### **GREEN CHEMISTRY AND CHEMICAL ENGINEERING**

# Water for Energy and Fuel Production

# Yatish T. Shah



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### Series Preface

### GREEN CHEMISTRY AND CHEMICAL ENGINEERING

### A BOOK SERIES BY CRC PRESS/TAYLOR & FRANCIS

The subject and discipline of chemistry and chemical engineering have encountered a new landmark in the way of thinking about, developing, and designing chemical products and processes. The revolutionary philosophy, termed "green chemistry and chemical engineering," focuses on the design of products and processes that are conducive to reducing or eliminating the use and/or generation of hazardous substances. In dealing with hazardous or potentially hazardous substances, there may be some overlaps and interrelationships between environmental chemistry and green chemistry. While environmental chemistry is the chemistry of the natural environment and the pollutant chemicals in nature, green chemistry proactively aims to reduce and prevent pollution at its very source. In essence, the philosophies of green chemistry and chemical engineering tend to focus more on industrial applications and practice rather than academic principles and phenomenological science. However, similar to the chemistry and chemical engineering philosophy, the green chemistry and chemical engineering derives from and builds on organic chemistry, inorganic chemistry, polymer chemistry, fuel chemistry, biochemistry, analytical chemistry, physical chemistry, environmental chemistry, thermodynamics, chemical reaction engineering, transport phenomena, chemical process design, separation technology, automatic process control, and so on. In sum, green chemistry and chemical engineering is the rigorous use of chemistry and chemical engineering for pollution prevention and environmental protection.

The Pollution Prevention Act of 1990 in the United States established a national policy to prevent or reduce pollution at its source whenever feasible. Adhering to the spirit of this policy, the Environmental Protection Agency (EPA) launched its Green Chemistry Program to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. The global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international communities of science, engineering, academia, industry, and government in all phases and aspects.

Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as a green solvent in separation technologies; application of supercritical water oxidation for destruction of harmful substances; process integration with carbon dioxide sequestration steps; solvent-free synthesis of chemicals and polymeric materials; exploitation of biologically degradable materials; use of aqueous hydrogen peroxide for efficient oxidation; development of hydrogen proton exchange membrane (PEM) fuel cells for a variety of power generation needs; advanced biofuel productions; devulcanization of spent tire rubber; avoidance of the use of chemicals and processes causing generation of volatile organic compounds (VOCs); replacement of traditional petrochemical processes by microorganismbased bioengineering processes; replacement of chlorofluorocarbons (CFCs) with nonhazardous alternatives; advances in design of energy-efficient processes; use of clean, alternative, and renewable energy sources in manufacturing; and so on. Even though this list is only a partial compilation, it is undoubtedly growing exponentially.

This book series "Green Chemistry and Chemical Engineering" by CRC Press/ Taylor & Francis is designed to meet the new challenges of the twenty-first century in the chemistry and chemical engineering disciplines by publishing books and monographs based on the cutting-edge research and development to the effect of reducing adverse impacts on the environment by chemical enterprise. In achieving this, the series will detail the development of alternative sustainable technologies that will minimize the hazard and maximize the efficiency of any chemical choice. The series aims at delivering the readers in academia and industry with an authoritative information source in the field of green chemistry and chemical engineering. The publisher and its series editor are fully aware of the rapidly evolving nature of the subject and its long-lasting impact on the quality of human life in both the present and the future. As such, the team is committed to making this series the most comprehensive and accurate literary source in the field of green chemistry and chemical engineering.

Sunggyu Lee

### Preface

The need for energy at both the individual level and the societal level is essential and rapidly growing. Throughout the history of the human race, man has found the sources of energy to make life more comfortable, convenient, and progressive. Energy is needed for all walks of life including industrial growth, transportation, manufacturing of products, and improvement of the quality of life. The modernization of society, increase in industrial productivity, increase in population, and man's constant desire for freedom to travel all contribute to the increasing demands on energy.

Fundamentally, there are 10 known sources of energy and fuel: oil, gas, solid fuels such as coal, oil shale, and bitumen (commonly known as solid fossil fuels), uranium (or nuclear), biomass, waste, solar, wind, geothermal, and water. Over the years, once the new sources of energy are discovered and harnessed, they have to compete for their share of the market. The demand for any given source of energy and fuel has gone up and down depending on the supply, competitive price, usability, and its influence to the environment. For example, in the 1800s, the source of energy (largely for heating and cooling) was biomass because oil, gas, coal, and uranium had not been discovered and the technologies to harness and use other sources of energy and fuels had not been developed. Over the years that followed, the percentage use of biomass steadily declined because of the availability, the need for use, and the pricing structure of other sources of energy and fuels. Over the past 100 years, our society and economy have been predominantly fossil fuel based.

The sources of energy and fuels have always been challenged by the need for better environment and economics. This is also a challenge for the development of new energy technologies. One source of energy and fuel cannot replace the other unless there are strong arguments based on the environment, economics, usability, and improvement of the quality of life. Often these forces compete with each other, and then local politics and social acceptance make the final decisions. One example is the recent rapid change in the use of renewable energy in favor of fossil energy due to a well-accepted notion that fossil energy, in general, affects our environment in more negative ways than the effects of renewable energies. This has led to the so-called green energy revolution. Even within fossil energy sources, it is generally believed that natural gas is less harmful to the environment than coal. This, along with changing supplies of gas, has led to the installation of more gas-driven power plants than those using coal. In our history, the changes in the sources of energy and fuels have been gradual because most technological developments in energy industries have been evolutionary and not revolutionary in their impacts.

Out of all sources of energy and fuels, one source that is most abundant, most green, most compatible with all other sources of energy and fuels, and most acceptable to the environmentalists is water. Nearly four-fifths of the world is surrounded by water. Water is everywhere underground and closely tied to the development of our fossil energy resources. Water is not only essential for all lives on this planet, but it is also the best under-tapped source of energy and fuels.

The main theme of this book is to convey the message that as we continue to find new sources of energy and fuels and continue the development of new technologies to meet our growing needs of energy, we need to be more vigilant in pursuing the role of water in the future energy landscape. Water can play a vital role in creating new energy sources that will keep our environment intact. For one thing, water is free and in plentiful supply. For the other thing, it carries the most important green source of energy, namely, hydrogen. In fact, there is a general belief that the best long-term solution for energy is hydrogen due to its least impact on environment.

We have used water without its appreciation due to its abundance. However, until now, we have not exploited all the versatility of water in its use to provide energy and fuels. New technological development over the past several decades have brought forward some of the most fascinating characteristics of water that was unknown before. These characteristics offer an even wider role for water in the future production of energy and fuel.

The book outlines, with concrete examples, five separate roles of water in the energy and fuel industry, which are as follows:

### 1. Benign roles of water in the production of energy and raw fuels

Water has played an important role in the recovery and purification of oil, gas, coal, oil shale, tar sand, and uranium. This role will become even more important as we (1) try to recover more unconventional sources of gas and oils, (2) use enhanced oil recovery methods more vigorously to work hard to get the remaining sources of oil, and (3) develop new technology such as "fracking process" to improve our efficiency of both conventional and unconventional oil and gas recovery. The use of water will also expand significantly with a substantial growth of recovery of bitumen from tar sand.

The water has also played a significant role as a thermal energy carrier and a reactor moderator in the nuclear power industry. With the commercialization of the next generation of nuclear reactors using "supercritical water," the importance of water in the nuclear industry will further increase. The importance of water as a benign energy carrier will also increase significantly because of the aggressive pursuit of enhanced geothermal systems across the world. An increased use of solar energy will also require more use of water as a thermal energy carrier. Finally, it is predicted that by 2040, electrical energy will be about 40% of our total energy usage. This growth of electrical energy will require more steam-driven turbines that will drive more electric generators.

### 2. Role of steam as a reactant

While steam has been used as a reactant for a variety of gasification and reforming processes in the past, this role will significantly increase because of (1) large growth in natural gas production (by unconventional gas recovery), which can be used for reforming (and hydrogen generation) and power plants; (2) the increased use of biomass gasification and reforming as it is a good source of hydrogen and it is renewable and environmentally friendly;

and (3) large growth in waste conversion industry to generate biogas that can also be reformed to produce hydrogen. In sum, the role of steam to produce hydrogen will significantly increase in outgoing years.

### 3. Role of water as a reactant, a reaction medium, and a catalyst

Recent developments showing the significant changes in the properties of water at elevated temperatures and pressures have galvanized a significant amount of R&D in making synthetic solid, liquid, and gaseous fuels from a variety of feedstock using water. At elevated temperatures and pressures, water possesses unique organic, liquid-like properties. The hydrothermal processes at high temperatures and pressures accelerate the conversion of biomass to more coal-like solids, oil-like liquids (biocrudes), and gases containing methane and hydrogen. This technology has a very bright and growing future.

Water has also been used as a medium to carry out the catalytic aqueousphase reforming of selective carbohydrates to produce hydrogen, syngas, alkanes, and other monofunctional products that can be further upgraded to produce a variety of fuels, fuel additives, and chemicals. This selective catalytic process has resulted in the birth of a new "Bioforming process," which also has a significant growth potential.

There have been other interesting developments in the use of water as a reactant. The acid-catalyzed hydrolysis has been successfully used to produce active and versatile chemicals such as levulinic acid, furfural, gamma-valerolactone from cellulose, and carbohydrates. These chemicals can provide platforms for many fuels, fuel additives, and useful chemicals. This technology has a bright future and has resulted in the development of the "Biofine process."

Anaerobic digestion of waste to produce hydrogen and methane has been practiced for a long time. This is one of the most efficient energy conversion processes. An increase in waste production worldwide (e.g., municipal solid waste that will reach close to one billion tons per year in few years) will increase the application of this process. Water is an important part of this biochemical process.

The use of water in hydrolysis and fermentation processes will also grow significantly as more emphasis on conversion of lignocellulose to ethanol and higher alcohols is mandated all over the world. The production of ethanol will significantly grow and increase the role of water in the fermentation industry.

### 4. Role of supercritical water in the production of synthetic fuels

Since the late 1970s, the use of supercritical water to convert all carbonaceous materials to synthetic fuels and chemicals has been rapidly increasing. Supercritical water possesses some very unique properties, which allow easy conversion of many carbon-based feedstock to liquid fuels, methane, and hydrogen. In recent years, this technology has been widely exploited to produce hydrogen. The growth in this technology will be accompanied by a significant growth in the use of water.

### 5. Role of water as a direct source for fuels and energy

Hydrogen can be generated by water dissociation. This subject has been very heavily researched in recent years. Technologies such as electrolysis,

photocatalytic and photobiological dissociation of water and thermochemical dissociation of water can provide some important breakthroughs for the production of hydrogen. The uses of solar and nuclear energies for this purpose have also been heavily examined.

Gas hydrates provide methane from water-based clathrate molecules. Gas hydrates are loosely bound methane molecules in water (or ice) cage. These naturally occurring compounds are the largest source of carbon in the world. The recovery of methane from the hydrates has been heavily researched all over the world.

Water has also been a direct source of energy by its use in dams for hydroelectricity (potential energy). This is one of the cleanest sources of energy and is rapidly growing all over the world. Besides hydroelectricity, in the recent years, other sources such as hydrokinetic energy that are imbedded in all types of moving water such as in tidal waves, offshore waves, undercurrents, and inland waterways are being harnessed. Tidal waves can provide both potential and kinetic energies for power. These are renewable, predictable, and clean sources of energy. Water can also provide power near the equator using ocean thermal energy conversion technologies that use the difference in surface temperature and temperature at the high depth to drive heat engines.

The potentials for each of these five applications are enormous. So far, we have only scratched the surface. In fact, together it appears that the future of energy and fuel land-scape is moving toward the expansion of the water industry with all other sources of energy and fuels as supporting players. The concept of water refinery is not unimaginable. The above-mentioned five roles of water are described in detail in 12 chapters of this book. The content of each chapter is described in the "Introduction" chapter.

The expanded use of water for energy and fuel production leads to another societal issue that will have to be managed. Clean water is essential for human and animal life. The expanded use of water for energy and fuel production may create a problem for the available amount of drinkable water for human and animal needs and useable water for agricultural needs. Just as there are tensions between the use of food materials such as corn, soybeans, maize, and other carbohydrates for fuels (such as ethanol), tensions will also be created by the use of water for energy and fuel production, and the need of clean water for human and animal needs as well as for agricultural purposes. The strategic management of water will be the next important societal issue. The treatment of water used in energy and fuel industries will become an independent industry by itself. This industry will have to manage the overall societal needs for the water to maintain the required strategic distribution of water among its different usages. Along with energy and fuel, a prudent use of water will be the next societal challenge. Water, however, will be the centerpiece of future energy and fuel landscape.

This book is very useful to all academic, industry, and government personnel who are engaged in R&D, pilot-scale development, and commercialization of new technologies for energy and fuel.

## Author

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# 1 Introduction

The energy and fuel landscape is changing faster than ever. We need energy and fuels for heat, power, electricity, and transportation. Generally, the major sources of raw fuels are oil, natural gas, coal, biomass, waste, and uranium. These raw fuels can provide either chemical or nuclear energy to generate power or raw materials for synthetic fuels and a host of chemicals and materials. Other major sources of energy for power production are solar, wind, geothermal, and water. Together, these 10 sources satisfy our needs for raw energy and fuels for residential, industrial, and transportation purposes. They also provide raw materials for important chemicals and materials.

The term "synthetic fuels," or "synfuels," generally refers to hydrogen, syngas (a mixture of hydrogen and carbon monoxide), methane, or a mixture of methane with other hydrocarbon gases, liquid alkanes (such as gasoline, diesel fuel, heating oil, jet fuel, naphtha, alcohols, biocrudes, and many other chemical additives), and intermediates as well as refined solid fuels (such as refined coal or oil shale, hydrochar, and biochars) that are all capable of direct use (as a source of chemical energy) to provide heat, electricity, or a source of energy for transportation purposes. These synthetic fuels also allow the storage of energy for an extended period of time.

### 1.1 GLOBAL ENERGY LANDSCAPE: PAST, PRESENT, AND FUTURE

In the twenty-first century, the energy industry is forced to diversify to address the three issues: (1) depletion of worldwide oil productions and reserves as well as refining capacity, (2) a stronger global demand for energy due to increased needs by China, India, and other developing nations, and (3) the effect of carbon emissions (in the form of volatile hydrocarbons and carbon dioxide) on global warming and climate change. During the last two decades, along with further expansion of clean energy sources such as wind, solar, hydroelectric, and geothermal, the development of renewable biomass energy (often called "bioenergy") has increased its momentum. Unlike fossil energy, bioenergy is proven to be carbon neutral because of the use of carbon dioxide by plants for photosynthesis. Renewable and carbonfree energy sources such as nuclear, solar, wind, and hydroelectric have also gained significant momentum due to push on "green energy."

Today, the power and fuel need is supplied by five separate types of energy industry. The largest supplier of power and fuel (>85%) is still "fossil energy," which is organic hydrocarbon based, and the fossil energy industry is attempting to reduce carbon emissions to the environment and its effect on global climate change. In this regard, more and more coal-based power plants are being replaced by the power plants that use the natural gas. In general, natural gas is more environmentally friendly than coal. The supply of natural gas is increasing because of the success in recovering new unconventional gas resources. The carbon-emitting fossil energy industry is still facing significant political pressures due to its harmful influence on the environment.

Over the last several decades (particularly in Europe and South America), much effort has been made to use renewable bioenergy, which uses biomass (and cellulosic waste), because this type of energy is carbon neutral in its natural life cycle. Carbon dioxide emitted by the use of biofuels is captured by plants and vegetables for their regenerations. Unlike fossil energy industry, bioenergy industry extensively uses aqueous processes (such as hydrothermal liquefaction, anaerobic digestion, hydrolysis, fermentation, aqueous-phase reforming, and supercritical gasification) along with the traditional thermochemical processes used in the fossil energy industry. This book illustrates the extensive use of water as a reactant to generate power and fuels in the bioenergy industry.

The remaining three types of energy industry that are also gaining an additional momentum in the recent years are all carbon-free energy industries and include (1) nuclear energy; (2) solar, wind, geothermal, hydroelectric, and hydrokinetic energies; and (3) hydrogen. These sources of energy do not emit any carbon in the environment. Nuclear energy has been in existence for a while, but its acceptance has been politically hindered because of safety issues. It is projected that its use will moderately grow over the next 30 years. Solar, wind, geothermal, hydroelectric, and hydrokinetic energy sources, which are time and/or location dependent, are renewable and are dependent on the natural elements. While each of these sources of energy will be an industry by itself, renewable nature and carbon-free characteristics unite them.

Hydrogen is the most abundant source of energy on this earth and it is the cleanest and most likely the solution to the energy needs of the world in the long term. Hydrogen economy may dominate "energy economy" in the long term, and it is slowly becoming an industry by itself. Unfortunately, hydrogen is found only in the compound form and its recovery as pure hydrogen requires fossil, biofuel, and water resources. While the generation of hydrogen from fossil and biofuels may cause carbon emissions, the use of hydrogen is carbon free. Water is the most abundant source of hydrogen and the generation of hydrogen from water can be carbon free. In the recent years, significant efforts have been made to recover hydrogen from water by innovative water dissociation technologies, most of which are outlined in this book. The research and development (R&D) in hydrocarbon-based, cellulose-based, carbohydrate-based, nuclear, and carbon-free energy sources will continuously change the future landscape of the energy industry.

Because of our quest to accommodate the growing needs of energy by the developing countries such as China, India, Brazil, Russia, and many African nations as well as to satisfy the need for reduced carbon emission to the environment, the global supply and demand picture will considerably change over the next several decades. ExxonMobil has carried out supply and demand projections for energy and fuels up to 2040 [1]. Similar reports (with somewhat different projections) have also been published by other oil companies (such as BP). Here we briefly summarize some of the important conclusions of the ExxonMobil report (EMR) [1].

- 1. Since 1800, the energy and fuel landscape has been constantly changing as new sources are developed and the old sources either dry up, or become relatively more expensive, less usable, or environmentally more unacceptable. The energy and fuel landscape from 1800 to 2040 has been graphically depicted by the EMR [1]. The best calculations from this graph are presented in Table 1.1. The data show that renewable fuel (biomass) was the sole source of energy in 1800. Over the last more than two centuries, its use has declined significantly because of the discovery of oil, gas, and coal reserves. For nearly a century, our energy production has largely been fossil fuel based. However, the renewable energy will be coming back due to more technological developments and favorable environmental impacts. Within fossil fuels, over the next several decades, the use of natural gas will significantly increase because of the new technological developments and less-favorable environmental impacts by coal. The table indicates that even in 2040, 75% of energy usage will still be provided by oil, gas, and coal and that oil and gas will supply 60% of the total energy demand. The extent of growth in the use of renewable energies (solar, wind, biomass, geothermal, and hydroelectric/hydrokinetic) will be significant. The level of increased percentage contribution by the renewable energies to overall energy consumption will depend on the rate of commercialization of these technologies.
- 2. The growth in energy demand projection during a 50-year (1990–2040) span by several countries is illustrated in Table 1.2 [1]. It is predicted that the growth in energy demand in Organisation for Economic Co-operation and Development (OECD) countries-most of the developed countries of the world-will be very small (around 18.5%), whereas the growth in each non-OECD country (except Russia/Caspian) will be >200%. Overall growth in non-OECD countries will be about 174%. The energy demand in Russia/Caspian region will actually go down during this period. This

Energy Landscape 1800–2040 Calculated from EMR								
Year	Fossil (%)	Nuclear (%)	Renewables (%)					
1800	2	0	98					
1850	10	0	90					
1900	50	0	50					
1950	76	0	24					
2000	82	7	11					
2040	75	9	16					
Source: E	xxonMobil, "The ou	tlook for energy: A view	to 2040," US Edition,					
E	xxonMobil Report, E	xxonMobil, Irving, TX, 2	2012. With permission.					
Note: The	numbers in the table	are approximate calculat	ions from the graphical					

**TABLE 1.1** 

The numbers in the table are approximate calculations from the graphical data reported in the EMR.

	Energy Demand (Quadrillion Btu's) and Growth					
Country	1990	2015	2040	Growth (1990–2040) (%)		
OECD countries	189	225	224	18.5		
Non-OECD countries	171	315	469	174		
China	33	105	138	318		
India	13	35	61	369		
Latin America	15	29	45	200		
Middle East	11	30	51	364		
Africa	17	29	62	265		
Russia/Caspian	57	43	43	-24.6		

### TABLE 1.2 Growth in Energy Demand Projections for OECD and Some Non-OECD Countries (1990-2040)

Source: ExxonMobil, "The outlook for energy: A view to 2040," US Edition, ExxonMobil Report, ExxonMobil, Irving, TX, 2012. With permission.

*Note:* The numbers in this table are best calculations/estimations from the graphical and tabulated data reported in the EMR.

projected growth will be due to (1) an increase in population, particularly in India and Africa, (2) increased demands for electricity in poor countries, and (3) increased industrial and transportation activities because of increased gross domestic product (GDP) and improved quality of life in these countries. Non-OECD countries will largely contribute to the total growth in energy demand in the world.

3. The growth in end-use demand in sectors and regions during the period 1990–2040 along with the growth in the CO<sub>2</sub> emissions is illustrated in Table 1.3 [1]. These results again show that energy demand in each sector (residential/commercial, industrial, and transportation) will significantly go up in non-OECD (except Russia) countries, whereas it will either increase moderately or go down in OECD countries. The energy demand in Russia will go down in every sector. The increased demand in non-OECD countries is for the same reasons outlined above. The largest growth across the world will be in electricity demand. In fact, the report predicts that in 2040, electricity demand will be about 40% of the total energy consumption in the world. OECD countries will focus on energy efficiency and environmental issues. Carbon dioxide emission in OECD countries will go down, whereas this will significantly go up in non-OECD countries. In 2040, 70% of the total CO<sub>2</sub> emission will be generated by non-OECD countries and the three major sources for CO<sub>2</sub> emissions will be industrial, transportation, and electricity [1]. While energy-related CO<sub>2</sub> emission per capita will go down in the United States and Europe, it will go up in India.

### TABLE 1.3 Growth in End-Use Demand and CO<sub>2</sub> Emissions in Sectors and Regions (1990–2040; 50-Year Span)

	Growth (1990–2040) (%)							
Sector								
	NA	Europe	Russia/Caspian	Africa	Asia/Pacific	LA	Middle East	
Residential/ commercial	33.3	17.6	-33	214	90	100	800	
Transport	24	36	-17	350	36	225	266	
Industrial electricity	6.6	-12	-25	183	225	200	300	
Demand	18.2	56	20	800	614	600	500	
CO <sub>2</sub> emission	-7	-27	-41	343	226	186	271	

*Source:* ExxonMobil, "The outlook for energy: A view to 2040," US Edition, ExxonMobil Report, ExxonMobil, Irving, TX, 2012. With permission.

*Note:* The numbers are calculated from the tabulated and graphical data presented in the EMR. LA, Latin America; NA, North America.

Other important changes will also occur in the energy landscape over the next 30 years. More shift from hydrocarbon-based energy to non-hydrocarbon-based energy supply will occur. The use of hydrogen for energy will become more prominent. R&D efforts to produce hydrogen from water and other sources using novel techniques will increase. The efforts to use "solar fuels" will become more prominent. As mentioned earlier, the renewable energy will play a larger role in the energy portfolio. In short, energy economy will become less and less dependent on the hydrocarbon industry. The EMR also gives more details on other factors such as the nature of transportation fuel, the nature of vehicle use, and their energy consumptions [1].

### **1.2 THE THEME AND OUTLINE OF THE BOOK**

While the world is craving for more sources of energy and fuels, one source of energy that is most abundant and environmentally acceptable is water. Water in all its forms (i.e., subcritical, supercritical, steam, heavy water) is the most important solvent in the development of new "energy economy." Four-fifths of the earth's surface is covered with water, which plays a very significant role in the generation of various forms of energy and fuels. The premise of this book is that water is essential not only for human health and environment but also for the development of a broad-based "energy economy."

The central theme of this book is to illustrate that as energy and fuel industries diversify, we are transitioning from predominantly oil- and fossil fuel-based economies to the economy where water plays a more and more important role in the supply of energy and fuels. The book shows that water contributes to the production of

energy and fuels in at least 12 different ways. Each of these methods will become more important as the need for energy and fuels grows and diversifies. The role of water is distinctly different in these 12 methods of water usage for the production of energy and fuel, which is discussed below. Each method is separately described in Chapters 2–13. The content of each chapter is briefly described below.

While the rest of the book is divided into 12 separate chapters based on 12 separate roles of water (in all its forms) in energy and fuel industries, these roles can also be classified in terms of the following five major functions played by the water:

- 1. The benign role of water in the production of raw fuels such as oil, gas, coal, uranium, and biomass as well as the benign role of water as a means for energy carrier in the form of hot water and steam (Chapters 2 and 3).
- 2. Role of steam as a reactant in the conversion of raw fuels to synthetic fuels, which can then be a direct source of energy (Chapter 4).
- 3. Role of water as a reactant, reaction medium, and catalyst in the conversion of raw fuels such as coal, biomass, and waste to useful synthetic fuels. Aqueous water under subcritical conditions can react with various feed-stock thermochemically in the presence of a catalyst or biochemically to produce gaseous, liquid, or solid synthetic fuels (Chapters 5–9).
- 4. Role of supercritical water in the conversion of fossil- and bio-based feedstock to synthetic fuels in the presence and absence of a catalyst. Supercritical water provides an excellent medium for many organic reactions (Chapter 10).
- 5. Water as a direct source of energy and fuels. Hydrogen can be generated by water dissociation. Gas hydrates provide methane from water-based clathrate molecules. Water can also be a direct source of energy when stored in dams (potential energy) or other sources of hydrokinetic energy such as in tidal waves, offshore sea and ocean waves, undercurrents, and inland waterways. In the equator region, power can also be generated using ocean thermal energy conversion technology, which harnesses the temperature difference between the ocean surface and the underwater to drive heat engine (Chapters 11–13).

### 1.2.1 CHAPTER 2: WATER FOR RAW FUEL PRODUCTION

Water plays a very important role in the generation of renewable source of energy, namely bioenergy and biofuels. The growth of all types of plants, vegetables, crops, and trees requires water. The growth of algae, which is one of the richest sources of oil, requires wetlands. Thus, water is a basic necessity for the production of biomass, a raw material for biofuels and bioenergy.

Water, however, also plays a vital role in the recovery of raw fuels such as oil, gas, coal, and uranium. The amount of water required (often denoted as "produced water") to recover raw fuels is so large that the treatment, disposal, and management of produced water has become a rapidly growing industry by itself. Some people consider fossil fuel industry as water industry with oil, gas, coal, and uranium as byproducts. For every barrel of oil produced, six to eight barrels of water is needed

or produced, which may grow to 12 barrels of water as "enhanced oil and gas recovery methods" become more important.

Chapter 2 illustrates the growing importance of water in raw fuel productions by examining the use of water in four specific cases: (1) the role of underground water and produced water in the recovery of oil and gas, and in particular an increased water usage for the recovery of coal bed methane and gas from geopressurized zones; (2) an increased use of water in enhanced oil recovery methods; (3) an important role of water in the newly developed and promising method called "fracking" in the recovery of unconventional gas (shale gas and tight gas); and (4) the use of water in mining, preparation, and extraction of coal, tar sands and heavy oils, uranium, and oil shale. The large expansion of tar sand industry will particularly enhance the use of water.

The four cases examined are the basis of existing and all future growth and diversification of raw fuel industries. While the large use of water for cases 1 and 4 described earlier is already known, it is the expanded use of water for all cases that will increase the importance of water in raw fuel production industries. As the existing oil wells age, the recovery of last remains from the oil wells will require more and more use of enhanced oil recovery methods. These methods use a number of techniques such as surfactant, polymer, alkaline flooding, and steam injection, which involve water or steam. In the case of unconventional oil recovery, pressurized steam is often used. Steam combustion is also used to increase fluidity of trapped oils.

The recoveries of unconventional gas such as shale gas, tight gas, and coal bed methane are the game changers in the natural gas industries.

Water has been used as a material for creating underground fractures in various geological structures to recover unconventional gas. This process is called fracking, and it opens up the tight geological structures by the injection of a high-pressure water in the ground either horizontally or at an angle. The fracking process increases the porosity of the tight geological structures and therefore releases the trapped gas. The pressurized water also contains additives (e.g., surfactants) and other chemicals. New unconventional gas industry will thus use significantly more water than old conventional natural gas industry. Chapter 2 briefly examines these and other relevant issues.

### 1.2.2 CHAPTER 3: WATER AS ENERGY CARRIER

Water also plays a benign but vital role in the recovery of various forms of energy. Chapter 3 illustrates this with four important applications of water and steam to recover energy: (1) nuclear reactor, (2) geothermal sources, (3) solar energy, and (4) thermal energy generated from the combustion of various types of fuels. In each case, water or steam plays a vital role in converting energy and carrying the thermal energy to generate electricity and heat.

Water has always been an effective "energy carrier." For example, in a nuclear reactor, water carries energy generated by the nuclear fission process in the form of steam (thermal energy) to convert it into electrical energy. Water also plays a role of reactor moderator, ensuring safety. More than 80% of current nuclear reactors use water as an energy carrier and/or reactor moderator. New nuclear reactors may use supercritical water as the next generation of reactor coolant and thermal energy carrier.

Water has also been used as a medium to transfer geothermal energy to heat pumps, air conditioners, or electrical devices by carrying geothermal energy in the form of steam for a subsequent energy conversion process. In future, the development of "enhanced geothermal systems" will require water not only as a geothermal energy carrier but also as a fluid required to open up deep compressed geological structures that carry geothermal heat. This dual role of water will make its use larger and more important in the recovery of geothermal energy. New geothermal recovery systems will also use existing underground infrastructure for oil and gas recovery for geothermal energy recovery.

Water can also be an effective "energy storage" device for renewable energy sources such as wind and solar energy that are time and location dependent. The electricity generated from these sources can be stored in the form of hydrogen through water dissociation, and this hydrogen can then be used to generate electricity during "off-time" periods. The stored energy can also be used for "peak energy" needs. While conversion of electrical energy into hydrogen is not the most efficient process, it provides another option for storing electrical energy instead of using conventional power grids, batteries, or capacitors. Unlike these conventional sources, once the electrical energy is stored by hydrogen, it will not dissipate over time. Water can also be used for thermal storage of excess electricity. Solar energy has also been used for heating and cooling homes and industrial buildings through the use of water. Water is once again an important thermal energy carrier for this use of solar energy.

Finally, steam turbine has been an effective device that uses steam to drive turbine which in turn generates electricity. Steam in this process is often produced using combustion heat generated from the burning of coal, oil shale, biomass, waste, and so on. Once again, steam is an effective energy carrier in the combustion processes to generate power. As mentioned earlier, the EMR [1] has predicted that by 2040, nearly 40% of our energy consumption will be in electric power. This expanded use of electricity will require a significant growth in the use of steam turbine. All of these benign roles of water as an energy carrier are briefly examined in Chapter 3.

### 1.2.3 CHAPTER 4: STEAM FOR SYNTHETIC GAS PRODUCTION

While the "steam gasification and reforming" process has been in place since the beginning of the fossil fuel industry, steam gasification and reforming of coal was not as popular and productive as steam reforming of natural gas. In the recent years, steam gasification and reforming of biomass has become more popular and productive for hydrogen generation.

The use of steam to recover gaseous synthetic fuels of different compositions is outlined in Chapter 4. Steam gasification and reforming of carbonaceous fuels (fossil as well as biomass) either alone or in combination with air (or oxygen), carbon dioxide, or hydrogen is a commercially accepted process. Depending on the nature of feedstock and operating conditions, the process generates gaseous fuel largely consisting of methane, carbon monoxide, carbon dioxide, water, and hydrogen. Minor amounts of other volatile hydrocarbons and nitrogen as well as impurities such as sulfur, nitrogen and chlorinated compounds may also be present in the product gases. For fossil fuels such as coal, shale oil, bitumen, tar sand, and crude oil, the gasification by steam alone has not been as effective as gasification by steam with oxygen, carbon dioxide, and hydrogen. The thermodynamics of steam gasification of coal are not very favorable [2]. Generally, such a gasification process predominantly generates pure syngas at temperatures higher than 1000°C–1200°C. The required temperature is, however, lower for biomass and low-rank coals. With excess steam and at high temperatures, the most dominant product is hydrogen with some carbon dioxide.

When steam gasification is carried out in the presence of catalysts, such as alkalis, and Ni-based or other supported noble metal catalysts (e.g., Ru, Rh catalysts), both gasification and reforming occur simultaneously. Along with steam gasification, steam reforming has been used for a long time to generate hydrogen needed for the ammonia and urea productions, petroleum refining, and other hydrogenation reactions producing chemicals. Ammonia is an important raw material for the fertilizer industry. Steam reforming is, to date, the most economical method for hydrogen production. In the recent years, steam reforming has been carried out along with dry reforming and partial oxidation reactions to generate syngas of various hydrogen– carbon monoxide compositions.

Chapter 4 evaluates various aspects of steam gasification and reforming technologies (SGRT) such as (1) the mechanism and kinetics of steam gasification and reforming processes in the presence and absence of other gases, (2) catalysis and reactors for steam gasification and reforming processes, and (3) effects of feedstock and operating conditions on the product distributions. The chapter also examines underground gasification and combustion and multistage processes for steam gasification and reforming. Finally, the effects of water gas shift reaction and simultaneous presence of dry reforming and partial oxidation reactions (i.e., tri-reforming) on the SGRT are also assessed.

In the recent years, novel approaches to steam reforming and gasification such as solar reforming and gasification and microwave-assisted reforming have also been investigated. Since steam reforming is an endothermic process, the use of solar energy for heating makes the process more energy efficient. Chapter 4 examines this and other novel steam gasification and reforming processes.

### 1.2.4 CHAPTER 5: SYNTHETIC FUEL PRODUCTION BY WATER UNDER SUBCRITICAL CONDITIONS

In recent years, the use of water under high-temperature and high-pressure conditions (in subcritical region) to carry out various thermochemical transformations has been increasing due to recognition that the properties of water change significantly with increase in temperature and pressure. These changes allow a number of organic reactions to occur in the aqueous medium. Water becomes nonpolar as temperature increases. Chapter 5 describes in detail this new-found role of water as a reaction medium for transformation of raw fuels such as coal, biomass, waste, and others to produce a variety of gaseous, liquid, and solid synfuels. The chapter first examines the changes in the properties of water as temperature and pressure increase. One of the most important transformations that occur is that water becomes nonpolar at higher temperatures. For example, the properties of water at 370°C are similar to those of acetone at 25°C. This transformation allows many hydrocarbon reactions to occur in the aqueous phase.

It is well known that fossil fuels, such as coal, oil, and gas, are the results of slow geological transformations of biomass waste and human and animal remains buried underground. These transformations have taken millions of years, resulting in fossil fuels such as coal and oil with higher carbon content and lower hydrogen and oxygen content than the original feedstock of biological nature.

Even within coal and oil, there are gradations of properties. For example, the highest ranking (i.e., longest geological age) anthracite coal contains the highest amount of carbon and the lowest amount of hydrogen and oxygen compared to younger coals such as bituminous, subbituminous, and lignite. The youngest lignite coal contains hydrogen/carbon ratio (H/C) and oxygen/carbon ratio (O/C) similar to that of biomass and peat. Just like biomass, lignite coal contains high oxygen concentration and high moisture content. All this is well illustrated by the famous Van Krevelen's plot [2], which shows H/C versus O/C for various types of fossil fuels and biomass. The plot shows that, in general, fossil fuels contain lower hydrogen and oxygen and higher carbon contents compared to those found in the biomass.

The chapter illustrates that the aging and geological transformation of biomass can be accelerated by the hydrothermal conversion processes. High thermal and pressure forces exerted during hydrothermal conversion processes rapidly convert biomass into more coal (hydrochar), oil (biocrude), or syngas similar to natural gas. Biomass is easily transformed to these products in high-temperature and high-pressure water because of strong thermochemical interactions between the biomass and the water.

Hydrothermal carbonization brings solid biomass properties closer to that of coal [3]. The hydrochar produced during this process exhibits properties that are closer to a subbituminous coal. Biomass produces cleaner hydrochar, which is an important raw material in the production of numerous types of gaseous and liquid fuels.

At higher temperatures and pressures under subcritical conditions, biomass can also be converted to oils. This process of hydrothermal liquefaction produces biocrude, which is similar to crude oil, and just like crude oil, it can also be upgraded. Finally, hydrothermal gasification produces methane, hydrogen, or syngas. The hydrothermal carbonization, liquefaction, and upgrading of biocrude as well as hydrothermal gasification processes have been successfully examined in the recent years, and some new commercial processes have been evolved based on these concepts. Chapter 5 briefly illustrates these topics.

The chapter also evaluates the coal–water chemistry in three different areas: (1) the effect of pretreatment of coal by water on coal liquefaction, (2) the liquefaction of coal in high-temperature and high-pressure water, and (3) the use of coal–water slurry in various combustion processes. The low-rank lignite coal is amenable to liquefaction in high-temperature water; however, the liquid product that is generated is of poor quality and requires significant upgrading. Coal–water slurry can be used as a fuel for combustion in boilers, gas turbines, and diesel engines. While the affinity of coal for water is not as pronounced as that of biomass, the chapter

illustrates that coal-water chemistry still needs to be further explored, particularly under high-temperature and high-pressure conditions.

### 1.2.5 CHAPTER 6: PRODUCTION OF SYNTHETIC FUELS BY AQUEOUS-PHASE REFORMING

Along with the hydrothermal conversion of biomass, an aqueous-phase reforming in subcritical water also plays an important role in the production of synfuels from a variety of oxygenated compounds in biomass. An aqueous-phase reforming process carries out selective conversion of sugar-based reactants such as glucose and fructose to hydrogen, syngas, or liquid alkanes and monofunctional groups depending on the nature of catalysts and other operating conditions. These compounds can be subsequently upgraded to liquid fuels using a variety of conventional refining operations.

The use of an aqueous-phase reforming process using a suitable catalyst to generate selective fuel products from various organic compounds is a relatively new and exciting technology. In this process, both catalytic materials and the nature of support are equally important. Chapter 6 gives a detailed and up-to-date account of the use of selective catalysis for the production of a variety of synfuels and/or useful platform chemicals in an aqueous-phase environment.

In the recent years, significant development work has been carried out to produce liquid fuels by upgrading (through a variety of condensation reactions) of monofunctional groups produced by aqueous-phase reforming process. This has led to the development of a "bioforming process" by Virent Inc., Madison, Wisconsin. The process is highly energy efficient and produces selective hydrocarbons that can be useful for specialized jet fuel, diesel, and other transportation fuel materials. The chapter outlines our present state of knowledge of this important and novel use of water chemistry to produce hydrogen and selective liquid transportation fuels.

### **1.2.6** Chapter 7: Production of Synthetic Fuels and Chemicals by Hydrolysis Followed by Selective Catalytic Conversions

Chapter 7 deals with another method of producing liquid fuels, fuel additives, and chemicals from a variety of feedstock using water. The method involves acid hydrolysis of a variety of carbohydrates, cellulose waste, and biomass to produce important platform chemicals such as furfural, levulinic acid (LA), and gamma-valerolactone (GVL). These chemicals can be catalytically upgraded to produce a variety of fuels, fuel additives, and useful chemicals.

The chapter describes the "biofine hydrolysis process," which fractionates lignocellulose into various fractions such as cellulose, hemicellulose, and lignin by hydrolysis and produces six-carbon (glucose) and five-carbon sugars (xylose). Instead of reforming these oxygenated compounds, as described in Chapter 6, five- and six-carbon sugars are catalytically converted to intermediate platform chemicals such as furfuryl and hydroxymethylfurfuryl (HMF) for five-carbon sugars and LA for six-carbon sugars. LA can also be further converted to GVL, another important platform chemical that can also be converted to a number of fuels, fuel additives, and chemicals. Formic acid and ligneous char are produced as byproducts for the biofine hydrolysis process. The chapter shows how different types of fuels, fuel additives, and chemicals for various industrial applications can be made using different upgrading strategies for the platform chemicals. The process can handle a variety of feedstock and is proven to be economical. A small commercial plant for this process is already in operation in Italy and larger commercial plants are being pursued in Ireland, the United Kingdom, and the United States.

### 1.2.7 CHAPTER 8: PRODUCTION OF HYDROGEN AND METHANE BY ANAEROBIC DIGESTION OF AQUEOUS WASTE

Aqueous-phase conditions are well known for carrying out biological reactions. An anaerobic digestion of aqueous agricultural and other biological waste can produce methane and hydrogen using suitable enzymes or consortia of microorganisms. Water can thus biochemically react with biomass to generate methane and hydrogen. Such reactions generate "landfill gas" (which is predominantly methane [about 55%] and carbon dioxide) from cellulosic waste. Landfill gas is an important raw material for power generation or for the production of other gaseous and liquid fuels via reforming and Fischer–Tropsch (FT) technologies.

Chapter 8 deals with the production of methane and hydrogen by biochemical anaerobic digestion of biomass and waste in aqueous environment. The chapter illustrates biochemical mechanisms to convert cellulosic waste into methane and hydrogen. Although landfill gas is a prime example of such conversion, the aqueous waste from numerous other types of waste such as animal and human manure, agricultural waste, forestry, and plant waste can also be converted to methane and hydrogen (commonly known as "biogas"). Anaerobic digestion of biological waste is one of the most energy-efficient and fastest growing industries in the world. The chapter examines various operational issues related to this industry.

### 1.2.8 CHAPTER 9: PRODUCTION OF ETHANOL BY AQUEOUS-PHASE FERMENTATION

The biochemical conversion of sugar, glucose, fructose, and so on to ethanol and other alcohols has been a long-standing industry. Although the fermentation process has been used for the production of beers, liquors, and so on, its application for the transportation fuels and their additives has become more important in the recent years because of an increased emphasis on renewable energy.

Fuel-grade ethanol can be produced from corn, starch, barley, or sugarcane by hydrolysis and fermentation processes. This has been commercialized for a long time. In the recent years, more emphasis has been placed on the conversion of lignocellulosic materials to ethanol by hydrolysis and fermentation processes. Recent research on new methods of pretreatments, acid and enzyme hydrolysis, and discovery of new microorganisms for fermentation has allowed this biological process to be applied to a broad range of lignocellulosic materials. New developments have also led to the production of higher alcohols such as butanol, which has a higher fuel value. Chapter 9 briefly examines our current state of art for these technologies and processes.

The future development of alcohol production from lignocellulosic materials will continue to require better methods of pretreatment, hydrolysis, and fermentation.

New microorganisms and enzymes will have to be developed to make these processes more efficient and economical. The fermentation process can generate specific types of products and will require basic understanding of the applications of genomics and proteomics to different types of lignocellulosic materials.

### 1.2.9 CHAPTER 10: PRODUCTION OF SYNTHETIC FUELS BY SUPERCRITICAL WATER

Water under supercritical conditions behaves very differently than at room temperature. Water has high solubility for many organic and cellulosic compounds under these conditions. The density, viscosity, and other properties facilitate the conversion of a variety of feedstock to fuels such as hydrogen, methane, and syngas. Since the pioneering work of Modell at Massachusetts Institute of Technology (MIT), this technology has made enormous progress and now many pilot-scale operations for the application of this technology to generate synfuels have become a reality.

In recent years, the interest in the use of supercritical water for the production of fuels and chemicals has been rapidly expanding. As mentioned earlier, the main reason is that the unique properties of supercritical water allow a variety of organic reactions to be carried out in the supercritical phase. In these reactions, water not only plays a benign role of solvent but also plays a role as an active reactant or a catalyst. Properties of water under supercritical conditions ensure that important organic reactions can be carried out in a homogeneous medium.

Supercritical water can play five different functions: (1) a medium in which numerous types of organic chemical synthesis occur, (2) a medium for partial or complete oxidation of numerous hazardous or nonhazardous materials, (3) a medium in which complex materials decompose and produce liquids and gases, (4) a medium for thermal or catalytic gasification of simple and complex materials to produce fuels such as methane and hydrogen, and (5) a medium to generate hydrogen by catalytic gasification and reforming of various carbonaceous materials. Chapter 10 outlines the role of supercritical water in each of these functions with a special emphasis on the functions that generate synthetic fuels.

Collectively, Chapters 4–10 illustrate various thermochemical, catalytic, and biotechnological options to convert coal, biomass, waste, and their mixtures to a variety of synthetic gaseous, liquid, and solid fuels. In all of these cases, water provides an important role of a reaction medium, a reactant, or a catalyst.

### 1.2.10 CHAPTER 11: PRODUCTION OF HYDROGEN BY WATER DISSOCIATION

Water can also be a direct source of fuel. Hydrogen can be generated from water by its dissociation. Hydrogen is the cleanest form of energy and may be the only long-term solution to our energy needs.

Chapter 11 examines three basic methods to dissociate water to produce hydrogen: electrolysis, photocatalytic or photobiological dissociation, and thermal or thermochemical dissociation. Various ramifications of each of these methods are also briefly examined. The chapter also briefly assesses other novel methods for the production of hydrogen from water.
One of the major issues with all these technologies for water dissociation is the low conversion efficiency. Various modifications of electrolysis, photocatalysis, and thermochemical methods have been tested in the literature. These are briefly assessed in the chapter as well. The use of solar and nuclear energy to dissociate water has also been extensively examined in the literature. These technologies are also surveyed in the chapter. A significant breakthrough in water dissociation technology can significantly change the energy landscape and push us more close to the hydrogen economy.

#### 1.2.11 CHAPTER 12: PRODUCTION OF METHANE FROM GAS HYDRATES

Chapter 12 deals with another direct source of fuel from water, that is, gas hydrates. Methane gas hydrates are naturally occurring methane trapped in water. These gas hydrates are unique substances that are found at the bottom of the sea and in arctic conditions such as in Alaska and Siberia. These naturally occurring hydrates require right temperature and pressure conditions for their stable formation. While hydrates are in general unstable, highly dispersed, and difficult to recover, there is more carbon in methane gas hydrates than in all other fossil fuels combined.

Gas hydrates are of great importance for a number of reasons. Naturally occurring methane gas clathrates contain enormous amounts of strategic energy reserve. In offshore hydrocarbon drilling and production operations, gas hydrates cause major and potentially hazardous flow assurance problems. Gas hydrates also pose potential danger to deep water drilling installations, pipelines, and subsea cables. The recovery of gas hydrates by carbon dioxide provides an opportunity to dispose carbon dioxide by sequestration. Gas hydrates also provide an increasing awareness of the relationship between hydrates and subsea slope stability. Finally, it creates long-term considerations with respect to hydrate stability, methane release, and global climate change. Some of these topics along with numerous methods for the recovery are briefly discussed in Chapter 12.

## 1.2.12 CHAPTER 13: WATER AS A DIRECT SOURCE OF ENERGY

Water is also a direct source for energy and power. This is accomplished by three different methods: hydroelectricity, hydrokinetic energy, and ocean thermal energy conversion.

The generation of power (hydroelectricity) with the potential energy from waterfalls using dams has been long known, and many dams across the world generate a significant amount of electricity from waterfalls. This is one of the cleanest sources of power and is practiced globally. The industry can be broken into large, small, mini-, micro-, and pico-plants depending on the level of the electricity generation. The use of this technology is continuing to grow all over the world.

More recently, more efforts have been made to harness the kinetic energy of the moving water in rivers, seas, and oceans. This method captures energy from sea and ocean waves and undercurrents, tidal waves, and inland waterways. New modern technologies are introduced that can generate hydrokinetic power using devices that can handle high-amplitude waves and fast currents. The chapter examines these

different technologies and their progress in the commercialization. The method is applicable globally and is gaining rapid acceptance.

The third method, ocean thermal energy conversion, is only applicable within  $20^{\circ}$  of the equator. In this method, the temperature difference (about  $20^{\circ}C-25^{\circ}C$ ) between the surface of ocean and the underwater is used to drive a heat engine, which in turn drives turbine to generate electricity. Although the economics of this method are not as favorable as the previous two methods, it has a number of side benefits in its use for desalination, aquaculture, seafood, hydrogen production, and other industries.

Chapter 13 examines our current state of art in all three methods. It is clear that a strong and growing global demand for energy and fuel will require technological developments for all sources of energy. New developments must be economical, usable, and environmentally acceptable. The energy and fuel landscape may change rapidly depending on the success of the new technology developments.

The 12 chapters outlined here demonstrate an important role of water in the development of future energy landscape. The chapters not only illustrate the versatility of water and its role as a solvent, energy carrier, reactant, catalyst, and a direct source of fuel and energy, but also show how water can help the growth of energy and fuel industry with a least environmental impact. As the production of energy and fuel diversifies, water will continue to play an increasingly important role in the new energy economy.

## 1.3 WATER-BASED REFINERY AND WATER MANAGEMENT FOR THE FUTURE

Besides numerous roles of water outlined in this book, the concept of water-based refinery may also be not unreal. The refinery, by definition, refines the crude feed-stock into useful fuels (or fuel additives) and chemicals. Over many decades, petro-leum refineries have converted crude oil of different compositions into various kinds of fuels and chemicals that meet the required industry standards. Analogous to petroleum refineries, coal conversion plants have also converted coal into useful gaseous and liquid fuels. The conversion of natural gas into syngas has also been a part of many refineries.

Unlike petroleum refineries for fossil fuel, biorefineries will be more versatile in that while parts of biorefinery can be integrated with the existing oil refineries, other parts will require more water-based processes. For example, gasification of biomass and conversion of biosyngas to liquid fuels can be integrated with the existing coal gasification and conventional FT process. Similarly, steam gasification and reforming of biomass would be similar to steam gasification of coal and reforming of gasification products. However, five other major technologies outlined in this book hydrothermal conversions under sub- and supercritical conditions, bioreforming and biofine processes and water dissociation technologies—are largely water based and the use of these technologies will require water-based refining processes. The use of water to obtain the hydrogen required for the refining operations will become more important as water dissociation technologies advance. The five technologies mentioned earlier and discussed in detail in this book show that a water-based refinery will be capable of generating all kinds of gaseous and liquid synfuels from biomass that is currently produced from fossil fuel in oil-based refinery.

Besides coal, oil, gas, and biomass, an important raw material for future energy and fuel industry is waste. The United States generates about 250 million tons of waste per year. The worldwide waste production will exceed 1 billion tons per year during this decade. Since it is also connected to the growth in world population, waste production is one of the fastest growing industries. The landfills around the world are full, and the new paradigm is that landfills are only temporary storage places for the waste and waste to energy and products should be more actively pursued. Since most waste contains between 50% and 85% cellulose, its conversion using water-based processes will become more important.

The future energy industry will also call for refineries that can process multiple feedstock, if possible. The use of mixed feedstock (such as coal and biomass, coal, and waste) may be the new reality of the future because of (1) the location- and time-dependent availability of various raw materials, (2) the desire to reduce carbon emission in the atmosphere, and (3) the cost reduction of building targeted refinery based on the feedstock. Some of the technologies such as gasification followed by gas-to-liquid conversion and supercritical water processing may handle such mixtures.

The expanded use of water for energy and fuel production leads to another societal issue that will have to be managed. Clean water is essential for human and animal life. The expanded use of water for energy and fuel production may create a problem for the available amount of drinkable water for human and animal needs and useable water for agricultural needs. Just as there are tensions between the use of food materials such as corn, soybeans, maize, and other carbohydrates for fuels (such as ethanol), tensions will also be created for the use of water for energy and fuel production and the need of clean water for human and animal needs as well as for agricultural purposes. The strategic management of water will be the next important societal issue. The treatment of water used in energy and fuel industries will become an independent industry by itself. This industry will have to manage the overall societal need for the water to maintain the required strategic distribution of water among its different usages. Along with energy and fuel, a prudent use of water will be the next societal challenge.

Water, however, will be the centerpiece of future energy and fuel landscape.

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# 2 Role of Water in Recovery and Production of Raw Fuels

#### 2.1 INTRODUCTION

We know that all biological products require water to survive and grow. Thus, bioenergy coming from different types of biomass requires the supply of water. Even the most oil-storing species such as algae requires wetland environment. This chapter, however, shows that water plays a very important role in the recovery and production of various types of fossil fuels and uranium (for nuclear energy). Water will continue to play an increasingly important role in the recovery and production of raw fuels such as conventional and unconventional gas and oils, and solid fuels such as coal, oil shale, tar sands, and uranium. In fact, the role of water in these processes is so important that the production, use, treatment, recycling, and management of water associated with the recovery of fossil fuels is becoming one of the fastest growing independent industries. This chapter illustrates the fact that the use of water and steam is not only essential for the recovery and production of various types of fossil fuels and uranium, but it will significantly increase over the next several decades [1].

There are those who say that fossil energy industry is effectively water industry with oil, gas, and coal as byproducts. This may be particularly true for oil and gas that generally reside with water in underground reservoirs. In North American onshore oil industry, eight barrels (bbl) of water are brought to surface for every bbl of oil. This produced water is often highly saline and contaminated by hydrocarbons: It is hazardous and requires treatment, disposal, and potential recycling. Handling this produced water is an integral part of the oil and gas industries.

In a recent global water intelligence report, the projected growth rate of the produced water from oil and gas industries was illustrated [2]. These produced volume of water forecast data are summarized in Table 2.1 [2]. The data shown in this table indicate that the produced water for oil and gas industries will grow from present 25 billion bbl per year to about 35 billion bbl per year by 2025. The largest growth in produced water will be due to the growth in unconventional gas and oil recoveries and more use of enhanced oil recovery (EOR) methods for the recovery of conventional gas and oil.

The growth in produced water volume will accompany an increase in produced water market activity. The report projects that the dollar value of the produced water market will grow from \$5 billion in 2010 to \$9.9 billion in 2025—nearly 100%

#### **TABLE 2.1**

## Produced Volume of Water and Percentage Increase (since 2007) Forecast in Oil and Gas Industries over the Next 15 Years

Year	Coal Bed Methane/Shale Gas	Oil Sand	On/Offshore	All Other Gas	Total
2007	4.5	2.8	14.5	2.8	24.6
2010	4.5 (0%)	2.8 (0%)	14.9 (2.8%)	2.8 (0%)	25.0 (1.6%)
2015	4.7 (4.4%)	3.2 (14.3%)	16.7 (15.2%)	2.9 (3.6%)	27.5 (11.8%)
2020	4.9 (8.9%)	4.5 (60.7%)	18.4 (26.9%)	3.0 (7.1%)	30.8 (25.2%)
2025 <sup>a</sup>	5.0 (11.1%)	5.5 (96.4%)	21.5 (48.3%)	3.0 (7.1%)	35.0 (42.3%)

Source: Global Water Intelligence, 12, 2-8, 2011. With permission.

Note: All numbers are in billion gallons of water per year.

<sup>a</sup> By 2025, the total increase in produced water will be more than 10 billion gallons per year.

growth in 15 years. The dollar value of the produced water equipment market will grow from \$693 million in 2010 to \$2.9 billion in 2025 [2]. This growth will accompany a significant growth in various water purification technologies.

While the use of water is essential for recovery of fossil fuels and uranium, the chapter illustrates at least four reasons why this usage will grow significantly (Table 2.1) over the next several decades. These four reasons are as follows:

- 1. The increased use of water for the recovery of unconventional gas such as coal bed methane, deep gas, and gas trapped in geopressurized zones. Water plays an important role in the underground storage of conventional oil as well as methane in coal bed. The removal of water from coal beds to release trapped methane will become more and more important. The water produced from this unconventional gas recovery will be more than that required for conventional gas capture [3–12]. Future growth in gas industry significantly depends on the recovery of these forms of gases. The chapter will briefly illustrate why more water will be required and produced to recover these gases.
- 2. More use of EOR methods to recover conventional and unconventional oils. The EOR methods (also often called tertiary oil recovery methods) heavily use water and steam. The thermal recovery methods such as steam flooding, cyclic steam stimulation, and *in situ* combustion, and the water flooding methods that include chemical flooding such as polymer flooding, micellar–polymer flooding, and alkaline flooding as well as microbial flooding and cyclic microbial recovery all use water. These methods have been very successfully applied to improve oil recovery efficiency of both conventional and unconventional oils. In future, the water-to-oil ratio in the EOR processes will further increase due to aging oil wells and expansion of more difficult recovery processes for unconventional oils [13–17]. By 2025, this ratio is likely to reach 12 bbl of water per each bbl of oil from the current number of eight.

3. The new "fracking" technique to recover unconventional shale gas will require a significantly large use of water. In recent years, the recoveries of shale and tight gases have revolutionized the gas industry. Shale deposits were formed about 350 million years ago. Shale is a very fine-grained sedimentary rock, which is easily breakable into thin parallel layers. It is a very soft rock, but it is impermeable to water in its natural state. The shales can contain natural gas usually when two thick black shale deposits "sandwich" a thinner area of shale. Due to the nonporous and impermeable properties of these shales, the extraction of natural gas from shale formation is more difficult.

Similarly, the "tight gas" is a gas that is stuck in a very tight and unusually impermeable hard rock or in a sandstone or limestone formation that is unusually impermeable and nonporous (tight sand). Unlike extracting conventional natural gas, a significant more effort has to be put into extracting gas from a tight formation. Recently, both shale and tight gases have been successfully recovered using a new technique of fracking, by which impermeable rocks in both cases are fractured using a horizontal or directional drilling technique, which uses high-pressure water solutions (with many chemical additives) to fracture impermeable and tight shale or sand matrix. The dramatic expansion of shale gas industry will require water (with chemicals) as "fracking fluid" to fracture impermeable shale rocks. Additional water will also be required to capture tight gas by the "fracking process" [18–37]. A significant increase in water requirement for this process may cause local conflicts due to competing needs for water. We will briefly discuss the role of water in this successful but somewhat controversial process.

4. Additional water will be required for the recovery of solid fuels such as coal, oil shale, tar sand, and uranium as these sources become harder to recover due to their locations and recovery methods. Both surface mining and deep mining are used in the recovery process. The extraction processes can be carried out outside the mine or *in situ*. A significant amount of water is used for these processes and water is essential for recovery and treatment of these fuels [38–42]. The use of water in the recovery of tar sands will grow very rapidly as more and more tar sands are discovered deeper into the ground and at a lower concentration in the sand.

## 2.2 INCREASED WATER USAGE FOR RECOVERY OF COAL BED METHANE AND GAS FROM GEOPRESSURIZED ZONES

Recovery of methane from coal beds is an attractive prospect for development because of the ability of coal bed to retain a large amount of methane gas; coal is able to store six to seven times more gas than an equivalent volume of rock common to conventional gas reservoirs. In most regions of the United States, coal bed methane wells produce between 100 and 500 thousand cubic feet of methane per day. The amount of methane in a coal deposit depends on the quality and depth of deposit. In general, the higher the energy value of the coal and the deeper the coal bed, the more methane in the deposit [3–12]. Like the United States, the extraction of coal bed methane is gaining a significant momentum in Canada as well [8]. In principle,

coal bed methane will be very important for all parts of the world where significant coal deposits are found.

In coal bed methane, the gas is trapped along with water in the porous coal bed. The pressure of water keeps methane loosely attached to coal and therefore preserves methane in coal deposits. The water pressure also allows bacterial actions between microorganisms in the water and coal to continue to generate new methane. The water needs to be released to allow methane to escape the coal bed. When the water is removed from the coal bed by pumping, the gas pressure is decreased and this allows methane to detach from coal and flow up to the gas well. As shown in Figure 2.1 [5,9], in the initial production stage of methane from the coal bed, the well mostly produces water. Once the water is nearly removed, the production of gas increases. Depending on the geological conditions, it may take several years to achieve a full-scale gas production. Generally, the well with the deeper coal bed produces gas with a short initial time lag due to the presence of less water. In general, the water produced from the coal bed is much higher than that obtained from conventional wells [6,7,12].

Coal bed methane wells are drilled using techniques similar to those used for conventional wells (Figure 2.2) [42]. When coal beds are shallow, less expensive modified water well drilling rigs can be used. In general, however, hydraulic fracturing (or fracking) is used as a primary means of stimulating gas flow in coal bed methane wells. The gas can also be stimulated using a cavitation technique [5,6,11,12]. In this technique, pressure in the reservoir is increased by the injection of water and air (or foam) into the well. The pressure is then suddenly released and this causes a violent blowout of gas, water, coal, and rock fragments from the well. This "surging action" can be repeated several times leaving larger holes and more fractures within coal seams, which in turn causes a faster rate of gas release. The quality of the produced water in both hydraulic fracturing and cavitation techniques mainly depends on the geology of the coal formation. Typically, saltier water is produced



**FIGURE 2.1** (See color insert.) Typical production curve for a coal bed methane well showing relative methane and water production. (Adapted from Rice, D., "Coal bed methane— An untapped energy resource and environment concern," US Geological Survey, Energy Resource Surveys Program, USGS Fact Sheet FS-019-97, 1997.)



**FIGURE 2.2** (See color insert.) Simplified illustration of a coal bed methane production well. (From Huth, E., Sule, M., Todman, L., Brant, J., and Templeton, M., "Treatment and reuse of coalbed methane produced water using pervaporation irrigation," 22nd Annual Produced Water Society Conference, January 17–19, 2012. With permission.)

from deeper coal formations. The produced water may contain nitrate, nitrite, chlorides, other salts, benzene, toluene, ethyl benzene, other minerals, metals, and high levels of the total dissolved solids [6,12]. The method of disposal of the produced water depends on (1) the quality of water and (2) the geographical location of the coal bed. Sometimes, the produced water can be an important source for (1) drinking water or (2) water used for the irrigation purposes [6].

Unlike in coal bed methane, in geopressurized zones, confinement of water causes thermal built-up partly because the rate of upward movement of water is not great enough to carry away geothermal heat added to the system and partly because water has a high-specific heat and a low thermal conductivity [6,11]. This thermal built-up further increases the pressure in the geopressurized zones. Water salinity is also increased with depth in the sand bed aquifers within geopressurized zones.

Geopressurized zones are underground natural formations that are at unusually high pressures for their depth. These zones are formed by the deposition of clays over more porous sand or silt and the gradual compaction of these clays over years. This compaction squeezes water and gas out of clay into more porous sand or silt. The gas in the sand under so-called geopressure is usually found at the depth of 10,000–25,000 ft. Thus, it carries some similarity with "deep gas" [6,7,11]. A combination of high depth and high pressure makes the extraction of gas from such zones very difficult. However, of all unconventional gas resources, geopressurized zones are mostly found in the Gulf Coast region. It is estimated that the amount of natural gas in the geopressurized zones can be anywhere between 5,000 and 49,000 Tcf. This presents an incredible opportunity because at present the total technically recoverable gas resource is about 1100 Tcf (see the National Energy Technology Laboratory [NETL] website for unconventional gas).

Gas in the geopressurized zones is usually dissolved in hot brine solution (about  $150^{\circ}\text{C}-200^{\circ}\text{C}$ ) under pressure. The high pressure makes gas recovery easy when the gas is tapped from these zones. However, this gas is accompanied by water that will have to be removed. The geopressurized zones contain three types of energy: (1) the unconventional gas reserve, (2) the high-pressurized fluids that can impart mechanical energy, and (3) the hot brine solution that may provide geothermal energy. The recovery of these energy resources will require high investment costs and large amount of water production, treatment, and usages [6,11,12] (see the NETL website).

#### 2.3 ENHANCED OIL RECOVERY (EOR) PROCESS

EOR is defined as the incremental ultimate oil that can be economically recovered from a petroleum reservoir over oil that can be recovered from the same reservoir by conventional primary and secondary methods. The intent of EOR is to increase the effectiveness of oil removal from the pores of the rock (displacement efficiency) and to increase the volume of the rock contacted by injected fluids (sweep efficiency) [16,17]. The oil remaining after conventional recovery operations is retained in the pore space of reservoir rock at a lower concentration than originally existed. This residual oil is found as either droplets trapped in the individual pores or cluster of pores or films partly coating the pore walls. Entrapment of this residual oil is predominantly due to capillary and surface forces as well as due to pore geometry.

Bypassing of oil in the reservoir occurs due to a number of reasons: (1) nonhomogeneity of the reservoir rock causing inefficient sweeping by the displacement fluids; (2) simultaneous effects of viscous, gravity, and capillary forces; and (3) high mobility of displacing fluid compared to that of oil. The net effect depends on the conditions at individual locations. In general, gravity forces cause vertical segregation of the fluids and water tends to underrun the oil-containing rock [16,17].

The recovery of conventional oil from a reservoir requires pressure gradient to push oil out from the reservoir to the surface. Initially, gas and water that accompany oil provide this pressure, and because of that as indicated earlier, when oil comes out of the ground, a significant amount of water (eight bbl of water per each bbl of oil) accompanies it. Initially, this process may be facilitated by pumping the fluid out of the ground by a pump. This is generally known as primary oil recovery process. This process generally recovers only 5%–15% of the oil from a well. Secondary oil recovery process, often involving pumping water down (water flooding) the well to maintain pressure on the oil, may increase the recovery to 30%. EOR techniques can increase the proportion of the oil brought to the surface to 60%. When the well is aged, the recovery of the remaining oil particularly requires the implementation of EOR techniques [16,17].

Fundamentally, three types of EOR processes are currently being used: (1) miscible displacement processes that use miscible hydrocarbons, carbon dioxide, or inert gas; (2) chemical processes that use surfactant polymer, polymer, or caustic solutions in water; or (3) thermal processes that use steam stimulation, steam flooding, hot water injection, or *in situ* combustion. In this chapter, we focus on the latter two processes because they use water or steam. Various methods used for EOR processes are described in two excellent books and numerous articles by Speight [16,17]. The present description closely follows his work along with other works reported in few additional publications [13–15].

#### 2.3.1 CHEMICAL PROCESSES

In general, due to their high cost, complex technology, and high risk, chemical flood processes account for <1% of the total tertiary recovery. The successful chemical processes for oil recovery require floodwater of precise salinity. Fundamentally, three types of chemical solutions—surfactant–polymer solution, polymer solution, and caustic alkaline solution—are used. Here we briefly describe the effectiveness of each of these processes.

#### 2.3.1.1 Surfactant–Polymer Solution (Microemulsion Flooding)

The injection of surfactant-polymer solution is a two-step process [16,17]. The first step is the injection of a surfactant slug commonly referred as either micellar solution or microemulsion. The purpose of the surfactant is to displace oil that cannot be displaced by water alone. The second step is the injection of polymer mobility buffer. The polymer provides mobility control for a more piston-like displacement.

In microemulsion flooding process, a stable solution of oil, water, electrolytes of salts, and one or more surfactants are injected into the formation that is then displaced by mobility buffer solution, which in turn is displaced by injection of water. Two approaches can be used in microemulsion flooding. In one approach, a relatively low-concentration (2–4 wt%) surfactant microemulsion is injected in large pore volumes of 15%-60%. In the second approach, a high-concentration (8–12 wt%) surfactant microemulsion is injected in a relatively small pore volume from 3% to 20%. As the time passes, the second approach merges with the first approach due to the dilution effect. Mobility control is important in the success of this process [16,17].

Microemulsion technique can be applied over a wide range of operating conditions. In microemulsion flooding, the slug must be designed for specific reservoir conditions of temperature, resident water salinity, and crude oil type. The success of the microemulsion–polymer flooding in a given reservoir depends on the proper assessment of the characteristics such as the nature of oil and water content, relative permeability, mobility ratios, formation fractures and variations in permeability, porosity, formation continuity, and rock mineralogy [16,17].

## 2.3.1.2 Polymer Solution

The addition of polymers in water increases the solution viscosity, thereby increasing the sweep efficiency. Two classes of polymers are normally used: polyacrylamides (PACs) and polysaccharides (PSAs). PAC (normally used in 50–1000 ppm concentration) decreases the mobility of the injected fluid by decreasing the permeability of the reservoir rock. Addition of PSA, however, increases the viscosity with a very low level of permeability reduction in the reservoir rock. The high viscosity of both solutions compared to water results in a significant long-range oil production.

Polymer flooding is most effective for heterogeneous reservoirs because they respond favorably to the improved vertical sweep efficiency. This technique is also preferred over microemulsion flooding for recovery of more viscous oils. Currently, polymer flooding is being used in a significant number of commercial field projects [16,17].

The injection of polymer solutions may face stability problems due to oxygen contamination. For PAC solutions, this may be alleviated using sodium hydrosulfite in low concentrations. In general, the degradation of polymer due to mechanical, chemical, thermal, and microbial reasons can be totally prevented by using specialized equipment or techniques [16,17].

## 2.3.1.3 Caustic Alkaline Solution

This method is inexpensive and preferred, but it provides low productivity. In this method, inorganic alkaline chemicals such as sodium hydroxide, sodium carbonate, or sodium orthosilicate are added to the water to enhance oil recovery by one or more of the following mechanisms: (1) interfacial tension reduction, (2) spontaneous emulsification, or (3) wettability alteration. For an efficient oil recovery, the pH range 12–13 is optimum. Sometimes the mobility ratio can be improved by an addition of polymer in the alkaline solution [16,17].

## 2.3.2 THERMAL PROCESSES

Thermal EOR processes are very popular and gaining more use due to the fact that they can be applied to both conventional and unconventional oil recovery. Three types of thermal processes are currently used: steam stimulation, hot water injection, and *in situ* combustion. We briefly examine each of these processes in Sections 2.3.2.1–2.3.2.3.

## 2.3.2.1 Steam Stimulation

Steam stimulation is a general term used when steam is injected into a well and then produced back out of the same well. The method is also referred as cyclic steam injection, steam soak, or huff and puff. The process uses up to 1000 bbl of water per day (in the form of superheated steam) for 10–30 days and then the well is shut in for about 1–4 weeks to allow the steam to soak in the well [16,17]. During this soaking period, heat dissipates into the reservoir and reduces the viscosity of oil

and expands the volume of oil causing fluid movement. This action facilitates oil recovery from the reservoir. The well begins its production level after the soaking period until the flow of oil slows down. Once this occurs, the process is repeated. After much of oil is recovered, cyclic steam flood is converted to steam injection. In this process, steam is injected from one well and the oil is recovered from other nearby wells [16,17].

Steam flood in some reservoirs results in a dramatic increase in oil production. This method which accounts for about 20% of EOR processes, has gained more popularity in recovery of unconventional oils such as heavy oils, tar sands, and shale oil [16,17]. The technique works well because of the crude oil expansion due to increased temperature, which continues as pressure drops. Steam flood wells are drilled on an ~5-acre spacing and require a reservoir depth of ~10 ft or more. The method is most effective in wells no deeper than 5000 ft.

#### 2.3.2.2 Hot Water Injection

Besides steam injection, hot water injection is often pursued. This method is, however, not as effective because of heat loss and resulting fingering phenomenon and loss of sweep efficiency [16,17].

#### 2.3.2.3 In Situ Combustion

*In situ* combustion can be dry (only using air) or wet or partially wet. In this process, fire is ignited by injecting compressed air into the injection wells and driven across the reservoir. The heat from fire reduces oil viscosity leading to drop in pressure and expansion of oil. The vapor can also be collected from the well and condensed at the well mouth. The process is not very efficient because a large amount of heat is not utilized.

The *in situ* combustion can be forward combustion or reverse combustion. In the forward combustion process, fire is ignited in the formation near the injection well, and with continuing air injection, the fire and produced oil are driven toward nearby producing wells. In the reverse combustion process, the fire is started near the compressed air injection well and allowed it to progress toward nearby wells. The process is then reversed; the air is injected from nearby wells and the original air injection well is used to collect the oil that is produced. The reverse combustion is often considered to be more efficient than the forward combustion. The combustion processes is more effective for heavy crude oil. In wet and partially wet injection processes, steam accompanies air [16,17].

As the existing oil well ages and new oil wells are discovered in more difficult locations, the use of EOR techniques to recover oils will significantly increase in future. This will require an additional usage of water or steam.

## 2.4 ROLE OF WATER IN THE FRACKING PROCESS

The natural gas can occur in the oil fields (known as associated gas), in coal seams (known as coal bed methane), in sandstone (tight and deep gas) or shale (shale gas), or in the fields not associated with oil or coal (i.e., nonassociated gas). The gas is also found in geopressurized zones. The most important game changer in recent years is shale gas largely due to the novel but controversial process of fracking [18–36].

The drilling and hydraulic fracturing of horizontal gas wells on average requires 3.5 million gallons of water. This water generally comes from surface water bodies or from groundwater, private water sources, municipal water, and reused produced water. Water, however, plays a very significant role in recovering unconventional gas such as deep gas, tight gas, gas from geopressurized zones, shale gas, and coal bed methane. Section 2.2 showed the increased usage of water for recovery of coal bed methane and the gas from geopressurized zones. In this section, we briefly discuss the additional usage of water required to recover shale gas and tight gas using the fracking process. This hydraulic fracturing process to release trapped gas in tight and nonporous geological matrix requires a substantial amount of water and chemical additives.

The recovery of shale gas and tight gas uses horizontal drilling and hydraulic fracturing (i.e., fracking). Over the next 25 years, the unconventional gas production will increase from 15% of the total current production to about 77% of the total gas production. Unconventional natural gas reserves are located at varying depths below the ground. In Texas' Barnett and Haynesville/Bossier plays, for example, the natural gas-producing areas are 1,000–12,000 ft below the ground. In Michigan and Illinois, natural gas-producing areas are much shallower ranging from hundreds of feet to 2000 ft below the ground. All of these reservoirs now use horizontal drilling and fracking process [17,29,35,36].

The drilling and hydraulic fracturing of a horizontal shale gas well uses large volumes of water. The EPA reports [30,31,34] that fracturing shale gas wells requires between 2.3 and 3.8 million gallons of water per well. An additional 40,000 to 1 million gallons of water is required to drill the well. This is considerably more water than is required for conventional gas because the wells to access shale gas and tight gas are deeper. The data [26,33,35] show that for shale gas in Marcellus region, 4.5 million gallons of water per well is required. Water requirements within Texas Eagle Ford shale area can be even greater where the fracking process can use up to 13 million gallons of water per well with additional water requirement for drilling the wells [17,18,22,36]. Within the state of Texas, the water requirement does depend on shale plays; for example, water requirement in Barnett shale play can range from 1 to 8 million gallons of water per well; in Haynesville and Bossier shale play, it can range from 1 to 10 million gallons per well; and in Woodford, Pearsall, and Barnett-PB shale plays, it can be as low as 1–5 million gallons per well [17–19,22,36].

The water used in the fracking process also contains some harmful chemicals such as acids, scale inhibitors, iron control agents, surfactants, friction reducing agents, corrosion inhibitors, gelling agents, and bactericide/biocide compounds. Once the fracking process is complete, the fracking fluid is withdrawn from the well, but this withdrawal rate can be as low as 20% of the injection rate. The remaining fluid can have a harmful effect on the underground water aquifers [20–22,24,30–32] due to its chemical contents. The water withdrawn from the well is accumulated in the surface pond and treated before it is reused or reinjected in the well. The fracking process not only requires a large amount of water but also creates a number of water-related issues such as (1) water withdrawals, (2) groundwater contamination associated with well drilling and production, (3) waste water management, (4) surface spills and

leaks, and (5) stormwater management. Water supply, purification, treatment, and management are very important and essential parts of the fastest growing shale gas industry.

## 2.5 WATER REQUIREMENT FOR MINING, PREPARATION, AND EXTRACTION OF SOLID FUELS

Mining of solid fuels such as coal, oil shale, tar sand (and heavy oil), and uranium, and their subsequent preparation and extraction require a large quantity of water [37–41,43–48]. We briefly address this issue in this section.

#### 2.5.1 OIL SHALE INDUSTRY

The mining and retorting of oil shale consumes a large amount of water. Aboveground retorting typically consumes between one and five bbl of water per each bbl of produced shale oil, depending on the technology [43–46,48]. Water is normally used for spent oil shale cooling and oil shale ash disposal. *In situ* processing, according to one estimate, uses about one-tenth as much water [47]. Also, water must be pumped out of oil shale mines. The resulting fall in water table may have negative effects on nearby arable lands and forests [43]. A 2008 programmatic environmental impact statement issued by the US Bureau of Land Management stated that surface mining and retort operations produce 2–10 US gallons of waste water per 1 short ton of processed oil shale [46].

#### 2.5.2 TAR SAND AND HEAVY OIL INDUSTRIES

Water requirement in tar sand industry is well reviewed by Speight [16,17,44] in his numerous books and other publications. Just like oil shale, tar sands and heavy oil are obtained from strip (surface) mining or underground mining. The mining is generally accompanied by extraction process to recover bitumen or heavy oil. In terms of bitumen separation and recovery, the "hot water process," to date, is the only successful commercial process to be applied to bitumen recovery from mined tar sand/ oil sand in North America.

The hot water process utilizes the linear variation of bitumen density and the nonlinear variation of water density with temperature so that bitumen that is heavier than water at room temperature becomes lighter than water at 80°C. Surface-active materials in the tar sand also contribute to the process. The two most important steps in the process are "conditioning" and "separation."

In the conditioning step, the tar sand is heated and mixed with water to form a pulp of 60%-85% by weight of solids at  $80^{\circ}C-90^{\circ}C$ . First the tar sand lumps are reduced in size by ablation. The conditioned pulp is screened through a double-layer vibrating screen. Water is added to the screened material and the pulp then enters the "separation" cell. The bulk of the sand settles in the cell and is removed from the bottom as tailings, but the majority of the bitumen floats to the surface and is removed as froth. A middling stream containing water and fine solids and some bitumen from the midway up the side of the cell wall is also recovered.

Froth from the hot water process may be mixed with a hydrocarbon diluent such as coker naphtha and centrifuged. The Suncor process described by Speight [16,17,44] employs a two-stage centrifuging operation. The final bitumen product contains 1–2 wt% mineral and 5–15 wt% water. About 2 tons of tar sands is required to produce one bbl of oil. Roughly 75% of the bitumen can be recovered from sand. More details on oil recovery from tar sands are given in excellent reviews of Speight [16,17,44].

Relatively large amount of water is required to process tar sands. Currently, tar sand extraction and processing require several bbl of water for each bbl of oil produced, though some of the water can be recycled. *In situ* production methods are used on bitumen deposits buried too deep for mining to be economically recovered. These techniques include steam injection, solvent injection, and firefloods (see various EOR methods in Sections 2.3.1 and 2.3.2).

#### 2.5.3 URANIUM MINING AND LEACHING

Uranium, a substance essential for nuclear energy, is recovered from the ground by the extraction process [41]. In 2009, a worldwide production of uranium amounted to 50,572 tons [41]. While this number is small compared to that for coal, oil shale, and tar sands, this mining process also requires a large amount of water. As with other types of hard rock mining, uranium is extracted by the three main methods: box cut mining, open pit mining, and *in situ* leaching (ISL). While water requirement for open pit mining or underground mining of uranium is similar to that of other minerals, coal, oil shale, and tar sand, the major water usage in uranium mining is in the implementation of the ISL process.

The ISL process is also known as solution mining, which involves leaving the ore where it is in the ground and recovering uranium from it by dissolving it and pumping the pregnant solution to the surface where the uranium is recovered. This process has a little surface disturbance and no waste is generated. Uranium ISL uses the native groundwater in the ore body that is fortified with a complexing agent and in most cases an oxidant such as hydrogen peroxide. In many cases, the complexing agent used is sulfuric acid. It is then pumped through the underground ore body to recover the minerals in it by leaching. Once the pregnant solution is returned to the surface, uranium is recovered in much the same way as in other uranium plants [41].

Often, the use of oxidant is replaced by high concentration of acid solution. In the United States, ISL mines use an alkali leach due to the presence of significant quantities of acid-consuming minerals such as gypsum and limestone in the host aquifers. Any more than two to five percent carbonate minerals means that alkali leach must be used in preference to the more efficient acid leach.

In uranium mine near Moab, Utah, uranium deposits were formed when oxygenated groundwater, which had leached uranium from crystal rocks, flowed down into aquifers, where it was reduced to form precipitate uraninite; the main ore of uranium. This corresponds to oxidized and reduced conditions in groundwater redox chemistry. The rocks formed in the oxidizing conditions are reduced by a reducing fluid. The reduced fluid carries uranium-bearing minerals [41]. While the uranium concentration in sea water is low at 3.3 mg per cubic meter of seawater, the total amount is large. Several countries such as the United Kingdom, France, Germany, and Japan are exploring the recovery of uranium from the seawater using inorganic adsorbents such as titanium oxide. Japan is also exploring the production of adsorbents by irradiation of polymer fiber. Uranium adsorption by the polymer adsorbent is about ten-fold high compared to that of conventional titanium oxide adsorbent. In 2012, Oak Ridge National Laboratory (ORNL) researchers announced the successful development of a new adsorbent material dubbed "HiCap" that vastly outperforms the previous best adsorbents. They showed that their adsorbents can extract five to seven times more uranium at uptake rates, which are seven times faster than the world's best adsorbents. HiCap also effectively removes toxic metals from water.

#### 2.5.4 COAL MINING AND PREPARATION

While coal mining also requires significant use of water and produces acid drainage that can affect local aquifers, the large use of water in the coal industry is also in the coal preparation plants [40]. Coal preparation plant requires washing, crushing, and removal of various impurities from coal. One area where significant water is used is in the removal of inorganic sulfur (iron pyrites) from coal by the floatation process. In this process, finely pulverized coal goes through a floatation process in which iron pyrite particles are removed from coal by gravity separation due to the density difference between pyrites and coal particles. The removal of sulfur, other impurities (like ash), and metals is important for the downstream operations for coal. For example, once the coal is finely pulverized and all ash and metals are removed, coal-water slurry becomes an important fuel for combustion purposes. The subject of coal-water slurry combustion is discussed in Chapter 5. The conversion of coal to oil by direct or indirect coal liquefaction processes also uses a significant amount of water. For 50,000 barrels per stream day (BPSD), water requirement can vary from 7,300 to 10,500 gallons per minute (GPM) depending on the nature of coal. For coproduction of Fischer-Tropsch (FT) liquids plus electric power of 25,000 BPSD and 1,250 MW plant, water requirement can be 20,800 GPM [40].

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# 3 Energy Recovery by Benign Hydrothermal Processes

## 3.1 INTRODUCTION

Water has been used as a benign thermal energy carrier for recovery of energy from various other sources. While the examples of use of water and steam as benign thermal energy carrier are numerous, this chapter focuses on four important applications of water and steam as energy carrier. Although water and steam are used for heating and cooling in all refineries and other process industries, this chapter focuses on the use of water and steam to carry energy created by other sources such as nuclear energy, geothermal energy, solar energy, and different types of fuel burning to generate electric power, and/or heating and cooling purposes. Four applications that are considered here include (1) the role of water as a coolant and a thermal energy carrier for the nuclear reactor, (2) the use of water and steam in the recovery of geothermal energy, (3) the use of water to store heat produced from solar energy, and (4) the role of steam to drive turbine for power generation from various types of fuel burning. In each of these applications, water or steam plays a benign but very important role for various types of energy conversion and recovery processes.

## 3.2 ROLE OF WATER IN PRODUCTION OF NUCLEAR POWER

As discussed in Chapter 2, the extraction of uranium requires a large quantity of water. This section illustrates the important role of water in the nuclear reactor. There are several types of nuclear reactors, that is, water cooled, gas cooled, fast neutron, and so on, currently used in commercial practice. However, as shown in Table 3.1 [1–4], a majority of the commercial nuclear reactors (>80%) currently in operation use water as a coolant and an energy carrier. In fact, water is not only a coolant but also a moderator of the nuclear reactors and provides both energy carrier and safety functions for the reactors. Some of the water-based nuclear reactors are briefly described below.

## 3.2.1 LIGHT WATER REACTOR

The light water reactor uses light water (hence enriched uranium) and this category contains two different types of reactor: pressurized water reactor (PWR) and boiling water reactor (BWR) [2]. The light water also combines the functions of coolant and moderator. In both PWR and BWR, the water flows through the reactor core,

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Reactor Type	Total NPP (%)	GWs	Coolant/Moderator				
PWR	65	270	Water/water				
BWR	20	81	Water/water				
PHWR (CANDU)	11.5	27	Heavy water/heavy water				
RBMK (light water)	2.5	10	Water/graphite				
Other	1	0.04	Water/graphite				
Source: Nuclear Engin	eering International H	andbook, 2011					
Note: The total number	r of reactors in the work	ld is 438 with 3	99.3 GW.				
PHWR, pressurized hear	vy water reactor.						

## TABLE 3.1 Water-Based Nuclear Power Plants (NPPs) in Commercial Operation

a zone containing a large array of fuel rods where it picks up the heat generated by the fission of  $U^{235}$  present in the fuel rods. The coolant transfers heat to turbine and returns back to the reactor core. This loop is called primary circuit. It is the pressure at which coolant flows through the reactor core that makes the distinctions between PWR and BWR. In both types of light water reactors, about one-third of the fuel is replaced every year (implying life cycle for any given rod to be about three years) because by that time the concentration of fission fragments produced as a result of fission reactions absorbs enough neutrons to interfere with the chain reaction. Thus, before  $U^{235}$  is exhausted, fuel rods are periodically replaced to maintain high efficiency of the fission process.

#### 3.2.2 BOILING WATER REACTOR

The BWR does not have a steam generator [1–3]. Instead, water in the BWR boils inside the pressure vessel and the steam–water mixture is produced when very pure water (reactor coolant) moves upward through the core absorbing heat. The uranium core in the reactor vessel creates heat. The control rods enter the reactor from below. The water boils and produces steam that is passed through a turbine, which in turn drives the electric generator. While the BWR has many similarities to the PWR, there is only one circuit with water at lower pressure (about 75 atm) in the BWR so that it boils in the core at about 285°C. About 12%–15% of water is in the upper part of the core as steam and this has a lower moderating effect. BWR units can operate in the load-following mode more readily than PWR. The steam passes directly to the turbines before being condensed and recycled. Both water and steam are thus a part of a close reactor circuit. The entire close loop along with the BWR is illustrated in Figure 3.1 [2].

As shown in the figure, the core of the BWR contains 3.5-4.0 m-long fuel rods (90–100) and assemblies (up to 750), which hold up to 140 tons of uranium. In most nuclear reactors, the fuel is enriched ceramic uranium oxide (UO<sub>2</sub> with melting point of 2800°C). The fuel pellets (usually about 1 cm in diameter and 1.5 cm long) are typically arranged in a long zirconium alloy tube to form a fuel rod. A fuel assembly is an open lattice that can be inserted and withdrawn from the reactor core.



**FIGURE 3.1** Schematic of a typical BWR. (Adapted from "Nuclear power reactors," a document of World Nuclear Association, July 2013.)

The BWR has a secondary control system that restricts the flow through the core so that the amount of steam in the upper part of the reactor can be adjusted. This is important because steam has a lower moderating effect and the steam produced in the fission zone is slightly radioactive, mainly due to short-lived activation products. The turbine is therefore housed in the same reinforced building as the reactor.

#### 3.2.3 PRESSURIZED WATER REACTOR

About 60% of the world commercial nuclear power reactors are PWRs [1–3]. A graphical illustration of this type of reactor and the attached cooling system is shown in Figure 3.2 [2]. Similar to the BWR, the PWR has a core where fission reactions occur and a containment structure; unlike the BWR, the PWR system has a primary cooling system and a secondary steam generation circuit.

A core in the PWR contains 80–100 tons of uranium in 150–250 fuel assemblies, each with 200–300 vertical rods. Each fuel rod contains a stack of pellets of enriched uranium oxide packed in a sealed tube of Zircalloy. The control rods containing neutron-absorbing materials such as boron or cadmium are used to fine-tune the reactor operation and shut down the reactor in an abnormal operation or in an event of a malfunction. Boric acid fluid is used as a secondary shutdown system.

As shown in Figure 3.2, the reactor vessel, the primary cooling system, and the steam generator for the secondary steam circulation system are enclosed in a meterthick concrete and steel containment structure to protect the reactor and provide seal for any radiation leakage. The escape of fission products that are formed during fission is prevented by (1) high melting temperature ceramic pellets themselves, as fission products are trapped in small pores, and (2) Zircalloy cladding that is corrosion resistant to low neutron absorption. Any fission gas that escapes from the pellets is accommodated in the small space at the top of the fuel rod.



**FIGURE 3.2** (See color insert.) PWR—A common type of LWR. (Adapted from "Nuclear power reactors," a document of World Nuclear Association, July 2013.)

In the PWR, ordinary water is used as a moderator and as a coolant. In a primary cooling system, water flows freely between the fuel rods, while being directed through fuel assembly in a predetermined fashion. Water is kept at 325°C under 150 atm pressure. As shown in Figure 3.2, the pressure is maintained by steam in a pressurizer. The water in the primary cooling system also serves as a moderator by controlling the negative feedback effect of steam production and the resulting slowdown of the fission reaction. Thus, generation of steam reduces heat generated by the fission reaction causing steam to condense back to water. This negative feedback effect provides one of the safety features of the reactor. An addition of boron to the primary cooling system can also be used as a secondary shutdown system. Thus, closed loop water recirculation system used for primary cooling is operated at 325°C and 150 atm.

The secondary steam generation circuit is operated under low pressure, and water in this circuit boils in the secondary steam generators that are towers containing long narrow tubes. The generated steam drives turbine, which in turn generates electricity. The condensed steam from the turbine is returned to the heat exchangers in contact with the primary circuit. The PWR thus differs from the BWR in that the steam to run the turbine is produced in a steam generator in the secondary steam generation circuit [1–3].

#### 3.2.4 PRESSURIZED HEAVY WATER REACTOR (CANDU)

CANada Deuterium Uranium (CANDU) is a pressurized heavy water nuclear reactor operated on natural uranium fuel  $U^{238}$  and uses heavy water ( $D_2O$ ) as a coolant and a moderator [2]. The CANDU reactor is capable of online refueling during operation. In this type of reactor, the heat from primary coolant is once again transferred

to a secondary boiling water loop. The main difference between this reactor and the light water reactor is the use of heavy water in CANDU.

## 3.2.5 GRAPHITE-MODERATED, DIRECT CYCLE (BOILING WATER) PRESSURE TUBE REACTOR

The graphite-moderated, direct cycle (boiling water) pressure tube reactor (RBMK) was designed in the former Soviet Union [2]. The reactor uses ordinary boiling water as a coolant and graphite as a moderator. This type of reactor is also capable of online fueling. Both CANDU and RBMK circulate water through pipes rather than in a pressure vessel surrounding the entire reactor. In both of these reactors, fuel rods can be reached while the reactor is in operation, and refueling takes place almost on a continuous basis. RBMK is, however, not currently used.

#### 3.2.6 SUPERCRITICAL WATER-COOLED REACTOR

Twenty percent of all electricity in the United States uses light water nuclear reactors [3,4]. The next-generation reactors, called supercritical water reactors, promise to increase reactor energy efficiency by as much as 13% while simplifying plant design. Water at about 374°C and about 220 atm pressure becomes supercritical where a phase difference between gas and liquid disappears. Heat produced by fission can also be converted into electricity in a reactor cooled by supercritical water. The supercritical state of water offers some distinct advantages of physical, thermal, and chemical properties for an efficient energy transformation operation in a nuclear reactor. The building of such reactors will, however, require materials that withstand high temperature and pressure. The commercial use of this type of reactor is still in its infancy.

It is clear from the above descriptions that water plays an essential role as an energy carrier and a reactor safety moderator in the nuclear power industry.

## 3.3 HYDROTHERMAL PROCESSES FOR RECOVERY OF GEOTHERMAL ENERGY

Geothermal energy is thermal energy generated and stored in the Earth [5–20]. This energy of the Earth's crust originates from the original formation of the planet (20%) and from the decay of radioactive minerals (80%). The difference in temperature between the core of the Earth and its surface drives a continuous conduction of heat from the core to the surface. The temperature of the Earth increases with an increased depth from the surface. The core of the Earth is believed to be over 5000°C due to radioactive decay.

The hot water and steam generated by the geothermal heat can be used for power generation. Approximately 10,715 MW of geothermal power is collected in 24 different countries [19]. The worldwide installed geothermal electric capacity is illustrated in Table 3.2 [19]. While the United States has more geothermal capacity than any other nation in the world, it has also been extensively explored in other parts of the world because geothermal power is renewable, reliable, sustainable, environmentally friendly, and cost effective [5,6]. For example, Philippines obtain >25% of its electricity from geothermal energy. The United States produces more than 3000 MW of power from

Giosai Geotilerinai capa	enty man dreater man so mit				
Country	Capacity as of 2010 (MW)				
United States	3086				
Philippines	1904				
Indonesia	1197				
Mexico	958				
Italy	843				
New Zealand	628				
Iceland	575				
Japan	536				
Iran	250				
El Salvador	204				
Kenya	167				
Costa Rica	166				
Nicaragua	88				
Russia	82				
Turkey	82				
Papua New Guinea	56				
Guatemala	52				

## TABLE 3.2Global Geothermal Capacity with Greater Than 50 MW

Source: "Geothermal energy," Wikipedia, the free encyclopedia, 2012.

geothermal energy largely used in eight states including California, Alaska, Oregon, and Nevada. California leads the nation with 80% of the total US energy consumption [19].

Conventional geothermal energy is generally limited to the areas near tectonic plate boundaries—the regions that are seismically active. Earthquakes and magma movement break up the rock covering allowing water to circulate. As the water rises to the surface, natural hot springs and geysers occur with water temperature as high as 200°C. Besides power, geothermal heat pump also uses the steady temperatures just underground to heat and cool buildings cleanly and inexpensively. About 28 GW of direct geothermal heat capacity is used for heating, spas, industrial processes, desalination, and agricultural applications [5].

The most common current way of capturing the geothermal energy is to tap into naturally occurring "hydrothermal convection" systems where cooler water seeps into the Earth's crust, is heated up by geothermal energy, and then rises to the surface. The hot water coming to the surface can be captured as steam, which in turn can drive turbine to generate electricity. The steam can also be effectively captured from holes that are drilled with a careful design.

Three methods—dry steam, flash steam, and binary cycle—are used to operate the power plants by geothermal energy [9,14]. While all of them use steam and hot water from the ground, in dry steam approach steam goes directly through the turbine then into a condenser where steam is condensed into water, which is returned to the ground. The recycling of water prolongs the life of the heat source. This method is schematically described in Figure 3.3a [14]. In the second approach shown in Figure 3.3b [14],

very hot water is depressurized or "flashed" into steam that can then be used to drive turbine. In the third "binary system" approach, the hot water is passed through a heat exchanger, where it heats a second fluid, such as isobutene, in a closed loop. The isobutene boils at a lower temperature than water, so it is more easily converted into steam to run the turbine. This method is schematically described in Figure 3.3c [14].



**FIGURE 3.3** (See color insert.) Three methods of recovering geothermal energy: (a) dry steam, (b) flash steam. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; National Renewable Energy Laboratory. Planta Solar 20. http://www.nrel.gov/csp/solarpaces/project\_detail.cfm/projectID=39.)



**FIGURE 3.3** (See color insert.) (Continued) Three methods of recovering geothermal energy: (c) binary cycle. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; National Renewable Energy Laboratory. Planta Solar 20. http://www.nrel.gov/csp/solarpaces/project\_detail.cfm/projectID=39.)

In general, the choice of the approach depends on the nature of the geothermal resource. If water comes out as steam, the dry steam approach is used. If water comes out as hot water at high enough temperature, the flash steam approach is used. Since most resources produce hot waters, an exchanger design (third approach) is more prevalent in common practice. The largest geothermal system now in operation is a steam-driven plant in an area called Geysers, north of San Francisco, California [13,14].

Geothermal energy (steam) can sometimes be accompanied by impurities that are harmful to the environment. The open systems such as geysers can emit some air pollutants such as hydrogen sulfide and trace amounts of arsenic and minerals along with steam. For the power plant run by hot water system such as Salton Sea reservoir in Southern California, a significant amount of salt can be built up in the pipes, which must be removed. This salt can be either put into landfill or reinjected back into the ground. The closed loop binary cycle system has no emission problem because everything is returned back to the ground.

Besides electricity, the geothermal heat can also be used to heat and cool homes, heat greenhouses, dry out fish and de-ice roads, improve oil recovery, and heat fish farms, spas, and local resorts among other applications. In Iceland, almost every building is heated with hot spring water. A convenient way to tap geothermal energy is to use heat pump, which supplies heating and cooling using geothermal energy. In this method, either air or antifreeze liquid is pumped through pipes that are buried underground and reentered into the buildings. In the summer, the liquid moves heat from the building into the ground, and in the winter, the opposite process takes place providing air and water to the heating system of the building. The system can be simple, in which heating and cooling using the ground source can occur by tubes running from outside the air, under the ground, and into the house ventilation system, or more complex, in which compressor and pumps are used as an electric air-conditioning system to optimize the heat transfer. These ground source heating and cooling systems are the most environmentally clean systems. The Department of Energy has pointed out that heat pumps operated by geothermal energy are more efficient and save more money than any other electrical systems. Currently, more than 600,000 homes in the United States use geothermal energy-driven heat pumps, and this number is increasing at the rate of 60,000 homes per year, with the largest growth in rural areas [6,14,19,20].

#### 3.3.1 ENHANCED GEOTHERMAL SYSTEMS

While geothermal heat can be obtained anywhere under the surface of the Earth, the conditions that make water circulate to the surface are found only in <10% of the Earth's surface [5,9,13,18,20]. A method to capture geothermal heat from dry areas is known as enhanced geothermal system (EGS) or "hot dry rock." The systematic steps demonstrating how EGSs work are graphically illustrated in Figure 3.4 [5,11,14]. As shown in this figure, the hot dry rock reservoirs, typically at greater depths below the Earth's surface than conventional sources, are first broken up by pumping highpressure water through them. Once the rock is perforated (by the hydraulic fracturing process), additional water not only expands perforations in the rock but also captures heat from the open rock. This steam is collected by a production well and brought to the surface, and it powers turbine to generate electricity. Finally, the cooled water is returned to the reservoir by injection wells to complete the circulation loop. The system can further be optimized by employing carefully designed multiple production wells. Plants that use a closed loop binary cycle described earlier release no fluids or heat-trapping emissions other than water vapor, which may be used for cooling. As indicated in the figure, water and steam play a key role in recovering geothermal energy from deep dry rocks.

The EGS process does carry some risk as hydraulic horizontal fracturing (fracking) used in the recovery of unconventional gas such as "shale gas" allows permeation of carbon dioxide or "fracking fluid" to water aquifers. The EGS can induce seismic activity that might occur from hot dry rock drilling and development, although the likelihood of this occurrence is low, when projects are located at an appropriate distance away from the major fault lines and properly monitored. Appropriate site selection, assessment, and monitoring of rock fracturing and seismic activity during and after construction are very critical. The EGS can produce a continuous power and it is feasible anywhere in the world, depending on the economic limits of the drilling depth. Good locations are over deep granite covered by a 3–5 km layer of insulating sediments that reduce the heat loss [6,7]. The EGS



**FIGURE 3.4** (See color insert.) Steps taken to recover geothermal energy via the EGS. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; Office of Energy Efficiency and Renewable Energy, *An Evaluation of Enhanced Geothermal Systems Technology*, US Department of Energy, Washington, DC, 2008.)

wells are expected to have a useful life of 20–30 years. The EGSs are currently being developed in many countries including France, Australia, Japan, Germany, the United States, and Switzerland. The largest current EGS project is being developed in Cooper Basin in Australia with a capacity of 25 MW [12]. A summary of the current commercial EGS projects under development is described in Table 3.3 [20].

## 3.3.2 COPRODUCTION OF GEOTHERMAL ELECTRICITY IN OIL AND GAS WELLS

Geothermal energy can also be captured by using the existing oil and gas wells. In many existing oil and gas reservoirs, a significant amount of high-temperature water and/or high-pressure conditions prevails, which will allow the production of electricity along with the production of oil and gas. In some cases, exploiting these sources can even enhance the extraction of oil and gas itself. A Massachusetts Institute of Technology (MIT) study indicates that in southern and southeastern states there is a potential for developing 44,000 MW of geothermal capacity by 2050 by coproducing electricity, oil, and natural gas at oil and gas fields [5,9,17,18]. The study also suggests that such advanced geothermal systems could supply 10% of

Country	Size (MW)	Plant Type	Depth (km)					
Germany (EU)	3	Binary	3.3					
Netherland (EU)	6	Thermal	2.0					
Australia	7–30	Binary	4.1					
Australia	25-50	Kalina	4.3					
United Kingdom	10	Binary	4.5					
United Kingdom	3	Binary	3.0-4.0					
	Country Germany (EU) Netherland (EU) Australia Australia United Kingdom United Kingdom	CountrySize (MW)Germany (EU)3Netherland (EU)6Australia7–30Australia25–50United Kingdom10United Kingdom3	CountrySize (MW)Plant TypeGermany (EU)3BinaryNetherland (EU)6ThermalAustralia7–30BinaryAustralia25–50KalinaUnited Kingdom10BinaryUnited Kingdom3Binary					

#### TABLE 3.3 Current Commercial EGS Projects under Development

Source: "Enhanced geothermal systems," Wikipedia, the free encyclopedia, 1-9, 2012.

<sup>a</sup> These projects are operational.

the US base load electricity by that year. Besides conventional oil and gas wells, horizontal wells created in deep oil shale rocks to recover shale gas by "fracking process" can also be helpful in recovering geothermal energy in oil shale rocks. The horizontal wells created for deep and tight gas as well as gas in geopressurized zones and coal bed methane reservoirs can also be useful for the recovery of geothermal energy along with the recovery of unconventional gas. Water and steam play a very critical role in these advanced geothermal systems [5,9,17,18].

#### 3.4 ROLE OF WATER IN STORAGE OF SOLAR ENERGY

The use of solar energy for home heating has been in existence for a long time [21–35]. In this method, solar panels installed on the top of the roof of the houses or buildings can absorb solar heat and this heat is stored in water and steam circulating under the solar panels. This heat can be stored and used continuously for the environmental control in residential houses and industrial buildings.

While solar energy can be stored and used in a number of different ways, water plays an important role in harnessing solar energy. Solar hot water systems use sunlight to heat water. In low geographical latitudes, domestic hot water use at moderate temperatures can be provided by solar water heating systems [21]. There are at least three types of solar heaters: evacuated tube collectors (most widely used), glazed flat plate collectors (used for domestic water heating), and unglazed plastic collectors (mainly used for the swimming pools in the United States) [22–24]. In 2007, the capacity of solar water heater systems installed worldwide was 154 GW, led by China (70 GW), Israel, and Cyprus [21–25].

Water is also heavily used in solar energy-driven heating, ventilation, and airconditioning (HVAC) systems in residential home as well as in industrial building. Water can be a good solar energy storage device that can be used to provide heating and cooling on a needed basis for daily and seasonal durations. Solar distillation can be used to make saline and brackish water potable. Solar energy can be used for water disinfection and water stabilization pond to treat wastewater. Solar concentrating technologies such as parabolic dish, trough, and Scheffler reflectors can provide process heating for commercial and industrial applications. For example, 50% of process heating, air-conditioning, and electrical requirement for a clothing factory in Shenandoah, Georgia, is provided by a solar energy project [21–25].

Finally, power generated by solar energy using photovoltaic (PV) systems needs to be stored. Off-grid PV systems have traditionally used rechargeable batteries to store excess electricity. Another approach is the use of pumped storage of hydroelectricity that stores energy in the form of water pumped when the energy is available from a lower elevation reservoir to a higher elevation one. The energy is recovered when demand is high by releasing the water to run through a hydroelectric power generator [25–35]. Solar energy can also be stored by producing solar fuels such as hydrogen using numerous techniques described in Chapter 11. The production of solar fuels mostly involves dissociation of water. Hydrogen can also be produced using solar reforming of fossil and biofuels using steam. Different techniques required to accumulate concentrated solar power are described in numerous references [25–35].

#### 3.5 STEAM TURBINE

A steam turbine is a device that extracts thermal energy from pressurized steam and uses it to do mechanical work on a rotating output shaft [36]. Because turbine generates rotary motion, it is particularly suitable to drive an electrical generator. In 1996, about 90% of all electricity generation in the United States used steam turbine [36]. The steam turbine is a form of heat engine that derives much of its improvement in thermo-dynamic efficiency through the use of multiple stages in the expansion of steam. Steam turbines are made in a variety of sizes ranging from <0.75 kW used for mechanical drives for pumps and compressors to 1.5 million kW used for electricity generators.

Basically five types of steam turbines are used: condensing, noncondensing, reheat, extraction, and induction [36]. *Condensing* turbines are most commonly found in the electric power plants. In this type, steam coming out of turbine is condensed (about 90%). Process steam applications mostly use back-pressure *noncondensing* steam turbine (commonly used in paper and pulp operations, refineries and desalination plants, etc.) in which exhaust pressure is controlled to suit the needs of the steam pressure. *Reheat* turbines are exclusively used in the electric power plants. Here, steam returns to the boiler from turbine, picks up more superheated steam, and returns back to turbine to continue its expansion. *Extraction* turbines are common in all applications. In this case, steam is released from the various stages of the turbine and used for industrial process needs and sent to boiler feedwater heaters to improve an overall cycle efficiency. *Induction* turbines introduce low-pressure steam at an intermediate stage to produce additional power.

Steam turbines are very valuable because they can be used for any fuel. For example, in a nuclear reactor, nuclear energy is converted to thermal energy by generating steam, and the steam can then be used to generate power by steam turbines. In combustion processes using coal, waste, biomass, or other fuels, heat generated by combustion is absorbed by water to generate steam, and the steam is then used to generate power via the use of a steam turbine. Steam is thus a very benign vehicle for energy conversion and heat and power generation.

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# 4 Steam Gasification and Reforming Technologies

## 4.1 INTRODUCTION

All carbon-based materials (i.e., coal, crude and heavy oil, shale oil, bitumen, tar sand, plastics, biomass, organic waste, etc.) can be converted to carbon monoxide, hydrogen, carbon dioxide, and methane in the gasification process by a controlled amount of oxygen and/or steam at temperatures higher than about  $700^{\circ}$ C. The product distribution generally depends on the temperature, pressure, residence time, catalyst, and the nature of the feedstock. The gas produced from steam gasification (with or without oxygen) is often called syngas (either synthesis gas or synthetic gas) or producer gas, both of which are fuel themselves that generate heat and energy. Unlike direct combustion of original raw materials, syngas (hydrogen and carbon monoxide) is much more versatile in that it can be used for combustion at much higher temperatures. It can be used in fuel cells (FCs) and can also serve as raw materials for the production of numerous chemicals and liquid fuels. The gasification also produces gaseous fuels that do not contain corrosive ash elements such as chloride and potassium [1–10].

Water in its gaseous form (i.e., steam) plays a very important role in overall gasification process. During gasification, carbonaceous material undergoes several important processes: (1) at temperatures around 100°C, the dehydration results in the generation of steam in the gas phase, and (2) further dehydration and pyrolysis of carbonaceous materials occur at temperatures around 200°C–300°C resulting in the loss of raw materials up to about 70% of their original weight. The nature of char produced by this reaction depends on the nature of the feedstock; (3) the volatile materials from char react with oxygen to produce carbon dioxide and carbon monoxide; (4) the char also reacts with steam to produce hydrogen and carbon monoxide; and (5) at higher temperatures, the water–gas shift reaction between carbon monoxide and steam produces hydrogen and carbon dioxide [1–10].

The equilibrium constants for various reactions involving carbon and intermediate products are illustrated in Figure 4.1 [1–3]. In the real process, at high temperatures, steam gasification predominantly produces hydrogen and carbon dioxide because of the dominance of water–gas shift reaction. Both carbon monoxide and carbon dioxide are favored during direct combustion [1,3,5].

To some extent, gasification and reforming are overlapping phenomena in that gasification involves the transformation of solid (and liquid) raw materials to the gas-phase products through a series of thermal reactions. Catalytic reforming involves the transformation of these intermediate products to hydrogen, carbon monoxide, and carbon dioxide by steam reforming, dry reforming,



**FIGURE 4.1** Equilibrium constant-temperature relations for carbon reactions with oxygen, steam, hydrogen, and carbon dioxide. (Adapted from Lee, S., Speight, J.G., and Loyalka, S.K., *Handbook of Alternative Fuel Technologies.* Taylor & Francis, Boca Raton, FL, 2007.)

partial oxidation, and water–gas shift reactions aided by a suitable catalyst. High-temperature gasification can also produce syngas; however, reforming catalyst allows the productions of hydrogen, carbon monoxide, and carbon dioxide at a lower temperature and at a faster rate. Generally, hydrocarbon-free product distribution by gasification requires temperatures in excess of 1000°C–1200°C. The catalytic reforming process can achieve the same type of product distribution at temperatures around 800°C.

Steam reforming is the oldest and most widely used technology available to convert hydrocarbons into a gaseous product containing hydrogen and carbon dioxide. The reaction between steam and hydrocarbons is an endothermic reaction and is carried at high temperatures (somewhere between 400°C and 1000°C) in the presence of a catalyst. Generally, Ni catalyst is used; however, in recent years, several other types of catalysts have been investigated. The stoichiometry of hydrocarbon reforming for maximum hydrogen production is described by the following reactions [11–17]:

$$C_n H_m + 2n H_2 O \rightarrow n CO_2 + \left(\frac{2n+m}{2}\right) \times H_2$$
 (4.1)

$$C_n H_m + n H_2 O \rightarrow n CO + \left(\frac{2n+m}{2}\right) \times H_2$$
 (4.2)

These two reactions are generally accompanied by the water-gas shift reaction as [18]

$$(X_n)CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{4.3}$$

The initial steps in steam reforming are the dissociative adsorption of the hydrocarbons on the metal sites of the catalyst and the reaction of the adsorbed  $C_xH_y$  species with the adsorbed H<sub>2</sub>O-derived species to produce CO and H<sub>2</sub> (Equation 4.2). With an active catalyst at temperatures below 600°C, reforming of hydrocarbons is irreversible with no intermediates and the only byproduct is carbon that forms on the catalyst. Besides the above reactions, the following reactions also occur at varying degrees:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
 (4.4)

$$2CO \rightarrow CO_2 + C \tag{4.5}$$

$$CH_4(g) \rightleftharpoons 2H_2(g) + C(s)$$
 (4.6)

Equation 4.1 is the combination of reforming and water-gas shift reactions. Equations 4.3, 4.4, and 4.6 are equilibrium-limited reactions. Under normal conditions, Equations 4.5 and 4.6 dominate, and they together produce coke on the catalyst. In general, both methanation and disproportionation reactions are equilibrium limited. The reformed fuel contains carbon monoxide that must be reduced to a low level (except for the use in high-temperature FCs [HTFCs]). To reduce carbon monoxide concentration at the desired level of <10 ppm, the reforming reaction is followed by a high-temperature and a low-temperature water-gas shift reaction, both of which are exothermic [18]. The residual carbon monoxide can be further reduced by its preferential oxidation. The mixture of hydrogen and carbon dioxide coming out of the preferential oxidation process can then undergo a separation process to remove carbon dioxide and generate pure hydrogen. The separation process can be a physical (absorption by molecular sieves), a chemical (absorption in an amine solution), or a membrane separation (usually Pd membrane) at high temperature. The separated carbon dioxide is used with ammonia to produce urea. The purified hydrogen is used in the production of ammonia and a host of other refining and chemical production operations.

The catalysts for steam reforming of hydrocarbons are mainly nickel based on oxide support to obtain high thermal stability. Nickel catalysts are preferred because of their low cost, reasonable thermal stability, and high activity [19–23]. At low temperatures (425°C–500°C), iron catalyst promoted with chromium oxide is sometimes used to enhance oxidation reaction. More details on the catalysis of steam and trireforming reactions are given in Sections 4.2.3, 4.3, and 4.4.

Currently, more than 65% of hydrogen production uses steam reforming of fossil fuel technology because it is a mature and reasonably inexpensive technology (compared to other processes). It does not require a new infrastructure. It also reduces the need for transport and storage of hydrogen. The disadvantages of the steam reforming process are as follows: (1) reformers are complex, large, and expensive; (2) reformers have high warm-up period; and (3) reformers introduce additional losses into the
energy conversion process. The reforming process can also create pollutants such as carbon dioxide, carbon monoxide, unburned original hydrocarbons, and nitrous oxide that can be generated by oxidation with air.

While steam gasification and reforming has huge potential to generate hydrogen, as discussed earlier, steam gasification of coal is more difficult than that of biomass. Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. It is more acceptable than coal because it is renewable and consumes atmospheric carbon dioxide during its growth, thus having a small net CO<sub>2</sub> impact compared to fossil fuels. However, hydrogen produced from biomass has major challenges. There are few commercial plants. While biomass is more reactive to steam compared to coal, the yield of hydrogen is low from biomass since the hydrogen content of biomass is low to begin with (~6% vs. 25% for methane) and the energy content is low due to 40% oxygen content of biomass. Since over half of the hydrogen from biomass comes from splitting water in the steam reforming reaction, the energy content of the feedstock is an inherent limitation of the process. Due to high oxygen content, the yield of hydrogen per unit weight of biomass is low. The low yield of hydrogen on a weight basis is, however, misleading since the energy conversion efficiency is high. For example, the steam reforming of bio-oil at 825°C with a fivefold excess of steam has an energy efficiency of 56% [24-26]. The cost of growing, harvesting, and transporting biomass is, however, high. Thus, even with reasonable energy efficiencies, it is not currently economically competitive with natural gas steam reforming for stand-alone hydrogen without the advantage of high-value coproducts. One way to make steam reforming of biomass more competitive is to use coal-biomass mixture as the feedstock [5,27–33]. This mixture will increase the hydrogen production rate, maintain the overall reactivity between steam and feedstock, and also reduce the emission of carbon dioxide. A 70/30 mixture of coal and biomass is CO<sub>2</sub> neutral for environmental purposes [2].

# 4.2 MECHANISMS, KINETICS, AND CATALYSIS OF STEAM GASIFICATION AND REFORMING

# 4.2.1 MECHANISM OF STEAM GASIFICATION

Steam gasification is an endothermic reaction and requires heat to move the reaction in the forward direction. Generally, excess steam is also required to promote the gasification reaction. However, excess steam affects the thermal efficiency of the process. The reaction can be expressed as [1]

$$C(s) + H_2O(g) = CO(g) + H_2(g) \dagger \Delta H_{298K}^0 = 131.3 \text{ kJ/mol}$$
 (4.7)

The equilibrium constant for this reaction is illustrated in Figure 4.1 and compared with the equilibrium constants for gasification with other gasifying agents such as oxygen, hydrogen, and carbon dioxide [1]. It is clear that the pure steam gasification is not as favored as the one with oxygen. Often steam is accompanied by oxygen and hydrogen to get more favorable rate of reaction and better product distribution. The steam gasification produces hydrogen and carbon monoxide. Its relative ratio depends on synthesis chemistry and process engineering as well as the presence of

other gasifying agents. Two reaction mechanisms for carbon-steam reactions over a wide range of gasification conditions are proposed [1,3]:

Mechanism A:

$$C_{f} + H_{2}O = C(H_{2}O)_{A}$$
 (4.8)

$$C(H_2O)_A \to CO + \Box H_2 \tag{4.9}$$

$$C_{f} + H_{2} = C(H_{2})_{B}$$
(4.10)

In this mechanism,  $C_f$  designates unoccupied carbon sites,  $C(H_2O)_A$  and  $C(H_2)_B$  are adsorbed species of water and hydrogen, respectively. Equations 4.8 and 4.10 are reversible, whereas Equation 4.9 is irreversible. This mechanism is referred to as inhibition by hydrogen adsorption because the adsorbed hydrogen prevents the adsorption of steam molecules and thus prevents the gasification reaction [1,3]

Mechanism B:

$$C_f + H_2O = C(O)_A + H_2$$
 (4.11)

$$C(O)_A \to CO \tag{4.12}$$

Here gasification rate is affected by the competitive reaction of chemisorbed oxygen with hydrogen, and this competition for sites limits the conversion of the adsorbed oxygen to carbon monoxide. Thus, this mechanism is often called "inhibition by oxygen exchange" [1,3].

Both of these mechanisms can express the gasification rate in the form as follows:

$$R = \frac{k_1 p_{\rm H_2}}{1 + k_2 p_{\rm H_2} + k_3 p_{\rm H_2O}} \tag{4.13}$$

where:

*R* is the rate of gasification  $P_{\rm H_2}$  and  $P_{\rm H_2O}$  are partial pressures of hydrogen and water  $k_1$  is the kinetic constant  $k_2$  and  $k_3$  are adsorption constants

and the expression fits the experimental data well. The rate expression can be derived, assuming pseudo-steady states for adsorbed species.

The above discussion assumes pure carbon and steam as a gasifying agent. The rate analysis gets more complex when coal and other gasifying agents are taken into the considerations. Carbon in coal is distributed within the coal matrix and its concentration depends on the rank of coal. The gasification of coal must therefore consider transport processes within the coal matrix and accessibility of carbon within the matrix. When other gasifying agents such as oxygen and hydrogen are added, their roles on overall gasification reactions must also be considered. Alkali metal salts

act as catalysts for steam gasification reactions. The order of catalyst activity of alkali metals on coal gasification reaction is Cs > Rb > K > Na > Li. For coal gasification, coke deposition during gasification on active catalyst sites also affects the catalyst life. The coking can be reduced by increasing the steam-to-carbon ratio [1–3].

### 4.2.2 MECHANISM OF STEAM REFORMING

As mentioned earlier, the steam reforming of methane is very attractive because methane contains the largest hydrogen/carbon (H/C) ratio in any hydrocarbon. Unfortunately, methane molecule is very stable with C–H bond energy of 439 kJ/mol. Such high bond energy makes methane resistant to many reactants and reactions. Furthermore, C–H bond in methane is very strong. Methane molecule can be, however, activated by group 8–10 transition metals and can be oxidized to produce syngas. Further conversion of CO by water–gas shift reaction generates the final product with large concentrations of hydrogen and carbon dioxide. Once the carbon dioxide is removed from the mixture of carbon dioxide and hydrogen by adsorption, absorption, or membrane separation process, pure hydrogen is obtained. The adsorption process allows the purity of hydrogen of about 999.999% at 25 bar feedstock pressure. In the recent years, the use of ceramic ion transport membranes (ITMs) with reformers has opened up the possibilities of the production of high-quality and low-cost hydrogen [5,6,33–35] (Barrio et al., 2012, pers. comm.).

Methane reforming by steam is an endothermic reaction and favored at lower pressures. While noble metal catalysts have been tested and used in the past, most commercial operations use nickel catalyst because of its low cost and high activity, stability, and selectivity. The activity of the catalyst depends on the catalyst surface area and the temperature (around 400°C–1000°C) for steam pressure up to 30 atm. The activity of the catalyst is usually described by the turnover frequency (TOF) that is generally  $0.5 \text{ s}^{-1}$  at around 450°C. This number corresponds to about 10% methane conversion. High conversion rate demands higher temperature because the reaction is limited by thermodynamics that is favored at higher temperature. Very high conversion requires the reactor to be operated at temperatures higher than around 900°C. Often the catalysts in the reformer are poorly used because heat transfer between gas and solid is a limiting factor in the reactor, which will be discussed later.

Numerous studies on mechanism of methane reforming have been reported and these are well reviewed by Wei and Iglesia [36], Rostrup-Nielsen et al. [37], and Bradford and Vannice [22,23]. The following discussion closely follows these reviews. Wei and Iglesia [36] have shown that the rate-limiting step for steam reforming is C–H bond activation. They proposed the following mechanism:

$$H_2O + * \to O^*(a) + H_2(g)$$
 (4.14)

$$CH_4(g) + 2^* \to CH_3^*(a) + H^*(a)$$
 (4.15)

$$CH_3^*(a) + * \rightarrow CH_2^*(a) + H^*(a)$$
 (4.16)

$$CH_2^*(a) + * \to CH^*(a) + H^*(a)$$
 (4.17)

$$CH^{*}(a) + O^{*}(a) \rightarrow CO^{*}(a) + H^{*}(a)$$
 (4.18)

$$CO^*(a) \to CO(g) + * \tag{4.19}$$

$$2H^{*}(a) \rightarrow H_{2}(g) + 2^{*}$$
 (4.20)

In the above equations, "\*" denote Ni (or catalyst in general) surface atom. In this mechanism, methane adsorbs dissociatively on the Ni surface producing methyl group and water molecule reacts with Ni surface atoms to produce adsorbed oxygen and gaseous hydrogen. The methyl group goes through further stepwise dehydrogenation steps. The final product of this dehydrogenation CH– reacts with adsorbed oxygen to produce syngas (CO and  $H_2$ ).

Along with the main reactions outlined above, the reforming reactions are accompanied by the carbon formation reactions:

$$2CO \rightarrow C + CO_2 \qquad \Delta H^0_{298\,\mathrm{K}} = -172.5 \,\mathrm{kJ/mol}$$
 (4.21)

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H_{298K}^0 = 74.9 \text{ kJ/mol}$$
 (4.22)

These two reactions deposit carbon on the catalyst in the form of filaments that ultimately deactivate catalyst. The carbon formation reactions are also counterbalanced by carbon-consuming reactions:

$$C + CO_2 \rightarrow 2CO \tag{4.23}$$

$$C + H_2 O \rightarrow CO + H_2 \tag{4.24}$$

Both of these reactions also depend on the operating conditions and the nature of the reactor design. Generally, at low temperatures, the Ni catalyst surface is covered with hydrocarbons, which degrades into a polymeric layer. However, at high temperatures, cracking of olefinic and aromatic hydrocarbons produces coke that deposits on the catalyst surface. Since NiC is not stable, carbon is formed in the form of filaments that grow on the catalyst surface. The size of Ni particles has a direct bearing on the location of filaments on the Ni surface. Smaller and more dispersed Ni particles reduce the formation of carbon filaments. Thus, Ni dispersion is an important variable on the catalyst activity and stability (degradation). The literature has shown that the size and location of Ni particle ensemble is an important variable for controlling the coke formation on the catalyst [34-40] (Barrio et al., 2012, pers. comm.). The coke formation can also be controlled by controlling the carbide formation. While alloys reduce carbide formation, they hide the active sites of nickel for the reforming reactions. The literature has also shown that the addition of a small amount of dopants (e.g., Sn) reduces coking without affecting the activity for the reforming reaction [34–40] (Barrio et al., 2012, pers. comm.). Carbon formation can also be reduced by the alloys of copper-nickel, sulfur-nickel, nickel-tin, and nickel-rhenium [34-40] (Barrio et al., 2012, pers. comm.).

## 4.2.3 CATALYSTS FOR STEAM GASIFICATION

Catalysts can be added to the steam gasification process in two forms: (1) as active bed additives or (2) as separate heterogeneous catalysts that are used in the steam reforming reactions [28,41–57]. The active additives are used to (1) reduce the amount

of tar formation; (2) promote several other chemical reactions to change the production rate, composition, and heating value of the gas; (3) promote char gasification; (4) prevent active agglomeration of the feedstock, char, and tar that can lead to reactor choking; and (5) remove carbon dioxide through the active adsorption process. The steam reforming catalysts also reform tar and produce gas of high quality.

### 4.2.3.1 Dolomite, Olivine, and Alkali Metal-Based Catalysts

These are generally cheap and disposable catalysts. Dolomite is a magnesium ore with the general formula MgCO<sub>3</sub>. CaCO<sub>3</sub> is considered to be a good catalyst for biomass gasification. Dolomite is also a good adsorbent for carbon dioxide and capable of removing tar very efficiently. It is, however, a very fragile substance and may quickly attrite in highly turbulent conditions within a fluidized bed. CaO additive was studied by Dalai et al. [41], who showed that the use of this additive reduced the gasification temperature to about 150°C to get the same level of gas production. Both carbon conversion and hydrogen production increased with impregnation of CaO in cellulose, cedar, and aspen. The production rates of gas and hydrogen also depended on the nature of feedstock; cedar and aspen performed better than cellulose.

Hu et al. [42] tested calcined olivine and dolomite in a fixed-bed reactor and found higher activities of calcined catalysts compared to those of natural catalysts. Other literature also showed that in the presence of olivine, tar conversion increased with an increase in temperature from 800°C to 900°C, and at 900°C and higher, all water-soluble heterocyclic compounds get converted [21] (Barrio et al., 2012, pers. comm.). With 17 wt% olivine in the sand at 900°C, the conversion of heavy polyaromatics increased from 48% to 71%. Calcined dolomite, however, increased the conversion up to 90%. Aznar et al. [44–46] showed that dolomite was very effective in removing tar coming from a blend of plastic waste with pinewood sawdust and coal in the temperature range of 750°C–880°C. Xu et al. [47] demonstrated that at 700°C, hydrogen concentration in the product increased by the use of CaO as an adsorption agent for carbon dioxide.

Monovalent alkali metals such as Li, Na, K, Rb, Cs, and Fr were also found to be catalytically active in steam gasification. Both K and Na are a part of biomass and accumulate in the ash, which in turn can act as a catalyst. This solves the problem of ash handling and the ash reduces the tar content in the gas phase. The ash catalytic activity, however, can be lost due to particle agglomeration. Sutton et al. [43] pointed out that direct addition of alkali metals can require (1) expensive recovery of catalyst, (2) increased char content after gasification, and (3) ash disposal problems. Lee [48] and Lee et al. [49] found that the addition of Na<sub>2</sub>CO<sub>3</sub> enhances the catalytic gasification of rice straw over a nickel catalyst and the additive increases the gas formation. They also found that the gas production rate is affected by the nature of the additive and follows the order: Na > K > Cs > Li. The use of activated alumina as a secondary catalyst was found to be effective by Simell et al. [50–52]; however, this catalyst deactivated faster due to coking compared to dolomite. Sami et al. [29] showed that both zirconia and alumina promoted toluene and ammonia conversions at lower temperatures, indicating enhanced oxidation activity of zirconia with alumina. Furthermore, H<sub>2</sub>S had a little effect on the activity of aluminadoped zirconia.

#### 4.2.3.2 Nickel-Based Catalysts

As mentioned earlier, the gasification and reforming in the presence of steam are overlapping reactions. Tar and lower hydrocarbons produced by the gasification can be simultaneously reformed in the presence of a suitable catalyst. Rostrup-Nielsen et al. [37] presented a very good review of applicability of transition metals (group VIII) and noble metal catalysts to steam gasification/reforming process. While a number of noble metal catalysts such as Ru and Rh have superior performance for steam reforming, the cost and easy availability of these catalysts compared to that of nickel, made the latter choice more practical. The literature has convincingly demonstrated the usefulness of nickel catalysts for biomass gasification [19-23,36,37,43]. Olivares et al. [53] showed that nickel reforming catalysts display 8-10 times more reactivity than calcined dolomite. Nickel catalysts can be, however, deactivated by the poisons such as sulfur, chlorine, and alkali metals. They can also be deactivated by the formation of coke. The coke deposition can be reduced by increasing steam/biomass ratio; however, this increases the energy cost and changes the gas-phase composition of the product. In general, Ni-gamma-alumina catalyst gave higher conversion and lower deactivation compared to Ni-alpha-alumina catalysts. The MgO/CaO addition to alumina also gives the catalyst more stability. Lanthanum-based pervoskite support was also found to be very effective. The topics of coking, catalyst deactivation, and effective support for the nickel are discussed in Sections 4.2.4, 4.3, and 4.4. Suffice to say that nickel-based catalysts have gained a significant support for steam gasification and reforming.

#### 4.2.4 CATALYSTS FOR STEAM REFORMING

In general, two types of sites are required for the steam reforming catalysts: the catalytic sites for hydrogenation and dehydrogenation and the acidic sites [22,23,28,36,37,41–56]. The acidic sites promote the formation of carbonium ions. For aromatization and isomerization reactions, the two types of sites are necessary. While, as mentioned earlier, Ni catalysts on oxide supports have been most extensively used in the industry, recent studies show that bimetallic catalysts such as Ni/Ru and Pt/Re have been more effective catalysts. Again, due to economical reasons, one of the catalysts needs to be nickel. Trimetallic catalysts of noble metal alloys have also been tested. In general, bi- and trimetallic catalyst activity and stability. Coke deposition on the catalysts has been the main reason for catalyst decay; however, coke can be removed by the oxidation at high temperatures. The coke deposition can vary from 15% to 25% on the catalyst [22,23,28,36,37,41–56].

The coke formation can occur by one or more of the following reactions:

$$CH_4(g) \rightleftharpoons 2H_2 + C(s)$$
 (4.25)

$$2CO(g) \rightleftharpoons CO_2(g) + C(s) \tag{4.26}$$

$$CO(g) + 2H_2(g) \rightleftharpoons H_2O(g) + C(s)$$
 (4.27)

$$\operatorname{CO}_2(g) + 2\operatorname{H}_2(g) \rightleftharpoons 2\operatorname{H}_2\operatorname{O}(g) + \operatorname{C}(s)$$
 (4.28)

Equation 4.25 is the famous Boudouard reaction. Coke can be formed from CO,  $CO_2$  as well as  $CH_4$ . Coke can also be formed from ethylene through the polymerization reaction as

$$C_2H_4 \rightarrow Polymers \rightarrow Coke$$
 (4.29)

The coke deposition at a sustained level should be avoided because it leads to several undesirable side reactions, loss in catalyst activity, and poor heat transfer between the catalyst and the gas phase. If the coke deposition becomes very extensive, it can block the open surface area causing an excessive pressure drop within the reactor and it can also cause localized "hot spots" that can induce "runaway" conditions for the reactor. Coke formation can be minimized by the use of an excess steam. The catalyst can also be regenerated periodically, by burning off the deposited coke through the oxidation reactions.

# 4.3 DRY REFORMING

While steam reforming has been extensively used to produce hydrogen, it is generally not a desirable process to make syngas of a diverse composition that may be needed for the downstream conversion of syngas to a variety of fuels and chemicals by Fischer–Tropsch (FT) and other processes [57–62]. To generate syngas of different composition, steam reforming is often coupled with dry reforming and partial oxidation. A combination of steam reforming, dry reforming, and partial oxidation is called "tri-reforming." Since both dry reforming and tri-reforming have strategic fuel values, they are briefly described in this and the following section.

Depending on the reaction conditions, steam reforming and water–gas shift reaction can also be accompanied by "dry reforming" reaction in which carbon dioxide produced from reverse water–gas shift reaction can react with hydrocarbons according to the following reactions:

$$\operatorname{CO}_2 + \operatorname{H}_2 \to \operatorname{CO} + \operatorname{H}_2 \operatorname{O} \quad \Delta H^0_{298\,\mathrm{K}} = 41.2 \,\mathrm{kJ/mol}$$

$$(4.30)$$

and

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298K} = 247.4 \text{ kJ/mol}$$
(4.31)

Here, the second "dry reforming" reaction is illustrated for methane. This reaction was first studied by Fischer and Tropsch in 1928. It is briefly covered here because of its close alignment with the steam reforming reaction. While the kinetic mechanisms for dry reforming and steam reforming reactions on conventional catalysts are very similar, generally steam reforming is faster and dry reforming requires higher temperature and is accompanied by more coke formation than steam reforming. While dry reforming provides a mechanism for chemical use of greenhouse gas "carbon dioxide," it is not the solution for the complete removal of carbon dioxide due to stoichiometry of various reactions occurring simultaneously. Generally, nickel and other noble metal catalysts, alone or composite bimetallic or trimetallic form, work well. The literature has shown that coking and catalyst deactivation issue can be partially addressed by the use of pervoskite and hydrotalcite (HT) catalyst supports with ABO<sub>3</sub> functionalities. Lanthanum- and strontium-based supports were found to be more effective. These catalysts reduce the degree of coking and the resulting catalyst deactivation. Dry reforming reaction produces  $H_2/CO$  ratio of 1, which is lower than 2 for partial oxidation and 3 for steam reforming.

Dry reforming gives good conversion generally at high temperature (around 850°C). Dry reforming is more endothermic than steam reforming and must be carried out at high temperature and low pressure to achieve maximum conversion. Besides noble metals, transition metal carbides (especially Mo) are also effective, but these catalysts are stable only at high temperatures.

There are at least two examples of the commercial process for the dry reforming of methane [57–62]. The industrial caloric process (CALCOR), which has been developed using nickel-based catalysts, is used for the production of CO-rich synthesis gas from natural gas or liquefied petroleum gas using a large excess of  $CO_2$ . Pure carbon monoxide is an important chemical feedstock, for example, in the production of acetic acid and phosgene, and it is important to produce on-site due to the transportation risks caused by its toxicity. This multistage process was developed by Caloric GmbH. In the first stage of the process, carbon dioxide and methane are reacted together producing a mixture of carbon monoxide, hydrogen, carbon dioxide, and water. The heat for the endothermic reaction is provided by the burning of fuel in a similar manner to the steam reforming process. In the next stage, carbon dioxide in the effluent stream is removed and recycled to the reformers. Carbon monoxide is separated from hydrogen (which can be used as a fuel and sold) and methane leaving only a very small amount of methane remaining in the product stream and giving purities up to 99.95%. The coking is prevented by packing the reactor with the catalyst that has varying activities and shapes.

The dry reforming of methane has also been practiced by the SPARG (sulfurpassivated reforming) process created by Haldor Topsøe [57–62]. It was commercialized at Sterling Chemicals Inc., Houston, Texas, in 1987. The process produces a variety of syngas compositions [57–62] and reduces H<sub>2</sub>/CO ratio from 2.7 to 1.8 without modification in steam reforming facility [38–43]. The process is operated at 915°C–945°C and coke deposition on Ni catalyst is reduced due to the treatment of the catalyst by sulfur. The process uses mixtures of CO<sub>2</sub> and H<sub>2</sub>O, and thus, it is a combined dry and steam reforming process. Impurities such as methane, hydrogen, or other hydrocarbons in the feed stream decrease the mechanical strength of polycarbonates produced from syngas via phosgene reaction path. Higher hydrocarbons are therefore removed in the pre-reforming step to reduce the product impurities as well as coke deposition on the catalyst. Sulfur in the product may require additional purification steps.

The literature indicates that the mechanism for dry reforming of  $C_1-C_3$  hydrocarbons is somewhat different from that of higher hydrocarbons [57]. The same holds for steam reforming reaction. The general route in the cases of  $C_1-C_3$  alkanes involves the dissociation of hydrocarbons and subsequent oxidation of carbon fragments; oxidative dehydrogenations of ethane and propane also proceed partially. The catalysts are in more reduced state and the activation of the hydrocarbon is the rate-controlling step. In the case of  $C_4$  and higher hydrocarbons, the first step of the process is direct hydrogenation of alkanes. Activation of carbon dioxide, but not the activation of hydrocarbon, is the rate-controlling step. Hydrogen formed interacts with carbon dioxide and shifts the equilibrium of the dehydrogenation reaction.

Just as for methane, a required condition for dry reforming of higher hydrocarbon is that the catalyst system adsorbs and activates carbon dioxide. The acidic property of  $CO_2$  necessitates the choice of a catalyst with basic properties. However, alkali metal and alkaline earth oxides are ineffective because of strong carbonate formation. Oxides of a moderate basicity are necessary, and moreover, they must participate in the redox process with  $CO_2$  reduction. While MnO was used in the earlier studies, its modification by oxides of K, Na, Cr, and La influences both its acceptor function and the degree of surface oxidation. It controls the mechanism of hydrocarbons and alcohol transformations. Possible other good candidates are  $La_2O_3$ , cesium oxides, and praseodymium oxides.  $La_2O_3$  showed the greatest interactions among  $CO_2$ , hydrocarbons, and alcohols. Binary oxide-based support system and dual metals can improve the performance. Promoters and the method of catalyst preparation also have an effect on the catalyst performance [57].

As mentioned earlier, the dry reforming of hydrocarbons leads to a variety of products and the transformation to syngas with different degrees of success depending on the operating conditions and the nature of the catalyst. The major issues with dry reforming are (1) endothermic nature of reaction requiring high-energy input for the reaction process, (2) difficulty in igniting the reaction at low temperature (lower than about 500°C), and (3) requiring very high temperature (>650°C) to reduce coke deposition on the catalyst. In sum,

- 1. The success of the CO<sub>2</sub> conversion depends on three factors: catalyst activity, catalyst stability (which depends significantly on the coke formation and the nature of the coke), and efficient heat transfer operations. While there are numerous catalysts examined in the literature, it is clear that nickel catalyst is still the most practical from an economic point of view at the commercial scale. Noble metal catalysts such as Rh, Ru, and Pt are more active and perhaps more stable, but they are too expensive to be of commercial value. Future research should be focus on bimetallic catalysts such as Ni—Ru. Ru is about 40–50 times less expensive than Rh, and therefore, it will carry more practical viability for the commercial process [57–62].
- 2. The nature of the catalyst support is also very important [57]. The support often interacts with metals, and because of that, it is often considered as part of the catalyst. The best situation is the uniform distribution of very active metals in small sizes distributed along the support and they do not migrate or sinter during high-temperature reforming process. Perovskite support offers special attraction because in this case metals are uniformly and tightly distributed in the support lattice. The catalyst must be a basic

in nature, but literature has shown that too much basicity does not help the reforming process. Along with Al<sub>2</sub>O<sub>3</sub>, lanthanum, cerium, and zirconium oxides need to be examined. Just like mixed metals, mixed supports should also be considered.

In more recent investigations on dry reforming, the overall objectives have been to devise (1) a process that has less coke deposition on the catalyst such that the catalyst is active and stable for a long period, (2) a process in which the catalyst ignites at as low temperature as possible, (3) a process that is heat efficient, (4) a process in which high conversion of  $CO_2$  and hydrocarbons is achieved, and (5) a process in which major products are carbon monoxide and hydrogen. As indicated earlier, the last objective is a particular problem without deep dehydrogenation when the hydrocarbons contain two or more carbon numbers.

## 4.4 TRI-REFORMING

Fundamentally, there are three types of high temperature reforming processes: stream reforming, dry reforming, and partial oxidation [57,63–65]. The term "tri-reforming" is applied to the process in which all of these reforming processes are combined in a single use. The three reforming processes are expressed by the following set of chemical reactions for methane:

1. Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H_{298\rm K}^0 = 206 \rm kJ/mol$
2. Dry reforming: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$\Delta H_{298\mathrm{K}}^0 = 247 \mathrm{kJ/mol}$
3. Partial oxidation: $CH_4 + O_2 \rightarrow CO + 2H_2$	$\Delta H_{298K}^0 = -38 \text{ kJ/mol}$

The water–gas shift reaction always accompanies these three reactions. The major technical problem of conducting steam reforming alone is carbon deposition on the catalysts that can lead to rapid deactivation and breakup of the catalyst. Carbon deposition can be substantially reduced by the use of an excess of water and a temperature of about 800°C. Other drawbacks of stream reforming are (1) the expensive generation of superheated steam (in excess) at high temperature; (2) the production of a significant amount of  $CO_2$  in the product gas causing the onset of reverse water–gas shift reaction ( $CO_2 + H_2 \rightarrow CO + H_2O$ ) particularly at high temperature; and (3) the  $H_2$ -to-CO ratio is higher than the optimum required for the downstream synthesis gas conversion to methanol, acetic acid, or hydrocarbons.

Partial oxidation offers some advantages over steam reforming. The reaction produces extremely high yields of syngas by an exothermic reaction, and therefore, the reactor would be more economical to heat. Oxygen is often used in steam reforming to provide heat and high methane conversion. Partial oxidation also gives a better ratio of hydrogen to carbon monoxide for subsequent conversion processes. The product gases from the reaction are low in carbon dioxide that must often be removed before the syngas can be used. Steam reforming and partial oxidation produce syngas of more moderate  $H_2/CO$  ratio (of about 2). This makes the direct use of syngas more versatile.

The dry reforming has the added advantage that it simultaneously consumes two greenhouse gases: hydrocarbons and  $CO_2$ . The best reducing agent for  $CO_2$ 

is hydrogen. While dry reforming converts carbon dioxide and hydrocarbons into useful syngas, the "tri-reforming" allows the process to produce the syngas with varying H<sub>2</sub>/CO ratios. The H<sub>2</sub>/CO ratio in syngas is very important for its further use for a variety of chemical products. Syngas can be converted to acetone, acetic acid, and ethylene by an exothermic reaction [22], while pure CO can be used for the production of acetic acid, formic acid, polyurethane, polycarbonates, methyl acrylates, and so on. Both dry reforming and steam reforming reactions are endothermic. The heat generated from partial oxidation reduces the need for expensive external heating. Both dry and steam reforming reactions require very high temperatures (>600°C) to reduce the cooking. While steam reduces carbon deposition, an addition of oxygen provides necessary heat that can jump start dry and steam reforming reactions and maintain the catalyst in a clean and carbon-free state through oxidation of coke on the catalyst surface. The extent to which oxygenates are added to the reforming reactions is strictly determined by the process conditions and the catalyst employed. Since dry reforming produces water, steam reforming always accompanies dry reforming, making these studies relevant for tri-reforming.

Finally, since the real systems where tri-reforming (a combination of steam reforming, dry reforming, and partial oxidation) will be applied consist of hydrocarbon mixtures, it is important to compare how different types of hydrocarbons will perform under the same operating conditions. Puolakka [65] made one such comparison and his results indicate that propane and ethanol give favorable product distributions compared to toluene and dodecane. Such results may help optimizing the composition of the mixed streams to get the best syngas (with desired  $H_2/CO$  ratio) production by tri-reforming. More work on "tri-reforming" is currently being pursued.

# 4.5 EFFECTS OF FEEDSTOCK AND OPERATING CONDITIONS ON PRODUCT DISTRIBUTIONS

# 4.5.1 STEAM GASIFICATION

# 4.5.1.1 Coal

Corella et al. [66] used the following model for steam gasification of coal at lowmedium (600°C-800°C) temperatures with simultaneous  $CO_2$  capture in a fluidized bed at an atmospheric pressure. The study also examines the effect of inorganic species on the gasification process.

The gasification of coal with steam follows the following set of reactions [66]: First, fast pyrolysis of coal follows the reactions:

$$Coal(C_{x}H_{y}O_{z}ISs) \rightarrow Tar 1 + Char 1 \rightarrow Tar 2 (CH_{0.85}O_{0.17}) + Char 2 (CH_{0.2}O_{0.13}ISs) + H_{2} + CO + CO_{2} + (4.32)$$
$$CH_{4} + C_{2}H_{4} + \cdots$$

Here, ISs are the inorganic species in the coal. The conversion of tar1 and char1 is a thermal reaction. Tar2 and char2 further react with steam and carbon dioxide as

$$\operatorname{Tar} 2(\operatorname{CH}_{0.85}O_{0.17}) + \operatorname{H}_2 O \to \operatorname{CO} + \operatorname{H}_2 + \cdots$$
 (4.33)

$$\operatorname{Char} 2(\operatorname{CH}_{0.2}\operatorname{O}_{0.13}\operatorname{ISs}) + \operatorname{H}_2\operatorname{O} \to \operatorname{CO} + \operatorname{H}_2 + \operatorname{Char} 3(\operatorname{C}_{xx}\operatorname{H}_{yy}\operatorname{O}_{zz}) + \operatorname{Ashes}(\operatorname{ISs}) (4.34)$$

$$\operatorname{Char} 2(\operatorname{CH}_{0.2}O_{0.13}\operatorname{ISs}) + \operatorname{CO}_2 \to \operatorname{CO} + \operatorname{H}_2 + \operatorname{Char} 3(\operatorname{C}_{xx}\operatorname{H}_{yy}O_{zz}) + \operatorname{Ashes}(\operatorname{ISs})$$
(4.35)

The above reactions are not in stoichiometric proportions. Steam reforming of methane and light hydrocarbons that may occur simultaneously is expressed as

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4.36}$$

$$C_2H_4 + H_2O \rightarrow 2CO + 3H_2 \tag{4.37}$$

Along with the shift reaction,

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$$
 (4.38)

All inorganic species with possible catalytic effects are designated as ISs. For example, iron-based species ( $Fe_2O_3$ ,  $Fe_3O_4$ , etc.) affect the rate of overall steam gasification reaction. Some of the reactions, in particular, reforming and water–gas shift reactions, are catalyzed by nickel. Inorganic species such as indium can also have a catalytic effect. Finally, alkaline and alkaline earth metallic species (sometimes called American Academy of Environmental Medicine [AAEM] species) such as K, Ca, Na, Cs, and Mg significantly influence the overall gasification process. AAEM species can be either parts of char generated or additives in the gasification of  $H_2$ ,  $CO_2$ , and  $CH_4$ ; and (3) tar content in the product gas. One of the AAEM species, CaO is a good absorbent for carbon dioxide to form calcium carbonate. During the gasification reaction, coke can be generated on CaO that can be removed by steam or carbon dioxide reactions with coke producing hydrogen and carbon monoxide. Thus, steam gasification of coal is often carried out with an addition of CaO so that the gasifier simultaneously removes carbon dioxide during the gasification process.

In general, carbon conversion and char gasification in a fluidized bed reactor increase with temperature between 600°C and 900°C. While tar yield (or tar content) and CO<sub>2</sub> capture decrease with an increase in the temperature in the same range. High contents of alkalis during gasification can also cause the problems of agglomeration, sintering, and melting, all of which are harmful to the smooth operation of the gasifier. Besides CaO, often calcined dolomites (CaO–MgO) and magnesium-based minerals silicates such as serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>], olivine (Mg<sub>0.9</sub>Fe<sub>0.1</sub>SiO<sub>4</sub>), and calcine limestones or calcites have also been tested.

The study showed that for a clean and efficient steam gasification of coal in a fluidized bed at low/medium temperatures, at an atmospheric pressure, and with

simultaneous capture of  $CO_2$ , the CaO/coal ratio is (1) a key parameter to obtain optimal product distribution, (2) a free parameter to be decided by the process designer, and (3) required to have relatively high values, clearly higher than 2 and perhaps as high as 80 or more. The type of coal or the types of ISs in the coal have some influence in the reaction network existing in the gasifier, but its influence is less than the effect of the temperature. Both product distribution and the usefulness of CaO are more controlled by temperature than AAEM, IS, and the nature of CaO.

Recently, Sharma [67,68] outlined a stepwise scheme to improve steam gasification reactivity of coal. In this scheme, coal is first refined using coal-derived solvents such as anthracene oil and paraffin oil. The refined coal has a higher amount of inorganic materials that can act as catalyst for the steam gasification to produce chemicals and char. The particle size of coal has no effect on the gasification reactivity, and the catalytic effects of minerals follow the order: Na > K > Ca > Ni [67]. The char is further subjected to steam gasification to produce syngas that can be further refined using steam reforming reaction. According to Sharma [67], the simplified set of reactions occurs during coal/char gasification as follows:

$$C_{90-120-240}H_{6-9-20}O_{x}S_{y}N_{z} + O_{2} + H_{2}O \rightarrow C_{n}H_{m} +$$
Other products (CO, CO<sub>2</sub>, etc.)
(4.39)

$$C_n H_m \to nC + mH \tag{4.40}$$

$$C + O_2 \rightarrow CO_2$$
  $\Delta H = -40.59 \text{ kJ/mol}$  (4.41)

$$C + O_2 \rightarrow 2CO$$
  $\Delta H = 159.7 \text{ kJ/mol}$  (4.42)

$$C + H_2O \rightarrow CO + H_2$$
  $\Delta H = 118.9 \text{ kJ/mol}$  (4.43)

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \qquad \Delta H = -40.9 \text{ kJ/mol}$$
(4.44)

$$C + 2H_2 \rightarrow CH_4$$
  $\Delta H = -87.4 \text{ kJ/mol}$  (4.45)

Shift reaction takes place only at high concentration of steam. The last reaction is important under pressure. Sharma [67] concluded that the main factors for the steam reactivity of gasification are (1) refining of coal that increases the surface area of coal, (2) volatile matters in residual coal and char (the more the volatile matter the more the reactivity), and (3) the concentration of mineral matter in coal and char. Sharma [68] also studied steam gasification reactions that can be useful for the reactor design. Exxon examined steam gasification of coal liquefaction residue [7]. Exxon technology utilized steam to sequentially gasify and hydrogenate both raw coal and carbon residue left in coal gasification. The study also used calcium hydroxide or a similar alkaline earth metal compound as possible catalysts for the process.

#### 4.5.1.2 Biomass

In the recent years, the steam gasification of biomass is gaining more importance because it produces gaseous fuel with high hydrogen content that can either produce electricity with high efficiency or provide a feedstock for various chemical and fuel productions. Steam gasification also (1) provides gases with high heating value, (2) reduces the diluting effect of nitrogen from air, and (3) eliminates the need for expensive oxygen separation plant. Catalytic gasification in a fluidized bed allows (1) lower temperature, (2) a variety of particle sizes, and (3) a variety of feedstock.

A serious issue in the broad implementation of steam gasification is the generation of unwanted materials such as tars, particles, nitrogen compounds, and alkali metals. Tar is a mixture of one- to five-ring aromatic hydrocarbons that can plug the reactor. Its removal is essential, which can be done either in the gasifier or by hot gas cleaning after the gasification process. Within the gasifier, tar can be reduced by choosing the appropriate operating parameters, inserting additive catalyst, or changing the gasifier design so that it cannot plug the reactor. The removal of tar thermally requires the operation of the gasifier at a temperature above 1000°C. The prevention of ash agglomeration however requires the gasifier at a temperature below 700°C. Ash frequently contains various oxides of Ca, K, Mg, P, Si, Na, and S that can agglomerate, deposit on the surface, and contribute to erosion and corrosion of the gasifier. Alkali metals can also react with silica to form silicates or with sulfur to form alkali sulfates, both of which are sticky and can cause sintering and defluidization [28,41-49,53-56,69-74] (Encinar et al., 2010, pers. comm.). Reforming tar using a Ni catalyst is an effective method for removing tar. The coke deposition in a reforming reaction can be reduced using excess steam. Catalytic steam gasification of biomass is a complete network of heterogeneous reactions [28,41-49,53-56,69-74] (Encinar et al., 2010, pers. comm.). The reactions can be described as follows:

Primary reactions:

$$C_x H_y O_z + H_2 O \rightarrow C(x-1) CO + \left(\frac{y}{2} + 1\right) H_2$$
 (4.46)

 $(C_x H_y O_z + H_2) \rightarrow (Heat)H_2 + CO + CO_2 + CH_4 + C_n H_{2m} + C(s) + Tars$  (4.47)

Secondary reactions:

$$C_n H_{2m} + n H_2 O \rightleftharpoons n CO + (n+m) H_2$$
(4.48)

Additional gas-phase reactions:

$$C + H_2 O \rightleftharpoons H_2 + CO$$
 (4.49)

$$C + CO_2 \rightleftharpoons 2CO$$
 (4.50)

$$C + 2H_2 \rightleftharpoons CH_4$$
 (4.51)

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$$
 (4.52)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
 (4.53)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$
 (4.54)



**FIGURE 4.2** A comparison of yields of hydrogen from beechwood at different temperatures via pyrolysis, supercritical water extraction, and steam gasification (with steam/solid = 2). (Adapted from Demirbas, M., *Energy Sources, Part A*, 28, 245–252, 2006.)

In order to operate gasification in the temperature range of 600°C–700°C, gasification is generally operated with reforming in the same reactor or in two stages.

Demirbas [72] compared the hydrogen production from conventional pyrolysis, steam gasification, and supercritical extraction. A comparison of hydrogen yield as a function of temperature for these three processes is illustrated in Figure 4.2 [72]. While the results described in this figure are for beech wood, similar results were obtained for corncob, olive waste, and wheat straw. The results show that an increase in the steam-to-biomass ratio increases the hydrogen production. At low temperature, supercritical extraction is the best process, whereas steam gasification produces the best results at higher temperatures. Inayat et al. [69] presented a model for steam gasification accompanied by CO<sub>2</sub> adsorption by CaO in a fluidized bed reactor. The model indicated that high steam-to-biomass ratio gave higher hydrogen production. While an increase in temperature gave an increased hydrogen production, at a very high temperature, reverse water-gas shift reaction changes the trend. The model showed that at a temperature of 950 K and a steam-to-biomass ratio of 3, hydrogen production was maximum. Demirbas [12,70,72,73] also studied other types of biomass such as hazelnut shell, tea waste, and spruce wood, and again showed that at higher temperatures, steam gasification gave higher hydrogen yield than conventional pyrolysis. Higher steam-to-biomass ratio also gave higher hydrogen production. Similar results for mosses and algae were reported by Demirbas [70]. Specific samples examined were Polytrichum commune, Thuidium tamarascinum, Cladophora fracta, Chlorella protothecoides, beech wood, and spruce wood. A kinetic model for steam gasification of a cellulose surrogate was presented by Salaices et al. [74].

Li et al. [71] examined catalytic steam gasification of municipal solid waste (MSW) in a combined (two-stage) fixed-bed reactor. The catalyst used was a trime-tallic catalyst (nano-Ni–La–Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and the MSW contained kitchen garbage,

wood and leaves, paper, textile, and plastics. The syngas composition was measured as functions of temperature, steam-to-MSW ratio, and catalyst-to-MSW ratio at an atmospheric pressure. The results showed >99% tar removal at 800°C with a significant production of hydrogen. The catalyst significantly improved hydrogen production. Higher temperature gave higher gas and hydrogen yields. While higher steam-to-MSW ratio gave better results, an excessive steam-to-MSW ratio lowered the gasification temperature and degraded the product quality. The optimum value of Steam/MSW ratio was found to be 1.33 under the operating conditions. The optimum value of the catalyst-to-MSW ratio was found to be about 0.5. A twostage (pyrolysis followed by catalytic steam gasification) process for olive waste was studied by Encinar et al. (2010, pers. comm.). The catalyst used was dolomite. The two-stage process produced gas, liquid, and solid, the yields of which were strongly dependent on the temperature and the amount of catalyst. Higher temperature and catalyst amount gave higher amount of gases and the presence of steam gave higher amount of hydrogen and carbon dioxide.

Hofbauer et al. [75–79] used a fast internally circulating fluidized bed (CFB; at a pilot scale) to gasify biomass with steam. Using a natural catalyst as bed material, and at a temperature of 750°C, tar content was significantly reduced and gas with high hydrogen content was obtained. The internal circulating bed allowed the flexibility in varying residence times needed to lower tar concentration. Herguido et al. [80] studied gasification of pine sawdust, pinewood chips, cereal straw, and thistles from energy crops in the presence of steam in a fluidized bed reactor. The product gases were hydrogen, CO, and CO<sub>2</sub>, and their amount and composition varied with the nature of biomass in the temperature range of  $650^{\circ}C$ -780°C.

A novel two-stage fluidized bed approach was used by Pfeifer et al. [81] in which the first stage carried out steam gasification of solid biomass to generate heat and power as well as provide raw materials for downstream chemical synthesis. The residual biochar from the first stage is combusted in the second stage and the hot bed materials from the second stage provide the heat needed for the first stage. This concept was also analyzed by Gopalakrishnan [82] and Matsuoka et al. [83]. The latter study showed that separating the combustion zone from the gasification zone resulted in high-efficiency gasification. They used  $\gamma$ -alumina as particles for bed materials and tested two different types of sawdusts. Since the residence time of the bed material can be controlled in the gasifier of the circulating dual bubbling fluidized bed system, the tars captured by the porous alumina particles (coke) as well as chars were effectively gasified. Since coke was preferentially gasified compared with char, higher carbon conversion and hydrogen yield can be achieved in this type of dual bed system than in the conventional CFB.

In the studies described earlier, the process generated gases with about 40 vol% hydrogen. Furthermore, an addition of carbonate adsorbed carbon dioxide and moved carbon dioxide from the gasification to the combustion zone (they called it adsorption-enhanced reforming [AER]). This concept has been successfully adapted by an 8 MW combined heat and power (CHP) plant in Güssing, Austria, since 2002. A new pilot plant of 100 kW has also been built to see the effect of the AER concept in improving hydrogen concentration to 75 vol% in the product gases. The possibilities of getting high hydrogen concentration, operating the reactors at low

temperature, and thereby improving energy conversion efficiency make this concept very attractive. As mentioned earlier, Salaices et al. [74] presented a very workable kinetic model for catalytic steam gasification of cellulose surrogate with Ni/alphaalumina catalyst in a CFB with a riser. The model successfully predicted the production of various gases such as hydrogen, carbon dioxide, carbon monoxide, water, and methane.

While a significant number of studies have investigated steam gasification in the presence of air (or oxygen) to improve carbon conversion and energy efficiency of the steam gasification process, Barrio et al. (2012, pers. comm.) examined the effect of hydrogen on the steam gasification process. They found that hydrogen inhibits the steam gasification reaction. They also concluded that the nature of char coming from beech or birch wood did not significantly affect the final results.

While a major effort on steam gasification is focused at a low temperature using a catalyst, Donaj et al. [84] and Gupta and Cichonski [85] examined the effectiveness of high-temperature steam gasification. Donaj et al. [84] examined the steam gasification of straw pellets at temperatures between 750°C and 950°C. The effect of the steam-to-feed ratio on carbon conversion was marginal (below 850°C), and in general, higher steam-to-feed ratio gave higher hydrogen production. Gupta and Cichonski [85] examined the steam gasification of paper, cardboard, and wood pellets in the temperature range of 700°C–1100°C. Once again in all cases, hydrogen production increased with the temperature and the steam-to-biomass ratio.

Lucas et al. [25] examined the high-temperature air and steam gasification (HTAG) of densified biofuels. The experiments were carried out in a fixed-bed updraft gasifier. The results showed that an increase in the feed temperature reduced the production of tars and soot and char residues, and also increased the heating value of the dry fuel gas produced. Butterman and Castaldi [86] showed that an increase in CO<sub>2</sub> feed rate enhanced the char conversion and the production of CO. The experiments produced a low concentration of methane and a high concentration of hydrogen (above 500°C for the herbaceous and nonwood samples and above 650°C for the wood biomass). The experiments also showed similarities between the gaseous products from biomass and MSW. The mass decomposition rates and the gas evolution profiles showed two distinct regions with transition around 400°C. Large pyrolysis char volumes correlated well with higher lignin compositions. The biomass fuels examined included woods, grasses, and other lignocellulosic samples. These included oak, sugar maple, poplar, spruce, white pine, Douglas fir, alfalfa, cordgrass, beachgrass, maple bark, pine needles, blue noble fir needles, pecan shells, almond shells, walnut shells, wheat straw, and green olive pit. The complete gasification occurred around 900°C-1000°C.

Aznar et al. [87] examined biomass gasification with steam $-O_2$  mixtures followed by a catalytic steam reformer and a CO-shift system. The use of two CO-shift converters downstream from a fluidized bed biomass gasifier, using steam $-O_2$  mixtures and a catalytic steam reformer, generated an exit gas with 73% hydrogen (by volume) on a dry basis and only 2.6% CO. The remaining gas contained CO<sub>2</sub>, O<sub>2</sub>, and CH<sub>4</sub>. The results showed that the H<sub>2</sub>O/CO ratio in the gas phase at the inlet of the hightemperature shift (HTS) reactor is a very important parameter in the system. CO conversion up to 90% was obtained, but to get this conversion, the steam/CO ratio greater than 2 at the inlet of the HTS reactor was needed. Due to low tar content in the inlet gas to the HTS reactor, a significant less deactivation of the catalyst in the shift reactor occurred.

### 4.5.1.3 Mixed Feedstock

In recent years, significant efforts have been made to gasify the mixtures of coal and biomass, coal and waste, or biomass and waste in the presence of steam. Seo et al. [30,88,89] used the successful two-stage fluidized bed model described earlier for coal-biomass blend in the temperature range of 750°C-900°C and the steam/fuel ratio of 0.5-0.8. Biomass-to-coal ratio was varied from 0 to 1. The study showed that the product gas yield, carbon conversion, and cold gas efficiency increased with increasing temperature and steam/fuel ratio. These parameters were higher for biomass gasification than those for coal gasification. A synergistic effect on gas yields was observed with a larger surface area, pore volume, and presence of micropores at a biomass/total feed ratio of 0.5. The calorific values of the product gas at 800°C were 9.89-11.15 MJ/m<sup>3</sup> with the coal, 12.10-13.19 MJ/m<sup>3</sup> with the biomass, and 13.77–14.39 MJ/m<sup>3</sup> with the coal–biomass blend. The maximum cold efficiency was 0.45 with a biomass/total feed ratio of 0.5. Sun et al. (2001, pers. comm.) examined various kinetic models for the gasification of biomass blended with waste filter carbon at temperatures around 850°C. Once again, high temperature and high flow of steam increased the gasification rate; the gasification rate of filter carbon was lower than that of wood chip. The data were taken for the steam pressure of 0.5 atm. A modified volume reaction kinetic model best fit all the data.

Kumabe et al. [27] showed that at 900°C, the mixture of woody biomass and coal in the presence of steam and air gave favorable results. The results of this study were similar to those described above; increase in biomass gave more gases and more hydrogen was produced at higher steam-to-feedstock ratio. Higher amount of biomass also gave lower amount of char and tar. The study produced gas with composition that was favorable to methanol, hydrocarbon fuels, and dimethyl ether (DME) under high biomass feed conditions. The co-gasification was carried out in a downdraft fixed-bed reactor and it provided cold gas efficiency ranging from 65% to 85%. Demirbas et al. [90], Demirbas and Caglar [91], and Demirbas [92,93] studied hydrogen production from various biomass samples, black liquor, biomass/coal, and biomass/heavy oil mixtures. In a most recent study, Demirbas [94] studied the effects of co-firing MSW with pulverized coal in a bubbling fluidized bed combustor. The results showed that the mixture produced less NO<sub>x</sub> and SO<sub>y</sub> in direct proportions to the MSW concentration in the mixture. Similarly, mixture produced less  $CO_2$  than coal alone. The mixture burning can, however, bring the problems with chlorine impurities in MSW that can lead to corrosion problems and inorganic impurities such as Si, Al, Ti, Fe, Ca, Mg, Na, K, S, and P that can significantly change the composition of ash and its melting and agglomeration characteristics. This change in ash characteristics may limit the market for its downstream use.

Numerous other investigators have also examined the steam gasification (some in the presence of air or oxygen) of a variety of coal-biomass mixtures. Chmielniak and Sciazko [95] produced syngas from steam gasification of coal-biomass mixture that was subsequently transformed to methanol, DME, ethylene, and gasoline.

Yamada et al. [31] also produced useful syngas from a mixture of coal and biomass briquettes. Kumabe et al. [27] examined steam gasification (with air) of a mixture of Japanese cedar and mulia coal and obtained useful syngas for the production of DME. Their gasification results were very similar to those described earlier and they obtained cold gas efficiency of 65%-85% during the gasification process. Pan et al. [96] examined steam gasification of residual biomass and poor coal blends. Pine chips from Spain were used as biomass, and the two types of coal—black coal (low grade) from Escatron, Spain, and Sabero coal from Sabero, Spain-represented poor-grade coals. Once again, reasonable quality of syngas was produced with an overall thermal efficiency of about 50%. Satrio et al. [97] examined steam gasification of coal-biomass mixture with the specially designed catalyst pellets with outside shell consisting of nickel on alumina and core consisting of calcium and magnesium oxides that can adsorb carbon dioxide. This catalyst design gave higher production of hydrogen. Finally, Ji et al. [32] studied steam gasification of a mixture of low-rank fuel mixture of biomass, coal, and sludge in a fluidized bed reactor at 900°C temperature. Just like other studies, higher temperature gave more gas and hydrogen but not high heating value of gas. The calorific value of syngas produced from sludge mixture, sludge, wood chips, and lignite was 13, 10, 6.9, and 5.7 MJ/m<sup>3</sup>, respectively.

An excellent review of problems associated with co-firing of coal and biomass fuel blends was given by Sami et al. [29]. This review critically assesses the effectiveness of this mixed feedstock for combustion and pyrolysis—two extreme cases of gasification. While they specifically do not discuss steam gasification and reforming, significant parts of their analysis are applicable to the process of steam gasification and reforming. Indrawati et al. [98] examined partial replacement of fossil energy by renewable sources such as rice husk, palm kernel shell, sawdust, and municipal waste in the cement production. While this study also does not specifically address steam gasification and reforming of mixed feedstock, the study points to another application of the mixed feedstock.

### 4.5.1.4 Tar

As indicated earlier, formation of tar is a major issue with steam gasification. Tar is a complex mixture of condensable hydrocarbons and it can contain one-ring to five-ring aromatic compounds with other oxygen containing hydrocarbon species [99–103]. Generally, tar is defined as  $C_6^+$  aromatic organics produced under gasification conditions. Tar is a problem during gasification because (1) it can deposit on the outlet pipes of the gasifier and also on the particulate filters; (2) it can clog fuel lines and injectors in the internal combustion engine; and (3) it reduces the gasifier's efficiency to produce additional useful fuel products such as hydrogen, carbon monoxide, carbon dioxide, and methane.

Baker et al. [99] illustrated the conceptual relationship between tar disappearance and the temperature during thermal steam gasification of carbonaceous materials. They also divided tar components in four different categories (Equation 4.55) [99]. The first category is easiest to crack and the fourth category (which mostly contains polycyclic aromatic hydrocarbons) is the most difficult to crack. Their analysis showed that at low temperatures (400°C), a significant amount of tar is produced, and at temperatures higher than around 1000°C, very little tar is produced. The literature has shown that as temperature increases, the nature of tar undergoes the following transformation [99–103]:

Mixed oxygenates (400°C) (primary)  $\rightarrow$ Phenolic ethers (500°C) (secondary)  $\rightarrow$ Alkyl phenolics (600°C) (tertiary-alkyl)  $\rightarrow$  (4.55) Heterocyclic ethers (700°C) (tertiary-PNA)  $\rightarrow$ PAH \* (800°C)  $\rightarrow$  Larger PAH (900°C)

In the above reaction, PAH\* is high-molecular-weight polynuclear aromatic hydrocarbons. Along with the temperature, tar concentration depends on the reaction time, the amount of oxygen, and the presence of a suitable catalyst during steam gasification. Higher oxygen concentration generally reduces tar concentration through the processes of cracking and oxidation among others. The conventional steam gasification operated at 700°C–800°C produces tar with naphthalenes, acenaphthylenes, fluorenes, phenanthrenes, benzaldehydes, phenols, naphthofurans, and benzanthracenes. While high-temperature steam gasification operating between 900°C and 1000°C produces tar that contains naphthalenes, acenaphthylenes, fluranthenes, pyrenes, acephenanthrylenes, benzanthracenes, benzopyrenes, 226 MW (molecular weight) polycyclic aromatic hydrocarbons (PAHs), and 276 MW PAHs. Milne et al. [100] further characterized tar in terms of primary, secondary, and tertiary products based on molecular beam mass spectroscopy. Some of the details of the constituents of primary, secondary, and tertiary products and their behavior with temperature are described by Milne et al. [100].

#### 4.5.1.5 Black Liquor

Huang and Ramaswamy [104] examined steam gasification of black liquor coming out of the paper and pulp industry at temperatures as high as 1500°C. Their results were in agreement with other reports. The carbon conversion was nearly complete at temperatures higher than about 750°C. Hydrogen concentration first increased with temperature but showed a maximum at high temperatures because of the dominance of reverse water–gas shift reaction. Higher steam gave higher hydrogen concentration in the product gas. Operating with a 0.3 < SBR < 0.6 in combination with high pressure of 30 atm, high temperature of 1000°C appears to be the most beneficial for obtaining smelt with no C(s) and maximizing Na and S capture in the melt. Here SBR is steam-to-dry black liquor ratio.

Black liquor gasification can be used to substitute the existing combustion process for potential higher energy efficiency, lower greenhouse gas emissions, and more safety. The steam gasification of black liquor technology can help the current paper and pulp mills technology to be extended into future biorefineries. In general, the equilibrium model examined by Huang and Ramaswamy [104] indicates that the hydrogen concentration in the product increased with a decrease in pressure and an increase in SBR, and it showed a maximum with an increase in temperature. Li and Heiningen [38] also illustrated the conversion data for a black liquor via steam gasification with and without catalysts. Whitty [105] examined steam gasification of black liquor char under pressurized conditions.

#### 4.5.1.6 Lignin

The gasification of lignin has been investigated by a number of investigators [106–108]. These and other studies have investigated various characteristics of pyrolysis and gasification of lignin, the effect of alkali addition on gasification and production of hydrogen and medium heating value gas during steam gasification of lignin. Most studies have examined lignin from paper and pulp industries as well as Westvaco Kraft lignin. In the latter category, Kraft-1, Kraft-2, and Alcell were gasified in the presence of steam at 600°C–800°C and they produced gases with 30–50 vol% hydrogen. Most studies used a fixed-bed reactor.

### 4.5.2 STEAM REFORMING

#### 4.5.2.1 Ethanol

As discussed in a subsequent chapter 9, alcohols and in particular ethanol can be easily obtained by the process of fermentation of sugar, glucose, fructose, and many lignocellulosic biomass [109–116]. In Brazil, ethanol is extensively produced using sugarcanes. Ethanol is easier and safer to store and transport because of its low toxicity and volatility and biodegradable characteristics. Ethanol can also be produced from various energy plants, waste materials from agro industries, or forestry residue materials as well as cellulosic and organic fractions of MSW. Easy availability of ethanol makes it a good candidate for steam reforming to produce hydrogen.

Unlike methanol and gasoline derived from fossil fuel sources, ethanol derived from biosources is carbon neutral to the environment. The carbon dioxide produced from the steam reforming of ethanol can be used to regenerate additional biomass. Bioethanol, generally containing about 12% ethanol in an aqueous solution, can be directly subjected to steam reforming, thus eliminating the distillation step required to produce pure ethanol. Since both water and ethanol can be converted to hydrogen, the process of steam reforming avoids the separation stage. The thermal efficiency of steam reforming of aqueous ethanol solution is very high (>85%) and this makes the process economically very attractive. The steam reforming of ethanol is carried out by the following reaction:

$$C_2H_5OH + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 \tag{4.56}$$

This reaction follows a number of steps that involve the dehydrogenation of ethanol to form acetaldehyde, which in turn decomposes to produce methane and carbon monoxide. Further reforming of methane and water–gas shift reaction leads to the formation of hydrogen. Since ethanol has high hydrogen content, the process produces a significant amount of hydrogen. There are, however, side reactions such as dehydration and decomposition of ethanol which produce methane, diethyl ether, and acetic acid that reduce the production of hydrogen. These side reactions can be minimized by the use of selective catalysts. In addition, the formation of large amounts of carbon monoxide reduces the hydrogen yield and it also requires complex gas cleanup process. Overall, ethanol is still one of the best raw materials for steam reforming to produce hydrogen.

An extensive number of studies to develop different types of catalysts for ethanol steam reforming have been reported in the literature [109–116]. Mas et al. [109] used Ni(III)-Al(III) lamellar double hydroxide as catalyst precursor. They developed a Langmuir-Hinshelwood type of kinetic model for steam reforming of ethanol for this catalyst. A general model was found to be valid for a wide range of water/ethanol feed ratio and temperatures. Biswas and Kunzru [110] examined the effects of copper, cobalt, and calcium doping on Ni-CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts for steam reforming of ethanol. The data were obtained in the temperature range of 400°C–650°C. The nickel loading was kept fixed at 30 wt%, whereas Cu and Co loading was varied from 2 to 10 wt% and Ca loading was varied from 5 to 15 wt%. For Cu- and Ca-doped catalysts, the activity increased significantly; however, Co-doped catalysts showed poor activity. The catalyst activity was in the order:  $Ni > NiCu_5 > NiCa_{15} > NiCo_5$ . For steam reforming reaction, the highest hydrogen yield was obtained on the undoped catalyst at 600°C. With calcium doping, in the temperature range of 400°C-550°C, higher hydrogen yield was obtained compared to those for undoped catalysts. Akdim et al. [111] compared the steam reforming of non-noble metal (Ni-Cu) with noble metals (Rh or Ir) supported over neutral SiO<sub>2</sub>, amphoteric Al<sub>2</sub>O<sub>3</sub>, and redox CeO<sub>2</sub>. The data showed that for each domain of temperature, quite different mechanistic routes were governing for the three tested systems. The data suggested some methods that improved the catalyst formula for the steam reforming of ethanol. Finally, the effect of support on catalytic behavior of nickel catalysts in the steam reforming of ethanol for hydrogen production was investigated by Fajardo et al. [112]. They studied Al<sub>2</sub>O<sub>3</sub>-, MgO-, SiO<sub>2</sub>-, and ZnO-supported nickel catalysts and showed that the catalyst behavior can be influenced by the experimental conditions and chemical composition of the catalysts.

The steam reforming of ethanol by different types of Co catalysts was investigated by Sekine et al. [113], Song et al. [115], and He et al. [116]. Sekine et al. [113] examined steam reforming of ethanol over Co/SrTiO<sub>3</sub> with an addition of another metal: Pt, Pd, Rh, Cr, Cu, or Fe. Ethanol conversion and H<sub>2</sub> yield improved significantly by adding Fe and Rh at 823 K; however, Rh addition promoted  $CH_4$  formation. Within Fe loading of 0.33–1.33 mol%, Fe addition increased the selectivity of steam reforming of ethanol. The addition of Fe on Co/SiO<sub>2</sub> catalyst was not very effective. High activity of Fe/Co/SrTiO<sub>3</sub> catalyst came from interaction among Fe, Co, and SrTiO<sub>3</sub>. Song et al. [115] showed that the use of novel synthesis methods such as solvothermal decomposition, colloidal crystal templating, and reverse microemulsion to prepare CeO<sub>2</sub>-supported Co catalysts gave better performance than the catalysts prepared using conventional incipient wetness impregnation method for ethanol steam reforming. The improvement can be attributed to a better cobalt dispersion and a better Co-CeO<sub>2</sub> interaction for the catalysts prepared using these novel methods. He et al. [116] examined a series of Co-Ni catalysts prepared from HT-like materials by coprecipitation for steam reforming of ethanol. The results showed that the particle size and reducibility of the Co-Ni catalysts are influenced by the degree of formation of HT-like structure and increasing Co content. All catalysts were active and stable at 575°C. The activity decreased in the order: 30Co-10Ni > 40Co-20Ni > 20Co > 10Co-30Ni > 40Ni. The 40Ni showed the strongest resistance to deactivation, whereas all Co-containing catalysts showed higher activity than 40Ni catalyst. The highest hydrogen yield was found for 30Co-10Ni catalyst in which XCo and Ni are intimately mixed and dispersed in the HT-derived support.

Dong et al. [114] examined hydrogen production by steam reforming of ethanol using potassium-doped  $12CaO-7Al_2O_3$  catalysts. The conversion of ethanol and  $H_2$  yield over  $C_{12}A_7O^{-}/x\%$ K catalyst mainly depended on the temperature, K-doping amount, steam-to-carbon ratio, and contact time. Based on numerous types of catalyst analysis, the authors concluded that the active oxygen species and doped potassium play important roles in the steam reforming of ethanol over  $C_{12}A_7-O^{-}/27.3\%$ K catalyst.

As shown earlier, the steam reforming of ethanol undergoes several reaction pathways depending on the catalysts and the reaction conditions. Therefore, the choice of the catalyst plays a vital role in the reforming process. Navarro et al. [13] pointed out that the reactions to avoid are  $C_4$  and  $C_2H_4$  inductive of carbon deposition on the catalyst surface. Thus, the catalysts that selectively produce hydrogen must (1) dehydrogenate ethanol, (2) break the carbon–carbon bonds of surface intermediates to produce CO and  $CH_4$ , and (3) reform these  $C_1$  products to generate hydrogen. As shown earlier, various oxide catalysts, metal-based catalysts (Ni, Co, Ni/Cu), and noble metal-based catalysts (Pt, Pd, Rh) have proven to be active for steam reforming of ethanol. The metallic function and the acid-based properties play an important role in the steam reforming. A good review of hydrogen selectivity and coking resistance of various types of catalysts is given by Navarro et al. [13].

### 4.5.2.2 Methanol

Methanol is an abundant chemical often produced from fossil fuels as well as biomass [117–134]. Industrially, it is produced at 250°C–300°C temperature and 80–100 atm pressure using a copper–zinc-based oxide catalyst. Methanol is an important feed-stock for the production of hydrogen and hydrogen-rich syngas. While methanol can be decomposed as

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H_{298K}^0 = 90.1 \text{ kJ/mol}$$

$$(4.57)$$

and this reaction is endothermic and can be catalyzed by a number of catalysts including Ni and Pd, in this chapter, we mainly focus on steam reforming of methanol. Methanol is a good feedstock because of its easy availability, high-energy density, and easy storage and transportation. Currently, a significant work is being carried out for low-temperature steam reforming to produce high-purity hydrogen for power generation in FC in automobiles. The steam reforming of methanol follows the reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H_{298K}^0 = 49.4 \text{ kJ/mol}$$
 (4.58)

While a number of catalysts have been examined, commercial Cu/ZnO water–gas shift reaction and methanol synthesis catalysts have been found to be effective for steam reforming of the methanol. Copper on  $ZrO_2$  support prepared by a numerous

different methods including precipitation, microemulsion, formation of amorphous aerogels, CuZr alloys, and so on have been successfully attempted. For this catalyst, a large surface area of the active metals needs to be maintained to avoid rapid deactivation. For this, zirconia support should be in the amorphous state under the calcination and reaction conditions. Cu/ZnO/ZrO<sub>2</sub> catalyst has been found to be active at a temperature as low as 170°C, but the catalyst deactivates rapidly at temperatures above 320°C. The deactivation can, however, be reduced by the incorporation of Al<sub>2</sub>O<sub>3</sub> that increases the temperature of crystallization of ZrO<sub>2</sub>, which remains amorphous at the reaction temperature. The incorporation of alumina also increases both the copper and the Brunauer, Emmett, and Teller (BET) surface area, thereby increasing the catalyst activity.

Henpraserttae and Toochinda [117] examined a novel preparation technique of Cu/Zn catalyst over  $Al_2O_3$  for methanol steam reforming. The study focused on the preparation methods of active Cu/Zn-based catalysts with and without urea by incipient wetness impregnations to lower the metal loading and the catalyst cost. The experimental data for methanol steam reforming were obtained in a fixed-bed reactor in the temperature range of 453–523 K to lower the energy costs. The data showed that the activity in the hydrogen production from the catalysts with urea was higher than that from the catalysts without urea. The impregnated catalysts can show the activity at temperatures as low as 453 K. The Cu/Zn catalysts prepared with an incipient wetness impregnated catalysts could be alternative catalysts for hydrogen production from methanol reforming with a lower cost of the catalyst compared with the co-precipitation method used in the commercial operation. More details on methanol synthesis technology from various raw materials are given by Lee [118].

The partial oxidation of methanol is attractive because it is an exothermic reaction and it follows the reaction:

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CO_2 + 2H_2 \qquad \Delta H^0_{298K} = -192.2 \text{ kJ/mol}$$
 (4.59)

The above reaction starts at the temperature as low as 215°C. Both the reaction rate and the selectivity for hydrogen increase very rapidly with temperature. The carbon monoxide formation in the entire temperature range is low. The literature has shown that production of hydrogen and carbon dioxide increases with copper content and it reaches the maximum with 40/60 atomic percentage of copper and zinc [117–134]. Unreduced copper-zinc oxide catalysts display very low activities and produce only carbon dioxide and water with very little hydrogen. The catalysts, however, become eventually reduced under high-temperature reaction conditions. The apparent activation energy and the TOF are higher at lower copper content and slightly decrease with an increase in the copper content and then achieve a constant value. These and some other similar data show that the reaction depends on both ZnO and CuO phases. Methanol conversion increases with oxygen partial pressure up to 0.063 atm. A further increase in oxygen partial pressure precipitously decreases methanol conversion. The incorporation of  $Al_2O_3$  (up to 15% Al) to the Cu/ZnO system results in a lower activity, implying that aluminum has an inhibiting effect on the partial oxidation of methanol.

Besides Cu/ZnO catalyst, Pd/ZnO catalyst has also been effective in methanol partial oxidation reaction. For 1 wt% Pd/ZnO catalyst, methanol conversion reaches 40-80% within the 230°C-270°C range. Methanol conversion and H<sub>2</sub> selectivity increase with an increase in temperature. The nature of support also affects the kinetics. Pd/ZrO<sub>2</sub> catalyst, while producing hydrogen and carbon dioxide, also shows a significant increase in the decomposition reaction.

A combination of steam reforming and partial oxidation results in an auto-thermal operation. Under this condition, the following reaction

$$CH_3OH + (1 - 2n) H_2O + nO_2 \rightarrow CO_2 + (3 - 2n)H_2 \quad (0 < n < 0.5) \quad (4.60)$$

with copper-based catalysts also perform well. On Cu/ZnO catalyst, initially methanol is combusted by oxygen and water is produced. When oxygen is depleted, methanol conversion and the production of hydrogen and carbon monoxide increase, and the water production goes down. When  $Al_2O_3$  is added to the catalyst, better performance for steam reforming is obtained. Purnama et al. [119] also found the beneficial effect of oxygen addition to the feed during steam reforming of methanol on Cu/ZrO<sub>2</sub> catalysts. In the auto-thermal operation, the relative ratio of oxygen, methanol, and steam plays an important role on hydrogen production. For Cu–ZnO (Al) catalyst, the best feed ratio of oxygen/methanol/steam was found to be 0.3/1/1. In general, oxy reforming of methanol is complex, but it also strongly interacts with water–gas shift reaction.

The auto-thermal operation of methanol for FC application in vehicles has been adopted by DaimlerChrysler, Toyota, and Nissan. Small-scale hydrogen production by reforming methanol is also commercialized. For its application in refueling station, hydrogen purification step is needed. This is generally carried out by either pressure swing adsorption (PSA) or membrane separation technology. In general, the cost of hydrogen production from methanol reforming is higher than that from methane reforming. The Mercator project funded by the European Commission is an integrated methanol steam reformer and selective oxidation system. The FC contains a series of catalytic plates with combustion of anode off-gas on one side and steam reforming of methanol on the other side.

A number of studies examined the metal-supported catalyst systems for steam reforming of methanol for FC applications [120–134]. Such catalysts overcome the slow heat transfer of packed-bed systems by integrating endothermic steam reforming with exothermic hydrogen combustion. A wash-coated aluminum heat exchanger showed the best performance using a suspension of commercial reforming catalysts. With an aluminum foam, 90% methanol conversion was achieved for a sustainable period of time (about 450 h). Lindström [120], Lindström and Pettersson [121–124,126,127], Lindström et al. [125,129], and Kolb et al. [128] examined methanol reforming over copper-based catalysts for FC applications.

A novel technology of steam reforming of methanol accompanied by palladium membrane separation to produce pure hydrogen was investigated by Pan and Wang [131,132] and Pan et al. [133]. This technique provides a possibility for bypassing the technical problems of storage and delivery of hydrogen by delivering methanol to forecourt hydrogen-dispensing stations and on-site hydrogen productions. Li et al.

[134] examined a strategy in which a coal-derived methanol is used as a hydrogen carrier. The steam reforming of methanol can generate hydrogen at the desired place.

#### 4.5.2.3 Liquid Hydrocarbons

Besides methane, methanol, and ethanol, gasoline, diesel, and jet fuel can also be important feedstock for the steam reforming to produce hydrogen [135–142] (Sun et al. 2001, pers. comm.). These three types of fuels contain a variety of hydrocarbons and sulfur. While these components themselves can be important feedstock for steam reforming, they are not as readily available on a large scale as various other fuels. The technical problems associated with these hydrocarbons include (1) the catalyst deactivation by sulfur in the feedstock and (2) the significant amount of coke deposition on the catalyst that eventually results in its deactivation. Along with steam reforming, in the recent years, catalytic partial oxidation of high hydrocarbons using short contact time (milliseconds) and high temperatures (850°C–900°C) over noble metal catalysts on porous monolithic ceramic supports have been examined [135–142] (Sun et al. 2001, pers. comm.). These reactions can be represented by a generalized reaction:

$$C_n H_m + \frac{n}{2} O_2 \rightarrow nCO + \frac{m}{2} H_2$$
(4.61)

The above reaction is about two times faster than the steam reforming reaction and the heat of reaction generated by this reaction depends on the oxygen-to-fuel ratio. Unlike steam reforming and partial oxidation of methane, methanol, and ethanol, steam reforming and partial oxidation of fuels involve dehydrogenation, C-C bond cleavages, total oxidation, steam reforming, CO<sub>2</sub> reforming, hydrocarbon cracking, methanation, and water-gas shift reaction all occurring simultaneously. In addition, these reactions occur for all different component hydrocarbons at different rates. Thus, the process is very complex and not clearly understood. In general, aromatics are less reactive and are more prone to the reaction producing cokes than aliphatic components and olefins. Through a complex set of reactions, fuels also produce hydrogen, carbon dioxide, carbon monoxide, and water along with a significant amount of lower hydrocarbons. The final product distribution depends on the temperature and the residence time. Several catalysts including nickel, platinum, rhodium, and bimetallic have been tested for hydrocarbons such as n-octane, n-heptane, and n-hexane [135-142] (Sun et al. 2001, pers. comm.). In general, ceria and zirconia supports or a mixture of ceria-zirconia supports has been found to be reasonably effective in averting coke deposition [135-142] (Sun et al. 2001, pers. comm.).

A combination of steam reforming, partial oxidation, and water–gas shift reaction has been tested to obtain an auto-thermal operation. Generally, partial oxidation and steam reforming are carried out in separate zones, with the first one controlled by the oxygen-to-carbon ratio and the second one by the steam-to-carbon ratio. The adiabatic temperature and the amount of hydrogen produced depend on the relative amounts of energy released in these two steps. Higher steam-to-carbon ratio reduces the carbon monoxide concentration in the product. For diesel fuel, thermodynamic equilibrium can be achieved at an oxygen-to-carbon ratio of 1 and a steam-to-carbon ratio of 1.25 at 700°C temperature.

The advanced thermal recycling (ATR) process requires catalysts and supports with high resistance to coking at high temperatures. Excess steam and/or oxygen helps avoid coking. Also at high temperature, sulfur is less of a problem. The noble metal catalysts (Pt, Rh, Ru) supported on ceria or zirconium or their mixtures work well. In the recent years, applications of pervoskite oxides (ABO<sub>3</sub>) for steam reforming of higher hydrocarbons and various fuels have been extensively examined [135–142] (Sun et al. 2001, pers. comm.). A group of six metal carbides has also shown a good success.

### 4.5.2.4 Glycerol

Glycerol has been a byproduct of a number of conversion processes, particularly transesterification of used oil, algae, and crop oils (there are about 350 of them) to produce diesel fuel [143–155] (Cheng et al., 2012, pers. comm.). This byproduct can also be effectively utilized to produce hydrogen by steam reforming process. Steam reforming of glycerol involves a complex set of reactions, numerous intermediates, and hydrogen that is accompanied by several other products. The hydrogen yield depends on the steam-to-glycerol ratio and follows the reactions:

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \tag{4.62}$$

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$$
 (4.63)

With an overall reaction as

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$$
 (4.64)

Simonetti et al. [148] showed that at about  $275^{\circ}$ C, glycerol can be catalytically converted to H<sub>2</sub>/CO mixture. Because of this low temperature, the endothermic steam reforming process can be combined with an exothermic FT process to make the overall process energy efficient for fuel generation from glycerol. The primary products for steam reforming of glycerol are hydrogen, methane, carbon dioxide, carbon monoxide, carbon, and unreacted water and glycerol. The formation of methane competes with the formation of hydrogen. According to steam reforming and decomposition reactions,

$$C_x H_y O_x + x H_2 O \rightarrow x CO_2 + \left(\frac{x+y}{2}\right) H_2$$
 Steam reforming (4.65)

$$C_x H_y O_x \rightarrow x CO + \frac{y}{2} H_2$$
 Decomposition reaction (4.66)

The maximum hydrogen concentration in the product can be either 77% or 57%. A study by Adhikari et al. [151,153] showed that at about 680°C, the upper limit of moles of hydrogen per mole of glycerol produced is six at an atmospheric pressure and at a steam-to-glycerol ratio of nine.

While nickel on alumina is a workable catalyst for steam reforming of glycerol, the effects of numerous promoters such as Ce, La, Mg, and Zr were examined at 600°C [143–155] (Cheng et al., 2012, pers. comm.). These results indicate that all promoters improved the production of hydrogen with zirconium giving the best results. The increase in hydrogen production can be due to an increased nickel concentration, an increased capacity to activate steam, and the stability of nickel phase.

Recent studies [143–155] (Cheng et al., 2012, pers. comm.) investigated various noble metal catalysts on a variety of supports at 500°C–600°C, an atmospheric pressure, and a steam-to-carbon molar ratio of 3.3. The results indicated the activity order: Ru = Rh > Ni > Ir > Co > Pt > Pd > Fe. Among  $Y_2O_3$ ,  $ZrO_2$ ,  $CeO_2$ ,  $La_2O_3$ ,  $SiO_2$ , MgO, and  $Al_2O_3$  supports,  $Y_2O_3$  (along with  $ZrO_2$  and  $CeO_2$ ) support gave the best glycerol conversion and hydrogen production. These studies also demonstrated that at low conversion and low temperature (225°C–275°C), Pt/C and Pt–Re/C gave stable results. For CeO<sub>2</sub> support, Zhang et al. [145] showed that at 400°C, Ir/CeO<sub>2</sub> gave the best glycerol conversion with 85% hydrogen selectivity, whereas Co/CeO<sub>2</sub> and Ni/CeO<sub>2</sub> gave 88% and 75% hydrogen selectivity at 425°C and 450°C, respectively. Glycerol has a higher tendency for coke formation compared to methane and this coke formation can be significantly reduced by increasing the steam-to-glycerol ratio in the feed. The catalytic steam reforming of glycerol (both conversion of glycerol and selectivity of hydrogen) is affected by the operating parameters such as the reaction temperature, the pressure, the steam-to-glycerol ratio, and the oxygen-to-glycerol ratio.

In a recent study, Maciel and Ishikura [144] have given an outstanding review of steam reforming of renewable feedstock for the production of hydrogen. They have considered methanol, ethanol, glycerol, glucose, and biomass as potential raw materials for steam reforming. Their overall analysis led to the following conclusions: (1) reforming should be carried out at lower temperatures and an atmospheric pressure to reduce the operating costs; (2) the catalyst should provide high selectivity to hydrogen and inhibit CO and byproduct formation such as methane; and (3) the catalyst must resist coke formation that reduces the number of active sites and hence the reaction rates, and implies a regeneration process that is costly. Feedstock issues such as supply, cost, logistics, and the value of byproducts are major factors in costeffectiveness of steam reforming process.

#### 4.5.2.5 Biomass

Just like methane and other hydrocarbons, biomass can also undergo partial oxidation and steam reforming in the presence of oxygen and steam at temperatures above around 725°C yielding gaseous products and chars [156–171]. The char can also be converted to gaseous products such as hydrogen, carbon dioxide, carbon monoxide, and methane under high-temperature conditions. The overall reaction is as follows:

$$C_x H_y O_z + H_2 O + O_2 \rightarrow H_2 + CO_x + CH_4 + HCs + char$$
(4.67)

The hydrogen production for a variety of biomass under different operating conditions has been examined in the literature [156–171]. The literature data indicate that in a fluidized bed reactor, under suitable operating conditions, as high as 60 vol% hydrogen can be produced from biomass. The major drawback of steam reforming of biomass is the tar formation that is not easily amenable to steam reforming process. The tar formation can be minimized by suitable operating conditions (i.e., operating at very high temperature), suitable gasifier design (i.e., entrained bed reactor), or incorporation of additives or promoters to the catalysts. At temperatures above around 1000°C, tar can be cracked, and for temperatures above around 1200°C, pure syngas can be obtained. Higher residence time can also help cracking of the tar. The additives such as dolomite and olivine to the nickel catalyst help to reduce the tar formation. Alkaline metal oxides are also used to reduce the tar formation.

Another important issue with biomass gasification and reforming is the formation of ash that can cause slagging, fouling, and agglomeration. The inorganic impurities in biomass can be removed by biomass pretreatment using leaching and extraction processes. The literature has shown the leaching and subsequent gasification to produce hydrogen as a viable process for olive oil waste [156–171].

Pacific Northwest National Laboratory studied the gasification of biomass to produce a variety of gaseous fuels using appropriate catalysts. The earlier studies used a catalytic steam gasification of biomass with concurrent separation of hydrogen in a membrane reactor that employed a permselective membrane to separate the hydrogen as it is produced [156–171]. The process was particularly well suited for wet biomass and may be conducted at temperatures as low as 300°C. One experiment was conducted at 4000 psi pressure and 450°C, although most others were at 15-30 psi. The process was named SepRx. Optimal gasification conditions were found to be at about 500°C, an atmospheric pressure, and a steam/ biomass ratio of 10/1. In the presence of a nickel catalyst, the product hydrogen concentration of 65 vol% was generated under these optimal conditions. Rapagna [168] examined steam gasification of almond shell in the temperature range of 500°C–800°C. Smaller particle size yielded more hydrogen. Rapagna and Foscolo [169] examined catalytic steam gasification in a fluidized bed reactor followed by a fixed-bed catalytic reactor. Over a temperature range of 660°C-830°C, the catalytic converter using different steam reforming nickel catalysts and dolomite gave as high as 60% hydrogen yield.

Steam gasification and steam reforming can be coupled processes. Mckinley et al. [165] examined various biomass gasification processes for the production of hydrogen. Turn et al. [166] showed that for a noncatalytic gasification of sawdust, the highest hydrogen yield was obtained at 825°C and for a steam/biomass ratio of 1.7. Zhou et al. [167], however, showed that for the production of hydrogen, adding steam to the gasification process was not as effective as adding steam to downstream nickel-catalyzed steam reforming process.

### 4.5.2.6 Mixed Feedstock

In the recent years, significant efforts have been made to gasify and steam reform mixed feedstock of coal and waste, coal and biomass, and various types of biomass. These studies are described in a recent publication by Lee and Shah [2] and others [5,29–32,172]. Gasification and steam reforming of mixed feedstock has a very bright future. De Ruyck et al. [172] examined the co-utilization of biomass and natural gas in a combined cycle through primary steam reforming of natural gas.

The study proposed a method in which external firing is combined with the potential high efficiency of combined cycles through co-utilization of natural gas with biomass. Biomass is burned to provide heat for partial reforming of the natural gas feed. In this way, biomass energy is converted into chemical energy contained in the produced syngas. Waste heats from reformer and biomass combustor are recovered through a waste heat recovery system. This way, biomass can replace up to 5% of the energy in the natural gas feed. It also shows that in the case of combined cycles, this alternate path allows for external firing of biomass without an important drop in cycle efficiency.

## 4.5.2.7 Carbon and Carbon Monoxide

These are perhaps the most basic steam reforming reactions leading to the production of a mixture of hydrogen and carbon monoxide and the subsequent reaction to produce hydrogen. The reactions are as follows [18]:

$$C + H_2O \rightleftharpoons CO + H_2$$
  $\Delta H = 131.2 \text{ kJ/mol}$  (4.68)

and

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
  $\Delta H = -41.1 \text{ kJ/mol}$  (4.69)

The first reaction is the basis of all different types of steam reforming reactions outlined earlier. The second reaction is called "water–gas shift reaction," and in this section, we mainly focus on this reaction. While the water–gas shift reaction was first reported in 1888 [173], it became the most popular for producing hydrogen in the Haber process for manufacturing ammonia. In the early stages of ammonia process, the hydrogen was obtained by burning coal, coke, and carbon according to reaction at a temperature about 1000°C [1]. At lower temperature, another reaction

$$C + 2H_2O \rightleftharpoons CO_2 + 2H_2 \qquad \Delta H = 90 \text{ kJ/mol}$$
(4.70)

produced needed hydrogen. Pure hydrogen can be obtained by separating  $CO_2$  using absorption, adsorption, or membrane separation technique. CO can be separated by liquefaction or copper liquor scrubbing. Later, Bosch and Wild [174] discovered that a mixture of carbon monoxide and steam can be converted to hydrogen and carbon dioxide at 400°C–500°C by iron and chromium oxides, thereby generating additional hydrogen for the Haber process. Thus, the use of water–gas shift reaction became a very important part of hydrogen generation from carbonaceous materials.

In the recent years, water–gas shift reaction has been extensively studied and new catalysts for this reaction have been developed. These catalysts are analyzed in a recent excellent review by Ratnaswamy and Wagner [18]. According to these authors, there are basically four types of catalysts for water–gas shift reaction. At moderately high temperature (350°C–450°C), promoted iron oxide catalysts are used and these catalysts are called HTS catalysts. At low temperatures (190°C–250°C), copper–zinc oxide catalysts are used and called low-temperature shift (LTS) catalysts. The third type of catalysts employs cobalt and molybdenum sulfides as active ingredients, and they are sulfur tolerant and used to treat "sour gas"-containing sulfur. They are therefore called sour gas catalysts. Finally, medium-temperature shift catalysts operate between 275°C and 350°C, and they are copper–zinc catalysts modified with iron oxide. Besides these four types of catalysts, Pt and Gold catalysts have been intensely investigated and promoters such as Cu and  $Al_2O_3$  have been added to the conventional iron and chromium oxide HTS catalysts.

As discussed earlier, the water–gas shift reaction is moderately exothermic and equilibrium controlled. The equilibrium constant first sharply decreases with an increase in the temperature above around 190°C and the levels of around 480°C. The rate expression is as follows [18]:

$$K_{\rm p} = \exp\left(\frac{4477.8}{T} - 4.33\right) \tag{4.71}$$

where:

T is expressed in kelvin

Thus, high forward conversion of water-gas shift reaction is favored at low temperature, and it is essentially unaffected by the total pressure. At high temperature, reverse water-gas shift reaction dominates. The reaction is reversible and the forward reaction rate is strongly inhibited by the reaction products:  $CO_2$  and  $H_2$ . Low CO level can be obtained by maintaining the reactor temperature at around 200°C. At low temperature, however, condensation of water and its contact with the catalyst should be avoided. The equilibrium carbon monoxide concentration is also affected by the steam-to-gas ratio. Higher steam-to-gas ratio lowers the product CO concentration and increases the hydrogen and carbon dioxide production rates. Since the water-gas shift reaction is always present and equilibrium controlled, in any steam reforming process a substantial amount of carbon dioxide is present in the reaction mixture. The presence of carbon dioxide also forces the "dry reforming" reaction between hydrocarbons and carbon dioxide. Thus, in any autothermal reactors, it is more than likely that steam reforming reaction, partial oxidation, water-gas shift reaction, and dry reforming reaction all occur simultaneously.

#### 4.5.2.8 Bio-Oil

Catalytic steam reforming of bio-oil at 750°C–850°C over a nickel-based catalyst is a two-step process that includes the shift reaction [24–26]:

$$Bio-oil + H_2O \rightarrow CO + H_2 \tag{4.72}$$

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \to \mathrm{CO}_2 + \mathrm{H}_2 \tag{4.73}$$

The overall stoichiometry gives a maximum yield of 11.2% based on wood. The overall reaction is

$$CH_{1,9}O_{0,7} + 1.26 H_2O \rightarrow CO_2 + 2.21 H_2$$
 (4.74)

For this process, bio-oil from regional facility is generally transported to central reforming facility. The process is compatible with other organic waste streams such as aqueous steam fractionation processes used for ethanol production and trap grease. Methanol and ethanol can also be produced from biomass by a variety of technologies and used for on-board reforming for transportation. Methane from anaerobic digestion could be reformed along with natural gas. A system analysis has shown that biomass gasification/shift conversion is economically unfavorable compared to natural gas reforming except for very low-cost biomass and potential environmental incentives.

# 4.6 STEAM GASIFICATION AND REFORMING REACTORS

# 4.6.1 STEAM GASIFICATION REACTORS

Fundamentally, three types of gasifiers are used in the commercial processes: fixed bed, fluidized bed and/or CFB, and entrained bed [5,8–10,33,75–83,125,127,156, 175–191]. In some specific applications, plasma and free radical gasifiers as well as molten salt gasification reactors are also used. Although in most conventional applications the first two types are most commonly used, all types of gasification reactors are briefly described below.

# 4.6.1.1 Fixed-Bed Gasifiers

There are two major types of fixed-bed gasifiers: countercurrent or "updraft" and cocurrent or "downdraft" gasifiers. In countercurrent gasifier, the carbonaceous materials (coal, biomass, waste, etc.) flow downward, whereas steam, oxygen, and/or air flow upward in the reactor. The ash is removed either dry or as slag. The slagging gasifiers have a lower ratio of steam to carbon achieving a temperature higher than the ash fusion temperature. The fuel must be permeable and noncaking. The throughput for this type of gasifier is relatively low. In this type of reactor, while thermal efficiency is high, both tar and methane productions are high and the product gases need to be extensively cleaned. The tar can be recycled. In gasification of rice hulls, the gas gets very hot (up to  $1000^{\circ}$ C) and has to be forced (by fan) into the reactor.

In both updraft and downdraft gasifiers, drying and devolatilization occur at the top of the reactor [56,191]. In the updraft reactor, this is followed by reduction and combustion. But in the downdraft gasifier, combustion precedes reduction. In an updraft reactor, in the devolatilization zone volatile species are released and considerable quantities of tars are formed. In the reduction zone, permanent gases are formed and finally char and remaining solids are combusted in the final combustion zone. The updraft reactor produces low tar content and the temperature in the gasification zone can also be controlled by co-feeding steam and air or humidifying air.

The product gases are cooled down to 200°C–300°C before leaving the gasifier. The overall energy efficiency of the updraft gasifier is high.

In a "down draft" reactor, both raw materials and gasification agent flow cocurrently downward. Heat needs to be added in the upper part of the bed either by combusting small portion of fuel or by some external sources. The produced gas leaves the reactor at high temperature, and most of the heat is transferred to the entering gasification agent. This creates an energy efficiency similar to that for "updraft" reactors. Since tar passes through the hot zones within the reactor, its level in the product gas is much lower than that in the "updraft" reactor [56,191].

The downdraft gasifier has four distinct zones [56,191]: (1) upper drying zone, (2) upper medium pyrolysis section, (3) lower medium oxidation zone, and (4) lower reduction zone. The temperature in the oxidation zone is 1000°C–1400°C and the tar produced is exclusively tertiary tar. The downdraft gasifier produces clean gas but has low thermal efficiency, and it is not suitable for handling biomass with high moisture and ash content.

Besides updraft and downdraft gasifiers, sometimes cross-flow gasifiers are used where raw materials (coal, biomass, etc.) flow downward and air or steam is introduced from the side. The product gases at about 800°C–900°C are withdrawn from the top of the gasifier. A hot combustion/gasification zone forms around the air entrance, with both pyrolysis and drying zones being formed higher up in the vessel. Ash is removed from the bottom of the reactor. The gasifier gives low-energy efficiency and produces high tar content.

The fixed-bed reactors are easy to design; however, they produce gas with low heating value and high tar content. The use of oxygen along with steam improves the product gas heating value. The heating value also significantly depends on the nature of the feedstock.

A novel HTAG unit was used to study biomass waste such as bark, charcoal, and wood pellets with diameters ranging from 6 to 12 mm as well as densified and not densified plastic wastes [56,75–84,178–181]. The facility consisted of a batch-type, countercurrent (updraft), fixed-bed vertical column gasifier. The reactor had three sections: a wind box, the feedstock section, and gas reaction section. The afterburning combustion chamber was coupled to a gasifier to burn completely produced fuel gas. After burner had an inlet for fuel gas, an outlet for flue gas, and a set of air nozzles to ensure complete combustion. Flue gas outlet channel was connected with the afterburning combustion chamber that was equipped with the cooling system. The air was preheated to 600°C with a capability to go up to 1300°C. The unit has worked very successfully.

#### 4.6.1.2 Suspended Bed Reactor

There are three types of suspended bed for steam gasification used in commercial practice: fluidized bed, CFB, and entrained bed.

#### 4.6.1.2.1 Fluidized Bed Reactor

In this type of reactor, fuel is fluidized by air (or oxygen) and steam. The ash is removed dry or as heavy agglomerates that defluidized. In dry ash gasifier, the temperature is relatively low, thus generating high methane content gases. The agglomerating gasifiers

have higher temperatures and are more suitable for high-rank coals. The flow rate in fluidized bed reactor is higher than that in fixed-bed reactor. The conversion per pass is usually low due to elutriation of carbonaceous materials. The mixing in the reactor is high giving more uniform temperature. Fluidized bed is most useful for raw materials such as biomass which form highly corrosive ash that can damage the walls of slagging gasifiers. The fluidized bed reactor is generally operated under "bubbling fluidized bed" conditions. A modeling and experimental validation of biomass–steam gasification in the bubbling fluidized bed reactor is given by Gopalakrishnan [82]. His analysis indicated that for steam gasification of biomass, an increase in temperature in such a reactor increases the production of hydrogen and carbon monoxide and decreases the production of carbon dioxide, decreases the production of hydrogen and carbon monoxide, and has no effect on the production of methane.

## 4.6.1.2.2 CFB Reactor

One way to improve conversion in fluidized bed reactor is to recycle solids back into the reactor. In this type of reactor, the solids coming out of reactor are separated from gas and recycled back into the reactor. This reactor thus provides more flexibility on the solids residence time within the reactor. The solids recycling also provides better solids mixing and uniform temperature distribution.

A variation of single CFB was examined by Matsuoka et al. [83] who examined a circulating dual bubbling fluidized bed system. In this system, two bubbling fluidized beds were used as a gasifier and a combustor. The gasifier and combustor had identical inner diameters (80 mm), and the static bed heights of the bed material in the gasifier and combustor were 270 and 150 mm, respectively. The inner diameter of the riser was 18 mm and its height from the top of the gasifier to the cyclone was about 1800 mm. Porous  $\gamma$ -alumina particles with a diameter of 75–150  $\mu$ m were used as refractory materials. The system was used to treat sawdust at temperatures ranging from 773 to 1073 K. The data were obtained at different steam-to-biomass ratios and different set of residence times. The system was found to be very efficient, and higher carbon conversion and hydrogen yield were achieved in this system compared to those obtained in conventional CFB.

Another variation of the dual fluidized bed steam gasification process was developed by Pfeifer et al. [81] at the Vienna University of Technology. This system is graphically depicted in Figure 4.5 later in the chapter. In this process, heat for the gasification reactor is provided by circulating bed material. This system was a further development of the so-called fast internally CFB (FICFB) technology [75–83,178–181,187]. In this technology, biomass enters a bubbling fluidized bed gasifier in which drying, thermal degasification, and partially heterogeneous char gasification take place at temperatures of about 850°C–900°C. Residual biomass char leaves the gasifier together with the bed material through an inclined, steam fluidized chute toward the combustion reactor. The combustion reactor serves for heating up the bed material and is designed as highly expanded fluidized bed (riser). Air is used as the fluidization agent in the riser. The circulating rate can be adjusted easily by changing the amount of primary and secondary air in the combustion chamber. After particle separation from the flue gas in a cyclone, the hot bed material flows back to the gasifier via a loop seal. The solids in both the loop seal and the chute are fluidized with steam, which effectively prevent gas leakage between gasification and combustion zone, and also allow high solid throughput. The temperature difference between the combustion and the gasification reactor is determined by the energy needed for gasification as well as bed material circulation rate. The system is inherently auto-stabilizing since a decrease in the gasification temperature leads to a higher amount of residual char, which results in more fuel for the combustion reactor. This, in turn, transports more energy into the gasification zone and therefore stabilizes the temperature. Both the gasifier and the combustor operate at atmospheric pressure. The process yields two separate gas streams: a high-quality producer gas and a conventional flue gas at high temperatures. The high-quality producer gas contains low amounts of tars and nitrogen, and high concentration of hydrogen. For practical use, olivine, a natural mineral, has proven to be a suitable bed material with enough resistance to attrition and moderate tarcracking activity [72-84]. This concept was proven to be more efficient for converting the primary fuel energy into producer gas than conventional dual fluidized bed steam gasification because of the lower operating temperature.

# 4.6.1.2.3 Entrained Bed Reactor

This type of reactor uses fine solids and high rate of gas flow to provide uniform temperature distribution and low residence time within the reactor [5]. The reactor is generally operated at high temperatures so that the tar and methane concentrations in the product gases are very low. The oxygen requirement in this type of gasifier is higher than those in other types of gasifiers. All entrained bed gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. These types of gasifiers do not suffer from corrosive slags and can better handle biomass that can generate corrosive slag.

For processing fuels with very high ash fusion temperatures, some limestone is mixed with fuel, which lowers the ash fusion temperature. The need for fine solids requires the fuel pulverization process before gasification. The reactor needs more energy due to fuel pulverization and the production of oxygen that is used for gasification.

# 4.6.1.3 Plasma and Free Radical Gasifiers

Both of these types of gasifiers use either thermolytic, photolytic, or high-voltage torch to supply heat for the gasification process. These are high energy intensive reactors and mostly produce clean syngas. They are not often used for steam gasification.

# 4.6.1.4 Molten Salt Steam Gasification Reactors

There are at least four different designs that use molten salt media to gasify coal in the presence of steam [1,3]. Two of these four designs, namely, Rockwell molten salt gasifier and Rummel–Otto single-shaft gasifier, are graphically illustrated in Figure 4.3a and b, respectively. Here, we briefly describe the remaining two, namely, Kellogg– Pullman molten salt process and Atgas molten iron coal gasification process.

# 4.6.1.4.1 Kellogg–Pullman Molten Salt Process

In this process, the coal is gasified in a bath of molten sodium carbonate through which steam is passed. The process offers the following advantages [1,3]:



**FIGURE 4.3** Schematics of two typical molten salt gasifiers: (a) Rockwell molten salt gasifier; (b) Rummel–Otto single-shaft gasifier. (Adapted from Lee, S., Speight, J.G., and Loyalka, S.K., *Handbook of Alternative Fuel Technologies.* Taylor & Francis, Boca Raton, FL, 2007; Lee, S., "Gasification of coal," in Lee, S., Speight, J.G., and Loyalka, S.K., eds., *Handbook of Alternative Fuel Technologies.* Taylor & Francis, Boca Raton, FL, 26–78, 2007.)

- 1. Salt bath supplies the necessary heat for gasification. Due to high and uniform temperature in the bath, products are free of impurities such as tars and tar acids.
- Gasification of caking coal without carbonization is possible due to uniform distribution of coal and steam and good contacting between the two reactants.
- 3. Complete gasification at a lower temperature is possible due to catalytic effect of sodium carbonate for coal steam gasification reactions.
In this process, the preheated oxygen and steam transport coal and unreacted recycled coal (after ash removal) in the molten salt gasifier. A significant portion of oxygen and steam is also admitted into the bottom of the reactor to provide the necessary gases for the complete gasification reactions. Sulfur in the coal is accumulated as sodium sulfide at equilibrium level and it reacts with molten salt as

$$Na_2CO_3 + H_2S \rightarrow Na_2S + CO_2 + H_2O$$

$$(4.75)$$

Ash accumulates in the melt and leaves with a bleed stream of salt where it is separated and the clean salt is recycled back into the reactor. The bleed salt is quenched in the water to dissolve sodium carbonate and the ash is separated by filtration. Sodium carbonate is further carbonated to make sodium bicarbonate (NaHCO<sub>3</sub>), which is then separated and heated to regenerate sodium carbonate for reuse in the reactor. The entrained salt and heat in the product gas are recovered and the purified gas stream is further processed to make synthesis gas, pipeline gas, or synthetic natural gas (SNG).

# 4.6.1.4.2 Atgas Molten Iron Coal Gasification

In this process, coal is injected with steam in the molten iron bath [1,3]. Thermal cracking of coal along with steam dissociation generates a mixture of carbon monoxide and hydrogen. The sulfur in coal is captured by iron and transferred to lime slag from which elemental sulfur is recovered. The Atgas process produces gases with a heating value of about 900 Btu/scf. The Atgas molten iron process has the following advantages over conventional fixed- and fluidized bed steam gasification processes:

- 1. Sulfur in coal is recovered as elemental sulfur, which can be sold, and this helps process economics. The product gas is essentially free of sulfur.
- 2. Gasification is carried at low pressure; hence, the coal feeding problem in pressurized operation is eliminated. Coking properties, ash fusion temperature and generation of coal fines, are not problematic.
- 3. Tar formation is minimal due to high-temperature operation.
- 4. The system is very flexible and does not cause any environmental problems. Relatively large coal particles can be handled without any pretreatment.
- 5. Reactor start-up and shutdown procedures are much simpler compared to those for fixed and fluidized bed reactors.

The coal and limestone are injected into the molten iron through tubes using steam as a carrier gas. Coal gasifies and produces carbon monoxide, and sulfur (both inorganic and organic) migrates to slag and reacts with lime to produce CaS. The product gas at 1425°C is cooled and compressed, and passes through a shift converter to convert CO into water gas with a H<sub>2</sub>-to-CO ratio of 3–1. The carbon dioxide is removed from the final product, and the gas is again cooled and passed through a methanator to produce methane by the reaction:  $CO + 3H_2 \rightarrow CH_4 + H_2O$ . Excess water is removed from the methane-rich product.

#### 4.6.2 STEAM REFORMING REACTORS

While hydrogen production can be achieved by a number of commercially proven technologies such as gasification of coal, biomass, and residue (waste); methanol decomposition; and steam reforming of methane, renewable materials, and liquid hydrocarbons, it is the last technology that produces the largest portion of hydrogen production [5,33,126,128,175–190]. With the considerable advances in unconventional production of natural gas that includes shale gas, deep gas, tight gas, coal bed methane, gas from geopressurized zones, and gas hydrates, the steam reforming of natural gas is likely to become even more important. An increase in natural gas production is likely to make the steam reforming of methane the choice of significant hydrogen production.

The design of a steam reforming plant requires the considerations that

- 1. The economics of the process is very scale dependent [33]. For example, for  $5 \times 10^6$  Nm<sup>3</sup>/day plant, the operating cost can be as low as \$80/kW of H<sub>2</sub>, whereas for 2300 Nm<sup>3</sup>/day plant, the same cost would be \$4000/kW for hydrogen.
- 2. The capital cost can be large due to large size of the plant (i.e., in large plants, reformer tubes can be as long as 12 m) and the need for expensive alloy materials for high-temperature and high-pressure operations.
- 3. The small-scale operation, while expensive, is often used for niche application such as FC technology and hydrogen refueling station, and this requires small and compact reformers at low cost.

Due to these considerations, both large- and small-scale reformers have been developed.

In normal commercial reformers, the steam-to-hydrocarbon ratio is kept high enough to prevent coking but to avoid overloading the reformer duty. Generally, the ratio of 3 is used. The inlet temperature of 760°C is used, and because reforming reaction is endothermic, additional heat is added as mixture flows down the catalyst-filled reformer tubes. A critical factor in the reformer heater design is keeping the tube wall temperature uniform and hot enough to promote reforming reaction. For this purpose, two types of heater design, side-fired reforming furnace and roof-fired heater design, have been employed [33].

In side-firing furnace, two parallel rectangular boxes are connected at the top with horizontal ductwork into the vertical convection stack. Several rows (typically four) are used to directly fire the tubes. A typical reformer furnace has 300 burners. Reformer tubes are 5 inch in diameter with a wall thickness of 0.5 inch and about 34 ft of wall is exposed to the burners. The tubes are generally 25% chrome, 20% nickel, or a high nickel steel such as HL40 [33].

The top-fired reformer is a rectangular box, the tubes are still vertical, and the inlet and outlet are pigtails to the pigtail inlet header and the outlet transfer line. The burners have a pencil-shaped flame design. All burners are located above the inlet manifold. Hydrogen plants with single reformer heaters and a capacity of up to 100,000 ft<sup>3</sup>/day are used in the vertical down-firing approach. The outlet transfer line from the reformer is used to generate high-pressure (650 psig) steam. The reformer effluent gas exits through the transfer line at about 760°C [33].

While the large commercial reformers are designed as described above, more compact and economical designs are used in the smaller scale reformers [120–134, 188–190]: (1) annular bed reformers, (2) plate-type reformers, (3) membrane reactors, (4) auto-thermal reactors, (5) ITM reformers, (6) sorbent-enhanced reformers, (7) plasma reformers, and (8) micro-channel reformers. These different designs consider the ways to improve the heat transfer rate, the area and the efficiency since reforming requires a large supply of heat due to an endothermic nature of the reaction. Improvement of material cost is another important consideration. Finally, a process that carries out simultaneous reaction and separation of hydrogen is important to improve the conditions for equilibrium and purity of hydrogen product. The following paragraphs briefly summarizes the descriptions of these eight reformers given in References 120–134.

The annular bed reformer is used for FCs and low hydrogen production (on the order of 2 kW) needs. In the latter case, it is generally operated at a low temperature of about 700°C and a low pressure of about 3 atm. These mild conditions reduce the cost of materials and produce an energy efficiency of about 70%–80%. This type of reformer is used by industries such as Haldor Topsoe, Ballard Power Systems, Sanyo Electric, and International Fuel Cells. The technology produces more compact reformers at a lower cost than conventional reformers.

Plate-type reformers are more compact than annular or conventional long tube reformers and are often used for proton exchange membrane (PEM) FC or residential-type FC (20 kW) applications. It has the same energy efficiency as that of annular reformer. The plates are arranged in a stack in which one side of the plate is coated with the catalyst and on the other side (anode) exhaust gas from FC undergoes catalytic combustion to supply heat for the endothermic steam reforming reaction. The unit is compact and low cost, and has good heat transfer and small heat-up period. For PEM FC applications, Osaka Gas Co., Japan, is developing a low cost reformer with an integrated plate design that carries out sulfur removal, steam reforming, water–gas shift reaction, and CO removal steps all in one unit making the final device more compact and economical. GASTEC is applying the technology for residential-type FCs and minimizing the cost by testing the variables such as combustion catalysts, coatings, and substrate materials.

In the membrane reactor, reforming, water–gas shift reaction, and further CO cleaning step all occur in the same unit. The reaction and separation functions are thus combined. The reactor operates under high pressure and uses the Pd membrane on one side through which  $H_2$  permeates with high selectivity. The constant removal of hydrogen on the downstream side allows equilibrium to be shifted to achieve better conversion by reforming at a lower temperature. The reactor also produces high-purity hydrogen.

In the auto-thermal reformer, endothermic reforming reaction is accompanied by partial oxidation reaction that generates enough heat to supply the heat needed for reforming reaction. Thus, the reactor does not need any external source for the heat. Arthur D. Little, Nuvera, Epyx, and a consortium of McDermott Technology/Catalytica, among others, have developed a 50 kW FC reformer of this type. Small-scale (10–50 kW) autothermal reactors have been developed for PEM FC by Honeywell, DaimlerChrysler, Analytical Power, and IdaTech, among others [120]. Generally, auto-thermal reactors use gasoline, diesel, and logistic fuels along with natural gas. The use of diesel and logistic fuels makes them specially useful for FC applications on ships [120]. In the ITM technology (being developed by a consortium of industries and universities headed by Air Product), one side of the membrane separates oxygen from air at around the room temperature and 0.03–0.20 atm pressure; on the other side, methane and steam react at high pressure (3–20 atm) to produce syngas. The membrane is made up of nonporous multicomponent oxides that operate at a temperature higher than 725°C and has high permeability and selectivity for oxygen transfer. Partial oxidation provides the heat for reforming reaction. The syngas can either be reformed to produce hydrogen or converted to produce fuels and chemicals. The ITM technology generally uses flat plate system.

In the sorbent-enhanced reforming (SER) technology, the steam reforming is accompanied by simultaneous removal of carbon dioxide and carbon monoxide by calcium oxide. The removal of carbon dioxide allows the reforming reaction to occur at 400°C–500°C as opposed to the normal reforming temperature of 800°C–1000°C. The reaction also produces reasonably pure hydrogen (90% H<sub>2</sub>, 9.5% CH<sub>4</sub>, 0.5% CO<sub>2</sub>, and <50 ppm CO), and this alleviates the downstream expensive purification processes such as water–gas shift reaction, preferential oxidation, and membrane separation.

Thermal plasma technology is a high-temperature (2,700°C to about 10,000°C) process to generate hydrogen and hydrogen-rich gas from a variety of feedstock. High temperature accelerates the rate of reforming process. The products generally contain ethylene and acetylene along with hydrogen, carbon monoxide, and carbon dioxide. The process can handle various reaction volumes, interelectrode gap, sulfur impurities, and carbon deposit. The process can be operated in auto-thermal mode. The process can generate a large range of fuel power (10–40 kW) and can give up to 90% conversion of methane.

One attractive method to improve the transport limitations in the reforming reactor is to use micro-channel reactor that can operate at 10 ms or lower residence time compared to conventional reactor that operates at the residence time of 1 s. Since intrinsic reforming reaction is very fast, at a high residence time, a significant portion of the catalyst volume in the steam reformer is wasted. The micro-channel reactor allows a reduction of plant volume by about a factor of 30, and thereby reducing both capital and operating costs for steam reforming of methane. Also, the micro-channel reactors allow high reaction rates by increasing the heat transfer rates. For highly active catalyst, equilibrium can be reached in less than 0.5–1 ms residence time. This indicates that further lowering of transport resistances can further reduce residence time to reach the desired equilibrium.

Besides the eight different types of reforming reactors that are being developed (particularly for small-scale applications), solar reforming reactors that use solar energy to carry out steam reforming reactions are gaining more popularity. These reactors are described in the following sections.

#### 4.7 NOVEL STEAM GASIFICATION AND REFORMING PROCESSES

#### 4.7.1 SOLAR GASIFICATION TECHNOLOGY

Solar thermochemistry refers to a number of process technologies such as thermal or thermochemical splitting of water, solar electrolysis, solar gasification, and reforming or cracking of water and other carbonaceous materials [192–214]. Many of these endothermic reactions are carried out by energy harnessed by concentrated solar beams. Solar gasification generally deals with upgrading and decaronization of fossil fuels. Such gasification is often carried out in the presence of steam. Successful solar gasification of carbonaceous materials was first reported in the 1980s in which coal, activated carbon, coke, and coal/biomass mixtures were employed in a fixed-bed windowed reactor. Charcoal, wood, and paper were gasified with steam in a fixed-bed reactor. More recently, steam gasification of oil shale and coal, biomass, waste tires and plastics, and coal in a fluidized bed reactor as well as petroleum coke and vacuum residue in fixed, fluidized, and entrained bed reactors were examined [192,193,195–199,202–210] (Piatkowski 2012, pers. comm.; Yeheskel et al., 2012, pers. comm.). In the last type of reactor, dry coke particles, coal–water slurries, and vacuum residues were tested for the steam gasification.

In a conceptual solar gasification process using steam, biomass is heated rapidly in a solar furnace to achieve flash pyrolysis at temperatures of about 900°C [192]. Some steam is added to the pyrolyzer to increase the gas yield relative to char. The char constituting about 10%-20% of the biomass by weight is steam gasified with external heating at temperatures of  $900^{\circ}$ C $-1000^{\circ}$ C; all of the volatile hydrocarbons are then steam reformed in a solar reformer. Steam for the process is generated from heat recovered from the product gas. The composition of the syngas is adjusted to the user's needs utilizing conventional operation involving the water–gas shift reaction and CO<sub>2</sub> stripping. This conceptual process can be modified in a number of different ways depending on the specific needs.

A number of gasification experiments were carried out using small quantities of biomass, coal, oil shale, and residual oil with external heat supplied by the Sun [192–207]. These experiments included cellulose gasification and oil shale gasification with carbon recovery approaching nearly 100% at a temperature of 950°C and short residence times [196,208,209]. While these experiments confirmed the applicability of the flash pyrolysis approach, they did not provide the data for design and scale-up of a solar gasification process. More work is being pursued to improve the design and scale-up capabilities of solar gasification process [192–207].

#### 4.7.2 SOLAR GASIFICATION REACTORS AND PROCESSES

A number of different types of solar steam gasification reactors have also been examined in the literature [192–206,209]. The reactor configuration examined by Z'Graggen [202] at Swiss Federal Institute of Technology (ETH) at Zurich consisted of a cylindrical cavity receiver of 21 cm in length and 12 cm in inside diameter, and an aperture of 5 cm in diameter for solar beams. The cavity-type geometry was designed to effectively capture the incident solar radiation and its apparent absorption is estimated to exceed 0.95. The cavity was made of Inconel 601 lined with  $Al_2O_3$  and insulated with an  $Al_2O_3/ZrO_2$  ceramic foam. The aperture was closed by 0.3-cm-thick clear fused quartz window mounted in a water-cooled aluminum ring that also served as a shield for spilled radiation. The window was actively cooled and kept away from particles and condensable gases.

Steam and particles were injected separately into the reactor cavity, permitting the separate control of mass flow rates and stoichiometry. Steam was introduced through several ports. The carbonaceous material feed unit was positioned on the top of the reactor vessel with its inlet port located at the same plane as the primary steam injection system, allowing for the immediate entrainment of particles by the steam flow. Reactor temperature was measured at 12 separate locations by thermocouples inserted in the Inconel walls. Both inlet and exit temperatures were also measured by the thermocouples. The dry, slurry, and liquid feeding of raw materials were carried out by different devices.

Piatkowski et al. [197], Piatkowski (2012, pers. comm.), and Piatkowski and Steinfeld [195] used a packed bed solar steam gasification reactor as shown in Figure 4.4. This reactor was specially designed for beam-down incident solar radiation,



**FIGURE 4.4** Section view of the packed-bed solar reactor featuring two cavities separated by an emitter plate, with the upper one serving as the radiative absorber and the lower one containing the reacting packed bed that shrinks as the reaction progresses. CPC, compound parabolic concentrator. (Reprinted from *Fuel Processing Technology*, 90, Piatkowski, N., Wieckert, C., and Steinfeld, A., Experimental investigation of a packed bed solar reactor for the steam gasification of carbonaceous feedstocks, 360–366, Copyright 2009, with permission from Elsevier.)

which was obtained through a Cassegrain optical configuration that made use of a hyperbolic reflector at the top of the solar tower to redirect the sunlight collected by a heliostat field to a receiver located at the ground level. The reactor had two cavities in series. The upper one absorbed the solar radiation and contained a small aperture to gather concentrated solar radiation. The lower cavity contained carbonaceous materials on the top of a steam injector. An emitter plate separated the two cavities.

A 3D compound parabolic concentrator (CPC) was incorporated in the aperture of the reactor, further augmenting the incident solar flux before passing it through a quartz window in the upper cavity. The emitter plate acted as a transmitter of the radiation to the lower cavity, thus avoiding the direct contact between the quartz window and the reactants and products. This set-up also provided uniform temperature in the lower cavity and a constant supply of radiant heat through the upper cavity that can act as energy storage, which was needed due to intermittent supply of radiant heat. This type of batch, two-cavity solar reactor, has been successfully used for the carbothermal reduction of ZnO and the detoxification of solid waste. The reactor can be operated with a wide variety of particle sizes, and as the reaction proceeds, both the particle size and the packed bed reactor volume decrease. The detailed dimensions and the operation of this type of reactor are given by Piatkowski and Steinfeld [195]. Piatkowski et al. [197] and Perkins et al. [196] also showed an effective use of such a reactor to produce syngas from coal, biomass, and other carbonaceous feedstock. Z'Graggen [198] and Z'Graggen et al. [202] produced hydrogen from petroleum coke using solar gasification process.

The solar energy is also used as the heat carrier for the pressurized coal gasification process. In this process, finely powdered coal is fed by a specially designed injection system. The oxidizing and fluidizing agent is a superheated steam. The heat required for the endothermic gasification reaction is introduced by means of a tubular heat exchanger assembly immersed in the fluidized bed. The technical feasibility of a solar power tower and pressurized gasifier integration has been demonstrated in a small pilot plant [194,199,202]. Solar energy has also been used to gasify biomass in different types of reactors [196,203,204,206,208,209].

#### 4.7.3 SOLAR REFORMING

The high temperatures required for solar reforming effectively limit the nature of solar energy collector [192,194,199–201,207–214] (Yeheskel et al., 2012, pers. comm.). The bulk energy production, whether in closed-loop or open-loop configurations, probably must be carried out on a large scale to compete with fossil fuels and probably requires the tower (central receiver) solar technology. Solar reforming can be carried out using different processes such as direct and indirect, each requiring different type of reformer configuration [192].

#### 4.7.3.1 ASTERIX: Solar Steam Reforming of Methane

Advanced Steam Reforming of Methane in Heat Exchange (ASTERIX) experiment, an earlier joint Spanish–German project, examined steam reforming of methane using solar-generated high-temperature process heat by an indirectly heated reformer [192,194,199]. The specific objectives of the ASTERIX experiments were to collect and store an amount of solar energy to obtain the maximum conversion of methane and to produce consistently high-quality synthesis gas. The experiment used gas-cooled solar tower (GAST) system to produce hot air (up to 0.36 kg/s at 1000°C and 9 bars) to drive separate steam reformer. This air was then fed back into the GAST cycle. The GAST technology program is described by Becker and Bohmer [194].

During normal operation, the heating medium, air, is taken from the GAST circuit (receiver) at a temperature of 1000°C over a suitable bench line and fed through the electric heater to the reforming reactor inlet. In this solar-only operating mode, air flows through the heater passively without any additional electric heating. Methane reforming is initiated at the process gas end of the reformer. A liquid natural gas storage tank directly provides the reforming unit with natural gas at the required pressure via the Liquid natural gas evaporator. The process gas mixture is heated by air from 500°C to about 850°C as it passes through the catalyst bed. The endothermic reforming reaction results in the production of hydrogen and carbon monoxide with a ratio of 3/1. More details of the ASTERIX experiment are given in References 192–194 and 199.

#### 4.7.3.2 The Weizmann Institute Tubular Reformer/Receiver

The WIS (Weizmann Institute of Science) operated a solar central receiver for the development of high-temperature technology including the storage and transport of solar energy via methane reforming [192,199,200] (Yeheskel et al., 2012, pers. comm.). The WIS had a designed facility for testing reformers up to about 480 kW absorbed energy. The facility was designed for either steam or carbon dioxide reforming and can accommodate the reformer that operates between 1 and 18 bars. The reformer systems were operated in coordination with a matching methanator system that recovered the energy from the reverse reaction [192].

A cavity receiver containing eight vertical reformer tubes (2 inch schedule 80 and 4.5 m long) was designed. The overall dimension of the device was about 5 m high, 4.5 m wide, and 3 m deep. The reactor was designed to produce syngas at 800°C. It resembled commercial reformers except that a solar cavity receiver had replaced the conventional gas-fueled radiant furnace [192].

#### 4.7.3.3 Soltox Process

In the Soltox process, a parabolic dish is used to concentrate sunlight through a quartz window into an internally insulated aluminum reactor vessel in which it is absorbed on a rhodium-coated reticulated ceramic foam absorber [192,199,201,207,210, 212–214]. Concentrated organic waste and steam are mixed and flow through the hot (>1000°C) catalyst bed, in which they react completely in fractions of a second to produce hydrogen, carbon dioxide, carbon monoxide, and halogen acids (which are easily neutralized to simple salts). The extremely good heat and mass transfer within the reactor result in a compact, highly efficient system [192–194].

When a vaporized organic waste is mixed with steam and passed through the reactor, highly specific, irreversible, endothermic reforming reactions take place on the catalyst-coated surface of the radiantly heated absorber to quantitatively destroy the waste. For example, trichloroethylene (TCE) reacts with steam to produce hydrogen, carbon monoxide, and hydrogen chloride. Because reforming is not a combustion process, neither fuel, nor air, nor oxygen needs to be supplied to the reactor. Thus, unlike incineration, solar-driven, high-temperature catalytic reforming produces neither  $NO_x$  nor products of incomplete combustion (PICs). Furthermore, variable absorber thickness and adjustable gas flow rates mean that residence times within the absorber and thus reaction times and destruction efficiency can be controlled [192–194].

## 4.7.3.4 Open-Loop Solar Syngas Production

The applications of open-loop solar syngas production include the following [188,189,192,199,214]:

- 1. Natural gas reforming for power plants—A number of European countries have imported natural gas via pipelines from North Africa and have reformed this gas to either syngas or hydrogen, increasing its calorific value by about 25% before combustion in gas turbine or FC power plants [192].
- Syngas production from municipal, agricultural, and organic industrial waste—In sunbelt countries, concentrated waste streams can be gasified to syngas with solar energy at potentially acceptable costs and with essentially no emissions to the atmosphere [192].
- 3. Soltox type processing—It provides an option for environmentally acceptable disposal of a number of toxic organic materials [192].

Open-loop syngas production can also be used for the generation of synthesis gas that is being supplied worldwide for the production of hydrogen, methanol, ammonia, and oxyalcohols.

### 4.7.3.5 Other Solar Reforming Processes

A number of studies have focused on the production of hydrogen by steam reforming of methane and other hydrocarbons using solar reactor [189,192,193,199–201,212,213] (Yeheskel et al., 2012, pers. comm.). A schematic of the solar reactor used by Seinfeld and coworkers is depicted in Figure 4.4. Yeheskel et al. (2012, pers. comm.) studied the chemical kinetics of high-temperature hydrocarbon reforming using a solar reactor. Watanuki et al. [189] examined methane steam reforming using a molten salt membrane reforming reactor. In this type of the reactor, the reforming reaction takes place in tubular reactors that consist of selective membranes, generally palladium, which separates hydrogen as it is produced. The principal advantages of a solar membrane reforming process compared to the conventional reforming process are as follows:

- 1. The reforming is carried out at a lower temperature (550°C). This means a significant reduction in the energetic consumption. Low-temperature reactors also use less costing materials for the reforming reactor tubes.
- 2. Hydrogen is obtained with a higher purity due to highly efficient membrane separation process.
- 3. Methane conversions up to 90% can be reached due to high hydrogen extraction through the membrane.

- 4. A big part of CO-CO<sub>2</sub> conversion is produced inside the reactor itself.
- 5. Emissions are reduced by about 34%–53% due to the use of concentrated solar energy to obtain the process heat.

In this study, steam reforming of methane proceeded with the original module having palladium membrane below the decomposition temperature of molten salt (around 870 K). The SOLREF (solar reforming) process [211] and its various options for solar reforming of natural gas by steam are also described by Moller [201]. A review of hydrogen production technologies from solar energy is also given by Suarez-Gonzalez et al. [212].

The above-described process can be easily adapted to solar gasification, but for this case, heavy hydrocarbons are used as feedstock. These are transformed into cleaner fuels for a combined cycle or in the process that can produce hydrogen. As mentioned earlier, a solar gasification plant using petroleum coke has been tested in the solar platform of Almería, Spain. The reactor has reached the hydrogen production efficiency of 60% working at 1500 K [192,199,202,211–213].

#### 4.7.4 MICROWAVE-ASSISTED REFORMING

In the recent years, a significant interest in the use of microwave to carry out hightemperature operations such as steam reforming, pyrolysis, dry reforming, and cracking has been reported [215–217]. Microwave heating is very different from conventional heating in that it heats the materials from inside out unlike outside in heating that normally takes place in conventional heating. This means that all heat is generated and absorbed by the materials and not the surroundings (like microwave cooking at home). The microwave heating, however, requires materials with good dielectric properties such that it not only absorbs microwave but also converts microwave energy into thermal energy. The use of porous, activated carbon for this purpose has been successfully demonstrated [215–217]. Oxides of various materials can also be useful for this purpose.

Menendez et al. [215–217] have shown that microwave-assisted reforming can give better results than the reforming carried out by conventional heating, particularly at lower temperatures. They studied both activated carbon and numerous catalysts deposited on the activated carbon. They also showed that microwave heating is more energy efficient than conventional heating. This approach has a significant potential. More research and development in this area is needed.

#### 4.7.5 UNDERGROUND COAL GASIFICATION

When coal is imbedded underground in steep seams, it is very difficult to mine. Often the energy from such steep coal seams is recovered by *in situ* underground gasification. Just like conventional gasification, underground gasification is often carried out with oxygen or with oxygen and steam mixture. Yang et al. [190,218] studied the product distribution from underground coal in China. They found that with pure oxygen gasification hydrogen volume percentage in product gas varied from 23.63% to 30.24% and carbon monoxide volume percentage varied from 35.22% to 46.32%. When oxygen–steam mixture was used for the gasification, the gas compositions virtually remained stable and CO + H<sub>2</sub> were basically between

61.66% and 71.29%. Moving-point gasification improved the changes in the cavity in the coal seams or the effect of roof in-break (i.e., hole in roof for solar energy) on gas quality. For steep seams, during oxygen–steam mixture gasification, the composition of  $CO + H_2$  remained within 58% and 72%. The average oxidation zone temperature reached 1200°C, and it was higher for forward gasification than for backward gasification. In general, for both types of seams, hydrogen concentration increased and carbon monoxide concentration decreased with an increase in steam-to-oxygen ratio. The hydrogen concentration reached about 60% at the steam/oxygen ratio of about 3.

#### 4.7.5.1 Underground Gasification Reactors

A typical underground gasification reactor is illustrated in Figure 4.5 [1,3]. In this type of reactor, the combustion process can be handled in either forward or reverse mode. The forward combustion involves the movement of the combustion front and injected air in the same direction. In the reverse combustion, the combustion front moves in the opposite direction to the injected air. The process involves drilling and subsequent linking of the two boreholes to enable gas flow between the two. Combustion is initiated at the bottom of one borehole (called injection well) and is maintained by the continuous injection of air and steam. A typical underground reaction system involves linking of a series of such a unit reactor system.

There are two principal methods for underground steam gasification which have been tried successfully: shaft methods and shaftless methods (and a combination of two). Selection of a specific method depends on the parameters such as natural permeability of coal seam; the geochemistry of coal deposit; the seam thickness, depth, width, and inclination; closeness to the metropolitan areas; and the amount of mining desired. Shaft methods involve driving of shafts and drilling of other large diameter openings which require the underground labor and shaftless methods use boreholes for gaining access to the coal seam which do not require any underground labor.

The shaft method can be further divided into three subdivisions: (1) chamber or warehouse method in which underground galleries are prepared and the coal panels are isolated with brick wall, (2) borehole producer method in which parallel underground galleries are created about 500 ft apart within the coal bed, and (3) stream method in which inclined galleries following the dip of the coal seam of steeply pitched coal beds are constructed parallel to each other.

The shaftless method carries out gasification through a series of boreholes drilled from the surface to the coal seam. The coal beds are made more permeable between the inlet and outlet boreholes by a chosen linking method, ignite the coal seam, and gasify it by passing air and steam from the inlet to the outlet borehole. In percolation or filtration method, multiple boreholes, at a distance that depends on the seam permeability, are used to gasify the underground coal.

The potential problems in all of these methods include (1) high and constant quality of product gas; (2) high-percentage recovery of coal energy; (3) control of ground-water contamination; (4) combustion control; (5) roof structure control; (6) product gas leakage control; (7) proper control of permeability, linking, and fracturing; and (8) proper monitoring of underground processes. An ideal underground steam gasification system must be the following: (1) it is operable on large scale; (2) no large deposit of coal remains ungassified; (3) the process is controllable and the quantity



**FIGURE 4.5** (a) Schematic of *in situ* underground gasification process. (b) Plane view of linked vertical well underground gasification plant operated near Moscow. (Adapted from Lee, S., Speight, J.G., and Loyalka, S.K., *Handbook of Alternative Fuel Technologies*. Taylor & Francis, Boca Raton, FL, 2007; Lee, S., "Gasification of coal," in Lee, S., Speight, J.G., and Loyalka, S.K., eds., *Handbook of Alternative Fuel Technologies*. Taylor & Francis, Boca Raton, FL, 2007; Lee, S., "Gasification of coal," in Lee, S., Speight, J.G., and Loyalka, S.K., eds., *Handbook of Alternative Fuel Technologies*. Taylor & Francis, Boca Raton, FL, 26–78, 2007.)

and quality of product gases are constant and uniform; (4) it is mechanically stable and removed from any leakages to the groundwater; and (5) the process requires a minimal or no underground work.

#### 4.7.6 OTHER NOVEL PROCESSES

Sato and White [219] showed that using a physical mixture of powdered Texas lignite and platinized titania, in the presence of water vapor and ultraviolet (UV) light, a catalytic reaction to produce  $H_2$  and  $CO_2$  at 23°C can be achieved. Quantum yields were very low, but improvements were thought to be possible. Belghit and El Issami [220] developed a theoretical model of a moving bed chemical reactor for gasifying coal with steam. The heat was supplied by a high-temperature nuclear reactor. Cypres [221] discussed the metallurgical process for hydrogen production from coal and other carbonaceous materials, including coal gasification in a molten iron bath. An argument was made to place such a gasifier in the vicinity of steel manufacturing plant.

A steam-iron process is one of the oldest commercial methods for the production of hydrogen from syngas [222–230]. Various types of oxides of iron were examined. Neither chemical composition nor porosity of the ores was found to govern the efficiency. Potassium salts enhanced the activity of both natural and synthetic oxides. A number of recent studies have examined the classical steam-iron (sponge iron) process for upgrading synthesis gas (mainly CO and H<sub>2</sub>) to pure hydrogen for use in FCs and other energy devices. Friedrich et al. [226] looked at this purification of nitrogen containing "reduction" gas from biomass gasifier using wood and wood wastes. The process involved two steps: (1) cleaning of gas from solid biomass, coal, or methane, and (2) energy storage in sponge iron. This study investigated woody biomass and commercially available sponge iron. The reactions are as follows:

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$
 (coal, biomass, or natural gas) (4.76)

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{4.77}$$

This process was stated to have little risk. Jannach et al. [230] extended the sponge iron process to FeO, as well as Fe as the oxidant. The sponge iron reaction was further studied by Hacker et al. [228,229] and Jannach et al. [230] in TGA (thermogravimetric analysis) and tube furnace devices. Other types of reactors were also examined by Fankhauser et al. [225] and Hacker et al. [227–229]. Biollaz et al. [223] explored the iron redox process to produce clean hydrogen from biomass. In the first step, iron oxide in the form of Fe<sub>3</sub>O<sub>4</sub> reacted with the reducing components of wood gas to produce FeO, CO<sub>2</sub>, and H<sub>2</sub>. The kinetics of the second step,  $3FeO + H_2O \rightarrow H_2 + Fe_3O_4$ , could be improved by adding other transitional metal oxides. The reduction of iron oxide with biosyngas to sponge iron and later oxidation of sponge iron with steam offers the potential of shifting and purifying biosyngas, and storing and transporting its energy. Bijetima and Tarman [222] described the steam–iron process for hydrogen production operated in a large-scale pilot facility. Economic advantages of the process were also presented. Another novel process is steam combustion to recover oil from reservoir. This enhanced oil recovery method is briefly examined in Chapter 2.

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# 5 Hydrothermal Processes in Subcritical Water

## 5.1 INTRODUCTION

As discussed in Chapter 4, gaseous water, steam, at high temperature and pressure is a powerful reactant to produce gaseous synthetic fuels from a variety of carbonaceous feedstock. While the products formed depend on the operating conditions, the catalyst, and the nature of feedstock, steam plays a very powerful role in the gasification and reforming processes. In recent years, significant efforts have been placed to explore the role of liquid water as a reactant and/or a reaction medium at high temperature and pressure for the production of a variety of synthetic gaseous, liquid, and solid fuels [1–10].

The properties of water at high temperature and pressure are significantly different from those at room temperature and pressure [5,11–13]. For many different types of carbohydrate feedstock, water provides an environment such that at a temperature of  $180^{\circ}C-250^{\circ}C$ , a residence time of 1-12 h, and a pressure above saturation pressure at this temperature range, hydrothermal carbonization (HTC) occurs producing mainly (50%-80%) solid char with about 5%-20% liquid dissolved in water and a small amount of gas (2%-5%). As the temperature increases to about  $270^{\circ}C-390^{\circ}C$ , the residence time of few hours, and the pressure below the critical pressure of about 213 atm, carbohydrates are converted to liquids by the process called hydrothermal liquefaction (HTL). The amount and nature of liquid produced depend on the nature of feedstock, the operating conditions, and the nature of the catalyst (if present). At much higher temperatures (>300^{\circ}C), hydrothermal gasification (HTG) occurs.

The chapter addresses this hydrothermal biomass-water conversion chemistry under subcritical conditions. The issues of purification, upgrading, and utilization of the products obtained from the three processes—HTC, HTL, and HTG—are also examined. In particular, a hydrothermal upgrading (HTU) process to upgrade the products from the HTL is briefly described.

The chapter also addresses various aspects of coal–water chemistry under hightemperature and high-pressure conditions. While water does not have as much affinity for coal as it has for biomass, water can also play an important role in coal liquefaction. The weathered coal created by pretreatment with water can have a significant negative effect on the yield and products of coal liquefaction. Water can also act as a hydrogen donor for the coal liquefaction process under high-temperature and high-pressure conditions. Finally, coal–water slurry, if prepared properly, can be a good feedstock for combustion in boilers, diesel engine, or gas turbines. The chapter briefly examines these three roles of water in coal–water interactions under subcritical conditions.

#### 5.1.1 PROPERTIES OF WATER AT HIGH TEMPERATURE AND PRESSURE

Water at room temperature and pressure is a rather benign, polar substance with low diffusivity, high dielectric constant (i.e., low permittivity), and low dissociation constant. These properties do not allow any meaningful reactions with organic molecules. As the temperature and pressure increase, the dielectric constant quickly decreases, the shared electron by oxygen and hydrogen atoms tends to circulate more evenly, and electronegativity of the oxygen molecule is reduced (i.e., less polar). When the temperature of the water increases from 25°C to 300°C, the dielectric constant decreases from 78.85 to 19.66, resulting in water molecules to become fairly nonpolar. This nonpolarity increases the affinity of water for organic hydrocarbons.

As the temperature and pressure increase, the dissociation constant also significantly increases. The dissociation constant for water at 300°C is about 500 times higher than that at room temperature. An increase in pressure also increases the ionization of water. At room temperature and pressure, low dissociation constant allows H<sup>+</sup> and OH<sup>-</sup> ions in hydrolysis or dissociation in equilibrium balance and the rate of acid- or base-catalyzed reaction rates is low. High dissociation constant at higher temperature and pressure facilitates more acid–base-catalyzed reactions [5].

For the above two reasons, water becomes a good solvent for typically nonpolar and hydrophobic hydrocarbons at high temperature and pressure. Water at  $300^{\circ}$ C possesses the properties of acetone at  $25^{\circ}$ C. The increased solubility of organics in water at high temperature enhances the possibilities of ionic reactions and the contacts of dissociated H<sup>+</sup> with hydrocarbons, thereby accelerating the activities of hydrolysis. These dramatic changes in physical and chemical properties thus allow various organic reactions to take place in the water [5,14]. In addition, water has the ability to carry out condensation, cleavage, and hydrolysis reactions and to affect the selective ionic chemistry, which are more compatible with the organic reactions. Thus, water becomes a medium similar to organic hydrocarbons in which different types of organic reactions can freely occur. As the temperature increases and crosses the critical temperature, water and organic hydrocarbons become more homogeneous in carrying out the various types of organic reactions. The role of water under supercritical conditions is discussed in Chapter 10.

High-temperature water, due to its properties, can act as a reactant and a catalyst for a second pathway to cascade organic molecular transformation of biomass (and to some extent coal) that leads to refined biomass, oil, or synthetic gaseous fuel. Water can cause organic material from biomass to disintegrate and reform by the addition of H<sup>+</sup> to open carbon bond into fragments that can then be converted to different types of hydrocarbons. Thus, hot water can be a catalyst for a series of ionic reactions. Hydrothermal operation differentiates itself from dry pyrolysis in that degradation of biomass in dry pyrolysis is caused by thermal forces, whereas the disintegration of biomass in water can occur due to acid- or base-catalyzed reactions. Water can act as a base to nibble certain organic molecules, and once the reaction conditions are changed, it can act as an acid promoting different sets of reactions. Thus, basic mechanisms for changes in hydrothermal operations (i.e., wet pyrolysis) are different from those occurring in the dry pyrolysis, and this difference is largely caused by the changes in the physical and chemical properties of water as its temperature increases [15]. To understand hydrothermal operation in sub- and supercritical regions, it is important to illustrate the behavior of various properties of water under these conditions. We will mainly focus on the water properties in the subcritical conditions. The properties of water under supercritical conditions are illustrated in Chapter 10. Interphase transport resistances can be considerably reduced at higher water temperatures. The water properties will vary considerably with temperature to facilitate various types of organic reactions and also the separations of products from byproducts. When feedstock contain inorganics such as sulfates, nitrates, and phosphates, hydrothermal operation can facilitate the recovery and recycling of these chemicals in their ionic forms for eventual use as fertilizers. Also, in hydrothermal operations, product streams are completely sterilized with respect to any possible pathogens including biotoxins, bacteria, and viruses. For temperatures greater than about 250°C and the contact time of few seconds, proteins are destructively hydrolyzed so that even prions would be destroyed [5,16].

Figure 5.1 illustrates the variations in dissociation constant, dielectric constant, and density as a function of temperature at ~30 MPa pressure. The figure shows that the density, the dissociation constant, and the static dielectric constant all vary significantly between the room temperature and the critical temperature. These changes cause enormous changes in the solvation behavior of water; it is changed from the polar, highly hydrogen-bonded solvent to the behavior of nonpolar solvent such as hexane. The dielectric constant changes from 80 to <2 in the temperature range of  $25^{\circ}C-450^{\circ}C$ .



**FIGURE 5.1** Variations of water density, static dielectric constant, and ion dissociation constant ( $K_w$ ) as a function of temperature at ~30 MPa. (From Peterson, A., Vogel, F., Lachance, R., Frolling, M., Antal, M., and Tester, J., *Energy & Environmental Science*, 1, 32–65, 2008. With permission.)

While the dissociation constant goes through a maximum with changes in temperature, it is also changed by about 5 orders of magnitude in nearly the same temperature range.

One of the indicators that water becomes polar to nonpolar solvent as temperature increases is the solubility of various inorganic salts and organic acids in water. Table 5.1 shows the solubility of various inorganic salts at 25 MPa pressure in water at different temperatures [5]. These data clearly indicate that as temperature increases, water becomes more nonpolar and the solubility of inorganic salts rapidly decreases. In fact, at very high temperature (in supercritical conditions), inorganic salts precipitate out of the water phase. Tables 5.2 and 5.3 show that the solubility of various fatty

	Salt Concentration (ppm)						
Temperature (°C)	CaCl <sub>2</sub>	KCI	NaCl	Na <sub>2</sub> SO <sub>4</sub>	CaSO <sub>4</sub>		
350	6000 <sup>a</sup>	_	_	60,000	0.6		
400	18	1000 <sup>a</sup>	1200 <sup>a</sup>	30	0.07		
450	6	200	250	0.7	0.004		
500	3	100	110	_	0.0017		
550	2	100 <sup>a</sup>	100	_	0.008		
Decrease <sup>b</sup>	9	10	12	_	8.75		

# TABLE 5.1 Solubility Limits of Various Salts in Water at 25 MPa

Source: Peterson, A., Vogel, F., Lachance, R., Frolling, M., Antal, M., and Tester, J., Energy & Environmental Science, 1, 32–65, 2008. With permission.

<sup>a</sup> The best extrapolated estimates from the graphical data.

<sup>b</sup> Decrease ratio indicates solubility at 400°C/solubility at 550°C.

# TABLE 5.2Fatty Acid Concentration in Water at Different Temperatures at 15 MPa

Temperature (°C)	Solubility (kg/kg)						
	<i>n</i> = 8	<i>n</i> = 10	<i>n</i> = 12	<i>n</i> = 14	<i>n</i> = 16	<i>n</i> = 18	
75	$4 \times 10^{-3}$	$7 \times 10^{-4}$	10-4	$1.5 \times 10^{-5}$	_	_	
100	$9 \times 10^{-3}$	10-3	$1.8 \times 10^{-4}$	$5 \times 10^{-5}$	_	_	
150	$4 \times 10^{-2}$	$7 \times 10^{-2}$	10 <sup>-3</sup>	$4 \times 10^{-4}$	$9 \times 10^{-6}$	_	
200	$1.5 \times 10^{-1}$	$2 \times 10^{-2}$	10-2	$1.5 \times 10^{-3}$	$8 \times 10^{-4}$	$5 \times 10^{-5}$	
225	1.2	10 <sup>-1 a</sup>	$5 \times 10^{-2}$	$5 \times 10^{-3}$	$5 \times 10^{-3}$	$6 \times 10^{-4}$	
Increase <sup>b</sup>	3000	142.8ª	500	333.3	_	_	

*Source:* Peterson, A., Vogel, F., Lachance, R., Frolling, M., Antal, M., and Tester, J., *Energy & Environmental Science*, 1, 32–65, 2008. With permission.

<sup>a</sup> The best extrapolated estimates from the graphical data.

<sup>b</sup> Increase numbers denote the ratio of fatty acid concentration at 225°C/fatty acid concentration at 75°C. *n*, number of carbon atoms in fatty acid.

# TABLE 5.3Water Concentration in Two Fatty Acids at DifferentTemperatures and at the Vapor Pressure of the System

	Solubility (kg/kg)				
Temperature (°C)	Coconut Fatty Acids	Tallow Fatty Acids			
100	0.05	0.01			
150	0.075	0.02			
200	0.1	0.05			
250	0.28	0.1			
300 <sup>a</sup>	0.70	0.23			
Increase <sup>b</sup>	14	23			

Source: Peterson, A., Vogel, F., Lachance, R., Frolling, M., Antal, M., and Tester, J., *Energy & Environmental Science*, 1, 32–65, 2008. With permission.

<sup>a</sup> The best extrapolated estimates from the graphical data.

<sup>b</sup> Increase ratio indicates solubility at 300°C/solubility at 100°C.

acids in water and vice versa increases with temperature, meaning that fatty acids dissolve well in high-temperature water allowing organic reactions to occur in the water phase. This is another indication of the fact that at high temperatures, water behaves more like an organic nonpolar solvent than a polar solvent.

In hydrothermal operations, water can act as a reactant as well as a solvent. Recently, Savage [14] outlined a number of organic reactions that can occur in the supercritical or near supercritical conditions. These reactions can be complete oxidation, decomposition of organic materials and compounds, and a variety of chemical syntheses. A review of chemical oxidation reactions near the critical region was also recently reported by Ding et al. [17]. The water thus provides a suitable medium for many hydrocarbon refinery operations involving a host of organic syntheses.

#### 5.2 HYDROTHERMAL CARBONIZATION (WET PYROLYSIS)

HTC is a thermochemical conversion process to convert biomass into a solid, coallike product in the presence of liquid water. This process is often called a wet or hydropyrolysis process and results in the production of "hydrochar" that has high carbon content and low oxygen content compared to original biomass. The main advantage of the HTC process over conventional pyrolysis process is that it can convert wet feedstock into carbonaceous material without having to remove water with an energy-intensive and energy-expensive drying process. The potential feedstock that can be used for this process are wet animal manures, human waste, sewage sludges, municipal solid waste (MSW), aquaculture and algal residues, and many other wet energy crops. The process is of course most beneficial when biomass is accompanied by a large amount of water. The solids produced from this process have been given many names such as char, biocoal or biochar, or more accurately hydrochar to differentiate it from the char or coal produced by the conventional dry pyrolysis. Significant reviews of hydrochar have been published recently particularly on its production processes [18–28]. The interest in hydrochar has increased very rapidly due to its connection to understand natural coal formation [18–20,27], its use in creating new innovative materials [21], and its application in soil quality improvement [22–28].

HTC can be an exothermic process, which lowers both oxygen and hydrogen content of the original feedstock mainly by dehydration and decarboxylation. The overall reaction identifying the heating value of the process can be expressed as [18–28]

$$C_6H_{12}O_5 \rightarrow C_{5,25}H_4O_{0,5} + 0.75CO_2 + 3H_2O$$
 (5.1)

The initial phase of this overall reaction, that is, hydrolysis of cellulose, is an endothermic reaction [29]. As shown in Figure 5.2, this process is not as harsh as dry pyrolysis in the reduction of hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios, and it produces "coal-like" material, which can be similar to bituminous or sub-bituminous coals. Typical effects of residence time and temperature on selected feedstock such as cellulose, peat bog, and wood are illustrated by Libra et al. [15]. Generally, the process occurs in the temperature range of 180°C–220°C at saturated pressure and for the reaction conditions that last for several hours. The process is accompanied by numerous reaction mechanisms such as hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization, which are further discussed in Sections 5.2.1 through 5.2.4. These are not consecutive but parallel reaction paths, and the detailed



**FIGURE 5.2** Comparison of H/C and O/C ratio variations for dry and wet pyrolysis processes (HTC) for various feedstock. (From Libra, J., Ro, K., Kammann, C., Funke, A., Berge, N., Neubauer, Y., Titirici, M., Fuhner, C., Bens, O., and Emmerich, K., *Biofuels*, 2, 89–124, 2011. With permission.)

nature of these mechanisms and their relative significance during the course of reaction primarily depend on the nature of the feedstock.

During the HTC process, biomass components are hydrolyzed to produce a large amount of monomers and oligomers [15]. Simultaneously, water-soluble extractables are also produced. These monomers, oligomers, and extractables then further undergo dehydration, decarboxylation, and condensation reactions. Many intermediates such as 5-hydroxymethylfurfural (HMF) are very reactive and some of them have high chemical values. These intermediates further undergo polymerization to produce humic acids, bitumen, and insoluble solids, some of which precipitate as HTC coal or hydrochar. Some components of biomass (e.g., crystalline cellulose) or oligomer cellulose do not hydrolyze under these reaction conditions. More details on the reaction mechanisms during the HTC process are given in the published literature [15,18,22–27,30–32].

Carbonization of biomass has a number of advantages over biological treatment. First, it takes only few hours as opposed to days and months taken by the biological process allowing more compact reactor design. While toxic feedstock cannot be converted biochemically, high temperature and chemical reactivity of hydrothermal environment can destroy pathogens and potential organic contaminants such as pharmaceutically active compounds [33–40]. HTC also produces useful gas, liquid, and solid products that can be further utilized, which contribute to greenhouse gas (GHG) and climate change mitigations, odor reduction, and soil amelioration [33–40]. The discussion in Sections 5.2.1 through 5.2.5 closely follows an excellent review by Libra et al. [15] and others [2,18–40].

#### 5.2.1 REACTION MECHANISMS

As mentioned earlier, HTC is accompanied by a series of chemical reactions such as hydrolysis, dehydration, decarboxylation, polymerization, and aromatization [14,15,18,21]. These reaction mechanisms are briefly described below.

Hydrolysis reactions during the HTC process mainly break down ether and ester bonds resulting in a wide range of products that include saccharides of cellulose and phenolic fragments of lignin. Along with other degradation mechanisms mentioned later, the intermediate products are also further hydrolyzed such as HMF converted to levulinic acid and formic acid. This transformation is further discussed in Chapter 7 on biofine process. Hemicellulose is hydrolyzed around 180°C and cellulose is hydrolyzed above ~200°C. The detailed mechanism of cellulose hydrolysis is given by Peterson et al. [5]. While initial hydrolysis reactions are favored by the alkaline conditions, further degradation of glucose is accelerated by the acidic conditions. In a pH range of 3–7, the rate of reaction is largely independent of H<sup>+</sup> and OH<sup>-</sup> concentrations. The hydrolysis of lignin occurs around 200°C and produces highly active low-molecular-weight substances. Some of these substances go through condensation reactions and precipitate from the solutions. In general, hydrolysis reactions are fast and transport limited. The structures produced from hemicellulose and lignin interact with each other resulting in high solubility of aromatic structures. At high temperatures, condensation reactions are likely to occur.

Chemical dehydration of biomass generally results in the elimination of hydroxyl group and the production of water. For example, the dehydration of cellulose is as follows [40]:

$$4(C_6H_{10}O_5)_n \rightleftharpoons 2(C_{12}H_{10}O_5)_n + 10H_2O$$
(5.2)

The rate of decarboxylation versus dehydration is generally measured by the factor F = mole of CO<sub>2</sub>/mole of H<sub>2</sub>O that varies from 0.2 for cellulose and 1 for lignite.

Condensation of fragments can also regenerate water during the HTC process, which results in a partial elimination of carboxyl groups producing  $CO_2$  and CO above 150°C [2,15,18,21]. Generally,  $CO_2$  is produced from carboxyl groups and CO is produced from carbonyl groups. One likely source for  $CO_2$  is formic acid that is formed in a significant amount by degradation of cellulose.  $CO_2$  can also be produced by condensation reactions, cleavage of intramolecular bonds, and destruction of oxidized molecules at high temperatures.

In an HTC process, intermediates that are created by dehydration and decarboxylation reactions are highly active and can polymerize to produce larger molecules. Condensation reactions are also accounted for the production of  $CO_2$ . The rate of carbonization is increasingly determined by stearic influences with a higher condensation degree of aromatics [15,18,19,21]. Thus, condensation polymerization is the main reason for the formation of biocoal in the HTC process. The condensation polymerization is most likely governed by the step-growth polymerization [15,18,19,21].

Cellulosic structures are capable of forming aromatic structures under hydrothermal conditions [2,15,18,19,21]. Aromatic structures show high stability under hydrothermal reaction conditions and may be considered as a basic building block of HTC coal. Alkaline conditions favor aromatization. Cross-linking condensation of aromatic rings also makes up the major constituents of HTC coal. A large number of aromatic bonds reduce the effects of HTC process on the carbon content. High temperature and residence time favor aromatization. Cellulose aromatizes most in the temperature range of  $200^{\circ}C-300^{\circ}C$ .

Besides the reaction mechanisms mentioned earlier, certain transformation reactions for crystalline structures in cellulose or certain oligomers are also possible. Their contribution at temperatures below 200°C appears to be small [15,18,19,21]. Demethylation has been used to explain the conversion of phenolic structure to catechol-like structure in HTC coal. The production of a small amount of methane substantiates this hypothesis. At temperatures higher than 200°C, pyrolytic reactions may also compete with the mechanisms mentioned earlier, although a significant amount of tar and CO (major products of pyrolysis) has not been found. Finally, Fischer–Tropsch (FT)-type reactions may also occur during the HTC process.

In general, wet pyrolysis is more effective on cellulose than on lignin. The literature data show that during HTC of lignin, the decline in the H/C ratio is not as severe as that of cellulose or even wood [15,18,19]. The decline in the H/C ratio of wood is in between that of lignin and cellulose.

#### 5.2.2 EFFECTS OF OPERATING CONDITIONS

A number of operating conditions such as (1) the water and solid concentrations, (2) the feed slurry pH value, (3) the reaction temperature and pressure, (4) the reaction residence time, and (5) the nature of feedstock affect the product distributions. These effects are well described in the literature [2,15,18–40]. Here we briefly summarize these literature results.

HTC process and formation of hydrochar requires the presence of water. It is known that the biomass above the water surface does not carbonize, although only small amount of water is necessary. The process of carbonization is accelerated by water because of its active role as a solvent, a reactant, and a catalyst during various steps of biomass degradation and subsequent condensation and aromatization processes. Water helps thermally driven pyrolysis. The initial step of hydrolysis is very important and the role of water for this step increases with an increase in temperature. Water facilitates the condensation polymerization of active intermediate species and also dissolves numerous compounds formed during the HTC process. The amount of water can also affect the transport of fragments from the influence of reactive centers. Generally, very low concentration of biomass in water may result in very low production of precipitated carbonized solids since most biomass may be dissolved. However, excessive biomass may result in some unreacted organic materials. Generally, increase in feed solid concentration increases the monomer concentration in the liquid phase. The key is to optimize the effect of residence time-solids concentration interplay on the extent of polymerization reaction. For each feedstock, there will be an optimum solids concentration to achieve the highest yield of carbonized solids.

It is known that during HTC, pH drops due to the formation of acetic, formic, lactic, and levulinic acids [15,18,19,21]. It is also known that natural coalification requires a neutral-to-weak acidic environment [15,18,19,21]. The effects of the nature and quantity of acids and bases on the product characteristics are well described in many of the studies mentioned earlier. In general, high pH values result in the product with a high H/C ratio, hydrolysis reactions are favored by the acidic conditions, and a weak acidic condition improves the overall rate of HTC [2,15,18–40].

Depending on the nature of the feedstock, an exothermal effect during hydrothermal operation can occur at as low as 100°C temperature (e.g., for peat). Temperature is the most important parameter in the HTC process. It is known that hydrolysis of glucose with subsequent dehydration may take several seconds at 270°C, but it will take up to several hours at 150°C. The rate of polymerization is also temperature dependent. The temperature has a definite influence on the nature of biomass that can be hydrolyzed. Hemicellulose hydrolyzes at 180°C and lignin at 200°C, but cellulose hydrolysis requires 220°C [2,15,18,19,21]. Pyrolytic reactions also become more important at higher temperatures.

The temperature also affects all the physical and chemical properties that are important in the HTC process. The viscosity of water is also decreased by twofold when the temperature is increased from the room temperature to around 350°C. Lower viscosity helps the water penetrate in porous biomass media. While pressure is
a more expensive process variable, it does not affect the HTC process as significantly as the temperature. While both dehydration and decarboxylation reactions are suppressed with an increase in pressure, this, however, does not significantly affect the overall HTC process. An increase in pressure facilitates (1) the removal of extractable, (2) solubilization of compressed gases and physical compacting of biocoal, and (3) hydrogen ion transfer and condensation polymerization between solids allowing the use of higher biomass/water ratio.

Although initial extraction and hydrolysis are rapid reactions, overall HTC process is a slow-limiting process. The diffusion-controlled transport mechanisms during biomass degradation and condensation polymerization govern the overall rate of reaction. Due to its slow nature, HTC coal yield increases with an increase in residence time.

Finally, feedstock characteristics such as chemical composition, volatile and noncombustible fractions, moisture content, particle size, and energy content significantly affect conversion efficiency and char characteristics. These effects are well described in the studies mentioned earlier [2,15,18–40].

#### 5.2.3 COMPARISON OF HTC AND DRY PYROLYSIS PROCESS

HTC process produce a high amount of solids, more water-soluble organics, and fewer gases that mainly contain  $CO_2$  [2,15,18,19,22]. The chemical structure of hydrochar more closely resembles coal than charcoal in terms of elemental composition and types of chemical bonds and their relative quantities. As discussed earlier, HTC hydrochar has higher H/C and O/C ratios than the char coming from dry pyrolysis (Figure 5.2). Thus, the ratio of decarboxylation to dehydration reaction is higher in HTC than in dry pyrolysis. Figure 5.2 shows that even though feed composition of animal-derived biomass is different from that of plant materials, the final hydrochar products coming from these materials have similar elemental compositions. The aromatic structure of hydrochar product is substantially different from that of char from dry pyrolysis. These and other structural differences indicate that different reaction mechanisms govern these two processes. Radical mechanism pathways taken in dry pyrolysis are completely suppressed in hot water in favor of ionic reactions.

HTC primarily starts out with hydrolysis reactions of biomacromolecules resulting in the production of oligosaccharides, hexoses, pentoses, and fragments of lignin [2,15,18,19,22]. These intermediates in the aqueous phase follow completely different reaction pathways than those in thermally driven dry pyrolysis. For example, in dry pyrolysis of glucose, the major product is anhydrous glucose, which appears only in a very small amount in the HTC process. In the HTC process, HMF is a crucial intermediate, which provides a standard platform for many subsequent reactions. Hydrolysis in the HTC process completely disintegrates the physical structure of biomass. This is not the case for dry pyrolysis. The degree of hydrolysis, however, depends on the temperature and process design [2,15,18,19,22]. Final H/C ratios produced by HTC of lignin and cellulose are different. This is a result of different reaction paths of these two processes. The literature has shown that HTC is more energy efficient as a pretreatment process than dry pyrolysis for wood combustion when the water content is >50% [2,15,18–40]. Generally, when the water content of feed slurry is >50%–70%, wet pyrolysis is preferred over dry pyrolysis. For such a slurry, dry pyrolysis will only be capable of producing charred material. However, HTC process can be used for a slurry containing 70%–90% water or even higher. The amount of external heat required will depend on the process design. Generally, HTC process with a slurry containing >40% water will have an energetic advantage over dry pyrolysis. HTC process needs to manage the required pressure and its effect on the safety and material issues. The energy from hot water also needs to be recovered. In general, energetic requirements to run the process and its auxiliary equipment are higher for a hydrothermal system than for dry pyrolysis.

#### 5.2.4 PRODUCT CHARACTERISTICS AND USAGES

HTC process largely produces hydrochar (solid) and liquid with dissolved nutrients. The fate of heavy metals and organic chemicals (present in the original feedstock or created by the reactions) is generally not known and must be traced during the process. Wet pyrolysis cannot destroy heavy metals. Since they have a toxic risk potential, their fate needs to be followed. If they accumulate in the solid char, which is subsequently used as soil nutrient, they can affect the food chain. Generally, except for zinc, heavy metal concentrations in char do not exceed the allowable limits [15,18,19,21,30–40]. Also, heavy metal contents of hydrochar obtained by wet pyrolysis are less than those obtained in biochar from dry pyrolysis [15,18,19,21,30–40]. Just like for heavy metals, a systematic knowledge of the fate of organic compounds during the HTC process is not well understood. Unlike heavy metals, new organic compounds can be formed during condensation, polymerization, and aromatization reactions. The fate of compounds such as polychlorinated biphenyl (PCB) and hexachlorobenzene (HCB) needs to be particularly followed along with all other organic chemicals during the HTC process [15,18,19,21,30–40].

For both animal manures and sewage sludge, hydrochar retains a significant level of calcium, potassium, and phosphorus. pH affects the mobility and sorption capability of the nutrients, particularly for the case of phosphorus. In the HTC process, dissolution of water-soluble minerals can be significant [15,18,19,21,30–40]; however, the nutrient content will also depend on the technique for dewatering the solid conversion product. The ratio between evaporation and dewatering governs the amount of plant nutrients that will be adsorbed or retained at the hydrochar interface. Nutrient retention should be an important parameter in the detailed process design.

Generally, an increase in temperature decreases the hydrochar yield and increases the yield of liquids and gases such as  $CO_2$ , CO, and  $H_2$ . An increase in temperature also decreases the H/C and O/C ratios in the hydrochar. The maximum allowable yields (which may be obtained at very large residence time) for various feedstock are illustrated by Libra et al. [15] and others [18,19,21]. A lower biomass solid concentration (i.e., high water concentration) generally gives a lower hydrochar yield. In general, 60%–84% of the biomass carbon remains in the hydrochar. The char composition is mainly affected by the nature of the feedstock, the temperature, and the reaction time. For all feedstock, an increase in temperature increases the carbon content and decreases the oxygen content of the hydrochar.

Hydrochar is often used for soil application as a fertilizer or a carbon sequester. Some discussion in this regard is given by Libra et al. [15] and others [30–40]. Experimental evidences indicate that depending on the nature of char, it can remain in soil for a long period. While less aromatic hydrochar stays longer in soils than uncarbonized carbon, it decomposes faster than the char from dry pyrolysis. The oxidation and degradation of char can be affected by the swelling–shrinking of clay materials by the weather. The degradation of hydrochar is also accelerated by labile carbon substrates and white-rot fungi, which are dominant char decomposers. In general, the degradation and stability of hydrochar in top soils of Earth's surface can be affected by surface erosion and dissolution as dissolved organic carbon or transported to subsoil as small particles with rain water. The char particles that are imbedded in subsoil surface are less susceptible to erosion and degradation.

Hydrochar promotes the fungal growth and soil aggregation [15,30–40]. It will very likely reduce the tensile strength, increase the hydraulic conductivity, and enhance the soil water holding capacity (WHC). Hydrochar does not have a very large internal surface area that may affect the penetration by water and nutrients and the resulting microbial activity. While the WHC of hydrochar is generally higher than that of mineral soils, it can be considerably reduced after it is fully dried. Hydrochars are more acidic than biochars and they do undergo aging process that can change the functional groups and therefore its effectiveness as nutrient. The hydrochar can also be used as (1) activated carbon adsorbents, (2) raw materials for the generation of nanostructured materials, (3) catalyst supports or as catalysts, (4)  $CO_2$  sorption materials, and (5) energy production and storage materials. These applications of hydrochar are described in more detail in an excellent review by Libra et al. [15].

The HTC process is accompanied by a large number of intermediate products due to complex reaction mechanism. The solids coming out of the HTC process represent the agglomerates of chemical substances. An elemental analysis of the hydrochar shows that it may approach lignite or even sub-bituminous coal depending on the reaction severity (Figure 5.2). An exception is resin whose H/C ratio remains unaffected by the HTC process. As mentioned earlier, HTC coal from lignin tends to have a lower hydrogen content, whereas coal from cellulose tends to achieve higher carbon content [15,18,19,21].

HTC coal (hydrochar) is soluble in benzol–alcohol mixtures, alkaline solutions, and ammonia [15]. The skeletal of HTC coal is very similar to that of natural coal, although it exhibits a higher amount of functional groups compared to natural bituminous coal. The removal of hydroxyl and carboxyl groups during the HTC process makes HTC coal with a lower hydrophobicity than the original materials [15,18,19,21]. While the inorganics largely remain in HTC coal, their relation with process conditions is not well known. While HTC coal has a small surface area, this area can be increased significantly (by 2 orders of magnitude) by removing extractables or by thermal treatment [15]. Observations of the nanostructure of HTC coal

reveal its potential technical applications as functionalized carbonaceous materials. Libra et al. [15] and others [30–40] show that with the use of proper starting materials and appropriate catalyst/template-assisted treatment methods, various types of nanospheres, nanocables, nanofibers, microcables, submicrotubes, and porous structures can be created from HTC coal.

#### 5.2.5 PROCESS CONSIDERATIONS

The HTC process generates more water than carbon dioxide. Water acts as a solvent and a reactant, and therefore carries a significant amount of inorganics and organics, many of which can be valuable chemicals. The solids in water can cause problems upon precipitation due to condensation or polymerization reactions. The wastewater of the HTC process can be processed with aerobic or anaerobic treatment to lower its total organic content. Some inorganics in water may be good nutrients for soil. The gases coming out of the HTC process mainly contain carbon dioxide with minor CO, CH<sub>4</sub>, and H<sub>2</sub> as well as traces of  $C_mH_n$ . The dissolution of carbon dioxide in the liquid phase may affect the critical temperature condition in the process. An increase in temperature generally decreases CO and increases H<sub>2</sub> and CH<sub>4</sub>. The progress of the HTC process can be monitored by following the production of carbon dioxide. The decarboxylation of feedstock is a major reaction during the HTC process [15,18,19,21]. While its high rate produces high heating value HTC coal, it also reduces carbon efficiency. Thus, the process should be optimized based on the end use of the final product.

In the HTC process, the ratio of biomass to water should be kept as high as possible to enhance polymerization. Less water will also give less energy loss and less pumping costs for the total throughput. The feedstock can be submerged in the water by mechanical compacting device to take advantage of the best reaction conditions. The residence time should be as large as possible to get the complete reaction to occur and minimize the loss or organics in the wastewater. A recirculation of water is one way to achieve this objective.

The reaction conditions should take advantages of the possible effects of organic acids; they may give faster polymerization and higher ash content of the produced HTC coal. While higher temperature accelerates the process and gives higher carbon content in the HTC product, high pressure required to achieve high temperature may be expensive. Pressure–temperature relationship should be optimized based on the intended use of the end product. Since hydrolysis is a diffusion-controlled reaction, small particle size of the feedstock may be beneficial. This, however, increases the energy demand and the investment cost [15,18,19,21].

# 5.3 HYDROTHERMAL LIQUEFACTION

Just like the HTC process, HTL is a wet pyrolysis process in which complex organic (particularly carbohydrate base) molecules from biowaste (manure and food processing waste), lignocellulose (crop residue), algae, and others are converted to crude oil type and other liquid fuel products as well as chemicals. To some extent, it mimics the natural geological process which is thought to be involved in the production of fossil fuels. HTL involves a direct liquefaction of biomass in the presence of water (and may be a catalyst) to liquid fuels in subcritical conditions. The process conditions for HTL thus differ from the HTC process described earlier in that generally HTL process requires the temperature range of about 250°C–400°C, a range that is higher than that used in the HTC process and that does not use the conditions of supercritical water. It is analogous to intermediate-temperature dry pyrolysis in that the objective of both processes is to produce liquid with minimum amounts of solids and gases.

The HTL process is not a selective catalytic process such as aqueous-phase reforming (APR) and its derivative technologies described in Chapter 6, in which hydrogen, alkanes, and monofunctional groups are produced at low temperature (range of 215°C–265°C) from a selective group of oxygenated biomass by a set of selective catalysts or biofine process described in Chapter 7. When high-temperature HTL reaction conditions are used with a selective group of catalysts, HTG process evolves. This process largely generates methane and carbon dioxide with some hydrogen. The HTG process is described in Section 5.4. Numerous excellent reviews on HTL are available in the literature [41–47] (Elliott, 2012, pers. comm.).

#### 5.3.1 REACTION MECHANISMS

HTL is a chemical transformation process of biomass in a heated and pressurized water environment where long-chain organic compounds break into short-chain hydrocarbons. All fossil fuels found underground, petroleum, natural gas and coal, and so on based on biogenic hypothesis, are formed through the HTL process from biomass buried beneath the ground and subjected to high pressure and temperature. In the recent years, it has been found that kerogens (which are a large part of oil shale) break down much easily in the presence of water than without it [41–48] (Elliott, 2012, pers. comm.). Gas hydrates and several carbon isotope studies have shown the involvement of water (and hydrogen from it) in the creation of natural gas. HTL process reaction paths depend on the temperature, the pressure, the reaction time, the water pH, the solids particle size, and the nature of the catalysts (if present).

While the exact reaction pathway for the HTL process is as yet not known, the study of Appell et al. [49–52] at Pittsburgh Energy Technology Center made some important points for the process. They studied liquefaction of wood particles with hydrogen and carbon monoxide at 370°C and 27 MPa pressure in the presence of sodium carbonate catalyst. Alkali salts such as sodium carbonate and potassium carbonate can initiate the hydrolysis of cellulose and hemicellulose into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation reactions. The amount of solids residue remained depends on the lignin content. Lignin contains alkyl phenols and free phenoxyl radicals formed by its thermal decomposition above 250°C, and it is likely to recombine and form the solids residue through condensation or repolymerization reaction.

Appell et al. suggested that during the conversion of carbohydrates to oil, sodium carbonate reacts with carbon monoxide and water to form sodium formate as

$$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCO_2Na + CO_2$$
(5.3)

which in turn reacts with cellulose in the wood wastes to form oil and regenerate sodium carbonate as

$$2C_6H_{10}O_5 + 2HCO_2Na \rightarrow 2C_2H_{10}O_4 + H_2O + CO_2 + Na_2CO_3$$
 (5.4)

Vicinal hydroxyl groups in the carbohydrates undergo dehydration to form an enol followed by its isomerization to ketone. The newly formed carbonyl group is reduced to the corresponding alcohol with formate ion and water. The hydroxyl ion then reacts with additional carbon monoxide to regenerate the formate ion.

The above set of basic reactions is accompanied by a multitude of side reactions producing a whole host of intermediates. Some of the beneficial side reactions are facilitated by the alkaline conditions. When two carbonyl groups become vicinal, a benzylic type of rearrangement occurs, which results in a hydroxyl acid. The hydroxyl acid readily decarboxylates causing a net effect of reducing the remainder of the carbohydrate-derived molecule [49–52].

For the HTL process, the segments produced by hydrolysis are further degraded by dehydration, dehydrogenation, decarboxylation, and deoxygenation. These types of reactions result in the formation of paraffin-type structures that have less oxygen than the original compounds.

There are several other features in this reaction mechanism. Aldol condensation may be a part of the reaction. This can occur between a carbonyl group on one molecule and two hydrogens on another molecule, resulting in the elimination of water. In the absence of a reducing agent such as CO or  $H_2$ , condensation reactions dominate, which lead to polymerization and the formation of solid-like products. The reducing agents keep the concentration of carbonyl groups low enough to produce liquid products instead of solid products.

Appell et al. [49–52] also pointed out that hydrogen radicals formed by the addition of CO and the presence of water–gas shift reaction can react with various carbonyl and hydroxyl groups to form paraffins and water, thus avoiding various condensation reactions. The addition of CO is thus more useful than that of molecular hydrogen (Table 5.4).

Effect of Reducing Gas on Maximum Liquid Oil Yield as a Function of Liquefaction Temperature							
Reducing Gas	Maximum Yield of Liquid Oil (wt%)						
Air	25						
Nitrogen	36						
Hydrogen	42						
Carbon monoxide	50						
Source: Akhtar, A. and An 1615–1624, 2011.	nin, N., <i>Renewable &amp; Sustainable Energy Reviews</i> , 15, With permission.						

Note: These are best estimates from the graphical data.

In the HTL process, other sets of complex reactions such as cracking and reduction of polymers such as lignin and lipids, hydrolysis of cellulose and hemicellulose to glucose and other simple sugars, hydrogenolysis in the presence of hydrogen, reduction of amino acids, dehydration, decarboxylation, C–O and C–C bond ruptures, and hydrogenation of various functional groups result in the production of liquids from biomass rather than solids as they occur in the HTC process [41–52] (Elliott, 2012, pers. comm.). More fundamental work in this area is still needed.

#### 5.3.2 EFFECTS OF OPERATING CONDITIONS ON HTL PROCESS

Unlike the HTC process, the main objective of the HTL process is to generate biooil of high quality. The process is designed to minimize the production of solids and gas. Numerous process parameters affect the performance of the HTL process and these are well examined in the literature [41–48,53–66] (Elliott, 2012, pers. comm.). The major process operating parameters are (1) temperature, (2) residence time, (3) solids concentration, (4) pressure, (5) biomass heating rate, (6) biomass particle size, (7) presence of hydrogen donor solvent and reducing gas environment, and (8) pH of slurry. Since the most important variable is the nature of feedstock, its effect on process performance is discussed in Section 5.3.3. The literature information on the effects of various operating parameters on the product distribution was well summarized in an excellent review by Akhtar and Amin [41]. Sections 5.3.2.1 through 5.3.2.3 briefly summarize their assessments.

#### 5.3.2.1 Pressure, Temperature, and Residence Time

In any HTL process, pressure must be at least equal or above the saturation pressure to maintain the process in a single-phase operation. High pressure allows a better manipulation of hydrolysis reaction and the reaction pathways are thermodynamically favorable to produce liquids and gases. High pressure also increases the solvent density, resulting in better extraction capability of the solvent. For a catalytic operation, however, high solvent density can block the active catalyst sites and therefore reduce C–C bond breakage and the resulting degradation rate.

Generally, high temperature increases both the concentration of free radicals and the probability of repolymerization of fragmented species. The hydrolysis and fragmentation of free radicals dominate in the early stages of the reactions, whereas repolymerization occurs in the later stages of the reaction, which in turn forms char. Generally, at very high-temperature bio-oil production is reduced due to (1) the secondary decompositions and Boudouard gas reactions that become active at high temperature leading to high gas formation or (2) the recombination of free radicals to form char. The overall process conditions and the presence of a catalyst generally dictate the dominant reaction mechanism. For most feedstock, however, the maximum bio-oil is obtained at temperatures around 300°C–350°C [41]. Also, the literature results show that the largest shift in the optimum temperature for bio-oil occurs for algae [67–79]. Both softwood and grass are generally more difficult to liquefy because of their higher lignin content and less reactive cellulose content.

Temperature (°C)	Residue (%)	<b>Oil</b> (%)	WS/W (%)	Gas (%)	O/S	O/G
150	72	6	21	1	0.083	6
200	56	13	26	5	0.23	2.6
250	32	33	29	6	1.03	5.5
300	16	38	30	16	2.37	2.37
350	16	27	33	24	1.69	1.37

# TABLE 5.5Yield of HTL Products as a Function of Temperature

*Source:* Akhtar, A. and Amin, N., *Renewable & Sustainable Energy Reviews*, 15, 1615–1624, 2011. With permission.

Note: These are the best calculations/estimations from the graphical data.

O/G, oil/gas ratio; O/S, oil/solid ratio; W, water; WS, water solubles.

Akhtar and Amin [41] compared the bio-oil productions from various studies and showed that bio-oil production showed an optimum in each study, although the exact location of the maximum oil production depended on the nature of the feedstock. At temperatures above 300°C, the gas production can also increase particularly when a suitable catalyst is used. The typical temperature dependence of the product distribution of solids residue, oil, water solubles plus water, and gas are illustrated in Table 5.5 [41]. Again, the exact phase composition will depend on the nature of the feedstock. The table also shows that both oil/solid and oil/gas ratios show maxima at a temperature around 300°C. Akhtar and Amin [41] suggested that a variation in the solids residue can be set as a reference point to measure the optimum liquefaction temperature for bio-oil yield for a given feedstock. As shown in the table, an increase in temperature increases gas yield and decreases residue yield. The oil yield shows an optimum with respect to the temperature at around 300°C.

The effect of the residence time on the HTL process has been examined by numerous investigators and this is well summarized by Akhtar and Amin [41]. Both biomass conversion and the nature of product distribution depend on the residence time. Since the initial hydrolysis process is fast, normally short residence is preferred in HTL. Boocock and Sherman [67] showed that the bio-oil production was suppressed at high residence time except when biomass concentration in the feed was very high. The effect of residence time on the bio-oil yield also depended on the temperature. At low temperatures, an increase in residence gave higher bio-oil yield [41], whereas at high temperatures (250°C–280°C), high residence time gave poorer bio-oil yields due to an increase in gas yields. In general, higher residence time gave higher biomass conversion. Qu et al. [69] found a decrease in heavy oil production at high residence time.

The effect of the residence time on the product distribution in the HTL process is complex once the biomass conversion is leveled off. The intermediate products formed during this time can form gas, liquid, or solid products by the secondary and tertiary reactions depending on the nature of intermediates and the prevailing local reaction environment. Karagoz et al. [70] showed that the decomposition products were not the same at low and high residence times for both low-temperature (180°C) and high-temperature (250°C) operations. In general, the composition and yield of bio-oil can be optimized by suitably adjusting the temperature and the residence time such that heavy residues containing asphaltenes and pre-asphaltenes are converted selectively to oil (and not gas). Often an addition of a reducing agent such as CO or H<sub>2</sub> prevents polymerization reactions and stabilizes the active free radicals.

#### 5.3.2.2 Biomass Particle Size, Heating Rate, and Concentration

While a reduction in a particle size of biomass (particularly for biomass such as wheat straw, barley straw, and switchgrass) is energy intensive, in general, a smaller particle size results in higher degree of hydrolysis and fragmentation. However, the literature data show that the particle size has a secondary effect on biomass conversion and product distribution in an HTL process because of high solvation and extraction powers of water at high temperature and pressure. Zhang et al. [64] found no effect of the particle size variation from 0.5 to 2 mm of grass perennials on the yield of bio-oils. Akhtar and Amin [41] recommended that the particle size between 4 and 10 mm should be suitable to overcome the heat and mass transfer limitations at a reasonable grinding cost.

While the studies mentioned earlier indicated the marginal effects of particle size on the herbaceous biomass liquefaction process, Kobayashi et al. [68] showed a significant effect of particle size of woody biomass on the HTL process. Wood powder pulverized by the vibration mill, cutter mill, and grinder was used as a liquefaction material. The wood powder was sieved between 212 and 500  $\mu$ m. Based on the results of water solubles and specific surface areas for three different milling processes obtained in this study, it was concluded that an increase in specific surface area increased the production of water soluble (saccharine); however, the difference in water solubles between the grinder and the cutter mill was only marginal. This indicated that the crystallinity of the wood powder also affects the water solubles yield.

Bio-oil production during the HTL process generally occurs at moderate heating rates. Slow heating rates usually lead to the formation of char residue due to secondary condensation and polymerization reactions. Very high heating rates also promote secondary reactions that generally result in more gas production. The heating rate is important for both dry and wet pyrolyses, although it is less important in the HTL process due to the better dissolution and stabilization of fragmented species in hotcompressed water medium. Zhang [45] and Zhang et al. [64] observed that for a heating rate range of 5°C–140°C/min during the HTL process for grassland perennials, bio-oil yield increased from 63% to 76% with an increase in the heating rate.

The solids concentration also affects the bio-oil production [41]. In general, high amount of water favors the production of liquids largely due to enhanced extraction and higher degree of solvation of biomass. The solvent enhances the stability and solubility of fragmented components, thereby reducing the production of solids residues and gases. At high biomass concentration, the interactions between the fragmented biomass components and the water decrease, the reactions among various fragments increase, and thus the influence of water on the product distributions diminishes. At high biomass concentration, the HTL process behaves much like the intermediate-temperature dry pyrolysis resulting in less bio-oil production.

#### 5.3.2.3 Gas and Liquid Properties

Generally, a reducing gas or a hydrogen donor stabilizes the fragmented products of liquefaction. Reducing the environment inhibits condensation, cyclization, and repolymerization of free radicals, thereby reducing the char formation [14,41]. The stabilization occurs by the following reactions [14,41]:

$$Ar^* + H_2 \to ArH + H^* \tag{5.5}$$

$$Ar^* + H^* \to ArH \tag{5.6}$$

While  $H_2$  is an effective reducing agent, it is also an expensive one. Often syngas (CO and  $H_2$ ), steam,  $N_2$  and Argon, and so on are also used to provide a reducing environment [41]. The effects of various reducing agents on the maximum bio-oil production for cattle manure by the HTL process are illustrated in Table 5.4. The results showed that CO was the most effective reducing agent and provided the maximum bio-oil yield of 50% at 310°C [41]. This is in line with the assertion of Appell et al. [49–52]. The temperature (310°C) at which the maximum occurred was independent of the nature of the gas. Air was ineffective because it led to combustion of biomass. The results also indicated that reactive gases gave better maximum oil yield than an inert gas such as nitrogen.

The use of hydrogen donor solvents such as tetralin and phenanthrene is also an effective way to stabilize free radicals and improve the bio-oil yield. This has been extensively examined to improve the yield in direct coal liquefaction processes. In general, this is, however, expensive for its commercial applications. A suitable catalyst can also induce or accelerate hydrogen transfer reactions to improve the bio-oil yield. However, catalyst stability and cost can be the limiting factors. In general, an adsorption of reducing gas (such as  $H_2$ ) on the catalyst surface can increase the probability of hydrogen transfer reactions.

While most of the literature studies have focused on the neutral and alkaline water conditions for the HTL process, recently Yin et al. [59] have examined the effect of water pH on reaction mechanism and product distribution of HTL of cellulose. The study examined the water pH of 3, 7, and 14 in the temperature range of  $275^{\circ}C-320^{\circ}C$ , and the residence time of 0-30 min. The results showed that the composition of the products from HTL varied with pH. In acidic and neutral conditions, the main liquid product was HMF. Under alkaline conditions, the main compound was C<sub>2-5</sub> carboxylic acid. At all pH levels, high temperature and long residence times had negative effects on the bio-oil yields. The reaction mechanisms also depended on the pH level. Under acidic conditions, polymerization of HMF to solids reduced the bio-oil production. Under neutral conditions, HMF was converted to both solids and gases. Under alkaline conditions, bio-oil was converted to gases by the formation of short-chain acids and aldehydes. Different reaction mechanisms and product characteristics mean different strategies required to improve the quality and quantity of bio-oil under different pH conditions.

#### 5.3.3 ROLE OF FEEDSTOCK

The nature of feedstock is the most important variable affecting the quantity and quality of bio-oil by the HTL process. HTL produces high-density liquid fuels and operates in the presence of water eliminating the need for feedstock drying that is important in dry pyrolysis process. The HTL process uses agricultural biomass and biowaste including crop residues and wood, food processing waste, animal and human manure, and algae. The HTL process can also be used as a pretreatment process for the subsequent fermentation of the feedstock that are difficult to convert.

While animal and food processing waste contain lipids, proteins, and small amounts of lignocellulose, crop residues and wood primarily contain lignocellulose. The primary basic compounds in these feedstock are various isomers of glucose (such as D-glucose and L-glucose), hemicellulose, cellulose, lignin, amino acids, proteins, lipids including fatty acids such as stearic acid and palimitic acid, and so on. Over the years, more and more efforts have been made to examine the effectiveness of the HTL process for a variety of lignocellulosic wastes containing different amounts of lignins and crystalline cellulose. Some of the materials examined are swine manure, garbage, Indonesian biomass residue, birch wood, sawdust, rice husk, phytomass, and chlorella [41-47] (Elliott, 2012, pers. comm.). These feedstock have been tested in the temperature range of  $280^{\circ}$ C– $375^{\circ}$ C, the pressure range of 5–50 MPa, and the residence time of 5–180 min depending on the feedstock. In some cases, sodium carbonate was used as a catalyst. The final yield varied from 21% (in case of garbage) to as high as 61% (in case of swine manure) [41–47] (Elliott, 2012, pers. comm.). More recently, HTL has been applied to algae for making biofuel. HTL can thus be applied to a variety of biomass with a varying degree of success. In the following discussion, feedstock is broken into three categories: biowastes, lignocellulosic wastes, and algae. These three categories cover the range of feedstock property variation.

#### 5.3.3.1 Biowastes

The best raw materials for the HTL process are perhaps biowastes such as various types of manures and wastewaters because they are mostly cellulosic (with very little lignin) and can be easily converted into bio-oil under hydrothermal conditions. In general, presence of high cellulose and hemicellulose content in biomass yields more bio-oil. Appell et al. [49-52] were the first to examine various waste streams such as urban refuse, cellulosic wastes, and sewage sludge, and found that at a temperature around 380°C, a pressure of 1500 psig, and a residence time of 20 min, even in the absence of a catalyst, an oil yield of about 24.5% was obtained. At low temperatures, oil was largely paraffinic and cycloparaffinic in the presence of carboxyl and carbonyl groups, whereas at high temperatures some aromatics were present. Following this pioneering study, a significant number of additional studies were published [41-48,53-68] (Elliott, 2012, pers. comm.), indicating that the applicability of the HTL process to cellulosic wastes is easy. These studies are also extensively described in a number of recent reviews [41-48] (Elliott, 2012, pers. comm.). The studies included swine manure, bovine manure, cellulose, activated sludge, sewage sludge, artificial garbage, protein-containing biomass (such as food wastes), various types of wastewaters (including wastewater from paper and pulp industries), glucose, glycine, dairy manure, poultry litter, and so on. Some of these studies are briefly described below.

A study by Minowa et al. [71–74] using glucose and glycine as model compounds of carbohydrates and proteins indicated that a significant oil production started at temperatures >250°C and increased with the temperature. This and other studies have shown that fatty acids and lipid are the main reactants in HTL process. Below 300°C, aliphatic compounds are the major source of bio-oil. Protein is widely involved in HTL reaction possibly by peptide bond splitting and amino acid conversion dehydration. Within the range of 300°C-450°C, the protein conversion reaction intensifies and the peptide bond begins to react. Saccharide reaction mainly belongs to the splitting of branched chains and the group transfer while considerable dehydration and cyclization of the main chain still appear to be dominant. The decomposition of an individual cellulosic biomass differs based on its structure. Decomposition is easier in hemicelluloses due to amorphous structure. Cellulose is little crystalline to decompose due to beta(1–4)-glycosidic linkages and relatively intermediate degree of polymerization (500–10,000). The major products of holocellulose degradation include cellohexaose, cellopentaose, cellotriose, cellobiose, fructose, glucose, erythrose, glycolaldehyde, glyceraldehyde, pyruvaldehyde, and furfurals [71-74].

#### 5.3.3.2 Lignocellulose

The presence of liquid water as solvent is essential for HTL of lignocellulose feedstock. Water in this case acts as a solvent and reactant along with its role as a vehicle for biomass and a carrier for the catalyst. Furthermore, water is simple to use, inexpensive, and environmentally benign.

Lignocellulose is the largest segment of the total biomass and contains a significant amount of lignin along with cellulose. It is the lignin component along with crystalline cellulose that is difficult to convert to bio-oil in the HTL process. In the absence of a catalyst, lignin produces very little bio-oil and ends up as a solids residue in the HTL process. While water is an excellent medium for the intermediate hydrolysis of cellulose and other higher molecular-weight carbohydrates to watersoluble sugars, it is not as effective for hydrolysis of heavily aromatic and multiring aromatic structures. The breakdown of lignin requires high temperature or the presence of a catalyst. Within lignocellulosic substances, softwood gives much lower yield than hardwood because of the difference in their lignin contents. Zhang [45] and Akhtar and Amin [41], among others, have given an extensive review of HTL of a variety of lignocellulosic biomass such as various energy crops, herbaceous products, forestry and other agricultural wastes, and various crop oil wastes. Midgett [42] examined the HTL process for materials such as tallow seed, switchgrass, and pine dust. Zhong and Wei [80] studied the effect of temperature on four different types of woods and concluded that the bio-oil yield was affected by both the temperature and the lignin content of the wood.

An interesting study was carried out by Sugano et al. [48] in which they examined the effectiveness of black liquor, paper regeneration wastewater, and the water on HTL of herbaceous eucalyptus biomass. Like softwood, this material contains lignin. The study showed that black liquor gave very low oil yield and high yield of water-soluble components. The liquefaction of eucalyptus by water resulted in high residue production due to dehydration and polymerization, such as the formation of aliphatic ester bonds. The paper regeneration wastewater gave low residue and high yield of bio-oil compared to water. It appears that condensation reaction observed during the liquefaction in water was inhibited because carboxylic acid formed during the liquefaction of eucalyptus was neutralized with the cations in the wastewater. In the temperature range of 150°C–350°C, process wastewater gave the best oil yield compared to other two solvents. The optimum temperature for bio-oil yield was 300°C. This study indicated that solvent pH and other additives can affect the bio-oil production of lignocellulosic materials.

Finally, high degree of polymerization (>10,000) and complex branching make lignin difficult to decompose even at high temperatures. The studies described earlier show that the conversion of lignin containing lignocellulosic materials requires catalysts to produce bio-oil instead of solids and gases. An extensive literature review of various catalyst studies for the HTL process applied to lignocellulosic biomass is given by Zhang [45].

#### 5.3.3.3 Algae

Ever since Glen Meier of Renewable Energy Group introduced the concept of producing fuel from algae, it has caught everybody's attention [75–79,81–88]. Like biowaste, algae do not compete with food materials for fuel. The HTL of algae has been given some attention in the recent years. Minowa et al. [89] converted *Dunaliella tertiolecta* with a moisture content of 78.4% directly into 37% oil by the HTL process operated at 300°C and 10 MPa. The oil had a viscosity of 150–330 MPa-s and a calorific value of 36 kJ/g, numbers comparable to that of fuel oil. Dote et al. [90] hydrothermally converted the artificially cultivated *Botryococcus braunii* Kützing Berkeley strain. The strain contained about 50% hexane solubles. The HTL process of this strain resulted in the production of 57% petroleum-like bio-oil at 300°C. Similar work was carried out for *Microcystis viridis* harvested from a lake.

Brown et al. [91] reported hydrothermal conversion of marine microalgae *Nannochloropsis* sp. into bio-oil in the temperature range of 200°C–500°C and for the residence time of 60 min. The highest bio-oil of 43 wt% was obtained at 350°C with a heating value of 39 MJ/kg, a number comparable to petroleum crude oil. The H/C and O/C ratios changed from 1.73 and 0.12 at 200°C to 1.04 and 0.05 at 500°C, respectively. The major components of bio-oil were phenol and its alkylated derivatives, heterocyclic N-containing compounds, long-chain fatty acids, alkanes, alkenes, derivatives of phytol, and cholesterol. Gases largely contained CO<sub>2</sub> and H<sub>2</sub>.

Metal catalysts had been used in microalgae liquefaction. Matsui et al. [92] investigated the liquefaction of *Spirulina*, a high protein algae in water at  $300^{\circ}\text{C}-425^{\circ}\text{C}$ using Fe(CO)<sub>5</sub>–S catalyst. Other metal catalysts used were Ru<sub>3</sub>(CO)<sub>12</sub> and Mo(CO)<sub>6</sub>. Continuous culturing of the *B. braunii* Berkeley strain in the secondary treated sewage was conducted and then liquefied by Sawayama et al. [93]. The liquefaction was carried out at 200°C, 300°C, and 340°C. The yield of the hexane-soluble fraction was 97% compared to that in the feedstock algal cells. The heating value of the liquefied oil obtained from this reaction was 49 MJ/kg and the viscosity was 64 MPa-s at 50°C. Different microalgae are not the same in producing oil through liquefaction. Recent literature have shown a wide variety of performances in the production rate of bio-oil and its quality [75–79,81–94]. The performance of HTL of microalgae has been improved by the use of a catalyst such as Na<sub>2</sub>CO<sub>3</sub> among others [75–79,81–94]. Zhou et al. [79] examined the HTL of marine macroalgae *Enteromorpha prolifera* in the temperature range of 220°C–320°C for 30 min and in the presence of 5 wt% Na<sub>2</sub>CO<sub>3</sub> catalyst. The highest bio-oil yield of 23 wt% with higher heating value of 28–30 MJ/kg at 300°C was obtained. These numbers are smaller than what are reported for microalgae [81]. The bio-oil contained ketones, aldehydes, phenols, alkenes, fatty acids, esters, aromatics, and nitrogen-containing heterocyclic compounds. Acetic acid was the main component of water-soluble components.

Vardon et al. [77,78] studied the HTL of Scenedesmus (raw and defatted) and Spirulina algal biomass at 300°C and 10–12 MPa pressure and compared the performance with that of Illinois shale oil and bio-oil produced by dry pyrolysis (at 450°C). Both wet and dry pyrolyses gave energy-dense bio-oil (35–37 MJ/kg) that approached shale oil (41 MJ/kg). Bio-oil yields (24%-45%) and physicochemical characteristics were highly influenced by the conversion route and feedstock selection. Sharp differences were observed for the mean bio-oil molecular weight (dry pyrolysis: 280–360 Da; HTL: 700–1330 Da) and the percentage of low-boiling compounds  $(bp < 400^{\circ}C)$  (dry pyrolysis: 62%–66%; HTL: 45%–54%). For wet algal biomass containing 80% moisture, the energy consumption ratio (ECR) for HTL (0.44–0.63) was more favorable than that for dry pyrolysis (0.92–1.24). In another study, Vardon et al. [77,78] showed that Spirulina algal biomass gave 32.6% biocrude as opposed to 9.4% for digested sludge under the same reaction conditions as mentioned earlier and for 30 min residence time. While swine manure, digested sludge, and Spirulina algae gave biocrudes of similar heating value (32–34.7 MJ/kg), they differ substantially in their detailed chemistry. The molecular weights tracked with obdurate carbohydrate content followed the order: Spirulina < swine manure < digested sludge.

Duan and Savage [81] were the first to evaluate the effects of various hydroprocessing catalysts on HTL of microalgae *Nannochloropsis* sp. The experiments were performed at 350°C with Pd/C, Pt/C, Ru/C, Ni/SiO<sub>2</sub>–alpha-Al<sub>2</sub>O<sub>3</sub>, CoMo/l<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (sulfide), and zeolite catalysts. In the absence of hydrogen, all catalysts gave higher yields of bio-oil, but the elemental compositions and heating value of bio-oil (about 38 MJ/kg) were insensitive to the nature of the catalyst used. Gases contained H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and lesser amounts of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. Ru and Ni catalysts produced nitrogen. The H/C and O/C ratios of the products were about 1.7 and 0.09, respectively. While the presence of hydrogen and higher pressure suppressed the gas formation, the bio-oil yield and its characteristics did not significantly change.

Generally, high lipid content of algal mass limits its conversion to bio-oil by the HTL process. Yu et al. [83] examined the HTL process for low-lipid microalgae *Chlorella pyrenoidosa* and found that at 280°C and 120 min reaction time, the bio-oil yield of 39.4% was obtained. The bio-oil yield, water solubles, and gases strongly depended on the temperature and reaction time. Biller and Ross [84] correlated the performances of various types of algal biomass in the HTL process by correlating the bio-oil yield with the biochemical content of the biomass. They examined microalgae *Chlorella vulgaris, Nannochloropsis oculata*, and *Porphyridium cruentum*, and cyanobacteria *Spirulina* 

and found that the yields of biocrudes from these species were 5-25 wt% higher than the lipid content of the algae depending on the biochemical composition. The yields of biocrudes follow the order: Lipids > proteins > carbohydrates.

Ross et al. [94] examined the effects of alkalis and organic acids on HTL of low lipid content *C. vulgaris* and *Spirulina* algae at 300°C and 350°C, respectively. The effects of the temperature and the catalyst types on the product yields and composition were examined. The catalysts used were alkali, potassium hydroxide, sodium carbonate, and the organic acids, acetic acid and formic acid. The yields of biocrudes were higher using an organic acid catalyst and these crudes had a lower boiling point and improved the flow properties. The higher heating value ranged from 33.4 to 39.9 MJ/kg. The biocrude contained 70%–75% carbon, 10%–16% oxygen, and 4%–6% nitrogen.

Biller et al. [87] examined a range of microalgae and lipids extracted from the terrestrial oil seed for the HTL process at 350°C and 150–200 atm pressure in the presence of a variety of heterogeneous catalysts. The results showed that the HTL process converted triglycerides to fatty acids and alkanes in the presence of certain heterogeneous catalysts. While heterogeneous catalysts increased biocrudes only slightly with the use of heterogeneous catalysts, higher heating value and deoxygenation of the products increased by up to 10% due to the presence of the heterogeneous catalysts.

#### 5.3.4 HTU PROCESS

The HTU process is a successful pilot-scale HTL process in which biomass reacts with liquid water at an elevated temperature and pressure but under subcritical conditions. The reactor is operated under complex phase equilibria due to the simultaneous presence of water, supercritical carbon dioxide, and various alcohols along with biocrude that contains 10%–13% oxygen. In subsequent upgrading, a large portion of oxygen is removed as carbon dioxide.

In the HTU process, biomass chips (or other organic materials) are first digested by water under pressure at about 200°C–250°C. The digested slurry is then passed into a reactor that is generally operated at 300°C–350°C, 12–18 MPa, and a residence time of 5–20 min. The feed slurry contains about 25% of biomass such as wood or other organic wastes. Once biomass is converted, the product biocrude that is a mixture of light (oil) and heavy (solid) materials is separated. Light biocrude is dehydrogenated and upgraded to premium diesel fuel or kerosene, or used as a refinery feedstock. Heavy biocrude is combusted along with coal to generate electricity.

The product biocrude has higher energy density than the feed biomass and it contains alcohols, acids, and numerous other water-soluble components. The typical data of a pilot plant and the typical feedstock, the reaction conditions, and the products of HTU process are given by Demirbas [3,4]. The process is simple and of high efficiency.

#### 5.4 HYDROTHERMAL GASIFICATION

The fast hydrolysis of organic molecules such as biomass at high temperature leads to a rapid degradation of the polymeric structure of biomass [6-11,91]. A series of consecutive reactions lead to the formation of gas whose composition depends

on the temperature and pressure of water, the contact time, and the catalyst if it is present. High solubility of intermediates in water, particularly at high temperature and pressure, allows further organic reactions to occur in aqueous media and prevents the formation of tar and coke. The reactive species originating from biomass (or other species) are diluted by solvation in water, thereby preventing polymerization to unwanted products. These conditions also lead to the formation of high gas yield at relatively low temperatures. The HTG process is thus the process of gaseous fuel generation in an aqueous medium, which differs from "steam gasification" in which solids react with gaseous steam to produce a set of gaseous products.

The goal of HTG under subcritical conditions is to obtain high quality and yield of fuel gas. Two most important components of fuel gas are hydrogen and methane. As discussed earlier, steam gasification and reforming generates gas with high hydrogen concentration. Thermochemical formation of methane is possible only by low-temperature hydrothermal route since in conventional steam or oxygen gasification process, temperatures are generally too high for the methane production from biomass. The HTG under subcritical conditions can be divided into two parts: (1) low-temperature APR and its derivative technologies, and (2) high-temperature catalytic gasification. The APR and its derivative technologies are discussed in Chapter 6. Here we address the subject of high-temperature catalytic gasification.

At higher temperatures up to supercritical temperature, in the presence of a catalyst, biomass or organic compounds are gasified mainly to methane and carbon dioxide. In the absence of a catalyst, this region of temperature (250°C to critical temperature, 374°C) is also called HTL region wherein carbohydrates are liquefied to various organic products. In the catalytic HTG process, the heat recovery is important for an efficient operation. The catalytic HTG process converts biomass/ water slurry into fuel gas and water that are subsequently separated. The gaseous fuel can be used for heat, power, or the generation of various chemicals. The role of catalysts on HTG is described in Section 5.4.1.

#### 5.4.1 CATALYSTS FOR HTG

The HTG can be divided into three regions depending on the range of temperature [6–11,95–105]. Osada et al. [98–101] identified region 1 as the one with a temperature range of 500°C–700°C; supercritical water in which biomass decomposes and the activated carbon can be used to avoid char formation or alkali catalyst to facilitate water–gas shift reaction. In this region, very little solids are remained and the main product of the gasification is hydrogen. In region 2, where the temperature range is 374°C–500°C that is again in the supercritical region, biomass hydrolyzes and metal catalyst facilitates gasification. In this region, the main product is hydrogen with some carbon dioxide, carbon monoxide, and methane. Both regions 1 and 2 producing fuel in supercritical water are discussed in Chapter 10.

In this section, we focus on region 3 where temperature is below the critical temperature of 374°C. In this case, biomass hydrolysis is slow and catalysts are required for gas formation. In the subcritical region, the gas product distribution will be dictated by the thermodynamic equilibrium at a given temperature and pressure. In general, in the subcritical region, more methane is produced compared to hydrogen. The partial pressure of water can also affect the gas composition. Higher partial pressure and lower biomass concentration can result in more steam reforming producing more hydrogen. An appropriate catalyst (such as nickel) can also reform methane to produce more hydrogen. The catalyst can also help to reduce the gasification temperature while maintaining useful kinetics. Lower temperature and pressure help in lowering the capital costs for the equipment as well as lowering the possible corrosion effect on the reactor walls, thus allowing the use of less costly alloys for the reactor vessel.

The catalysts for biomass gasification under subcritical conditions are discussed in an excellent review by Elliot [9]. His analysis is briefly described below.

Elliot et al. [102–105] examined the subcritical gasification of biomass feedstock that included cellulose, lignin, hollocellulose (cellulose and hemicellulose), and a Douglas fir wood flour using nickel catalyst and added sodium carbonate cocatalyst. The results showed that at 350°C, the catalyst gave 42% of carbon fed compared to 15% of carbon fed in the absence of catalyst. Both hydrogen and methane concentrations were higher for the catalytic operations compared to those without catalyst. The carbon monoxide concentration was close to zero in the presence of catalyst. With regard to the activity of alkali additions, the activity follows the order: Cs > K > Na. The study by Elliot et al. [102–105] also indicated that conventional support for nickel, namely, alumina (other than alpha-alumina), silica, various ceramic supports, minerals such as kieselguhr and other silica-alumina, were unstable in a hot liquid water environment due to mechanisms such as carbon, monoclinic zirconia or titania, and alpha-alumina.

Elliot evaluated the base metal catalysis, noble metal catalysis, and activated carbon catalysis for HTG. His important conclusions are summarized as follows:

- Of all the base metal catalysts examined [102–105], such as nickel, magnesium, tungsten, molybdenum, zinc, chromium, cobalt, rhenium, tin, and lead, nickel was found to be the most active and stable catalyst. Various supports such as kieselguhr, silica-alumina, alpha-alumina, alumina-magnesia in spinel form, and carbon examined in the literature [6–11,91,102–105] gave a varying degree of success. The most useful promoters were ruthenium, copper, silver, and tin impregnated at 1 wt%.
- 2. For noble metal catalysis, while some conflicting results are reported by various investigators [6–11,91,95–105], in general, platinum, palladium, and silver showed minor activities to HTG at 350°C; iridium had some activities but the best activities were shown by ruthenium and rhodium. Rutile form of titania and carbon supports was found to be effective. Vogel et al. [96] and Vogal and Hildebrand [97] found ruthenium doping on nickel catalyst on carbon to be effective for HTG.
- 3. While activated carbon and charcoal were found to be the effective catalysts by some investigators [6–11,91,95–105], these results were mostly obtained under supercritical conditions.

The study by Minowa and Ogi [71] indicated that the cellulose gasification depends on the nature of support and the size of metal particles on the support. They presented the following mechanism for the cellulose gasification:

Cellulose 
$$\xrightarrow{\text{Decompose}}$$
 Water soluble products  $\xrightarrow{\text{Gasification/Ni}}$   
Gases  $(H_2 + CO_2) \xrightarrow{\text{Methanation/Ni}}$  Gases  $(CH_4 + CO_2)$  (5.7)

Vogel group [96,97] indicated that Raney nickel was more effective than alphaalumina-supported nickel. They also studied the nickel catalysts with ruthenium, copper, and molybdenum doping. The most effective results were obtained from ruthenium doping on nickel catalysts. Elliot [9] and Elliot et al. [102–105] reported that at 350°C, bimetallic Ru/Ni, Ru/C, and Cu/Ni gave favorable gas production by HTG of a variety of biomass. Favorable yields were obtained for lignin gasification by Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/C, and Rh/C catalysts.

Favorable results for HTG of various biomass have been obtained for both batch and continuous systems. Ro et al. [95] showed that the subcritical HTG of hog manure feedstock can be the net energy producer for the solids concentration >0.8 wt%. While the costs for gasification are higher than those for anaerobic digestion lagoon system, the land requirement for the gasification process and the cost of transportation and tipping fees are lower. In addition, the catalytic gasification process would destroy pathogens and bioactive organic compounds, and will produce relatively clean water for reuse. The ammonia and phosphate byproducts generated in gasification have also the potential value in the fertilizer market.

# 5.5 COAL–WATER CHEMISTRY

While the affinity of coal with water is not as pronounced as that of biomass, evidences have shown that chemical interactions between coal and water can be significant. Here, we examine these interactions for three different cases: (1) the effect of pretreatment of coal by water on the coal conversion during coal liquefaction, (2) the effect of water on coal liquefaction at high temperatures and pressures, and (3) the effectiveness of coal–water slurry as a fuel for combustion in boilers, diesel engines, and gas turbines.

#### 5.5.1 EFFECT OF WATER PRETREATMENT OF COAL ON COAL LIQUEFACTION

The effect of water pretreatment of coal on coal liquefaction was studied by Serio et al. [106,107] (Serio et al., 2012, pers. comm.) and Ross and Hirschon [108]. Serio et al. examined four different types of coals (Zap lignite, Wyodak subbituminous, Illinois No. 6 bituminous, and Pittsburgh bituminous) pretreated by water at 4000 psig and 350°C and for the treatment times from 5 to 1200 min in a batch reactor. For each experiment, the yields of gases, water-soluble materials, and residues were determined. The residues were subjected to an analysis by a variety of techniques such as thermogravimetry coupled with Fourier transform infrared

spectroscopy (TG-FTIR), solvent extraction, donor solvent liquefaction, and FTIR. The study resulted in the following conclusions:

- 1. At short pretreatment times, the process loosened up the coal structure resulting in the increase of extractables and the yield. The oxygen content also decreased when coal was subjected to an accelerated aging process. However, the liquefaction yields appear to decrease relative to the raw coal.
- 2. At longer pretreatment times, the process partly recombines the structure resulting in a decline of extractable and tar yields. Oxygen continues to be removed, but ether groups go through a maximum. The liquefaction yields were closer to values for the raw coal.
- 3. The solvent adduction may be the reason for the decline in liquefaction yields for coals with short pretreatment times.
- 4. For Illinois coal, the yields were very sensitive to the amount of oxygen exposure. The participation by the oxidized form of pyrite in the liquefaction pretreatment chemistry appeared possible.

Bienkowski et al. [109,110] evaluated the effect of steam pretreatment on coal liquefaction. For a Wyodak coal stored under water (to avoid weathering), they pretreated the coal using 750 psig steam for 30 min at 200°C. Pretreatment of suction dried coal at 200°C increased the production of extractables at 400°C from 30.5% to 38.5%. While an increase in the pretreatment temperature to 240°C increased the yield to 40.3% an increase in the pretreatment temperature to 320°C reduced the conversion to 33.8%. Bienkowski et al. [109,110] argued that an increase in the pretreatment temperature increased coal matrix loosening and stabilization of some reactive components of the coal resulting in higher conversion. A further increase in temperature set up higher rate of retrogressive reaction, which in turn decreased the conversion. Bienkowski et al. [110] also found that an addition of ammonia in both the pretreatment and subsequent liquefaction stages gave even higher conversion due to the reactions between hydrogen and oxygen functional groups.

Graff and Brandes [111,112] (Graff and Brandes, 2012, pers. comm.) and Brandes et al. [113] observed higher yields of liquid products from pyrolysis and solvent extraction of Illinois No. 6 coal that was pretreated by steam at 320°C–360°C and 50 atm pressure. A similar pretreatment with helium had no effect and the exposure to air of steam-pretreated coal lost the increase in yields. The study concluded that the pretreatment disrupts the hydrogen bonds, reduces the number of covalent cross-links, and increases the hydroxyl groups in the coal [111,112] (Graff and Brandes, 2012, pers. comm.). The exposure to air weathers the coal with a negative effect on liquefaction yield. Khan et al. [114] showed that the steam pretreatment at a pressure of 1100–1300 psig and a temperature of 300°C–320°C for five coals of different ranks did not increase the tar yields when pyrolyzed at a slow heating rate. The steam treatment reduced the concentration of oxygen functional groups for the low-rank coals and increased the tar yields when pyrolyzed at a rapid heating rate.

Ross et al. [115–119] evaluated the effects of water pretreatment on Illinois No. 6 and Wyodak subbituminous coals and found no effects on toluene solubles in a

subsequent donor solvent liquefaction process. Significant changes were, however, observed in the composition and molecular weight distributions of the liquid products of the liquefaction process due to water pretreatment. The pretreatments were carried out at 250°C and 38 atm pressure. The coal liquefaction was carried out at 400°C and 500 psi H<sub>2</sub> pressure for 20 min in the tetralin solvent.

#### 5.5.2 COAL LIQUEFACTION IN HIGH-PRESSURE AND HIGH-TEMPERATURE WATER

A number of studies [52,120–124] have examined the coal liquefaction in water at high temperature and pressure. Mikita et al. [52] and Blaustein et al. (Blaustein et al., 2012, pers. comm.) found tetrahydrofuran (THF) conversion of Illinois No. 6 coal in water to be about 67%, in water and solvent-refined coal (SRC) II solvent about 87%, and in water and 1000 ppm of Mo about 90% for reactions at 385°C, 1200 psig H<sub>2</sub> pressure, and 30 min residence time. A synergism was observed at low ratios ( $\leq$ 0.5) of donor solvent to coal upon combination of SRC II distillate and water. A similar effect was not observed when cyclododecane replaced water. The addition of Mo catalyst precursors to the water allowed a complete elimination of donor solvent without loss in conversion.

Yoneyyama et al. [120] examined noncatalytic hydrogenation of several bituminous and subbituminous coals with or without water addition at 400°C. By comparison, similar experiments in nitrogen or undecane  $(n-C_{11})$  were also carried out. In nitrogen or hydrogen atmosphere, water promoted coal conversion, but the addition of undecane neither changed nor decreased the conversions. For higher rank coal, undecane inhibited coal conversion in nitrogen. The conversion of coals using nitrogen and water increased with increasing carbon content of coals. However, when hydrogen and water were used, there existed no clear relationship between the coal conversion and the carbon content of coals. Under pressurized hydrogen, coals containing pyrites gave significantly larger conversions implying their catalytic role in the conversion of coals, and the effect was more obvious for the coals containing larger amount of pyrite.

Ross and Blessing [121] and Ross et al. [122,123] found that for Illinois No. 6 coal in the CO/H<sub>2</sub>O system at 4000–5000 psig pressure and 400°C (under supercritical conditions), better toluene solubles were achieved than for tetralin under the same conditions. The CO/H<sub>2</sub>O system was more effective than the H<sub>2</sub>/H<sub>2</sub>O system and the latter system was not very effective for demineralized coal. The results were explained in terms of an ionic mechanism involving the initial formation of formate ion by which hydrogen is donated to the coal.

Recently, Anderson [124] examined hydrothermal dissolution of coal and found that at high temperature and pressure, coal dissolution is rapid and can be taken to completion. Breaking cross-linking structures will convert high-molecular-weight structures into low-molecular-weight products that can be processed and used as high-value chemical feedstock. Product is a pumpable liquid that can be further processed. Up to 90% of the original carbon is recoverable as water-soluble product. Finally, inorganic components (pyrites, calcite) are readily converted to soluble products that can be recovered and/or treated in the liquid phase.

The studies described earlier clearly indicate that water plays an active role as a reactant for the coal liquefaction under high-temperature and high-pressure conditions. The reactive role of water is further increased near and above the supercritical conditions. Thus, water should be evaluated as a possible solvent for the coal liquefaction process.

#### 5.5.3 COAL-WATER MIXTURE AS FUEL

A slurry of finely powdered coal and water (coal-water mixture as fuel [CWF]) has been found to be an effective fuel for combustion purposes. Presence of water in CWF reduces harmful emissions into the atmosphere, makes the coal explosion proof, and also makes the coal equivalent to liquid fuel [125–129] (Penn State's coalwater slurry fuel program, 2012, pers. comm.). CWF can be used in place of oil and gas in any size of heating and power station. It can be used in oil and coal boilers. It can also be used in the diesel engine power plants and the combined cycle gas turbines. While the energy efficiency of CWF may be somewhat lower (by about 3%) compared to natural gas and oil, depending on the geographical area, the price per unit energy of CWF can be 30%–70% lower than the equivalent oil or gas. Low emissions and low BTU cost make CWF a very cost-effective and environmentfriendly fuel for heat and power generation. Another advantage of CWF production process is the separation of noncarbon material that reduces the ash content by about 2% in CWF, making it a viable alternative to diesel fuel #2 for use in large stationary engines or diesel electric locomotives [125-129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

While the first patent on coal-water fuels was granted in 1891 [125], the real development of coal-water fuels from high-quality coal commenced in earnest in the United States, Germany, and the former Soviet Union in the 1960s. In the United States, the research was accelerated in 1970 and early 1980 following oil embargo and subsequent increase in oil price. While the original objectives of the research were to produce a cheap substitute for heavy oils in boilers, in the subsequent years fuels that met environmental regulations and that can also be used for diesel engines and turbines became important. The use of CWF in boilers, diesel engines, and turbines required different level of chemical and physical properties and specialized equipment for handling and transporting slurries [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

While the thermal efficiency of CWF in boilers is around 2%–3% lower than that of coal, the intense environmental regulations in 1990 for clean coal technology forced more research for cleaner and the one with better physical and chemical properties of CWF. The R&D leads to processes that can produce ultralow-ash feed coals, especially for high-value metallurgical applications, such as the production of electrode carbons [125–129]. Processes include advanced physical processing to produce "super coal" that has a very low residual ash and very fine particle size so 60%–70% coal in CWF can be burned cleanly and possess the physical and chemical properties that are acceptable to boilers, diesel engines, and turbines. The use of CWF in diesel engines and turbines particularly required very fine coal particles in the slurry. The research led to the development of chemical processes that

either remove fine residual ash (e.g., ultra clean coal [UCC] and CENfuel), from coal or coal dissolution processes that produce ash free synthetic coal-like material (e.g., Hypercoal). Although none of these processes reached immediate commercial development, these advanced coal beneficiation techniques gave a significant impetus to the use of CWF for the following reasons [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.):

- CWF produced from ultra clean coal can replace fuel oils used in highefficiency gas turbines and low-medium speed diesel engines. The cycle efficiency for gas turbines or diesel engines is not negatively impacted by the water content in CWF.
- CWF facilitates pipeline transportation and storage, and gives additional reductions in greenhouse gases (GHGs). The convenience of easy transport of CWF is a benefit for many countries with overloaded transport infrastructure.
- 3. Large and fuel-efficient diesel engines for stationary power generation are especially suitable for retrofit to burn CWF. Small gas turbines and diesel engines can also utilize CWF with high efficiency.

The preparation of CWF involves crushing the coal particles to  $10-65 \,\mu$ m particle size, although the particle size of  $10-25 \,\mu$ m is more desirable. This can be achieved by the standard grinding or crushing processes. This is generally followed by the wet milling and homogenization process using standard milling processes. Some additives may be used to facilitate the process. CWF has been prepared with a number of coals such as lignite, flame and gas flame coals, anthracite, and brown coals [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.). If CWF is to be used for gas/oil boilers, the ash content should be <10%. For coal boilers, no limit on ash content is necessary. According to the literature [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.), CWF for brown coal (lignite) has been successfully tested. For flame coal with 40–45 vol% slurry and gas flame coal and gas coal with 28–40 vol% slurry, the systems are well developed. For anthracite with 7–28 vol% slurry, CWF is possible and has been successfully tested [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. 2012, pers. 2012, pers. 2013, slurry and gas flame coal and gas coal with 28–40 vol% slurry, the systems are well developed. For anthracite with 7–28 vol% slurry, CWF is possible and has been successfully tested [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. 2012, pers. 2012, pers. 2012, pers. 2014, pers. 2015, pers. 2014, pers. 2015, pers. 2014, pers. 2014,

CWF can be used in several different applications [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.) such as a possible substitute for heavy-grade fuel oils such as diesel #6, bunker C, and bunker D residual fuel oils. When a particle size is  $\leq 80 \ \mu$ m, it can be used as co-fuel and substitute fuel in diesel engines [125–129]. Low-speed marine and modular power plant diesels can operate on pure CWF. Medium-speed diesels such as locomotives sometimes need coinjection of CWF and diesel #2 fuel that acts as an ignition source for the CWF. For the use of CWF in gas turbines, fine particles such as 5–10  $\mu$ m of coal are needed to substitute petroleum and natural gas in these usages. The particle size of coal is an important factor in making homogeneous CWF that can be easily atomized in various types of engines [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

Coal impurities prohibit the use of CWF in turbines and diesel engines. Although CWF with significantly higher specifications than coals used in previous turbine and diesel engine tests is now possible with the development of the UCC product described in Section 5.5.3.1.1. Several programs initiated by the Department of Energy in the late 1970s help the development better injection systems for the use of CWF in diesel engines and turbines. The major considerations for CWF use are ignition timing, plugging, and sticking issues [125–129]. The use of CWF in diesel engines are now possible. Direct firing of coal requires micronizing to <20–30  $\mu$ m for diesel engines and <10  $\mu$ m for gas turbines and producing a CWF containing around 50 wt% coal. In the past, CWF was largely used for the compression ignition (diesel) engine [125–129]. The characteristics of injection and combustion of CWF in diesel engines are significantly different to those for diesel fuels due to the combined effects of poorer atomization and the time required to evaporate the slurry water. However, combustion and thermal efficiencies matching diesel fuel have been achieved for CWF at up to 1900 rpm [125–129].

The most researched area has been the design of the injectors, which gives the optimum atomization of fuel for the best combustion and thermal efficiencies. Coal particle size and rheology of coal–water mixture play a very important role in efficient atomization. The engine modifications such as purged shuttle fuel pump plunger, electronically timed injection, diamond compact injector tip nozzles, tungsten carbide-sprayed cylinder liner and top ring set, and pilot injection of diesel are some of the engine modifications considered for the successful direct injection of CWF [125–129]. The fate of mineral matter and its effect on the engine wear and how to minimize coal agglomeration during the evaporation of individual CWF droplets are also required further investigations [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

#### 5.5.3.1 Production of CWF

The production of CWF requires sophisticated treatment of coal to remove mineral matters and sulfur, and prepare a very fine particle size such that CWF can be used as a replacement of heavy fuel oil not only in boilers but also in diesel engines and gas turbines. The preparation of such coal follows multiple steps: physical cleaning, advanced coal processing projects, advanced coal milling, and chemical cleaning.

Physical cleaning of coal is carried out by a wide array of solid–liquid and solid– solid separation processes. Floatation technologies and various dewatering systems are some of the processes used for this purpose. The objective is to remove ash and other mineral matters without losing coal. Most of the current milling, separation, and dewashing techniques allowed coal particles to get down to  $30-40-\mu m$ size. Further removal of impurities and mineral matters required the applications of chemical methods.

Advanced physical coal cleaning was developed by Bechtel and AMAX [130]. The primary objective was to produce UCCs suitable for conversion to stable and highly loaded CWF. The main specification was an ash content of <1%-2%. The separation technologies were advanced column froth floatation and selective agglomeration. A more novel process for preparation of ultraclean micronized coal was researched in China, based around high-pressure water jet milling [131,132]. It was

found that hydraulically milled coal significantly increased the liberation of minerals (97% vs. 90% for ball milling) and led to an improved overall mineral separation.

Ultrafine coal milling is an essential part of firing coal into gas turbines or diesel engines. For gas turbines, the particle size of  $\leq 10 \ \mu\text{m}$  is desirable. For diesel engine, the top size of 20  $\mu$ m has been specified, although this depends on the size and speed of the engine. Milling energy depends on both the type of mill and the material especially at small particle size required for CWF in turbines and engines. A number of advanced mills that are now available include ball mills, centrificial or planetary mills, nutating mills, opposed flow jet mills, impact jet mills, spiral jet mills, and high-pressure water jet mill [125–129] (Penn State's coal-water slurry fuel program, 2012, pers. comm.). While nutating mill appears to offer the lowest energy consumption, the final choice of mill may depend on the interaction of milling with the deashing process. Another factor affecting the choice may be the particle size distribution required for the deashing technology to be employed for each CWF product.

Two types of processes for chemical cleaning of coal are (1) those that attempt to dissolve the mineral components of coal (e.g., UCC, CENfuel) and (2) those that dissolve the coal leaving a mineral-rich insoluble coal byproduct (e.g., Hypercoal). We briefly examine these three important processes in Sections 5.5.3.1.1 through 5.5.3.1.3.

# 5.5.3.1.1 Ultra Clean Coal

The UCC production process [116] involves two main steps: a caustic pressure leach to convert silicates and clays to dissolved sodium silicates and sodalite-type minerals. The sodalite material is then dissolved in acid so that it can be removed with the filtrate in a simple filtering operation [125–129]. The key features of the technology are as follows:

- 1. Since coal pulverization is not required, the solid-liquid separation easy.
- Digestion removes both extraneous and a large portion of minerals within the coal particles. The process also removes most of alkalis, all of the inorganic sulfur, and some of the organic sulfur. The UCC product contains about 30% moisture.
- 3. The process is capable of treating most bituminous coals.

The process is capable of meeting gas turbine specifications for all bituminous coals [125–129,133] (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

#### 5.5.3.1.2 CENfuel

CENfuel produces ultralow-ash coal by an acid regeneration and with the removal of other deleterious elements from coal. In the process, the main ash components such as  $SiO_2$ ,  $Al_2O_3$ , and  $TiO_2$  are removed by leaching granular coal (2 mm) with an aqueous solution of hydrofluoric acid and fluosilicic acids. Sulfoides such as iron pyrites are not affected by leach. The rich liquor contains soluble fluosilicates and undissolved FeS particles. The liquor is passed to a distillation unit where metal fluorides are recovered and removed from the system. The residue

is dried and stored. The spent liquor is dried and sent to the gas absorber where hydrogen fluoride (HF) and  $H_2SiF_6$  are recovered and excess  $H_2SiF_6$  is passed to a hydrolyzer for conversion to silica and HF is returned to the dissolution circuit [134,135]. More improved process contains two dissolution steps [125–129] involving hydrofluoric acid and fluosilicic acids (Penn State's coal-water slurry fuel program, 2012, pers. comm.).

# 5.5.3.1.3 Hypercoal

Hypercoal is a low-ash, low-alkali coal product produced by dissolving the coal matter into an organic solvent, then flashing off the solvent for recycling to the dissolution step of the process [125–129,136] (Penn State's coal-water slurry fuel program, 2012, pers. comm.). The insolubles are retained in the high-ash byproduct coal. Hypercoal process is very different from UCC process in that this process aims to separate solvent-soluble coaly matter from the ash and insoluble coal, thereby producing a high-ash coproduct. The process involves five steps: slurry preparation, extraction at 360°C temperature, separation of the extracts, removal of alkali from the liquid component and removal of ultrafine particles by filtration, and finally drying of the final product. A number of solvents such as tetralin, 1-methyl-naphthalene, dimethylnaphthalene, and light cycle oil have been used as solvents for extraction. The key features of the technology are as follows [125–129]:

- 1. On a dry coal basis, the yield can be as high as 80%. The process removes most alkalis from raw coal.
- 2. The higher ash (coproduct) is suitable for domestic power generation.
- 3. The process can be applied to all subbituminous and bituminous coals. Yields are lower for subbituminous coals than for bituminous coals. Yields for subbituminous coals can be increased by pretreating the coal with HCl or weaker acids.

# 5.5.3.2 Fuel Preparation and Transportation

The science and technology behind the production of UCC CWF has been well published [125–130] (Penn State's coal-water slurry fuel program, 2012, pers. comm.). Most systems involve the preparation of coal–water slurries containing 60%–70% coal, together with additives to provide slurry stabilization and to lower the viscosity. The energy density of such slurry is about 18 GJ/m<sup>3</sup>. Additives consist of dispersants and stabilizers. The dispersants such as sodium sulfonate of naphthalene, polystyrene, polymethacrylate, and polyolefin maintain the separation of coal particles within the slurry [125–130]. Stabilizers include additives such as cellulose or xanthum gums. For gas turbines and diesel engines, the water penalty for CWF is much smaller and probably negligible when the overall power cycle is considered, and therefore, CWF slurry transportation is a preferred form. Final preparation of CWF requires that the coal is either premilled dry before slurry preparation or milled (micronized) wet as either a part of slurry preparation process or immediately prior to combustion. In general, wet milling has lower cost and lower energy consumption [125–130]. In China and Japan, CWF has been produced in large plants for more than 30 years. In a typical CWF production plant, the coal is mixed with water and some additives (to help forming good mixture) and passed through one or more pulverizers and multiple milling (high-load and low-load) processes. For boiler application of CWF, high slurry concentration (65–70 wt%) and better stability requires a wide particle size distribution (often bimodal) with mass mean particle size between 5 and 10  $\mu$ m. This is often achieved by using several mills and/or recycle streams.

The efficient atomization of CWF slurry in a combustor governs the required particle size and slurry concentration. For gas turbine and diesel engine applications of CWF, generally lower slurry concentration and mass mean particle size of coal are required. For diesel engines, the preferable slurry concentration is 50–55 wt% with a mass mean particle size of 5–15 microns. For turbines, the preferable slurry concentration is 55–60 wt% with a mass mean particle size of 4–6 microns. Since the cost of milling and pulverizing rises exponentially with a decrease in particle size below 30–50 microns, low particle sizes required in diesel engines and turbines will necessitate the use of special milling and pulverizing processes.

CWF exhibits the rheological properties different from fuel oils. Fuel oils tend to be more Bingham fluids. CWF is pourable and pumpable, but its viscosity decreases significantly with the shear caused by agitation and pumping. Also unlike fuel oils, the viscosity of CWF is unaffected by the temperature. Slurry viscosities are strongly affected by the coal characteristics, concentration, and flow conditions. Currently, CWF containing 65%–70% coal has an apparent viscosity around 1000 MPa-s at room temperature. This is too high for atomization of slurry in the combustion chamber, and it is normally reduced either adding water (10%–20%) or heating before the injection, which can promote flashing.

The use of CWF in diesel engines and gas turbines besides its use as a substitute for heavy oil in boilers requires the following considerations and additional research:

- CWF is more difficult to atomize than diesel fuel due to its much higher viscosity. The effective atomization is more critical to combustion due to the effect of droplet size on ignition delay (which is caused by the time required for water evaporation) and burnout. Pressure atomization can be improved by increasing the liquid velocity through the nozzles; however, this greatly increases the nozzle wear.
- CWF causes chronic wear of injection nozzles, with wear being exacerbated by cavitation effects.

More research has been continuing to address these issues. However, CWF combustion has a very promising future.

#### 5.5.3.3 Combustion of CWF

Fu et al. (2012, pers. comm.) carried out the earlier combustion experiments for CWF in a boiler using oxygen-enriched air. Their study for 700 hp watertube boiler with bituminous coal indicated that the use of oxygen-enriched air resulted in the required lower air preheating and the improvement in the carbon burnout.

The reduction in the volume of flue gas lowered the heat losses and increased the boiler efficiency. The air-preheating temperature was reduced by  $192^{\circ}F$  by enriching combustion air by 22.8% volume of oxygen. The boiler performance was significantly improved even with a small addition of oxygen (2%-3%) in air. With the use of staged air admissions, the NO<sub>x</sub> emission was also reduced by one-third. This was, however, accompanied by some decrease in combustion efficiency. The use of oxygen-enriched air in the primary combustion stage increased flame stability, reduced carbon burnout, and moderately reduced the overall NO<sub>x</sub> emissions. The carbon conversion (96%–98%) and the boiler efficiencies (81%–83%) remained high in their entire study.

The issues of CWF atomization and its effect on the optimization of combustion efficiencies in boilers, diesel engines, and gas turbines are continued to be investigated. Coal–water slurry has, however, proven to be an important synthetic fuel. It has a significant economic potential [137] and its application to generate heat and power will continue to grow [138–140].

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# 6 Aqueous-Phase Reforming and BioForming Process

# 6.1 INTRODUCTION

In Chapter 5, we examined the conversion of biomass to biochar, bio-oil, and fuel gases such as methane and hydrogen in water at high temperature and pressure but under subcritical conditions. We showed that water under high-temperature and high-pressure conditions possesses unique physical and chemical properties that allow its strong interactions with biomass to generate solid, liquid, and gaseous fuels. Water, in this case, not only acts as a solvent but also as a reactant and a catalyst to carry out wet pyrolysis reactions. The quality of products depends on the reaction temperature, pressure, reaction time as well as the presence of any catalyst. The chapter also showed that water at high temperature possesses the properties very similar to several organic chemicals and is capable of carrying out various types of organic chemical reactions. While the level of the conversion by the hydrothermal processes (hydrothermal carbonization [HTC], hydrothermal liquefaction [HTL], or hydrothermal gasification [HTG]) can be improved with the use of a suitable catalyst, these processes are basically nonselective.

Biomass can produce hydrogen and liquid fuels in a number of different ways. These production methods can be thermochemical, biochemical, or catalytic. Current processes to convert biomass to liquid fuels include (1) fermentation of glucose to ethanol, (2) pyrolysis or high-pressure liquefaction of biomass to bio-oils, (3) gasification of biomass to syngas followed by Fischer-Tropsch (FT) synthesis to alkanes, (4) anaerobic digestion of cellulosic waste to produce hydrogen and methane, (5) Mobil process of conversion of carbohydrates to aromatic hydrocarbons and coke with Zeolite Socony Mobil (ZSM)-5 catalyst, and (6) supercritical water extraction or gasification of biomass to hydrogen or liquid fuels. In this chapter, we describe yet another selective process to generate hydrogen, syngas, alkanes, and monofunctional groups using low-pressure catalytic process in an aqueous environment. Monofunctional groups can also be further upgraded to various liquid fuels (such as diesel, gasoline, and jet fuel) using a selective catalytic process known as "bioforming process." Numerous excellent reviews on both aqueous-phase reforming (APR) and bioforming process are available in the literature [1–14].

We briefly examine in this chapter a set of catalytic reactions that can be carried out for a select group of oxygenated compounds such as sugar, glucose, sorbitol,
glycerol, ethylene glycol, and methanol (with carbon/oxygen [C/O] ratio close to one) to produce hydrogen, syngas, lower alkanes ( $C_1-C_6$ ), and various monofunctional groups. The monofunctional groups can be subsequently converted to a variety of liquid fuels such as gasoline, diesel, and jet fuels (or their additives) with another set of catalysts. This overall process is called "APR and its derivative technologies" or bioforming process [1]. The selective APR reactions generally occur in the temperature range of 215°C–265°C. The upgrading of monofunctional groups generally requires a somewhat higher temperature. The nature and quality of products strongly depend on the feedstock and the nature of the catalyst, support, and promoter along with other operating conditions such as temperature, pressure, acidity of slurry and catalyst, and solid concentration in the feed slurry. Unlike the process of hydrothermal conversion described in Chapter 5, this is a very selective catalytic process targeted to only certain types of compounds, producing targeted fuels and chemicals [1–6].

### 6.2 AQUEOUS-PHASE REFORMING

The pioneering work carried out by Dumesic et al. [1-6] showed that carbohydrates such as sugars (e.g., glucose) and polyols such as methanol, ethylene glycol, glycerol, and sorbitol can be efficiently converted to hydrogen and carbon dioxide at 500 K by reforming under aqueous conditions. The process can be applied to all carbohydrates found in wastewater from biomass processing of cheese whey, beer brewery, sugar processing as well carbohydrate streams from agricultural products, such as corn and sugar beets and hemicellulose from any biomass [4,15]. Typical feedstock that can be used for APR and bioforming process are listed in Table 6.1 [4,15]. The secondary feedstock mentioned in the table are first converted to primary feedstock (by hydrolysis and/or hydrogenation processes depending on the feedstock), before using them for APR process. The produced hydrogen can be used to hydrogenate many components of lignocellulosic biomass to produce glycols and other polyols, thus enlarging the feedstock possibilities for APR. The hydrogen can also be used to produce ammonia and fertilizer, an additive to gasification products to produce liquid fuels via FT synthesis and fuel source for polymer electrolyte membrane (PEM) fuel cells.

Besides hydrogen, APR can also produce syngas (CO and  $H_2$ ), alkanes, and monofunctional groups depending on the nature of the catalyst and the operating conditions. As will be discussed later, the production of hydrogen and syngas requires the breakage of C–C bonds within oxygenated compounds, whereas the production of alkanes and monofunctional groups requires the breakage of C–O bonds within the oxygenated compounds. With most feedstock examined so far, the alkane production is limited to six carbon atoms. More feedstock, catalysts, and reactor designs are needed to produce  $C_8-C_{15}$  alkanes from the biomass-derived reactants. The alkanes and monofunctional groups can be further upgraded catalytically by creating new C–C bondages (through condensation reactions) to produce higher alkanes and liquid fuels. The light fuel additives such as pentane and hexane have limited values due to their high volatility. Various reaction paths that can be produced by APR process are schematically illustrated in Figure 6.1 [4].

# TABLE 6.1 Typical Feedstock for Aqueous-Phase Reforming

#### **Primary Feedstock**

Water-soluble oxygenated hydrocarbons such as sugars, sugar alcohols, saccharides, and other polyhydric alcohols

#### Secondary Feedstock<sup>a</sup>

Sugar crops Grain crops Agricultural waste (cornstalks, straw, seed hulls, sugarcane leavings) Bagasse, nutshells, manure (from cattle, poultry, and hogs) Wood materials (wood or bark, sawdust, timber slash, mill scrap) Municipal waste (waste paper, yard clippings) Energy crops (poplars, willows, alfalfa, switchgrass, prairie bluestem, corn, soybean)

- Source: Huber, G.W., Cortright, R.D., and Dumesic J.A., Angewandte Chemie International Edition, 43, 1549–1551, 2004. With permission; Davda, R. and Dumesic, J., Angewandte Chemie International Edition, 42, 4068, 2003. With permission; Tao, J., Shishi, C., and Fahai, C., Chemical Industry and Engineering Progress, 31, 1010–1017, 2012. With permission; Alonso, D.M., Bond, J.Q., and Dumesic, J.A., Green Chemistry, 12, 1493–1513, 2010. With permission; Cortright, R., Davda, R., and Dumesic, J., Nature, 418, 964–967, 2002. With permission; Huber, G. and Dumesic, J., Catalysis Today, 111, 119–132, 2006. With permission; Blommel, P.G. and Cortright, R.D., "Production of conventional liquid fuels from sugars," A White Paper for European Platform on Biofuels, 2012. With permission.
- <sup>a</sup> These are used to generate primary feedstock.

# 6.3 APR VERSUS STEAM REFORMING

The low-temperature APR to produce hydrogen has significant advantages over conventional steam reforming mentioned in Chapter 4 in that

- 1. The process occurs in one liquid phase eliminating energy requirement to vaporize water and carbohydrates. Steam reforming requires high temperature and is accompanied by a phase change.
- 2. The raw materials for APR are nonflammable and nontoxic allowing them to store and handle safely and conveniently. We have established technologies for the storage of sugar, starch, and carbohydrates.
- 3. The temperature and pressure used in APR favors the thermodynamics of water-gas shift reaction allowing high conversion of CO in one reactor. This allows the production of nearly pure hydrogen stream (with very low CO concentration).
- 4. The conventional PSA, cryogenic separation, and membrane technologies are easily applicable to the product stream to separate carbon dioxide from hydrogen since pressures used in APR vary from 15 to 50 atm. Steam reforming is often carried out at low pressure, thus requiring pressurization



**FIGURE 6.1** (See color insert.) Possible reaction paths for APR for water-soluble oxygenated hydrocarbons. (Reprinted from *Green Chemistry*, 12, Alonso, D.M., Bond, J.Q., and Dumesic, J.A., Catalytic conversion of biomass to biofuels, 1493–1513, Copyright 2010, with permission from Elsevier.)

of the product to carry out effective separation. Pure hydrogen can thus be produced more easily by APR process.

- 5. Low temperatures used in APR minimize the decomposition reactions for carbohydrates and resulting coking of the catalysts. Coking of the catalyst is a significant issue in the conventional steam reforming.
- 6. APR can produce hydrogen in a single reactor as opposed to conventional steam reforming process that will generally require a multistage process.
- 7. Since APR produces hydrogen, syngas, lower alkanes, and monofunctional groups (which can be further processed to generate different types of liquid fuels), the operating conditions and catalysts can be manipulated to obtain the desired selectivity among various products. This process thus offers more product possibilities than conventional steam reforming process. It should, however, be reemphasized that APR is a selective process that can only be used for a certain type of feedstock. However, steam reforming can be used for all carbonaceous feedstock.

# 6.4 THERMODYNAMICS OF APR

The discussion in this section closely follows excellent reviews by Dumesic et al. [1-6,16] on the subject. The prevailing thermodynamic forces for the steam reforming of alkanes and oxygenated compounds along with the water–gas shift reaction are illustrated in Figure 6.2 in the form of a plot of Gibbs free energy versus



**FIGURE 6.2** DG/RT vs. temperature for production of CO and H<sub>2</sub> from vapor-phase reforming of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>6</sub>H<sub>14</sub>; CH<sub>3</sub>(OH), C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>, and C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>; and water–gas shift reaction. Dotted lines show the values of ln(P) for the vapor pressures vs. the temperature of CH<sub>3</sub>(OH), C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>, and C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub> (pressure in units of atmosphere). (Reprinted from *Applied Catalysis B: Environmental*, 56, Davda, R., Shabaker, J., Huber, G., Cortright, R., and Dumesic, J., A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metalcatalysts, 171–186, Copyright 2005, with permission from Elsevier.)

temperature [1–6,16]. The favorable thermodynamic forces for these reactions require negative Gibbs free energy. Based on this condition, the figure shows that both oxygenate reforming (of methanol, ethylene glycol, glycerol, sorbitol, and glucose) and water–gas shift reactions are favorable at low temperatures. Also, methanation reaction is favorable at reasonably low temperatures. However, steam reforming reactions for methane and other alkanes are only favorable at higher temperatures.

The concept of APR is based on the fact that at moderate temperature and pressure, oxygenated carbohydrates react with water to produce either alkanes or hydrogen and carbon monoxide by the following reforming reaction [1-6,16]:

$$C_n H_{2n+2} + n H_2 O \rightleftharpoons n CO + (2n+1) H_2$$
(6.1)

Also, at these temperatures and pressures, the following water-gas shift reaction is favored:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 (6.2)

Figure 6.2 presents the Gibbs free energy ( $\Delta G^{\circ}/RT$ ) associated with the steam reforming of a series of alkanes such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>6</sub>H<sub>14</sub> normalized per mole of CO produced along with that for the water–gas shift reaction. For a reaction to occur, negative free energy value in Figure 6.2 is needed. These results show that while water–gas shift reaction is favorable at low temperature, the thermodynamics of steam reforming of alkanes is only favorable at higher temperatures (e.g., *T* > 675 K for C<sub>6</sub>H<sub>14</sub> and *T* > 900 K for CH<sub>4</sub>). Thus, at lower temperatures, lower alkanes cannot be reformed to syngas.

The oxygenated hydrocarbons having a C/O ratio of 1:1 form carbon monoxide and hydrogen according to the following reaction [1–7,16]:

$$C_z H_{2y} O_z \rightleftharpoons z CO + y H_2$$
 (6.3)

The Gibbs free energy diagrams for some typical oxygenated compounds such as methanol (CH<sub>3</sub>OH), ethylene glycol  $[C_2H_4(OH)_2]$ , glycerol  $[C_3H_5(OH)_3]$ , and sorbitol  $[C_6H_8(OH)_6]$  are also shown in Figure 6.2. These results indicate that the APR of these compounds at low temperatures are thermodynamically favorable. Sorbitol is generally obtained by the hydrogenation of glucose  $[C_6H_6(OH)_6]$ . Thus, oxygenated hydrocarbons can be reformed at much lower temperatures than the alkanes with similar carbon number. A combination of aqueous (or steam) reforming of oxygenated carbohydrates and water–gas shift reaction will allow the production of hydrogenation of hydrogenation.

Figure 6.2 also illustrates the logarithms of vapor pressure as a function of temperature for methanol, ethylene glycol, glycerol, and sorbitol. For the first three substances, steam reforming (in the gas phase) can be carried out at temperatures of  $\geq$ 550 K, while for sorbitol, vapor-phase steam reforming requires a temperature of at least 750 K. Thus, at low temperatures (<750 K), reforming of sorbitol (and glucose) can be carried out in the aqueous phase producing hydrogen and syngas. The favorable thermodynamics for APR of oxygenated compounds illustrated in this figure prompted a significant research to evaluate favorable kinetic conditions to produce hydrogen, syngas, and alkanes via the APR process [1–7,16].

Since the thermodynamics of steam reforming of alkanes at low temperatures are not favorable, hydrogen and carbon dioxide formed from oxygenates at lower temperatures are not stable and alkanes can be formed by the methanation and FT reactions between hydrogen and carbon monoxide and carbon dioxide. For example, at 500 K, the equilibrium constant for methanation reaction is favorable [1–7,16]:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$
 (6.4)

Thus, forming hydrogen selectively and inhibiting the formation of alkanes would require a catalyst that promotes C-C scission followed by the water–gas shift reaction and inhibits C-O scission followed by the hydrogenation.

# 6.5 KINETICS AND CATALYSIS OF APR PROCESS

As shown in Figure 6.1, the APR process can be tailored toward the four distinct kinetic steps depending on the desired product [1–6,11–33] (Tanksale et al., 2008, pers. comm.). APR can produce hydrogen, syngas, alkanes, or monofunctional groups depending on the catalyst and support system, promoters, and other operating conditions.

The original purpose of APR was to generate either hydrogen or alkanes by an APR of sugar, other oxygenated compounds, and polyols (with a ratio of 1:1). The kinetics of APR depends on the temperature, the pressure, the nature of the catalyst and its support, the presence of promoters, the pH of the slurry, the acidity of catalyst active sites, and the nature of the feedstock. Here, we briefly examine the effects of these operating variables on the APR process. While the literature has shown numerous ways to generate hydrogen from biomass under high-temperature conditions, APR is unique in that it is the only process that can be carried out in liquid water [5,34–57]. While APR can only be used for selective feedstock without their pretreatments, it is faster than anaerobic digestion process for generating hydrogen from cellulosic waste [5,34–57].

#### 6.5.1 EFFECTS OF TEMPERATURE, CARBON NUMBER, AND PRESSURE

As shown in Figure 6.1, APR provides multiple options of reaction paths depending on the operating conditions. Figure 6.3 illustrates that hydrogen selectivity decreases with an increase in carbon number of oxygenated compounds and an increase in temperature. The temperature effect shown in this figure is valid for all oxygenated feedstock. The literature has shown that compounds such as furanone and acetic acid are not amenable to the production of hydrogen by APR [1–7,16]. The hydrogen selectivity depends on the nature of the bond breaking in oxygenated compounds; the breakage of C–C bond favors the hydrogen formation and the breakage of C–O bond favors the formation of alkanes. Following the preferred pathway is the key to the hydrogen formation. Dumesic et al. [1–6,16] also showed that an increase in pressure reduced the hydrogen selectivity. For example, for the reaction of 5 wt% sorbitol over Pt–SiAl at 498 K, the hydrogen selectivity at 25.8 atm pressure was 21, whereas the same selectivity at a pressure between 33.1 and 52.1 atm was <2 [1–6,16].

### 6.5.2 EFFECTS OF CATALYSTS AND SUPPORTS

As shown in Table 6.1, the major primary feedstock for APR are glucose (and sorbitol), alcohols, ethylene glycol, and glycerol. For all of these feedstock, Dumesic et al. [1-6,16], among others [5,15,17-26,27-57] (Tanksale et al., 2008, pers. comm.), have clearly shown that the nature of metal and support has an important influence on the reaction paths and the rates of reactions in the APR process. The product selectivity can be tuned depending on the metal and support. For example, Pt-black and Pt supported on  $Al_2O_3$ ,  $TiO_2$ , and  $ZrO_2$  have been demonstrated to be active and selective for the APR of methanol and ethylene glycol to produce hydrogen. Catalysts based on Pd have shown similar activity compared to Pt analogs. Ru, Rh, and Ni, however, showed lower activity for hydrogen.



**FIGURE 6.3** Selectivities vs. oxygenated hydrocarbon.  $H_2$  selectivity (circles) and alkane selectivity (squares) from APR of 1 wt% oxygenated hydrocarbons over 3 wt% Pt/Al<sub>2</sub>O<sub>3</sub> at 498 K (open symbols and dashed curves) and 538 K (filled symbols and solid curves). (Reprinted from *Applied Catalysis B: Environmental*, 56, Davda, R., Shabaker, J., Huber, G., Cortright, R., and Dumesic, J., A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metalcatalysts, 171–186, Copyright 2005, with permission from Elsevier.)

Davda et al. [16] and others [15–33] (Tanksale et al., 2008, pers. comm.) have examined the effectiveness of various group VIII metal catalysts, such as Ru, Rd, Pt, Ir, Pd, and Ni, for APR. The studies compare the selectivity for hydrogen, alkanes, and carbon dioxide by Pt, Pd, Ru, Rh, and Ni catalysts for various oxygenated compounds and at various temperatures. The results show that  $CO_2$  selectivity was the highest for Pt and Ni catalysts, and the lowest for Rh and Pd catalysts. The alkanes selectivity was the highest for Ru and Rh catalysts followed by Pt and Ni. Very little alkanes were produced by Pd catalysts. Finally, Pt and Pd (followed by Ni) showed good reforming activity and high hydrogen production rates. Good catalysts for hydrogen production by APR should show high activity for water–gas shift reaction and for cleavage of C–C bonds. Both Pd and Pt catalysts gave poor activity for C–O scission and subsequent methanation and FT reactions [1–6].

In the final analysis, since Pt catalysts gave good product distributions for all three (hydrogen, carbon dioxide, and alkanes) components, Pt was considered to be the best catalyst. Ni catalyst, although cheap, gave preference to alkanes. Park et al. [29] studied the production of biohydrogen by APR of polyols over Pt catalysts supported on three-dimensionally bimodal mesoporous carbon (3D-BMC). The 3D-BMCs with mesopores of tunable size (controlled through the polymerization of the carbon precursor) were synthesized. After loading with platinum, the

catalysts were used in APR of polyols, and superior performance was shown in terms of carbon conversion, hydrogen yield, selectivity, and hydrogen production rate compared to Pt catalysts supported on activated carbon or two-dimensional CMK-3 (ordered mesoporous carbon synthesized by silica hard template).

The study by Davda et al. [2,16,41,58,59] also indicated that the best support for Pt was  $Al_2O_3$  for hydrogen production and the effect of support on reforming activity and selectivity is greater than that of metal dispersion. They also analyzed bimetallic catalysts and concluded that Ni–Sn catalysts show potential for APR. The selectivity for hydrogen and alkanes for different oxygenates at 225°C and 265°C using Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is illustrated in Figure 6.3 [16].

### 6.5.3 EFFECTS OF PROMOTERS AND ACIDITY OF LIQUID AND SOLIDS

The addition of a promoter can also have some effect on the catalyst performance. Re was found to be an effective promoter for Pt/C catalyst. The selectivity of Pt–Re/C was found to be different from that of Pt/C. Hydrogen selectivity with promoter was lower, although hydrogen productivity was higher. Following reduction, Pt–Re/C catalyst was significantly more active for APR of glycerol than Pt/C catalyst. The presence of Re created surface acidity that favored a pathway of C–O bond breaking (dehydration), resulting in lower hydrogen and CO(CO<sub>2</sub>) selectivity and higher alkanes selectivity [1–6,16]. The literature [1–6,16] also showed that an addition of KOH (base) affected APR selectivity of glycerol for 3%Pt3%Re/C catalyst.

The effects of liquid and solid acidities on carbon selectivity for sorbitol at 538 K and 57.6 bar with Pt/Al catalysts were also examined by Dumesic et al. [1-6,16]. The results indicated that lower pH of both liquids and solids produce higher carbon number alkanes. In general, an increase in acidity by either the use of acid catalyst support (i.e., SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) or the addition of the mineral acid such as HCl to increased the feed alkanes selectivity due to the increased rate of dehydration and hydrogenation pathways compared to hydrogenolysis and reforming reactions. The nickel supported on SiO<sub>2</sub> or AI<sub>2</sub>O<sub>3</sub> was found to have low selectivity for hydrogen and favored the formation of alkanes. However, an addition of an Sn promoter to Raney R–Ni-based catalysts enhanced the production of hydrogen from sorbitol, glycerol, and ethylene glycol [1–6,16]. While the promoters and acidity can be used to produce alkanes, some C–C bond needs to be broken to produce hydrogen needed for the production of alkanes. For example, the hydrogenation and complete deoxygenation of sorbitol results in the following set of reactions [1–6,16]:

$$C_6H_{14}O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O$$
 (6.5)

However, complete deoxygenation occurs as [1–6,16]

$$C_6H_{14}O_6 \rightarrow 13/19C_6H_{14} + 36/19CO_2 + 42/19H_2O$$
 (6.6)

These reactions indicate the need for hydrogen for the production of alkanes.

#### 6.5.4 EFFECTS OF FEEDSTOCK

As shown in Table 6.1, while APR can be applied to both the primary and secondary feedstock, so far, most of the work has been focused on the primary feedstock such as sugar, glucose, sorbitol, alcohols, ethylene glycol, and glycerol. As Virent's BioForming process based on APR develops, it is intended to apply to the secondary feedstock as well. This will require some acid and/or enzyme hydrolysis pretreatments to the feedstock. Here we briefly review some of the reported studies on APR for both the primary and secondary feedstock. For the primary feedstock, the discussion is further broken into two parts: (1) individual compounds having high vapor pressure such that APR is carried out in both gas and liquid phases, and (2) individual compounds having low vapor pressure such that APR occurs largely in the aqueous environment. Since the literature for APR of biomass-derived products is extensive [1–7,12,14,16,17,56,60–64], here we focus only on few recent studies on individual compounds and materials [1–7,12,14,16,17,56,60–64].

# 6.5.4.1 APR of Ethylene Glycol, Alcohols, and Glycerol (Primary Feedstock with High Vapor Pressure)

APR of these compounds can occur in both the liquid and gas phases due to their high vapor pressure under the reaction conditions. Dumesic et al. [4,16,48,49] have extensively studied APR of ethylene glycol, particularly for alumina-supported Pt catalysts. Their results are well reviewed by Alonso et al. [4] and Davda et al. [16]. Two recent novel studies are by D'Angelo et al. [31] who examined APR of ethylene glycol in a novel microchannel reactor and Chu et al. [38] who examined APR of ethylene glycol on Co/ZnO catalysts prepared by the coprecipitation method. APRs of various alcohols (methanol, ethanol, and other polyols) are well examined by Dumesic et al. [1–6,16,48], Park et al. [29], Cruz et al. [50], and Zhang et al. [54].

The Department of Energy has identified glycerol as one of the 12 important platform chemicals from biomass (see Chapter 7). In Chapter 4, we examined a significant work reported on the steam reforming of glycerol. The reforming reaction with glycerol results in [1-7,16]

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \tag{6.7}$$

APR of glycerol has also been widely studied, as indicated by the large amount of literature on the subject [34–36,44,47,51–57,65]. The subject is also extensively covered in a number of reviews by Dumesic et al. [1–6], Davda et al. [16], and Vaidya and Rodrigues [47]. Here we examine only few recent studies on the subject in brief detail.

Tuza et al. [65] examined the production of renewable hydrogen by APR of glycerol over Ni–Cu catalysts derived from hydrotalcite precursors. The reforming was carried out in a batch reactor at 250°C and 270°C. The catalyst with 5% of Cu showed high  $H_2$  selectivity at 250°C. At 270°C, there was consumption of  $H_2$  with time due to hydrogenolysis of glycerol. The study proposed the main reaction routes, which

considered liquid byproducts. At 250°C, hydrogen selectivity was always higher than 80% and the formation of CO was very low (<3%). The addition of Cu decreased the formation of methane.

Wen et al. [39] examined the activities and stabilities of Pt. Ni, Co, and Cu catalysts and supports for  $H_2$  production by APR of glycerol. The experimental data were taken in a continuous flow fixed-bed reactor. It was found that the activity of the metal catalysts increased in the order of Co, Ni, Cu, and Pt. Additionally, Pt was highly stable, whereas Ni and Co showed a significant deactivation with time on stream. It was also found that the activity of Pt catalysts on various supports follows the order: SAPO-11 < active carbon (AC) < HUSY <  $SiO_2 < MgO < Al_2O_3$ . Moreover, the basic support resulted in high activity and higher hydrogen molar concentration, whereas acidic support and neutral Al<sub>2</sub>O<sub>3</sub> support tended to increase alkanes formation. It was shown by X-ray diffraction (XRD) that Pt was caused to sinter on all of the supported Pt catalysts during the reaction. In addition, a trace amount of carbon deposition was found on all of the supported Pt catalysts. However, no remarkable deactivation was observed over Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/SiO<sub>2</sub>, Pt/AC, and Pt/ HUSY catalysts. Two zeolite-supported catalysts showed low activities as well as the collapse of the support. In addition, little influence of the collapse of the support on the stability of Pt/HUSY was observed. Pt/SAPO-11 catalyst exhibited very high deactivation.

Cho et al. [57] examined APR of glycerol over Ni-based catalysts for hydrogen production. The reforming was carried out at 225°C, 23 bar, and liquid hourly space velocity (LHSV) = 4 h<sup>-1</sup>. The Ni-based catalyst was prepared by an incipient wetness impregnation method. It was found that Ni (20 wt%)–Co (3 wt%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed higher glycerol conversion and hydrogen selectivity than Ni (20 wt%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. There were no major changes in Ni particles after the reaction over Ni–Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The results suggest that the Ni–Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be applied to the hydrogen production system using APR of glycerol.

# 6.5.4.2 APR of Sugar and Glucose (Primary Feedstock with Low Vapor Pressure)

Tanksale et al. [42] examined the hydrogen production by APR of sugar solutions using metal-supported catalysts. The aim of this study was to examine the influence of several reaction parameters on hydrogen production using liquid-phase reforming of sugar solution over Pt, Pd, and Ni supported on nanostructured supports. It was found that the desired catalytic pathway for H<sub>2</sub> production involves cleavage of C–C, C–H, and O–H bonds that adsorb on the catalyst surface. Thus, a good catalyst for the production of H<sub>2</sub> by liquid-phase reforming must facilitate the C–C bond cleavage and promote the removal of adsorbed CO species by the water–gas shift reaction, but the catalyst must not facilitate the C–O bond cleavage and hydrogenation of CO or CO<sub>2</sub>. Apart from studying various catalysts, a commercial Pt/ $\gamma$ -alumina catalyst was also examined at three different temperatures: 458, 473, and 493 K. On the surface of some of the spent catalysts, the amorphous and organized form of coke was found. APR of sugar solution was also studied by Blommel and Cortright [15], Cortright [8,66], and Held [67]. APR of cellulose can form hydrogen by the following reaction [1–6,16]:

$$C_6O_6H_{12} + 6H_2O \rightarrow 6CO_2 + 12H_2$$
 (6.8)

Also, dehydration/hydrogenation results in the formation of alkanes as

$$C_6O_6H_{12} + 7H_2 \rightarrow C_6H_{14} + 6H_2O$$
 (6.9)

which gives the combined reaction as

$$1.6C_6O_6H_{12} \rightarrow C_6H_{14} + 3.5CO_2 + 2.5H_2O$$
 (6.10)

Alkanes contained 95% of the heating value and only 30% of the mass of the biomass-derived reactant.

Davda et al. [16] proposed that a way to increase hydrogen selectivity from glucose is to operate in two stages: (1) to carry out the low-temperature hydrogenation step followed by the high-temperature reforming process and (2) to co-feed hydrogen with liquid reactant stream to the reforming reactor. This co-feeding argument leads them to propose a reactor scheme shown in Figure 6.4 to obtain the product of desired specification using APR [16].

For biomass application, APR of glucose is very important because it is the basic sugar component of all starch and carbohydrates [1–6,16,48]. The hydrogenation of glucose leads to the formation of sorbitol, and both glucose and sorbitol can be reformed to form carbon dioxide and hydrogen. As the glucose concentration in the feed increases, the hydrogen selectivity decreases. Also, these reactions are favored at low temperatures. The reforming of both glucose and sorbitol can occur on Pt and Ni-Sn alloy by cleavages of C-C bonds followed by the water-gas shift reaction [1-6,16]. The alkanes are produced on the acidic sites of metals from both glucose and sorbitol. Glucose also produces acids, aldehydes, and so on through homogeneous side reactions. Since undesirable side reactions are first order with respect to glucose and the desirable reactions have a fractionorder dependence on glucose, an increase in glucose concentration reduces hydrogen selectivity [1-6,16]. The hydrogenation of glucose to sorbitol also occurs at a higher rate at low temperature (400 K) and high hydrogen pressure. Recently, Wen et al. [39] examined the catalytic properties of Ni on alumina for the APR of glucose.

#### 6.5.4.3 APR of Biomass and Cellulose (Secondary Feedstock)

APR has also been tested on biomass and cellulose waste paper [37,45]. Valenzuela et al. [37] studied APR of woody biomass in a batch reactor. In this study, APR was used to produce hydrogen from actual biomass. The experiments were carried out in a 100 mL Parr micro reactor heated to 225°C. Both acid hydrolysis of woody biomass and subsequent APR of soluble molecules by a  $Pt/Al_2O_3$  catalyst were carried out in a single reactor. The experiments showed that increasing the acid concentration from 1% to 5% resulted in more than a twelve-fold increase in  $H_2$  concentration in the product gas. However, hydrogen accounted for only 18% of



FIGURE 6.4 Summary of the process conditions employed to obtain a product of the desired specifications using the APR process. (Reprinted from Applied Catalysis B: Environmental, 56, Davda, R., Shabaker, J., Huber, G., Cortright, R., and Dumesic, J., A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metalcatalysts, 171–186, Copyright 2005, with permission from Elsevier.)

the noncondensable gas phase with  $CO_2$  as a major product. The presence of the Pt/Al<sub>2</sub>O<sub>3</sub> reforming catalyst enhanced both the selectivity and the yield of hydrogen in the gas phase. This was also accompanied by a noticeable decrease in carbon monoxide production due to a faster water-gas shift reaction catalyzed by platinum. In comparison with other feeds such as glucose, wastepaper, and ethylene glycol, the amount of hydrogen produced from biomass was of a comparable magnitude per gram of feed, although biomass yielded more hydrogen per gram of carbohydrate than either glucose or wastepaper. Baseline experiments were carried out to confirm that the observed hydrogen production was originated from the biomass.

Tungal and Shende [45] reported APR of wastepaper in the presence of a homogeneous Ni(NO<sub>3</sub>)<sub>2</sub> catalyst for biocrude and H<sub>2</sub> production. In this study, reforming of aqueous wastepaper slurry (0.1 g/cc) was performed using 5 wt% catalyst at  $200^{\circ}\text{C}-275^{\circ}\text{C}$ . At  $250^{\circ}\text{C}$ , about 44 wt% biocrude and 3.8 mol% H<sub>2</sub> were observed after 120 min of reaction time. Other gases observed in the products were CO<sub>2</sub>, CO, and CH<sub>4</sub>. The liquid phase (biocrude) contained sugars (7.5 wt%), hydroxy-methylfurfural (HMF)/furfural (~1 wt%), oxygenated hydrocarbons (42.4 wt%), and monocarboxylic acids (49.1 wt%) such as acetic, formic, propionic, and lactic (2-hydroxypropionic) acids.

### 6.5.5 NOVEL REACTOR DESIGNS

The operating conditions and the nature of the catalyst not only affect the selectivity between hydrogen and alkanes, but also the level of CO production. A low CO concentration in the product requires an ultra shift operation in which the reaction conditions are such that the water–gas shift reaction is favored. The lowest level of CO requires the lowest partial pressure of  $CO_2$  and  $H_2$  in the gas phase so that the forward water gas reaction is thermodynamically favored. These conditions are achieved by operating the reactor at the saturation pressure for water (at the reaction temperature) and using low feed concentration of oxygenates [16].

Very few studies have been done on the novel reactor design to carry out the APR process. As mentioned earlier and shown in Figure 6.4, Davda et al. [16] proposed that a way to increase hydrogen selectivity from glucose is to operate in two stages. D'Angelo et al. [31] studied APR of biocarbohydrates in a catalytically stable wash-coated micro reactor, in which multiphase hydrogen removal enhanced hydrogen efficiency. A coating method to deposit a Pt-based catalyst on the microchannel walls was selected and optimized. APR reactivity tests were performed using ethylene glycol as the model compound. Optimum results were achieved with a static wash coating technique in which a highly uniform and well-adhered 5  $\mu$ m layer was deposited on the walls of a 320 µm internal diameter (ID) microchannel in one single step. During APR of ethylene glycol, the catalyst layer exhibited high stability over 10 days after limited initial deactivation. The microchannel presented higher conversion and selectivity to hydrogen than a fixed-bed reactor. They concluded that the benefits of using a micro reactor for APR can be further enhanced by utilizing the increased Pt loadings, higher reaction temperatures, and larger carbohydrates (e.g., glucose). The use of micro technology for APR can allow a significant reduction in the reformer size, thus rendering it promising for distributed hydrogen production.

Subsequently, D'Angelo et al. [9] used the 1.7 m long, 320  $\mu$ m ID microchannel reactor with a 5  $\mu$ m Pt-based wash-coated catalyst layer described earlier to study APR of sorbitol. The performance of this microchannel reactor was correlated to the mass transfer properties, reaction kinetics, hydrogen selectivity, and product distribution. While mass transfer did not affect kinetically controlled sorbitol consumption, it did affect hydrogen selectivity and the product distribution. Compared to a fixed-bed reactor, the hydrogen selectivity in the microchannel reactor was higher by a factor of 2. The yield of side products (mainly C<sub>3</sub> and heavier hydrodeoxygenated species) was suppressed, whereas the yield of hydrogen was increased from 1.4 to 4.0 moles per mole of sorbitol fed.



**FIGURE 2.1** Typical production curve for a coal bed methane well showing relative methane and water production. (Adapted from Rice, D., "Coal bed methane—An untapped energy resource and environment concern," US Geological Survey, Energy Resource Surveys Program, USGS Fact Sheet FS-019-97, 1997.)



**FIGURE 2.2** Simplified illustration of a coal bed methane production well. (From Huth, E., Sule, M., Todman, L., Brant, J., and Templeton, M., "Treatment and reuse of coalbed methane produced water using pervaporation irrigation," 22nd Annual Produced Water Society Conference, January 17–19, 2012. With permission.)



**FIGURE 3.2** PWR—A common type of LWR. (Adapted from "Nuclear power reactors," a document of World Nuclear Association, July 2013.)



**FIGURE 3.3** Three methods of recovering geothermal energy: (a) dry steam. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; National Renewable Energy Laboratory. Planta Solar 20. http://www.nrel.gov/csp/solarpaces/project\_detail.cfm/projectID=39.)



(b)



**FIGURE 3.3** (Continued) Three methods of recovering geothermal energy: (b) flash steam and (c) binary cycle. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; National Renewable Energy Laboratory. Planta Solar 20. http://www.nrel.gov/csp/solarpaces/project\_detail.cfm/projectID=39.)



FIGURE 3.4 Steps taken to recover geothermal energy via the EGS. (Adapted from Union of Concerned Scientists, *How Geothermal Energy Works*, Union of Concerned Scientists, Cambridge, MA, 2012; Office of Energy Efficiency and Renewable Energy, *An Evaluation of Enhanced Geothermal Systems Technology*, US Department of Energy, Washington, DC, 2008.)



**FIGURE 6.1** Possible reaction paths for APR for water-soluble oxygenated hydrocarbons. (Reprinted from *Green Chemistry*, 12, Alonso, D.M., Bond, J.Q., and Dumesic, J.A., Catalytic conversion of biomass to biofuels, 1493–1513, Copyright 2010, with permission from Elsevier.)



**FIGURE 6.5** Schematic pathways to convert sugar and polyols to biofuel through production of monofunctional intermediates. (Reprinted from *Green Chemistry*, 12, Alonso, D.M., Bond, J.Q., and Dumesic, J.A., Catalytic conversion of biomass to biofuels, 1493–1513, Copyright 2010, with permission from Elsevier.)



FIGURE 6.6 Virent's BioForming® process to produce liquid transportation fuels from biomass feedstock. APR enables the process to partially defunctionalize carbohydrate feedstock for further catalytic upgrading. (Reprinted from White Paper for European Platform on Biofuels, Blommel, P.G. and Cortright, R.D., Production of conventional liquid fuels from sugars, Copyright 2012, with permission from Elsevier.)



**FIGURE 6.7** Detailed two-stage reactor setup for BioForming process: Panel (a) illustrates the catalytic steps used to convert glucose and xylose to gasoline-range hydrocarbons; panel (b) summarizes the molar carbon and heating value yields of the resulting products. (Reprinted from White Paper for European Platform on Biofuels, Blommel, P.G. and Cortright, R.D., Production of conventional liquid fuels from sugars, Copyright 2012, with permission from Elsevier.)



C Biofine Technology

**FIGURE 7.1** A schematic of the overall Biofine process that includes product upgrading. (From Fitzpatrick, S. and Nace, P., "Biofine Technology, LLC: Renewable chemicals and biofuels," Paper presented for Sustainable Bioplastics Council of Maine, 2012. With permission.)



# C Biofine Technology

**FIGURE 7.4** A complete process flow diagram of the Biofine process. (From Fitzpatrick, S. and Nace, P., "Biofine Technology, LLC: Renewable chemicals and biofuels," Paper presented for Sustainable Bioplastics Council of Maine, 2012. With permission.)



**FIGURE 7.5** Biorefinery products "family tree." (From Fitzpatrick, S. and Nace, P., "Biofine Technology, LLC: Renewable chemicals and biofuels," Paper presented for Sustainable Bioplastics Council of Maine, 2012. With permission.)

о но Ц он	но Он	HO HO NH <sub>2</sub>
Succinic acid	3-Hydroxypropionic acid	Glutamic acid
	но стори	но
Aspartic acid	Glycerol	4-Hydroxybutyrolactone
O HO Haconic acid	O U O U O U O U O H	0 HO OH
ОН ОН ОН ОН ОН		
Xylitol	Sorbitol	Glucaric acid
Diofine Technology		

**FIGURE 7.6** "Select 12" platform chemicals from biomass as identified by the Department of Energy. (From Fitzpatrick, S. and Nace, P., "Biofine Technology, LLC: Renewable chemicals and biofuels," Paper presented for Sustainable Bioplastics Council of Maine, 2012. With permission.)



**FIGURE 7.7** Process chain to produce maximum yields of DMB from organic waste and residue. (From Hayes, D., DiBANET project, 2013. With permission.)



**FIGURE 11.1** Thermochemical routes for solar hydrogen production. (From Meier, A. and Sattler, C., "Solar fuels from concentrated sunlight," SolarPACES, Solar Power and Chemical Energy Systems, IEA report, 2009. With permission.)



**FIGURE 11.2** Exergy efficiency—Variation of the exergy efficiency as a function of the process operating temperature for a blackbody cavity receiver converting concentrated solar energy into chemical energy. (From Meier, A. and Sattler, C., "Solar fuels from concentrated sunlight," SolarPACES, Solar Power and Chemical Energy Systems, IEA report, 2009. With permission; Fletcher, E.A. and Moen, R.L., *Science*, 197, 1050–1056, 1977. With permission.)



**FIGURE 11.3** Thermochemical route based on metal oxide–redox reactions. (From Meier, A. and Sattler, C., "Solar fuels from concentrated sunlight," SolarPACES, Solar Power and Chemical Energy Systems, IEA report, 2009.)



**FIGURE 11.4** Rotary solar reactor for the thermal dissociation of zinc oxide to zinc and oxygen at above 1700°C. (From Meier, A. and Sattler, C., "Solar fuels from concentrated sunlight," SolarPACES, Solar Power and Chemical Energy Systems, IEA report, 2009.)



**FIGURE 11.5** Monolithic dual-chamber solar receiver reactor for continuous hydrogen production. (From Meier, A. and Sattler, C., "Solar fuels from concentrated sunlight," SolarPACES, Solar Power and Chemical Energy Systems, IEA report, 2009.)



**FIGURE 12.1** Various molecular structures of gas hydrate and clathrate depending on guest molecules. (From "Methane hydrates," A communication by Center for Gas Hydrate Research, Heriot-Watt University, Edinburgh, The Hydrate forum Org., 2012. With permission.)



**FIGURE 12.2** Gas hydrate stability fields for (a) nominal marine settings. (From Tohidi, 2013, pers. comm. With permission.)



**FIGURE 12.2** (Continued) Gas hydrate stability fields for (b) permafrost settings. (From Tohidi, 2013, pers. comm. With permission.)



**FIGURE 13.1** Cross section of a conventional hydroelectric dam. (Adapted from "Hydroelectricity," Wikipedia, the free encyclopedia, 1–7, 2012.)



**FIGURE 13.3** WaveRoller wave energy farm installation in Peniche, Portugal. (Adapted from "Wave power," Wikipedia, the free encyclopedia, 2013.)



**FIGURE 13.4** Wave Dragon seen from reflector. (Adapted from "Wave power," Wikipedia, the free encyclopedia, 2013.)



**FIGURE 13.5** A horizontal-axis hydrokinetic rotating device, tidal turbine. (Adapted from "How hydrokinetic energy works?" Union of Concerned Scientists, 1–5, 2012.)



**FIGURE 13.6** Cross-flow turbine used in Alaska Rivers: ORPC's TidGen<sup>TM</sup> power system. [Adapted from "Hydrokinetic energy (in river, tidal, and ocean current)," *Alaska Energy Wiki*, Alaska Center for Energy and Power, 1–4, 2012.]



**FIGURE 13.7** The world's first commercial scale and grid-connected tidal stream generator— SeaGen—in Strangford Lough. (Adapted from "Tidal power," Wikipedia, the free encyclopedia, 2013.)



**FIGURE 13.9** A schematic of OTEC process with applications. (Adapted from "Ocean thermal energy conversion," Wikipedia, the free encyclopedia, 2013.)



**FIGURE 13.10** Cumulative marine and hydrokinetic energy installed capacity by technology, world market: 2008–2017. (Adapted from Gauntlett, D. and Asmus, P., "Executive summary: Hydrokinetic and Ocean Energy; Renewable power generation from ocean wave, tidal stream, river hydrokinetic, ocean current, and ocean thermal technologies," Research report by Pike Research, Cleantech Market Intelligence, Boulder, CO, 2012.)