Integrated Short Contact Time Hydrogen Generator (SCPO)

Bio-Derived Liquids to Hydrogen Working Group Kick-Off Meeting
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Baltimore, Maryland

Ke Liu & Gregg Deluga
GE Global Research Center

Lanny Schmidt
Univ. of Minnesota

Ted Krause
Argonne National Lab

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SCPO Project Objectives & Highlights

Project Team

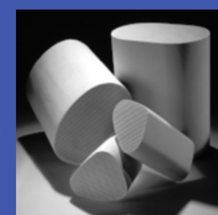
GE Global Research
- System & Economic Analysis
- Catalyst Dev. & High P Valid.
- Prototype Reactor Design
- Overall Project Management

University of Minnesota
- CPO Catalyst Discovery
- Parametric Testing & Modeling
- Catalyst Characterization

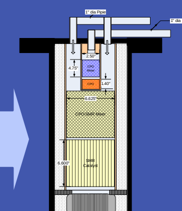
Argonne National Laboratory
- SMR Catalyst Discovery
- Catalyst Durability
- Catalyst Characterization

Project Objective: To Develop a Compact Hydrogen Generator that can Deliver H_2 at a Cost of <$3.00/kg

Lab Screen



Prototype Scale



Pilot

Technical Approach
- Develop S-tolerate Short Contact Time Catalysts
- Develop & Design Comp. CPO, SMR, WGS & HEX
- Demonstrate Critical Components

Anticipated Benefits

- Compact, Low Cost, H2 Generation Technology
- Applications in Refueling Stations, NGCC NOx Reduction & CO2 Capture

Deliverables

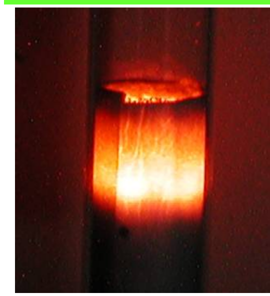
- Short Contact Time Catalysts
- Demonstration of Critical Technology & Components
- Reactor & Process Model for Scale-up

- DOE award announced in November 2004
- Initiated in January 2005

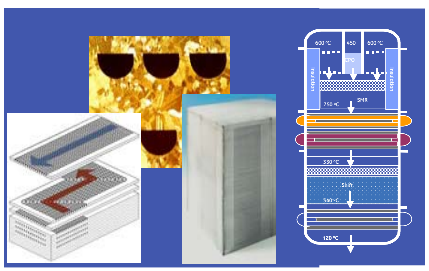
Staged Catalytic Partial Oxidation

Approaches & Features of SCPO

Sulfur Tolerate CPO Catalysts



+ Syngas Clean-up + Compact HEX & Active Cooling WGS



+ Novel System Design & integration

=Compact/Cost Effective Reformer System

Potential Application

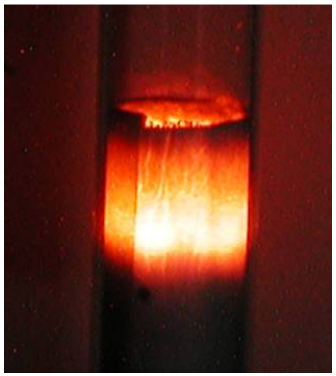
Develop Technologies for Following Potential Applications:

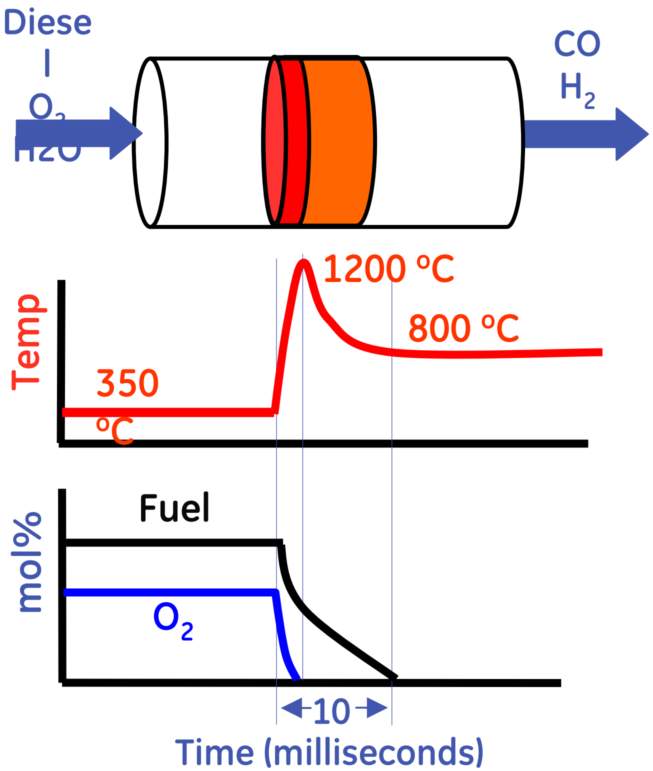
- ❑ H2 Fueling Stations
- ❑ Sulfur tolerate CPO technology for GT turn-down & NOx reduction & SOFC.
- ❑ Active Cooling WGS for NGCC & IGCC with CO2 Capture
- ❑ Sulfur tolerate SMR technology for NGCC with partial CO2 capture

Risks ⟷ Tasks & Plan to Retire Them

Risks	Tasks & Plan to Retire Them
➢Sulfur poisons CPO & SMR catalysts ➢SMR reactor bulky & expansive ➢Sulfur/Cl poisons WGS catalyst & PSA sorbents	➢Sulfur tolerate CPO & SMR catalyst development. ➢Integrate compact HEX with SMR catalyst ➢Multi-function sorbents to removal COS, H2S & HCl… before WGS. ➢Sorption kinetics study with TGA
➢Low CO conversion due to equilibrium limit in a single stage WGS reactor	➢Active cooling WGS technology development

Why Staged Catalytic Partial Oxidation (SCPO) ?





CPO: (Exothermic)
$Diesel + O_2 \rightarrow CO + H_2$

SMR: (Endothermic)
$Diesel + H_2O \rightarrow CO + H_2$

Quantify Performance/Cost Trade-offs

Minimize "Cost of Hydrogen"

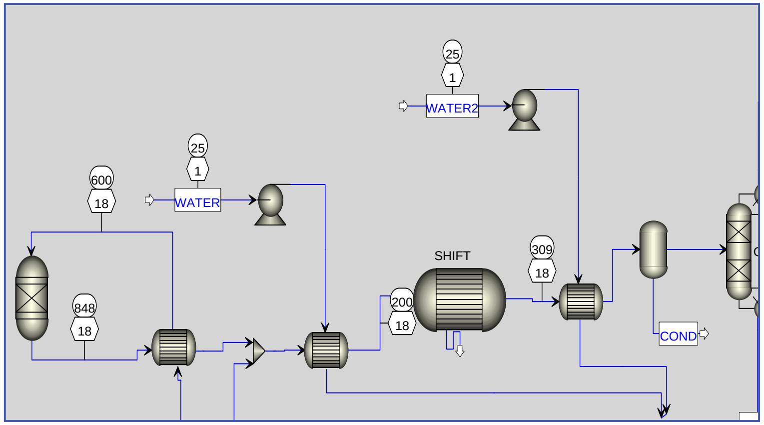
High Efficiency
- High fuel conversion
- Low steam/C
- Low O_2/C
- High PSA recovery
- Low vent temperature
- Minimum losses
- Utilization of waste heat

Low Capital Cost
- Compact (high space velocity)
- Energy Integration

Safe Operation

High Reliability

Process Model & Flow-Match



DOE H_2A Model

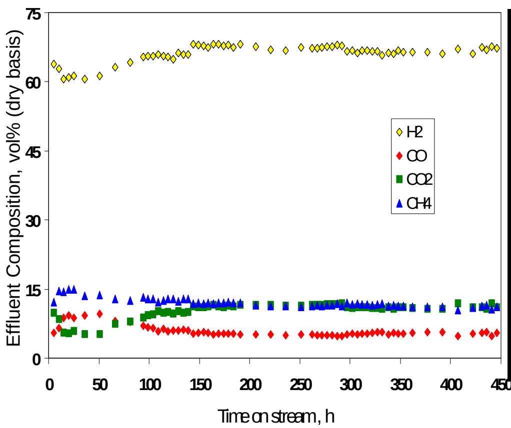
H2A Model
For Cost of H2

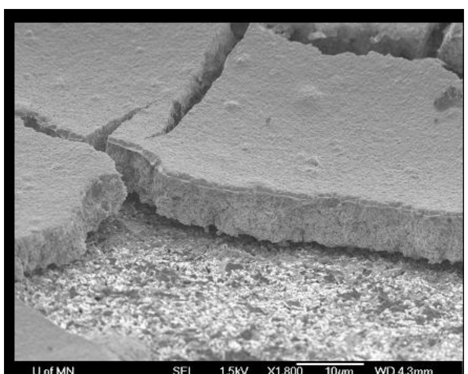
Approach: Leverage Partners' Facilities & Knowledge Base

Integrated Activities

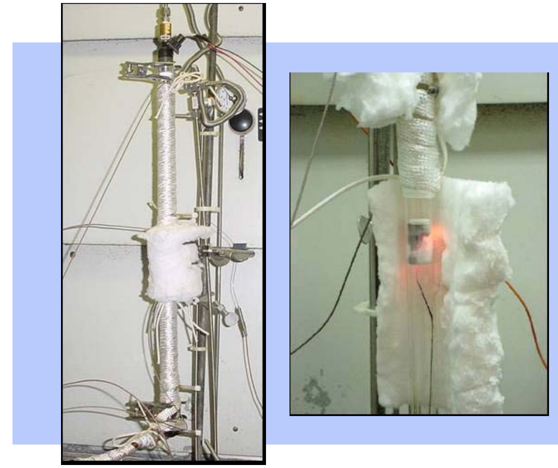
- GE design the overall system & define system conditions
- ANL & U of Mn have created catalysts and tested them at conditions GE identified
- U of Mn: New CPO catalyst & kinetics model
- ANL: New SMR catalyst & long term stability of catalysts
- Goal: Increase GHSV & S tolerance to lower capital cost.

Example Data





U of Mn Invented the CPO



ANL Has the State-of-Art Cat Testing Facilities

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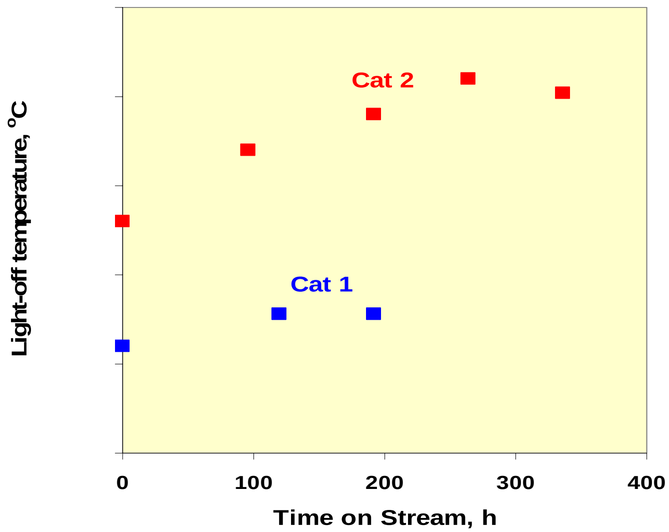
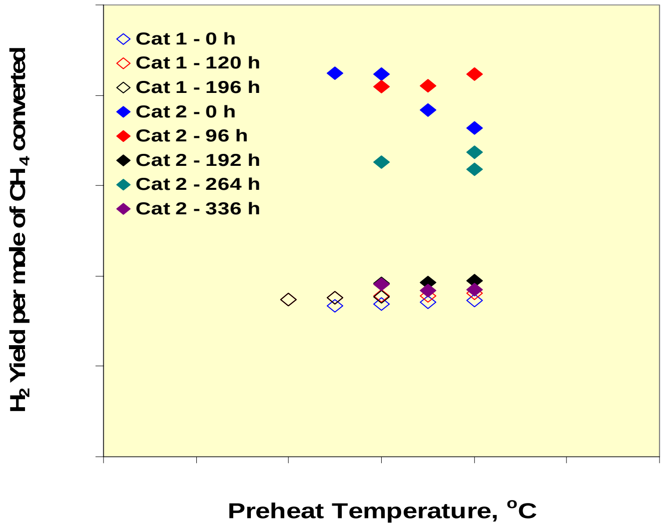
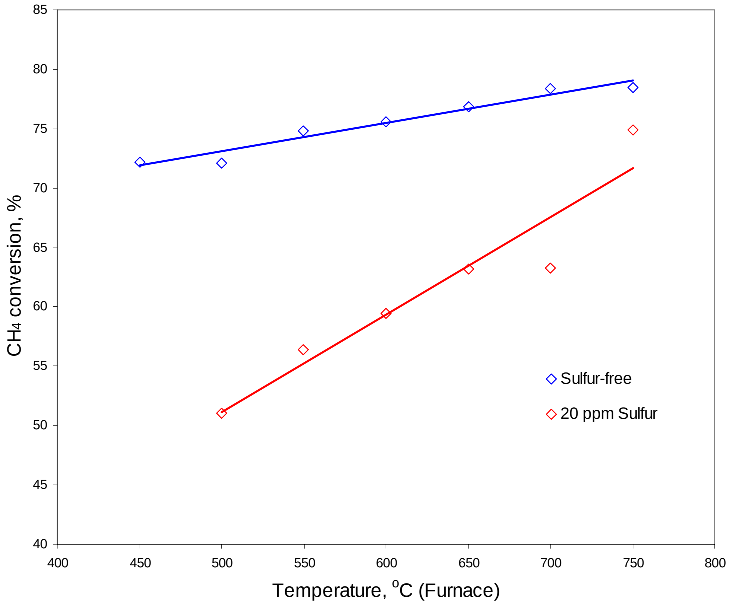
Evaluating the S-Tolerate & Durability of CPO Catalysts





Sulfur impact decreases as T increases

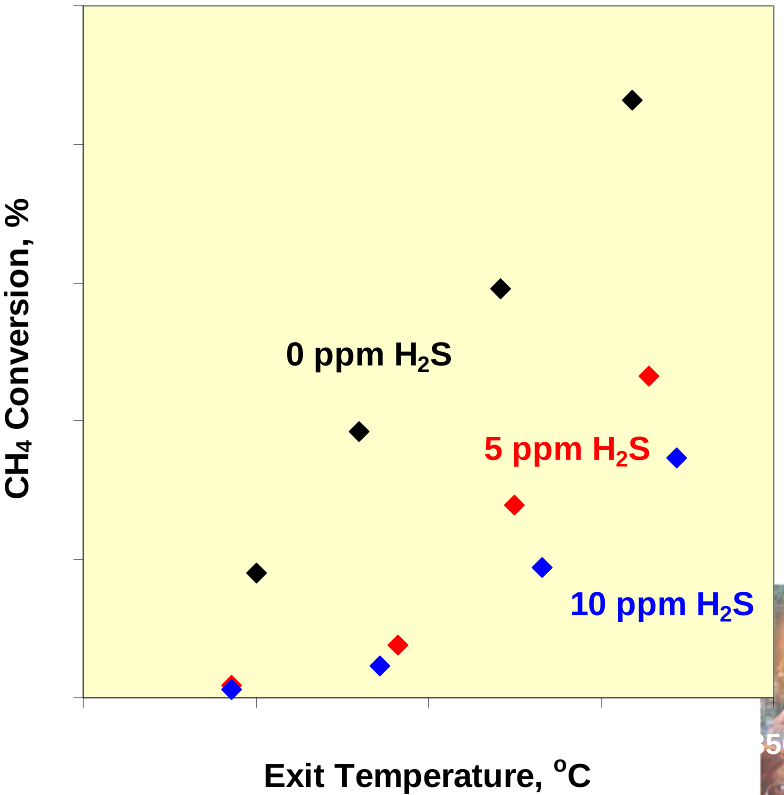


It's More Challenge to Develop S- Tolerance SMR Catalyst Than CPO Catalyst

Sulfur poisoning of SMR catalysts:

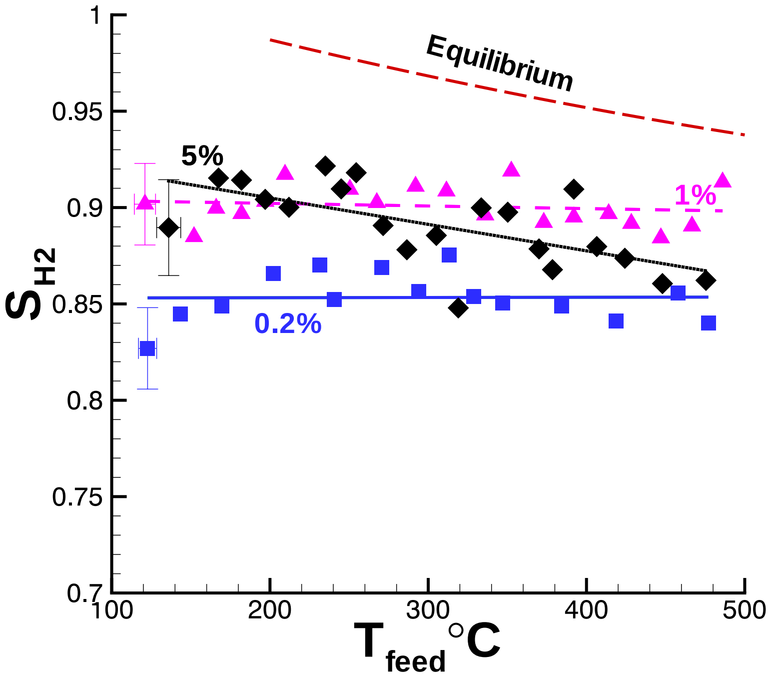
- Rapid decrease in activity when exposed to a few ppm of H_2S
- Activity stabilizes after initial decrease with only a very slight decrease in activity observed over next 8-24 h
- Essentially complete recovery of activity when H_2S is removed

Long-term effect of sulfur on catalyst performance and stability is unknown and being investigated

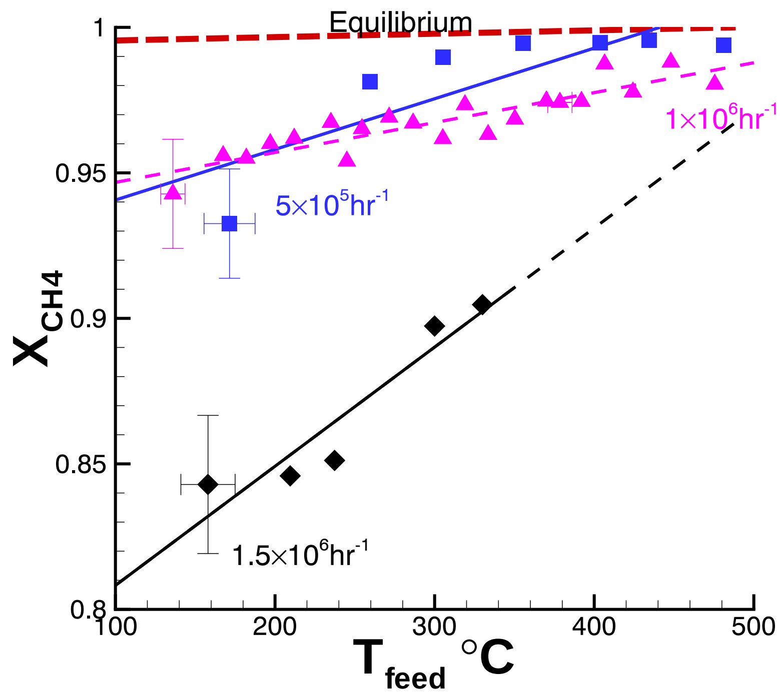


The Metal Loading of CPO Can Be Reduced

Metal Loading Effect



Space Velocity Effect



- Reaction zone is pushed to the back with increasing flow. Experiments with 3mm monoliths show that at $1\times10^{6}hr^{-1}$ the reaction is not complete
- Support determines the mass & heat transfer which are the limiting factors

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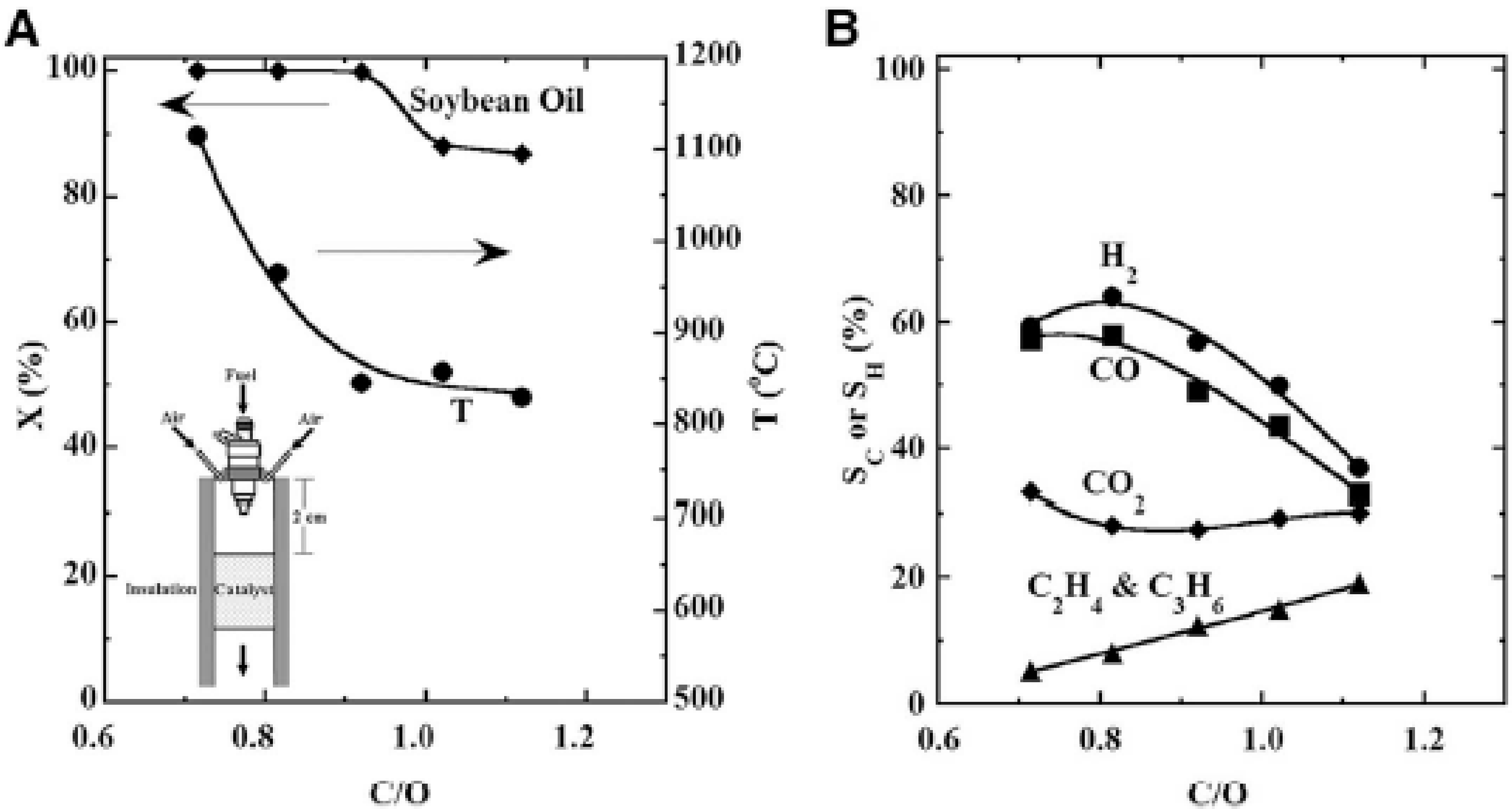
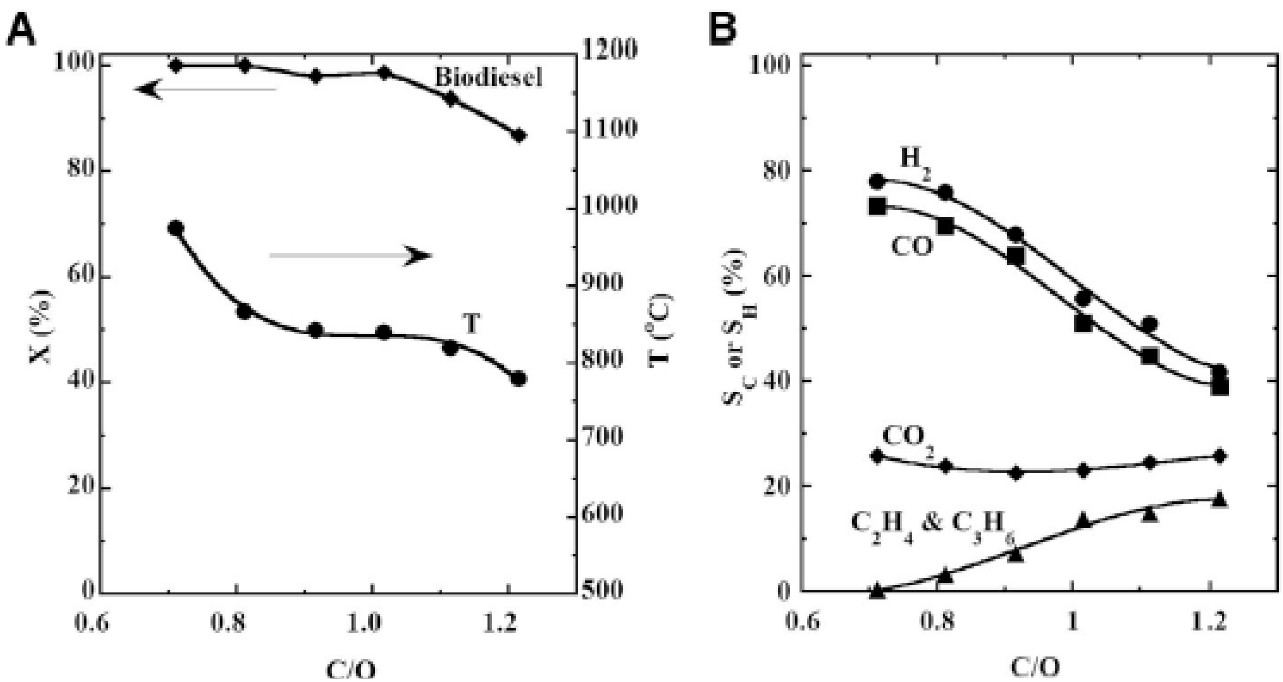
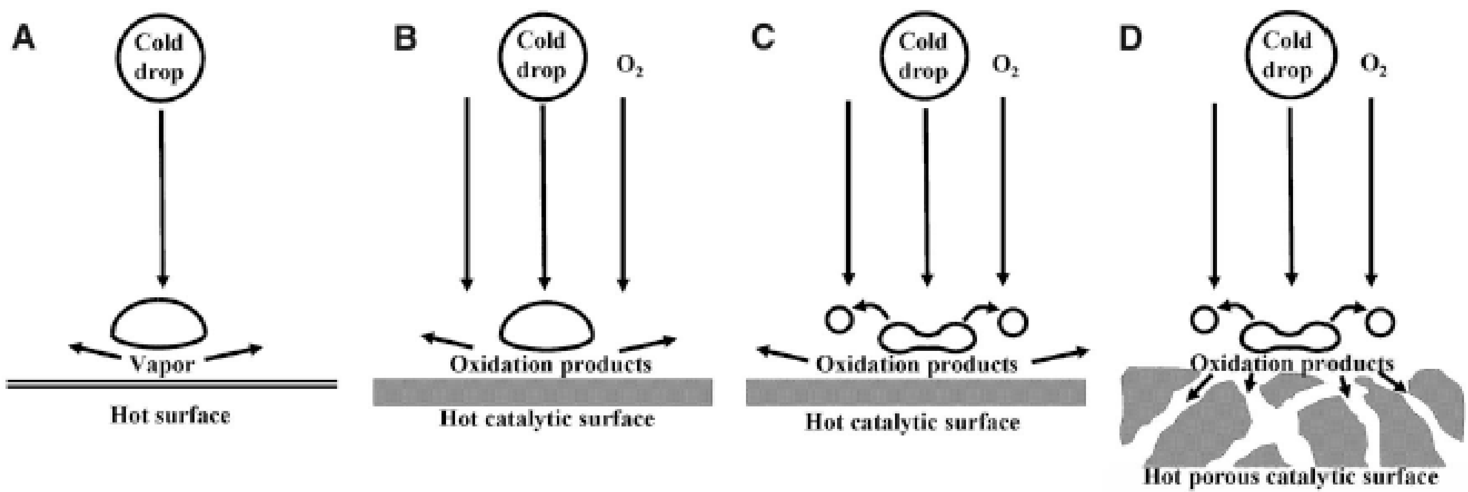
Renewable Hydrogen from CPO of Soybean Oil



J. R. Salge, B. J. Dreyer, P. J. Dauenhauer & L. D. Schmidt, 2006

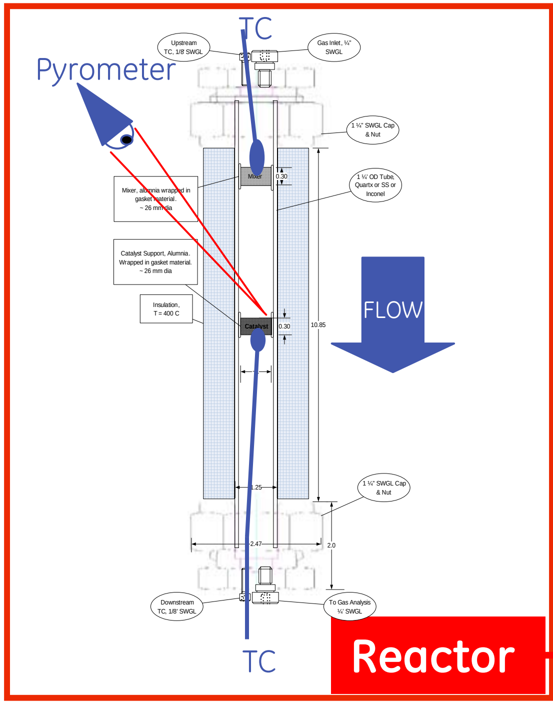
Renewable Hydrogen from CPO of Heavy Bio-diesel

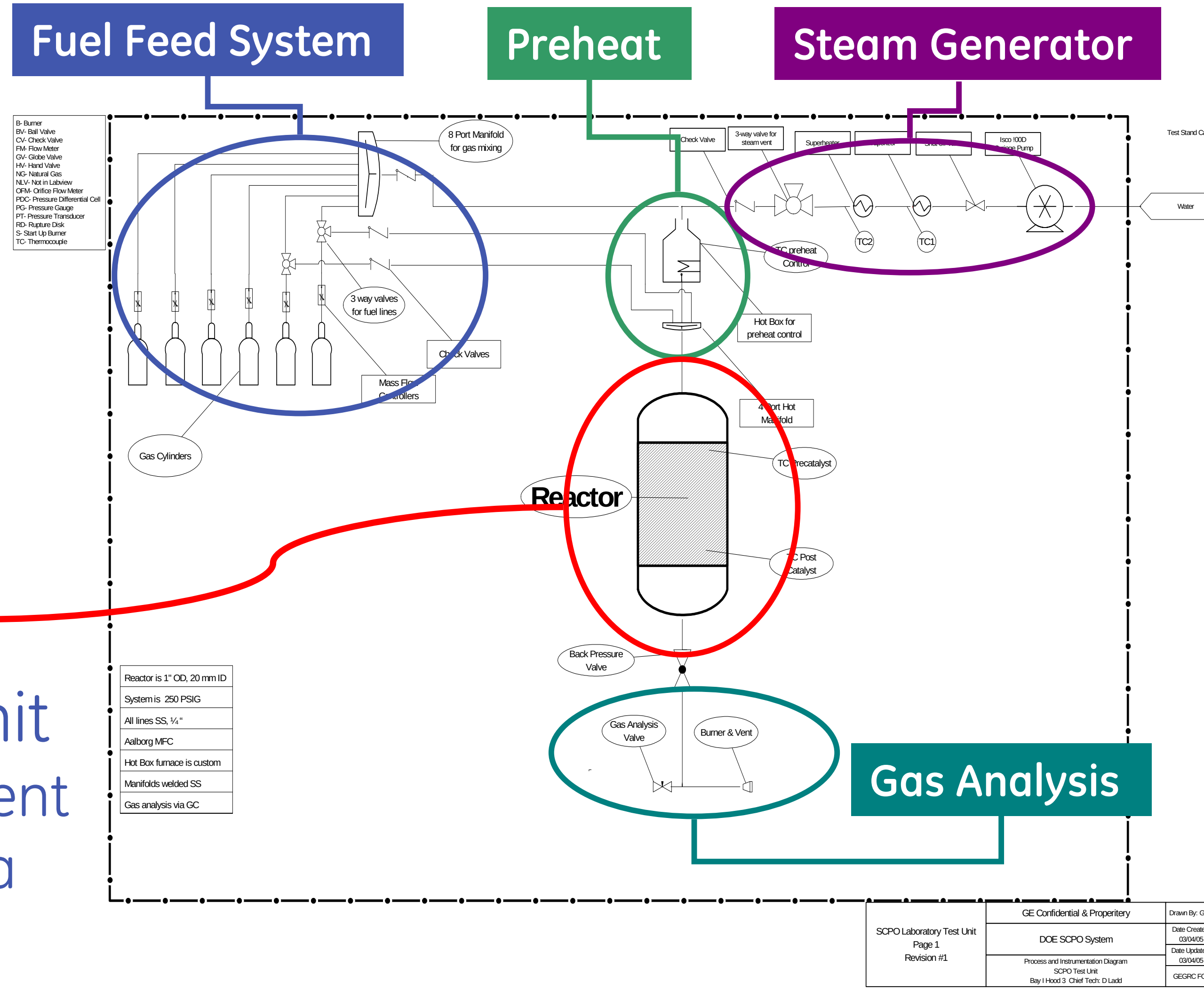




J. R. Salge, B. J. Dreyer, P. J. Dauenhauer & L. D. Schmidt, 2006

Leverage GE Reformer Design Experience





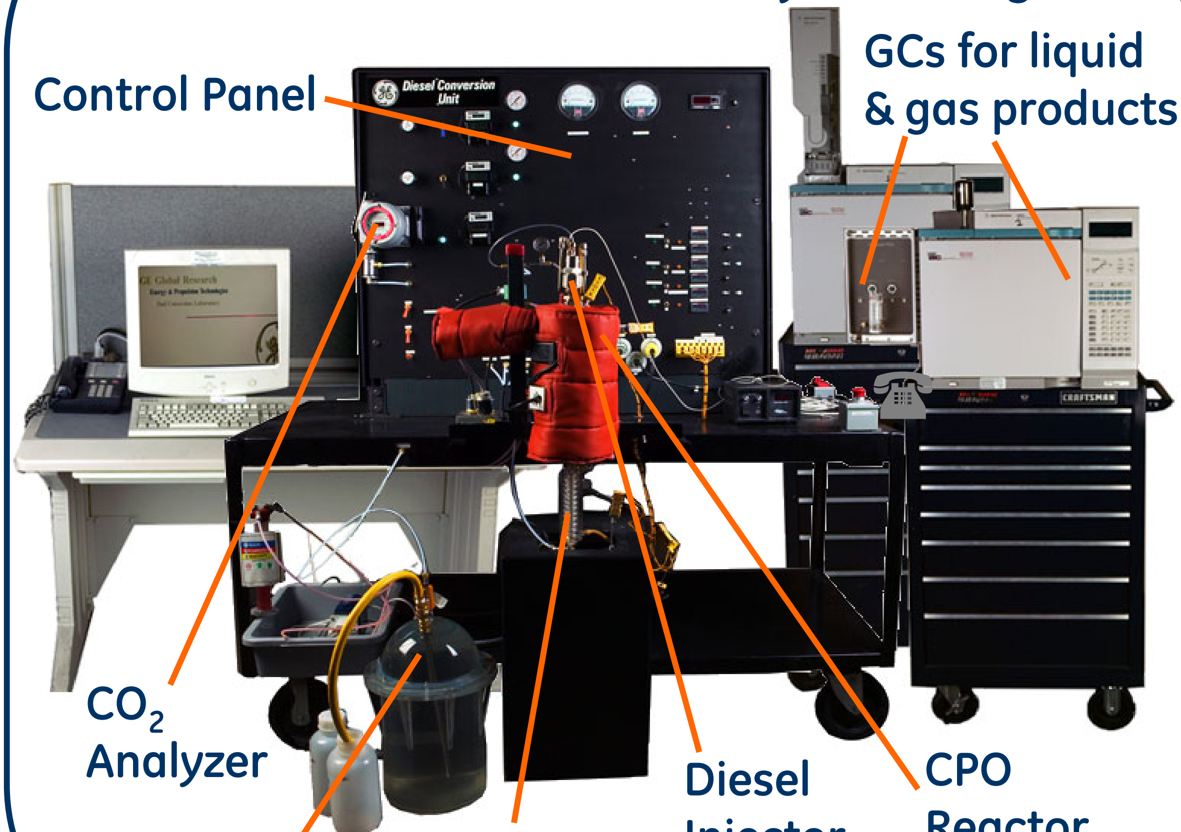
SCPO lab-scale unit

—catalyst development

—system design data

Diesel Conversion Unit Built at GE

Experimental Setup for
Diesel Conversion & Catalyst Testing

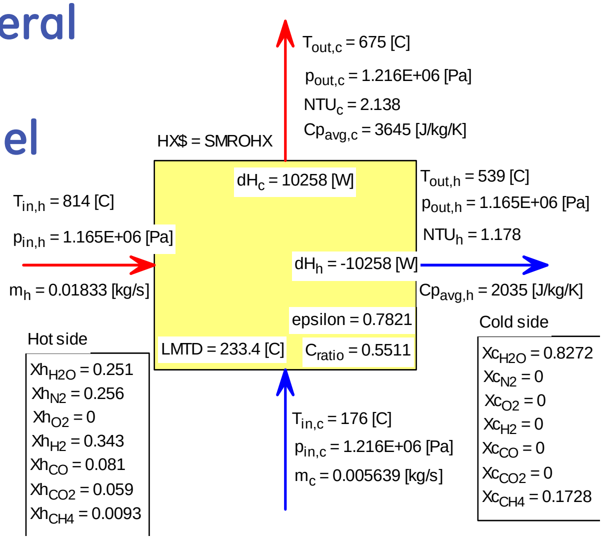


<u>Capabilities</u>

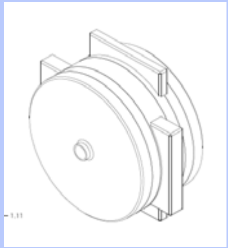
- Quantification of products
  - Gas
  - Liquid
  - Coke
- Mass balance
- Catalyst optimization

Progress & Results: Heat Exchanger Design Process

General HEX Model



HEX Technologies Evaluated




Compact shell/tube Technology

Diffusion Bonded Technology

Design of Modular, Manufacturability, Compact Heat Exchangers for SCPO

- Vendor database for GRC
- Leverage experience
- Visited vendors
- 6-Sigma tradeoff analysis

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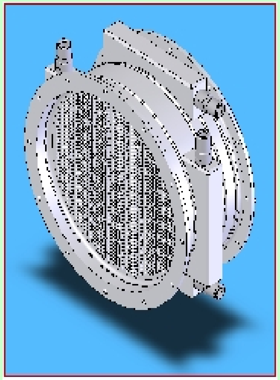
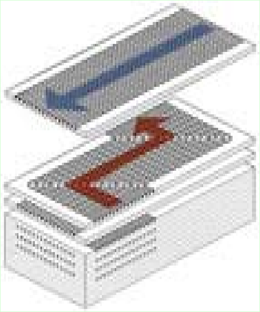
Results: Identified HEX Technology Among >50 Vendors

- GRC created HEX specifications
- Built Hex vendor database (>100 vendors)
- Vendors dropped off:
  - Missing form factor
  - No high T designs
  - Slow responses
  - Expensive
- Identified 3 vendors
  - Designs and quotes
  - Visited all of them

Vendor 1



Vendor 2

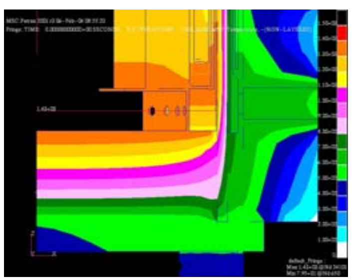


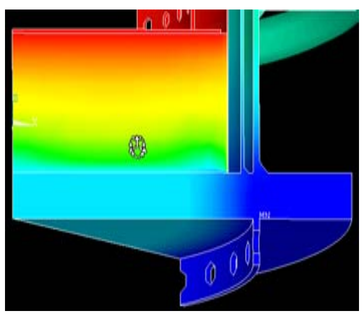
Vendor 3

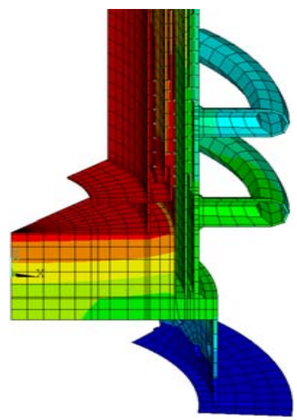
Modeling & Analysis Tools will be Used to Ensure Proper Design

Material/Criterias	Importance	SS304	Inconel 600	Inconel 601	Inconel 690	Inconel 693	Inconel 625	Inconel 617	Inconel 800H	Inconel 800HT	RA330	RA333	RA602CA
Maximum Temperature (F)			2000	2100	2000	2100	2000	2000	1900	1900	2200	2200	2200
Material Properties and Resistance													
Thermal Coefficient of Expansion	3		4	4	4	4	5	5	3	3	3	4	4
Oxidation Resistance	4	1	3	4	4	5	5	4	2	2	3	4	5
Carburization Resistance	4	1	4	4	4	5	4	5	3	3	3	4	4
Rupture Life test	4		4	4	2	4	5	5	4	4	3	4	5
Metal Dusting in a Reduced Enviroment	4		3	2	4	5	3	4	1	1	3	3	3
Costs and Availability													
Cost per ft	5		5	5	1	1	4	1	5	5	5	1	1
Lead time	5		5	5	2	1	5	2	4	4	4	2	1
	Total		118	118	83	98	128	102	94	94	102	87	90

Material of construction selected







Thermal & stress modeling performed to ensure expected vessel lifetime. The design satisfy ASME codes.

Leverage prior experience in ACR development

PSA System Evaluation

Separation Summary

- 2 leading PSA technologies evaluated, none currently reach DOE goal of 90 % recovery
- Compressor systems for both storage and feed composition have been found and quotations received
- Alternative technologies for feed compositions (oxygen membranes) were evaluated.
- Pressure of SCPO system becomes important for purification
- Storage systems for hydrogen have been studied

Specifcations for Hydrogen Purity				
Species	DOE Proposal Specification	CGA Industrial H2, Grade B	Vendor A (120 PSI)	Vendor B (120 PSI)
H2	98%	99.95%	99.996	99.95
CO	<1 ppm	<10ppm	<1.0 ppm	ND
CO2	<100 ppm	<10 ppm	<1.0 ppm	ND
N2	balance	<400 ppm	44.4 ppm	500 ppm
CH4	<100 ppm	<10 ppm	<1.0 ppm	<1 ppm
Recovery			75%	79%

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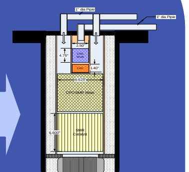
SCPO Program Highlights & Accomplishments

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

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

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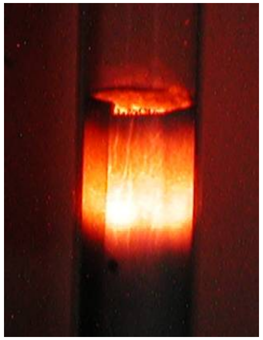
- ➢ System analysis/design completed.
- ➢ Economic analysis completed
- ➢ Reactor sizing / design completed
- ➢ HEX technology selected, design completed
- ➢ Designed, built, shakedown high-P CPO unit
- ➢ Tested CPO catalysts use both NG & Diesel
- ➢ Design & build the integrated SMR reactor
- ➢ Control strategy, start-up & shut-down procedure developed
- ➢ Completed cost analysis using GE's process model & DOE's H2A model
- ➢ Conducted preliminary FMEA analysis, major risks identified

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

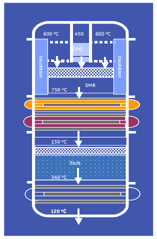
Staged Catalytic Partial Oxidation (SCPO) Reformer for Hydrogen Production from HCs & Bio-Liquids

CPO Can Reform/Gasify Heavy Bio-liquids !

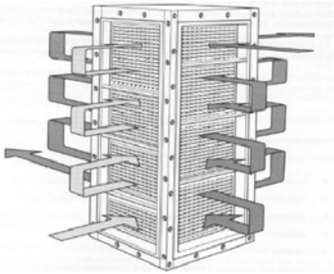
- ❑ Most cost effective distributed hydrogen production unit
  - ➢ Compact (Reformer vessel 5 times smaller than ACR)
  - ➢ Modular design for mass production
- ❑ Ease of ownership
  - ➢ "Maintenance free" – reformer vessel life > 10 years
  - ➢ Catalyst life > 5 years
  - ➢ Fuel flexibility – can be operated with various grades of NG, ethanol & methanol…
  - ➢ Automatic, unmanned operation
- ❑ Environmentally sound
  - ❑ Higher efficiency than ATR/CPO
  - ❑ No emissions except: N_2, CO_2 & Water



➢Patented staging of CPO & SMR catalysts.
➢ Leverages proven catalysis technologies



Estimated SCPO reformer vessel size: < 150 lit



Compact heat exchanger design will further reduce the SCPO size

http://heat-exchangers.globalspec.com/