techniques for Detailed Kinetic Models	224
13.1.5	Integration of Detailed Kinetic Modeling Tools and Model Delivery Technology.....	225
13.1.6	Molecule-Based Kinetic Modeling of Naphtha Reforming.....	226
13.1.7	Mechanistic Kinetic Modeling of Heavy Paraffin Hydrocracking.....	226
13.1.8	Molecule-Based Kinetic Modeling of Naphtha Hydrotreating	227
13.1.9	Automated Kinetic Modeling of Gas Oil Hydroprocessing	228
13.1.10	Molecular Modeling of Fluid Catalytic Cracking.....	229
13.1.11	Automated Kinetic Modeling of Naphtha Pyrolysis.....	229
13.2	Conclusions.....	229
Index	231