# *Fuel Processors for PEM Fuel Cells*

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College of Engineering
May 25, 2004

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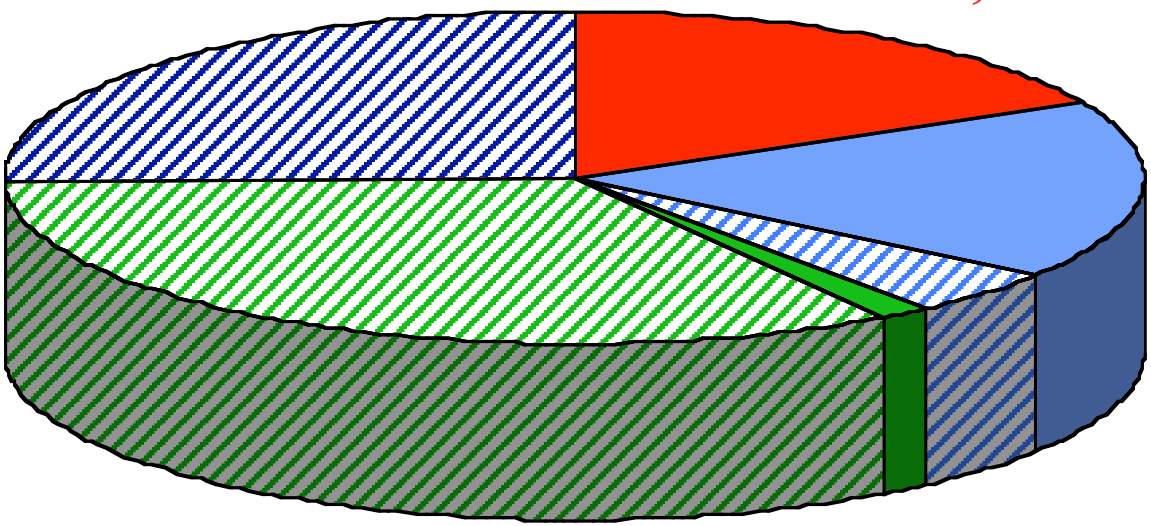
# Project Objectives

- Develop high performance, low-cost materials
  - High capacity sulfur adsorbents for liquid fuels
  - High activity and durable Autothermal Reforming (ATR), Water Gas Shift (WGS) and Preferential Oxidation (PrOx) catalysts
- Design and demonstrate microreactors employing high performance catalysts
- Design and demonstrate microvaporizer/combustor
- Design and demonstrate thermally integrated microsystem-based fuel processors
- Evaluate system cost

# Total Budget (as of March, 2004)




| | DoE | Cost-Share | |
|---|---|---|---|
| Received | 1,250k | 517k | 41% |
| Due | 1,750k | 383k | 22% |

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# Fuel Processor (Fuel Cell) Technical Barriers

- Fuel Processor Startup/Transient Operation
  - Improved catalysts, sorbents and reactors
  - Thermal integration
  - Decreased unit operations
- Durability
  - Improved impurity tolerance
  - Improved resistance to coking and sintering
- Emissions and Environmental Issues
- Hydrogen Purification/CO Cleanup
  - Improved catalysts, sorbents and reactors
- Fuel Processor System Integration and Efficiency
- Cost
  - Improved catalysts, sorbents and reactors
  - Integration and decreased unit operations



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# Fuel Processor (Fuel Cell) Technical Targets

| Characteristics | Units | Current Status (2003) | Target for Year: 2005 | 2010 |
|---|---|---|---|---|
| Energy efficiency | % | 78 | 78 | 80 |
| Power density | W/L | 700 | 700 | 800 |
| Specific power | W/kg | 600 | 700 | 800 |
| Cost | $/kWe | 65 | 25 | 10 |
| Cold startup time to max power<br>@ -20 °C ambient temperature<br>@ +20 °C ambient temperature | <br>min<br>min | <br>TBD<br><10 | <br>2.0<br><1 | <br>1.0<br><0.5 |
| Transient response (10% to 90% power) | sec | 15 | 5 | 1 |
| Emissions | | <Tier 2 Bin 5 | <Tier 2 Bin 5 | <Tier 2 Bin 5 |
| Durability | hours | 2000 | 4000 | 5000 |
| Survivability | °C | TBD | -30 | -40 |
| CO content in product stream<br>Steady state<br>Transient | <br>ppm<br>ppm | <br>10<br>100 | <br>10<br>100 | <br>10<br>100 |
| $H_2S$ content in product stream | ppb | <200 | <50 | <10 |
| $NH_3$ content in product stream | ppm | <10 | <0.5 | <0.1 |

# Approach

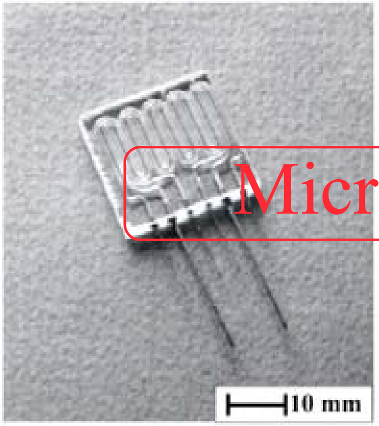
High Performance Materials

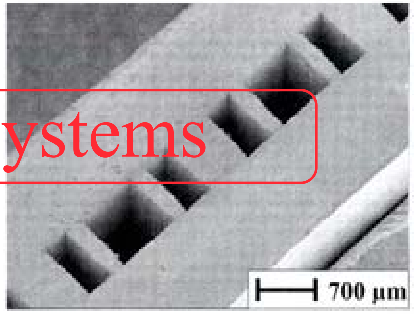
+

High Degree of Integration

+

Microsystems




Project Director: Levi Thompson (ltt@umich.edu)

Co-PIs: Gulari, Savage, Schwank & Yang (ChE); Assanis, Im, Ni & Wooldridge (ME); Dahm & Powell (Aero)

Subcontractors: Ricardo, Inc. (MI); Osram Sylvania; IMM (Germany); MesoFuel (NM)

# Project Safety

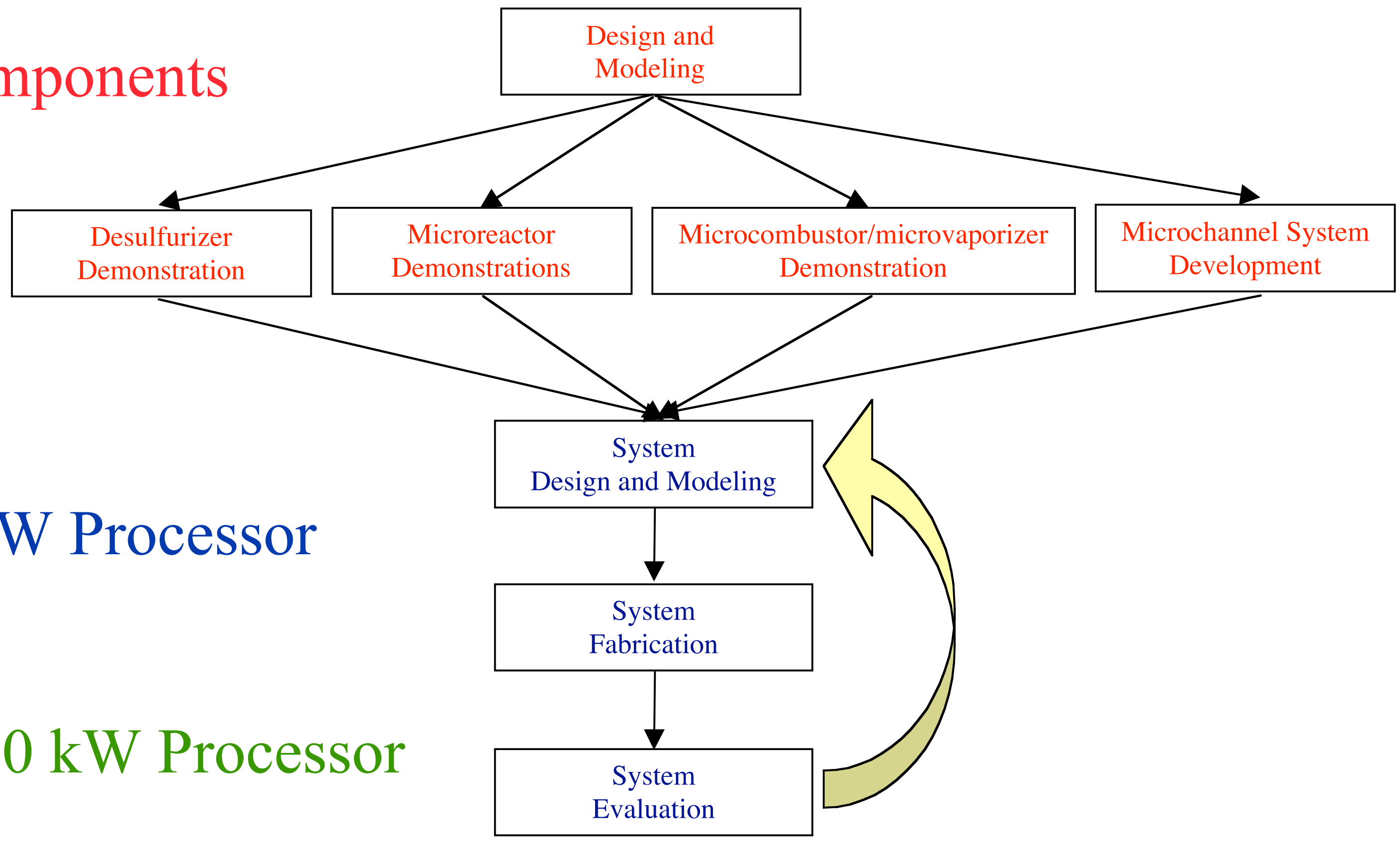
- Preliminary Identification of Safety Vulnerabilities (e.g. FMEA, HAZOP)
- System Safety Assessment
- Risk Mitigation Plan
- Safety Performance Assessment
- Communications Plan

# Project Timeline

Phase I: Components

Phase II: 1 kW Processor

Phase III: ≤10 kW Processor

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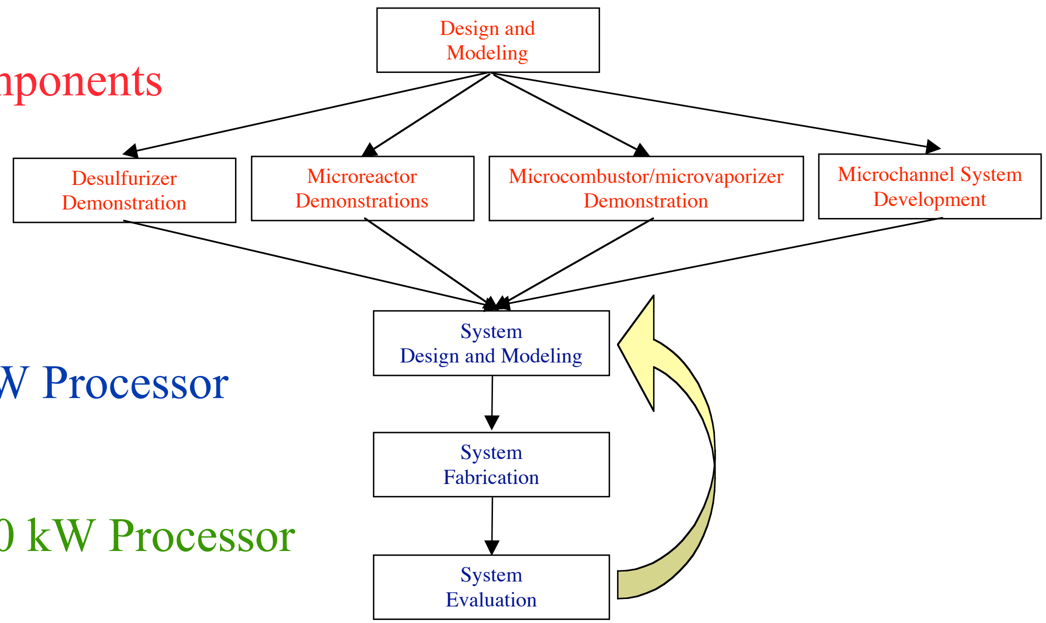
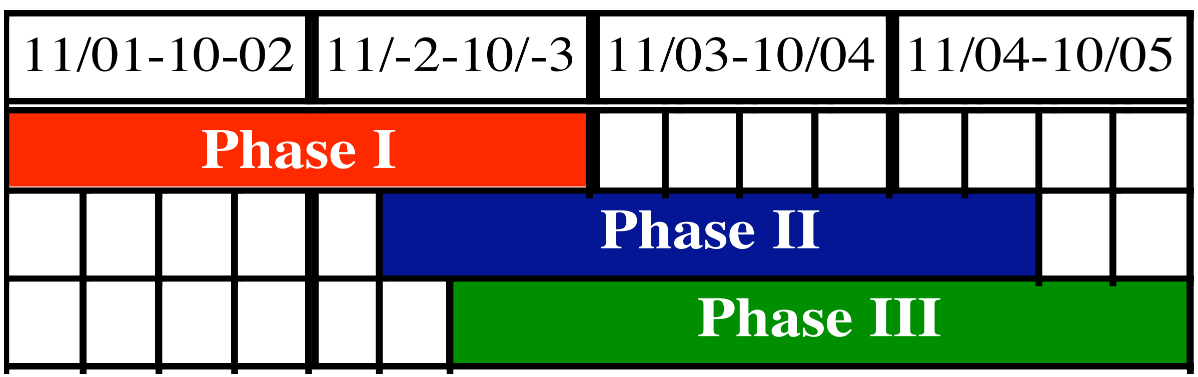
# Project Timeline

Phase I: Components

Phase II: 1 kW Processor

Phase III: ≤10 kW Processor

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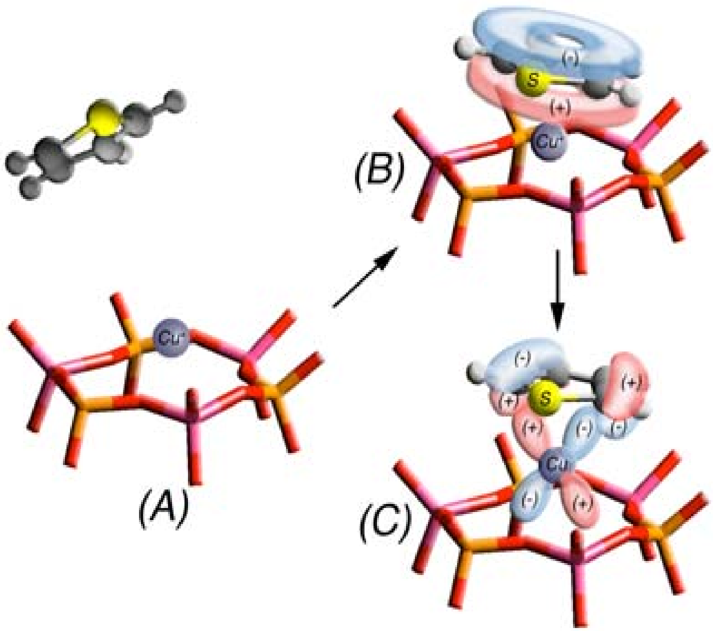
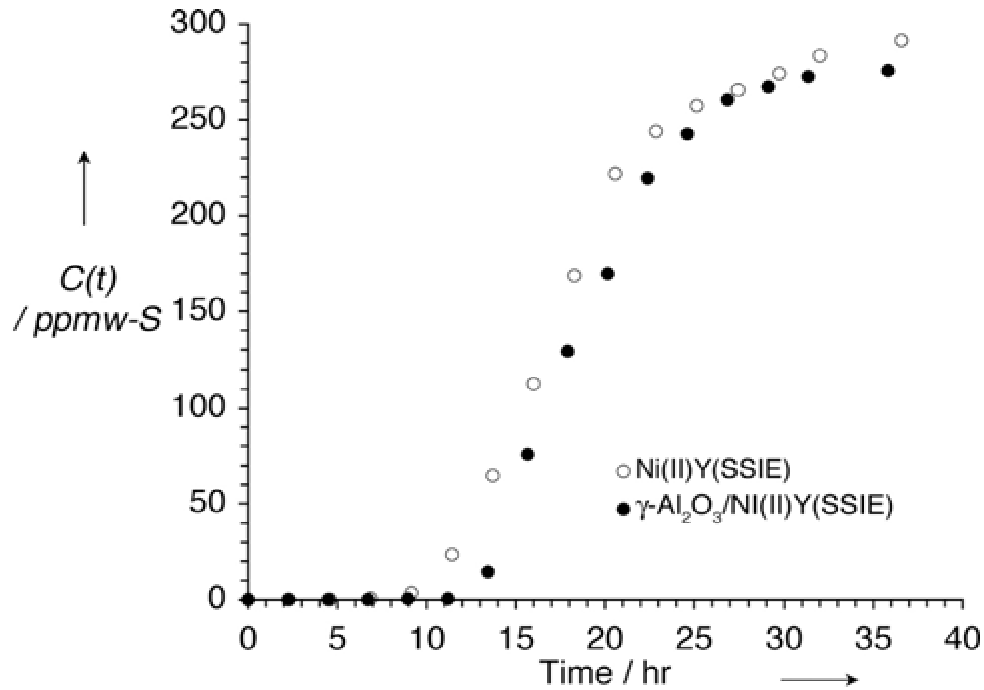
# Desulfurization of Fuels by Adsorption




**π-Complexation Mechanism:**

- Cu ions occupy faujasite 6-ring windows sites. Thiophene approaches site.
- σ-donation of thiophene π-electrons to the 4s orbital of Cu(I) or Ni(II)
- d-$\pi^*$ backdonation of electrons from 3d orbitals of Cu(I) or Ni(II) to $\pi^*$ orbitals of thiophene

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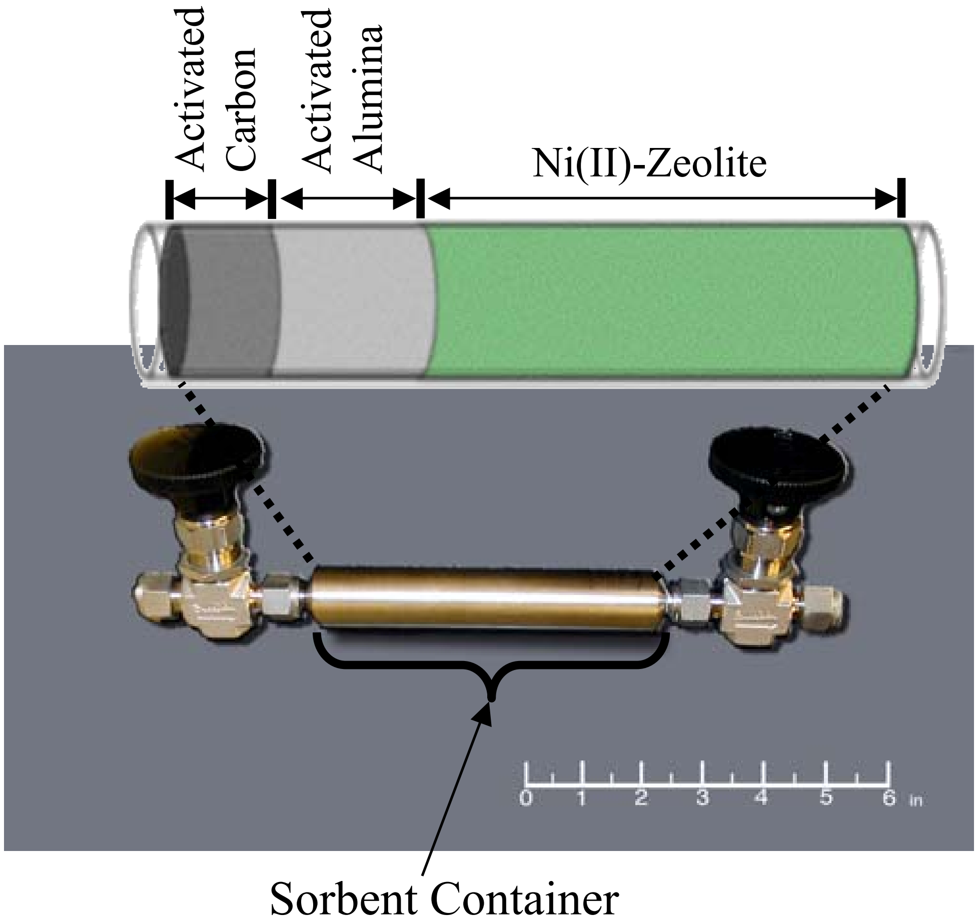
# Sulfur Adsorber Prototype




- Three Sorbent Layers
  - Activated Carbon (12.4 wt%)
  - Activated Alumina (23 wt%)
  - Ni(II)-Y (64.6 wt%)
- Gasoline Rate: 50 mL/hr
- Equivalent $H_2$ Output: 2.8 moles/hr (100 W)
- Effluent Concentration: ~ 0.3 ppmw sulfur
- Operation Cycle: 9-10 hrs

Yang et al., U.S. and foreign patents applied.

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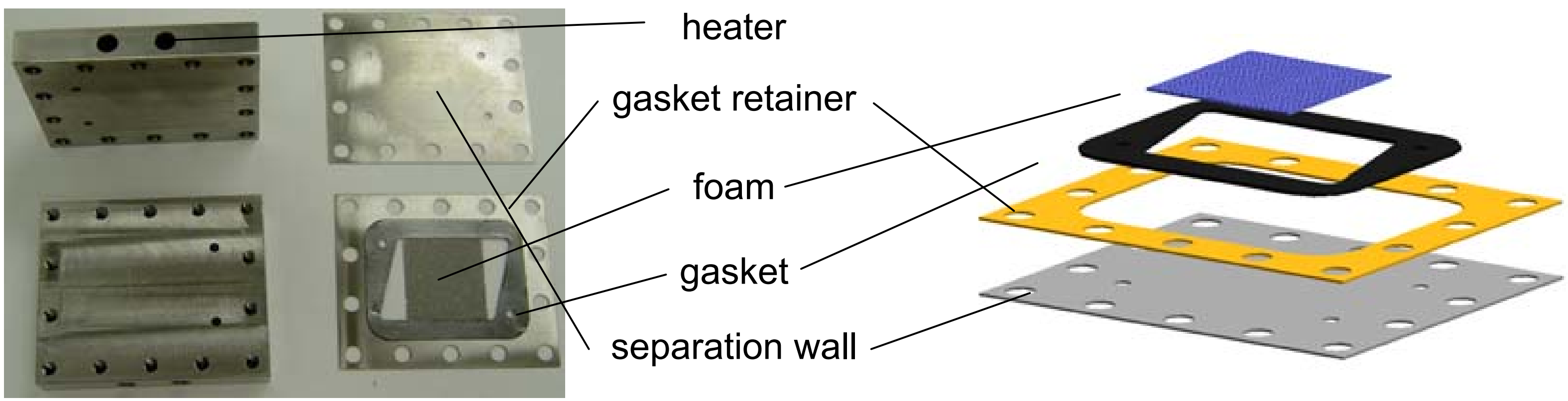
# Microreactors

- Materials of Construction
  - Silicon Microfabrication
  - Micromachined Metals
  - Low Temperature Co-Fired Ceramics (LTCC)
- Metal Microreactors
  - 1st Generation (GEN1) Micro-reactor
    - Design and Fabrication
  - 2nd Generation (GEN2) Micro-reactor
    - Design Overview and Achievements
- Semi-solid Forming (SSF) Process

# GEN2 Prototype Design

- Flexible design
- Assembled reactor module is 77 x 64 x 54 mm (25 stacks)

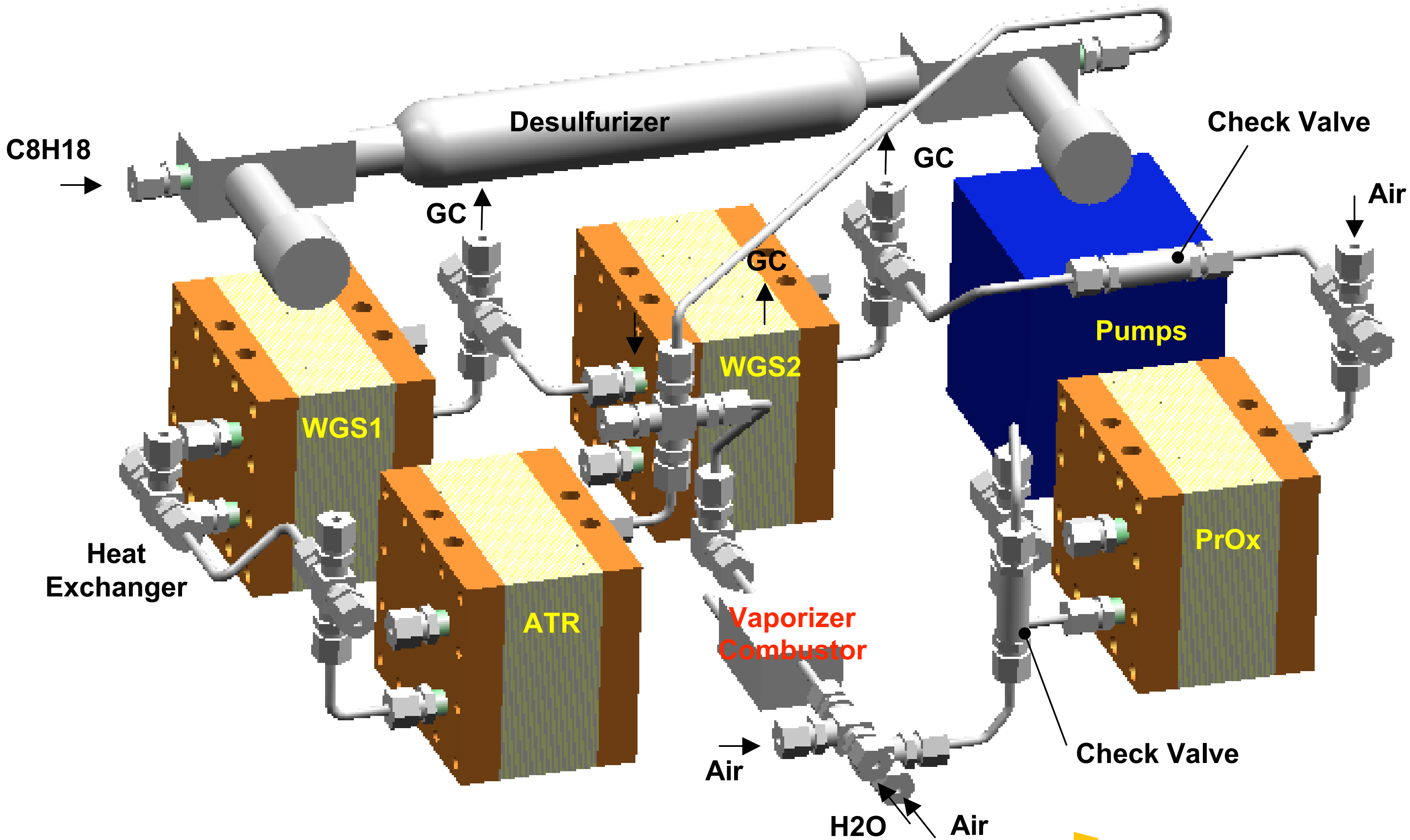
Assembled module




Fabricated Parts

Core Layers

# Breadboard System

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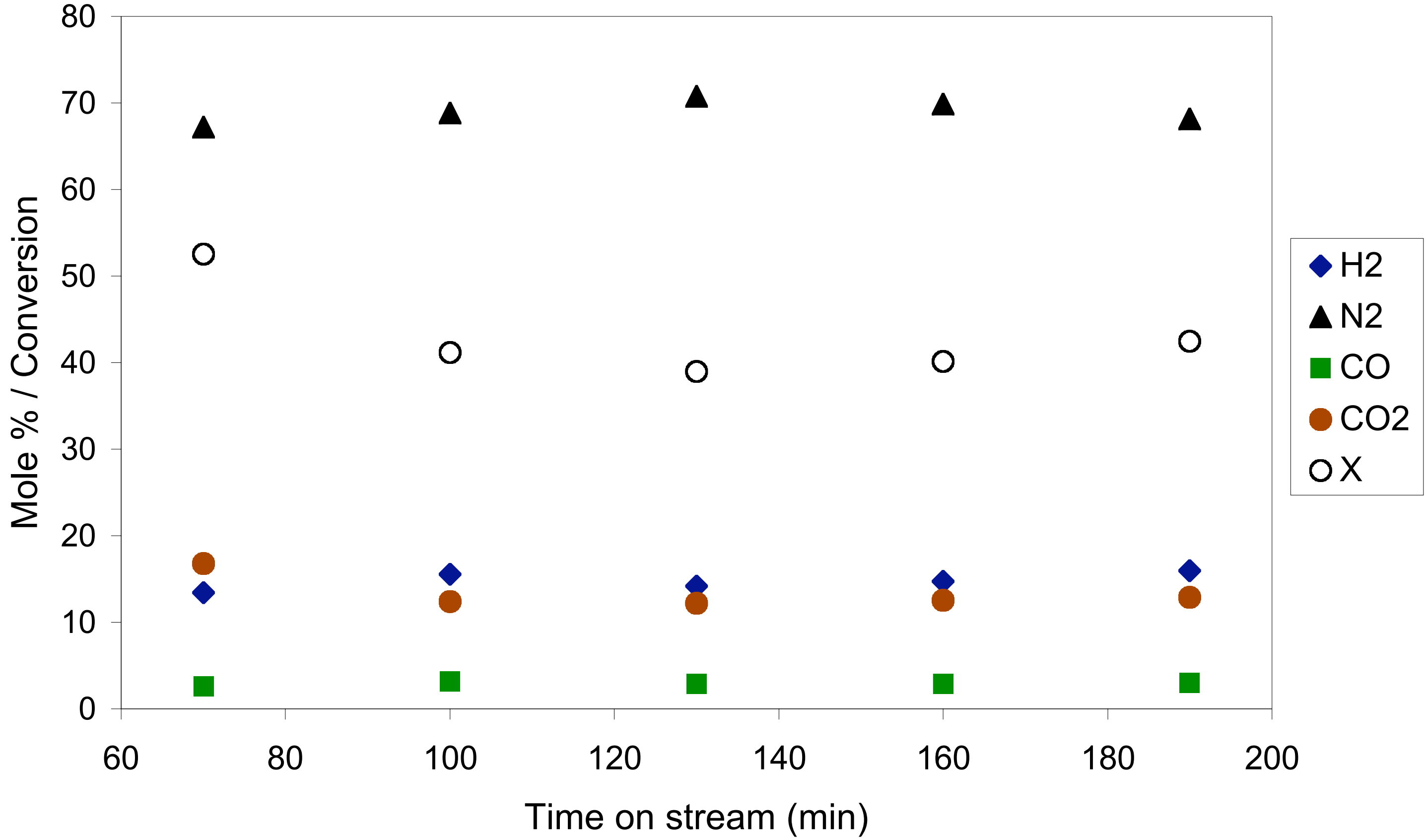
# ATR Prototype Results ($100\ W_e$)




Experimental Conditions: $H_2O/C = 2.0$, $O/C = 1.0$

Reactor Skin Temperature: 590 °C; Reactor Exit Temperature:385 °C

1.5 SLPM air, 0.6 mL/min Iso-octane, 1.1 mL/min $H_2O$

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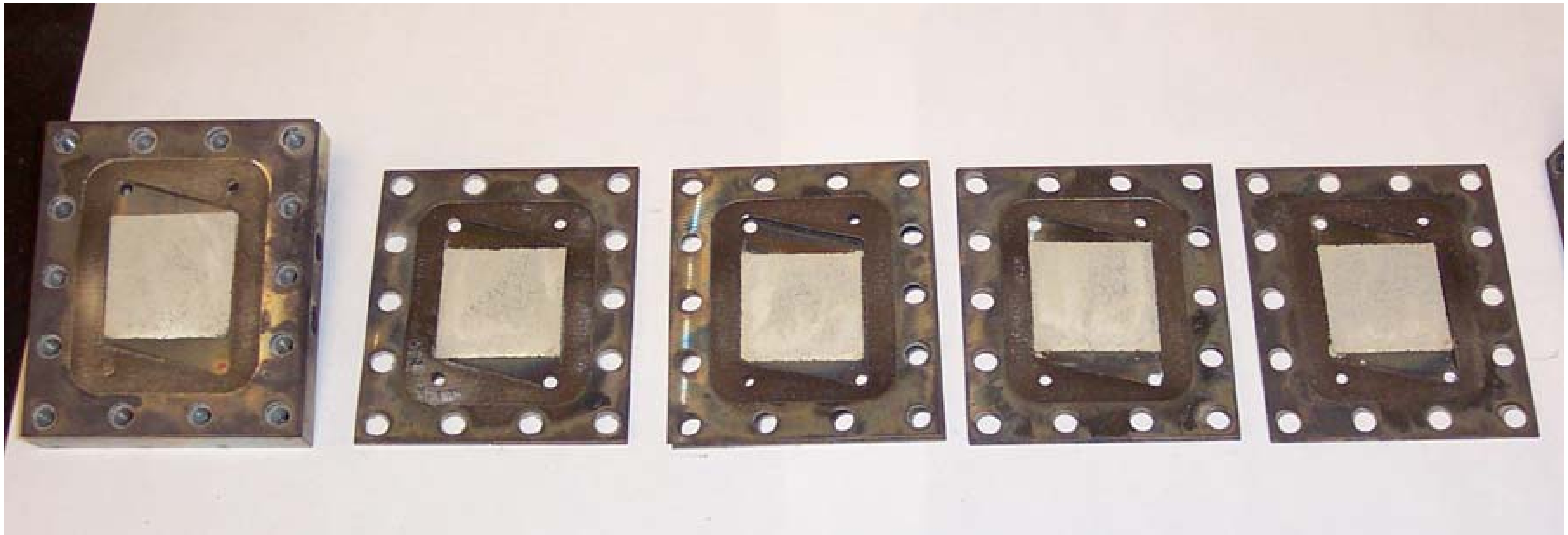
# Minimal Coke Deposition



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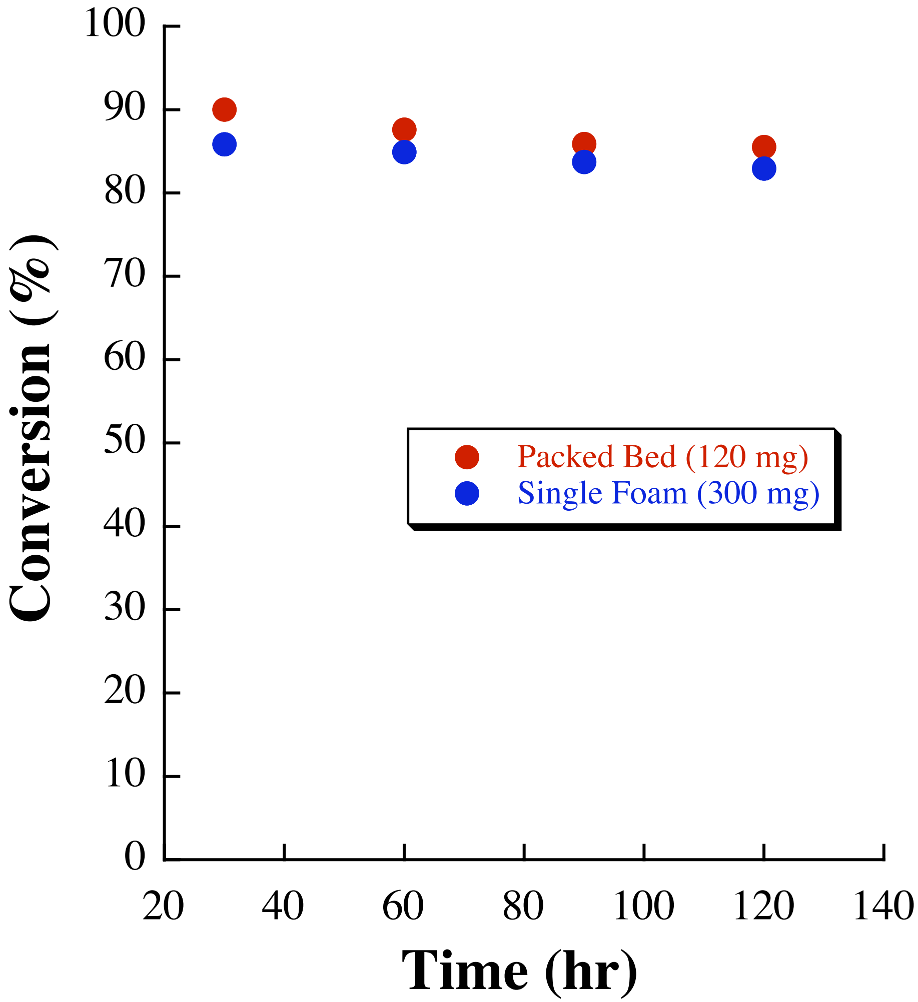
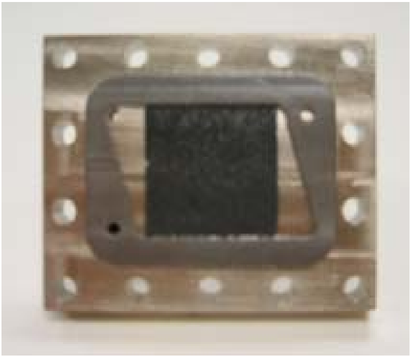
# WGS Prototype Results




- Temperature: 240°C
- Flow rate: 40 ccm (1 $W_e$)
- GHSV: 53,333 $h^{-1}$
- Feed composition



| | |
|---|---|
| CO | 10% |
| $H_2O$ | 31% |
| $CO_2$ | 6% |
| $H_2$ | 39% |
| $N_2$ | 15% |



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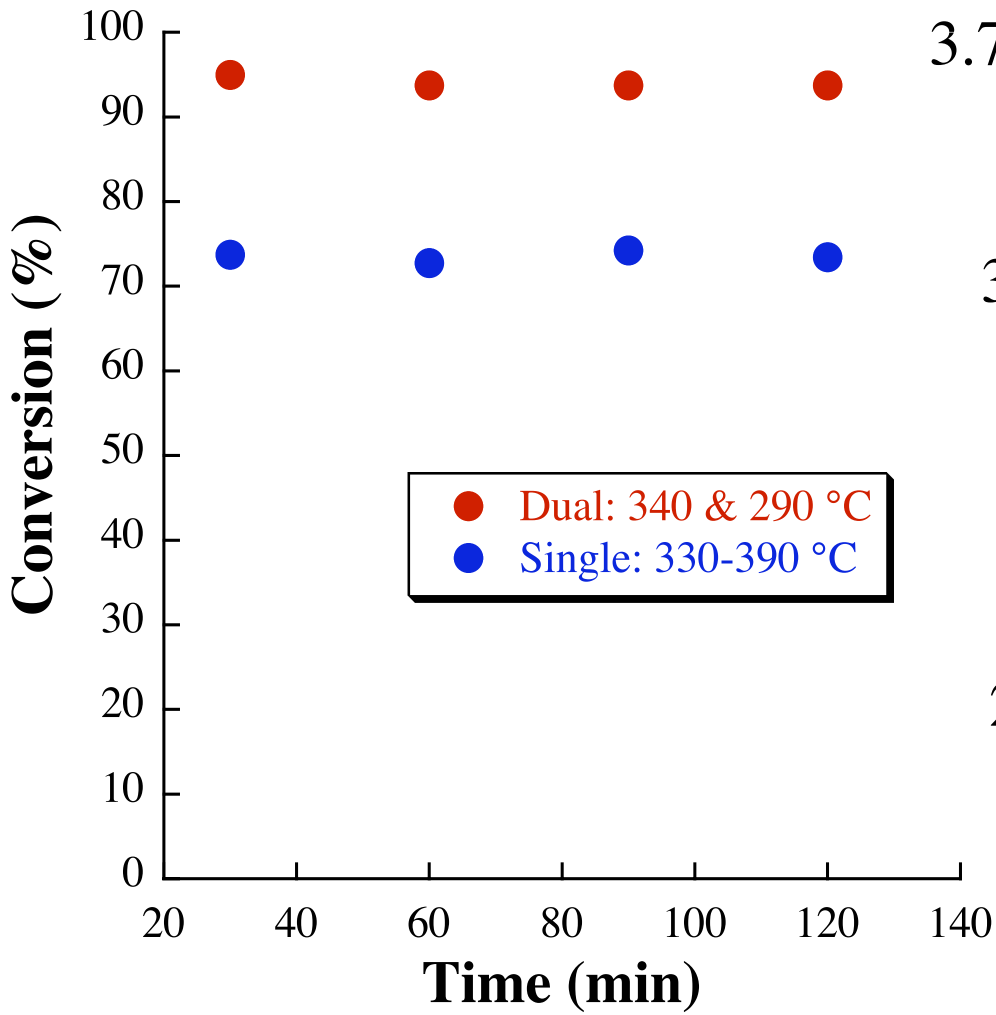
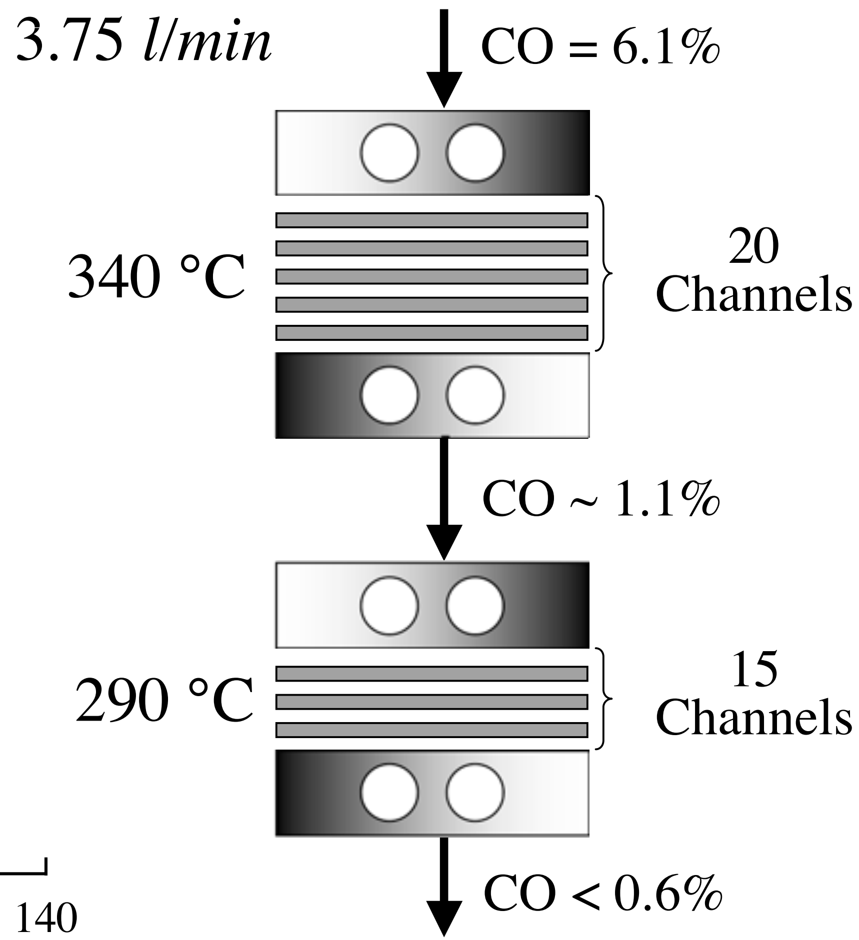
# WGS Prototype Results ($100\ W_e$)



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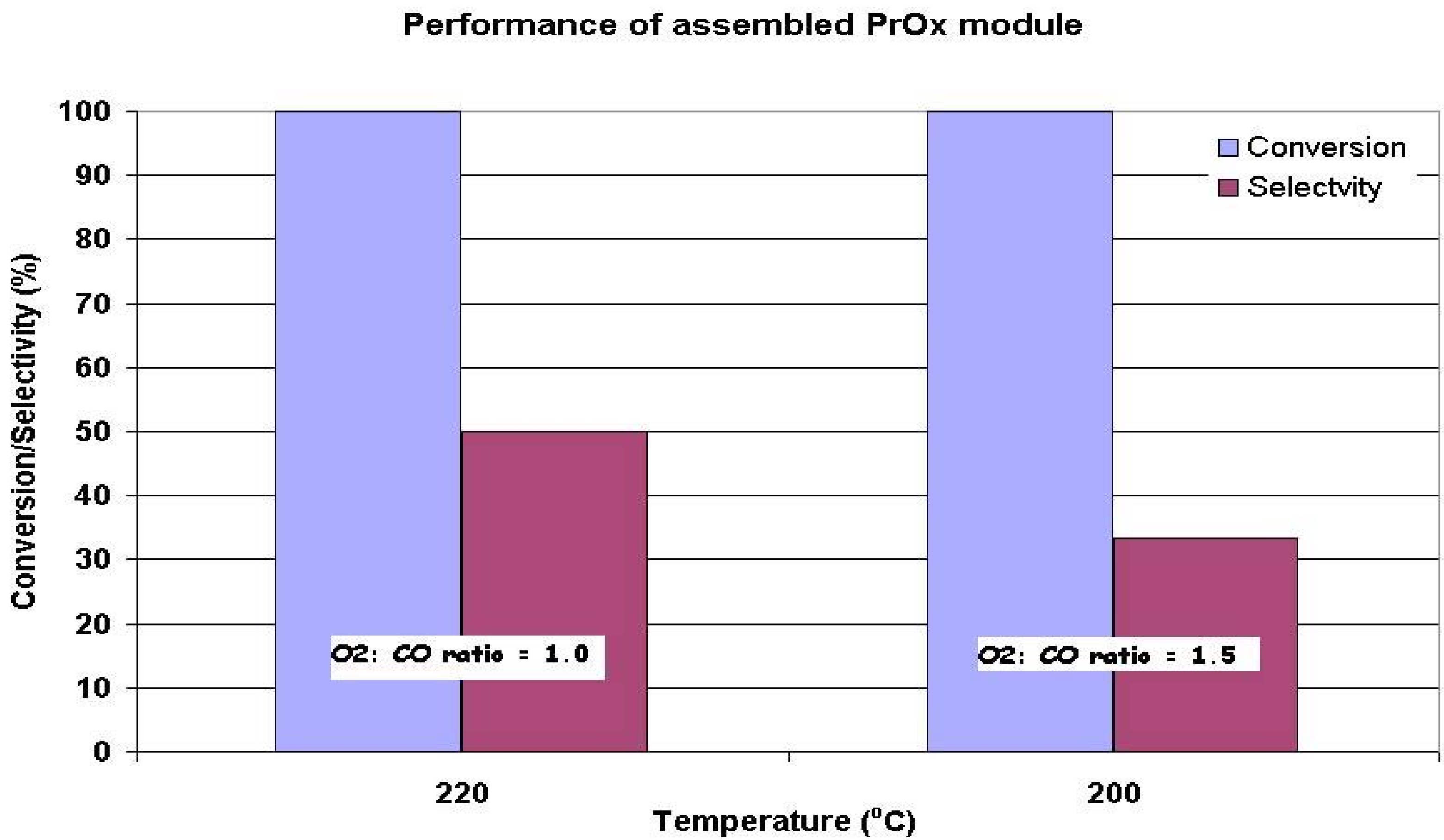
# PrOx Prototype Results

- 4 % $Pt\text{-}Al_2O_3$ sol-slurry hybrid washcoat
- WHSV = 50 lit $hr^{-1}$ g-$cat^{-1}$
- Increased catalyst loading of ~250 mg/foam
- Inlet stream compositions (simulated WGS exhaust):
  - CO : 0.79 – 0.81 %
  - $O_2$ : 0.81 – 1.19 %
  - $CO_2$ : 14.91 – 15.28 %
  - $H_2$ : 30.58 – 31.32 %
  - $H_2O$ : 15.54 %
  - $N_2$ : 36.23 – 36.99 %

# PrOx Prototype Results

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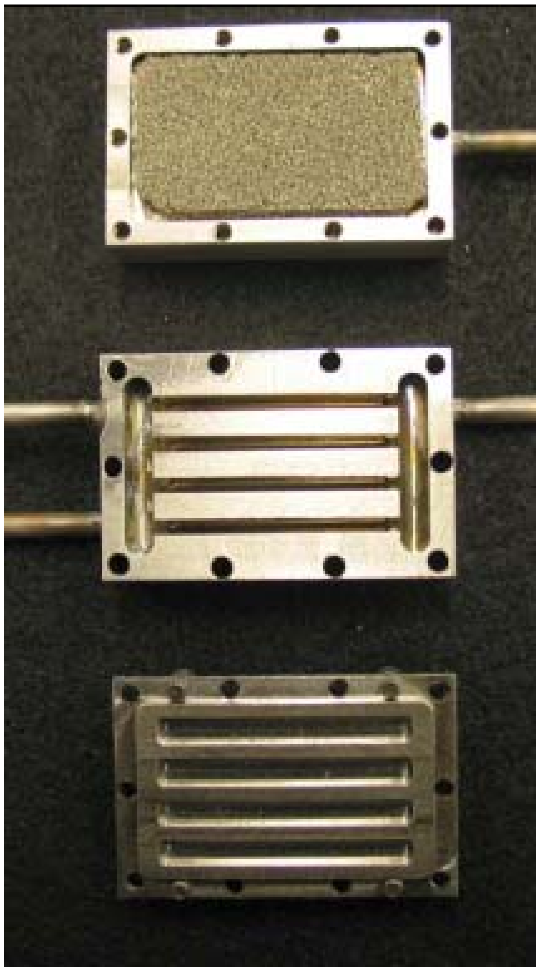
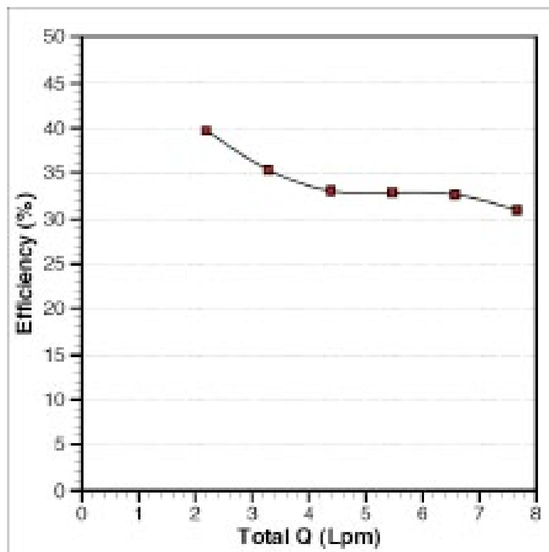
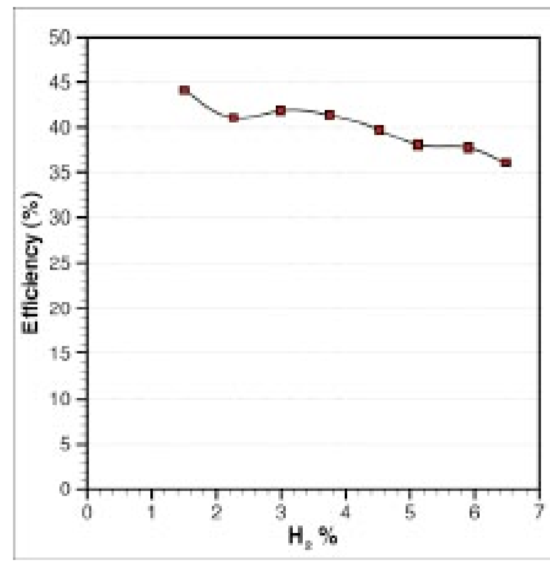
# Catalytic Tailgas Combustor Prototype



Burner Characteristics:

- 100 W nominal capacity mesoscale burner
- 80 ppi Pt-coated FeCrAlloy metal foam
- 8.0 L/min tailgas low-$H_2$ surrogate flow rate



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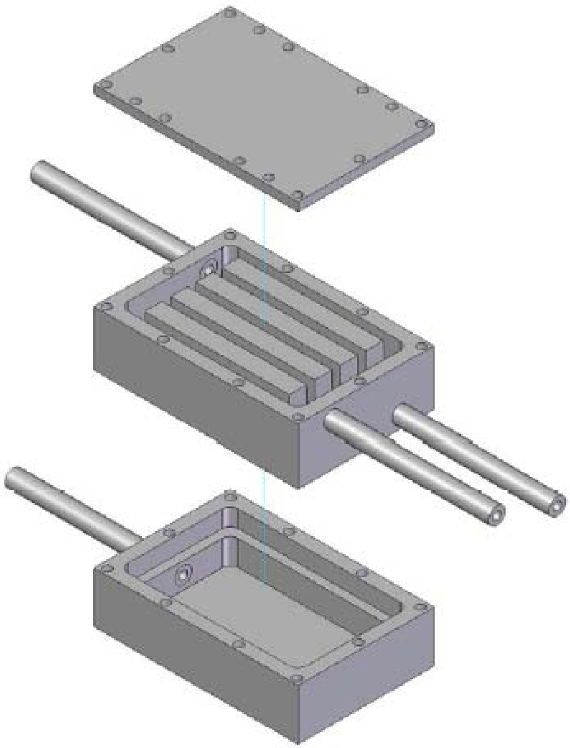
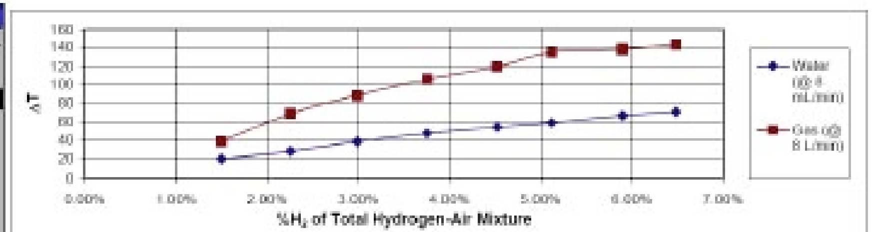
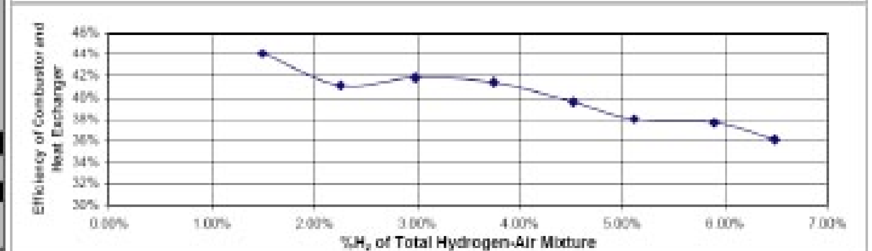
# Catalytic Tailgas Burner and Heat Exchanger Prototype

- Performance tests conducted for 1.5% - 8% $H_2$ concentrations
- Current test results show single-sided efficiencies of 35-45%
- Double-sided efficiencies anticipated in 65-80% range



| Constants | | |
|---|---|---|
| Hydrogen Flammability Limits | | |
| $\Phi_{min}$ = | 0.14 | |
| $\Phi_{max}$ = | 2.54 | |
| $MW_{H2}$ | 2.02 | g/mole |
| $MW_{Air}$ | 29 | g/mole |
| $MW_{H2O}$ | 18.02 | g/mol |
| $\rho_{H2}$ | 0.0899 | kg/m^3 |
| $\rho_{Air}$ | 1.225 | kg/m^3 |
| $\rho_{H2O}$ | 993 | kg/m^3 |
| $c_p$ of $H_2O$ | 4188.6 | J/kgK |
| $c_p$ of $H_2$ | 29.26 | J/molK |
| | 14485.15 | J/kgK |
| $c_p$ of Air | 1500.00 | J/kgK |
| LHV of $H_2$ | 140000 | kJ/kg |
| Stoich | $f_s$ = | 34.17 |
| Water Flow | 8.0 | mL/min |
| Rate | 1.32E-04 | kg/s |




| Φ | $H_2$ Flow | Air Flow | Total | $H_2$ % | q from $H_2$ | Gas In | Gas Out | Gas ΔT | $H_2O$ In | $H_2O$ Out | $H_2O$ ΔT | $H_2O$ Δq | Gas Δq | q Lost | η |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.04 | 0.12 | 7.9 | 8.0 | 1.50% | 25.2 | 304 | 342 | 38 | 302 | 322 | 20 | 11.1 | 1.5 | 13 | 44.1% |
| 0.06 | 0.18 | 7.8 | 8.0 | 2.26% | 37.8 | 304 | 373 | 69 | 302 | 330 | 28 | 15.5 | 5.4 | 17 | 41.1% |
| 0.08 | 0.24 | 7.8 | 8.0 | 2.99% | 50.3 | 304 | 392 | 88 | 302 | 340 | 38 | 21.1 | 6.6 | 23 | 41.9% |
| 0.10 | 0.30 | 7.7 | 8.0 | 3.75% | 62.9 | 306 | 412 | 106 | 302 | 349 | 47 | 26.1 | 7.3 | 30 | 41.4% |
| 0.12 | 0.36 | 7.6 | 8.0 | 4.52% | 75.5 | 307 | 427 | 120 | 301 | 355 | 54 | 29.9 | 7.0 | 39 | 39.7% |
| 0.14 | 0.41 | 7.6 | 8.0 | 5.12% | 86.0 | 308 | 443 | 135 | 302 | 361 | 59 | 32.7 | 8.0 | 45 | 38.0% |
| 0.16 | 0.47 | 7.5 | 8.0 | 5.90% | 98.6 | 308 | 446 | 138 | 302 | 369 | 67 | 37.2 | 5.2 | 56 | 37.7% |
| 0.17 | 0.52 | 7.5 | 8.0 | 6.48% | 109.1 | 308 | 451 | 143 | 303 | 374 | 71 | 39.4 | 3.8 | 66 | 36.1% |
| | Lpm | Lpm | Lpm | | W | K | K | K | K | K | K | W | W | W | |

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# GEN2 100 $W_e$ Prototype Design

| | Vap/Com | ATR | WGS | | PrOx |
|---|---|---|---|---|---|
| Temperature (°C) | 450 | 600 | 340 | 290 | 220 |
| Modules | 1 | 1 | 1 | 1 | 1 |
| Catalyst Type | | $Ni/CeZrO_2$ | $Au/CeO_2$ | $Au/CeO_2$ | $Pt/Al_2O_3$ |
| Catalyst Weight (g) | | 1.5 | 6 | 4.5 | 2.4 |
| No. of Foam cores | | 10 | 20 | 15 | 30 |
| Foam Volume (cc) | | 4 | 8 | 6 | 12 |
| Power Density (W/L)* | | | | | |
| Based on Foam | 5,500 | 25,000 | 7,142 | | 8,333 |
| Target | 5,882 | 10,417 | 2,525 | | 9,091 |



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# Interactions and Collaborations

- Osram Sylvania (some IP transfer): Joel Christian - scale up of catalysts
- Ricardo: Marc Wiseman - system optimization and cost analysis
- Mesofuel: Doyle Miller - heat exchanger design and fabrication
- IMM: Volker Hessel - reactor design optimization

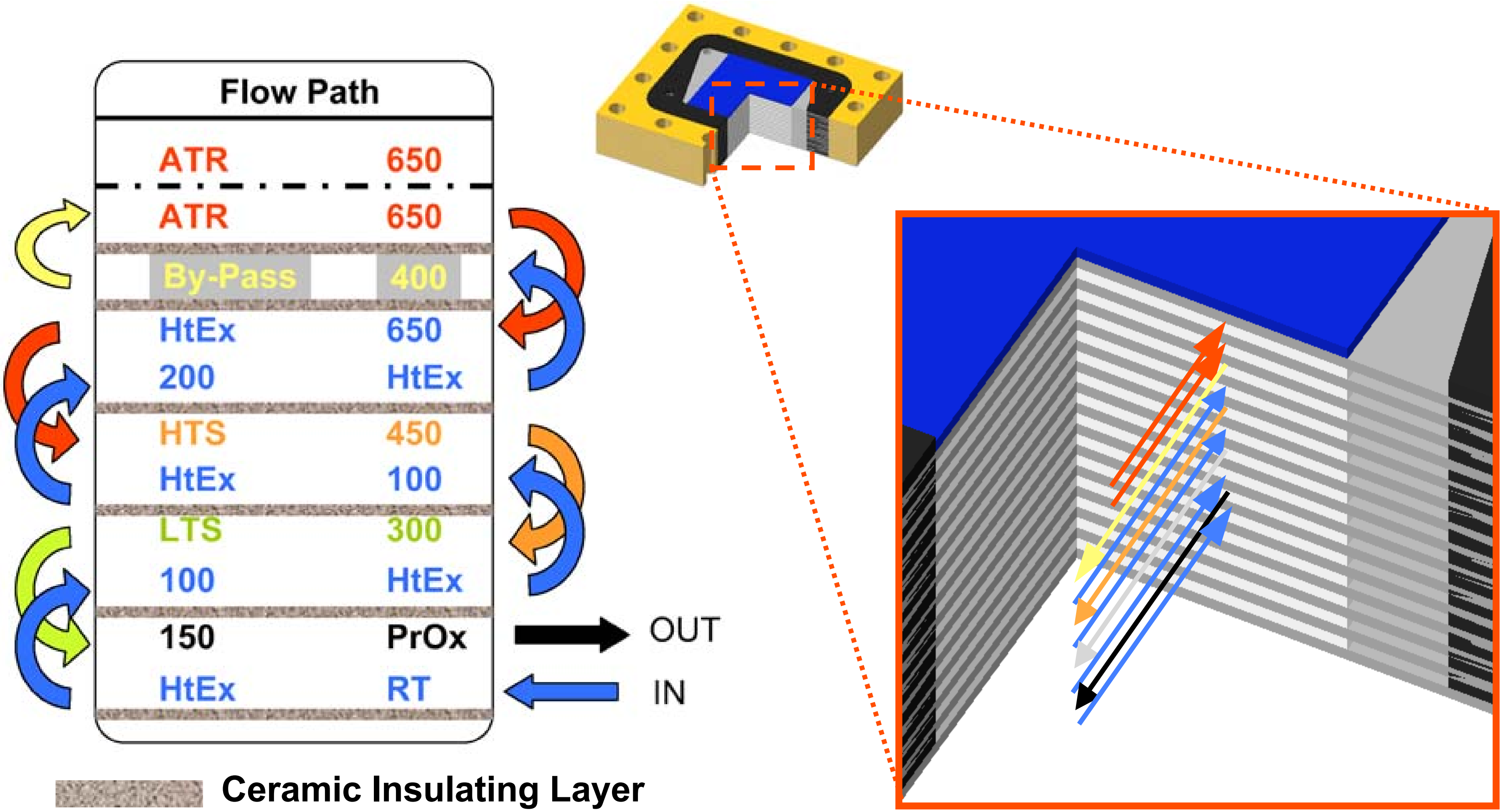
# Responses to Previous Year Reviewers' Comments

- Capacity of Cu(I) zeolite too low
- Coking of Ni-based ATR catalysts
- Verify performance of WGS catalysts
- Bottoms up approach
- Slow progress in developing microreactors
- Minimal involvement by companies
- Microprocessor work appears to be similar to PNNL
- Recommendations: Sulfur-tolerant ATR and hot gas sulfur sorbent

# Future Work

- Remainder of FY03
  - Increase module power densities
    - Increase catalyst loading and utilization
    - Decrease parasitic weight (reactor and foam)
  - Assemble 100 W breadboard fuel processor
  - Evaluate cost and final size
  - Estimate start-up time
- FY04 (through end of 2004)
  - Demonstrate integrated module
  - Assemble 1 kW breadboard fuel processor

# Stack Level Integration

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# Thank You

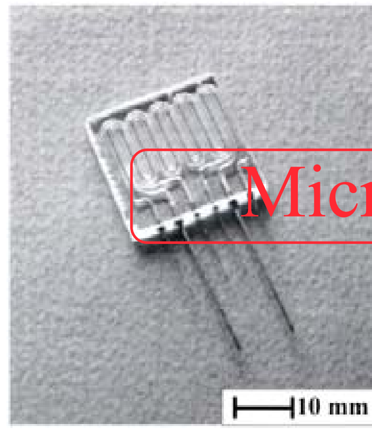
High Performance Materials

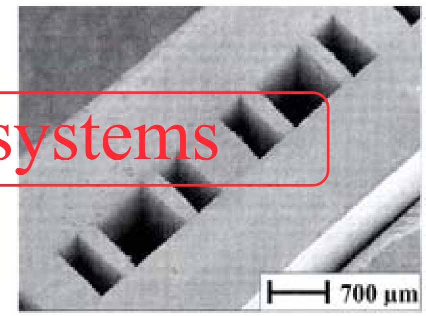
+

High Degree of Integration

+

Microsystems

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