

Beyond Oil and Gas: The Methanol Economy

*George A. Olah, Alain Goeppert,
and G. K. Surya Prakash*



WILEY-VCH Verlag GmbH & Co. KGaA

**Beyond Oil and Gas:
The Methanol Economy**

*George A. Olah, Alain Goeppert,
and G. K. Surya Prakash*

More Titles by these Authors

George A. Olah (Editor), G. K. Surya Prakash (Editor)

Carbocation Chemistry

2004

ISBN 0-471-28490-4

George A. Olah, Árpád Molnár

Hydrocarbon Chemistry

2nd Edition

2003

ISBN 0-471-41782-3

George A. Olah, Kenneth K. Laali, Qi Wang, G. K. Surya Prakash

Onium Ions

1998

ISBN 0-471-14877-6

Beyond Oil and Gas: The Methanol Economy

*George A. Olah, Alain Goeppert,
and G. K. Surya Prakash*



WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Dr. George A. Olah

Dr. Alain Goeppert

Prof. Dr. G. K. Surya Prakash

Loker Hydrocarbon Research Institute
University of Southern California
837 W. 37th. Street
Los Angeles, CA 90089-1661
USA

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: Applied for

British Library Cataloguing-in-Publication Data:

A catalogue record for this book is available from the British Library.

Bibliographic information published by

Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>.

© 2006 WILEY-VCH Verlag GmbH & Co.
KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany.
Printed on acid-free paper.

Typesetting Hagedorn Kommunikation,
Viernheim

Printing Betz Druck GmbH, Darmstadt
Bookbinding Litges & Dopf Buchbinderei
GmbH, Heppenheim

Cover Grafik-Design Schulz, Fußgönheim

ISBN-13: 978-3-527-31275-7

ISBN-10: 3-527-31275-7

Contents

Chapter 1

Introduction 1

Chapter 2

Coal in the Industrial Revolution, and Beyond 11

Chapter 3

History of Oil and Natural Gas 18

Oil Extraction and Exploration 22

Natural Gas 23

Chapter 4

Fossil Fuel Resources and Uses 27

Coal 28

Oil 32

Tar Sands 37

Oil Shale 38

Natural Gas 39

Coalbed Methane 46

Tight Sands and Shales 47

Methane Hydrates 47

Outlook 49

Chapter 5

Diminishing Oil and Gas Reserves 51

Chapter 6

The Continuing Need for Hydrocarbons and their Products 60

Fractional Distillation 63

Thermal Cracking 64

Chapter 7

Fossil Fuels and Climate Change 72

Mitigation 81

Chapter 8

Renewable Energy Sources and Atomic Energy 84

Hydropower 87

Geothermal Energy 91

Wind Energy 94

Solar Energy: Photovoltaic and Thermal 97

Electricity from Photovoltaic Conversion 98

Solar Thermal Power for Electricity Production 100

Electric Power from Saline Solar Ponds 101

Solar Thermal Energy for Heating 102

Economic Limitations of Solar Energy 102

Biomass Energy 103

Electricity from Biomass 103

Liquid Biofuels 104

Ocean Energy: Thermal, Tidal, and Wave Power 108

Tidal Energy 109

Waves 110

Ocean Thermal Energy 110

Nuclear Energy 111

Energy from Nuclear Fission Reactions 113

Breeder Reactors 118

The Need for Nuclear Power 119

Economics 121

Safety 121

Radiation Hazards 124

Nuclear Byproducts and Waste 125

Emissions 127

Nuclear Power: An Energy Source for the Future 127

Nuclear Fusion 128

Future Outlook 131

Chapter 9

The Hydrogen Economy and its Limitations 133

The Discovery and Properties of Hydrogen 133

The Development of Hydrogen Energy 135

The Production and Uses of Hydrogen 138

Hydrogen from Fossil Fuels 140

Hydrogen from Biomass 141

Photobiological Water Cleavage 142

Water Electrolysis 142

Hydrogen Production Using Nuclear Energy 144

The Challenge of Hydrogen Storage	145
Liquid Hydrogen	147
Compressed Hydrogen	148
Metal Hydrides and Solid Absorbents	149
Other Means of Hydrogen Storage	150
Hydrogen: Centralized or Decentralized Distribution?	150
Safety of Hydrogen	153
Hydrogen in Transportation	154
Fuel Cells	155
History	155
Fuel Cell Efficiency	156
Hydrogen-Based Fuel Cells	159
PEM Fuel Cells for Transportation	162
Regenerative Fuel Cells	165
Outlook	166

Chapter 10

The “Methanol Economy”: General Aspects	168
---	-----

Chapter 11

Methanol as a Fuel and Energy Carrier	173
Properties and Historical Background	173
Present Uses of Methanol	175
Use of Methanol and Dimethyl Ether as Transportation Fuels	177
Alcohol as a Transportation Fuel in the Past	177
Methanol as Fuel in Internal Combustion Engines (ICE)	180
Methanol and Dimethyl Ether as Diesel Fuels Substitute in Compression Ignition Engines	182
Biodiesel Fuel	186
Advanced Methanol-Powered Vehicles	187
Hydrogen for Fuel Cells from Methanol Reforming	187
Direct Methanol Fuel Cell (DMFC)	191
Fuel Cells Based on Other Fuels and Biofuel Cells	195
Regenerative Fuel Cell	196
Methanol for Static Power and Heat Generation	196
Methanol Storage and Distribution	197
Methanol Price	200
Methanol Safety	201
Emissions from Methanol-Powered Vehicles	205
Methanol and the Environment	206
Methanol and Issues of Climate Change	208

Chapter 12**Production of Methanol from Syn-Gas to Carbon Dioxide 209**

- Methanol from Fossil Fuels 212
- Production via Syn-Gas 212
- Syn-Gas from Natural Gas 215
- Methane Steam Reforming 215
- Partial Oxidation of Methane 216
- Autothermal Reforming and Combination of Steam Reforming and Partial Oxidation 217
- Syn-Gas from CO₂ Reforming 217
- Syn-Gas from Petroleum and Higher Hydrocarbons 218
- Syn-Gas from Coal 218
- Economics of Syn-Gas Generation 219
- Methanol through Methyl Formate 219
- Methanol from Methane Without Syn-Gas 220
- Selective Oxidation of Methane to Methanol 221
- Catalytic Gas-Phase Oxidation of Methane 221
- Liquid-Phase Oxidation of Methane to Methanol 224
- Methanol Production through Mono-Halogenated Methanes 226
- Microbial or Photochemical Conversion of Methane to Methanol 228
- Methanol from Biomass 229
- Methanol from Biogas 235
- Aquaculture 237
- Water Plants 237
- Algae 238
- Methanol from Carbon Dioxide 239
- Carbon Dioxide from Industrial Flue Gases 242
- Carbon Dioxide from the Atmosphere 243

Chapter 13**Methanol-Based Chemicals, Synthetic Hydrocarbons and Materials 246**

- Methanol-Based Chemical Products and Materials 246
- Methanol Conversion to Olefins and Synthetic Hydrocarbons 248
- Methanol to Olefin (MTO) Process 249
- Methanol to Gasoline (MTG) Process 251
- Methanol-Based Proteins 252
- Outlook 253

Chapter 14

Future Perspectives 254

The “Methanol Economy” and its Advantages 256

Further Reading and Information 260

References 274

Index 283

Preface

Humankind, for its continued existence, requires not only such essentials as food, clean water, shelter, and clothing materials, but also large amounts of energy. Ever since cavemen succeeded in kindling fire, our ancestors have used a variety of sources for heating and cooking, ranging initially from wood and vegetation followed by peat moss and other carbon-based fuels. Since the industrial revolution, the major source of energy was coal to which, during the twentieth century, oil and natural gas were added. The latter resources – termed “fossil fuels” – were formed by Nature over eons, but once combusted they are not renewable on our human time scale and are thus increasingly depleted by overuse. Our readily accessible oil and gas reserves may not last much past the twenty-first century, while coal reserve may be available for another century or two. We need, therefore, to find new ways and resources for the future.

This book discusses a new approach based on what we call the “Methanol Economy[®]”. The production of methanol directly from still-available fossil fuel sources, and the recycling of carbon dioxide via hydrogenative reductions, are – we believe – feasible and convenient ways to store energy generated from all possible sources including, alternative energy sources (solar, hydro, wind, geothermal, etc.) and atomic energy. In the short term, new efficient production of methanol not only from still-available natural gas resources (without going through the syn-gas route) but also by the hydrogenative conversion of carbon dioxide from industrial exhausts, offer feasible new routes. In the long term, recycling of the carbon dioxide captured from the air itself will be possible. Air, in contrast to oil and gas resources, is available to everybody on Earth, and its CO₂ content represent an inexhaustible recyclable carbon resource. Methanol produced from this CO₂ (using any energy source to produce the required hydrogen from water), is an excellent fuel on its own for internal combustion engines or fuel cells of the future. It can be also readily converted, via its dehydration to ethylene and propylene, into synthetic hydrocarbons and their products. Consequently, it can free mankind’s dependence on our diminishing oil and natural gas (even coal) resources. At the same time, by being able to recycle excess CO₂ we can mitigate or eliminate a major source of global climate change – that is, warming of the Earth – caused by human activities.

We are fully aware that to solve our outlined problems for the future, including energy storage and transportation, non-oil- and gas-based fuels and raw materials for the production of synthetic hydrocarbons and their products (to which we are accustomed in our everyday life) and new approaches are needed. Much has been said about the future in view of our diminishing and non-renewable fossil fuel resources. The outlined “Methanol Economy” is one of the feasible and achievable solutions, which deserves serious further consideration and development. We hope that this book will call more attention to this approach, and spur future activities in the area.

Los Angeles, December 2005

*George A. Olah
Alain Goeppert
G. K. Surya Prakash*

Acronyms, Units and Abbreviations

Acronyms

AFC	Alkaline Fuel Cell
BP	British Petroleum
BWR	Boiling Water Reactor
CEA	Commissariat à l'Energie Atomique (France)
CEC	California Energy Commission
CIA	Central Intelligence Agency
DMFC	Direct Methanol Fuel Cell
DOE	Department of Energy (United States)
EDF	Electricité de France
EIA	Energy Information Administration (DOE)
EPA	Environmental Protection Agency (United States)
EU	European Union
GDP	Gross Domestic Product
GHG	Greenhouse Gas
IAEA	International Atomic Energy Agency
ICE	Internal Combustion Engine
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IPCC	International Panel on Climate Change
ITER	International Thermonuclear Experimental Reactor
LNG	Liquefied Natural Gas
MCFC	Molten Carbonate Fuel Cell
NRC	National Research Council (United States)
NREL	National Renewable Energy Laboratory (United States)
OECD	Organization for Economic Cooperation and Development
OPEC	Organization of Petroleum Exporting Countries
ORNL	Oak Ridge National Laboratory
OTEC	Ocean Thermal Energy Conversion
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PFBC	Pressurized Fluidized Bed Combustion
PV	Photovoltaics

PWR	Pressurized Water Reactor
R/P	Reserve/Production ratio
SUV	Sport Utility Vehicle
TPES	Total Primary Energy Supply
UNO	United Nations Organization
UNSCEAR	United Nations Scientific Committee on Effects of Atomic Radiation
URFC	Unitized Regenerative Fuel Cell
USCB	United States Census Bureau
USGS	United States Geological Survey
WCD	World Commission on Dams
WCI	World Coal Institute
WEC	World Energy Council
ZEV	Zero Emission Vehicle

Units and Abbreviations

b and bbl	barrel
Btu	British thermal unit
°C	degree Celsius
cal	calorie
g	gram
h	hour
ha	hectare
kWh	kilowatt-hour
m	meter
Mb	megabarrel (10 ⁶ barrels)
ppm	parts per million
toe	tonne oil equivalent
s	second
Sv	Sievert
t	metric tonne
W	watt