Green Catalysis and Reaction Engineering

Discover tools to perform Life Cycle Analysis (LCA) and develop sustainable chemical technologies in this valuable guide for chemists, engineers and practitioners. Tackling one of the key challenges of modern industrial chemical engineering, this book introduces tools to assess the environmental footprint and economics of key chemical processes that make the ingredients of everyday products such as plastics, synthetic fibers, detergents and fuels. Describing diverse industrial processes in detail, it provides process flow diagrams including raw material sourcing, catalytic reactors, separation units, process equipment and recycle streams.

The book clearly explains elements of LCA and how various software tools, available in the public domain and commercially, can be used to perform LCA. Supported by real-world practical examples and case studies provided by industrial and academic chemists and chemical engineers, this is an essential tool for readers involved in implementing LCA and developing next-generation sustainable chemical technologies.

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An Integrated Approach with Industrial Case Studies

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Dedicated to Appa and Amma
For their love, many sacrifices and dedication in nurturing and educating their six children

Contents

Preface

Humanity stands before a great problem of finding new raw materials and new sources of energy that shall never become exhausted. In the meantime, we must not waste what we have, but must leave as much as possible for coming generations.

Nobel laureate Svante Arrhenius (1925)

The purpose of this book is to show how life cycle assessment, when paired with technoeconomic analysis, can more effectively guide the development of sustainable chemical processes. It is true that the principles of green chemistry and engineering provide qualitative guidelines for developing greener processes. However, if we want to assess such technologies *quantitatively* in terms of their sustainability, we will need clear metrics and methods to compare them with conventional processes and products.

A 2018 United States Government Accountability Office report on chemical innovation for sustainability (www.gao.gov/products/GAO-18-307) concluded that quantitative sustainability assessment is essential for the real-world adoption of sustainable technologies. The 2019 United Nations Environment Program report (www.unenvironment.org/resources/report/global-chemicals-outlook-ii-legacies-innovative-solutions) arrived at the same conclusion. This book is therefore timely: it shows how to use existing tools to assess the sustainability of chemical processes in the early stages of development, in order to identify key economic and environmental problem areas. Identifying these areas is essential for making well informed business decisions and for encouraging investment in the kind of research that will eventually lead to the commercialization of green chemical technologies.

This book demonstrates various methods of quantifying the environmental impact of chemical manufacturing processes. In particular, it focuses on the chemical precursors we find in everyday products such as plastic bottles, synthetic fibers, shampoos, detergents and fuel additives. These commodity chemicals include ethylene (Chapter 3), ethylene oxide (Chapter 4), terephthalic acid (Chapter 5), propylene oxide (Chapter 6), butyraldehyde (Chapter 7), nonanals (Chapter 8) and *iso*octane (Chapter 9). Due to their high manufacturing capacities (billions of pounds per year), they rank among the top 18 chemicals that together account for nearly 75% of the chemical industry's overall greenhouse gas emissions (Chapter 1). Their global demand has been steadily increasing and so has their environmental footprint.

Aiming to reduce the environmental burden of such chemicals and the conventional processes they are involved in, a number of research groups have proposed concepts

for greener processes. The approaches include (a) developing greener technologies for existing feedstock; (b) replacing existing petroleum or coal-based feedstock with renewable feedstocks such as those derived from biomass; and (c) replacing the target product itself with functionally equivalent and more benign substitutes. This book provides several examples of such alternatives – sustainable technologies formulated on the basis of innovations in catalyst design, tunable reaction media (e.g., supercritical fluids, gas-expanded liquids and ionic liquids) and novel reactor concepts which integrate reaction and separation (Chapter 2). Specific examples of these technologies include (a) homogeneous ethylene oxide and propylene oxide processes using methyltrioxorhenium as a catalyst and hydrogen peroxide as an oxidant that eliminates CO_2 as a byproduct (Chapters 4 and 6); (b) the development of highly selective heterogeneous olefin epoxidation catalysts composed of earth-abundant materials (Chapters 4 and 6); (c) an intensified one-step spray reactor concept for the inherently-safe formation of polymer-grade terephthalic acid and 2,5-furandicarboxylic acid at high yields and purity (Chapter 5); (d) highly selective hydroformylation of olefins in gas-expanded liquids (as benign and tunable solvents) with reduced energy intensity (Chapters 7 and 8); (e) soluble polymer-supported homogeneous hydroformylation catalysts that are easily retained in solution by nanofiltration membranes (Chapter 8); and (f) a stable solid acid catalyzed alkylation process for producing *iso*octane (Chapter 9).

One can't meaningfully compare conventional and alternative processes without reliable data. The data for conventional manufacturing processes used throughout this book is sourced from the open literature, including patents. Simulations of the greener alternatives rely on reported laboratory-scale data. Most of the examples of greener process concepts were drawn from my research program, which made the data needed for process simulation readily available. However, convenience has not been the only reason for this choice: the writing of this book is the fruit of nearly three decades' worth of research and teaching dedicated to finding sustainable alternatives to energy-intensive and environmentally-problematic chemical processes. Indeed, it was while teaching *Development of Sustainable Catalytic Processes*, a course for chemical engineering and chemistry graduate students at the University of Kansas, that I refined the examples which appear in the following pages.

Several features of this book distinguish it from other excellent books in the areas of green chemistry/catalysis, authored and edited by leaders in the field (such as David Allen, Paul Anastas, James Clark, Joseph DeSimone, Philip Jessop, Walter Leitner, Roger Sheldon, David Shonnard, William Tumas, John Warner and Julie Zimmerman). Allen and Shonnard have shown how to quantify the negative effects of chemical processes in various segments of the environment (such as air, water and soil). The other books enunciate the principles of green chemistry and engineering; provide examples of various types of reactions (such as oxidations, carbonylations, hydrogenations, hydroformylations and alkylations) performed in benign media (such as dense carbon dioxide and ionic liquids) with conventional and renewable feedstocks; and describe novel catalysts (chemo and bio) and continuous reactors that integrate separation with reduced usage of material and energy. They focus mainly on

the chemistry aspects of processes. This book supplements these efforts by also focusing on the engineering aspects and shows how lab-scale data from a "greener" catalytic process concept can be used to simulate a detailed process flow diagram that includes downstream separation of products, recycling of unreacted feedstock and catalyst and safety considerations. Detailed process-engineering simulations like these form the basis of technoeconomic and environmental impact analyses, which allow one to determine whether the greener concepts in question are in fact more sustainable than their conventional counterparts. This book also includes cradle-to-gate and gate-to-gate impact assessments. These delineate the environmental burden associated with raw material extraction and the chemical manufacturing process and, thus, encourage a life cycle approach to identifying bottlenecks and recommend process improvements for enhancing sustainability. Finally, this book makes ample use of publicly available toxic release inventory (TRI) data, reported by chemical companies and power generating stations, in order to assess methods for estimating environmental impact.

This book is intended for multiple audiences. Students, researchers and practitioners of green chemistry and engineering will find in the proposed comparative economic and environmental impact analysis approach a useful sustainability assessment framework. Readers can update this framework for themselves by incorporating new sustainability criteria (such as toxicology, product biodegradability and even social dimension) as and when appropriate metrics and tools emerge. The book can be used in a graduate-level course; as mentioned, several parts of it have already been used in a multidisciplinary graduate course at KU. The book may also be useful to undergraduates majoring in chemical engineering, supplementing their capstone process-design and environmental assessment/safety courses. Of particular value to instructors and students are the detailed operating parameters and methods provided for simulating the process-flow diagrams of several industrially important chemical manufacturing processes (Chapters 3–9). These could be used for process-design projects that not only perform traditional economic analysis but also incorporate environmental impact assessment exercises. For freshmen studying chemical engineering and chemistry, the book can serve as a general introduction to major industrial chemical manufacturing processes and the sustainability challenges they pose. Instructors will also find a rich array of examples to include in chemical reactor design and separations courses, such as alternative chemistries, reactors, feedstocks and solvents that reduce adverse environmental impact. I have used several examples of sustainable chemistry and reactor alternatives described in the book in the undergraduate *Chemical Engineering Kinetics and Reactor Design* course at KU.

My hope is that this book will be a useful teaching tool, promoting quantitative sustainability assessment as an indispensable research methodology for chemists and chemical engineers in their quest to achieve a greener chemical industry.

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