Handbook of Alternative Fuel Technologies

Sunggyu Lee
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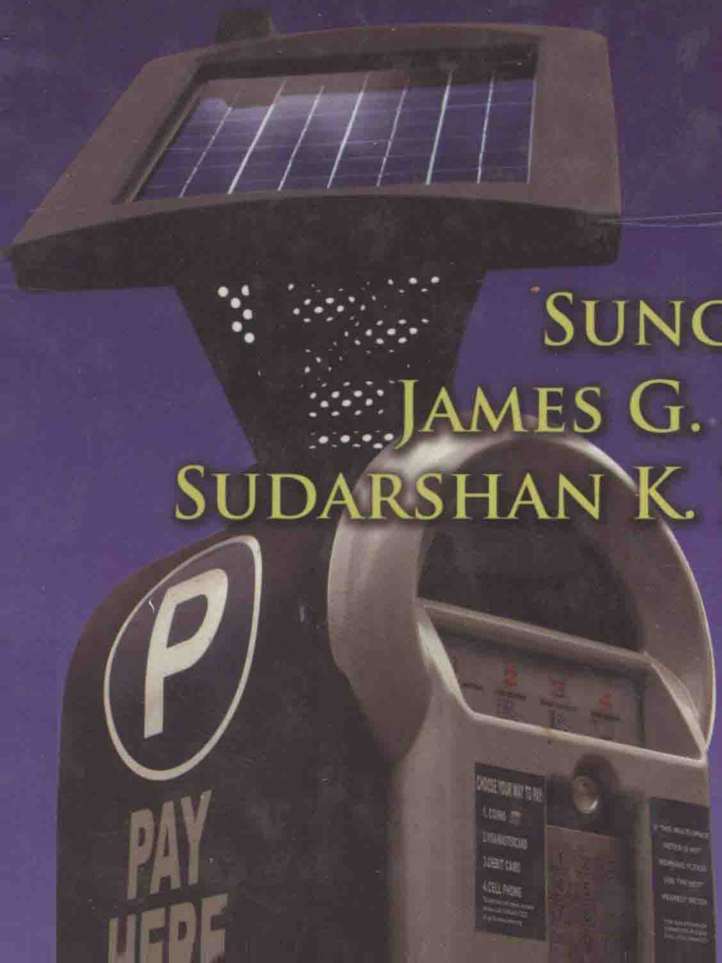

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HANDBOOK OF ALTERNATIVE FUEL TECHNOLOGIES

Preface

Energy has always been the foremost resource that humans have relied on for survival and productive activities. Industrialization and technological advancement of modern society have also been possible through the effective use of energy. There is a strong correlation between the index for quality of life and energy consumption. Heightened economic strength of a country, technological prosperity of a society, higher production output of an industry, improved finances of a household, and increased activities of an individual are also realized by effective utilization of energy.

A number of important factors have historically dominated the trend, market, and type of energy utilization. These factors are: (1) resource availability, (2) convenience of energy utilization, (3) efficiency of conversion, (4) technological feasibility, (5) portability and ease of transportation, (6) sustainability, (7) renewability, (8) cost and affordability, (9) safety and health effects, and (10) environmental acceptance and impact. The technological success and prosperity of petrochemical industries in the 20th and early 21st centuries can largely be attributed to the vast utilization of fossil fuels, especially petroleum, as well as technological breakthroughs and innovations by process industries. Industry and consumers have seen and come to expect a wide array of new and improved polymeric materials and other chemical and petrochemical products. However, the fossil fuel resources upon which industry is heavily dependent are limited in available quantities and are expected to be close to depletion in the near future.

The unprecedented popularity and successful utilization of petroleum resources observed in the 20th century may have to decline in the 21st century owing to a lack of resource availability, thus making prospects for future sustainability seem grim. Public appetites for convenient fuel sources and superior high-performance materials are, however, growing. Therefore, additional and alternative sources for fuels and petrochemical feedstocks are not only to be developed further but are also needed for immediate commercial exploitation. Use of alternative fuels is no longer a matter for the future; it is a realistic issue of the present.

Additional and alternative sources for intermediate and final products, whether fuels or petrochemicals, directly contribute to the conservation of petroleum resources of the world by providing additional raw material options for generating the same products for consumers. Examples may include wood alcohol for methanol, corn fermentation for ethanol, biodiesel from soybean or algae, BTX (benzene, toluene, and xylenes) from coal, biogas or bioliquid from agricultural wastes, hydrogen as transportation fuel, bio-hydrogen from a variety of biological sources, jet fuel from shale oil or crop oil, Fischer–Tropsch fuel from coal or biomass, bisphenols from agricultural sources, liquid transportation fuels from a natural gas source by ZSM-type catalysis, ethylene/propylene via conversion of synthesis gas, use of coal-derived acetylene for petroleum-derived ethylene as a building block chemical, and liquid fuels from spent tires or mixed wastes, etc.

If usable energy or deliverable power is the final product to be desired, alternate sources for energy may strongly and directly affect the lifestyle of consumers, as well as their energy consumption patterns. A good example can be found in electric cars that are powered by powerful rechargeable batteries. These powerful batteries serve no use for conventional gasoline motors, whereas, in turn, premium gasoline is not needed in these electric cars. Another good example is the solar house whose climate control inside the house is provided only by solar energy. Other examples include LPG vehicles, dimethylether (DME) buses, hybrid cars, E-85 vehicles, hydrogen vehicles, solar-powered equipment and vehicles, wind energy powered equipment, and geothermal heating and cooling, etc.

During the past several decades, there has been a considerable increase in research and development in areas of environmentally acceptable alternative fuels. Synthetic fuels were of prime interest in the 1970s, due to a sudden shortage of petroleum supply kindled by an oil embargo in 1973, as well as public concern about dwindling petroleum reserves. Although synfuels seemed to be a most promising solution to the conservation of petroleum resources (or, at least, frugal use of the resources) and the development of additional sources for conventional liquid fuels, some of the focus has been shifted toward environmental acceptance of the fuel and the long-term sustainability of world prosperity in the last decade of the 20th century. Efforts have been made to reduce emissions of air pollutants associated with combustion processes whose sources include electric power generation and vehicular transportation. Air pollutants that have been targeted for minimization or elimination include SO_x, NO_x, CO_x, VOCs, particulate matters (PM), mercury, and selenium. These efforts have significantly contributed to the enhancement of air quality and associated technologies.

Concerns of global warming via greenhouse gases have further intensified the issue of environmental acceptance of fuel consumption. Combustion of fossil fuels inevitably generates carbon dioxide due to an oxidation reaction of hydrocarbon and carbonaceous materials. Carbon dioxide is known as a major greenhouse gas with emissions that need to be significantly reduced. Therefore, new developments in alternative fuels and energy have focused more on nonfossil sources or on mitigation and fixation of carbon dioxide in fossil fuel utilization. Renewable energy sources are certainly very promising due to their long-term sustainability and environmental friendliness. Of particular interest are solar (solar thermal and photovoltaic), wind, hydropower, tidal, and geothermal energies, in addition to biomass (wood, wood waste, plant/crop-based renewables, agricultural wastes, food wastes, and algae) and biofuels including bioethanol, biohydrogen, and biodiesel. It should be noted that hydropower is also regarded as a "conventional" energy source, as it has provided a significant amount of electrical energy for over a century. Government mandates, tax incentives, and stricter enforcement of environmental regulations are pushing environmentally friendly alternative fuels into the marketplace at an unprecedented rate.

The number of alternative-fueled vehicles in use in the world is expected to increase sharply. These alternative-fueled vehicles are powered by liquefied petroleum gas (LPG), liquefied natural gas (LNG), ethanol 85% (E85), methanol 85% (M85), electricity, neat methanol (M100), ethanol 95% (E95), dimethylether (DME), and hydrogen, among which hydrogen presently accounts for very little but is considered the most promising by many. It should be noted that this list of alternative fuels in vehicles only represents the successful results of previous developments and does not include recent advances and breakthroughs in the field. Research and development efforts in alternative-fueled vehicles and utilization of renewable energy sources have intensified in the past few years. Alternative-fueled vehicles and emission-free cars are expected to gain more popularity, due in part to enforcement of stricter emission standards, the unmistakable fate of depletion for conventional transportation fuels, and numerous tax incentives for such vehicles. This intensified interest is coupled with the record-high prices of gasoline- and petroleum-based products experienced all over the world. Perhaps the key difference between the 1973 oil embargo era and the present is that this time around, efforts are likely to firmly latch-on to the roster of ongoing priorities most exigent to mankind.

Energy from wastes cannot be neglected as a valuable energy source. If effectively harnessed, energy from wastes, including municipal solid waste (MSW), agricultural refuses, plastics and spent tires, and mixed wastes can be employed to alleviate the current burden for energy generation from fossil fuel sources. Moreover, energy generation from wastes bears extra significance in reducing the volume of wastes, thus saving landfill space and utilizing resources otherwise of no value. Environmental aspects involving waste energy generation are to be fully addressed in commercial exploitation.

A great number of research articles, patents, reference books, textbooks, monographs, government reports, and industry brochures are published and referenced everyday. However, these literary sources are not only widely scattered and massive in volume, but they are also lacking in scientific consistency and technological comprehensiveness. Further, most of the published articles focus on the justification and potential availability of alternative fuel sources rather than environmental and technical readiness of the fuel as a principal energy source for the future postpetroleum era.

This handbook aims to present comprehensive information regarding the science and technology of alternative fuels and their processing technologies. Special emphasis has been placed on environmental and socioeconomic issues associated with the use of alternative energy sources, such as sustainability, applicable technologies, mode of utilization, and impacts on society.

Chapter 1 focuses on the current concerns in the area of consumption of conventional energy sources and highlights the importance of further development and utilization of alternative, renewable, and clean energy sources. This chapter presents past statistics as well as future predictions for each of the major conventional and alternative energy sources of the world.

Chapter 2 deals with the science and technology of coal gasification to produce synthesis gas. Synthesis gas is a crucially important petrochemical feedstock and also serves as an intermediate for other valuable alternative fuels such as methanol, dimethylether, ethanol, gasoline, diesel, and hydrogen. As the technology developed for gasification of coal has been widely modified and applied to processing of other fuel sources such as oil shale and biomass, details of various gasifiers and gasification processes are presented in this chapter.

Chapter 3 covers the science and technology of coal liquefaction for production of clean liquid fuels. All aspects of pyrolysis, direct liquefaction, indirect liquefaction, and coal–oil coprocessing liquefaction are addressed in detail. This chapter has significant relevance to the production of alternative transportation fuels that can replace or supplement the conventional transportation fuels. The scientific and technological concepts developed for coal liquefaction serve as foundations for other fuel processes.

Chapter 4 deals with the science and technology of coal slurry fuels. Major topics in this chapter include slurry properties, hydrodynamics, slurry types, transportation, and environmental issues.

Chapter 5 discusses the liquid fuels obtained from natural gas. Special emphasis is also placed upon the Fischer–Tropsch synthesis whose chemistry, catalysis, and commercial processes are detailed.

Chapter 6 presents the science and technology of resids. Properties and characterization of resids as well as conversion of resids are detailed in this chapter.

Chapter 7 describes the occurrence, production, and properties of oil sand bitumen and the methods used to convert the bitumen to synthetic crude oil. Properties of the synthetic crude oil are also discussed.

Chapter 8 explores the science and technology of oil shale utilization. In particular, occurrence, extraction, and properties of oil shale kerogen are discussed. A variety of oil shale retorting processes as well as shale oil upgrading processes are described.

Chapter 9 focuses on the synthesis of methanol from synthesis gas. Chemical reaction mechanisms, catalysis, and process technologies of methanol synthesis are described.

Chapter 10 deals with the production of fuel ethanol from corn. The chapter elucidates the chemistry, fermentation, and unit operations involved in the production process. Moreover, the chapter discusses the environmental benefits of the use of ethanol as internal combustion fuel or as oxygenated additives.

Chapter 11 discusses the detailed process steps and technological issues that are involved in the conversion of lignocellulosic materials into fuel ethanol.

Chapter 12 deals with a variety of process options for energy generation from biomass. Biomass characterization, environmental benefits, and product fuel properties are also discussed.

Chapter 13 focuses on the energy generation from waste materials. Particular emphasis is placed on beneficial utilization of municipal solid wastes, mixed wastes, polymeric waste, and scrap tires.

Chapter 14 describes the occurrence, renewability, and environmentally beneficial utilization of geothermal energy. Geothermal power plants, district heating, and geothermal heat pumps are also discussed.

Chapter 15 deals with the science and technology of nuclear energy. The chapter describes nuclear reactor physics, nuclear fuel cycles, types of reactors, and electricity generation from nuclear reactors. Public concerns of safety and health are also discussed.

Chapter 16 presents the basic concepts of fuel cells. This chapter also describes a number of different types of fuel cells and their characteristics. Hydrogen production and storage are also discussed in this chapter.

This book is unique in its nature, scope, perspectives, and completeness. Detailed description and assessment of available and feasible technologies, environmental health and safety issues, government regulations, issues for research and development, and alternative energy network for production, distribution, and consumption are covered throughout the book. For R & D scientists and engineers, this handbook serves as a single-volume comprehensive reference that will provide necessary information regarding chemistry, technology, and alternative routes as well as scientific foundations for further enhancements and breakthroughs.

This book can also be used as a textbook for a three credit-hour course entitled "Alternative Fuels," "Renewable Energy," or "Fuel Processing." The total number of chapters coincides with the total number of weeks in a typical college semester. This book may also be adapted as a reference book for a more general subject on fuel science and engineering, energy and environment, energy and environmental policy, and others. Professors and students may find this book a vital source book for their design or term projects for a number of other courses.

All chapters are carefully authored for scientific accuracy, style consistency, notational and unit consistency, and cross-reference convenience so that readers will enjoy the consistency and comprehensiveness of this book.

Finally, the authors are deeply indebted to their former graduate students, colleagues, and family members for their assistance, encouragement, and helpful comments.

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Authors

Sunggyu Lee is professor of chemical and biological engineering at the University of Missouri–Rolla. He is the author or coauthor of six books and over 400 archival publications. He received 23 U.S. patents in the field of chemical process technologies. He has advised more than 80 graduate students for their doctoral and master's degrees. He is also the editor of the *Encyclopedia of Chemical Processing*, published by Taylor & Francis. A specialist in chemical reaction kinetics and process engineering, and an active member of the American Institute of Chemical Engineers, Dr. Lee has designed more than 25 pilot, commercial, and demonstration plants, and advised companies such as B.F. Goodrich, Water Technologies Limited, and Northern Technology International Corporation. He received his B.S. (1974) and M.S. (1976) degrees in chemical engineering from Seoul National University, Korea, and his Ph.D. degree (1980) in chemical engineering from Case Western Reserve University, Cleveland, Ohio. He taught at the University of Akron for 17 years and also at the University of Missouri–Columbia for 9 years before joining the University of Missouri–Rolla in 2006.

James G. Speight has more than 38 years of experience in areas associated with the properties and recovery of reservoir fluids; the refining of conventional petroleum, heavy oil, and tar sand bitumen; the properties of fuels and synthetic fuels, including gas-to-liquids; natural gas; coal; and oil shale. He received his B.S. degree in chemistry and his Ph.D. in organic chemistry from the University of Manchester, England, where he was a research fellow in chemistry from 1965 to 1967. He served on the Alberta (Canada) Research Council from 1967 to 1980, and for the next four years was with Exxon Research and Engineering Company. At Western Research Institute he was chief scientific officer and executive vice president from 1984 to 1990 and chief executive officer from then until 1998, when he began focusing on consulting with CD&W, Inc., giving lectures on energy and environmental issues, and authoring work in his field. He has taught over 60 courses and has prepared more than 400 publications, reports, and presentations, including more than 25 books and bibliographies related to fossil fuel processing and environmental issues. He has been editor of *Petroleum Science and Technology* (founding editor); *Energy Sources. Part A: Recovery, Utilization, and Environmental Effects*; and *Energy Sources. Part B: Economics, Planning, and Policy.*

Academic posts include adjunct professor of chemical and fuels engineering, University of Utah and visiting professor at the University of Trinidad and Tobago, Technical University of Denmark (Lyngby), University of Petroleum (Beijing, China), University of Regina (Saskatchewan, Canada), and University of Akron (Ohio).

His awards include the Diploma of Honor, National Petroleum Engineering Society, 1995, for outstanding contributions to the petroleum industry; the Gold Medal, Russian Academy of Sciences, 1996, for outstanding work in the area of petroleum science, 1996; Specialist Invitation Program Speakers Award, NEDO (New Energy Development Organization, Government of Japan), 1987 and 1996, for contributions to coal research; Doctor of Sciences degree, Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia, 1997, for exceptional work in petroleum science; Einstein Medal, Russian Academy of Sciences, 2001, in recognition of outstanding contributions and service in the field of geologic sciences; and the Gold Medal — Scientists Without Frontiers, Russian Academy of Sciences, 2005, in recognition of his continuous encouragement of scientists to work together across international borders.

Sudarshan K. Loyalka was educated at the Birla College of Engineering (now Birla Institute of Science and Technology), Pilani, India (B.S. Mech., 1964) and Stanford University, Palo Alto, California (M.S., 1965; Ph.D., 1967, in nuclear engineering). He has been on the faculty of the University of Missouri–Columbia since 1967 and is Curators' Professor of Nuclear and Chemical Engineering. His research interests are in transport theory, aerosol mechanics, the kinetic theory of gases, and neutron reactor physics and safety. He is a Fellow of both the American Physical Society (since 1982) and the American Nuclear Society (since 1985). He has published about 200 papers and has advised approximately 80 graduate students. Dr. Loyalka has received the David Sinclair Award (1995) of the American Association for Aerosol Research and the Glenn Murphy Award (1998) of the American Association for Engineering Education.

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1 Global Energy Overview

Sunggyu Lee

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1.1 WORLD ENERGY CONSUMPTION

World energy consumption has been steadily increasing for a variety of reasons, which include enhancements in quality of life, population increase, industrialization, rapid economic growth of developing countries, increased transportation of people and goods, etc. There are many types of fuel available worldwide, the demand for which strongly depends on application and use, location and regional resources, cost, "cleanness" and environmental impact factors, safety of generation and utilization, socioeconomic factors, global and regional politics, etc. The energy utilization cycle consists of three phases: generation, distribution, and consumption, all of which must be closely balanced for an ideal energy infrastructure. Any bottlenecking or shortage would immediately affect the entire cycle as a limiting factor. If there is a decrease in production of a certain type of fuel, the distribution and consumption of this specific fuel would also decrease; so that fuel switching from this type to another, as well as forced conservation becomes inevitable. Further, based on the supply and demand principle, the consumer price of this fuel type would undoubtedly rise. Even a breakdown in the transportation system of a certain fuel type would affect the consumer market directly, and consequences such as fuel shortage and price hike would be realized at least for a limited time in the affected region.

Table 1.1 summarizes world energy consumption for each of the principal fuel types from 1980 to 2003.[1] As shown, all these types have recorded steady increases for the period. Coal and hydroelectric power show the slowest increase in consumption for the period, whereas renewable and nuclear energy have recorded the steepest increases, indicating that these are the emerging energy sources with the greatest

TABLE 1.1
World Net Consumption of Primary Energy by Energy Type, 1980–2003

Energy Type	1980	1985	1990	1995	2000	2001	2002	2003
Petroleum (1000 barrels per day)	63,108	60,089	66,576	70,018	76,946	77,701	78,458	80,099
Dry natural gas (trillion cubic feet)	52.89	62.24	73.37	78.64	88.21	89.31	92.51	95.50
Coal (million short tons)	4,126	4,898	5,269	5,116	5,083	5,165	5,250	5,439
Hydroelectric power (billion kilowatt-hours)	1,722.8	1,953.6	2,151.7	2,461.3	2,651.8	2,559.6	2,619.1	2,654.4
Nuclear electric power (billion kilowatt-hours)	684.4	1,425.5	1,908.8	2,210.0	2,450.3	2,517.2	2,546.0	2,523.1
Geothermal, solar, wind, wood, and waste electric power (billion kilowatt-hours)	31.1	55.5	131.5	177.5	249.5	259.8	292.1	310.1

future in the world energy market. Coal and hydroelectric power, however, are more conventional and established, and the world will still have to depend on these for a long time. The higher rates of growth for renewable and nuclear energy consumption also show their strong potential as alternative fuels that ultimately will replace and supplement the conventional fuel types in a variety of applications and end uses.

Among the conventional fossil fuels, the increased consumption of natural gas outpaced the other fossil fuel types, i.e., coal and petroleum, for the period reported in Table 1.1. This is attributable to stronger demands for natural gas in industrial and residential heating, increased installations of natural-gas-based electric power plants, and new discoveries of large natural gas deposits. Several times in the 21st century, the world has experienced significant shortages and price hikes of natural gas, mainly due to imbalances between supply and demand.

1.2 U.S. ENERGY CONSUMPTION

Figure 1.1 shows the total U.S. energy consumption[2] in quadrillion Btu's. One quadrillion is $10,^{15}$ which is equal to 1000 trillion. Based on the data, it is noted that U.S. total energy consumption has tripled over the past 50 years, i.e., from 1950 to 2000. Over the first 25 years of this period the increase was about 2.4 times, whereas it was about 1.3 times over the following 25 years. The slowdown of the pace of U.S. energy consumption was noticed immediately after the oil crisis of 1973. Many factors may have contributed to this: to name a few, increase in energy conversion efficiency, energy conservation across the board, energy efficient products, and even climates becoming milder due to global warming. However, if we consider separately the period from 1973 to 1988, for which total U.S. energy consumption was fairly

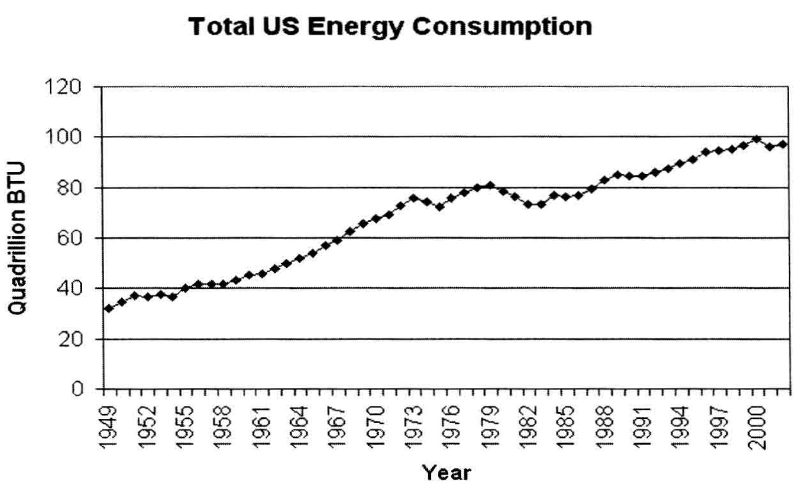

FIGURE 1.1 Total U.S. energy consumption. (From Web site by Maxwell School of Syracuse University, U.S. Energy Consumption, accessible through http://wilcoxen.cp.maxwell.syr.edu/pages/804.html. With permission.)