ENERGY CONVERSION ENGINEERING

Towards Low CO_2 Power and Fuels

AHMED F. GHONIEM

ENERGY CONVERSION ENGINEERING

This unique textbook equips students with the theoretical and practical tools needed to model, design, and build efficient and clean low-carbon energy systems. Students are introduced to thermodynamics principles, including chemical and electrochemical thermodynamics, moving on to applications in real-world energy systems, demonstrating the connection between fundamental concepts and theoretical analysis, modeling, application, and design. Topics gradually increase in complexity, nurturing student confidence as they build toward the use of advanced concepts and models for low- to zero-carbon energy conversion systems. The textbook covers conventional and emerging renewable energy conversion systems, including efficient fuel cells, carbon capture cycles, biomass utilization, geothermal and solar thermal systems, hydrogen, and low-carbon fuels. Featuring numerous worked examples, over 100 multi-component homework problems, and online instructor resources including a solutions manual, this textbook is the perfect teaching resource for an advanced undergraduate and graduate-level course in energy conversion engineering.

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To the memory of my mother, Fatima Fouad Hussain

And to my wife, Elizabeth

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Preface

In the early 2000s I started thinking about the next set of challenges to face us. After much reading and discussions with colleagues in my own and other disciplines (a short sabbatical was helpful), I concluded that it would be energy and its environmental impact. Not the lack of resources – conventional and non-conventional – but the rapid rise in consumption and increase of carbon dioxide concentration in the atmosphere. Not that it was a new challenge, either; many studies had concluded the same, over decades. I decided to expand my research portfolio to work on potential solutions, and introduced a senior undergraduate–graduate subject that we called "Fundamentals of Advanced Energy Conversion." The course focuses on energy conversion engineering, considering thermal, mechanical, chemical, and electrical energy forms, starting with fundamental principles and tools of analysis, and expanding toward systems. The course has not been solely about CO_2 reduction in energy and power systems, but this is an important theme that runs through the material. I cover material needed to evaluate the efficiency and CO_2 production in power plants, alternative and more efficient power plant designs including electrochemical systems, renewable concepts such as concentrated solar thermal, geothermal, and biomass, CO_2 capture-based power plants, and alternative fuels production and utilization, such as with hydrogen. The course includes an introduction to nuclear energy, wind, photovoltaics, and energy storage. I wrote lecture notes to help the students follow our coverage. These notes grew into this textbook, after many iterations that included help from students, associates, and colleagues.

While energy systems have relied mostly on burning fossil fuels to produce heat/thermal energy and converting this to work (then electricity by driving generators), things are changing, and the material in this book covers some of these changes. Newer energy conversion processes incorporate more machinery and other devices to improve efficiency, reduce CO_2 emission, capture CO_2, convert chemical energy to electricity directly, store energy in different forms, convert hydrocarbon to other fuels, produce hydrogen by reforming, thermolysis or electrolysis, and more. It is important to expose students studying energy conversion, at an early stage, to elements of general thermodynamics, including availability analysis and chemical and electrochemical thermodynamics, to broaden their perspectives as to what is possible, and to use examples of existing systems and systems under development to encourage them to think beyond systems covered in introductory courses. The application of this generalized treatment to power plants for efficient electricity production using chemical energy (fossil or renewable) and heat (from conventional or renewable sources) can follow. Beyond this, it is important to address the growing challenge of global warming by, besides emphasizing carbon-free energy, covering concepts related to carbon capture and storage. For this reason, introduction to gas separation processes and how they integrate with energy conversion in power plants is needed.

An underlying theme in the class, and in the coverage throughout this book, is energy conversion for electricity (power) production in a carbon-constrained world in which fossil fuels will continue to be used, renewable energy utilization will expand, nuclear energy may also grow, and integration/coproduction will be practiced. Thus, the overall theme is the conversion of thermal and chemical energies to work, efficiently and with reduced CO_2 release into the atmosphere. The focus of the coverage is on power plant fundamentals, or the power island part of the plant. In a carbon-constrained world, conversion efficiency is at a premium and hence all systems must be designed to operate near their ideal limit by reducing entropy production/exergy destruction. Thus, fundamental principles governing this near-ideal behavior are emphasized. These fundamental principles are very important and must be made clear first using simple systems, then discussed again within the context of complex systems. Efficiency can also be gained by integrating or combining different conversion subsystems, or using direct conversion – that is, skipping the production of mechanical work. Integrating power plants with chemical processes for gas separation is important for CO_2 capture designs. And a deeper understanding of the underlying chemistry is important for both, and in discussion of conversion of biomass to energy and fuels.

Chapter 1 frames the overall challenge of energy conversion by reviewing sources, consumption, and environmental concerns, especially as related to CO_2 emissions, accumulation in the atmosphere, and associated global warming. Evidence of growing consumption of energy, especially fossil fuels, and projections supporting the same trend in the intermediate future is shown. CO_2 emissions by fuel and sector (power generation, transportation, industry, etc.) are also used to prioritize intervention options, and international agreements to cap emissions show the urgency of action. Increased electrification of transportation and the economy overall adds more urgency to improving the efficiency and reducing the carbon intensity (CO_2 emission per unit of electricity generated) from power plants, the focus of this book.

While the book focuses on thermodynamics and chemistry (or thermochemistry) fundamentals used extensively in the analysis of existing energy systems and new higher-efficiency and low-CO_2 designs, it expands on system design to include recent studies of complex power plants that can capture CO_2 while burning gaseous and solid fuels. The coverage goes beyond the constraints of "heat-to-work" that most mechanical engineering students are familiar with in their undergraduate studies. Thus, fundamentals of chemical and electrochemical thermodynamics are treated in separate chapters which assume no prior introduction to these topics. A later chapter is dedicated to gas separation processes used in air separation, fuel reforming and hydrogen production, CO_2 separation from combustion gases, and more, and following chapters show how these processes are integrated in power plants, and their impact on efficiency. Solved examples are used to show how simplifying assumption can be used to make quick estimates, and very detailed analyses using computer simulations are used to show how to make more accurate calculations.

The book can be loosely divided into four parts: fundamentals in Chapters 2–4; analysis of power plant systems using conventional and renewable energy in Chapters 5–9; power plants for carbon capture and sequestration in Chapters 10–13; and biomass energy in Chapter 14. In each chapter, coverage gets progressively more specialized toward the end of the chapter, and coverage in the book overall gets more advanced toward the later parts. While in most chapters the emphasis is on using principles of thermodynamics to analyze the performance of simple and complex energy systems, in a couple of chapters I cover material related to kinetics and transport to highlight the need for non-equilibrium effects while estimating the performance of some systems (fuel cells in Chapter 7) and reactors (biomass gasification in Chapter 14). Some instructors can skip these sections (and others) without loss of continuity as desired. Especially in later chapters, I include some state-of-the-art systems and concepts, such as membrane reactors and chemical looping for combustion and gasification, some still at the research stage, to show recent progress and innovations in the field.

Chapters 2–4 cover the fundamentals of thermodynamics, chemical thermodynamics, and electrochemical dynamics, starting with basic concepts of mass and energy conservation, equilibrium, and entropy as a property of matter. These concepts are gradually generalized beyond thermal energy, to chemical energy to electrochemical energy. In the latter, charge conservation, direct conversion, and cell components are introduced.

Chapter 2 is essentially a review of the first and second laws, availability concepts, and their elementary applications. It starts with a quick review of thermodynamics with a formulation that focuses on evaluating the efficiency of heat-to-work conversion, that is availability or exergy analysis. It also reviews gas mixtures and entropy of mixing as an introduction to gas separation and its application in removing CO_2 from hydrocarbon combustion products, or in air separation for oxygen production. Special emphasis is given to the ideal energy of separation as an introduction to gas separation processes (discussed in detail in Chapter 10). It ends with a discussion of liquefaction and its application to hydrogen storage, among other topics. The chapter introduces mass transfer equilibrium and the concept of chemical potential. It reviews and extends the concept of thermodynamic efficiency beyond heat engines, an area revisited frequently in the rest of the book.

Chapter 3 covers chemical thermodynamics – that is, mass and energy conservation in chemical reactions and their application to combustion and thermochemical processes for the conversion of chemical energy to thermal energy and vice versa. Most students will have been introduced to chemical thermodynamics before, but will see its applications beyond combustion and in fuel reforming, hydrogen production, and water splitting in this chapter. Extension to the application of the second law is used to introduce equilibrium and the calculation of mixture composition under given constraints. Again, use of this powerful concept in new and conventional energy applications is explored using several examples and ongoing research. Extensions of equilibrium to define conditions under which maximum conversion efficiency of a "chemical engine" is achieved is also explored. This sets the stage for covering electrochemical thermodynamics. The chapter also seeks a deeper understanding of thermochemistry by discussing applications in syngas production and conversion to other chemicals, which is covered in more detail in later chapters.

Chapter 4 covers chemical reactions that involve charge exchange or transfer – that is, electrochemical reactions and reduction–oxidation or redox pairs. With the growing importance of fuel cells and “chemical engines” that convert chemical energy directly to work, it is important to expose students of energy conversion to fuel cells and batteries, where the whole operation is governed by electrochemical reactions. Conservation is extended beyond mass and energy and into charges in each chemical reaction. Work obtained from a chemical reaction, under equilibrium conditions, is the Gibbs free energy of the reaction. The same calculations are used to derive expressions for the voltage across the electrodes on an electrochemical cell. The chapter also introduces the concept of electrolysis – that is, converting electricity (work) to chemical energy via an electrochemical reaction. These are also related to energy storage (either chemical or electrical).

Chapters 5–9 discuss the “applications” of Chapters 2–4 to systems used in electricity generation (power plants), including fossil and renewable sources (as well as nuclear plant apart from the reactor itself). Several concerns, such as the temperature of the heat source, the overall conversion efficiency, and whether indirect conversion (chemical to heat to mechanical to electrical) or direct (chemical to electrical), are considered. Also addressed is combining conversion approaches or hybridizing different conversion technologies. Of special importance are systems designed to maximize conversion while using low-temperature sources that are typical of “waste heat” or renewable heat sources such as geothermal and solar. In these chapters, most examples and problem sets can be solved using hand calculations with the help of math software, but using equation solvers and packages such as EES (Engineering Equation Solver) should be encouraged.

In Chapters 5 and 6, we use material from Chapter 2 to develop expressions for efficiency of heat-to-power or thermomechanical conversion, first in high-temperature cycles using gas turbines then in intermediate cycles using Rankine cycles and working fluids undergoing phase change. In Chapter 5, simple and higher efficiency Brayton cycles for ideal gas are reviewed. The concept is extended to closed cycles, as well as those using unconventional working fluids such as CO_2, as well as how to enable the cycles to operate at even higher temperatures. Similar coverage is done for Rankine cycles using steam as a working fluid in Chapter 6. The focus is on how to minimize entropy generation (or exergy destruction) and improve efficiency. Pinch-point analysis is introduced and supercritical cycles are discussed for steam and CO_2 working fluids. Organic Rankine cycles play an important role in low-temperature applications and waste heat recovery. Finally, cooling and its impact on the cycle efficiency are discussed.

In Chapter 7, we go back to electrochemical conversion and cover elements of fuel cell operation, including electrochemical kinetics and charge transfer, and their impact of fuel cell efficiency. This is one of a few places in the book where we cover finite rate processes (kinetics and transport) and their impact on the operation of the conversion system, with sufficient detail so as to derive expressions for efficiency that account for these loss mechanisms. Relations are obtained between the finite current, cell voltage, and overall conversion efficiency. The chapter also summarize some of the most popular fuel cells and their performances. The emphasis is on conversion efficiency under different operating conditions and the impact of the cell design on losses.

Chapter 8 explores how to combine more than one cycle and/or a cycle with a fuel cell to improve the overall conversion efficiency. The traditional combined Brayton–Rankine cycle is covered, with the emphasis on how to use the pinch point to improve its efficiency. Another new concept considered here is oxy-combustion cycles in which fuel is burned in a mixture of oxygen and recycled CO_2 and/or water. These enable CO_2 capture, and while discussed in detailed in a later chapter, they are introduced here as an application of traditional cycle analysis. Two forms of oxy-combustion cycles are discussed: a combined cycle with the Brayton cycle operating on CO_2 as a working fluid, and a cycle with significant water recycling. Finally, hybridizing conventional cycles with fuel cells is also discussed.

Chapter 9 extends cycle analysis to renewable energy sources where low- and intermediate-temperature sources impose further constraints on the system design, starting with a brief characterization of each source and its geographic availability. We start with geothermal energy, where the source is at low temperature. In some cases, “collecting” the heat and the power island must be considered while maximizing the efficiency. Also discussed are approaches to hybridizing these sources and integrating them with fossil energy to overcome the intermittency problem and avoid the need for expensive storage. We describe interesting developments in integration involving solar reforming and its impact on efficiency.

Chapters 10, 11, and 13 focus on how to use fossil fuels for power generation while limiting CO_2 release into the atmosphere, essentially exploring carbon (dioxide) capture technologies (known as CCS for carbon capture and sequestration/storage, or CCUS for carbon capture use and storage) in ways compatible with the fuel and the cycle. Since a fuel must still be burned, these approaches have been classified into post-combustion, oxy-combustion, and pre-combustion, depending on where the CO_2 is separated. Since gas separation is an essential part of the system, the section starts with a chapter dedicated to reviewing these processes, and in particular their energy requirements, in order to assess how incorporating these processes in power cycles could affect their efficiency.

In Chapter 10, a new topic is introduced, namely gas separation, with the aim to discuss some of the related fundamentals before introducing power cycles that have been proposed for CO_2 capture (CCS or CCUS). Material in this chapter is likely to be new for mechanical engineering students, although most chemical engineering students should have been introduced to some of these concepts previously. The coverage is limited to some of the essential fundamentals used to model the separation process, which can be used to estimate the energy required under some operating conditions. The chapter covers absorption using liquid solvents, both physical and chemical, adsorption using solid sorbents, cryogenic separation, and membrane (porous and dense) separation. Some examples are given for how these processes are applied to different energy systems (including but also beyond power plants).

Chapters 11 discusses carbon (dioxide) capture from natural gas power plants, starting with classification of the different approaches followed by details for each. Simplified models that have been proposed are discussed and examples for the impact on efficiency penalty are solved. Many proposed power plant cycles that enable CO_2 capture via pre-combustion, post-combustion, and oxy-combustion are discussed. These include the "water" and Graz cycles, among others. Advanced materials on novel concepts including chemical looping combustion and membrane reactors in which air separation and combustion are integrated are also covered. Analytical treatment using simplified assumptions is used, and the results of analysis using computer models that relax these assumptions are also shown.

Chapters 12 and 13 focus on coal, one of the most widely used fuels for electricity production, and the one with the highest CO_2 emissions per unit of electricity produced. Chapter 12 starts with source characterization. Conventional systems, using boilers, and new plant designs that start with gasification in an integrated gasification combined cycle (IGCC) are reviewed, emphasizing the environmental performance of both. Because of its significance in both power plants and fuel and chemicals production, coal gasification is discussed in more detail, including types of gasifiers and processes to transform syngas to chemicals and fuels (these concepts extend beyond coal; any source of syngas can be used for the production of higher-value chemicals). In Chapter 13, CCS applications are discussed starting with post-capture using amines and membranes. Oxy-combustion of coal under atmospheric or higher pressure have received much attention and hence their results are reviewed. Pre-capture using gasification is also discussed, especially for applications using different feed technologies and with membrane separation of hydrogen. Finally, chemical looping combustion of coal is reviewed.

In Chapter 14 the topic of biomass is covered, starting with characterization, a quick review of organic chemistry, the composition of biomass and its derivatives, their constituents, and their energy contents. Conversion of biomass to thermal energy and biofuels is often characterized as biochemical or thermochemical, with subcategories in each. Mass and energy balances in bioconversion are shown in some detail, and the efficiency and products of each are presented. In thermochemical conversion, the dependency of the products on the process temperature (and heating rate) are shown, and reactor systems for low-temperature torrefaction and intermediate-temperature gasification are described. The chapter ends with a detailed gasification model for biomass in fluidized beds – an exercise combining single particle conversion with bed material heat and mass transport. This section, being the last in the book, involves the most complex modeling section, which is likely to go beyond what can be covered in a course. Nevertheless, it sets the stage for follow-up coverage.

Knowledge of college-level physical chemistry and introductory-level engineering thermodynamics is assumed, and the book can be used in senior-level undergraduate thermodynamics as well as energy conversion classes. More of the material can be covered in graduate courses. In my experience it is not possible to cover the material of the entire book in one semester, but one may choose to skip parts in each chapter, especially toward the end of the chapter, without losing continuity. It is also possible to skip entire chapters if they do not fit in the curriculum (e.g., Chapter 4 on equilibrium treatment of fuel cells or Chapter 7 on finite current performance, or Chapters 10, 11, and 13 on gas separation and carbon capture). There are plenty of solved examples to help the student, as well as homework problems for assignments. For doing the homework, familiarity with equation solvers packages is very helpful, and software such as EES will be very productive. Students familiar with ASPEN will find it useful while going through the examples in the later chapters, but it is not necessary or required.

The class at MIT has been taken by students mostly from mechanical engineering, but also from chemical engineering, nuclear engineering, material science and engineering, and occasionally by students from the school of science.

An early version of the PowerPoint slides used in teaching the class can be found on MIT OpenCourseWare. This will be replaced soon with a much-updated version that I used in 2019. In the class I teach at MIT, I ask the students to do a term project – some samples of these can also be found on the website.

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Nomenclature

A

Helmholtz free energy

a

Surface area

AF

Air-fuel ratio

$A_{f,b}$

Pre-exponential factor in the rate constant

A_s

Surface area

C_l

Speed of light

CV

Control volume

c

Molar concentration

c_p

Specific heat at constant pressure

d

Diameter

D

Diffusion coefficient

E

Total stored energy

E_a

Activation energy

e

Total specific internal energy

e^-

Electron

$\boldsymbol{F}$

Force

$\mathfrak{I}_a$

Faraday's number

FU

Fuel utilization

g_r

Gravitational acceleration

G

Gibbs free energy

H

Enthalpy

$\mathbf{H}$

Magnetic field

h

Specific enthalpy

HR

Heat rate

h_{conv}

Convective mass transfer coefficient

He

Henry's constant

I

Irreversibility

I

Number of different chemically distinct components

I

Total current

i

Current density, current per unit area

J

Flux of species, uncharged and charged

k_s

Elastic constant

KE

Total kinetic energy

K_p

Pressure-based equilibrium constant

k

Reaction rate constant

k

Isentropic index

K

Equilibrium constant

L

Length

$\dot{m}$

Mass flow rate

M

Molecular weight

MW

Molecular weight

m

Mass

N_a

Avogardo’s number

N

Number of molecules

$\dot{N}$

Molar flux

n

Number of moles

n

Unit vector

$\dot{n}$

Molar flow rate

n_e

Number of electrons in an electrochemical reaction

p

Pressure

PE

Potential energy

$\mathcal{P}$

Power

PP

Pinch point

$\mathcal{P}$

Power per unit area, or power density

Q

Heat transfer

$\tilde{P}_i$

$= D_i/(\mathfrak{R}Tt)$, Permeability (used mostly for porous membranes)

$\tilde{P}_i$

$= (D_i/\mathfrak{R}T)S_i$, Permeability coefficient (used for non-porous membranes)

$\mathfrak{R}$

Universal gas constant

R

Pressure ratio across membrane

$\mathbb{R}$

Resistance

S

Entropy

s