Contents

Preface XI

List of Contributors XIX

- Part I Industrial Applications
- 1 Industrial Applications of Reactive Distillation 3
- 1.1 Introduction 3
- 1.2 Etherification: MTBE, ETBE, and TAME 14
- 1.3 Dimerization, Oligomerization, and Condensation 15
- 1.4 Esterification: Methyl Acetate and Other Esters 16
- 1.5 Hydrolysis of Esters 18
- 1.6 Hydration 20
- 1.7 Hydrogenation/Hydrodesulfurization/Hydrocracking 20
- 1.7.1 Benzene to Cyclohexane 21
- 1.7.2 Selective Hydrogenation of C₄ Stream 21
- 1.7.3 Hydrogenation of Pentadiene 21
- 1.7.4 C₄ Acetylene Conversion 22
- 1.7.5 Hydrodesulfurization, Hydrodenitrogenation, and Hydrocracking 22
- 1.7.6 Miscellaneous Hydrogenations 22
- 1.8 Chlorination 23
- 1.9 Acetalization/Ketalization 23
- 1.10 Recovery and Purification of Chemicals 24
- 1.11 Difficult Separations 25
- 1.12 Chemical Heat Pumps 26
- 1.13 RD with Supercritical Fluids 26
- 1.14 Conclusions 26
- 2 Reactive Distillation Process Development in the Chemical Process Industries 30
- 2.1 Introduction 30
- 2.2 Process Synthesis 32
- 2.3 Process Design and Optimization 35

- VI Contents
 - 2.4 Limitations of the Methods for Synthesis and Design:
 - the Scale-Up Problem 37
 - 2.5 Choice of Equipment 38
 - 2.6 Some Remarks on the Role of Catalysis 46
 - 2.7 Conclusions 46
 - 2.8 Acknowledgments 47
 - 2.9 Notation 47

3 Application of Reactive Distillation and Strategies in Process Design 49

- 3.1 Introduction 49
- 3.2 Challenges in Process Design for Reactive Distillation 51
- 3.2.1 Feasibility Analysis 51
- 3.2.2 Catalyst and Hardware Selection 51
- 3.2.3 Column Scale-Up 51
- 3.3 MTBE Decomposition via Reactive Distillation 52
- 3.3.1 Conceptual Design 52
- 3.3.2 Model Development 54
- 3.3.2.1 Catalyst Selection and Reaction Kinetics 55
- 3.3.2.2 Phase Equilibrium Model 55
- 3.3.2.3 Steady-State Simulation 56
- 3.3.3 Lab-Scale Experiments 57
- 3.3.4 Pilot-Plant Experiments 58
- 3.4 Conclusions 61
- Part II Physicochemical Fundamentals
- 4 Thermodynamics of Reactive Separations 65
- 4.1 Introduction 65
- 4.2 Process Models for Reactive Distillation 66
- 4.2.1 Outline 66
- 4.2.2 Case Study: Methyl Acetate 66
- 4.3 Equilibrium Thermodynamics of Reacting Multiphase Mixtures 70
- 4.4 Fluid Property Models for Reactive Distillation 74
- 4.4.1 Outline 74
- 4.4.2 Examples 75
- 4.4.2.1 Hexyl Acetate: Sensitivity Analysis 75
- 4.4.2.2 Methyl Acetate: Prediction of Polynary Vapor-Liquid Equilibria 77
- 4.4.2.3 Butyl Acetate: Thermodynamic Consistency 81
- 4.4.2.4 Ethyl Acetate: Consequences of Inconsistency 82
- 4.4.2.5 Formaldehyde + Water + Methanol:
 - Intrinsically Reactive Complex Mixture 83
- 4.5 Experimental Studies of Phase Equilibria in Reacting Systems 88
- 4.5.1 Outline 88
- 4.5.2 Reactive Vapor–Liquid Equilibria 90
- 4.5.2.1 Batch Experiments 90
- 4.5.2.2 Flow Experiments 91

- 4.5.2.3 Recirculation Experiments 92
- 4.6 Conclusions 92
- 4.7 Acknowledgments 93
- 4.8 Notation 93
- 5 Importance of Reaction Kinetics for Catalytic Distillation Processes 97
- 5.1 Introduction 97
- 5.2 Reactive Ideal Binary Mixtures 98
- 5.2.1 Reaction-Distillation Process with External Recycling 100
- 5.2.1.1 (∞,∞)-Analysis 101
- 5.2.1.2 (∞ , N_{\min})-Analysis 102
- 5.2.2 Distillation Column with Reactive Reboiler 103
- 5.2.3 Fully Reactive Distillation Column 106
- 5.3 Kinetic Effects on Attainable Products 109
- 5.3.1 Singular Point Analysis 110
- 5.3.2 Ideal Ternary Mixtures 112
- 5.3.2.1 Case a: $a_{AC} = 0.2$, $a_{BC} = 3.0$ 112
- 5.3.2.2 Case b: $a_{AC} = 5.0$, $a_{BC} = 3.0$ 112
- 5.3.3 Non-Ideal Mixtures 115
- 5.3.3.1 Synthesis of MTBE 115
- 5.3.3.2 Synthesis of TAME 117
- 5.3.4 Systems with Liquid-Phase Splitting 121
- 5.3.5 Systems with Interfacial Mass-Transfer Resistances 126
- 5.4 Determination and Analysis of Reaction Kinetics 129
- 5.4.1 Physicochemical Transport Phenomena 129
- 5.4.2 Process Evaluation by Dimensionless Numbers 131
- 5.4.3 Formulation of Reaction Rate Expressions 133
- 5.4.4 Importance of Transport Resistances for Column Operation 135
- 5.5 Conclusions 138
- 5.6 Acknowledgments 139
- 5.7 Notation 140
- Part III Process Design

6 Feasibility and Process Alternatives for Reactive Distillation 145

- 6.1 Introduction 145
- 6.2 Motivation 147
- 6.3 Flash Cascade Model 153
- 6.4 Feasibility Hypothesis 156
- 6.5 Bifurcation Analysis of the Flash Cascade Model 160
- 6.6 Conclusions 165
- 6.7 Notation 165

VIII	Contents

- Hardware Selection and Design Aspects 7 for Reactive Distillation Columns 169 Introduction 169 7.1 Hardware for Homogeneous Reactive Distillation 169 7.2 Case Study for Methyl Acetate Production 173 7.2.1 Hardware for Heterogeneous Reactive Distillation 177 7.3 Different Hardware Configurations 177 7.3.1 Hardware Selection Aspects 183 7.3.2 The Side-Reactor Concept 185 7.4 7.5 Conclusions 187 Acknowledgments 188 7.6 **Development of Unstructured Catalytic Packing** 8 for Reactive Distillation Processes 190 Introduction 190 8.1 Requirements for RD Catalytic Packing 190 8.2 State of the Art: Catalytic Packing for RD Processes 191 8.3 8.3.1 Commercial Packing 191 8.3.2 Alternative Concepts 193 8.3.2.1 Catalysts Made of Pure Catalytic Material 193 8.3.2.2 Catalysts Supported on Carrier Materials 194 8.4 New Catalyst Concept: Porous Polymer/Carrier Composite 195 Requirements for the Carrier Materials 198 8.4.1 8.4.2 Requirements for the Polymerization Process 199 8.5 Preparation of Sulfonated Ion-Exchange Polymer/Carrier Catalysts 200 8.6 Performance of Polymer/Carrier Catalysts 203 8.6.1 Influence of Polymer Content and Reactant Concentration 204 8.6.2 Influence of Reaction Temperature 205 8.6.3 Influence of Cross-Linking 207 8.6.4 Influence of Cross-Linking at Low Polymer Content 207 8.6.5 Influence of Cross-Linking at High Polymer Content 209 8.7 Outlook: Extension to Other Synthetic Processes With Integrated Separation 210 8.7.1 Reactive Stripping 210 8.7.2 Reactive Chromatography 211 8.7.3 Polymer-Assisted Solution-Phase Organic Synthesis 212 8.8 Conclusions 212 Modeling and Process Control Part IV 9 Modeling of Homogeneous and Heterogeneous Reactive Distillation Processes 217 9.1 Introduction 217 Equilibrium Stage Models 217 9.2 9.3 Non-equilibrium Stage Modeling 220
 - 9.3.1 The Conventional NEQ Model 220

- 9.3.2 NEQ Modeling of Reactive Distillation 223
- 9.3.3 Homogeneous Systems 223
- 9.3.4 Heterogeneous Systems 225
- 9.3.5 NEQ Cell Model 227
- 9.3.6 Properties, Hydrodynamics, and Mass Transfer 232
- 9.4 Comparison of EQ and NEQ Models 232
- 9.5 A View of Reactive Distillation Process Design 237
- 9.6 Notation 238

10 Nonlinear Dynamics and Control of Reactive Distillation Processes 241

- 10.1 Introduction 241
- 10.2 Multiplicity and Oscillations in Chemical Process Systems 242
- 10.3 Methyl Formate Synthesis 245
- 10.3.1 Singularity Analysis of a One-Stage Column 246
- 10.3.2 ∞/∞-Analysis of Lab-Scale Column 247
- 10.3.3 Continuation Analysis of Lab-Scale Column 248
- 10.4 Ethylene Glycol Synthesis 249
- 10.4.1 Singularity Analysis of a One-Stage Column 250
- 10.4.2 Continuation Analysis of Industrial Size Distillation Column 251
- 10.5 MTBE and TAME Synthesis 257
- 10.5.1 MTBE Synthesis 257
- 10.5.2 TAME Synthesis 258
- 10.5.3 Kinetic Instabilities for Finite Transport Inside the Catalyst 260
- 10.5.4 Oscillatory Behavior 261
- 10.6 Classification 262
- 10.7 Nonlinear Wave Propagation 264
- 10.8 Control 271
- 10.8.1 Control Structure Selection 271
- 10.8.2 Control Algorithms 274
- 10.9 Conclusions 276
- 10.10 Acknowledgments 278

Index 283