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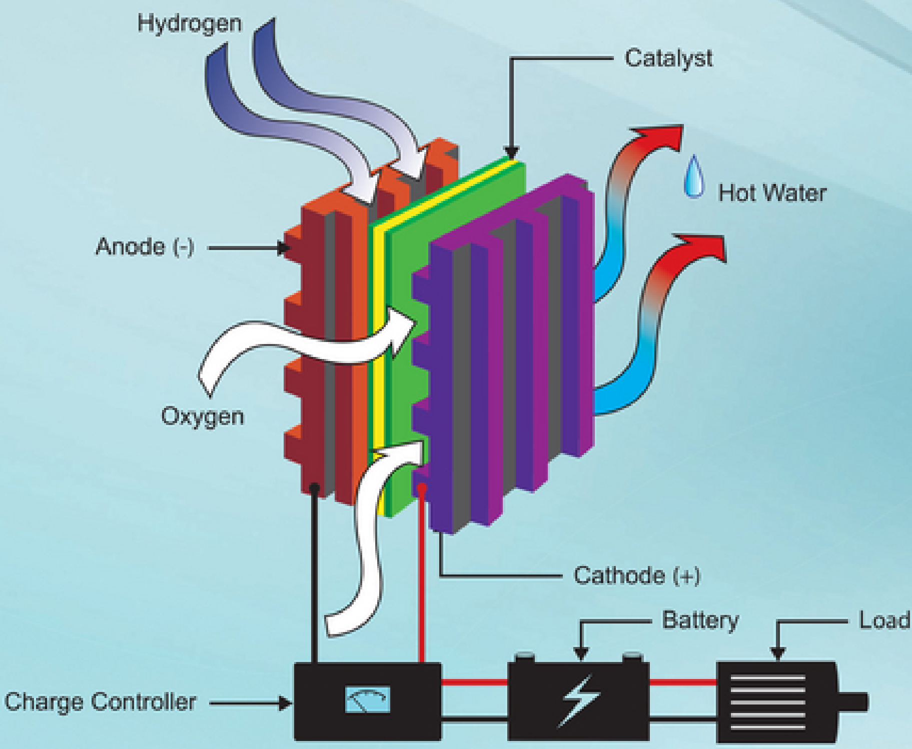
INTRODUCTION TO HYDROGEN TECHNOLOGY



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Second Edition

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PREFACE

Hydrogen gas continues to occupy a unique place in the world as it possesses properties that other elements do not. Consequently, scientists and engineers have been working on using it for improving the existing technology. The scientific literature on hydrogen technology is astronomically growing with the result that a large number of hydrogen-powered devices have entered the market and are being used in mobile phones, laptops, automobiles, utility vehicles, and so on. In addition, fuel cells have been developed to produce stationary power in a number of countries; it is predicted that the utilization will grow to 1.25 million fuel cells in the next 5 years.

The second edition of this book is to keep pace with the above developments and contains updated information on renewable energies, world petroleum production, and greenhouse gases. The new generation of solar cells is included in this book. Each chapter of the first edition is updated by including new developments. Of particular importance is fuel value of biodiesels, solid carbon fuel cells that is being considered for new developments, new Nafion membranes produced by grafting for polymer electrolyte membrane fuel cell, improved electrode materials for molten carbonate, and solid oxide fuel cells. The chapter on hydrogen technology is modified to address infrastructure technology.

Two new chapters—Hydrogen Production and Batteries—are added in this edition. The Hydrogen Production chapter reviews the various developments in improving the water decomposition efficiency and the resulting environmental impact factor. In this chapter, nine different methods of hydrogen production are considered, which, hopefully, will lower the cost of hydrogen. The Batteries chapter is included to provide a deeper examination of how hydrogen is used as a fuel in a fuel cell to generate electricity. With battery, electricity is generated from the stored energy. In essence, both are generating electricity for practical applications. Hence, for comparison of the chemistries involved in the two ways of generating electricity, this chapter hopefully will stimulate the reader for appreciating the suitability of the two methods toward fulfilling the greenhouse gas effect in the atmosphere.

In the first edition, it was mentioned that UN's Intergovernmental Panel on Climate Change had been enforcing the need to reduce the greenhouse gases in the atmosphere. The second phase (2013–2020) of Kyoto agreement has begun, and the United Nations Framework Convention on Climatic Change (UNFCC) passed a resolution in Paris in 2015 (http://unfccc.int/paris_agreement/items/9485.php) to stabilize the concentrations of greenhouse gases in the atmosphere such that there would be minimum interference with the climatic system. The hydrogen technology can go a long way to fulfilling this goal.

Finally, this book, if it is used as a textbook for a course, contains problems at the end of each chapter.

The authors thank Profs. Paul Craig and Sophia Maggelakis for their support in bringing out this edition.

K.S.V. Santhanam, Roman J. Press, Massoud J. Miri, Alla V. Bailey, and Jerry A. Takacs
June 3, 2017,
Rochester, NY

ABOUT THE COMPANION WEBSITE

This book is accompanied by Instructor website:

www.wiley.com/go/santhanam/hydrogentech_2e

On this website you will find

- Multiple choice questions as a preparation for class room examinations.
- Problems and their solutions.
- Appendix

CHAPTER 1

Available Energy Resources

1.1 CIVILIZATION AND THE SEARCH FOR SUSTAINABLE ENERGY

Many thousands of years ago, our ancestors knew how to produce fire and they used it for several different purposes, including warming themselves and preparing food. They discovered that energy could be liberated from burning wood. The energy-liberating material was defined as fuel, and this led to the recognition that wood is a fuel. Early civilizations depended on this fuel for a long time. To improve their living conditions, humans searched for new forms of sustainable energy. This exploration resulted in the invention of wind-driven wheels that could be used to pump water from wells. Before this discovery, water was pulled from wells by human energy. This led to a correlation that wind is a source of energy. The wheel was also found useful for transportation forming a part of a chariot that could be rotated when drawn by horses.

During the 18th century, the most commonly used forms of energy were derived from wood, water, horses, and mills. The composition and structure of these materials were mysteries, and more so how the energy was liberated from them. These mysteries led to detailed investigations into the structure of matter by numerous scientists, including J.J. Thompson, J. Dalton, M. Faraday, M. Curie, N. Bohr, A. Einstein, and J. Gibbs. This search for understanding the composition and structure of matter resulted in astounding discoveries in science, including the discovery and understanding of molecules and atoms.

The energy liberates upon combustion and products of combustion were established during this period. During the 18th century, as mentioned in the beginning of the paragraph, it was demonstrated that alcohol could be produced by the destructive distillation of wood, and that alcohol could be used as a source of energy. A realization that wood could be replaced by alcohol and that it could do the job much more effectively resulted in the use of alcohol as a source of energy. Coal was used as a source of energy for running steam engines.

In the 19th century, organic chemists synthesized hydrocarbons and determined the energies available from them. The 20th century led to the search for naturally available sources of hydrocarbons, and the discovery, that oil and natural gas contain them, paved the way for their utilization as energy sources in transportation. The rapid utilization and resulting depletion of these naturally occurring sources by mankind is leading to the search for viable alternatives. In addition, hydrocarbon-based energy sources are responsible for pollution of

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the atmosphere. These energy sources release carbon dioxide and carbon monoxide gases. Such gases are causing global warming (Section 1.3).

The 21st century is facing challenging problems, with faster depletion of fossil fuels and pollution arising from their use. Energy sources that are sustainable and producing negligible pollution are needed. In this context, hydrogen and fuel cells are being considered, but their exploration and use require policy decisions. Historically, the United States depends heavily on imported oils, and the infrastructure has been built on the imported oils and natural gases. In order to switch over to other fuels free from the restrictions discussed earlier, a smooth transitional infrastructure needs to be evolved.

A symbol of early human ingenuity is the first step pyramid, built for King Zoser in 2750 BC in Saqqará/Egypt. Similarly, the "energy pyramid" represents another advancement in human ingenuity. As the "food pyramid" represents a balanced approach to a healthy lifestyle, the energy pyramid (Figure 1.1) represents a balanced approach to consuming renewable and nonrenewable energy sources. With the gradual depletion of most nonrenewable sources of hydrocarbon-based fuels, the energy pyramid contains a diverse proportion of renewable fuels—hydro, solar, and wind power, along with various biomass-produced fuels.

During the 19th century, hydrogen was experimented as an energy source, and Sir William Grove demonstrated in 1839 that hydrogen and oxygen would combine to produce electricity. The product of the reaction was water. He called the device a fuel cell. In this method of producing electricity, there is no pollution generated and it is environmentally friendly for transportation. These two factors are very important in the 21st century. President George W. Bush spoke of the potential of hydrogen as a future energy source in his address to the National Building Museum on February 6, 2003. He stated, "Hydrogen fuel cells represent one of the most encouraging, innovative technologies of our era," and predicted that any obstacles in building hydrogen-based technology could be overcome by thoughtful research by scientists and engineers. This trend is continued by President Obama's administration by speeding up the hydrogen-powered transportation and energy production.

The United States is in a unique situation in its energy consumption. Growth was exponential in the second half of the 20th century. The United States consumes 25% of the

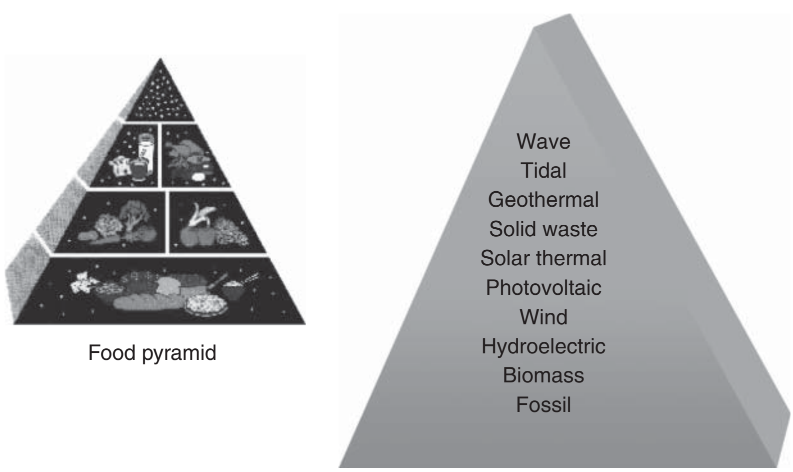

Figure 1.1 Energy pyramid.

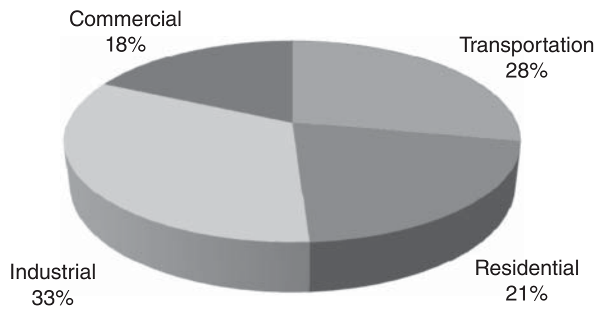

Figure 1.2 US energy use by sector.

world's energy supplies, which are distributed over the following four sectors: industrial commercial, transportation, and residential use (Figure 1.2). A deeper analysis shows that these four sectors showed a 300% increase in the annual usage since 1950. This trend has resulted in faster depletion of fossil fuels and greater environmental effects. Petroleum and gas reserves (fuels) are being rapidly depleted at a rate of a thousand times faster than the fuels are formed and stored. With the economic viability of the United States closely linked to fuel supplies from unstable regions around the globe, additional problems are likely to arise in the future. If domestic supplies of fuels decline, the need for importing fuels will increase. With current evidence for the imported fuel prices increasing year by year, the fuel needs and cost are likely to severely escalate in the near future.

Increased use of fossil fuels has had negative environmental effects: oil spills endanger aquatic and plant life, contaminate beaches and soil, and cause erosion of large masses of land. It also results in global warming effects. If we wish to solve all these problems, then we have to find alternative sources of energy. Hydrogen is one of the alternative energy sources that the world could rely on safely.

Industrialized society is built on the existing infrastructure and is primarily fueled by petroleum. If fuel prices are stable, then the infrastructure requires very little change and the status quo can be maintained. Unfortunately, the status quo does not address the problems of the future. Future needs can be met only by recognizing the problems generated by petroleum-based technology and making efforts to find energy sources free from these problems. Hydrogen-based technology appears to be an ideal solution in this context.

Hydrogen-based technology offers attractive options for use in an economically and socially viable world with negligible environmental effects. Hydrogen is everywhere on earth in the form of water and hydrocarbons. In other words, hydrogen as fuel produces water as the by-product, and water is the source for hydrogen. It is an ideal energy carrier and hence could play a major role in a new decentralized infrastructure that would provide power to vehicles, homes, and industries. Hydrogen is nontoxic, renewable, clean, and provides more energy per dollar. Hydrogen is also the fuel for energy-efficient fuel cells.

Fossil fuels such as oil and gas are being currently used to harvest hydrogen. This is not ideal as it does not solve environmental issues that arise with the usage of fossil fuels. In the future, it will be necessary to use renewable energy sources such as wind, hydro, solar, biomass, and geothermal instead.

The stationary power generation based on fuel cell technology is a viable energy source and has been implemented in several places in the world. This technology provides a drastic reduction in carbon dioxide output in comparison to the existing technology.

Leading automotive companies, such as GM, Ford, Opel, Daimler-Chrysler, and Toyota, have even made significant progress in developing advanced fuel cell propulsion systems using hydrogen. Hydrogen-powered fuel cells are approximately two times more efficient than gasoline engines. With 650 million vehicles worldwide fueled by gasoline, the market potential is immense. Fuel cells power modules, using either proton exchange membranes or solid oxide, can potentially be the source of distributed electric power generation for business and home use.

The purpose of this book is to introduce the reader to the fundamental, chemistry-based aspects of hydrogen technology. It also provides information on renewable energy, hydrogen production, and fuel cells. The latest developments and current research on alternative fuels are discussed. The core topics include acid–base chemistry, reaction topics, chemical equilibrium, thermodynamics, electrochemistry, organic chemistry, polymers, photochemistry, and environmental chemistry. The topics covered in this text are highly relevant to current international and national concerns about overconsumption of our planet's natural resources and the political implications of the United States' dependence on foreign oil to meet the majority of its energy needs. There are many reasons to search for renewable sources of energy—including, but not limited to, energy conservation, pollution avoidance, and prevention. Hydrogen, being one of the cleanest and most abundant alternative energy, will most likely play a critical role in a new energy infrastructure by providing a cleaner source of power to vehicles, homes, and industries.

The authors are members of the Rochester Institute of Technology Renewable Energy Enterprise (RITree). They sincerely hope that this book will give a very good background on chemical aspects of hydrogen technology, including its potential in fuel cells and impact on environment. It is also the hope of the authors that this publication will contribute to the preparation of a workforce ready for future challenges in the areas of energy consumption, generation, and the rapid commercialization of both hydrogen-powered transportation and nonautomotive applications.

1.2 THE PLANET'S ENERGY RESOURCES AND ENERGY CONSUMPTION

On this planet, sources of energy are fossil fuels, the sun, the wind, water, and the earth (the latter includes geothermal and nuclear energy). Fossil fuels-oil, natural gas, and coal-and nuclear energy are abundantly used at present. Since these energy sources are expected to be depleted within a couple of centuries, they have been called "nonrenewable" energy sources. Only about 20% of our energy needs come from renewable sources. Examples in this category are solar energy, wind energy, hydro energy, biomass, geothermal energy, tidal energy, and *hydrogen*. These sources are not very efficient and research needs to be done to improve their efficiencies.

1.2.1 Energy Consumption

The total world consumption of energy amounted to 400 Quad (=quadrillion) Btu in 2000.[1] A human being consumes about 0.9 GJ/day of energy, equivalent to burning 32 kg of coal per day, or as average energy supply, 10.4 kW. Any human being needs as nutrition only 0.14 kW or about 1% of the energy consumed per capita. Essentially, all human activities

1 1 Quad = 1.055 × 1018 J.

involve consumption of energy, for example, construction of buildings, production of consumer goods, medicine, food, packaging of products, transportation, heating and cooling, administrative work, and even activities in our leisure time. Between 1850 and 1970, the world population tripled with the result that energy consumption increased by a factor of 12.

CRITICAL THINKING QUESTIONS

A What are the sources of energy considered in the global energy consumption?

B Which continent is consuming the highest Quadrillion Btu?

Answer: A

(a) Crude oil (b) oil-derived sources (c) natural gas (d) coal and lignite (e) power production and (f) renewables.

Answer: B

Based on US Energy Information Administration (EIA),

North America: 116.191 Quadrillion Btu

Central and South America: 28.674 Quadrillion Btu

Europe: 81.45 Quadrillion Btu

Eurasia: 46.09 Quadrillion Btu

Middle East: 32.213 Quadrillion Btu

Africa: 17.335 Quadrillion Btu

Asia and Oceania: 202.19 Quadrillion Btu

World: 524.076 Quadrillion Btu

Based on the 2012 data provided by EIA, Asia and Oceania consume the highest, and Africa is the lowest ranked in total primary energy consumption.

1.2.2 Regional Differences

Energy consumption is not evenly distributed over the countries of the world. The developed rich countries, for example, the United States, Europe, and Japan, consume about 80% of the worldwide energy and represent 20% of the world's population. Consumer habits differ from region to region. In the United States, people drive larger, lesser-fuel-efficient automobiles and buy larger homes than in many other countries, such as China or India. Currently, an American on the average uses 10 times more energy than the average Chinese and 20 times more than the average Indian. However, energy consumption is rising faster in the developing countries.

1.2.3 Distribution by Economic Sector

Transportation accounts for 30% of the world's energy consumption, mainly due to the use of passenger cars. About one billion cars are used worldwide and about a quarter of all of the world's automobiles are driven in the United States. In Europe and Japan, more mass transportation is used, often encouraged by government policies such as high taxes for car registration and subsidies for mass transport. Since most automobiles run on petroleum-based gasoline, the higher use of mass transportation significantly reduces production of greenhouse gases and global warming (see Section 1.3) and causes less pollution.

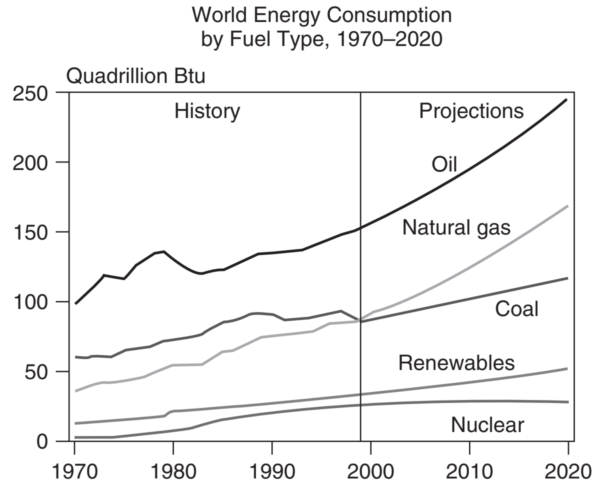

Figure 1.3 Consumption by type of energy source. [*Source*: EIA (Energy Information Administration), International Energy Outlook 2000, PPT by J. E. Hakes; http://tonto.eia.doe.gov/FTPROOT/presentations/ieo2000/sld002.htm.]

Approximately a third of the world's energy is used in residential and commercial buildings, for heating, cooling, cooking, and other appliances. Americans use about 2.4 times the energy of Europeans, due to larger homes and more appliances. The average size of the living space for a citizen in the United States is about 25 times that of a person on the African continent. Another third of the world's energy is used in industry for the production of various goods, such as consumer products, cars, buildings, and food.

1.2.4 Differentiation by Type of Energy Resource

Figure 1.3 shows the consumption by energy source for the last three decades along with projections up to 2020. In 2000, close to 150 Quad Btu of the energy we used was from petroleum, followed by another 70 Quad Btu from natural gas, about 70 Quad Btu from coal, and 15 Quad Btu nuclear fuel. The remainder was from renewable energy resources.

1.2.5 Meeting the Energy Demands of the Future

Improved technology has helped to increase energy efficiency, particularly of the renewable energy resources. However, since the world's economy is also steadily increasing, the consumption of energy grows by about 2% every year, and the demand for energy will only increase.

1.3 THE GREENHOUSE EFFECT AND ITS INFLUENCE ON QUALITY OF LIFE AND THE ECOSPHERE

We live on a planet that derives energy for all our activities from the sun. We wash our clothes in water and dry them in the sun. We get hydroelectric power from the evaporation of water by the heat of the sun. The green plants (trees, algae, etc.) on our planet perform photosynthesis using solar energy. There are many other applications of solar energy, such as in solar heaters, photovoltaic cells producing electricity, photogalvanic, and photobiological processes.

CRITICAL THINKING QUESTIONS

1 What is global warming?
   It is a term used to describe the rapid change of the earth's climate.

2 Explain the different factors associated with the global warming.
   a) Increased global air temperatures
   b) Increased annual precipitation
   c) Shorter winters
   d) Shrinking ice covers
   e) Presence of mosquito-borne diseases at higher altitudes
   f) Rising sea levels

The sun produces solar radiation by a nuclear process, and the solar spectrum spans a wavelength of about 0.03–14,000 nm. Of these different wavelengths of radiation emitted by the sun, the highly energetic ones (γ-rays, X-rays, and ultraviolet rays) spanning a wavelength region of 0.03–300 nm, are filtered by the atmosphere above our planet. The other wavelengths enter our atmosphere. The radiation that reaches the earth's surface is now subjected to reflection by the atmosphere, the clouds, and the earth's surface. The total solar radiation that is reflected amounts to about 30%. The balance of 70% of incoming solar radiation is absorbed by the atmosphere, clouds, land, and oceans. Table 1.1 gives the estimated contributions by the different entities toward reflection and absorption. However, solar energy powers the life on the earth solely by absorption. Almost all of the short wavelength radiation coming from the sun (ultraviolet light) is absorbed by the ozone layer in the stratosphere. This absorption is very important as it protects life on the earth.

Figure 1.4 shows the path for the greenhouse effect and the solar radiation that is emitted and the radiation reaching the earth. Note that only part of the solar radiation reaches the earth.

TABLE 1.1 Pathways for the dissipation of solar radiation

	Reflection (%)
Atmosphere	6
Clouds	20
Surface	4
Absorption (%)	
Atmosphere	16
Clouds	3
Land and oceans	51

Source: http://en.wikipedia.org/wiki/Greenhouse_effect.

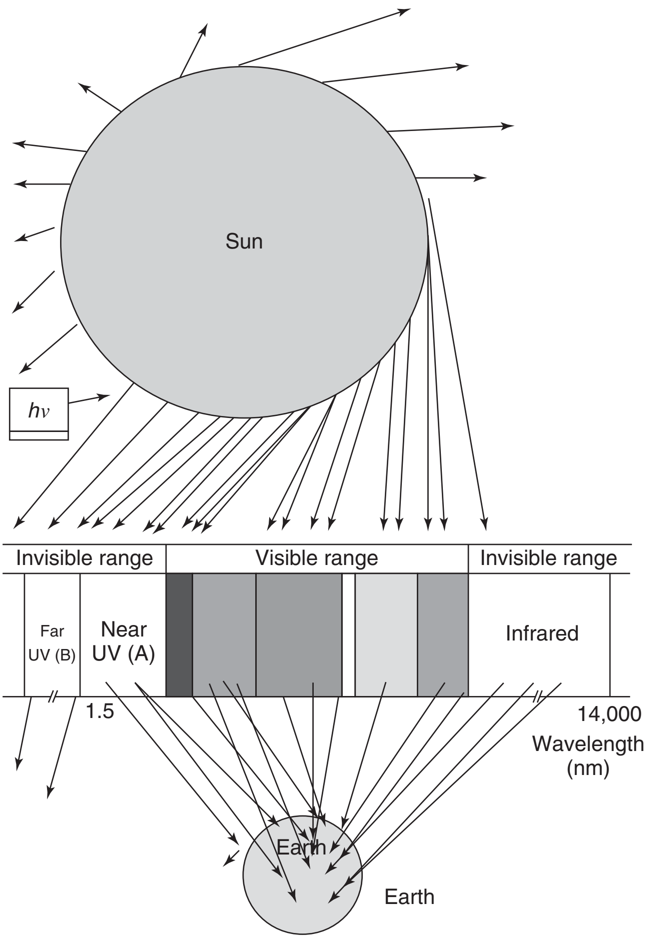

Figure 1.4 Solar radiation.

1.3.1 What Is the Effect of Solar Radiation Reaching the Earth?

The solar radiation reaching the earth heats the surface. This heating effect can be calculated from the radius of the earth (R) [0.635×10^7 m], solar constant (S) that describes the average amount of radiation that earth receives from the sun [1.37 kW/m^2], and Albedo (A) [the fraction of the radiation reflected by the planet] of the earth as given by equation 1.1.

$$\text{Amount of solar radiation reaching the earth's surface} = \pi R^2 S(1 - A) \tag{1.1}$$

This radiation heats up the earth to an effective temperature, T_e. The photons of the wavelengths shown by arrows pointing to earth in Figure 1.4 reach the entire surface and are not localized. If the earth emits radiation as a blackbody, the infrared radiation emitted will follow Stefan–Boltzmann law, according to which

$$\text{Amount of radiation reemitted by earth} = 4\pi R^2 k T_e^4 \tag{1.2}$$

where k = Stefan–Boltzmann constant.

Equating (1.1) with (1.2)

$$T_e = [S(1 - A)/4k]^{1/4} \tag{1.3}$$

By substituting the constants in equation 1.3, it is possible to estimate the effective temperature T_e. The earth's temperature based on this equilibrium model would be about $T_e = 253$ K(−20°C). This is not a suitable condition for life as it would be a frozen world. However, this situation does not exist because of the greenhouse effect and we have an average temperature on the earth of about 288 K (15°C).

1.3.2 How the Temperature Is Kept Higher Than the Equilibrium Model

We have considered in the earlier discussions that the sun's radiation is a blackbody radiation that reaches the earth. The temperature of the sun is much higher than the earth (5880 K vs 288 K), and also the earth's surface (earth diameter = 1.27×10^7 m and surface area 0.51×10^{15} m^2) is much smaller than the sun (diameter = 1.39×10^9 m and surface area = 0.609×10^{19} m^2). Due to these factors, Wien's displacement law proposes that the wavelength of radiation emitted by the earth should be longer than the one coming from the sun. It is typically in the infrared region of 1000 nm. The sun's radiation that reaches the earth is a visible wavelength of about 500 nm. As the earth radiates infrared radiation, it is absorbed by molecules in the atmosphere, typically molecules such as carbon dioxide, water vapor, nitrous oxide, ozone, and methane. These molecules have the capability to absorb the infrared radiation and reemit it to keep the earth's temperature higher than predicted by the equilibrium model. The molecules absorbing the earth's radiation are called greenhouse gases and the process is known as the greenhouse effect. In other words, the greenhouse effect is a process of absorption of infrared radiation emitted from the earth by the greenhouse gases. Thus, most of the thermal radiation of the earth does not escape and is contained in the atmosphere. Only about 6% of the total radiation from the earth escapes into space. For infrared radiation to be absorbed, the molecule should have a permanent dipole moment or asymmetric stretching or bending that can cause a temporary dipole moment. In the atmosphere, nitrogen and oxygen molecules are available in high concentrations and do not contribute to infrared absorption; this is due to the fact that these molecules do not have permanent dipole moment. The molecules such as water vapor, nitrous oxide, ozone, and methane have permanent dipole moment with the exception of carbon dioxide that possesses temporary dipole moment.

1.3.3 Quality of Life

The quality of our living depends on the environment we have around us. The effective temperature, T_e, is one of the deciding factors. If the atmosphere around us has a higher carbon dioxide level, then it will absorb more of the radiation emitted by the earth and reradiate it to the earth. This results in higher T_e on the earth and consequently in global warming. If global warming continues to take place, then a stage might be reached when our existence is threatened. Here we could compare the greenhouse effect of other planets. Venus is rich in carbon dioxide and hence it causes the greenhouse effect on its surface, where the temperature is such that a metal like lead can melt. On the other hand, Mars has very small amounts of greenhouse gases and hence produces a minimum greenhouse effect.

The carbon dioxide level in the earth's atmosphere has increased due to heavy industrialization from the original value of 313 ppm in 1960 to the present value of 375 ppm.

The average temperature of the earth has increased by 0.5°C. This has been discussed as global warming in several scientific meetings. If this trend were to continue, then after a very long time, the effective temperature may not be tolerable for our living. At this stage, increased water evaporation will take place that will affect the quality and quantity of drinking water. It may cause higher rainfalls that may result in flooding. Another possible concern is in a rising sea level that can also cause flooding of the land. Increased temperature may cause spread of infectious diseases, forest fires, and demand for more air conditioning for our living (Table 1.2).

Figure 1.5 gives the carbon dioxide level before Christ (BC) and expected level in 2015.

1.3.4 The Ecosphere

Based on our current understanding of the greenhouse effect, it is desirable to examine the ecosphere, which is not only made up of the environment but also includes all the living things. It extends from the stratosphere to the deep abyss of ocean, with several interacting entities. We may divide the ecosphere into local ecosystems. Among these ecosystems within ecosystems, there may be interactions that will affect the atmosphere. With increasing industrialization (producing more carbon dioxide that is let into the atmosphere) and deforestation (absence of photosynthesis resulting in more carbon dioxide in the atmosphere) in the ecosphere, more of the greenhouse gases will surround us that would result in increasing the temperature on the earth. Another problem that we face is the destruction of the ozone layer (this layer filters ultraviolet rays from reaching the earth) by the

TABLE 1.2 Polluted air: causes and remedies

Type of pollution	Gases involved	Sources	Remedies
Universal problem Greenhouse gas effect	CO_2, CFC, CH_4, N_2O, and O_3	Fuel combustion Forest fires Volcano eruption Chlorofluorocarbons (CFC) Volatile organic compounds Peroxy acetyl nitrate	Lesser usage of fossil fuels Using nonpolluting fuels Forest conservation Stopping volcanoes (???)
Acid rain	Sulfur and nitrogen oxides, ammonia and hydrochloric acid vapors	Caused by combustion of fuels and industrial gases Chemical pulping used in paper industries	Using gas absorbers for desulfuration and denitration Efficient combustion
Ozone layer	Fluorocarbons, CH_3CCl_3, CCl_4, O_3	Decomposition of O_3 with Cl in UV light	Substitution and collection of CFO
Local problem-smog	SO_2, HCl, CO, sulfuric acid mist	Industrial waste gas Combustion of coal	Smoke treatment
Photochemical smog	NO_x, SO_x, nonmethane HC	Combustion of fuel	Same as acid rain

CFC, chlorofluorocarbons; CFO, chlorofluoro oxides; ???, questionable.

References: Energy and air pollution, World energy outlook special report, International Energy Agency, OECD/IEA, 2016; S. Cole, G. Ellen (14 December 2015). "New NASA Satellite Maps Show Human Fingerprint on Global Air Quality." *NASA*. Retrieved 14 December 2015.

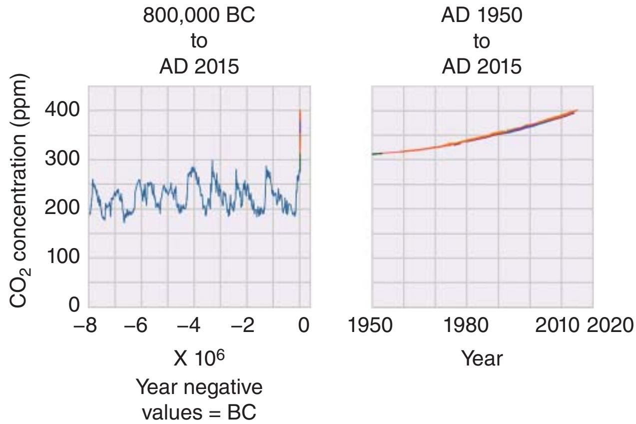

Figure 1.5 Global atmospheric concentrations of carbon dioxide over time. [www.epa.gov/climatechange/indicators.]

fluorocarbons that will allow shorter wavelength radiation from the sun to penetrate through the layer and will have significant interaction with our ecosystem. This may bring about destruction of plants, animals, and humans living on our planet. Although the physical and chemical processes involved in greenhouse effect suggests caution in our industrialization and deforestation, it may be several millions of years before the effective temperature can reach the limit of destruction of life on our planet due to the above-mentioned causes.

The greenhouse gas effect has not been accepted by some scientists. The skeptics consider it as a normal and natural process on the planet that will not affect our living. However, those who accept the greenhouse effect tend to think that it can be reduced by controlling industrial and automobile exhausts. This step would reduce the carbon dioxide level in the atmosphere. Several countries are enforcing the automobile emission controls to a very low level (0–2%). Reductions can also be achieved by use of fuels that do not produce greenhouse gases. In this context, hydrogen technology plays a role as it is used as a fuel to power cars (as fuel cells) and in home heating. The "Kyoto Protocol" enforces that industrialized countries should bring down the emissions of greenhouse gases by 5% by 2010 as compared to 1990.

Toward the end of 2015—at the Climate conference in Paris—195 countries adopted the first universal global climate deal, also known as Paris Agreement. This document describes sets of global actions to avoid dangerous climate change by limiting global warming to 1.5°C.

1.4 NONRENEWABLE ENERGY RESOURCES

Energy sources are nonrenewable when they are depleted in a foreseeable time, typically within a couple of hundred years. Nonrenewable energy is abundantly used and makes up most of our energy resources. Among the nonrenewable sources, the most prevalent are fossil fuels, which formed more than 200–300 million years ago, either from plants, resulting in coal, or from microorganisms, leading to petroleum and gas. Another nonrenewable supply of energy is available nowadays as nuclear fuel, based on the fission of heavy nuclei such as uranium-235. Besides these conventional sources, there are also oil sand and natural gas hydrates, which, however, require more complex extraction methods such as hydraulic fracturing (fracking) and are not commercially used in a significant quantity yet because of their relatively expensive extraction and production costs. The origin, production, use, and specific problems for each nonrenewable energy source will be further discussed as follows.

1.4.1 Petroleum

Petroleum was formed from microorganisms that were covered by sand and silt below the earth's surface. Under pressure and heat, the organic material initially formed waxy solids, so-called kerogen, a precursor to gaseous and liquid organic compounds. Crude oil, or simply oil, as petroleum is also called, is typically a yellow/black viscous liquid that contains gaseous, liquid, and solid hydrocarbons. We will use terms *oil* and *petroleum* interchangeably. In refineries, the petroleum is separated into purer fractions by a distillation process. The details on the fractionation of oil are described in Section 2.6.3.1. Figure 1.6 and Table 1.3 show the regions and major countries and their oil reserves.

Typically, oil is obtained by drilling into reservoirs beneath the earth's surface, including from platforms in the oceans. The oil reserves of the world amounted to 148 Gt in 2004. The area of the world in which the most oil is found is the Middle East, which has about 65% of the world reserves. Most of the world's oil is produced by the following countries: Saudi Arabia, Iran, Iraq, Kuwait, and the United Arab Emirates. These and other countries are members of the OPEC (Organization of Petroleum Exporting Countries). Other major oil-producing non-OPEC countries are Russia and Mexico. If nonconventional oil reserves are included, Canada would possess significant reserves based on oil sand. Figure 1.7 indicates how oil production has increased within the last decades.

If we continue to consume petroleum at the current rate, we should run out of this fossil fuel in the next 40–50 years by most estimates. Over half the petroleum used by Americans comes from countries other than the United States. Most of the oil is consumed for gasoline

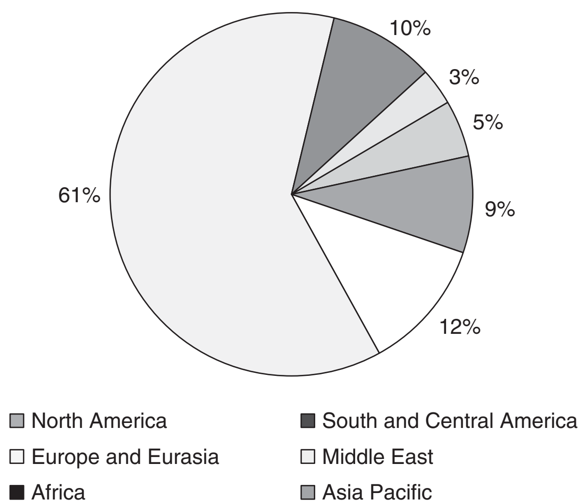

Figure 1.6 Oil reserves in the world in 2005. [*Source*: Based on data from BP, available at http://www.bp.com/productlanding.]

TABLE 1.3 Oil reserves by country in billions of barrels

Africa and the Middle East			North America, Central America, and South America			Europe, Asia, and Oceania		
	Low estimate	High estimate		Low estimate	High estimate		Low estimate	High estimate
Africa			North America			Western Europe		
Algeria	11.4	11.8	Canada	16.5	178.0	United Kingdom	4.1	4.5
Libya	33.6	39.1	Mexico	12.9	14.8			
Nigeria	35.3	35.9	United States	21.3	29.3	Norway	7.7	8.0
Total	100.8	113.8	Total	50.7	222.1	Total	16.2	17.3
Middle East			Central and South America			Eastern Europe and Former USSR		
Iran[a]	125.8	132.7	Brazil	10.6	11.2	Russia	60	72.4
Iraq[a]	115	115	Venezuela	52.4	361.2	Kazakhstan	9	39.6
Kuwait[a]	48	101.5	Total	76	401.1	Total	79.2	121.9
Qatar	15.2	15.2						
Saudi Arabia[a]	261.9	264.3						
UAE[a]	69.9	97.8						
Total	657.3	733.9						
TOTAL WORLD RESERVES: 1016.4–1650.7						Asia and Oceania		
						China	15.4	16.0
						Australia	1.5	4
						India	4.9	5.6
						Indonesia	4.3	4.3
						Total	36.2	39.8

[a]This reserve number cannot be verified.

Source: Wikipedia 2007 (orig.: EIA) http://wikipedia.com, secondary source: http:www.eia.doe.gov/, last accessed 6/1/2007.

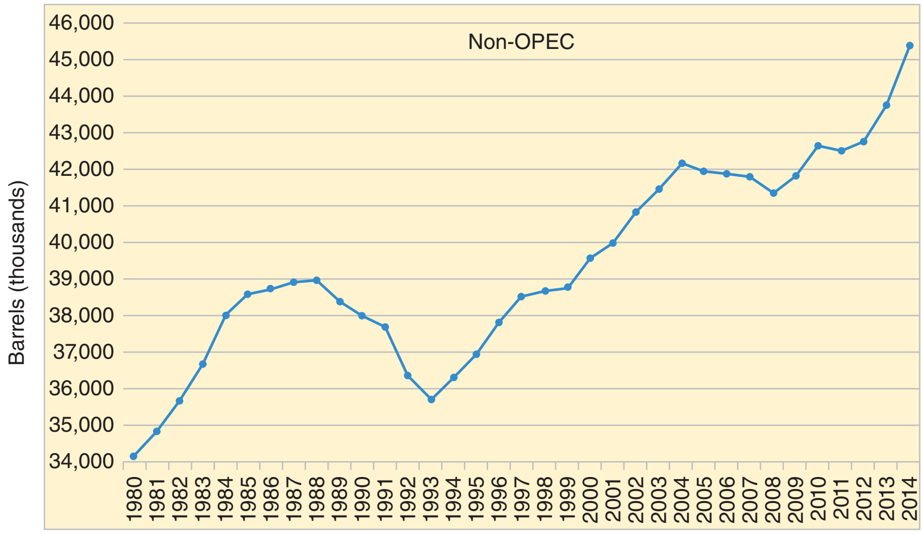

Figure 1.7 World petroleum production. [*Source*: Energy Information Administration/Annual Energy Review 2005 (http://www.eia.doe.gov/emeu/aer/pdf/pages/sec_10.pdf).]

production, and more than half for fuels altogether, including diesel oil, heating oil, and airplane fuel. However, oil is also used to make more valuable products such as plastics, rubber, and medicines.

1.4.2 Natural Gas

Because natural gas is formed by similar anaerobic processes as oil, involving the decay of microorganisms several million years ago, most natural gas reservoirs are geographically close to oil reservoirs (conventional natural gas). Natural gas that occurs by itself in bedrock is distinguished as unconventional natural gas. A substantial amount of natural gas is methane, with amounts ranging between 50% and 90%, with the remainder consisting of hydrocarbons with 2–4 carbons. Table 1.4 shows the countries' natural gas reserves. Natural gas is frequently transported through pipelines. Alternatively, it is liquefied at low temperatures (−160°C) and used as LNG (liquefied natural gas) and transported in containers. Due to its lower viscosity, LNG can be more easily transported and processed than oil. It is mostly used as fuel in industry and residential homes. Similar to oil, it is also used effectively as precursor for the production of plastics and pharmaceuticals. Since natural gas is a purer mixture of hydrocarbons and contains less by-products than oil, it produces less environmentally problematic products when burned. For example, the level of nitrogen oxides or particulate matter is negligible. Another advantage of natural gas is that it is cheaper than oil. Similar to most volatile hydrocarbons, natural gas is highly flammable and therefore potentially hazardous. Natural gas itself does not have a characteristic smell. For detection in case of leakage, sulfur-containing compounds such as mercaptans are added to it. These additives can be easily detected by their garlic-like smell and thus indicate whether the gas is present. The world's natural gas reserves are forecasted to last about 60 more years—slightly longer than our oil reserves.

TABLE 1.4 World natural gas reserves: world proven natural gas reserves by country, 2005 and 2006

	2005	2006	% change 06/05
North America	7,420.0	7,590.0	2.3
Canada	1,633.0	1,665.0	2.0
United States	5,787.0	5,925.0	2.4
Latin America	7,312.0	7,716.0	5.5
Argentina	439.0	415.0	−5.5
Bolivia	740.0	740.0	0.0
Mexico	408.0	388.0	−4.9
Trinidad and Tobago	530.0	530.0	0.0
Venezuela	4,315.0	4,708.0	9.1
Latin America others	880.0	935.0	6.2
Eastern Europe	58,878.0	58,890.0	0.0
Romania	628.0	628.0	0.0
Former USSR	58,099.0	58,113.0	0.0
Eastern Europe others	151.0	149.0	−1.3
Western Europe	5,561.0	5,396.0	−3.0
Germany	257.0	255.0	−0.8
Netherlands	1,387.0	1,347.0	−2.9
Norway	3,007.0	2,892.0	−3.8
United Kingdom	481.0	481.0	0.0
Western Europe others	429.0	421.0	−1.9
Middle East	72,834.0	72,319.0	−0.7
Iran, I.R.	27,580.0	26,850.0	−2.6
Iraq	3,170.0	3,170.0	0.0
Kuwait	1,572.0	1,572.0	0.0
Oman	995.0	980.0	−1.5
Qatar	25,636.0	25,636.0	0.0
Saudi Arabia	6,900.0	7,154.0	3.7
UAE	6,060.0	6,040.0	−0.3
Middle East others	921.0	917.0	−0.4
Africa	14,132.0	14,165.0	0.2
Algeria	4,504.0	4,504.0	0.0
Angola	270.0	270.0	0.0
Egypt	1,895.0	1,940.0	2.4
Libya, S.P.A.J.	1,491.0	1,420.0	−4.8
Nigeria	5,152.0	5,210.0	1.1
Africa others	821.0	821.0	0.0
Asia and Pacific	14,928.0	14,824.0	−0.7
Australia	2,605.0	2,605.0	0.0
Bangladesh	436.0	435.0	−0.2
China	2,449.0	2,449.0	0.0
India	1,101.0	1,075.0	−2.4
Indonesia	2,769.0	2,659.0	−4.0
Malaysia	2,480.0	2,480.0	0.0
Myanmar	538.0	538.0	0.0
Pakistan	798.0	798.0	0.0
Papua New Guinea	428.0	435.0	1.6
Asia and Pacific others	1,324.0	1,350.0	2.0
Total world	181,065.0	180,899.0	−0.1
OPEC	89,419.0	89,193.0	−0.3
OPEC percentage	49.4	49.3	

Source: http://www.opec.org/library/Annual%20Statistical%20Bulletin/interactive/FileZ/Main.htm see then also: Oil and gas data, T34 World proven natural gas reserves by country, 1980–2006, last accessed: 6/1/2007.

1.4.3 Coal

Coal is the most abundant fossil fuel and is used to produce most (approximately 60%) of the world's electricity. It was formed about 300 million years ago (earlier than petroleum) from highly compressed residues of plants. Chemically, coal consists mainly of carbon, ash, which represents silicates and metals, and some sulfur. Some metals in coal are toxic, and sulfur is not desired, since it leads during combustion to sulfur oxides, which are hazardous in the environment. Coal appears in nature in different grades. At high pressure and low moisture anthracite is formed, which has, with 95%, the highest carbon content. Bituminous coal, which is relatively soft, contains 60–80% carbon. Subbituminous coal has a lower carbon content of about 40%; however, its lowest sulfur content makes it useful. At lower pressure and higher moisture lignite is formed, which only contains 25% carbon. Coal was obtained traditionally by underground mining, but more recently there is a trend to surface mining. The latter leads to less human casualties, however, causing more changes to the landscape and environment. Table 1.5 displays the world's reserves of coal.

TABLE 1.5 Proved recoverable coal reserves at end-2006 (million tons)

Country	Bituminous and anthracite	Subbituminous and lignite	Total	Share
United States	111,338	135,305	246,643	27.1
Russia	49,088	107,922	157,010	17.3
China	62,200	52,300	114,500	12.6
India	90,085	2,360	92,445	10.2
Australia	38,600	39,900	78,500	8.6
South Africa	48,750	0	48,750	5.4
Ukraine	16,274	17,879	34,153	3.8
Kazakhstan	28,151	3,128	31,279	3.4
Poland	14,000	0	14,000	1.5
Brazil	0	10,113	10,113	1.1
Germany	183	6,556	6,739	0.7
Colombia	6,230	381	6,611	0.7
Canada	3,471	3,107	6,578	0.7
Czech Republic	2,094	3,458	5,552	0.6
Indonesia	740	4,228	4,968	0.5
Turkey	278	3,908	4,186	0.5
Greece	0	3,900	3,900	0.4
Hungary	198	3,159	3,357	0.4
Pakistan	0	3,050	3,050	0.3
Bulgaria	4	2,183	2,187	0.2
Thailand	0	1,354	1,354	0.1
North Korea	300	300	600	0.1
New Zealand	33	538	571	0.1
Spain	200	330	530	0.1
Zimbabwe	502	0	502	0.1
Romania	22	472	494	0.1
Venezuela	479	0	479	0.1
Total	478,771	430,293	909,064	100.0

Source: http://www.wikipidia.com. Secondary source: http://www.eia.doe.gov/oiaf/aeo/supplement/pdf/suptab_114.pdf, last accessed: 4/1/2008.