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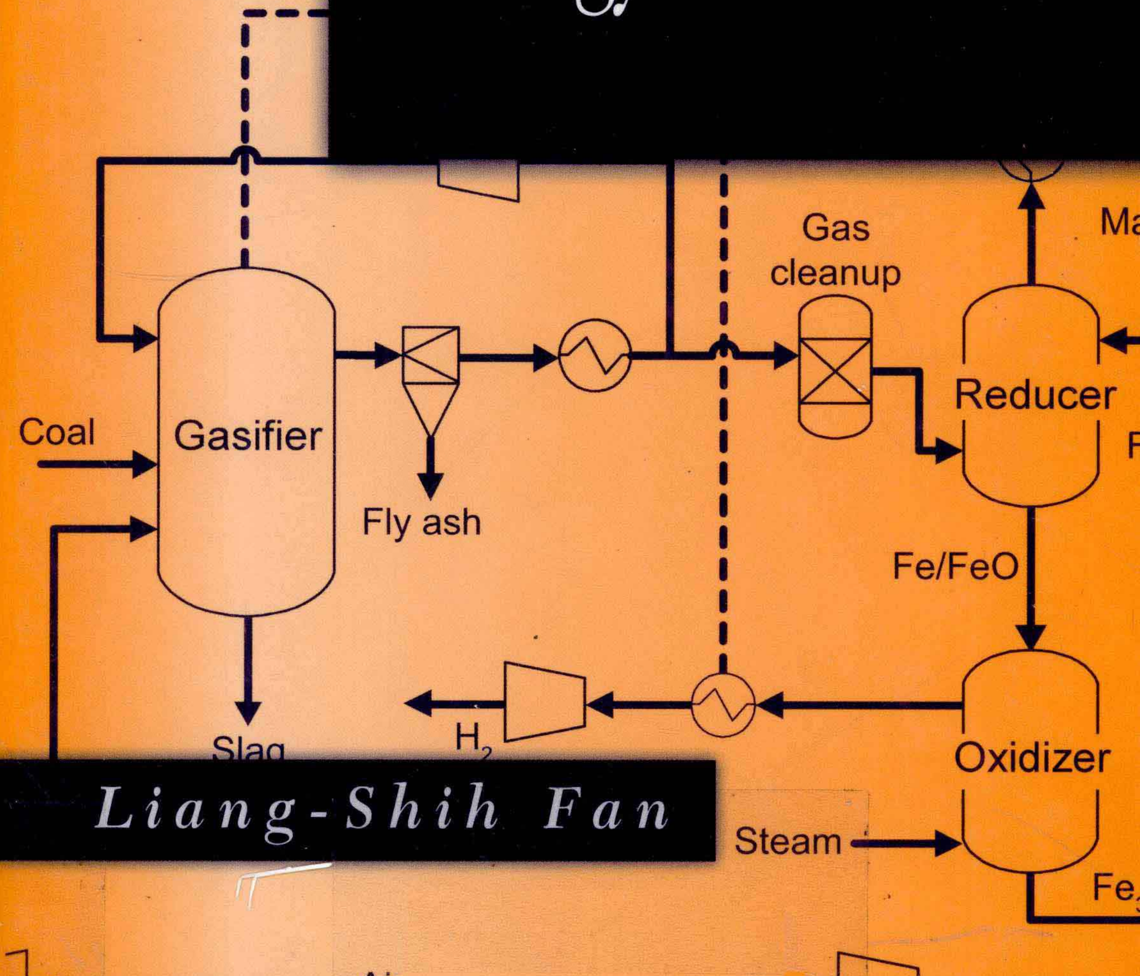
Chemical Looping Systems for Fossil Energy Conversions



Liang-Shih Fan

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CHEMICAL LOOPING SYSTEMS FOR FOSSIL ENERGY CONVERSIONS

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Dedicated to

Fan Club Members
for Their Indefatigable Spirit and Devotion
to the Exploration of Engineering Science and Technology
and for Their Friendship

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PREFACE

A given chemical reaction often can be decomposed into multiple subreactions using chemical intermediates. When this reaction is carried out in a process system, the subreaction schemes can be designed to minimize the exergy (available energy) loss in this reactive process system, whereas the desired products or undesirable by-products generated from the reaction can be separated with ease, yielding an economically viable process system. A reaction scheme of this nature is called chemical looping. The processes associated with chemical looping are called the chemical looping processes.

The concept of chemical looping has been widely applied in chemical industries, for example, in the production of hydrogen peroxide (H_2O_2) from hydrogen and oxygen using 9,10-anthraquinone as the looping intermediate. Fundamental research on chemical looping reactions also has been applied to energy systems, for example, the splitting of water (H_2O) to produce oxygen and hydrogen using ZnO as the looping intermediate. The chemical looping applications to fossil energy systems, specifically coal-based systems, were practiced commercially with the Steam Iron Process in the 1900s–1940s and were demonstrated at a pilot scale with the Carbon Dioxide Acceptor Process in the 1960s and 1970s. Currently, no chemical looping processes use fossil fuels in commercial operation. The key factors hampering the continued use of these earlier processes were that the looping particles were not sufficiently reactive or recyclable and that the energy conversion efficiencies were low. These factors led to higher product costs for using the chemical looping processes, compared with the other direct fossil fuel conversion processes.

With CO_2 emission control now being a requirement, interest in chemical looping technology has resurfaced. In particular, chemical looping processes are appealing because of their unique ability to generate a sequestration-ready CO_2 stream. Renewed fundamental and applied research since the early 1980s has emphasized improvement over the earlier shortcomings. New techniques have been developed for direct processing of coal or other solid carbonaceous feedstock in chemical looping reactors. With a significant progress under way in particle design and chemical looping reactor development, as demonstrated in the operation of several pilot- or subpilot-scale units worldwide, the chemical looping technology can be commercially viable in the future for processing fossil fuels or carbonaceous fuels in general.

This book contains six chapters and a CD. Chapter 1 presents an overview of the global energy demand and supply from fossil, nuclear and renewable sources, and of the current or conventional fossil energy conversion processes along with the chemical looping processes. It also discusses both coal combustion and coal gasification with an emphasis on the conversion efficiencies of their process applications and gaseous pollutant control methods, including CO_2 capture and sequestration. The exergy and its conversion efficiency concepts are described, as well as their applications to the selection of coal conversion process alternatives. Examples of chemical looping reactions and chemical looping processes using fossil fuels and their conversion to hydrogen, chemicals, liquid fuels, and electricity are elaborated.

Chapter 2 is devoted to the subjects of solid particle design, synthesis, properties, and reactive characteristics as the looping media employed in the processes are in solid form and the success of the chemical looping technology applications strongly depends on the performance of the particles. The looping processes can be applied for combustion and gasification using, directly or indirectly, gaseous carbonaceous fuels such as natural gas and syngas or solid carbonaceous fuels such as coal, petroleum coke, and biomass as feedstock.

Chapters 3–5 describe the design, analysis, optimization, energy conversion efficiency and economics of the looping processes, as well as current or conventional processes for combustion and gasification applications. Chapter 3 illustrates the chemical looping processes for combustion with gaseous or solid carbonaceous fuels as feedstock. Chapter 4 describes chemical looping processes for gasification using gaseous fuels as feedstock. Discussion includes applications of the reducer in these processes that serve as a reformer for treating C_1–C_4+ hydrocarbons. Chapter 5 elucidates the chemical looping processes for gasification using solid carbonaceous fuels as feedstock, in which the reducer serves the function of a gasifier used in the traditional processes.

Chapter 6 presents potential chemical looping applications, including hydrogen storage and onboard hydrogen production, the Carbonation-Calcination Reaction (CCR) Process for carbon dioxide capture, carbon dioxide and hydrogen reaction processes, chemical looping integrated with solid oxide fuel cells, enhanced steam methane reforming, tar sand digestion, and oxygen uncoupling. The CD appended to the book provides the detailed procedure and results of the simulation of various chemical looping reactors and processes based on the ASPEN PLUS (Aspen Technology, Inc., Houston, TX) software. Note that, unless otherwise stated, the unit of tonnage used in the book is the metric ton.

The book can be used as a research reference and/or used for teaching courses on energy and environmental reactions and process engineering with a focus on carbonaceous energy processing. Part of the book has been used for the senior process design course at The Ohio State University, in which student groups are asked to choose between a traditional process and a chemical looping process for coal conversion to hydrogen. The key part of the problem statement for this course is given as follows:

> ABC Energy Ltd., a major hydrogen producer in Ohio, is evaluating the feasibility of a potential process to produce hydrogen and electricity from coal using a traditional coal gasification reactor (gasifier). The coal processing rate of the gasifier is set to be 1,000 MW_{th}. Your group in the R&D division of the company is going to compare two processes that produce hydrogen from coal. You will need to submit a comprehensive evaluation report to the division manager addressing the technological and economic advantages and disadvantages of the traditional process versus one of the two new chemical looping processes, that is, the Syngas Chemical Looping Process or the Calcium Looping Process. You will also need to recommend to the manager which process, that is, the traditional process or chemical looping process, is a better choice for the new coal-to-hydrogen process.

This book will offer students an in-depth understanding of the technical aspects of the process options along with scale-up challenges in their deliberation about the process choice. This book also can be used to supplement undergraduate or graduate courses in chemical reaction engineering, thermodynamics, and process analysis/simulation. Material of particular relevance to these courses includes the contact mode of multiphase reactors, multiphase reactor design, reaction kinetics, thermodynamic analysis, process integration, and ASPEN Plus® process simulation.

This book was written in collaboration with ten of my graduate students who had worked or are working on chemical looping technology or related subjects as their dissertation research topics at The Ohio State University. The students who participated in writing this book and are still in the program are Dr. Fanxing Li (Post-Doctoral Research Associate), Shwetha Ramkumar, Liang Zeng, Deepak Sridhar, Hyong Ray Kim, and Fei Wang. The students who had participated, but left the program are Dr. Ah-Hyung Alissa Park (currently Lenfest Junior Professor in Applied Climate Science at Columbia University), Dr. Luis Velazquez-Vargas (currently Research Engineer at Babcock and Wilcox Company), Dr. Puneet Gupta (currently Research Engineer at CRI/Criterion), and Dr. Mahesh Iyer (currently Group Leader of Hydrogen Technology at Shell Global Solutions). Completion of this book would not have been possible without their extensive knowledge and insights into the intricate fundamental and applied nature of the chemical looping problems, as well as without their enthusiasm and commitment to this book, as it is apparent from the citations in the text. Dr. Alissa Park and Dr. Fanxing Li devoted an enormous amount of time to coordinating its writing. Their gracious and helpful efforts are deeply appreciated. I am, however, solely responsible for the presentation of this book including its scope, topic selection, structure, logic sequence, format and style.

My team and I are very grateful to Dr. Chau-Chyun Chen, Eric Sacia, Siwei Luo, Zhenchao Sun, Prof. Sankaran Sundaresan, Prof. Arvind Varma, Prof. Da-Ming Wang, William Wang, Wan-Yi Wu, Cindy Yizhuan Yan, and Fu-Chen Yu who reviewed one or more chapters of the book or the CD and provided valuable suggestions and comments. We would also like to express our gratitude to Debbie Bauer, Francis Coppa, Prof. Luis F. de Diego, Mark Hornick, Svein Harald Ledaal, Dr. Shiying Lin, Dr. Ke Liu, Dr. Adam Luckos, Prof. Anders Lyngfelt, Sylfest Myklatun, Dr. Tobias Pröll, George Rizeq, Dr. Ho-Jung Ryu, Dag Schanke, Prof. Laihong Shen, Dr. Tore Torp, and Greg Wolf who kindly granted permission to use their photos and valuable information in this book. Our special thanks are extended to those industrial and governmental colleagues, with whom we have had the privilege of working for many years, for generously sharing their knowledge and insights into the industrial applications: Jackie Bird, John Bloomer, Lou Benson, Robert Brown, Daniel Cicero, Dan Connell, James Derby, Jeff Gerken, Mark Golightley, Steve Grall, Robert Morris, Bartev Sakadjian, Hamid Sarv, Mark Shanagan, Kevin Smith, Dr. Robert Statnick, Gary Stiegel, Dr. Ted Thomas, and Richard Winschel. Over the years, several agencies including the Ohio Coal Development Office, U.S. Department of Energy, and U.S. Air Force, along with an industrial consortium consisting of Babcock and Wilcox, Consol Energy, Air Products, Shell, CRI/Criterion, AEP, Duke Energy, First Energy, and Specialty Minerals provided significant funding in support of my team's research, development, and demonstration efforts. Much of the results reported in this book are based on these efforts. Their support is most gratefully acknowledged. Our thanks also go to Samuel Bayham for his excellent figure drawings, Carol Mohr for her outstanding editorial assistance in the preparation of the manuscript, and Haeja Han for her help in the preproduction of the book.

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CHAPTER 1

INTRODUCTION

L.-S. Fan

1.1 Background

Energy is the backbone of modern society. A clean, relatively cheap, and abundant energy supply is a prerequisite for the sustainable economic and environmental prosperity of society. With the significant economic growth in the Asia Pacific region and the expected development in Africa, the total world energy demands are projected to increase from 462.4 quadrillion BTU in 2005 to much more than 690 quadrillion BTU by 2030,[1] as shown in Figure 1.1. The projected energy supply through 2030 will be drawn from oil, coal, natural gas; renewable forms of energy; and nuclear energy, in that order. Figure 1.1 reveals that fossil fuels account for more than 86% of the world's energy supply.[1]

The impact of the global warming induced by the CO_2 emission from fossil energy conversion processes has been an issue of international concern. An energy solution prompted by the combination of ever-increasing energy consumption and rising environmental concerns thus requires a consideration of coupling fossil energy conversion systems with economical capture, transportation, and safe sequestration schemes for CO_2. A long-term energy strategy for low or zero carbon-emission technologies also would include nuclear energy and renewable energy. Nuclear power is capable of generating electricity at a cost comparable with the electricity generated from fossil fuels.[2] Other than electricity, the heat generated from a nuclear plant can be used for hydrogen generation in hydrogen-producing thermochemical or high-temperature electrolysis plants.[3] A variety of social and political issues, as well as

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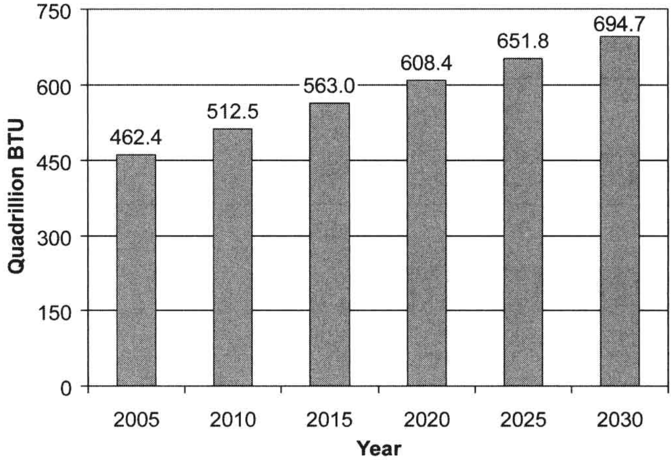
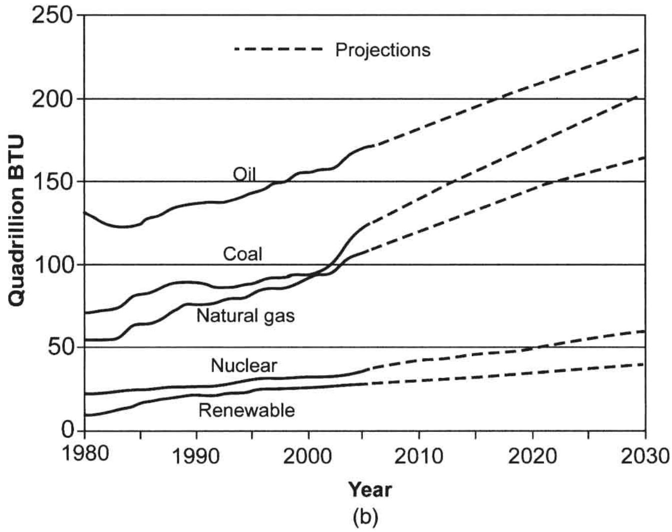


(a)



(b)

Figure 1.1. Projected global energy (a) demand and (b) supply.[1]

operational safety and permanent waste disposal concerns, however, would limit nuclear energy's widespread utilization in overall energy production.[2,4]

1.1.1 Renewable Energy

Renewable energy (i.e., hydro, wind, solar, biomass, and geothermal) is attractive because of its regenerative and environment-friendly nature. Among the renewable energy sources, hydraulic power provides the largest share of the total renewable energy supply.[5] For example, in 2005, the world's total hydroelectricity capacity was 750 GW accounting for 63% of the total renewable energy supply or 19% of the world's electricity supply for that year.[5] In the United States, hydropower electricity generation is equivalent to 95,000 MW and accounts for 7% of total U.S. electricity generation, supplying 28 million households.[6] Hydraulic power is less costly compared with other renewable energy sources. Once the hydroelectric plant is built, it does not require a significant amount of operational costs or raw materials. Also, when the overall energy life cycle is considered, a hydroelectric plant emits less greenhouse gases compared with a fossil fuel power plant. Despite these advantages, hydraulic power is subject to geological constraints. Moreover, the construction of hydroelectric plants often can be disruptive to the surrounding ecosystems and the life of inhabitants.[7]

Biomass, defined as "any organic matter, which is available on a renewable basis, including agricultural crops and agricultural wastes and residues, wood and wood wastes and residues, animal wastes, municipal wastes, and aquatic plants"[8], is a versatile renewable resource that can be converted into electricity, H_2, and biofuels. Biomass can be directly combusted to generate heat or electricity; it also can be gasified to produce syngas for power generation or liquid fuel synthesis. Other than direct combustion and gasification, alcohol-based biofuels such as bioethanol and biobutanol can be produced from sugar or starch crops through fermentation; biodiesel is produced from vegetable oils and animal fats through transesterification; and biogas can be produced from anaerobic digestion of waste or other organic material.[9] Biomass is often considered to be a carbon neutral energy source, because plant matter is produced from atmospheric CO_2 through photosynthesis. Although biomass is advantageous in several ways, the carbon savings, which are affected by the agricultural practices, for starch-crop-based bioethanol fermentation are doubtful. The life-cycle analysis indicates that the energy consumed in cultivation, transportation and conversion of biomass into bioethanol may be greater than the energy contained in the resulting fuel.[10,11] According to a more recent study, bioethanol has a positive net energy when the conversion by-products are accounted for properly.[12] The study, however, estimated that ~42 joules (J) of energy from fossil fuels will be consumed to produce 100 J of ethanol from corn through fermentation.

The more advanced cellulosic ethanol production technique, which is under development, converts cellulose such as agricultural residues, forestry wastes, municipal wastes, paper pulp, and fast-growing prairie grasses into ethanol. As a result of the significantly reduced feedstock cost, the cellulosic ethanol production process can be more economical than traditional biofuel production techniques. Moreover, the energy input for generating the biofuel potentially can be reduced, leading to reduction in net CO_2 emissions.[13] There are, however, technological challenges in the cellulosic biomass pretreatment prior to fermentation. The thermochemical conversion, such as gasification (as in coal gasification), of cellulosic biomass has been considered an attractive approach to generating not only biofuels but also biochemicals and electricity.

Wind, as another source of renewable energy, is used mainly for electricity generation through turbines on wind farms. Wind power can generate electricity at ~5.6 cents per kilowatt-hour.[4] Under the current tax credit subsidy of 1.9 cents per kilowatt-hour (in 2006 dollars) in the United States, wind power is economically competitive with coal-fired power plants. Within the last decade, the global generation of wind power has increased at an average rate of more than 25% per year.[14] The global capacity of wind turbines reached a record high of 73.9 GW at the end of 2006.[15] The major drawbacks of wind power are its intermittency and highly variable nature, which imposes difficult challenges on grid management. Wind turbines also can be noisy and visually intrusive, but the offshore installation option (turbines installed more than 10 km away from shore) and the recently proposed airborne turbine option[16] would eliminate these aesthetic concerns.

The sum of the solar power that reaches the earth's surface is estimated to be more than 5,000 times the current world energy consumption, and solar electric generation has a higher average power density than any other renewable energy source.[17] Solar energy often is used to generate electricity via photovoltaic cells (solar cells) or heat engines (steam engines or Stirling engines). Apart from electricity generation, solar energy also can be converted into chemical energy such as hydrogen and syngas through solar chemical processes.[18] The major disadvantage of solar power, however, is the high cost of the photovoltaics, which leads to the electricity generated from solar power costing approximately four times that of electricity generated from fossil fuels.[14] The solar chemical processes are still under demonstration in the prototype phase.

Although renewable energy sources are attractive from the environmental viewpoint, they face complex constraints for large-scale application. Even when both the decrease in renewable energy costs and the increase in fossil fuel prices are taken into account, only approximately 8.5% (see Figure 1.1) of the total energy demands in 2030 are projected to come from renewable sources. For primarily economic reasons, fossil fuels, including crude oil, natural gas, and coal, will continue to play a dominant role in the world's energy supply for the foreseeable future.

1.1.2 Fossil Energy Outlook

Among various fossil energy sources, oil is expected to maintain its leading status and its consumption will increase for the foreseeable future. Compared with natural gas and coal, crude oil is relatively easy to be pumped, transported, and processed into high-energy density liquid fuels and chemicals. The 2008 British Petroleum (BP) energy review[19] reported the estimated total oil reserves to be 1.24 trillion barrels, with more than 60% of these reserves located in the Middle East, but the high crude oil prices[1] and limited oil reserves are expected to decrease the share of crude oil in the overall energy supply from 37% to 33%.[1]