Hydrogen and Syngas Production and Purification Technologies

Edited by

Ke Liu
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BP Products North America, Inc.

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Preface

Hydrogen and synthesis gas (syngas) are indispensable in chemical, oil, and energy industries. They are important building blocks and serve as feedstocks for the production of chemicals such as ammonia and methanol. Hydrogen is used in petroleum refineries to produce clean transportation fuels, and its consumption is expected to increase dramatically in the near future as refiners need to process increasingly heavier and sour crudes. In the energy field, the developments made recently in IGCC (Integrated Gasification Combined Cycle) and fuel cell technologies have generated a need to convert the conventional fuels such as coal or natural gas to either pure hydrogen or syngas for efficient power generation in the future. In addition, the dwindling supply of crude oil and rising demand for clean transportation fuels in recent years led to intensive research and development worldwide for alternative sources of fuels through various conversion technologies, including gas-to-liquid (GTL), coal-to-liquid (CTL) and biomass-to-liquid (BTL), which involve both hydrogen and syngas as key components.

The purpose of this multi-authored book is to provide a comprehensive source of knowledge on the recent advances in science and technology for the production and purification of hydrogen and syngas. The book comprises chapters on advances in catalysis, chemistry and process for steam reforming and catalytic partial oxidation of gaseous and liquid fuels, and gasification of solid fuels for efficient production of hydrogen and syngas and their separation and purification methods, including water-gas-shift, pressure swing adsorption, membrane separations, and desulfurization technologies. Furthermore, the book covers the integration of hydrogen and syngas production with future energy systems, as well as advances in coal-to-liquids and syngas-to-liquids (Fischer-Tropch) processes. All the chapters have been contributed by active and leading researchers in the field from industry, academia, and national laboratories. We hope that this book will be useful to both newcomers and experienced professionals, and will facilitate further research and advances in the science and technology for hydrogen and syngas production and utilization toward clean and sustainable energy in the future.

We sincerely thank all the authors who spent their precious time in preparing various chapters for this book. We would like to express our sincere gratitude to our family members and colleagues for their constant support and patience while we completed the task of preparing and editing this book. We are also grateful to all

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Chapter 1

Introduction to Hydrogen and Syngas Production and Purification Technologies

Chunshan Song

Clean Fuels and Catalysis Program, EMS Energy Institute, and Department of Energy and Mineral Engineering, Pennsylvania State University

1.1 IMPORTANCE OF HYDROGEN AND SYNGAS PRODUCTION

Clean energy and alternative energy have become major areas of research worldwide for sustainable energy development. Among the important research and development areas are hydrogen and synthesis gas (syngas) production and purification as well as fuel processing for fuel cells. Research and technology development on hydrogen and syngas production and purification and on fuel processing for fuel cells have great potential in addressing three major challenges in energy area: (a) to supply more clean fuels to meet the increasing demands for liquid and gaseous fuels and electricity, (b) to increase the efficiency of energy utilization for fuels and electricity production, and (c) to eliminate the pollutants and decouple the link between energy utilization and greenhouse gas emissions in end-use systems.[1]

The above three challenges can be highlighted by reviewing the current status of energy supply and demand and energy efficiency. Figure 1.1 shows the energy supply and demand (in quadrillion BTU) in the U.S. in 2007.[2] The existing energy system in the U.S. and in the world today is largely based on combustion of fossil fuels—petroleum, natural gas, and coal—in stationary systems and transportation vehicles. It is clear from Figure 1.1 that petroleum, natural gas, and coal are the three largest sources of primary energy consumption in the U.S. Renewable energies

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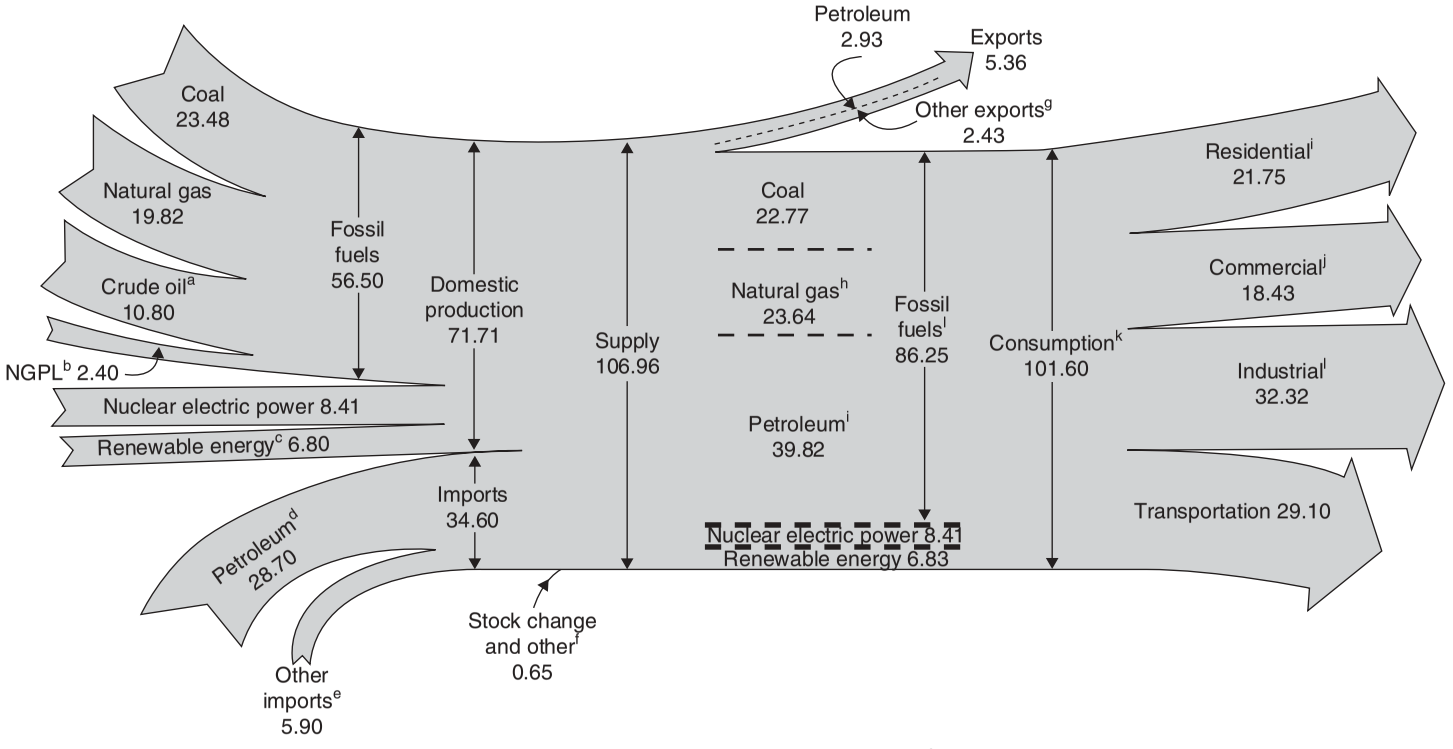

Figure 1.1. Energy supply by sources and demand by sectors in the U.S. in 2007 (in quadrillion BTU).[2]

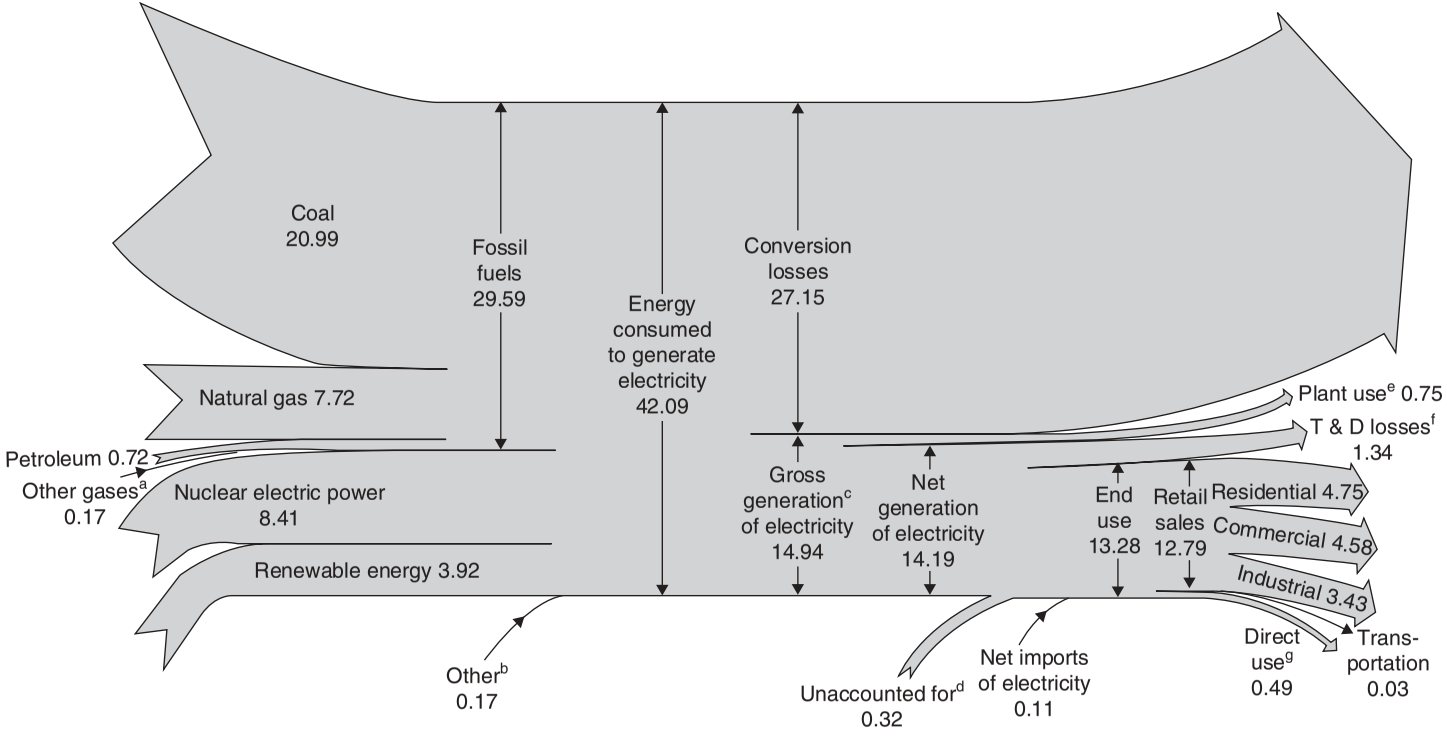

Figure 1.2. Energy consumption for electricity generation in the U.S. in 2007 (in quadrillion BTU).[2]

are important but are small parts (6.69%) of the U.S. energy flow, although they have potential to grow.

Figure 1.2 illustrates the energy input and the output of electricity (in quadrillion BTU) from electric power plants in the U.S. in 2007.[2] As is well known, electricity is the most convenient form of energy in industry and in daily life. The electric power plants are the largest consumers of coal. Great progress has been made in the electric power industry with respect to pollution control and generation technology with certain improvements in energy efficiency.

What is also very important but not apparent from the energy supply–demand shown in Figure 1.1 is the following: The energy input into electric power plants represents 41.4% of the total primary energy consumption in the U.S., but the electrical energy generated represents only 35.5% of the energy input, as can be seen from Figure 1.2. The majority of the energy input into the electric power plants, over 64%, is lost and wasted as conversion loss in the process. The same trend of conversion loss is also applicable for the fuels used in transportation, which represents 28.6% of the total primary energy consumption. Over 70% of the energy contained in the fuels used in transportation vehicles is wasted as conversion loss. This energy waste is largely due to the thermodynamic limitations of heat engine operations dictated by the maximum efficiency of the Carnot cycle.

Therefore, the current energy utilization systems are not sustainable in multiple aspects, and one aspect is their wastefulness. Fundamentally, all fossil hydrocarbon resources are nonrenewable and precious gifts from nature, and thus it is important to develop more effective and efficient ways to utilize these energy resources for sustainable development. The new processes and new energy systems should be much more energy efficient, and also environmentally benign. Hydrogen and syngas production technology development represent major efforts toward more efficient, responsible, comprehensive, and environmentally benign use of the valuable fossil hydrocarbon resources, toward sustainable development.

Hydrogen (H_2) and syngas (mixture of H_2 and carbon monoxide, CO) production technologies can utilize energy more efficiently, supply ultraclean fuels, eliminate pollutant emissions at end-use systems, and significantly cut emissions of greenhouse gases, particularly carbon dioxide, CO_2. For example, syngas production can contribute to more efficient electrical power generation through advanced energy systems, such as coal-based Integrated Gasification Combined Cycle (IGCC), as well as syngas-based, high-temperature fuel cells such as solid oxide fuel cells (SOFCs)[3] and molten carbonate fuel cells (MCFCs). Syngas from various solid and gaseous fuels can be used for synthesizing ultraclean transport fuels such as liquid hydrocarbon fuels, methanol, dimethyl ether, and ethanol for transportation vehicles.

1.2 PRINCIPLES OF SYNGAS AND HYDROGEN PRODUCTION

With gaseous and liquid hydrocarbons and alcohols as well as carbohydrate feedstock, there are many process options for syngas and hydrogen production. They are

steam reforming, partial oxidation, and autothermal reforming or oxidative steam reforming. With solid feedstock such as coal, petroleum coke, or biomass, there are various gasification processes that involve endothermic steam gasification and exothermic oxidation reaction to provide the heat *in situ* to sustain the reaction process.

The following equations represent the possible reactions in different processing steps involving four representative fuels: natural gas (CH_4) and liquefied propane gas (LPG) for stationary applications, liquid hydrocarbon fuels (C_mH_n) and methanol (MeOH) and other alcohols for mobile applications, and coal gasification for large-scale industrial applications for syngas and hydrogen production. Most reactions (Eqs. 1.1–1.14 and 1.19–1.21) require (or can be promoted by) specific catalysts and process conditions. Some reactions (Eqs. 1.15–1.18 and 1.22) are undesirable but may occur under certain conditions.

- Steam reforming

$$CH_4 + H_2O = CO + 3H_2 \quad (1.1)$$
$$C_mH_n + m\,H_2O = m\,CO + (m + n/2)H_2 \quad (1.2)$$
$$CH_3OH + H_2O = CO_2 + 3H_2 \quad (1.3)$$

- Partial oxidation

$$CH_4 + O_2 = CO + 2H_2 \quad (1.4)$$
$$C_mH_n + m/2\,O_2 = m\,CO + n/2\,H_2 \quad (1.5)$$
$$CH_3OH + 1/2\,O_2 = CO_2 + 2H_2 \quad (1.6)$$
$$CH_3OH = CO + 2H_2 \quad (1.7)$$

- Autothermal reforming or oxidative steam reforming

$$CH_4 + 1/2\,H_2O + 1/2\,O_2 = CO + 5/2\,H_2 \quad (1.8)$$
$$C_mH_n + m/2\,H_2O + m/4\,O_2 = m\,CO + (m/2 + n/2)\,H_2 \quad (1.9)$$
$$CH_3OH + 1/2\,H_2O + 1/4\,O_2 = CO_2 + 2.5H_2 \quad (1.10)$$

- Gasification of carbon (coal, coke)

$$C + H_2O = CO + H_2 \quad (1.11)$$
$$C + O_2 = CO_2 \quad (1.12)$$
$$C + 0.5O_2 = CO \quad (1.13)$$
$$C + CO_2 = 2CO \quad (1.14)$$

- Carbon formation

$$CH_4 = C + 2H_2 \quad (1.15)$$
$$C_mH_n = x\,C + C_{m-x}H_{n-2x} + x\,H_2 \quad (1.16)$$
$$2CO = C + CO_2 \quad (1.17)$$
$$CO + H_2 = C + H_2O \quad (1.18)$$

- Water-gas shift

$$CO + H_2O = CO_2 + H_2 \quad (1.19)$$
$$CO_2 + H_2 = CO + H_2O \text{ (reverse water-gas shift [RWGS])} \quad (1.20)$$

- Selective CO oxidation

$$CO + O_2 = CO_2 \quad (1.21)$$

$$H_2 + O_2 = H_2O \quad (1.22)$$

Reforming or gasification produces syngas whose H_2/CO ratio depends on the feedstock and process conditions such as feed steam/carbon ratio and reaction temperature and pressure. Water-gas shift reaction can further increase the H_2/CO ratio of syngas produced from coal to the desired range for conversion to liquid fuels. This reaction is also an important step for hydrogen production in commercial hydrogen plants, ammonia plants, and methanol plants that use natural gas or coal as feedstock.

1.3 OPTIONS FOR HYDROGEN AND SYNGAS PRODUCTION

Both nonrenewable and renewable energy sources are important for hydrogen and syngas production. As an energy carrier, H_2 (and syngas) can be produced from catalytic processing of various hydrocarbon fuels, alcohol fuels, and biofuels such as oxygenates. H_2 can also be produced directly from water, the most abundant source of hydrogen atom, by electrolysis, thermochemical cycles (using nuclear heat), or photocatalytic splitting, although this process is in the early stage of laboratory research.

As shown in Table 1.1, by energy and atomic hydrogen sources, hydrogen (and syngas in most cases) can be produced from coal (gasification, carbonization), natural gas, and light hydrocarbons such as propane gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming), petroleum fractions (dehydrocyclization and aromatization, oxidative steam reforming, pyrolytic decomposition), biomass (gasification, steam reforming, biologic conversion), and water (electrolysis, photocatalytic conversion, chemical and catalytic conversion). The relative competitiveness of different options depends on the economics of the given processes, which in turn depend on many factors such as the efficiency of the catalysis, the scale of production, H_2 purity, and costs of the feed and the processing steps, as well as the supply of energy sources available.

Among the active ongoing energy research and development areas are H_2 and syngas production from hydrocarbon resources including fossil fuels, biomass, and carbohydrates. In many H_2 production processes, syngas production and conversion are intermediate steps for enhancing H_2 yield where CO in the syngas is further reacted with water (H_2O) by water-gas shift reaction to form H_2 and CO_2.

Current commercial processes for syngas and H_2 production largely depends on fossil fuels both as the source of hydrogen and as the source of energy for the production processing.[4] Fossil fuels are nonrenewable energy resources, but they provide a more economical path to hydrogen production in the near term (next 5–20 years) and perhaps they will continue to play an important role in the midterm (20–50 years from now). Alternative processes need to be developed that do not

Table 1.1. Options of Hydrogen (and Syngas) Production Processing regarding Atomic Hydrogen Source, Energy Source for Molecular Hydrogen Production, and Chemical Reaction Processes

Hydrogen Source	Energy Source	Reaction Processes
1. Fossil hydrocarbons	1. Primary	1. Commercialized process
Natural gas[a]	Fossil energy[c]	Steam reforming[d]
Petroleum[b]	Biomass	Autothermal reforming[d]
Coal[a,b]	Organic waste	Partial oxidation[d]
Tar sands, oil shale	Nuclear energy	Catalytic dehydrogenation[e]
Natural gas hydrate	Solar energy	Gasification[d]
		Carbonization[d]
2. Biomass	Photovoltaic	Electrolysis[f]
3. Water (H_2O)	Hydropower	2. Emerging approaches
4. Organic/animal waste	Wind, wave, geothermal	Membrane reactors
5. Synthetic fuels	2. Secondary	Plasma reforming
MeOH, FTS liquid, etc.		
6. Specialty areas	Electricity	Photocatalytic
Organic compound	H_2, MeOH, etc.	Solar thermal chemical
		Solar thermal catalytic
Metal hydride, chemical complex hydride	3. Special cases	Biologic
Ammonia, hydrazine	Metal bonding energy	Thermochemical cycling
Hydrogen sulfide	Chemical bonding energy	Electrocatalytic
7. Others	4. Others	3. Others

[a]Currently used hydrogen sources for hydrogen production.

[b]Currently used in chemical processing that produces H_2 as a by-product or main product.

[c]Currently used as main energy source.

[d]Currently used for syngas production in conjunction with catalytic water-gas shift reaction for H_2 production.

[e]As a part of industrial naphtha reforming over Pt-based catalyst that produces aromatics.

[f]Electrolysis is currently used in a much smaller scale compared with steam reforming.

depend on fossil hydrocarbon resources for either the hydrogen source or the energy source, and such alternative processes need to be economical, environmentally friendly, and competitive. H_2 separation is also a major issue as H_2 coexists with other gaseous products from most industrial processes, such as CO_2 from chemical reforming or gasification processes. Pressure swing adsorption (PSA) is used in current industrial practice. Several types of membranes are being developed that would enable more efficient gas separation. Overall, in order for hydrogen energy to penetrate widely into transportation and stationary applications, the costs of H_2 production and separation need to be reduced significantly from the current technology, for example, by a factor of 2.

1.4 HYDROGEN ENERGY AND FUEL CELLS

The main drivers for hydrogen energy and fuel cells development are listed in Table 1.2. Hydrogen production has multiple application areas in chemical industry, food industry, and fuel cell systems. Due to the major advantages in efficiency and in environmental benefits, hydrogen energy in conjunction with fuel cells has attracted considerable attention in the global research community. H_2 production is a major issue in hydrogen energy development. Unlike the primary energy sources such as petroleum, coal, and natural gas, hydrogen energy is a form that must be produced first from the chemical transformation of other substances. Development of science and technology for hydrogen production is also important in the future for more efficient chemical processing and for producing ultraclean fuels.

The development of H_2-based and syngas-based energy systems require multifaceted studies on hydrogen sources, hydrogen production, hydrogen separation, hydrogen storage, H_2 utilization and fuel cells, H_2 sensor, and safety aspects, as well

Table 1.2. Drivers for Hydrogen Energy and Fuel Cell System Development

Category	Drivers	Remarks
Basic reaction	$H_2 + 1/2\ O_2 = H_2O$ $\Delta H = -241.8$ kJ/mol (Gw, LHV) $\Delta H = -285.8$ kJ/mol (Lw, HHV)	LHV refers to the reaction with H_2O as vapor
Technical	Efficiency—major improvement potential with fuel cells Environmental advantage—no emissions of pollutants and CO_2	Overcome the thermodynamic limitations of combustion systems
Sustainability	Bridge between nonrenewable (fossil) and renewable (biomass) energy utilization Sustainable in terms of hydrogen atom sources	Hydrogen atom from H_2O
Political and regional	Energy security and diversity Dependence on import of oils	Wide range of resources can be used
Economical	New business opportunities Niche application/market development Potential role and domain for new players	Gas producers and other industrial and small business organizations
Specific applications	Portable power sources Quiet power sources Remote power sources Space explorations Military applications	On-site or on-board fuel cells for stationary, mobile, and portable systems

as infrastructure and technical standardization. The production and utilization of hydrogen energy is also associated with various energy resources, fuel cells, CO_2 emissions, and safety and infrastructure issues. Hydrogen energy and fuel cell development are closely related to the mitigation of CO_2 emissions. Fuel cells using hydrogen allow much more efficient electricity generation; thus, they can decrease CO_2 emission per unit amount of primary energy consumed or per kilowatt-hour of electrical energy generated.

1.5 FUEL PROCESSING FOR FUEL CELLS

Hydrogen and syngas production process concepts can be applied to fuel processing for fuel cells, as outlined in Figure 1.3.[5] In general, all the fuel cells operate without combusting fuel and with few moving parts, and thus they are very attractive from both energy and environmental standpoints. A fuel cell is two to three times more efficient than an internal combustion (IC) engine in converting fuel to electricity.[6] On the basis of the electrolyte employed, there are five types of fuel cells. They differ in the composition of the electrolytes and in operating temperature ranges and are in different stages of development. They are alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), proton exchange membrane fuel cells (PEMFCs), MCFCs, and SOFCs. In all types, there are separate reactions at the anode and the cathode, and charged ions move through the electrolyte, while electrons move round an external circuit. Another common feature is that the electrodes must be porous,

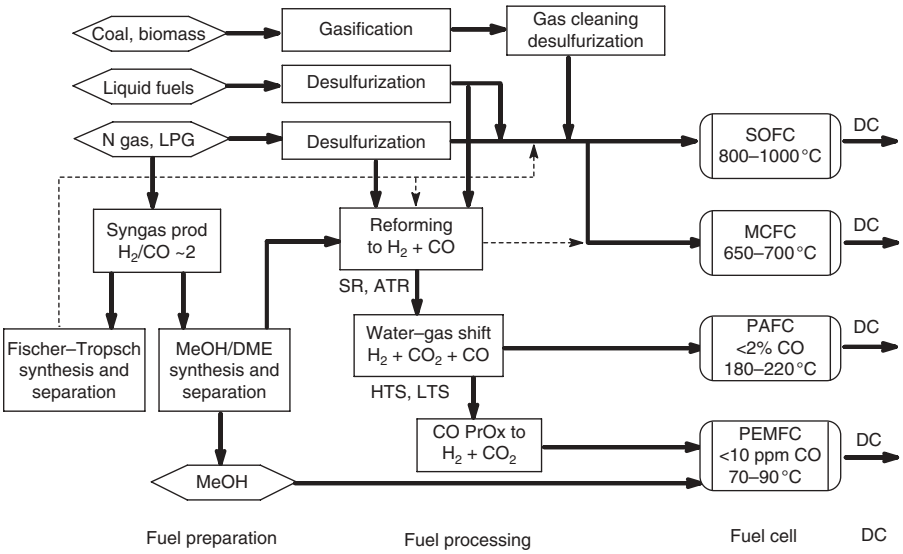

Figure 1.3. Fuel processing of gaseous, liquid, and solid fuels for syngas and hydrogen production for different fuel cells (modified after Song[5]).

because the gases must be in contact with the electrode and the electrolyte at the same time.

A simplified way to illustrate the efficiency of energy conversion devices is to examine the theoretical maximum efficiency.[7] The efficiency limit for heat engines such as steam and gas turbines is defined by the Carnot cycle as maximum efficiency = $(T_1 - T_2)/T_1$, where T_1 is the maximum temperature of fluid in a heat engine and T_2 is the temperature at which heated fluid is released. All the temperatures are in kelvin (K = 273 + degrees Celsius), and therefore, the lower temperature T_2 value is never small (usually >290K). For a steam turbine operating at 400 °C, with the water exhausted through a condenser at 50 °C, the Carnot efficiency limit is (673 − 323)/673 = 0.52 = 52%. (The steam is usually generated by boiler based on fossil fuel combustion, and so the heat transfer efficiency is also an issue in overall conversion.) For fuel cells, the situation is very different. Fuel cell operation is a chemical process, such as hydrogen oxidation to produce water ($H_2 + 1/2O_2 = H_2O$), and thus involves the changes in enthalpy or heat (ΔH) and changes in Gibbs free energy (ΔG). It is the change in Gibbs free energy of formation that is converted to electrical energy.[7] The maximum efficiency for fuel cell can be directly calculated as maximum fuel cell efficiency = $\Delta G/(-\Delta H)$. The ΔH value for the reaction is different depending on whether the product water is in vapor or in liquid state. If the water is in liquid state, then $(-\Delta H)$ is higher due to release of heat of condensation. The higher value is called higher heating value (HHV), and the lower value is called lower heating value (LHV). If this information is not given, then it is likely that the LHV has been used because this will give a higher efficiency value.[7]

Hydrogen, syngas or reformate (hydrogen-rich syngas from fuel reforming), and methanol are the primary fuels available for current fuel cells. Reformate can be used as a fuel for high-temperature fuel cells such as SOFC and MCFC, for which the solid or liquid or gaseous fuels need to be reformed.[5,8,9] Hydrogen is the real fuel for low-temperature fuel cells such as PEMFC and PAFC, which can be obtained by fuel reformulation on-site for stationary applications or on-board for automotive applications. When natural gas or other hydrocarbon fuel is used in a PAFC system, the reformate must be processed by water-gas shift reaction. A PAFC can tolerate about 1%–2% CO.[10] When used in a PEMFC, the product gas from the water-gas shift must be further processed to reduce CO to <10 ppm.

1.6 SULFUR REMOVAL

Sulfur is contained in most hydrocarbon resources including petroleum, natural gas, and coal. Desulfurization of fuels, either before or after reforming or gasification, is important for syngas and hydrogen production and for most fuel cell applications that use conventional gaseous, liquid, or solid fuels.[5,11] Sulfur in the fuel can poison the fuel processing catalysts such as reforming and water-gas shift catalysts. Furthermore, even trace amounts of sulfur in the feed can poison the anode catalysts in fuel cells. Therefore, sulfur must be reduced to below 1 ppm for most fuel cells, preferably below 60 ppb.

1.7 CO_2 CAPTURE AND SEPARATION

CO_2 capture and separation have also become an important global issue in the past decade, not only for H_2 and syngas purification, but also for the greenhouse gas control. When syngas is used for making liquid fuels, CO_2 may be recovered and added to the feed gas for reforming to adjust the H_2/CO ratio. A new process concept called tri-reforming has been proposed[12] and established for using CO_2 in reforming for producing industrially useful syngas with desired H_2/CO ratios for the Fischer–Tropsch synthesis and methanol synthesis. CO_2 utilization and recycling as fuels and chemicals are also important long-term research subjects. Many recent publications have discussed the CO_2 issues including new ways to capture CO_2 by solid sorbents.[1,13,14]

1.8 SCOPE OF THE BOOK

To facilitate the advances in science and technology development for hydrogen and syngas production and purification as well as fuel processing for fuel cells, this book was developed based on the contributions from many active and leading researchers in industry, academia, and national laboratory. Following Chapter 1 as an introduction and overview, Chapters 2–5 deal with the production of syngas and subsequent syngas conversion to hydrogen. In Chapter 2, catalytic steam reforming technologies are reviewed by Velu Subramani of BP, Pradeepkumar Sharma of RTI, and Lingzhi Zhang and Ke Liu of GE Global Research. This is followed by the discussion on catalytic partial oxidation and autothermal reforming in Chapter 3 by Ke Liu and Gregg Deluga of GE Global Research, and Lanny Schmidt of the University of Minnesota. These two chapters collectively cover the production technologies using gaseous and liquid feedstocks. In Chapter 4, coal gasification is reviewed as a solid-feed-based hydrogen and syngas production approach by Ke Liu and Zhe Cui of GE Global Research and Thomas H. Fletcher of Brigham Young University. Coal gasification technology development is also an area of research and development programs of the U.S. Department of Energy.[15,16] It should be mentioned that the basic processing approach of coal gasification is also applicable in general to the gasification of petroleum coke and biomass. Since the hydrocarbon resources including gaseous, liquid, and solid fuels all contain sulfur, which is environmentally harmful and poisonous to process catalysts, Chapter 5 is devoted to a review of desulfurization technologies for various sulfur removal options from liquid and gaseous fuels by Chunshan Song and Xiaoliang Ma of Pennsylvania State University. The step in the hydrogen production process following reforming or gasification and desulfurization is the water-gas shift, which is covered in Chapter 6 by Alex Platon and Yong Wang of Pacific Northwest National Laboratory.

Chapters 7–10 cover the syngas purification and separation. When reforming and water-gas shift are applied to PEMFC systems, trace amounts of CO in the gas that poisons anode catalyst must be removed. This is achieved by preferential CO oxidation, which is covered in Chapter 7 by Marco J. Castaldi of Columbia

University. Membrane development is a promising approach for efficient gas separation in various applications. Chapter 8 provides an overview on hydrogen membrane separation and application in fuel processing by David Edlund of IdaTech. In Chapter 9, CO_2-selective membrane development is reviewed by Jin Huang, Jian Zou, and W.S. Winston Ho of Ohio State University. The CO_2 membrane application for fuel processing is also discussed. For the commercial hydrogen production technologies, PSA is an important technology, for which the state of the art is reviewed by Shivaji Sircar of Lehigh University and Timothy C. Golden of Air Products and Chemicals.

For practical applications, integrated production technologies are highly desired and often provide more efficient and also flexible processing options in response to demands. Chapter 11 focuses on the integration of H_2/syngas production technologies with future energy systems, which is discussed by Wei Wei, Parag Kulkarni, and Ke Liu of GE Global Research.

One of the most important applications of syngas is the synthesis of liquid fuels and chemicals. It is well known that syngas with different H_2/CO ratios can be used for the Fischer–Tropsch synthesis of liquid hydrocarbon fuels for the synthesis of methanol and dimethyl ether, as well as ethanol and higher alcohols. Chapter 12 provides an overview of coal and syngas to liquid technologies, which is authored by Ke Liu, Zhe Cui, Wei Chen, and Lingzhi Zhang of GE Global Research. The indirect coal-to-liquids (CTL) technology via syngas conversion has its root in Germany as reflected by the well-known Fischer–Tropsch synthesis, which can also be applied to natural gas-to-liquids (GTL) and biomass-to-liquids (BTL) development.

We hope this book will provide the balanced overview of science and technology development that will facilitate the advances of hydrogen and syngas production for clean energy and sustainable energy development.

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