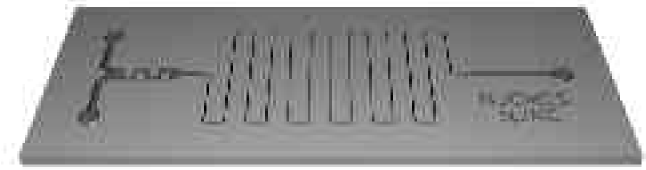
Microchemical Systems: New Solutions to Chemical Engineering Problems Through Miniaturization



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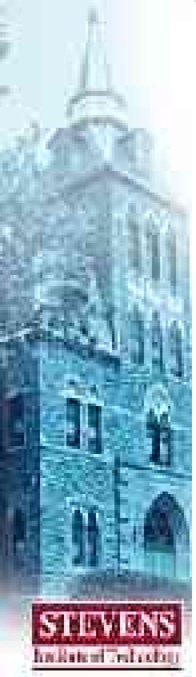
June 24, 2004

Outline

- Introduction to Stevens and NJCMCS
- Definition of MCS
- Advantages of MCS
- Major application areas
    - Miniaturization and Intensification
- Examples
    - Extended: Fuel processing for portable power (CPM)
    - Brief: Catalytic hydrogenation for pharaceuticals (CPI)



Stevens Institute of Technology

- **Private University founded in 1871**
- **The Stevens family: First Urban Ferry Business in New York Harbor**
- **1700 undergraduates, 2800 graduates**
- **Engineering, Science, Technology Management**
- **Incoming Freshman GPA: 3.8 and SAT 25%-75%: 1200-1400**

New Jersey Center for MicroChemical Systems (NJCMCS)

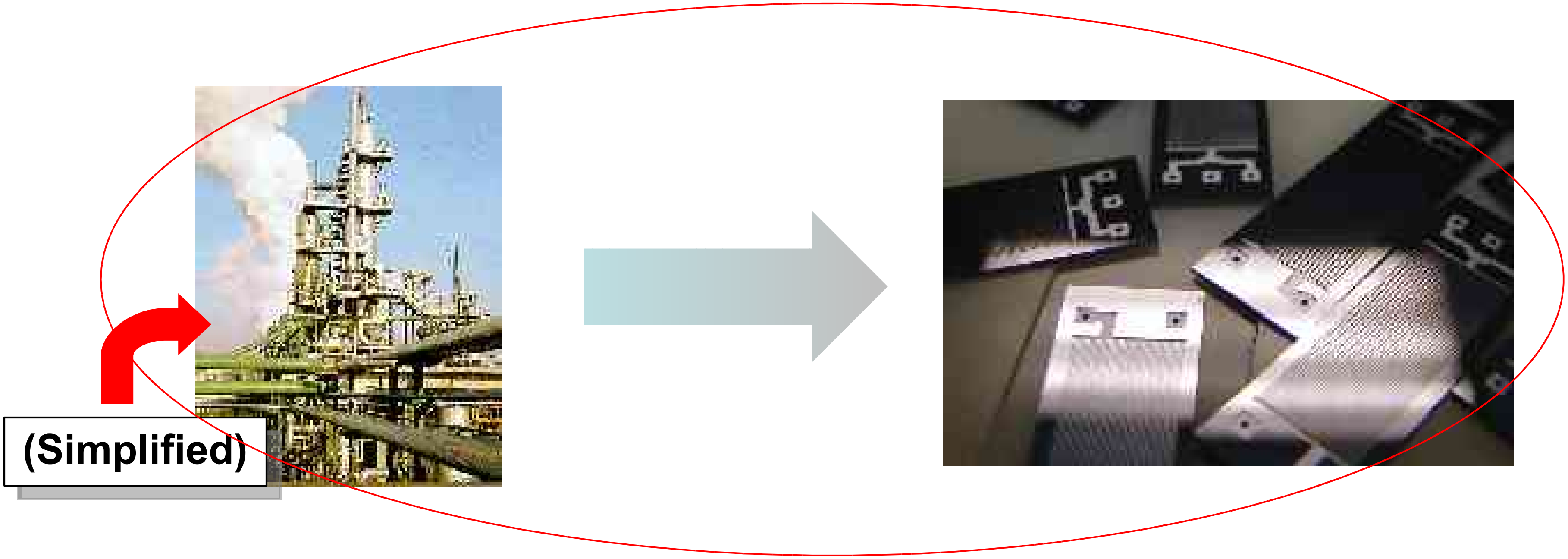
- Official start in September 2002
  - $7.5M commitments to date
  - $10.0M pending for state-wide infrastructure
- Vision
  - Leadership for microchemical device/system <u>understanding</u>, <u>design</u> methodology and <u>tools</u> development
- Systems-level concept demowith our key partners
  - Army-Picatinny, Bristol-Myers Squibb, FMC, and Lucent-Bell Labs
  - Portable power, pharmaceutical, and chemical applications

NJCMCS People

- Besser Group
  - Dr. L. Bednarova, S. Ouyang, K. Shah, H. Gadre, W. C. Shin, S. McGovern
- Lawal Group
  - Dr. R. Halder, Dr. D. Qian, J. Adeosun, S. Tadepalli, Y. Voloshin
- Lee Group
  - Dr. Y.-F. Su, J. Meyer, H. Chen, H. Qiu
- Affiliated Faculty
  - Profs. R. Blanks, H. Du, T. Fischer, S. Koven, M. Libera, E. Whittaker
- Consultants
  - Dr. A. Kaufman, Dr. J. Manganaro, F. Shinneman, M. Urken
- Center Administration
  - Prof. Lee (Director) and Prof. Besser and Prof. Lawal (Co-directors)
  - Aqsa Quresh and Pat Downes

Main contributors to the contents of this seminar.

Microchemical Systems



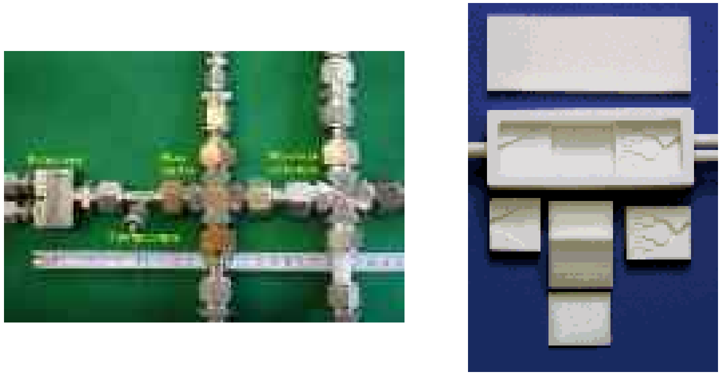
(Simplified)

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

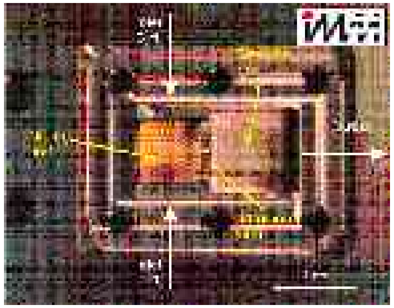
Distinction from Lab-on-Chip: chemical <u>production</u> vs. analysis

Microreactors—What Are They?

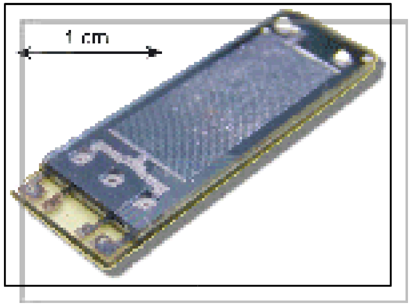
- “Microreactor” traditionally means lab bench reactor
- Dimensions 1/10 of those in bench reactors



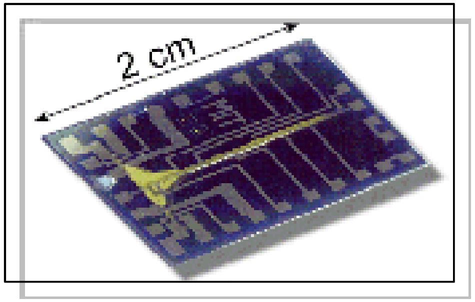
(Forschungszentrum Karlsruhe GmbH)



(Ehrfeld, et.al., IMM)



(Besser, et.al., IfM)

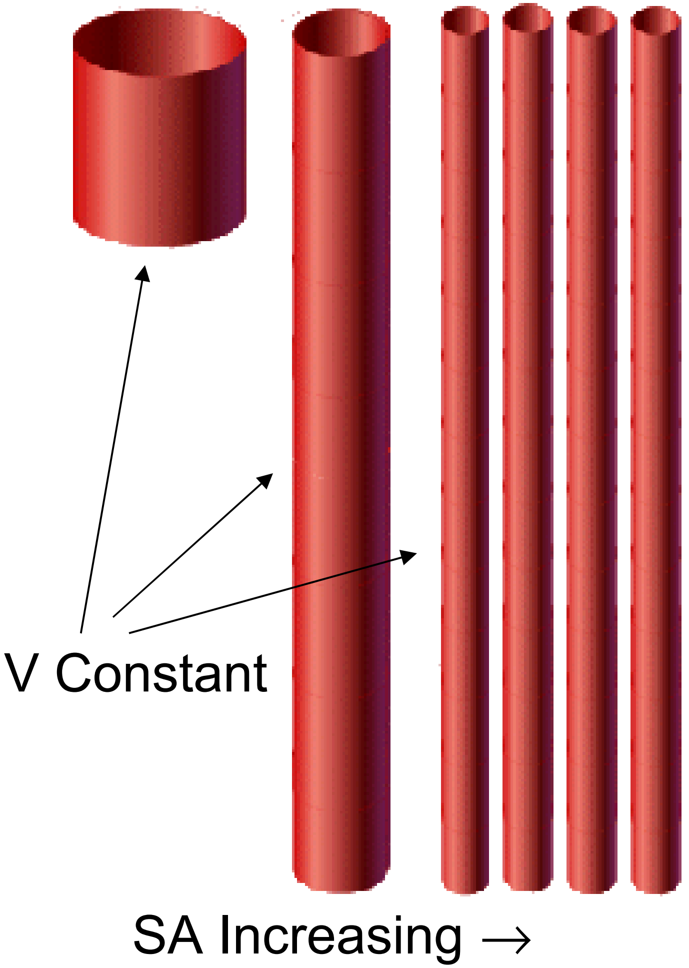


(Jensen, et.al., MIT)

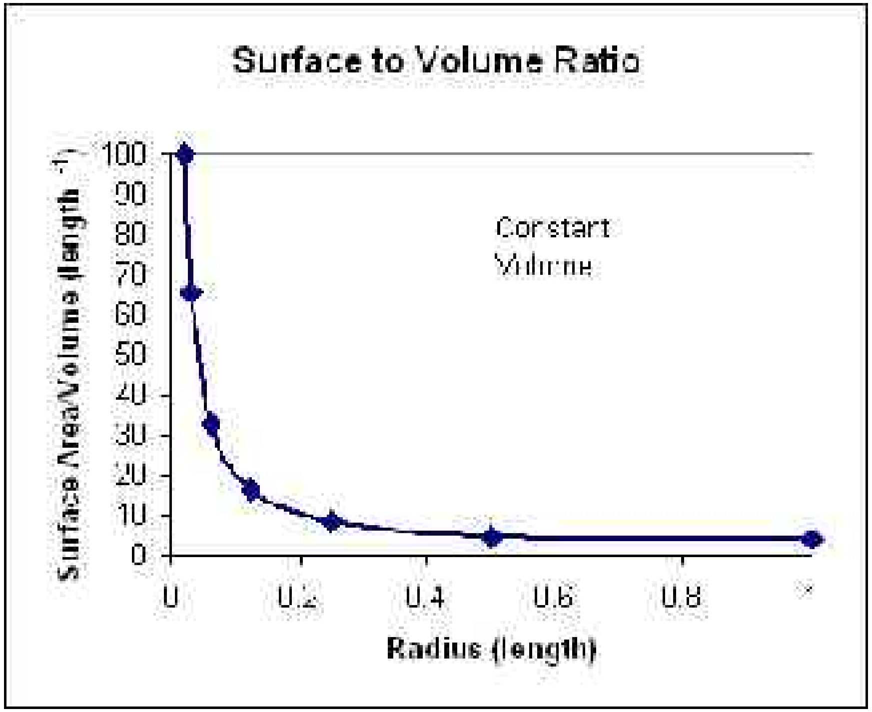
Benefits of Miniaturization—Why?

- Surface to Volume Ratio
  - Low Transport Resistances
- Low Inventory (“Hold Up”)
- Robust Materials
- Cost

Benefits: Surface to Volume


V Constant

SA Increasing →



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

Benefits: Low Transport Resistances

Example: Overall Heat Transfer Coefficient

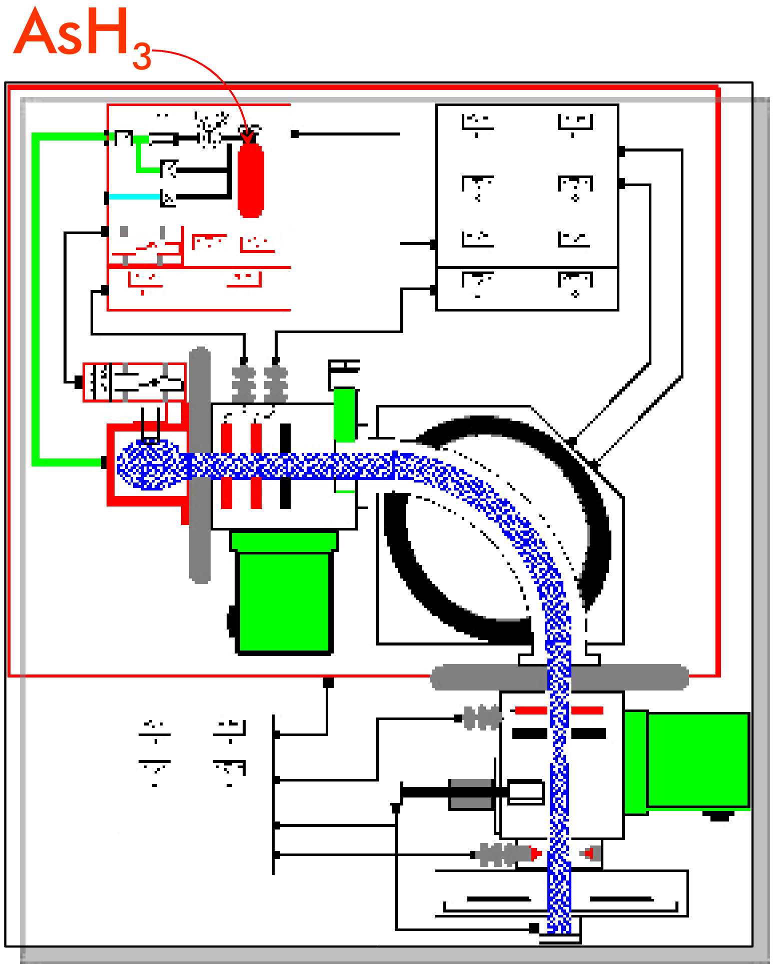
Hx Type	***U (W/m²K)***
Tubular	150-1200
Spiral	700-2500
Plate	1000-4000

Microchannel: 3800-6800 W/(m²K)

(Stevens undergrad design project)

(500x500 μm^2 x 1.5 cm channels)

Benefits: Low-Inventory (Hold-Up)



Schematic of As^+ Ion Implanter

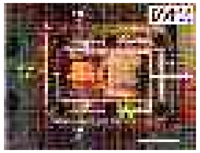
- Safety
- Environment

Phosgene Reactor, Geismar, LA

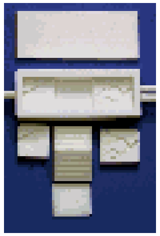
Benefits: Robust Materials

- High strength, high melting point materials:
  - Metals
  - Ceramics
  - Silicon
- Array of fabrication processes (MEMS technology)
- Non-traditional reactor materials
  - Polymers

SS 304



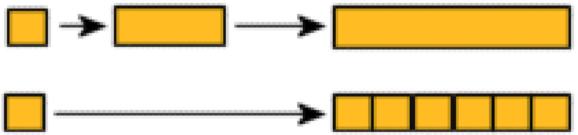
Al_2O_3



Si

Benefits(?): Cost

- Reactor Fabrication
  - – High volume batch
    - Si integrated circuit fabrication model
    - Metal/ceramic micromachining techniques ($)
    - Interface of reactor to plant ($?)
- Scale-Up Process



  - – Linear process
  - – Characterize unit module; scale up throughput by addition of modules

Major Application Directions

Chemical Process Miniaturization

- Same functionality per volume as macro
- Miniature size is distinguishing factor
- Portability often important

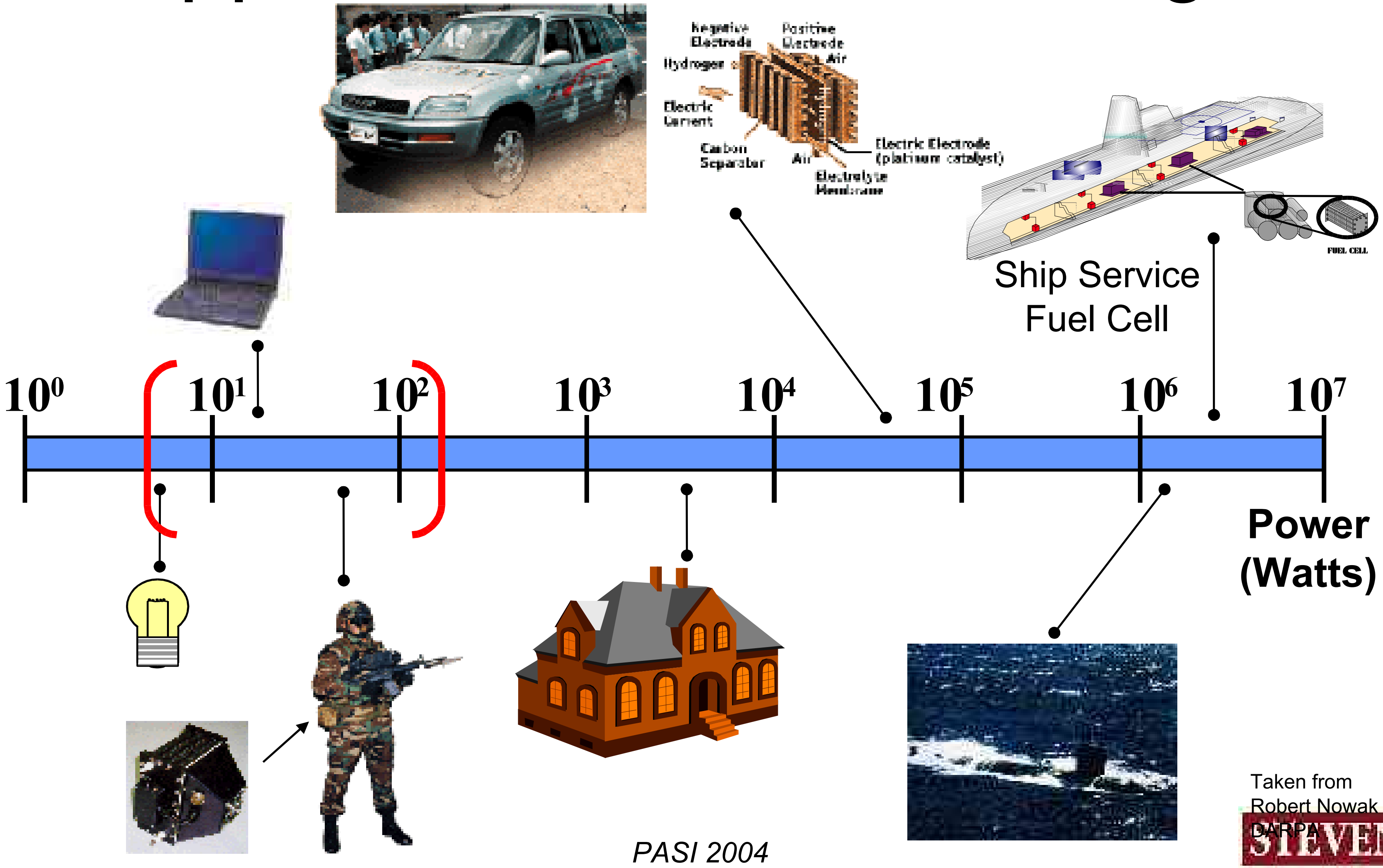
Example: H_2 generation for small fuel cells

Chemical Process Intensification

- Higher functionality density than macro
- Size reduction is not paramount
- May access new chemistry routes
- Generally leverages

Example: hydrogenation of pharma intermediate.

Fuel Cells: Applications & Power Ranges

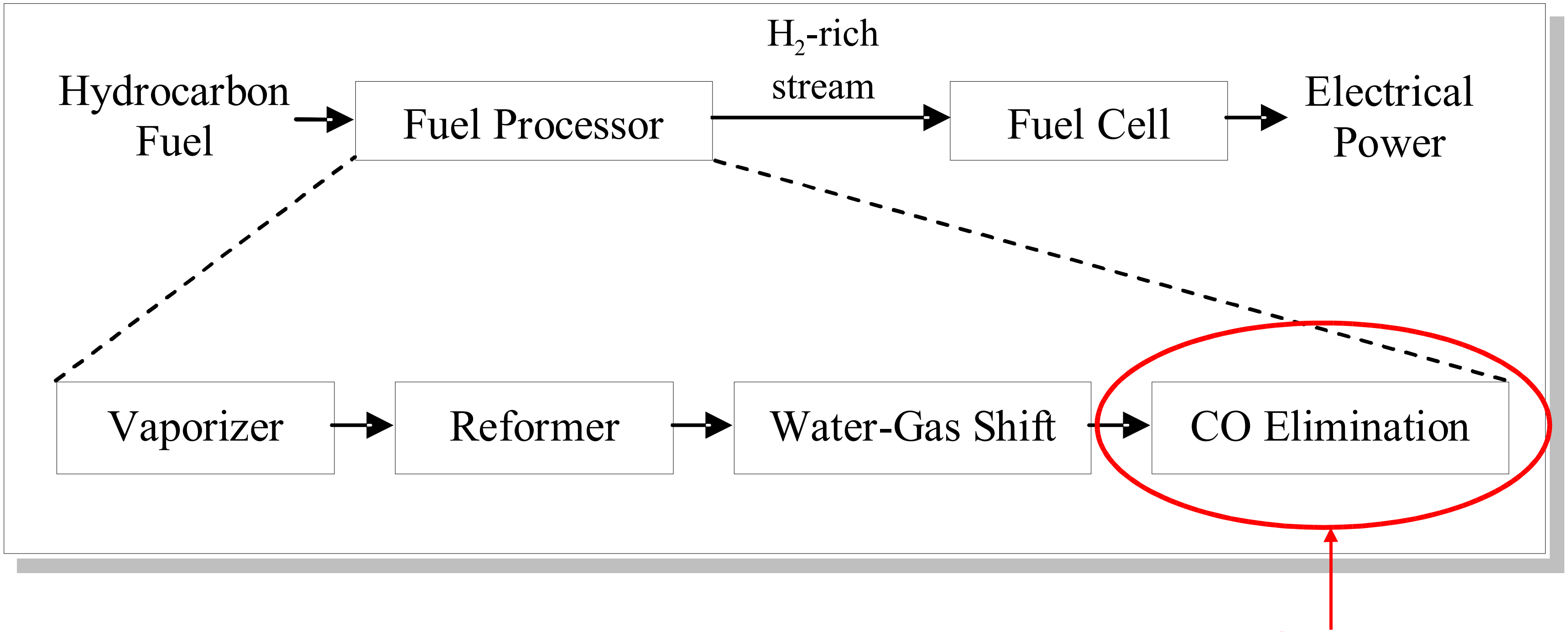


Taken from
Robert Nowak
DARPA

Can We Use Microchemical Systems for Portable Power?

- MCS: Superior heat and mass transfer
  - Thermal management, excellent mixing
- MCS: Compactness
  - Energy density:
    - Advanced Li-MnO_2 battery: 169 W-h/kg
    - MeOH: 6000 W-h/kg

Model Study: Preferential Oxidation (“PrOx”)



PrOx reactor

CO poisons PEM fuel cell catalysts

CO must be reduced below 10 ppm for viability (PEMFC)

CO Poisons FC Catalyst

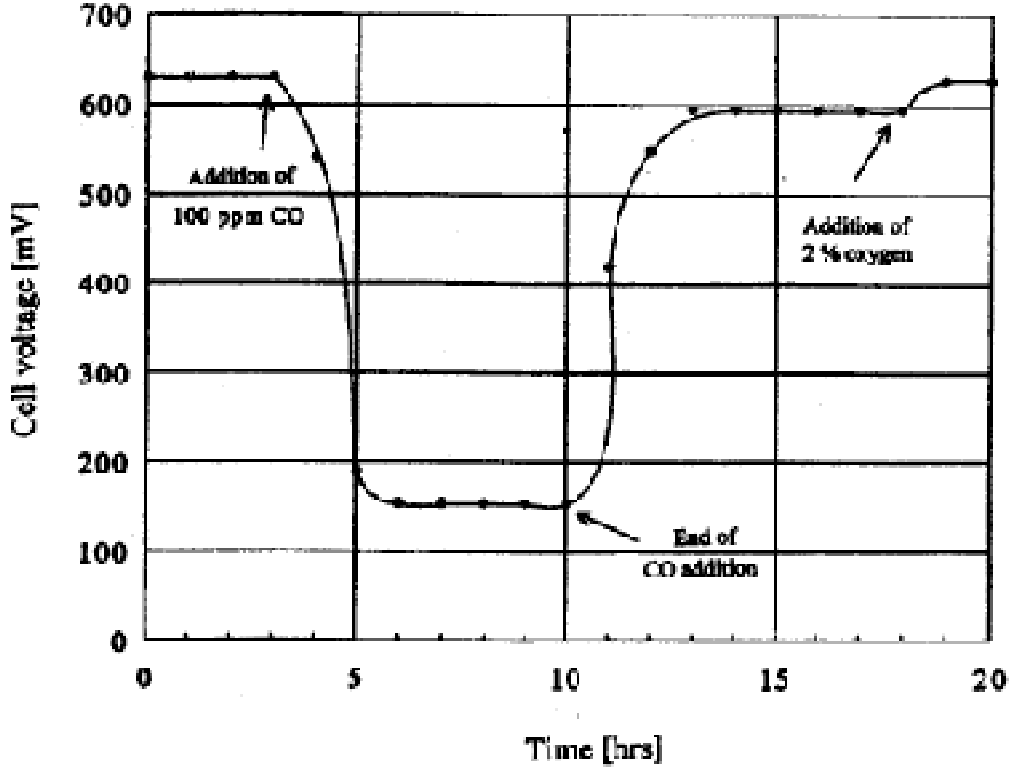


Fig. 1. Effect of CO on a PEM fuel cell operated on hydrogen at a current density of 100 mA cm^{-2}, $T = 70$°C, cathode and anode Pt loading 0.2 mg cm^{-2}.

(M.Gotz and H. Wendt, *Electrochemica Acta*, **43**, 3847 (1998)).

Goals for PrOx Project

- Construct strong support infrastructure for *MCS* understanding and design
- Apply this infrastructure to understanding PrOx for portable fuel cells
- Demonstrate a PrOx reactor for a 1-W_e fuel processing system

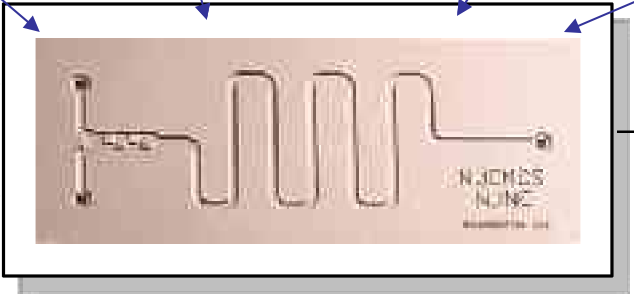
PrOx Design Challenges

Surface Engineering

Microfabrication

Kinetic Simulation

Fluidic Modeling



Air @ 2 μmole/s

Reformate @ 20 μmole/s

CO: 1.7%

H_2: 68.5%

H_2O: 8.1%

CO_2: 21.7%

CH_3OH: 27 ppm

To PEMFC

Treated Reformate

CO: 9 ppm

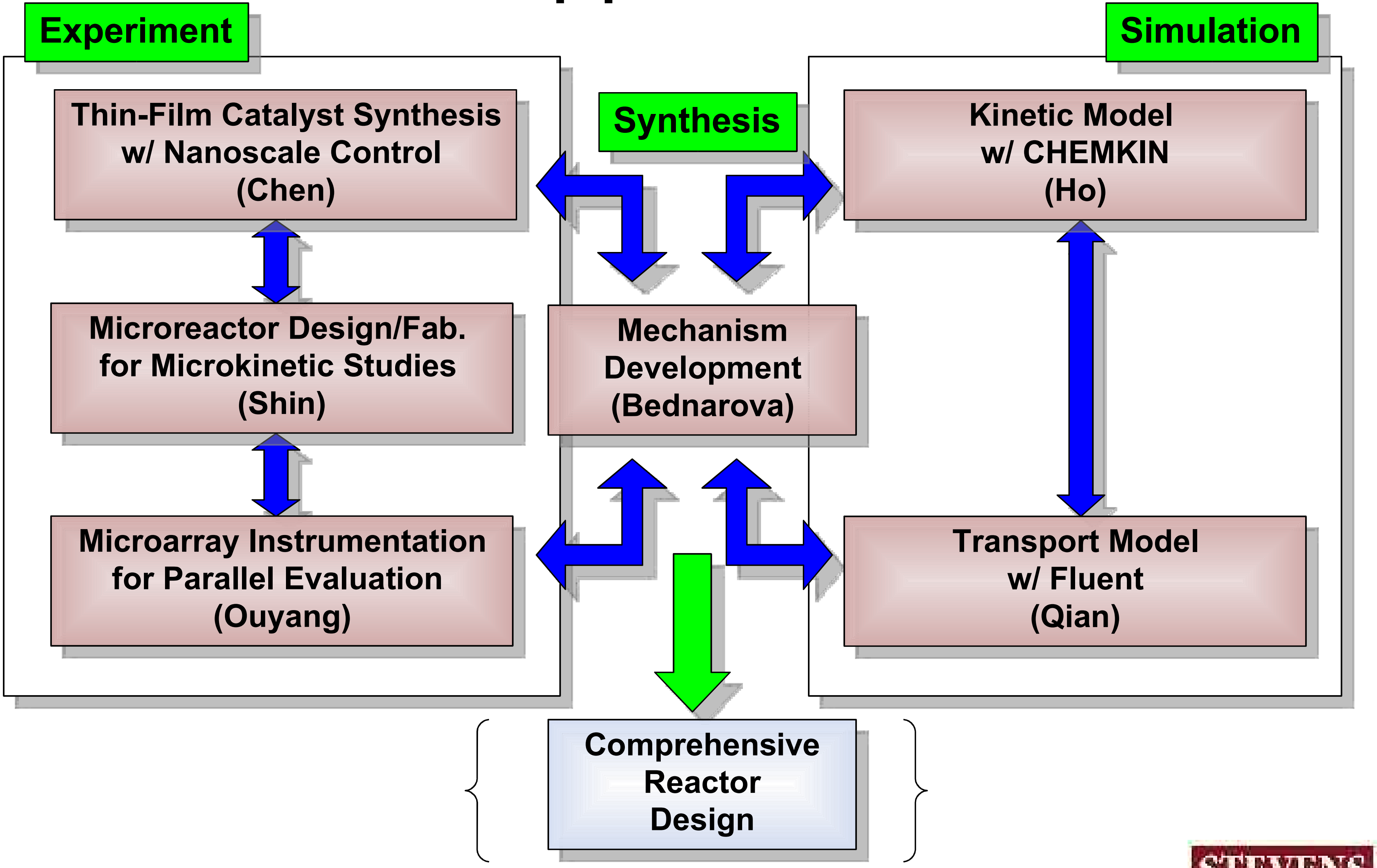
Low H_2 conversion

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Design Criteria

- **150-200°C and ~1 atm**
- **Minimum volume, ΔP**
- **Conversion, selectivity, stability.**

Approach



Experiment

Thin-Film Catalyst Synthesis w/ Nanoscale Control (Chen)

Microreactor Design/Fab. for Microkinetic Studies (Shin)

Microarray Instrumentation for Parallel Evaluation (Ouyang)

Synthesis

Mechanism Development (Bednarova)

Simulation

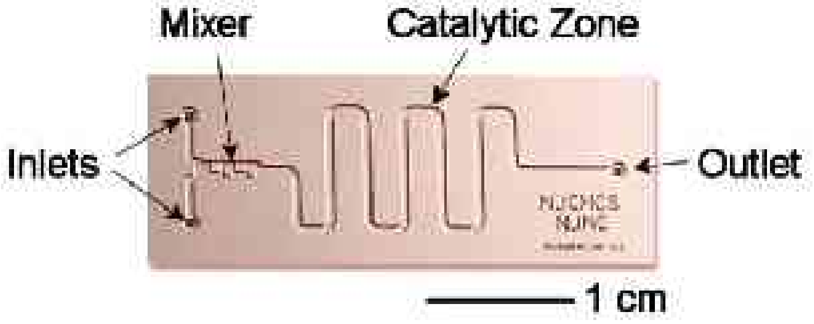
Kinetic Model w/ CHEMKIN (Ho)

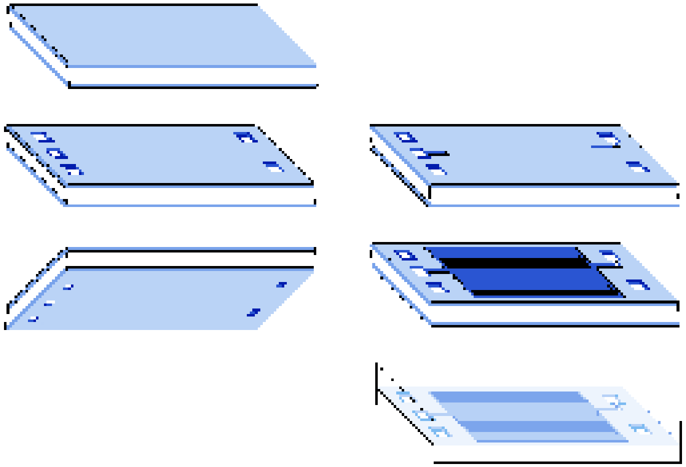
Transport Model w/ Fluent (Qian)

Comprehensive Reactor Design

Microreactor Fabrication

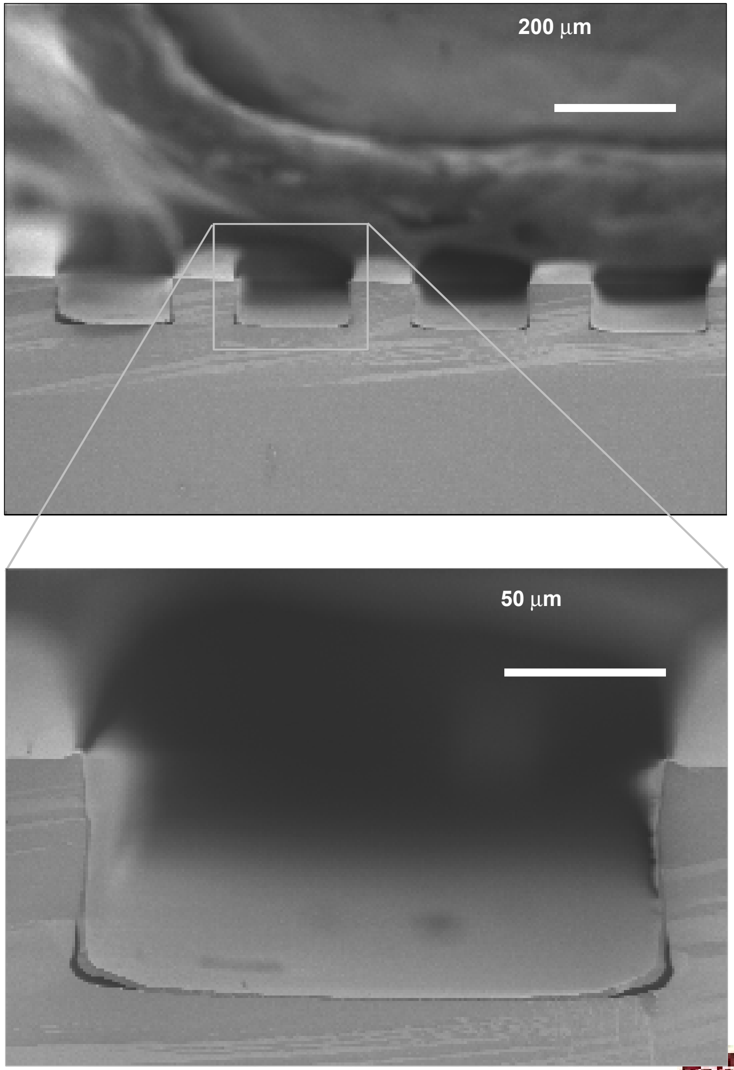
- Photo-patterning process
- High-rate silicon dry etching (DRIE)
- Anodic bonded Pyrex cover
- Batch processing
- 8-in. Si wafers, Bell Labs-NJNC



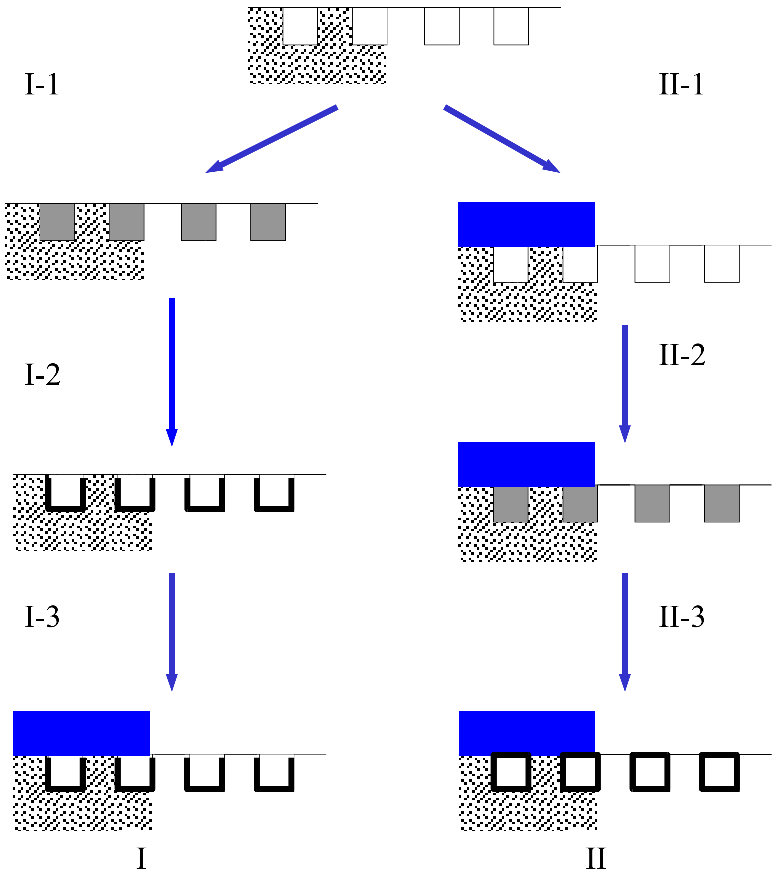


Thin-Film Wall Catalyst: Why?

- Low pressure drop compared to packed bed
- Less clogging
- Better mass transport than packed bed or washcoat

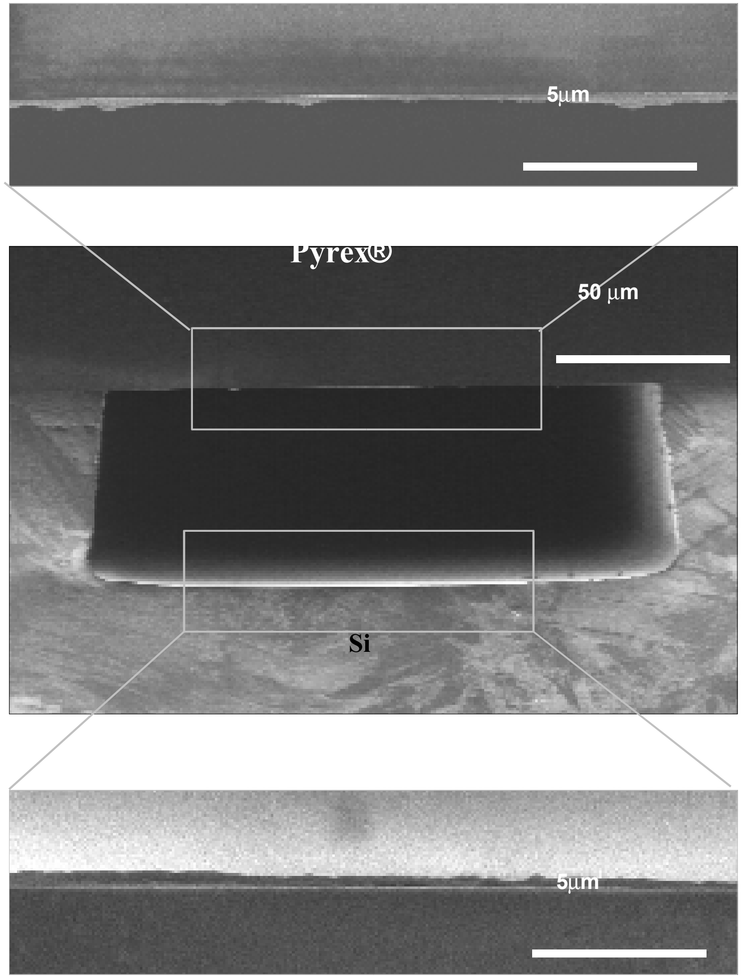


Catalyst Infiltration



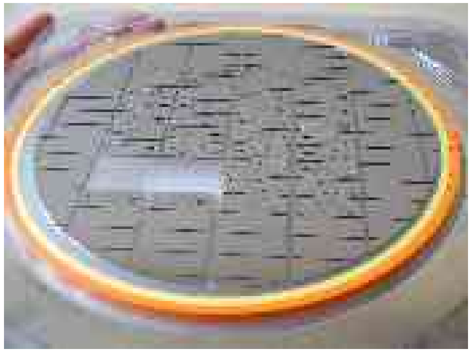
Open Channel

Closed Channel

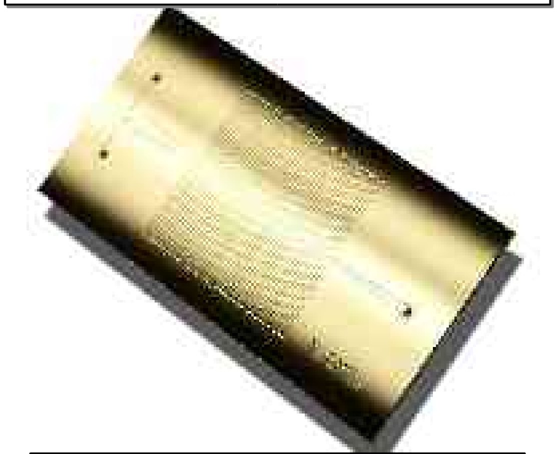


Closed Channel Infiltrated

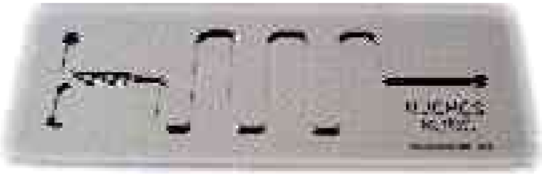
Microreactors Fabricated for PrOx Research Project



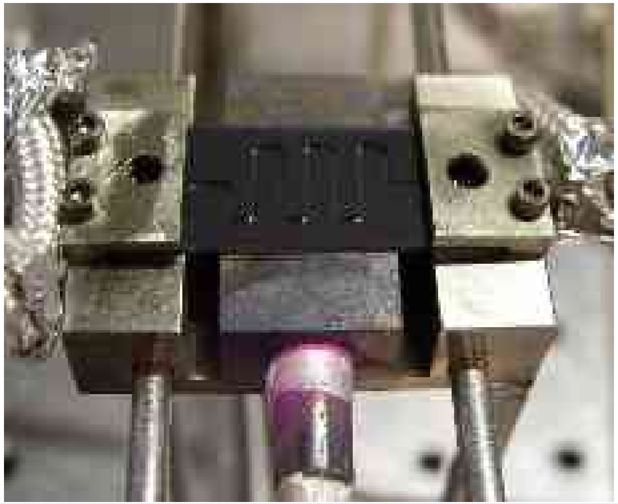
8-in. Si wafer, Bell Labs



Long-channel reactor

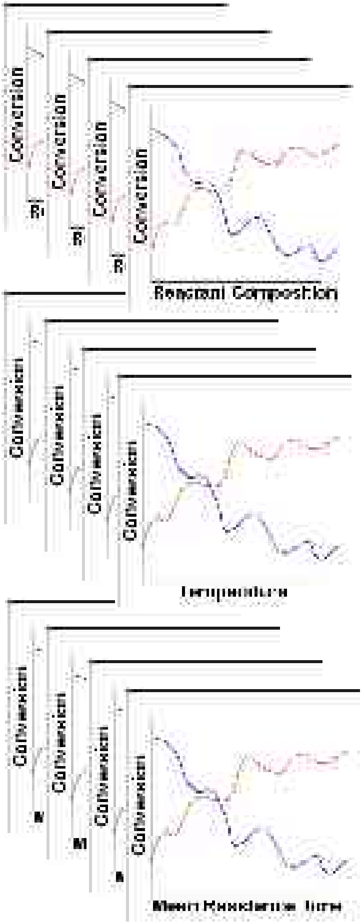


Short-channel reactor



Short-channel reactor under test

Gathering Process-Relevant Information—How?



Microkinetic array

Four reactors in parallel

Independent reaction parameters

Shared analytical

No cross-contamination

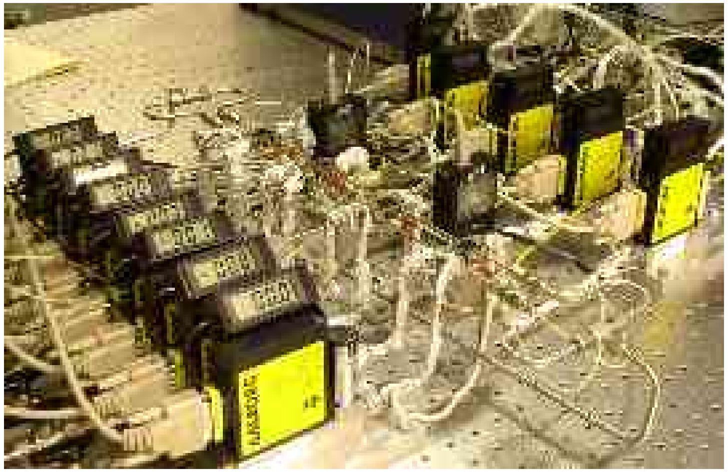
Individual microreactors

Independent reaction control

Fast sample loading and unloading

Process relevant reaction info

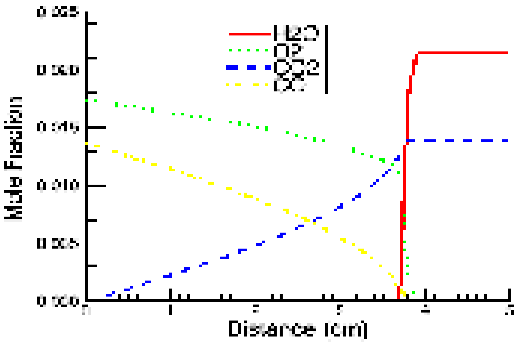
Test reactor found to mitigate CO in 0.25 W_e flow with ≈1mg catalyst

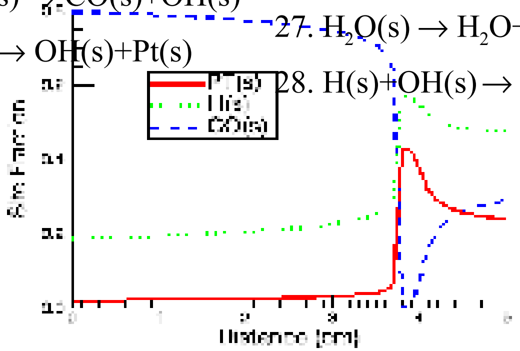


CHEMKIN Simulation: Prediction of Reaction Behavior

- Solution of kinetic rate eqns. all species
- Eight gas/surface species along channel
- Virtual experiments
- New experiment directions generated

1. $H_2 + Pt(s) + Pt(s) \rightarrow H(s) + H(s)$
2. $O_2 + Pt(s) + Pt(s) \rightarrow O(s) + O(s)$
3. $H_2O + Pt(s) \rightarrow H_2O(s)$
4. $CO_2 + Pt(s) \rightarrow CO_2(s)$
5. $CO + Pt(s) \rightarrow CO(s)$
6. $CO(s) \rightarrow CO + Pt(s)$
7. $CO_2(s) \rightarrow CO_2 + Pt(s)$
8. $C(s) + O(s) \rightarrow CO(s) + Pt(s)$
9. $CO(s) + Pt(s) \rightarrow C(s) + O(s)$
10. $CO(s) + O(s) \rightarrow CO_2(s) + Pt(s)$
11. $CO_2(s) + Pt(s) \rightarrow CO(s) + O(s)$
12. $CO(s) + OH(s) \rightarrow CO_2(s) + H(s)$
13. $CO_2(s) + H(s) \rightarrow CO(s) + OH(s)$
14. $H(s) + O(s) \rightarrow OH(s) + Pt(s)$
15. $OH(s) + Pt(s) \rightarrow H(s) + O(s)$
16. $H_2O(s) + Pt(s) \rightarrow H(s) + OH(s)$
17. $OH(s) + OH(s) \rightarrow H_2O(s) + O(s)$
18. $H_2O(s) + O(s) \rightarrow OH(s) + OH(s)$
19. $H + Pt(s) \rightarrow H(s)$
20. $H(s) \rightarrow H + Pt(s)$
21. $O + Pt(s) \rightarrow O(s)$
22. $O(s) \rightarrow O + Pt(s)$
23. $OH + Pt(s) \rightarrow OH(s)$
24. $OH(s) \rightarrow OH + Pt(s)$
25. $H(s) + H(s) \rightarrow Pt(s) + Pt(s) + H_2$
26. $O(s) + O(s) \rightarrow Pt(s) + Pt(s) + O_2$
27. $H_2O(s) \rightarrow H_2O + Pt(s)$
28. $H(s) + OH(s) \rightarrow H_2O(s) + Pt(s)$



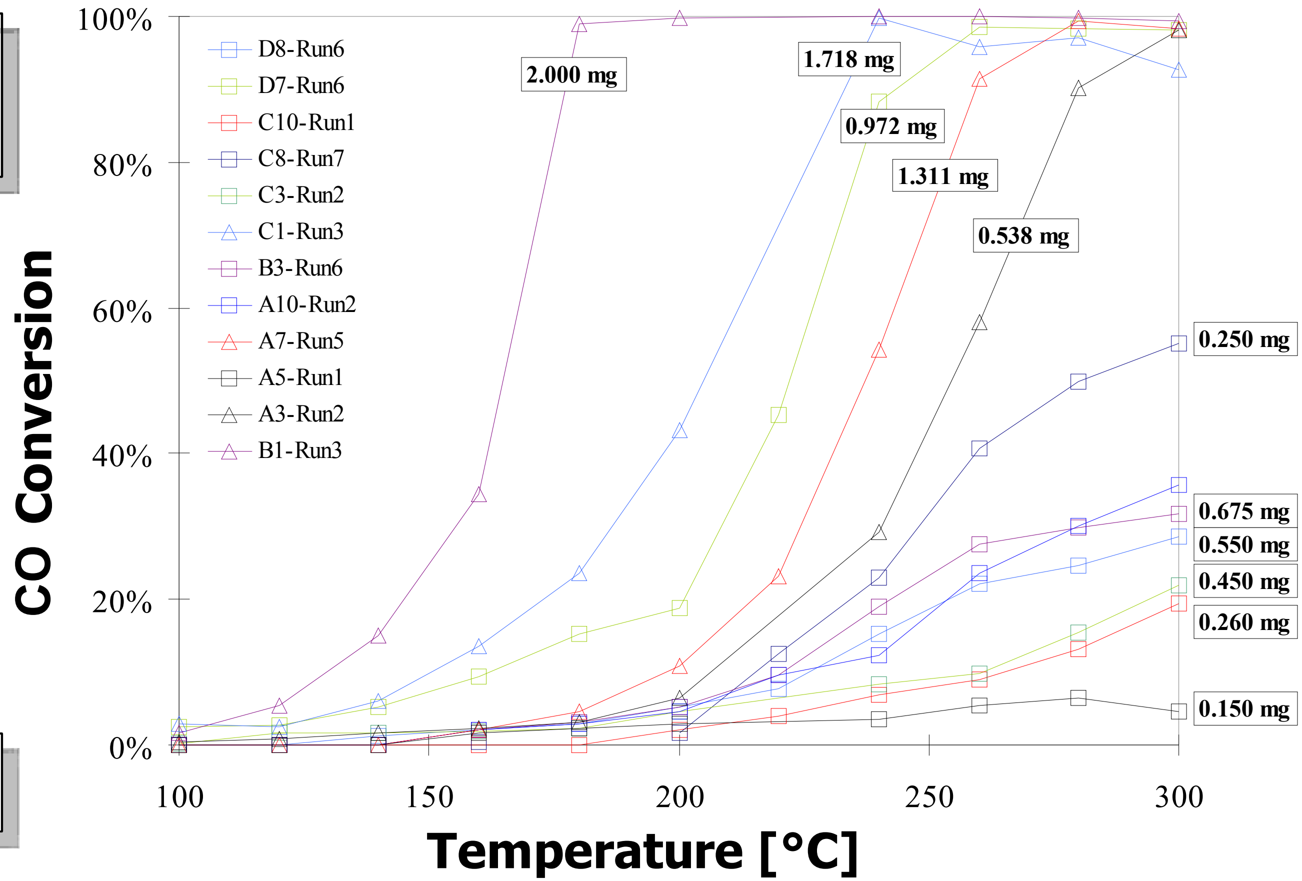


How Does the Reactor Perform?

- What is the conversion behavior?
- What is the selectivity?
- How productive is the reactor?
- What are the transport limitations?
- What is the activation/deactivation behavior?
- What is the catalyst stability?

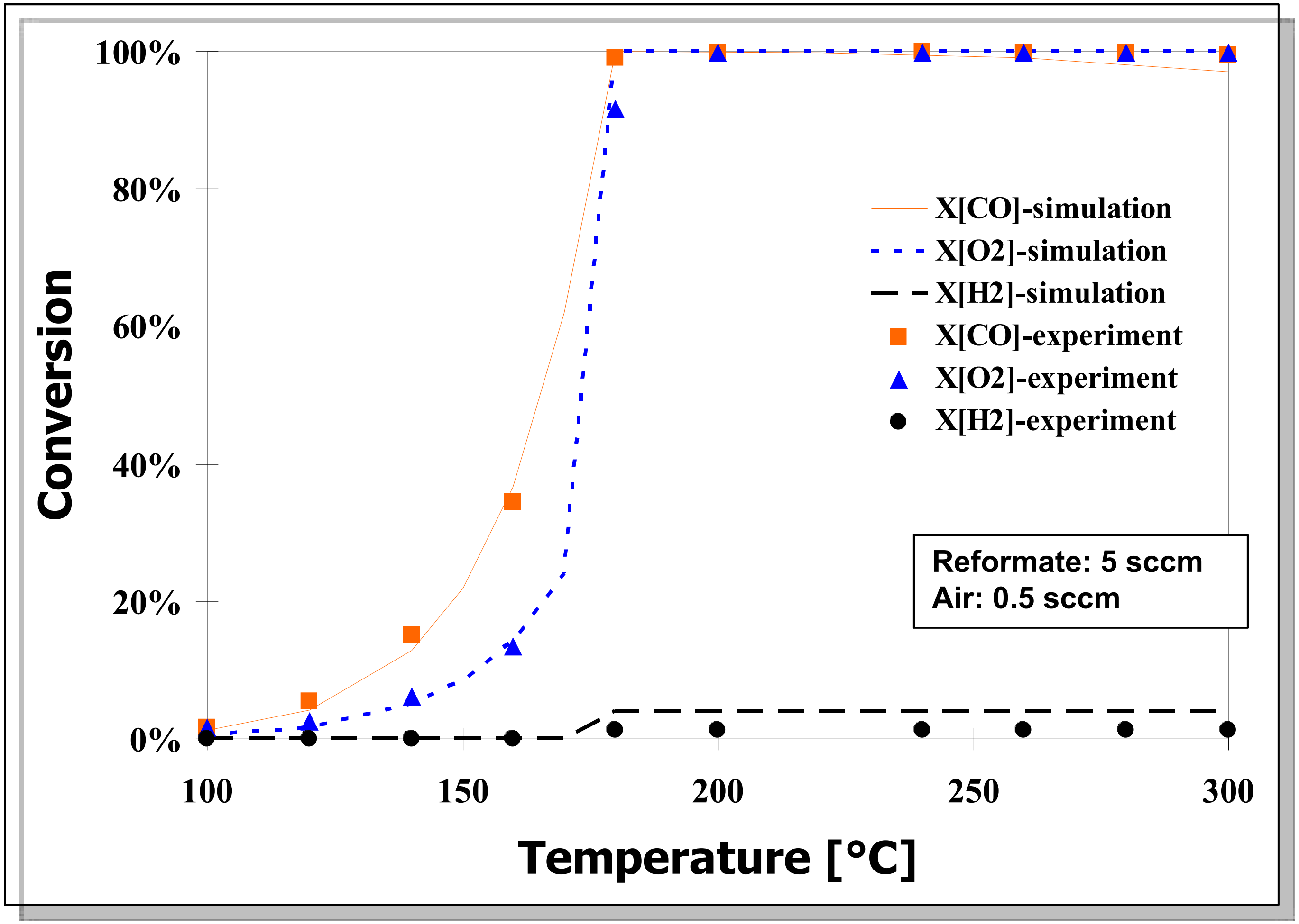
Conversion Behavior

$$Conv = \frac{\dot{n}_{in} - \dot{n}_{out}}{\dot{n}_{in}}$$



Reformate: 5 sccm
Air: 0.5 sccm

Comparison: Experiment vs. Simulation



Reformate: 5 sccm
Air: 0.5 sccm

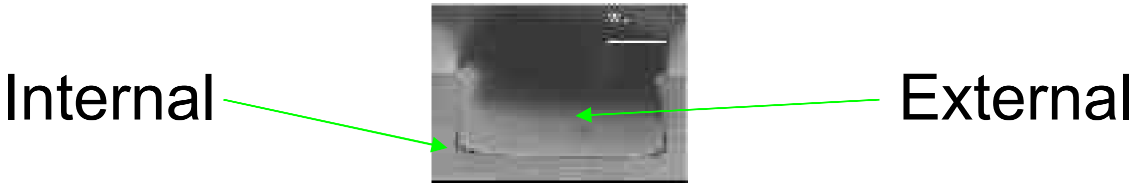
Catalyst Activity Comparison

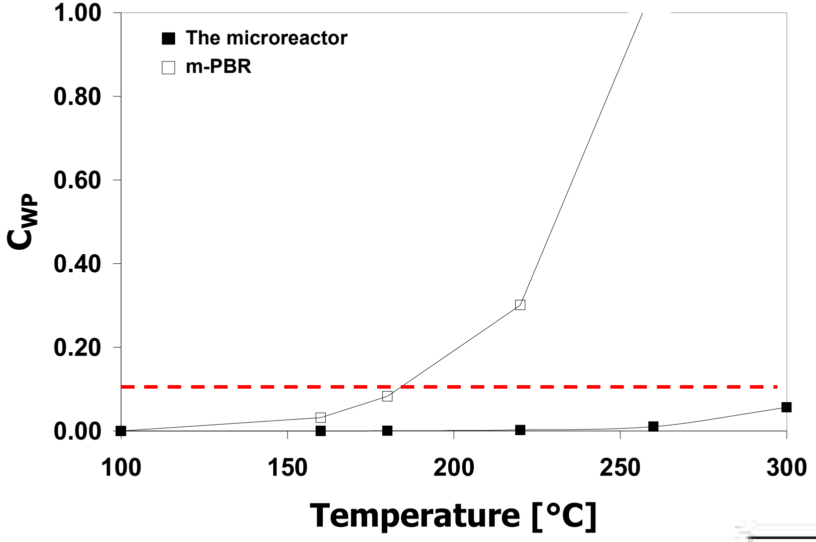
TOF=molecules produced/active site/sec

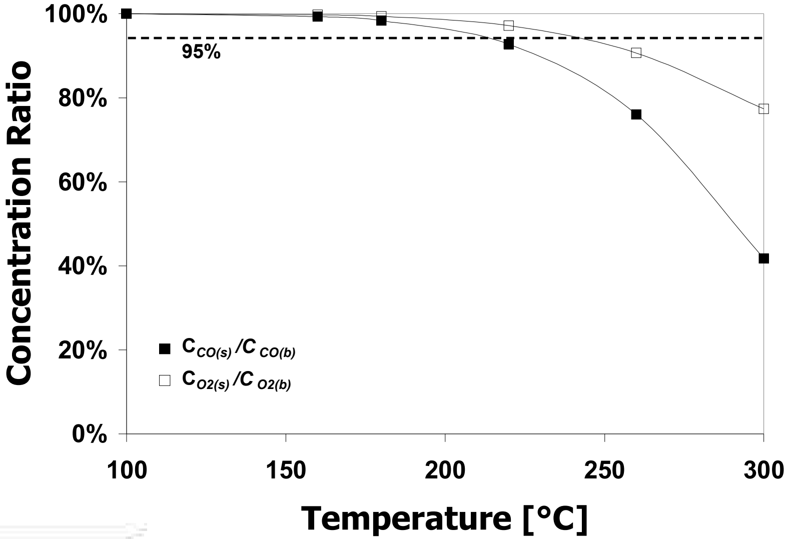
≈same activity as others at lower temperature (<150°C)

better activity at higher temperature (>200°C)

Mass Transport Limitation

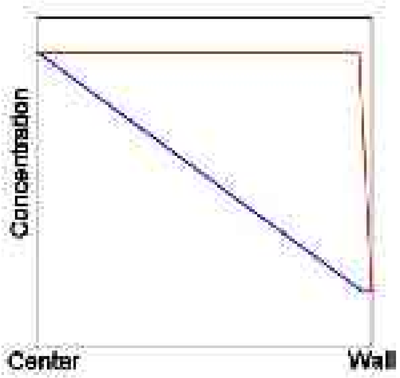






$C_{WP}=\eta\varphi^2$ $\qquad \varphi^2=\frac{-r'_{O_2}(obs)\rho_c L_c^2}{D_e C_{O_2(s)}}$

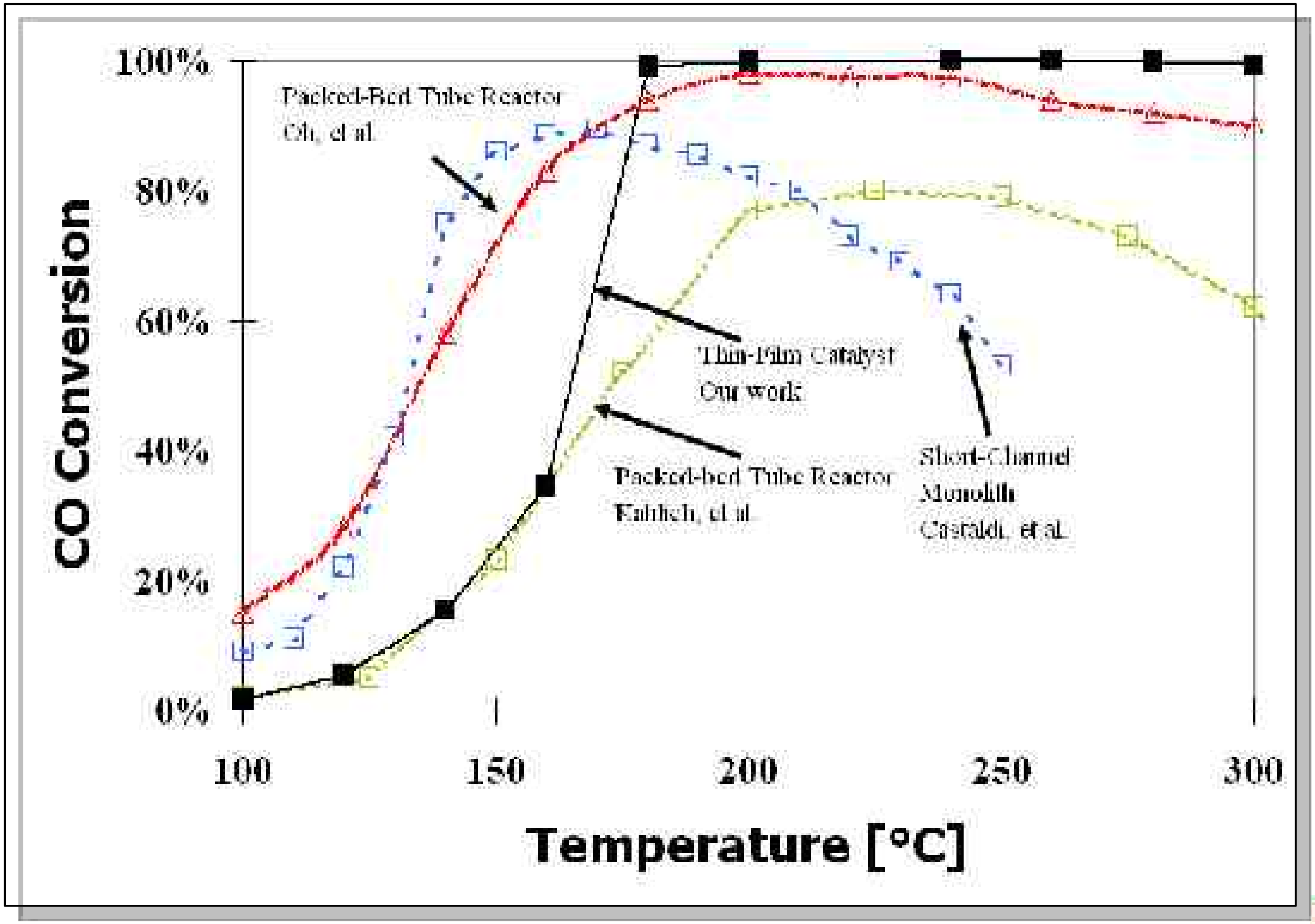
$C_{WP} \ll 1$



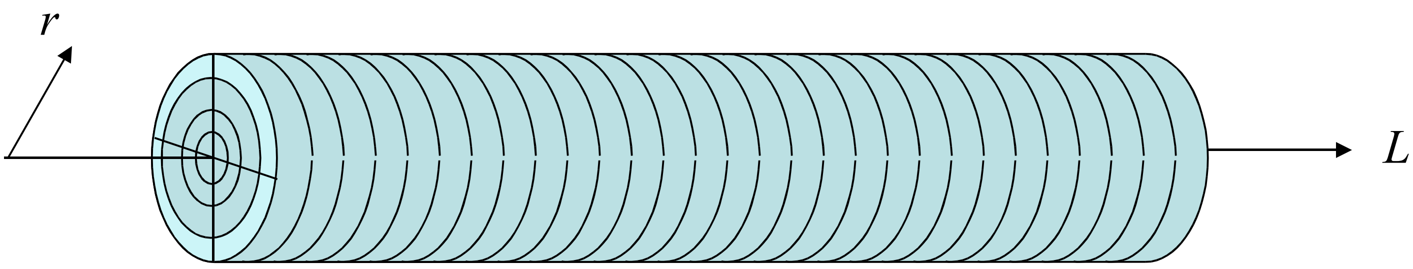
$C_{CO(s)}/C_{CO(b)} > 0.95$

$C_{O_2(s)}/C_{O_2(b)}$ ¿ 0.95

Conversion Comparison



2-D Finite Difference Model

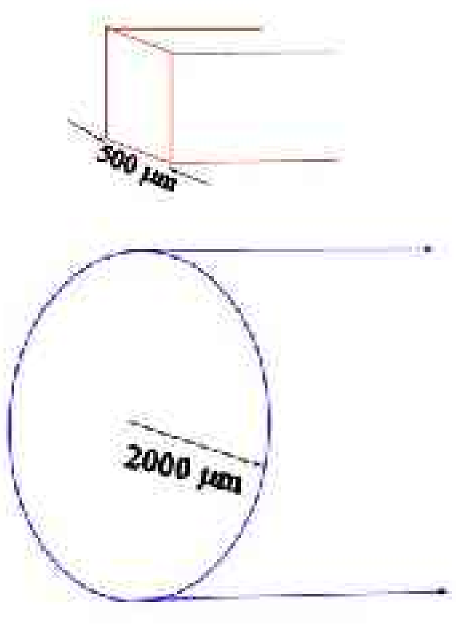


T_{wall} = Constant

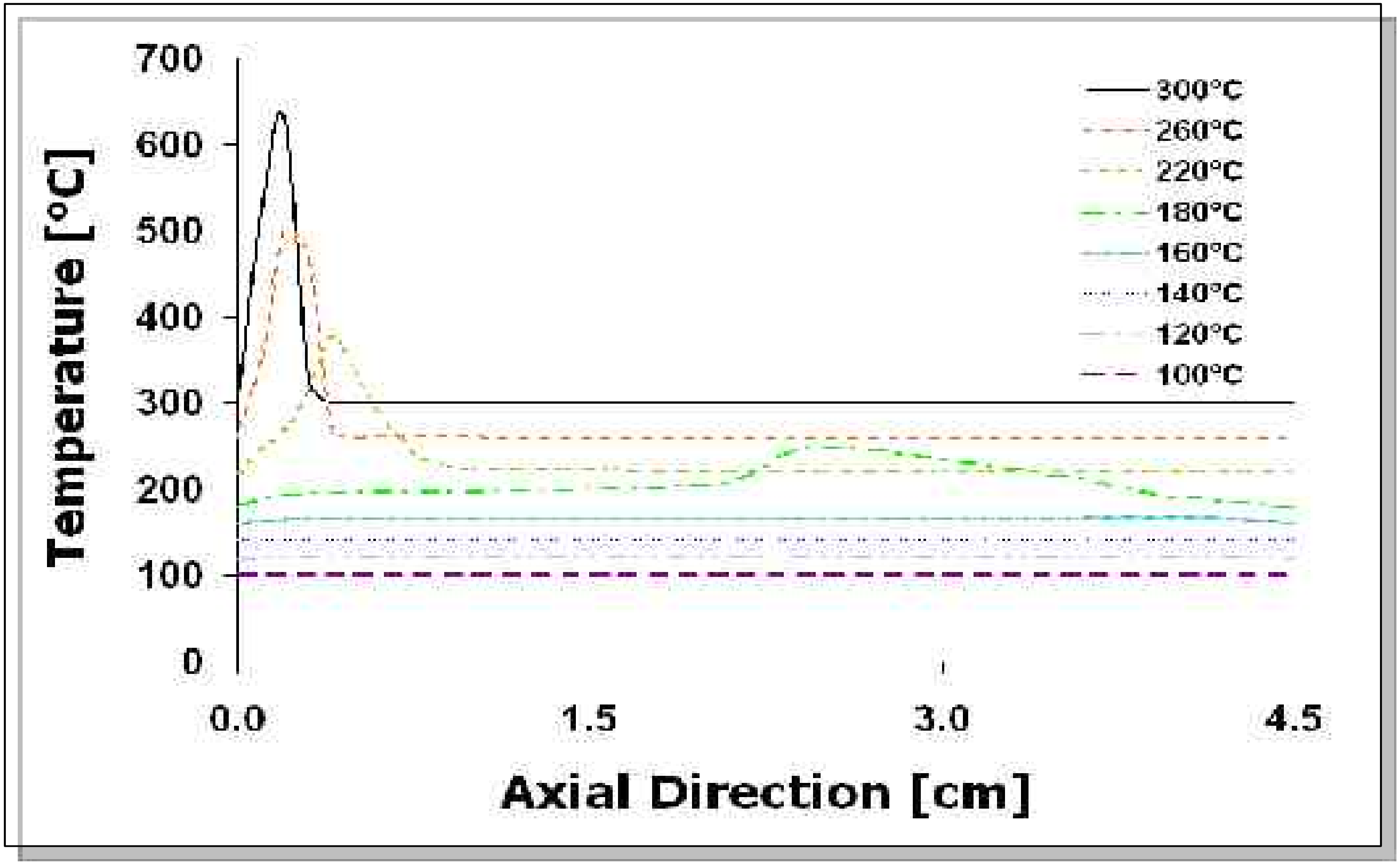
$$CO + \frac{1}{2}O_2 \xrightarrow{\Delta H = -67\,kcal/mol} CO_2$$

$$H_2 + \frac{1}{2}O_2 \xrightarrow{\Delta H = -58\,kcal/mol} H_2O$$

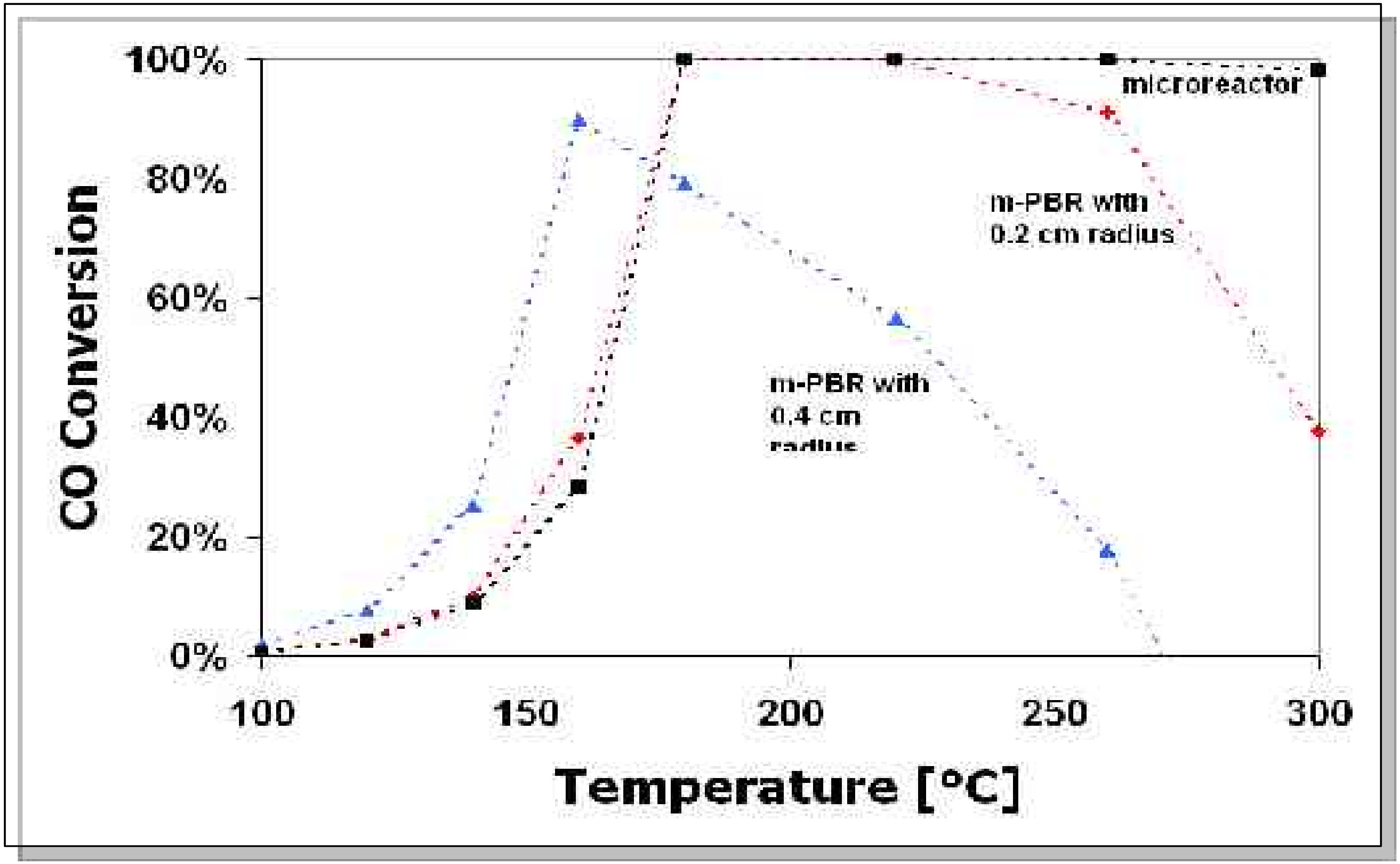
$$CO_2 + H_2 \xrightarrow{\Delta H = 9.8\,kcal/mol} CO + H_2O$$



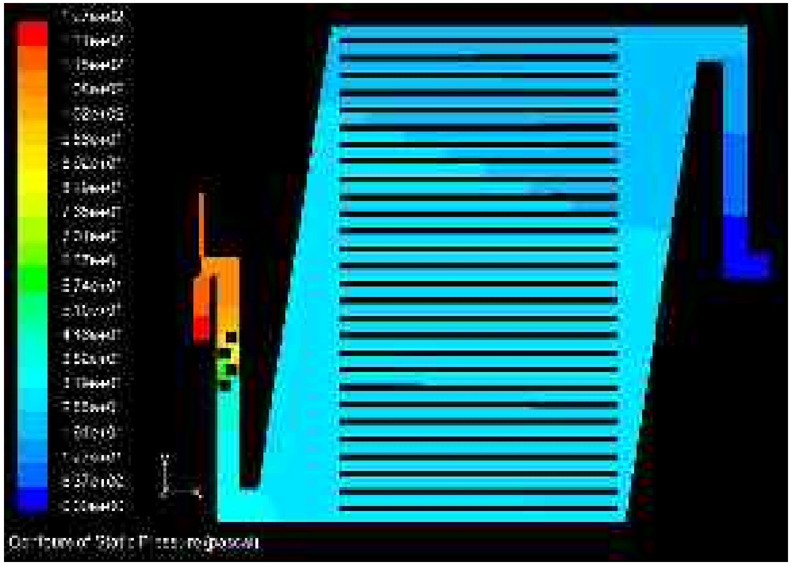
Temperature Non-Uniformity: Hot Spots

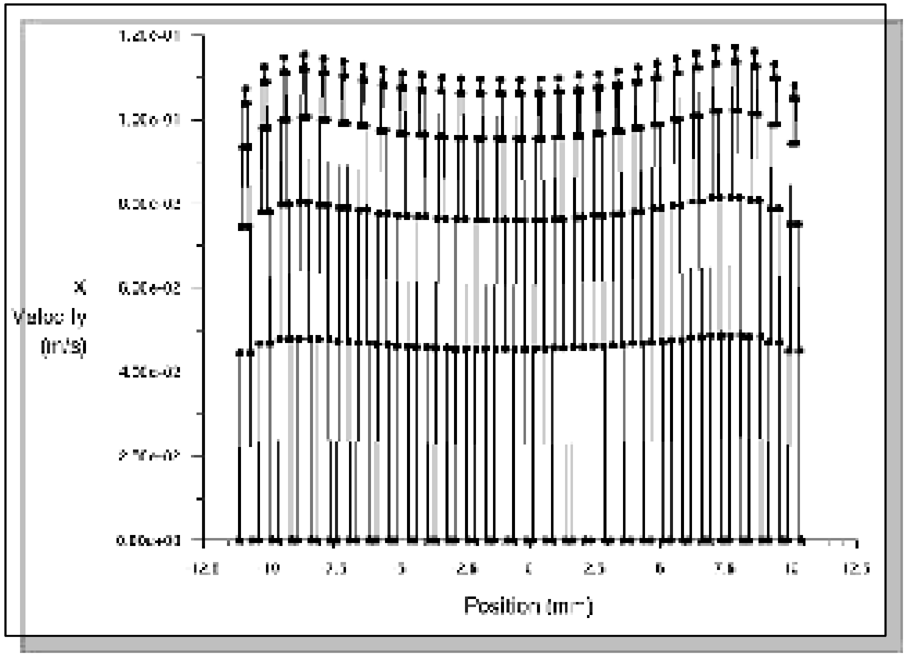


Predicted Conversion Characteristics



Flow Distribution Optimization

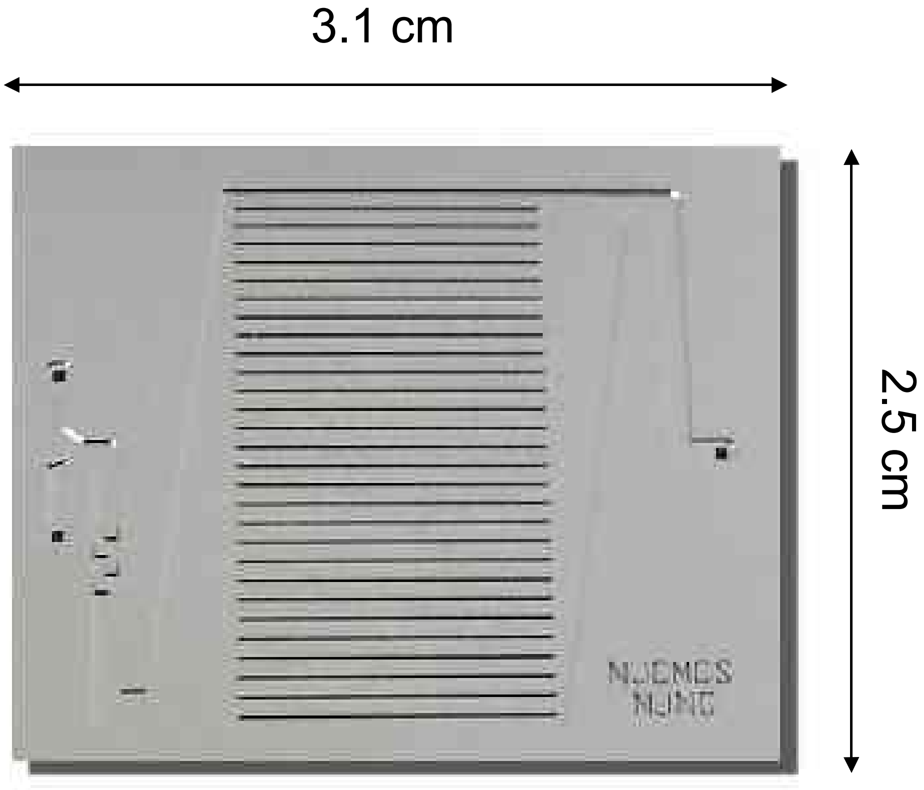




(Computational Fluid Dynamics Model)

2-D design for equal flow distribution in channels

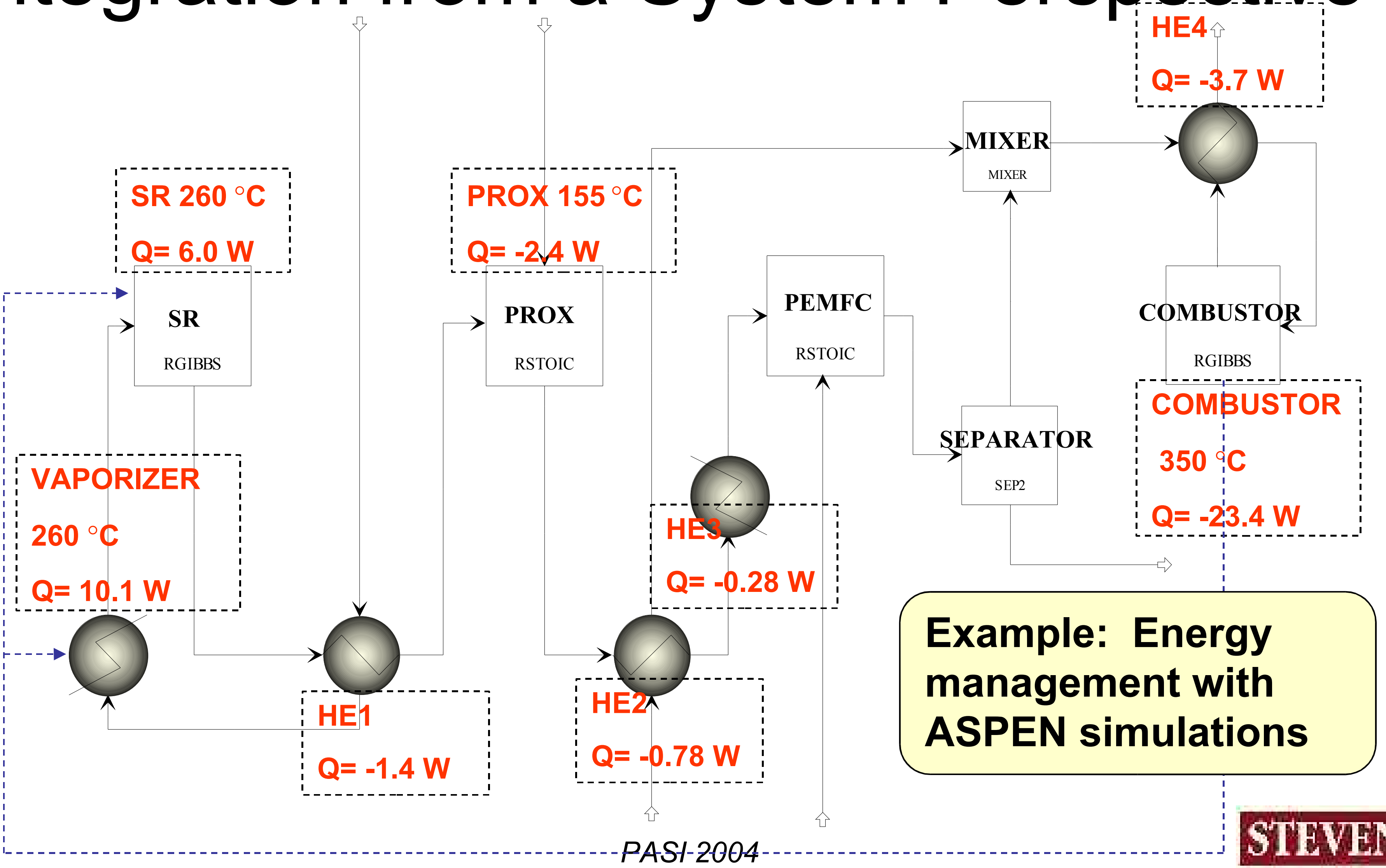
Fabricated 1W_e PrOx Reactor



4 Reactors on 4-in. Wafer

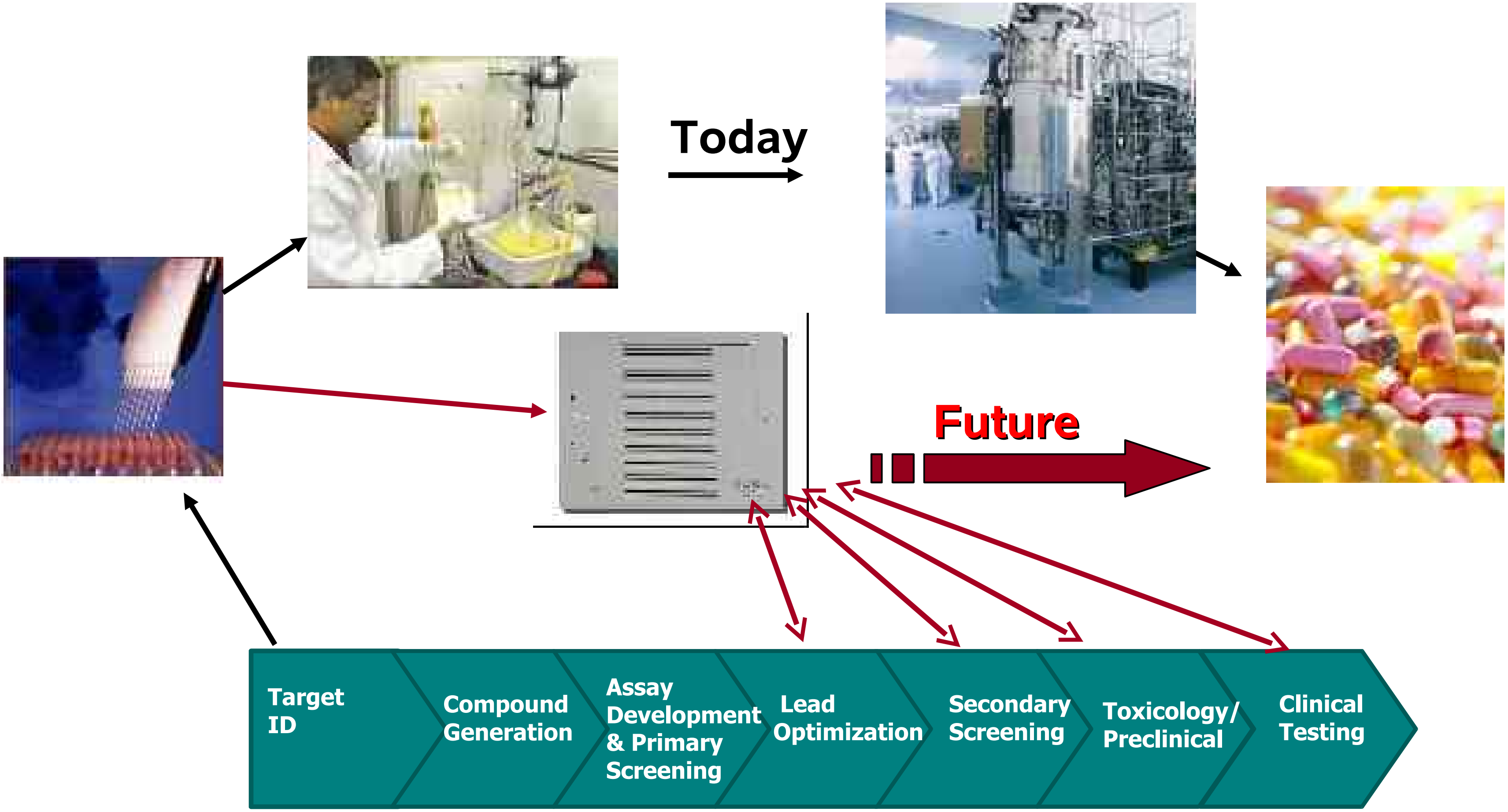
Actual Chip;29 x (450 x 400 μm^2) Channels

Next Step: Component Integration from a System Perspective



Example: Energy management with ASPEN simulations

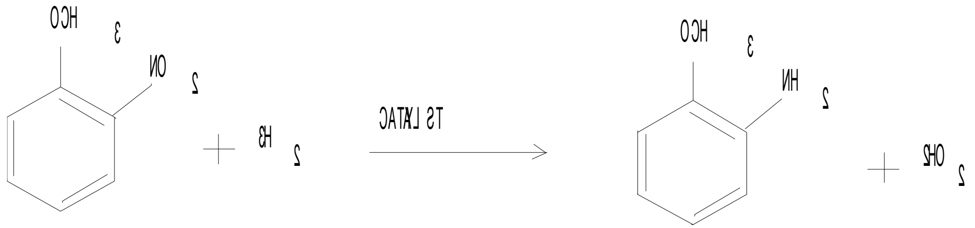
Bringing New Drugs Faster and More Safely to the Marketplace



Adapted from S. Kiang, Bristol-Myers Squibb, 2003

Intensification for Pharma: Catalytic Hydrogenation

o-nitroanisole

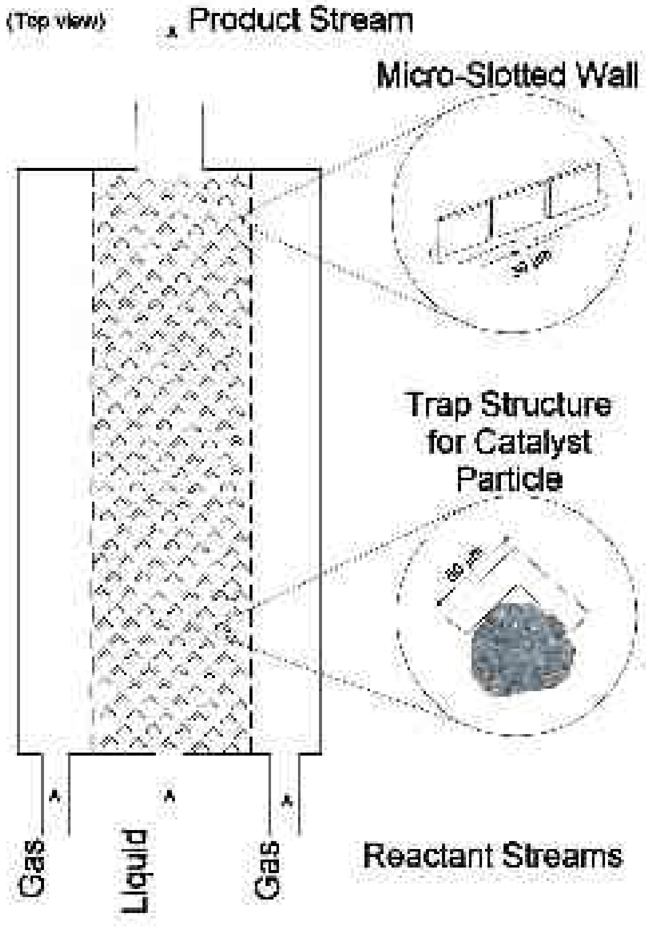


o-nitroanisidine

20% of all pharma manufacturing processes

- Currently: batch reactors, >100 l in size → Continuous flow microreactors
- H_2 at high pressure (safety) → Low H_2 hold-up
- Highly exothermic-low duty cycle, high heat removal (cost, energy efficiency) → Superb heat extraction, high-duty cycle, low peak cooling;
- Residence time several hours → Residence time minutes
- Selectivity 50%; several purifications needed → High selectivity through T control

Intensification for Pharma: Catalytic Hydrogenation



Challenges:

Transport Effects in Multiphase flow

Effective Reactants Mixing

Minimization of Pressure Drop

Minimization of Heat and Mass Transfer Resistances

Catalyst Selection/Preparation/Deposition for High Yield and Selectivity

Intrinsic Kinetics Analysis for Microreactor Design

Microreactor Design & Optimization

Conclusions

- MCS/Microreactors possess special properties due to their **small dimensions** (< 500 μm), large **surface-to-volume** ratio, and **materials** options.
- MCS will be used to enable the generation of hydrogen for small fuel cell systems (**miniaturization**).
- MCS will allow access to novel chemical environments for the production of special chemical products like pharmaceuticals (**intensification**).

Collaborators and Sponsors

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- P. Ho, Reaction Design
- D. Ivanov, NJ Institute of Technology
- D. Kientzler, Bristol-Myers Squibb
- S. Pau, Lucent-Bell Labs
- W. Mansfield, Lucent-Bell Labs

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