

Integrated Short Contact Time Hydrogen Generator (SCPO)

2007 DOE H2 Program Annual Review Meeting

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imagination at work

Project ID # PDP9

Overview

Timeline

Project start date: 05/30/2005
Project end date: 05/30/2008
Percent complete: 38%

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: \$890K

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 H₂ Cost < \$3.00/gge H₂

Partners

- University of Minnesota
- Argonne National Lab



SCPO Program Highlights & Accomplishments in 2006

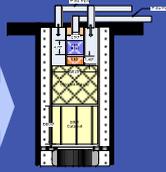
Project Overview



Laboratory



Large Scale



Demo

Technical Approach

- Develop S-tolerate Short Contact Time CPO & SMR Catalysts
- Design Compact Reformer System (SCPO)
- Demonstrate Critical Components



- Designed, built, shakedown high-P CPO unit
- Tested CPO catalysts use both NG & Diesel
- Design & build the integrated SMR&WGS reactor
- System analysis and design
- Economic analysis
- Develop new bio-liquids reforming program
- Coordinate R&D activities GE, ANL & UoM, and report to DOE the progress quarterly.



Project Objective

To Develop a Compact Hydrogen Generator that can Deliver H₂ at a Cost of <\$3.0/kg



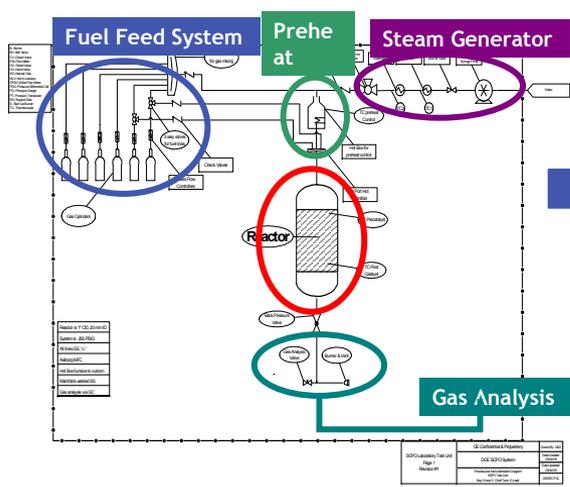
- S-tolerate CPO catalyst discovery
- S-tolerate CPO catalyst development
- CPO catalyst characterization: XRD, XPS



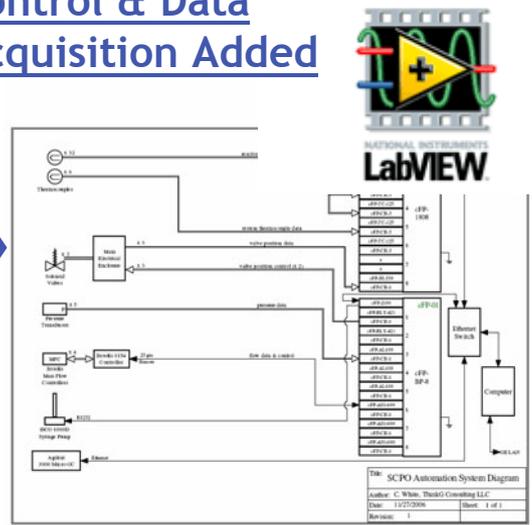
- SMR catalyst discovery
- Vendor CPO & SMR catalyst screening
- CPO & SMR catalyst durability test w/wo sulfur dope
- SMR & CPO catalyst characterization

Task 1: Premix CPO with Sulfur Tolerate CPO Catalyst

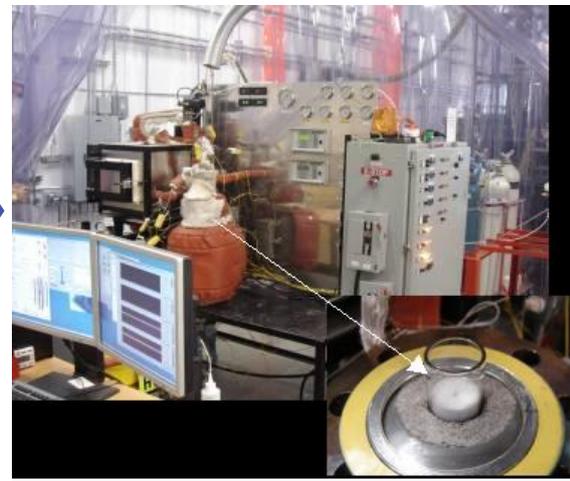
System Designed



Control & Data Acquisition Added



System Constructed



Test in 2007

Status

- Completed the shake-down and started the high-P CPO tests
- Two catalysts tested at diff conditions, high quality data obtained.

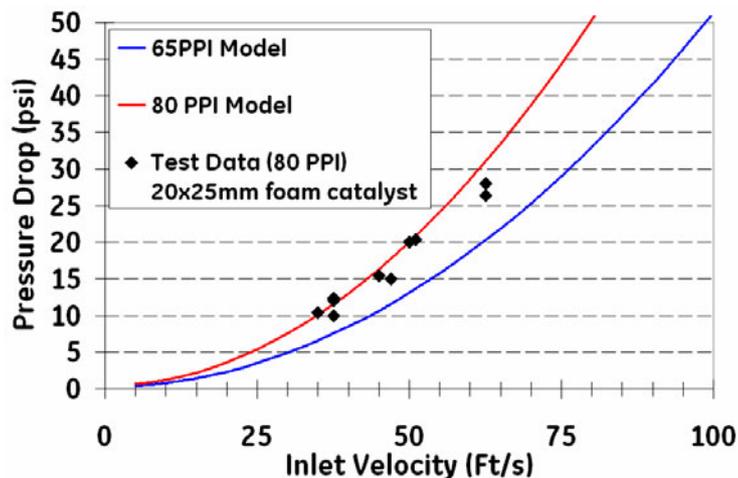
Plans:

- Heavy usage in Q1 of 2007
- Integration with Mixer
- Integration with SMR & WGS

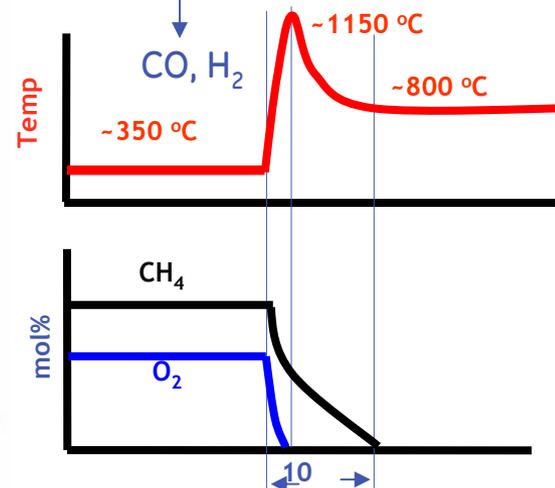
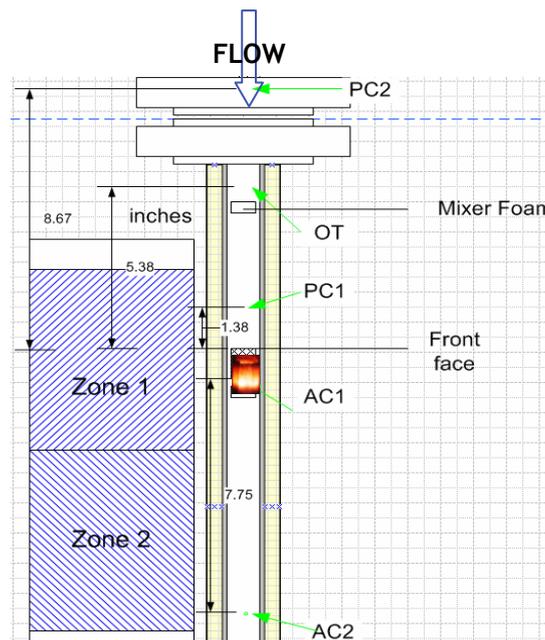
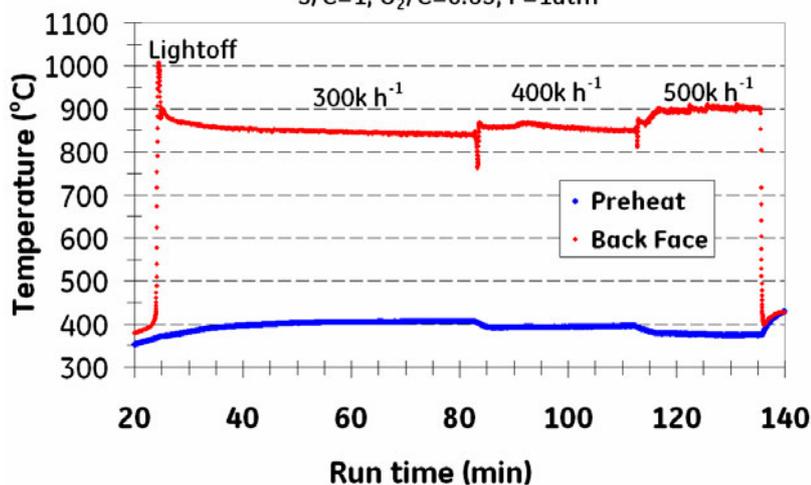


High-P CPO Data Obtained in FCL

Pressure Drop versus PPI

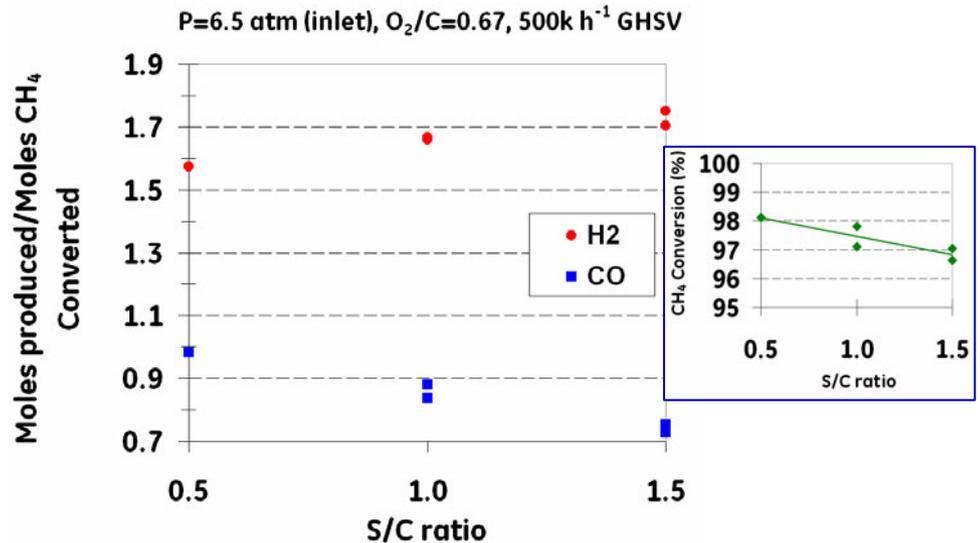
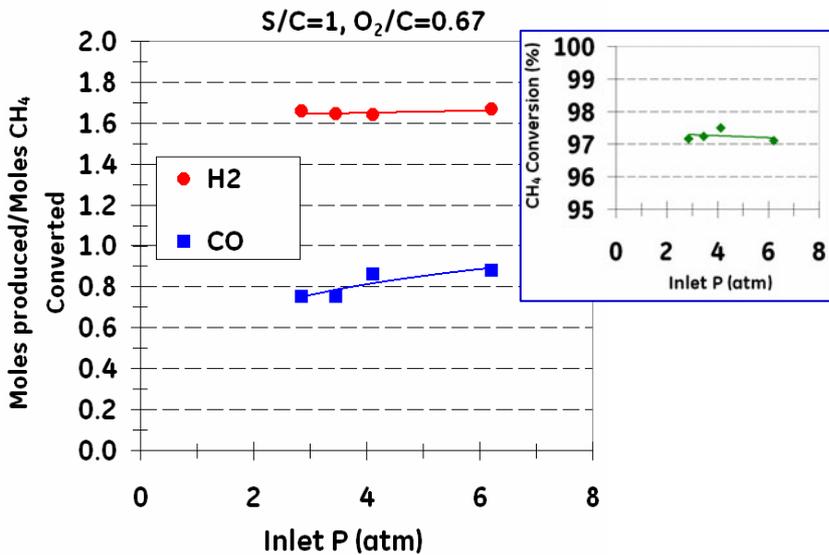
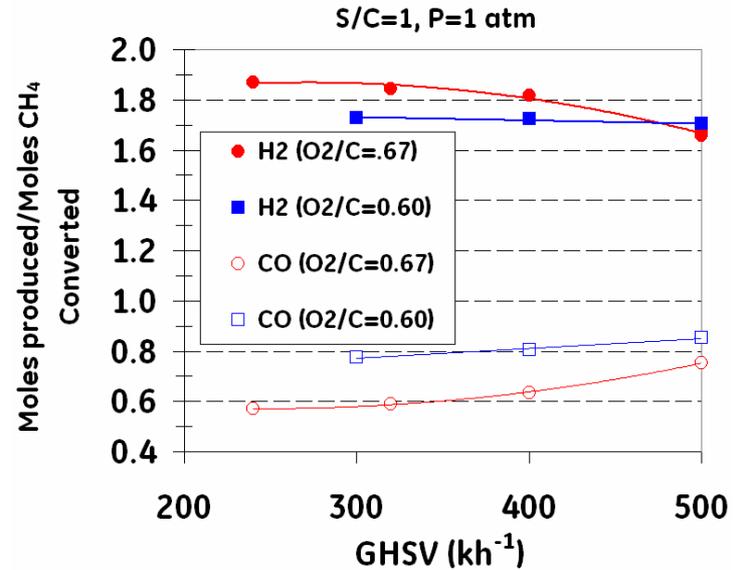
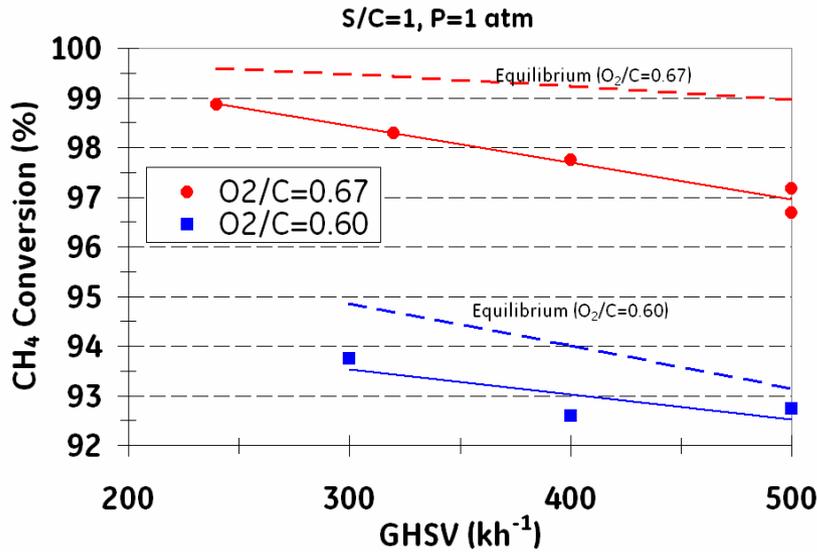


S/C=1, O₂/C=0.65, P=1atm



Time (milliseconds)

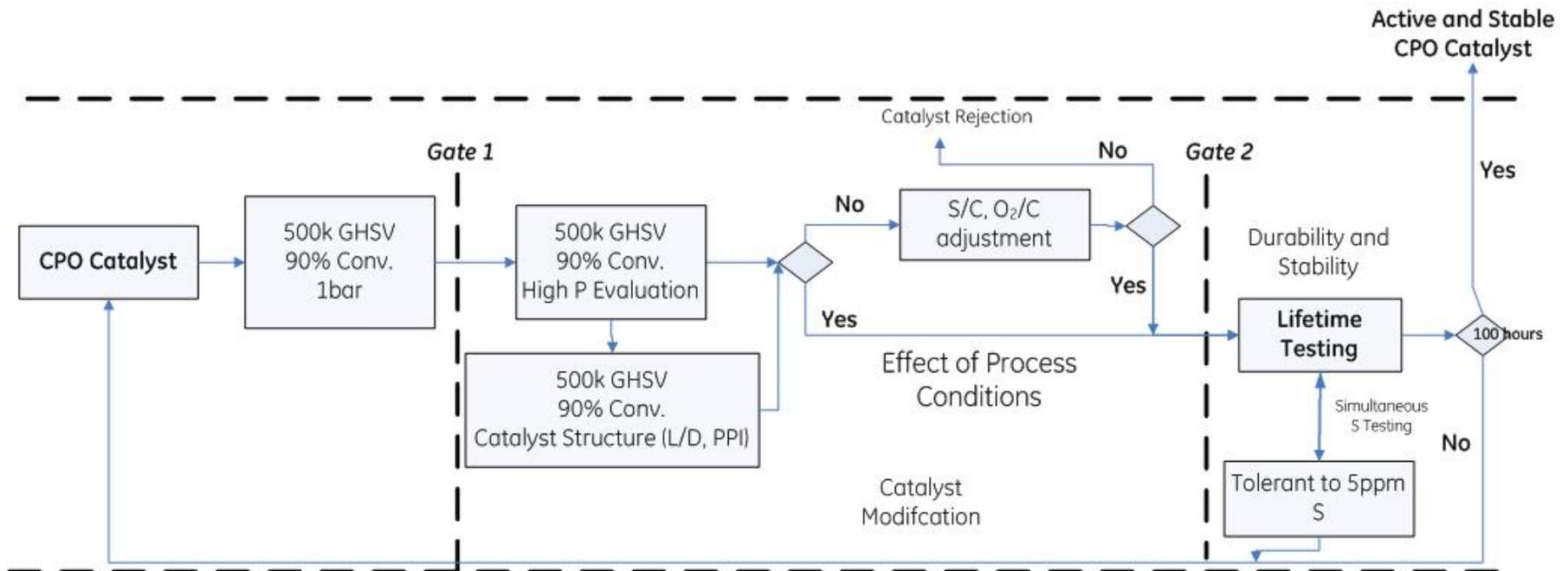
Results: Catalyst Testing-Baseline Performance



Future Work: Ongoing Catalyst Testing

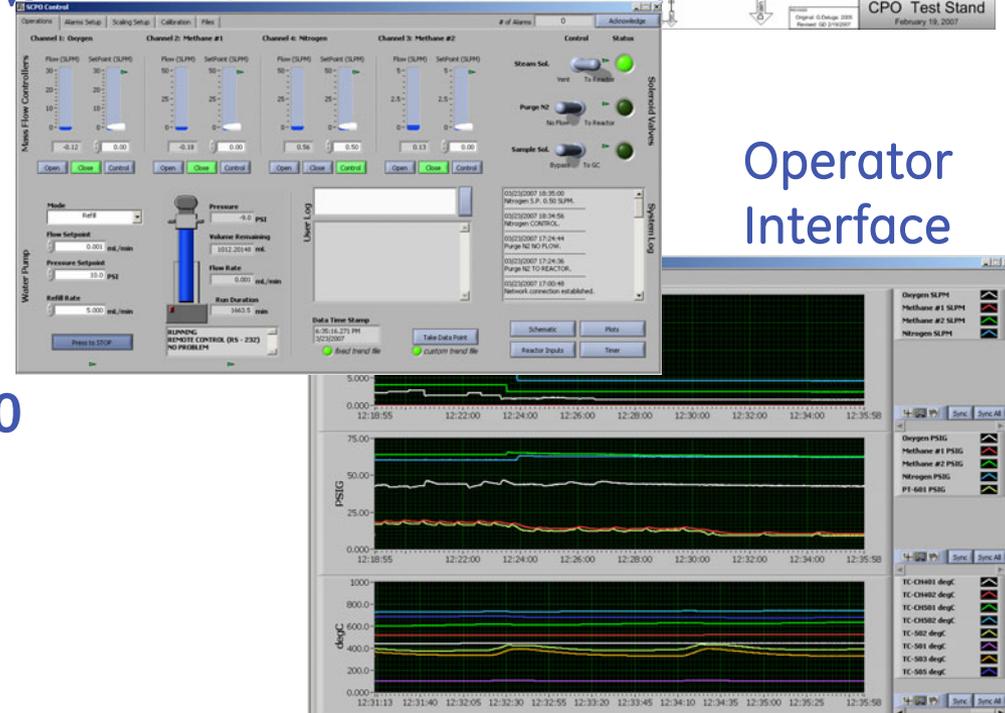
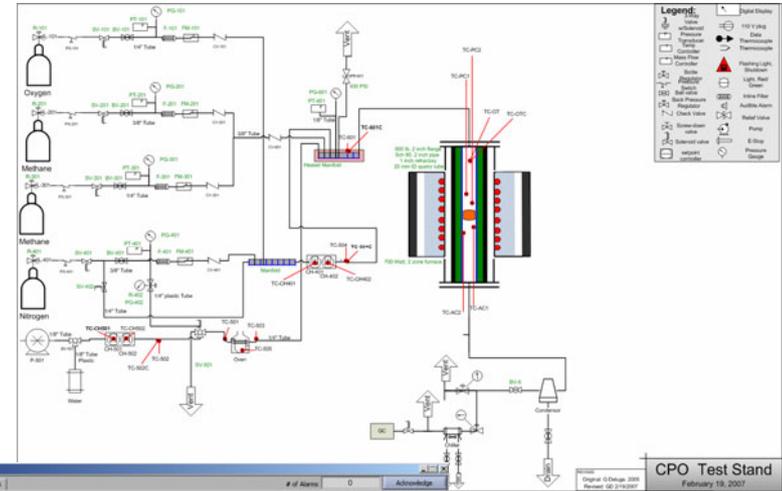
- Have Begun Catalyst Testing

- Atmospheric and high pressure screening
- Evaluating process conditions
 - GHSV, Temp., Pressure Drop, S/C, and O₂/C



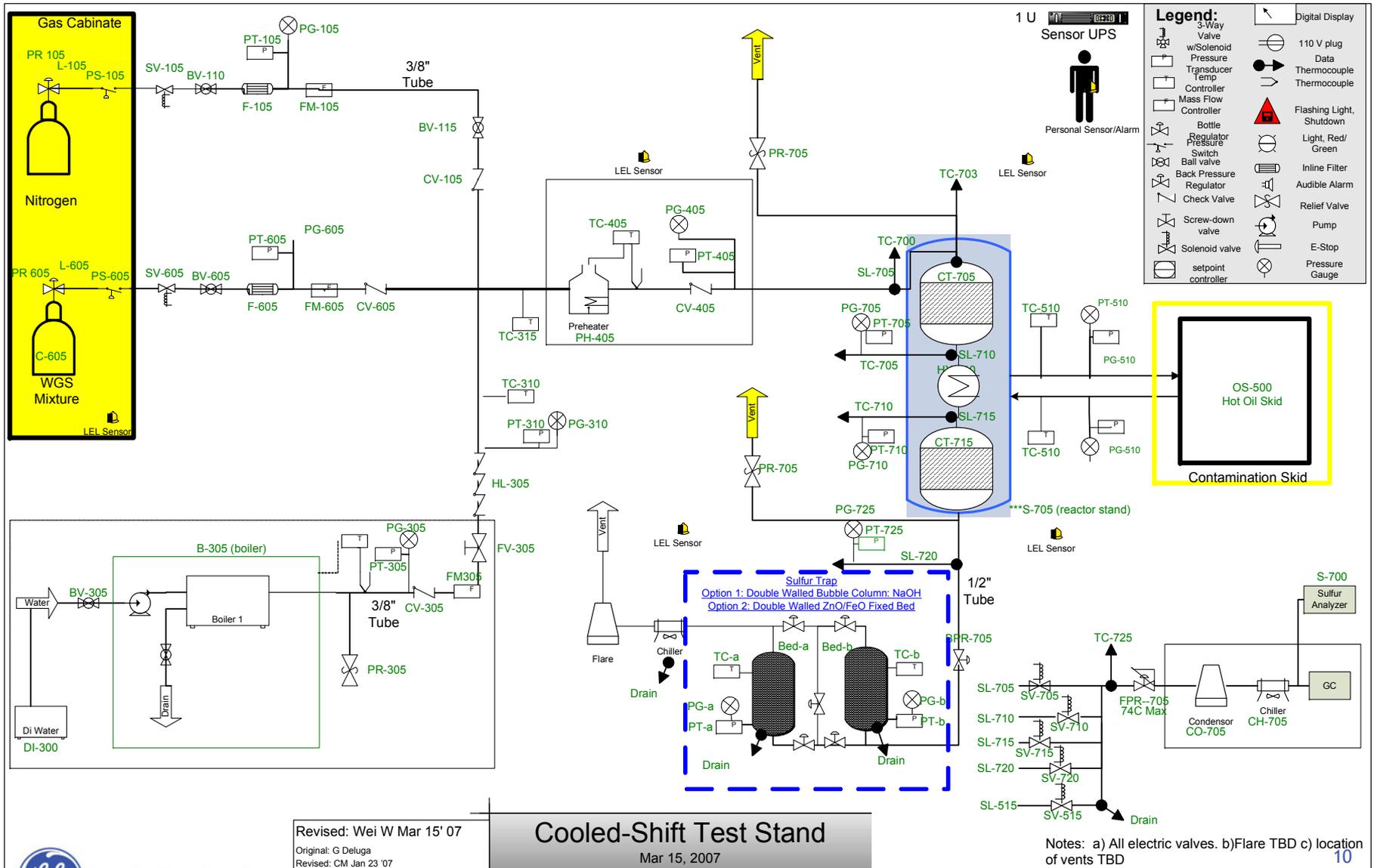
Future Work: Ongoing Catalyst Testing

- System construction completed and commissioned
 - HAZOP and FMEA Safety Review and System modifications
 - System Calibration and Shakedown with Catalyst
 - Currently testing optimized catalysts
 - Up to 1,000,000 GHSV and 400 psig

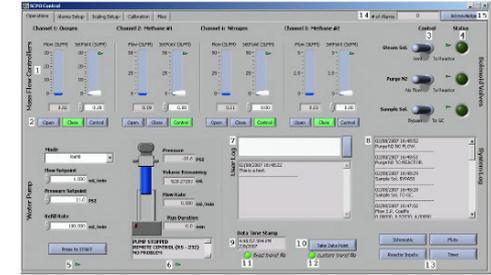
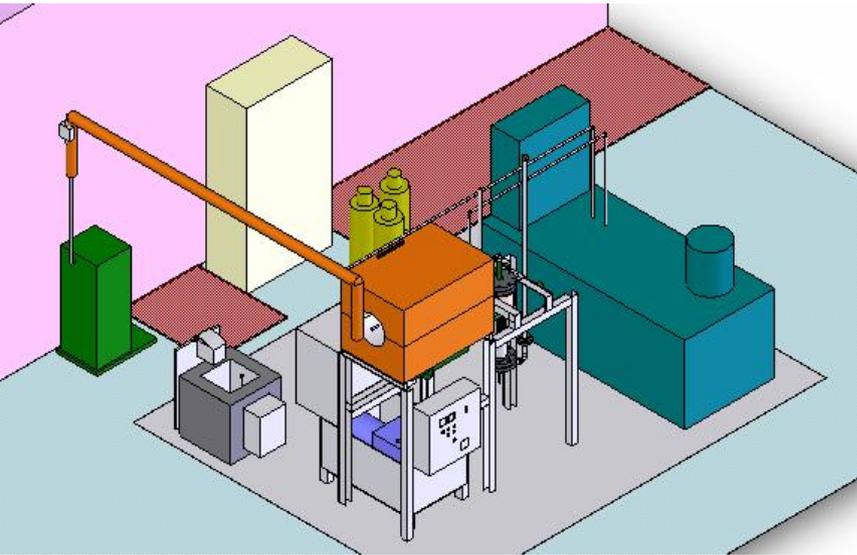


Operator Interface

Task 2 & 3 SMR & Shift Experiments

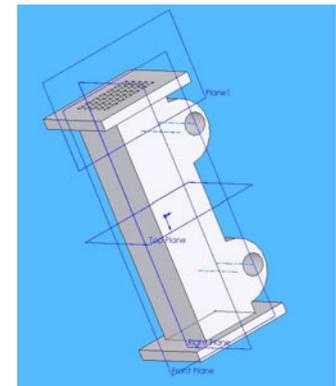
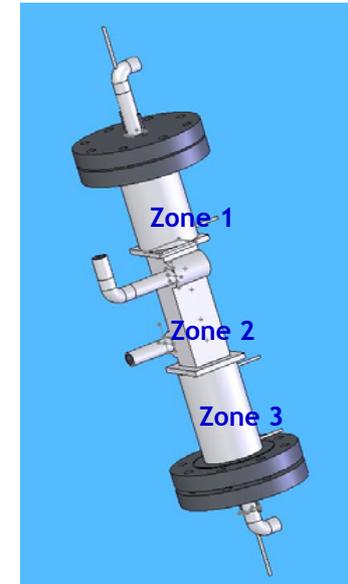


Task 2 &3: SCPO SMR/WGS Test Rig and Control System



- Labview: Schematic/Blueprint of all controls complete
- Programming in progress: Includes flow control, data monitoring and acquisition, and alarm warnings.

- 60Kg/ day Test Rig installation in progress
- Hood & Safety System installed (gas detection, E-stops)
- Burner installation and plumbing 90% complete
- Control system design complete: Labview coding in process
- Shakedown May 31. Full test status July 1.
- Footprint of the 1500 kg/day SCPO unit including PSA: 15ft x 10ft (Preliminary estimates, size depends on the compactness of packaging)



ANL - FY07 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 H₂S
- > Base metal catalysts (4 catalysts from two commercial vendors)
 - *Activity* (Status: in progress)
 - *Durability* (Status: in progress)

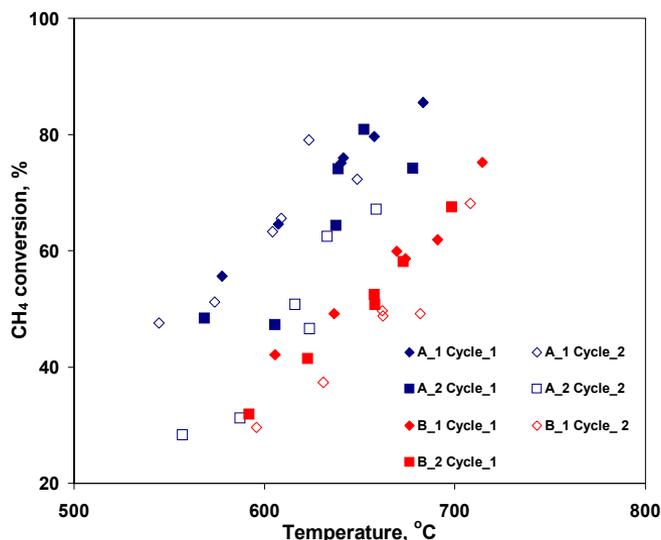
Water-gas shift catalyst evaluation

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

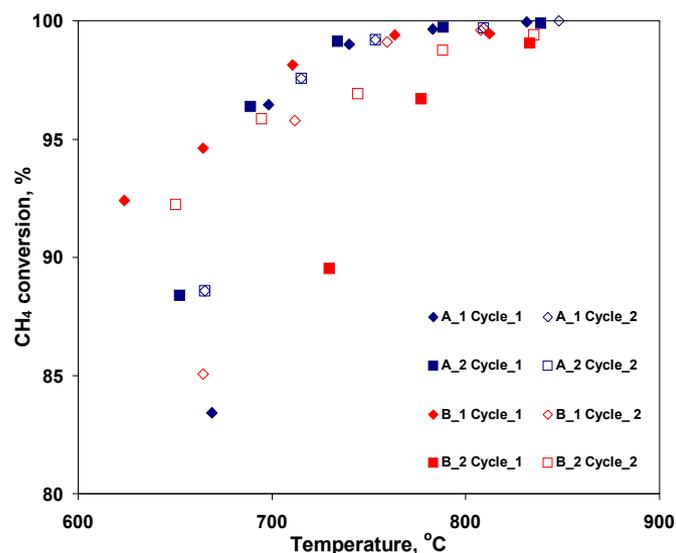
FY07 funding: \$125K

SMR Catalysts Were Evaluated for Activity and Durability

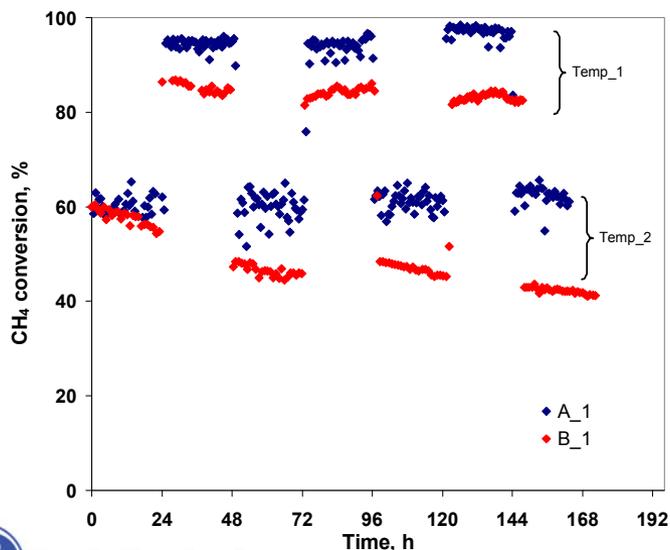
Activity - Low Temp SMR Conditions



Activity - High Temp SMR Conditions



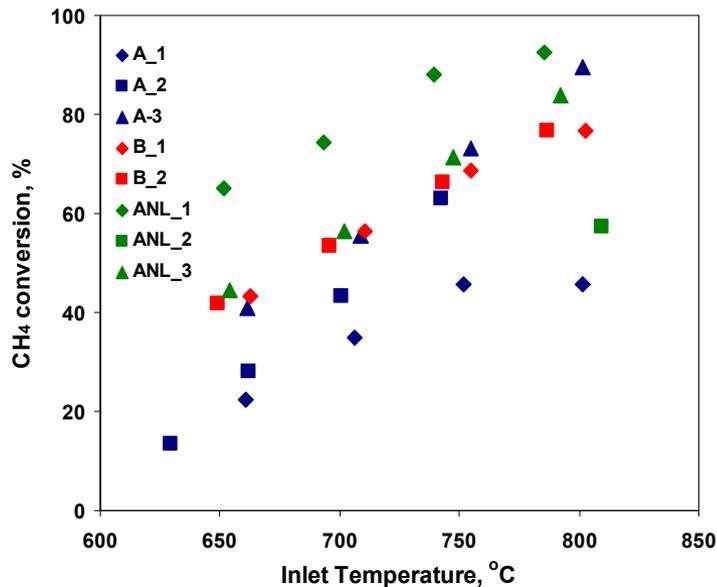
Durability – Low Temp SMR Conditions



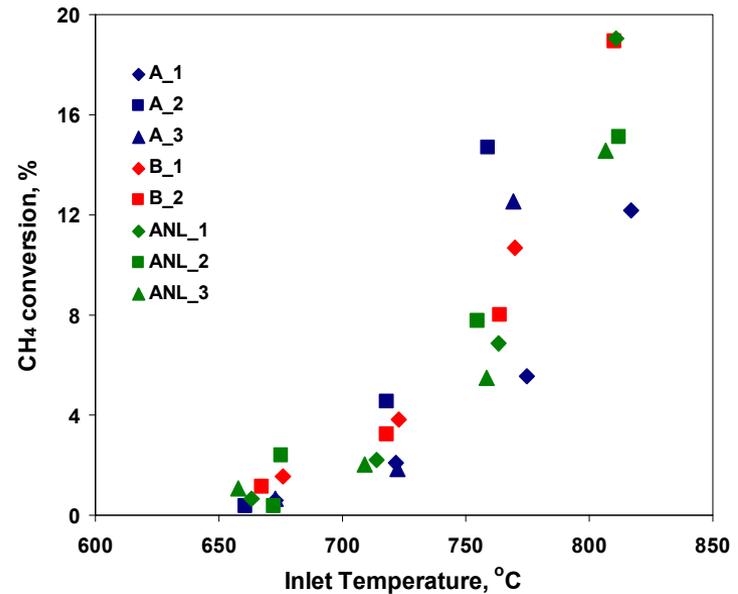
- Activity was evaluated by cycling catalyst between low and high T SMR conditions over a period of 48 hours.
- Durability was evaluated for low T SMR conditions by cycling between temperatures.
- Identified the catalyst that exhibits the best combination of activity and durability.

All Precious Metal SMR Catalysts Have Poor Sulfur Tolerance

0 ppm H₂S



5 ppm H₂S



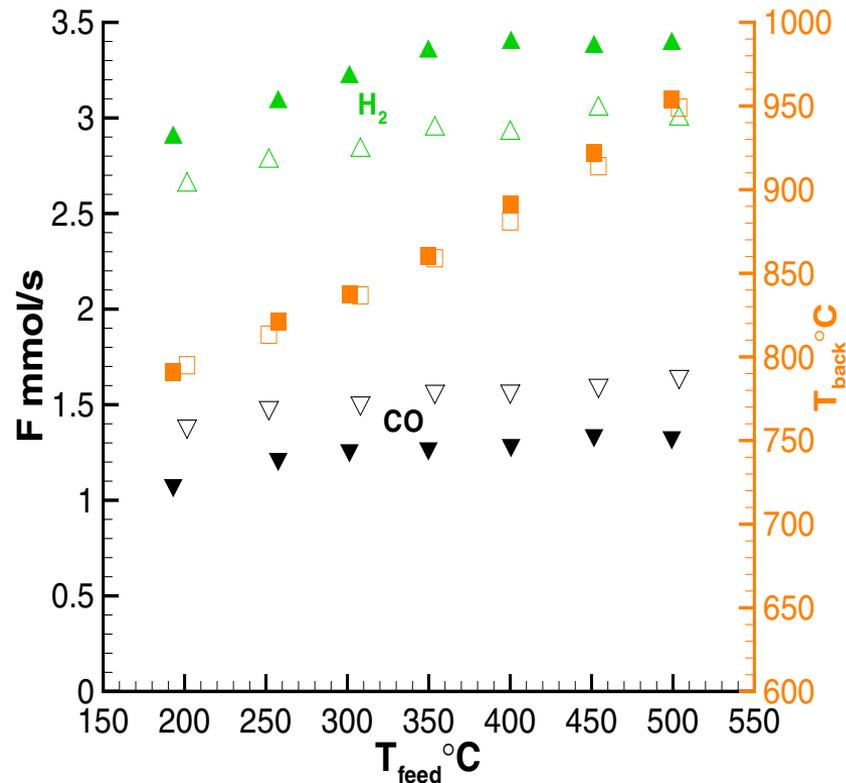
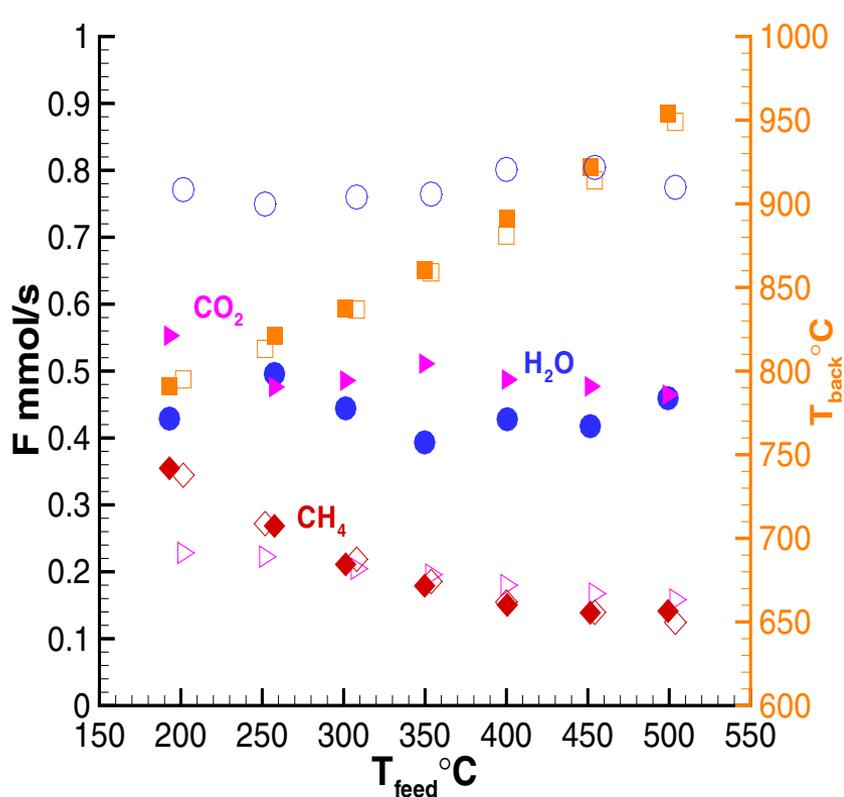
- Sulfur poisoning was generally reversible, even at 20 ppm H₂S. Most of the activity could be recovered over 1-2 h by raising the temperature or lowering H₂S concentration.
- No evidence of carbon buildup on catalysts.
- Increasing the metal loading led to high rates in the absence of H₂S but had no effect on improving the sulfur tolerance (Argonne catalysts).

UoMn Accomplishments



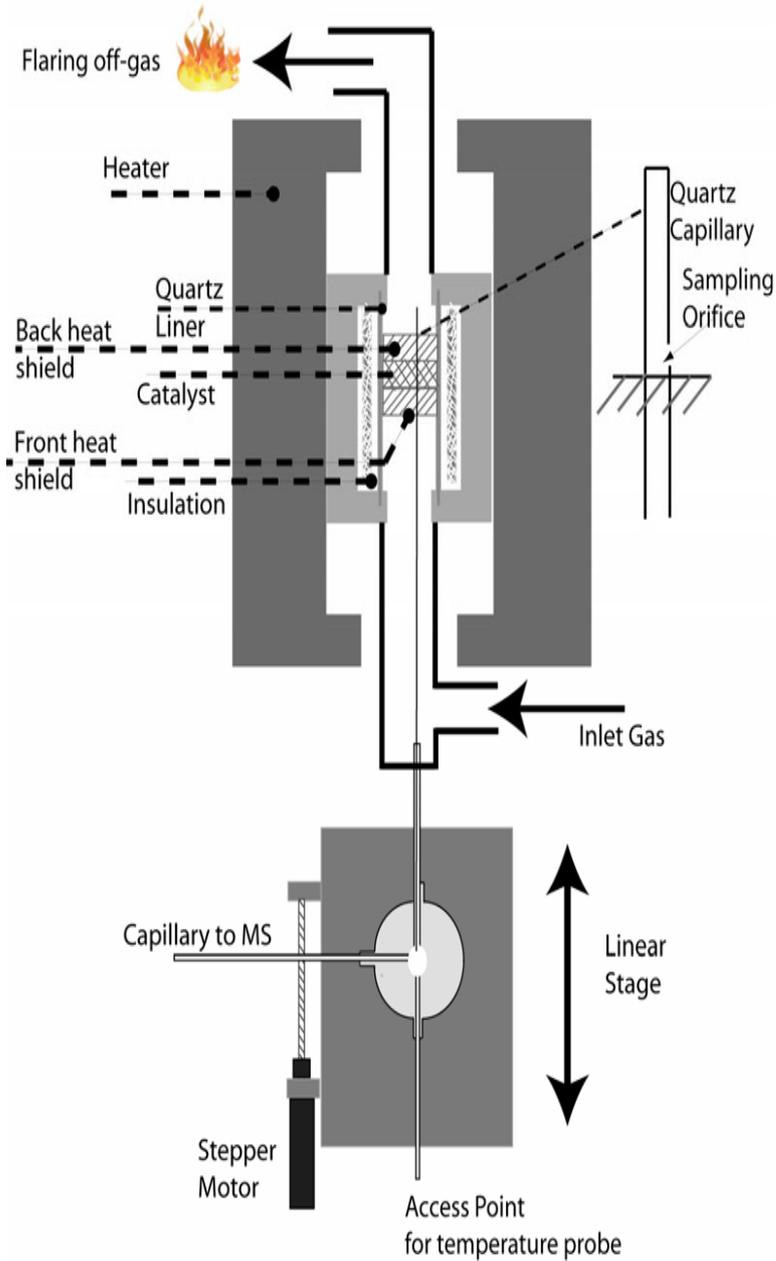
- Completed screening of catalyst systems. 10 systems were investigated and Rh-Ce was shown to have the best performance
- Investigated the effect of steam addition in the system at high space velocities
- Characterized the catalyst using surface analysis (XRD, XPS). This showed that the catalyst is reduced under reaction conditions to oxidation state 0.
- Developed an experimental technique that allows to sample inside the reactor while running experiments

Effect of Steam Addition



- Open symbols are with steam replaced by N_2 .
- The water flow is $F_{\text{H}_2\text{O}}^{\text{in}} - F_{\text{H}_2\text{O}}^{\text{out}}$
- No effect from SR but WGS does play a role
- $\text{O}_2/\text{C}=0.68$, $\text{S}/\text{C}=1$, $\text{GHSV } 750,000\text{h}^{-1}$

Spatial Profiles Inside the Foam Catalyst

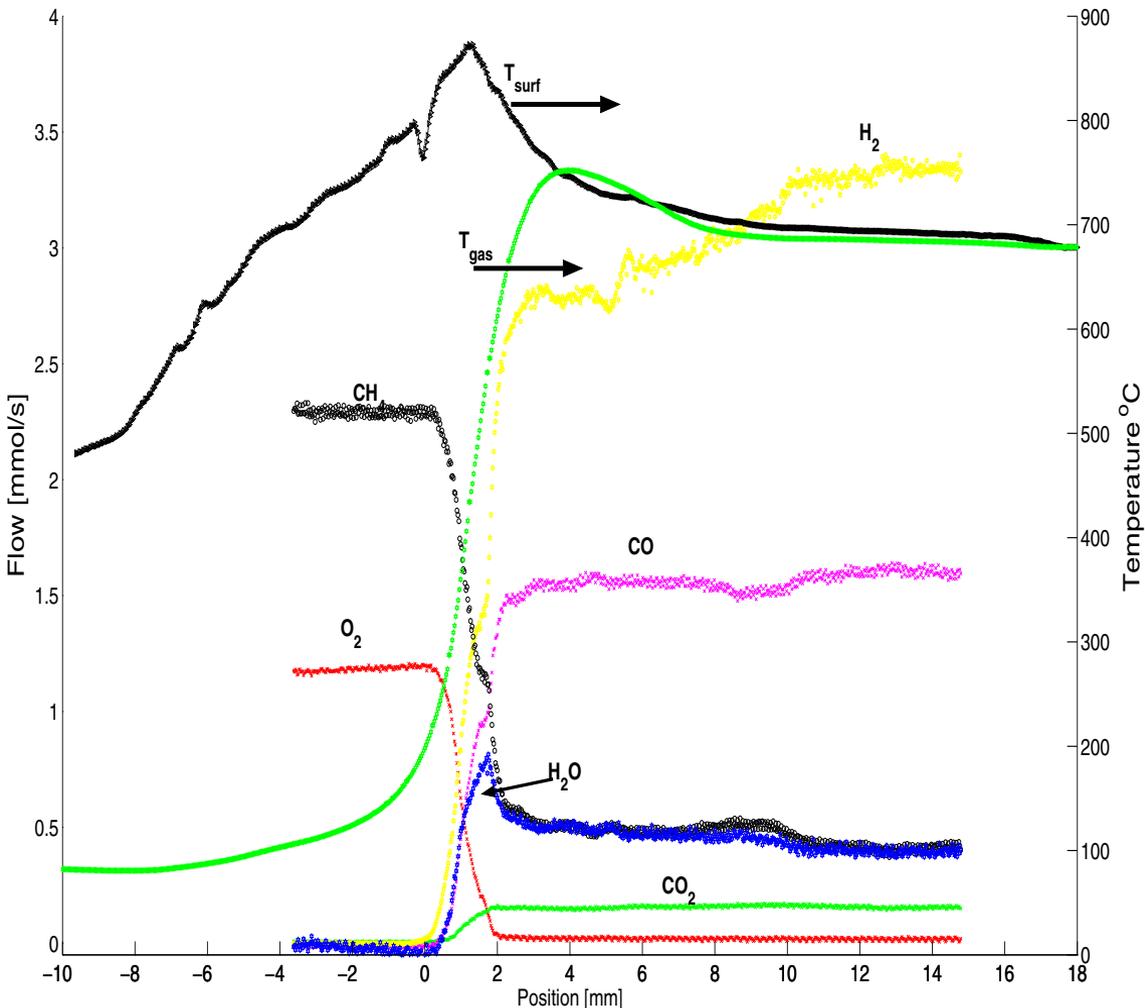


- Developed a system that allows to *in situ* sampling in a system with very high temperature and species gradients
- Unprecedented spatial resolution ($\sim 300\mu\text{m}$) on the order of the characteristic length of the support
- Sampling method introduces minimal disturbance in flow. Sample rate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

Results From Spatial Profiles



Rh 0.5%–2%Ce 80ppi GHSV 275,000 h⁻¹ O₂/C=0.5



- 0mm is the front face of the catalysts
- 2 zones can be identified:
 - First a short ~2mm oxidation zone, where all O₂ is consumed.
 - Second a longer endothermic steam reforming zone
- Very high temperature gradients in the front of the catalyst

Sulfur Adsorption Tests via TGA

•Absorption Tests / Optimization

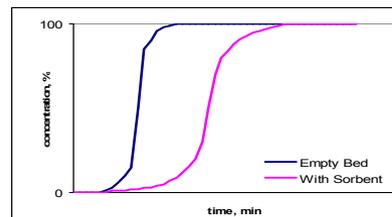
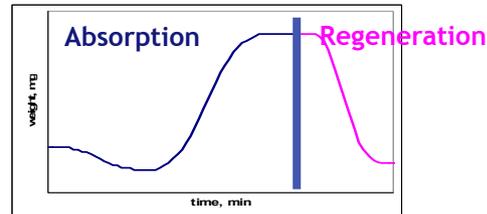
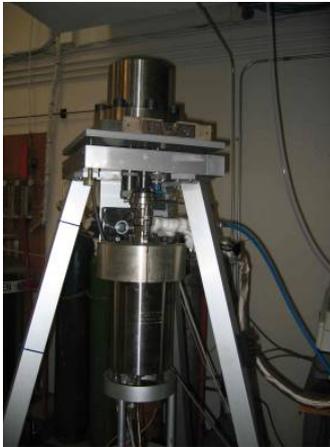
- Temperature (P is determined by gasification condition)
- H₂S Level
- Particle Size (2 levels: study effect of pore-diffusion)
- Absorption Kinetics
- Optimized Absorption Conditions

•Regeneration Tests / Optimization

- Temperature
- O₂ Concentration (Air/N₂ ratio)
- Optimized Regeneration Conditions
- Sorbents Lifetime (Absorption / Regeneration)
- Fixed Bed or Fluidized Bed Reactor is Suggested

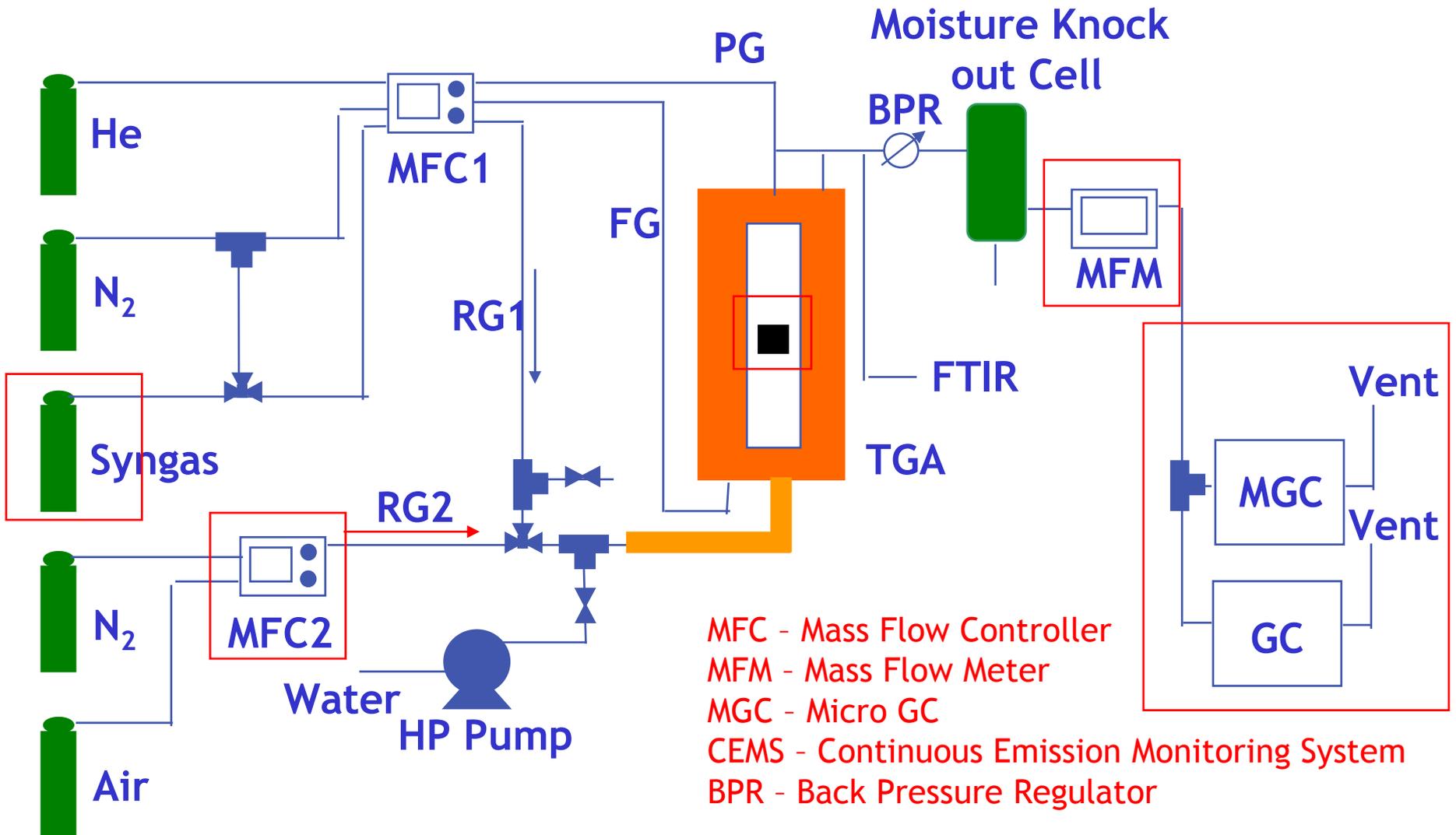
$$r = \frac{dx}{dt} = f(x, p_{H_2S}, T) = K p_{H_2S}^m (1 - x)^n$$

$$K = k \cdot \exp\left(-\frac{E}{RT}\right)$$



- Break-through point for the sorbent
- Absorption/regeneration kinetics
- Optimized operating condition
- Solid residence time in reactor (absorber/regenerator)
- Fluidized bed reactor/regenerator design

P&ID - TGA System



Summary & Highlights

- High-P CPO data obtained from our high-P CPO unit. Conducting tests daily now. Preparing more CPO catalysts.
- Prepared the catalyst & shipped to Niskayuna; Completed the pre-mixer design, the mixer is being fabricated. Modified the test rig. Pre-mixer CPO tests is being conducted
- SMR & Cooled shift test rig are being built, and the hood is installed, and major equipments are in place.
- Completed the shift kinetics modeling based on literature kinetics found recently. Completed the preliminary economics analysis.
- Completed the IP & literature analysis on WGS catalysts.
- ANL & UoMn continuity generate good test data for GE
- System analysis/design completed; System pressure trade off analysis completed
- Base case catalysts identified, Reactor sizing / design completed.
- HEX technology tradeoff completed, HEX technology selected, design completed
- Control strategy, start-up & shut-down procedure developed
- Completed cost analysis using GE's process model & DOE's H2A model

Conclusions & Recommendations

- SCPO will be a leading technology for H₂ production from NG. It is a cost-effective distributed H₂ production technology based on the economic analysis of different H₂ production technologies. With minor catalyst and process condition 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....

Design and built high-P CPO unit and tests are being conducted. Designed and building the SMR & WGS reactors test rig, and conduct testing in 2nd half of 2007.