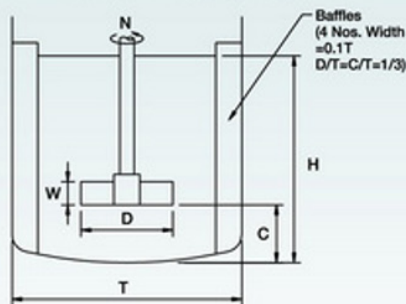
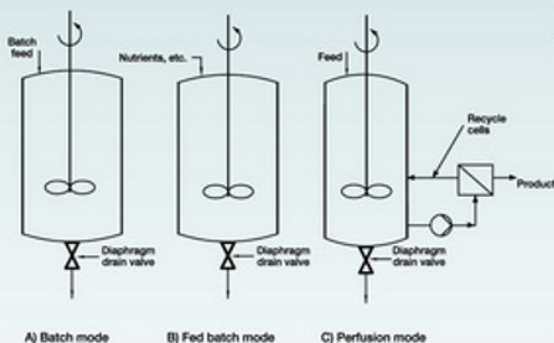
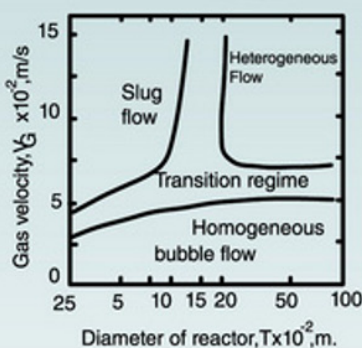
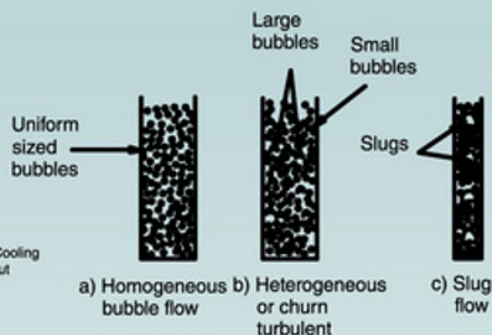
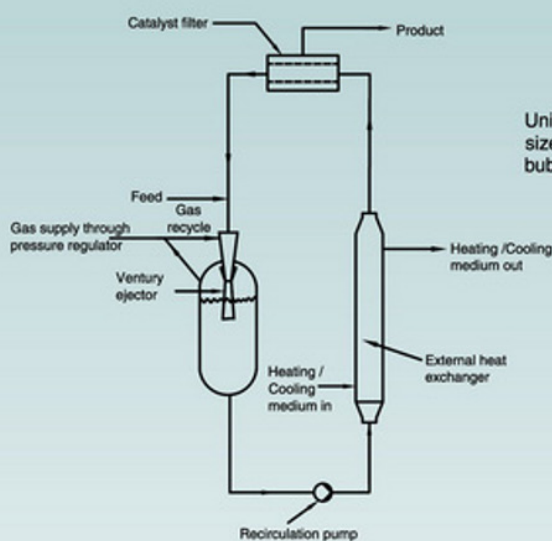




Design of Multiphase Reactors

Vishwas Govind Pangarkar



DESIGN OF MULTIPHASE REACTORS

DESIGN OF MULTIPHASE REACTORS

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Prajá-pataye Swaáhá. Prajá-pataye Idam Na Mama.

*This ancient Sanskrit Mantra can be explained as follows:
“I offer the spiritual and material resources used to produce
this work to Prajapaty (the Cosmic creator of Life).
Oh Creator, this is not mine, but Thine.”*

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FOREWORD

Multiphase reactors are widely used in the chemical industry. The design and scale-up of such reactors is always a difficult task and is not adequately covered in traditional chemical reaction engineering books. The book by Pangarkar is a welcome addition to this field and brings a new perspective of combining the theory with practice.

The book opens with examples of industrial applications and addresses many issues associated with the success of industrial multiphase processes, such as catalyst selection, selectivity, environmental issues. It proceeds then to address the key problem of design and scale-up. The transport–kinetic interaction is vital to understand the design of these reactors. The author illustrates this clearly for various cases of both gas–liquid and gas–liquid–solid systems. Next, reactor selection is discussed in detail including the need for efficient heat management culminating with guidelines for selection of reactors. This is vital in industrial practice as a wrong type of reactor can lead to inefficient or poor process. Fluid dynamic aspects and scale-up based on similarity principles are examined next. Stirred tank reactor design is then examined through detailed analyses of both conventional multiphase chemical reactions and cell culture technology. A second case study deals with venturi loop reactor that is widely used for high-pressure hydrogenations in the fine chemicals sector. The last case study deals with sparged reactors that are of great relevance in gas to liquid fuels in the current context. These case studies are provided in a clear manner with appropriate worked examples and show how the theory can be applied to practice. Overall the book will be valuable for industrial practitioners and will help them to design these reactors in a fundamentally oriented way.

From a teaching point of view, many schools do not offer advanced courses in multiphase reactor design. Further, existing courses also do not cover it adequately. Lack of appropriate textbook may be one reason why this material that is so vital to

industrial practice is not effectively covered. By including a number of appropriate case studies, Pangarkar has remedied this and fulfilled an important gap in the current teaching of Chemical Reactor Design. This book could therefore be used for special topic course or in a second course in Chemical Reaction Engineering. I presume that such a course is currently taught in Institute of Chemical technology, Mumbai, formerly known as UDCT. Both Pangarkar and I were fortunate to do our doctoral work in this field in this prestigious school and I have contributed to this field with my earlier coauthored book (with R. V. Chaudhari) *Three Phase Catalytic Reactor*, which has been quite popular with industrial practitioners and academicians. I believe that this book by Pangarkar will be equally popular and I endorse and recommend it to my colleagues in academia and industry.

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PREFACE

A practicing chemical engineer invariably comes across one or the other type of a multiphase reactor. The preponderance of multiphase reactors in the chemical process industry has given rise to widespread research directed toward understanding their behavior particularly with a view to develop reliable design and scale-up procedures. The literature is replete with information on various types of multiphase reactors. Additional information is being regularly generated on various aspects of multiphase reactors. The efforts in this direction are using increasingly sophisticated tools like Laser Doppler Anemometry/Velocimetry, computational fluid dynamics, etc. It will be long before the last word is written on design of multiphase reactors. Although this fresh information is welcome, the time and money required for it is disproportionately high, and hence there is a need for simpler, yet theoretically sound, methods to be applied.

Engineering is the bridge that spans the distance between Art and Science. Engineering can convert a seemingly intractable problem into a technically approachable one. Danckwerts (1961) pointed out that the tendency to go more scientific calls for some caution and that “we ought to produce more powerful teaching methods for developing both insight and the qualitative analysis of the problem.” The fine balance between Science and Engineering in any text must be maintained since as another doyen of chemical engineering, Thomas Sherwood (1961) noted “if perspective is lost through enthusiasm for scientific and mathematical analyses, an engineer will be less effective in industry.” The profound statements of these all-time great chemical engineers are extremely relevant to the present state-of-the-art methods for design of multiphase reactors. Astarita (1997) while agreeing with Danckwerts and Sherwood argued that the enthusiasm for computational analyses must be separated from simple

creative arguments. This book is an attempt to practice what Albert Einstein suggested **Everything should be made as simple as possible, but not simpler.**

A number of excellent texts dealing with design of multiphase reactors have been published (Shah 1979; Ramachandran and Chaudhari 1983; Doraiswamy and Sharma 1984; Trambouze et al. 1988; Westerterp et al. 1988; Harriott 2003). This book attempts to provide process design procedures for a variety of industrially important multiphase reactors. The basis of the procedures developed is that whereas the intrinsic kinetics of any multiphase reaction do not vary with the type of the reactor used and its scale, the transport parameters (in particular the gas–liquid/solid–liquid mass transfer coefficients) depend on both the type of reactor and its size. The intrinsic kinetics can be determined on small scale under appropriate conditions, but the transport properties need to be specific to the type and size of the reactor. This book therefore focuses on the development of credible correlations for predicting the mass transfer coefficients. It relies extensively on the findings of my research group at the University Department of Chemical Technology (UDCT), Mumbai, in developing these simple procedures. The tradition of industrial consulting at UDCT, an institute established by the very desire of the chemical industry, enabled me to understand the industrial world and its problems. Industrial consulting is a rich source of valuable research tips. It leads to quality research of industrial relevance combined with academic punch. This consulting experience over the last 40 years starting with Late Mr. Chandrakant Khagram (Evergreen Pvt. Ltd., Mumbai) provided me with a perspective that no classroom learning could have substituted. The concepts of “turbulence similarity,” “relative suspension,” and “relative dispersion” used in Chapters 6, 7A, and 7B have their roots in this industrial interaction. Theory without practice is generally considered “dry.” However, experience convinced me that practice without theory can be disastrous.

This book should be of special interest to process design engineers in the chemical, fine chemicals, and allied industries. Chapter 7A uses the concepts of relative suspension/dispersion mentioned earlier for a simple spreadsheet-based design procedure for the highly complex stirred reactor. Chapter 8 is the first comprehensive chemical engineering–based treatment of the venturi loop reactor. This reactor has no serious competition in the fine chemicals industry. Unfortunately, most of the information pertaining to it is proprietary. The spreadsheet-based design provided in Chapter 8 should be of special interest to the fine chemicals sector. Chapter 7B is also probably a similar, first of its type treatment of stirred reactors for cell culture technology, a frontier area in healthcare. As explained in Chapter 3, specific reactor types are best suited to specific applications in the chemical industry. The treatment of various reactors has been arranged into chapters, more or less, in a self-contained manner. There is, however, some inevitable repetition among chapters, which I hope, would only serve to reinforce understanding in the respective context. The commonality in terms of basic design features has, however, not been ignored as evinced, for instance, in Chapters 7A and 7B.

The chemical and allied industry is continuously evolving. Newer molecules/processes are being developed. In most cases, the time span between discovery and commercial exploitation tends to be very short. Therefore, the process designer has

to either quickly do a reliable design of a suitable multiphase reactor or use an available one. Either way, the simplified spreadsheet-based design procedures for the stirred and venturi loop reactor should find favor with the process design engineering fraternity.

The author is grateful to his students: Aditi Deshpande, Bhushan Toley, Biswa Das, Dhananjay Bhatkhande, Keshavan Niranjana, Manoj Kandakure, Niteen Deshmukh, Prasad Pangarkar, Prashant Mandare, Rajendra Prasad, Randheer Yadav, Sameer Bhongade, Sanjay Kamble, Satish Bhutada, Sri Sivakumar, Venkatesh Shirure, Yogesh Borole and colleague Professor Sudhir Sawant for help in literature details, checking of the spreadsheets and overall comments on the flow of information and readability of the book. Professor Sawant's support on a personal level at crucial stages is also gratefully acknowledged. Special thanks are due to Vishwanath Dalvi and Arun Upadhyaya for regressions of published data. The author gratefully acknowledges help from Mr. Manoj Modi (Reliance Industries Ltd., Mumbai, India) during the initial stages of the project on venturi loop reactor. The diligence of Rahul Bagul and timely corrections by Ajay Urgunde in the artwork is highly appreciated.

Finally, my family, who walked the path and endured my long working hours over the past 7 years, deserve all thanks.

The author sincerely hopes that the information given in this text will make the life of the process design engineer easier. The reductionist approach adopted should appeal to students who wish to unravel the complexities of chemical process equipments through simple arguments.

The workbook files are available at the Wiley Book Support site (<http://booksupport.wiley.com>).

VISHWAS GOVIND PANGARKAR

Nashik, India

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1

EVOLUTION OF THE CHEMICAL INDUSTRY AND IMPORTANCE OF MULTIPHASE REACTORS

1.1 EVOLUTION OF CHEMICAL PROCESS INDUSTRIES

Multiphase reactors have been at the cutting edge of technology development in the chemical industry. This premier status of multiphase reactors can be best appreciated in the context of the evolution of the chemical industry itself. It is therefore appropriate to discuss specific aspects relating to the growth and progress of the chemical process industries. This introduction starts with the evolution of the modern chemical industry and discusses the importance of green and sustainable methods and the inevitability of catalysts and multiphase catalytic reactors for carrying out highly efficient catalytic reactions.

The chemical process industries took a long and arduous road of development from modest beginnings through processes such as brewing and distillation; manufacture of soap, sugar, and paper, etc. in small-scale units. Most of the development was based on serendipity and empiricism rather than application of sound chemical engineering principles. In view of the poorly defined methodology, the advancement was slow. The seventeenth and eighteenth centuries witnessed practically no scientific progress that could bring about significant improvements in chemical engineering principles required for rational design.

In the early 1920s, a need was felt to have a unified approach for different disciplines of chemical engineering, and thus, the concept of unit operations (Walker et al. 1923) was introduced. Subsequently, the concept of unit processes (Groggins 1958), which allowed treatment of individual reaction types on a unified basis, was

added. For example, hydrogenations, esterifications, nitrations, etc. were organized on the basis of related thermodynamics, kinetics, and, to a lesser extent, the hardware for each type of process. Groggins showed that unit operations and unit processes are intimately connected through the governing chemical engineering principles. Indeed, from this point onward, chemical engineering has been mathematically defined as $\text{ChE} = \text{Unit operations} + \text{Unit processes}$.

Extensive research efforts, particularly in the Western world that began in the second half of the twentieth century, laid the foundations of the modern chemical industry. The information generated is, however, still not sufficient for many objectives. For example, *a priori* design procedures for majority of the process equipment are still lacking. Indeed, in many chemical engineering design problems, we find that experience must supplement pure theory. This is an indication that chemical engineering is still largely an art rather than science, where we can evaluate the parameters exactly. For comparison, in electrical engineering, we can precisely calculate the drop in voltage, given the resistance of a conductor and the current it carries. It would be difficult to do the same for the pressure drop in a simple two-phase pipe flow. We need to resort to empirical/semiempirical approaches in a majority of the cases because of lack of sufficient knowledge of the phenomena involved. This example should serve as an indicator of the difference in chemical engineering and other basic engineering disciplines.

In the initial stages, the chemical process industries were restricted to inorganic chemicals (sulfuric acid, nitric acid), sugar, paper, fertilizers, etc. Most hydrocarbons were derived from coal.

From the mid-1950s onward, petroleum crude took over from coal as the principal supplier of hydrocarbons. The major impetus to the organic chemicals sector came from the availability of inexpensive petroleum crude in large quantities. Products derived from petroleum crude had capability to undergo a variety of complex reactions to yield different products that the evolving society required. Chemical engineering became a much more complex profession than in the 1920s. Some basic changes were occurring but were not obvious. The refining and petrochemical industries started producing specialized products with well-defined functions/properties. Products such as high-octane gasoline and specific lubricants were considered as commodity products notwithstanding their careful formulation that gave the specific desired end result. These formulations also underwent changes brought about by various considerations such as environmental impact. An example is that of replacement of tetraethyl lead in gasoline by more benign antiknock compounds. The chemical process industries were slowly shifting from the commodity/bulk chemicals to specialty/functional products (Cussler and Moggridge 2001). This paradigm shift called for more specialists than generalist chemical engineers. According to a 2004 survey (Jenck et al. 2004), “the global chemical industry represents a significant part of world trade and economic activity with 10 million employees and a combined turnover of some USD 1600 billion excluding pharmaceuticals, and at USD 2200 billion including pharmaceuticals, representing 4–5% of world income. It contributes 9% of world trade whilst emitting only 4% of global carbon dioxide.” Evidently, the carbon dioxide emissions of the chemical process industries are an insignificant

fraction of the total global carbon dioxide emissions. In spite of these highly revealing statistics, most chemical majors are curtailing greenhouse gas emissions as a part of overall sustainability measures (McCoy 2008). Indeed, processes for utilizing this liability (CO_2 , generated by other sectors) for value-added products are receiving increasing research attention (Section 1.3.1.1). A recent review by Muller et al. (2014) discusses the thermodynamic feasibility of potential reactions for converting CO_2 to value-added chemicals. This review points out the severe thermodynamic limitations imposed by the low energy level of CO_2 . The following conclusion have been derived: Thermodynamically, favorable routes for producing useful chemicals require (i) high-energy reactants such as epoxide that overcome the low energy level of CO_2 , (ii) *in situ* hydrogenation of the intermediate, or (iii) formation of at least two water molecules per mole of CO_2 . Such efforts are indicative of an industry that is conscious of its societal responsibility despite the fact that it bears a very small burden of the CO_2 generated.

The chemical process industries have been at the receiving end of the regulatory authorities not because of their greenhouse gas emissions but due to their toxic emissions. Both of these prompted a drive for sustainable processing. The sustainability aspect needs to be dealt with in some detail. The rapid expansion of the petroleum refining and petrochemicals industry through a *laissez-aller* approach resulted in unbridled consumption of vital resources with simultaneous generation of hazardous waste. The development of the industry was disorganized with little attention being paid to the damage caused to the ecosystem. Over the past five to six decades, release of toxic wastes in all forms (solid/liquid/gaseous) has caused serious damage to the ecosystem. Rachel Carson's 1962 book *Silent Spring* was the first recorded warning of the catastrophic nature of the rapid, unsavory expansion. Rachel Carson argued that man is not above nature but is an integral part of it and hence must ensure peaceful coexistence with all species involved. The chemical and allied industries were the main culprits in the eyes of the society that suffered episodes such as the "Love Canal" and "Bhopal" tragedies. As a result of the severe criticism, the chemical industry is now closely looking at safety, health, and environment (SHE) issues while developing a new process or designing a new plant. However, the SHE aspects as practiced are related to decisions that are essentially of short-term nature to avoid contingencies typified by "firefighting" situations. In the 1980s, a more mature approach "sustainable development" was advocated as a long-term objective. *Our Common Future* published by the World Commission on Environment and Development defined sustainable development as "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs." This definition abhors senseless consumption and waste creation. A complementary definition of sustainable development given in 1991 in *Caring for the Earth: A Strategy for Sustainable Living* by IUCN, UNEP, and WWF was "Improving the quality of human life while living within the carrying capacity of the supporting eco-system." The 2002 World Summit on Sustainable Development expanded the previous definitions, identifying "three overarching objectives of Sustainable Development as (1) eradicating poverty, (2) protecting natural resources, and (3) changing unsustainable production and consumption patterns." Sustainability

has been at the core of human philosophy as evinced by the following excerpt from ancient Vedic literature:

“Whatever I dig from thee, O Earth, may that have quick growth again.
O Purifier; may we not injure thy vitals or thy heart (Atharva Veda)”

This quote should be a clear message to all engaged in various industries and in particular the chemical process industries. Sustainability was the theme of 21st International Symposium on Chemical Reaction Engineering (LaMarca et al. 2010).

1.2 SUSTAINABLE AND GREEN PROCESSING REQUIREMENTS IN THE MODERN CHEMICAL INDUSTRY

The reader may wonder about the need for all this philosophy and its relation to the design and scale-up of multiphase reactors. The origin, advent, and ubiquity of multiphase reactors lie in the quest for curtailing wastage of resources through highly selective alternatives to less selective processes practiced earlier. The statement of Sir John Cornforth (cf. Adzima and Bowman 2012) sums up the final goal of chemical synthesis on large scale:

The ideal chemical process is that which a one-armed operator can perform by pouring the reactants into a bath tub and collecting pure product from the drain hole.

Chemical engineers and chemists always envied the highly selective synthesis of complex molecules in nature. The specificity of enzymatic reactions was also known for a long time. The brewing industry that performed a simple sugar to alcohol reaction was the first known use of enzymes to provide a product of great joy to many. The chance discovery of penicillin triggered the quest for antibiotics to treat various diseases. The subsequent specific varieties of antibiotics were refinements brought about by the application of life sciences/synthetic chemistry. The specificity of enzymatic reactions created enormous interest, particularly for complex molecules, which could only be made with great difficulty and low selectivity by synthetic organic chemistry. This second paradigm shift arose out of the industry's aim of making complex products from inexpensive raw materials at selectivity levels achievable only in nature. The advantages of biotechnology brought it to the forefront. Consequently, chemical majors such as DuPont, DSM, etc. made major investments in life sciences divisions. In the recent past, there is a growing interest in biological therapeutics and stem cell therapy (subject of Chapter 7B).

Selectivity is important across the broad spectrum of the chemical process industry. Therefore, there is a continuous quest for more selective syntheses. The most prominent approach adopted by the team of chemical engineers and chemists is to develop highly selective catalysts (Section 1.3). The ultimate aim would be complete selectivity for conversion of a given reactant to the desired product with minimum energy requirement and without any hazard.

This approach called “green chemistry” was first enunciated by Anastas and Warner (1998) in their book *Green Chemistry: Theory and Practice*. The American Chemical Society’s Green Chemistry Institute has identified the following 12 distinguishing features of green chemistry:

1. Prevention

It is better to prevent waste generation than to treat or clean up waste after it has been created. The earlier messy Bechamp reductions using Fe–HCl and generating a highly acidic waste sludge are replaced by clean catalytic processes using suitably designed multiphase reactors (Section 1.3 and Chapters 7A and 8).

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Special types of processes that yield high selectivity are being introduced.

3. Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to perform their desired function while minimizing their deleterious effects. Product design has emerged as a new discipline.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (such as solvents and separation agents) should be made unnecessary wherever possible. When unavoidable, the auxiliary substances should be safe to handle. Water-based systems are desirable because of the absence of toxicity and low (practically no) cost.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be an important aspect in view of their environmental and economic impacts. Minimization of energy requirement should be a perpetual exercise. If possible, synthetic methods should be conducted at ambient temperature and pressure. Section 1.3.1.1 discusses some recent trends for achieving this objective. All worked reactor design examples in this book (Sections 7A.10, 8.13, and 9.5) include estimation of energy requirement to compare the energy efficiency of different reactors.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting, wherever technically and economically practicable. Energy from biomass is a very important contemporary research activity. First-generation fuel (ethanol) technologies were based on plant sugars and starch. In second-generation biofuels, lignocellulosic species, considered to be much less expensive, were contemplated, while the third-generation biofuels comprise fuel components derived from algae. There are conflicting reports/conclusions for each type. Hammerschlag’s (2006) analysis of literature data from 1990 on ethanol’s

return on investment indicated that corn-based ethanol can substantially reduce petroleum crude oil consumption when used to replace gasoline. This study further showed that cellulosic ethanol is still better in terms of reducing oil consumption. A later report (Pala 2010) also supported the energy efficiency of the biomass (grass) to ethanol route. However, in terms of cultivation, corn is advantageous because it has multiple uses against limited uses for grass. The idiom “There is no free lunch in science or nature” applies and, indeed, dictates the economics. In a rare paper, the proponents and opponents of bioethanol joined to analyze the discrepancies in their individual assessments (Hall et al. 2011). The conclusion was that the practicality of a biomass to fuel (ethanol, in this case) must be ascertained on the basis of energy return on investment (EROI) with the best data available. In another recent critical analysis, Bahnholzer and Jones (2013) have shown that biomass to chemicals route is ridden with several problems. The shelving of the USD 300 million worth biomass to ethanol project of BP has been cited as a commercially significant example. Estimates of Bahnholzer and Jones from the data of Salehi et al. (2013) indicate that even the gas to liquid (GTL) conversion is inefficient since it consumes 1.8 MJ energy from natural gas for producing 1 MJ in terms of the liquid fuel. However, GTL is relatively attractive because it converts a low-mass and low-energy density raw material to a higher density type, thereby improving the quality of the fuel. GTL has substantial commercial logic when there is a specific demand for liquid fuel, particularly when the raw material is “stranded gas.” Further, liquid fuel is easier to transport, and therefore, GTL has some justification. An example of such positive upgradation cited by Bahnholzer and Jones (2013) is conversion of fossil fuels to electricity. This conversion also has an inherent inefficiency. However, the final energy product is far superior to the fossil fuel employed as the raw material. The latter is used mainly in utility and to an extent directly in transport. Electricity, on the other hand, has multiple applications besides being more easily transported as compared to a fossil fuel. In this regard, Bahnholzer and Jones suggested that EROI may not be a vital factor in evaluating an improved energy delivery service as compared to simple conversions such as biomass to fuel. Overall, for conversion of low-mass and low-energy density substances such as biomass to low-value chemicals, this approach has very little justification. The obvious reason is consumption of excessively high energy (very highly carbon negative) than what is available from the product of the process. The arguments made by Bahnholzer and Jones are compelling and cast a serious doubt on the biomass to chemical (ethanol)/algal routes. The situation could, however, be different for biomass-based specialty (nutraceuticals)/functional chemicals where the value addition and economic incentive is greater. The use of valuable multipurpose electricity for low-value products has also been heavily criticized by Bahnholzer and Jones (2013). They argued that “It simply is impractical to make fuels (and also low value chemicals) from electricity because the energy losses during the conversion are simply too large.”

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection–deprotection, and temporary modification of physical–chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste. This also implies reduction of multistep syntheses to much lesser, preferably a single step. Examples of this strategy pertaining to selective aqueous-phase photocatalytic oxidations of hydrocarbons are discussed in Section 1.3.1.1 (Izumi et al. 1980; Yoshida et al. 1997; Gonzalez et al. 1999; Du et al. 2006).

9. Catalysis

Catalytic processes are superior to processes that use stoichiometric reagents (Bechamp reduction cited earlier). There is a continuous improvement in catalysts. Many acid-catalyzed reactions (esterifications, hydrations, alkylations) have been replaced by benign ion exchange resins in the H^+ form (Wasker and Pangarkar 1992, 1993). The newer catalysts are not only more selective but also more active in enhancing reaction rates. In some cases, for instance, replacement of mineral acids by ion exchangers allows the use of low-cost material of construction and facile separation/recycle of the catalyst while simultaneously eliminating ultimate neutralization of the product by a base.

10. Design for Degradation

Chemical products should be designed so that at the end of their function, they break down into innocuous products and do not persist in the environment.

11. Real-Time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control to avoid formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances used in a chemical process should be chosen to minimize the potential for accidents, including release of toxic substances, explosions, and fires. Examples of such safe chemistries and the corresponding multiphase reactors available are discussed later in Sections 1.3.1.1 and 1.6. The possibility of a runaway reaction can be eliminated through the use of microstructured multiphase reactors, which afford order of magnitude of higher heat transfer coefficients as compared to the conventional reactor/heat exchanger combination. Section 1.3.1.1 describes “direct” introduction of a specific functional groups as an alternative to their “indirect” introduction.

Source: American Chemical Society’s Green Chemistry Institute (cf. Ritter 2008).

In the foregoing, only points that are relevant to multiphase reactions/reactors are dealt. Points 1, 2, 6, 9, and 12 are synonymous, implying (directly or indirectly) high selectivity of conversion of a given reactant to the desired product. The limit of selective processes is the acid–base (electron transfer) reaction. This reaction goes not only to completion but is also instantaneous (Section 1.7). The same cannot be

envisaged even of combustion reactions. These have a highly favorable free energy change, yet these reactions are never complete. If they were, we would not have the problem of presence of carbon monoxide in, for example, auto exhausts. A highly selective process also implies no or very little wastage of the reactant through formation of undesired products. When these undesired products have no utility, they have to be discarded. Further, when these species are toxic and are disposed without any treatment, serious ecological problems arise. Risking repetition, a highly selective process is also the least polluting or requires least treatment prior to disposal of the undesired by product.

The earlier discussion clearly points out the direction in which the modern chemical process industry is moving. Katzer (2010) has articulated the case for sustainable research, development, and demonstration (RD&D). As argued by Katzer, sustainable development needs to be an organized effort, combining skills and expertise of various disciplines. An excellent example is that of solar energy. Meaningful development in economically viable solar electricity generation will need combined efforts of material scientists, architects, and government agencies so that individual households and commercial premises can have sustainable supply that will always be carbon negative. Solar energy to electricity is the ultimate upgradation of energy in the sense of Bahnholzer and Jones. Even considering the energy used in making the solar energy conversion/storage systems, this approach should be a winner. There is an urgent need for increasing the conversion efficiency and reduction of capital costs through innovation in this field (Johnson 2013; Jacoby 2014).

There are several instances of innovative ideas originating from nonscientists. These will again need to be taken up and developed for the benefit of the society. Katzer has given examples of “success and failures” across a broad spectrum of scientific activities. In the field of chemical processing, the overriding considerations that must be employed in future plans involve sustainable processing, including green chemistry and engineering. An ideal reaction would have to be highly selective, nonhazardous, nonpolluting, and self-sufficient in terms of energy requirement. This is certainly a tall order. Current research activity both in terms of the process (Wiederkehr 1988; Choudary et al. 2000; Kolb et al. 2001; Chaudhari and Mills 2004; Jenck et al. 2004; Chen et al. 2005; Andrews et al. 2009, 2010; Buchholz 2010; Adzima and Bowman 2012) and hardware, in terms of multiphase reactors (Dudukovic et al. 2002; Stitt 2002; Boger et al. 2004), is directed at achieving at least some of the aforementioned objectives. What needs to be done at a much higher level can be illustrated by the excellent example of nitrogenous fertilizers based on ammonia. The latter is obtained industrially by the Haber–Bosch process. Andrews (1977) has shown that these fertilizers are thermodynamically extremely inefficient in providing nitrogen to the plants. Ammonia is made by an energy-intensive process that abstracts precious hydrogen from carbon–hydrogen feedstock. Eventually, prior to the final step of uptake of the nitrogen by the plants, this expensive hydrogen is almost totally wasted through oxidation to water by nitrate-forming bacteria. In turn, the plants have to spend more photosynthesis-derived energy to reduce the nitrate back to ammonia. Plant biochemistry does not allow swift absorption of large quantities of ammonia. The most efficient route would be through fixing of nitrogen as

nitrites. However, commercially viable processes for this route do not exist (Andrews 1977). As a result, a very large amount of hydrocarbon feedstock is being consumed for the production of urea through ammonia by the Haber–Bosch process. There is an urgent need for INVENTING alternate sustainable methods for this very important activity that provides food to the ever-growing world population. As indicated earlier, the other area that requires immediate attention is conversion of solar energy to electricity. This field has witnessed innovation, but if the world is to meet its increasing energy needs, innovation may not be sufficient. There is a clear need for INVENTION in this field so that a quantum jump in efficiency with corresponding lower costs and longer life can be achieved.

1.3 CATALYSIS

A report of the American Chemical Society (1996) indicates that more than 90% of industrial chemicals are produced by catalytic processes. At the heart of a highly selective process is the catalyst. The term “catalyst” was first introduced by J. J. Berzelius in 1835. A catalyst is a material that promotes a given reaction without undergoing any change in itself. The catalyst only enhances the rate of the reaction without affecting any of the related thermodynamic phenomena. As compared to the noncatalytic path, the catalytic path offers a low-energy barrier route for the reactant to undergo the specified reaction. There are nearly 30,000 chemicals produced worldwide and production of most of the processes involves catalysis in at least some of the steps (Weissmermel and Arpe 2003). In the beginning, the fine chemicals sector, in particular, used routes employing stoichiometric reagents (chromic acid/permanganate for oxidation, borohydrides, Bechamp reaction for reduction, etc.). These processes not only raised safety and health concerns but also created a waste stream containing hazardous inorganic salts. Current specifications on all chemicals for human consumption do not allow use of any heavy metal intermediates or even heavy metals as materials of construction in a process. Therefore, the use of the earlier routes has been completely phased out. These have been replaced by benign, selective, and eco-friendly multi-phase catalytic routes. However, in the specialty sector involving small volume production of high-value products, some processes may still use less benign methods.

The Haber–Bosch catalytic process for production of ammonia is perhaps an invention that had the most dramatic impact on the human race (Ritter 2008). The inexpensive iron-based catalyst for ammonia synthesis, which replaced the original, more expensive osmium and uranium catalysts, made it possible to produce ammonia in a substantially effective manner. The objective here was not improvement in selectivity but higher reaction rates for rapid approach to the equilibrium conversion at the specified temperature and pressure. Higher rates meant lower catalyst volume and smaller high-pressure reactors. The iron catalyst was improved by addition of several promoters such as alkali metals. In contrast to this simple single reaction case of ammonia synthesis, most organic reactions are complex with multiple pathways.

Armor (2011) has given a brief but excellent account of the history of modern catalysis. The following major stages/product lines in which catalysts play an

important role have been identified: (i) basic chemical industry consisting of petroleum refining and petrochemicals. Houdry's fluid catalytic cracking catalyst was developed around 1930. This was the harbinger of the burgeoning petrochemical industry that fed many other sectors such as polymers, pharmaceuticals, agrochemicals, and other specialty chemicals. Parallel to the petrochemicals from petroleum crude, pre-World War II Germany had developed the coal to chemicals route. This was later abandoned in the Western world. However, the same flourished in crude oil-starved South Africa, (ii) transportation fuels sector that later became an integral part of modern refineries. Development of catalysts for naphtha reforming, alkylation, isomerization, etc. was the first phase in this stage. With increasing demands on cleaner fuels, hydro-desulfurization catalysts were developed. Later with increasing crude prices, catalytic hydrocracking was added in the "bottom of the barrel" approach to crude utilization; (iii) polymers obtained from catalytic processes appeared on the scene with introduction of nylon by DuPont in the 1930s. A large variety of polymers with uses ranging from industrial to household to apparel were added to this list; (iv) beginning with 1950, a host of specialty and fine chemicals were made by catalytic routes. These included active pharmaceutical ingredients, agrochemicals, synthetic dyes, surface coatings (paints), fragrance and flavor chemicals, etc.; (v) automobile emission control catalysts were introduced in the later half of the 1970s as a sequel to the increasing concerns about NO_x , diesel soot emissions, etc.; and (vi) increase in petroleum crude prices brought into focus biodiesel obtained from catalytic transesterification of vegetable oils. Currently, better catalysts are also being developed for coal gasification and Fischer–Tropsch synthesis to yield a variety of products from coal. The latter is being considered as a substitute for petroleum crude (Levenspiel 2005). Hydrogenation is an important process addressed in this book. Chen et al. (2005) have reviewed the literature on hydrogenation catalysts for fine and intermediate chemicals. With increasing demands on high selectivity combined with clean processes, the quest for appropriate catalysts intensified. Very few reactions such as the nitro to amino in the presence of abundant hydrogen supply and a good hydrogenation catalyst have high selectivity, such as those desired in industrial processes. An example is the extensively studied catalytic epoxidation of ethylene to ethylene oxide. This process is used worldwide on a very large scale. The silver-based catalyst with several additives can achieve selectivity very close to ~86% predicted by one of the mechanisms proposed. Yet, the quest for a better catalyst combination for this reaction continues. A catalyst that gives even 1% higher selectivity can reap rich dividends. This reaction is a classical example of application of catalysis science. With plant scales in the range of several hundred thousand tonnes per year, the stakes are very high. The margin for error is very small.

Fischer–Tropsch synthesis is another industrially important case where the quest for a catalyst with higher rate as well as selectivity continues. This synthesis is exothermic, and catalysts with higher activity (higher rates) will impose a burden on the heat exchanging capacity of the multiphase reactor used. Development of better catalysts must be accompanied by multiphase reactors that can cater to the higher exotherm associated with faster rates. Section 3.4.1.4 discusses the various available reactor options.

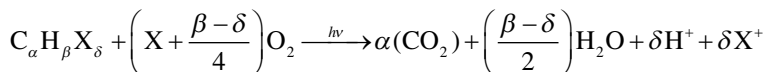
Catalysis is generally classified into two types depending on the physical nature of the catalyst employed: (1) heterogeneous, in which the catalyst is immiscible with the reaction medium and is present as a separate phase, and (2) homogeneous, in which the catalyst is soluble in the reaction medium. Multiphase reactors are used in both categories.

1.3.1 Heterogeneous Catalysis

Heterogeneous catalysis is the most preponderant type in industrial applications. Some of the common features of heterogeneous catalysis are (i) relatively severe temperature and pressure conditions, (ii) applicable for both batch and continuous modes of operation, (iii) relatively long catalyst life if poisons are eliminated, (iv) facile separation of the catalyst after completion of the reaction, etc. Therefore, almost all important areas, such as processing of petroleum crude (e.g., catalytic reforming, catalytic cracking, hydrocracking, hydro-desulfurization, etc.) and other processes for bulk chemicals such as ammonia and Fischer–Tropsch synthesis, manufacture of sulfuric acid, etc. use heterogeneous catalysts. This long list extends to fuels (for transportation, energy, etc.) and generation of building blocks (for further consumption by pharmaceutical and fine chemicals industries) from petroleum crude oil. For more details, the reader is referred to Cybulski et al. (2001), Weissrermel and Arpe (2003), and Moulijn et al. (2013).

1.3.1.1 Selective Photocatalysis: A Paradigm Shift in Synthetic Chemistry

Photocatalysis has been widely investigated for degradation of refractory organic compounds as an advanced oxidation process (Bhatkhande et al. 2002, 2003, 2004; Kamble et al. 2003, 2006; Pujara et al. 2007). The major advantage of this approach is complete mineralization (complete reduction of chemical oxygen demand, COD) of refractory pollutants at ambient conditions. Semiconductor materials have been used as the photocatalyst. In majority of these investigations, Degussa P25, a 70:30 mixture of anatase and rutile forms of TiO_2 , has been used. A typical photocatalytic mineralization reaction is described by the following stoichiometry:

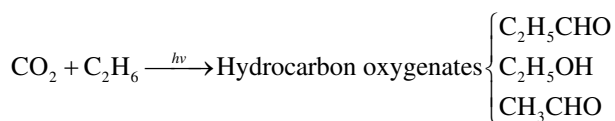


The generally accepted mechanism for photocatalytic transformations in aqueous media is the attack of OH^\cdot on the organic moiety. Bhatkhande et al. (2002) have discussed the various mechanisms proposed for photocatalytic pathways. In the case of aromatic compounds, it has been shown that hydroxy aromatic compounds are formed through the mediation of OH^\cdot . It has also been shown that a maximum of three hydroxyl groups can be attached after which the compound becomes highly unstable and decomposes to CO_2 and water. This is evident because no aliphatic compounds are formed. This mechanism can be used to obtain di- and trihydroxy compounds (Brezova et al. 1991; Centi and Misono 1998; Ye and Lu 2013). Other hydroxylated compounds such as *o* (salicylic acid) and *p* (-hydroxy benzoic acids)

are also potential candidates. Salicylic acid is the precursor for aspirin, the more than century-old wonder drug manufactured on a very large scale. The conventional process for salicylic acid starting with phenol is relatively time-consuming and generates large quantities of waste streams. Photocatalytic hydroxylation of benzoic acid can be a neat and nonpolluting alternative.

Unfortunately, it is not easy to control the extent of oxidation of the substrate for selective formation of a partially oxidized species or addition of specific number of hydroxyl groups at the desired position in the substrate. Notwithstanding this drawback, there has been considerable research interest in selective photocatalytic oxidation. Du et al. (2006) have shown that with a proper combination of the incident photon wavelength and photocatalyst, it is possible, for instance, to obtain almost complete selectivity for oxidation of cyclohexane to cyclohexanone. It may be noted that cyclohexanone is manufactured in large quantities as an intermediate for ϵ -caprolactam. A sizeable quantity of cyclohexanone is obtained by oxidation of cyclohexane, a process that has very bad memories (Flixborough, United Kingdom). The major problem in this conventional route is formation of cyclohexanol, which must be separated and catalytically dehydrogenated to improve the cyclohexanone yield. This latter part of the process consumes substantial quantities of energy. Therefore, there has been a quest for a selective, safe, and hazard-free process for oxidation of cyclohexane to cyclohexanone. The investigation of Du et al. (2006) shows great promise to replace the conventional oxidation route.

There is a surfeit of attractive applications of selective photocatalysis that can be game changers. An example is the elegant innovative approach suggested by Wang et al. (2005) that involves the use of inexpensive ethane and a liability greenhouse gas, CO_2 , to obtain value-added products. The proposed reaction is:



The use of an inexpensive feedstock such as natural gas for producing value-added products is a very interesting concept, particularly in view of large-scale availability of lower alkanes from shale gas in the United States and other new natural gas finds. The current route to formaldehyde through methanol involves relatively high capital cost in production of syngas and its conversion to methanol followed by oxidation to formaldehyde. Direct conversion of alkanes to aldehydes can allow significant reduction in both capital cost and energy consumption. Applications of photocatalysis in converting CO_2 to value-added products such as formaldehyde, formic acid, methanol, etc. is another highly attractive concept that has been exhaustively surveyed by Usubharatana et al. (2006).

Palmisano et al. (2007) have reviewed pertinent literature up to 2007. Fagnoni et al. (2007) have presented an excellent review of the literature on photocatalysis for the formation of the C–C bond. Table 1.1 summarizes some recent investigations besides those covered by Palmisano et al.

TABLE 1.1 Some Important Investigations on Selective Photocatalytic Oxidation

Substrate	Main products	Photocatalyst employed	References
Ethane	Acetaldehyde, ethanol, formaldehyde, CO ₂	MoO ₃ /SiO ₂ , ZnO–TiO ₂ /SiO ₂	Wada et al. (1991); Kobayashi (2001)
CO ₂	Formaldehyde, formic acid, methanol, and trace amount of methane	Various photocatalysts reviewed	Usubharatana et al. (2006)
Styrene	Styrene oxide, phenyl acetaldehyde, benzaldehyde	TS-1	Laha and Kumar (2001)
Ethane	Acetaldehyde, ethanol, formaldehyde, CO ₂	MoO ₃ /SiO ₂ , ZnO–TiO ₂ /SiO ₂	Wada et al. (1991); Kobayashi (2001)
Benzene	Maleic acid, hydroquinone, resorcinol, catechol, phenol, CO ₂ Very poor selectivity to non-CO ₂ products	TiO ₂ /mica	Shimizu et al. (2002)
Ethane + CO ₂	Propanal, ethanol, acetaldehyde	ZnO–TiO ₂ /SiO ₂	Wang et al. (2005)
Ethyl benzene	Acetophenone	Degussa P25	Gonzalez et al. (1999)
Cyclohexane	Cyclohexanone (partially cyclohexanol). Total selectivity to cyclohexanone possible through careful control of operating conditions	V ₂ O ₅ /Al ₂ O ₃ ; TiO ₂	Giannotti et al. (1983); Mu et al. (1989); Gonzalez et al. (1999); Teramura et al. (2004); Du et al. (2006); Almeida et al. (2010)
Toluene	Benzaldehyde; benzyl alcohol	Degussa P25	Gonzalez et al. (1999)
Methyl cyclohexane	1-, 2-, 3-, and 4-methyl cyclohexanol, 2- and 3-methyl cyclohexanone.	Degussa P25	Gonzalez et al. (1999)
Benzyl alcohol	Benzaldehyde	Degussa P25/Cu (II)	Spasiano et al. (2013)
Nitrobenzene	Amino benzenes and ketones	Ti (IV) without precious metals	Imamura et al. (2013)
Ethanol	Acetaldehyde	V ₂ O ₅ on TiO ₂ on commercial ZnS-based phosphor	Ciambelli et al. (2011); Sannino et al. (2013)
Phenol	Catechol, hydroquinone	Specially prepared anatase TiO ₂ nanocrystals	Ye and Lu (2013)
Amino alcohols	1,3-Oxazimes	Ru(bpy) ₃ Cl ₂	Mathis et al. (2013)
Hydroamination of alkynes	Amines, enamines, and imines	Supported gold nanoparticles	Zhao et al. (2013)

It is evident from this summary that there is an increasing interest in heterogeneous photocatalysis as a green and safe substitute to conventional chemical transformations.

Bhatkhande et al. (2002) have surveyed the literature pertaining to the substitution of OH[•] on the aromatic ring. In most cases, the attack occurs at a position favored by the existing functional group. However, exceptions have been observed depending on various factors such as the source and strength of radiation, catalyst used, etc. For instance, nitrobenzene should favor formation of *m*-nitrophenol. Contrary to this meta-directing effect in nitrobenzene, Bhatkhande et al. (2003) observed large amounts of *p*-nitrophenol (almost twice as compared to *m*-nitrophenol) when concentrated solar radiation was used. On the other hand, with UV radiation ($\lambda_{\text{max}} = 253$ and 365 nm), no intermediates were observed, implying that this type of radiation was strong enough to completely degrade the substrate without noticeable formation of intermediates. Evidently, tuning of the oxidation level and selectivity for a desired isomer is possible through a combination of the related parameters (Du et al. 2006).

Photocatalytic reactions occur on the surface of the photocatalyst. Evidently, all participants in the reaction, the oxidant, and substrate should be present on the catalyst surface. Supply of the oxidant is obviously dictated by the process parameters that generate it. These are the type of photocatalyst and the strength and intensity of the incident photons. The substrate has to be supplied to the catalyst from the bulk liquid phase, and therefore, mass transfer factors play an important role. Finally, the affinity of the substrate with the surface of the photocatalyst decides its surface concentration. Therefore, factors that affect adsorption of the substrate on the photocatalyst play a crucial role. These are (Bhatkhande et al. 2002) (i) the nature of the photocatalyst surface, (ii) the substrate itself, (iii) the isoelectric pH of the photocatalyst, (iv) pH of the solution being treated, and (v) presence of anions. Degussa P25 has been used as the model photocatalyst in most investigations. It has been generally found that adsorption is maximum in the vicinity of the zero point charge pH (zpc). Further, ionized substances (organic acids at high pH or organic bases at low pH) suffer from poor adsorption. Therefore, when such substrates are involved, the solution pH must be such that it is near the zpc of the catalyst. Bhatkhande et al. (2002, 2003) and Kamble et al. (2003, 2006) found that anions present in the reaction mixture generally had a detrimental effect on the attack of OH[•]. In particular, typical hydroxyl scavengers (Cl⁻, HCO₃⁻, CO₃⁼) exhibited strong negative effect on the extent of adsorption. This effect can be advantageously applied for slowing the attack of OH[•] and regulate the selectivity for the intermediate in the photocatalytic attack on the substrate. This is in addition to the various other methods suggested for enhancing the selectivity (Du et al. 2006). In conclusion, it can be argued that it is possible to fine-tune selectivity for a given product by employing conditions that (i) regulate the adsorption of the substrate and desorption of the product desired, (ii) reduce the strength (λ) and dosage (intensity) of the photons, etc. as discussed by Du et al. (2006). Evidently, selective photocatalysis is a highly

attractive route that can bring about paradigm changes in the current processes for certain chemical syntheses.

The discussion on this topic will not be complete without a brief discussion on different types of photocatalytic reactors that can be used. A photocatalytic reaction is essentially a heterogeneous reaction involving the substrate, an electron acceptor (oxygen from air in most cases), a solid photocatalyst, and the incident photons. Thus, all parameters that affect the performance of a three-phase (gas–liquid–solid) reactor need consideration while choosing the type of reactor to be used. An additional and probably the most important parameter that governs the rate of a photocatalytic reaction is the photon intensity distribution in the reactor (Pareek 2005; Pareek et al. 2008; Motegh et al. 2013). This additional variable needs to be included in the modeling and design of a photocatalytic reactor. Basically, two types of photocatalytic reactors have been employed: (1) fixed film of photocatalyst (Usubharatana et al. 2006) and (2) suspended photocatalyst. A comparison reveals the advantages and drawbacks of each type. The fixed bed type has the advantage that it does not require separation of the photocatalyst. However, this advantage is more than offset by problems concerning inadequate mass transfer from the liquid to the photocatalyst, lack of photon penetration beyond the top layer of the photocatalyst, and consequent nonutilization of major fraction of the photocatalyst. The suspended or slurry-type photoreactor provides excellent mass transfer and utilization of the photocatalyst. The requirement of photocatalyst is also relatively very low (<1 wt%; typically 0.1 wt%). Kamble et al. (2004) and Pujara et al. (2007) have described slurry reactors for both solar and artificial UV radiation.

Selective photocatalysis requires electrical energy to generate photons. The arguments of Bahnholzer and Jones (2013) against use of electricity for producing commodity chemicals have been discussed earlier. Notwithstanding, such clear exposition of this folly, examples of the same abound. An example is the use of ultrasound for intensification of reactions such as transesterification of vegetable oils, enzymatic hydrolysis of lignocellulose, etc. Efficiency of conversion of primary power to ultrasonic power is relatively very low (maximum 30–40%), and the actual utilization of ultrasound energy for reaction is unlikely to be far different than the above value. Contrary to this, for many examples in Table 1.1, the EROI should be attractive. Natural gas to aldehydes (instead of methanol route), benzoic acid to salicylic/*p*-hydroxy benzoic acid (instead of phenol-based Kolbe–Schmitt transformation), and cyclohexane to cyclohexanone (instead of conventional oxidation) are some examples for which a simple comparison of existing processes with selective photocatalytic oxidation route should reveal the immense benefits in terms of EROI.

Conclusion: The earlier discussion clearly shows the significant advantages of selective photocatalysis. It is evident that this route requires milder conditions, far less capital investment while yielding high selectivity under proper conditions. Thus, it can bring about radical changes in certain chemical syntheses. It must be emphasized that considerable efforts will be needed to develop the concepts discussed earlier to the level of mature technologies.

1.3.2 Homogeneous Catalysis

Homogeneous catalysis is of a more recent origin as compared to heterogeneous catalysis. Although industrial applications of homogeneous catalysis are much less in comparison to heterogeneous catalysis, it has some significant advantages. Some general features of homogeneous catalysts are as follows:

1. **Advantages:** mild reaction conditions, high activity and selectivity, better mechanistic understanding, etc.
2. **Drawbacks:** difficult and expensive separation of the soluble catalyst from the product.

The advantages of homogeneous catalysis outweigh the drawbacks, and therefore, the interest in homogeneous catalysis is growing. In view of this, some basic information on homogeneous catalysis is presented in the following.

Most of the processes involving homogeneous catalysis (e.g., carbonylation, hydroformylation, oxidation, telomerization, copolymerization, metathesis, etc.) utilize inexpensive feedstocks available from processing of petroleum crude and produce important bulk and fine chemicals for polymer, pharmaceutical, paints, and fertilizer industries (Parshall 1980, 1988a; Masters 1981; Cornils and Herrmann 1996, 1998; Beller and Bolm 1998; Choi et al. 2003; Weissermel and Arpe 2003; Gusevskaya et al. 2014). As mentioned earlier, the separation and recycle of the catalyst is relatively complex. This is achieved through precipitation of the catalyst by addition of nonpolar solvents, high vacuum distillation, extraction of products into a second phase, etc. In spite of this complicated recovery and recycle, about 25% of the industrial catalytic reactions involve homogenous catalysis. The most attractive feature of homogeneous catalysis is better mechanistic understanding of its micro “processes” (catalytic cycles), which allows the possibility of influencing steric and electronic properties of these molecularly defined catalysts. Therefore, homogeneous catalysis is highly promising for innovative chemistry for specialty materials that are otherwise difficult to produce by conventional processes. This is an overriding and clear advantage over heterogeneous catalysis. Understanding of heterogeneous catalysis is still poor despite the advent of highly sophisticated instrumental techniques (Section 1.5). Indeed, heterogeneous catalysis is termed as an alchemist’s “black art” because of this poor mechanistic understanding (Schlogl 1993). This is clearly illustrated by a comparison of examples of hydroformylation on one hand and Fischer–Tropsch reaction on the other. While both represent catalytic carbon monoxide chemistry, the molecular structure of the homogeneous catalyst is precisely known to be trigonal-bipyramidal, *d*8-Rh-I, whereas for the Fischer–Tropsch reaction occurring on solid surfaces, no clear molecular level mechanism is known (Herrmann 1982). The progress of homogeneous catalysis is particularly significant and rapid in the area of fine chemicals. The main objective is to achieve high atom efficiency or *E* factors. Thus, the goal of “green chemistry” as a synonym to environmentally benign chemicals and processes, including sustainable development, is

more reliably performed through homogeneous catalysis rather than heterogeneous catalysis (Cornils and Hermann 2003).

The performance of homogeneous catalysts depends not only on the physical conditions of the reaction but also on the type of the metal, ligands, promoters, and cocatalysts. Selectivity is one of the most important issues in a majority of the cases. Generally, transition metal complexes are used as catalysts because of their stability in varying oxidation states. Systematic catalyst characterization with vastly improved techniques has allowed significant progress in the field of coordination chemistry. Consequently, this high level of fundamental understanding has resulted in significantly higher selectivities for homogeneous catalytic processes. Further, it has also allowed use of milder conditions than before. In addition, for an important class of homogeneous-catalyzed reaction such as hydroformylation, the complex problem of catalyst–product separation has been effectively tackled with the development of various techniques reviewed by Cole-Hamilton (2003). A list of some important industrial applications of homogeneous catalytic processes is presented in Table 1.2.

The major defining characteristics for a homogeneous catalyst are (i) activity that is quantified by “turnover number (TON) or frequency” and (ii) selectivity.

TON indicates the number of product molecules that are produced per mole of the catalyst. Turnover frequency is simply the TON expressed in the rate form (i.e., TON per unit time). The difference between activities of homogeneous and heterogeneous catalysts is generally not larger than an order of magnitude when a given reaction can use either of them as a catalyst (Bhaduri and Mukesh 2000). As discussed earlier, in view of the increasing pressure on premium raw materials, there is growing need of catalytic technologies particularly for conversion of inexpensive feedstock to chemicals. These technologies are aimed at providing new routes for fine chemicals, pharmaceuticals and specialties, waste minimization, and conservation of energy. Higher selectivities can be realized with homogeneous catalysis as a result of its better mechanistic understanding. Combined with the use of less expensive feedstocks, such routes have some elements of sustainable processing. Among others, the major industrial products of homogeneous catalysis are products of hydroformylation reaction. Indeed, hydroformylation is acting as a model for other homogeneous catalytic reactions and is being viewed as a convenient way to produce fine chemicals from laboratory scale to industrial scale.

1.4 PARAMETERS CONCERNING CATALYST EFFECTIVENESS IN INDUSTRIAL OPERATIONS

Selectivity and activity of a catalyst has a profound influence on the economics of a commercial process. Selectivity of a reaction can be of different types. These types are explained in Figure 1.1 using the examples of reactions of vinyl acetate monomer.

TABLE 1.2 Industrial Applications of Homogeneous Catalysis

Process	Catalyst	References
Oxidation of ethylene to acetaldehyde	$\text{PdCl}_2/\text{CuCl}_2$	Jira (1969, 2009)
Oxidation of <i>p</i> -xylene to terephthalic acid/ester	$\text{Co/Mn salts} + \text{Br}^-$	Partenheimer (1995)
Polymerization of ethylene to HDPE/LDPE	Ni complex	Lutz (1986)
Hydrocyanation of butadiene to adipic acid	Ni complex	Ludecke (1976)
Asymmetric hydrogenation of acetamido cinamic acid (3-methoxy-4-acetoxy derivative) (l-dopa process)	$\text{Rh (diene) (solvent)]}^+/\text{DIPAMP}$	Knowles (1983)
Hydroformylation of propene to butyraldehyde	NaCo(CO)_4 $\text{HCo(CO)}_3\text{PBU}_3$ $\text{HRh(CO)(PPh}_3)_3$ Rh/TPPTS	BASF AG (1977a, b) Johnson (1985) Anon (1977) Cornils and Kuntz (1995)
Hydroformylation of higher olefins to oxo alcohols	$\text{HCo(CO)}_3\text{PBU}_3$	Greene and Meeker (1967)
Hydroformylation of diacetoxybutene to 1-methyl-4-acetoxy butanal (vitamin A intermediate)	$\text{HRh(CO)(PPh}_3)_3$ Rh catalyst	Fitton and Moffet (1978) Pommer and Nuerrenbach (1975)
Carbonylation of methanol to acetic acid	Rh/iodide $\text{Co}_2(\text{CO})_8$ Ir/iodide	Roth et al. (1971) Hohenschutz et al. (1966) Watson (1988)
Carbonylation of methyl acetate to acetic anhydride	Rh/MeI Rh/MeI	Coover and Hart (1982) Agreda et al. (1992)
Carbonylation of ethylene to propionic acid	$\text{Ni(OCOC}_2\text{H}_5)_2$	Hohenschutz et al. (1973)
Carbonylation of acetylene to acrylic acid	Ni salts or carbonyls	Blumenberg (1984)
Carbonylation of benzyl chloride to phenyl acetic acid	$\text{Co}_2(\text{CO})_8$	Casssar (1985); Parshall and Nugent (1988b)
Carbonylation of 1-(4-isobutylphenyl) ethanol to ibuprofen	$\text{PdCl}_2(\text{PPh}_3)_2/\text{HCl}$	Elango (1990)
Oxidative carbonylation of methanol to dimethyl carbonate	$\text{PdCl}_2\text{--CuCl}_2$	Ugo et al. (1980)
Hydroformylation of ethylene oxide to 2-hydroxy propanal	$\text{Co}_2(\text{CO})_8$	Powell et al. (1999)

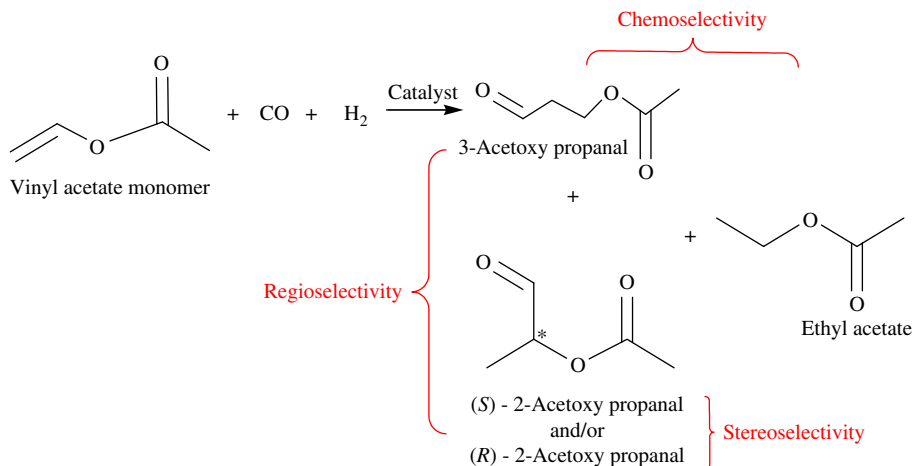


FIGURE 1.1 Examples of various types of selectivity.

1.4.1 Chemoselectivity

This refers to the selectivity based on major chemical transformation and side reaction. For example, hydroformylation of vinyl acetate monomer with synthesis gas can yield two species: (1) aldehydes, acetoxy propanals, and (2) ester, ethyl acetate, as shown in Figure 1.1. In this case, acetoxy propanals are the desired hydroformylation products, whereas ethyl acetate is formed by an undesired hydrogenation of vinyl acetate monomer. The chemoselectivity would therefore be decided by the relative amounts of the acetoxy propanals and ethyl acetate formed.

1.4.2 Regioselectivity

This refers to the selectivity based on the chemical isomers formed due to presence of two or more possibilities capable of bond making or breaking. Again, considering the earlier example of hydroformylation of vinyl acetate monomer, two isomers of acetoxy propanal are possible: (1) 3-acetoxy propanal and (2) 2-acetoxy propanal as shown in Figure 1.1. The 3-acetoxy propanal is obtained by formation of an aldehyde group at the terminal carbon of the vinyl acetate monomer double bond. On the contrary, in the case of 2-acetoxy propanal, the aldehyde group is formed at the internal carbon of the vinyl acetate monomer double bond. The regioselectivity would therefore be decided by the relative amounts of the 3- and 2-acetoxy propanals formed during the reaction.

1.4.3 Stereoselectivity

If one or more of the products has an element of chirality present in them, possibility of formation of products having different chiral structures emerges. The elements of chirality could be attributed to chiral carbon or absence of a plane of symmetry. In the example being discussed, vinyl acetate monomer is a prochiral species for

hydroformylation. During hydroformylation, the 2-acetoxy propanal formed has a chiral carbon atom at position 2, indicated by * in Figure 1.1. Therefore, two stereoisomers, *R* and *S*, 2-acetoxy propanal, are possible. The stereoselectivity would consequently be decided by the relative amounts of the *R*- and *S*-2-acetoxy propanals formed during the asymmetric hydroformylation reaction.

1.5 IMPORTANCE OF ADVANCED INSTRUMENTAL TECHNIQUES IN UNDERSTANDING CATALYTIC PHENOMENA

Advances in instrumental techniques have given a major boost to understanding of catalysis science. Several powerful tools such as high-resolution electron spectroscopy, X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), secondary ion mass spectroscopy (SIMS), photoelectron spectroscopy, low energy ion scattering (LEIS), etc. have been of great use in understanding the catalyst surface structure (Thune and Niemantsverdriet 2009). An excellent contemporary example of use of these techniques is the work of Gerhard Ertl, which fetched him the Nobel Prize for Chemistry for 2007 (http://nobelprize.org/nobel_prizes/chemistry/laureates/2007/press.html). The citation applauded the groundbreaking efforts “for his studies of chemical processes on solid surfaces.” The combination of random selection and evolutionary strategies with high-throughput approaches of combinatorial chemistry has also played a major role in the discovery of new heterogeneous catalysts. Multielement combinations appear to dominate catalyst evolution, particularly in the development of heterogeneous catalysts. The active catalytic species are generally impregnated on a suitable support. In most cases, the support is a material with a well-developed pore structure and high surface area. A major exception to this rule is the famous support for the catalyst used in oxidation of ethylene to ethylene oxide. This support is the antithesis of the general support theory. It has a surface area of $\sim 1 \text{ m}^2/\text{g}$ as against several hundred square meters for other supports. The logic is obvious; the ethylene oxide formed is highly reactive due to the epoxide ring. It must be released quickly from the oxidation site to prevent its further oxidation to carbon dioxide and water. If the catalyst has extensive pores, the product ethylene oxide trapped in these pores is readily oxidized. This logic should also be applied to hydrogen peroxide based epoxidation of allyl chloride to epichlorohydrin using TS-1 catalyst. The latter with an epoxide ring tends to participate in side reactions if not released rapidly from the catalytic site. Some of these side products are very difficult to separate from the main product, epichlorohydrin. The latter has stringent purity requirement as a raw material for epoxy compounds.

The catalyst preparation process is highly specific to generate a catalyst for a specific reaction and also with specific selectivity. A large body of literature describes such procedures/recipes. Control of the nature (crystal type, size) of the active species on the atomic level is considered to be an important factor. Thus, atoms of a given metal can exhibit different behavior since these have different properties (energy levels) at different locations in the crystallite. The multielement catalysts widely used in current practice are much more complicated since atoms of the different metals that

serve specific purposes must be at specific locations in a given cluster of the multi-metal structure. In the case of zeolites, the shape and size of pores allow shape selectivity because the active sites in the pores of the zeolites are tailored for the reactant of choice. In view of this, many reactions that involve isomers/reactants of different sizes use specific zeolites to keep undesired reactants out of the scene of the reaction.

1.6 ROLE OF NANOTECHNOLOGY IN CATALYSIS

As mentioned earlier, in the majority of heterogeneous-catalyzed reactions, a catalyst with high surface area is preferred because it presents a very large number of active sites. In addition, the nature of the catalyst and its distribution on the support are equally important. There has been a continuing effort to increase the catalyst surface area and simultaneously eliminate other drawbacks of conventional catalysts such as loss through leaching, sintering, etc. Nanotechnology is gaining increasing importance as a means of achieving the aforementioned goals. Sophisticated instrumental techniques (scanning tunneling microscopy, scanning probe microscopy, atomic force microscopy) have literally opened the gates for the “nano world” (Gerber and Lang 2006). For more details, the reader is advised to refer to Kung (2001) and Filipponi (2007).

1.7 CLICK CHEMISTRY

Conventional chemical synthesis usually employs a combination of several chemical reactions to obtain the desired end product. The overall process is tedious, results in a number of undesired by-products, etc. as discussed in Section 1.2. Adzima and Bowman (2012) have given an excellent and exhaustive review of a new paradigm termed “click chemistry” by Kolb et al. (2001). Sharpless and his group have done pioneering work on this new technique that uses a modular approach consisting of facile and dependable chemical transformations that yield relatively very high atom efficiencies and require only simple separations. These near-perfect reactions occur on a “click” as if they are “spring loaded” (Kolb et al. 2001). Kolb et al. (2001), Kolb and Sharpless (2003), and Adzima and Bowman (2012) list the following broad criteria that define a click reaction:

1. The feedstock comprises of readily available reactants.
2. It obeys the reaction stoichiometry.
3. The quantity of the final product is in precise stoichiometric proportion.
4. It is completely selective, implying no side reactions/by-products. This includes stereospecificity but not essentially enantioselectivity.
5. The main click reaction product is stable being in its lowest free energy state. It compares with the final state of a released spring (Kolb et al. 2001).
6. Product isolation is either not necessary or facile.

7. It occurs under relatively mild/ambient conditions.
8. Akin to the carbonylation reactions in nature, water is the favored solvent.
9. The reaction occurs rapidly although not necessarily as spontaneous as the release of a spring.
10. A highly favorable explicit thermodynamic driving force ($>80\text{ kJ/mol}$) is the key to the speedy completion of the reaction leading to a specific single product.

Click chemistry is likely to be a very attractive complement to combinatorial methods that are widely used in drug discovery and related process development. The latter is very arduous, involving a large number of complex individual chemical reactions to build the desired molecule. These individual reactions lack selectivity, and as a result, (i) the yield is low and (ii) isolation/purification poses serious problems. Indeed, in most cases, the complex separation processes contribute a significant portion to the overall cost. The major advantage of click chemistry is its potential for evolving novel structures that could be different than already identified pharmacophores (Kolb and Sharpless 2003).

Some of the important click reactions are (Kolb and Sharpless 2003; Adzima and Bowman 2012) azide-alkyne; azide-sulfonyl cyanide; benzyne-azide cycloaddition and hetero Diels–Alder reactions; nucleophilic ring opening of strained molecules such as epoxides, aziridines, etc.; non-aldol-type reactions; and additions to carbon–carbon multiple bonds through oxidation-type reactions such as epoxidation, hydroxylation, etc. For more details, the reader is referred to a recent review by Adzima and Bowman (2012).

1.8 ROLE OF MULTIPHASE REACTORS

It has been mentioned earlier that more than 90% of industrial chemicals are produced by catalytic processes. Most of these processes involve multiphase systems. Even those processes that use “homogeneous catalysts” such as hydroformylation, carbonylation, oxidation, etc. involve reactants originally present in two phases (Table 1.2). Three-phase reactions involving gas–liquid–solid (catalyst) contacting, such as hydrogenation, alkylation (solid catalyst), hydro-desulfurization, Fischer–Tropsch synthesis, etc. comprise the most widely used class. Fixed-bed, sparged, and stirred contactors were the workhorses for carrying out these reactions. For the last two, there was relatively poor understanding of the hydrodynamics involved, which reflected in lack of reliable procedures for predicting their performance/transport characteristics. It is needless to say that the hardware in terms of the multiphase contacting device is just as important as the catalyst system. Indeed, this hardware is an integral part of a reliable technology. For instance, new highly active catalysts for the Fischer–Tropsch process will require corresponding reactors that can cater to the increased amount of heat released. Catalytic reactions that involve very high pressures ($>5\text{ MPa}$) also pose serious problems for conventional (e.g., stirred) reactors, and hence, suitable alternatives need to be evolved. Sustained research and development

efforts on various aspects of multiphase contacting devices have allowed better understanding of the underlying principles. These in turn have helped in developing relatively better design procedures. In addition, new types of multiphase contactors such as the venturi loop reactor and microstructured devices have also been introduced.

In summary, the progress of the modern chemical industry relies heavily on catalysis for high selectivity/green chemistry and sustainable technology. However, the effectiveness of a catalyst system is pivotally dependent on the availability of appropriate multiphase contacting devices, which are commonly referred to as multiphase reactors. Chapter 3 gives a detailed discussion on the types of multiphase reactors available and the rationale for their selection for a specific reaction system.

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2

MULTIPHASE REACTORS: THE DESIGN AND SCALE-UP PROBLEM

2.1 INTRODUCTION

The overall process occurring in a multiphase reactor can be divided into a number of steps occurring in series. Figures 2.1 and 2.2 show typical concentration profiles for a reaction involving two (gas–liquid) and three (gas–liquid–solid) phases, respectively. The gaseous solute dissolves in the liquid phase and can react directly with the liquid-phase reactant as in Figure 2.1 or with it as an adsorbed species on a solid catalyst (Fig. 2.2). The various resistances required to be overcome in transferring a gaseous solute to the liquid-phase/solid catalyst surface where the reaction takes place are shown using the film model as the basis. This book is mainly devoted to the chemical, petrochemical, and fine chemicals industries. Majority of the reactions encountered in these industries, for example, hydrogenation and oxidation, involve sparingly soluble gases. For these reactions, the gas film resistance can be neglected since the gas-phase reactant has a very low solubility in the liquid phase. The notable exceptions are chlorination and sulfonation with gaseous SO_3 . In view of this, prediction of the mass transfer coefficients is restricted to the gas–liquid ($k_L a$) and solid–liquid mass transfer (K_{SL}) steps in terms of general nature of concentration profiles for the gaseous solute. Concentration profiles for specific cases for the different regimes of mass transfer accompanied by a chemical reaction are covered under the relevant cases later in this chapter.

Since the two diffusional processes and the subsequent reaction occur in series, the step that is the slowest controls the overall rate. As the first step in the design

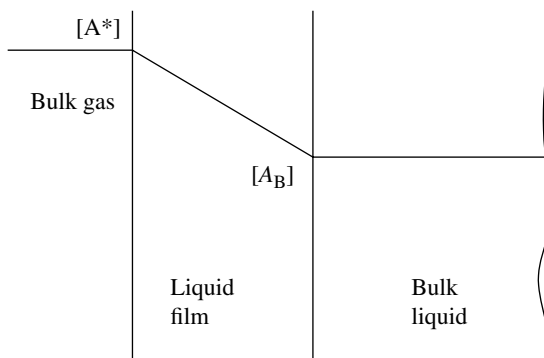


FIGURE 2.1 Typical concentration profiles for a gas–liquid reaction. (Reproduced with permission from Doraiswamy and Sharma (1984). © John Wiley & Sons Inc.)

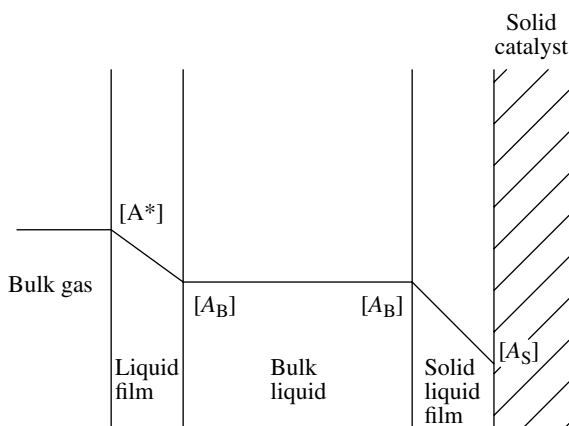


FIGURE 2.2 Typical concentration profiles for solid-catalyzed gas–liquid reaction. (Reproduced with permission from Doraiswamy and Sharma (1984). © John Wiley & Sons Inc.)

procedure, the rate-governing step(s) among those shown in Figures 2.1 and 2.2 needs to be identified. In this respect, two important aspects must be considered: (1) intrinsic kinetics and its invariance with the type/scale of multiphase reactor used and (2) rates of transport processes and their dependence on type/scale of the multiphase reactor chosen.

2.2 THE SCALE-UP CONUNDRUM

The process development starts at the laboratory level. For catalytic reactions, the first step obviously involves screening of various catalysts. Data on selectivity, activity, and life of the catalyst are acquired at this stage, typically approximately on gram level. Commercially available completely automated high-throughput screening

techniques, which can simultaneously test a large number of catalysts, are used for this purpose to save time and labor costs (Archibald et al. 2002). Most benchtop experiments are conducted with relatively pure reactants. These studies are followed by testing with the feed composition that is expected in commercial operation. Issues regarding poisoning of the catalyst by species present in the commercial feed composition are also addressed at this stage. Most of the work up to this stage is carried out in glass kettles if the pressure is atmospheric or in laboratory autoclaves for higher pressures. It is important that the laboratory equipment should at least have similar geometry with the prototype that is likely to be used as discussed later in Section 5.2.1. The round bottom flask (RBF) fitted with a Teflon paddle that is popular with chemists should be avoided in this stage. The hydrodynamics (flow pattern) in this RBF is completely different than the fully baffled cylindrical variety used in industrial practice. Clearly, the hydrodynamic dependent transport properties are vastly different in these two equipments. After having identified a catalyst with high selectivity, activity, and good life, the process of scaling up of the bench-scale data starts. Most research and development departments have a multipurpose pilot plant that is used to ascertain the viability of the process on the kilogram scale. There is hardly any process that has not gone through the pilot plant stage. A notable exception is the first atomic bombs that were used in World War II. The reasons were clear (i) the relatively very small time frame available and (ii) the element of secrecy and surprise.

The reactor is the focus of this book and its scale-up is our foremost consideration. Because of the “art” involved in chemical engineering, an intermediate-scale study is required to gain the confidence for investing on the large scale. There is no “high-throughput screening” alternative for this case. The major question that arises is, what is this “intermediate scale” at which a pilot study needs to be carried out? The basic reactor choice has to be made on the basis of the thermodynamic and reaction engineering aspects of the reaction involved as discussed later in Section 3.2. Most process licensors have experience with running commercial plants set up on the technology supplied earlier. Besides this, they also have pilot plants for continuous improvements. For a given process, a number of critical equipments like reactors, separation trains, etc. have to be scaled up. In such cases, data on operating commercial plants always get precedence over theoretical estimates. An example in this author’s experience was the packed height of a pump-around section in a fractionator. The mass transfer equipment supplier’s correlation predicted a height that was at variance with the process licensor’s data sheet by a factor of 6! The mass transfer equipment supplier insisted that they had a well-tested correlation, whereas the process licensor could show a working plant under practically the same conditions with their specified height providing the desired result. In this case, the choice was clear: “the cake had been made and it tasted good!” Hence, no alternate recipe (correlation for calculating the height) could challenge the successfully operating commercial unit.

In the absence of reasonable pilot-scale data, process designers tend to be conservative and substantial factors of safety are provided. At this stage, the dangers of overdesign need to be emphasized. As an example, consider a continuous flow