

The background of the cover is a photograph of an industrial chemical plant. The top half is dark, showing a complex network of pipes and structural beams. The bottom half is a lighter, orange-tinted image of a similar industrial structure, possibly a distillation column or reactor, with a worker visible in silhouette. The overall aesthetic is technical and industrial.

INDUSTRIAL ORGANIC CHEMICALS

Second Edition

HAROLD A. WITTCOFF, BRYAN G. REUBEN, JEFFREY S. PLOTKIN

CONTENTS

PREFACE	xxiii
PREFACE TO THE FIRST EDITION	xxv
LIST OF ACRONYMS AND ABBREVIATIONS	xxvii
CHAPTER 0 HOW TO USE INDUSTRIAL ORGANIC CHEMICALS, SECOND EDITION	1
0.1 Why this Book was Written and how it is Structured / 1	
0.2 North American Industry Classification / 3	
0.3 Units and Nomenclature / 4	
0.4 General Bibliography / 4	
0.4.1 Encyclopedias / 5	
0.4.2 Books / 6	
0.4.3 Journals / 9	
0.4.4 Patents / 9	
0.4.5 Statistics / 11	
0.4.6 CD-ROM and On-Line Databases / 12	
CHAPTER 1 THE CHEMICAL INDUSTRY	15
1.1 The National Economy / 15	
1.2 Size of the Chemical Industry / 20	

- 1.3 Characteristics of the Chemical Industry / 21
 - 1.3.1 Maturity / 21
 - 1.3.1.1 Realignment of Business Segments / 26*
 - 1.3.2 Participation in International Trade / 28
 - 1.3.3 Competition from Developing Countries / 29
 - 1.3.4 Capital Intensity and Economies of Scale / 32
 - 1.3.5 Criticality and Pervasiveness / 33
 - 1.3.6 Freedom of Market Entry / 35
 - 1.3.7 Strong Health and Safety Regulation / 36
 - 1.3.8 High Research and Development Expenditures / 41
 - 1.3.9 Dislocations / 46
- 1.4 The Top Chemical Companies / 48
- 1.5 The Top Chemicals / 50
- Notes and References / 53

CHAPTER 2 CHEMICALS FROM NATURAL GAS AND PETROLEUM

57

- 2.1 Petroleum Distillation / 61
- 2.2 Petroleum Refining Reactions / 67
 - 2.2.1 Steam Cracking / 67
 - 2.2.1.1 Choice of Feedstock / 70*
 - 2.2.1.2 Economics of Steam Cracking / 71*
 - 2.2.1.3 Mechanism of Cracking / 76*
 - 2.2.2 Catalytic Cracking / 76
 - 2.2.3 Catalytic Reforming / 79
 - 2.2.4 Oligomerization / 82
 - 2.2.5 Alkylation / 84
 - 2.2.6 Hydrotreating and Coking / 84
 - 2.2.7 Dehydrogenation / 86
 - 2.2.8 Isomerization / 87
 - 2.2.9 Metathesis / 87
 - 2.2.9.1 Metathesis Outside the Refinery / 89*
 - 2.2.9.2 Mechanism of Metathesis / 90*
- 2.3 The Refinery—A Perspective / 92
 - 2.3.1 The Function of the Refinery and the Potential Petroleum Shortage / 92
 - 2.3.2 Unleaded Gasoline and the Clean Air Act / 93
- 2.4 Separation of Natural Gas / 96
- Notes and References / 96

CHAPTER 3 CHEMICALS AND POLYMERS FROM ETHYLENE 100

- 3.1 Ethylene Polymers / 105
 - 3.1.1 Discovery of Low- and High-Density Polyethylenes / 105
 - 3.1.2 Low-Density Polyethylene / 106
 - 3.1.3 High-Density Polyethylene / 107
 - 3.1.4 Linear Low-Density Polyethylene / 108
 - 3.1.5 Very High Molecular Weight Polyethylene / 109
- 3.2 Ethylene Copolymers / 109
 - 3.2.1 Chlorosulfonated Polyethylene / 109
 - 3.2.2 Ethylene-Vinyl Acetate / 110
 - 3.2.3 Ionomers / 111
 - 3.2.4 Copolymer from "Incompatible" Polymer Blends / 111
 - 3.2.5 Ethylene-Propylene Elastomers / 111
 - 3.2.6 Ultra-Low-Density Polyethylene / 112
 - 3.2.7 Photodegradable Copolymers / 112
- 3.3 Oligomerization / 113
 - 3.3.1 Dimerization / 113
 - 3.3.2 Ziegler Oligomerization of Ethylene / 114
 - 3.3.3 Other Ethylene Oligomerization Technologies / 115
 - 3.3.4 The Shell Higher Olefins Process (SHOP) / 116
- 3.4 Vinyl Chloride / 119
- 3.5 Acetaldehyde / 121
- 3.6 Vinyl Acetate / 124
- 3.7 Ethylene Oxide / 126
 - 3.7.1 Ethylene Glycol / 127
 - 3.7.2 Proposed Non-Ethylene Oxide Processes for Ethylene Glycol Production / 129
- 3.8 Styrene / 132
- 3.9 Ethanol / 135
- 3.10 Major Chemicals from Ethylene—A Summary / 137
- 3.11 Lesser Volume Chemicals from Ethylene / 139
 - 3.11.1 Hydroformylation—Propionaldehyde, Propionic Acid, and *n*-Propanol / 140
 - 3.11.2 Ethyl Halides / 141
 - 3.11.3 Acetaldehyde Chemistry / 142
 - 3.11.4 Metal Complexes / 146
 - 3.11.5 Ethylenediamine and Related Compounds / 147

- 3.11.6 Ethylene Oxide and Ethylene Glycol Derivatives / 149
 - 3.11.6.1 Oligomers / 149
 - 3.11.6.2 Glycol Ethers and Esters / 149
 - 3.11.6.3 Ethylene Carbonate / 150
 - 3.11.6.4 Aminoethyl Alcohols (Ethanolamines) and Derivatives / 153
 - 3.11.6.5 Ethylenimine / 154
 - 3.11.6.6 1,3-Propanediol / 155
 - 3.11.6.7 Ethylene Glycol Derivatives / 156
 - 3.11.7 Vinyl Chloride and Ethylene Dichloride Derivatives / 158
 - 3.11.8 Vinyl Fluoride and Vinylidene Fluoride / 159
 - 3.11.9 Ethylene Dibromide / 160
 - 3.11.10 Ethanol Derivatives / 161
 - 3.11.11 Vinyl Esters and Ethers / 162
- Notes and References / 163

CHAPTER 4 CHEMICALS AND POLYMERS FROM PROPYLENE 167

- 4.1 On-Purpose Propylene Production Technologies and Propane Dehydrogenation / 168
- 4.2 Propylene via Deep Catalytic Cracking / 169
- 4.3 Propylene via Olefin Metathesis / 169
- 4.4 Propylene via Selective C₄/C₅ Cracking / 171
- 4.5 Main Polymers and Chemicals from Propylene / 172
 - 4.5.1 Propylene Polymers and Copolymers / 172
- 4.6 Oligomerization / 175
- 4.7 Acrylic Acid / 176
- 4.8 Acrylonitrile / 181
 - 4.8.1 Uses of Acrylonitrile / 183
- 4.9 Cumene, Cumene Hydroperoxide, and Phenol / 184
- 4.10 Acetone and Isopropanol / 187
 - 4.10.1 Methyl Methacrylate / 188
 - 4.10.2 Methyl Isobutyl Ketone and other Acetone Derivatives / 193
- 4.11 Propylene Oxide / 195
 - 4.11.1 Propylene Oxide Applications / 198
 - 4.11.2 Projected Propylene Oxide–Propylene Glycol Processes / 199

- 4.11.3 Other Novel Syntheses of Propylene Oxide / 200
 - 4.11.3.1 *Direct Oxidation* / 200
 - 4.11.3.2 *Use of Peracids or Hydrogen Peroxide* / 201
 - 4.11.3.3 *Electrochemical Processes* / 202
 - 4.11.3.4 *Biotechnological Approaches* / 204
- 4.12 *n*-Butyraldehyde and Isobutyraldehyde / 205
 - 4.12.1 Uses for Butyraldehyde and Isobutyraldehyde / 207
 - 4.12.2 Other Oxo Products / 208
- 4.13 Major Chemicals from Propylene—A Perspective / 209
- 4.14 Lesser Volume Chemicals from Propylene / 211
 - 4.14.1 Allyl Chloride and Epichlorohydrin / 211
 - 4.14.2 Glycerol / 214
 - 4.14.3 Acrylamide / 215
 - 4.14.4 Acrolein / 216
 - 4.14.5 Acrylonitrile Derivatives / 218
- Notes and References / 218

CHAPTER 5 CHEMICALS AND POLYMERS FROM THE C₄ STREAM

223

- 5.1 Chemicals and Polymers from Butadiene / 226
 - 5.1.1 Acrylonitrile–Butadiene–Styrene Resins (ABS) / 230
 - 5.1.2 Hexamethylenediamine / 231
 - 5.1.3 Lesser Volume Chemicals from Butadiene / 236
 - 5.1.3.1 *Cyclization* / 236
 - 5.1.3.2 *Dimerization and Trimerization* / 237
 - 5.1.3.3 *Diels–Alder Reactions* / 239
 - 5.1.3.4 *Adipic Acid* / 240
 - 5.1.3.5 *1,4-Butanediol* / 241
 - 5.1.3.6 *trans-1,4-Hexadiene* / 241
 - 5.1.3.7 *Dimethyl-2,6-naphthalene Dicarboxylate* / 241
 - 5.1.3.8 *Butadiene Monoepoxide* / 241
- 5.2 Chemicals and Polymers from Isobutene / 242
 - 5.2.1 Methyl *tert*-butyl Ether / 243
 - 5.2.2 Butyl Rubber / 244
 - 5.2.3 Polyisobutenes and Isobutene Oligomers and Polymers / 244

- 5.2.4 *tert*-Butanol / 245
- 5.2.5 Methyl Methacrylate / 245
- 5.2.6 Lesser Volume Chemicals from Isobutene / 245
- 5.3 Chemicals and Polymers from 1- and 2-Butenes / 248
- 5.4 Chemicals from *n*-Butane / 249
 - 5.4.1 Acetic Acid / 249
 - 5.4.2 Maleic Anhydride / 249
- Notes and References / 251

CHAPTER 6 CHEMICALS AND POLYMERS FROM THE C₅ STREAM

255

- 6.1 Separation of the C₅ Stream / 256
- 6.2 Isoprene / 259
- 6.3 Cyclopentadiene and Dicyclopentadiene / 263
- 6.4 Pentene-1 and Piperylene / 265
- Notes and References / 266

CHAPTER 7 CHEMICALS AND POLYMERS FROM BENZENE

267

- 7.1 Phenol / 269
 - 7.1.1 Phenolic Resins / 275
 - 7.1.2 Bisphenol A / 276
 - 7.1.2.1 Epoxy Resins / 277
 - 7.1.2.2 Polycarbonate Resins / 277
 - 7.1.2.3 Lesser Volume Uses for Bisphenol A / 280
 - 7.1.3 Cyclohexanone / 281
 - 7.1.4 Alkylphenols / 283
 - 7.1.5 Chlorinated Phenols / 283
 - 7.1.6 2,6-Xylenol and Cresols / 284
 - 7.1.7 Aniline from Phenol / 284
- 7.2 Cyclohexane / 285
 - 7.2.1 Adipic Acid / 285
 - 7.2.1.1 Nylons from Adipic Acid / 289
 - 7.2.2 Caprolactam / 290
- 7.3 Aniline / 294
 - 7.3.1 4,4'-Diphenylmethane Diisocyanate (MDI) / 296
- 7.4 Alkylbenzenes / 299
- 7.5 Maleic Anhydride / 301
- 7.6 Chlorinated Benzenes / 301

7.7 Dihydroxybenzenes / 302

7.8 Anthraquinone / 308

Notes and References / 309

CHAPTER 8 CHEMICALS AND POLYMERS FROM TOLUENE 312

8.1 Hydrodealkylation and Disproportionation / 313

8.2 Solvents / 314

8.3 Dinitrotoluene and Toluene Diisocyanate / 314

8.4 Lesser Volume Chemicals from Toluene / 316

Notes and References / 318

CHAPTER 9 CHEMICALS AND POLYMERS FROM XYLENES 320

9.1 *o*-Xylene and Phthalic Anhydride / 322

9.1.1 Uses of Phthalic Anhydride / 323

9.2 *m*-Xylene and Isophthalic Acid / 327

9.2.1 Uses of Isophthalic Acid / 328

9.3 *p*-Xylene and Terephthalic Acid—Dimethyl Terephthalate / 329

9.3.1 Oxidation of *p*-Xylene / 329

9.3.2 Alternate Sources for Terephthalic Acid / 331

9.3.3 Poly(ethylene terephthalate) / 332

9.3.4 Lower Volume Polymers from Terephthalic Acid / 334

9.4 Major Chemicals from Xylenes: A Summary / 335

Notes and References / 336

CHAPTER 10 CHEMICALS FROM METHANE 338

10.1 Hydrocyanic Acid / 338

10.2 Halogenated Methanes / 341

10.2.1 Chloromethane / 342

10.2.2 Dichloromethane / 343

10.2.3 Trichloromethane / 343

10.2.4 Tetrachloromethane and Carbon Disulfide / 344

10.2.5 Bromomethane / 347

10.3 Acetylene / 347

10.3.1 1,4-Butanediol / 349

10.3.2 Lesser Uses for Acetylene / 352

- 10.4 Synthesis Gas / 353
 - 10.4.1 Steam Reforming of Methane / 354
 - 10.4.2 Variants of Steam Reforming / 355
 - 10.4.3 Partial Oxidation of Hydrocarbons / 356
 - 10.4.4 Solid Feedstocks / 357
 - 10.4.5 Hydrogen / 357
- 10.5 Chemicals from Synthesis Gas / 358
 - 10.5.1 Ammonia and Its Derivatives / 358
 - 10.5.1.1 Urea and Melamine Resins / 360
 - 10.5.2 Methanol / 362
 - 10.5.2.1 Formaldehyde / 364
 - 10.5.2.2 Acetic Acid / 365
 - 10.5.2.3 Acetic Anhydride / 368
 - 10.5.2.4 Methanol to Gasoline / 370
 - 10.5.2.5 Methanol to Olefins / 371
 - 10.5.2.6 Lower Volume and Proposed Uses for Methanol / 373
 - 10.5.2.7 C_1 -Based Development Processes / 375
- 10.6 Carbon Monoxide Chemistry / 377
 - 10.6.1 Proposed Chemistry Based on Carbon Monoxide / 378
- 10.7 Gas-to-Liquid Fuels / 382
 - 10.7.1 Sasol GTL Technology / 382
 - 10.7.2 Shell Middle Distillate Synthesis / 383
 - 10.7.3 Other GTL Technologies / 383
- Notes and References / 384

CHAPTER 11 CHEMICALS FROM ALKANES

387

- 11.1 Functionalization of Methane / 388
 - 11.1.1 Methane to Methanol-Formaldehyde / 388
 - 11.1.2 Dimerization of Methane / 389
 - 11.1.3 Aromatization of Methane / 390
- 11.2 Functionalization of C_2 - C_4 Alkanes / 391
 - 11.2.1 Oxidation of C_2 - C_4 Alkanes / 391
 - 11.2.2 Dehydrogenation of C_2 - C_4 Alkanes / 393
 - 11.2.3 Aromatization of C_2 - C_4 Alkanes / 394
- 11.3 Carbon Black / 394
- Notes and References / 395

CHAPTER 12	CHEMICALS FROM COAL	399
12.1	Chemicals from Coke Oven Distillate / 400	
12.2	The Fischer–Tropsch Reaction / 404	
12.3	Coal Hydrogenation / 406	
12.4	Substitute Natural Gas (SNG) / 407	
12.5	Synthesis Gas Technology / 407	
12.6	Calcium Carbide / 408	
12.7	Coal and the Environment / 409	
	Notes and References / 409	
CHAPTER 13	FATS AND OILS	411
13.1	Fatty Acids / 416	
13.2	Fatty Nitrogen Compounds / 419	
13.3	“Dimer” Acid / 421	
13.4	Aminoamides and Imidazolines / 423	
13.5	Azelaic, Pelargonic, and Petroselinic Acids / 423	
13.6	Fatty Alcohols / 424	
13.7	Epoxidized Oils / 426	
13.8	Ricinoleic Acid / 426	
13.9	Glycerol / 428	
13.10	Alcoholysis of Fats and Oils / 428	
	13.10.1 Cocoa Butter / 429	
13.11	The Future of Fat and Oil Chemistry / 430	
	13.11.1 Non-Caloric Fat-Like Substances / 430	
	13.11.2 Alkyl Polyglycosides / 430	
	13.11.3 Fatty Acid-Based Fuels and Lubricants / 431	
	Notes and References / 432	
CHAPTER 14	CARBOHYDRATES	435
14.1	Sugars and Sorbitol / 435	
	14.1.1 Furfural / 442	
14.2	Starch / 443	
14.3	Cellulose / 446	
14.4	Gums / 449	
14.5	Fermentation and Biotechnology / 450	
	14.5.1 Amino Acids / 453	

- 14.5.2 Polymers / 454
- 14.5.3 Proteins by Recombinant DNA Technology / 455
- 14.5.4 A Fermentation Scenario / 455
- 14.5.5 Can Ethanol Be Justified as a Fuel? / 456
- Notes and References / 457

CHAPTER 15 HOW POLYMERS ARE MADE

459

- 15.1 Polymerization / 464
- 15.2 Functionality / 465
- 15.3 Step- and Chain-Growth Polymerizations / 469
 - 15.3.1 Free Radical Polymerization / 471
 - 15.3.2 Chain Transfer / 473
 - 15.3.3 Copolymerization / 475
 - 15.3.4 Molecular Weight / 477
 - 15.3.5 Polymerization Procedures / 478
 - 15.3.6 Ionic Polymerization / 480
 - 15.3.7 Living Polymers / 486
 - 15.3.8 Block Copolymers / 486
 - 15.3.9 Graft Copolymers / 489
 - 15.3.10 Metal Complex Catalysts / 489
 - 15.3.11 Metal Oxide Catalysts / 493
 - 15.3.12 Metallocene and Other Single-Site Catalysts / 494
 - 15.3.12.1 *Single-Site Nonmetallocene Catalysts / 498*
 - 15.3.12.2 *Late Transition Metal Catalysts / 498*
 - 15.3.12.3 *Commercial Prospects / 500*
- 15.4 Examples of Step Polymerization / 501
 - 15.4.1 Phenoplasts and Aminoplasts / 501
 - 15.4.2 Polyurethanes / 503
 - 15.4.3 Epoxy Resins / 506
 - 15.4.4 Dendritic and Hyperbranched Polymers / 508
- 15.5 Polymer Properties / 512
 - 15.5.1 Crystallinity / 512

- 15.5.2 Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature / 516
- 15.5.3 Molecular Cohesion / 517
- 15.5.4 Stress–Strain Diagrams / 518
- 15.6 Classes of Polymers / 520
- Notes and References / 521

CHAPTER 16 INDUSTRIAL CATALYSIS

527

- 16.1 Catalyst Choice / 528
 - 16.1.1 Reaction Velocity and Selectivity / 529
 - 16.1.2 Recovery of Unchanged Catalyst / 531
 - 16.1.3 Catalyst Deactivation / 532
 - 16.1.4 Access to Nonequilibrium Products / 532
- 16.2 Homogeneous and Heterogeneous Catalysis / 533
 - 16.2.1 Reactors for Heterogeneous Catalysts / 534
 - 16.2.2 “Immobilization” of Homogeneous Catalysts / 535
- 16.3 Catalyst Markets / 536
- 16.4 Catalysis by Acids and Bases / 539
- 16.5 Dual Function Catalysis / 543
- 16.6 Catalysis by Metals, Semiconductors, and Insulators / 544
 - 16.6.1 Catalysts for Automobile Emission Control / 545
- 16.7 Coordination Catalysis / 546
 - 16.7.1 Catalysts for Stereoregular Compounds / 547
 - 16.7.2 Asymmetric Synthesis / 549
- 16.8 Enzymes / 550
 - 16.8.1 Catalytic Antibodies / 552
- 16.9 Shape-Selective Catalysts / 553
- 16.10 Phase-Transfer and Fluorous Biphasic Catalysis / 556
- 16.11 Catalysts of the Future / 558
 - 16.11.1 Catalyst Design / 558
 - 16.11.2 Higher Selectivities / 559
 - 16.11.3 Catalysts with Greater Activity / 559
 - 16.11.4 Pollution Problems / 560
 - 16.11.5 Catalysts for New Reactions / 560
 - 16.11.6 Catalysts that Mimic Natural Catalysts / 560

16.11.7 Catalyst Discovery via High Throughput
Experimentation / 561

Notes and References / 562

CHAPTER 17 SUSTAINABILITY AND GREEN CHEMISTRY 567

- 17.1 Energy Sources / 569
- 17.1.1 Wind Power / 570
- 17.1.2 Wave Power / 570
- 17.1.3 Solar Power / 571
- 17.1.3.1 Photovoltaic Cells / 571
- 17.1.3.2 Artificial Photosynthesis / 572
- 17.1.4 Methane Hydrate / 574
- 17.1.5 The Hydrogen Economy / 575
- 17.1.5.1 Fuel Cells / 576
- 17.2 Pollution / 580
- 17.2.1 The Ozone Layer / 581
- 17.2.2 Global Warming / 585
- 17.2.3 Trace Chemicals / 587
- 17.2.3.1 Pesticides / 587
- 17.2.3.2 Nonpesticide Lipophiles / 588
- 17.2.4 Air Pollution / 589
- 17.2.4.1 Sulfur Dioxide and Particulates / 589
- 17.2.4.2 Automobile Exhaust Emissions / 590
- 17.2.5 Water Treatment / 593
- 17.2.6 Solid Wastes / 594
- 17.2.6.1 Waste Prevention / 595
- 17.2.6.2 Recycling / 595
- 17.2.6.3 Combustion—Incineration / 596
- 17.2.6.4 Sanitary Landfill / 598
- 17.2.7 Petrochemical Industry Wastes / 599
- 17.2.8 Other Environmental Problems / 600
- 17.3 Green Chemistry / 601
- 17.3.1 The Decline in Acetylene Chemistry / 602
- 17.3.2 Nylon / 603
- 17.3.3 Replacement of Phosgene / 603
- 17.3.4 Monomethylation by Dimethyl Carbonate / 604
- 17.3.5 Liquid and Supercritical Carbon Dioxide
and Water / 605

17.3.6	Ionic Liquids / 607	
17.3.7	Photocatalysts / 608	
17.3.8	Paired Electrosynthesis / 608	
17.3.9	Sertraline Synthesis / 609	
17.3.10	Catalytic Dehydrogenation of Diethanolamine / 611	
17.3.11	Genetic Manipulation / 611	
17.3.12	Polyhydroxyalkanoates / 612	
17.4	Valediction / 613	
	Notes and References / 614	
APPENDIX 1	A NOTE ON COST CALCULATIONS	620
APPENDIX 2	UNITS AND CONVERSION FACTORS	624
APPENDIX 3	SPECIAL UNITS IN THE CHEMICAL INDUSTRY	626
INDEX		629