CARBON-NEUTRAL FUELS AND ENERGY CARRIERS

Edited by
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Nazim Z. Muradov and T. Nejat Veziroğlu

Preface

Carbon is the backbone of life on Earth. Starting from the discovery of fire, our civilization depends vitally on carbon for its energy; carbon made possible the industrial revolution and the rise in the standard of living we currently enjoy. On the other hand, recently, the word "carbon" has acquired a rather negative connotation mostly due to its association with carbon-bearing fossil fuels and, especially, with the product of their combustion—carbon dioxide (CO_2). Fossil fuels are currently being blamed for the ever-increasing levels of CO_2 in the atmosphere, climate change, air pollution, smog, oil spills, and other forms of environmental damage to the biosphere.

Today, more than 29 billion tons of man-made carbon dioxide emissions from a variety of sources (mostly from power generation, transportation and industrial sectors) are annually being pumped into the atmosphere. Some ominous signs of the adverse effects of these emissions on the Earth's ecosystems and climate have already started manifesting themselves in the form of retreating glaciers, hotter summers, stronger storms, increasing floods, etc.

In the face of ever-increasing levels of fossil fuel-derived CO_2, there have been attempts to estimate the tolerable limits of atmospheric CO_2 concentrations in terms of the global mean temperature rise. Analysis of scientific literature on climate impacts indicates that, in the majority of cases, a doubling of preindustrial atmospheric CO_2 concentration and an associated temperature increase of 2°C above the preindustrial level are considered a critical point beyond which a potentially catastrophic impact on the planet's ecosystem might occur. The danger is that beyond this 2°C point in the temperature increase, there exists not only elevated risk of extreme climate impacts and events, but also an increased possibility of strong positive carbon cycle feedbacks that would lead to an even stronger climate impact with the real potential of reaching a "tipping point" (or a runaway situation). These are real concerns that have to be addressed to avert the irreversible changes in the environment and climate.

There is a growing consensus that in order to maintain the present standard of living and establish an environmentally sustainable energy future, new approaches to managing energy resources and fuels have to be developed and implemented. Concerns over an insecure energy supply and the adverse environmental impact of carbonaceous fuels have triggered considerable efforts worldwide to find carbon-free or low-carbon alternatives to conventional fossil fuels. In particular, it is understood that many existing challenges can be solved in conjunction with the development and implementation of carbon-neutral energy systems (i.e., systems that do not increase atmospheric CO_2 concentration).

This book emphasizes the vital role of carbon-neutral energy sources, transportation fuels, and associated technologies in the establishment of a sustainable energy future. From a bird's-eye view, it tries to answer the following question: Will humankind be able to secure enough clean energy and fuels to further prosper and live in harmony with the environment against a backdrop of an ever-growing demand for energy, rapidly depleting resources of affordable fossil fuels, and deteriorating global ecological situation? To answer this question, we solicited help from world-renown experts in a wide range of research areas from photochemistry and fuel-generating enzymes to nuclear and automotive technologies. Without their valuable contributions, a project of this magnitude would not have been possible. We would like to thank all the lead authors and coauthors for their time and efforts, as well as their valuable suggestions and recommendations.

Due to its multidisciplinary nature, this comprehensive sourcebook is organized into 15 chapters, each reflecting a specific area of up-to-date research and development activities. It begins with an introductory chapter where we analyze the Earth's carbon budget with a special emphasis on the effect of human activities on the global carbon cycle, as well as proposed measures to stabilize the atmospheric CO_2 concentration at an acceptable level. The chapter provides a brief overview of a wide range of state-of-the-art technologies for the utilization of carbon-free energy resources and advanced transportation fuels and assesses their technical and commercial potential to meet the target of 10–30 TW of carbon-neutral power by mid-century. Although the technical potential of carbon-free energy resources is by far adequate to meet all humankind energy needs for the foreseeable future, it is realized that switching from fossil fuels currently providing about 80% of primary energy to non-fossil-based energy systems may require too many changes and, consequently, too much time to accomplish that transition. On the other hand, some experts believe that we cannot afford a long transition period because of potentially irreversible changes in global climate caused by the extensive use of fossil fuels.

In Chapter 2, Professor Carl-Jochen Winter (Germany) provides a comprehensive analysis of two main carbon-free energy carriers: electricity and hydrogen. As one of the pioneers of the hydrogen movement, Professor Winter provides the historical and technological background of the hydrogen economy concept. In this wide-ranging chapter, he describes various aspects of future hydrogen economy: hydrogen production, storage and distribution systems, its environmental and climatic relevance, and traditional and new application areas.

Chapter 3 (lead author—Dr. Kenneth Schultz, United States) focuses on the role of nuclear power in the production of carbon-neutral energy and fuels. Advantageously, nuclear energy does not inherently involve any direct use of fossil fuels or generation of CO_2 or other greenhouse gases. Thus, nuclear energy has the potential to make major contributions to the production of carbon-neutral fuels and energy carriers by providing a major carbon-free source of primary energy. In this chapter, a team of authors from a number of leading U.S. research institutions explore how nuclear energy can contribute to the production of carbon-neutral fuels using state-of-the-art nuclear technologies.

Several chapters are dedicated to the efficient utilization of renewable energy resources (solar, wind, geothermal, etc.) and the storage of intermittent renewable energy. In Chapter 4, Professor Gabriele Centi and coauthors (Italy) discuss the role of catalysis and photocatalysis in solving complex scientific problems related to solar-powered conversion of water and CO_2 to carbon-neutral fuels. In Chapter 5, Professor Arif Hepbasli (Turkey) emphasizes the importance of conducting exergetic analysis of renewable energy sources such as solar, wind, and geothermal energy from the viewpoint of designing optimal sustainable energy systems of the future. Electrochemical reduction of CO_2 to fuels is discussed by Professor Serguei Lvov and coauthors (United States) in Chapter 6. The cost-effective around-the-clock utilization of intermittent renewable resources such as solar, wind, wave, and tidal energy would not have been possible without efficient energy storage systems. This aspect is discussed by Professor Bent Sørensen (Denmark) in Chapter 7, which provides an overview of state-of-the-art systems for the storage of intermittent renewable energy resources.

A large section of the book is devoted to different aspects of bioenergy and biofuels production and utilization, and the potential role of bio-inspired energy systems. In Chapter 8, Professor Helmut Tributsch (Germany) discusses the concept of "energy-bionics," inferring that mankind should follow the energy example of nature on a high technological level. This chapter provides specific examples of scientific and technological concepts that aim at reaching this goal. Chapter 9 written by Professor Georg Schaub and Dr. Kyra Pabst (Germany) discusses on thermochemical technologies for the production of

synthetic hydrocarbons from lignocellulosic biomass. Fundamental aspects of fermentative bio-hydrogen production are discussed by Professor Debabrata Das and Dr. Chitralekha Nag Dasgupta (India) in Chapter 10. In Chapter 11, a team of U.S. researchers led by Dr. Paul King addresses biomimetic and photobiological aspects of solar fuel production. Dr. Levin and coauthors (Canada) discuss and analyze the prospects of practical applications and outlook for fermentative biofuels such as bioethanol and biobutanol in Chapter 12. The current status and technological aspects of biodiesel production from oily biomass and algae are the focus of Chapter 13 written by Dr. Maximino Manzanera (Spain).

It is universally accepted that the world will continue to rely on fossil fuels to supply the bulk of its primary energy for many decades; thus, finding ways to curb the fossil-derived CO_2 emissions is a major challenge. The concept of fossil fuel decarbonization is considered by many as a feasible and potentially cost-effective near-to-mid-term solution for drastically reducing man-made CO_2 emissions originating from coal, petroleum, and natural gas. In Chapter 14, Dr. Nazim Muradov (United States) assesses the current state of knowledge and technological development with regard to the fossil decarbonization concept and its potential role in the portfolio of carbon mitigation options. The transportation sector consumes a significant fraction of primary energy resources (mostly petroleum) and emits enormous amounts of CO_2 emissions; therefore, it is important to develop and implement effective measures that would help in reducing oil consumption and cut CO_2 emissions in transportation. In Chapter 15, Dr. Sandy Thomas (United States) uses a dynamic computer simulation model to compare various vehicle and fuel options over the entire twenty-first century with regard to greenhouse gas emissions, oil consumption, and urban air pollution.

In summary, this book provides a comprehensive overview of carbon-neutral energy sources and fuels that will play an increasingly important role in the near-to-mid-term future; it highlights the enormous technical, economic, and environmental challenges facing their introduction to the world marketplace. This multidisciplinary reference book is unique in its scope and the diversity of topics covered, and it will be handy to all scientists, engineers, and students working and studying in practically all areas related to alternative energy sources and fuels. It will be a good supplement to textbooks on alternative fuels, renewable energy sources, and hydrogen economy. Nontechnical readership may also find this book useful from the viewpoint of introduction to the field of alternative energy and transportation fuels.

We realize that there is a divergence of opinions and viewpoints especially on such complex issues as energy, environment, and climate, and, therefore, wherever possible, the authors have tried to present a balanced view of the subject. We have made every effort to avoid overlapping in this multiauthored book, but, undoubtedly, some redundancy may still remain from one chapter to the other. For these and any other remaining flaws present in this book, we take full responsibility.

We hope that this book will contribute to an improved understanding and appreciation of the energy and environmental sustainability problems. It is very important to recognize the scope of problems and available options early in order to adequately plan long-term strategies for the transition to sustainable carbon-neutral energy systems, because failure to do that will have an enormous negative impact on our planet and future generations.

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Green Chemistry and Chemical Engineering

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. While 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 derives from and builds upon 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 is 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 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. The global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international community of science, engineering, academia, industry, and governments in all phases and aspects.

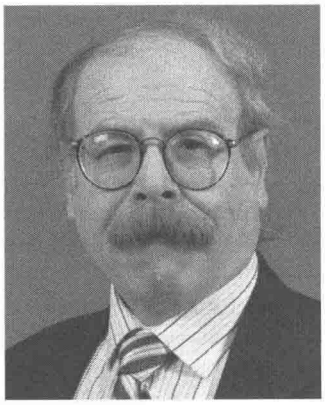
Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as green solvent in separation technologies; the application of supercritical water oxidation for the destruction of harmful substances; process integration with carbon dioxide sequestration steps; solvent-free synthesis of chemicals and polymeric materials; the exploitation of biologically degradable materials; the use of aqueous hydrogen peroxide for efficient oxidation; the development of hydrogen proton exchange membrane fuel cells for a variety of power generation needs; advanced biofuel productions; the devulcanization of spent tire rubber; the avoidance of the use of chemicals and processes causing the generation of volatile organic compounds; the replacement of traditional petrochemical processes by microorganism-based bioengineering processes; the replacement of chlorofluorocarbons with nonhazardous alternatives; advances in the design of energy-efficient processes; the 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 by CRC Press/Taylor & Francis Group is designed to meet the new challenges of the twenty-first century in the disciplines of chemistry and chemical engineering 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. And 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. It aims at providing 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

Editors

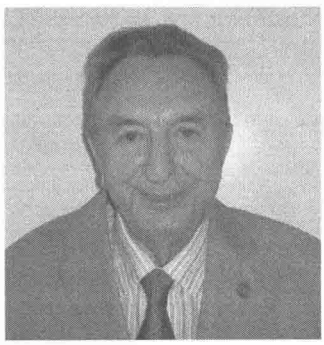


Nazim Z. Muradov is the principal research scientist at the Florida Solar Energy Center, University of Central Florida, Cocoa, Florida. He holds a DSc in physical chemistry (1990), a PhD in kinetics and catalysis (1975), and an MS in petrochemical engineering (1970). Dr. Muradov's main areas of research include thermocatalytic and photocatalytic hydrogen production systems, solar-powered water-splitting cycles, fossil fuel decarbonization, biomass-derived fuels, reformers for fuel cell applications, radiant detoxification of hazardous wastes, nanostructured carbon materials, and catalytic processing of hydrocarbons.

Dr. Muradov is a member of the board of directors of the International Association for Hydrogen Energy (IAHE) and a member of the board of trustees and the scientific council of the Madrid Institute for Advanced Studies, IMDEA Energia (Spain). He has also been an associate editor of the *International Journal of Hydrogen Energy* since 2006.

Dr. Muradov has authored and coauthored about 200 publications, 36 patents, a book and several book chapters. His paper "From hydrocarbon to hydrogen-carbon to hydrogen economy" (coauthored with T. Nejat Veziroğlu) was identified by Thomson Reuters' *Essential Science Indicators* to be one of the most cited papers in the research area of hydrogen economy, and it was featured as a fast-moving front paper on the *ScienceWatch*® Web site.

Dr. Muradov is a recipient of the University of Central Florida (Institutes and Centers) Distinguished Researcher of the Year Award (1996) and the UCF Research Incentive Award (2003). In 2010, he was granted the honorary title of the IAHE Fellow.



Dr. T. Nejat Veziroğlu, a native of Turkey, graduated from the City and Guilds College, the Imperial College of Science and Technology, University of London, with degrees in mechanical engineering (ACGI, BSc), advanced studies in engineering (DIC.), and heat transfer (PhD).

In 1962, after doing his military service in the Ordnance Section, serving in some Turkish government agencies, and heading a private company, Dr. Veziroğlu joined the Engineering Faculty at the University of Miami. In 1965, he became the director of graduate studies and initiated the first PhD program in the School of Engineering and Architecture. He served as chairman of the Department of Mechanical Engineering from 1971 through 1975, established the Clean Energy Research Institute in 1973, and was the associate dean for research from 1975 through 1979. He took a three-year leave of absence (2004–2007) and founded UNIDO-ICHET (United Nations Industrial Development Organization—International Centre for Hydrogen Energy Technologies) in Istanbul, Turkey. On May 15, 2009, he attained the status of professor emeritus at the University of Miami.

Dr. Veziroğlu organized the first major conference on hydrogen energy: The Hydrogen Economy Miami Energy (THEME) Conference, Miami Beach, March 18–20, 1974. At the opening of this conference, he proposed the hydrogen energy system as a permanent solution for the depletion of fossil fuels and the environmental problems caused by their utilization. Soon after, the International Association for Hydrogen Energy (IAHE) was established, and Dr. Veziroğlu was elected president. As president of IAHE, he initiated the biennial world hydrogen energy conferences in 1976 and the biennial world hydrogen technologies conventions in 2005.

In 1976, Dr. Veziroğlu started the publication of the *International Journal of Hydrogen Energy* (*IJHE*) as its editor-in-chief in order to publish and disseminate hydrogen energy–related research and development results from around the world. IJHE has continuously grown—it now publishes 24 issues a year. Dr. Veziroğlu has also published about 350 papers and scientific reports, edited 160 volumes of books and proceedings, and has coauthored the book *Solar Hydrogen Energy: The Power to Save the Earth*.

Dr. Veziroğlu has memberships in 18 scientific organizations; has been elected to the grade of fellow in the British Institution of Mechanical Engineers, the American Society of Mechanical Engineers, and the American Association for the Advancement of Science; and is the founding president of the International Association for Hydrogen Energy. He has been the recipient of several international awards. He was presented the Turkish Presidential Science Award in 1974, made an honorary professor in Xian Jiaotong University of China in 1981, awarded the I. V. Kurchatov Medal by the Kurchatov Institute of Atomic Energy of the USSR in 1982 and the Energy for Mankind Award by the Global Energy Society in 1986, and elected to the Argentinean Academy of Sciences in 1988. In 2000, he was nominated for the Nobel Prize in Economics for conceiving the hydrogen economy and striving toward its establishment.

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Energy Options in a Carbon-Constrained World: An Advent of Carbon-Neutral Technologies

Nazim Z. Muradov and T. Nejat Veziroğlu

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1.1 Introduction

Carbon is the basis and the backbone of life on the Earth. It is assumed that life can only exist on planets that have carbon and water (this widely accepted assumption is referred to as *carbon–water chauvinism*). Due to its unique electronic structure carbon atom can easily form strong bonds with other atoms forming vitally important molecules from the simplest molecule methane to such complex molecules as DNA and RNA that control the continuation of life on the Earth (the human body contains 18.5 wt.% of carbon). Through so-called carbon cycle (discussed in the following sections) carbon atoms can be recycled countless times over millions of years.

Our civilization vitally depends on carbon for its energy (starting from the discovery of fire). Carbon is the major constituent of all fossil fuels that made possible the