INCORPORATING CHEMICAL PROCESS MINIATURIZATION INTO THE ChE CURRICULUM

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The world is undergoing sweeping changes in science and engineering through a fast-paced revolution in miniaturization technologies. Following methods and processes from the microelectronics industry, engineers and scientists are contributing to the rapid development of micro-electro-mechanical devices (MEMS) and related adaptations of chemically- and biologically-based microsystems—changing both our depth of understanding and our modes of interaction with the world around us. A broad range of devices is being created—from sensors for detecting biological and chemical agents to micro-scale pumps, valves, separators, and reactors.

This exciting growth offers tremendous potential to the chemical process industries through chemical process miniaturization (CPM). CPM technologies will find application in a variety of ways, including environmental sensing and control, improved operation of chemical processes (*e.g.*, rates and yields), stronger economic performance through reduced capital costs, and increased safety for processing hazardous materials.

The unique principles governing CPM and the strong interdisciplinary nature of such an endeavor motivates us to engage our students in the discovery of fundamental chemical engineering principles linked to CPM applications. Our goal in the chemical engineering program at Louisiana Tech University is to integrate rapid advances from both the literature and our research work into the chemical engineering undergraduate and graduate curriculum to initiate students' interest and participation in this innovative area of chemical processing. We are developing curricular modules in the areas of micro-scale fluid behavior, reaction kinetics, physical chemistry, and biochemistry applications, highlighting the special physical and chemical features of CPM.

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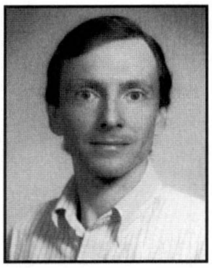

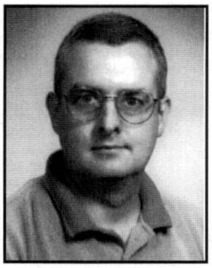

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ADVANTAGES OF THE MICRO-SCALE

The reactor forms the heart of a tremendous variety of industrial processes. Likewise, the chemical reactor will constitute the core process in a "micro chemical plant." Micro-scale systems are characterized by processing units of sub-millimeter dimensions and extremely large surface area-to-volume (S/V) ratios. Heat transfer and temperature control play an important role in chemical reaction processes. Because of the inherently large surface area-to-volume ratios, microreactor systems offer the advantage of optimizing heat removal and maintaining a constant temperature for equilibrium considerations. Through relatively small amounts of injected chemicals per unit of processing equipment and accompanying high rates of heat transfer, these systems offer significant improvements in process safety.

A further benefit CPM provides is a reduction in safety hazards[1] and environmental pollution by eliminating the need for transportation and storage of toxic or explosive chemicals.[2] CPM can provide as-needed, on-line produc-

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tion with a modular system. Additionally, a much higher throughput per unit volume can be accomplished when compared to a conventional packed-bed reactor. At the micro-scale, fluids are generally transported in laminar flow. Mass transfer therefore occurs primarily through diffusion (*e.g.*, little or no turbulent mixing). While this is a serious limitation in traditional systems, microstructures capitalize on this "diffusion-only" transport phenomenon by bringing the moving fluid into close proximity with the reactive surfaces. Shrinking the system geometry can result in tremendous increases in the rates of chemical reaction, heat, and mass transfer. Indeed, it has been observed that "diffusion is 100 times faster when a system is 10-fold smaller."[3] Scale-up is accomplished simply by creating an array of microreactors (*i.e.*, linear scale-up). This is far quicker and more cost-efficient than the traditional approach of proceeding through bench scale and pilot plant to full production. The realization of these advantages will further enhance the process economics, particularly for processes relying on very expensive reactants. Beyond chemical catalysis, the miniaturization of mixing, separations, and other unit operations offers similar process improvements to those described.

Process parameters, which cannot be further optimized in macro-scale reactors, can be improved in microreactors. The large S/V ratios promote rapid response of the chemical process to control modulations. Microfabrication processes enable control over the diffusional path length of reactants through the construction of precisely dimensioned microchannels. Secondary reactions may be reduced or eliminated, resulting in products of high purity.

As research tools, the advantages of miniaturized chemical processing units can be used to study poorly understood processes. On a production level, these advantages may also reduce the need for costly separation processes—often the most expensive part of traditional chemical processing at the macro-scale.

With these advantages of scaling to the micrometer (or even nanometer) level, large exchange rates at the catalytically active surfaces are realized. For fluid reactions catalyzed at solid surfaces, a high degree of conversion is expected. There should be similar advantages for mass fluxes through membranes in reactors and separators. As a result of the precise, regular features of micro-reactor channels, the equilibration of space, velocity, and temperature across and along the reactor channels is expected. This should increase selectivity compared to conventional packed-bed reactors that have a well-known non-isothermal temperature profile. Conventional packed-bed reactors often experience channeling, whereby fluids flow through paths of least resistance using only a fraction of the reactor bed. This problem in operating efficiency can virtually be eliminated in channel-based microreactors. Microreactors are essentially a "pores-only" model of a packed bed—thereby greatly reducing or eliminating diffusion resistances. Using micro-channel devices, heterogeneous catalysis and reaction kinetics can be isolated and studied in ways not otherwise possible.[4,5]

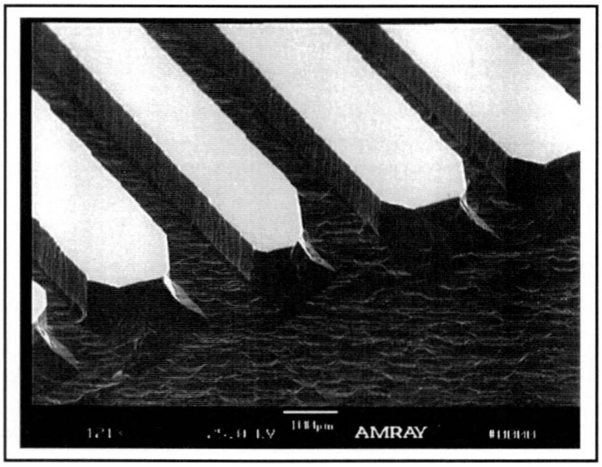

Figure 1. *An SEM photograph of a microreactor section. Channels are chemically etched in silicon. Cross-sectional dimensions are approximately 100 µm x 100 µm.*

While numerous advantages are potentially available, certainly not all chemical processes are suitable for adaptation to chemical process miniaturization. Obviously, the tremendous flow rates of bulk/commodity chemicals and petroleum products are outside the range of consideration in the near term. Further obstacles to employing CPM are seen with processes requiring solids/liquids handling. The suitability for its use with high-cost reactants, high-value products or with substances of a hazardous nature justifies both the ongoing research in CPM and the dissemination of this knowledge to students of chemical engineering.

MICROFABRICATION

An example of microfabrication suitable for introducing CPM at the undergraduate level is the manufacture of a micro-scale reactor. Figure 1 depicts a set of parallel microchannels approximately 100 micro-meters in depth.

These channels were achieved by chemical etching ("wet-etching")—a process adapted from the microelectronics industry. A catalyst, such as platinum, is then applied by "sputtering" onto the channel surfaces. A simplified schematic of this process is presented in Figure 2. The wet-etching procedure shown depicts one of a growing number of manufacturing techniques available for constructing chemical processing equipment at the micro-scale. Photolithography, micromachining, hot-embossing, ion-beam etching, and X-ray lithography are only a few of the many microfabrication techniques used. Beyond silicon wafer processing, micro-scale structures are now being fabricated in a variety of polymeric materials.[5,6] The relative "newness" and unfamiliarity of these techniques to chemical engineering students warrants an overview in an introductory CPM course.

Micro-reactor configurations other than the parallel array of microchannels are being developed. One example is the integration of membrane technologies with microreactors.[7] This combination can provide a means of product purification and the reduction of product inhibition simultaneously with reaction. The use of polydimethylsiloxane (PDMS or silicon rubber) with biological enzymes is being studied for use as a biologically-based microreactor.[6]

INTRODUCTION OF CPM TO THE CHEMICAL ENGINEERING CURRICULUM

An overview of the development of microfabrication technologies is necessary as a basis for allowing students to place CPM within the context of recent advances in the field. An introductory course was offered at Louisiana Tech for the first time in the fall quarter of 2000 (see Table 1). For those students interested in pursuing more detailed training, additional courses are offered that further address microfabrication principles and techniques (also shown in Table 1). A course focused on chemical process miniaturization stands uniquely apart and can augment the existing curricular emphases in surface science and microelectronics processing technology currently provided by several chemical engineering programs around the country.

We believe it is also necessary to integrate into our existing chemical engineering courses the special elements of flow, heat transfer, and reaction kinetics that arise in micro-scale systems. Table 2 outlines the courses currently offered in Louisiana Tech's chemical engineering program that are being examined for suitable introduction of CPM topics. For example, technical electives such as air pollution control and biochemical engineering provide an excellent avenue for presenting novel micro-scale applications, including environmental sensors, catalytic convertors,[9] and bioreactor systems.

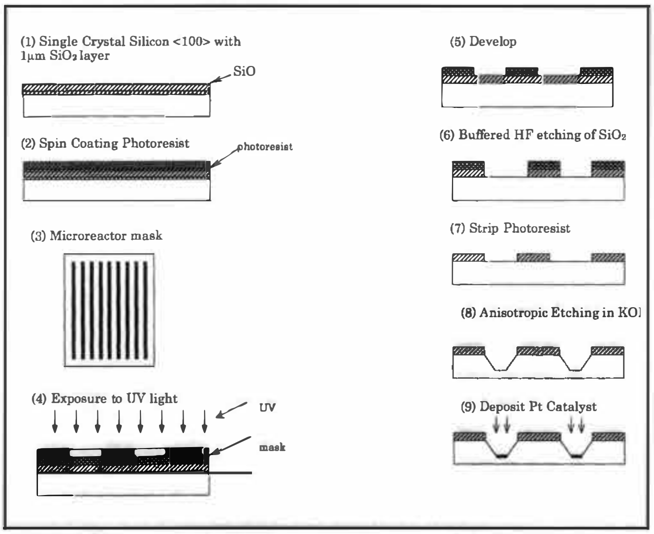

Figure 2. *Steps for microreactor fabrication.*

BACKGROUND

A brief overview illustrates some of the unique features of micro-scale processes. These topics will be introduced, where appropriate, to the existing chemical engineering courses.

Fluid flow Fluid flow in typical tubes and channels behaves as a continuum and follows well-known continuum mechanics. Continuum flow is characterized by a linear pressure drop along the channel length. As the lateral dimension of the channel decreases to tens of microns, the fluid continuum begins to break down. Continuum mechanics combined with a slip function at the walls is used to describe flow in this regime. Arkilic, *et al.*,[10] have measured a nonlinear pressure drop in this so-called slip-flow regime.

Further reduction in channel dimension causes the flow continuum to break down completely. The flow in this instance has a statistical description rather than a continuum and is often called Knudsen flow. CPM requires a focus on reactive systems experiencing fluidic flow across these three regimes—continuum, slip-flow, and Knudsen or free molecular flow.

Chemical reaction For reactions occurring in microreactors, fluid molecules move along the micro-channel, reacting when they come into contact with the catalyst-coated wall. Kinetic theory is used to describe these wall collisions and subsequent reaction rates.

Heat transfer Reactions occurring in the channels are either exothermic or endothermic. In conventional packed-bed reactors, this causes the temperature to vary within the reactor. This change in temperature may adversely affect the formation of desired products or unwanted byproducts. Analogous to micro-heat exchangers, micro-reactors have an enormous heat transfer area per unit reactor volume. This characteristic gives the micro-reactor an equilibrium advantage due to the relative ease of accomplishing the necessary heat transfer to maintain a constant temperature throughout the reactor. Constructed of the proper materials and control systems, micro-reactors should be able to operate isothermally. With regard to heat transfer, studies with micro-heat exchangers have exhibited excellent performance.[11] Heat transfer rates are enhanced at the small scale.

PREVIOUS WORK

As with any emerging field of engineering or science, the "history" or "roots" of its existence is vital for laying a proper foundation upon which future practitioners can build. In the absence of a text at present, we use recent literature citations along with our own experience to "tell the story" of CPM.

The concept of free molecular flow and its deviation from a continuum model was examined by Knudsen early this century. Recently, Norberg, *et al.*,[8] studied fluid flow and chemical reaction in microchannels. Observed molecule/wall interactions were more complex than simple diffuse scattering. In their reaction studies, platinum was sputtered onto a silicon surface, serving to catalyze the reaction of oxygen and hydrogen to water.

Lerou, *et al.*,[12] studied the technical feasibility of microfabricated unit operations such as flow metering, mixing, and heat exchange within a hazardous chemical process. The point of their investigation was to demonstrate the safety advantages of dealing with dangerous chemicals (such as phosgene, methyl isocyanate, cyclohexyl isocyanate) by microprocessing. In a continuation of the same study, Srinivasan, *et al.*,[1,13] conducted oxidation reactions in a reactor with a channel depth of 550 microns. They concluded that these potentially explosive reactions can be conducted in microreactors with a higher degree of control and safety than with conventional reactors.

TABLE 1
Courses in Microstructures and Microfabrication Techniques at Louisiana Tech

- Chemical Microsystems (ChE)
- Micromechanical Systems I (ME)
- Micromechanical Systems II (ME)
- Fundamentals of Micro-Scale Heat Transfer (ME)
- Micro-System Measurements (ME)
- Lithography Processes (ME)
- Engineering Photonics (ME)
- Microsystems Metrology (ME)
- Micromechanical Machining Processes (ME)
- Microfabrication Principles (EE)
- Microfabrication Applications and Computer-Aided Design (EE)
- Advanced Microfabrication Principles with CAD (EE)

TABLE 2
Existing Courses Under Consideration for Integrating Chemical Process Miniaturization Principles and Technologies

- CMEN 304 - Undergraduate Transport Phenomena
- CMEN 402 - Chemical Reaction Kinetics and Reactor Design
- CMEN 443 - Air Pollution Control
- CMEN 451 - Biochemical Engineering
- CMEN 504 - Graduate Reaction Kinetics and Reactor Design
- CMEN 514 - Graduate Transport Phenomena

Wegeng, *et al.*,[11] are investigating combustion and partial oxidation of hydrocarbons in microchannel reactors. They are attempting to achieve greater product selectivity and higher yield through precise temperature control and residence time.

Weismeier and Honicke[14] are working with microchannels etched into metal blocks. In one instance, 100 micrometer channels were machined into copper. The copper was then oxidized to cuprous oxide (Cu_2O) for catalyzing oxidation of alkenes.

The potential of microreactor systems to serve analytical needs is being investigated by Jacobsen, *et al.*[15] In their work, various unit operations (*e.g.*, mixing, reaction, and separation) are performed on an etched-glass plate. This "lab on a chip" offers performance equivalent to full-scale analytical devices at a fraction of the production cost and with the requirement of only a fraction of traditional sample volumes.

Schuth[16] suggests that membrane reactors should be particularly suited to the micro-scale. A membrane reactor separates a product molecule from the reaction stream, thereby "beating" the equilibrium limitations and greatly increasing conversion. Shindo, *et al.*,[17] constructed a 6-millimeter packed-bed reactor that dehydrogenated cyclohexane to benzene. The hydrogen product was removed through a palladium-silver membrane wall. Conversion was increased from 18.9% (at equilibrium) to greater than 99%.

At Louisiana Tech, modeling and experimental microreactor studies are underway to investigate gas-solid catalyzed and liquid-phase enzyme reactions in microchannels.[18-22] A variety of operating conditions and reactor configurations are being examined to experimentally validate system modeling and simulation of such systems. By involving a number of undergraduates in our research activities through introduction of this material into the curriculum, we hope to help our students develop an interest in CPM and to become conversant in the language of micro-scale technologies. Using our work and the growing body of scientific and engineering knowledge in this area, we can help them envision the role of the micro-scale in the future of chemical engineering.

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Miniaturization in the Curriculum

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CONCLUDING REMARKS

Science and technology is moving forward at a breathtaking pace. Never before in history have so many changes occurred so rapidly. Noteworthy in the public arena are the incredible advances in information technology and in biology—particularly the advent of the Internet and potential advances through the human genome project. We anticipate the influence of chemical process miniaturization to be no less significant in the chemical process industries.

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