# International Edition

Daniel A. Crowl/Joseph F. Louvar

# **Chemical Process Safety**

**Fundamentals with Applications** 

Second Edition

Prentice Hall International Series in the Physical and Chemical Engineering Sciences



# **Contents**

# Preface xiii Nomenclature xv

-	T 4 T 4	-
	Introduction	

1-1	Safety Programs 2	
1-2	Engineering Ethics 4	
1-3	Accident and Loss Statistics 4	
1-4	Acceptable Risk 12	
1-5	Public Perceptions 14	
1-6	The Nature of the Accident Process	15
1-7	Inherent Safety 20	
1-8	Four Significant Disasters 23	
	Flixborough, England 23	
	Bhopal, India 25	
	Seveso, Italy 26	
	Pasadena, Texas 27	
	Suggested Reading 29	
	Problems 30	

## 2 Toxicology 35

2-1	How Toxicants Enter Biological Organisms 36	
	Gastrointestinal Tract 37	١
	Skin 37	
	Respiratory System 38	
2-2	How Toxicants Are Eliminated from Biological Organisms	3
2-3	Effects of Toxicants on Biological Organisms 40	
2-4	Toxicological Studies 41	

2-4 TOXICOTOGICAL STUDIES 41
2-5 Dose versus Response 42

3

4

2-6 2-7 2-8	Models for Dose and Response Curves 48 Relative Toxicity 54 Threshold Limit Values 54 Suggested Reading 59 Problems 59
Ind	ustrial Hygiene 63
3-1	Government Regulations 64 Laws and Regulations 64 Creating a Law 64 Creating a Regulation 64 OSHA: Process Safety Management 68 EPA: Risk Management Plan 71
3-2	Industrial Hygiene: Identification 74  Material Safety Data Sheets 74
3-3	Industrial Hygiene: Evaluation 78  Evaluating Exposures to Volatile Toxicants by Monitoring 79  Evaluation of Worker Exposures to Dusts 83  Evaluating Worker Exposures to Noise 84  Estimating Worker Exposures to Toxic Vapors 85
3-4	Industrial Hygiene: Control 94 Respirators 96 Ventilation 97 Suggested Reading 103 Problems 104
Sou	rce Models 109
4-1	Introduction to Source Models 109
4-2	Flow of Liquid through a Hole 112
4-3	Flow of Liquid through a Hole in a Tank 116
4-4	Flow of Liquids through Pipes 121 2-K Method 124
4-5	Flow of Vapor through Holes 130
4-6	Flow of Gases through Pipes 136 Adiabatic Flows 136 Isothermal Flows 143
4-7	Flashing Liquids 151
4-8	Liquid Pool Evaporation or Boiling 157
4-9	Realistic and Worst-Case Releases 159
4-10	Conservative Analysis 159 Suggested Reading 161 Problems 162

Contents

#### 5 Toxic Release and Dispersion Models 171

- 5-1 Parameters Affecting Dispersion 172
- 5-2 Neutrally Buoyant Dispersion Models 176
  - Case 1: Steady-State Continuous Point Release with No Wind 180
  - Case 2: Puff with No Wind 181
  - Case 3: Non-Steady-State Continuous Point Release with No Wind 182
  - Case 4: Steady-State Continuous Point Source Release with Wind 183
  - Case 5: Puff with No Wind and Eddy Diffusivity Is a Function of Direction 183
  - Case 6: Steady-State Continuous Point Source Release with Wind and Eddy Diffusivity Is a Function of Direction 184
  - Case 7: Puff with Wind 184
  - Case 8: Puff with No Wind and with Source on Ground 185
  - Case 9: Steady-State Plume with Source on Ground 185
  - Case 10: Continuous Steady-State Source with Source at Height *H*, above the Ground 186
  - Pasquill-Gifford Model 186
  - Case 11: Puff with Instantaneous Point Source at Ground Level, Coordinates Fixed at Release Point, Constant Wind Only in x Direction with Constant Velocity u 190
  - Case 12: Plume with Continuous Steady-State Source at Ground Level and Wind Moving in x Direction at Constant Velocity u 191
  - Case 13: Plume with Continuous Steady-State Source at Height  $H_r$  above Ground Level and Wind Moving in x Direction at Constant Velocity u 192
  - Case 14: Puff with Instantaneous Point Source at Height H, above Ground Level and a Coordinate System on the Ground That Moves with the Puff 103
  - Case 15: Puff with Instantaneous Point Source at Height *H*, above Ground Level and a Coordinate System Fixed on the Ground at the Release Point 194
  - Worst-Case Conditions 194
  - Limitations to Pasquill-Gifford Dispersion Modeling 194
- 5-3 Dense Gas Dispersion 195
- 5-4 Toxic Effect Criteria 199
- 5-5 Effect of Release Momentum and Buoyancy 212
- 5-6 Release Mitigation 213 Suggested Reading 214 Problems 215

#### 6 Fires and Explosions 225

- 6-1 The Fire Triangle 225
- 6-2 Distinction between Fires and Explosions 227

7

7-2

Static Electricity 307

Fundamentals of Static Charge 307

6-3	Definitions 227
6-4	Flammability Characteristics of Liquids and Vapors 229
	Liquids 230
	Gases and Vapors 233
	Vapor Mixtures 233
	Flammability Limit Dependence on Temperature 235
	Flammability Limit Dependence on Pressure 236
	Estimating Flammability Limits 236
6-5	Limiting Oxygen Concentration and Inerting 238
6-6	Flammability Diagram 240
6-7	Ignition Energy 248
6-8	Autoignition 249
6-9	Auto-Oxidation 249
6-10	Adiabatic Compression 249
	Ignition Sources 251
6-12	Sprays and Mists 252
6-13	Explosions 252
	Detonation and Deflagration 253
	Confined Explosions 255
	Blast Damage Resulting from Overpressure 265
	TNT Equivalency 269
	TNO Multi-Energy Method 271
	Energy of Chemical Explosions 274
	Energy of Mechanical Explosions 276
	Missile Damage 279
	Blast Damage to People 279
	Vapor Cloud Explosions 281
	Boiling-Liquid Expanding-Vapor Explosions 282
	Suggested Reading 282
	Problems 283
Des	igns to Prevent Fires and Explosions 291
7-1	Inerting 292
	Vacuum Purging 292
	Pressure Purging 295
	Combined Pressure-Vacuum Purging 297
	Vacuum and Pressure Purging with Impure Nitrogen 298
	Advantages and Disadvantages of the Various Pressure and Vacuum Inert-
	ing Procedures 299
	Sweep-Through Purging 299
	Siphon Purging 301
	Using the Flammability Diagram To Avoid Flammable Atmospheres 301

8

	Charge Accumulation 308
	Electrostatic Discharges 309
	Energy from Electrostatic Discharges 311
	Energy of Electrostatic Ignition Sources 312
	Streaming Current 313
	Electrostatic Voltage Drops 316
	Energy of Charged Capacitors 316
	Capacitance of a Body 321
	Balance of Charges 324
7-3	Controlling Static Electricity 330
	General Design Methods To Prevent Electrostatic Ignitions 331
	Relaxation 332
	Bonding and Grounding 332
	Dip Pipes 333
	Increasing Conductivity with Additives 336
	Handling Solids without Flammable Vapors 337
	Handling Solids with Flammable Vapors 337
7-4	Explosion-Proof Equipment and Instruments 337
	Explosion-Proof Housings 339
	Area and Material Classification 339
	Design of an XP Area 340
7-5	Ventilation 340
	Open-Air Plants 340
	Plants Inside Buildings 341
7-6	
7-7	Miscellaneous Designs for Preventing Fires and Explosions 347
	Suggested Reading 347
	Problems 348
Intr	oduction to Reliefs 353
8-1	Relief Concepts 354
8-2	Definitions 356
8-3	Location of Reliefs 357
8-4	Relief Types 360
8-5	Relief Scenarios 364
8-6	Data for Sizing Reliefs 365
8-7	Relief Systems 368
	Relief Installation Practices 368
	Relief Design Considerations 368
	Horizontal Knockout Drum 371
	Flares 375
	Scrubbers 376
	Condensers 376
	Suggested Reading 376
	Problems 377

9	Relief	Sizing	383
---	--------	--------	-----

- 9-1 Conventional Spring-Operated Reliefs in Liquid Service 384
- 9-2 Conventional Spring-Operated Reliefs in Vapor or Gas Service 389
- 9-3 Rupture Disc Reliefs in Liquid Service 394
- 9-4 Rupture Disc Reliefs in Vapor or Gas Service 394
- 9-5 Two-Phase Flow during Runaway Reaction Relief 395
   Simplified Nomograph Method 401
- 9-6 Deflagration Venting for Dust and Vapor Explosions 404
   Vents for Low-Pressure Structures 406
   Vents for High-Pressure Structures 408
- 9-7 Venting for Fires External to Process Vessels 411
- 9-8 Reliefs for Thermal Expansion of Process Fluids 415 Suggested Reading 418 Problems 420

#### 10 Hazards Identification 429

- 10-1 Process Hazards Checklists 432
- 10-2 Hazards Surveys 432
- 10-3 Hazards and Operability Studies 448
- 10-4 Safety Reviews 454
- 10-5 Other Methods 459 Suggested Reading 460 Problems 460

#### 11 Risk Assessment 471

- 11-1 Review of Probability Theory 472
  Interactions between Process Units 474
  Revealed and Unrevealed Failures 480
  Probability of Coincidence 484
  - Probability of Coincidence 484 Redundancy 486
  - Common Mode Failures 486
- 11-2 Event Trees 486
- 11-3 Fault Trees 491

Determining the Minimal Cut Sets 494

Quantitative Calculations Using the Fault Tree 497

Advantages and Disadvantages of Fault Trees 498

Relationship between Fault Trees and Event Trees 498

11-4 QRA and LOPA 499

Quantitative Risk Analysis 499

Layer of Protection Analysis 500

Consequence 503

Frequency 503

Suggested Reading 507

Problems 508

Contents

#### 12 Accident Investigations 515

- 12-1 Learning from Accidents 515
- 12-2 Layered Investigations 516
- 12-3 Investigation Process 518
- 12-4 Investigation Summary 519
- 12-5 Aids for Diagnosis 521

Fires 522

Explosions 522

Sources of Ignition in Vessels 523

Pressure Effects 523

Medical Evidence 525

Miscellaneous Aids to Diagnosis 525

12-6 Aids for Recommendations 528

Control Plant Modifications 528

User-Friendly Designs 529

Block Valves 529

Double Block and Bleed 530

Preventive Maintenance 530

Analyzers 531

Suggested Reading 532

Problems 532

#### 13 Case Histories 535

13-1 Static Electricity 536

Tank Car Loading Explosion 536

Explosion in a Centrifuge 536

Duct System Explosion 537

Conductor in a Solids Storage Bin 537

Pigment and Filter 536

Pipefitter's Helper 536

Lessons Learned 536

13-2 Chemical Reactivity 540

Bottle of Isopropyl Ether 540

Nitrobenzene Sulfonic Acid Decomposition 540

Organic Oxidation 541

Lessons Learned 541

13-3 System Designs 546

Ethylene Oxide Explosion 546

Ethylene Explosion 546

Butadiene Explosion 546

Light Hydrocarbon Explosion 547

Pump Vibration 547

Pump Failure 547

Ethylene Explosion (1) 548

	Ethylene Explosion (2) 548	
	Ethylene Oxide Explosion 548	
	Lessons Learned 549	
13-4	Procedures 551	
	Leak Testing a Vessel 552	
	Man Working in Vessel 552	
	Vinyl Chloride Explosion 552	
	Dangerous Water Expansion 553	
	Phenol-Formaldehyde Runaway Reaction 553	
	Conditions and Secondary Reaction Cause Explosion	554
	Fuel-Blending Tank Explosion 555	
	Lessons Learned 556	
13-5	Conclusion 556	
	Suggested Reading 557	
	Problems 557	

#### Appendix A: Unit Conversion Constants 561

# **Appendix B: Flammability Data for Selected Hydrocarbons** 565

# **Appendix C: Detailed Equations for Flammability Diagrams** 571 Equations Useful for Placing Vessels into and out of Service 576

## Appendix D: Formal Safety Review Report for Example 10-4 581

### **Appendix E: Saturation Vapor Pressure Data** 591