Microchemical Systems for Current Problems in Process Engineering

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Outline

• SIT and NJCMCS
• MCS: A Definition
• Projects and Tools of NJCMCS
• Example: Portable H₂ Generation
• Example: Pharmaceutical Hydrogenation
• Conclusions
• Acknowledgements
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
  - Portable power, pharmaceutical, and chemical applications
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**

- Heat Management
- Mixing
- Surface Reaction
- Explosion-Safety

V Constant

SA Increasing →

![Graph showing Surface to Volume Ratio](image)
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)

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Application Areas

Critical Chemicals

H₂ Generation for Portable Power

Pharmaceutical Manufacturing

Biomedical Systems

New!

H₂O₂ by direct combination

Micro Fuel Processing

Pharmaceutical Manufacturing

Catalyst Integration Under Development

Selective-Area Infiltration

Net-Shape Cellular

Hydrophobic Surface

Hydrophilic Microchannel

Loading Reproducibility without Surface Contamination

Window Radius

Cell Radius

Skeleton Density

Tunable Multifunctional and Multiscale Structures

- Lawal et al., “Reactor Integration Issues,” Wednesday, 4:35 pm.
Tools: Modeling & Simulation

- **CFD**
- **PROX** 155 °C, Q = 2.4 W
- **PEMFC**
- **HEX** Q = -0.28 W
- **MIXER**
- **SEPARATOR**
- **SR PROX PEMFC COMBUSTOR**
- **MIXER**
- **SEP2**
- **RGIBBS**

**Heat Transfer**

**Process (ASPIN)**

Tools: Micro-Kinetic Test Bed

- **Individual microreactor**
- **Low dead volume**
- **No cross-contamination**
- **Low catalyst mass requirement**
- **Fast sample loading and unloading**
- **Process relevant reaction info**

Ouyang, et al., 2000

- **CFD + Reaction**
- **Heat Transfer**
- **Elementary Kinetics**

**Tools:**
- Modeling & Simulation
- CFD
- CFD + Reaction
- Heat Transfer
- Elementary Kinetics

**Micro-Kinetic Test Bed Features:**
- Independent reaction control
- Fast sample loading and unloading
- Low dead volume
- Low catalyst mass requirement
- No cross-contamination
- Process relevant reaction info
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Fuel Cells:
Applications & Power Ranges

Power (Watts)

10⁰ 10¹ 10² 10³ 10⁴ 10⁵ 10⁶ 10⁷

Ship Service Fuel Cell

Taken from Robert Nowak DARPA
Fuel Cells: Next Generation Portable Power Sources

- As alternatives to batteries in advanced portable power applications
- Offers high energy density. Allows portable devices to operate for longer times with less recharging
  Methanol: 4780 Wh/l, Li-ion secondary battery: 300 Wh/l

- Chemical Process Miniaturization: size and portability drives the use of microreactor technology in the field of fuel processing
- Advantageous heat and mass transport, lightweight, improvement in efficiency and productivity, fast response time

Fuel cell & fuel Processing

- Electrochemical devices that convert chemical energy of fuel directly to electricity
- Development of an efficient way of delivering fuel to the cell
- Generating hydrogen by processing of easily stored liquid hydrocarbons

Methanol to hydrogen: Components of fuel processor
Understanding Fundamentals of Preferential Oxidation in a Microchannel as Foundational to Rational Microreactor Design

Temperature Dependence of $X_{CO}$

- Falloff was caused by the reactor temperature gradients and r-WGS reaction (Oh et al., Choi et al., Venderbosch et al., Roberts et al.)
- No detailed study on the effect of reactor size for r-WGS reaction in PrOx

3D Reactor Model

- Ouyang, “PrOx Models” Tues. Poster
- Reconversion of CO$_2$ to CO overtakes PrOx at highest temperature

Temperature Dependence of $X_{CO}$

CO Conversion

Temperature [°C]

- Greater diameter, catalyst "thickness"
- More severe hot spot formation
- Greater r-WGS activity


Microscale Fuel Processing: Issues and Challenges

- Miniaturization of system components
- Heat management
- System complexity and packaging
- Kinetics evaluation for each unit operation
- Compatible Balance of Plant (BOP) components
- Water management
- Internal energy demand
- Dynamic control
- Fate of exhaust gases
**Approach**

**Challenges**

- **Miniaturization of system components**
  - Chemical process miniaturization using silicon microreactor technology

- **Heat management**
  - Development of a silicon microreactor based methanol reformer as a key fuel processing component. Design, fabrication, and packaging of steam reformer in the context of complete thermal integration to directly address the heat management issue

**Micro Steam Reformer**

**Reforming reaction**

\[ CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \]  
\( \Delta H_\text{r} = 50 \text{ kJ/mol} \)

On metal oxide catalyst (CuO/ZnO-based)

- SR microreactor design: Chip size: 4 cm × 2 cm × 500 micron
  - Reaction zone: 1 cm × 1 cm × 400 micron (0.04 cc)

- Pressure drop for reaction zone packed with catalyst estimated from Ergun equation. For catalyst of size 60 micron, the reactor with bed length of 1 cm resulted in a pressure drop of 1.865 Pa

- The reactor includes a flow manifold, a reaction zone, and filter structures at outlet to trap catalyst particles
Flow Modeling
Internal Heat Management: Microfabricated Vacuum Insulation

- Critical to thermal integration
- Best commercial insulators = 0.02 W/mK
- For sub-atmospheric pressures, K decreases with pressure
- Engineering of K with pressure and depth of cavity
- Gap filled with low-pressure gas: = 0.001 W/mK
- Microfabrication enables straightforward approach to this structure

Vacuum cavity, P = 0.001-0.1 torr

Vacuum Insulation Design: 3D Thermal Simulation

\[(m.Cp.T)_{in} : 0.0738 W\]
\[(m.Cp.T)_{out} : 0.174 W\]

T = 155º C

Combustor zone

Insulation

PrOx zone

0.22 W Heater
Vacuum Insulation Design: 3D Structural Modeling

Pressure differential force results in deformation and high stress generation in silicon and glass during bonding.

Glass

Si

P ∼ 0

Deformation: 1.02 micron

For Vacuum bonding, 800 micron thick wafer should be used.

Integrated Unit

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

Insulation

T Sensors

500 micron

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

SR reactor
(4 cm × 2 cm)

Heater

50-µm depth
Atm. pressure
k = 0.04 W/mK
Incorporation of catalyst in the form of packed bed by vacuum loading. Catalyst loading achieved: 51 mg
Thermal/Reaction Characterization
Experiments in Progress

Research Impact
- Understanding of critical thermal parameters. Improvement in thermal model
- Weight, volume, and performance comparison with battery technology
- Help conceive applications and limitation of silicon microchemical technology for micro fuel processing and provide impetus for subsequent development

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Evolution in Pharmaceutical Industry

- Procedure Based
- Disincentive to Innovate
- Cost Burden to Industry
- Stretch Resources of Reg. Agency

Protect the Public → Little/No Standard Procedures → Regulation → c. 1960

- Sulfanilamide; FDC 1938
- Thalidomide; KHA 1962

Pharmaceutical Manufacturing

- Driving Forces For Change
  - Rising R&D Costs-Less Molecules (NMEs)
  - Healthcare Industry Pressure to Lower Costs
  - Competition-patent expir., generics, globalization

- Focus on Manufacturing
  - High Cost of Mfg.>R&D
  - 5-10% Waste
  - Labor Intensive
  - Quality by testing
  - High Capital Cost
    - large facilities
    - <50% utilization

(Hussain, FDA, 2004)
Breaking Old Paradigms

**Procedural Basis**
- Good vs. bad
- Rigidity
- Slow/no change

**Science Basis**
- Notion of variation
- Innovation based on data
- Timely implementation

**Batch**
- Large
- Flexible
- Batch-to-batch non-uniform.

**Continuous**
- Compact
- Fixed
- Steady state uniformity

**Post-Sampling**
- After the fact
- Human intervention
- Reactive

**In-Line Monitoring**
- Continuous monitor
- Remote
- Proactive

Paradigm Breaker: Microreaction

**Mass-Transport Limited** ↔ **Fast Mixing**

**Highly Exothermic** ↔ **Fast Heat Transport**

**Sensitive to Extreme T,P** ↔ **Short Residence Time**

**Safety, Liability** ↔ **Small Volumes, Quenching**
Barriers to Microreaction

**Philosophical**
- “Not invented here”
- Industrialization demos lacking

**Technical**
- Support infrastructure
  - availability
  - standardization
  - design engineering

**Financial/Strategic**
- Huge existing investment

Concrete demos needed

Careful implementation strategy needed
Difference Micro Makes

>500 organic synthetic reactions studied in microsystems

(Hessel 4/05)

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

Yield

\[ \begin{array}{c|c|c|c|c|c|c|c|c|c} 
\text{Yield} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\text{Yield Gain} & -20\% & -10\% & 0\% & 10\% & 20\% & 30\% & 40\% & 50\% \\
\end{array} \]
Precise Control of Reactant Energy Distribution

Temperature Distribution

Side Reactions

Consecutive Reactions


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• Pharmaceutical Manufacturing: Background
• Microreaction for Pharmaceutical Hydrogenation
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Project Goals

Lab Scale Microreactor/Heat Exchanger Demo
(3 yrs.)

Pilot Plant Scale Demonstration
(2 yrs.)

Design, fabricate, evaluate, optimize

Prelude to commercialization

Demonstrate model reactions at moderate conditions (<130°C, 50 psi)

1 kg/hr

Generic catalyst deposition methods

70-90% reduction in energy reqt.

Generic reaction/catalyst screening tools

Screening Tool Reactor Modeling

Final Design:

L=20 mm
W=18 mm
D=350 μm
n=14,082
ε=0.846
w=0.532 mg

dp=50 μm
dp=25 μm

Gas

Liquid

3H₂ + OCH₃NO₂ → OCH₃NH₂ + 2H₂O

o-nitroanisole → o-anisidine
Catalyst Trap Reactor

Initial Reaction Results

<table>
<thead>
<tr>
<th>Gas Flow rate (sccm)</th>
<th>5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flow rate (mL/min)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Pressure, psia</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
<td>Catalyst loading (mg)</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Conversion%</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>Selectivity%</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>Yield%</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>Relative Productivity</td>
<td>0.10</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Residence-time dependent yield
Compares well to capillary test
To come: elevated pressure
Mapping of flow regimes
Gas-Liquid Interface

1 sccm 12 sccm

Conclusions

- NJCMCS: a unique center devoted to MCS
- Multidisciplinary model: understanding, designing, implementing MCS
- Hydrogen production: good application for MCS
- Pharmaceutical industry: another great opportunity
- Hydrogenation: a strong example for implementation
- Progress in initial expts and tool development, stay tuned
- Visit us in Hoboken!
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