



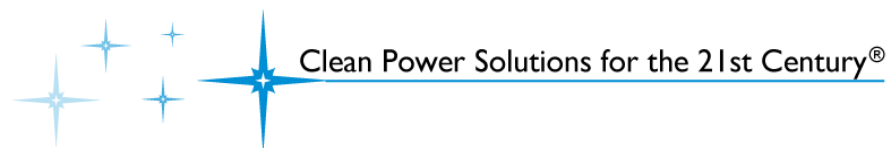
# Diesel Fuel Processing: Water Neutrality, Sulfur Cleanup, Coke Minimization

DOE Phase II SBIR (COTR: Joe Stoffa)

Christian Junaedi, Jeff Weissman, Subir Roychoudhury

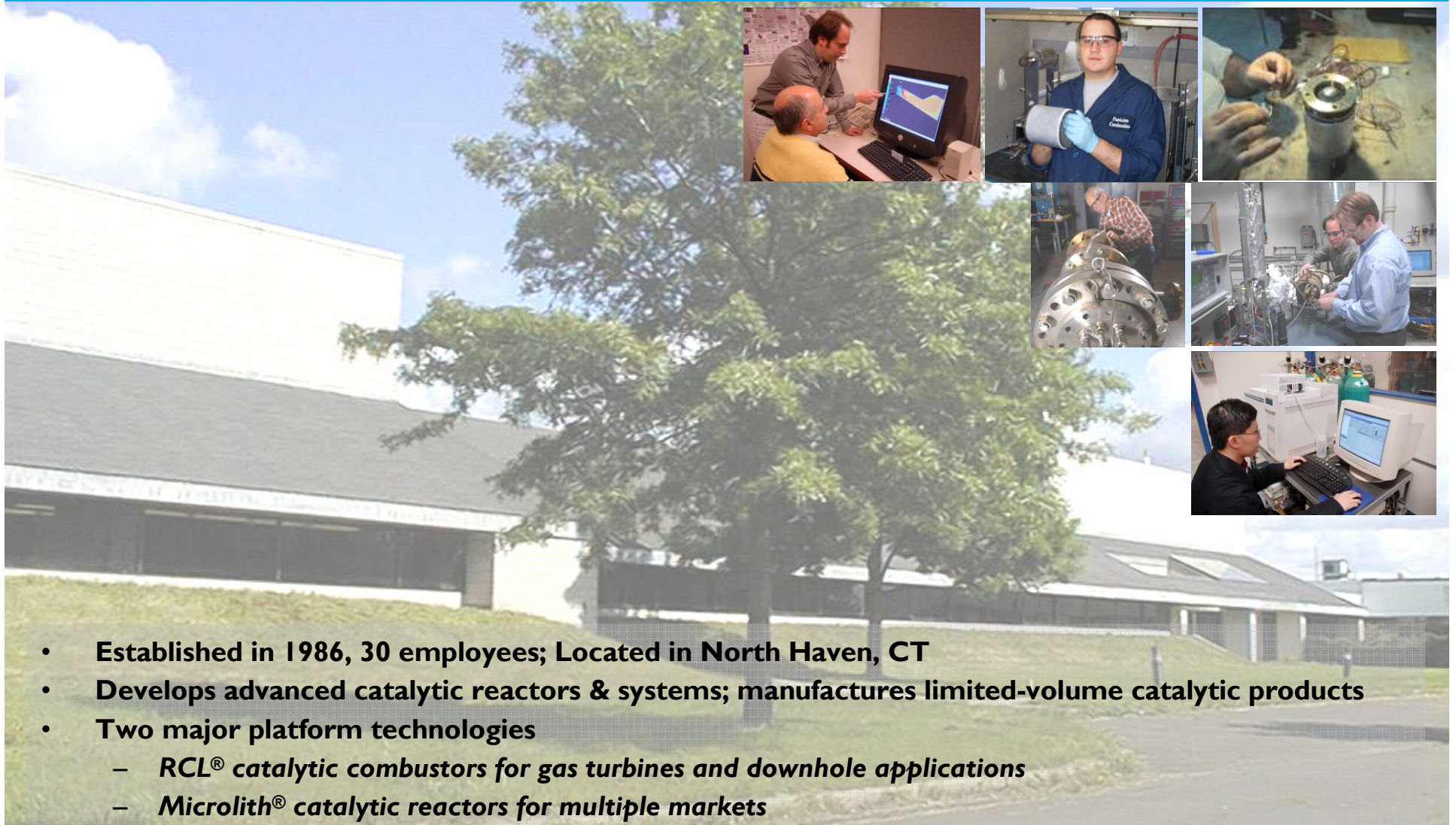
*Precision Combustion, Inc. (PCI), North Haven, CT*

11th Annual SECA Workshop  
Pittsburgh, PA; July 29, 2010





# Precision Combustion, Inc.



- Established in 1986, 30 employees; Located in North Haven, CT
- Develops advanced catalytic reactors & systems; manufactures limited-volume catalytic products
- Two major platform technologies
  - *RCL<sup>®</sup> catalytic combustors for gas turbines and downhole applications*
  - *Microlith<sup>®</sup> catalytic reactors for multiple markets*



# PCI Technology Overview

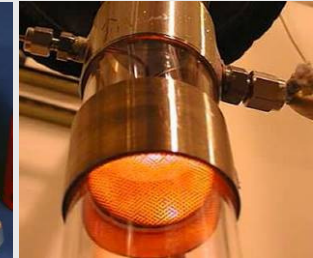
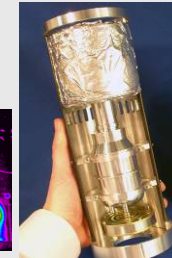
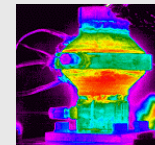
- RCL<sup>®</sup> Catalytic Combustion

- Best New Technology Award 2006 – IGTI, ASME
- Full scale GT engine testing underway at OEM's



- Microlith<sup>®</sup> Catalytic Reactors – Tibbetts & Army Innovation awards

- Catalytic Burners & Converters
  - JP-8/Diesel/H<sub>2</sub>/anode gas burners
  - Stirling Engine Burners (as low as 50 We)
  - Catalytic after-treatment - automobiles



- Ultra-compact Fuel Processing

- ATR, Waterless CPOX & CSR for liquid and gaseous fuels (e.g. JP-8, diesel, methane, propane, biofuels)
- Reformers for SOFC, PEM & MCFC applications
- 1 - 250 kW<sub>e</sub> Fuel processing Systems



- Regenerable Sorption Reactors:

- Chem-bio filters
- Air revitalization for long-duration manned spaceflight







# Reforming Areas Under Development At PCI

## Reforming Processes:

Auto-thermal reforming  
Catalytic Partial Oxidation  
Steam Reforming

## Reforming reactors:

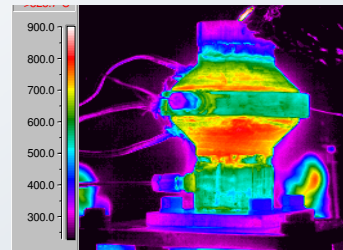
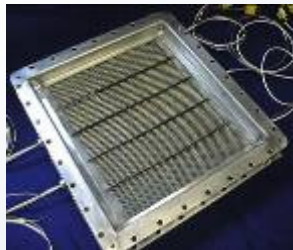
WGSR, PROX  
Burners (startup, AGB, purge)  
Scales: 50 We – 250 kWe

## Fuels:

Liquids: Diesel, JP-8, Jet-A, E-85  
FT fuels, Methanol, Gasoline  
Gases: Natural Gas, Propane

## BOP:

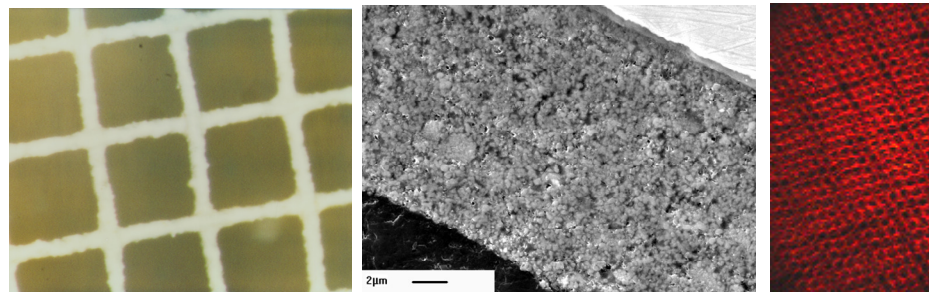
Pumps, Blowers, Nozzles  
Igniters, HX, Steam generation,  
F/A/S mixing, Controls  
Sulfur Cleanup, System Integration



*“Put The Fuel in Fuel Cells”*



# Microlith® Technology



Small, durable, catalytically coated metal mesh with very high surface area



Continuous catalyst coating line with batched furnace and rigorous QA, QC in place



## Microlith® Catalytic Reactors

- Ultra compact
- Short contact time
- Rapid thermal response
- High heat & mass transfer
- High surface area/unit volume
- Low catalyst usage & small size  $\Rightarrow$  Low cost

PCI holds multiple patents on catalyst structure, reaction methods, and apparatus



# Significant Results

- **Microlith Auto Thermal Reformer (ATR)**
  - System layout
  - Water neutrality
    - Condensation
    - Anode Gas Recycle
  - Catalyst sulfur tolerance and sulfur cleanup
  - Coke minimization for operation w. SOFC stacks
- Microlith Waterless Diesel reformer (CPOX)
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  - Long term operation w. sulfur containing distillate fuels
- Larger scale reformers w. gaseous/liquid fuels



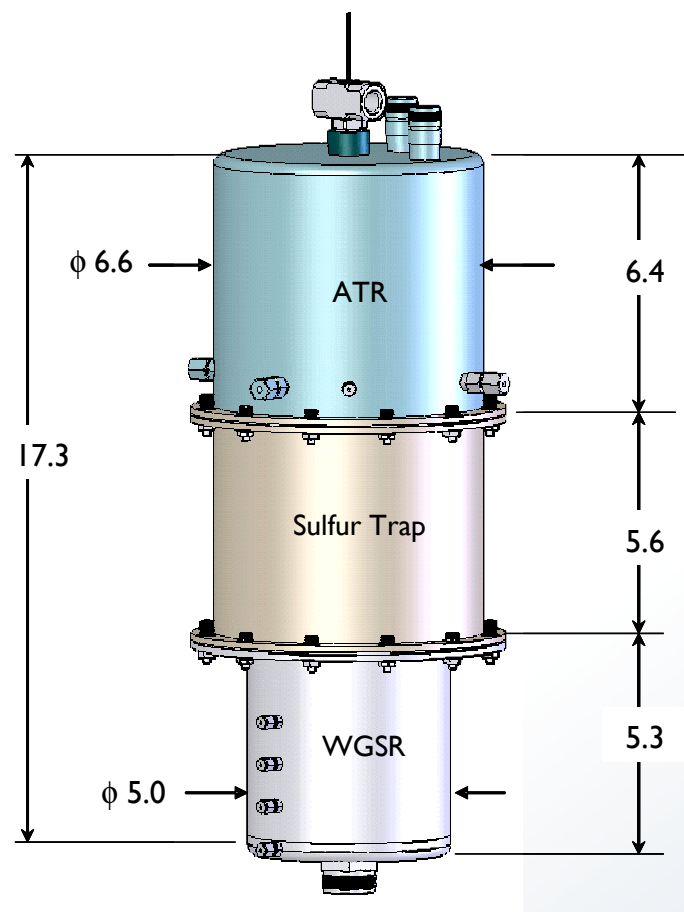
# Integrated Fuel Processor



5 – 10 kW<sub>th</sub> reformer integrated w. fuel/air/steam injector, igniter, steam generating HX, sulfur trap.  
Cabinet w. balance of plant components (fuel, water tanks, pumps, controls, power supply, etc.)



# Standalone Fuel Processor (HT-PEM/PEM)



25 kW<sub>th</sub> ATR w. fuel/air/steam injector, igniter, steam generating HX, sulfur trap, WGSR





# Standalone Fuel Processor Metrics

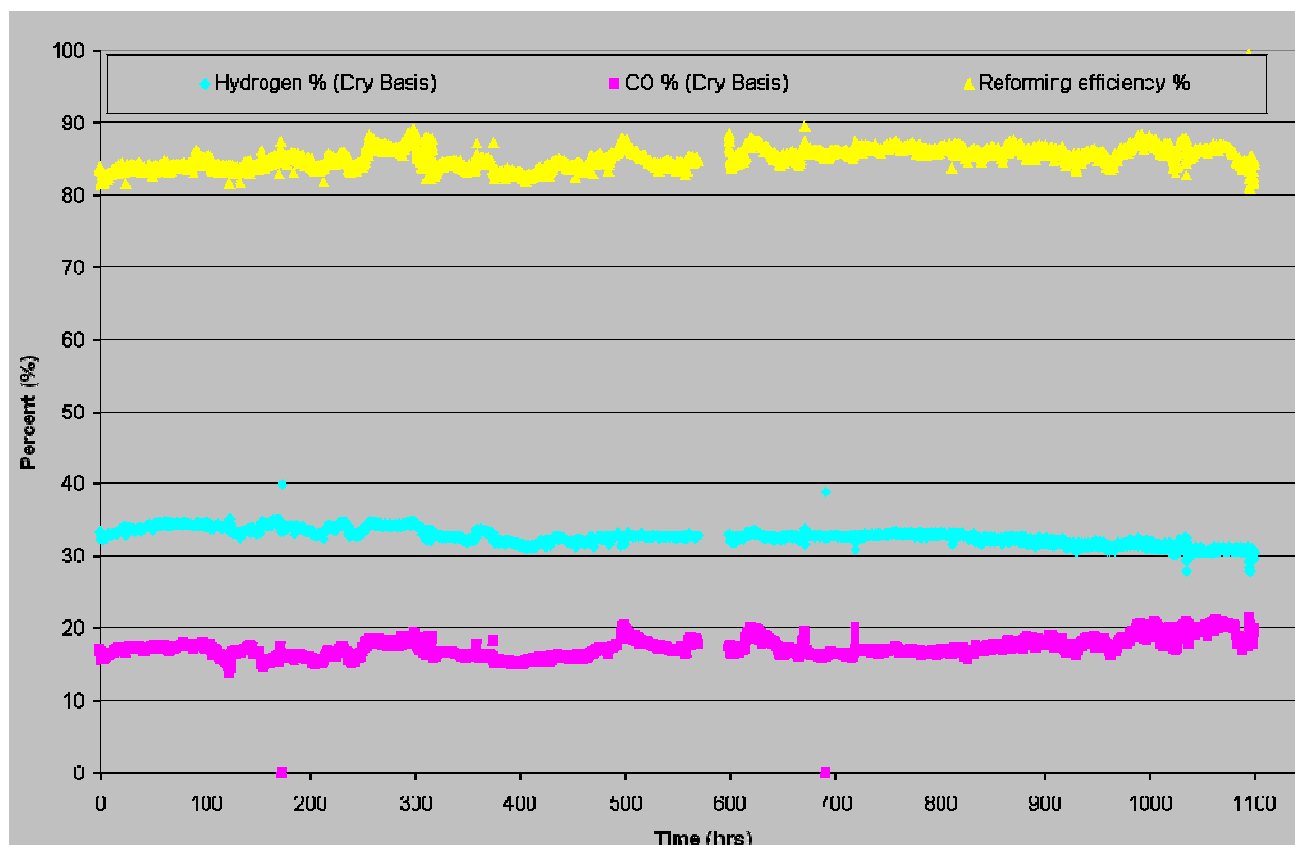
- Reforming efficiency: ~85% (ratio of LHV)
- Size: 3 liters; Weight: 5 kg (for 5 kW<sub>th</sub>)
- Operate at low S:C ratios (AGR/water)
- Start up in CPOX (1 min), transition to ATR (7 min)
- Modular, readily-serviceable components
- Stand-alone pumps & blowers implemented
- 12 V battery for startup & controls
- Readily integrated w. SOFC, PEM, H<sub>2</sub> generation systems
- Durability: 1000 hrs w/o failure w. JP-8 (~400 ppm<sub>w</sub> sulfur)



Convert JP-8\*/Diesel<sup>+</sup> into sulfur free (<1 ppm<sub>v</sub>) reformat



# Reformer + Stack Interface Testing



JP-8 w. low S (Average  $\sim 15 \text{ ppm}_w \text{ S}$ ); Higher HC's  $< 20 \text{ ppm}$ .

Operated with  $1 \text{ kW}_e$  SOFC stack – Stable Operation w/o coking for 1100 hours



# Test Summary

- Automated start, shutdown, load changes
- Closed loop feedback control w. safety interlocks
- DC Gross efficiency of 34% achieved
- Maximum power of 1.5 kWe obtained
- On post inspection, no carbon detected



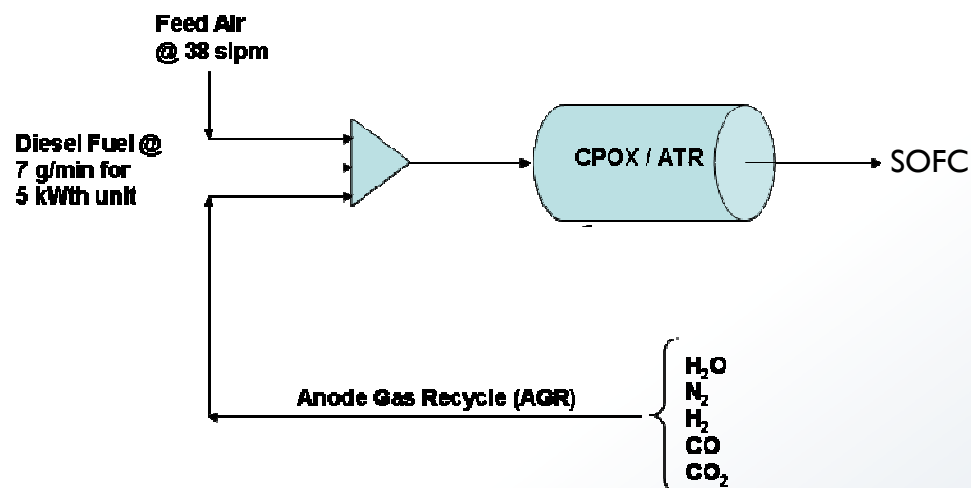
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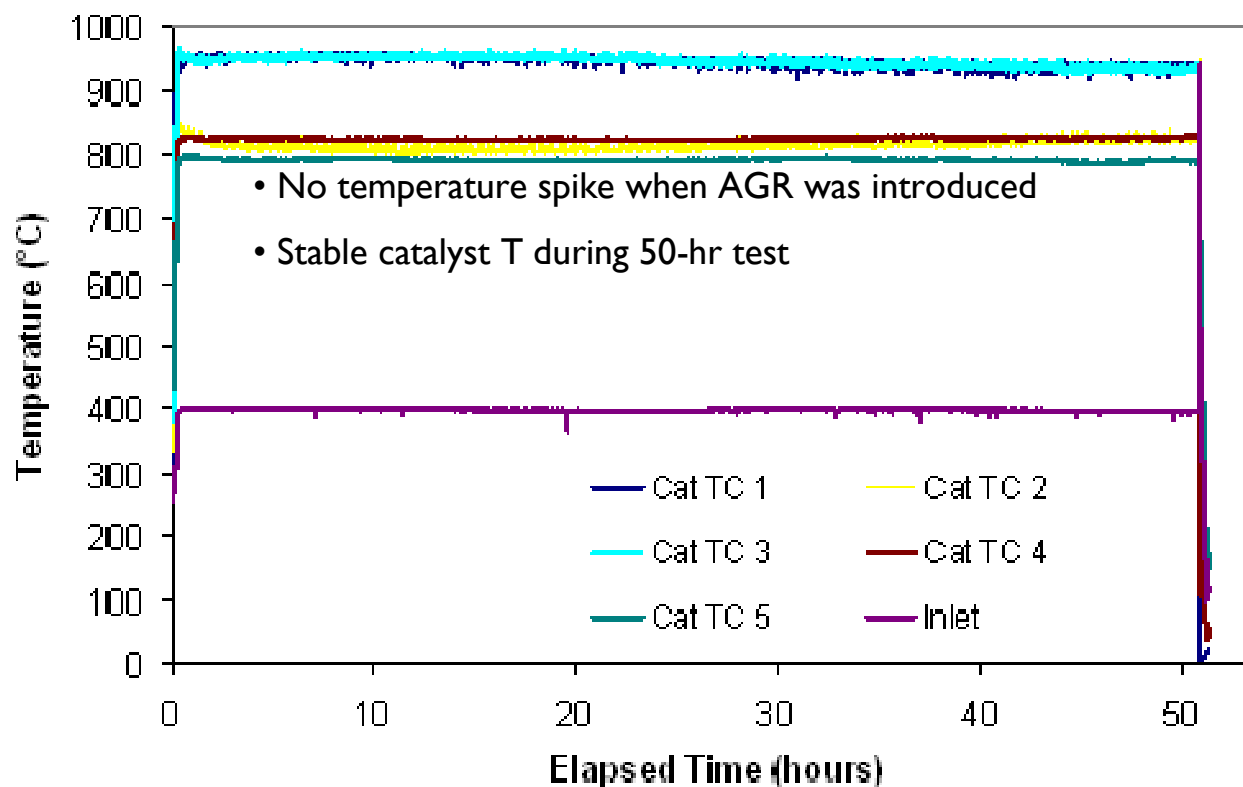
# Water Recovery: Direct Anode Recycle (AGR)



- Used surrogate gas mixture to simulate AGR composition and flow rate
  - Assumptions: 60% SOFC Fuel Utilization; 50% AGR split to achieve target O/C and S/C
- Reactor startup under CPOX (waterless); then transitioned to ATR (w. AGR)
- Stable reactor operation w. no temperature excursions
- Successfully demonstrated 50-hr durability of ATR using AGR for water neutral operation
- Test results in good agreement w. thermodynamic equilibrium analysis; no HCs slippage



## AGR Approach – T Profile (50-hr Durability Test)



# AGR Approach 50-hr Durability Test: Product Composition

Species	Conc. (mole %, dry basis)	
	50-hr test (average)	ASPEN model
H <sub>2</sub>	12.4	12.4
CO	14.8	15.3
CO <sub>2</sub>	12.6	10.9
N <sub>2</sub>	60.2	61.4
CH <sub>4</sub>	0.02	0



# Water Recovery: Condensation Approach

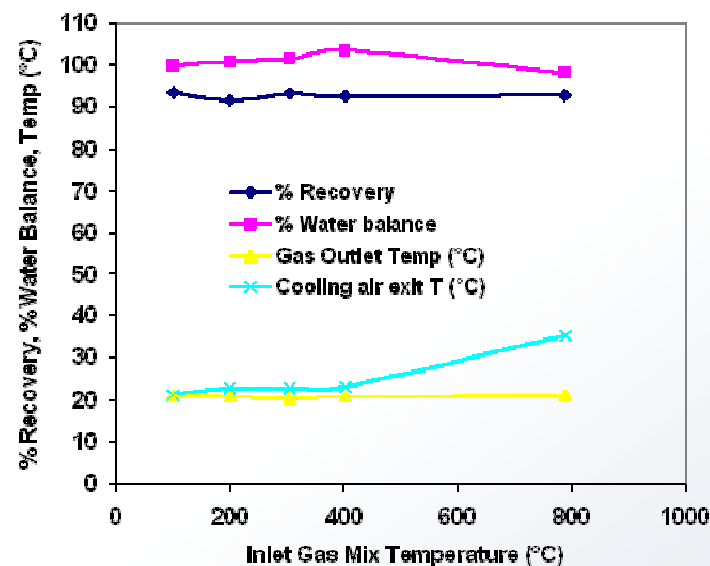
Required % H<sub>2</sub>O recovery is a function of:

- % hydrogen in the hydrocarbon feed
- Reformer product H<sub>2</sub> and H<sub>2</sub>O
- Fuel Utilization in the Fuel Cell
- Location of anode gas burner in the system
- Bypass ratio & Recycle ratio
- Ambient conditions





## Results from Increasing Condenser Inlet T



- Condenser inlet T was increased from 100 to ~800°C.
- 21°C cooling air, 32.7 mol% H<sub>2</sub>O, 5 kWth system.
- ~93% water recovery achieved at 800°C.

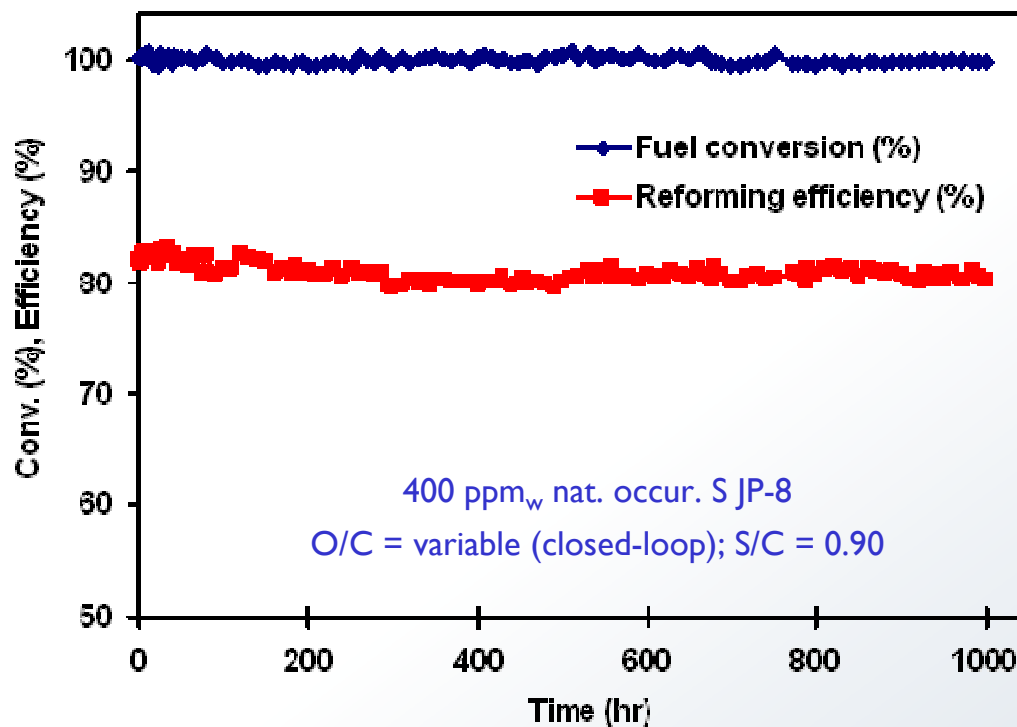


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## Effect of 400 ppm<sub>w</sub> “Real S” for 1000 hrs



- Stable/complete fuel conversion, Reforming efficiency, H<sub>2</sub>+CO mole % over time
- Total organics (primarily C2, C3) <100ppm at end of test.
- Fuel-bound S converted to H<sub>2</sub>S and removed (<1 ppm) downstream of reforming reactor
- NETL Rh-pyrochlore formulation adapted to Microlith. Significant cost reduction potential identified.



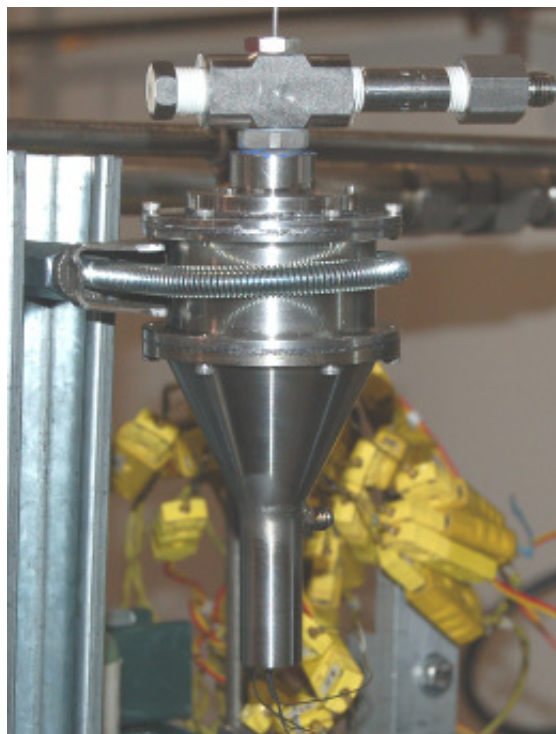
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# Diesel CPOX Reactor embodiment



~30 cc reactor + fuel/air injector + igniter

Reformate Composition

H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Propylene	Propane
22	0.0	54	0.4	21	2	0.3	0.0	0.1	0.0



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# CSR Reactor 500-hr Durability Test Summary

- 500-hr durability testing successfully completed (one catalyst w/o regeneration/replacement)
- Operated both CSR & burner w. 2 ppm<sub>w</sub> S synfuel for 450 hrs (50 hrs w. n-C12)
- Stable CSR reformat w. ~70 mol% H<sub>2</sub> (dry basis)
- Product composition in good agreement with thermodynamic prediction

CSR exptl data at 1.5 kW<sub>th</sub> and 1 atm vs. thermodynamic equilibrium

	<b>Exptl Product Mol %, S/C=3.0, P = 1 atm</b>	<b>Equilibrium Mol. %, S/C=3.0, P = 1 atm</b>
<b>H<sub>2</sub></b>	<b>69-71</b>	<b>68.5</b>
<b>CO</b>	<b>10.7-14.0</b>	<b>9</b>
<b>CO<sub>2</sub></b>	<b>14.0-19.3</b>	<b>17.6</b>
<b>CH<sub>4</sub></b>	<b>0.8-4.0</b>	<b>4.9</b>

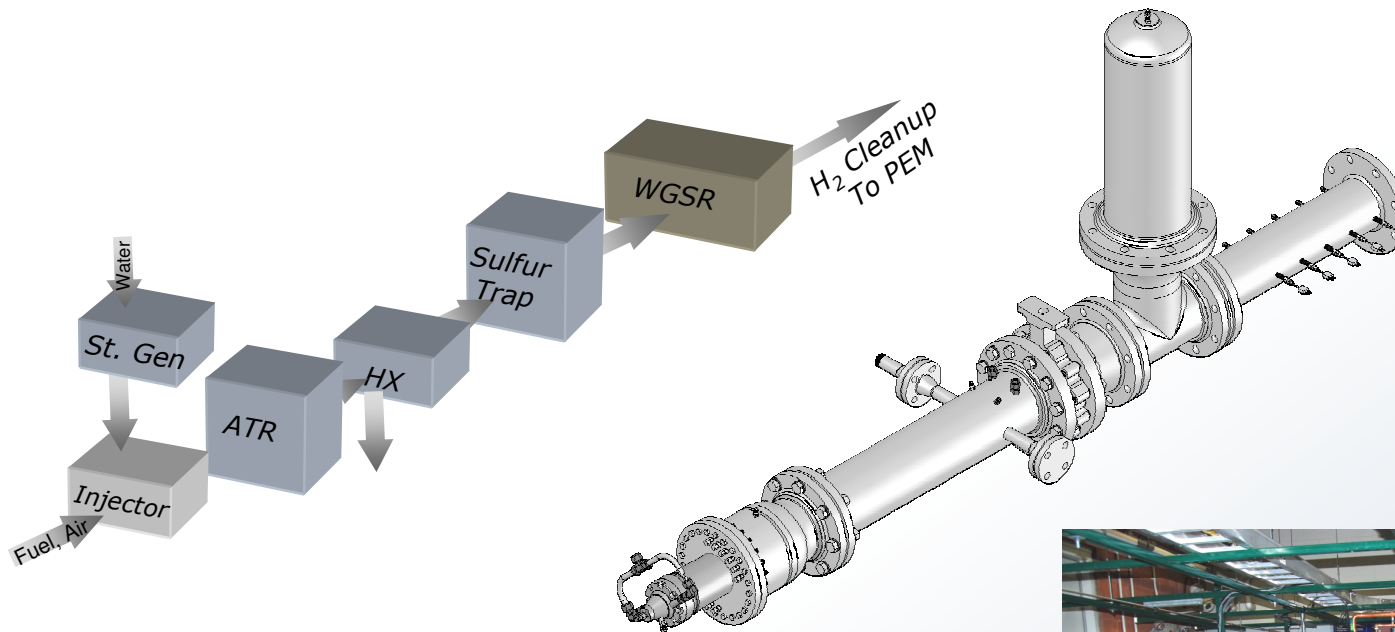


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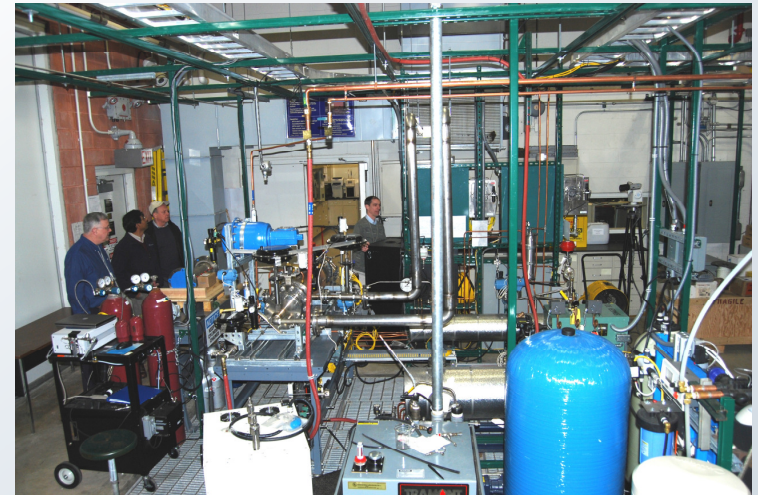
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# 200 kW<sub>th</sub> Fuel Processor (ATR + Sulfur Trap + WGSR – ONR)

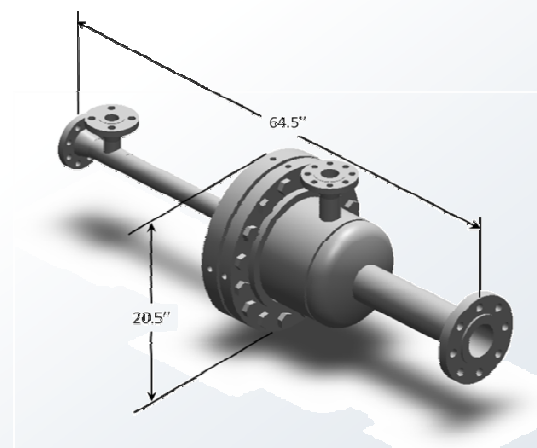
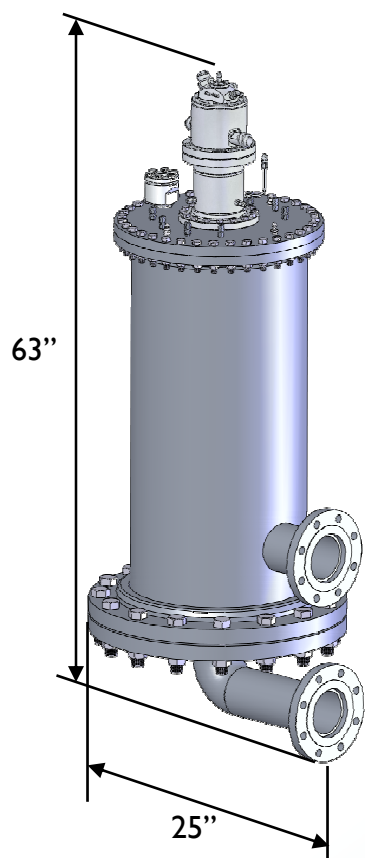


- Simple layout
- Compact footprint
- ATR Size: 3 liters
- Operating pressure: 7 atm
- Reforming efficiency: 70% - 80%
- 1 mW<sub>th</sub> scale-up ongoing





# Scale-up: 250 kW<sub>e</sub> to 5 MW<sub>th</sub> Fuel Processors



- 250 kW<sub>e</sub> Fuel Processing System Design & Hardware consisting of fuel/air/steam injector, ATR, steam generator hex, and downstream sulfur clean-up
- 5 MW<sub>th</sub> natural gas CPOX hardware



# Summary

- Auto Thermal Reforming – *Diesel*:
  - Stable, long-term operation w. SOFC stacks
  - Compact package, w. high reforming efficiency (~85%) with JP-8
  - Water neutral operation verified via AGR and Condensation
  - Stable, long-term operation w. 400 ppm<sub>w</sub> fuel sulfur
  - Higher HC's < 100 ppm
- Steam reforming:
  - Catalytic ox. & endothermic design w. high heat flux – compact reactor
  - Stable, long-term operation w. distillate fuels (S-8)
  - Sulfur tolerance up to 25 ppm<sub>w</sub> (no degradation over 50 hrs.)
- Catalytic Partial Oxidation (waterless) – *diesel*:
  - Stable, long-term operation in a compact package.
- Scale-up:
  - 200 kW<sub>th</sub> to 5 MW<sub>th</sub> demonstrated w. liquid & gaseous fuels



# Acknowledgment

We are grateful to the DOE for their support,

And

The engineers and technicians at PCI.

