GREEN CHEMISTRY AND CHEMICAL ENGINEERING

CHEMICALS FROM BIOMASS

Integrating Bioprocesses into Chemical Production Complexes for Sustainable Development

DEBALINA SENGUPTA

RALPH W. PIKE

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Series Preface

Green Chemistry and Chemical Engineering

The subjects and disciplines of chemistry and chemical engineering have encountered a new landmark in the way of thinking about, developing, and designing chemical products and processes. This revolutionary philosophy, termed "green chemistry and chemical engineering," focuses on the designs of products and processes that are conducive to reducing or eliminating the use and generation of hazardous substances. In dealing with hazardous or potentially hazardous substances, there may be some overlaps and interrelationships between environmental chemistry and green chemistry. While environmental chemistry is the chemistry of the natural environment and the pollutant chemicals in nature, green chemistry proactively aims to reduce and prevent pollution at its very source. In essence, the philosophies of green chemistry and chemical engineering tend to focus more on industrial application and practice rather than academic principles and phenomenological science. However, as both chemistry and chemical engineering philosophy, green chemistry and chemical engineering derives from and builds upon organic chemistry, inorganic chemistry, polymer chemistry, fuel chemistry, biochemistry, analytical chemistry, physical chemistry, environmental chemistry, thermodynamics, chemical reaction engineering, transport phenomena, chemical process design, separation technology, automatic process control, and more. In short, green chemistry and chemical engineering is the rigorous use of chemistry and chemical engineering for pollution prevention and environmental protection.

The Pollution Prevention Act of 1990 in the United States established a national policy to prevent or reduce pollution at its source whenever feasible. And adhering to the spirit of this policy, the Environmental Protection Agency (EPA) launched its Green Chemistry Program to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. The global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international community of science, engineering, academia, industry, and governments in all phases and aspects.

Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as green solvent in separation technologies; application of supercritical water oxidation for destruction of harmful substances; process integration with carbon dioxide sequestration steps; solvent-free synthesis of chemicals and polymeric materials; exploitation of biologically degradable materials; use of aqueous hydrogen peroxide for efficient oxidation; development of hydrogen proton exchange membrane (PEM) fuel cells for a variety of power generation needs; advanced biofuel production; devulcanization of spent tire rubber; avoidance of the use of chemicals and processes causing generation of volatile organic compounds (VOCs); replacement of traditional petrochemical processes by microorganism-based bioengineering processes; replacement of chlorofluorocarbons (CFCs) with nonhazardous alternatives; advances in the design of energy efficient processes; use of clean, alternative, and renewable energy sources in manufacturing; and much more. This list, even though it is only a partial compilation, is undoubtedly growing exponentially.

This book series on green chemistry and chemical engineering by CRC Press/Taylor & Francis Group is designed to meet the new challenges of the twenty-first century in the chemistry and chemical engineering disciplines by publishing books and monographs based on cutting-edge research and development to the effect of reducing adverse impacts on the environment by chemical enterprise. And in achieving this, the series will detail the development of alternative sustainable technologies that will minimize the hazard and maximize the efficiency of any chemical choice. The series aims at delivering the readers in academia and industry with an authoritative information source in the field of green chemistry and chemical engineering. The publisher and its series editor are fully aware of the rapidly evolving nature of the subject and its long-lasting impact on the quality of human life in both the present and future. As such, the team is committed to making this series the most comprehensive and accurate literary source in the field of green chemistry and chemical engineering.

Sunggyu Lee

Preface

The vision for this book is the development of new plants that are based on renewable resources that supply the needed goods and services for existing petrochemical plants. The vision includes converting existing plants to ones that are based on renewable resources requiring nonrenewable resource supplements. Identifying and designing new chemical processes that use renewable feedstock as raw materials and show how these processes can be integrated into existing chemical production complexes are key to having a sustainable chemical industry. Also, identifying and designing new industrial processes that use carbon dioxide as a raw material are an important option in mitigating the effects of global warming.

The existing plants in the chemical production complex in the Lower Mississippi River Corridor produce a wide range of basic and specialty chemicals, monomers, and polymers. They were used as a base case to demonstrate the integration of new, biomass-based plants into an existing infrastructure of plants. Potential bioprocesses were evaluated based on selection criteria, and simulations of these bioprocesses were performed in Aspen HYSYS®. The bioprocesses were then converted to input–output block models. A superstructure of plants was formed, which was optimized to obtain the optimal configuration of existing and new plants (chemical complex optimization).

The optimal configuration of plants was based on economic, environmental, and sustainable costs and credits (triple bottom line). The optimal solution to this mixed integer, multicriteria, nonlinear programming problem was obtained using global solvers. Detailed results were provided that showed a triple bottom line increase, raw material cost decrease, utility cost increase, and pure carbon dioxide vented to the atmosphere reduced to zero in the optimal structure. Five case studies were performed demonstrating the versatility of the analysis, and the optimization software, Chemical Complex Analysis System, can be downloaded.

A methodology for the optimal integration of bioprocesses in an existing chemical production complex was developed and demonstrated. This methodology can be used to evaluate energy-efficient and environmentally acceptable plants and have new products from greenhouse gases. Based on these results, the methodology could be applied to other chemical complexes for new bioprocesses, reduced emissions, and energy savings. Detailed process designs for fermentation, transesterification, anaerobic digestion, gasification, and algae oil production can be downloaded for modification, as needed, along with optimization programs.

This book can serve as a text for a senior or first-year graduate course in bioprocess engineering, since it covers essentially all aspects of this topic.

These include bioprocess raw materials and products, design of bioprocess, economic and sustainability analysis, optimization of chemical complexes, and applications to existing processes and chemical production complexes.

Practicing engineers in the bioprocessing industries will find that this rapidly growing field requires a stand-alone text like this that covers all parts of biomass conversion to products. This book describes the technical and scientific expertise needed to bring the engineer and scientist "up to speed" in this field. The importance and rapid expansion of this field is covered in the *Wall Street Journal's* feature article, "Just One Word: Bioplastics," in the October 18, 2010, issue that describes the "huge potential" of plastics from plant materials.

The material is organized into seven chapters, a postscript, and appendices. In Chapter 1, a description of the production of chemicals from renewable resources is given, with the research vision being to develop the methodology for new plants based on renewable resources that supply the needed goods and services for existing plants. The criteria for optimal configuration of plants and optimization theory are introduced in this chapter. In Chapters 2 and 3, detailed literature reviews and analyses are covered for biomass as feedstock and for the production of chemicals from biomass. Conceptual designs of bioprocesses are constructed, as described in Chapter 4, and include detailed information about the bioprocesses. Five processes are developed in Aspen HYSYS® with cost estimations from Aspen ICARUS®. Information from other process simulation software, for example, SuperPro Designer®, is applied for the corn-to-ethanol fermentation process. In Chapter 5, bioprocess plant models are formulated for optimization using input and output streams, equilibrium rate equations, parameters, and thermodynamic information from HYSYS plant models. Two other processes included in this chapter are for the production of algae oil from carbon dioxide and for the production of syngas from corn stover by steam reforming. Then interconnections in the bioprocesses are developed for optimization.

In Chapter 6, the superstructure of chemical and biochemical plants was formulated by integrating the bioprocess and carbon dioxide–consuming plants with the base case of existing chemical plants in the Lower Mississippi River Corridor. Carbon dioxide from the integrated chemical complex was utilized for the production of algae and for chemicals from carbon dioxide. The optimal structure was obtained by maximizing the triple bottom line, which included product sales, economic costs (raw material and utility), environmental costs (67% of raw material costs), and sustainable costs and credits. The optimal solution gave the plants that were included in the optimal structure. Comparisons between the base case and optimal structure were given for triple bottom line costs, the pure and impure carbon dioxide emissions, the energy requirements for plants, and the capacity of the plants. Multicriteria optimization was used to determine Pareto optimal solutions for the optimal structure. Monte Carlo simulation was used to determine the parameter sensitivity of the optimal solution. Comparisons of results with approaches were included in this chapter.

In Chapter 7, optimization was used to evaluate five cases. Case I was a modification to evaluate integration of bioprocesses in the existing base case without carbon dioxide being used for chemicals or algae oil production. The other four cases examine other aspects obtained from the optimization. The postscript gives the conclusions from this methodology and extensions that can be used for future developments.

The existing plants used for the base case were developed with industrial colleagues led by Tom A. Hertwig of Mosaic Corporation, and their assistance was invaluable. The assistance of the members of the Total Cost Assessment Users' Group at the AIChE, and especially Lise Laurin for guidance in using the Total Cost Assessment Methodology, is gratefully acknowledged.

Authors

Debalina Sengupta received her bachelor of engineering degree in chemical engineering from Jadavpur University, Calcutta, India, in 2003. She worked as a software engineer in Patni Computer Systems from 2003 to 2004. In 2005, she joined the Department of Chemical Engineering at Louisiana State University, Baton Rouge, Louisiana. She received her doctor of philosophy degree in chemical engineering under the guidance of Professor Ralph W. Pike for her research entitled "Integrating bioprocesses into industrial complexes for sustainable development" in 2010. Her expertise is in optimization of industrial complexes and sustainability analysis using total cost assessment methodology. She is now working as an ORISE postdoctoral fellow at the United States Environmental Protection Agency. Her current research is focused on sustainable supply chain design of biofuels and includes life cycle assessment (LCA) for ethanol as biofuel. Her research interests include model development for ethanol biorefineries for LCA and assessing environmental releases from biorefineries.

Ralph W. Pike is the director of the Minerals Processing Research Division and is the Paul M. Horton Professor of Chemical Engineering at Louisiana State University. He received his doctorate and bachelor's degrees in chemical engineering from Georgia Institute of Technology. He is the author of a textbook entitled *Optimization for Engineering Systems* and coauthor of four other books on design and modeling of chemical processes. Pike has directed 15 doctoral dissertations and 16 master's theses in chemical engineering. He is a registered professional engineer in Louisiana and Texas. His research has been sponsored by federal and state agencies and private organizations, with 107 awards totaling $5.6 million, and has resulted in over 200 publications and presentations. His research specialties are optimization theory and applications for the optimal design of engineering systems, online optimization of continuous processes, optimization of chemical production complexes, and related areas of resources management, sustainable development, continuous processes for carbon nanotubes, and chemicals from biomass.

Pike is a fellow of the American Institute of Chemical Engineers and is chair of the Environmental Division and past chair of the Fuels and Petrochemicals Division. He is an active member of the Institute for Sustainability and the Safety and Chemical Engineering Education (SACHE) Committee of the Center for Chemical Process Safety. He was the meeting program chairman for the 74th Annual Meeting and has cochaired 66 sessions on optimization, sustainability, transport phenomena, and reaction engineering. He has held all of the positions in the Baton Rouge Section of the AIChE. Pike is also on the editorial boards of *Environmental Progress and Renewable Energy* and *Clean*

Technology and Environmental Policy. He has served as coeditor in chief of *Waste Management*, an international journal devoted to information on prevention, control, detoxification, and disposition of hazardous, radioactive, and industrial wastes. He is a member of the American Chemical Society and Sigma Xi, the scientific society.

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