A Look At Microchemical Systems

What are MCS? What are some key limitations?

Prof. R.S. Besser

Chemical Engineering
Stevens Institute of Technology, Hoboken, NJ

Stevens Institute of Technology

Founded 1871
Stevens family: Commercialized urban ferry transport in NYC
4500 students: 1700 trad. undergrad; 2800 grad (most p-t)
Freshmen: 3.8 GPA; SAT: 1200-1400 (25%-75%)
Chem/Biomed/Matls Engineering → NJ Center for Microchemical Systems
New Jersey Center for MicroChemical Systems (NJCMCS)

- Official start in September 2002
  - $10.0M commitments to date
- Vision
  - Leadership for microchemical device/fundamental understanding, design methodology and tools development
- Mission
  - Original research, education of new PhDs
- Systems-level concept demo with partners
  - Army-Picatinny, Bristol-Myers Squibb, FMC, Lucent-Bell Labs/NJNC
  - Applications: portable power, pharmaceutical processing, critical industrial chemicals, biomedicine

Microchemical Systems

Miniature reaction and other unit operations, possessing specific advantages over conventional chemical systems

Not Lab-on-Chip: chemical production vs. analysis
Key Benefit: Surface to Volume

SA Increasing → V Constant

Heat Management
Mixing
Surface Reaction
Explosion-Safety

Transport and Residence Time Advantages

\[ A + B \rightarrow C \]

Mass transport limited
mixing
heterogeneous rxn

Heat transport limited
Temp uniformity, control

Residence time tuning to limit exposure
selectivity
decomposition
access to extreme T and P
Surface to Volume: Superb Transport

Example: Overall Heat Transfer Coefficient

<table>
<thead>
<tr>
<th>Hx Type</th>
<th>$U$ (W/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubular</td>
<td>150-1200</td>
</tr>
<tr>
<td>Spiral</td>
<td>700-2500</td>
</tr>
<tr>
<td>Plate</td>
<td>1000-4000</td>
</tr>
</tbody>
</table>

Microchannel: **3800-6800 W/(m²K)**

(Stevens undergrad design project)

(500x500 μm² x 1.5 cm channels)

- **SIT and NJCMCS**
- **MCS: a Definition**

**Key Limitations in MCS and Examples of How We Are Exploring Them**

- **Geometry Limitation in Heat Removal**
- **Thermal Integration Limitation in a Multiunit System**
- **Multiphase Mixing Limitation**
- **Integrated Process Control Limitation**
Fuel Cells: Applications & Power Ranges

Power (Watts)

Fuel Cells & Fuel Processing

- As alternatives to batteries
- Offers high energy density. Allows portable devices to operate for longer times with less recharging
- Generating hydrogen by processing of easily stored liquid hydrocarbons
- Methanol reforming: attractive source of H₂ for portable PEMFC

Next Generation Portable Power Sources

Vaporizer
Steam
Reformer (SR)
Preferential oxidation (PrOx)

Methanol
Vaporizer
Steam
Reformer (SR)
Preferential oxidation (PrOx)

H₂, CO₂, CO

Combustor
Air

Unconverted H₂ from anode of fuel cell

Water

Electrical Energy

Methanol

PEM Fuel Cell

Methanol to hydrogen: Components of fuel processor

Rutgers, 2/23/06
Geometry Limitation in Heat Removal

- Exothermic reactions at high processing rates generate lots of heat
- Thermal resistance leads to temperature non-uniformities ("hot spots")
- Critical reactions are sensitive to temperature variations
- Can MCS help?--How small is small enough?

Looking for Improvements with MCS: Preferential Oxidation of CO₂

CO → CO₂

**Chemical Reaction Equations**

\[
CO + \frac{1}{2} O_2 \xrightarrow{\Delta H = -67 \text{ kcal/mol}} CO_2 \\
H_2 + \frac{1}{2} O_2 \xrightarrow{\Delta H = -58 \text{ kcal/mol}} H_2O
\]

**Graphical Representation**

- **CO Conversion vs. Temperature**
  - **Negligible CO conversion drop**
  - **Significant CO conversion falloff**

**3D Reactor Model**

\[
CO_2 + H_2 \xrightarrow{\Delta H = 9.8 \text{ kcal/mol}} CO + H_2O
\]

**Reconversion of CO₂ to CO**

Temperature Dependence of $X_{CO}$

Importance of Geometry

Greater diameter \rightarrow More severe hot spot formation \rightarrow Greater r-WGS activity

Key Limitations in MCS and Examples of How We Are Exploring Them

- Geometry Limitation in Heat Removal
- Thermal Integration Limitation in a Multiunit System
- Multiphase Mixing Limitation
- Integrated Process Control Limitation
Microfabricated reactors are flat and sheet-like

1. High Surface to Volume
2. Lossy, bad for heat retention
3. Good for inter-unit heat transfer
4. But units need to operate at their individual optimal temperatures


Vaporizer-reformer stack (O.J. Kwon et al.)

Solid State Research Center, Motorola Labs

Pattekar Kothare, IEEE-JMEMS

Integrated Fuel Processor

200-µm depth
P = 0.005 torr
k = 0.0006 W/mK

T Sensors

Insulation

500 micron

Reaction zone (1 cm x 1 cm), catalyst packed bed or cartridge

180°C

260°C

350°C

SR reactor
(4 cm x 2 cm)

Inlet

Si

Heater

Temp. sensor-center of heater

Rutgers, 2/23/06

50-µm depth

Atm. Pressure, k = 0.04 W/mK

250µm

350µm
Incorporation of catalyst in the form of packed bed by vacuum loading. Catalyst loading achieved: 51 mg.

**Thermal Characterization**

**Thermal Characterization**: Measure critical thermal parameters like Q required, transfer of heat between components, temperature profiles in different components, insulation effectiveness, and heat loss mechanisms.

- **Ambient pressure testing**: Device placed in bowl of insulation.
- **Vacuum testing**: To distinguish multiple modes of heat transport in the system by eliminating convective losses.

![Graphs showing temperature vs. heater power for Combustor, Steam Reformer, and Preferential oxidation.](image)
Thermal Characterization:
Understanding Heat Loss Mechanism

Experiments | $Q_{\text{total}}$ | $T_{\text{comb}}$ | $T_{\text{reactor}}$ | $T_{\text{PrOx}}$ | $Q_{\text{cond.}}$ | $Q_{\text{conv.}}$ | $Q_{\text{rad.}}$ | $h_{\text{conv.}}$
--- | --- | --- | --- | --- | --- | --- | --- | ---
Vacuum suspended | 3.4 | 443 | 260 | 181 | | | 0.3 | 2.9 | 1.5
Atm. suspended | 5.6 | 517 | 259 | 166 | | | 2.6 | 3.1 | 10.3
Vacuum with Al foil | 2.2 | 404 | 262 | 190 | | | 0.3 | 1.9 | 1.5
Atm. with Al foil | 4.7 | 476 | 261 | 166 | | | 1.9 | 2.8 | 10.3
Vacuum, covered with fiberglass insulation | 1.7 | 386 | 263 | 181 | 1.5 | 0.2 | | 0.5
Atm., covered with fiberglass insulation | 2.8 | 411 | 263 | 181 | 1.7 | 1.1 | | 7.0

Thermal Characterization: Conclusion

1. Both radiation and convection important
2. Combination insulation (vac, low-k, reflective) is most effective (insulation design)
3. Think about 3D architectures instead of sheets (packaging)
Key Limitations in MCS and Examples of How We Are Exploring Them

- Geometry Limitation in Heat Removal
- Thermal Integration Limitation in a Multiunit System
- Multiphase Mixing Limitation
- Integrated Process Control Limitation

Multiphase (S,L&G) Mixing Is Difficult Without Turbulence

*And the pressure drop becomes enormous*

- Two-phase flow
  - Bubble ↔ Taylor/Slug ↔ Annular
  - Best G-L mass transfer
  - What flow regimes exist within the microreactor?
  - How do flow regimes affect the reaction conversion?
  - Can we design a microreactor to operate in bubble mode and still be kinetically-controlled?
Pharmaceutical Hydrogenation

\[
3\text{H}_2 + \ce{OCH3-NO2} \rightarrow \ce{OCH3-NH2} + 2\text{H}_2\text{O}
\]

- Safety
- Temperature control
- Selectivity
- Attrition
- Energy consumption of cooling
- Separation of catalyst from product

Reactor Concept

- Separate gas & liquid channels
- Slotted walls-allow gas access along entire length
- Catalyst traps-engineering porosity for \(\Delta P\)
- Access to range of \(u_G/u_L\)
**Catalyst Trap Microreactor**

- Liquid Inlet Port
- Slotted Wall
- Trap Posts
- Trapped Catalyst Particles

**Wetted Traps**

- Dried Traps
- Wetted Traps
- G-L Interface
- Gas
- Liquid

- Indication of the type of flow regime present.
- Traps function as a network of "mini-batch" reactors. *Measured conversion exceeds model prediction.*
Conversion Results (in progress)

Still limited by G/L area?
Can we achieve higher yields in L-dominated region where productivity is greater?

Key Limitations in MCS and Examples of How We Are Exploring Them

- Geometry Limitation in Heat Removal
- Thermal Integration Limitation in a Multiunit System
- Multiphase Mixing Limitation
- Integrated Process Control Limitation
Integrated Process Control Needs for Portable MCS-Based Systems

- Integrated sensing (temperature, flow, pressure, etc.)
- Integrated actuation (valves, heaters, etc.)
- Control strategy
- Miniature
- Autonomous

We Need a MicroFlow Sensor. Build One.

Principle of a Simple Flow Sensor: Calorimetric Sensor

2. Trigger temperature changes of sensing resistors by convective movement of the fluid stream.
3. Temperature changes lead to resistance changes.
4. Monitoring resistance changes through voltage drop.
Will It Work and How (CFD Simulation)

Temperature profiles with different flow rate

Temperature difference between static and flow conditions

Design & Fabrication

Anodic-bonded sensor chips with microreactor

Sensor chips microreactor
**Flow Sensor Performance Limitations**

- **Sensitivity**
  Limited primarily by resistance of sense resistors within thermally affected zone

- **Response time ≅ 70 msec**
  Limited primarily by mass of Pyrex substrate above thermally affected zone

---

**Flow Sensor Development**

*(Transient Thermal Response)*

**Lumped Thermal Capacitance Model:**

Biot number << 1

*(Internal Conduction Resistance/External Convection Resistance)*

---

**Heat loss from thermal mass** = Convection to gas flow + Conduction to substrate

\[
Vc \rho \frac{dT}{dt} = q_{\text{convection}} + q_{\text{conduction}}
\]

\[
Vc \rho \frac{dT}{dt} = -A_i h_i (T - T_s) - L K \frac{d}{d y} (T - T_{py})
\]
Flow Sensor Development

Summary

- Satisfactory sensitivity
- Matched to the flow range of microreactor (10 sccm)

Limitations on sensitivity
  - R of the sensing resistor, separation of heater and sensor, and
    the heating power

Limitations on response time
  - With reduction of Pyrex thickness, response time could be
    reduced to < 10 msec

- Integratability, manufacturability, cost


A Control Scheme is Needed

Block diagram of feedback control system for microreactor system
Microchemical System Control

Experimental Plan

- **Control Unit** (PID, Fuzzy, etc.)
  1. Labview algorithm implementation

- **Sense** (T-sensor, Flow-sensor, GC)
  1. Reactor temp.
  2. Flow rate
  3. Conversion

- **Sensing Zone** (Flow & Temp.)
- **Reaction Zone** (Steam Reforming of MeOH)
- Micro Heater (beneath reactor)

- **Actuation**
  1. Microheater
  2. External prop. valve*

- **CH₃OH + H₂O ↔ CO₂ + 3H₂**

1. Perform the reaction with different control schemes. (Fuzzy logic, PID, etc.)
2. Demonstrating effective control scheme and condition for SR-reaction.

**Geometric Limitation on Heat Transfer**
1. 500 μm vs. 2 mm made a big difference

**Thermal Integration of Separate Units**
1. Minimum design 1.3 W

**Multiphase Mixing**
1. Do novel flow regimes offer an advantage?

**Miniature Integrated Control**
1. Limitations of integrated flow sensor manageable.
Microchemical Systems

1. Surface to volume ratio

Acknowledgements

People
Prof. Woo Lee, SIT
Prof. A. Lawal, SIT
Dr. Pauline Ho, Reaction Design
Dr. C.S. Pai, NJNC
Mr. B. Mansfield, NJNC
Mr. Ashley Taylor, NJNC
Dr. Stanley Pau, ASU
Prof. Suphan Koven, SIT
Dr. D. Ivanov, NJIT
Dr. K.R. Farmer, Fisher
Mr. Steve Nicolich, TACOM
Dr. Art Kaufman
X. Ouyang, Ida-Tech
L. Bednarova, Ultracell

Agencies, Institutions
U.S. Department of Energy
Defense Advanced Research Projects Agency
New Jersey Commission on Science and Technology
Stevens Institute of Technology
TACOM-ARDEC
Office of Naval Research
Cornell Nanofabrication Facility (NSF)

People (cont.)
K. Shah, W. Shin
S. McGovern, H. Gadre