CONTENTS

PREFACE xvii

1 INTRODUCTION 1
1.1 History 2
1.2 Basics of Reactive Distillation 3
1.3 Neat Operation Versus Excess Reactant 7
1.4 Limitations 8
  1.4.1 Temperature Mismatch 8
  1.4.2 Unfavorable Volatilities 9
  1.4.3 Slow Reaction Rates 9
  1.4.4 Other Restrictions 9
1.5 Scope 9
1.6 Computational Methods 10
  1.6.1 Matlab Programs for Steady-State Design 10
  1.6.2 Aspen Simulations 10
1.7 Reference Materials 11
PART I  STEADY-STATE DESIGN OF IDEAL QUATERNARY SYSTEM  

2  PARAMETER EFFECTS  
2.1 Effect of Holdup on Reactive Trays  
2.2 Effect of Number of Reactive Trays  
2.3 Effect of Pressure  
2.4 Effect of Chemical Equilibrium Constant  
2.5 Effect of Relative Volatilities 
  2.5.1 Constant Relative Volatilities  
  2.5.2 Temperature-Dependent Relative Volatilities  
2.6 Effect of Number of Stripping and Rectifying Trays  
2.7 Effect of Reactant Feed Location 
  2.7.1 Reactant A Feed Location ($N_{FA}$)  
  2.7.2 Reactant B Feed Location ($N_{FB}$)  
2.8 Conclusion  

3  ECONOMIC COMPARISON OF REACTIVE DISTILLATION WITH A CONVENTIONAL PROCESS  
3.1 Conventional Multiunit Process 
  3.1.1 Assumptions and Specifications  
  3.1.2 Steady-State Design Procedure  
  3.1.3 Sizing and Economic Equations  
3.2 Reactive Distillation Design 
  3.2.1 Assumptions and Specifications  
  3.2.2 Steady-State Design Procedure  
3.3 Results for Different Chemical Equilibrium Constants 
  3.3.1 Conventional Process  
  3.3.2 Reactive Distillation Process  
  3.3.3 Comparisons  
3.4 Results for Temperature-Dependent Relative Volatilities 
  3.4.1 Relative Volatilities  
  3.4.2 Optimum Steady-State Designs  
  3.4.3 Real Chemical Systems  
3.5 Conclusion  

4  NEAT OPERATION VERSUS USING EXCESS REACTANT  
4.1 Introduction  
4.2 Neat Reactive Column  
4.3 Two-Column System with Excess B 
  4.3.1 20% Excess B Case  
  4.3.2 10% Excess B Case
4.4 Two-Column System with 20% Excess of A 81
4.5 Economic Comparison 85
4.6 Conclusion 86

PART II STEADY-STATE DESIGN OF OTHER IDEAL SYSTEMS 87

5 TERNARY REACTIVE DISTILLATION SYSTEMS 89

5.1 Ternary System Without Inerts 90
5.1.1 Column Configuration 90
5.1.2 Chemistry and Phase Equilibrium Parameters 90
5.1.3 Design Parameters and Procedure 92
5.1.4 Effect of Pressure 94
5.1.5 Holdup on Reactive Trays 94
5.1.6 Number of Reactive Trays 94
5.1.7 Number of Stripping Trays 94

5.2 Ternary System With Inerts 99
5.2.1 Column Configuration 99
5.2.2 Chemistry and Phase Equilibrium Parameters 99
5.2.3 Design Parameters and Procedure 100
5.2.4 Effect of Pressure 102
5.2.5 Control Tray Composition 103
5.2.6 Reactive Tray Holdup 105
5.2.7 Effect of Reflux 107
5.2.8 Chemical Equilibrium Constant 109
5.2.9 Feed Composition 109
5.2.10 Number of Reactive Trays 113
5.2.11 Number of Rectifying and Stripping Trays 113

5.3 Conclusion 116

6 TERNARY DECOMPOSITION REACTION 119

6.1 Ternary Decomposition Reaction: Intermediate-Boiling Reactant 120
6.1.1 Column Configuration 120
6.1.2 Chemistry and Phase Equilibrium Parameters 120
6.1.3 Design Parameters and Procedure 121
6.1.4 Holdup on Reactive Trays 123
6.1.5 Number of Reactive Trays 124
6.1.6 Number of Rectifying and Stripping Trays 126
6.1.7 Location of Feed Tray 126

6.2 Ternary Decomposition Reaction: Heavy Reactant with Two-Column Configurations 127
6.2.1 Column Configurations 127
6.2.2 Chemistry and Phase Equilibrium Parameters 128
6.2.3 Design Parameters and Procedure 128
6.2.4 Reactive Holdup 129
6.2.5 Number of Reactive Trays 131
6.2.6 Number of Rectifying Trays 132

6.3 Ternary Decomposition Reaction: Heavy Reactant with One-Column Configurations 134
6.3.1 Feasibility Analysis 134
6.3.2 Column Configuration 139
6.3.3 Design Parameters and Procedure 139
6.3.4 Reactive Tray Holdup 139
6.3.5 Number of Reactive Trays 139
6.3.6 Number of Rectifying Trays 140
6.3.7 Location of Feed Tray 143
6.3.8 Comparison Between These Two Flowsheets 143

6.4 Conclusion 143

PART III STEADY-STATE DESIGN OF REAL CHEMICAL SYSTEMS 145

7 STEADY-STATE DESIGN FOR ACETIC ACID ESTERIFICATION 147
7.1 Reaction Kinetics and Phase Equilibria 147
  7.1.1 Reaction Kinetics 147
  7.1.2 Phase Equilibria 149
7.2 Process Flowsheets 153
  7.2.1 Type I Flowsheet: MeAc 153
  7.2.2 Type II Flowsheet: EtAc and IPAc 156
  7.2.3 Type III Flowsheet: BuAc and AmAc 157
7.3 Steady-State Design 158
  7.3.1 Design Procedure 158
  7.3.2 Optimized Design 160
7.4 Process Characteristics 168
  7.4.1 Type I: MeAc 168
  7.4.2 Type II: EtAc and IPAc 168
  7.4.3 Type III: BuAc and AmAc 170
7.5 Discussion 175
7.6 Conclusion 177

8 DESIGN OF TAME REACTIVE DISTILLATION SYSTEMS 179
8.1 Chemical Kinetics and Phase Equilibrium 180
  8.1.1 Chemical Kinetics 180
  8.1.2 Phase Equilibrium Using Aspen Plus 181
  8.1.3 Conceptual Design 186
8.2 Component Balances 194
8.3 Prereactor and Reactive Column 195
  8.3.1 Base Case Design of Reactive Column 195
  8.3.2 Effect of Design Parameters on Reactive Column 199
8.4 Pressure-Swing Methanol Separation Section 208
8.5 Extractive Distillation Methanol Separation Section 209
8.6 Economic Comparison 210
8.7 Conclusion 212

9 DESIGN OF MTBE AND ETBE REACTIVE DISTILLATION COLUMNS 213
  9.1 MTBE Process 213
    9.1.1 Phase Equilibrium 214
    9.1.2 Reaction Kinetics 214
    9.1.3 Aspen Plus Simulation Issues 214
    9.1.4 Setting up the Aspen Plus Simulation 215
    9.1.5 Effect of Design Parameters 221
    9.1.6 Chemical Equilibrium Model 229
  9.2 ETBE Process 231
    9.2.1 Kinetic Model 231
    9.2.2 Process Studied 232
    9.2.3 User Subroutine for ETBE 232
    9.2.4 Chemical Equilibrium Model 234
    9.2.5 Effects of Design Parameters 236
  9.3 Conclusion 237

PART IV CONTROL OF IDEAL SYSTEMS 239

10 CONTROL OF QUATERNARY REACTIVE DISTILLATION COLUMNS 241
  10.1 Introduction 242
  10.2 Steady-State Design 243
  10.3 Control Structures 245
  10.4 Selection of Control Tray Location 246
  10.5 Closed-Loop Performance 247
    10.5.1 CS7-R Structure 247
    10.5.2 CS7-RR Structure 248
  10.6 Using More Reactive Trays 249
    10.6.1 Steady-State Design 249
    10.6.2 SVD Analysis 250
    10.6.3 Dynamic Performance of CS7-RR 253
## 10.7 Increasing Holdup on Reactive Trays

10.8 Rangeability

10.9 Conclusion

## 11 CONTROL OF EXCESS REACTANT SYSTEMS

11.1 Control Degrees of Freedom

11.2 Single Reactive Column Control Structures
   11.2.1 Two-Temperature Control Structure
   11.2.2 Internal Composition Control Structure

11.3 Control of Two-Column System
   11.3.1 Two-Temperature Control
   11.3.2 Temperature/Composition Cascade Control

11.4 Conclusion

## 12 CONTROL OF TERNARY REACTIVE DISTILLATION COLUMNS

12.1 Ternary System Without Inerts
   12.1.1 Column Configuration
   12.1.2 Control Structure CS1
   12.1.3 Control Structure CS2
   12.1.4 Control Structure CS3

12.2 Ternary System With Inerts
   12.2.1 Column Configuration
   12.2.2 Control Structure CS1
   12.2.3 Control Structure CS2
   12.2.4 Control Structure CS3
   12.2.5 Conclusion for Ternary A + B ⇔ C System

12.3 Ternary A ⇔ B + C System: Intermediate-Boiling Reactant
   12.3.1 Column Configuration
   12.3.2 Control Structure CS1
   12.3.3 Control Structure CS2
   12.3.4 Control Structure CS3

12.4 Ternary A ⇔ B + C System: Heavy Reactant
   With Two-Column Configuration
   12.4.1 Column Configuration
   12.4.2 Control Structure CS1
   12.4.3 Control Structure CS2

12.5 Ternary A ⇔ B + C System: Heavy Reactant
   With One-Column Configuration
   12.5.1 Column Configuration
   12.5.2 Control Structure CS1
   12.5.3 Control Structure CS2
   12.5.4 Control Structure CS3
   12.5.5 Conclusion for Ternary A ⇔ B + C System
PART V  CONTROL OF REAL SYSTEMS 353

13  CONTROL OF REACTIVE DISTILLATIONS FOR ACETIC ACID ESTERIFICATION 355

13.1  Process Characteristics 355
   13.1.1  Process Studies 355
   13.1.2  Quantitative Analysis 356

13.2  Control Structure Design 362
   13.2.1  Selection of Temperature Control Trays 363
   13.2.2  Control Structure and Controller Design 366
   13.2.3  Performance 368
   13.2.4  Alternative Temperature Control Structures 376

13.3  Extension to Composition Control 380

13.4  Conclusion 388

14  PLANTWIDE CONTROL OF TAME REACTIVE DISTILLATION SYSTEM 389

14.1  Process Studied 389
   14.1.1  Prereactor 390
   14.1.2  Reactive Column C1 391
   14.1.3  Extractive Column C2 391
   14.1.4  Methanol Recovery Column C3 397

14.2  Control Structure 397
   14.2.1  Prereactor 397
   14.2.2  Reactive Distillation Column C1 399
   14.2.3  Extractive Distillation Column C2 399
   14.2.4  Methanol Recovery Column C3 401

14.3  Results 403

14.4  Conclusion 406

15  CONTROL OF MTBE AND ETBE REACTIVE DISTILLATION COLUMNS 407

15.1  MTBE Control 407
   15.1.1  Steady State 407
   15.1.2  Control Structure with C4 Feedflow Controlled 408
   15.1.3  Control Structure with Methanol Feedflow Controlled 416

15.2  ETBE Control 418
   15.2.1  Control Structure with Flow Control of C4 Feed 419
   15.2.2  Control Structure with Flow Control of Ethanol Feed 424
## PART VI  HYDRID AND NONCONVENTIONAL SYSTEMS  429

16  DESIGN AND CONTROL OF COLUMN/SIDE REACTOR SYSTEMS  431

16.1  Introduction  431

16.2  Design for Quaternary Ideal System  433
   16.2.1  Assumptions and Specifications  434
   16.2.2  Reactor and Column Equations  435
   16.2.3  Design Optimization Procedure  436
   16.2.4  Results and Discussion  437
   16.2.5  Reactive Column with Optimum Feed Tray Locations  445

16.3  Control of Quaternary Ideal System  446
   16.3.1  Dynamic Tubular Reactor Model  446
   16.3.2  Control Structures  447

16.4  Design of Column/Side Reactor Process for Ethyl Acetate System  458
   16.4.1  Process Description  458
   16.4.2  Conceptual Design  459

16.5  Control of Column/Side Reactor Process for Ethyl Acetate System  474
   16.5.1  Determining Manipulated Variables  475
   16.5.2  Selection of Temperature Control Trays  479
   16.5.3  Controller Design  481
   16.5.4  Performance  481
   16.5.5  Extension to Composition Control  485
   16.5.6  Comparison with Reactive Distillation Temperature Control  485

16.6  Conclusion  485

17  EFFECTS OF BOILING POINT RANKINGS ON THE DESIGN OF REACTIVE DISTILLATION  487

17.1  Process and Classification  487
   17.1.1  Process  487
   17.1.2  Classification  490

17.2  Relaxation and Convergence  492

17.3  Process Configurations  495
   17.3.1  Type I: One Group  496
   17.3.2  Type II: Two Groups  501
   17.3.3  Type III: Alternating  507

17.4  Results and Discussion  511
   17.4.1  Summary  511
   17.4.2  Excess Reactant Design  514

17.5  Conclusion  518
18 EFFECTS OF FEED TRAY LOCATIONS ON DESIGN AND CONTROL OF REACTIVE DISTILLATION 519

18.1 Process Characteristics 519
  18.1.1 Modeling 521
  18.1.2 Steady-State Design 522
  18.1.3 Base Case 522
  18.1.4 Feed Locations Versus Reactants Distribution 523
  18.1.5 Optimal Feed Locations 527

18.2 Effects of Relative Volatilities 529
  18.2.1 Changing Relative Volatilities of Reactants 529
  18.2.2 Changing Relative Volatilities of Products 530
  18.2.3 Summary 532

18.3 Effects of Reaction Kinetics 533
  18.3.1 Reducing Activation Energies 533
  18.3.2 Effects of Preexponential Factor 536

18.4 Operation and Control 538
  18.4.1 Optimal Feed Location for Production Rate Variation 538
  18.4.2 Control Structure 539
  18.4.3 Closed-Loop Performance 541

18.5 Conclusion 544

APPENDIX CATALOG OF TYPES OF REAL REACTIVE DISTILLATION SYSTEMS 545

REFERENCES 563

INDEX 573