

CHEMICAL REACTION ENGINEERING

A Story of Continuing Fascination

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Chemical engineering in its most general sense is broadly centered on two aspects of chemical processing: transformation engineering and separation engineering. Transformation engineering addresses the engineering of physical and chemical change, while separation engineering deals with the principles and tools by which the products of transformation can be obtained at stated levels of purity.

The engineering of chemical change constitutes the core of chemical reaction engineering. Given the centrality of chemical change in any chemical process, it is surprising that the principles and practices of chemical change did not coalesce into a well-defined area until the late 1950s. It was called "applied kinetics" before that time. Part 3 of *Chemical Process Principles*, by Hougen and Watson,^[1] was perhaps the first book to attempt a coherent educational presentation of the principles of reactor design.

The subsequent development of chemical reaction engineering (CRE) was rapid, almost dramatic, in the 1960s and 1970s. The increasing use of sophisticated methods, so aptly and appropriately discussed by Aris,^[2] provides a reflective backdrop to the continuing research in this area. The field has expanded so vastly and so heterogeneously, through the export of its basic theme (interaction between chemical and physical factors) to other areas of chemical transformation, that its own scope—if one can conceive of a scope for this "moving boundary problem"—is now being increasingly linked ("confined" is not the right word) to chemical and petrochemical processes. Among these are biochemical reaction engineering, microelectronic reaction engineering, polymer reaction engineering, and electrochemical reaction engineering.

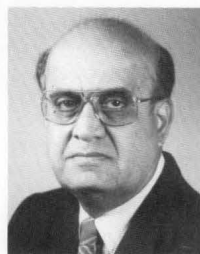
In the author's opinion, this is an irreversible change (perhaps in the right direction), and chemical reaction engineering will continue to grow vertically within its own province, but always overlapping interactively with the boundaries of its progeny. In any case, considering the quick dispersal of knowledge that is evident today and the commonality of many prin-

ciples, one can only conceive of different *disciplines* of CRE. The areas mentioned above are precisely that. If all of them are to come under a single umbrella, then CRE, already interdisciplinary, would be truly ubiquitous.

Over the years, chemical reaction engineering has progressed along two rather different paths. In Europe the emphasis has been more on the application of new and exciting concepts to conventional technologies, including the "bread and butter" conventions. On the other hand, in the United States conventional technologies have not normally held much attraction for academia, except perhaps in some areas such as catalysis. There is much to be said in favor of both approaches, but what is likely to emerge as we move into the 21st Century is a balanced synthesis of the two paths.

UNDERGRADUATE PROGRAMS IN CRE

Concepts of CRE are taught in different courses. The emphasis in undergraduate curricula usually tends to be on homogeneous reactions, catalytic reactions, and occasionally on multiphase reactions involving two or more reactive phases. It is important that students get a broad exposure to various areas and systems covered by CRE in the junior year—in addition to a more rigorous course involving a few selected systems (depending on the interest and expertise of the instructor). It is not uncommon in today's world to find a graduating student who has had little or no exposure to the emerging areas of a subject, including CRE. This is a situation that must be addressed immediately. Students must be given a firmer grounding in order to cope with the challenges of the next century.



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Another concept that should be implemented is a scaled-down version of the think-tank concept in which the student is given a design problem and makes no *a priori* assumption as to the type of reactor to be used. This is beautifully brought out in a Danckwerts Memorial Lecture by O. Levenspiel^[3] where he illustrates the concept with a specific example. This approach stimulates thinking and analysis, and every effort should be made to provide a course, or some kind of an individualized or tutorial mechanism, to foster an "educational think tank" of the type proposed.

COMPLEMENTARY ROLES OF ANALYSIS AND APPLICATION

All too often, at the end of a course the student has learned most of the principles but has no clue as to the systems (existing or potential) where they might be used. Sharma and Doraiswamy^[4] addressed this problem in their book, where many examples are given which illustrate principles or design situations. Furthermore, the student should acquire a feel for numbers, *e.g.*, What is a "slow" reaction? What is the range of effective thermal conductivities of common catalysts? What is the range of liquid-side mass transfer coefficients in some real systems? The argument that these concepts can be acquired later is moot and less than comforting.

This brings us to the pedagogic problem of analysis vs. application. Many books, including Bird, Stewart, and Lightfoot's *Transport Phenomena*,^[5] tend to be analysis oriented. There is great merit in that approach—it was certainly the correct approach at a time when there was an overdose of empiricism and when descriptive and "experience" aspects of process technology held sway. But it is increasingly evident that analysis and application must complement each other. In CRE courses, for example, one can talk of controlling regimes and can present detailed analytical methods for discerning the controlling regimes, but it should be supplemented with industrial (or even laboratory) examples of reactions conforming to those regimes. Thus, if one is considering the mass transfer regime, it would be instructive to illustrate with examples such as dehydrogenation of cyclohexane, decomposition of hydrogen peroxide, and hydrogenation of phenol (to name a few).

It should also be mentioned that a regular graduate course in CRE should involve a problem where the student is required to design a reactor for a selected reaction, starting from the base level—a literature search for getting the correct rate equation. (This is slightly different from Levenspiel's concept where the reaction is new and no information is available.) Rase's *Chemical Reactor Design for Process Plants*^[6] contains such examples in its second volume. In today's context, however, these examples should have a higher content of analysis and modeling.

MORE CHEMISTRY IN CRE

And—let's face it—the basis of all chemical engineering is, after all, chemistry, and the average chemical engineering student's knowledge of chemistry is less than it should be. Either during a course in CRE or by additional coursework in chemistry, students must be required to gain a firmer feel for chemistry—definitely for inorganic and organic chemistry, and biochemistry and polymer chemistry in special cases. Here, students of biochemical engineering or polymer reaction engineering are at an advantage since they enjoy greater exposure to the chemistry aspects of the subject than do students in a regular CRE course in chemical engineering. Such exposure at an early stage enhances the student's ability not only to deal with everyday problems subsequently encountered on the job, but also in later years to formulate exciting problems of current or potential relevance. The need for more chemistry in chemical engineering was stressed by the author in a lecture (delivered at Wisconsin some years ago^[7]) which included a number of examples to strengthen the argument.

SOME RESEARCH AREAS

In a field that covers such a large mix of possibilities, it would be presumptuous to list areas for continued or future attention. Even so, there are certain areas which have the potential for significant impact on the chemical industry (used in its broadest sense). The following suggestions are perceptions not uncolored by the author's personal fancy or evaluation, and should therefore be viewed in that light.

Catalysis and Catalytic Reaction Engineering

In an age where there is an increasing tendency to

frown on conventional topics, catalysis is a refreshing exception. It is among the oldest areas in chemistry, and yet it continues to be new. Perhaps its main driving forces are the omnipotence of catalysis and the intriguing fact that, in spite of its long run, it is just beginning to emerge from the shadows of empiricism. We are still a long way from answering the question "Can one design a catalyst for a given requirement?"—this could be the main reason for the unrelenting research in this area. With the help of sophisticated instruments, we are now looking at catalysis at its most fundamental level, particularly with the objectives of identifying the participating sites, mapping their energy levels, and understanding the basis of selectivity. Iowa State University has a strong school of research in these areas.

From the point of view of catalytic reaction engineering and starting with the early publications of Amundson,^[8] we seem to have almost reached the end of the line where steady-state analysis is concerned, and the state-of-the-art has been fully covered by Aris^[9] (also see Levenspiel^[10] and Froment and Bischoff^[11]). That is not so, however, with respect to unsteady state analysis (including multiplicity), for which some new mathematical tools have been developed.^[12] The role of adsorption and the use of nonideal isotherms has all but evaded the attention of reaction engineers, and only recently have we started to look at adsorption, catalysis, and reactor design in their totality.^[13] This is presently an active area of research at Iowa State University, and a recent conference in Poland addressed the problem, perhaps for the first time in an international forum. Another approach that is gaining ground in catalytic processes is the simultaneous consideration of feedstock, catalyst, reactor, selectivity, and separation. I believe that these trends will continue well into the 21st Century.

An area of catalytic reactor design that will gain momentum is gas phase polymerization in fluidized bed reactors. Following the first flush of success of fluidized beds in the petroleum and petrochemical industries, interest in the area waned when it was found that fluidization was no panacea for reactor evils. It began to wax again when coal conversion processes revived attention—but with a difference: fluidization of large particles. Perhaps the stage is now set for another revival—in the area of polymerization.

In addition to heterogeneous catalysis, we have homogeneous catalysis, where innovative coordination chemistry and catalyst recovery play vital roles. An exciting example is reductive carbonylation of

methanol. It is here that early exposure to inorganic chemistry would be most useful. It would also be useful in catalyst preparation technology, and it is in this area that our ignorance coefficient is woefully high. Impregnation and drying of catalysts are still almost entirely empirical operations. The analysis of Varma and collaborators in a series of ten papers (see, for example, Part 9 which contains all previous references^[14] and Part 10, to appear soon) shows that an optimum catalyst profile in the pellet can increase catalyst activity and selectivity in many reactions. This underscores the need for a more rigorous espousal of catalyst manufacturing science.

Solid State Reaction Engineering

Today, research in solid state materials is a frontier of enquiry. Solid-solid reactions were first mentioned in the mid-80s^[4] as an area of interest in chemical reaction engineering. With the increasing participation of chemical engineers in materials development, this interest has grown to an astonishing level today. Materials of interest include structural composites, ceramic materials, new metal compositions, and microelectronic materials. The engineering science analysis of the reactions involved in these preparations has been late in coming, but it now appears to have taken root. There is little doubt that this interest will rise exponentially in the years ahead. Take microelectronics as an example of the role of CRE in these materials; here we have processes such as deposition, etching, diffusion, and implantation, in which different types of reactors are employed to carry out both homogeneous and heterogeneous reactions. CRE inputs are just beginning to flow into the analysis of these operations. There is a need to introduce electronic materials concepts at the undergraduate level, perhaps as an elective.

Plasma-enhanced chemical vapor deposition using a variety of techniques is an important method of preparing solid state materials, particularly catalytic materials. A strong school of research as Iowa State University is exploring the preparation, characterization, and use of such materials.

Reaction-Cum-Separation (or the reactor-separator combo)

One way to cut capital costs (and increase conversion and selectivity in some cases) is to carry out the reaction and separation steps in a single piece of equipment, or to devise technologies where useful side-products are formed. The earliest example of the first kind is the well-known Solvay tower in which a number of operations occur simultaneously

to ultimately produce soda ash. Indeed, the Solvay tower is a veritable combo of multiple operations. Although this reactor combo is no longer a complete black box, many aspects of it still are. But that is only one major example. A number of other, less complicated, examples of reaction-cum-recovery can be cited: the removal/recovery of acid gases such as CO₂, H₂S, SO₂, recovery of valuable products from waste or dilute streams, or reaction-cum-crystallization in the manufacture of such important products as citric and adipic acids.

There is increasing interest, particularly in schools outside the United States, in the analysis of combo reactors. The type of research involved here is usually concerned with the application of new and innovative ideas in the so-called conventional manufacturing processes. At Iowa State, research in crystallization has been in progress since the 1950s, and more recently the problem of reaction-cum-crystallization has been added to this continuing program.

In the removal of oxygen present in levels below 2% in gases like CO₂, it would be desirable to develop absorbents with the ability to mimic hemoglobin-type regenerative action. Some manganese compounds probably have such an ability. In the separation of *p*- and *m*-xylenes the difference in reactivity of the two can be successfully exploited. Thus, one can selectively alkylate *m*-xylene (with the *para* isomer untouched) using acetaldehyde to give dixylyethane (DXE).^[15] DXE, when cracked, gives half the amount of the *meta* isomer back along with the industrially useful side-product dimethylstyrene. Innumerable other instances can be quoted involving reactive extraction, dissociation extraction reaction, and dissociation extraction crystallization to buttress the contention that this is indeed an exciting area of research with unlimited scope for the use of novel concepts.

This area of research can serve as an example to strengthen the point made earlier that there should be more chemistry in CRE education and research. In a lecture the author heard some years ago, the point was made that many companies do not expect significant chemistry input from chemical engineers. It would seem that chemistry input of the kind mentioned here must come primarily from reaction engineers exposed to a lot of chemistry. (Here, chemistry means the chemistry of relatively large and complex molecules encountered in, say, drugs and pesticides manufacture.) It is significant that one sees a greater degree of chemistry orientation in biotechnology and polymer science and engineering.

Microphase Reaction Engineering

Reaction of a component from a liquid phase (which we will call Phase 1) with another reactant of limited solubility diffusing from a second phase can be hastened if a small quantity of a microphase can be added to the system. If the particle size of the microphase is smaller than the diffusion scale of the reactant, then these particles can get inside the liquid film and transport more of the reactant from Phase 2 into Phase 1. From two excellent reviews on the subject,^[16,17] it seems clear that the use of a microphase (which may be a simple adsorbent like active carbon, a catalyst, or a liquid dispersed as a colloid) can in some cases enhance the reaction rate by almost an order of magnitude.

Extension of this concept to include (1) sparingly soluble solute in Phase 1 itself, (2) a precipitated product with particles small enough to enter the liquid film (or the fluid element in the language of the penetration theory), capture more of the reactant from the neighborhood of the second phase and discharge it into the bulk of Phase 1, and (3) micellar catalysis, has shown interesting possibilities. Particularly in cases like the production of citric acid (where each of the two major steps involved contains a precipitating product phase), control of conditions to reduce particle size to microphase levels can lead to remarkable enhancements in the precipitation rate. This is obviously a kind of precipitate-induced autocatalysis and offers much challenge both for the theoretician and the experimentalist.

Organic Synthesis Engineering (selectivity engineering?)

Much of the progress in CRE has been in areas relating to the production of high tonnage chemicals. It is only in the last ten to fifteen years that another focus has emerged: reaction engineering of small volume chemicals. It is surprising that most of the hundreds of reactions involved in organic synthesis have remained outside the pale of CRE. Indeed, one is hard put to think of more than a few important organic name reactions that have been subjected to rigorous analysis. Examples are: Henkel reaction by Doraiswamy and collaborators,^[18,19] Grignard reagent preparation by Hammerschmidt and Richarz,^[20] and Kolbe-Schmitt reaction by Phadtare and Doraiswamy.^[21]

With the increasing importance of small-volume chemicals, particularly in the field of drugs and drug intermediates, one would be greatly surprised if reaction engineers do not, almost as a natural course, extend their domain to include this area as a formal

part of CRE research. One sees considerable activity in Europe (particularly in Bourne's school) and in some industrial research and development centers in Europe and the USA, but a more pronounced involvement of CRE groups in academia is desirable.

Several ways of improving selectivity have been used by chemists,^[22] some of which are being pursued vigorously by chemical engineers. Phase transfer catalysis is an outstanding example of the former in which some reaction engineering groups are evincing keen interest. Other means of increasing selectivity are through the use of micelles, microphases, catalysts like zeolites and molecularly engineered layered structures, and controlled levels of micromixing. The last is particularly attractive from an engineering science point of view, as attested to by the extensive publications of Bourne and collaborators (for example, Baldyga and Bourne^[23]). Another rewarding line of approach is the use of ultrasonics. The finding by Luche and Damiero^[24] that ultrasonification can enhance yields in the Barbier reaction augers well for the increasing role of ultrasonics in synthesis engineering.

A field of research in organic synthesis with great potential for enhanced selectivity and ease of operation is the possibility of extending the concept of supported liquid-phase catalysts to include supported reagents—with all the attendant advantages. The edited book of Hodge and Sherrington^[25] provides clear evidence of the favorable role of the solid support. With the extensive knowledge we now have of fluid-solid (catalytic and noncatalytic) reactions, this field offers great scope for innovative approaches to, among other things, the reaction-diffusion problems inherent in such systems. Use of photochemistry and enzymes in organic synthesis can also greatly enhance specificity. These are well-known areas to the chemist and biochemist, but there is a definite need for increased CRE input.

Other Areas

There are many other areas that merit attention and where there is bound to be continuing interest. Among these are

- interfacial engineering, an area that covers a multitude of systems, including catalysis, colloids, and micellar action
- multiphase reactions (which involve at least one liquid phase) extensively used in the manufacture of fine chemicals
- gas-solid noncatalytic reactions, so common in pollution abatement, preservation of monuments, ore processing, and catalyst regeneration
- analysis of operation "at the edge" in solid cata-

lyzed reactions, meaning operating under conditions where the diffusion and kinetic effects are balanced to maximum advantage

- increased attention to forced cycling
- use of appropriate solvents (for liquid phase reactions) such as dimethylsulfoxide to increase reactivity
- use of ion exchange resins to replace liquid phase acid/base catalysts
- control strategies in multistep synthesis of pharmaceuticals (including computerized optimization of the synthetic route)
- use of aqueous-aqueous extraction in reactive separation
- reaction-cum-separation strategies for recovery of valuable products from dilute solutions, or removal of polluting components therefrom
- hazard analysis and prevention

Many of the areas listed are not "new topics," but certainly all of them thrive on the use of innovative concepts. Areas such as recovery of valuable products from dilute solutions are replete with examples of the use of reaction as a tool for separation and recovery. A general strategy of intensification in which isolated studies have been reported, and which has the potential for treatment as an area of research, is the role of dilution in process technology. An attempt was made by the author some years ago^[7] to put together the various aspects of intensification by dilution, *i.e.*, dilution of the gas and solid phases in catalytic reactions, dilution of solid in gas-solid reactions, and "natural intensification" due to dilution in biological systems. Increased effort in this area could be very rewarding.

CONCLUSION

Education in CRE must explore new possibilities, some of which have been described in this article. Among these are a mini think-tank, a broad exposure to the reaction engineering of a variety of systems to supplement the prevailing practice of enlarging on a few, and initiation of electives in some emerging areas such as solid-state reaction engineering and interface engineering.

The overview presented here with respect to research is indicative of the areas of present/potential relevance. The element of challenge will continue, whether the areas are new or traditional. While the researcher in CRE, like his counterparts in many other areas, must continue to vigorously explore new and emerging fields, let us not throw the conventional areas overboard. Recovery of value-added products from dilute solutions (or waste

streams) is an outstanding example of applying new concepts to old problems. Whether or not they attract one's fancy, their importance will continue undiminished. So the educator, the researcher, and the funding agencies must look at new concepts in traditional areas with almost the same enthusiasm as at the emerging areas. Nucleation and growth must remain simultaneous.

The chemical industry, notwithstanding the strains and vicissitudes imposed by a fluctuating economy and an increasing appreciation of environmental concerns, permeates practically every facet of our lives and depends for its continued development on invention as well as innovation. Invention is getting a novel idea which works; innovation is overcoming all hurdles to its economic use.^[26] There is scope for both in CRE. To ensure continued dominance, academic research must become increasingly bold, industrial research must be supported rather than managed, and both must be more accommodative of shifts in approach and the delays they entail.

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REVIEW: Design Project

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ever, the authors do provide some insight into hazardous operations analysis and general safety considerations.

The nitric acid process selected is the traditional one without the more modern modification of reaction gas compression. Surprisingly little is said about the need for cleanup of the tail gases from the absorber. The authors have provided a relatively simple process with a great deal of supporting data. This should have appeal to faculty members who understand quite well that it is an onerous chore to dig up all the supporting information for a realistic case study.

The use of this text in the design course should follow an introductory design course which treats such matters as equipment cost estimating, profitability studies, profit and loss statements, and the like. The authors point this out in the introductory material. If only one semester is allocated to design, it is the opinion of this reviewer that adoption of this book would be a mistake. On the other hand, if a second semester (or quarter) is available, material in the book can support one or more worthwhile case study projects. □