Basic Principles and Calculations in Chemical Engineering

Eighth Edition

BASIC PRINCIPLES AND CALCULATIONS IN CHEMICAL ENGINEERING

EIGHTH EDITION

David M. Himmelblau
James B. Riggs

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This book is dedicated to the memory of
David M. Himmelblau (1923–2011) and his contribution to
the field of chemical engineering.

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PREFACE

This book is intended to serve as an introduction to the principles and techniques used in the field of chemical engineering as well as biological, petroleum, and environmental engineering. Although the range of subjects deemed to be in the province of chemical engineering has broadened over the last twenty years, the basic principles of this field of study remain the same. This book presents the foundation of specific skills and information that are required for the successful undergraduate and postgraduate study of chemical engineering as well as the professional practice of chemical engineering. Moreover, your remaining chemical engineering classes will rely heavily on the skills that you will develop in this course: your ability to solve abstract problems as well as the application of material and energy balances. One can view the study of the field of chemical engineering as a tree with material and energy balances being the trunk and the subjects of thermodynamics, fluid flow, heat transfer, mass transfer, reactor kinetics, process control, and process design being the branches off the trunk. From this perspective, it is easy to see the importance of mastering the material that follows.

The primary objective of this book is to teach you how to systematically formulate and solve material and energy balance problems. More important, you should learn to systematically formulate and solve all types of problems using the methods presented in this text. In addition, this text serves to introduce you to the breadth of processes that chemical engineers work with, from the types of processes found in the refining and chemical industries to those found in bioengineering, nanoengineering, and the microelectronics industries. While the analysis used in this book will be based largely on a macroscopic scale (i.e., representing a complex system as a uniform system), your later engineering courses will teach you how to formulate microscopic material and energy balances that can be used to more completely describe these systems. In fact, you will learn in these classes that to formulate a microscopic balance you only have to apply the balances presented in this textbook to a very small volume inside the process of interest.

This text is organized as follows:

- Part I Introduction: background information (Chapters 1–2)
- Part II Material Balances: how to formulate and solve material balances (Chapters 3–6)
- Part III Gases, Vapors, and Liquids: how to describe gases and liquids (Chapter 7–8)
- Part IV Energy: how to formulate and solve energy balances (Chapters 9–11)

Expecting to "absorb" the information and skills in this text by reading and listening to lectures is a bit naïve. It is well established that one learns by doing, that is, applying what you have been exposed to. In this regard, our text offers a number of resources to assist you in this endeavor. Probably the most important resources for your study of this material are the Self-Assessment Tests at the end of each section in the book. In particular, the Self-Assessment questions and problems are particularly valuable because by answering them and comparing your answers to the answers posted in Appendix A, you can determine what it is that you do not fully understand, which is quite an important piece of information. A number of valuable resources are provided to you on the CD that accompanies this book, which includes the physical property software, which provides timesaving access to physical properties for over 700 compounds and elements; Polymath for solving sets of equations, which comes with a 15-day free trial; and the Supplemental Problems Workbook with over 100 solved problems and process equipment descriptions. For more specific information on the resources available with this textbook and the accompanying CD, refer to the "Read Me" section that follows.

It is our sincere hope that this textbook and materials not only inspire you to continue to pursue your goal to become a chemical engineer, but also make your journey toward that goal easier.

Jim Riggs
Austin, Texas

READ ME

Welcome to *Basic Principles and Calculations in Chemical Engineering.* Several tools exist in the book in addition to the basic text to aid you in learning its subject matter. We hope you will take full advantage of these resources.

Learning Aids

1. Numerous examples worked out in detail to illustrate the basic principles
2. A consistent strategy for problem solving that can be applied to any problem
3. Figures, sketches, and diagrams to provide a detailed description and reinforcement of what you read
4. A list of the specific objectives to be reached at the beginning of each chapter
5. Self-Assessment Tests at the end of each section, with answers so that you can evaluate your progress in learning
6. A large number of problems at the end of each chapter with answers for about a third of them provided in Appendix E
7. Thought and discussion problems that involve more reflection and consideration than the problem sets cited in item 6
8. Appendixes containing data pertinent to the examples and problems
9. Supplementary references for each chapter
10. A glossary following each section

11. A CD that includes some valuable accessories:
   a. Polymath—an equation-solving program that requires minimal experience to use. Polymath is provided with a 15-day free trial. Details on the use of Polymath are provided. A special web site gives significant discounts on educational versions of Polymath for various time periods: 4 months, 12 months, and unlimited use: www.polymath-software.com/himmelblau
   b. Software that contains a physical properties database of over 700 compounds.
   c. A Supplementary Problems Workbook with over 100 completely solved problems and another 100 problems with answers.
   d. The workbook contains indexed descriptions of process equipment and animations that illustrate the functions of the equipment. You can instantly access these pages if you want to look something up by clicking on the page number.
   e. Problem-solving suggestions including checklists to diagnose and overcome problem-solving difficulties that you experience.
   f. Additional chapters and appendixes

12. A set of steam tables (properties of water) in both SI and American Engineering units in the pocket in the back of the book

Scan through the book now to locate these features.

Good Learning Practices (Learning How to Learn)

You cannot put the same shoe on every foot.
Publilius Syrus

Those who study learning characteristics and educational psychologists say that almost all people learn by practicing and reflecting, and not by watching and listening to someone else telling them what they are supposed to learn. “Lecturing is not teaching and listening is not learning.” You learn by doing.

Learning involves more than memorizing

Do not equate memorizing with learning. Recording, copying, and outlining notes or the text to memorize problem solutions will be of little help in really understanding how to solve material and energy balance problems. Practice will help you to be able to apply your knowledge to problems that you have not seen before.

Adopt good learning practices

You will find that skipping the text and jumping to equations or examples to solve problems may work sometimes but in the long run will lead to frustration. Such a strategy is called "formula-centered" and is a very poor way to approach a problem-solving subject. By adopting it, you will not be able to generalize, each problem will be a new challenge, and the interconnections among essentially similar problems will be missed.

Various appropriate learning styles (information processing) do exist; hence you should reflect on what you do to learn and adopt techniques best suited to you. Some students learn through thinking things out in solitary study. Others prefer to talk things through with peers or tutors. Some focus best on practical examples; others prefer abstract ideas. Sketches and graphs used in explanation usually appeal to most people. Do you get bored by going over the same ground? You might want to take a battery of tests to assess your learning style. Students often find such inventories interesting and helpful. Look in the CD that accompanies this book to read about learning styles.

Whatever your learning style, what follows are some suggestions to enhance learning that we feel are appropriate to pass on to you.

Suggestions to Enhance Learning

1. Each chapter in this book will require three or more hours to read, assimilate, and practice your skills in solving pertinent problems. Make allowance in your schedule so that you will have read the pertinent material **before** coming to class. Instead of sitting in class and not fully understanding what your professor is discussing, you will be able to raise your understanding to a much higher level. It is not always possible, but it is one of the most efficient ways to spend your study time.
2. If you are enrolled in a class, work with one or more classmates, if permitted, to exchange ideas and discuss the material. But do not rely on someone to do your work for you.
3. Learn every day. Keep up with the scheduled assignments—don't get behind, because one topic builds on a previous one.
4. Seek answers to unanswered questions right away.
5. Employ active reading; that is, every five or ten minutes stop for one or two minutes and summarize what you have learned. Look for connecting ideas. Write a summary on paper if it helps.

Suggestions for How to Use This Book Effectively

How can you make the best use of this book? Read the objectives before and after studying each section. Read the text, and when you get to an example, first cover up the solution and try to solve the stated problem. Some people, those who learn by reading concrete examples, might look at the examples first and then read the text. After reading a section, solve the self-assessment problems at the end of the section. The answers are in Appendix A. After completing a chapter, solve a few of the problems listed at the end of the chapter. R. P. Feynman, the Nobel laureate in physics, made the point: "You do not know anything until you have practiced." Whether you solve the problems using hand calculators or computer programs is up to you, but use a systematic approach to formulating the information leading to a proper solution. Use the supplement on the CD in the back of the book (print it out if you need to) as a source of examples of additional solved problems with which to practice solving problems.

This book functions as a savings account—what you put in, you get out, with interest.

ACKNOWLEDGMENTS

We are indebted to many former teachers, colleagues, and students who directly or indirectly helped in preparing this book, and in particular the present edition of it. We want to thank Professor C. L. Yaws for his kindness in making available the physical properties software database that is the basis of the physical properties package in the CD that accompanies our book, and also thanks to Professors M. B. Cutlip and M. Shacham who graciously made the Polymath software available. Far too many instructors using the text have contributed their corrections and suggestions to list them by name. Any further comments and suggestions for improvement of this textbook would be appreciated.

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ABOUT THE AUTHORS

David M. Himmelblau was the Paul D. and Betty Robertson Meek and American Petrofina Foundation Centennial Professor Emeritus in Chemical Engineering at the University of Texas, where he taught for 42 years. He received his B.S. from MIT in 1947 and his Ph.D. from the University of Washington in 1957. He was the author of 11 books and over 200 articles on the topics of process analysis, fault detection, and optimization, and served as President of the CACHE Corporation (Computer Aids for Chemical Engineering Education) as well a Director of the AIChE. His book, *Basic Principles and Calculations in Chemical Engineering*, has been recognized by the American Institute of Chemical Engineers as one of the most important books in chemical engineering.

James B. Riggs earned his B.S. in 1969 and his M.S. in 1972, both from the University of Texas at Austin. In 1977, he earned his Ph.D. from the University of California at Berkeley. Dr. Riggs was a university professor for 30 years, the first five years being spent at West Virginia University and the remainder at Texas Tech University. He was appointed Professor Emeritus of Chemical Engineering at Texas Tech University after he retired in 2008. In addition, he has a total of over five years of industrial experience in a variety of capacities. His research interests centered on advanced process control and online process optimization. During his academic career he served as an industrial consultant and founded the Texas Tech Process Control and Optimization Consortium, which he directed for 15 years. Dr. Riggs is the author of two other popular undergraduate chemical engineering textbooks: *An Introduction to Numerical Methods for Chemical Engineers*, Second Edition, and *Chemical and Bio-Process Control,* Third Edition. He currently resides near Austin in the Texas Hill Country.

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CHAPTER 1

What Are Chemical Engineering and Bioengineering?

Your objectives in studying this chapter are to be able to

1. Appreciate the history of chemical engineering and bioengineering
2. Understand the types of industries that hire chemical and bioengineers
3. Appreciate the diversity of the types of jobs in which chemical and bioengineers engage
4. Understand some of the ways in which chemical and bioengineers can contribute in the future to the resolution of certain of society's problems

Looking Ahead

In this chapter we will present some features of the professions of chemical and bioengineering. First, we will present an overview of the history of these fields. Next, we will consider where graduates of these programs go to work. Finally, we will present types of projects in which chemical and bioengineers might participate now and in the future.

1.1 Introduction

Why did you choose to work toward becoming a chemical or bioengineer? Was it the starting salary? Did you have a role model who was a chemical or bioengineer, or did you live in a community in which engineers were prominent? Or were you advised that you would do well as a chemical or bioengineer because you were adept at math and chemistry and/or biology? In fact, most prospective engineers choose this field without fully understanding the profession (i.e., what chemical and bioengineers actually do and what they are capable of doing). This brief chapter will attempt to shed some light on this issue.

Chemical and bioengineers today hold a unique position at the interface between molecular sciences and macroscopic (large-scale) engineering. They participate in a broad range of technologies in science and engineering projects, involving nanomaterials, semiconductors, and biotechnology. Note that we say "participate" because engineers most often work in multidisciplinary groups, each member contributing his or her own expertise.

1.2 A Brief History of Chemical Engineering

The chemical engineering profession evolved from the industrial applications of chemistry and separation science (the study of separating components from mixtures), primarily in the refining and chemical industry, which we will refer to here as the **chemical process industries (CPI)**. The first high-volume chemical process was implemented in 1823 in England for the production of soda ash, which was used for the production of glass and soap. During the same time, advances in organic chemistry led to the development of chemical processes for producing synthetic dyes from coal for textiles, starting in the 1850s. In the latter half of the 1800s a number of chemical processes were implemented industrially, primarily in Britain.

And in 1887 a series of lectures on chemical engineering which summarized industrial practice in the chemical industry was presented in Britain. These lectures stimulated interest in the United States and to some degree led to the formation of the first chemical engineering curriculum at MIT in 1888. Over the next 10 to 15 years a number of U.S. universities embraced the field of chemical engineering by offering fields of study in this area. In 1908, the American Institute of Chemical Engineers was formed and since then has served to promote and represent the interests of the chemical engineering community.

Mechanical engineers understood the mechanical aspects of process operations, including fluid flow and heat transfer, but they did not have a background in chemistry. On the other hand, chemists understood chemistry and its ramifications but lacked the process skills. In addition, neither mechanical engineers nor chemists had backgrounds in separation science, which is critically important to the CPI. In the United States, a few chemistry departments were training process engineers by offering degrees in industrial chemistry, and these served as models for other departments as the demand for process engineers in the CPI began to increase. As industrial chemistry programs grew, they eventually formed separate degree-granting programs as the chemical engineering departments of today.

The acceptance of the "horseless carriage," which began commercial production in the 1890s, created a demand for gasoline, which ultimately fueled exploration for oil. In 1901, a Texas geologist and a mining engineer led a drilling operation (the drillers were later to be known as "wildcatters") that brought in the Spindletop Well just south of Beaumont, Texas. At the time, Spindletop produced more oil than all of the other oil wells in the United States. Moreover, a whole generation of wildcatters was born, resulting in a dramatic increase in the domestic production of crude oil, which created a need for larger-scale, more modern approaches to crude refining. As a result, a market developed for engineers who could assist in the design and operation of processing plants for the CPI. The success of oil exploration was to some degree driven by the demand for gasoline for the automobile industry, but ultimately the success of the oil exploration and refining industries led to the widespread availability of automobiles to the general population because of the resulting lower cost of gasoline.

These early industrial chemists/chemical engineers had few analytical tools available to them and largely depended upon their physical intuition to perform their jobs as process engineers. Slide rules were used to perform calculations, and by the 1930s and 1940s a number of nomographs were developed to assist them in the design and operation analysis of processes for the CPI. Nomographs are charts that provide a concise and convenient means to represent physical property data (e.g., boiling point temperatures or heat of vaporization) and can also be used to provide simplified solutions of complex equations (e.g., pressure drop for flow in a pipe). The computing resources that became available in the 1960s were the beginnings of the computer-based technology that is commonplace today. For example, since the 1970s **computer-aided design (CAD)** packages have allowed engineers to design complete processes by specifying only a minimum amount of information; all the tedious and repetitive calculations are done by the computer in an extremely short period of time, allowing the design engineer to focus on the task of developing the best possible process design.

During the period 1960 to1980, the CPI also made the transition from an industry based on innovation, in which the profitability of a company depended to a large degree on developing new products and new processing approaches, to a more mature commodity industry, in which the financial success of a company depended on making products using established technology more efficiently, resulting in less expensive products.

Globalization of the CPI markets began in the mid-1980s and led to increased competition. At the same time, developments in computer hardware made it possible to apply process automation (advanced process control, or APC, and optimization) more easily and reliably than ever before. These automation projects provided improved product quality while increasing production rates and overall production efficiency with relatively little capital investment. Because of these economic advantages, APC became widely accepted by industry over the next 15 years and remains an important factor for most companies in the CPI.

Beginning in the mid-1990s, new areas came on the scene that took advantage of the fundamental skills of chemical engineers, including the microelectronics industry, the pharmaceutical industry, the biotechnology industry, and, more recently, nanotechnology. Clearly, the analytical skills and the process training made chemical engineers ideal contributors to the development of the production operations for these industries. In the 1970s, over 80% of graduating chemical engineers took jobs with the CPI industry and government. By 2000, that number had dropped to 50% because of increases in the number taking jobs with biotechnology companies, pharmaceutical/health care companies, and microelectronics and materials companies. The next section addresses the current distribution of jobs for chemical engineers.

1.3 Where Do Chemical and Bioengineers Work?

Table 1.1, which lists the percentages of all chemical engineers by employment sector between 1996 and 2007, shows that the percentage of chemical engineers in these developing industries (pharmaceutical, biomedical, and microelectronics industries) increased from 7.1% in 1997 to 19.9% in 2005.

Chemical engineers are first and foremost process engineers. That is, chemical engineers are responsible for the design and operation of processes that produce a wide range of products from gasoline to plastics to composite materials to synthetic fabrics to computer chips to corn chips. In addition, chemical engineers work for environmental companies, government agencies including the military, law firms, and banking companies.

The trend of chemical engineering graduates taking employment in industries that can be designated as bioengineering is a new feature of the twenty-first century. Not only have separate bioengineering or biomedical departments been established, but some long-standing chemical engineering departments have modified their names to “chemical and bioengineering” to reflect the research and fresh interests of students and faculty.

Table 1.1 Chemical Engineering Employment by Sector (from AIChE Surveys)

	1996	2000	2002	2005	2007
Chemical, industrial gases, rubber, soaps, fibers, glass, metals, paper	33.3	32.5	25.2	28.1	25.5
Food, ag products, ag chemical	4.5	5.1	5.6	5.7	5.0
Energy, petroleum, utilities	14.1	1.9	5.1	4.5	3.7
Electronics, materials, computers	1.4	1.9	5.1	4.5	3.7
Equipment design and construction	13.8	12.6	10.6	12.6	14.3
Environmental, health, and safety	6.4	4.7	4.4	4.2	3.4
Aerospace, automobile	1.1	0.9	1.8	2.0	2.1
Research and development	3.9	3.8	4.4	4.2	3.4
Government	3.6	3.6	3.5	3.7	4.4
Biotechnology	1.5	2.2	2.4	4.4	3.7
Pharmaceutical, health care	4.2	6.5	6.1	8.4	7.6
Professional (including education)	4.7	4.5	8.6	7.0	8.4
Other	7.4	8.6	9.6	-	1.5

A bioengineer uses engineering expertise to analyze and solve problems in chemistry, biology, and medicine. The bioengineer works with other engineers as well as physicians, nurses, therapists, and technicians. Biomedical engineers may be called upon in a wide range of capacities to bring together knowledge from many technical sources to develop new procedures, or to conduct research needed to solve problems in areas such as drug delivery, body imaging, biochemical processing, innovative fermentation, bioinstrumentation, biomaterials, biomechanics, cellular tissue and genetics, system physiology, and so on. They work in industry, hospitals, universities, and government regulatory agencies. It is difficult to find valid surveys of specific companies or topics to classify bioengineering graduates' ultimate locations, but roughly speaking, one-third of graduates go to medical school, one-third continue on to graduate school, and one-third go to work in industry with a bachelor's degree.

1.4 Future Contributions of Chemical and Bioengineering

The solution of many of the pressing problems of society for the future (e.g., global warming, clean energy, manned missions to Mars) will depend significantly on chemical and bioengineers. In order to more fully explain the role of chemical and bioengineers and to illustrate the role of chemical and bioengineers in solving society's technical problems, we will now consider some of the issues associated with carbon dioxide capture and sequestration, which is directly related to global warming.

Because fossil fuels are less expensive and readily available, we would like to reduce the impact of burning fossil fuels for energy, but without significantly increasing the costs. Therefore, it is imperative that we develop low-cost CO_2 capture and sequestration technologies that will allow us to do that.

An examination of Figure 1.1 shows the sources of CO_2 emissions in the United States. What category would you attack first? Electric power generation is the number-one source. Transportation sources are widely distributed. No doubt power generation would be the most fruitful.

Carbon capture and storage (CCS) is viewed as having promise for a few decades as an interim measure for reducing atmospheric carbon emissions relatively quickly and sharply while allowing conventional coal-fired power plants to last their full life cycles. But the energy costs, the disposal challenges, and the fact that adding CCS to an existing plant actually boosts the overall consumption of fossil fuels (because of the increased consumption of energy to collect and sequester CO_2, more power plants have to be built so that the final production of net energy is the same) all suggest that CCS is not an ultimate solution.

One interim measure under serious consideration for CCS that might allow existing conventional coal-fired power plants to keep producing until they can be phased out at the end of their full lives involves various known technologies. An existing plant could be retrofitted with an amine scrubber

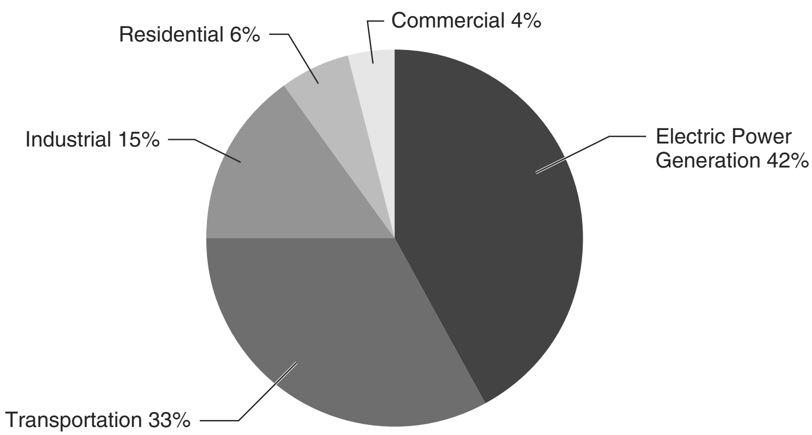

Figure 1.1 Major sources of carbon dioxide emissions in the United States excluding agriculture

to capture 80% to 95% of CO_2 from combustion gases; the CO_2 would then be condensed into a liquid that would be transported and stored somewhere indefinitely where it could not leak into the atmosphere. If several hundreds or thousands of CCS systems were deployed globally this century, each capturing 1 to 5 metric tons of CO_2 per year collectively, they could contribute between 15% and 55% of the worldwide cumulative mitigation effort.

However, the engineering challenges are significant. First, CCS is an energy-intensive process, so power plants require significantly more fuel to generate each kilowatt-hour of electricity produced for consumption. Depending on the type of plant, additional fuel consumption ranges from 11% to 40% more—meaning not only in dollars, but also in additional fossil fuel that would have to be removed from the ground to provide the power for the capture and sequestration, as well as additional CO_2 needing sequestration by doing so. Current carbon-separation technology can increase the price tag of producing electricity by as much as 70%. Put another way, it costs about $40 to $55 per ton of carbon dioxide. The annual U.S. output of carbon dioxide is nearly 2 billion tons, which indicates the economic scale of the problem. The U.S. Department of Energy is working on ways to reduce the expenses of separation and capture.

By far, the most cost-effective option is partnering CCS not with older plants, but with advanced coal technologies such as integrated-gasification combined-cycle (IGCC) or oxygenated-fuel (oxyfuel) technology. There is also a clear need to maximize overall energy efficiency if CCS itself is not merely going to have the effect of nearly doubling both demand for fossil fuels and the resultant CO_2 emitted.

Once the CO_2 has been captured as a fairly pure stream, the question is what to do with it that is economical. In view of the large quantity of CO_2 that must be disposed of, disposal, to be considered a practical strategy, has to be permanent.

Any release of gas back into the atmosphere not only would negate the environmental benefits, but it could also be deadly. In large, concentrated quantities, carbon dioxide can cause asphyxiation. Researchers are fairly confident that underground storage will be safe and effective.

This technology, known as carbon sequestration, is used by energy firms as an oil-recovery tool. But in recent years, the Department of Energy has broadened its research into sequestration as a way to reduce emissions. And the energy industry has taken early steps toward using sequestration to capture emissions from power plants.

Three sequestration technologies are actively being developed: storage in saline aquifers in sandstone formations [refer to S. M. Benson and T. Surles, "Carbon Dioxide Capture and Storage," *Proceed. IEEE*, **94**, 1795 (2006)], where the CO_2 is expected to mineralize into carbonates over time;

injection into deep, uneconomic coal seams; and injection into depleted or low-producing oil and natural-gas reservoirs.

Preliminary tests show that contrary to expectations, only 20% maximum of CO_2 precipitates form carbonate minerals, but the majority of the CO_2 dissolves in water. Trapping CO_2 in minerals would be more secure, but CO_2 dissolved in brine is an alternate disposal outcome.

Other suggestions for the reduction of CO_2 emissions include permanent reduction in demand, chemical reaction, various solvents, use of pure O_2 as the oxidant, and so on. See J. Ciferno et al., *Chemical Engineering Progress*, 33–41 (April, 2009), and F. Princiotta, "Mitigating Global Climate Change through Power-Generation Technology," *Chemical Engineering Progress*, 24–32 (November, 2007), who have a large list of possible avenues of approach. The bottom line is that a solution for CO_2 emissions reduction is not just a matter of solving technical problems but a matter of cost and environmental acceptance. Based on the nature of these challenges, it is easy to see that chemical and bioengineers will be intimately involved in these efforts to find effective solutions.

1.5 Conclusion

The chemical engineering profession evolved from society's need for products and energy. Today and into the future, chemical and bioengineers will continue to meet society's needs using their process knowledge, their knowledge of fundamental science, and their problem-solving skills.

Looking Back

In this chapter we reviewed the history of chemical engineering and presented information on the current and projected future status of the profession.

Glossary

Chemical process industries (CPI) The chemical and refining industries.

Computer-aided design (CAD) packages Software programs that are used to design and/or analyze systems including chemical processes.

Web Site

www.pafko.com/history/h_whatis.html

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