DOE Hydrogen Program

Integrated Short Contact Time Hydrogen Generator (SCPO)

2008 DOE H2 Program Annual Review Meeting

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GE Global Research Center

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Project ID # PDP17

Overview

Timeline

Project start date: 05/30/2005
Project end date: 10/31/2008
Percent complete: 90%

Budget

Total project funding
- > DOE share: $2.6M
- > Contractor share: $1.4M

Funding received in FY05: $490K
Funding received in FY06: $400K
Funding received in FY07 : $1.37M
Funding received in FY08 : $0

No-cost extension granted to 10.31.08

Barriers

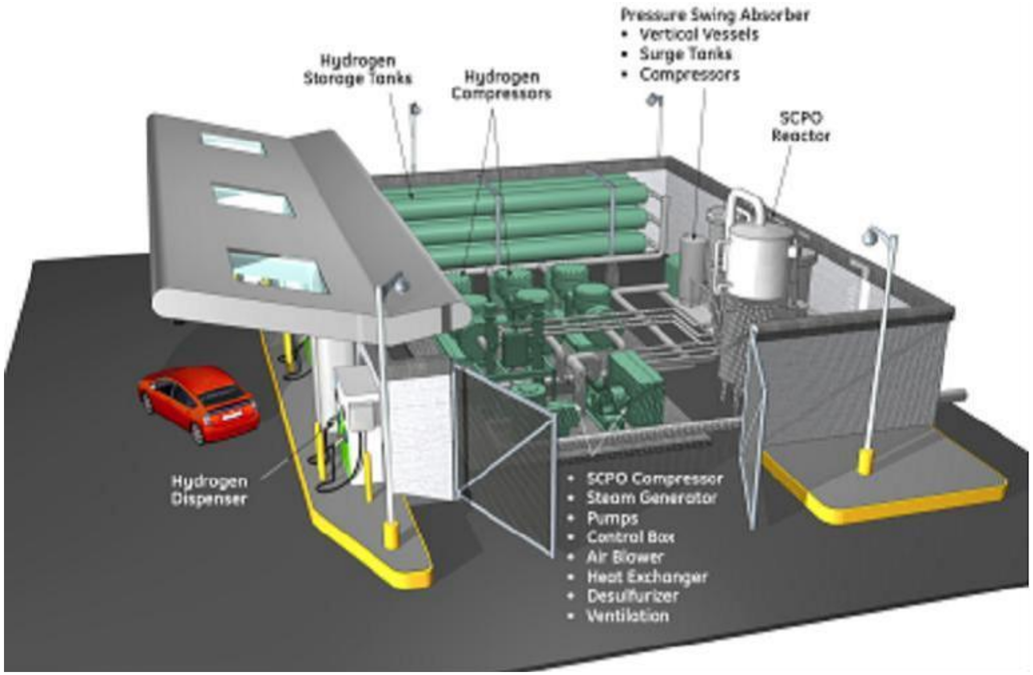
- Technical Barriers Addressed:
  - A. Cost of Fuel Processor
  - C. Operation and Maintenance (O&M)
  - D. Feedstock Issues
  - E. Catalyst sulfur tolerance & durability
- Technical Targets (2010):
  - Total Energy Efficiency (%LHV) > 75%
  - Total H_2 Cost $2.00-$3.00/gge H_2

Partners

- University of Minnesota
- Argonne National Lab

Objectives

The main objective of the SCPO project is the development of a low-cost, compact reforming technology that is fuel flexible; developed to operate on on fossil fuels but adaptable to renewable fuels.



•This technology integrates three catalysts into a single compact reactor: catalytic partial oxidation (CPO), steam methane reforming (SMR), and water gas shift (WGS).

•Demonstrated via testing of high-pressure pilot-scale CPO, SMR and WGS reactors in GE Global Research's lab at Irvine, California.

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Approach

Project Team

GE Global Research

Energy and Economic Analyses, HTS Catalyst Development, Pilot-Scale System Design/ Fabrication/Operation, and Overall Project Management

University of Minnesota

Short Contact Time Catalyst Identification, Preparation, and Parametric Testing

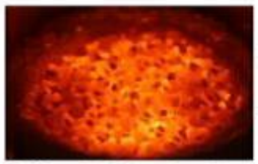
ARGONNE

Argonne National Lab

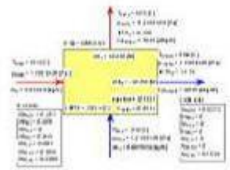
Catalyst Durability, Lifing and Characterization

3-Year, $4-Million Program to Develop a Compact Integrated Hydrogen Generator Based on SCPO Technology

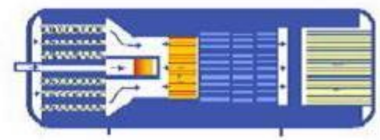
Project Objective: *To develop a compact hydrogen generator that can deliver H_2 at a cost of <$3.00/Kg with >75% efficiency*



Short Contact Time Catalyst Development



System Design and Analysis



Pilot-Scale System Design and Operation

Technical Approach

- Develop short contact time catalysts
- Design compact integrated reformer based on SCPO technology
- Demonstrate feasibility of the concept on a pilot-scale system

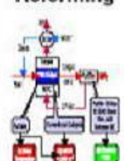
Anticipated Benefits

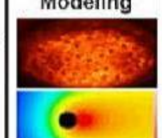
- Revolutionary, compact, highly efficient and low cost H_2 generation technology
- Applications in H_2 refueling stations and coproduction of H_2 and electricity with CO_2 separation

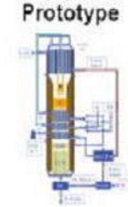
Program Deliverables

- Short contact time reforming and shift catalysts
- Pilot-scale H_2 generator meeting DOE targets

Current	Short Contact Time Catalyst Screening	Lab-Scale Short Contact Time Catalysts	Bench-Scale Catalyst Development and SCPO Prototype Demonstration	SCPO System Scale-Up and Commercialization
Conventional Reforming	UoM, ANL, GE Catalyst Testing	UoM, ANL, GE Catalysts and Process Modeling	GE SCPO Prototype	Hydrogen Generator



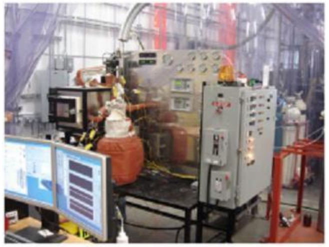


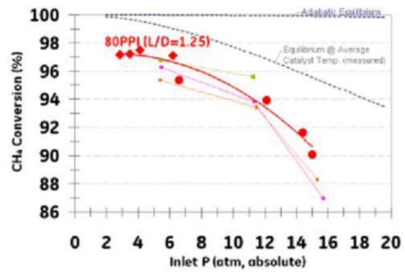


Development of SCPO Based Hydrogen Generator

SCPO & Warm Gas Cleanup 2007-2008 Major Milestones

Catalytic Partial Oxidation (CPO)





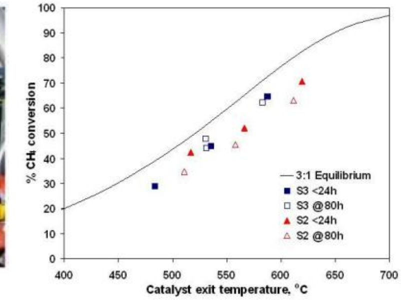
•Prepared catalyst test samples for in-house and Premix tests and compared to commercial formulation

•Completed 40 experimental runs in CPO system up to 500kh^{-1} GHSV and 275 psig. (70Kg/day H_2 production level)

•Completed screening, spatial profiling, and sulfur exposure tests

•Integrated results into modeling efforts for cost analysis and Gas Turbine integration systems analysis

Steam Methane Reforming (SMR)



•Completed design, construction and shakedown of combined SMR/WGS system in 2007

•Completed precious metal and nickel based SMR catalyst screening, long term testing, and sulfur tolerance at Argonne National Lab

•Completed SMR system large scale demonstrations at FCL

•Integrated results into heat transfer modeling

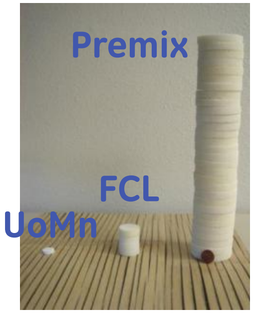
Premix design for CPO/Gas Turbine

•Designed, fabricated reactor & premixer

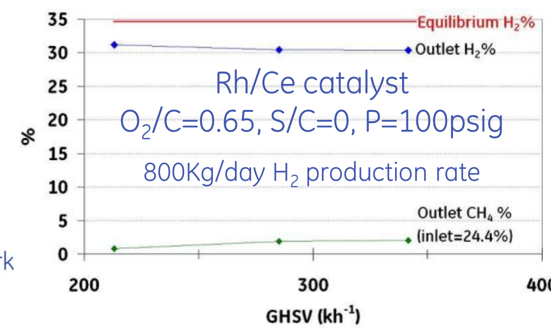
• Retrofitted experimental facility with reactor

• Completed test matrix from 250-500 kh^{-1} GHSV at different steam concentrations

•Achieved near equilibrium H_2 production



Relative Test Size



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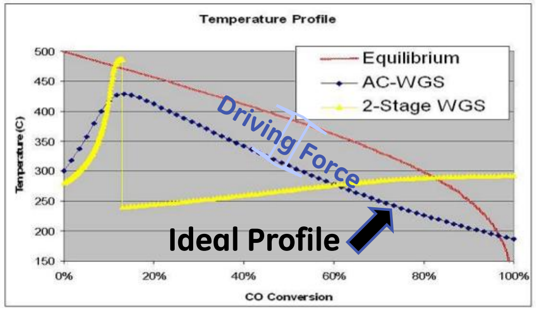
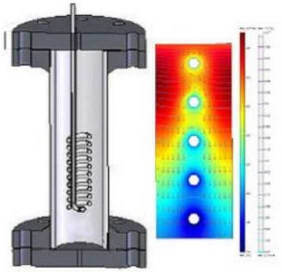
Water Gas Shift (WGS)





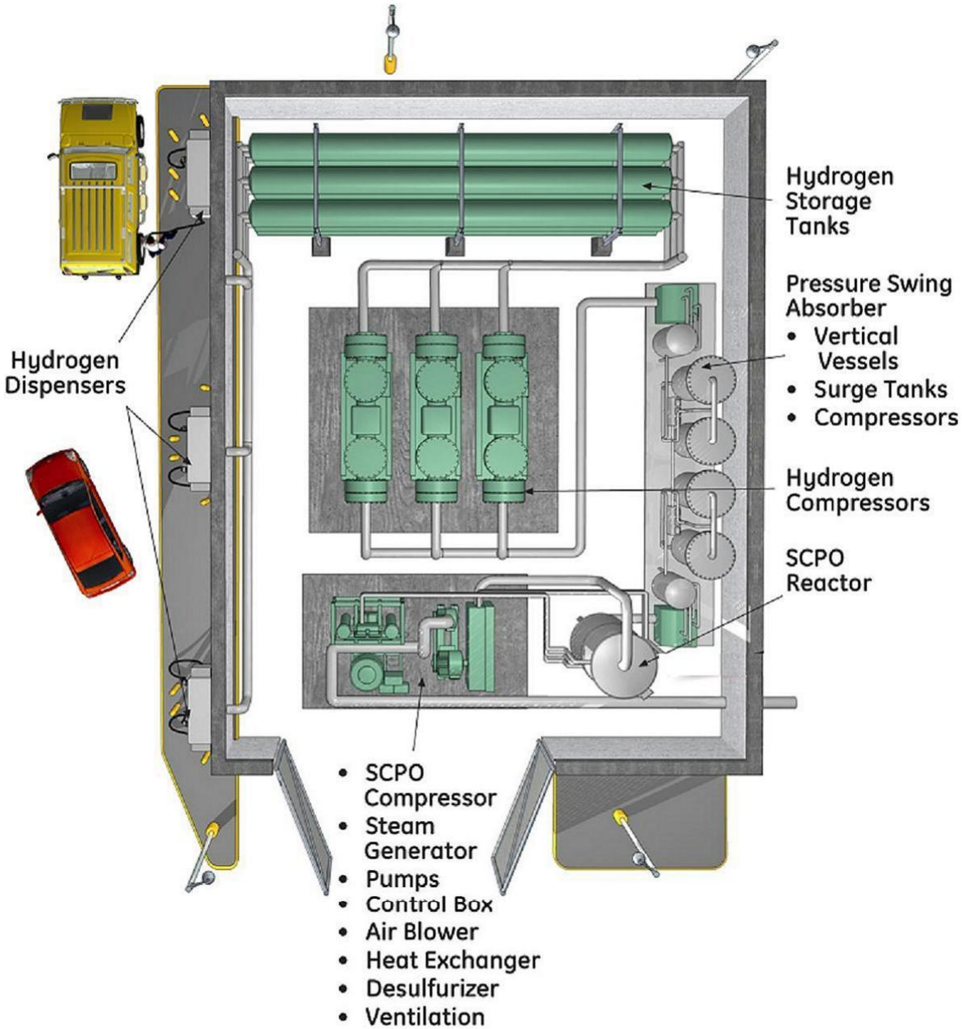
Residence Time (s); Proportional to vessel size & catalyst loading

•Completed design, system modeling and reactor fabrication

•Completed WGS catalyst screening at Argonne National Lab

•Completed aggressive HAZOP review for 2007 and baseline WGS catalyst testing

Distributed Hydrogen Fueling Station Using GE SCPO Technology



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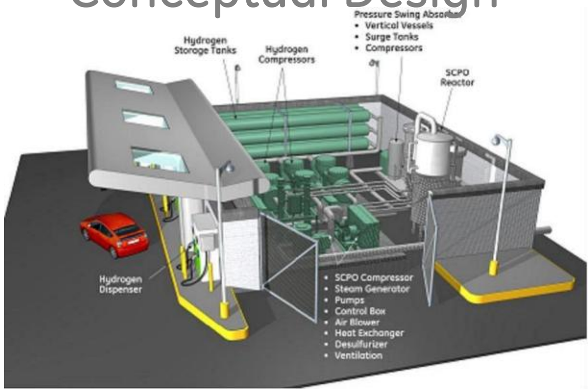
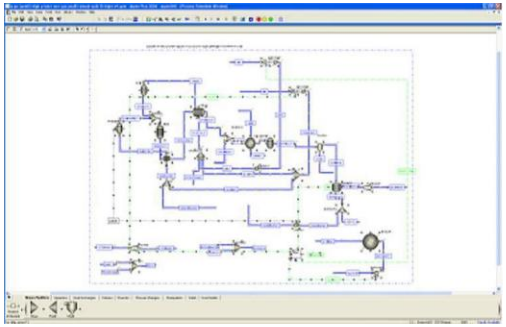
SCPO Cost of Hydrogen Estimation Approach

Conceptual Design



Process Evaluation (Assumptions)



Updated CPO Performance w/ Experimental Data

	Prior Assumption	Experimental
SCPO Conversion	99.56%	98.18%
SMR Conversion	74.16%	79.10%
Production Unit Hydrogen Efficiency (%)	73.0%	75.4%
Production Step Efficiency (%)	70.3%	72.5%
Total System Efficiency (%)	66.5%	68.5%

H2A Model

$ Technology Economics

Updated Cost of Hydrogen:

$3.025/kg

CTQ

Catalyst & Process R&D

DOE deliverables met in 2008

Project continues to develop and demonstrate CPO catalyst technology

Cost of Hydrogen Updates

	Prior Assumption	Experimental
SCPO Conversion	99.56%	98.18%
SMR Conversion	74.16%	79.10%
Production Unit Hydrogen Efficiency (%)	73.0%	75.4%
Production Step Efficiency (%)	70.3%	72.5%
Total System Efficiency (%)	66.5%	68.5%
Hydrogen Selling Price and Cost Contributions (Year 2005 $)		
	Previous H2A	Updated H2A
Required Hydrogen Selling Price ($(Year 2005)/kg of H2)	$3.052	$3.025
Capital Costs ($/kg of H2)	$1.384	$1.384
Fixed O&M ($/kg of H2)	$0.578	$0.578
Feedstock Costs ($/kg of H2)	$0.828	$0.802
Other Raw Material Costs ($/kg of H2)	$0.000	$0.000
Byproduct Credits ($/kg of H2)	$0.000	$0.000
Other Variable Costs (including utilities) ($/kg of H2)	$0.262	$0.261

Aspen model of the SCPO system was updated using the SCPO and SMR experimental data ➔ Updated H2A cost analysis

GE Test Facilities

Controlled and Monitored Gas Delivery

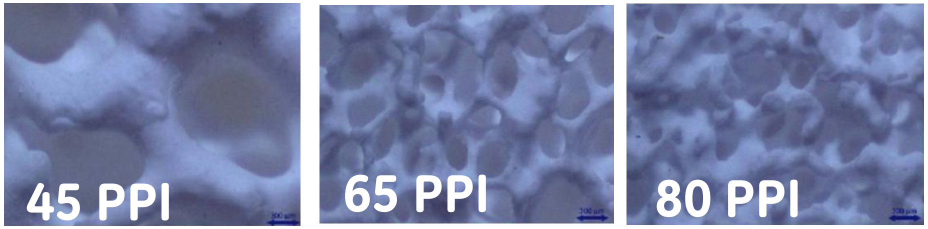
Steam Methane Reforming (SMR)

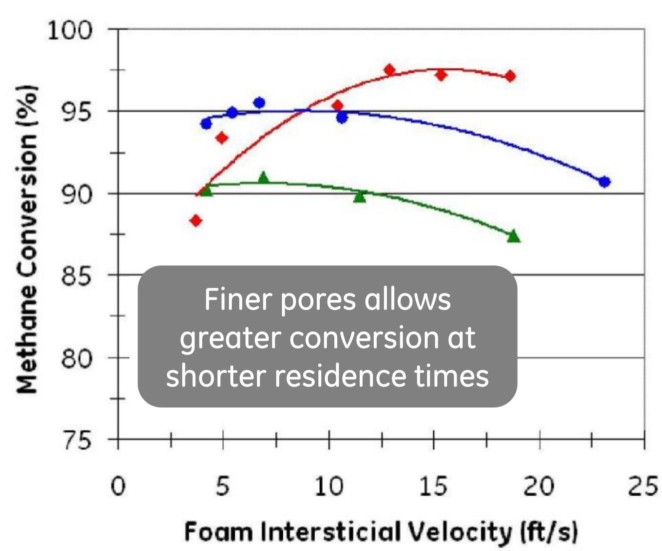
Catalytic Partial Oxidation (CPO)

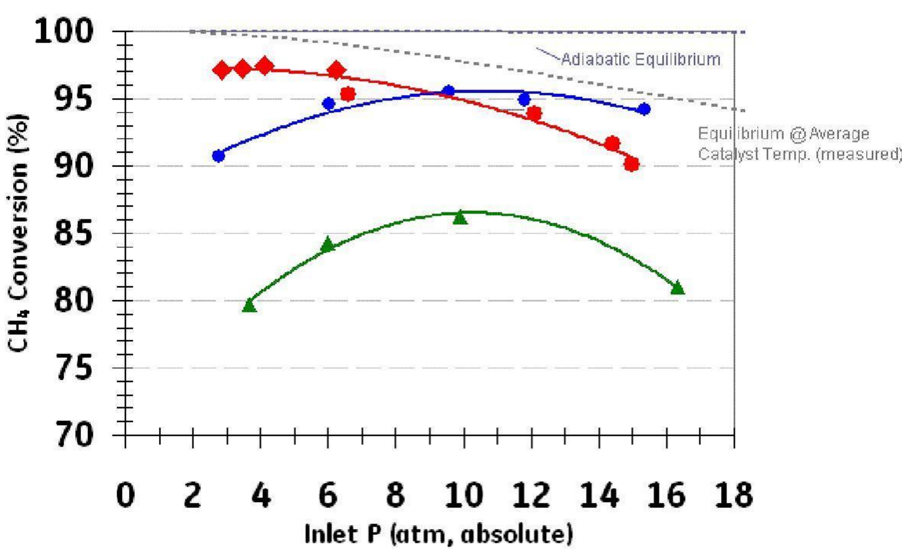
Water-Gas-Shift (WGS)

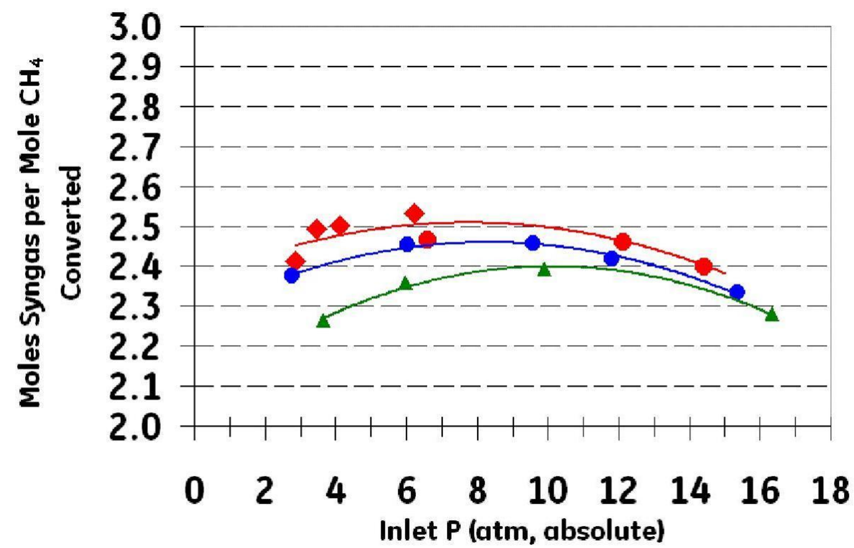
Task 1 Premix CPO and Sulfur Tolerant Catalysts

CPO Catalyst Performance Versus Structure

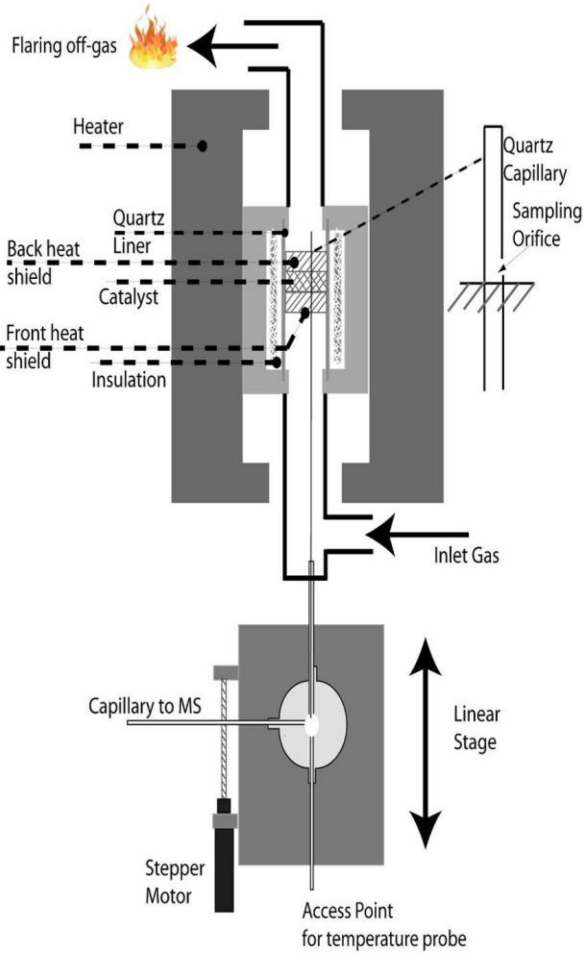




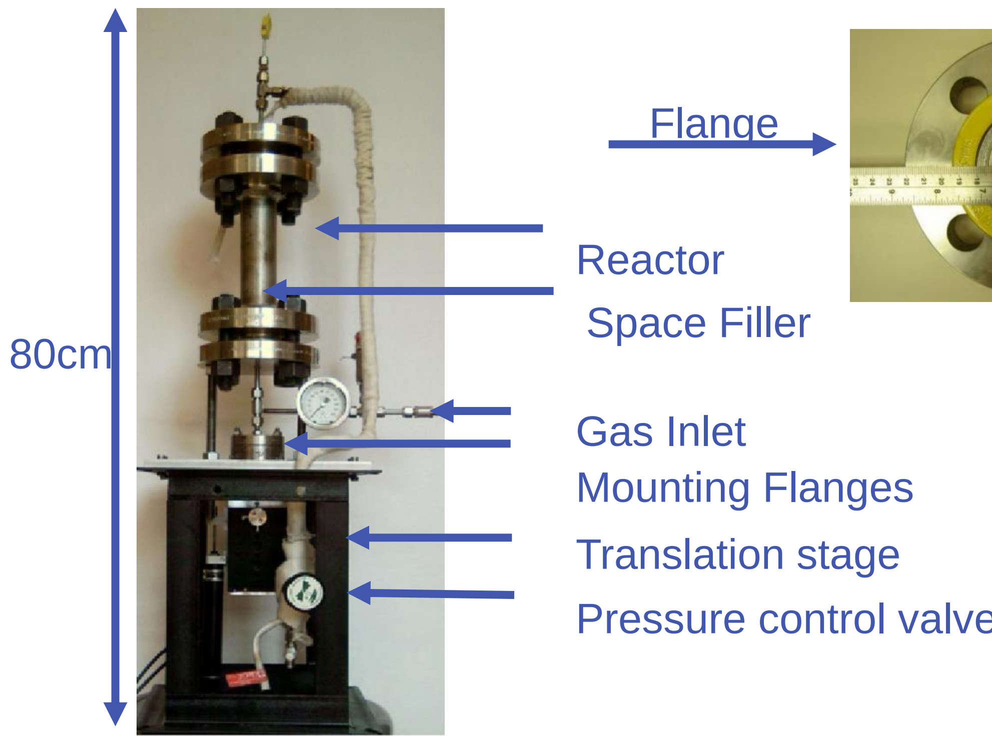


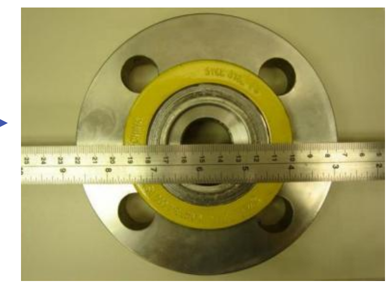


Spatial Profiles Inside the Foam Catalyst



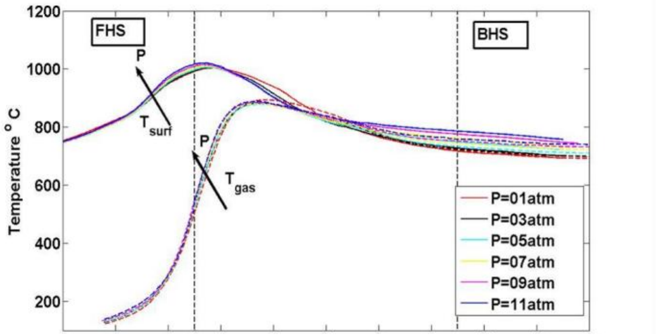
- Developed a system that allows to *in situ* sampling in a system with very high temperature and species gradients
- Unprecedented spatial resolution (~300μm) on the order of the characteristic length of the support
- Sampling method introduces minimal disturbance in flow. Sample rate 10ml/min, total flow 5000ml/min
- Analysis is done by mass spectroscopy which is continuously calibrated by gas chromatography

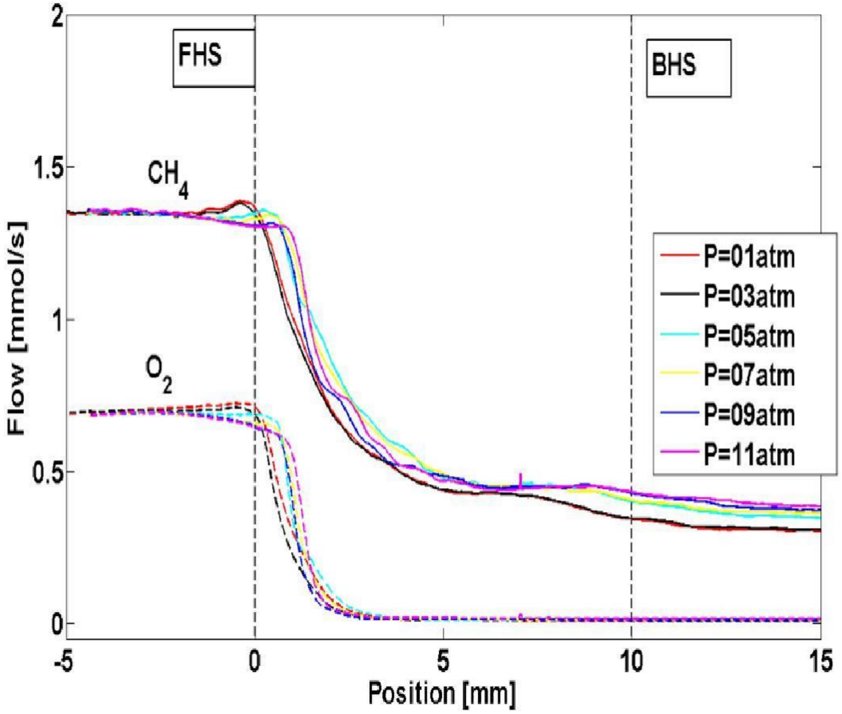


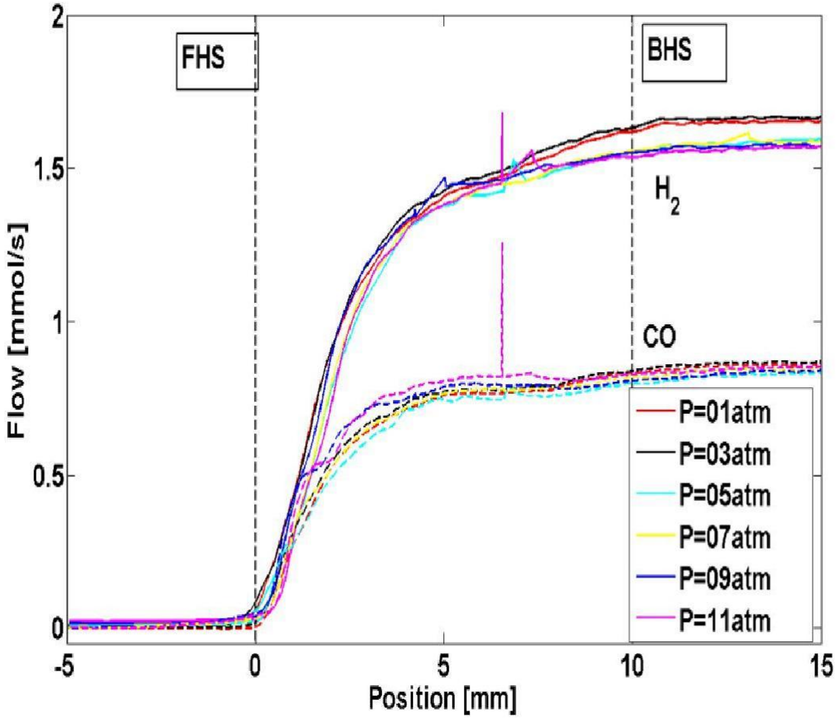


Temperatures and Species at GHSV 164,000h^{-1} O_2/C=0.5

- The effect of pressure is not great

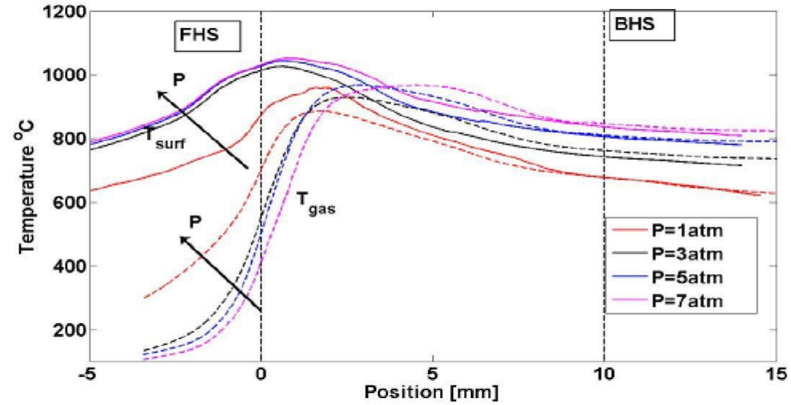


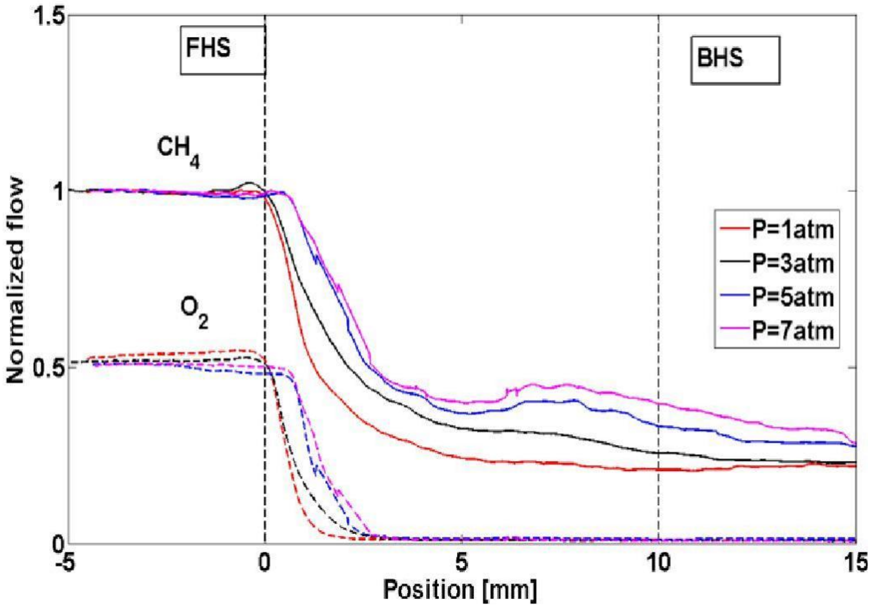


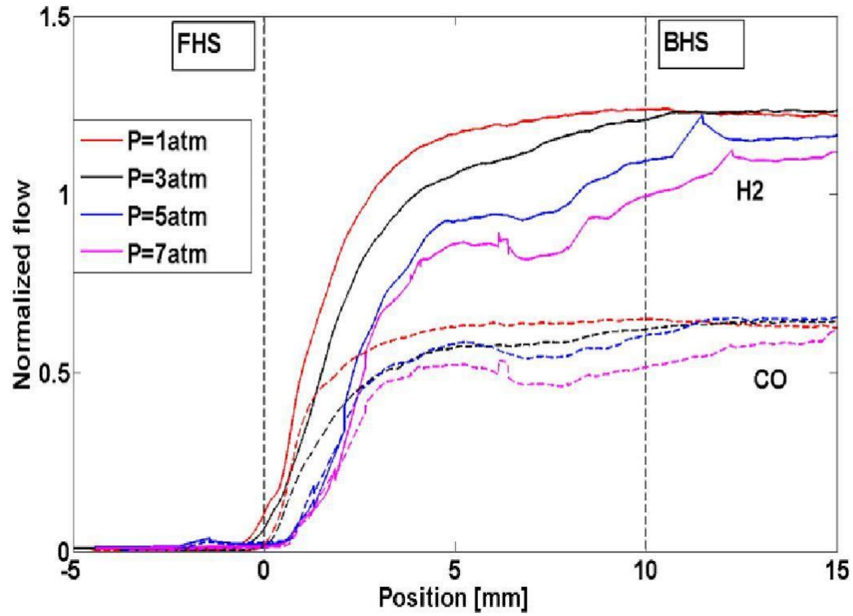


Constant Inlet Velocity

- Oxidation zone varies as expected with changes in pressure







Mass transfer effects

$$Sh = \frac{k^m L}{\mathscr{D}} = cRe^a Sc^b$$

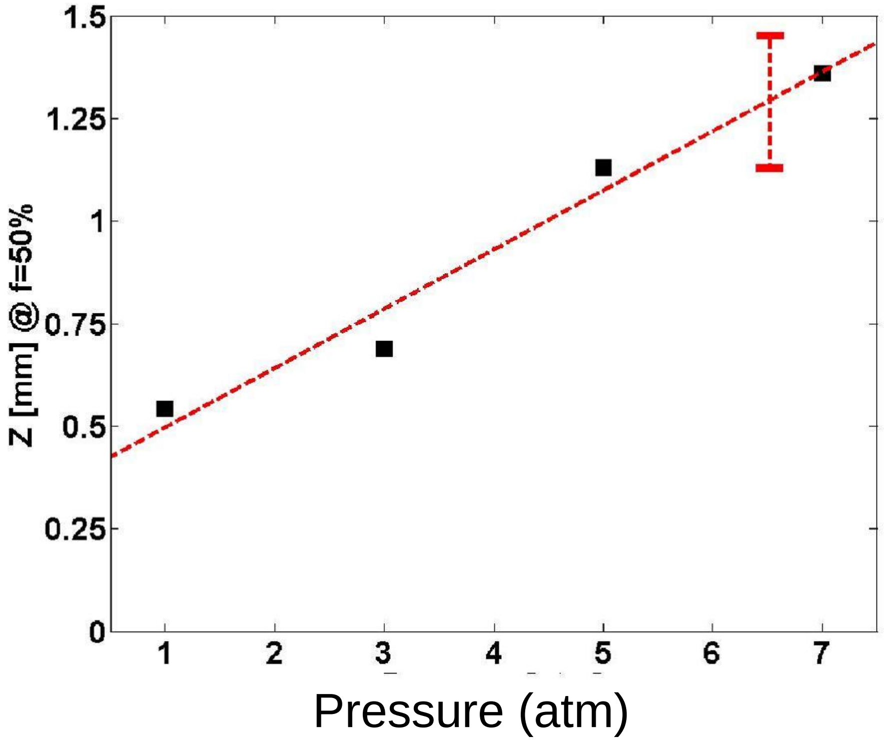
$$Sh \propto \left(\frac{1}{\sqrt{T}}\right)^a$$

$$-\frac{\mathrm{d}Y_{O2}}{Y_{O2}} = \frac{S}{V}\frac{k^m_{O2}}{u}\mathrm{d}z$$

$$z = \ln\left(\frac{1}{f}\right)\frac{V}{S}\frac{\overbrace{\bar{u}}^{Constant}}{k^{\bar{m}}_{O_2}}$$

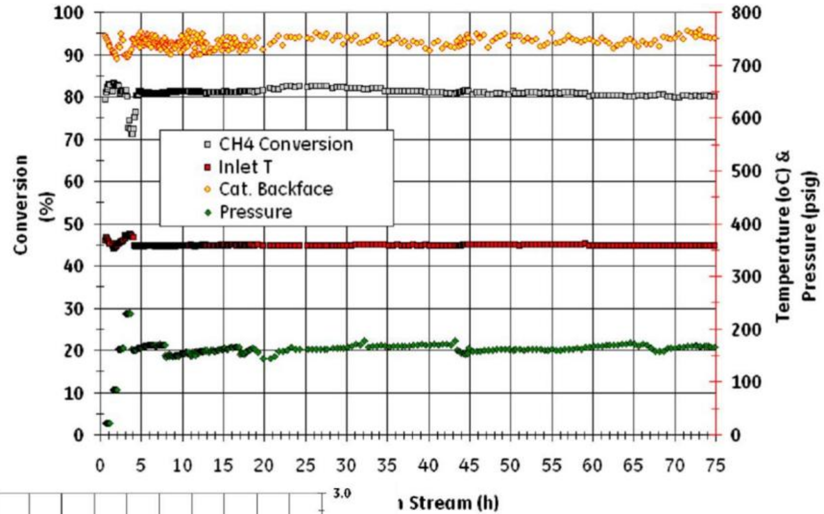
$$z \propto \frac{P}{T^{\frac{3}{2}-\frac{1}{2}a}} \sim P$$

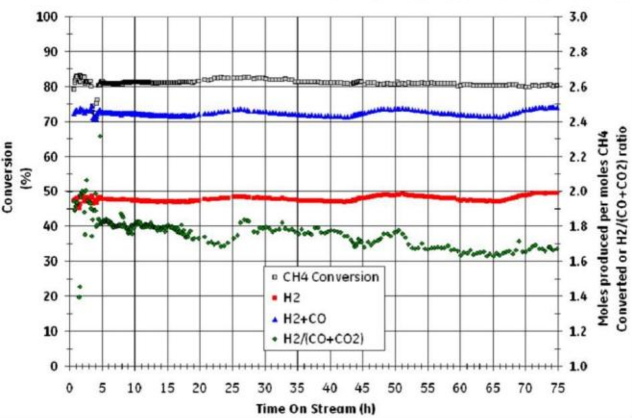
- Point of 50% oxygen conversion is predicted

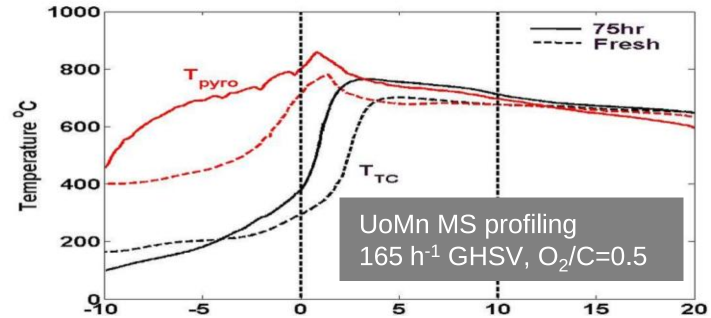


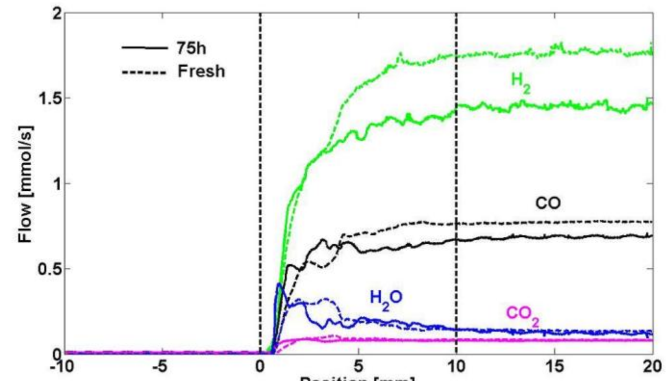
CPO short term life testing followed by mass spec profiling

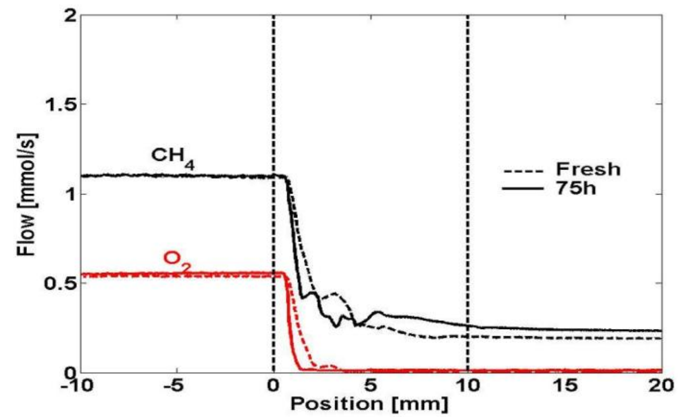
75 hour life test of GE baseline catalyst: 80 PPI pre-capillary drilled, L/D=0.65
Conditions: 500,000 h^{-1} GHSV, S/C=1, O_2/C=0.67











No significant changes seen through catalyst profile after 75 hours online with no sulfur;

However, profiling shows the catalyst seems to be losing steam-reforming capability most likely due to phase transformations in the γ-alumina wash coat.

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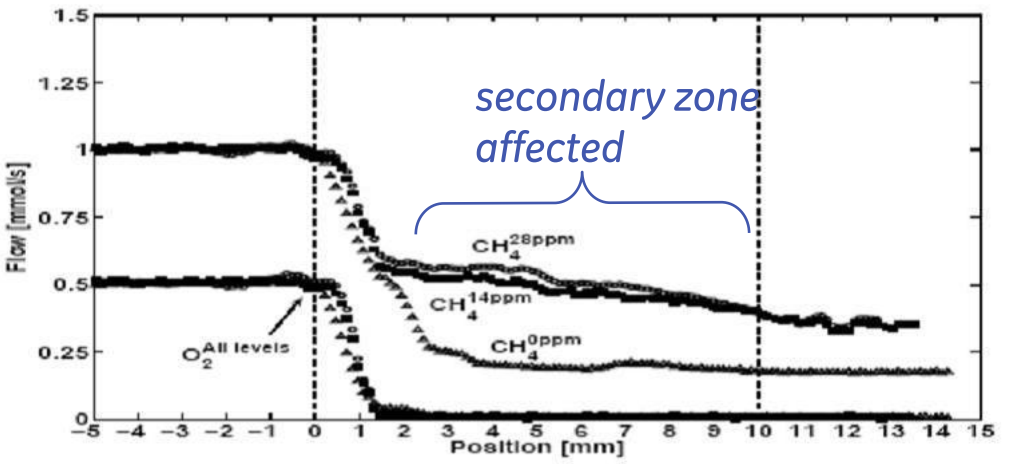
Effect of Sulfur on CPO

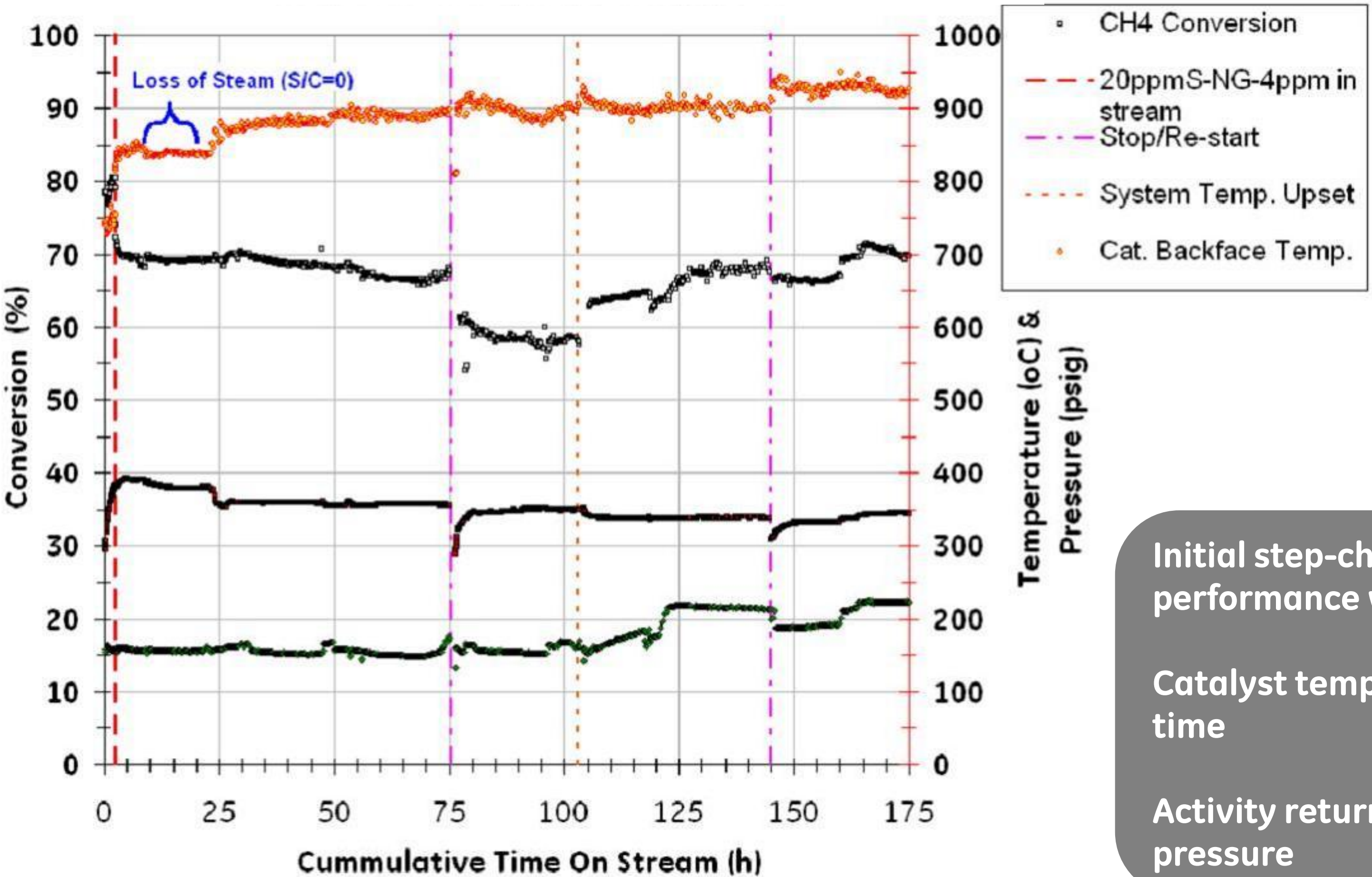
UoMn data shows that sulfur inhibits the steam reforming zone, but *is steady over 50 hours* of testing with CH_3SH

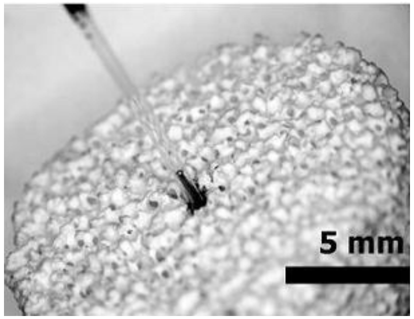
GHSV 1.4×10^5 h^{-1}. C/O=1.

	0 ppm	14 ppm S	28 ppm S
X_{CH4}	83%	68%	65%
X_{O2}	100%	100%	100%
$S_{H,H2}$	89%	79%	76%
$S_{C,CO}$	91%	90%	88%
$S_{C,CO2}$	9%	9%	9%



Longer term CPO performance with sulfur





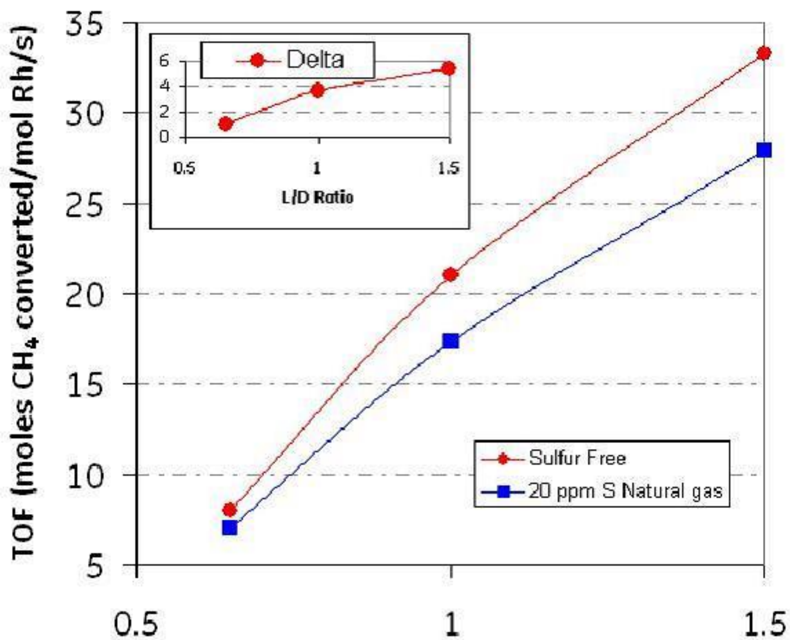
Initial step-change loss in performance with sulfur.

Catalyst temperature rising with time

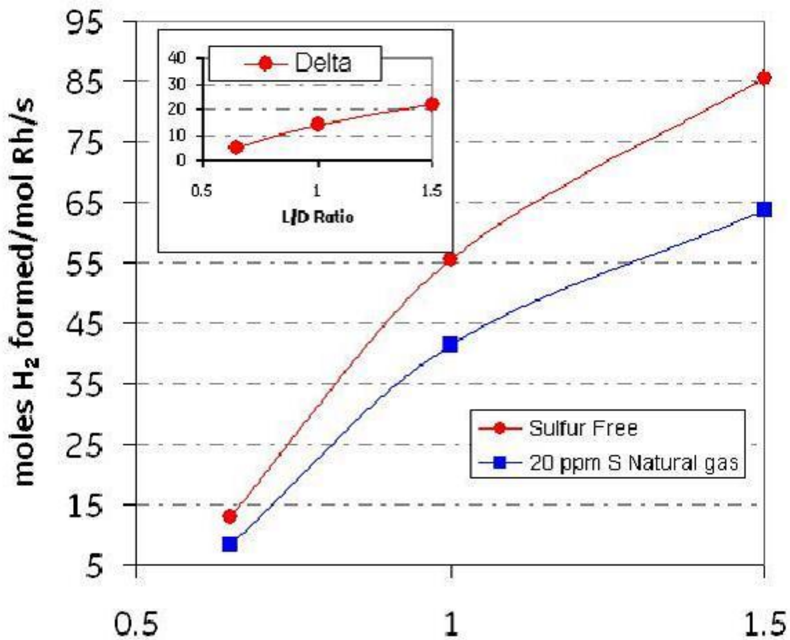
Activity returned with increase in pressure

Methane turnover and hydrogen formation in CPO with and without sulfur:

GE baseline formulation



Different Catalysts



Different Catalysts

We are evaluating step-loss in performance as well as longer term deactivation

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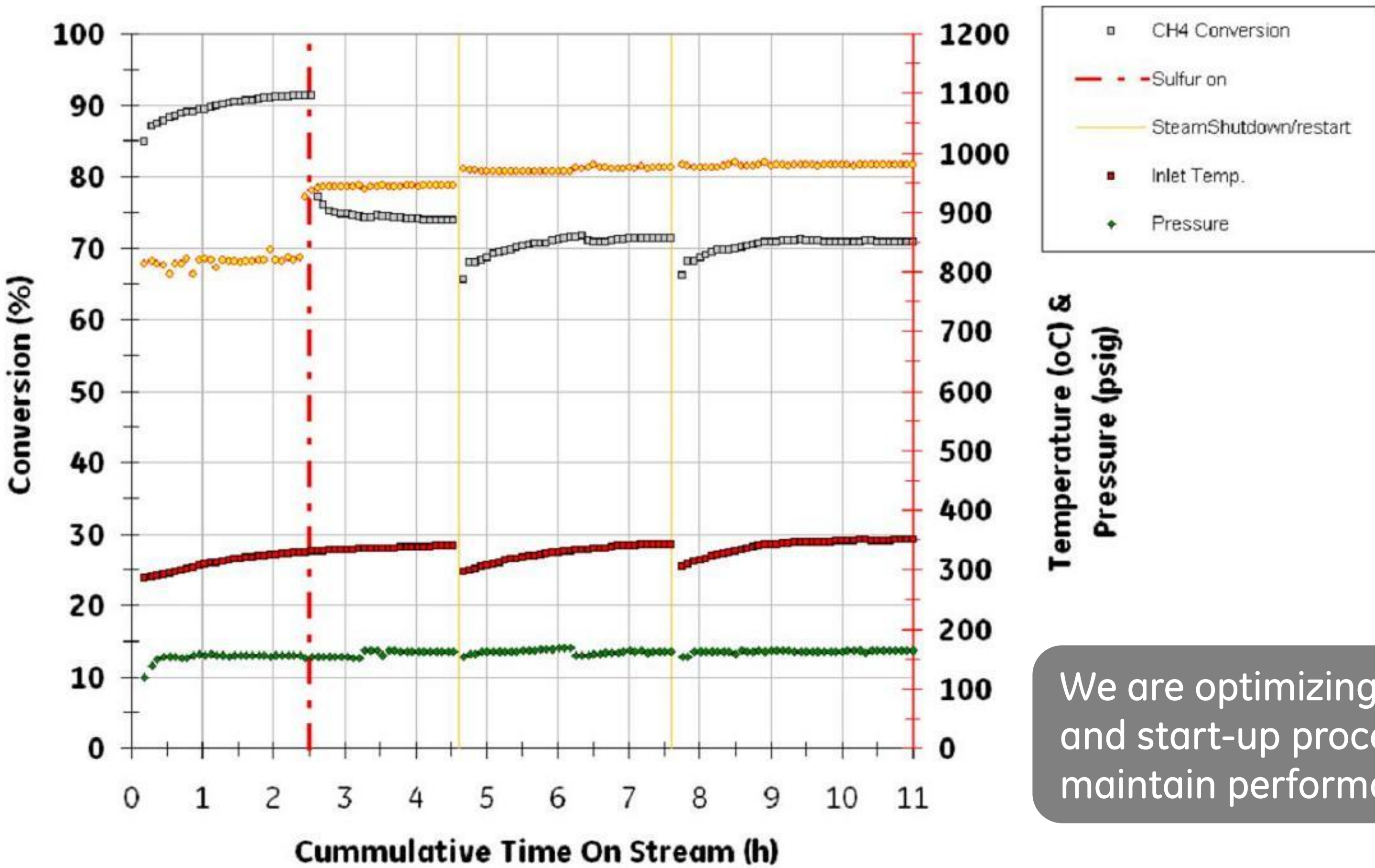
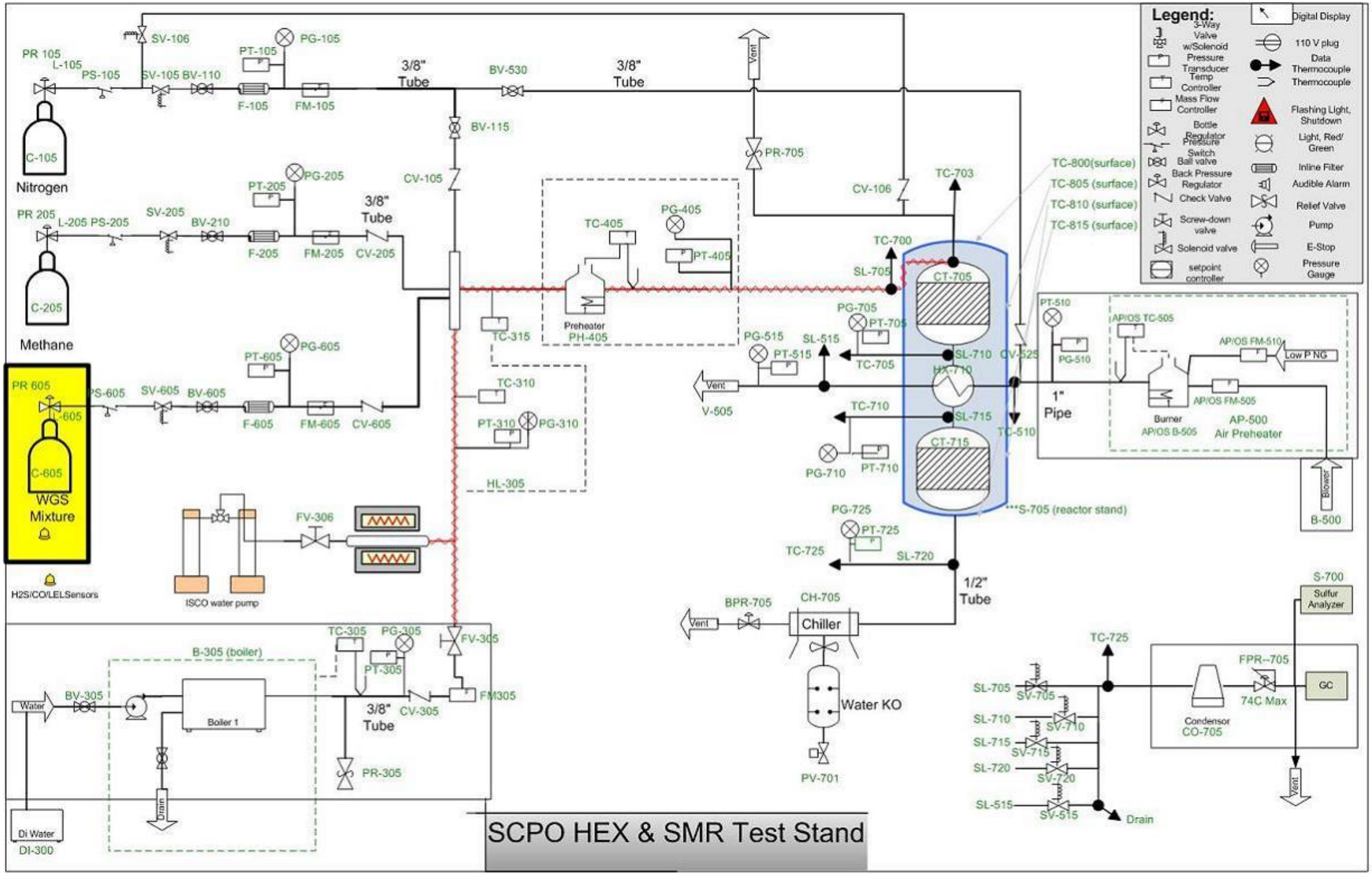
Optimizing start/stop CPO behavior in the presence of sulfur

CPO performance of GE baseline formulation using 20 ppm S simulated natural gas (Steamed stop/starts)

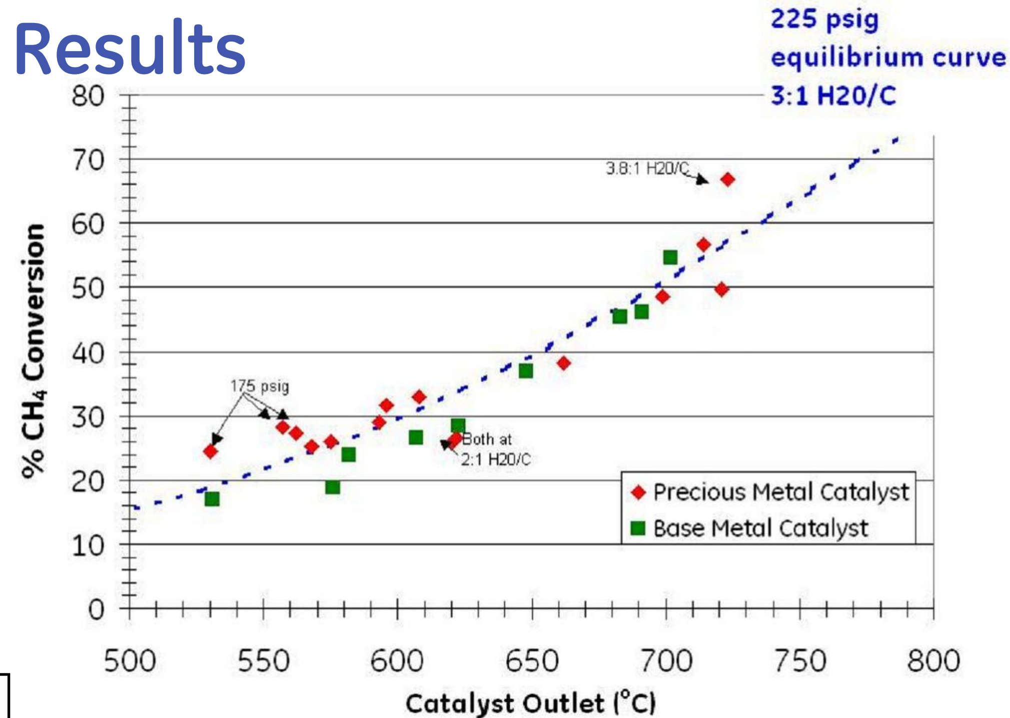


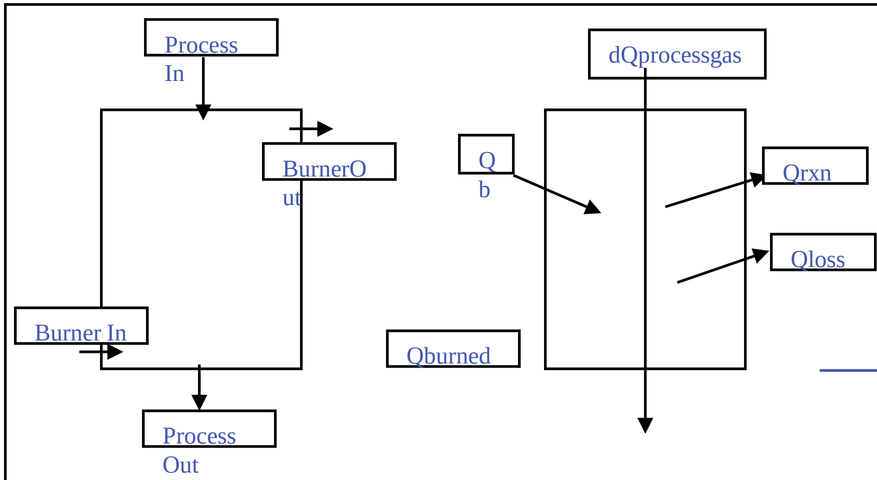
We are optimizing shutdown and start-up procedures to maintain performance

Task 2 & 3 SMR & Shift Experiments



Steam Methane Reforming Results

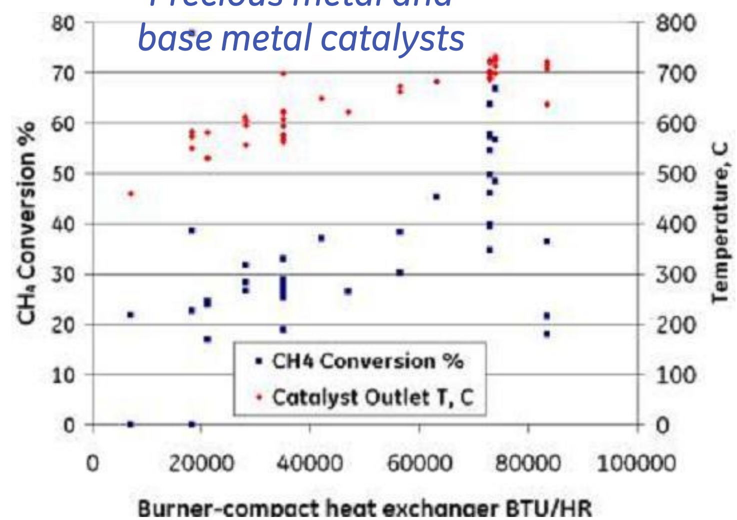




Heat lost by burner = Heat Loss + Heat to Reaction + Heat increase in process

Qb = Qloss + Qrxn + Qprocgas

Precious metal and base metal catalysts



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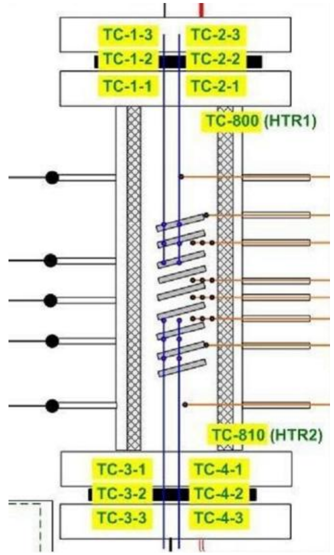
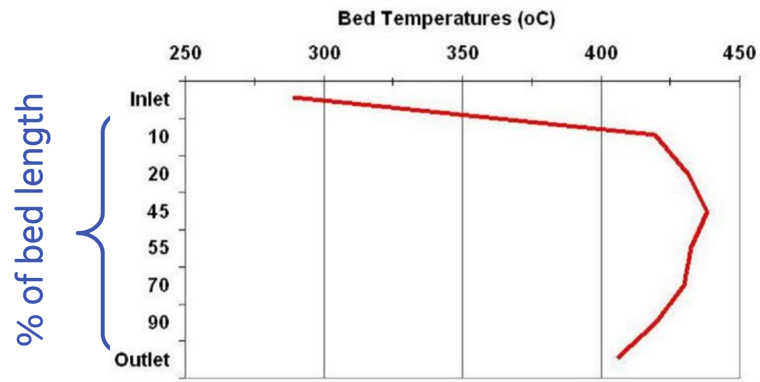
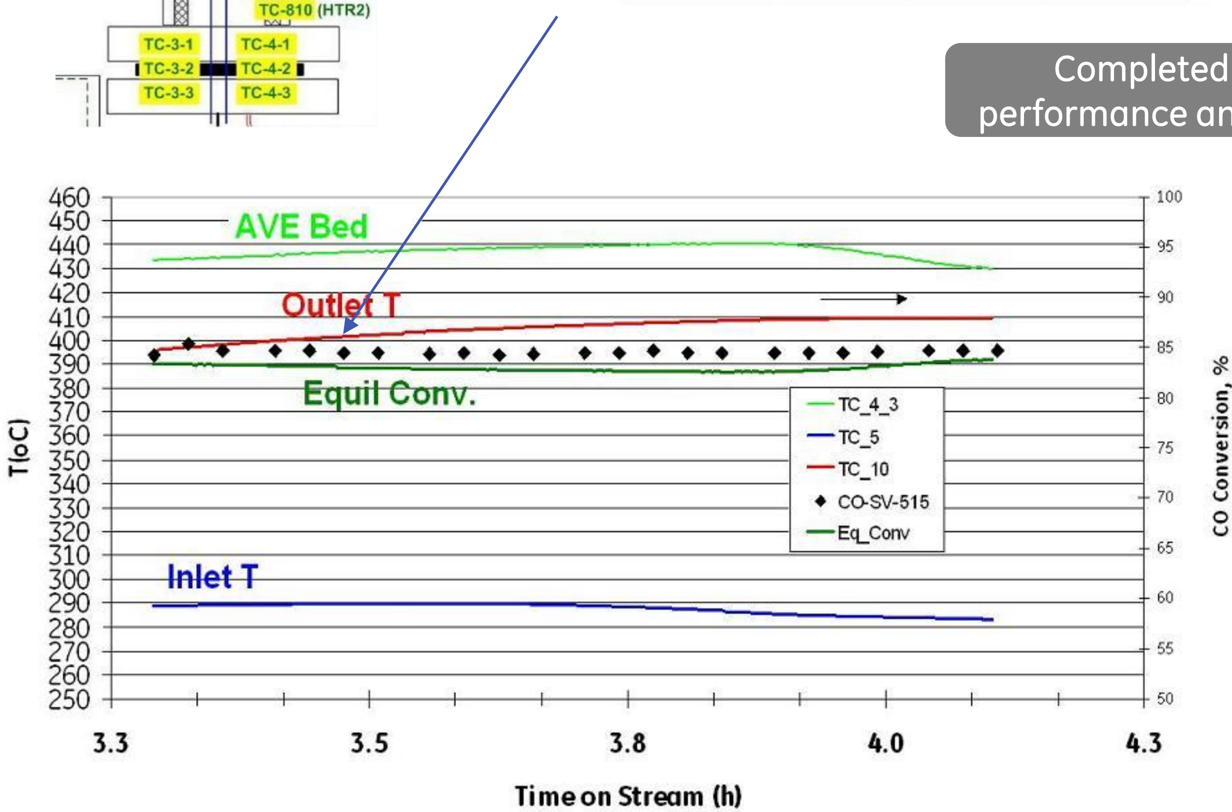
SMR testing reached equilibrium conversion and heat transfer correlated to performance

Task 3. Water Gas Shift Catalyst & Reactor Designs





Completed low GHSV WGS catalyst performance and heat balance tests in 2007



ANL – FY07 and 08 Workscope and Status

Steam reforming catalyst evaluation and development

> Precious metal catalysts (3 catalysts from vendor A; 2 catalysts from vendor B; and 3 catalysts from Argonne)
  - *Activity (*Status: completed*)*
    - Low temperature SMR conditions
    - High temperature SMR conditions
  - *Durability (*Status: completed*)*
    - Low temperature SMR conditions
  - *Sulfur-tolerance (*Status: completed*)*
    - Low temperature SMR conditions at 5 and 20 ppm H_2S
    - CPO extended sulfur test

> Base metal catalysts (4 catalysts from two commercial vendors)
  - *Activity (*Status: complete*)*
  - *Durability (*Status: complete*)*

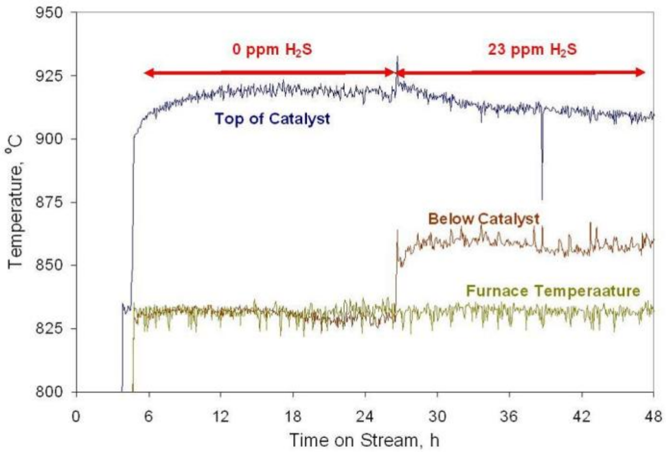
Water-gas shift catalyst evaluation

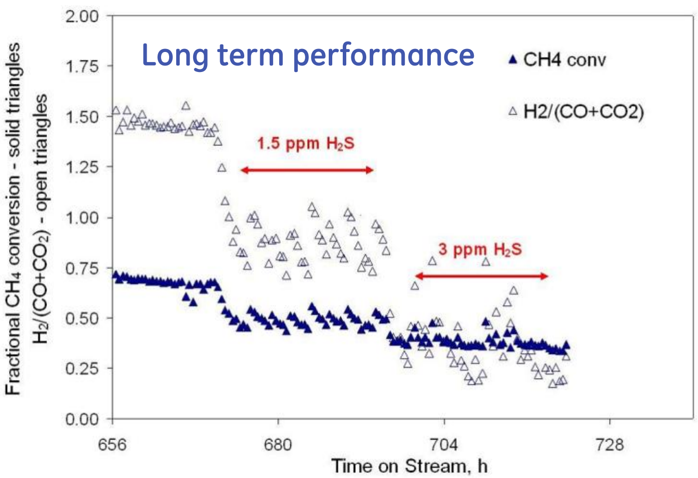
> Precious and base metals (1 PM and 1 base metal catalyst, two different vendors)
  - *Activity (*Status: complete*)*
  - *Durability (*Status: in progress*)*

WGS and SMR Catalysts Were Evaluated for Activity and Durability

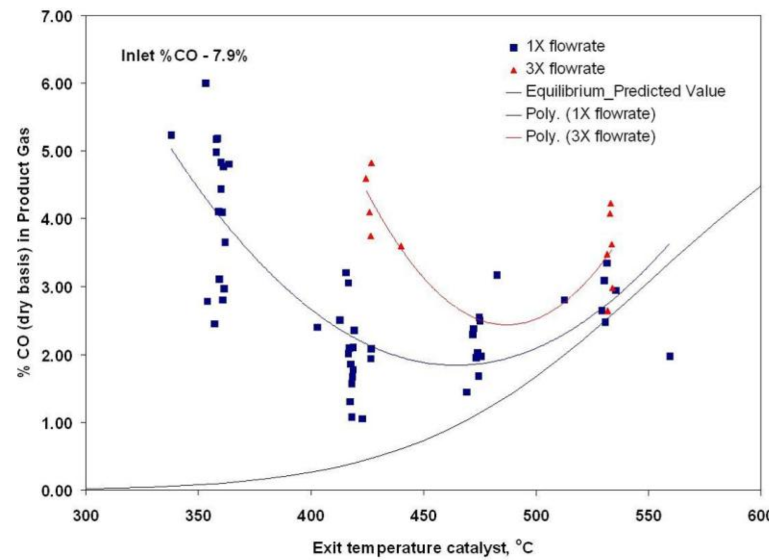
PM SMR Catalysts evaluated under CPO conditions

Temperature profile observed for a commercial PM SMR catalyst operating under CPO conditions





Activity - High Temp WGS Conditions



Activity was evaluated as a function of steam-to-carbon ratio (total carbon equal to the sum of CO, CO_2, and CH_4), temperature, and space velocity.

Durability was evaluated for SMR under CPO conditions, not acceptable for sulfur tolerance.

Identified the catalyst that exhibits the best combination of activity and durability for both SMR and WGS and validated kinetics.

imagination at work

Summary & Highlights

- Project extended to Oct. 31, 2008 for refined economics and CPO catalyst testing
- Completed SMR demonstration and kinetics validation
- Completed WGS demonstration and most of the kinetic data validation
- High-P CPO data obtained from our high-P CPO unit continues to synergize with UoMn characterization work.
- Initial work on sulfur tolerance is promising and we are characterizing activity loses
- Completed cost analysis using GE's process model & DOE's H2A model

  Economic analysis has been refined with new experimental data
- Base case catalysts identified, Reactor sizing / design completed.
- HEX technology tradeoff completed, HEX technology selected, design completed
- Control strategy, start-up & shut-down procedure being developed.

Conclusions & Recommendations

- SCPO will be a leading technology for H_2 production from NG. It is a cost-effective distributed H_2 production technology based on the economic analysis of different H_2 production technologies. With minor modification, we can extend the feed to gasoline, diesel, ethanol & methanol.

- The technologies developed in this program has good synergies with application in fuel blending, NGCC with CO2 capture, SOFC & syngas production for GTL….

Refinement of the system analysis for updated costs and further development of the CPO catalyst (sulfur tolerance) will be the focus points for the remainder of the project year.