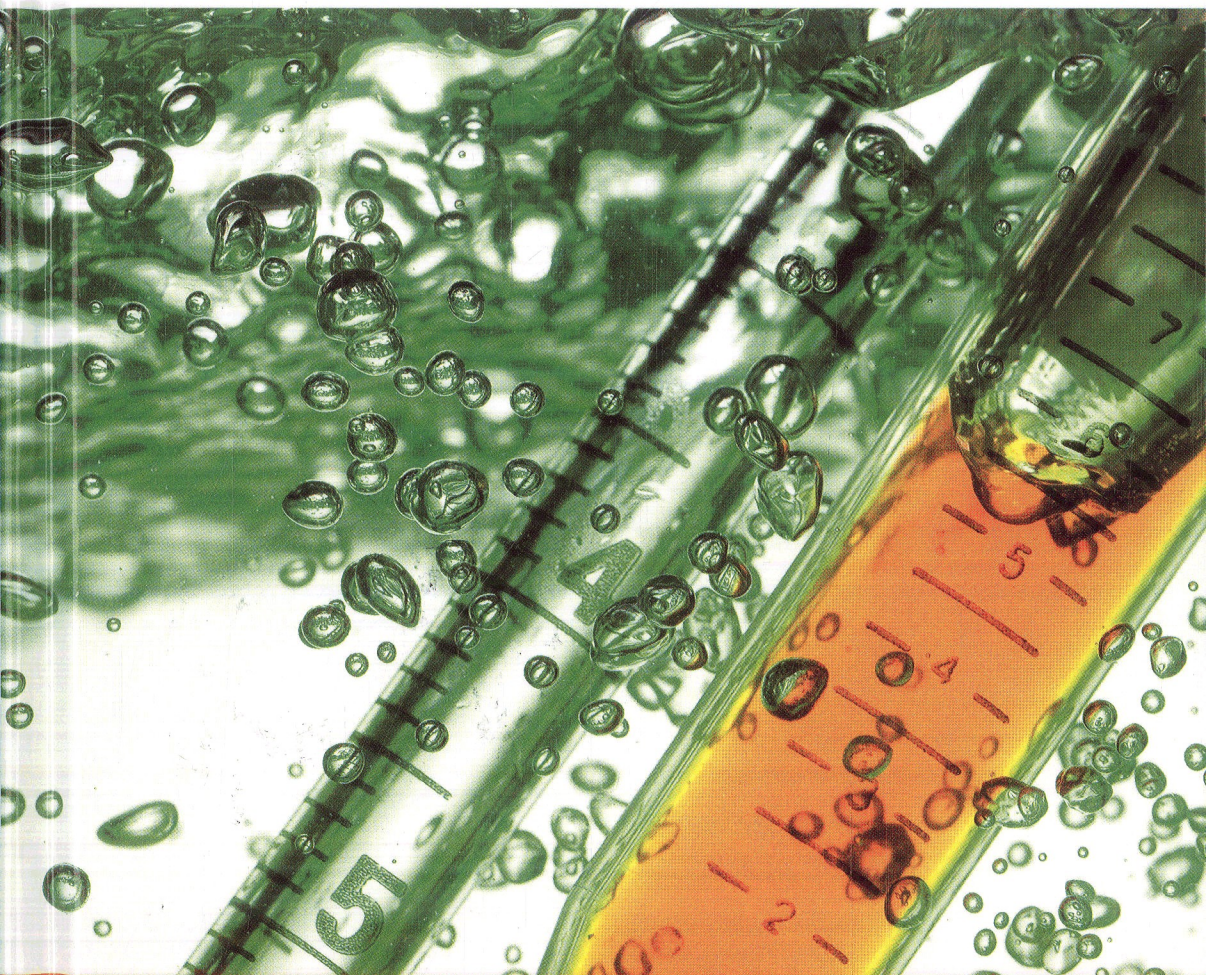


2nd Edition

Green Chemistry

An Introductory Text

Mike Lancaster



RSC Publishing

Contents

Chapter 1	Principles and Concepts of Green Chemistry	1
1.1	Introduction	1
1.2	Sustainable Development and Green Chemistry	3
1.2.1	Green Engineering	4
1.3	Atom Economy	7
1.4	Atom Economic Reactions	9
1.4.1	Rearrangement Reactions	9
1.4.2	Addition Reactions	11
1.5	Atom Un-economic Reactions	13
1.5.1	Substitution Reactions	13
1.5.2	Elimination Reactions	15
1.5.3	Wittig Reactions	16
1.6	Reducing Toxicity	17
1.6.1	Measuring Toxicity	19
	Review Questions	21
	Further Reading	22
Chapter 2	Waste: Production, Problems, and Prevention	23
2.1	Introduction	23
2.2	Some Problems Caused by Waste	25
2.3	Sources of Waste from the Chemical Industry	26
2.4	Cost of Waste	29
2.5	Waste Minimization Techniques	33
2.5.1	The Team Approach to Waste Minimization	34
2.5.2	Process Design for Waste Minimization	36
2.5.3	Minimizing Waste from Existing Processes	38

2.6	On-site Waste Treatment	39
2.6.1	Physical Treatment	41
2.6.2	Chemical Treatment	42
2.6.3	Biotreatment Plants	46
2.7	Design for Degradation	47
2.7.1	Degradation and Surfactants	48
2.7.2	DDT	49
2.7.3	Polymers	50
2.7.4	Some Rules for Degradation	51
2.8	Polymer Recycling	52
2.8.1	Separation and Sorting	53
2.8.2	Incineration	55
2.8.3	Mechanical Recycling	56
2.8.4	Chemical Recycling to Monomers	57
	Review Questions	60
	Further Reading	60
Chapter 3	Measuring and Controlling Environmental Performance	61
3.1	The Importance of Measurement	61
3.1.1	Lactic Acid Production	62
3.1.2	Safer Gasoline	65
3.2	Introduction to Life Cycle Assessment	66
3.2.1	Four Stages of LCA	68
3.2.2	Carbon Footprinting	72
3.3	Green Process Metrics	74
3.4	Environmental Management Systems (EMS)	77
3.4.1	ISO 14001	77
3.4.2	The European Eco-Management and Audit Scheme (EMAS)	81
3.5	Eco-Labels	82
3.6	Legislation	83
3.6.1	Integrated Pollution Prevention and Control (IPPC)	84
3.6.2	REACH	87
	Review Questions	88
	Further Reading	89
Chapter 4	Catalysis and Green Chemistry	90
4.1	Introduction to Catalysis	90
4.1.1	Comparison of Catalyst Types	92
4.2	Heterogeneous Catalysts	94
4.2.1	Basics of Heterogeneous Catalysis	94
4.2.2	Zeolites and the Bulk Chemical Industry	97

4.2.3	Heterogeneous Catalysis in the Fine Chemical and Pharmaceutical Industries	105
4.2.4	Catalytic Converters	114
4.3	Homogeneous Catalysts	117
4.3.1	Transition Metal Catalysts with Phosphine or Carbonyl Ligands	117
4.3.2	Greener Lewis Acids	121
4.3.3	Asymmetric Catalysis	122
4.4	Phase Transfer Catalysis	128
4.4.1	Hazard Reduction	129
4.4.2	C–C Bond Formation	130
4.4.3	Oxidation using Hydrogen Peroxide	131
4.5	Biocatalysis	132
4.6	Photocatalysis	135
4.7	Conclusions	137
	Review Questions	137
	Further Reading	138

Chapter 5 Organic Solvents: Environmentally Benign Solutions **139**

5.1	Organic Solvents and Volatile Organic Compounds	139
5.2	Solvent-free Systems	141
5.3	Supercritical Fluids	144
5.3.1	Supercritical Carbon Dioxide (scCO ₂)	146
5.3.2	Supercritical Water	156
5.4	Water as a Reaction Solvent	157
5.4.1	Water Based Coatings	162
5.5	Ionic Liquids	163
5.5.1	Ionic Liquids as Catalysts	165
5.5.2	Ionic Liquids as Solvents	166
5.6	Fluorous Biphasic Solvents	170
5.7	Comparing Greenness of Solvents	172
5.8	Conclusions	173
	Review Questions	174
	Further Reading	174

Chapter 6 Renewable Resources **175**

6.1	Biomass as a Renewable Resource	175
6.2	Energy	175
6.2.1	Fossil Fuels	175
6.2.2	Energy from Biomass	179
6.2.3	Solar Power	186
6.2.4	Other Forms of Renewable Energy	188
6.2.5	Fuel Cells	189

6.3	Chemicals from Renewable Feedstocks	194
6.3.1	Chemicals from Fatty Acids	196
6.3.2	Polymers from Renewable Resources	204
6.3.3	Some Other Chemicals from Natural Resources	210
6.4	Alternative Economies	215
6.4.1	Syngas Economy	216
6.4.2	Hydrogen Economy	217
6.5	Biorefinery	218
6.6	Conclusions	219
	Review Questions	220
	Further Reading	220

Chapter 7 Emerging Greener Technologies and Alternative Energy Sources 221

7.1	Design for Energy Efficiency	221
7.2	Photochemical Reactions	224
7.2.1	Advantages of and Challenges Faced by Photochemical Processes	225
7.2.2	Examples of Photochemical Reactions	227
7.3	Chemistry using Microwaves	231
7.3.1	Microwave Heating	231
7.3.2	Microwave-assisted Reactions	232
7.4	Sonochemistry	236
7.4.1	Sonochemistry and Green Chemistry	237
7.5	Electrochemical Synthesis	239
7.5.1	Examples of Electrochemical Synthesis	241
7.6	Conclusions	244
	Review Questions	244
	Further Reading	245

Chapter 8 Designing Greener Processes 246

8.1	Introduction	246
8.2	Conventional Reactors	247
8.2.1	Batch Reactors	247
8.2.2	Continuous Reactors	250
8.3	Inherently Safer Design	252
8.3.1	Minimization	254
8.3.2	Simplification	255
8.3.3	Substitution	255
8.3.4	Moderation	256
8.3.5	Limitation	257
8.4	Process Intensification	258

8.4.1	Some PI Equipment	260
8.4.2	Some Example of Intensified Processes	263
8.5	In-process Monitoring	266
8.5.1	Near-infrared Spectroscopy	268
8.6	Process Safety	269
	Review Questions	270
	Further Reading	270

Chapter 9 Industrial Case Studies 271

9.1	Introduction	271
9.2	Methyl Methacrylate	271
9.3	Greening of Acetic Acid Manufacture	273
9.4	EPDM Rubbers	277
9.5	Vitamin C	280
9.6	Leather Manufacture	282
9.6.1	Tanning	284
9.6.2	Fatliquoring	288
9.7	Dyeing to be Green	288
9.7.1	Some Manufacturing Improvements	289
9.7.2	Dye Application	292
9.8	Polyethylene	293
9.8.1	Radical Process	293
9.8.2	Ziegler–Natta Catalysis	294
9.8.3	Metallocene Catalysis	295
9.8.4	Post Metallocene Catalysts	297
9.9	Eco-friendly Pesticides	298
9.9.1	Insecticides	298
9.10	Epichlorohydrin	301
	Review Questions	302

Chapter 10 The Future's Green: An Integrated Approach to a Greener Chemical Industry 304

10.1	Society and Sustainability	304
10.2	Barriers & Drivers	305
10.3	Role of Legislation	307
10.4	Green Chemical Supply Strategies	309
10.5	Greener Energy	311
10.6	Conclusions	312
	Review Questions	312
	Further Reading	313

Subject Index 314