Hydrogen and Syngas Production and Purification Technologies

Edited by

Ke Liu GE Global Research Center

Chunshan Song Pennsylvania State University

Velu Subramani BP Products North America, Inc.



A John Wiley & Sons, Inc., Publication

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A Joint Publication of the Center for Chemical Process Safety of the American Institute of Chemical Engineers and John Wiley & Sons, Inc.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada

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Library of Congress Cataloging-in-Publication Data:

Hydrogen and syngas production and purification technologies / edited by Ke Liu, Chunshan Song, Velu Subramani.

p. cm. Includes index. ISBN 978-0-471-71975-5 (cloth) 1. Hydrogen as fuel. 2. Synthesis gas. 3. Coal gasification. I. Liu, Ke, 1964– II. Song, Chunshan. III. Subramani, Velu, 1965– TP359.H8H8434 2010 665.8'1-dc22

2009022465

Printed in the United States of America 10 9 8 7 6 5 4 3 2 1

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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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the staff members at John Wiley & Sons for their great and sincere efforts in editing and publishing this book.

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Introduction to Hydrogen and Syngas Production and Purification Technologies

CHUNSHAN SONG

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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





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 (H₂) and syngas (mixture of H₂ 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, CO₂. 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 (CH₄) 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

$$CH_4 + H_2O = CO + 3H_2$$
 (1.1)

$$C_m H_n + m H_2 O = m CO + (m + n/2) H_2$$
 (1.2)

- $CH_3OH + H_2O = CO_2 + 3H_2$ (1.3)
- · Partial oxidation

$$CH_4 + O_2 = CO + 2H_2$$
 (1.4)

$$C_m H_n + m/2 O_2 = m CO + n/2 H_2$$
 (1.5)

$$CH_3OH + 1/2 O_2 = CO_2 + 2H_2$$
 (1.6)

$$CH_3OH = CO + 2H_2 \tag{1.7}$$

· Autothermal reforming or oxidative steam reforming

$$CH_4 + \frac{1}{2} H_2O + \frac{1}{2} O_2 = CO + \frac{5}{2} H_2$$
(1.8)

$$C_m H_n + m/2 H_2 O + m/4 O_2 = m CO + (m/2 + n/2) H_2$$
 (1.9)

$$CH_3OH + 1/2 H_2O + 1/4 O_2 = CO_2 + 2.5H_2$$
 (1.10)

• Gasification of carbon (coal, coke)

$$C + H_2O = CO + H_2$$
 (1.11)

$$\mathbf{C} + \mathbf{O}_2 = \mathbf{C}\mathbf{O}_2 \tag{1.12}$$

$$C + 0.5O_2 = CO$$
 (1.13)

$$C + CO_2 = 2CO \tag{1.14}$$

Carbon formation

$$CH_4 = C + 2H_2 \tag{1.15}$$

$$C_m H_n = x C + C_{m-x} H_{n-2x} + x H_2$$
(1.16)

$$2\mathrm{CO} = \mathrm{C} + \mathrm{CO}_2 \tag{1.17}$$

$$CO + H_2 = C + H_2O (1.18)$$

· Water-gas shift

$$CO + H_2O = CO_2 + H_2$$
 (1.19)

$$CO_2 + H_2 = CO + H_2O$$
 (reverse water-gas shift [RWGS]) (1.20)

- 6 Chapter 1 Introduction to Hydrogen and Syngas Production and Purification Technologies
 - · Selective CO oxidation

$$\mathrm{CO} + \mathrm{O}_2 = \mathrm{CO}_2 \tag{1.21}$$

$$H_2 + O_2 = H_2 O$$
 (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 CO₂.

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

H	ydrogen 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	Ga	asification ^d
					Carbonization ^d
2.	Biomass		Photovoltaic		Electrolysis ^f
3.	Water (H ₂ O)		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.	So	lar 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

Table 1.1. Options of Hydrogen (and Syngas) Production Processing regarding AtomicHydrogen Source, Energy Source for Molecular Hydrogen Production, and ChemicalReaction Processes

^aCurrently used hydrogen sources for hydrogen production.

 $^{\mathrm{b}}\mathrm{Currently}$ used in chemical processing that produces H_2 as a by-product or main product.

^cCurrently used as main energy source.

 $^d\mbox{Currently}$ used for syngas production in conjunction with catalytic water-gas shift reaction for H_2 production.

^eAs a part of industrial naphtha reforming over Pt-based catalyst that produces aromatics.

^fElectrolysis 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 CO₂ 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

Category	Drivers	Remarks
Basic reaction	$H_2 + 1/2 O_2 = H_2O$ $\Delta H = -241.8 \text{ kJ/mol} (Gw, LHV)$ $\Delta H = -285.8 \text{ kJ/mol} (Lw, HHV)$	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 ₂ O
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

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

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 Song⁵).

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 CO₂ CAPTURE AND SEPARATION

 CO_2 capture and separation have also become an important global issue in the past decade, not only for H₂ 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 H₂/CO ratio. A new process concept called tri-reforming has been proposed¹² and established for using CO_2 in reforming for producing industrially useful syngas with desired H₂/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 solidfeed-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, CO₂-selective membrane development is reviewed by Jin Huang, Jian Zou, and W.S. Winston Ho of Ohio State University. The CO₂ 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 H₂/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.

ACKNOWLEDGMENTS

We wish to thank all the authors for their contributions and for their patience in the long process of manuscript preparation, editing, and book production. We also gratefully acknowledge the acquisition editors and editorial office of Wiley publisher for their support of the book project and for their editorial assistance. Finally, we wish to thank the Pennsylvania State University, GE Global Research, and BP Refining Technology for their support of the efforts by the editors for contributing to and editing this book.

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Catalytic Steam Reforming Technology for the Production of Hydrogen and Syngas

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2.1 INTRODUCTION

Hydrogen (H₂) has a long tradition as an energy carrier as well as an important feedstock in chemical industries and in refineries. It has a very high energy density. As shown in Table 2.1, 1 kg of H₂ contains the same amount of energy as 2.6 kg of natural gas/methane (CH₄) or 3.1 kg of gasoline. This makes H₂ an ideal fuel in applications where weight rather than volume is an important factor, such as providing lift for balloons or zeppelins and recently as a fuel for spacecraft.

The use of H₂-rich gas, known as "town gas," produced from coal and containing about 50% H₂ with the rest mostly CH₄ and carbon dioxide (CO₂), for lighting and heating began in early 1800s and continued until mid-1900s.¹ Town gas was celebrated as a wonder, bringing light and heat to the civilized world. Later, the discovery of oil and natural gas reserves slowly displaced the supply of town gas. The use of H₂ as a feedstock for the production of ammonia and fertilizer began in 1911. Today, ammonia synthesis has become one of the major uses of H₂.

The worldwide H_2 production at present has been estimated to be about 12 trillion standard cubic feet (SCF)/year, including about 1.7 trillion SCF/year of merchant H_2 .² Most of this H_2 is consumed for the synthesis of ammonia and methanol. A significant portion is also used in refineries for upgrading crude oils by

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Hydrogen and Syngas Production and Purification Technologies, Edited by Ke Liu, Chunshan Song and Velu Subramani

Fuel	Major Chemical Compound	Energy Density (MJ/kg)	H/C Ratio
Hydrogen	H_2	142.0	_
Natural gas	CH_4	55.5	4
Biogas-I ^a	CH_4 , CO_2	28-45	2-3.2
Biogas-II ^b	CH ₄ , H ₂ , CO ₂ , CO	4–14	0.7-2.0
LPG	$C_3 - C_4$	50.0	2.5-2.7
Methanol	CH ₃ OH	22.5	4
Ethanol	C ₂ H ₅ OH	29.7	3
Gasoline	$C_4 - C_{12}$	45.8	1.6-2.1
Jet fuel	Up to C_{25}	46.3	1.6-2.0
Diesel	C ₉ -C ₂₄	45.3	1.8–2.3

Table 2.1. Energy Density and Hydrogen to Carbon Ratio of Various Hydrocarbon and Alcohol Fuels

^aBiogas from anaerobic digester.

^bBiogas from gasifier.

processes such as hydrocracking and hydrotreating to produce gasoline and diesel. Pure H_2 streams have also been used in a number of hydrogenation reactions, including hydrogenation of edible oils, aromatics, hydrocarbons, aldehydes, and ketones for the production of vitamins, cosmetics, semiconductor circuits, soaps, lubricants, margarine, and peanut butter.

There is a growing worldwide demand for H_2 in refineries because of the need to process heavier and dirtier feedstocks, combined with the desire to produce much cleaner transportation fuels that are almost free from sulfur to meet the stringent environmental regulations imposed in several countries.^{3,4} Processing of heavier and higher-sulfur crude oils will require a greater H_2 stream. In addition, the evolving interest in using H_2 as a future energy carrier, especially in the automotive sector, will result in a large demand for H_2 in the future.

 H_2 can be produced from a variety of feedstocks, including fossil fuels such as natural gas, oil, and coal and renewable sources such as biomass and water with energy input from sunlight, wind, hydropower, and nuclear energy. H_2 production from fossil fuels and biomass involves conversion technologies such as reforming (hydrocarbons, oils and alcohols), gasification, and pyrolysis (biomass/coal), while other conversion technologies such as electrolysis and photolysis are used when the source of H_2 is water (Fig. 2.1). The former processes produce syngas, which is a mixture of H_2 and CO with a H_2 /CO ratio dictated by the type of fuel source and the conversion technology used. The syngas obtained is subjected to several downstream processes, which produce pure H_2 . The discussion in this chapter will focus on reforming of fossil fuels and biofuels for the production of syngas, which does not involve downstream gas cleanup and conditioning.

Reforming occurs when a hydrocarbon or alcohol fuel and steam and/or oxygen is passed through a catalyst bed under optimum operating conditions. Depending



Figure 2.1. Technological options for the production of hydrogen from various carbon-containing feedstocks. IGCC, Integrated Gasification Combined Cycle.



Figure 2.2. Possible H_2/CO ratios obtained from various syngas production processes. Adapted from Rostrup-Nielsen et al.¹⁰

upon whether steam or oxygen or a mixture of steam and oxygen is used, the reforming technology is termed "steam reforming," "partial oxidation," and "autothermal reforming (ATR)," respectively. Reforming of natural gas with CO₂, also known as "dry reforming," has also been reported in recent years.^{5–10} Among the reforming technologies, steam reforming is the preferred process for hydrogen and syngas today because it offers relatively a higher H₂/CO ratio (close to 3) since a part of hydrogen comes from water. The H₂/CO ratio can be varied over a wide range as shown in Figure 2.2, as the reforming reactions are coupled with the shift reaction at the downstream.¹⁰ Catalytic steam reforming (CSR) involves the extraction of H_2 molecules from a hydrocarbon or alcohol fuel and water over a base metal or noble metal-supported catalysts. CSR is widely employed to produce H_2 -rich gas from various gaseous and liquid hydrocarbon fuels. Steam reforming of hydrocarbon fuels, especially steam reforming of natural gas containing methane, is a well-developed technology and practiced commercially for large-scale H_2 production.^{3–6,8–10} Research in this area is still being pursued actively to further improve process efficiency. Knowledge gained from natural gas reforming is applied to the reforming of higher hydrocarbons, alcohols, and biofuels for the manufacture of H_2 or syngas depending on the end use. The chemistry, thermodynamics, catalysts, kinetics, reactions mechanisms, and technology developments in the CSR of various hydrocarbon and alcohol fuels for H_2 or syngas production are discussed in detail in the following sections.

2.2 STEAM REFORMING OF LIGHT HYDROCARBONS

2.2.1 Steam Reforming of Natural Gas

2.2.1.1 Chemistry

Natural gas is an odorless and colorless naturally occurring mixture of hydrocarbon and nonhydrocarbon gases found in porous geologic formations beneath the earth's surface, often in association with petroleum or coal. The principal constituent is methane (CH₄) and its composition is regionally dependent. Table 2.2 summarizes the composition of natural gas by region.⁸

Methane reacts with steam in the presence of a supported nickel catalyst to produce a mixture of CO and H_2 , also known as synthesis gas or syngas as represented by Equation 2.1. This reaction is also referred to as steam methane reforming (SMR) and is a widely practiced technology for industrial production of H_2 . However, the SMR is not really just one reaction as indicated in Equation 2.1 but involves contributions from several different catalyzed reactions such as water-gas shift

Region	Methane	Ethane	Propane	H_2S	CO ₂
U.S./California	88.7	7.0	1.9	_	0.6
Canada/Alberta	91.0	2.0	0.9	_	_
Venezuela	82.0	10.0	3.7	_	0.2
New Zealand	44.2	$11.6(C_2-C_5)$	-	_	44.2
Iraq	55.7	21.9	6.5	7.3	3.0
Libya	62.0	14.4	11.0	_	1.1
U.K./Hewett	92.6	3.6	0.9	_	_
U.R.S.S./Urengoy	85.3	5.8	5.3	_	0.4

 Table 2.2.
 Composition of Natural Gas by Region⁸

(WGS), reverse water-gas shift (RWGS), CO disproportionation (Boudouard reaction), and methane decomposition reactions as described in Equations 2.2–2.5:

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g) \qquad \Delta H_{298}^\circ = +205.9 \text{ kJ/mol}, \quad (2.1)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$
 $\Delta H_{298}^o = -41 \text{ kJ/mol},$ (2.2)

$$2CO(g) \rightarrow CO_2(g) + C \qquad \Delta H_{298}^\circ = -172.4 \text{ kJ/mol},$$
 (2.3)

$$CH_4(g) \to C + 2H_2(g)$$
 $\Delta H_{298}^{\circ} = +74.6 \text{ kJ/mol},$ (2.4)

$$C + H_2O(g) \rightarrow CO + H_2(g)$$
 $\Delta H_{298}^\circ = +131.3 \text{ kJ/mol},$ (2.5)

$$CO(g) + 0.5O_2(g) \rightarrow CO_2(g) \qquad \Delta H_{298}^{\circ} = -283 \text{ kJ/mol},$$
 (2.6)

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$
 $\Delta H_{298}^{\circ} = -205.9 \text{ kJ/mol.}$ (2.7)

The steps involved in the SMR process for the production of pure H_2 can be divided into (a) feed pretreatment, (b) steam reforming, (c) CO shift conversion, and (d) hydrogen purification. For natural gas, the only pretreatment required is desulfurization, which usually consists of a hydrogenator for the conversion of sulfurcontaining species into H₂S followed by a zinc oxide bed for H₂S scrubbing. After desulfurization, the natural gas is fed into a reformer reactor, where it reacts with steam to produce H₂, CO, and CO₂ through reactions represented by Equations 2.1-2.5. The reformer is comprised of several reactor tubes filled with reforming catalysts and kept in a furnace that provides heat necessary for the endothermic reaction and operated in the temperature range between 500 and 900 °C and pressure above 20 atm.^{3-6,8-10} Since the reaction produces an increase in the net number of product molecules, additional compression of the product would be necessary if the reaction were run at <20 atm. Although the stoichiometry for Equation 2.1 suggests that only 1 mol of H₂O is required for 1 mol of CH₄, the reaction in practice is being performed using high steam-to-carbon (S/C) ratio, typically in the range 2.5-3 in order to reduce the risk of carbon deposition on the catalyst surface. The gas exiting the reformer is cooled to about 350 °C and then subjected to the WGS reaction in a high-temperature shift (HTS) converter. The current process for the industrial production of pure H₂ (over 99.99%) employs pressure swing adsorption (PSA) for the purification of H₂ after the shift reaction. The PSA off-gas, which contains CO, CO₂ unreacted CH_4 , and unrecovered H_2 is used to fuel the reformer.

Alternative technologies to the PSA process for H_2 purification include, after the HTS reaction, a low-temperature shift (LTS) reaction followed by CO₂ scrubbing (e.g., monoethanolamine or hot potash).¹¹ The LTS reaction can increase the H_2 yield slightly. However, the product stream, after the HTS, needs to be cooled to about 220 °C. Preferential oxidation (Prox) and/or methanation reaction as shown in Equations 2.6 and 2.7, respectively, removes the traces of CO and CO₂. The product H_2 has a purity of over 97%.

2.2.1.2 Thermodynamics

As shown in Equation 2.1, the SMR reaction results in gas volume expansion and is strongly endothermic ($\Delta H_{298}^{\circ} = +205.9 \text{ kJ/mol}$). Therefore, the reaction is thermodynamically favorable under low pressure and high temperatures. The changes in enthalpy (ΔH) and Gibbs free energy (ΔG) during the reaction can be calculated, along with the corresponding equilibrium constants (shown in Table 2.3). The thermodynamic data presented in the table provides knowledge in identifying operation conditions and feasibility. The reaction requires certain temperatures to achieve sufficient activity. Figure 2.3 shows the variation of ΔG as a function of temperature in the form of an Ellingham-type diagram for three representative reactions during the SMR process: SMR, methane decomposition, and carbon gasification. ΔG declines as temperature increases for all three reactions, again reflecting the endothermic nature of those reactions. It can be seen that methane decomposition (line a), which leads to coke deposition, occurs at relatively low temperature, around 500 °C. However, the SMR and carbon gasification reactions require fairly high temperatures (>700 °C) to move forward. This makes heat transfer a critical reactor design component. It also puts stringent thermal requirement for materials used for reactor and pipeline manufacture.

The equilibrium methane conversions with increasing temperature calculated at different S/C ratios and pressure between 1 and 20 bar are shown in Figure 2.4. The methane conversion increases with higher S/C ratios (S/C varies from 1 to 5) and decreases with increasing pressures (1–20 bar pressures were studied). A complete

Temperature (°C)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	Log K
25	205.885	141.932	-24.868
75	208.156	131.025	-19.66
125	210.269	119.801	-15.718
175	212.225	108.32	-12.626
225	214.026	96.629	-10.133
275	215.675	84.764	-8.078
325	217.179	72.755	-6.354
375	218.541	60.626	-4.886
425	219.769	48.397	-3.621
475	220.867	36.085	-2.52
525	221.841	23.703	-1.551
575	222.698	11.264	-0.694
625	223.442	-1.222	0.071
675	224.077	-13.747	0.757
725	224.608	-26.303	1.377
775	225.037	-38.883	1.938
825	225.369	-51.481	2.449
875	225.608	-64.092	2.916
925	225.76	-76.711	3.345
975	225.831	-89.335	3.739
1000	225.838	-95.648	3.925

Table 2.3. Thermodynamic Data for the Steam Methane Reforming (SMR) Reaction



Figure 2.3. Variation of ΔG as a function of temperature in the form of an Ellingham-type diagram for the SMR process.

conversion of methane could be achieved around 700 °C at 1 bar pressure and the S/C ratio of above 2.5, while a temperature of above 900 °C would be required to achieve the complete methane conversion at 20 bar pressure. It has been reported that all currently available steam reforming catalysts promote carbon formation to different extents. Presence of excess stream can suppress carbon deposition and avoid plant shutdown caused by catalyst deactivation. Therefore, although stoichiometrically only S/C = 1 is needed for the SMR reaction, a 3.0 to 3.5 ratio is commonly used in practical applications.¹² In modern H₂ plants, driven by economic and efficiency considerations, reactor and process designs are improved to reduce the steam consumption, with a typical ratio of S/C = 2.5.¹⁰

Equilibrium H_2 and CO compositions can also be derived thermodynamically. Depending on the ultimate application for the gas product, H_2 /CO ratio can be further tailored by integrating with secondary reactor stage (e.g., WGS) or by optimizing catalysts or operating conditions.

2.2.1.3 Catalyst

Natural gas steam reforming has been widely practiced in the industry, and a large body of catalyst development research can be found in literature. This section is not meant to be a comprehensive literature review on steam reforming catalysis, but outlining major research aspects in steam reforming catalyst development. Contributions from the following authors on steam reforming literature reviews are highly acknowledged: Trimm,¹³ Bartholomew,¹⁴ Rostrup-Nielsen,¹⁵ Twigg,¹² Trimm,¹⁶ and Sehested.¹⁷

In industrial practice, steam reforming of natural gas has been performed at high temperatures over Ni-based catalysts. Ni has been the favored active metal because



Figure 2.4. Equilibrium methane conversions at different temperatures, steam/carbon ratios, and pressures obtained by thermodynamic calculations.

of its sufficient activity and low cost. Ni is typically supported on alumina, a refractory and highly stable material. These catalysts are shaped into an optimal form, often in the shape of multichannel wheels in order to have a better heat and mass transfer and to minimize the pressure drop under the industrial operating conditions. The catalyst performs in excess of 5 years (>50,000h) of continuous operation. Potential suppliers of steam reforming catalyst include Haldor Topsoe, Johnson Matthey, Süd-Chemie, and BASF.⁶ The Ni-based catalysts suffer from catalyst deactivation by coke formation and sintering of metallic Ni active phase. Research has been undergoing to address these issues employing different approaches, including catalyst preparation, promoter incorporation, and support materials.

Conventional Ni-Al₂O₃ catalysts are prepared by wet-impregnating Ni onto the Al_2O_3 support. This method has poor control of metal distribution on the support and yields weak binding between metal and the support. As indicated from literature, weakly attached Ni particles tend to aggregate and form large particles, which catalyze coke formation reactions.^{18–20} Catalyst preparation was examined to strengthen the interaction between Ni particles and the support or enhance metal dispersion on the support, aiming to achieve higher stability during steam reforming. As revealed from Fonseca and Assaf's work,²¹ in comparison with traditional impregnation technique, catalysts synthesized using hydrotalcite precursors displayed high methane reforming activity and long-term stability. Use of hydrotalcite precursors produces homogeneous dispersion of anions during catalyst synthesis. Ni can be uniformly dispersed in the final calcined catalyst structure. Zhang et al. examined one pot sol-gel technique for Ni-Al₂O₃ preparation.²² Compared with conventional impregnation, sol-gel technique yields catalysts with highly dispersed Ni particles on the surface and a strong metal-support interaction. This suppresses the carbon filament formation and filament growth, thereby increasing catalyst stability. Zhang et al. studied synthesized nanocomposite Ni-based catalysts using a novel sol-gel method and obtained highly active and extremely stable reforming catalysts.²³ By dipping presynthesized Mg-Al mixed oxides into Ni nitrate solution, Takehira et al. obtained eggshell-type loaded Ni catalysts.²⁴ These catalysts showed high and stable reforming activity owing to highly dispersed and stable Ni metal particles concentrated in the catalyst surface layer. Catalysts based on hexa-aluminate-type oxides were prepared to uniformly disperse active species (Ni or other active metals) in the lattice.²⁵ A new concept in catalyst preparation is to combine catalyst and CO₂ sorbent into one material for steam reforming. As described by Satrio et al.,²⁶ small spherical pellets were prepared in the form of a layered structure, with a CO₂ sorbent core enclosed by a porous protective shell made of alumina-supported Ni catalysts. This material offers *in situ* CO₂ removal and hydrocarbon reforming, thereby achieving 95% H₂ yield.

Trace amount of promoters was reported to markedly suppress coke formation during steam reforming. Presence of promoters can modify Ni ensemble size on the surface and inhibit coke deposition.¹⁶ Alkali metals such as K and alkaline earth metals such as Mg and Ca are frequently used to improve catalyst stability. This was attributed to higher reactivity of carbon formed on the surface and neutralization of acidic sites of the support materials (acidic support catalyzes hydrocarbon cracking and polymerization reactions).^{15,27} A small amount of molybdenum or tungsten (0.5 wt % MoO₃ or WO₃) into Ni catalysts was demonstrated by Borowiecki et al. to increase the coking resistance without loss in catalytic activity.²⁸⁻³⁰ Lanthanides (La, Ce, Gd, Sm) emerge as promising promoters for Ni-supported catalysts.³¹⁻³⁴ Noble metals including Rh, Pt, and Pd were examined by Nurunnabi et al. and promoted reforming activity and stability.³⁵⁻³⁸ Studies on bimetallic Ni-based catalysts showed high stability for hydrocarbon reforming. Formulations examined

include Ni–Co, Ni–Mo, Ni–Re, and Ni–Cu.^{34,39,40} Exposure of Ni catalysts to very low concentration of sulfur was found beneficial for coke resistance. It is a debating topic whether this is due to ensemble size control or interference with carbon dissolution during whisker formation process as indicated by Trimm.¹⁶

The typical Al₂O₃ support for steam reforming catalysts is acidic and favors hydrocarbon cracking and polymerization. In addition to using promoters to modify Al₂O₃ support properties, researchers are seeking for alternative supports. Matsumura and Nakamori compared ZrO₂ with Al₂O₃ as support for Ni catalysts. Ni-ZrO₂ exhibited better performance than Ni-Al₂O₃ catalysts, particularly at low reaction temperatures, which was attributed to more hydroxyls groups formed on the ZrO₂ surface.⁴¹ Compared with Al₂O₃, MgO support promotes surface carbon gasification, which markedly suppresses coke deposition. Ni-MgO solid solution catalysts demonstrated stable performance over long-term operation.⁴²⁻⁴⁴ The solid solution creates a strong ionic environment at the metal particle-support interface and effectively minimizes Ni particle clustering and carbon formation. CeO₂ is a popular support for reforming catalysts because its high oxygen storage capacity prevents coke formation reaction.^{34,45} Similarly, the lattice oxygen in perovskites materials facilitates the oxidation of CH_x fragments adsorbed on metallic nickel and reduces coking. Urasaki et al. compared the decoking abilities of a series of perovskite-supported Ni catalyst including LaAlO₃, LaFeO₃, SrTiO₃, BaTiO₃, and La_{0.4}Ba_{0.6}Co_{0.2}Fe_{0.8}O_{3-δ}, and high activity and stability were measured in LaAlO₃ and SrTiO₃ catalytic systems.⁴⁶ New formulations have been developed. Ross reported some promising results over Mo and W carbides for natural gas dry reforming with CO_{2} . 47

Another major type of steam reforming catalysts is based on noble metals. The serious coking problem with Ni is caused by the formation, diffusion, and dissolution of carbon in the metal.¹⁶ However, carbon does not dissolve in noble metals, yielding much less coking in those systems. Ru, Rh, Pd, Ir, and Pt were examined for their reforming performance. Ru and Rh displayed high reforming activities and low carbon formation rates.⁴⁸ However, the cost and availability of noble metals limit their application.

2.2.1.4 Kinetics

There is a vast amount of literature studies on the kinetics of SMR. A variety of kinetics models or rate expressions have been reported. There are no general agreements on the rate equations. Discrepancies exist and some may even contradict. Kinetic parameters are largely influenced by catalysts and operation conditions. Neglecting diffusion and heat transfer limitations may yield misleading results. An overview of steam reforming kinetics has been provided in Twigg's catalysis handbook published in 1989.¹² The table of selected kinetic equations for hydrocarbon reforming from the book has been included here, which is still of high value now.

A few of representative kinetic studies in recent years are discussed in this section. Gokon et al.⁴⁹ discussed different kinetics models employed for methane reforming studies, including the Langmuir–Hinshelwood (LH), basic (BA),

Eley–Rideal (ER), and stepwise (SW) mechanisms. The LH model was tested by Mark et al. in the CO₂ reforming of methane.⁵⁰ It assumed that both reactant species of CH₄ and CO₂ are adsorbed onto the catalyst active sites separately. Adsorbed reactants then associatively react on the active sites and lead to H₂ and CO product formation. The basic model is established on the basis that the reactant species of CH₄ and CO₂ follow the first-order behavior. In the ER mechanism, one of the two reactants (either CH₄ or CO₂) is adsorbed onto the catalyst surface in adsorption equilibrium. The adsorbed species then react with the other reactant from the gas phase, and H₂ and CO are formed subsequently.⁵¹ The SW mechanism assumes that CH₄ dissociatively adsorbed (active carbon and hydrogen species) on the catalytic surface. The active carbon reacts with CO₂ in the gas phase and produces two equivalents of CO.

Rostrup-Nielsen et al.¹⁰ and Trimm and Önsan⁵² described the kinetics of the SMR reaction based on LH rate expressions reported by Xu and Froment.⁵³ These studies have considered that H_2 , CO, and CO₂ are produced in the SMR reaction through methane steam reforming and WGS reactions. Also, CO₂ is formed not only through the WGS reaction, but also by the steam reforming reaction with a higher S/C ratio. The rate expressions for stoichiometric methane steam reforming to syngas, WGS, and methane steam reforming with an excess of steam to produce H_2 and CO₂ are given in Equations 2.8–2.10, respectively,

CH₄ + H₂O = 3H₂ + CO;
$$r_1 = \frac{k_1 \cdot P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^2 \cdot Z^2} (1 - \beta),$$
 (2.8)

$$CO + H_2O = H_2 + CO_2; \qquad r_2 = \frac{k_2 \cdot P_{CO} \cdot P_{H_2O}}{P_{H_2} \cdot Z^2} (1 - \beta), \qquad (2.9)$$

CH₄ + 2H₂O = 4H₂ + CO₂;
$$r_3 = \frac{k_3 \cdot P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^{3.5} \cdot Z^2} (1 - \beta),$$
 (2.10)

where

$$Z = 1 + K_{a,CO}P_{CO} + K_{a,H2}P_{H2} + K_{a,CH4}P_{CH4} + K_{a,H2O}(P_{H2O}/P_{H2})$$

$$\beta = \text{reaction quotient } (Q_R)/Kp,$$

$$K_a = \text{adsorption constant, and}$$

Kp = equilibrium constant.

The rate constants (k_1 , k_2 , and k_3) for these three reactions and the adsorption constants (K_a) for CH₄, H₂O, CO, and H₂ determined experimentally by two different research groups are compared in Table 2.4.¹⁰

Wei and Iglesia^{54–57} recently reported isotopic and kinetic studies for the SMR and CO₂ reforming of methane over Ni- and noble metal-based catalysts. They considered the sequence of elementary steps involved in the steam reforming and CO₂ reforming of methane as well as methane decomposition and WGS reactions as shown in Figure 2.5. Accordingly, CH₄ decomposes to chemisorbed carbon (C*) via sequential elementary H-abstraction steps, which becomes faster as H atoms are sequentially abstracted from the CH₄ reactant. This cascade process leads to a low

Parameter	Data by Xu and Froment	Data by Avetnisov et al.
$\overline{k_1}$	$4.23 \times 10^{15} \exp(-240.1/\text{RT})$	$1.97 \times 10^{16} \exp(-248.9/\text{RT})$
k_2	$2.00 \times 10^{6} \exp(-67.1/\text{RT})$	$2.43 \times 10^5 \exp(-54.7/\text{RT})$
k_3	$1.02 \times 10^{15} \exp(-243.9/\text{RT})$	$3.99 \times 10^{18} \exp(-278.5/\text{RT})$
$K_{\rm a,CO}$	$8.23 \times 10^{-5} \exp(70.65/\text{RT})$	$3.35 \times 10^{-4} \exp(65.5/\text{RT})$
$K_{\rm a,H2}$	$6.12 \times 10^{-9} \exp(82.90/\text{RT})$	$2.06 \times 10^{-9} \exp(58.5/\text{RT})$
$K_{\rm a,CH4}$	$6.65 \times 10^{-4} \exp(38.28/\text{RT})$	$6.74 \times 10^{-3} \exp(34.1/\text{RT})$
K _a , _{H2O}	$1.77 \times 10^5 \exp(-88.68/\text{RT})$	$9.48 \times 10^4 \exp(-74.9/\text{RT})$

 Table 2.4. Kinetic Constants for the Steam Methane Reforming and Water-Gas Shift Reactions^{10,53}

 k_1 , k_2 , and k_3 are rate constants of Equations 2.8–2.10, respectively.

 $K_{a,CO}$; $K_{a,H2}$; $K_{a,CH4}$; and $K_{a,H2O}$ are adsorption constants for CO, H₂, CH₄, and H₂O, respectively. Catalyst used was Ni/MgAl₂O₄ with an Ni metal surface area of $3 \text{ m}^2/\text{g}$. Activation energies and heats of adsorption (values in the parentheses) are in kilojoule per mole.



Figure 2.5. Sequence of elementary steps involved in the CH₄ reforming and water-gas shift reactions over Ni-based catalysts. Adapted from Wei and Iglesia.⁵⁴

CHx* coverage and to C* as the most abundant carbon-containing reactive intermediate. Chemisorbed carbon is then removed by steam or CO_2 as a coreactant. These elementary steps are consistent also with kinetic and isotopic measurements on other noble metal-based catalysts such as Pt and Ir studied by them. When exposed metal atoms are the abundant surface species, only the rate constant for the activation of

Catalyst	Turnover Rate (s ⁻¹)	Rate Constant (s/kPa)	Activation Energy (kJ/mol)	Preexponential Factor (s/kPa)
Ni/MgO	4.0	0.2	105	3.8×10^{3}
Pt/ZrO ₂	13.1	0.66	75	2.0×10^{2}
Ir/ZrO ₂	12.4	0.62	87	9.9×10^4

 Table 2.5.
 Kinetic Parameters for the Steam Methane Reforming over Ni-, Pt-, and

 Ir-Based Supported Catalysts⁵⁴⁻⁵⁷

Reaction conditions: temperature: 600 °C; CH4 partial pressure: 20 kPa; H2O partial pressure: 25 kPa.

the first C–H bond in CH_4 appears in the rate expression, and the reaction rates become first order in CH_4 and independent on the concentration of the coreactant, steam, or CO_2 . The rate equation is shown in Equation 2.11,

$$r_{\rm f} = k P_{\rm CH4},\tag{2.11}$$

where $r_{\rm f}$ is the rate of the forward reaction for the SMR, *k* is the rate constant, and $P_{\rm CH4}$ is the partial pressure of CH₄. The kinetic parameters such as turnover rate, rate constant, activation energy, and the preexponential factor for the SMR over supported Ni, Pt, and Ir catalysts determined under the same experimental conditions are gathered in Table 2.5.^{54–57} Additional kinetic equations for the steam reforming of methane and other higher hydrocarbons reported in the literature are gathered in Table 2.6.

2.2.1.5 Mechanism

Methane is a stable and highly symmetrical molecule. The bond energy, which is essentially the average enthalpy change in a gas-phase reaction to break all similar bonds, of C–H bond in methane is 416 kJ/mol. The activation of the rigid C–H bond by dissociative adsorption of methane is the most critical and the rate-determining step (RDS) in the SMR reaction, and this occurs with different rates over Ni- and noble metal-based supported catalysts.^{10,54–58} The activated methane molecule then undergoes surface reaction with adsorbed oxygen atom obtained from the dissociation of H₂O as described in Equations 2.12–2.20,^{10,58}

$$CH_4 + 2^* \to CH_3^* + H^* \quad (RDS),$$
 (2.12)

$$CH_3^* + * \leftrightarrow CH_2^* + H^*, \tag{2.13}$$

$$CH_2^* + * \leftrightarrow CH^* + H^*, \tag{2.14}$$

$$CH^* + * \leftrightarrow C^* + H^*, \tag{2.15}$$

$$H_2O + 2^* \leftrightarrow OH^* + H^*, \tag{2.16}$$

$$OH^* + * \leftrightarrow O^* + H^*, \tag{2.17}$$

$$C^* + O^* \leftrightarrow CO^* +^*, \tag{2.18}$$

- $CO^* \leftrightarrow CO + ^*,$ (2.19)
- $2\mathrm{H}^* + 2^* \leftrightarrow \mathrm{H}_2 + 2^*, \tag{2.20}$

				0	
Hydrocarbon (hc)	Catalyst	Temperature (°C)	Pressure (bar)	Rate Equation	Remarks
CH ₄	Ņ	500-900	1-15	$[hc](1-K_5'/K_5)$	Plant design model
CH_4	Ni	500-900	1 - 15	$[hc](1-K_6'/K_6)$	Plant design model
CH_4	Ni	500-900	1-15	$[hc][H_2O]^2(1-K_6'/K_6)$	CO ₂ from CH ₄ , then reverse shift to give CO
CH_4	Industrial Ni	500-900	21-41	[hc]	Rate constant is pressure
	catalyst			$(1-K'_5/K_5)[H_2]$	dependent because of diffusion
CH_4	Ni foil	470-800	1-41	$[hc][H_2O]$	Rate constant is pressure
				$[H_2O] + a[H_2]^2 + b[H_2]^3(1 - K'_5/K_5)$	dependent. Adsorption of hc to form =CH ₂ , then reaction
					with gas-phase n ₂ O
CH_4	Ni/α-Al ₂ O ₃	350-450	1–2	$\frac{[\ln c][H_2O]^2}{1-a[\ln c](1-K'_6/K_6)}$	Rate-determining step reaction of adsorbed hc and gas-phase
					H_2O ; H_2 inhibits reaction
CH_4	Commercial	638	1 - 18	$-K_{co}([CO] - K[CH_4][H_2O]/[H_2O]^3)$	Equation is for CO formation,
	Ni catalyst			$1 + a[H_2O] + b[CH_4][H_2O]/[H_2]^3 + c[CH_4][H_2O]^2/[CH_2]^4$	similar one for CO ₂ formation. Rate-determining
					step is desorption of CO and
					CO ₂ after the reaction of CH ₄
					gas with adsorbed H ₂ O
					(Continued)

Table 2.6. Selected Kinetic Equations for Hydrocarbon Steam Reforming

Hydrocarbon (hc)	Catalyst	Temperature (°C)	Pressure (bar)	Rate Equation	Remarks
CH4	Ni/Al ₂ O ₃ or SiO ₂	670–770	16–26	$[hc][H_2O]^2(1-K_6'/K_6)$ Ra	ate constant is pressure lependent because of itfinsion: $E_{\alpha} = 38$ 5–60 k1/mol
CH_4	Rh, etc./SiO ₂	350-600	1	$[hc]^{\circ}[H_2O]^{0.5}$ G_2°	aseous products at -30.302 million for shift reactions and CH $_4$ + H ₂ O \rightarrow CO + 3H ₅
C_3H_6	Ni/SiO ₂ or C	500-750	1	$[hc]^{0.75}[H_2O]^{0.5}$ Tw n E	wo-site mechanism; nondissociative hc adsorption: Ea = 64 kJ/mol
C_2H_6	Ni/Cr ₂ O ₃	300–360	1	$\frac{[hc]^{\circ}}{1+a[hc]/[H_{2}]}$ Ra	ate-determining step hc idsorption; reaction via =CH ₂
<i>n</i> -C ₆ H ₁₄ , etc. <i>n</i> -C ₇ H ₁₆	Ni Rh/	500-800 550-800	1-30 1	[hc]°[H ₂ O]° - CF tf C C C C C C C C C C C C C C C C C C C	<i>a</i> = 46kJ/mol H ₄ and CO greater than hermodynamics involving CH ₄ + H ₂ O=CO + 3H ₂ and chift reaction. CH ₄ direct from
n -C $_7$ H $_{16}$	Rh/MgW ₄	500	1	$\frac{[hc][H_2O]}{1+a[hc]}$ As As p	ic and from methanation s above. Zero order for heat nigh [hc]. CO_2 primary product: $Ea = 78$ kJ/mol

 Table 2.6.
 Continued

n -C $_{6}$ H $_{14}$	Ni/K	500-800	1 - 20		CH ⁴ less than thermodynamics
	polyaluminate				involving
					$CH_4 + H_2O = CO + 3H_2$ and
					CO ₂ less than shift
					equilibrium at high H ₂ O/hc
					ratio. CO primary product
C ₃ H ₈ , etc.	Ni/Al ₂ O ₃ or	450-500	1	1	As above, but CO ₂ less than
	Mg silicate				shift equilibrium, CO from
					reverse shift, CH ₄ from CO/
					$CO_2 + H_2$
Toluene	$Rh/\gamma - Al_2O_3$	520	1	$[hc]^{\circ}[H_2O]^{\circ}$	Two-site adsorption. Some
					gasification via dealkylation,
					π -bonded ring and =CH ₄
Toluene	$Rh/\gamma - Al_2O_3$	500-600	1	1	Gasification via adsorbed
					six-membered aromatic and
					CH_x species
Toluene	$Rh/\gamma - Al_2O_3$	400-500	1	$[hc]^{n}[H_{2}O]^{(1-n)/2}$	N = 0.1. Two-site adsorption
					followed by surface reaction:
					Ea = 138 kJ/mol
Toluene	Rh/α - Cr_2O_3 ,	625	1 - 20	$[hc][H_2O]$	Single-site adsorption.
	etc.			$\overline{(1+a[hc])+b[H,O]^2}$	Rate-determining step is
					surface hc and H ₂ O reaction:
					Ea = 115 kJ/mol
Letters a, b, and	c are constants.				

[x], partial pressure of species x; Ea, activation energy; K, equilibrium constants; K', K calculated from nonequilibrium concentrations.



Figure 2.6. Potential energy diagram for the steam methane reforming over Ni(111) and Ni(211) surfaces based on the density functional theory (DFT) study. Adapted from Rostrup-Nielsen et al.¹⁰

where the asterisks (*) denotes the adsorption sites on the catalyst surface. Wei and Iglesia^{54–57} also considered the involvement of similar elementary steps in SMR and CO_2 reforming of methane over Ni- and noble metal-based catalysts and showed the elementary reactions schematically as shown in Figure 2.5 and described above in the kinetics section.

Rostrup-Nielsen and coworkers, based on the density functional theory (DFT) calculations for the SMR over Ni(111) and Ni(211) surfaces, showed the energies of intermediate species formed on the surface and activation barrier separating the intermediates along the reaction path (Fig. 2.6).^{10,58} The data indicate that the C or CH species are the most stable intermediates on these surfaces. For the reverse reaction, methanation, the dissociation of CO has a large activation barrier on the perfect Ni(111) surface but is favored on the stepped Ni(211) surface. Hence, the steps on the Ni(111) surface are predicted to be the sites where CO dissociates. The reaction energy, (the final point in the figure) 292 kJ/mol calculated from this DFT study, corresponds to a reaction enthalpy of 230 kJ/mol, and this is in good agreement with the experimental value of 206 kJ/mol.

2.2.1.6 Modeling and Simulation

Process modeling and simulation significantly improves the efficiency of system design and development and economic analysis, which is important for the success of SMR industry operation. The behavior of the process can be simulated with diverse mathematical models. Many parameters have been factored into the modeling process, including reactor type, mass and heat transfer, operation conditions (temperature, pressure, feed composition), kinetic modeling, and flow distribution pattern. Knowledge derived from these studies provides understanding of the complex process and facilitates developmental work. This section introduces examples of process modeling and simulation work available in the literature, most of

which were performed in SMR reactors combined with H_2 removal or CO_2 sorption.

Lee et al.⁵⁹ simulated a hybrid reaction system of SMR and *in situ* noncatalytic removal of CO₂ by the carbonation of CaO to CaCO₃ in a moving bed reactor where reforming catalyst and CaO-based CO₂ acceptor in pellets move concurrently with gaseous reactants. Effects of parameters like feed rates of CaO and CH₄, and the reactor bed temperature on steady-state behavior of the hybrid reaction have been determined. In another paper, these researchers simulated the transient behavior of SMR coupled with simultaneous CO₂ removal by carbonation of CaO pellets in a packed bed reactor for hydrogen production.⁶⁰ A mathematical model was developed to describe both the SMR reaction and the CaO carbonation-enhanced SMR reaction at nonisothermal, nonadiabatic, and nonisobaric operating conditions. It has been successfully validated with reaction experiments. Apparent carbonation kinetics of the CaO pellet prepared has been determined using thermogravimetric analysis (TGA) carbonation experiments at various temperatures and has been incorporated into the model. Effects of major operating parameters (bed temperature, pressure, steam to methane feed ratio, and flow rate) on the transient behavior of the CaO carbonation-enhanced SMR have been investigated using the model. Therefore, the optimum operation conditions can be identified to achieve desired CO₂ uptake capacity, to lower CO concentration in the product, and to maximize H₂ yields.

Ochoa-Fernández et al.⁶¹ studied the kinetics of CO_2 sorption on a solid adsorbent, namely lithium zirconate, in an oscillating microbalance. The solid sorbent has been prepared by a novel route resulting in a high capacity, good stability, and much improved sorption rates, making it suitable for its application in sorption enhanced hydrogen production by SMR. A kinetic equation for the sorption as a function of CO_2 partial pressure and temperature has been developed. The hydrogen production by sorption-enhanced reaction process has been simulated by a dynamic one-dimensional pseudo-homogeneous model of a fixed-bed reactor, where a hydrotalcite-derived Ni catalyst has been used as steam reforming catalysts. Simulation results show that hydrogen purer than 95% with a concentration of carbon monoxide lower than 0.2 mol% can be produced in a single step.

Cao et al.⁶² mathematically described and experimentally demonstrated the microstructured catalysts used for SMR reaction in microchannel reactors. Porous metal substrates (FeCrAlY) were used to form engineered catalysts with Rh. Two types of structures were evaluated in the microchannel reactors and simulated with the developed heterogeneous reactor model. The modeling technique described in the paper provides a convenient way to evaluate variables in designing more efficient catalysts for SMR. Yu et al.⁶³ performed a simulation study to investigate the performance of a porous ceramic membrane reactor for hydrogen production through SMR. The results show that the methane conversions much higher than the corresponding equilibrium values can be achieved in the membrane reactor due to the selective removal of products from the reaction zone. The comparison of isothermal and nonisothermal model predictions was made. It was found that the isothermal assumption overestimates the reactor performance and the deviation of calculation results between the two models is subject to the operating conditions. The effects

of various process parameters such as the reaction temperature, the reaction side pressure, the feed flow rate, and the steam to methane molar feed ratio, as well as the sweep gas flow rate and the operation modes, on the behavior of membrane reactor were analyzed and discussed.

Rakib and Alhumaizi⁶⁴ mathematically studied a bubbling fluidized bed membrane reactor for SMR reaction, with the permselective Pd membranes removing hydrogen from the reaction system to enhance the methane conversion. Oxygen fed into the reaction system can decrease the endothermicity of the overall reaction by the combustion of methane, thereby reducing the need of external firing. Operation at low feed steam:carbon ratios is also possible with the steam required for the reforming reaction being provided as a product from the combustion reactions, although problems related to coking also need to be addressed at very low ones. Because of the high endothermicity and fast kinetics of the steam reforming reactions, to provide heat effectively to the reaction, an *in situ* heat generation by combustion is employed. As an alternative, a higher feed temperature can be used as well. However, since higher oxygen:methane ratios also tend to consume more of the methane itself, this cannot be increased much, and an optimum value exists with respect to the favorable production of pure hydrogen from the reactor permeate side.

Wang and Rodrigues⁶⁵ reported the fundamental analysis of the sorptionenhanced steam methane reforming (SE-SMR) process in which the simultaneous removal of carbon dioxide by hydrotalcite-based chemisorbent is coupled. A twosection reactor model has been developed to describe the SE-SMR reactor, decoupling the complexity in process analysis. The model defines two subsequent sections in the reactor: an equilibrium conversion section (upstream) and an adsorption reforming section (downstream). The material balance relationship in the equilibrium conversion section is directly determined by thermodynamic equilibrium calculation, providing an equilibrated atmosphere to the next section. The adsorption reforming section is described using an isothermal multicomponent dynamic model into which the SMR reactions and the high-temperature CO₂ adsorption are embedded. The multiple requirements (including H₂ purity, H₂ productivity, CH₄ conversion enhancement, and carbon oxide concentrations) are taken into account simultaneously so as to analyze and define feasible operation window for producing high-purity hydrogen with ppm-level CO impurity. The performances of the reactors with different dimensions (laboratory scale and pilot scale) are explored, highlighting the importance of operation parameter control to the process feasibility.

Posada and Manousiouthakis⁶⁶ discussed the heat and power integration studies for a conventional methane reforming based hydrogen production plant with the purpose of finding minimum hot/cold/electric utility cost. Hot methane and steam were fed into the SMR reformer, where the reversible reactions (r_1) , (r_2) , and (r_3) were the main global reactions taking place. Heat and power integration results in utility profit due to electricity production in excess of process needs. Heat integration alone resulted in a 36% reduction in utility costs. Operation at the minimum hot/ cold or hot/cold/electric utility cost did not require hot utility with a consequent reduction of carbon dioxide emissions of 6.5%.

Takeuchi et al.⁶⁷ reported a membrane reactor as a reaction system that provides higher productivity and lower separation cost in chemical reaction processes. In this paper, packed bed catalytic membrane reactor with palladium membrane for SMR reaction has been discussed. The numerical model consists of a full set of partial differential equations derived from conservation of mass, momentum, heat, and chemical species, respectively, with chemical kinetics and appropriate boundary conditions for the problem. The solution of this system was obtained by computational fluid dynamics (CFD). To perform CFD calculations, a commercial solver FLUENTTM has been used, and the selective permeation through the membrane has been modeled by user-defined functions. The CFD simulation results exhibited the flow distribution in the reactor by inserting a membrane protection tube, in addition to the temperature and concentration distribution in the axial and radial directions in the reactor, as reported in the membrane reactor numerical simulation. On the basis of the simulation results, effects of the flow distribution, concentration polarization, and mass transfer in the packed bed have been evaluated to design a membrane reactor system.

Zanfir and Gavriilidis⁶⁸ presented a theoretical study of the influence of flow arrangement on the thermal behavior of a catalytic plate reactor (CPR) for SMR reaction using methane catalytic combustion as heat source. A two-dimensional model is presented. CPR performance and the thermal behavior is strongly affected by overall and local balance between heat generated on the exothermic side and heat consumed on the endothermic one, which in turn is influenced by flow arrangement. Simulations for co-current and countercurrent flow were carried out for similar inlet conditions and catalyst loadings. It was found that the reactor is better balanced thermally for concurrent operation. For countercurrent arrangement, higher conversions and better utilization of the overall heat generated in the exothermic process are achieved at the expense of pronounced temperature extremes. Thus, reforming conversion for countercurrent operation is 62.8% compared with 52% for concurrent operation, while maximum transverse temperature difference for concurrent operation is only 16.5K compared with 310K for countercurrent operation. This increases the chances of the reactor runaway and of homogeneous combustion being initiated. Utilization of a nonuniform catalyst distribution can overcome the heat imbalance by inducing favorable reactant depletion along the reactor during countercurrent flow.

Gallucci et al.⁶⁹ investigated the SMR reaction from a modeling viewpoint, considering the effect of different parameters on methane conversion. For example, considering the influence of the lumen pressure on methane conversion at constant temperature, it has been found that increasing this parameter increases the equilibrium methane conversion for the membrane reactor, while it decreases for the traditional one. Moreover, in a realistic membrane reactor (i.e., considering a simulation performed using kinetic expressions), the behavior of methane conversion versus lumen pressure at various temperatures shows a minimum value, depending on the membrane thickness, on the reactor length, and on the temperature.

2.2.1.7 Reactor Design and Development

The SMR reaction results in the production of H_2 and CO_2 and is a strongly endothermic reaction and favored at high temperatures. Heat transfer is critical to ensure fast kinetics as the reaction moves forward. To enhance SMR reaction, the following approaches can be employed:

- Integration of SMR reaction and products (H₂ or CO₂) separation steps to shift the equilibrium and enhance the reaction rate in the forward direction. This also lowers the reforming temperature to achieve the same conversion level.
- Novel reactor design with improved mass and heat transfer. Efficient heat transfer facilitates reaction kinetics and decreases energy consumption. As such, reactor size and cost can be significantly reduced.
- Alternative heating sources to increase system efficiency. This may lead to additional benefit of reducing CO₂ emissions.

A look into the recent advances taking place in the equipment and reactor designs reveals that much emphasis has been laid on preparing and experimenting with the membrane reactors and CO_2 sorption-enhanced reactors. There are extensive studies on Pd-based membrane for selective separation of H₂. Cost of Pd has been proven to be insignificant among the total cost considering typical membrane thickness of $5-10 \mu$.⁷⁰ With H₂ permeable membrane reactor configuration, ultrapure H₂ can be obtained and high-pressure CO₂ can be readily sequestrated or for other application. As reported by Patil et al.,⁷¹ permselective Pd metallic membranes for H₂ removal (500–600 °C operating temperature) was integrated inside a fluidized bed reactor along with selective O_2 addition through dense perovskite membranes (900–1000 °C operating temperature). CH₄ conversion over 95% could be obtained. Ultrapure H₂ (no more than 10 ppm CO) can be generated from light hydrocarbons such as CH₄, which meets the requirement for feeding proton exchange membrane fuel cells (PEMFCs). Instead of fitting a ceramic substrate to a thin Pd-based layer that lacks mechanical stability, Tong and coworkers performed a series of studies on controlled deposition of Pd or Pd alloy (Pd-Ag, Pd-Ce) composite membranes onto porous stainless steel (PSS) tubes for SMR.72-75 The deposited membrane exhibited stable homogeneous structure and provided high hydrogen permeable flux and complete selectivity of H_2 versus argon or helium. Under typical operation temperature (\sim 500 °C) and pressure (100–300 kPa), a methane conversion of over 97% was measured. Pd-based membrane supported on PSS was also reported by Ayturk et al.⁷⁰ Long-term stability at high temperature with high methane conversion (>95%) has been achieved.

Research on other types of materials for H_2 separation has been motivated by relatively high cost of Pd and possible membrane degradation by acidic gases and carbon as summarized in Tsuru et al.⁷⁶ These authors examined microporous silica membranes together with an Ni catalyst layer for SMR reaction. However, this type of membrane allows the permeation of hydrogen as well as other gases in reactants and products, which markedly reduces hydrogen selectivity and limits methane

conversion (up to 0.8 under their testing conditions). Improvement in methane conversion and H_2 selectivity was reported in Nomura et al.,⁷⁷ who synthesized a catalyst composite silica membrane using a counter diffusion chemical vapor deposition method and observed higher H_2 selectivity (H_2/N_2 permeance ratio over 1000).

There are many studies available in literature on CO₂ sorption-enhanced SMR. Pure CO₂ from the reaction is suitable for sequestration or other use.⁷⁸ Primary efforts were in the development of CO₂ sorbent materials and improvement of multicycle stability. Johnsen et al.⁷⁹ studied dolomite as a CO₂ sorbent in a bubbling fluidized bed reactor. The operating temperature and pressure are 600 °C and 1 atm, respectively. By cycling between CO_2 absorption and regeneration to reduce prebreakthrough and subsequent conversion decline, an H₂ concentration of >98% could be obtained. Dolomite was found to be a better sorbent than limestone. Ca(OH)₂ or $CaOSiO_2$ is another major type of adsorbent that is effective for CO_2 separation. They displayed superior performance during hydrocarbon gasification compared with other metal oxides including MgO, SnO, and Fe₂O₃.⁸⁰ Wu et al.⁸¹ characterized the production of hydrogen with a sorption-enhanced steam methane reaction process using $Ca(OH)_2$ as the CO₂ adsorbent. Ninety-four percent H₂ concentration can be reached, which is nearly 96% of the theoretical equilibrium limit, much higher than the equilibrium concentration of 67.5% without CO₂ sorption under the same conditions of 500 °C, 0.2 MPa pressure, and a steam-to-methane ratio of 6. In addition, the residual mole fraction of CO₂ was less than 0.001. Li₂ZrO₃ synthetic sorbents are also reported in literature with better multicycle stability, but the costs are prohibitive.79,82

Kusakabe et al.⁸³ proposed selective CO oxidation membrane concept to facilitate SMR reaction. Yttria-stabilized zirconia (YSZ) membrane was deposited on the surface of a porous alumina support tube by sol-gel procedure. This again was impregnated with Pt and Rh aqueous solution to produce a Pt- or Rh-loaded YSZ membrane. With addition of O_2 in the feed, oxidation of CO can bring CO concentration to the level appropriate for PEMFC (<30 ppm).

A substantial amount of work on new reactor design has been undergoing to enhance mass and heat transfer efficiency and SMR kinetics as a result. Xiu et al.⁸⁴ applied the subsection-controlling strategy to design adsorptive SMR reactor. The whole process was divided into four steps within one bed, with adsorbent/catalyst packing ratio and wall temperature separately regulated in each subsection. By maintaining a pressure swing sorption-enhanced SMR cyclic process, a product stream with H₂ purity over 85% purity, CO concentration below 30 ppm, and CO₂ concentration below 300 ppm can be reached.

Roychoudhury et al.⁸⁵ reported the use of microlith catalytic reactors (patented by Precision Combustion, Inc. (PCI)) for ATR, WGS, or Prox. The microlith substrates are composed of a series of ultrashort channel length, low thermal mass, catalytically coated metal meshes with very small channel diameters. This design allows fast heat and mass transfer, reduces the reactor size, and improves the overall performance. ATR test showed high resistance to coking, especially at low steam/C ratios.

Chikazawa et al.^{86,87} evaluated the feasibility of small sodium-cooled reactor as a diversified power source in terms of economical and safety potential and reviewed

the application of this type of reactor for hydrogen generation from natural gas reforming. This type of reactor demonstrates high thermal efficiency and availability, yields a compact reactor design, and simplifies the cooling system. Glockler et al.⁸⁸ and Kolios et al.⁸⁹ reported the multifunctional reactor concept. This design is capable of integrating exothermic and endothermic reactions in microstructured devices and employing recuperative heat exchange between the process streams. This offers efficient heat recovery. Hoglen and Valentine⁹⁰ applied Coriolis meters in SMR technology. Accurate control of S/C ratios provides high operation efficiency.

Velocys, which is a spinout company from Battelle Memorial Institute, has developed microchannel process technology for large-scale chemical processing. Hydrogen can be produced from the compact microchannel unit at high heat and mass transfer rates. As discussed by Tonkovich et al.,⁹¹ a microchannel methane steam reforming reactor integrates catalytic partial oxidation of methane prior to catalytic combustion with low excess air (25%) to generate the required energy for endothermic methane steam reforming in adjacent channels. This design improves process intensification and results in significant capital and operating cost savings for commercial applications. Galvita and Sundmacher⁹² proposed a periodically operated two-layer (reduction and reoxidation) reactor design concept for steam reforming of methane. In the reduction phase, methane is converted at "layer 1" into CO and H₂ using partial oxidation. The products are fed to "layer 2" where CO₂ and H₂O are produced. In the reoxidation phase, the reactor is fed with pure steam, which reoxidizes the catalytic materials and is itself converted into CO-free H₂ gas. This process generates high-quality H₂ and eliminates additional H₂ purification units at a reduced cost.

SMR reactor design can also be approached by employing other energy sources. Nozaki et al.^{93,94} reported improvement of SMR performance (much higher methane conversion) by combination of catalysts and barrier discharges. Use of barrier discharge greatly reduces energy cost and increases energy efficiency. Solar steam reforming has been examined by Moller et al.⁹⁵ Using the solar reformer technology, up to 40% fuel savings can be expected compared with a conventional plant. CO₂ emission reduction is another benefit. Another clean energy source is nuclear power. Fukushima and Ogawa⁹⁶ presented a conceptual design of low-temperature hydrogen production and high-efficiency nuclear reactor technology.

2.2.2 Steam Reforming of C₂-C₄ Hydrocarbons

While natural gas reforming is the primary process for the industrial production of H_2 , the reforming of other gaseous hydrocarbons such as ethane, propane, and *n*-butane have been explored for the production of H_2 for fuel cells.^{52,97} The reforming of propane and *n*-butane received particular attention in recent years, because they are the primary constituents of liquefied petroleum gas (LPG), which is available commercially and can be easily transported and stored on-site. LPG could be an attractive fuel for solid oxide fuel cells (SOFCs) and PEMFCs for mobile applications.^{98–101} The chemistry, thermodynamics, catalysts, kinetics, and reaction mechanism involved in the reforming of C_2 – C_4 hydrocarbons are briefly discussed in this section.

2.2.2.1 Chemistry and Thermodynamics

Steam reforming reaction of ethane, propane, and *n*-butane are represented by Equations 2.21-2.23, while the thermodynamic data for these reactions are summarized in Tables 2.7-2.9, respectively:

$$C_2H_6(g) + 2H_2O(g) \rightarrow 5H_2(g) + 2CO(g); \Delta H_{298}^\circ = +374.3 \text{ kJ/mol},$$
 (2.21)

$$C_{3}H_{8}(g) + 3H_{2}O(g) \rightarrow 7H_{2}(g) + 3CO(g); \Delta H_{298}^{\circ} = +497.7 \text{ kJ/mol}, \quad (2.22)$$

$$n-C_4H_{10}(g) + 4H_2O(g) \rightarrow 9H_2(g) + 4CO(g); \Delta H_{298}^\circ = +651.3 \text{ kJ/mol.}$$
 (2.23)

These are endothermic reactions and the endothermicity increases with increasing carbon number of the hydrocarbon. These reactions are generally carried out in a wide temperature range between 300 and 900 °C over a nickel-based or noble metal-based supported catalyst. Under the reaction operating conditions, other reactions such as cracking into carbon and hydrogen (Eqs. 2.24–2.26) followed by carbon gasification, cracking into methane (Eq. 2.27) followed by steam reforming of methane can also occur. Methane formation can also occur by methanation of carbon oxide and H₂ (Eq. 2.28) formed in the cracking reactions. Similar to the SMR process, the steam reforming of higher hydrocarbons in practice is also performed

Temperature (°C)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	Log K
25	374.3	215.6	-37.782
75	351.3	193.2	-28.995
125	354.8	170.3	-22.344
175	358.1	146.9	-17.126
225	361.0	123.2	-12.92
275	363.7	99.2	-9.454
325	366.0	75.0	-6.548
375	368.1	50.6	-4.075
425	370.0	26.0	-1.944
475	371.6	1.3	-0.09
525	373.1	-23.5	1.539
575	374.3	-48.4	2.98
625	375.4	-73.3	4.266
675	376.3	-98.4	5.419
725	377.1	-123.4	6.458
775	377.7	-148.5	7.401
825	378.2	-173.6	8.258
875	378.5	-198.7	9.042
925	378.7	-223.9	9.761
975	378.8	-249.0	10.422
1000	378.8	-261.6	10.734

Table 2.7. Thermodynamic Data for the Steam Reforming of Ethane: $C_2H_6(g) + 2H_2O(g) \rightarrow 5H_2(g) + 2CO(g)$

Temperature (°C)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	Log K
25	497.701	297.577	-52.139
75	503.172	263.571	-39.548
125	508.015	228.822	-30.022
175	512.331	193.495	-22.555
225	516.185	157.711	-16.539
275	519.624	121.56	-11.585
325	522.685	85.112	-7.433
375	525.398	48.422	-3.903
425	527.787	11.535	-0.863
475	529.875	-25.513	1.781
525	531.681	-62.69	4.103
575	533.224	-99.973	6.158
625	534.518	-137.34	7.988
675	535.572	-174.772	9.629
725	536.398	-212.254	11.109
775	537.008	-249.772	12.448
825	537.413	-287.314	13.668
875	537.623	-324.871	14.781
925	537.652	-362.432	15.802
975	537.517	-399.991	16.741
1000	537.392	-418.768	17.183

Table 2.8. Thermodynamic Data for the Steam Reforming of Propane: $C_3H_8(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO(g)$

at higher S/C ratios, typically between 1 and 3, in order to reduce the risk of carbon deposition. While higher operating pressures are preferred for industrial applications, the reactions are generally operated at atmospheric pressure for fuel cell applications. The syngas produced can be fed directly into SOFC. HTS and LTS and/or Prox reactions are also needed in the downstream of the steam reformer to remove CO from the reformed gas for PEMFC applications:

$$C_2H_6(g) \rightarrow 3H_2(g) + 2C; \Delta H_{298}^\circ = +84.7 \text{ kJ/mol},$$
 (2.24)

$$C_3H_8(g) \to 4H_2(g) + 3C; \Delta H_{298}^\circ = +103.8 \text{ kJ/mol},$$
 (2.25)

$$n-C_4H_{10}(g) \rightarrow 9H_2(g) + 4C; \Delta H_{298}^\circ = +126.2 \text{ kJ/mol},$$
 (2.26)

$$C_nH_m + xH_2O \rightarrow yH_2 + (n-1)CO + CH_4,$$
 (2.27)

$$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}; \Delta H_{298}^\circ = -206 \text{ kJ/mol.}$$
 (2.28)

2.2.2.2 Catalysts and Kinetics

The Ni-based catalysts known for the steam reforming of natural gas are also active for the steam reforming of C_2 - C_4 hydrocarbons. However, carbon deposition and