9

CURRENT AND FUTURE STATE OF ENERGY PRODUCTION AND CONSUMPTION

9.1 INTRODUCTION

In 2010, China became the world's largest energy user, consuming over 2.4 million kilotons of oil equivalent, surpassing the United States for the first time (data provided by the World Bank). China and the United States also represent the world's largest contributors to CO_2 emissions, with over 7 and 5.5 million kilotons of CO_2 emissions, respectively. While the total consumption of energy between these two countries is close, there is a larger gap in the CO_2 emissions, a result of the fuel mix used for the energy supply.

The fuel mix used in the United States has changed dramatically over the years. Most of the energy originally came from wood, then by the late 1800s coal replaced wood and by the mid-1900s oil and natural gas were the primary energy sources. In the 1970s nuclear power emerged but fossil fuels still provide the bulk of our energy sources today. Figure 9.1 reveals how the historical mix has changed over time and indicates that the addition of new energy resources takes an extensive length of time to effectively propagate into the energy mix [1].

Green Chemistry and Engineering: A Pathway to Sustainability,
Anne E. Marteel-Parrish and Martin A. Abraham.

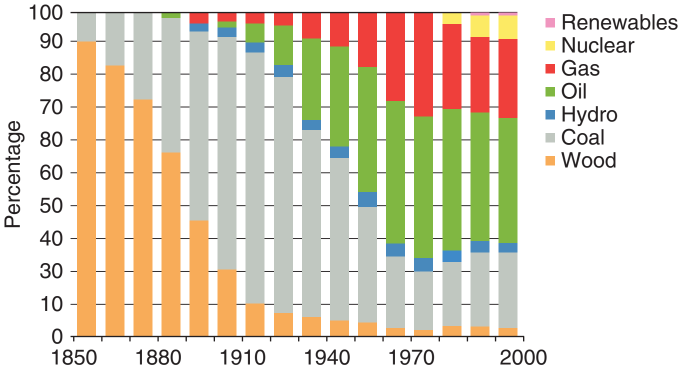


Figure 9.1. Change in the U.S. energy mix over the last 150 years [1]. (Reprinted by permission from Macmillan Publishers Ltd.)

The Energy Information Administration of the U.S. Department of Energy publishes annually a report compiling energy information for the United States, including the sources and sector analysis shown in Figure 3.9. In 2011, the United States consumed a total of 97.3 quadrillion BTU of energy, of which 36% came from petroleum, 26% was produced from natural gas, 20% came from coal, 9% was from renewable sources, and 8% was produced through nuclear power. Among the energy consumers, the transportation sector takes up the greatest share, consuming 28% of the total energy produced and 71% of the petroleum resources. The generation of electric power consumes 40% of the total energy supply, produced from a diverse resource mix, and is then distributed into final end-use sectors [2].

The current U.S. energy mix is based on a complex system of technologies for the production, distribution, and use of fuels and electricity. The Committee of America's Energy Future identified five critical characteristics of this system in 2009 [3, p. 11]:

1. Burning of carbon-based fossil fuels accounted for 85% of U.S. energy needs.
2. The impact of burning fossil fuels is seen mostly in the emission of greenhouse gases, and specifically carbon dioxide (CO_2). In 2007, 6 billion tons of CO_2 was released per year into the atmosphere by the United States alone. However, in the United States, CO_2 emissions have been declining due to the increasing use of renewables and less carbon intensive fuels including natural gas. In developing countries such as China, CO_2 emissions are still increasing due to their rapid economic development and the reliance on the cheapest fuels available: fossil fuels.

   The growth of carbon dioxide emissions is predicted to pose great challenges to international efforts to minimize the impacts of global warming. China and India together use about 19% of the world's energy resources. The U.S. Energy Information Administration expects that by 2020 China and India will consume about one-third of the world's energy resources while the United States will likely reduce its energy consumption slightly [4, p. 28].

The increase in consumption of fossil fuel energy also means a surge in the production of greenhouse gas emissions.

3. Another measure of energy use is annual gross domestic product (GDP) per unit of energy use, which could be one way to measure the energy efficiency of a country. Among OECD countries, Switzerland ranks as the most efficient, at \$11.7 per kg of oil equivalent, in 2010 (World Bank data). The United States was far behind, at \$5.9 per kg of oil equivalent.
4. Energy consumption is connected with economic prosperity. Oil consumption dropped in 2008 and 2009 due to the worldwide economic recession. In the United States, the transportation sector is almost entirely dependent on petroleum. In 2008, more than half of the petroleum consumed in the United States was imported, and in some cases, from unstable and fragile regions of the world [3, p. 14]. Competition for and access to energy plays a central role in U.S. foreign policy. Energy security remains a strong national interest. Recent advances in the use of alternative resources and new discoveries of oil and gas that can be accessed through hydraulic fracturing are beginning to change the political equation, but as with all changes in energy infrastructure, they take significant time to work through this complex system.
5. The energy system's assets are either being depleted or are getting old. There is a great debate as to the total amount of petroleum that can be recovered through existing and proposed technologies. Some experts agree that new technologies will allow increased fossil resource production, whereas others claim that the maximum level of global petroleum production has already been or will soon be reached (and that therefore international conflicts and booming oil barrel prices will arise). Economic theory indicates that as fossil resources become more scarce, prices will go up, which also means that greater cost can be expended to extract those resources. Nonetheless, alternative sources will eventually become more economical, leading to changes in the energy mix.

Infrastructure issues, particularly of transmission and distribution systems, are also of major concern. Many U.S. coal plants are 50–60 years old, beyond their normally expected lifetimes. Retrofits of these plants have kept them operational, but EPA requirements for increased environmental controls limit the economic benefits to continued improvements. Because of cost issues, power companies are beginning to switch to gas-fired power plants. These systems produce less CO_2 emissions than coal plants and have the added advantage that they can be shut down when less energy is needed. New nuclear plants are also being considered, using modular technologies that are more efficient than the 30 year old plants needing to be replaced. Replacing the current and sometimes obsolete infrastructure will be time consuming and pricey.

Since the world's energy consumption is expected to increase by 44% before 2030, there is a global recognition that reducing our reliance on fossil fuels for energy is not only necessary but is the only step toward sustainability. Transforming the way energy is produced, distributed, and consumed is the biggest challenge of the 21st century. But it is not a new challenge: since Franklin D. Roosevelt, several presidents have expressed a need to address environmental impacts and security issues arising from energy production. For example, in 1977, Jimmy Carter introduced a “National Energy Plan”; in 1997, Bill Clinton released the “Federal Energy R&D for the Challenges of the 21st Century”; and in 2001, George W. Bush’s published a report on “Reliable, Affordable, and Environmentally Sound Energy for America’s Future.”

As the leader of one of the world’s largest consumer of energy resources, Barack Obama signed Executive Order 13514 in October 2009, which “sets sustainability goals for Federal agencies and focuses on making improvements in their environmental, energy and economic performance” [5]. This Executive Order on federal sustainability focuses on federal agencies “to meet a number of energy, water, and waste reduction targets, including:

- 30% reduction in vehicle fleet petroleum use by 2020;
- 26% improvement in water efficiency by 2020;
- 50% recycling and waste diversion by 2015;
- 95% of all applicable contracts will meet sustainability requirements;
- Implementation of the 2030 net-zero-energy building requirement;
- Implementation of the storm water provisions of the Energy Independence and Security Act of 2007, Section 438; and
- Development of guidance for sustainable Federal building locations in alignment with the Livability Principles put forward by the Department of Housing and Urban Development, the Department of Transportation, and the Environmental Protection Agency” [5].

The world’s reliance on fossil resources and continued economic growth pose great threats to the sustainability of the world’s energy production. The Kyoto Protocol, adopted in 1997 and put in force in 2005, aimed to reduce the CO_2 emissions by 5.2% from the period 2005–2012. However, the protocol was never ratified by major emitters, such as the United States, and has therefore had limited impact. Current goals to extend the provisions of the Kyoto Protocol through 2020 have not succeeded, as individual countries evaluate the impacts of the proposed plans on their economic growth. While nations debate, the CO_2 levels in the atmosphere continue to rise, and climate variations grow more severe. The National Oceanic and Atmospheric Administration reports December 2012 atmospheric CO_2 at 394.28 ppm, an increase of approximately 1% from the year previously, and an increase of roughly 25% since 1960, as indicated in Figure 9.2 [6].

As described, conversion of a fuel is used to produce energy for the power grid and all other energy needs. Common fuels include natural gas, coal, and oil, but the same processes can be used for renewable materials such as biomass. This is also the basic process that produces energy.

The boiler works by combusting the fuel in the presence of air to produce an exhaust gas at a very high temperature. The gas exchanges heat with the water,

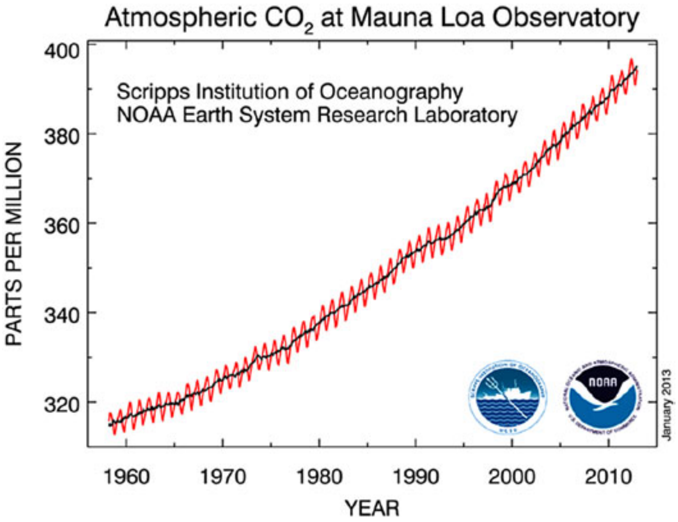


Figure 9.2. Carbon dioxide levels in the atmosphere as reported by NOAA, 1960–present [6].

converting it to steam in the process, through a series of heat exchange tubes. In addition, the radiant heat from the burning fuel can also be recovered in the burner.

The energy from the combusted fuel produces heat, which is transferred to a water stream to produce high-temperature steam, which is ultimately used to power a turbine. The full system, shown in Figure 9.3, consists of four subsystems [7]:

- The water system that transports water into the boiler.
- The fuel system, which controls the fuel flow.
- The draft system, which controls the way in which air is transported through the boiler.
- The steam system, associated with collecting the produced steam.

Most chemical reactions require an energy input for the reaction to occur in a timely fashion on an industrial scale. Given that one of the principles of green chemistry states that “energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized,” it is important to understand energy needs of the chemical process. To do so requires one to know first how energy is produced in chemical reactions and second how it can be measured through basic thermodynamic functions.

9.2 BASIC THERMODYNAMIC FUNCTIONS AND APPLICATIONS

When a reaction occurs, there is an energy change in going from the reactants to the products; this energy change is termed the heat of reaction. To measure the total heat or energy emitted or consumed by a reaction, we use a thermodynamic function

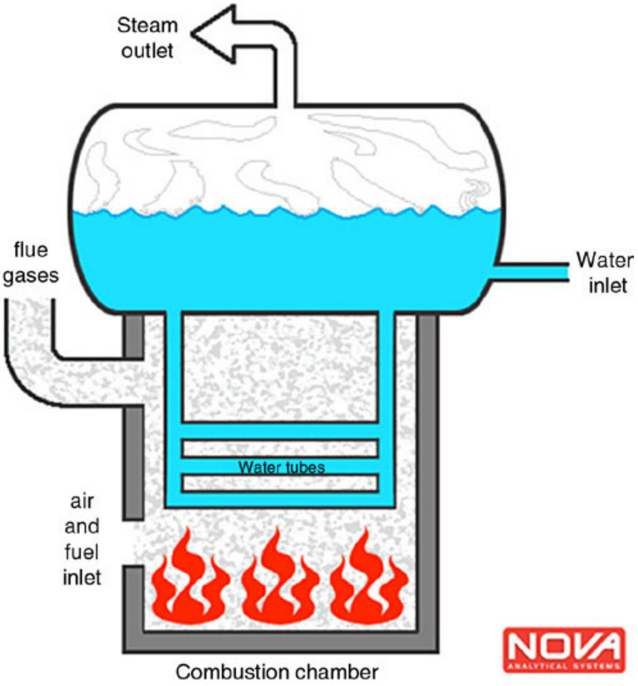
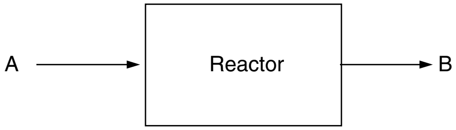


Figure 9.3. Simplified diagram of a steam boiler [7]. (Courtesy of D. Sheasby, NOVA Analytical System, Tenova Group.)

called enthalpy (H). Consider an isomerization reaction, where butylene is converted to isobutylene, for example. We can draw a diagram of this situation:



If we define the reactant and the product with a common standard state, then the energy change associated with this process is the difference between the enthalpy of the product and the enthalpy of the reactant. This is defined as the heat of reaction, ΔH_r, with Δ symbolizing a change in energy between the enthalpy of the products and the enthalpy of the reactants. According to the energy balance then,

$$\Delta H_r = n(H_{out} - H_{in}) \tag{9.1}$$

with n being the number of moles of the products and reactants.

We can extend this to a situation in which the reaction is somewhat more complex, involving multiple reactants and products, each produced with different stoichiometric coefficients. In so doing, we get a summation over all of the species, which provides

$$\Delta H_{\mathrm{r}} = \sum (nH)_{\mathrm{products}} - \sum (nH)_{\mathrm{reactants}} \tag{9.2}$$

We can put this definition on a molar basis, by dividing by the number of moles,

$$\Delta \bar{H}_{\mathrm{r}} = \sum (v_i H_i) \tag{9.3}$$

to put this in terms of the stoichiometric coefficient, ν_{i}. Recall that ν_{i} is negative for a reactant and positive for a product. Then, the total heat of reaction can be expressed as

$$\Delta H_{\mathrm{r}} = \frac{\overline{\Delta H_{\mathrm{r}}}}{v_{\mathrm{A}}} n_{\mathrm{A}} \tag{9.4}$$

All that remains is to define a common standard state, so that the evaluation of the enthalpy of the products and the reactants is consistent.

We handle the consistency problem by defining the enthalpy of an elemental species, in its normal state at 25 °C, to be identically equal to zero. Thus,

$$H(\mathrm{C, solid, 25\,°C}) \equiv 0$$
$$H(\mathrm{O_2, gas, 25\,°C}) \equiv 0$$

Then, when we wish to determine the enthalpy of any compound, we write a hypothetical reaction in which the compound is formed from its component elements

$$\mathrm{C(s)} + 2\,\mathrm{H_2(g)} \rightarrow \mathrm{CH_4}$$

and find that the heat of reaction is calculated as

$$\begin{aligned}\Delta H_{\mathrm{r}} &= H(\mathrm{CH_4}) - 2H(\mathrm{H_2}) - H(\mathrm{C}) \\ &= \Delta H_{\mathrm{f}}(\mathrm{CH_4})\end{aligned}$$

A reaction that leads to the formation of the compound from its elements is termed a formation reaction; the heat of formation ΔH_{f} is the energy generated (or consumed) through the formation of the component from its elements. These values are tabulated for many compounds and are available in the literature.

Once the values of the enthalpies for each compound are known, then we can calculate the enthalpy change using the heat of formation. For example, in the reaction

$$\mathrm{CH_4} + \mathrm{H_2O} \rightarrow \mathrm{CO} + 3\,\mathrm{H_2}$$

the heat of reaction is given by

$$\Delta\bar{H}_r = 3\Delta H_f(H_2) + \Delta H_f(CO) - [\Delta H_f(CH_4) + \Delta H_f(H_2O)]$$

Often the heat of formation of a species is determined through a combustion reaction, so the heat of combustion is defined and tabulated specifically. The heat of combustion is simply the heat of reaction that would be obtained for the combustion of the species under consideration. Thus, for the combustion of methane

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O(1)$$

we can calculate

$$\Delta\overline{H_r} = \Delta\bar{H}_C = 2\Delta H_f(H_2O) + \Delta H_f(CO_2) - [\Delta H_f(CH_4)]$$

Remember that ΔH_f for O_2 is equal to zero. Note that the heat of combustion is just a specific case of heat of reaction, in which the compound reacts with the stoichiometric amount of oxygen to produce carbon dioxide, water (as a liquid), and other combustion products. Several other heats of reaction can be calculated, as shown in Highlight 9.1.

It is important to note that the heat of reaction is dependent on the phase of the species in the reacting system. Thus, it is essential to use the heat of formation for liquid water if liquid water is produced. The difference between the heat of formation of the liquid and the vapor species will be identical to the heat of vaporization of that component.

It is not possible to measure values of heat of reaction for every conceivable reaction. Fortunately, it is possible to develop equivalent chemical reactions for complex systems based on simpler reactions. Hess law states that for an equation of a reaction which is the sum of two or more equations: ΔH_r of the total reaction is equal to the sum of ΔH_r values of the underlying reactions.

Highlight 9.2 illustrates how Hess law is applied.

Highlight 9.1 Calculation of Heat of Reaction

Calculate the heat of reaction for the hydration of ethylene, given by the chemical equation

$$C_2H_4\,(g) + H_2O\,(1) \rightarrow C_2H_5OH\,(1)$$

***Solution*:**

The heat of reaction is given according to the general equation

$$\Delta\bar{H}_r = \sum(v_i \Delta H_{f,i})$$

where we substitute the standard heat of formation for the enthalpy of each species. The standard heat of formation is provided for each of the species, along with the stoichiometric coefficient for each species, in the following table:

Species	ν_i	ΔH_f
C_2H_4	−1	+ 52.28 kJ/mol
H_2O (l)	−1	−285.84 kJ/mol
C_2H_5OH (l)	+1	−277.63 kJ/mol

Substituting in the values provides

$$\begin{aligned}\Delta\overline{H}_r &= (-1)\left(52.28\ \text{kJ/mol}\right) + (-1)(-285.84\ \text{kJ/mol}) + (+1)(-277.63\ \text{kJ/mol})\\ &= 44.07\ \text{kJ/mol}\end{aligned}$$

The sign of ΔH_r indicates the direction of energy transfer. In this example the heat of reaction is negative, which means that energy is transferred from the system to the surroundings and therefore this reaction is called *exothermic* (there is a production of energy). In the opposite case (positive heat of reaction), the reaction is named *endothermic* (in this case there is a transfer of energy from the surroundings to the system).

Highlight 9.2 Application of Hess Law

Using the two following thermochemical equations:

$$(1)\quad N_2O_4\ (g) \rightarrow 2\ NO_2\ (g) \qquad \Delta H_f = 57.2\ \text{kJ}$$

$$(2)\quad NO\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow NO_2\ (g) \quad \Delta H_2 = -57.0\ \text{kJ}$$

find ΔH_r for the following reaction:

$$2\ NO\ (g) + O_2\ (g) \rightarrow N_2O_4\ (g)$$

Solution:

2 NO (g) + O_2 (g) → N_2O_4 (g) is your target expression. In the target expression identify which reactants are desired in what quantities and which products are desired in what quantities.

Look at the known thermochemical expressions and decide how each needs to be changed to give reactants and products in the quantities that are in the target expression.

To have 2 NO as a reactant, all of the stoichiometric coefficients in Equation 2 need to be multiplied by 2. Proportionally the value of ΔH_2 also needs to be multiplied by 2.

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g) \quad 2\ \Delta H_2 = -114.0\ \text{kJ}$$

To have N_2O_4 as product, Equation 2 needs to be flipped, which also means that the sign of ΔH_1 needs to be changed to a negative one.

$$2\ \mathrm{NO}\ (\mathrm{g}) \rightarrow \mathrm{N_2O_4}\ (\mathrm{g}) \quad -\Delta H_\mathrm{f} = 57.2\ \mathrm{kJ}$$

When adding the two equations above, we obtained the target expression:

$$2\ \mathrm{NO(g)} + \mathrm{O_2}\ (\mathrm{g}) \rightarrow \mathrm{N_2O_4}\ (\mathrm{g})$$

and the overall heat of reaction for the target expression is

$$\Delta H_\mathrm{r} = 2\,\Delta H_2 - \Delta H_1 = -114.0\ \mathrm{kJ} - 57.2\ \mathrm{kJ} = -171.2\ \mathrm{kJ}$$

9.3 OTHER CHEMICAL PROCESSES FOR ENERGY TRANSFER

Traditional chemical processing relies on the transfer of energy in the form of heat or work, but it is also possible to use other processes to transfer the necessary energy to promote a chemical reaction. Because the energy transfer may be more efficient or targeted, the yield and selectivity can be improved, often eliminating the need for a catalyst, reducing the separation requirements, and eliminating waste. This section evaluates several of these less common energy transfer techniques.

9.3.1 Microwave-Assisted Reactions

Microwave frequencies are part of the electromagnetic spectrum and typically range from 110 to 140 GHz, between infrared radiation and radio waves. Energy can be transported through microwave radiation. Most kitchens now include a microwave oven, which converts electrical energy into microwaves that are transmitted to food. The absorption of the microwave energy by the food leads to an increase in the temperature of the food. Similar processes are also found in industrial processes for drying and curing products, or to generate plasma such as in the plasma enhanced chemical vapor deposition (PECVD). Because the microwave energy allows for efficient energy transfer directly into materials, it can be used to provide higher yields in shorter reaction times when compared to conventional thermal heating. Some researchers claim that there is a special microwave effect and several explanations are put forward [8]:

- Instantaneous high temperatures at the surface of the solid.
- Facilitation of contact between solid and liquid reagents.

The use of microwave chemistry is spreading rapidly wherever polar materials are present and often no solvent is required. When a polar solvent is present, the success of the chemical reaction depends on the efficient conversion of energy absorbed by the solvent. Because of the increased efficiency of energy transfer, reactions can happen in a microwave without the presence of a catalyst.

9.3.2 Sonochemistry

Ultrasound, or high intensity sound, provides another means of transferring energy through a fluid. The key element of ultrasound is the creation of acoustic cavitation, which is defined as the collapse of gas bubbles in a liquid and which generates very high local temperatures (about 5000 °C) and high pressures (over 1000 atm).

Ultrasound is fairly common for processes involving solids in a liquid or two immiscible liquids. Reactions involving ultrasound require shorter reaction times with improving rates and superior selectivity. Most of these reactions require quality mixing between species. In one example, ultrasonic baths are used to clean the surface of jewelry pieces by cavitation. While sonication has also been used widely in the field of microbiology and biochemistry (to help with digestion of cells), the use of ultrasound has been extended to the polymer field and can be scaled up to large volumes in batch or continuous flow systems. Copolymers of polyethylene and acrylamide have been built using ultrasonic cleavage of polyethylene in the presence of acrylamide [9].

Most recently, sonochemistry was used as an efficient extraction technique. Extraction of carvone and limonene from caraway seeds has been successful. Sonochemistry helped increase the yield, lower the extraction temperature, and produce a purer extract than those obtained with conventional methods [10].

9.3.3 Electrochemistry

Electrochemistry, also defined as oxidation/reduction reactions involving electron transfer between electrodes (usually metals, conductors of electricity) and ionic solutions (or electrolytes), was founded by John Daniell and Michael Faraday in the 1830s.

In previous chapters, we described the redox reaction, essentially an exchange of electrons between species. The redox reaction can be promoted through the application of an external voltage. An electrochemical process can promote a chemical reaction through the application of electricity across a cell, or one in which current is generated through the chemical reaction.

The best example of an electrochemical reaction is in the traditional battery. The earliest batteries, and those still used in automobiles, contained a liquid electrolyte, usually an acid, which would react with a solid surface, for example, lead, promoting a chemical reaction that transferred electrons through an electric circuit.

Electrochemical processes can be seen in action in nature (photosynthesis is an electrochemical process) and in commercial applications such as the coating of objects with metals through electrodeposition or through electroplating to protect metals from corrosion. It can also be used as a greener way to recover metal ions from waste streams, to remove low-molecular-weight ionic compounds through electrodeionization for the production of pure drinking water, or to regenerate an expensive metal or toxic compound in situ.

The fuel cell represents another electrochemical reaction. The fuel cell requires a constant source of fuel, usually hydrogen, in order to continue to produce electricity. The electrochemical reaction involves the oxidation of hydrogen to produce water, representing the greenest energy opportunity (except that the production of hydrogen to power the fuel cell may not be as green as desired).

9.3.4 Photochemistry and Photovoltaic Cells

Photochemical processes use photons from light sources as the source of energy. There are several advantages for using photons as they are clean with no waste production (assuming the original energy source did not produce any wastes), the reaction temperatures are lower than in traditional thermal processes, and they may provide higher selectivity as light is directly shining on the essential reagents. Photochemistry is used by nature for photosynthesis (conversion of carbon dioxide and water into glucose using sunlight) but is also used in the commercial production of vitamin A and vitamin D_3; this is one of the only industrial processes relying on photochemistry since there is no viable thermal alternative to the production of these two valuable products.

Many organic and inorganic chemical reactions are induced by light. An example of an organic photochemical reaction is the preparation of benzyl chloride ($C_6H_5CH_2Cl$) from toluene ($C_6H_5CH_3$) and chlorine (Cl_2). When the diatomic molecule of chlorine is exposed to light, breakage of the Cl–Cl bond occurs and two chlorine radicals are then formed:

$$\mathrm{Cl-Cl+H\nu \rightarrow 2Cl\bullet}$$

The chlorine radical is then used to convert toluene to the benzyl radical:

$$\mathrm{Cl\bullet + C_6H_5CH_2 \rightarrow C_6H_5CH_2\bullet + HCl}$$

The benzyl radical reacts with the second chlorine radical to form benzyl choride:

$$\mathrm{C_6H_5CH_2\bullet + Cl\bullet \rightarrow C_6H_5CH_2Cl}$$

Approximately 100,000 tons of benzyl chloride is produced annually using this gas-phase photochemical reaction.

An example of a photoreactive organometallic reaction is a decarbonylation reaction (removal of a carbonyl group). When organometallic compounds (containing a metal center and organic-based ligands) are subjected to UV irradiation, their ligands are dissociated upon irradiation with UV light. For example, a solution of molybdenum hexacarbonyl ($Mo(CO)_6$) in tetrahydrofuran (THF) will become

$Mo(CO)_5(THF)$ upon UV irradiation. In this case one of the CO ligands is removed and replaced by THF. Since THF is easily dissociated, it can be replaced by another ligand in the second reaction step. This reaction is particularly useful for carbonylation chemistry since metal carbonyls resist thermal substitution and do not dissociate when heated.

Photochemically activated reactions are finding uses in modern applications such as the combustion of carbon nanotubes at high temperatures, which then break open and reorganize in the shape of horns giving the popular name "nanohorns," promising materials for chemical and bio-sensors. Their strong catalytic property is suitable for fuel cell applications and their porosity is ideal for gas storage.

Another application of converting light to electricity is photovoltaic cells. This will be discussed in Section 9.4.1.2 on solar energy applications.

9.4 RENEWABLE SOURCES OF ENERGY IN THE 21st CENTURY AND BEYOND

In order to reduce reliance on fossil fuels, new technologies that take advantage of renewable sources of energy are needed. Several clean sources of electricity, such as solar, wind, and geothermal, may be appropriate depending on the application. Hydropower represents a traditional renewable energy source. These renewable sources are described in this section.

9.4.1 Solar Energy

9.4.1.1 From Where Does It Come?

Solar energy is probably the most well-known and promising renewable source of energy. The sun generates natural nuclear energy through nuclear fusion (when the two nuclei of atoms are combined or are "fused" together to form a single heavier nucleus).

Solar energy would be sufficient to produce the entire amount of electricity needed in the world as the total amount of radiation hitting the earth is about 7000 times the total current global energy consumption. In 2009, The Union of Concerned Scientists mentioned that "all the energy stored in Earth's reserves of coal, oil, and natural gas is matched by the energy from just 20 days of sunshine" [11]. Solar energy also has the advantage of being available everywhere on earth.

However, solar energy is an intermittent energy source, as it can only be harvested during daylight hours. In addition, the intensity of the solar radiation varies significantly depending on weather conditions, location in the world, and the season. On average, the energy available varies between 3 and 9 $kWh/m^2/day$ in North America while in Northern Europe, it fluctuates between 2 and 3 $kWh/m^2/day$. However, the variation can be substantial as the southern regions of France receive $2\frac{1}{2}$ times more solar radiation than the northern regions. Because of the intermittency, it is necessary to store solar energy, or convert it to heat or electricity and transport it where needed, even in the most remote areas of our planet.

The sun is categorized as a renewable source of energy since it has emitted radiation for billions of years, independent of how much of this energy humans have used and are currently using. There are many ways to use solar energy: either in the form of heat (solar-thermal energy) or in the form of electricity (solar-photovoltaic energy).

9.4.1.2 Where Can We Use It? Current and Future Applications

Using the sun's energy for heat is not a new process. Before early civilizations mastered the art of fire, solar energy was the only source of heat accessible. Solar thermal energy is used to maintain temperature within a greenhouse. In remote locations, solar energy can be used to heat water in a solar still and create hot water for showers in a remote location.

On average, about 14% of the total energy consumed in the United States is devoted to heating water and accounts for one-third of the average total household energy consumption [12, p. 175]. As an alternative to heating water in a conventional gas water heater, it is possible to take advantage of natural sunlight through a solar hot water system, in which the radiative energy from the sun is captured by the water. There are two types of solar-thermal collectors: concentrating and nonconcentrating. With concentrating collectors, the area exposed to the sun (collector area) is much greater than the area absorbing the radiation (absorber area); therefore, the concentration of the sun's radiation is very intense at the absorber area. Flat-plate collectors or nonconcentrating collectors usually consist of water tubes located between a transparent cover called glazing and a black absorber plate. The solar radiation passes through the transparent cover (can be glass) and the water tubes attached to the black absorber plate are used to remove the heat from the absorber. In this case, there is no difference between the area of the collector and absorber. Nonconcentrating collectors are effective in producing water at temperatures up to 95 °C, which would be sufficient to produce hot water for domestic uses or in-floor radiant heating or to heat swimming pools. Above this temperature, concentrating collectors are needed. Solar collectors are extremely popular in various countries: 90% of Israeli homes are equipped with solar water heaters; it is also the leading domestic heating technology in 10 countries of the European Union such in Germany, Greece, and France. Only 4 m^2 of collector is needed to supply hot water for a family of four people in France [12, p. 176].

There are also a number of ways to utilize solar energy passively, which counts on using the natural energy flows into or out of a building without the consumption of fossil fuels. This is simply done by designing the architecture of a house in a smart way. For example, one can imagine that a house made of thick stone walls could be ideal in a region where it is hot during the day and the temperatures decrease at night. The heat absorbed by the walls during the day is then released into the interior of the house at night. Most of the houses in the north of France are not equipped with air conditioning; they rely on the natural heating and cooling effect of their infrastructure.

Solar energy can also be used to cook food. Solar cookers, which do not require the use of fuel, are built and available in the shape of solar panel cookers, hotpots, and solar kettles. Since solar cooking works effectively in remote locations, it can reduce problems associated with deforestation and desertification in developing countries that rely heavily on wood and biomass as sources of energy for cooking.

A more efficient way to reach the high temperatures required for industrial applications, or produce electricity, is through the use of concentrated solar power plants in conjunction with thermal power plants. This technique is effective in regions of the world where the sun shines at least 2500 hours per year. While this type of process is not widespread, nearly 1600 MW of power was generated through concentrating solar power in 2011, in places including California and the EU. Through the use of parabolic reflectors or mirrors, the solar radiation can be directed onto an absorber tube containing a fluid such as oil or water, and this fluid can be heated to very high temperatures. Often the sunlight is concentrated into a collector on top of a "power tower," and this design is commonly termed "heliostat power plants." The steam generated is used to power an electrical generator. In California, the Luz solar power station totaling 850 parabolic trough mirrors is able to produce electricity equivalent to 380 kWh/y/m^2. The whole facility requires a ground area of 1.5 km^2 and an area of mirrors equivalent to 465,000 m^2. The solar radiation is converted to electricity with 14% efficiency. In Spain, a solar-thermal power plant near Seville contains 624 heliostatic solar mirror panels, which provides electricity for about 6000 households. It is expected that this plant will increase its capacity by 2013 and will be able to supply about 180,000 households in the near future.

Sunlight can also be converted directly into electricity using the photovoltaic effect (based on the creation of a p-n junction; p for positively doped (lack of electrons and creation of holes) and n for negatively doped (presence of extra negative charges), as illustrated in Figure 9.4.

For a semiconductor in the presence of light, an electron can be excited and moves from p-silicon (see Figure 9.4) into the n-silicon. As the electrons move, the p-silicon

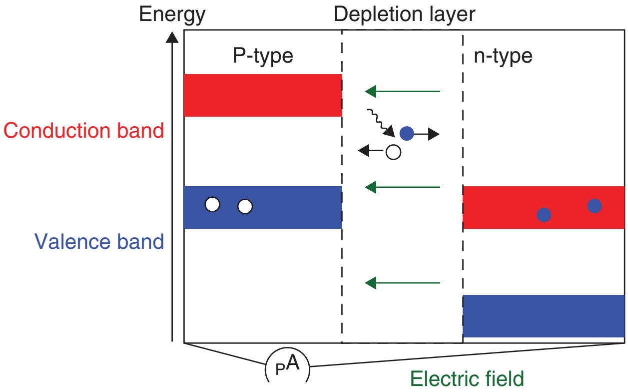


Figure 9.4. Illustration of electron–hole movement in a p-n junction [13]. (Courtesy of Marianne Breinig and James Hitchcock, University of Tennessee, Knoxville.)

becomes positively charged and the n-silicon becomes negatively charged, creating a net electric field. In the photovoltaic cell, this semiconductor device is connected to an electric circuit through which the electrons migrate back to the p-silicon, creating an electric current that can be used for power.

Photovoltaic cells are often made of silicon-based semiconductor materials, which efficiently absorb light and release free electrons, but they can also be made from more complex and less environmentally friendly materials such as cadmium and tellurium. Photovoltaic cells are typically from 1 to 10 cm wide and are connected together in modules to bring the current and voltage to acceptable levels. The amount of electricity produced depends on the amount of solar radiation, which varies depending on the weather and time of the day. Usually only about 25% of the solar energy is converted into electricity under ideal conditions; the remainder is dissipated as heat.

Produced electricity can be used directly to power devices such as small calculators or road signs and lighting or communication equipment, or it may be placed directly onto the electric grid. Because solar power is intermittent, a solar energy system must include battery storage that can provide energy when it is cloudy outside. The photovoltaic cells usually produce a direct current (DC), which needs to be converted to alternating current (AC) for most households and appliances through an inverter.

9.4.1.3 How Much Does It Cost?

A typical domestic solar-thermal hot water heater system costs between $1000 and $2000. In parts of the globe where it is mostly sunny all year, a solar-photovoltaic installation can supply about 40% of all electricity needs at a cost of about $50,000. If more electricity is generated than needed, owners can sell it back to the electric utility provider and make a profit.

For commercial solar-thermal power plants, construction costs are estimated to be twice those associated with a modern coal power station and three times the costs of a gas power station. Commercial solar-photovoltaic power plants cost between $0.20/kWh and $0.60/kWh (compared to the cost of $0.035–0.060/kWh for a coal-fired power station and $0.040–0.063/kWh for a gas-fired power station) [14].

In 2011, the international cost of residential electricity averaged about $0.16/kWh. Residential solar electricity is more expensive than the average grid electricity. Improvements in performance and reduced production costs through economies of scale project that solar-photovoltaic costs will decrease to about $0.10/ kWh by 2020, placing the cost of a solar system on par with coal by 2017 and with natural gas by 2022 [15]. In addition, solar produces no greenhouse gases during the generation of electricity.

9.4.1.4 What Are the Upsides and Downsides of Solar Energy?

One of the main advantages of solar power is that sunlight is ubiquitous and despite the initially large investment, operation and maintenance are inexpensive. No waste or greenhouse gas is generated while heat or electricity is produced. Solar energy can also be used in remote locations, where connection to the electric grid is not practical.

The main drawback is that solar energy is not available during the night and its effectiveness depends very much on the location and climate conditions. While the cost of domestic solar energy cannot yet compete with electricity produced through fossil resources, it is expected that extensive development and research will lead to economically competitive photovoltaic systems. On the other hand, converting solar radiation into thermal energy can be done rather cheaply and is already used extensively in many parts of the world.

9.4.2 Wind Power

9.4.2.1 From Where Does It Come?

Wind power has been used since antiquity, mostly for sail boats and then for windmills. In the Asian world, wind was mostly used to pump water and irrigate fields. Wind is nowadays used to produce electricity via wind turbines.

Airflows on earth are created by the difference in atmospheric pressure between various locations on the surface of the earth and various altitudes. This movement of air can be tapped for its energy content and converted to electricity. A single small wind turbine can provide sufficient energy for domestic purposes, or clusters of wind turbines on land or offshore called wind farms can be used to supply electricity to large communities or for addition to the electric grid.

Commercial wind turbines are composed of several parts: on the top of a tower that can be in excess of 100 m tall, three giant blades of 30 meters or more in length rotate a horizontal shaft, turning a generator that converts mechanical energy into roughly 3 MW electricity. Inside the tower there is a cable that carries electricity to transmission lines and a computer system that controls the rotation and direction of the blades.

9.4.2.2 Where Can We Use It? Current and Future Applications

Wind power technologies have developed significantly over the past several decades, allowing for installation of wind farms especially in China, Europe, and the United States. The largest single wind farm is located in Texas, with a total capacity of 781 MW. Offshore wind energy is now also becoming more prevalent, including the largest capacity offshore wind farm located in the United Kingdom having a capacity of 300 MW. The United States ranks first in energy generated by wind, with 1.168 quadrillion BTU produced in 2011.

Larger wind turbines produce more energy, because the larger diameter blade is available to capture a greater proportion of the mechanical energy passing by the turbine. As a result, the size of turbine blades has increased dramatically since 1980. The diameter of a typical wind turbine was 15 meters in 1980 and in 2003 the diameter reached 124 meters. Research is going on to even increase the diameter to 160 meters by 2020 and therefore intensify the recovered power since the power generated is proportional to the cube of the wind velocity. Turbines are also becoming taller, to take advantage of the higher wind velocity at increased altitude, as well as allowing for longer turbine blades.

Land-based wind turbines are installed in windy areas and where the population is low. There are limited available land sites and many local populations would prefer wind turbines to not be erected in sight. Wind tends to increase along shorelines, and thus an important emerging alternative to land-based wind turbines are offshore turbines. They are similar to the ones used on land but they require reinforced foundations. The offshore wind turbines operate more regularly than the inland ones since the wind is more regular offshore and turbulence is reduced, generating increased wind speed.

The theoretical limit for efficiency of a wind turbine is 59%, but because the wind does not always blow at a constant speed, most wind farms achieve an efficiency closer to 30%. The electricity generated by wind can be harvested and delivered to the grid but because wind is intermittent, energy must be stored to be available when the wind is not blowing. This limits the contribution of wind power tremendously for electricity grid capacity.

9.4.2.3 How Much Does It Cost?

Even if wind is free, wind farms need to be built, operated, and maintained and cost about \$1000 to \$2000 per kW to build. Some claim that with the operating and maintenance costs, the cost of a productive wind farm is in the same range as coal, gas, and nuclear power plants [16]. Wind-based technology costs from \$0.045 to \$0.140/kWh. The capacity of a wind turbine is dependent on the wind speed and therefore cost can vary radically. Every little increase in wind speed (even just 5 km/h) will multiply exponentially the power generated by a wind turbine. A wind speed of 14–90 km/h is needed for wind turbines to operate productively.

Some residential wind turbines can be installed and are used to charge batteries. An interesting hybrid system that couples wind energy with solar photovoltaic provides a more continuous source of energy, since it is often windier at night and in poor weather.

9.4.2.4 What Are the Upsides and Downsides of Wind Power?

As mentioned for the sun, wind is a renewable source of energy and can be used efficiently in specific regions of the world. While it is the cheapest of all the renewable sources of energy, the production of electricity from wind power does not generate greenhouse gases (however, this is not the case in the construction and maintenance phase). The footprint of land-based wind turbines is small and therefore the land around them can be used for other purposes.

One of the main drawbacks is the initial investment associated with wind, which is still higher than that for coal, oil, or nuclear systems. The other major inconvenience is that the wind does not always blow everywhere and its speed is not consistent. Therefore, the reliability of wind power for grid electricity is low. The sites of wind turbines are often remote; storage and transportation of electricity are accumulative issues driving the cost up.

Besides the visual impact of wind turbines and their controversial aesthetic aspect, they are also blamed for their noise and for their contribution to the increased death of migratory birds.

Regarding offshore wind turbines, an additional problem lies in anchoring the turbines, for which their foundations need to resist higher winds but also waves. This also causes environmental concerns linked to the destruction of the seabed flora.

Even if wind power can only be competitive in specific situations, its price has decreased notably in the last decade and future improvements in terms of storage and transmission of wind energy are expected.

9.4.3 Geothermal Solution

9.4.3.1 From Where Does It Come?

Below the crust of our planet is a reservoir of geothermal energy coming from the original formation of the planet about 4.5 billion years ago (20%) and from radioactive decay of minerals such as uranium, thorium, and potassium (80%).

Geothermal derives from the Greek: "geo" means "earth" and "thermal" means "hot." The difference in temperature between the core of the planet and its surface implies that there is a geothermal gradient that moves the thermal energy in the form of heat from the core to the surface of the earth. This is the major factor involved in accessibility of geothermal energy; the second factor is the permeability of the rocks near the surface of the earth, which determines the rate of heat conduction to the surface.

Because of these two factors, while geothermal energy is available everywhere on earth, the intrinsic nature of the local geology and the temperature gradients are driving the use of geothermal energy. Variations in gradients can be quite large: the average geothermal temperature gradient near the surface of the earth is 3.3 °C/100 meters compared to Iceland, famous for its hot springs, where the gradients may reach 30 °C/100 meters.

9.4.3.2 Where Can We Use It? Current and Future Applications

Geothermal energy can be used either for thermal energy production or for electricity generation. In fact, geothermal energy has been used for several thousands years to heat water for homes, for cooking, and for agriculture.

Geothermal sources may either be low temperature (<149 °C) or high temperature. Low-temperature sources are most appropriate for direct application, such as the production of hot water for homes or for heat. A closed loop recycle system includes a well drilled up to 400 ft into the ground to extract high underground temperatures into a liquid working fluid, which is then distributed at the surface as heat. Slightly below the ground surface, the temperature is a fairly constant 10 °C. A heat pump may be employed to move heat from a building to the subsurface, acting as a natural air conditioning system.

For the production of electricity, only high- or medium-temperature sources are appropriate. For commercial applications only hydrothermal sources are suitable and, depending on their depth, several applications such as the use of dry steam at high temperature for electricity production are worth being pursued. The temperature difference between the fluid extracted from deep underground and that extracted near the surface provides the driving force for an exchange of energy that can be extracted through a turbine to generate electricity.

The United States with about 77 geothermal power plants is the leader in the production of geothermal energy, producing about 3000 MW in 2007. There are several commercial projects underway in France, Japan, and Australia. In France, the increase in geothermal energy was 30% in 2005. The average increase in the world is at a level of 4% every year [12, p. 210].

9.4.3.3 How Much Does It Cost?

The typical cost of geothermal energy is around $0.05/kWh. It is therefore a little more expensive than coal, gas, and nuclear but still cheaper than wind and solar-based energy. Prices to install a residential geothermal system vary considerably: from $7000 to $30000 for a 2000 square foot home. However, most of the cost comes from the installation and the price of the heat pump, which can be somewhere between $11,000 and $30,000. The impact on the energy bill is considerable: from $100 per month with geothermal heat compared to $600 with an oil furnace [17].

9.4.3.4 What Are the Upsides and Downsides of Geothermal Energy?

The main advantage of geothermal energy is that it is a continuous energy resource available throughout the day. There is an abundance of geothermal resources in the world but some parts of the world are particularly favored due to local geological conditions. Geothermal energy is quite flexible in that it can produce both heat and electricity and generates very low CO_2 emissions. The footprint is much smaller than for wind and solar energy and the environmental impact is very low.

However, in the majority of the cases geothermal heat pumps are necessary for large-scale production of heat and this generates some greenhouse gases. Some claim that geothermal energy is not truly renewable since hydrothermal resources for electricity production will eventually be depleted.

Even if geothermal energy will be increasingly exploited in the future and is currently the third most used renewable energy resource in the world, it only accounts for 0.4% of the worldwide energy.

9.4.4 Hydropower

9.4.4.1 From Where Does It Come?

Hydropower uses the water flows in a river or channel or the movement from the waves in a sea or ocean. It has been used for centuries to do mechanical work, such as milling grain, sawing timber, or extracting metal ore. Today, it is the most commonly used source of renewable energy for electricity generation.

To harness the energy from water, which flows or falls, water is directed into a channel or pipe and is then pushed against turbines or blades to make them rotate. There are two main types of hydropower usage, either using the current of a river or using a pumped storage or dam system. Dam systems rely on the height of the water and rate of the water flow. This is not always consistent as the availability of flowing water can vary considerably throughout the year. In a pumped water storage system, water is stored in different leveled reservoirs (one above the other). The excess electricity stored as grid electricity is then used to drive pumps that move the water back into the higher reservoir. This is then used to generate electricity during periods of peak demand.

9.4.4.2 Where Can We Use It? Current and Future Applications

Hydropower accounts for 16% of all of the electricity produced in the world. Countries that have easy access to water, such as Canada, Brazil, and Norway, use hydroelectric power stations extensively. In cases in which the water flow is insufficient or unsustained, a dam can be installed to create a lake; the water that flows through the spillway of the dam can be converted to electricity for the power grid. The largest hydropower plant in the world is Itaipu, located on the Paraná River, across the Brazil–Paraguay border. Twenty-five percent of the electricity consumed by Brazil and 90% of that consumed by Paraguay is provided by the Itaipu hydroelectric dam, which was elected one of the seven modern Wonders of the World in 1994.

Pumped storage systems are a very effective way to store energy. In a pumped storage system, two reservoirs at different elevations act together. Electricity is used during periods of low demand to pump water from one reservoir to the other, creating an elevation difference. When required, the water is allowed to flow from the higher elevation, and the mechanical energy of flow is converted to work, which is then used to drive a turbine and produce electricity.

9.4.4.3 How Much Does It Cost?

The main cost of the power station is in the construction cost, which covers 80–90% of the total lifetime cost. The capital expenditures are high but the operational costs are low. It is estimated that the lifetime cost of a new hydroelectric power station is \$0.065–0.100 per kWh, which makes it more expensive than wind but cheaper than solar. When hydropower is available in a country, it is the first energy source exploited to produce electricity. China is the prime producer of electricity from hydropower, followed by Canada.

9.4.4.4 What Are the Upsides and Downsides of Hydropower?

The major downsides of hydropower are the limited number of locations where hydropower plants can be built and when these locations are appropriate, the cost is huge. However, there is no intermittency and it is an excellent way to generate peak electricity. There is no CO_2 emitted during the production of electricity but some is produced during the construction of the hydroelectric power plant.

Nevertheless, the environmental and societal impacts of hydropower are greater than for wind, solar, or geothermal energy. The construction of dams involves emissions of greenhouse gases, noise as well as sediment disturbance, and possible impact of water quality. It demands shifting rivers and extraction of millions of tons of earth and rock, therefore affecting the ecology, impacting the nearby river flows, and also relocating populations. When a dam submerges upstream land, the existing plant and fish life is impacted. Rivers become disconnected, meaning that fish can't travel the river; as a result, populations of fish, especially salmon, usually decrease as hydroelectric power plants are built.

Lastly, dam accidents have happened. Most recently in 2009, an accident occurred at RusHydro's largest plant at Sayano-Shushenskaya in eastern Siberia. Seventy-five people were killed when the turbine and engine rooms were flooded, damaging almost all turbines when the ceiling collapsed. A widespread power failure followed. More people are killed through dam failures than through nuclear reactor accidents.

9.4.5 The Case of Hydrogen Technology

The hydrogen atom is the smallest and lightest of all elements and also the most abundant element of the universe (75% of the visible mass of the universe is composed of hydrogen). It is found in a large variety of compounds such as in water, hydrocarbons such as methane, and biomass, but it is rarely found as a diatomic molecule of H_2. When this flammable gas is burned in oxygen, it forms water and also releases energy.

Hydrogen is not a primary source of energy since it does not exist as a separate entity and energy needs to be provided to remove it from other compounds. It is known as an energy carrier, a means of transmitting energy from one place or form to another. For example, hydrogen may be used to produce electricity in a fuel cell, but that hydrogen might be produced by electrolysis of water. The electrolysis consumes electricity to produce hydrogen, whereas the fuel cell converts hydrogen to water with the production of electricity.

Hydrogen is mostly produced from natural gas or coal through reforming with steam to produce syngas—a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and water vapor (H_2O). It can also be formed by the electrolysis of water, which consists in passing an electric current through water to dissociate it into H_2 and O_2 at high temperatures or pressures. Electrolysis only accounts for 4% of the production of hydrogen while fossil fuels provide the rest [18].

Besides its use in industrial chemical processes and in the food processing industry, hydrogen was the main energy fuel for the NASA space program. Because of hydrogen's unique properties, storage and distribution limit the potential uses for hydrogen as a fuel for motor vehicles or for generating electricity. Some limited applications can be envisioned; for example, hydrogen fuel cells combined with an electric motor can replace the typical internal combustion engine. A hydrogen fuel cell functions like a battery, where the two sides are separated by a proton exchange membrane (PEM). Fuel cells make electricity from hydrogen and oxygen with the emission of only heat and water. In theory, a hydrogen fuel cell can achieve 80% efficiency, but in practice, the overall efficiency is often much less. Hydrogen has seen some success, as it was used to power buses in London and Beijing during the Olympic Games in 2012 and 2008, respectively. Air Products is the leading producer of hydrogen and has engineered about 130 fueling stations in the world. Vehicles powered by hydrogen do not generate greenhouse gas emissions, and they are quieter and more efficient than their gasoline and diesel counterparts. Hydrogen can also be made from waste and from renewable resources such as the sun or biomass.

9.4.6 Barriers to Development

Not one renewable source of energy stands out in terms of productivity, cost, or accessibility. The main issue associated with renewable electricity sources is the high cost, followed by the lack of well-established transmission and storage capacity. Integrating renewably generated electricity with grid electricity requires a significant change in the electrical grid, allowing for both inputs and outputs to the system based on availability and demand. The so-called smart grid will allow distributed energy generation but requires a substantial change in infrastructure, at a significant cost. Modernization is made difficult by regional ownership of transmission and distribution systems, and the current regulatory system that is not designed to benefit utility companies that make improvements for future innovations.

In order to reach the goal of having 20% of electricity generated by renewable sources of energy by 2030, a consistent and long-term mix of policies, regulations, public investments, and incentives must be provided to jump start future deployment of these new technologies.

9.5 CONCLUDING THOUGHTS ABOUT SOURCES OF ENERGY AND THEIR FUTURE

The current context regarding power generation is one of uncertainty. We can't predict the future. Burton Richter took the lead in ranking winners, losers, and maybes in his book, *Beyond Smoke and Mirrors: Climate Change and Energy in the*

21st Century in 2010 [18]. In his winners list, is coal (with carbon capture and storage), hydroelectric, geothermal (near-surface systems), nuclear, natural gas (as a replacement for coal), solar heat and hot water, and solar photovoltaic (for off-grid applications only). The losers are coal (without carbon capture and storage), oil for transportation, and corn ethanol and hydrogen for transportation. There are still some question marks associated with geothermal for deep mining for heat, the high cost associated with solar-thermal electric and solar-photovoltaic as well as advanced biofuels. Of course, there needs to be a spot left for new technologies not invented yet.

REFERENCES

1. Chu, S.; Majumdar, A. *Nature*, **2012**, 488, 294–303.
2. `http://www.eia.gov/totalenergy/data/annual/pdf/sec2_3.pdf.`
3. National Academy of Sciences, National Academy of Engineering, and National Research Council. *America's Energy Future-Technology and Transformations*, The National Academies Press, Washington, DC, 2009.
4. Miller, D.; Mann, M. *Energy Production and Alternative Energy*, Greenhaven Press, Farmington Hills, MI, 2011.
5. `http://www.whitehouse.gov/administration/eop/ceq/sustainability.`
6. `http://www.esrl.noaa.gov/gmd/ccgg/trends/.`
7. `http://nova-gas.blogspot.com/2011_12_01_archive.html.`
8. Matlack, A. *Introduction to Green Chemistry*, Marcel Dekker, New York, 2001, p. 465.
9. Fujiwara, H.; Tanaka, J.; Horiuchi, A. *Polym. Bull.*, **1996**, 36, 723
10. Chemat, A.; Lagha, A.; AitAmar, H.; Bartels, P. V.; Chemcat, F. *Flavor and Fragrance Journal*, **2004**, 19, 188–195.
11. Union of Concerned Scientists. "How Solar Energy Works," 2009, www.ucsusa.org.
12. Ngo, C.; Natowitz, J. B. *Our Energy Future: Resources, Alternatives, and the Environment* John Wiley & Sons, Hoboken, NJ, 2009.
13. `http://web.utk.edu/~cnattras/Phys250Fall2012/modules/module%204/conduction_in_solids.htm.`
14. `http://www.iea.org/textbase/nppdf/free/2010/projected_costs.pdf.`
15. `http://solarcellcentral.com/cost_page.html.`
16. Nicholsen, M. *Energy in a Changing Climate*, Rosenberg Publishing Pty Ltd, Australia, 2009, p. 61.
17. `http://www.qualitysmith.com/request/articles/articles-hvac/geothermal-heat-pump-cost/.`
18. Richter, B. *Beyond Smoke and Mirrors: Climate Change and Energy in the 21st Century*; Cambridge University Press, New York, 2010, p. 74.