CHAPTER FIFTEEN

The Twenty-First Century Energy Mix

Many scenarios of the twenty-first century energy mix expect society to use several different energy sources. They view hydrogen as a major carrier of energy, but not as an energy source. Even though the assumptions, methods, and results presented in these scenarios are debatable, they all show an energy infrastructure in transition. We discuss a set of energy forecasts later in this chapter. First, we consider the role hydrogen may play as a major component of the twenty-first century energy mix.

15.1 HYDROGEN AND FUEL CELLS

Hydrogen is found almost everywhere on the surface of the earth as a component of water. It has many commercial uses, including ammonia (NH₃) production for use in fertilizers, methanol (CH₃OH) production, hydrochloric acid (HCl) production, and use as a rocket fuel. Liquid hydrogen is used in cryogenics and superconductivity. Hydrogen is important to us because it can be used as a fuel. We first describe the properties of hydrogen before discussing the production of hydrogen and its use as the primary fuel in fuel cells.

PROPERTIES OF HYDROGEN

Hydrogen is the first element in the Periodic Table. The nucleus of hydrogen is the proton, and hydrogen has only one electron. At ambient conditions on Earth, hydrogen is a colorless, odorless, tasteless, and nontoxic gas of diatomic molecules (H₂). Selected physical properties of hydrogen, methane, and gasoline are shown in Table 15-1. A kilogram of hydrogen, in either the gas or liquid state, has a greater energy density than the most widely used fuels today, such as oil and coal (Appendix D-1). The heating value of a fuel is the heat released when the fuel is completely burned in air at room temperature and the combustion products are cooled to room temperature [Cengel and Boles, 2002, page 254]. The lower heating value is the heating value obtained when the water produced by combustion is allowed to leave as a vapor. The higher heating value is the heating value obtained when the water produced by combustion is completely condensed. In this case, the heat of vaporization is included in the higher heat of combustion of the fuel. The energy conversion efficiencies of cars and jet engines are normally based on lower heating values, and the energy conversion efficiencies of furnaces are based on higher heating values. Lower heating value and higher heating value are sometimes abbreviated as LHV and HHV respectively.

Hydrogen is considered a clean, reliable fuel once it is produced because the combustion of hydrogen produces water vapor. Hydrogen can react with oxygen to form water in the exothermic combustion reaction 2H₂ + O₂ → 2H₂O. The heat of combustion of the reaction is 62,000 BTU/lbm of hydrogen (1.4 × 10⁶ J/kg). Hydrogen combustion does not emit toxic greenhouse gases such as carbon monoxide or carbon dioxide. When hydrogen is burned in air, it does produce traces of nitrogen oxides. Hydrogen is considered a carrier of energy because it can be used as a fuel to provide energy. It is not considered an energy source because energy is required to produce molecular hydrogen H₂ from water.

HYDROGEN PRODUCTION

Hydrogen can be produced by electrolysis.¹ Electrolysis is the non-spontaneous splitting of a substance into its constituent parts by supplying electrical energy. In the case of water, electrolysis would decompose the

---

¹ For a more detailed explanation of electrolysis, see Appendix D-1.
H₂O + electrical energy → H₂ + ½O₂  \hspace{1cm} (15.1.1)

It is difficult to electrolyze very pure water because there are few ions present to flow as an electrical current. Electrolyzing an aqueous salt solution enhances the production of hydrogen by the electrolysis of water. An aqueous salt solution is a mixture of ions and water. The addition of a small amount of a nonreacting salt such as sodium sulfate (Na₂SO₄) accelerates the electrolytic process. The salt is called an *electrolyte* and provides ions that can flow as a current.

We illustrate the electrolysis process in Figure 15-1 using the electrolysis of molten table salt (sodium chloride or NaCl). Electrolysis is an oxidation-reduction (redox) reaction. Recall that oxidation involves the loss of electrons, and reduction involves the gain of electrons. The redox reaction takes place in an electrolytic cell. The electrolytic cell is a cell with two electrodes: the anode, and the cathode. Oxidation occurs at the anode, and reduction occurs at the cathode. The voltage source in Figure 15-1 provides the potential difference needed to initiate and support the redox reaction. In the figure, a negatively charged chlorine ion with one extra electron loses its excess electron at the anode and combines with another chlorine atom to form the chlorine molecule (Cl₂). The electrons flow from the anode to the cathode, where a positively charged sodium ion gains an electron and becomes an electrically neutral atom of sodium.

The redox reaction can be treated as two half-reactions. The first half-reaction is oxidation at the anode. Oxidation occurs when electrons are released by the reducing agent in the oxidation half-reaction. In the case of electrolysis of a water-table salt solution, two oxidation half-reactions occur at the anode:

\[
\begin{align*}
anode - oxidation: \\
2\text{H}_2\text{O}(l) & \rightarrow 4\text{H}^+(aq) + \text{O}_2(g) + 4e^- \\
2\text{Cl}^- (l) & \rightarrow \text{Cl}_2(g) + 2e^-
\end{align*}
\hspace{1cm} (15.1.2)
\]

The parenthetic symbols denote liquid phase (l), aqueous phase (aq), and gas phase (g). A reducing agent is a substance that donates electrons in a reaction. The hydrogen atom from a water molecule is the reducing agent at the anode. Electrolysis of a water-table salt solution is illustrated in Figure 15-2.

The second half-reaction is reduction at the cathode. Reduction occurs when the oxidizing agent acquires electrons in the reduction half-reaction. In the case of electrolysis of a water-table salt solution, two reduction half-reactions occur at the cathode:

\[
\begin{align*}
cathode - reduction: \\
4\text{H}_2\text{O}(l) + 4e^- & \rightarrow 2\text{H}_2(g) + 4\text{OH}^-(aq) \\
\text{Na}^+(aq) + e^- & \rightarrow \text{Na}(s)
\end{align*}
\hspace{1cm} (15.1.3)
\]

The parenthetic symbol (s) denotes solid phase. An oxidizing agent is a substance that accepts electrons in a reaction. The hydroxyl radical OH⁻ from a water molecule is the oxidizing agent at the cathode for the upper reaction, and the sodium cation is the oxidizing agent for the lower reaction.

The overall reaction for electrolysis of a water-table salt solution in an electrolytic cell is

\[
\begin{align*}
\text{overall:} \\
2\text{H}_2\text{O}(l) & \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \\
2\text{NaCl} & \rightarrow 2\text{Na}(s) + \text{Cl}_2(g)
\end{align*}
\hspace{1cm} (15.1.4)
\]
chlorine is highly reactive and toxic. One of the problems facing society is the problem of how to produce hydrogen using an environmentally acceptable process.

Two possible sources of energy for producing hydrogen in the long-term are nuclear fusion and solar energy. Ausubel [2000] has suggested that the potential of nuclear energy will be realized when nuclear energy can be used as a source of electricity and high-temperature heat for splitting water into its constituent parts. The process of decomposing the water molecule at high temperatures is called thermal decomposition. Heat in the form of steam can be used to re-form hydrocarbons and produce hydrogen.

Steam re-forming exposes a hydrocarbon such as methane, natural gas, or gasoline to steam at 850°C and 2.5 × 10^6 Pa [Sørensen, 2000, pages 572–573]. The reformation requires the two reactions

\[
C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2
\]

\[
CO + H_2O \rightarrow CO_2 + H_2
\]

(15.1.5)

where \(C_nH_m\) represents the hydrocarbon. Both reactions produce hydrogen. A process such as absorption or membrane separation can be used to remove the carbon dioxide by-product. The production of carbon dioxide, a greenhouse gas, is an undesirable characteristic of steam re-forming.

Some bacteria can produce hydrogen from biomass by fermentation or high-temperature gasification. The gasification process is similar to coal gasification described in Section 13.8.

**FUEL CELLS**

Hydrogen is considered a carrier of energy because it can be transported in the liquid or gaseous states by pipeline or in cylinders. Once produced and distributed, hydrogen can be used as a fuel for a modified internal combustion engine or as the fuel in a fuel cell. **Fuel cells** are electrochemical devices that directly convert hydrogen or hydrogen-rich fuels into electricity using a chemical rather than a combustion process.

A fuel cell consists of an electrolyte sandwiched between an anode and a cathode (Figure 15-3). The electrolyte in Figure 15-3 is a mixture of potassium hydroxide (KOH) and water. The electrolyte solution is maintained at a lower pressure than the gas cavities on either side of the porous electrodes. The pressure gradient facilitates the separation of hydrogen and oxygen molecules. The load in the figure is a circuit with amperage \(A\) and voltage \(V\). Hydrogen is fed to the anode (negative electrode) and oxygen...
The historical trend toward decarbonization reflects the contention by many energy forecasters that hydrogen will be the fuel of choice in the future. These forecasters believe that power plants and motor vehicles will run on hydrogen. The economies that emerge will depend on hydrogen and are called hydrogen economies. The concept of a hydrogen economy is not new. The use of hydrogen as a significant fuel source driving a national economy was first explored in the middle of the twentieth century as a complement to the adoption of large-scale nuclear electric generating capacity. Concerns about global climate change and the desire to achieve sustainable development have renewed interest in hydrogen as a fuel.

A future that depends on hydrogen is not inevitable. Hydrogen economies will require the development of improved technologies for producing, storing, transporting, and consuming hydrogen. We have already discussed some of the challenges involved in the production of hydrogen. As another example of the technological challenges that must be overcome in a transition to a hydrogen economy, let us consider the storage of hydrogen.

Hydrogen can be stored in the liquid or gaseous state, but it must be compressed to high pressures or liquefied to achieve reasonable storage volumes because of the low density of the diatomic hydrogen molecule. The energy content of hydrogen gas is less than the energy contained in methane at the same temperature and pressure. The volumetric energy density of liquid hydrogen is approximately 8700 MJ/m³. This is about one third the volumetric energy density of gasoline. The relatively low volumetric energy density of hydrogen creates a storage problem if we want to store hydrogen compactly on vehicles.

Researchers have learned that hydrogen can be stored effectively in the form of solid metal hydrides. A metal hydride is a metal that absorbs hydrogen. The hydrogen is absorbed into the spaces, or interstices, between atoms in the metal. According to Silberberg [1996, page 246], metals such as palladium and niobium “can absorb 1000 times their volume of H₂ gas, retain it under normal conditions, and release it at high temperatures.” This form of storage may be desirable for use in hydrogen-powered vehicles.

Hydrogen can be hazardous to handle. A spectacular demonstration of this fact was the destruction of the German zeppelin Hindenburg. The Hindenburg used hydrogen for buoyancy. In 1937, the Hindenburg burst into flames while attempting a mooring in Lakehurst, New Jersey. At first
it was widely believed that the zeppelin became a ball of fire when the hydrogen ignited. An early solution to the flammability problem was to use less flammable gases such as helium in lighter-than-air ships. In the 1990s, a former NASA scientist named Addison Bain reanalyzed the data and showed that the Hindenburg fire was more likely started by the ignition of a flammable material that was used to coat the cloth bags that contained the hydrogen than by the ignition of hydrogen. Today it is believed that hydrogen may have contributed to the Hindenburg fire, but was not its cause.

Hydrogen forms an explosive mixture with air when the concentration of hydrogen in air is in the range of 4% to 75% hydrogen. For comparison, natural gas is flammable in air when the concentration of natural gas in air is in the range of 5% to 15% natural gas. Furthermore, the ignition energy for hydrogen–air mixtures is approximately one-fifteenth the ignition energy for natural gas–air or gasoline–air mixtures. The flammability of hydrogen in air makes it possible to consider hydrogen a more dangerous fuel than natural gas. On the other hand, the low density of hydrogen allows hydrogen to dissipate more quickly into the atmosphere than a higher-density gas such as methane. Thus, hydrogen leaks can dissipate more rapidly than natural gas leaks. Adding an odorant to the gas can enhance the detection of gas leaks.

The environmental acceptability of hydrogen fuel cells depends on how the hydrogen is produced. If a renewable energy source such as solar energy is used to generate the electricity needed for electrolysis, vehicles powered by hydrogen fuel cells would be relatively clean because hydrogen combustion emits water vapor. Unfortunately, hydrogen combustion in air also emits traces of nitrous oxide (NO₂) compounds. Nitrogen dioxide (x = 2) contributes to photochemical smog and can increase the severity of respiratory illnesses.

15.3 SUMMARY OF ENERGY OPTIONS

The literature contains several publications that present a description of the energy sources that are available or are expected to be available during the twenty-first century. Energy options known today include fossil fuels, nuclear energy, solar energy, renewable fuels, and alternative sources. They are briefly described in the following paragraphs as a summary of available energy sources [Fanchi, 2000].

Fossil fuels are the dominant energy source in the modern global economy. They include coal, oil, and natural gas. Environmental concerns are motivating a change from fossil fuels to an energy supply that is clean. Clean energy refers to energy that has little or no detrimental impact on the environment. Natural gas is a source of relatively clean energy. Oil and gas fields are considered conventional sources of natural gas. Two nonconventional sources of natural gas are coalbed methane and gas hydrates.

Coalbeds are an abundant source of methane. The presence of methane gas in coal has been well known to coal miners as a safety hazard, but is now being viewed as a source of natural gas. Coalbed methane exists as a monomolecular layer on the internal surface of the coal matrix. Its composition is predominately methane, but can also include other constituents, such as ethane, carbon dioxide, nitrogen, and hydrogen. The gas, which is bound in the micropore structure of the coalbed, is able to diffuse into the natural fracture network when a pressure gradient exists between the matrix and the fracture network. The fracture network in coalbeds consists of microfractures called cleats. Gas flows through the microfractures to the production well.

Gas hydrates are chemical complexes that are formed when one type of molecule completely encloses another type of molecule in a lattice. In the case of gas hydrates, hydrogen-bonded water molecules form a cage-like structure in which mobile molecules of gas are absorbed or bound. Although gas hydrates can be found throughout the world, difficulties in cost-effective production have hampered development of the resource. Gas hydrates are generally considered troublesome for oil and gas field operations, but their potential commercial value as a clean energy resource is changing the industry perception. The potential as a gas resource is due to the relatively large volume of gas contained in the gas hydrate complex.

Nuclear energy is presently provided by nuclear fission. Nuclear fission is the process in which a large, unstable nucleus decays into two smaller fragments. It depends on a finite supply of fissionable material. Nuclear fusion is the combination, or fusing, of two small nuclei into a single larger nucleus. Many scientists expect nuclear energy to be provided by nuclear fusion sometime during the twenty-first century. Fusion reactions are the source of energy supplied by the sun. Attempts to harness and commercialize fusion energy have so far been unsuccessful because of the technical difficulties involved in igniting and controlling a fusion reaction. Nevertheless, fusion energy is expected to contribute significantly to the energy mix by the end of the twenty-first century, even though a prototype commercial-scale nuclear reactor is not expected to exist until 2015 or later.