STATUS OF MICROCHEMICAL SYSTEMS DEVELOPMENT IN THE UNITED STATES OF AMERICA

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The advances in microelectronics have revolutionized computers, communication systems, and appliances, to name a few. These advances have also spurred the development of microelectro mechanical systems (MEMS). The work at Sandia National Laboratory, Lawrence Livermore National Laboratory, UC Berkeley, CalTech, MIT, UW Madison, and UCLA is indicative of these efforts, which have developed silicon actuators/levers, gears and gear reduction units, diaphragm pressure sensors, motors, transmissions, locks, mirrors and hinges, and more. Some of these devices have been combined to yield intricate mechanical systems-on-a-chip. Efforts are moving toward integrated microelectronic/micromechanical systems-on-a-chip; the acceleration sensors for deploying air bags is an example of the commercialization of micromachined systems-on-a-chip.

The substantive efforts to develop microchemical systems are the subject of this discussion. Although such miniaturization is in its early stages, it is driven by considerable incentive and the opportunity to revolutionize heat exchangers, heat pumps, combustors, gas absorbers, solvent extractors, fuel processors, and other similar systems [1]. In the future, these lightweight, compact, and high-performance systems will be important in transportation, construction, military applications, environmental restoration, space exploration, global climate control, and industrial chemical processing.

The quest for the miniaturization of chemical systems is progressing in a number of novel and energetic efforts that are building upon many of the precision engineering techniques developed for the electronics industry. But there is a lot of pioneering work because these systems require new devices, different construction materials, new system architectures, and appropriate working fluids. This miniaturization of chemical systems is being driven by some important needs. One that has pushed development is the need for miniature analytical systems for chemicals and pathogens such as HIV, DNA, and toxic chemicals. There are many needs for such instruments in medicine, forensics, agriculture, and environmental control. Other prominent needs driving development include 1) military requirements for human-portable heating, cooling, and power generating units; 2) transportation demands for hydrogen rich streams for fuel cells; and 3) chemical processing systems capable of processing the rocks, soil, and atmosphere on planets such as Mars.

MICROCHEMICAL ANALYSIS SYSTEMS

Oak Ridge National Laboratory is known for its work on miniature systems for chemical and biochemical analyses [2, 3]. Glass microchips are fabricated with a channel network etched into the surface. These microchips represent the ability to miniaturize benchtop analytical methods with the advantages of speed, automation, and volumetric reduction of sample and waste. Such operations as mixing, separation, and identification of reagents have been demonstrated. And the laboratory-on-a-chip has moved analytical methods to the field. The device is about the size of a dime and performs chemical separations including electrophoresis, chromatography, and micellar electrokinetic capillary chromatography, which allows identification of ionic and neutral species in solution. The device is fabricated by micromachining a two-dimensional channel structure into an insulating substrate such as glass, fused silica, or crystalline quartz. The channels, which are about 50 microns wide and 5 microns deep, are closed by directly bonding a cover plate over them. Fluid volumes of reagents and samples are in quantities of picoliters. Cylindrical reservoirs at the channel ends contain electrodes for performing fluid manipulations by electrokinetic motion.

The Microtechnology Center at Lawrence Livermore National Laboratory (LLNL) is developing microanalytical systems to analyze DNA, test for HIV, and identify pathogens and poisons used in biological and chemical warfare. The thrust is for sampling and analysis in the field, allowing real-time detection. LLNL has developed a portable, battery-powered DNA analyzer that is small enough to fit in a briefcase. The heart of the instrument is a tiny heated chamber on a chip of silicon, where the polymerase chain reaction occurs; a fluorescent signal is used to analyze the DNA and determine whether it matches that of a particular subject. Another analytical device is a portable miniature gas chromatograph that uses a micromachined capillary column etched on two silicon wafers that are bonded together. The circular column is about 100 microns wide and several meters long; the entire instrument occupies about 164 cubic centimeters (10 cubic inches).

In the Defense Advanced Research Projects Agency (DARPA) of the Department of Defense, the MicroFluidic Molecular Systems (MicroFlumes) program uses “beyond components” and “beyond miniaturization” thinking to develop microfluidics-enabled automated microchips for chemical and biochemical analysis [4, 5]. Fluid-based protocols and operations such as chemical/biochemical reaction, transport, synthesis, and engineering are being taken from the laboratory to the field by 1) developing chip-scale fluid-handling capability (to replace such components as pumps, valves, reservoirs, and tubing) and 2) integrating this new microfluidics capability with automated sample acquisition, sample preparation, analysis/detection, and digital I/O. This results in the ability to automatically perform multiple reaction and analysis techniques in one microinstrument. A unique feature is that the channel network can pump, mix, heat, separate, or perform other functions within the channel network itself. The key to success is working at microscale dimensions and using the levels of integrated control made possible by microfabrication.

MICROCHEMICAL REACTOR SYSTEMS

MIT is developing micromachined chemical reactors [6, 7] in work supported by DuPont, DARPA, and the National Science Foundation. It is envisioned that this microchemical reactor system can be used to provide point-of-use, on-demand production to improve safety by eliminating storage and transportation of toxic and hazardous chemicals and reducing the potential damage due to accidents. The microreactor is made of silicon and contains submillimeter flow channels with integrated heaters and flow and temperature sensors. These on-chip features allow for better process control, faster response, and flexible operation.

The microreactor consists of a T-shaped channel for gas flow etched in a 15 by 25 mm silicon wafer. The channel, which has a height of about 0.55 mm and a width of about 1.3 mm, is capped at the top by a 1-micron-thick silicon nitride membrane and sealed at the bottom with an aluminum plate that has three gas inlet-outlet holes. The reactants enter at the horizontal end of the T-shaped channel, mix at the entrance, and react in the vertical reaction channel. The products exit at the vertical end of the T. The top face of the silicon nitride membrane has thin-film platinum lines deposited that serve as resistive heaters and flow and temperature sensors. The potential application of the reactor to partial-oxidation reactions was explored by using platinum-catalyzed ammonia oxidation as a model reaction. The main problems reported were that, when the microreactor was operated at temperatures greater than 700°C, the membrane deformed and some of the platinum catalyst was lost to the gas stream. Results indicate that the reaction hot zone is very localized, while the channel walls and the bulk of the chip remain at room temperature. This could potentially make microreactors safer to operate than conventional reactors.

Researchers at Pacific Northwest National Laboratory (PNNL) have investigated several micro-channel reactor units. One, an integrated microchannel stainless steel combustor/evaporator, generates heat using the heat of reaction obtained from the gas-phase combustion of methane or hydrogen [8]. The technical objective is to demonstrate that a microchannel combustor can produce at least 25 watts of thermal energy per square centimeter of heat transfer profile area and transfer that energy to a cooling unit. This is approximately 20 times higher than the heat transfer rate of a conventional water heater. The most important problem for the microcombustors is maintaining the flame in a small volume. There are also problems maintaining the desired temperature in the combustion chamber and efficiently removing the heat and the combustion products.

In this system, oxygen (or air) and fuel are introduced into the combustion chamber where an ignition wire is used to initiate combustion. Microchannels have been fabricated on the underside of the burner to provide cooling for the combustion region during the combustion process. The combustion products then enter a microchannel heat exchanger that enhances heat transfer between the combustion products and the combustor solid surfaces. The overall size of the system is 41 x 60 x 20 mm. Tests were conducted on micromachined combustor channels 300 microns wide, 500 microns deep, and 35 mm long; results showed that the system could achieve heat fluxes greater than 30 W/cm^2 with combustion efficiencies greater than 85%. Combustion efficiency is defined as the ratio of the heat transferred to the water relative to the heating value of the fuel. Flame quenching problems increased as the combustor size decreased, indicating that flame quenching will set a limit on the degree of miniaturization that is possible in this type of combustor.

PNNL researchers have also investigated catalytic microchannel reactors made from high-temperature metal alloys for several applications. Nickel foam catalyst, fully coated with rhodium, is one of the concepts being tested. This porous metal catalyst is packed into the microchannels and provides a large surface area, high heat-transfer rates, and low pressure drops. While slow kinetics are a current paradigm in conventional reactor systems, fast kinetics are possible in microchannel reactors. While multisecond reactions may be necessary in conventional reactors, millisecond reactions occur in microchannel reactors. This improvement is attributed to the diffusion lengths, which are reduced by at least two orders of magnitude, and to achieving efficient heat transfer, which prevents “hot spots” and “cold spots” and enables high throughputs.

A methane partial oxidation reactor was operated with fast kinetics at 900°C over a rhodium catalyst to produce carbon monoxide and hydrogen. A second microreactor uses the water-gas shift reaction to convert the carbon monoxide to hydrogen and water. Methane conversion efficiencies were more than 85% with 11 millisecond residence time and 100% with 25 millisecond residence time. The main problem noted with this system was the depletion of catalyst powders at high flow rates. The use of catalysts in microchannel reactors is so promising that PNNL is now developing engineered microstructures to find those best suited to microchemical reactors. This includes investigations with coated foam metals and the development of mesoporous catalytic materials.

At PNNL there are efforts to use microchannel reactors to develop a system for in-situ propellant production on Mars. The Sabatier reaction combines carbon dioxide (which would come from the Mars atmosphere) with hydrogen (which would be carried from Earth) to produce methane propellant and water vapor. An electroloysis unit would dissociate the water into oxygen and hydrogen. Some hydrogen would be used in a palladium catalyst microchannel converter to preheat the feed stream. This system is favorable because the catalytic combustion does not affect the ruthenium catalyst and the Sabatier reaction doesn't affect the palladium catalyst. Tests showed that the ruthenium catalyst on a titanium dioxide support provides 85% conversion at 250°C with a reactor residence time of 0.1 second.

A microtechnology-based fuel processor is being developed at PNNL in support of compact power generating systems. The U.S. Department of Energy (DOE) is supporting development of a fuel-cell powered automobile that would use methanol as its hydrogen source. A similar system could be used for portable power generation for the military. The total power generating system incorporates a methanol vaporizer, a partial oxidation reactor, a water-gas shift reactor, a preferential oxidation reactor, and a fuel cell. The heat for vaporization of the methanol comes from the reaction of the fuel cell anode effluent with air as it passes through the catalyst in the microchannel vaporizer. The main technical challenges facing further development of a vaporizer are minimizing channel fouling and discovering how to regenerate the unit.

MICROCHEMICAL SEPARATIONS SYSTEMS

PNNL researchers have designed and tested microchannel devices for efficient contacting of two liquids in solvent extraction [9]. Previous efforts have tested such devices as gas absorbers. This solvent-extraction work is a step in the development of compact efficient devices for chemical separations. The microchannel contactor results in substantially higher throughput per total system volume compared with conventional technologies.

Solvent extraction requires intimate contact of two immiscible liquids to facilitate mass transfer of one or more solutes from one fluid to another. The architecture employed in this work consists of two micromachined channels separated by a contact plate. The channels are separated by a micromachined contactor plate of 25-micron-thick Kapton substrate that has a matrix of uniform holes which are 25 microns in diameter. The solvent and feed streams can be operated co-currently or countercurrently. This arrangement allows for intimate contact of the two immiscible fluids as they flow through very thin channels that are smaller than the normal mass transfer boundary layer.

The mass transfer resistance has contributions from each flow stream, from the contactor plate, and from the interface. The pressures inside the contactor must be carefully controlled to prevent breakthrough of the fluids through the holes in the contactor plate. If the interface is immobilized, the two liquid films can flow in counter-current directions, allowing for a more effective separation in the contactor. PNNL is seeking to reduce the overall size of the equipment and improve operating efficiency by 1) reducing the thicknesses of the films and 2) improving mass transfer efficiency in the contactor plate. Tests were conducted using microcontactor channels 1 cm wide, 10 cm long and 200 to 500 microns high. Results with cyclohexane-water feed and cyclohexane solvent indicate that the micromachined contact plates worked at least as well as commercial microporous membranes and have significant potential for improved performance. Also, with channel heights of less than 300 microns, diffusion through the contactor plate is the limiting factor in mass transfer.

MICROTHERMAL SYSTEMS

A compact microtechnology-based heat pump is being developed by PNNL researchers [10] for a range of microclimate control applications, including portable cooling and distributed space conditioning. The miniature absorption heat pump will be sized to provide 350 W cooling, will have dimensions of 9 x 9 x 6 cm, and will weigh about 0.65 kg. Compared with a macroscale absorption heat pump, this represents a 60% reduction in volume. A complete portable cooling system, including the heat pump, an air-cooled heat exchanger, batteries, and fuel, is estimated to weigh 4 to 5 kg, compared with the 10 kg of alternative systems. Size and weight reductions are obtained by developing the system that can simultaneously take advantage of the high heat and mass transfer rates attainable in microscale structures while being large enough to allow electric powered pumping.

The absorption heat pump uses a lithium bromide and water mixture as the working fluid and is driven primarily by the thermal energy produced by the combustion of liquid hydrocarbon fuels. Electric power is required to operate the solution pump and fan, but its overall power requirements are an order of magnitude lower than those of a conventional vapor compression system. Microtechnology-based components are used for the combustor, desorber, evaporator, regenerative heat exchanger, condenser, absorber, and solution pump. The heat pump uses a microchannel combustor that can produce at least 30 W/cm^2. The desorber and absorber use a proprietary micromachined structure to maintain a film thickness of approximately 100 microns. The evaporator, regenerative heat exchanger, and condenser consist of arrays of microchannels with widths from 100 to 300 microns and depths of up to 1 mm. The solution pump is a commercially available unit; while larger than needed, it suffices for the proof-of-principle demonstration of this miniature absorption heat pump.

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