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Chemical Engineering Science and Green Chemistry – The Challenge of Sustainability

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1.1
Sustainability Challenge for the Chemical Industry

The challenge of sustainability is well illustrated by the global ecological footprint "wedge" (Figure 1.1). It shows that the global footprint is exceeding the ecological reserve since 1960s [1]. Footprint is only one aspect of sustainability, reflecting the use and availability of resources and damage to natural environment. The sustainability challenge could be paraphrased as achieving economic prosperity, while ensuring social equality and well-being and not destroying the environment [2]. The ecological footprint is one of the more critical aspects for today: it reflects several important relationships that must be understood in order to identify the path to feasible solutions of the sustainability challenge. The key relationship is between human aspirations and our ways of attaining them. Here, we will not go into the topic of aspirations. This is discussed in detail in sustainability literature and includes satisfaction of basic needs, aspirations of a certain standard of living, aspirations toward self-fulfillment and self-realization, which are highly context specific. What is important for us is that there appears to be a clear positive link between the standard of living and the energy intensity per capita. This ultimately stems from two factors: (i) the way we attain the increases in our standard of living and (ii) basic thermodynamics. Our standard of living today depends on access to manufactured goods used in production of building materials, clothing, food, modern education and entertainment technology, modern healthcare, and so on. In turn, manufacturing necessarily involves expenditure of energy, as we transform matter into more complex and ordered forms [3]. As population grows and a larger proportion of the population increases its standard of living, the demand for energy and resources will grow, due to the link between the standard of living and the energy required to achieve it. At present, the developed countries with a high human development index (HDI) [4] and the ecological footprint far exceeding their own resources, export their waste to, and import resources from, the

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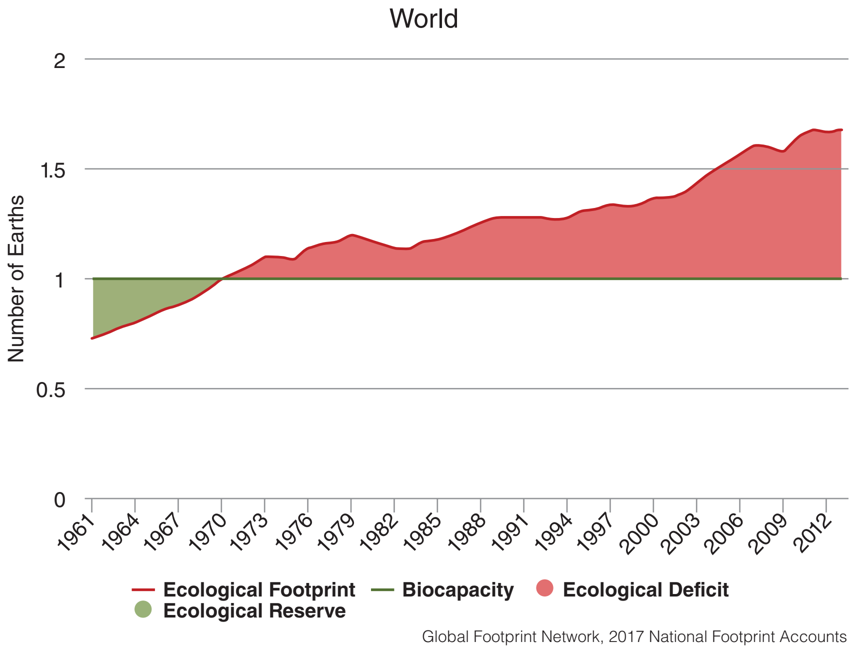


Figure 1.1 A comparison of ecological footprint, represented as a number of Earths, versus biocapacity. (Global Footprint Network [5].)

countries with low HDI and low ecological footprint. This leads to inequality and exploitation, and this situation of course cannot continue indefinitely.

The second reason why it is critical to decouple HDI from energy demand is the apparent anthropogenic effect on climate. The vary rapid increase in global population of humans and their aspirations toward better life result in a rapidly increasing demand for energy [6–8]. At present, this results in the increase in the rate of emissions of carbon dioxide that today far exceeds the rate of biological and geological sequestration of atmospheric carbon [9], resulting in the observed climate change.

The fundamental challenge of sustainability, therefore, is to decouple the quality of life and human aspirations from energy and material intensities of achieving them.

In this respect, chemical industry will play a significant role. Chemistry is ubiquitous in everyday life and is responsible for the majority of innovations in all aspects of life, from agriculture and food to healthcare, sport, entertainment, and fashion. It is also the major source of innovation in the energy-efficient technologies. Calculation of the environmental impact of the manufacture of materials for energy generation and energy-efficient technologies, and comparison with the saved emissions by these technologies (Figure 1.2) shows the significance of chemistry to finding ways of decoupling HDI and ecological footprint. These data focus on carbon emissions, which today are regarded as the most important

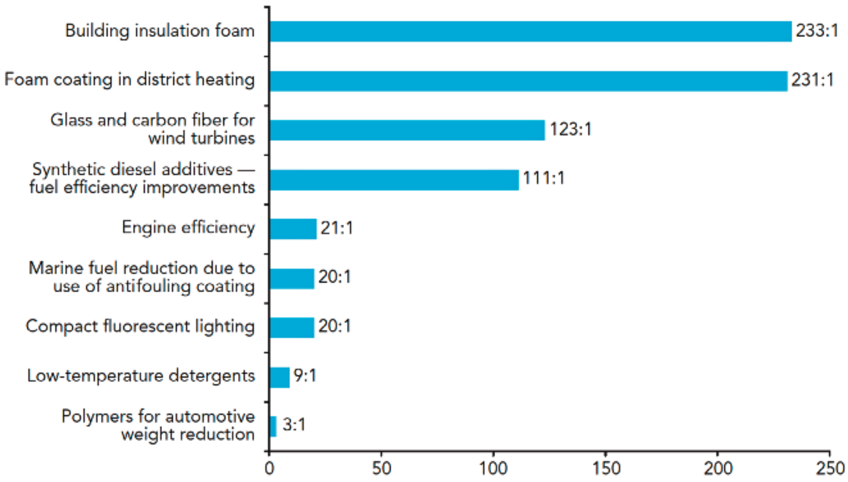


Figure 1.2 Examples of the green house gas emission savings enabled by chemistry, represented as a ratio of emission savings to emissions incurred. (Adapted from Refs [10, 11].)

target as the driver of climate change [7]. Among the larger contributions to the reduction of carbon emissions by innovation in chemistry are development of insulation materials and materials for construction of wind turbines; fuel technology, including fuel additives for better combustion; shift to lower carbon fuels; novel materials for energy-efficient lighting, and detergents for low-temperature cleaning. Thus, the manufacture of novel materials is an important technological solution for reduction of carbon emissions, as it directly affects two of the major anthropogenic sources of carbon emissions, namely, transport and housing. Of course, the manufacture of materials is, basically, chemistry.

These solutions are not affecting the way how energy is being produced, but are directed at efficiency of the use of energy: A reduction in the waste of energy should result in lowering the demand for energy production. The last decade saw a rapid uptake of renewable energy technologies, in particular wind and solar power. As a result, a new energy technology paradigm has emerged – chemistry as a major industrial energy storage system (Figure 1.3). This paradigm is based on the proposition that excess power will be available from renewable energy installations at low-demand off-peak times during a day. This low-cost electricity could be used to convert unreactive molecules, CO_2 and

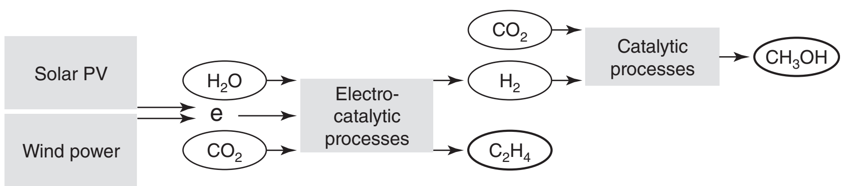


Figure 1.3 Chemical industry as an energy storage solution.

H_2O, into basic chemical feedstocks, such as methanol and olefins, in what has been termed "CO_2 recycling technology" [12]. In a way this approach parallels the biological conversion of carbon dioxide into molecules of higher *exergy* [13], driven by constant supply of solar energy, but at a higher intensity (defined as production rate per unit area).

An estimate of the potential scale of the CO_2 recycling technology has been given for the example of using the potentially available electricity to synthesize methanol from CO_2: This technology can produce 1.2×10^9 metric tones of methanol from CO_2 per year [12]. This is an order of magnitude larger amount than the global methanol production via current conventional technology. Of course, in this case the CO_2-derived methanol is not a final product, but a convenient to transport source of an activated C1 group for further conversion to bulk chemical products. This technology may have a very significant impact on the overall chemical supply chain and, consequently, reduce emissions from the manufacture of chemicals.

To understand the impact of CO_2 recycling technology on global emissions, it is necessary to compare life cycle impacts from conventional routes to methanol, with the proposed CO_2-based technologies. The global warming potential or green house gas (GHGs) emissions, evaluated in the units of kilogram CO_2 equivalents per kilogram of product, is one of the most important indicators. The total contribution of the CO_2 recycling technology to GHG is comprised of three main contributions: direct use of CO_2 as a feedstock, avoiding CO_2 emissions from conventional routes to methanol, and CO_2 emissions due to the new processes. These values would vary depending on the CO_2 recycling technology used. As an example, the estimate of GHG reduction from introduction of the solar–thermal methanol synthesis is $-1.71\,\text{kg}\ CO_2$ equiv. kg^{-1} compared to GHG emissions from conventional methanol synthesis of 0.67 [14]. Here, the negative sign means the reduction of carbon emissions in the wider system of the chemical supply chain.

The second route to utilization of CO_2, shown in Figure 1.3, is via electrocatalytic reduction of CO_2 to ethylene [15]. A much larger reduction in GHG emissions compared to that of methanol synthesis would be expected for the case of the production of ethylene from CO_2, since GHG emissions from conventional ethylene production range between 2.5 and 8.9 [16].

The merger of chemical and energy industries is a major opportunity to rapidly and significantly reduce global carbon emissions from the three main contributions to anthropogenic emissions of carbon dioxide: energy generation, transport (through fuel substitution), and chemical manufacturing itself.

As manufacturing of molecules and materials might in the future be integrated into new energy technologies and become one of critical solutions to the reduction of carbon emissions, *what* is being manufactured and the impact of chemical products during and after their use comprise the second aspect of the sustainable chemical technologies. Chemical industry is producing tens of thousands of chemical compounds. Very few of these are bulk platform chemicals produced in millions of tones per year, with the majority being produced at an annual rate of approximately 1000 tonnes. Today, chemical manufacturing is experiencing its fastest growth in the developing countries. It is already projected that developing countries will be responsible for manufacturing of 37% of high-volume industrial chemicals by 2030 [10]. Thus, emissions to atmosphere and pollution of natural environment associated with the manufacture and use of chemicals are set to increase, unless significant changes are introduced into the industry through use of green and sustainable chemistry. World Health Organization (WHO) estimates that 25% of the burden of disease is linked to environmental factors, including chemical pollution [17]. As controls of the use, storage, and disposal of toxic chemicals are lacking mainly in the developing countries, the rapid increase in the size of chemical industries in these countries may lead to the increase in the damage to human health and the environment.

The impact of chemicals on the environment is increasingly better documented, however, the lack of knowledge of the interactions of chemicals with the environment is a significant problem, especially for the large number of existing chemicals, introduced into manufacturing and products before current toxicity, and environmental impact testing regimes were introduced into legislations [18]. Thus, consideration of *what* is being produced and used in the final products, especially the products that are highly distributed and end up in the environment, is an urgent priority for chemical and chemistry-using industries.

1.2 From Green to Sustainable Chemistry

The 12 principles of green chemistry formulated at the end of 1990s (Table 1.1) have marked an important step in developing our understanding of the relationship of chemistry research with the environmental impact of chemical industry and chemical products [19]. The focus of the principles is on delivery of the *target useful functions* without the specific to the chemicals' negative effects, such as toxicity or material intensity (through use of auxiliary substances in the synthesis). This is the principle of *ideality*, well known in the innovation literature [20–22]. The very simple idea behind green chemistry principles is that if materials being released into environment do not possess inherent hazards, are benign toward environment, and have low material and energy intensities in manufacturing and use, than the problems we are forced to solve now would not be further exacerbated. Green chemistry has seen remarkable successes, especially with regard to developing solvent guides and processes using alternative solvent media [23–29], application of catalysis and biocatalysis in organic synthesis [30], and the significant progress of the chemistry of biofeedstocks [31–34], among many others. It is safe to state that today the principles of green chemistry are embedded in everyday work of most chemists. Furthermore, there is an increasing appreciation of the intimate link of green chemistry with engineering. This stems from the basic idea that green chemistry is a

Table 1.1 Green chemistry principles [19].

It is better to prevent waste than to treat or cleanup waste after it is formed
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product
Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment
Chemical products should be designed to preserve efficacy of function while reducing toxicity
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used
Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure
A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable
Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances
Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires

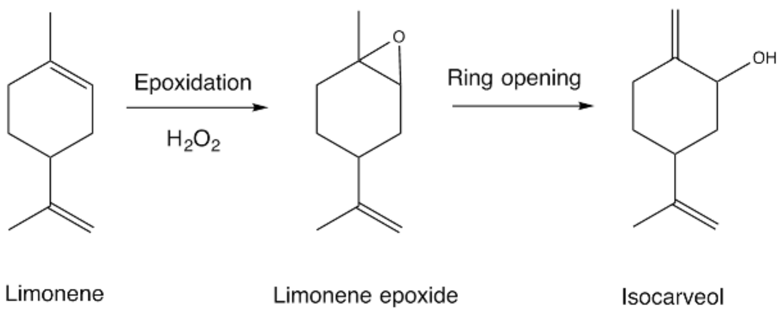
system's approach [35], and decisions about molecules, modes of activation, solvents, feedstocks, and operating conditions will necessarily affect decisions about processes, mass and energy integration, supply chain, and business models. Green chemistry has evolved into sustainable chemistry.

In a broader context of sustainability, OECD defined *sustainable chemistry* as "the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes" [36]. The technical areas of sustainable chemistry closely match the principles of green chemistry, but the impact of these is evaluated with respect to human health and the environment, safety of workers and users, energy and resources consumption, and economic viability. The emphasis on evaluation of the impacts over the life cycle of products and processes and at different levels – local, country, regional, and global – warrants the use of the term *sustainable*, rather than the narrower definition of the scientific and technical challenges defined by the green chemistry principles. The problem of developing better chemistry has become truly a system-level problem and no discipline is better suited to contribute the development of sustainable chemistry as chemical/biochemical engineering, the discipline deeply routed in systems analysis and tools.

1.3
Chemical Engineering Science for Sustainability

Understanding behavior of hierarchical interacting systems is the core of chemical engineering discipline. The manufacture of chemicals is a structured hierarchical complex system with multiple dynamic interactions at different levels of the hierarchy and between the levels [37]. As a result, any changes proposed to such a system, for example, replacing a stoichiometric synthesis with a catalytic process, replacing elements of the supply chain based on the new criteria of inherent safety or the origin of the feedstocks, and so on, require system-level changes. Any solution proposed in isolation from the rest of the system would not be successful until its effects on the overall system's behavior are understood, and are *positive*. We can trace the history of discourse on systems in chemical manufacturing to the development of ideas of industrial ecology [38, 39], system-level process design [40, 41], hierarchical indicators for environmental impact of green chemistry and technology [42], and the adoption of life cycle assessment (LCA) in chemistry and chemical technology [43–49]. In particular, indicators and LCA are the methods that allow quantification of the outcome of new developments in terms of their *positive* contribution to the reduction of the environmental impact of the economically feasible processes. This requires a brief explanation.

In many cases there is a compromise between economically optimal or environmentally optimal solutions. We can use as an illustration a recent study of conversion of a biowaste-derived terpene feedstock into a useful but not easily accessed platform molecule (Scheme 1.1). The conceptual process was optimized toward two simultaneous objectives, the minimum values of a cost function and a CO_2 emissions indicator, with process operating conditions being the optimization variables [46]. The results are reproduced in Figure 1.4. The optimization rapidly converges to a minimum of both objectives, as shown in Figure 1.4a. Upon expanding the minimum solution, we see that it is, in fact, a series of Pareto optimal solutions with a trade-off between cost and GHG. The set of Pareto solutions is of interest as these solutions correspond to the lowest environmental



Scheme 1.1 Conversion of biowaste-derived limonene to isocarveol.

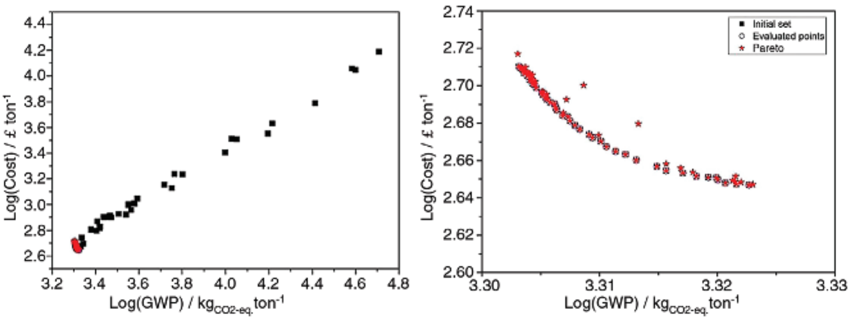


Figure 1.4 (a) A course of optimization over 100 iterations in attaining a simultaneous minimum of a cost function and global warming potential in the synthesis of isocarveol from terpenes and (b) the expanded optimal region showing the set of simultaneously optimal Pareto solutions. (Reproduced with permission from Ref. [46]. Copyright 2017, John Wiley & Sons, Inc.)

impact (in terms of CO_2 emissions) and the best economic potential. Any of the solutions on the Pareto front are optimal, and further criteria, considering in detail the operating conditions of each of the solutions, should be considered to select the process for implementation.

The consideration of the process itself, within the system boundary of the conversion of limonene to isocarveol is not enough to justify that this process gives a positive contribution to sustainable chemical supply chain. The results given in Figure 1.4 are obtained using life cycle assessment cradle-to-gate system boundary, starting from how the specific biowaste is separated to give pure limonene as a feedstocks. Within this system boundary it was clear that using the waste of paper manufacturing as a source of limonene is significantly more attractive than orange peel, due to the much lower CO_2 emissions and lower cost [46]. Here, comparative LCA allows the quantification of the potential impact of the introduction of new technology.

The transition from green to sustainable chemistry is the inclusion of the wider system in the domain of problems of chemistry and chemical engineering. Using the same example with which we began this chapter, the CO_2 recycling technology, the only reason why manufacturing of bulk feedstocks from CO_2 may become a serious proposition is the rapid drop in the cost of renewable electricity, which occurred mainly due to political and economic decisions. The development at the system level of energy infrastructure translates into changes in the supply chains, business models, process technology, and ultimately, requires novel chemistry and novel engineering solutions.

The desired attributes of green engineering solutions have been well articulated by the principles of green *chemical* engineering, reproduced in Table 1.2 [50]. These attributes closely follow the principles of green chemistry [19], with the addition of the system-level attributes, such as conservation of exergy [13], expressed in Table 1.2 as embedded entropy and complexity, and

Table 1.2 Principles of green engineering [50].

Designers need to strive to ensure that all material and energy inputs and outputs are as inherently nonhazardous as possible
It is better to prevent waste than to treat or cleanup waste after it is formed
Separation and purification operations should be designed to minimize energy consumption and materials use
Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency
Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials
Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition
Targeted durability, not immortality, should be a design goal
Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw
Material diversity in multicomponent products should be minimized to promote disassembly and value retention
Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows
Products, processes, and systems should be designed for performance in a commercial "afterlife"
Material and energy inputs should be renewable rather than depleting

many features that have recently been formulated in the concept of "circular economy" [51].

The challenges of sustainability require system-level solutions and, in particular, ability to model interactions within complex dynamical systems, such as the developing integrated chemistry-energy systems or biorefining systems, among many others. Within chemical engineering science, the ability to identify the critically important mechanisms within a chemical system, for example, what factors affect stability of catalysts under industrial operating conditions, and the ability to explore scenarios of technology development within broad system boundaries are some of the current important areas of development of the field. We can now look at some current trends in chemical engineering science.

1.4 Trends in Chemical Engineering Science

The new challenges of sustainability require new tools and solutions from the chemical engineering science. If we take as an example, how current grand challenges are viewed by an authoritative and representative engineering community, US National Academy of Engineering (Table 1.3), access to bulk chemical products or fossil energy are not on the list, but clean water, renewable energy,

Table 1.3 NAE 2017 grand challenges for engineering [52].

Make solar energy economical
Provide energy from fusion
Develop carbon sequestration methods
Manage the nitrogen cycle
Provide access to clean water
Restore and improve urban infrastructure
Advance health informatics
Engineer better medicines
Reverse engineer the brain
Prevent nuclear terror
Secure cyberspace
Enhance virtual reality
Advance personalized learning
Engineer the tools of scientific discovery

carbon sequestration, and better medicines are. I would argue that solutions to these challenges require much closer integration of chemical engineering with the neighboring sciences, and developing the capability for transcending many length scales that connect molecular systems with manufacturing systems and the final applications. These trends – (i) of merger of chemical engineering with physical, biological, and medical sciences and (ii) setting much broader system boundaries for problems – are evident in current chemical engineering literature and the subject matter of research in leading chemical engineering departments in universities around the world.

Recently, several publishers launched journals that are explicitly aimed at the interdisciplinary space between sciences and chemical engineering. These include *ACS Sustainable Chemistry and Engineering*, RSC's *Reaction Chemistry and Engineering*, RSC's *Molecular Systems Design and Engineering*, Elsevier's *Sustainable Chemistry and Pharmacy*, and so on, as well as the already well-established interdisciplinary chemistry–chemical engineering–material science journals, such as *ChemSusChem* and *Green Chemistry*. If we look at research in the top chemical engineering university departments using, for example, a QS ranking to define "top," we find biomedical research, nanomaterial's engineering, artificial intelligence, data science, robotics, sensors, and so on. It appears that principles of chemical engineering are becoming an integral part of discovery sciences while the neighboring sciences are becoming an integral part of the chemical engineering design toolbox. For this reason, it seems rather timely to present in a single volume the new topics and capabilities within the field of chemical engineering that have emerged recently.

1.5 Topics Covered in This Book

This volume of the Green Chemistry series provides an outlook on recent and new trends in chemical engineering, emerging in response to the challenge of *sustainable chemistry*, as a next chapter in the evolution of this field. Chemical engineering is becoming increasingly linked with molecular sciences and tools of molecular and materials design. Part One of the book deals with two large topics in molecular design and engineering – engineering of solvents and design of functional nanomaterials. Solvents is a critical topic for green chemistry, as in many areas of chemical industry that suffer from large waste-to-product output ratios, the E-factor [53]; it is large because of the significant use of solvents in both synthesis and reactor cleaning. With the increasing attention to bio-based chemical supply chains, the role of solvents is likely to further increase. However, replacing solvents is a challenging problem since solvents frequently are not inert in the reactions and new solvents need to be designed to not only provide the favorable solvation properties at reasonable cost and with little environmental impact, but also to favorably affect the reaction outcome. Nano-structured functional materials are becoming increasingly used in the most wide ranging applications. Ensuring the control over structure, composition and morphology at nanoscale, and especially in bulk manufacture of nanomaterials has become a significant barrier for commercialization of functional nanomaterials. Design of scalable manufacturing of nanomaterials should account for the need to control nanoscale processes via manipulated variables many orders of magnitude larger in the length scale. Hence, a significant attention is being paid to various novel synthetic methods that allow such control. This also emphasizes the need for new approaches to modeling that link multiple length and time scales for processes.

Applied mathematics has always been a critical component of chemical engineering curriculum and practice. However, today new mathematical methods are being adopted as chemical engineering faces new challenges and merges with new disciplines. Part Two deals with the state of the art in conceptual process design and optimization. Many of the current challenges in process design are system-level problems: reactor networks, optimization of complete flow sheets, optimization of heat integration networks, and super-structure optimization. In addition to traditional optimization tools, some areas of chemical process design have turned to data-driven methods, such as machine learning and Bayesian statistics-based design of experiments. These are some of new enabling technologies that are described in Part Three.

Part Two also deals with the innovations in unit operations and manufacturing in chemical industry. Process intensification [54] (PI) has become a standard tool within the chemical engineering design toolbox. However, we also observe new trends, such as wide adoption of PI within pharmaceutical and specialty chemical industries, where adoption of continuous flow manufacturing [55] is opening new business opportunities [56], for example, the potential to manufacture drugs on demand at a point of sale. To achieve this a radical increase in productivity, of the traditionally highly inefficient complex multistep syntheses, is required. This could be achieved in microreactors. Chapter 6 is dedicated to the state of the art in microreactor design, including their modeling. The problems and opportunities of adoption of PI in industry are discussed in detail in Chapter 7. Further advances on new business models that are emerging with the increased adoption of green chemistry solutions is the subject of Chapter 8. Chemical leasing is a concept that has already found applications in leasing of noble metals and some solvents. However, a series of pilot projects undertaken recently in Europe show how this approach may be adopted to other chemical products in new types of business-to-business relationships. Another aspect of PI is the rapid adoption of additive manufacturing technology in chemical industry. Chapter 9 describes the new opportunities that are being opened up for chemical synthesis and process design by additive manufacturing.

Biotechnology is deliberately given a very narrow focus in this book. Traditional areas of biotechnology, such as fermentation, tissue engineering, bioseparations, and biorefining, have been the subject of significant attention. However, one area of biotechnology has seen little coverage in the chemical engineering literature, but is likely to be the most disruptive – synthetic biology. Being able to design new reaction pathways using non-native biocatalytic reaction pathways is a major step forward for synthetic chemistry. Already, several successes in green chemistry are due to developing much shorter reaction sequences via adoption of enzymatic or whole-cell transformations. Chapter 4 deals with the systematic approach to the development of non-native biocatalytic transformations.

The final part of the book, Part Three, is dedicated to several key enabling technologies. Out of many, only three are included in this volume. Spectroscopy as a tool for process monitoring is well known and, in principle, well-studied area, but it is only now that it is becoming an essential tool for industrial chemical processes. There are still very few suppliers of industrial-grade spectroscopic equipment for real-time analysis under operating conditions, but the range of potential applications is vast, and the potential for energy and materials savings must not be underestimated. Chapter 10 describes the state of the art and current challenges of spectroscopic process monitoring. Chapter 11 deals with the more advanced technique of magnetic resonance imaging, which has seen remarkable developments over the last decade. The possibility to measure flow velocity maps under operating conditions, measure diffusion coefficients inside porous catalysts, and distinguish between bulk and adsorbed phases within catalysts and other materials, are some of recent highlights from MRI. As we progressively tackle more complex chemical problems, the opportunities to increase the number of state variables that could be directly observed are critical to our ability to design new processes using rational design principles, rather than trial and error. This opens up a debate about the role of physical and surrogate models in process development, addressed to some extent in the final chapter of the book, Chapter 12. This chapter deals with another recent addition to chemical engineering-enabling technologies: robotics and machine learning and artificial intelligence (AI).

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