

GREEN CHEMISTRY AND CHEMICAL ENGINEERING

Fotis Rigas • Paul Amyotte

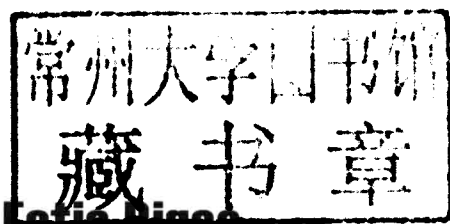
Hydrogen Safety



CRC Press
Taylor & Francis Group

GREEN CHEMISTRY AND CHEMICAL ENGINEERING

Hydrogen Safety



Fotis Nigas

Paul Amyotte



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an informa business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2013 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed in the United States of America on acid-free paper
Version Date: 20120531

International Standard Book Number: 978-1-4398-6231-5 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Hydrogen Safety

GREEN CHEMISTRY AND CHEMICAL ENGINEERING

Series Editor: Sunggyu Lee

Ohio University, Athens, Ohio, USA

Proton Exchange Membrane Fuel Cells: Contamination and Mitigation Strategies

Hui Li, Shanna Knights, Zheng Shi, John W. Van Zee, and JiuJun Zhang

Proton Exchange Membrane Fuel Cells: Materials Properties and Performance

David P. Wilkinson, JiuJun Zhang, Rob Hui, Jeffrey Fergus, and Xianguo Li

Solid Oxide Fuel Cells: Materials Properties and Performance

Jeffrey Fergus, Rob Hui, Xianguo Li, David P. Wilkinson, and JiuJun Zhang

**Efficiency and Sustainability in the Energy and Chemical Industries:
Scientific Principles and Case Studies, Second Edition**

Krishnan Sankaranarayanan, Jakob de Swaan Arons, and Hedzer van der Kooi

Nuclear Hydrogen Production Handbook

Xing L. Yan and Ryutaro Hino

Magneto Luminous Chemical Vapor Deposition

Hirotsugu Yasuda

Carbon-Neutral Fuels and Energy Carriers

Nazim Z. Muradov and T. Nejat Veziroğlu

Oxide Semiconductors for Solar Energy Conversion: Titanium Dioxide

Janusz Nowotny

Lithium-Ion Batteries: Advanced Materials and Technologies

Xianxia Yuan, Hansan Liu, and JiuJun Zhang

Process Integration for Resource Conservation

Dominic C. Y. Foo

**Chemicals from Biomass: Integrating Bioprocesses into Chemical Production Complexes
for Sustainable Development**

Debalina Sengupta and Ralph W. Pike

Hydrogen Safety

Fotis Rigas and Paul Amyotte

Series Preface

The subjects and disciplines of chemistry and chemical engineering have encountered a new landmark in the way of thinking about developing and designing chemical products and processes. This revolutionary philosophy, termed *green chemistry and chemical engineering*, focuses on the designs of products and processes that are conducive to reducing or eliminating the use and/or generation of hazardous substances. In dealing with hazardous or potentially hazardous substances, there may be some overlaps and interrelationships between environmental chemistry and green chemistry. Whereas environmental chemistry is the chemistry of the natural environment and the pollutant chemicals in nature, green chemistry proactively aims to reduce and prevent pollution at its very source. In essence, the philosophies of green chemistry and chemical engineering tend to focus more on industrial application and practice rather than academic principles and phenomenological science. However, as both a chemistry and chemical engineering philosophy, green chemistry and chemical engineering derive from and build on organic chemistry, inorganic chemistry, polymer chemistry, fuel chemistry, biochemistry, analytical chemistry, physical chemistry, environmental chemistry, thermodynamics, chemical reaction engineering, transport phenomena, chemical process design, separation technology, automatic process control, and more. In short, green chemistry and chemical engineering are the rigorous use of chemistry and chemical engineering for pollution prevention and environmental protection.

The Pollution Prevention Act of 1990 in the United States established a national policy to prevent or reduce pollution at its source whenever feasible. And adhering to the spirit of this policy, the Environmental Protection Agency (EPA) launched its Green Chemistry Program in order to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. Global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international communities of science, engineering, academia, industry, and government in all phases and aspects.

Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as a green solvent in separation technologies; application of supercritical water oxidation for destruction of harmful substances; process integration with carbon dioxide sequestration steps; solvent-free synthesis of chemicals and polymeric materials; exploitation of biologically degradable materials; use of aqueous hydrogen peroxide for efficient oxidation; development of hydrogen proton exchange membrane (PEM) fuel cells for a variety of power generation needs; advanced biofuel

productions; devulcanization of spent tire rubber; avoidance of the use of chemicals and processes causing generation of volatile organic compounds (VOCs); replacement of traditional petrochemical processes by microorganism-based bioengineering processes; replacement of chlorofluorocarbons (CFCs) with nonhazardous alternatives; advances in design of energy-efficient processes; use of clean, alternative, and renewable energy sources in manufacturing; and much more. This list, even though it is only a partial compilation, is undoubtedly growing exponentially.

This book series on Green Chemistry and Chemical Engineering by CRC Press/Taylor & Francis is designed to meet the new challenges of the twenty-first century in the chemistry and chemical engineering disciplines by publishing books and monographs based on cutting-edge research and development to the effect of reducing adverse impacts on the environment by chemical enterprise. In achieving this, the series will detail the development of alternative sustainable technologies that will minimize the hazard and maximize the efficiency of any chemical choice. The series aims at delivering the readers in academia and industry with an authoritative information source in the field of green chemistry and chemical engineering. The publisher and its series editor are fully aware of the rapidly evolving nature of the subject and its long-lasting impact on the quality of human life in both the present and future. As such, the team is committed to making this series the most comprehensive and accurate literary source in the field of green chemistry and chemical engineering.

Sunggyu Lee

Preface

This book on the safe handling and use of hydrogen is intended as much to provoke thought and dialogue as to provide practical guidance. We of course hope that readers will find the information we present to be helpful in their endeavors to bring the envisaged hydrogen economy into reality. But we also hope that important areas of safety research, often viewed as being nontechnological, will be welcomed into the discussion of hydrogen safety along with the more familiar technological topics.

The book is organized to first address questions associated with the hazards of hydrogen and the ensuing risk in its use within industry and by the public. What are the properties of hydrogen that can render it a hazardous substance? How have these hazards historically resulted in undesired incidents? How might these hazards arise in the storage of hydrogen and with its use in vehicular transportation?

We then turn to the issues of inherently safer design and, in accordance with the previous comment on so-called nontechnological topics, safety management systems and safety culture. The European Commission (EC) Network of Excellence for Hydrogen Safety, *HySafe*, is singled out for separate coverage, as are various case studies associated with hydrogen and constructional materials. We conclude with a brief look at future research requirements and current legal requirements for hydrogen safety.

Our approach, then, has been to attempt a balanced view of hydrogen safety. Such a perspective comes not only from our respective areas of expertise, but also a collective belief that the safety of any material or activity is most effectively addressed through a combination of the physical sciences and engineering principles together with the management and social sciences. Non-hydrogen-related industries have undergone painful experiences in this regard; there should be no need for industrial applications involving hydrogen to experience the same difficulties.

Coauthor Fotis Rigas would like to acknowledge and thank his family, and especially his wife, Betty, for their (almost) uncomplaining and enduring patience during his long-drawn-out academic activities. He also wishes to express his gratitude to Ms. Allison Shatkin, senior editor in Materials Science and Chemical Engineering of CRC Press/Taylor & Francis, for entrusting him and coauthor Paul Amyotte with the task of writing this book.

Coauthor Paul Amyotte would like to acknowledge and thank his family for their loving support in all his professional undertakings. He is especially grateful to his wife, Peggy. He also extends gratitude to Dalhousie University, and in particular Dr. Joshua Leon, dean of Engineering, for his recent appointment as C. D. Howe Chair in Engineering.

The Authors

Fotis Rigas is an associate professor of Chemical Engineering at National Technical University of Athens in Greece and has been a Visiting Professor at National Autonomous University of Mexico. His current research and academic activities are in the areas of process safety and bioremediation of contaminated sites. He has published or presented over 150 papers in the fields of his activities and is a reviewer of papers in 34 international journals.

Paul Amyotte is a professor of Chemical Engineering and the C. D. Howe Chair in Engineering at Dalhousie University in Canada. His research and practice interests are in the areas of inherent safety, process safety, and dust explosion prevention and mitigation. He has published or presented over 200 papers in the field of industrial safety and is the editor of the *Journal of Loss Prevention in the Process Industries*.

List of Acronyms

ADNR (inland waterways)	Regulation for the Carriage of Dangerous Substances on the Rhine (EU)
ADR (road)	Accord Européen Relatif au Transport International des Marchandises Dangereuses par Route - European Agreement Concerning the International Carriage of Dangerous Goods by Road
AIChE	American Institute of Chemical Engineers
ALARP	As Low As Reasonably Practicable Principle
ATEX	Appareils destinés à être utilisés en Atmosphères Explosives (EU Directive)
BAMs	Bulk Amorphous Materials
BLEVE	Boiling Liquid Expanding Vapor Explosion
CCPA	Canadian Chemical Producers' Association
CCPS	Center for Chemical Process Safety
CEI	Dow Chemical Exposure Index
CFCs	Chlorofluorocarbons
CFD	Computational Fluid Dynamics
CL	Checklist
CNG	Compressed Natural Gas
COD	Code of Practice
CPU	Central Processing Unit
CSB	Chemical Safety Board (USA)
CSChE	Canadian Society for Chemical Engineering
CVCE	Confined Vapor Cloud Explosion
DDT	Deflagration-to-Detonation Transition
DGR	IATA Dangerous Goods Regulations
DNR	Department of Naval Research
DOE	United States Department of Energy
EIGA	European Industrial Gases Association
EPR	European Pressure Reactor
ETA	Event Tree Analysis
FDS	Fire Dynamics Simulator Code
F&EI	Dow Fire and Explosion Index
FMCSA	Federal Motor Carrier Safety Administration
FMEA	Failure Modes and Effects Analysis
FTA	Fault Tree Analysis

FVM	Finite Volume Method
GH ₂	Compressed Hydrogen Gas
HAZOP	Hazard and Operability Analysis
HIAD	European Hydrogen Incident and Accident Database
HRAM	Hydrogen Risk Assessment Method
HSE	Health and Safety Executive
HTHA	High-Temperature Hydrogen Attack
IATA	International Air Transport Association
IChemE	Institution of Chemical Engineers (UK)
IEA	International Energy Agency
IGC	Industrial Gases Council
IMO (sea)	International Maritime Organization
ISD	Inherently Safer Design
ISO	International Standards Organization
ITER	International Thermonuclear Experimental Reactor
LBLOCA	Large Break Loss of Coolant Accident
LDL	Lower Detonability Limit
LFL	Low Flammability Limit
LH ₂	Liquid Hydrogen
LLNL	Lawrence Livermore National Laboratory
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
MH	Metal Hydride
MHIDAS	Major Hazard Incident Database Service
MIACC	Major Industrial Accidents Council of Canada)
MIC	Methyl Isocyanate
MIL-STD 882	Military Standard 882
MOC	Management of Change
MOFs	Metal-Organic Frameworks
MVFRI	Motor Vehicle Fire Research Institute
NASA	National Aeronautics and Space Administration
NBP	Normal Boiling Point
NFPA	National Fire Protection Association
NHTSA	National Highway Traffic Safety Administration
NIST	National Institute of Standards and Technology
NRA	National Railway Authority
NTP	Normal Temperature and Pressure
NWC	Naval Weapons Center
OHA	Operating Hazard Analysis
OHSAS	Occupational Health and Safety Assessment Series

OSHA	U.S. Occupational Safety and Health Administration
PAR	Passive Auto-Catalytic Recombiners
PED	European Pressure Equipment Directive
PHA	Preliminary Hazard Analysis
PRD	Pressure Relief Devices
PSM	Process Safety Management
QRA	Quantitative Risk Assessment
RID (rail)	Règlement Concernant le Transport International Ferroviaire des Marchandises Dangereuses – Regulation Concerning the Transport of Dangerous Goods by International Railway
RRR	Relative Risk Ranking
SHHSV	Stationary High-pressure Hydrogen Storage Vessel
SRB	Solid Rocket Boosters
SST	Shear Stress Transport Models
STP	Standard Temperature and Pressure
SUV	Suburban Utility Vehicle
SwRI	Southwest Research Institute
TNT	Trinitrotoluene
TPED	Transportable Pressure Equipment Directive
TRD	Thermal Relief Device
UFL	Upper Flammability Limit
UDL	Upper Detonability Limit
UN ECE	United Nations' Economic Commission for Europe
UVCE	Unconfined Vapor Cloud Explosion
WI	What-If Analysis

Contents

Series Preface	xi
Preface.....	xiii
The Authors	xv
List of Acronyms	xvii
1. Introduction	1
References	3
2. Historical Survey of Hydrogen Accidents.....	5
2.1 Significant Disasters	7
2.1.1 The Hindenburg Disaster	7
2.1.2 Hydrogen Release during Maintenance Work	9
2.1.3 Pressurized Hydrogen Tank Rupture.....	9
2.1.4 The <i>Challenger</i> Disaster	10
2.2 Incident Reporting	11
References	16
3. Hydrogen Properties Associated with Hazards.....	19
3.1 General Consideration.....	19
3.2 Hydrogen Gas Properties Related to Hazards	20
3.3 Liquefied Hydrogen Properties Related to Hazards	24
References	25
4. Hydrogen Hazards	27
4.1 Physiological Hazards.....	27
4.1.1 Asphyxiation	27
4.1.2 Thermal Burns	28
4.1.3 Cryogenic Burns	31
4.1.4 Hypothermia	32
4.1.5 Overpressure Injury	32
4.2 Physical Hazards.....	33
4.2.1 Hydrogen Embrittlement.....	33
4.2.1.1 Types of Embrittlement	34
4.2.1.2 Mechanical Properties Deterioration	35
4.2.1.3 Main Factors of Hydrogen Embrittlement	35
4.2.1.4 Hydrogen Embrittlement Control.....	36
4.2.2 Thermal Stability of Structural Materials	36
4.2.2.1 Low-Temperature Mechanical Properties	36
4.2.2.2 Low-Temperature Embrittlement.....	37
4.2.2.3 Thermal Contraction.....	38

4.3	Chemical Hazards	39
4.3.1	General Considerations and Accident Statistics.....	39
4.3.2	Flammability of Hydrogen.....	40
4.3.2.1	Hydrogen-Air Mixtures	42
4.3.2.2	Hydrogen-Oxygen Mixtures	43
4.3.2.3	Effects of Diluents	43
4.3.2.4	Effects of Halocarbon Inhibitors	44
4.3.2.5	Autoignition Temperature	45
4.3.2.6	Quenching Gap in Air.....	45
4.3.3	Ignition Sources	46
4.3.3.1	Sparks.....	47
4.3.3.2	Hot Objects and Flames	48
4.3.4	Explosion Phenomena.....	49
4.3.4.1	Terms and Definitions	49
4.3.4.2	Detonation Limits	51
4.3.4.3	Ignition Energy.....	53
4.3.4.4	Detonation Cell Size.....	53
4.3.4.5	Consequences of Hydrogen-Air Explosions.....	56
4.3.4.6	Damage of Structures from Thermal Radiation and Blast Waves.....	57
4.3.4.7	Safety Distances from Hydrogen Storage Facilities	58
4.3.4.8	Deflagration-to-Detonation Transition.....	59
4.3.4.9	Accidental Hydrogen Generation in Nuclear Reactors.....	59
4.3.5	Environmental Concerns.....	60
	References	62
5.	Hazards in Hydrogen Storage Facilities	65
5.1	Storage Options	65
5.1.1	Storage as Liquid Hydrogen.....	66
5.1.2	Storage in Porous Media	67
5.2	Hazard Spotting.....	68
5.2.1	Refrigerated Storage Conditions.....	69
5.2.2	Cryogenic Storage Conditions	71
5.3	Hazard Evaluation	73
5.3.1	Methodology	73
5.3.2	ETA Method Application.....	74
5.4	Qualitative Prediction of Cloud Travel.....	75
5.5	Gas Dispersion Simulation	76
5.5.1	CFD Modeling	76
5.5.2	CFD Simulations of Gaseous and Liquefied Hydrogen Releases	76
5.5.3	Releases in Confined Spaces	83
5.5.4	Thermal Hazards from Hydrogen Clouds.....	85

5.5.5	Simulations in the Chemical Industries	86
5.5.6	Simulations in the Nuclear Industry	89
References	92
6.	Hazards of Hydrogen Use in Vehicles	97
6.1	Hydrogen Systems in Vehicles	97
6.1.1	Internal Combustion Engines	97
6.1.2	Hydrogen Storage in Vehicles	98
6.1.3	Safety Comparisons of Hydrogen, Methane, and Gasoline.....	99
6.2	Accidents Caused by Hydrogen Use in Vehicles.....	102
6.2.1	Hydrogen Vehicle Hazards	102
6.2.2	Hydrogen Tanks Onboard.....	104
6.2.3	Accidental Release of Hydrogen from Vehicles	110
6.2.4	Fueling Stations.....	114
References	116
7.	Inherently Safer Design	119
7.1	Hierarchy of Risk Controls	120
7.2	Minimization (Intensification)	123
7.3	Substitution	125
7.4	Moderation (Attenuation)	126
7.5	Simplification	128
7.6	Other Examples	129
7.7	Measurement of Inherent Safety	131
References	136
8.	Safety Management Systems	143
8.1	Introduction to Safety Management Systems.....	143
8.2	Process Safety Management.....	146
8.2.1	PSM Element 1—Accountability: Objectives and Goals	154
8.2.2	PSM Element 2—Process Knowledge and Documentation.....	155
8.2.3	PSM Element 3—Capital Project Review and Design Procedures.....	156
8.2.4	PSM Element 4—Process Risk Management.....	157
8.2.5	PSM Element 5—Management of Change	163
8.2.6	PSM Element 6—Process and Equipment Integrity	163
8.2.7	PSM Element 7—Human Factors	164
8.2.8	PSM Element 8—Training and Performance	165
8.2.9	PSM Element 9—Incident Investigation.....	167
8.2.10	PSM Element 10—Company Standards, Codes, and Regulations	167
8.2.11	PSM Element 11—Audits and Corrective Actions	168

8.2.12	PSM Element 12—Enhancement of Process Safety Knowledge	168
8.3	Safety Culture	169
	References	171
9.	HySafe: Safety of Hydrogen as an Energy Carrier	177
9.1	Overview of EC Network of Excellence for Hydrogen Safety	178
9.2	HySafe Work Packages and Projects	179
9.3	e-Academy of Hydrogen Safety	183
	References	186
10.	Case Studies	189
10.1	Case Study Development	189
10.2	Use of Case Studies	192
10.2.1	Case Study Legacy Lessons	193
10.2.2	Case Study Engineering Lessons	195
10.2.3	Case Study Management Lessons	195
10.3	Incident Investigation Reports	195
10.4	Other Examples	199
10.4.1	Hydrogen and Explosible Dusts	199
10.4.2	Hydrogen Sulfide	202
	References	204
11.	Effects of Hydrogen on Materials of Construction	207
11.1	Hydrogen Embrittlement	209
11.2	Loss of Thermal Stability	212
11.3	Ongoing Research	213
	References	214
12.	Future Requirements for Hydrogen Safety	217
12.1	Hydrogen Safety Research Gaps Identified in the Literature	217
12.2	Hydrogen Safety Needs: Some Thoughts on Research	220
12.2.1	General Process Safety Research Needs	220
12.2.2	Hydrogen-Specific Process Safety Research Needs	225
	References	225
13.	Legal Requirements for Hydrogen Safety	229
13.1	General Aspects and Definitions	229
13.1.1	ATEX Directive	230
13.1.2	Other Official Documents	231
13.2	Hydrogen Facilities	232
13.2.1	Electrical Considerations	233
13.2.2	Bonding and Grounding	233

13.2.3	Hydrogen Transmission Lines	234
13.2.4	Elimination of Ignition Sources	234
13.2.5	Hot Objects, Flames, and Flame Arrestors	235
13.2.6	Design and Construction of Buildings	235
	13.2.6.1 Explosion Venting	235
	13.2.6.2 Test Facilities	235
13.2.7	Placarding in Exclusion and Control Areas.....	236
13.2.8	Protection of Hydrogen Systems and Surroundings.....	236
	13.2.8.1 Barricades	236
	13.2.8.2 Liquid Spills and Vapor Cloud Dispersion.....	237
	13.2.8.3 Shields and Impoundment Areas	238
13.2.9	Quantity-Distance Relationships.....	238
13.3	Hydrogen Fueling of Vehicles.....	238
	13.3.1 Guidelines for Hydrogen Systems on Vehicles	239
	13.3.1.1 Compressed Hydrogen Systems	239
	13.3.1.2 Liquid Hydrogen Systems.....	241
	13.3.1.3 Liquid Fuel Reformers Onboard.....	243
	13.3.2 Guidelines for Hydrogen Fueling Facilities.....	244
	13.3.2.1 Compressed Hydrogen Fueling	244
	13.3.2.2 Liquid Hydrogen Fueling	248
13.4	Storage, Handling, and Distribution of Liquid Hydrogen	250
	13.4.1 Customer Installations	251
	13.4.2 Transport and Distribution of Liquid Hydrogen	252
	13.4.2.1 Road Transport	252
	13.4.2.2 Tank Container Transport by Railway.....	253
	13.4.2.3 Transport by Waterways and Sea	253
	References	254
14.	Conclusion.....	255
Index.....		257