



Environmentally friendly processes

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Abstract

Environmental concerns have raised public awareness of environmental issues and are driving forces for regulation. The impact of regulation on the cost of production is expected to become important in determining the international competitiveness of the US chemical industry. In response to cost pressures, industry has launched a number of initiatives aimed at improving efficiency and reducing environmental impact. Some of these environmental success stories are receiving increased national attention due to programs such as the Presidential Green Chemistry Challenge Awards Program. In addition to traditional metrics for evaluating process performance, such as productivity, environmental considerations increasingly are important in process development.

Chemical processes evolve through life cycle phases, beginning with research, and then moving to process engineering, plant operation, and eventually, decommissioning. The number of technology options available for reducing environmental impact are highest early on in the life cycle and then decrease drastically. In contrast, costs associated with resolving an environmental problem typically increase exponentially as the process matures and the scale of equipment gets larger. There is, therefore, a considerable incentive to address and resolve environmental issues early in the life cycle.

Chemical reactions responsible for producing high value-added products are, in most cases, also responsible for generating by-products and pollutants. New chemical and biochemical approaches are providing new reaction concepts. As in the development of traditional chemical and petrochemical processes, reaction engineering, broadly defined as the field that quantifies the engineering aspects of chemically reactive systems, is providing enabling tools that accelerate the development of environmentally friendly processes. Core reaction engineering methods are being utilized for kinetic modeling, reactor selection, scale-up, and design. Meanwhile, the research frontiers are providing new reaction engineering tools, from computational chemistry to probe the nature of catalytic active sites to computational fluid dynamics modeling for designing the internals of reaction-separation systems.

The long-term goal is to develop processes having 100% raw materials utilization, or zero waste. The near-term strategy for controlling emissions is to institute pollution prevention programs and install cost-effective end-of-pipe technologies. These technologies typically control generic classes of air pollutant emissions such as carbon monoxide, volatile organic compounds (VOCs), nitrogen oxides (NO_x) and sulfur oxides (SO_x). Technologies for treating wastewater are also available. Over time, a shift in focus is expected, from mere compliance to a point where environmentalism, like safety, is fully integrated into the corporate culture. The present paper discusses the role of reaction engineering in the development of environmentally-friendly processes. Select examples of processes, from the author's experience, that benefit from reaction engineering will be presented. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Industrial growth on a global scale has spawned environmental concerns on a global level. These concerns transcend local problems, such as point-source pollutant emissions and site remediation, to truly global problems, such as ozone depletion and global warming. They have

raised public awareness of environmental issues and are driving forces for *regulation*. The impact of regulation on the cost of production is expected to become more important in determining the chemical industry's competitiveness than in earlier years when the US industry and producers in a few countries were dominant in world markets (Office of Technology Policy, 1996).

The US chemical industry is important to the nation's economic health. In 1994, the industry directly supported nearly a million jobs and shipped more than 70,000 products valued at \$341.3 billion. On a value-added

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basis, the industry provided about 1.9% of the gross domestic product (GDP). Chemical industry exports accounted for more than \$1 out of every \$10 of US goods exported in recent years. The industry trade surplus, of \$18.4 billion in 1994, has increased to \$20.5 billion in 1997 (Office of Technology Policy, 1996; Storck, 1998). In contrast, the 1994 US environmental industry supported 1.27 million jobs and reported revenues of \$172.5 billion. Total 1993 pollution abatement and control expenditures were reported at about \$110 billion: \$31.9 billion for air, \$39.0 billion for water, and \$38.8 billion for solid waste (US Department of Commerce, 1997). It is generally believed that environmental issues *cost the industry* approximately 3% of sales revenue, or about \$10 billion each year (Carberry, 1998).

Regulatory and cost pressures are driving forces for developing environmentally-friendly and energy-efficient products and processes. A long-term framework for developing an environmental agenda has been proposed. In the concept of “*industrial ecology*”, industrial plants are designed as if they were a series of interlocking man-made ecosystems interfacing with the natural global environment. The need for such systems is driven by the fact that the scale of industrial production is now so great that even formerly-tolerable emissions, such as carbon dioxide, are becoming a threat. For example, industrial flows of nitrogen and sulfur are reported to be equivalent or greater than natural flows, while flows of metals (such as lead, cadmium, nickel, vanadium, and the like) are twice natural flows (Tibbs, 1993). Since the long-term survival of the industrial system depends on the functioning of a natural global ecosystem, the environmental agenda must allow the two systems to coexist. The industrial ecology approach, over time, will require a shift in focus from mere compliance to a point where environmentalism, like safety, is fully integrated into the corporate culture (see Fig. 1).

Industry recognizes the need to proactively reduce pollutant emissions rather than to react to increasingly stringent regulations. A key approach for reducing emis-

sions is *pollution prevention* (Allen and Rosselot, 1997). Companies are developing programs to improve efficiency in the use of materials, energy and water, and to develop inherently-safer processes, distribution, and products. For example, DuPont has committed to a 15% reduction in energy required per pound of product by the year 2000, from a 1991 base. In addition, the company has documented a 20 billion gallons per year reduction in influent water use since 1993, on a global basis (Chemical Engineering, 1997). Along with traditional objectives such as productivity and safety, environmental considerations have become important.

In the US, *green chemistry* is receiving national attention. The Presidential Green Chemistry Challenge Awards Program was established in 1995 to “recognize and support fundamental and innovative chemical methodologies that are useful to industry and that accomplish pollution prevention through source reduction” (US EPA, 1996–97). Awards during the past two years are listed in Table 1. Environmentally-oriented and “lower-emissions” research proposals are being supported by organizations, such as the American Institute of Chemical Engineers, the Council for Chemical Research, the Department of Commerce, the Department of Energy, the Environmental Protection Agency, and the National Science Foundation (see e.g., Beaver, 1996). These initiatives will likely accelerate the development of new tools and new chemical and process concepts.

Life cycle assessment (LCA), an environmental auditing tool that quantifies the environmental burdens of an activity, can help a company reduce environmental risk and thereby acquire a competitive advantage in the marketplace. A schematic of a life cycle framework is shown in Fig. 2. LCA provides a methodology for the cradle-to-grave analysis of materials and energy that includes raw material extraction, the manufacturing process, product use, and product disposal. It involves an inventory (of wastes, emissions, raw materials and energy usage associated with the entire life cycle of the product) and an assessment of the environmental impact at each life cycle stage. The methodology can be used to compare the environmental impact of each of several possible options. The data for such an analysis is often difficult to obtain. The cost of acquiring the data, however, often is offset by savings that result from identifying options that avoid future environmental costs. LCA has been used typically for products and not for processes.

The *atom utilization* (or by-products per pound product) is an indicator of the raw materials efficiency of a chemical process. Atom utilization varies widely across the chemical process industry. The basic chemicals industry can be viewed as quite efficient in its use of raw materials with overall yields of over 90%. On the other hand, when viewed on a wet basis, the amount of waste generated in chemical manufacturing is high, pointing to the need for lower overall water usage (Allen, 1996).

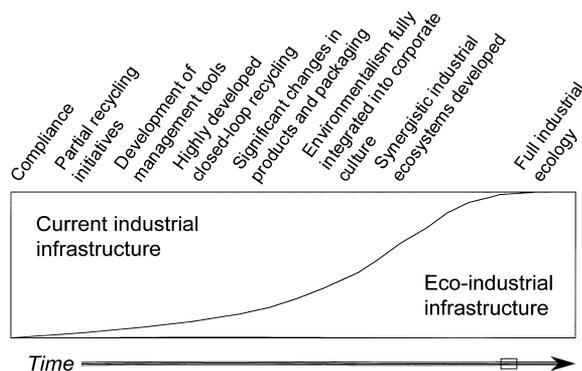


Fig. 1. Schematic of the industrial ecological approach over time (Tibbs, 1993).

Table 1
US Presidential Green Chemistry Challenge Awards in 1996 and 1997 (US EPA, 1996–1997)

Type	Year	Title
Alternative synthetic Pathways	1996	The catalytic dehydrogenation of Diethanolamine
	1997	BHC Company Ibuprofen Process
Alternative solvents/ reaction conditions	1996	The development and Commercial Implementation of 100 Percent Carbon Dioxide as an Environmentally Friendly Blowing Agent for the Polystyrene Foam Sheet Packaging Market
	1997	DryView™ Imaging Systems
Designing safer chemicals	1996	Designing an Environmentally Safe Marine Antifoulant
	1997	THPS Biocides: A new Class of Antimicrobial Chemistry
Small business	1996	Production and Use of Thermal Polyaspartic Acid
	1997	Coldstrip™, A Revolutionary Organic Removal and Wet Cleaning Technology
Academic	1996	Conversion of Waste Biomass to Animal Feed, Chemicals, and Fuels
	1997	Design and Application of Surfactants for Carbon Dioxide

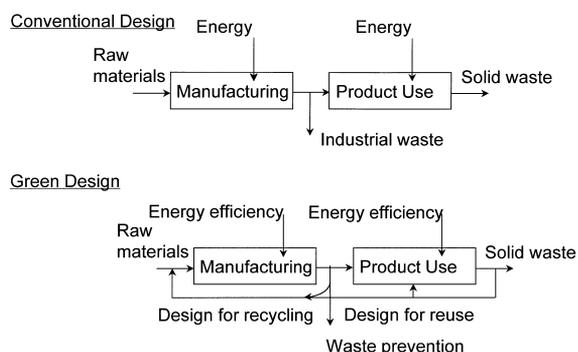


Fig. 2. Life cycle framework for clean manufacturing technology and green design (Office of Technology Assessment, 1992).

By-products per pound of product are much higher in the pharmaceutical industry. Product manufacture, in this segment, may require that a number of stoichiometric organic synthesis steps be conducted in series. As a result, the overall yield can be low even if the yield for each individual synthesis step is high. Given the high-value nature of pharmaceutical products, the economic driving force for increasing selectivity has been relatively low. New environmentally-oriented chemistry and processes in this industry have been recently reviewed (Mills and Chaudhari, 1997).

From an environmental standpoint, a process may possess a number of *desirable attributes* (Table 2). Clearly, as discussed above, higher atom utilization or product selectivity is extremely desirable. Beyond the obvious impact on production, conversion impacts costs associated with product refining and recycle. The ability to reduce or eliminate the use of hazardous raw materials or solvents is an advantage. Higher energy efficiency by improving heat integration and introducing novel process concepts is desirable. There is a high interest in finding new uses for byproducts and in developing pro-

Table 2
Some environmental process objectives

Higher product selectivity
High conversion
Improved energy efficiency
Use of benign solvents
Raw materials substitution
Conversion of hazardous products to less hazardous products prior to shipment
On-site production of hazardous materials
Conversion of by-products to products
Lower secondary emissions
Low aqueous waste

cesses that convert by-products to useful products. There is a trend away from the large-scale manufacture, transportation, storage and handling of hazardous chemicals. In some cases, the control of one pollutant can lead to a secondary emission problem (e.g., the formation of toxic chlorinated products during the catalytic oxidation of halogenated hydrocarbons). Such secondary emissions must be reduced or eliminated.

An *optimization framework* that includes the environmental costs associated with a process is needed. This involves first defining a process boundary and accounting for raw materials, energy and wastes flowing across the boundary. For example, the boundary for a vinyl chloride monomer manufacturing process may include processes for making ethylene and chlorine feed (Stefanis et al., 1995). The next step is to define an objective function, such as total process cost:

$$\text{Minimize } \sum_{i=1}^N C_i \text{ or } \left\{ \sum_{k=1}^M C_{\text{process}, k} + \sum_{j=1}^L C_{\text{environ}, j} \right\}, \quad (1)$$

where $C_{\text{process},k}$ are process-related costs and $C_{\text{environ},j}$ are environmental costs. Such an approach has recently been reported for a nitric oxide plant (Kniel et al., 1996). $C_{\text{environ},j}$ can include leveled end-of-pipe equipment and operating costs, waste disposal costs, and the hidden costs associated with environmental monitoring and reporting. The cost of emissions from the standpoint of human health and the environment can also be included. Though several methods for doing this have been proposed (e.g. Stefanis et al., 1995), a good general method is not yet available. Regardless of whether or not such costs are included, the optimum design of a process likely will change as environmental costs become significant.

As in the development of traditional chemical and petrochemical processes, *reaction engineering*, broadly defined as the field that quantifies the engineering aspects of chemically reactive systems, provides *enabling tools* that accelerate process development. Core reaction engineering methods are useful for kinetic modeling, reactor selection, scale-up, and design. Reactor models, that link independent process variables (e.g., reactor type, operating conditions) to performance variables (e.g., conversion and selectivity), together with the appropriate explicit and implicit constraints, are essential for process optimization. In addition, the research frontiers are providing tools for new process development, from computational chemistry to probe the nature of catalytic active sites to Computational Fluid Dynamics modeling for designing the internals of reaction-separation systems. The increased use of reaction engineering in developing biochemical processes is anticipated. Biochemical processes for producing chemicals such as acrylamide, cyclodextrin, hydroquinone, and ethanol are commercial in Japan (Tanaka et al., 1993).

A comprehensive review of the environmental field is a considerable challenge. The status of a number of environmental technologies has been discussed in the Proceedings of the 5th World Congress of Chemical Engineering (AIChE, 1996). A summary of environmental developments in Europe is also available (DECHEMA, 1990). The present paper, while recognizing the considerable advances in the development of both products and processes, will primarily address *process development*. The life cycle phases for a typical process will first be presented. Some examples from the authors' experience, where reaction engineering is playing a key role in improving environmental performance, will then be discussed. The discussion is biased toward catalysis and catalytic reactors.

2. Process life cycle phases

Chemical processes typically evolve through *life cycle phases*. Life cycle phases have recently been discussed in a monograph on inherently safer chemical processes

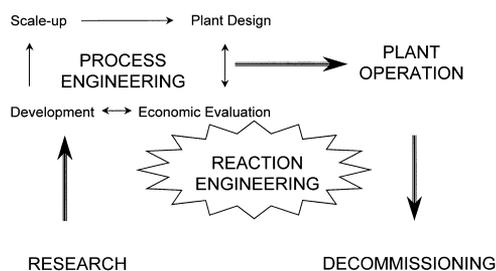


Fig. 3. Schematic of life cycle phases of a typical chemical process (adapted from Bollinger et al., 1996).

(Bollinger et al., 1996). They include research, process engineering, plant operation and, eventually, decommissioning (Fig. 3). The research phase typically explores the feasibility of a chemical process concept. Reactor and process design is accomplished during the extensive process engineering phase. This phase includes development of kinetics and mathematical modeling, first at the laboratory scale and later at the pilot scale. Durability issues are typically investigated at this stage. If questions regarding feasibility arise, the project may return to the research phase, or be discontinued. Commercial modeling software may be used to design unit operations and to develop a preliminary flow sheet. The flow sheet is used for economic evaluation. If economic criteria are met, the plant is designed and constructed. During the life of the process, materials used in manufacture, such as spent catalysts and by-product wastes, may have to be disposed from time to time.

The *number of options* available for reducing environmental impact decreases drastically as the project progresses from one life cycle phase to the next. A larger number of alternatives are available at the research phase. The constraints on what can be reasonably considered increase as the project continues. Extensive reactor and process modifications can be only implemented prior to commissioning of a new plant. During plant operation, the scope of changes is impacted by the economics of modifying downstream processing units and installed utilities. If environmental compliance issues still remain after the plant is commissioned and optimized, end-of-pipe technologies provide the only remaining option.

The *costs* associated in implementing an option dramatically increase as the size of the equipment gets larger. Within the context of process safety, it is believed that, relatively speaking, fixing a safety-related problem costs \$1 at the research stage, \$10 at the process flow sheet stage, \$100 at the final design stage, \$1000 at the production stage, and \$10,000 at the post-incident stage (Bollinger et al., 1996). Cost parallels are likely to be similar in the case of environmental problems as well. There is, therefore, a considerable incentive to address and resolve environmental issues early in the life cycle.

3. Research

In many cases, the catalytic active site, responsible for making product, also generates undesired by-products and pollutants. Beyond reducing raw materials efficiency, these undesired materials have to be separated and disposed. *Discovery research* aimed at identifying a 100%-selective active site is ongoing both in industry and in academia. As an example, a catalyst that decreases by-product pollutant CCl_4 selectivity during the manufacture of phosgene has been recently discovered. The conventional coconut carbon-based catalyst produced about 500 ppm of CCl_4 in the exhaust, which had to be reduced to below 100 ppm to meet the tighter regulations. The new catalyst has reduced CCl_4 levels to below 50 ppm and produces more phosgene (Cicha and Manzer, 1998). The identification of such catalysts would be especially welcome in partial oxidation catalysis.

Computational chemistry is being increasingly used to probe the active site. For example, a new, more-selective transport riser-regenerator process for oxidation of *n*-butane to maleic acid has been discussed (Lerou and Ng, 1997). The process concept was based on the finding that the reaction proceeds via a redox mechanism that involves oxygen on the surface of the vanadium pyrophosphate catalyst (Haggin, 1995). Computational chemistry is providing insights on how the oxygen interacts on the catalyst surface. Optimization calculations of the monovanadium species at the density functional theory (DFT) level are providing clues on how oxygen moves from one vanadium to another (Dixon et al., 1997) and may provide leads for further improving selectivity.

A detailed understanding of the reaction rate mechanism is useful for identifying operating conditions that minimize by-products and developing new catalysts. In the partial oxidation of methane to formaldehyde, macrokinetic analysis has revealed that formaldehyde and carbon dioxide are primary products over a $\text{MoO}_3/\text{SiO}_2$ catalyst. In contrast, formaldehyde is the primary product over $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst. A *microkinetic approach*, using a single set of physically realistic input assumptions, has identified the elementary steps needed to fit the data for both of these catalysts (Amiridis et al., 1991). Reaction pathways for each catalyst are shown in Fig. 4. The approach can also be used as a design tool to identify catalyst properties that may provide improved selectivity. A monograph discussing the microkinetic approach is now available (Dumesic et al., 1993). Such analyses are particularly important in the design of catalytic devices for the removal of pollutants in the ppm range where customary approximations in catalytic reaction engineering are unreliable over wide ranges of process variables (Boudart, 1994).

In addition to tools that allow a mechanistic understanding of the surface chemistry, there is a need for tools that represent and track molecular species in *complex*

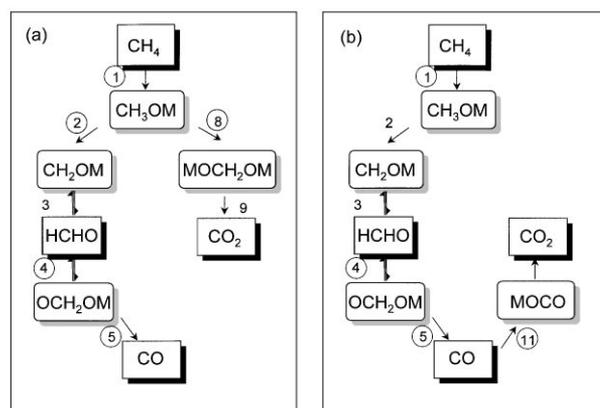


Fig. 4. Active steps in the microkinetic model for methane partial oxidation over (a) $\text{MoO}_3/\text{SiO}_2$, and (b) $\text{V}_2\text{O}_5/\text{SiO}_2$ (Amiridis et al., 1991).

feeds. This is especially true in petroleum refining where regulations are placing restrictions on the composition of the fuel. For example, reformulated gasoline regulations mandate a minimum level of oxygenated compounds and that the aromatic (especially benzene) content, sulfur content, and vapor pressure be controlled. Models that contain an increased level of molecular detail, far beyond the traditional lumped approaches, are needed. The structure oriented lumping (SOL) approach provides a methodology for representing molecular structure, describing process chemistry, and estimating molecular properties (Quann and Jaffe, 1996). Such models can help track molecules as they are processed in the refinery and provide insights on how to optimize refinery operation to meet regulatory requirements or to generate a higher-value product slate.

Molecular modeling is being used to estimate *transport coefficients* in zeolites (Theodorou et al., 1996). There is a continuing need to extend the work to more complex feed and catalyst systems. An example, from the pharmaceutical industry, is the hydroxylation of phenol with hydrogen peroxide over ZSM-5 and TS-1 to yield hydroquinone. The use of hydrogen peroxide, although expensive when compared to molecular oxygen, is preferred because it is simpler and safer to use. The reaction has 99% selectivity to dihydroxybenzenes and produces very little by-product salt. In contrast, the conventional route using Fenton's reagent produces 10 kg of salt per kg of product. A second example is the acylation of alkyl benzene with carboxylic acids over Ce-Y zeolite to yield aromatic ketones. The conventional route uses stoichiometric quantities of AlCl_3 along with acid chlorides, which creates environmental problems (Mills and Chaudhari, 1997).

Traditional reaction engineering methods for analyzing and optimizing *intra- and inter-particle resistances* have been used extensively in the industry. As new chemistries emerge, there may be a need to extend our

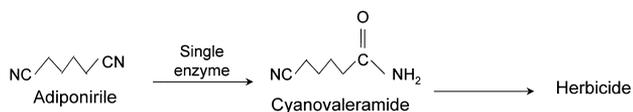


Fig. 5. Biochemical routes to chemical intermediates (C&E News, 1998).

understanding to these new systems. An example is the hydrolysis of adiponitrile (Fig. 5), using a supported enzyme catalyst, for the production of 5-cyanoveralderamide, an agricultural intermediate (Di Cosimo, 1998). The conventional manganese dioxide catalyst is not reusable, difficult to recover and reactivate and, for selectivity reasons, operates at lower than 20% conversion. The bioconversion process, in contrast, has high conversion and high selectivity.

An interesting example in which diffusion, reaction, and the *mechanical properties* of the catalyst support are all important is in ethylene polymerization. During early polymerization, the catalyst pores fill up with polymer product. Ethylene continues to diffuse through the product even after the pores are filled and, eventually, the support fragments like popcorn (Webb et al., 1991). As polymerization continues, the active sites separate from each other as the polymer grains grow in size. Reaction engineering models of polymer grain growth are largely due to Ray and his coworkers (e.g., Floyd et al., 1986). The discovery of homogeneous “single-site” metallocene catalysts, that are at least an order of magnitude more active than conventional catalysts, has created a need to “heterogenize” the homogeneous catalyst, engineer support pore structure, and optimize process operation. Metallocene catalysts are making it possible to create

plastics with physical properties finely tuned to particular uses. The development of single polymers (versus polymer blends) having specialized properties is expected to reduce polymer usage and the amount of waste and simplify polymer recycle (Ewen, 1997).

An improved understanding of the *deactivation* mechanism can accelerate process development. An example is the shape-selective catalytic cracking of normal paraffins over ZSM-5 to improve the low temperature fluidity of fuels. A reaction engineering analysis of the cracking and deactivation behavior of ZSM-5 crystals using a model n-dodecane feed suggested that cracking is intra-crystal diffusion limited, coking occurs uniformly throughout the crystal and that poisoning, due to nitrogen species such as 5,6 benzoquinoline, occurs via a shell progressive mechanism. This explains why the smallest crystals, though the most active initially, are more easily poisoned (Fig. 6) and provides guidance on the desired crystal size (Kennedy et al., 1991). The process, originally developed to improve operating efficiency and reduce energy costs, has largely replaced prior solvent extraction technology which produced fugitive emissions of solvent. The ZSM-5 process eliminates these fugitive emissions and cracks the normal paraffins to useful, gasoline-range products (McWilliams, 1993).

Environmentally benign *alternative solvents*, such as supercritical carbon dioxide, are being increasingly investigated. For example, methyl methacrylate has been polymerized in a supercritical carbon dioxide medium by using a specially engineered free radical initiator and a polymeric stabilizer. The carbon dioxide is easily separated from the reaction mixture, and the approach offers the possibility of avoiding the generation of hazardous waste streams (Illman, 1994). Supercritical

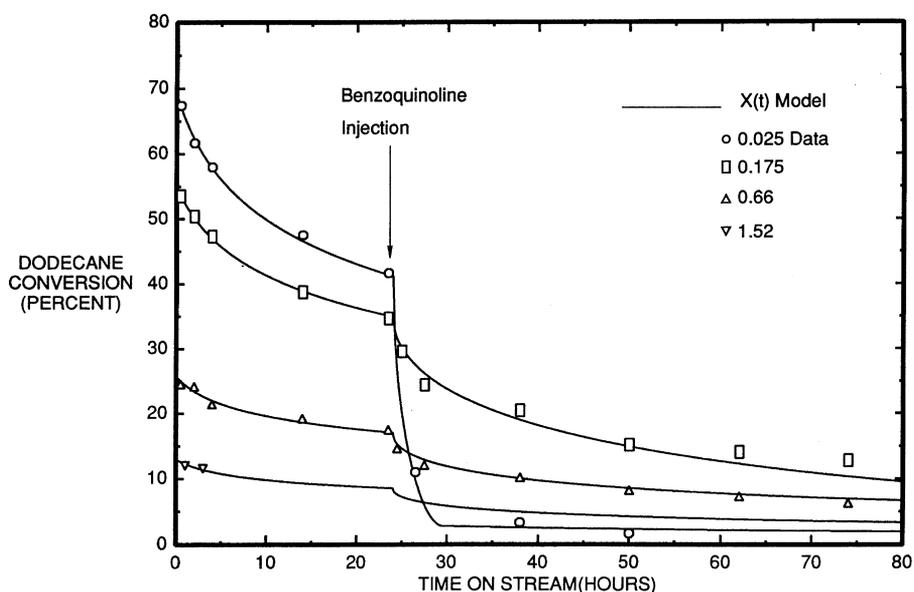


Fig. 6. Dodecane conversion over ZSM-5 crystals of various sizes (in microns). A nitrogen-containing poison is injected at 25 h (Kennedy et al., 1991).

fluids are being considered in a number of industrial applications, such as extraction of food and pharmaceutical compounds and fragrances, dyeing and cleaning textile fibers, and synthesis of nanopowders and polymers. The role of supercritical fluids in the synthesis of organic chemicals has been recently reviewed (Dinjus et al., 1997). From a reaction engineering standpoint, a continuing need to develop physical property databases and kinetics for these new chemistries is indicated.

As *novel technologies* are developed, new reaction engineering tools may be needed.

- The environmental opportunities for electrochemical technology have been recently discussed (Fenton, 1998). As an example, a process for the direct gas phase electrolysis of anhydrous hydrochloric acid to chlorine in a polymer electrolyte membrane fuel cell (PEMFC) is being developed (Trainham et al., 1995). The process converts by-product hydrochloric acid to chlorine for reuse.
- The electrical engineering aspects of inductively heating a granular bed of conductive particles has recently been examined (Duquenne et al., 1994). The suitability of using induction heating for endothermic reactions has been discussed in the literature (Gardner, 1991).
- Hydrogen cyanide has been produced in small quantities from methane and ammonia over a Pt/Al₂O₃ catalyst housed in a microwave cavity. Selectivity is found to be higher than that of thermal processes (Wan and Koch, 1994).
- Reactor design aspects of a loop reactor using a sonochemical power ultrasound module have been discussed for the hydrolysis of methyl benzoate (Martin and Ward, 1992).
- Photocatalytic reactors are being developed for the oxidation of organic compounds in air and water systems. Reactor design issues include conversion and selectivity to partially-oxygenated products (Braun et al., 1993).

4. Process engineering

The engineering phase provides an opportunity for assessing the design aspects of a new process. Typical technical goals include a detailed quantification of reaction products, reactor modeling and the development of scale-up criteria, durability evaluation and process synthesis. An obvious first step is to explore *reactor design and operating conditions* that reduce byproduct selectivity. Theoretical analyses of conditions that minimize waste for series and parallel reaction networks are available (Allen and Rosselot, 1997; Hurme, 1995). For example, for parallel reactions, the ratio of the rate of the undesirable to the desirable reaction for power law

kinetics is given by

$$R = \frac{A_u}{A_d} e^{-(E_u - E_d)/RT} C_A^{m^2 - m_1} \quad (2)$$

The values of the reaction rate constants in Eq. (2) provide guidance on reactor selection and on operating conditions favoring the desired reaction. Such analysis has been used to study allyl chloride synthesis, acrylonitrile synthesis, a reactive distillation process, and a petrochemical process (Hopper et al., 1994). The authors report that emissions from two of these processes have been reduced by implementing changes proposed by modeling.

Mixing and flow distribution hardware can have a large influence on product distribution. Computational fluid dynamics (CFD) code allows the numerical solution of the equations of motion (mass, momentum, and energy) in a flow geometry of interest. Species material balance equations may also be solved to include chemical reactions. Many challenges in the implementation of CFD code remain. Some examples include models for multiphase flow, the effects of turbulent micro-mixing of fast reactions with characteristic times comparable to the time scale of the smallest (Kolmogorov) eddies, and the computational effort required to solve problems with wide ranges of geometrical scales and time-dependent behavior. CFD can provide guidance on the design of reactor internals, such as feed nozzles, baffles, distributor plates, and impellers. When reactions are included, CFD can provide semi-quantitative information on the effect of reactor geometry on product and by-product selectivity (Preisigke, 1995). Neglecting micro and meso-mixing can sometimes lead to large errors in predicted selectivity (Baldyga et al., 1997), even when velocity and turbulence fields agree quite well with experiment. A review of literature together with an identification of future needs in the chemical processing industry has been recently published (Harris et al., 1996).

The design of *reactors for high temperature, short contact time operation* poses a challenge. Syngas has been produced over noble metal surfaces directly from methane at temperatures of $\sim 1,000^\circ\text{C}$ and contact times of ~ 1 m second (Schmidt and Goralski, Jr., 1997). Reactor design considerations include high mass and heat transfer rates, narrow residence time distributions, elimination of homogeneous processes which lead to multiple products, flames and explosions, and materials of construction issues (Schmidt et al., 1996). For rational reactor design, models must contain detailed kinetic descriptions of both heterogeneous and homogeneous reactions. Detailed gas-phase and surface kinetics and transport processes have been included in a model for the catalytic ignition of H₂/air mixtures over platinum catalysts (Bui et al., 1997). These approaches will have to be extended to include methane and higher alkanes.

Transient analysis of the diffusion, reaction and adsorption processes are important in the design and operation of solid-supported liquid-catalyst reactors. Such reactors have been proposed to replace conventional refinery alkylation technology that uses liquid hydrofluoric and sulfuric acids. In this concept, the reactor is packed with a high surface area support material that strongly adsorbs a fluorinated sulfonic acid catalyst. Reactants, together with a small amount of supplemental acid, are fed to the reactor to produce alkylate (Hommeltoft, 1996). Alternately, the reverse flow reactor concept has also been discussed. In this case, reactant flows over the bed driving the acid front toward the reactor exit. At periodic intervals, the flow of reactant is reversed (Hommeltoft, 1991). This reactor concept is the mass transfer analog of the heat storage concept practiced in reverse-flow oxidation reactors. The approach is the next best thing to the development of a commercially viable solid acid alkylation catalyst (e.g., see Rao and Vatcha, 1996; Corma and Martinez, 1993).

There is a trend toward reactors that *combine reaction and separation* processes. An example is the synthesis of methyl-tert-butyl-ether (MTBE), a reformulated gasoline additive, from methanol and isobutylene. In contrast to the conventional approach of using fixed bed catalytic reactors followed by distillation columns, a distillation column containing catalyst is used (e.g., see Smith, 1984). The overall material balance for reactive distillation is (Doherty and Buzad, 1992)

$$x_{F,i} - \frac{D/B}{D/B + 1} x_{D,i} - \frac{1}{D/B + 1} x_{B,i} + Da \sum_{j=1}^{N_r} \left(x_{j,3}^2 - \frac{x_{j,1}x_{j,2}}{K} \right), \quad i = 1, 2, \quad (3)$$

where x is the mole fraction of component i in the liquid phase, D and B denote the flow of distillate and bottoms, Da is the Damkohler number, and the last term in parenthesis represents the reaction rate for a reversible reaction. Potential advantages to this approach include reduced thermodynamic limitations to conversion (as the MTBE moves down the column and away from the reaction zone), a simpler separation system, fewer pieces of process equipment (e.g., valves, flanges, heat exchangers, etc.) reducing the possibility of fugitive emissions, and lower capital and energy costs (Allen, 1996). The approach does reduce the operating degrees of freedom, since the catalyst temperature is limited to a range where separation is possible as well. Another example, reported in the trade literature, is the process for producing methyl acetate in which about seven process steps are consolidated into a single reactive distillation vessel. Compared to the traditional process, reduced investment, improved operability, and an energy savings of over 70% are claimed (Chem. Eng. Prog., 1990). Other reaction-

separation systems, based on porous inorganic and other membranes, are also being investigated (Allen and Rosselot, 1997).

Separate reactor and separation systems can be optimally combined to increase product yield. Such is the case for the methane oxidative coupling reaction to convert abundant natural gas to C_2 products. Progress on developing catalysts having high conversion and selectivity has been slow in recent years. The fundamental properties of these catalysts, such as p -semiconductivity and oxygen anion mobility, have been investigated in more detail and a kinetic model has been proposed (Zanthoff et al., 1992). The desired products of the reaction, ethylene and ethane, are far more reactive with oxygen than methane and are therefore easily oxidized to carbon oxides. Process concepts that couple catalytic reactors with adsorbers have been investigated for increasing the overall yield at high conversion. The simulated counter-current moving-bed chromatographic reactor (SCMBCR) periodically cycles the methane-oxygen feed mixture between four reactor units and four separating columns to achieve a yield of 50% (Tonkovich et al., 1993). Modeling work on the SCMBCR reactor has been reported (Tonkovich et al., 1994). C_2 hydrocarbon yield of up to 88% has been claimed using a gas recycle loop reactor combined with an appropriate molecular sieve trap in the recycle loop (Jiang et al., 1994).

Process technology for the *on-site manufacture* and immediate use of hazardous chemicals eliminates the need to transport, store and handle hazardous chemicals. Methylisocyanate has been conventionally produced by the phosgenation of methylamine and then stored and shipped as needed. A two-step process for the on-site generation of methylisocyanate from methylamine has been developed. Methylamine is first reacted in a bubble-column reactor to form methylformamide. The oxidative dehydrogenation of methylformamide using a silver catalyst yields methylisocyanate (Rao and Heinsohn, 1985). The approach of developing small modular reactors for making hazardous chemicals, such as HCN and phosgene, is also being explored. The ultimate in modularization and miniaturization is the development of microreactors (Lerou et al., 1995).

An alternate approach to on-site generation is to develop *technology that renders materials non-hazardous* prior to shipping. Hydrocyanation technology is being used to prepare nitriles, which can then be shipped to the customer for further functionalization. A different but related approach, used in the delivery of HCN to mine sites for gold extraction, is to reduce the risk of exposure by converting HCN to solid NaCN prior to shipment (Bell et al., 1995).

There is an active interest in finding new uses for by-products or *converting by-products to useful products*. A vintage example is refinery hydrodesulfurization, which selectively removes organic sulfur in gasoline

and distillate fuel and converts it to hydrogen sulfide. Hydrogen sulfide can be routed to a Claus plant and converted to salable elemental sulfur. Parenthetically, the reduced sulfur content in gasoline beneficially affects the oxidation performance of the automobile catalytic converter (since sulfur oxides inhibit noble metal catalysts). In the chemical industry, by-products from the process for making hexamethylenediamine, a nylon 6,6 intermediate, are being converted to branched diamines, used in comonomers and curatives (Bell et al., 1995).

Reaction engineers are called upon to design reactors as new chemistries are discovered. A much cited example of a “green” chemistry is the new process for manufacturing the drug ibuprofen. The conventional process utilizes a six-step stoichiometric process having a molar efficiency of about 40%. The first step involves the reaction of isobutylene and an acetylating agent using an environmentally undesirable AlCl_3 catalyst. The new process uses a reactive-extractor system with liquid HF as catalyst (Lindley et al., 1991). The product is hydrogenated over a Raney[®] catalyst to form the alcohol. The alcohol is carbonylated by carbon monoxide using a Pd catalyst to make product with an overall molar efficiency of about 80% (Chemical Engineering, 1997). Another example is the enzyme-based synthesis of dopamine. A reactor model has revealed that reactor volume can be minimized by using separate sequential (rather than simultaneous) enzymatic reactions (Anderson et al., 1992). More *user-friendly software* for screening alternate reactor concepts will clearly be useful.

5. Plant operation

At this stage, the nature and emissions of pollutants are known. *Regulatory compliance and cost* issues often drive technology selection and the timing for implementation. Pollution prevention approaches can be effectively used to minimize emissions. Obvious approaches include good housekeeping, simple process modifications, product reformulation, raw material substitution, and recycling. Each unit operation in the process can be examined from the pollution reduction standpoint (Allen and Rosselot, 1997). A rational methodology to pollution prevention, that involves selecting the waste stream, generating ideas for emissions reduction, and implementing the most cost-effective changes, has recently been discussed (Dyer and Mulholland, 1998a).

In some special cases, a detailed understanding of process chemistry can result in the development of *in-process additives* for emissions reduction. An example of this is for the fluid catalytic cracking (FCC) process, that converts high-boiling feeds to transportation fuels. Process emissions of particulates, carbon monoxide (CO), nitrogen oxides (NO_x), and sulfur oxides (SO_x) have to be

reduced because of regulations. In response to these pressures, manufacturing methods have been modified to produce more attrition resistant catalysts. In-process additives, having the same size distribution as FCC catalysts, have been developed to control emissions. Noble metal-promoted additives have reduced regenerator CO and NO_x emissions. SO_x transfer additives have been developed to reduce SO_x emissions. The SO_x transfer mechanism is shown schematically in Fig. 7. SO_x is adsorbed by the additive in the regenerator and released as H_2S together with product gases from the FCC riser (Cheng et al., 1998).

5.1. End-of-pipe technologies

These technologies control *generic classes* of air pollutant emissions (such as CO, volatile organic compounds (VOCs), NO_x and SO_x). Sometimes, technology for dealing with atypical pollutants (e.g., methyl bromide from polyester plants, nitrous oxide from adipic acid plants, etc.) is needed. The specific choice of control technology, in most cases, is driven by the need to meet regulatory compliance at the lowest cost. The most cost-effective strategy for a given application, depends on a number of factors, including the nature of the pollutant, its concentration, the flow rate of the exhaust, and regulations.

Reaction engineering contributions to emission control go back to the early days of the 3-way *automobile catalytic converter* (Hegedus and Gumbleton, 1980). Bead catalysts with non-uniform intraparticle impregnation patterns were developed and later analyzed (e.g., see Gavriilidis et al., 1993, and references therein). Reaction engineering tools were used to predict poisoning behavior of catalysts and to optimize pore structure for maximum poison resistance (e.g., see Pereira et al., 1988, and references therein). More recently, work has been reported on modeling the Electrically Heated Converter (EHC), which is an option for meeting the tough regulatory standards in California (see Oh et al., 1993). The EHC is a catalyst-coated metal pre-converter device that is resistively heated by an electric current just prior to engine ignition. Electric heating reduces the CO and hydrocarbon emissions during the first 2 min following the cold start of the engine, which account for as much as 80% of the emissions during a typical driving cycle.

5.1.1. Volatile organic compound (VOC) control

The two primary options for destroying VOCs are by thermal or catalytic oxidation. *Thermal oxidizers* are robust combustion devices that achieve high destruction efficiency if properly operated at the 3Ts: temperature, turbulence, and residence time. Fuel costs and emissions of carbon monoxide and nitrogen oxides (formed in the flame tube of the oxidizer) can be issues. *Catalytic oxidizers* may be bead beds or monoliths. The active

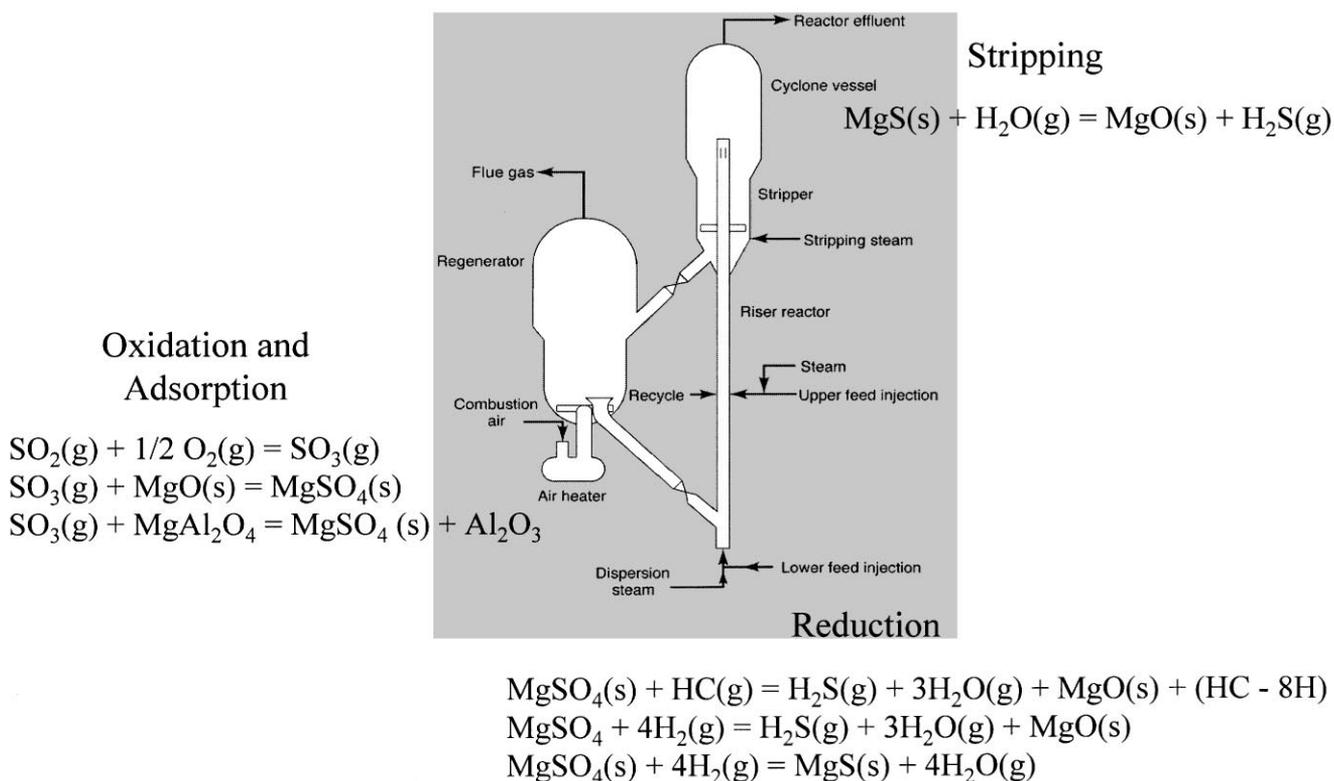


Fig. 7. Mechanism for in-process SO_2 transfer additive for SO_x control (adapted from Cheng et al., 1998).

catalytic ingredients (usually noble metals) are typically supported on a high surface area alumina (Spivey, 1987). The activity and durability of these catalysts have been addressed for select applications (e.g., see Libanati et al., 1998, and references therein). Sometimes, as in the case of the destruction of N_2O from adipic acid plants, new catalysts are needed (Anseth and Koch, 1994). Catalytic systems can typically operate at a much lower excess oxygen concentration than thermal oxidizers.

The destruction of *halogenated hydrocarbons*, often used as solvents, cleaners and degreasers, is a significant challenge. In thermal systems, complete combustion has to be ensured by proper design and operation of the flame, to avoid emissions of toxic chlorinated partial oxidation products (Chang et al., 1986). Noble metal catalysts deactivate in the presence of halogens and more robust catalyst formulations are needed. The performance of supported-molten salt catalysts (Saraf et al., 1989), zeolite-supported chromium (Chatterjee and Greene, 1991), and combined sorbent-catalyst systems (Greene et al., 1996) has been discussed.

Under normal operation, VOC oxidation catalysts operate at or near external mass transfer-limited conversion. Since this conversion provides an upper bound on control efficiency, there have been considerable efforts aimed at increasing the mass transfer-limited performance of *monolithic structures* at a fixed pressure drop.

Under mass transfer-limited control (k_m is the external mass transfer coefficient)

$$k_m = -SV \ln(1 - \psi)/\alpha \quad (4)$$

where SV is the space velocity, α is the geometric surface area per volume and ψ is the conversion. A variety of cell geometries and metal structures have been evaluated. Mass transfer correlations have been developed for several of these structures. For example, as shown in Fig. 8, Camet metal monoliths were found not to follow the mass transfer-pressure drop analogy and have a higher mass transfer limited conversion at a given pressure drop compared to commercial square-channeled ceramic monoliths (Gulian et al., 1991). Theoretical calculations aimed at increasing the destruction efficiency of metal structures are providing some design guidance (Anderson and Schoon, 1993). The development of a thinner-walled, steel monolith substrate having a heat capacity that is 40% that of commercial monoliths has been reported. A catalyst based on this substrate is claimed to have a 30% higher "overall purifying efficiency" at a third of the pressure drop (Chemical Engineering, 1997).

New process concepts for dealing with halogenated hydrocarbons have recently been proposed. A new fixed-bed reactor technology *combines oxidation with dry scrubbing*. The reactor contains a base metal oxide

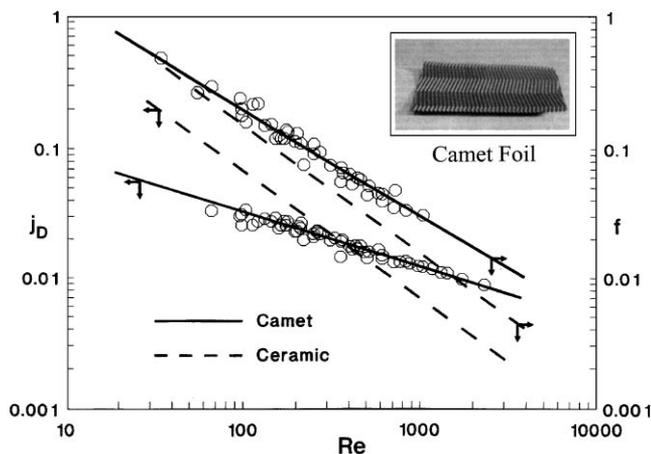


Fig. 8. Variation of f and j_D for square channel ceramic and Camet catalysts (Gulian et al., 1991).

catalyst (such as Mn or Mg) supported on an alkali or alkaline earth (such as Na, K, or Ca) metal carbonate. The halogenated hydrocarbon is oxidized to carbon dioxide, water and acid gas. The acid gas reacts with the metal carbonate support as soon as it is formed. Eventually, the support is consumed and has to be regenerated or replaced (Berty, 1997). Another proposed approach is the catalytic hydrogenation of chlorinated solvents (Kim and Allen, 1997). In this approach, there is a need to carefully analyze the exhaust for the presence of toxic partially halogenated products.

Scrubbing of VOCs is an attractive option for treating exhausts having low concentration but high exhaust flow. From a materials standpoint, the search has been to identify materials that have high capacity and regenerability. Pressure swing and temperature swing fixed bed adsorbers have been used for a long time. *Wheel concentrators* are being more recently deployed. The VOCs are desorbed by passing hot regenerative gas through a small sector of the wheel (Schwartz and Pereira, 1994). Typically, the VOC concentration in the regenerative gas is higher than the concentration of the exhaust by a factor of 6–10. VOCs in the regenerative gas may be oxidized or recovered. Membranes also present a viable option for concentrating VOCs.

Most oxidizers have built-in recuperative or regenerative heat recovery systems. Recuperative systems are shell and tube heat exchangers. The *regenerative* or “hot rocks” systems transfer heat by direct heating and cooling of solids. Though the original regenerative or “reverse-flow” concept patent was issued a long time ago (Cottrell, 1938), regenerative catalytic and thermal systems for VOC control have been commercialized in the US only in the past decade. Reaction engineering work on reverse-flow reactors is largely due to Matros and Eigenberger and their coworkers (e.g., see Matros and Bunimovich, 1996; Matros and Bunimovich, 1995; Eigenberger and Nieken, 1994).

5.1.2. Nitrogen oxides (NO_x) control

NO_x is defined as the sum of the nitric oxide (NO) and nitrogen dioxide (NO_2) concentration in the exhaust. The easiest way to reduce nitrogen oxides is to prevent them from forming in the first place. Nitrogen oxides are primarily formed by the oxidation of fuel-bound nitrogen and by reaction of air-derived nitrogen with oxygen at high temperature. The latter pathway for nitrogen oxide formation can be minimized by reducing high temperature hot spots, increasing turbulence, and increasing the residence time. An example is a *low- NO_x burner* in which gradual mixing with the centrally injected fuel is achieved by radial stratification of the flame. This stratification is achieved by a combination of swirling air flow and strong positive radial density gradients in the flame (Beer, 1994). Another approach is the development of an inward-fired premixed radiant burner that operates at high levels of excess air (Bartz et al., 1996). A third approach is via catalytic combustion.

In *catalytic combustion*, the catalyst lights off combustion reactions which are sustained in the gas phase after the catalyst. Peak temperatures obtained are significantly lower than those achieved in admixed or premixed flames. Along with materials developments, proposed reactor designs include two or more reactors in series, e.g., the first stage for light off, the second for controlled conversion, the third stage for high temperature stability (Zwinkels et al., 1993; Dalla Beta et al., 1993a). As shown in Fig. 9, *hybrid heat exchange-catalyst reactors* having only a fraction of the metal monolith structure coated with catalyst are being developed to control conversion and thereby limit the maximum temperature of the catalyst (Retallic and Alcorn, 1993; Dalla Beta et al., 1993b).

Yet another concept for preventing nitrogen oxide formation is that of “*hybrid catalytic combustion*”, which combines a partial oxidation reactor with air staging. Natural gas and a small fraction ($\sim 7.5\%$) of the required air are fed to the heat exchange-catalyst reactor which is externally cooled by about half the required air. The reaction products, together with the remaining air are combusted in the primary zone of the combustor. The heated air is injected into the secondary zone and sent to a gas turbine (Colket et al., 1993). Reaction engineering can play a useful role in the design and optimization of these heat exchange-reactor concepts.

The commercial catalytic method for controlling NO_x requires the injection of ammonia which, in the presence of a V_2O_5/TiO_2 catalyst, *selectively reacts with NO_x* to form nitrogen (SCR). Exhaust gases containing NO_x also often contain SO_x . The reaction engineering aspects of the SCR process have been examined both for NO_x reduction and SO_2 oxidation (Beeckman and Hegedus, 1991; Tronconi et al., 1994). NO_x conversion is intraparticle diffusion limited while SO_2 oxidation is kinetically limited. Optimization of the pore structure has increased NO_x activity and durability while minimizing SO_2

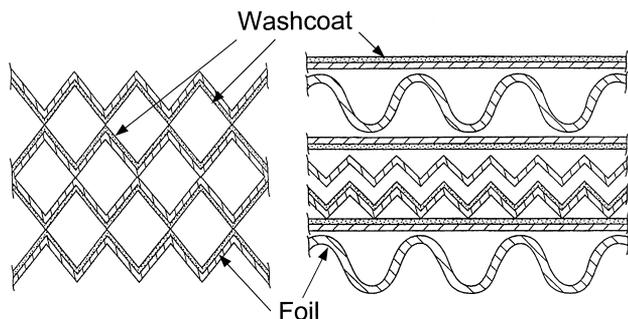


Fig. 9. Catalyst structure employing integral heat transfer (Dalla Betta et al., 1993).

oxidation selectivity. An issue with this technology is the cost of catalyst and monitoring systems and the emission of unconverted (or slip) ammonia.

In some cases, control technologies can be *integrated into plant operations*. An example of such integration is the Ljungstrom regenerative air preheater used in coal fired power plants. The air preheater is a large wheel (up to 20 to 30' in diameter), packed with metal sheets, that rotates between the feed and exhaust stream of a coal-fired power plant. Hot exhaust gases, at a temperature of about 350°C, directly heat the packed metal sheets. As the hot packing rotates to the cool inlet side, it exchanges heat with the inlet air to the plant. An approach undergoing evaluation is to coat the metal sheets in the top section of the wheel with SCR catalyst (or pack the top layer with ceramic SCR catalyst) and then to inject ammonia for increased control of NO_x emissions (Michelfelder and Michalak, 1986). The objective function, for purposes of optimization, is to maximize NO_x conversion subject to a lower bound on regenerative heat transfer and an upper bound on pressure drop.

There is some progress on *replacing ammonia in SCR with a hydrocarbon*, such as methane. The most desirable way of controlling NO_x is to catalytically decompose it into nitrogen and oxygen. Steady-state NO_x decomposition in the presence of excess oxygen has only been demonstrated relatively recently; however, the catalyst is inhibited by oxygen and water and poisoned by sulfur oxides (see Pereira and Amiridis, 1995, and references therein).

5.1.3. Combined technologies

In special cases, technologies may be combined to provide a cost-effective control option. For example, noble metals are good oxidation catalysts. In addition, when ammonia is added, noble metals are known to convert NO_x at lower temperatures than V₂O₅/TiO₂ catalysts. These observations present the possibility of operating the reactor in a narrow temperature window with ammonia injection to *simultaneously control both carbon monoxide oxidation and NO_x*. A downside of this

technology is that noble metals are sensitive to the presence of low levels of sulfur in the exhaust and that the product of the NO_x reaction is N₂O. The technology has been commercialized primarily for natural gas-fired systems (Pereira et al., 1990).

There may also be opportunities to *trade emissions of one pollutant against another*. For example, in the case of natural gas-fired cogeneration plants, nitrogen oxide emissions may be controlled by injecting steam or water into the gas turbine combustion chamber. A negative consequence, however, is that emissions of CO and unburned hydrocarbons can increase. These emissions may be controlled by installing an oxidation catalyst. If only modest (< 50%) reduction in NO_x emissions is needed, this approach can obviate the need for a more expensive SCR system (Pereira and Thomas, 1993).

Processes for sulfur oxides reduction involve either wet or dry scrubbing and have been around for several decades (Cooper and Alley, 1994). More recent work aimed at technologies for *combined sulfur oxide and nitrogen oxide control* is based on the recognition that coal combustors, that generate a large fraction of the sulfur oxides, are also large emitters of nitrogen oxides. Developmental technologies include solid adsorption-regeneration processes, electron beam irradiation processes (oxidation followed by scrubbing), denox–desox (SCR followed by sulfur dioxide oxidation and scrubbing), combined denox–desox wet scrubbing, dry injection processes, and electrochemical reduction processes (Chicanowicz et al., 1991).

5.1.4. Wastewater treatment

Wastewater treatment is a significant issue for the chemical processing industry. *Biofiltration and biotreatment* are being increasingly used for treating air and water streams, respectively. Natural microorganisms are used together with natural materials (such as mulch, soil, etc.) or synthetic substrates (shaped pellets, monoliths, etc.). Considerations in biofilter design have been reviewed recently (Govind et al., 1993). Batch activated sludge data has been used to elucidate the performance of activated sludge systems and to design continuous flow reactors (Argaman, 1991). Reaction engineering work on the design and operation of anaerobic treatment processes has been discussed. Stoichiometry and kinetics, mass transfer and reactor type have been found to be important in such processes (Lema et al., 1991). Research horizons include the development of reliable bio-monitors and methods for minimizing and disposing the biomass produced.

The practicing engineer is often called upon to troubleshoot problems associated *metals emissions in wastewater*. Commercial simulation packages, such as the OLI Software System, which has a database containing the thermodynamic and physical properties for over 3000 inorganic and organic species, are now available for

estimating the solubility of metal hydroxides/oxides in water as a function of pH (Dyer et al., 1998b).

The need to better understand the *thermochemical and kinetic aspects of aqueous treatment systems* is expected to become increasingly important. Experimental and modeling work on the base catalyzed hydrolysis of acrylonitrile suggests that concentration reduction has a double exponential dependence on pH. The model predicts that dramatic reductions in concentration may be realized at higher pH, suggesting the use of basic conditions (LaMarca et al., 1996). Reaction engineering tools can quantify the time required to achieve the required pollutant destruction and thereby provide a sound technical basis for the water treatment and site remediation technologies.

6. Decommissioning and disposal

The safe handling and disposal of plant equipment has been discussed by Bollinger et al. (1996). There are also materials that have to be disposed, from time to time, during plant operation. For example, the disposal of *spent catalyst* is an important issue for chemical and power plants. Noble metal spent catalysts are routinely reclaimed for their metals value. Spent hydrotreating catalysts contain about 5 wt% NiO or CoO and 15 wt% MoO₃. Demetallation catalysts can pick up an additional 10 w% Ni, and as much as 100% V, from heavy feeds. These catalysts may be reclaimed to recover cobalt, molybdenum, nickel, vanadium, and alumina. (C & E News, 1992a). Refining typically entails dissolution in strong acid or base followed by wet chemical recovery. Reclamation economics can vary widely depending on the sometimes-fluctuating price of metals. It is estimated that 1/3 of the market for vanadium is met by reprocessing spent demetallation catalysts (C & E News, 1992b).

A number of proprietary technologies are being developed for treating *waste polymers*. An attractive option is to depolymerize the waste for reuse. However, this is difficult to do in cases where the waste is a blend of individual polymers. As option receiving some research attention is to blend the polymer together with heavy oil feed and to crack it in a refinery FCC unit (Lin et al., 1998). The addition of polymers may affect FCC performance, especially if the polymers contain heteroatoms, such as chlorine and nitrogen.

7. Conclusions

Regulatory pressure and their impact on the cost of production are driving forces for the development and deployment of inherently-less polluting processes. From the standpoint of the number of options available and cost, it is desirable to deal with environmental issues

early in the process life cycle rather than during plant operation. While the near-term approach is regulatory compliance, in the longer term, environmental considerations, like safety, will become an integral part of process design. Continued development and application of reaction engineering tools will accelerate the development of both environmentally-friendly processes and end-of-pipe technologies.

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