PCI
Precision Combustion

Compact Fuel Reformers – *kW to MW scales.*

DOE Phase II SBIR (Enhancement); COTR: Joe Stoffa

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

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Clean Power Solutions for the 21st Century®

Precision Combustion, Inc.

38,000 sq ft total space

- Established in 1986
- Privately held, Small Business
- Located in North Haven, CT
- We put the “Fuel” in “Fuel Cells”
  → Fuel reformation for syngas/H_2 generation
- Collaborators include: U.S. Govt., Large & small corporations, Universities, …..
- Develop advanced catalytic reactors/systems; manufacture limited-volume prototypes

Outline

- Developments under the DOE SBIR program
- Microlith-based Auto Thermal Reformer (ATR) scale-up
- Microlith-based Waterless Partial oxidation Reformer (CPOX)
- Advances in Microlith-based Catalytic Steam Reforming (CSR)
- Concluding Remarks

SBIR Phase 1/2/Enhancement Objectives

- ✓ Experimentally demonstrate feasibility of water neutral reformer operation
- Develop and optimize a low pressure drop fuel injector/nozzle
  - Permit stable, steady state operation, cold start, 5:1 turndown
  - Coking avoidance w. complete fuel conversion to C1 products
  - ~85% reforming efficiency.
- Compare different catalyst options to meet commercially viable APU targets.
  - Examine benefits of Rh-pyrochlore catalysts for diesel reforming.
- Examine reformer performance w. specific bio-fuels
- ✓ Examine fuel processor operation with SOFC stacks
- Identify design simplification of BOP to meet commercially viable APU targets

Low Air-Pressure Nozzle Development

Goals:

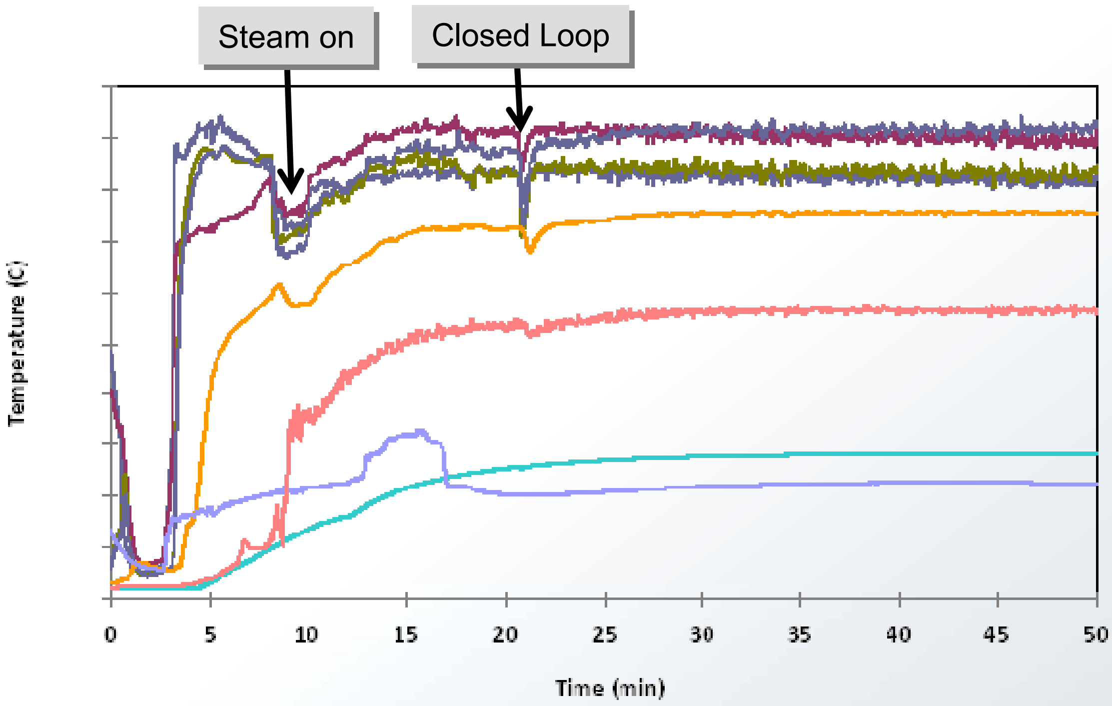
- Achieve proper atomization & vaporization of the fuel.
- Stable introduction & mixing of steam & air for optimum ATR performance.
- Ability to cold-start & maintain low pressure air source for minimal parasitic losses.

Results to date:

- Low air ΔP at 5 kW_{th}
- Uniform fuel atomization, vaporization & mixing
- Cold start capability demonstrated
- Steam stability (from internal steam generator)
- 5:1 turndown possible
- Long-term durability ongoing w. Tier II/ULSD Diesel

Low Air-side Pressure-drop Nozzle Testing

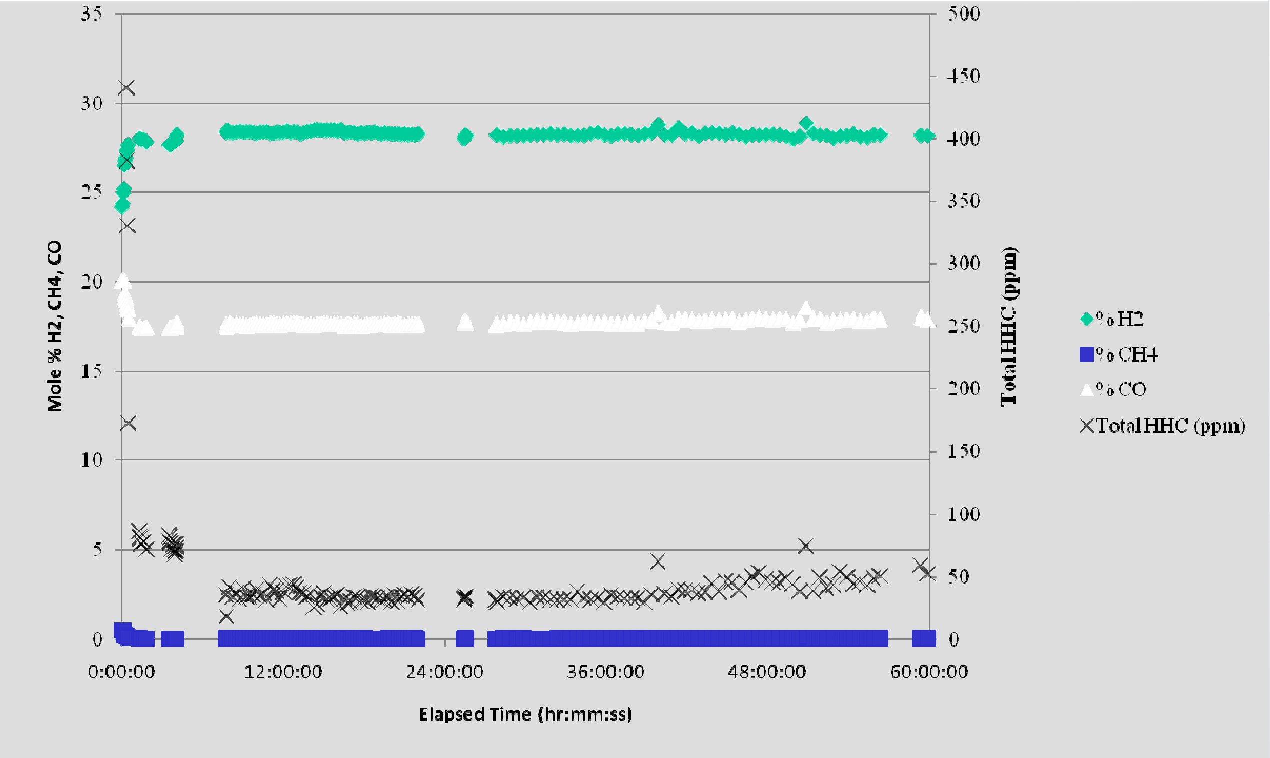
Temperature profile during start-up & introduction of steam



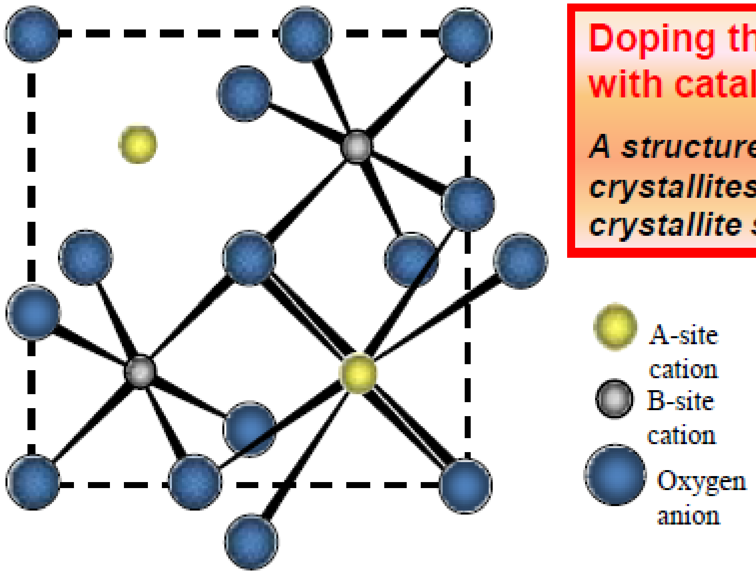
Low air pressure drop is required for reduced parasitic loads

Low Pressure Nozzle Development – ATR Performance

- Operated low ΔP nozzle w. ATR at 3 kWth for ~100 hrs
- Stable HHC's of < 50 ppmv (dry basis)



Pyrochlore Oxide-Based Catalyst Systems



Doping the lattice of certain oxide-based compounds with catalytic metals results in…

A structured catalytic surface with nano-sized metallic crystallites that serves as a template to control metallic crystallite size and dispersion.

Pyrochlores ($A_2B_2O_7$) are viable reforming catalysts because they exhibit:

- High chemical and thermal stability [1]
- Mechanical strength to accommodate substitutions [2]
- Active metal can be substituted into B-site to improve catalytic activity
- Substitution with lower valence elements in A-site and B-site can create oxygen vacancies, which may increase lattice oxygen-ion mobility to reduce carbon formation.

<u>*Source:*</u> D. Shekhawat, "Structured Oxide-Based Reforming Catalyst Development," 11th Annual SECA Workshop, Pittsburgh, PA – July, 2010

NATIONAL ENERGY TECHNOLOGY LABORATORY

Rh-Pyrochlore Catalyst Development at PCI

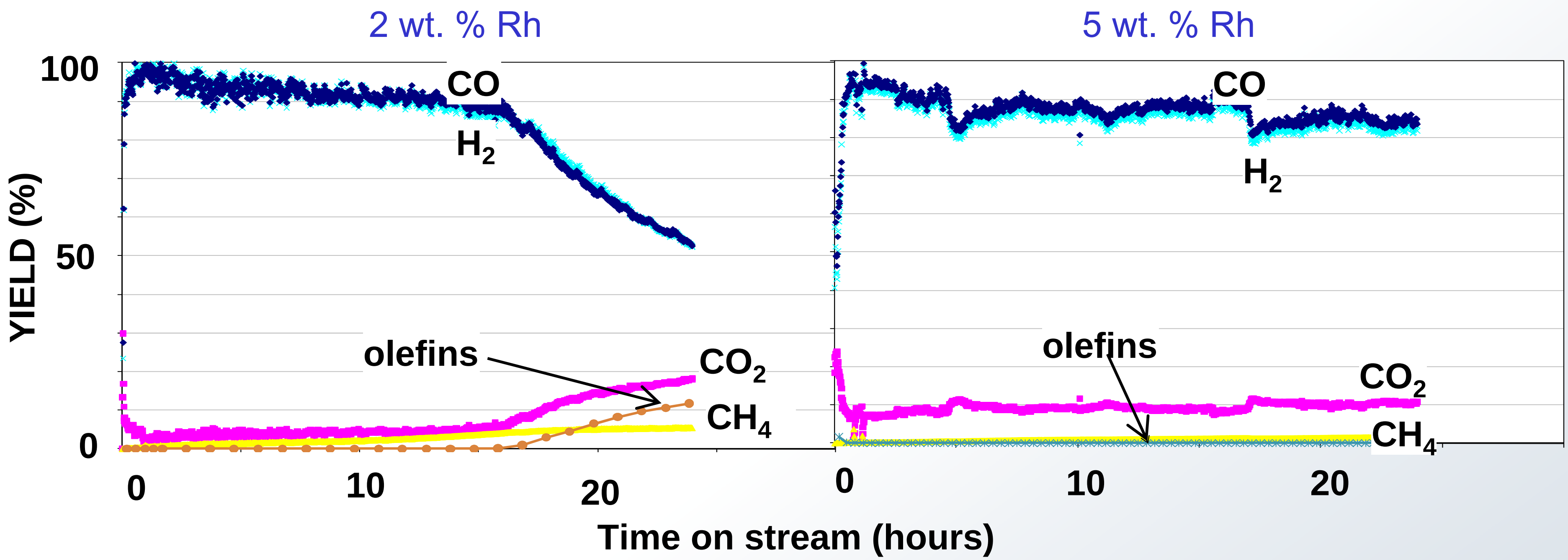
Goals:

- Demonstrate NETL pyrochlore catalyst as reliable, cost effective alternative for fuel reforming.
  - Apply catalyst to Microlith Catalyst Substrate
- Potential reduction in Rh metal cost.
  - Rh-pyrochlore has potential for same activity/durability level at much less Rh usage
  - Understand active form of rhodium

PCI prepared $(La,Ca)_2(Zr,Rh,Y)_2O_{7-\delta}$ powders:

- 0, 2 and 5 wt. % Rh in pyrochlore were synthesized
- Rh and Y content balanced
- La and Ca content adjusted for charge balance

Performance of 2 wt.% vs. 5 wt.% Rh in Pyrochlore



- Tests were performed using NETL's microreactor using low-sulfur diesel fuel.
- O/C of 1.1 (mole ratio) to maintain peak T of ~900°C.

PCI confirmed that 5 wt. % Rh has better stability over 2 wt. % in $(La,Ca)_2(Zr,Rh,Y)_2O_{7-\delta}$ Oxide

Rh Pyrochlore Coating Development & Test Results

- Optimize coating of 5 wt.% Rh pyrochlore catalyst on PCI's Microlith substrate.
- Maximize loading, dispersion & adhesion; minimize cost & processing time.
- To date, 4 iterations have been performed by adjusting washcoat formulation & catalyst application method.
- Catalyst performance tests were performed at PCI w. 1.6 ppm_w sulfur JP-5 (similar aromatics w. Tier II Diesel).

Performance comparison at the same operating conditions

Iteration #	Conversion to C1s (%)	LHV-based Efficiency (%)	Ethane + Ethylene (ppmv, wet basis)	Propane + Propylene (ppmv, wet basis)
1	94.1	73.9	1175	260
2	97.1	75.5	1100	290
3	~100	79.3	634	64
4	~100	78.8	198	0
5*	100	85	0	0

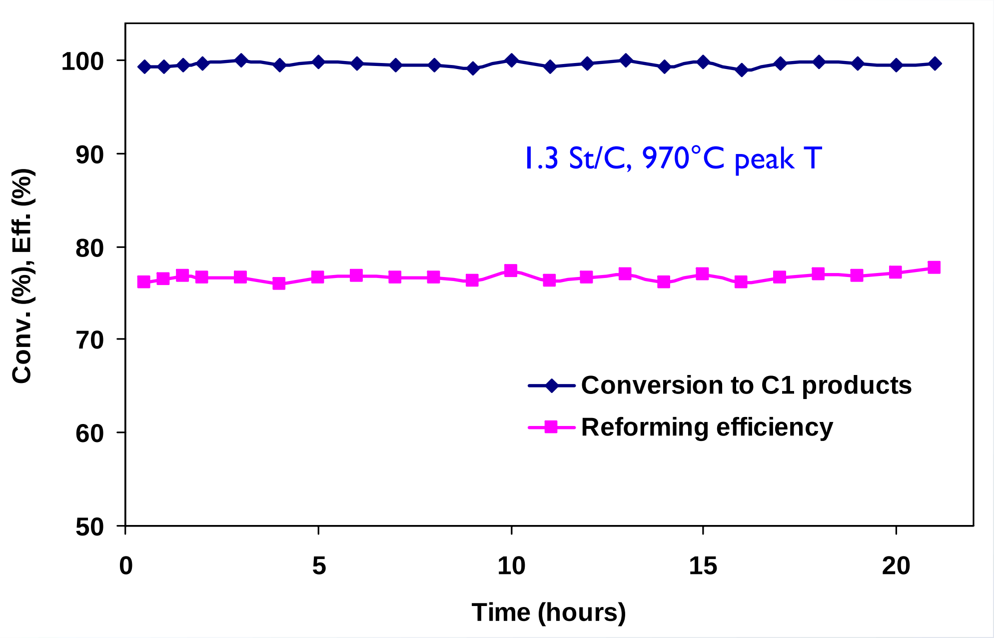
*5: Target values as achieved by non-pyrochlore PCI catalyst

- Reduced coke precursors (i.e., higher hydrocarbons, including C2s & C3s) from >1000 ppm_v to 200 ppm_v.
- Increased fuel conversion to C1 products (i.e., CO, CO_2, CH_4) & reforming efficiency.
- Work is ongoing to further reduce higher hydrocarbons (HHCs) level in reformate stream.

Pyrochlore Catalyst Evaluation: Durability Test

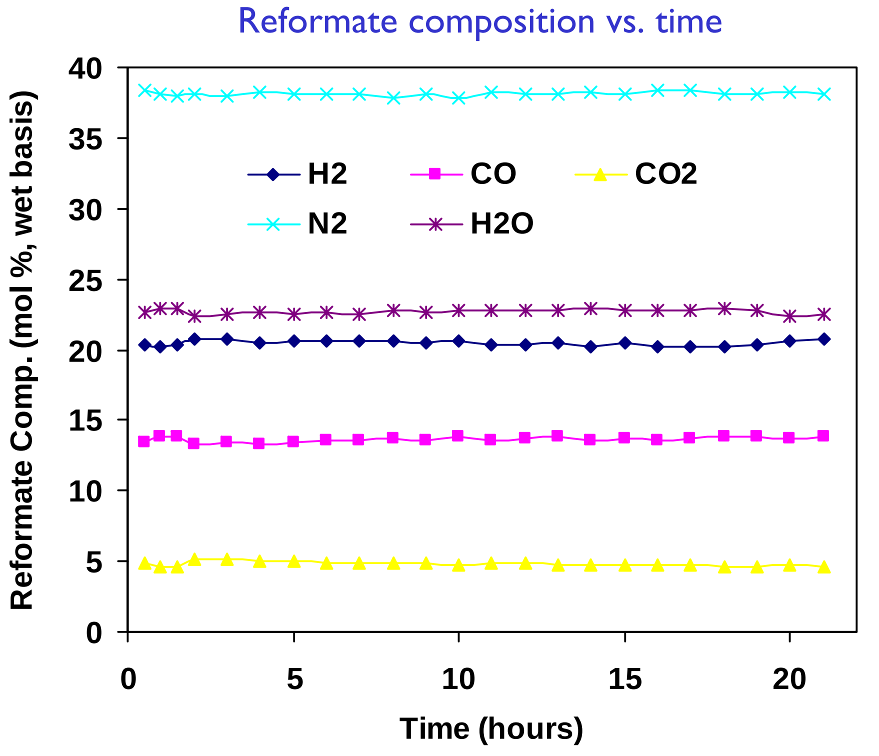
- 21-hr test with 1.6 ppm_w sulfur JP-5: 1.3 St/C.
- Stable fuel conversion (~100%) and reforming efficiency (~78-79%)

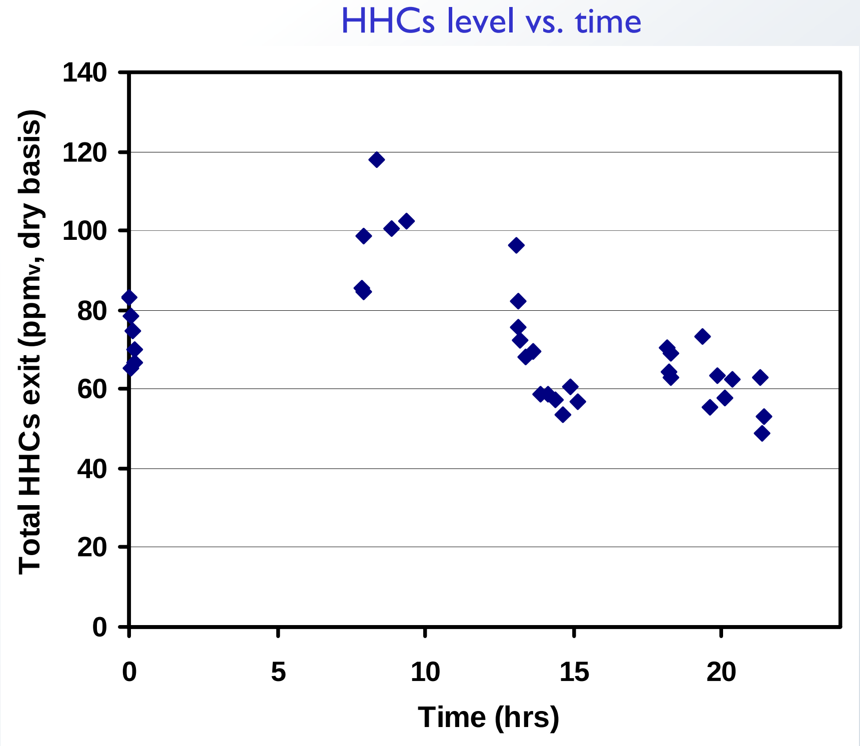
Conversion & Reforming efficiency vs. time



Pyrochlore Catalyst Evaluation: Durability Test

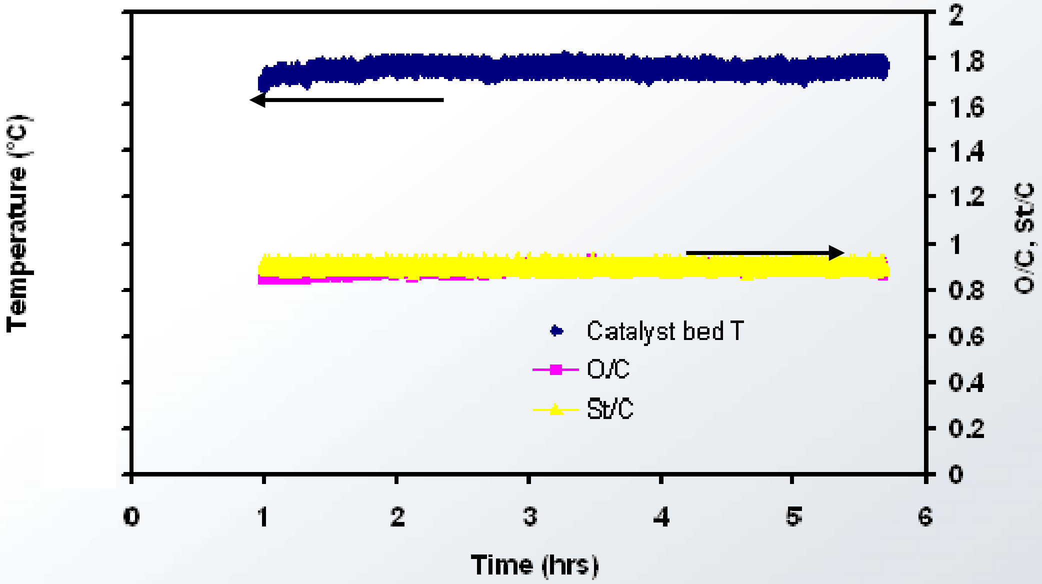
- Stable ATR reformate composition
- Total C2s = <120 ppm$_v$ (wet basis); no C3s detected by GC


Reformate composition vs. time


HHCs level vs. time

ATR Reforming of Biodiesel: Test Condition & T Profile

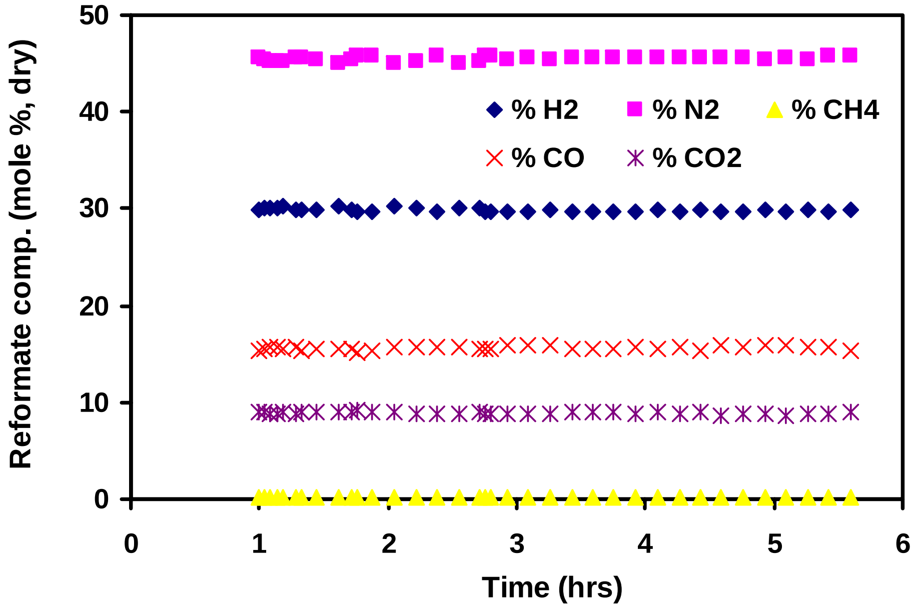
- Acquired Biodiesel 99 (B-99) from a residential heating oil company.
- Made 50/50 blend of B-99 and Tier II Diesel (ULSD).
- ATR testing using PCI's Rh catalyst was performed w. blended fuel (B-50).
- Fuel sample is being analyzed at an outside lab to obtain fuel specs (e.g., aromatics, sulfur level, H content, net heat of combustion, etc.)
- Test conditions: St/C of 0.9, O/C of ~0.9



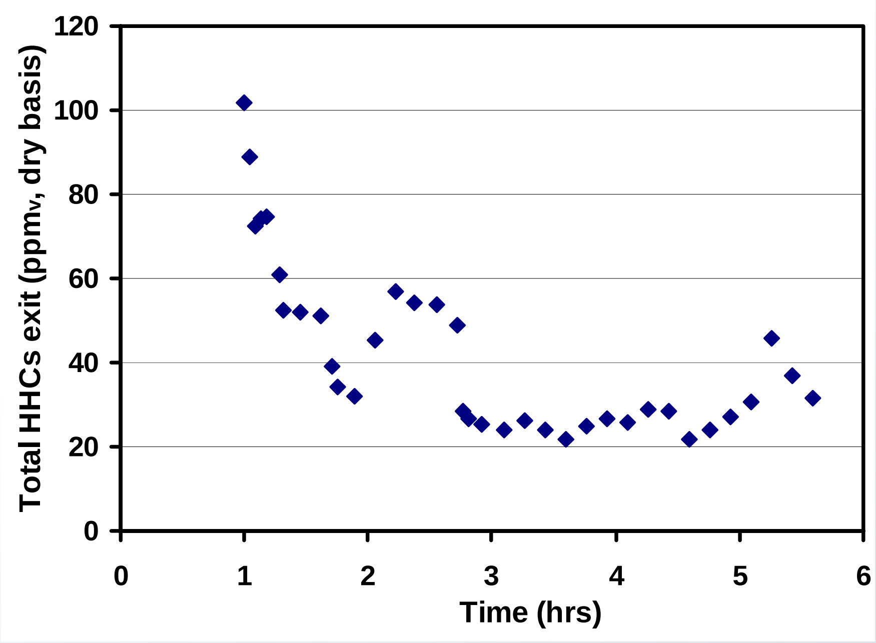
Steady State Temperature, O/C & St/C Profile

ATR Reforming of Biodiesel: Reformate Composition

Reformate composition vs. time



HHCs level vs. time

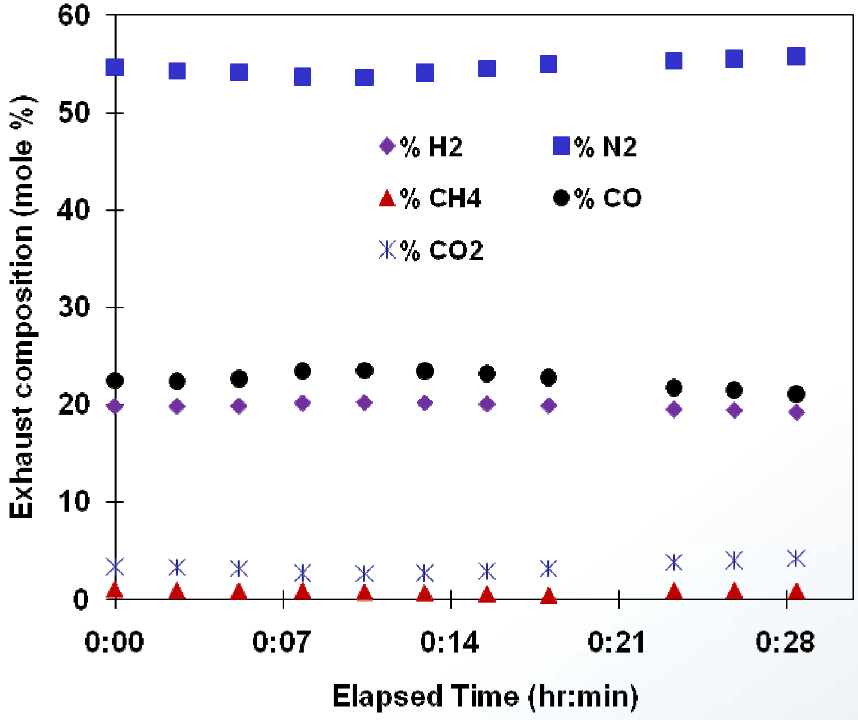


- Stable reformate composition: ~30% H_2 and 15% CO (dry basis).
- Higher hydrocarbons level decreased over time during the 6-hr test, steady at ~30 ppm_v (dry basis).
- Preliminary test demonstrated feasibility for efficient biodiesel reforming to syngas.
- More tests ongoing to develop performance map & to evaluate durability at optimum conditions.

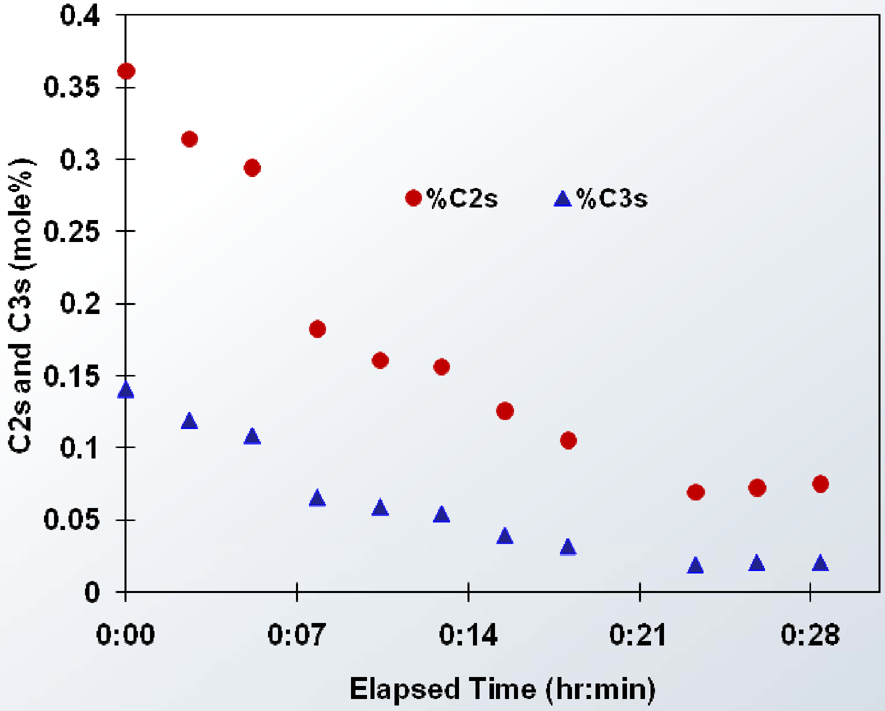
Waterless CPOX of Camelina Oil

Oil Flow rate: 2.5 – 3.0 g/min;

CPOX reformate composition (mol %, dry basis)



Higher hydrocarbons (mol %, dry basis)

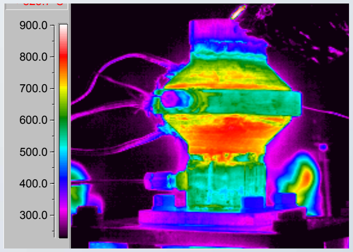


Camelina Oil (50% polyunsaturated fatty acids), Source: Montana Gluten Free, Belgrade, MT

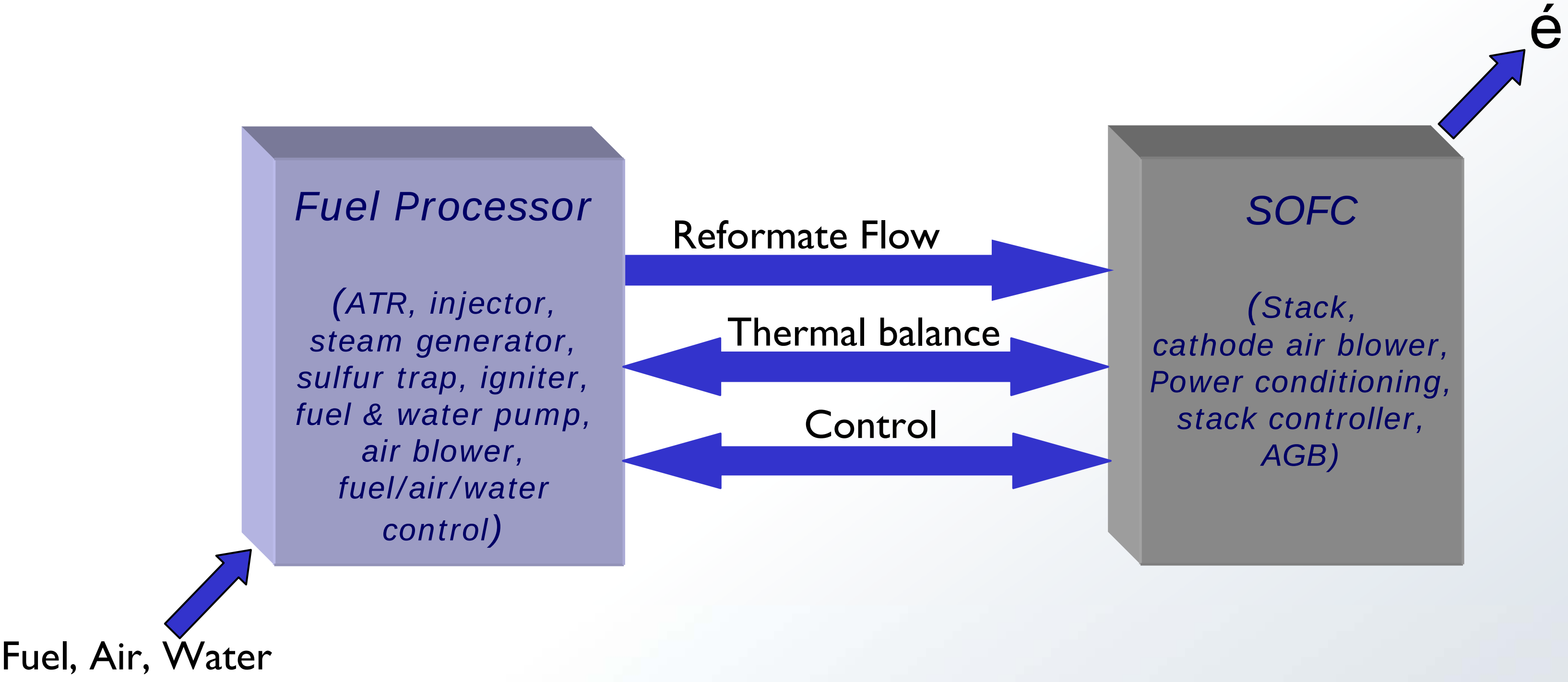
BOP Development

BOP encompassing:

- Heat Exchangers (steam generators, condensers, cathode air, preheater, etc.)
- Fuel/air/steam injector (low ΔP, uniform mixing, no coking, turndown, etc.)
- Air, fuel, water pumps, valves (controllable, accurate, with low parasitics)
- Burner (anode gas, startup, handle dynamics)
- Control algorithm (feedback control, embedded software, stack/reformer interface)
- System packaging (battery hybridization, fuel storage, gravimetric/volumetric density, insulation, etc.)
- FMEA (Safety; MIL Specs: Vibe, Environmental, Life, etc.)
- Costs (Use COTS equipment where possible for reduced cost)



Stack Fueling



Fuel Processor

(ATR, injector, steam generator, sulfur trap, igniter, fuel & water pump, air blower, fuel/air/water control)

Reformate Flow

Thermal balance

Control

SOFC

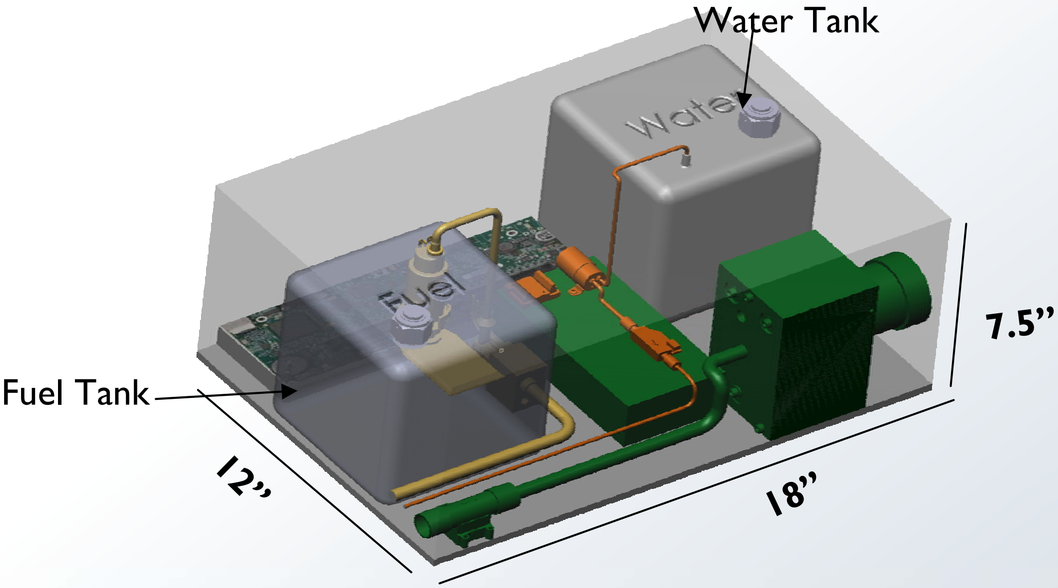
(Stack, cathode air blower, Power conditioning, stack controller, AGB)

é

Fuel, Air, Water

Capable of Startup, load following, shutdown

Reformer + BOP Packaging (5 kWth)



Steady state parasitic power needs: 50 – 60 We

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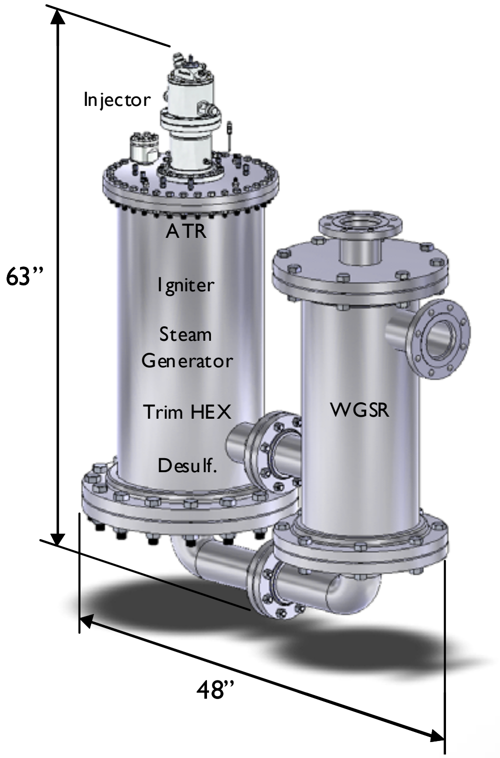
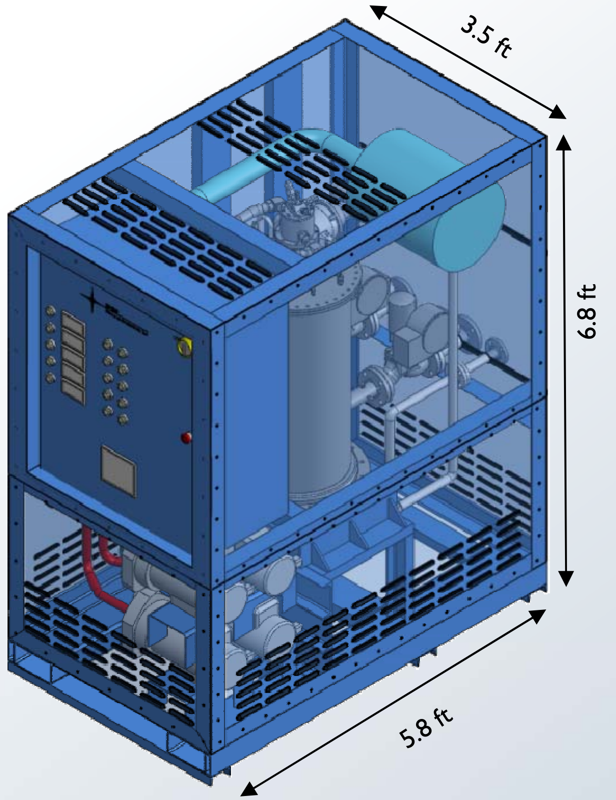
ATR Scale-up: 1 MW_{th} ATR System for ONR





Modular 250 kW_e Fuel Processing System consisting of fuel/air/steam injector, ATR steam generator hex, sulfur clean-up, controls, pumps, blowers, filters, sensors.

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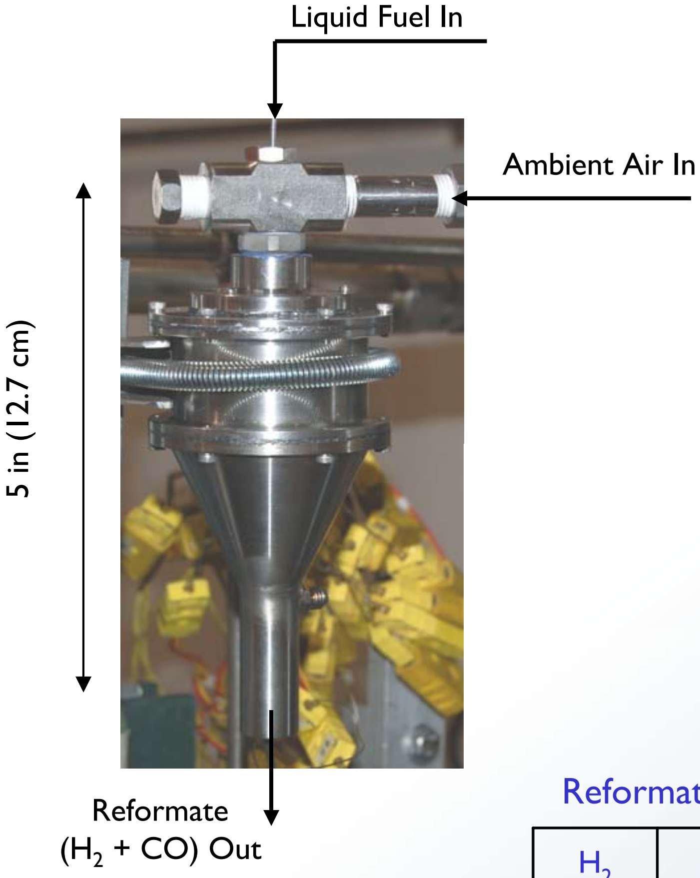
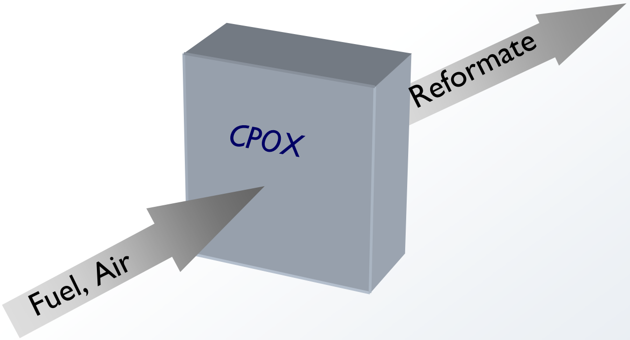
Catalytic Partial Oxidation Reactor (Waterless CPOX)

5 kW_{th} CPOX reactor w. fuel/air injector, igniter





- Operates at O/C ≈ 1; And S/C = 0
- Direct partial oxidation (w/o deep oxidation)
- Ambient air + fuel in ⇒ reformate out
- High H_2 selectivity
- Startup time <1min (ambient to steady state).
- Stable steady state operation w. multi start/stop over 1000 hrs
- Collaboration w. automotive OEM

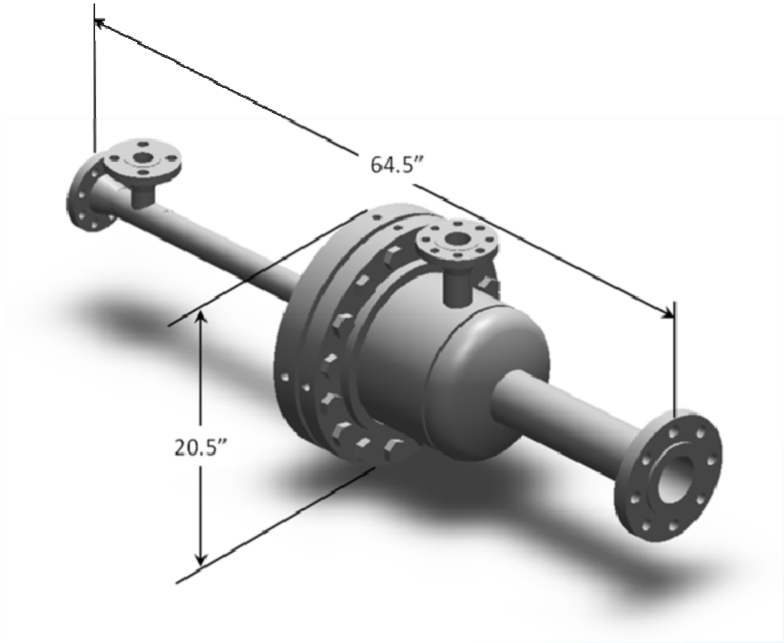
Reformate composition (mole %) for operation w. distillate fuel:

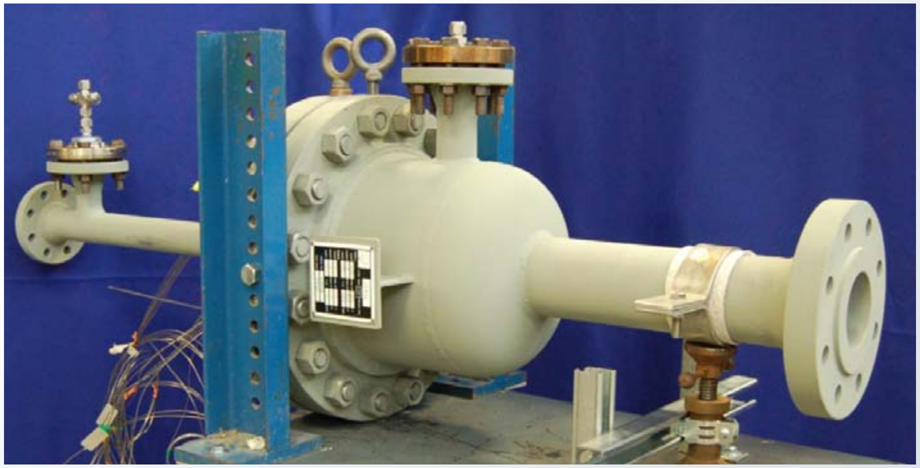
H_2	O_2	N_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
22	0	54	0.4	21	2	0.3	0.0	0.1	0.0

CPOX Scale-up: 5 MW(th) Natural Gas Processor

5 MWth reactor to reform natural gas to produce syngas

Prototype tested & delivered





- Performance testing successfully completed.
- 1000 hrs of sub-scale durability completed (Target 8000 hrs).

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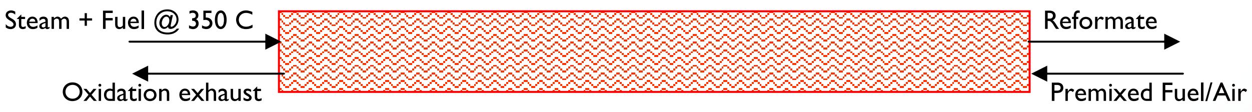
Catalytic Steam Reforming Reactor (CSR)


Steam + Fuel @ 350 C

Oxidation exhaust

Reformate

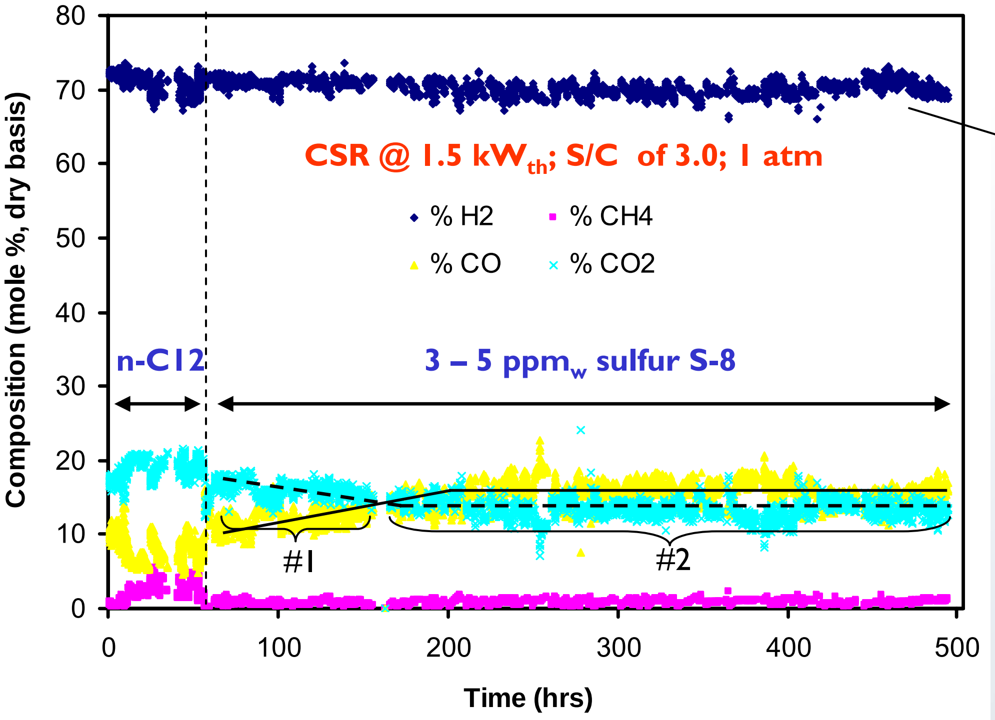
Premixed Fuel/Air


3 kWth Reactor (Endothermic + Exothermic)
(2 in Dia X 14 in. long)

- CSR prototype consists of catalytic exothermic (burner) & catalytic endothermic (CSR).
- Catalytic burner instead of flame-stabilized burner improves thermal uniformity, distribution, durability & control.
- ~10x higher overall heat transfer coeff. vs. conventional HEX (w. open annular space) → compact reactor.
- Up to 3 kWth CSR operation at 3 atm; ~15 SLPM H_2 produced (at ~65-70 mole % of reformate)
- Product composition in good agreement w. thermodynamic prediction

CSR Reactor 500-hr Durability Test

Product composition vs. time (500-hr test)



Minimal change in H_2 (Δ=1%)

- CSR operated w. n-C12 for first 50 hrs; then used 2-3 ppm S synfuel for 450 hrs.
- Sulfur presence in synfuel suppressed WGS → higher CO (Δ=2-3%) and lower CO_2 (Δ=2-3%) in product.
- #1: change in CO and CO_2 concentrations over 100-hr operation.
- #2: after initial change, reformate composition stable for the remaining 350-hr operation.

CSR Reactor 500-hr Durability Test Summary

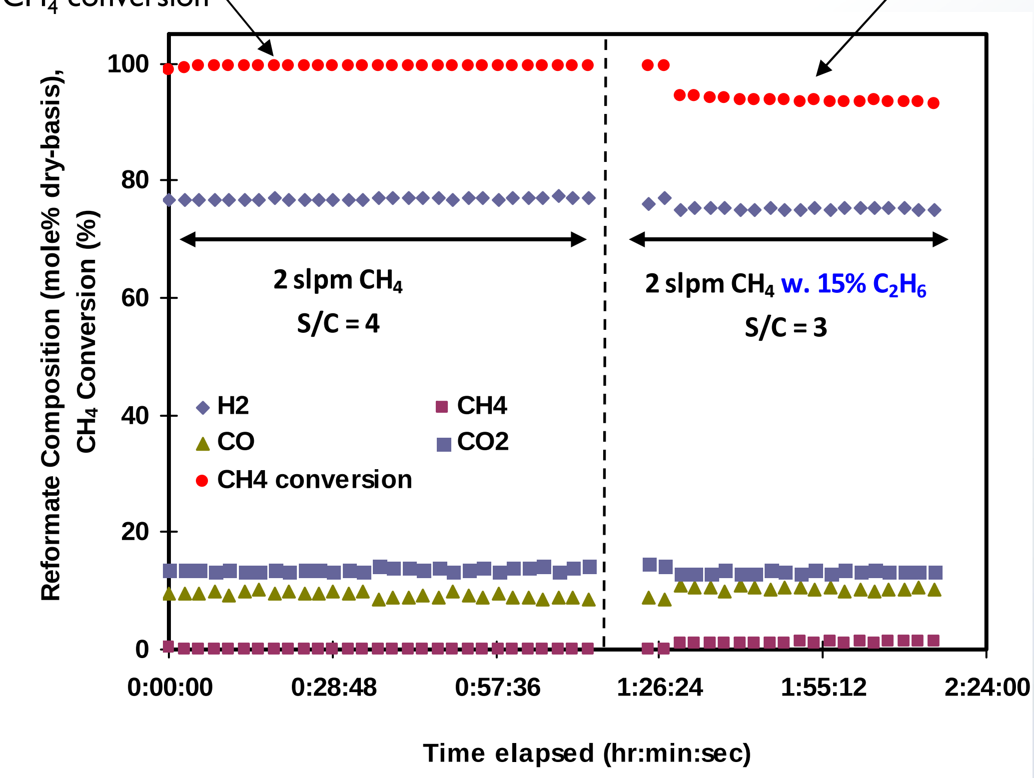
- 500-hr durability testing successfully completed (one catalyst w/o regeneration/replacement)
- Operated both CSR & burner w. 2 ppm_w sulfur synfuel for 450 hrs (50 hrs w. n-C12)
- Stable CSR reformate w. ~70 mol% H_2 (dry basis)
- Product composition in good agreement w. thermodynamic prediction

CSR exptl data at 1.5 kW_{th} and 1 atm vs. thermodynamic equilibrium

	Exptl Product Mol%, St/C=3.0, P = 1 atm	Equilibrium Mol%, St/C=3.0, 1 atm, 650°C
H_2	69-71	70.8
CO	10.7-14.0	11.8
CO_2	14.0-19.3	15.6
CH_4	0.8-4.0	1.9
LHV-based efficiency (w. CH_4)	~119% (synfuel)	115%

Methane/Natural Gas Steam Reforming

- Steam Reformer (Endothermic) side: Methane @ 1.1 kW_{th} and S/C of 3 – 4
- Burner (Exothermic) side: liquid fuel (synfuel S-8 w. 2-5 ppm_w sulfur)
- Stable CSR reformate w. ~75 mol% H_2 (dry basis)


Complete CH_4 conversion

~93% CH_4 conversion w. complete C_2H_6 conversion

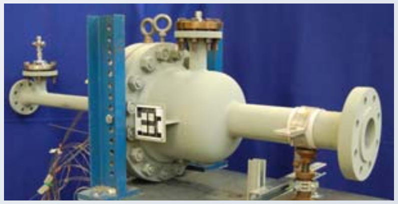
CSR Scale-up: 7-10 kWth Operating at 10 atm

7-10 kWth CSR for up to 10 atm operation w. low sulfur diesel and distillate fuels

- CSR prototype consists of catalytic exothermic (burner), catalytic endothermic (CSR), St. Gen Hex & mixer.
- Catalytic burner instead of flame-stabilized burner increases thermal uniformity, distribution, durability & control.

Summary

- Auto Thermal Reforming (ATR) – *Diesel*:
  - Compact package w. high reforming efficiency (up to ~85%)
  - Water neutral operation feasible via AGR & condensation approaches
  - Demonstrated nozzle with air pressure drop for reduced parasitics
  - Rh-pyrochlore catalyst development shows potential for cost-effective reforming
    - Successfully coated NETL pyrochlore onto Microlith substrate; more tests ongoing
  - Scaled-up to 1 MWth reactor for reforming of diesel & distillate fuels
- Catalytic Partial Oxidation (waterless CPOX) – Diesel & natural gas:
  - Stable, long-term operation in a compact, simple package.
  - Scaled-up to 5 MWth reactor for natural gas reforming



- Catalytic Steam Reforming (CSR) – Diesel & natural gas:
  - Catalytic oxidation & endothermic design w. high heat flux – compact reactor
  - Stable, long-term operation w. distillate fuels (S-8) w. 3 – 5 ppm sulfur
  - Scale-up to 7.5 kWth is ongoing

Acknowledgment

We are grateful to the DOE and ONR for their support,

And

The engineers and technicians at PCI.