# Integrated Short Contact Time Hydrogen Generator (SCPO)

## 2007 DOE H2 Program Annual Review Meeting

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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 $H_2$ Cost < $3.00/gge H2

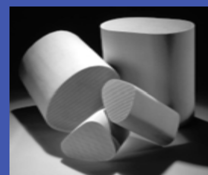
## Partners

- University of Minnesota
- Argonne National Lab

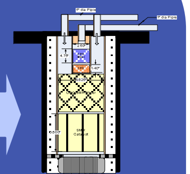
# SCPO Program Highlights & Accomplishments in 2006

## 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 $H_2$ at a Cost of <$3.0/kg

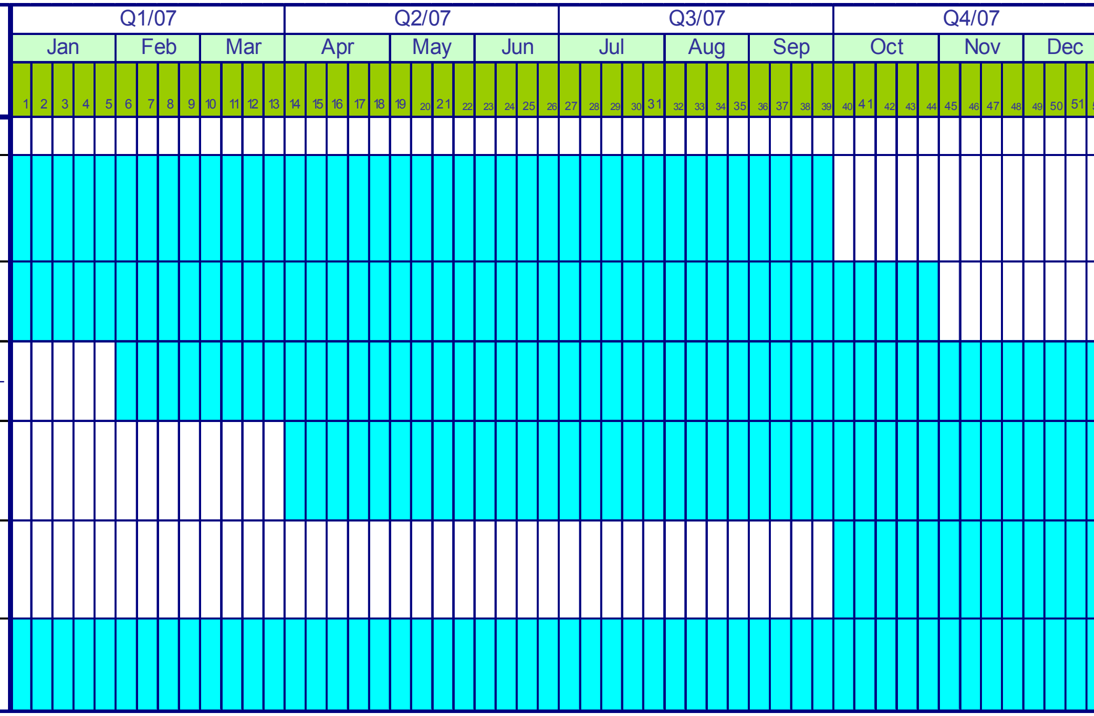
- ➢S-tolerate CPO catalyst discovery
- ➢S-tolerate CPO catalyst development
- ➢CPO catalyst characterization: XRD, XPS


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

# SCPO Tasks, Schedule & Budget

**2007 Tasks & Schedule for SCPO & Warm Gas Clean-up**

| Tasks | Subtasks |
|---|---|
| Task 1: Premix CPO + Sulfur Tolerate CPO Catalyst | 1). Pre-mix + CPO Catalyst tests at GE Niska; 2). Low P tests at UoM; 3). High P tests at GE Irvine; 4). Durability tests & APS analysis at |
| Task 2: Compact SMR Reactor | 1). Low P tests at ANL; 2). High P tests at GE; 3). Durability Tests at ANL |
| Task 3: Cooled WGS Reactor | 1). Design, build C-WGS unit; 2). Test C-WGS; 3). Evaluate the benefit of C-WGS for SCPO & IGCC |
| Task 4: Sorption Kinetics Study with TGA | 1). Multi-pollutants detection; 2). Adsorption kinetics; 3). Regeneration kinetics |
| Task 5: System & Economic Analysis | 1). Aspen system model based on new test results; 2). Economic model ( H2A) based on new test results and updated system design. |
| Task 6: Project Management & Reporting | 1). Coordinate the R&D activities of GE-ANL-UoM. Manage the overall SCPO project. |




## 2007 Budget:

| | |
|---|---:|
| Materials (k$): | 360 |
| Labor (k$): | 1030 |
| Total Funding (k$): | 1390 |

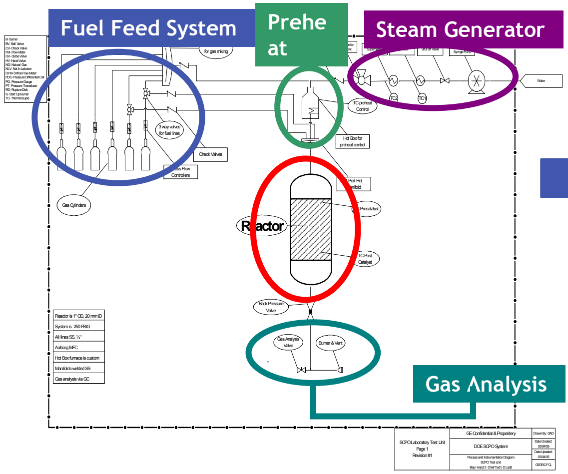
Note: The material budget includes $80K to UoMn

**YTD Labor:** $322K
**YTD Material:** $87K
**YTD Total:** $409K

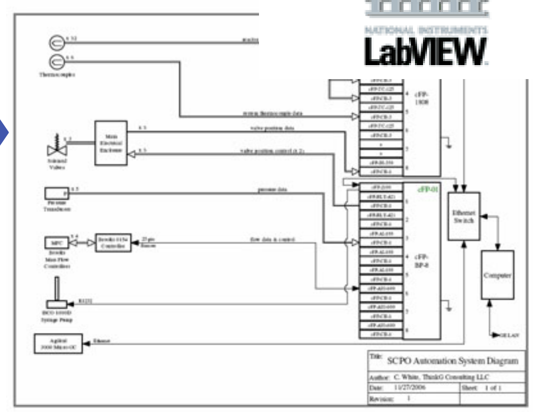
**TTD Labor:** $1,304K
**TTD Material:** $630K
**TTD Total:** $1,935K

# Task 1: Premix CPO with Sulfur Tolerate CPO Catalyst

## System Designed




## Control & Data Acquisition Added




## System Constructed

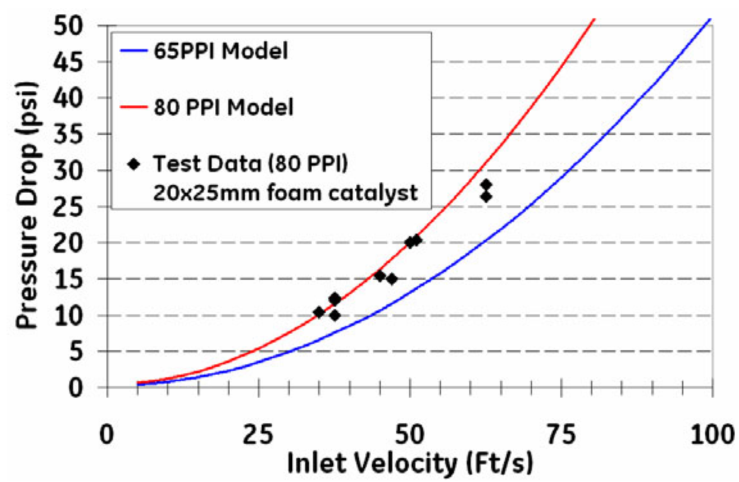
## Test in 2007

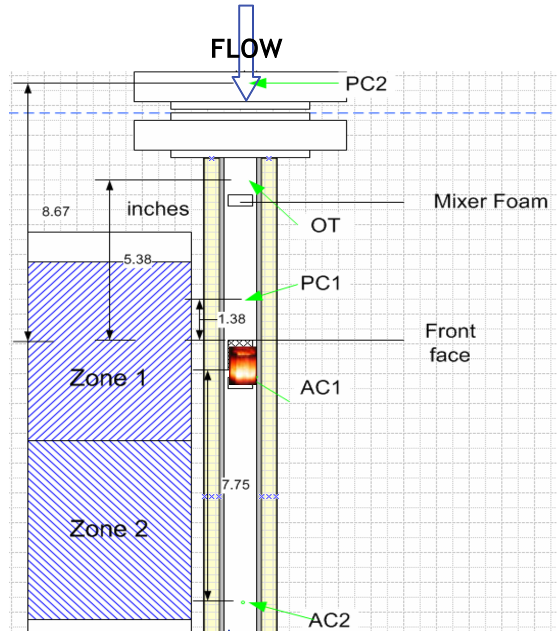
Status
• Completed the shake-down and started the high-P CPO tests
• Two catalysts tested at diff conditions, high quality data obtained.

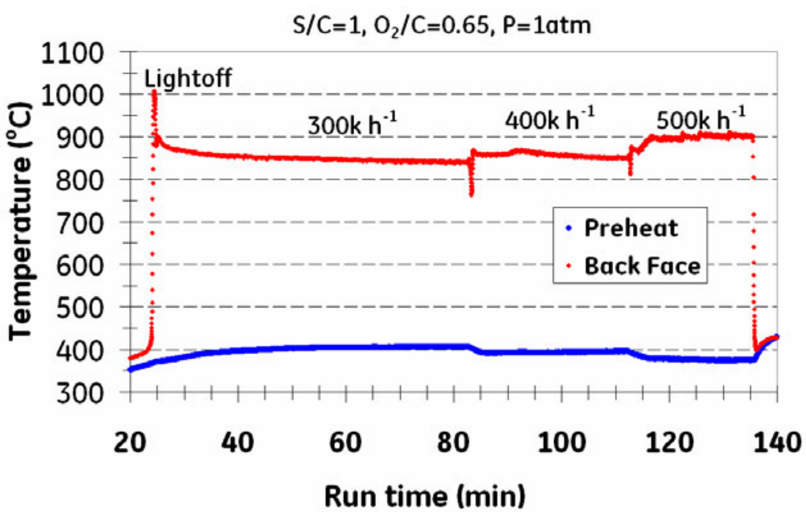
Plans:
•Heavy usage in Q1 of 2007
•Integration with Mixer
•Integration with SMR & WGS

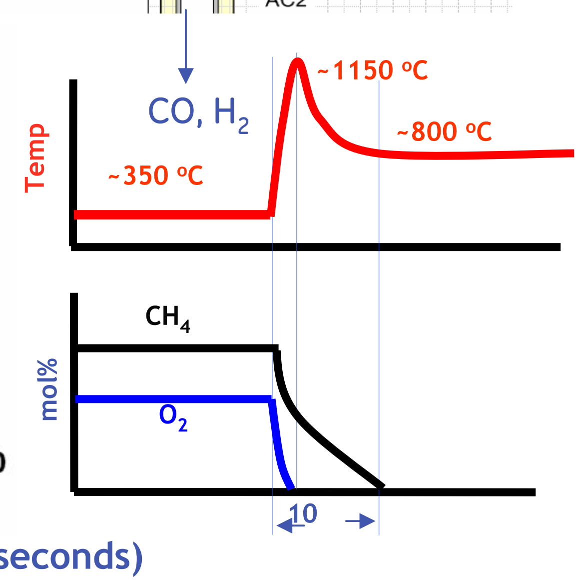
# High-P CPO Data Obtained in FCL

## Pressure Drop versus PPI

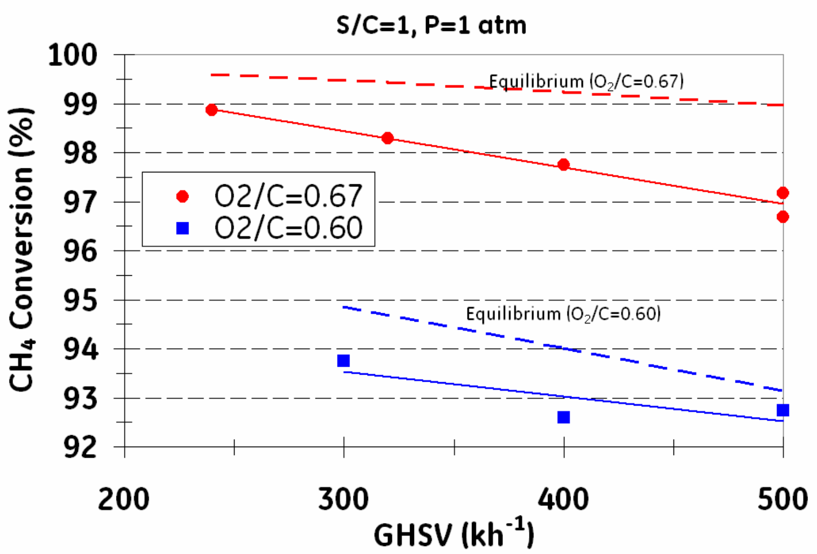


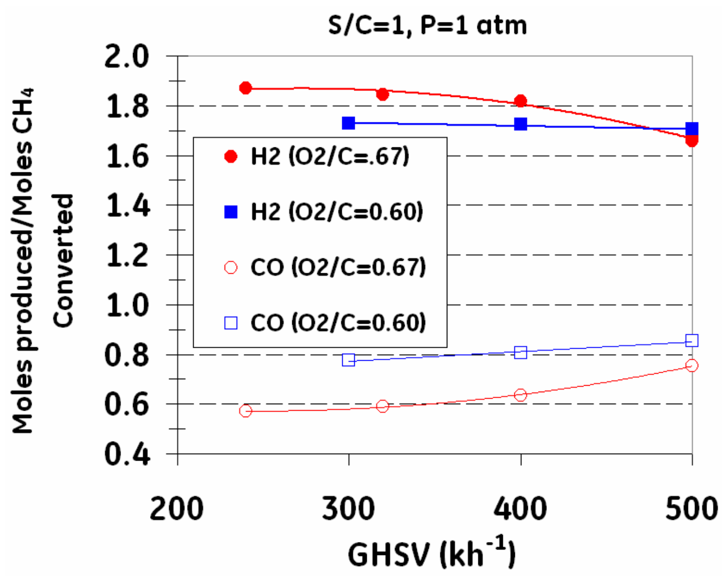



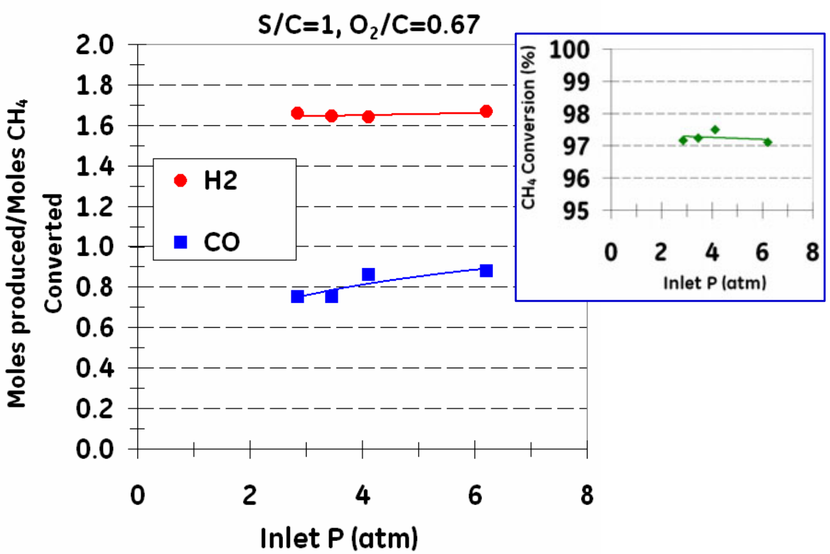



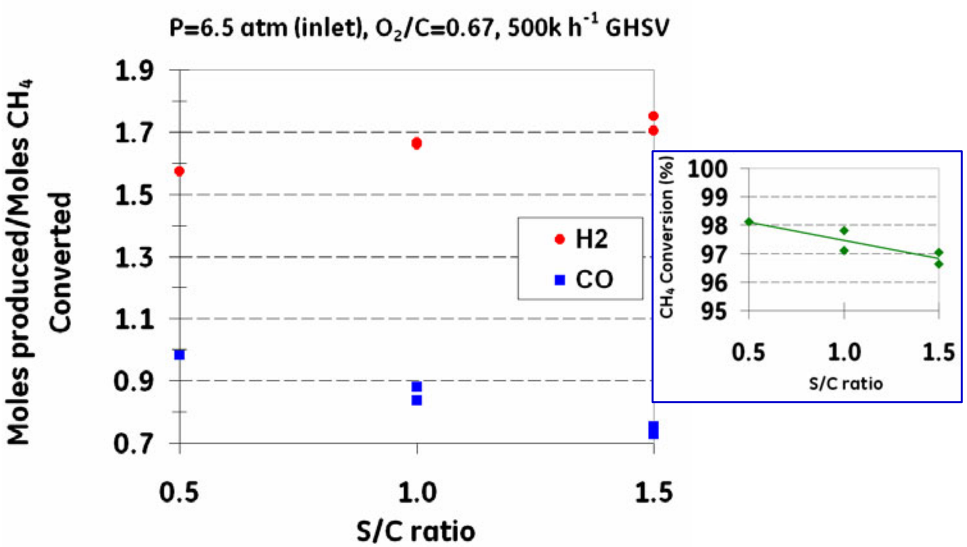



# Results: Catalyst Testing-Baseline Performance



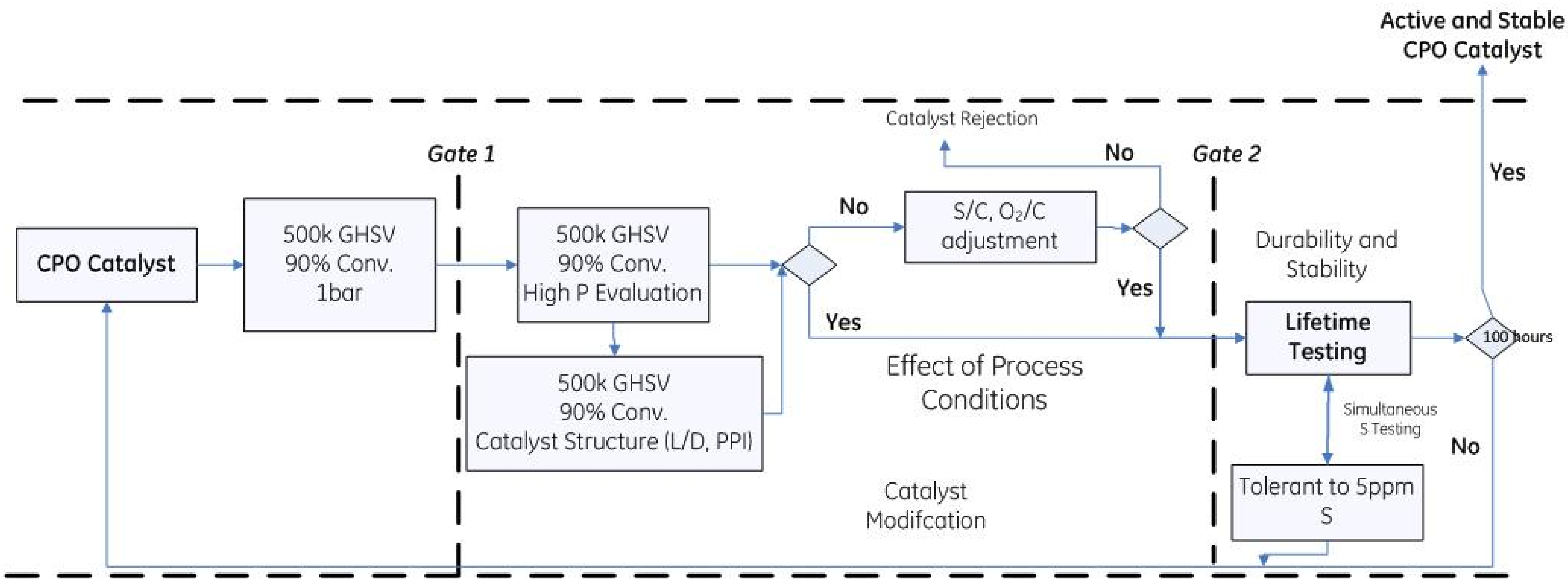



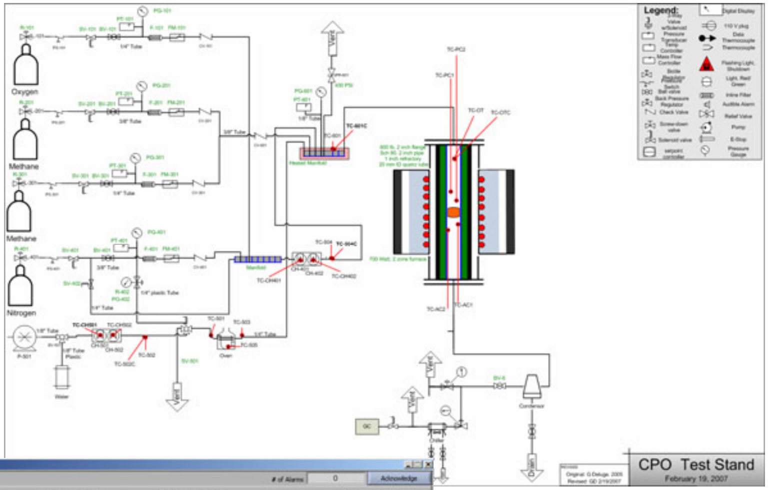
# Future Work: Ongoing Catalyst Testing

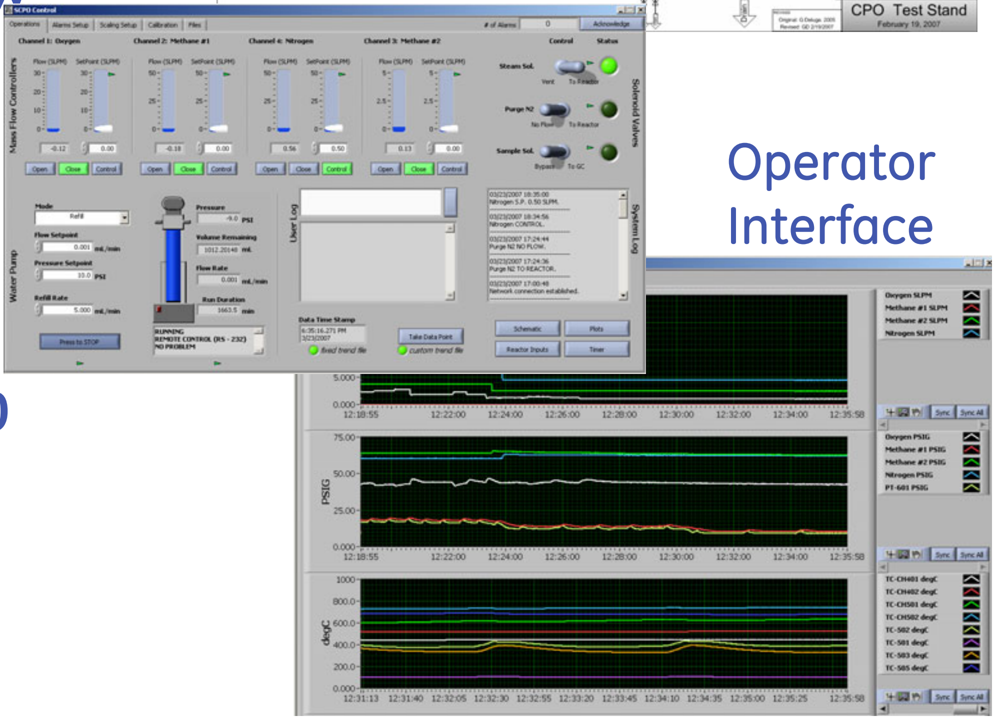
- **Have Begun Catalyst Testing**
  - Atmospheric and high pressure screening
  - Evaluating process conditions
    - GHSV, Temp., Pressure Drop, S/C, and $O_2$/C



# Future Work: Ongoing Catalyst Testing

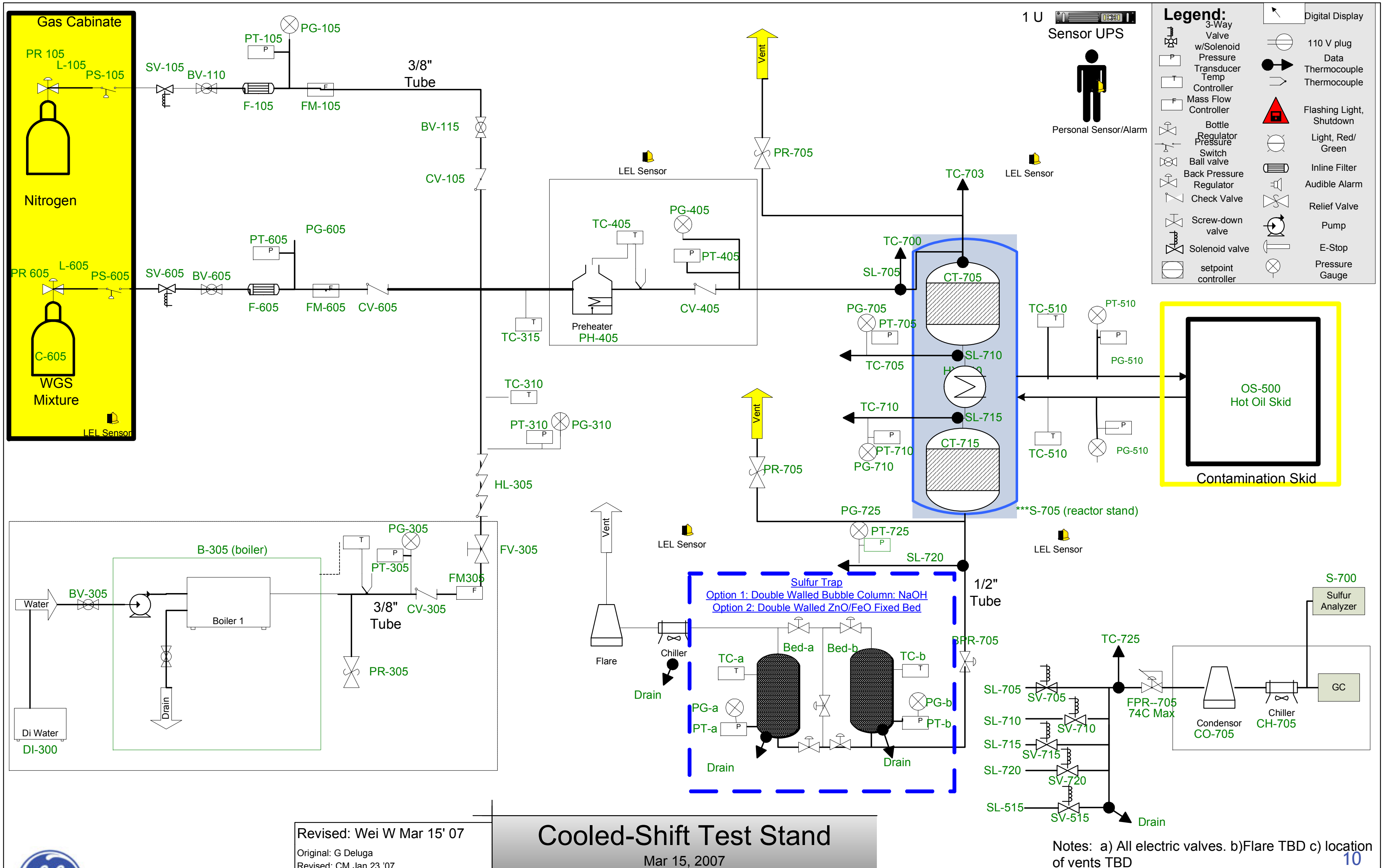
- System construction completed and commissioned
  - HAZOP and FMEA Safety Review and System modifications
  - System Calibration and Shakedown with Catalyst
  - Currently testing optimized catalysts
  - Up to 1,000,000 GHSV and 400 psig



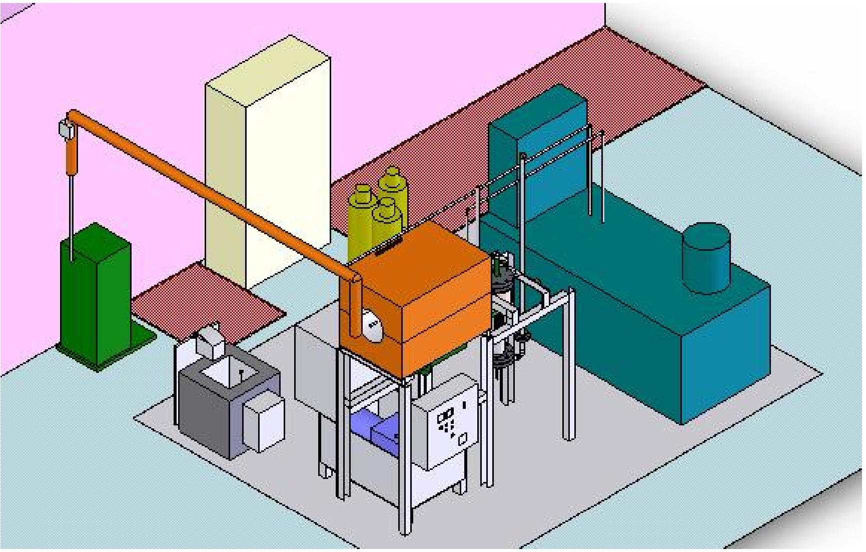



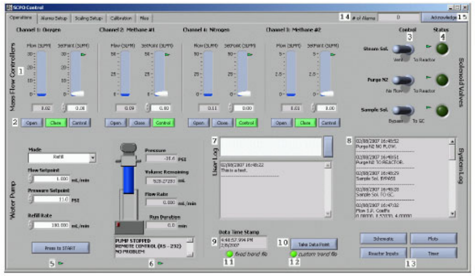

Operator Interface

# Task 2 & 3 SMR & Shift Experiments



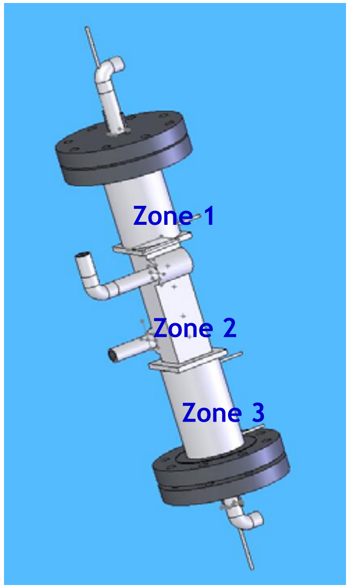
# Task 2 &3: SCPO SMR/WGS Test Rig and Control System

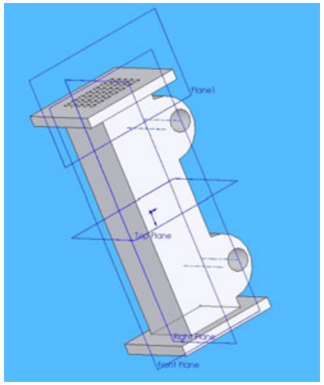




- Labview: Schematic/Blueprint of all controls complete
- Programming in progress: Includes flow control, data monitoring and acquisition, and alarm warnings.

- 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 $H_2S$
- Base metal catalysts (4 catalysts from two commercial vendors)
  - *Activity (*Status: in progress*)*
  - *Durability (*Status: in progress*)*

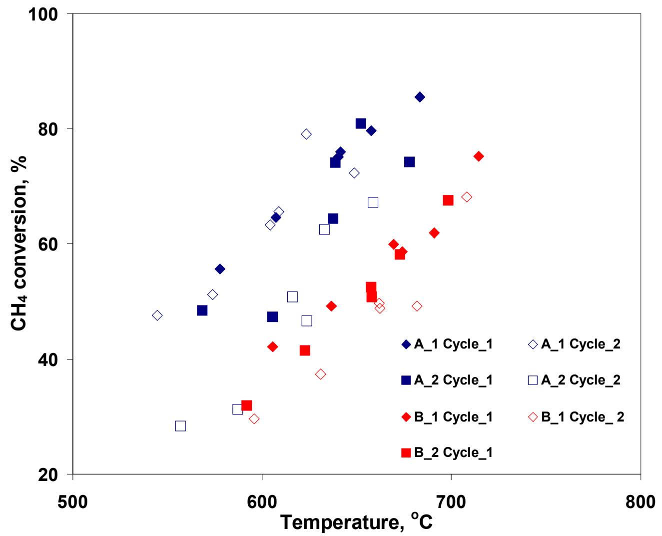
Water-gas shift catalyst evaluation

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

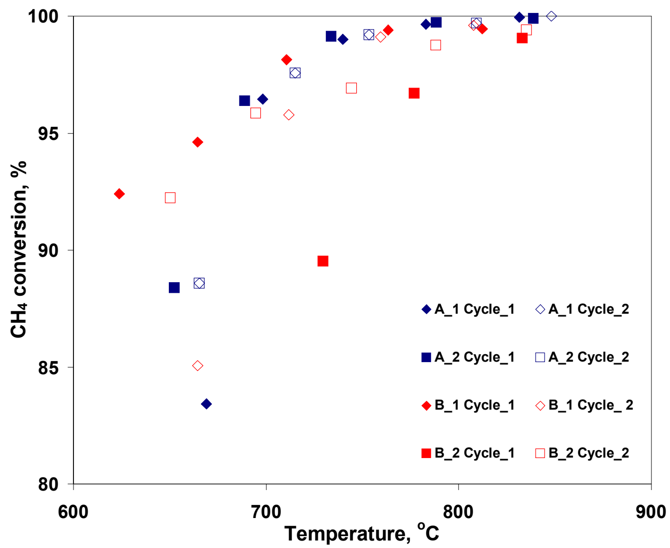
**FY07 funding: $125K**

# SMR Catalysts Were Evaluated for Activity and Durability

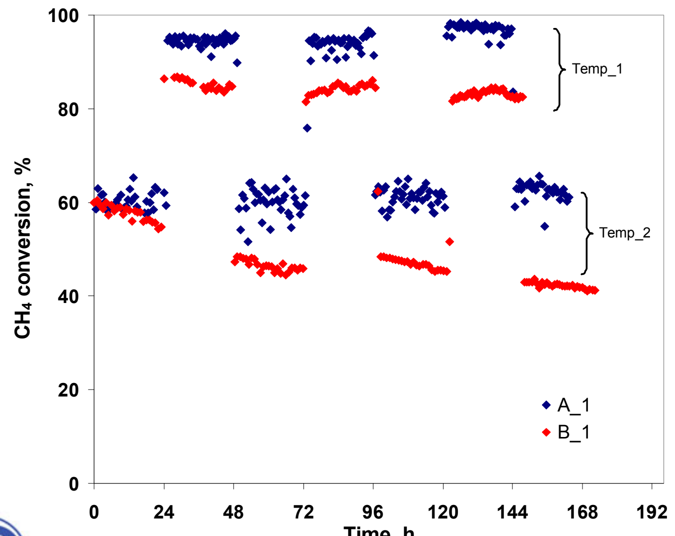
**Activity - Low Temp SMR Conditions**




**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.

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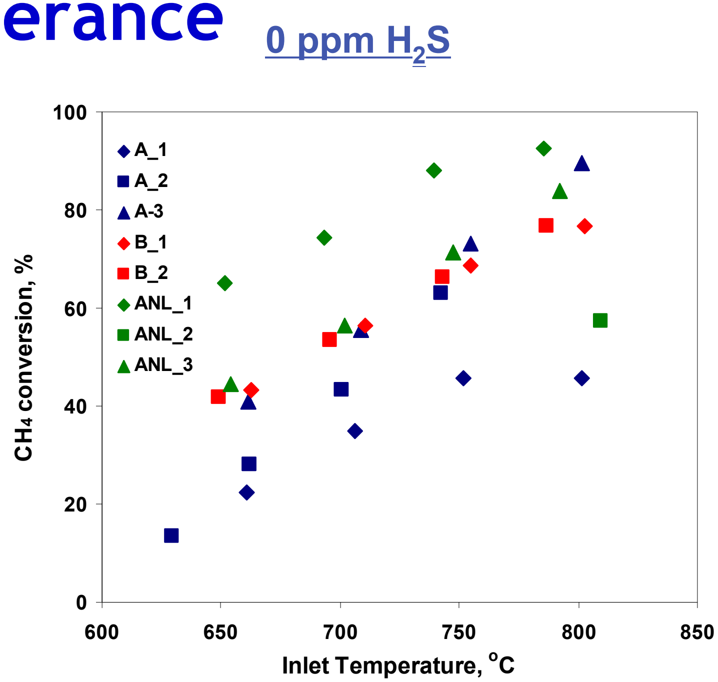
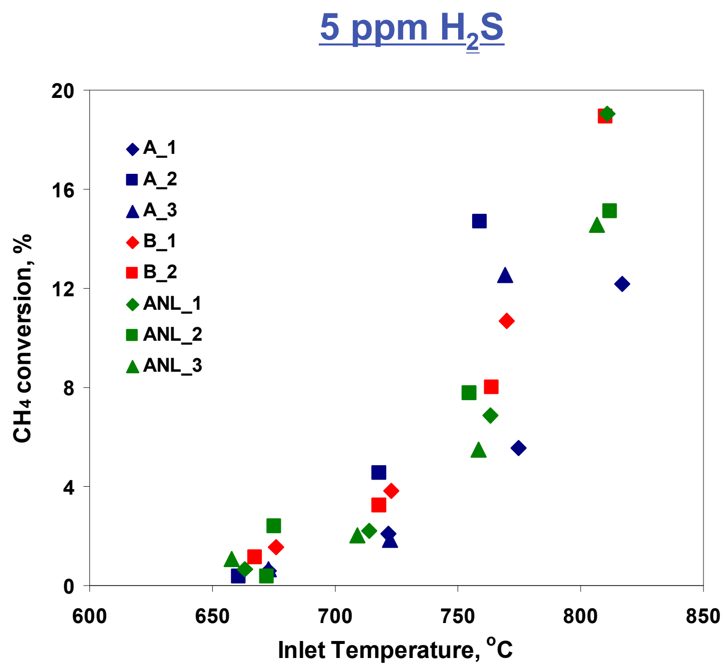
# All Precious Metal SMR Catalysts Have Poor Sulfur Tolerance




- Sulfur poisoning was generally reversible, even at 20 ppm $H_2S$. Most of the activity could be recovered over 1-2 h by raising the temperature or lowering $H_2S$ 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).

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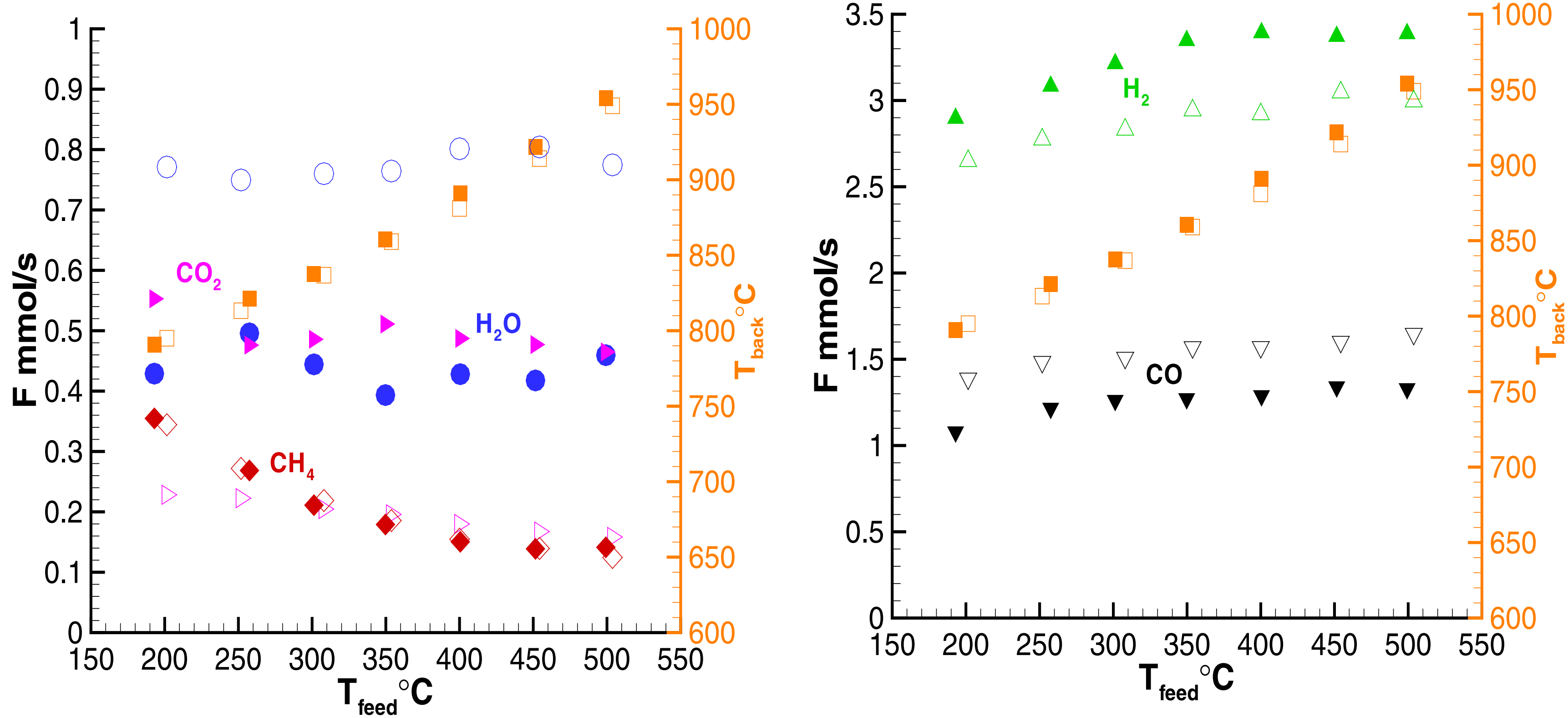
# UoMn Accomplishments

- 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 $F_{H20}^{in}$-$F_{H2O}^{out}$
- No effect from SR but WGS does play a role
- $O_2$/C=0.68, S/C=1, GHSV 750,000$h^{-1}$

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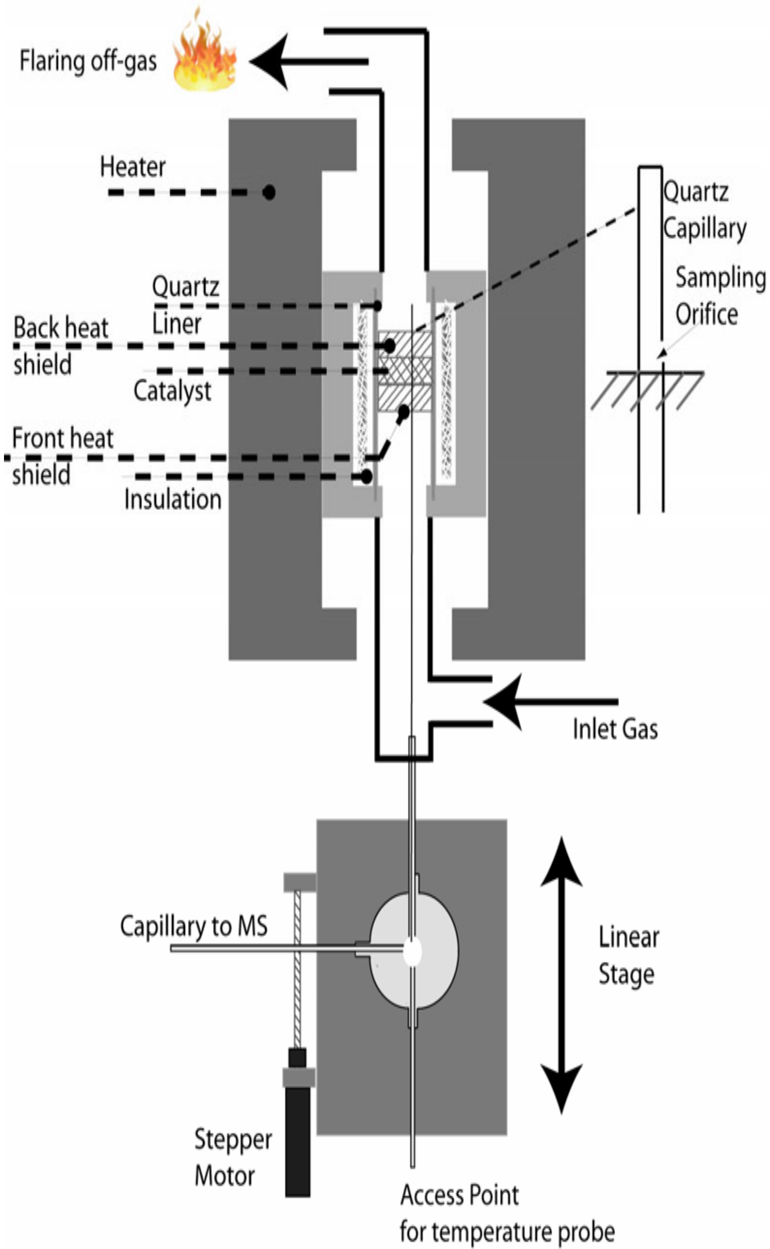
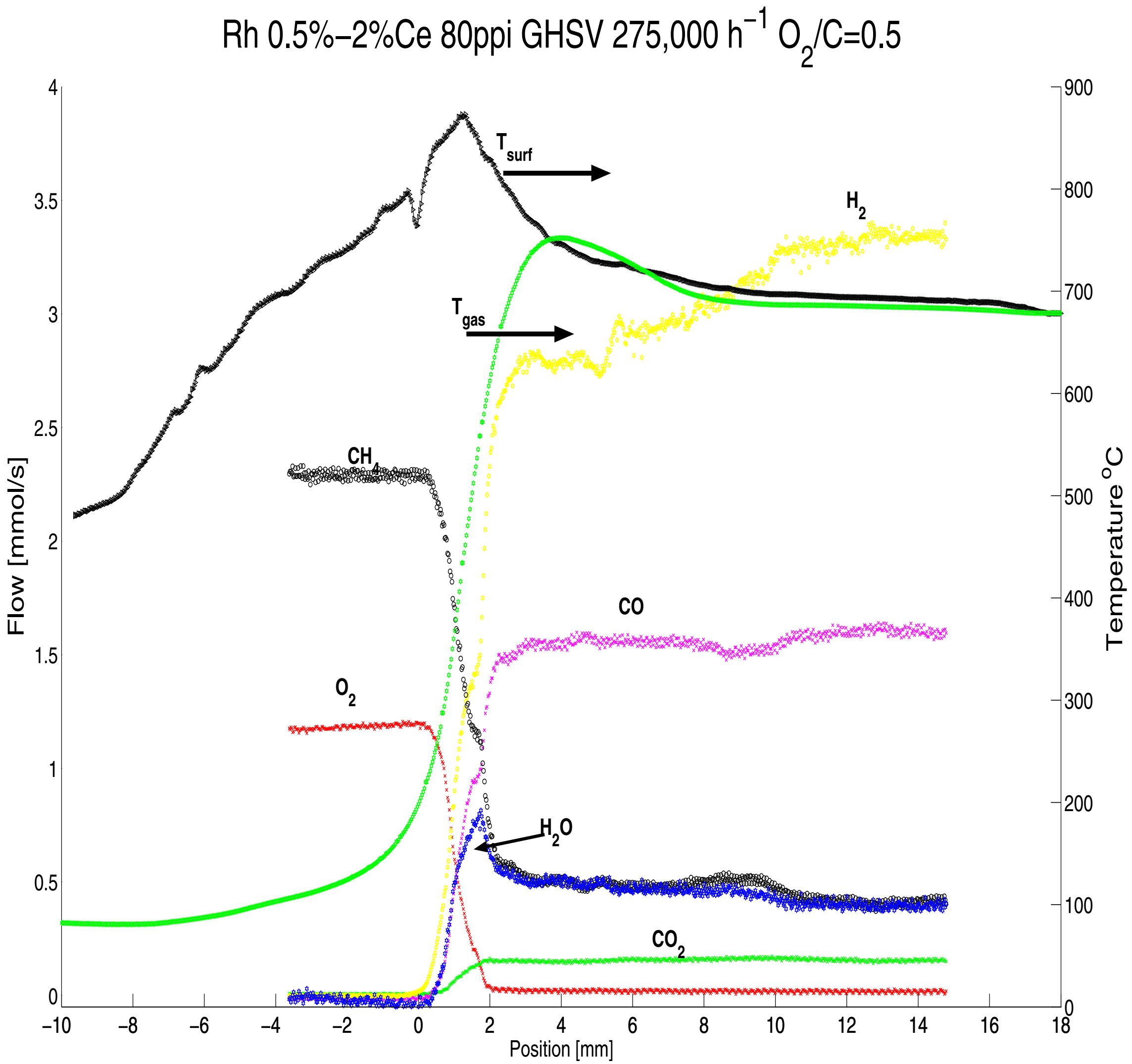
# Spatial Profiles Inside the Foam Catalyst




- 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

# Results From Spatial Profiles




- 0mm is the front face of the catalysts
- 2 zones can be identified:
- First a short ~2mm oxidation zone, where all $O_2$ is consumed. Second a longer endothermic steam reforming zone
- Very high temperature gradients in the front of the catalyst

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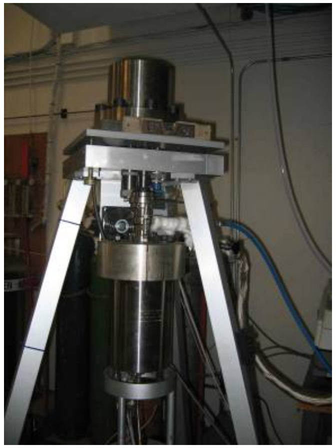
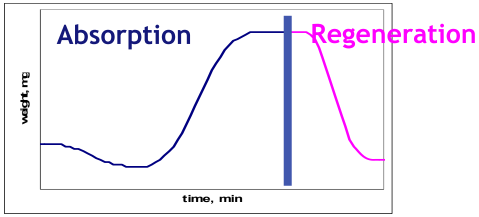
# Sulfur Adsorption Tests via TGA

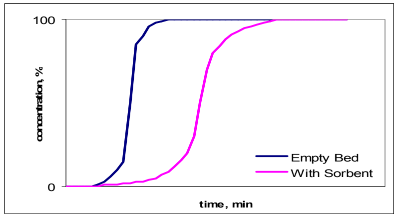
- Absorption Tests / Optimization
  - Temperature (P is determined by gasification condition)
  - $H_2S$ Level
  - Particle Size (2 levels: study effect of pore-diffusion)
  - Absorption Kinetics
  - Optimized Absorption Conditions
- Regeneration Tests / Optimization
  - Temperature
  - $O_2$ Concentration (Air/$N_2$ ratio)
  - Optimized Regeneration Conditions
- Sorbents Lifetime (Absorption / Regeneration)
  - Fixed Bed or Fluidized Bed Reactor is Suggested

$$r = \frac{dx}{dt} = f\left(x, p_{H2S}, T\right) = K p_{H2S}{}^{m} (1 - x)^{n}$$

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

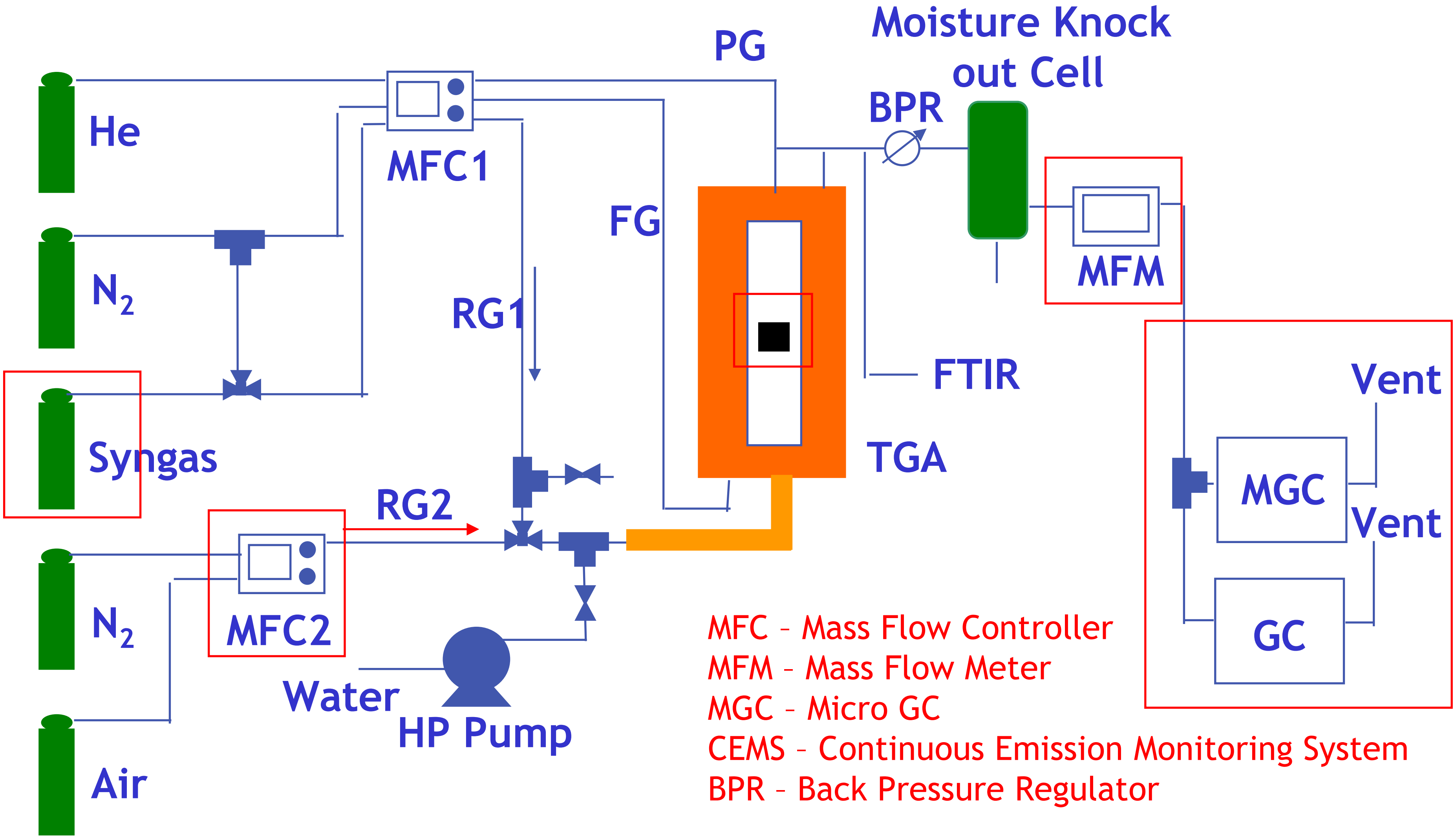





- Break-through point for the sorbent
- Absorption/regeneration kinetics
- Optimized operating condition
- Solid residence time in reactor (absorber/regenerator)
- Fluidized bed reactor/regenerator design

# P&ID - TGA System




MFC – Mass Flow Controller
MFM – Mass Flow Meter
MGC – Micro GC
CEMS – Continuous Emission Monitoring System
BPR – Back Pressure Regulator

# 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 $H_2$ 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 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 2$^{nd}$ half of 2007.