# Contents

Preface XI List of Symbols XIII

### 1 Overview of Micro Reaction Engineering 1

- 1.1 Introduction 1
- 1.2 What are Microstructured Devices? 2
- 1.3 Advantages of Microstructured Devices 2
- 1.3.1 Enhancement of Transfer Rates 2
- 1.3.2 Enhanced Process Safety 5
- 1.3.3 Novel Operating Window 7
- 1.3.4 Numbering-Up Instead of Scale-Up 7
- 1.4 Materials and Methods for Fabrication of Microstructured Devices 9

v

- 1.5 Applications of Microstructured Devices *10*
- 1.5.1 Microstructured Reactors as Research Tool 11
- 1.5.2 Industrial/Commercial Applications 11
- 1.6 Structure of the Book 13
- 1.7 Summary *13* 
  - References 14

### 2 Basis of Chemical Reactor Design and Engineering 19

- 2.1 Mass and Energy Balance 19
- 2.2 Formal Kinetics of Homogenous Reactions 21
- 2.2.1 Formal Kinetics of Single Homogenous Reactions 22
- 2.2.2 Formal Kinetics of Multiple Homogenous Reactions 24
- 2.2.3 Reaction Mechanism 25
- 2.2.4 Homogenous Catalytic Reactions 26
- 2.3 Ideal Reactors and Their Design Equations 29
- 2.3.1 Performance Parameters 29
- 2.3.2 Batch Wise-Operated Stirred Tank Reactor (BSTR) 30
- 2.3.3 Continuous Stirred Tank Reactor (CSTR) 35
- 2.3.4 Plug Flow or Ideal Tubular Reactor (PFR) 39
- 2.4 Homogenous Catalytic Reactions in Biphasic Systems 45

VI Contents

2.5	Heterogenous Catalytic Reactions 49
2.5.1	Rate Equations for Intrinsic Surface Reactions 50
2.5.1.1	The Langmuir Adsorption Isotherms 51
2.5.1.2	Basic Kinetic Models of Catalytic Heterogenous Reactions 53
2.5.2	Deactivation of Heterogenous Catalysts 57
2.6	Mass and Heat Transfer Effects on Heterogenous Catalytic
	Reactions 59
2.6.1	External Mass and Heat Transfer 60
2.6.1.1	Isothermal Pellet 60
2.6.2	Internal Mass and Heat Transfer 69
2.6.2.1	Isothermal Pellet 69
2.6.2.2	Nonisothermal Pellet 77
2.6.2.3	Combination of External and Internal Transfer Resistances 79
2.6.2.4	Internal and External Mass Transport in Isothermal Pellets 79
2.6.2.5	The Temperature Dependence of the Effective Reaction Rate 81
2.6.2.6	External and Internal Temperature Gradient 82
2.6.3	Criteria for the Estimation of Transport Effects 83
2.7	Summary 84
2.8	List of Symbols 86
	References 87
3	Real Reactors and Residence Time Distribution (RTD) 89
3.1	Nonideal Flow Pattern and Definition of RTD 89
3.2	Experimental Determination of RTD in Flow Reactors 91
3.2.1	Step Function Stimulus-Response Method 92
3.2.2	Pulse Function Stimulus-Response Method 93
3.3	RTD in Ideal Homogenous Reactors 95
3.3.1	Ideal Plug Flow Reactor 95
3.3.2	Ideal Continuously Operated Stirred Tank Reactor (CSTR) 95
3.3.3	Cascade of Ideal CSTR 96
3.4	RTD in Nonideal Homogeneous Reactors 98
3.4.1	Laminar Flow Tubular Reactors 98
3.4.2	RTD Models for Real Reactors 100
3.4.2.1	
	Tanks in Series Model 100
3.4.2.2	Dispersion Model 101
3.4.2.2 3.4.3	Tanks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105
3.4.2.2 3.4.3 3.5	Tanks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107
3.4.2.2 3.4.3 3.5 3.5.1	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2 3.5.2.1	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110Dispersion Model111
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2 3.5.2.1 3.5.2.2	Tanks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110Dispersion Model111Tanks in Series Model112
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2 3.5.2.1 3.5.2.2 3.6	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110Dispersion Model111Tanks in Series Model112RTD in Microchannel Reactors115
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2 3.5.2.1 3.5.2.2 3.6 3.6.1	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110Dispersion Model111Tanks in Series Model112RTD in Microchannel Reactors115RTD of Gas Flow in Microchannels117
3.4.2.2 3.4.3 3.5 3.5.1 3.5.2 3.5.2.1 3.5.2.2 3.6 3.6.1 3.6.2	Ianks in Series Model100Dispersion Model101Estimation of RTD in Tubular Reactors105Influence of RTD on the Reactor Performance107Performance Estimation Based on Measured RTD108Performance Estimation Based on RTD Models110Dispersion Model111Tanks in Series Model112RTD in Microchannel Reactors115RTD of Gas Flow in Microchannels117RTD of Liquid Flow in Microchannels118

- 3.7 List of Symbols *126* References *127*
- 4 Micromixing Devices 129
- 4.1 Role of Mixing for the Performance of Chemical Reactors *129*
- 4.2 Flow Pattern and Mixing in Microchannel Reactors *136*
- 4.3 Theory of Mixing in Microchannels with Laminar Flow 137
- 4.4 Types of Micromixers and Mixing Principles 143
- 4.4.1 Passive Micromixer 144
- 4.4.1.1 Single-Channel Micromixers 144
- 4.4.1.2 Multilamination Mixers 146
- 4.4.1.3 Split-and-Recombine (SAR) Flow Configurations 148
- 4.4.1.4 Mixers with Structured Internals 149
- 4.4.1.5 Chaotic Mixing 149
- 4.4.1.6 Colliding Jet Configurations 150
- 4.4.1.7 Moving Droplet Mixers 151
- 4.4.1.8 Miscellaneous Flow Configurations 153
- 4.4.2 Active Micromixers 154
- 4.4.2.1 Pressure Induced Disturbances 154
- 4.4.2.2 Elektrokinetic Instability 155
- 4.4.2.3 Electrowetting-Induced Droplet Shaking 156
- 4.4.2.4 Ultrasound/Piezoelectric Membrane Action 156
- 4.4.2.5 Acoustic Fluid Shaking 157
- 4.4.2.6 Microstirrers 157
- 4.4.2.7 Miscellaneous Active Micromixers 158
- 4.5 Experimental Characterization of Mixing Efficiency 158
- 4.5.1 Physical Methods 158
- 4.5.2 Chemical Methods 159
- 4.5.2.1 Competitive Chemical Reactions 159
- 4.6 Mixer Efficiency and Energy Consumption 171
- 4.7 Summary *172*
- 4.8 List of Symbols 173 References 173
- References 175

## 5 Heat Management by Microdevices 179

- 5.1 Introduction 179
- 5.2 Heat Transfer in Microstructured Devices 181
- 5.2.1 Straight Microchannels 181
- 5.2.2 Curved Channel Geometry 189
- 5.2.3 Complex Channel Geometries 191
- 5.2.4 Multichannel Micro Heat Exchanger 191
- 5.2.5 Microchannels with Two Phase Flow 193
- 5.3 Temperature Control in Chemical Microstructured Reactors 195
- 5.3.1 Axial Temperature Profiles in Microchannel Reactors 197
- 5.3.2 Parametric Sensitivity 201

VIII Contents

5.3.3	Multi-injection Microstructured Reactors 212
5.3.3.1	Mass and Energy Balance in Multi-injection Microstructured
	Reactors 213
5.3.3.2	Reduction of Hot Spot in Multi-injection Reactors 218
5.4	Case Studies 221
5.4.1	Synthesis of 1,3-Dimethylimidazolium-Triflate 221
5.4.2	Nitration of Dialkyl-Substituted Thioureas 222
5.4.3	Reduction of Methyl Butyrate 223
5.4.4	Reactions with Grignard Reagent in Multi-injection Reactor 224
5.5	Summary 226
5.6	List of Symbols 226
	References 228
6	Microstructured Reactors for Fluid-Solid Systems 231
6.1	Introduction 231
6.2	Microstructured Reactors for Fluid-Solid Reactions 232
6.3	Microstructured Reactors for Catalytic Gas-Phase Reactions 233
6.3.1	Randomly Micro Packed Beds 233
6.3.2	Structured Catalytic Micro-Beds 235
6.3.3	Catalytic Wall Microstructured Reactors 238
6.4	Hydrodynamics in Fluid–Solid Microstructured Reactors 239
6.5	Mass Transfer in Catalytic Microstructured Reactors 243
6.5.1	Randomly Packed Bed Catalytic Microstructured Reactors 244
6.5.2	Catalytic Foam Microstructured Reactors 245
6.5.3	Catalytic Wall Microstructured Reactors 246
6.5.4	Choice of Catalytic Microstructured Reactors 253
6.6	Case Studies 255
6.6.1	Catalytic Partial Oxidations 255
6.6.2	Selective (De)Hvdrogenations 257
6.6.3	Catalytic Dehydration 259
6.6.4	Ethylene Oxide Synthesis 259
6.6.5	Steam Reforming 260
6.6.6	Fischer – Tropsch Synthesis 261
6.7	Summary 261
6.8	List of Symbols 262
	References 262
7	Microstructured Reactors for Fluid-Fluid Reactions 267
7.1	Conventional Equipment for Fluid – Fluid Systems 267
7.2	Microstructured Devices for Fluid–Fluid Systems 268
7.2.1	Micromixers 269
7.2.2	Microchannels 271
7.2.2.1	Microchannels with Inlet T. Y. and Concentric Contactor 271
7.2.2.2	Microchannels with Partial Two-Fluid Contact 271

Contents IX

7.2.2.3 Microchannels with Mesh or Sieve-Like Interfacial Support Contactors 271 7.2.2.4 Microchannels with Static Mixers 272 7.2.2.5 Parallel Microchannels with Internal Redispersion Units 272 7.2.3 Microstructured Falling Film Reactor for Gas-Liquid Reactions 272 7.3 Flow Patterns in Fluid-Fluid Systems 273 Gas-Liquid Flow Patterns 273 7.3.1 7.3.1.1 Bubbly Flow 273 Taylor Flow 274 7.3.1.2 7.3.1.3 Slug Bubbly Flow 279 7.3.1.4 Churn Flow 279 7.3.1.5 Annular and Parallel Flow 280 Liquid – Liquid Flow Patterns 280 7.3.2 Drop Flow 281 7.3.2.1 7.3.2.2 Slug Flow 281 7.3.2.3 Slug-Drop Flow 282 Deformed Interface Flow 7.3.2.4 282 7.3.2.5 Annular and Parallel Flow 283 Slug-Dispersed Flow 283 7.3.2.6 7.3.2.7 Dispersed Flow 283 7.4 Mass Transfer 284 7.4.1 Mass Transfer Models 285 Characterization of Mass Transfer in Fluid – Fluid Systems 7.4.2 286 7.4.3 Mass Transfer in Gas–Liquid Microstructured Devices 287 7.4.3.1 Mass Transfer in Taylor Flow 287 7.4.3.2 Mass Transfer in Slug Annular and Churn Flow Regime 292 7.4.3.3 Mass Transfer in Microstructured Falling Film Reactors 293 7.4.4 Mass Transfer in Liquid-Liquid Microstructured Devices 296 Slug Flow (Taylor Flow) 296 7.4.4.1 7.4.4.2 Slug-Drop and Deformed Interface Flow 297 7.4.4.3 Annular and Parallel Flow 297 Slug-Dispersed and Dispersed Flow 298 7.4.4.4 7.4.5 Comparison with Conventional Contactors 299 7.5 Pressure Drop in Fluid – Fluid Microstructured Channels 300 7.5.1 Pressure Drop in Gas-Liquid Flow 301 7.5.2 Pressure Drop in Liquid – Liquid Flow 304 Pressure Drop – Without Film 304 7.5.2.1 7.5.2.2 Pressure Drop – With Film 305 7.5.2.3 Power Dissipation in Liquid/Liquid Reactors 307 7.6 Flow Separation in Liquid – Liquid Microstructured Reactors 307 7.6.1 Conventional Separators 308 Types of Microstructured Separators 308 7.6.2 7.6.2.1 Geometrical Modifications 309 7.6.2.2 Wettability Based Flow Splitters 310

- X Contents
  - 7.6.3 Conventional Separator Adapted for Microstructured Devices 315
  - 7.7 Fluid Fluid Reactions in Microstructured Devices *315*
  - 7.7.1 Examples of Gas–Liquid Reactions 317
  - 7.7.1.1 Halogenation 317
  - 7.7.1.2 Nitration, Oxidations, Sulfonation, and Hydrogenation 318
  - 7.7.2 Examples of Liquid Liquid Reactions 319
  - 7.7.2.1 Nitration Reaction *319*
  - 7.7.2.2 Transesterification: Biodiesel Production 320
  - 7.7.2.3 Vitamin Precursor Synthesis 320
  - 7.7.2.4 Phase Transfer Catalysis (PTC) 321
  - 7.7.2.5 Enzymatic Reactions 322
  - 7.8 Summary 323
  - 7.9 List of Symbols 324
    - References 325

#### 8 Three-Phase Systems 331

- 8.1 Introduction 331
- 8.2 Gas-Liquid-Solid Systems 331
- 8.2.1 Conventional Gas-Liquid-Solid Reactors 331
- 8.2.2 Microstructured Gas-Liquid-Solid Reactors 333
- 8.2.2.1 Continuous Phase Microstructured Reactors 333
- 8.2.2.2 Dispersed Phase Microstructured Reactors 334
- 8.2.2.3 Mass Transfer and Chemical Reaction 336
- 8.2.2.4 Reaction Examples 341
- 8.3 Gas-Liquid-Liquid Systems 346
- 8.4 Summary 347
- 8.5 List of Symbols 347
  - References 348

Index 351