Diesel Reforming for Fuel Cell Auxiliary Power Units

SECA Core Technology Program Review

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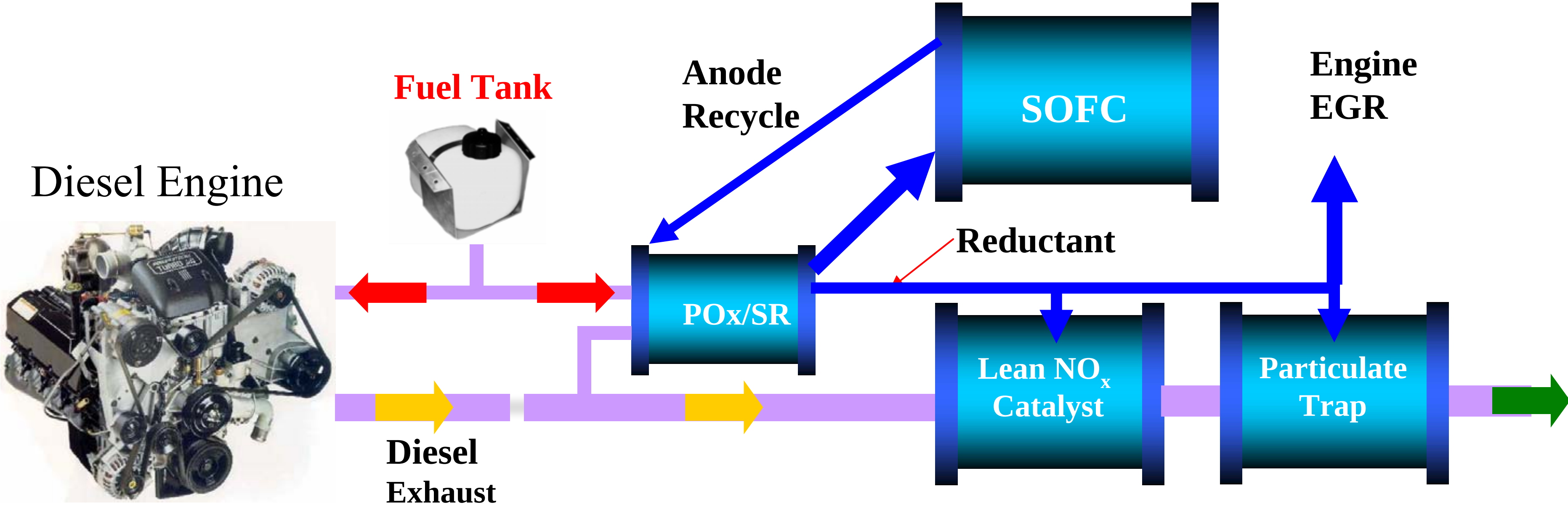
Applications of Diesel Reformers in Transportation Systems



Reforming of diesel fuel can have simultaneous vehicle applications:

- **SECA application: reforming of diesel fuel for Transportation SOFC / APU**
- Reductant to catalyze NOx reduction, regeneration of particulate traps
- Hydrogen addition for high engine EGR
- Fast light-off of catalytic convertor

Our goal is to provide kinetics, carbon formation analysis, operating considerations, catalyst characterization and evaluation, design and models to SECA developers.

Diesel Fuel Processing for APUs
Technical Issues

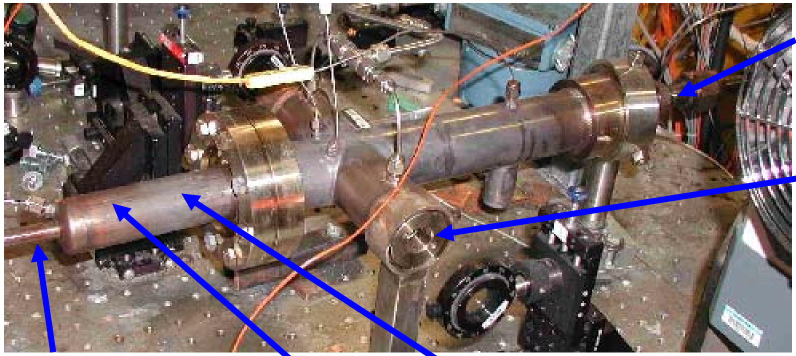
- Diesel fuel is prone to pyrolysis upon vaporization
  - Fuel/Air/Steam mixing
  - Direct fuel injection
- Diesel fuel is difficult to reform
  - Reforming kinetics slow
  - Catalyst deactivation
    - Fuel sulfur content
    - Minimal hydrocarbon slip
    - Carbon formation and deposition
    - High temperatures lead to catalyst sintering
- Water availability is minimal for transportation APUs
  - Operation is dictated by system integration and water content
    - water suppresses carbon formation

Diesel Reforming
Objectives and Approach

- **Objectives:** **Develop technology suitable for onboard reforming of diesel**
  - Research fundamentals (kinetics, reaction rates, models, fuel mixing)
  - Quantify operation (recycle ratio, catalyst sintering, carbon formation)
- **Approach:** **Examine catalytic partial oxidation and steam reforming**
  - Modeling
    - Carbon formation equilibrium
    - Reformer operation with anode recycle
  - Experimental
    - Carbon formation
    - Adiabatic reformer operation
      - Anode recycle simulation
      - Direct diesel fuel injection, SOFC anode and air mixing
      - Catalyst temperature profiles, evaluation, durability
      - Hydrocarbon breakthrough
    - Isothermal reforming and carbon formation measurements
      - Catalyst evaluation, activity measurements
      - Carbon formation rate development

Diesel Reforming
Measurements and Modeling

Adiabatic Reactor with nozzle



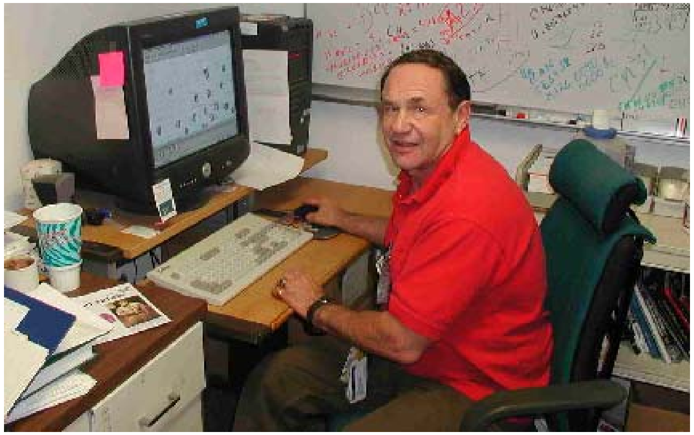
Window for Catalyst Reaction Zone Observation

Windows for laser diagnostics

Air / anode recycle

Nozzle

Catalyst (Pt/Rh)



Furnace

Iso-thermal system

- Measure kinetics
- Steam reforming / POx
- Light-off
- Carbon formation

Iso-thermal Microcatalyst

Modeling

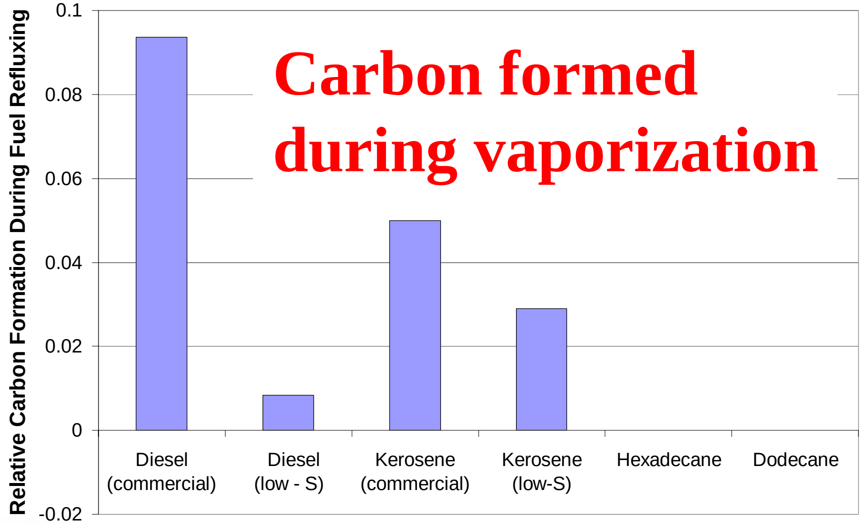
Equilibrium

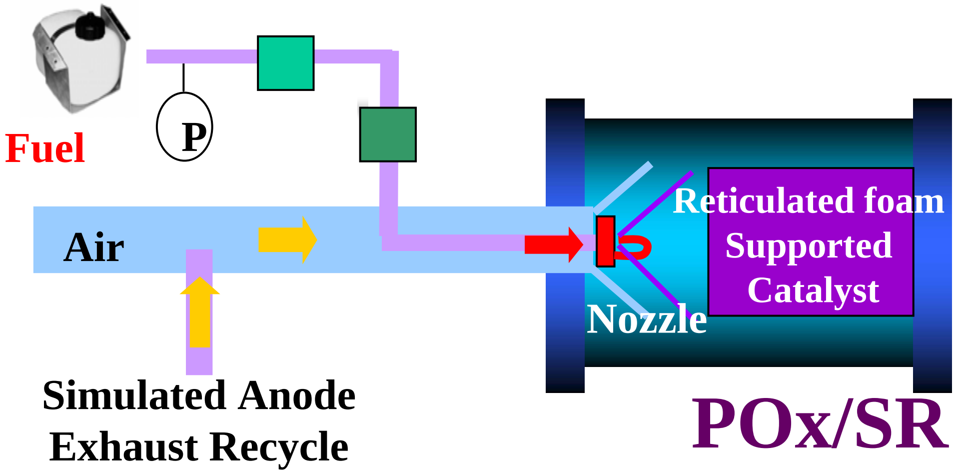
Kinetic

Composition

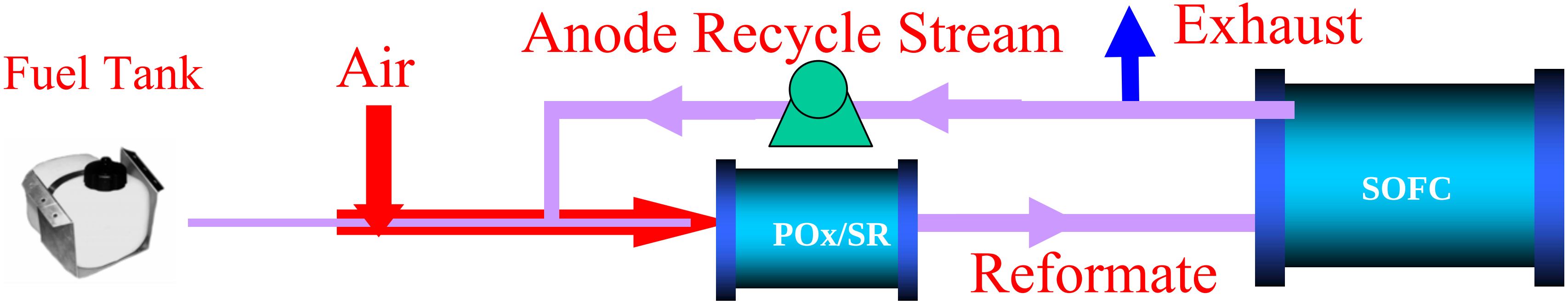
Direct Injection Fuel Nozzle Operation

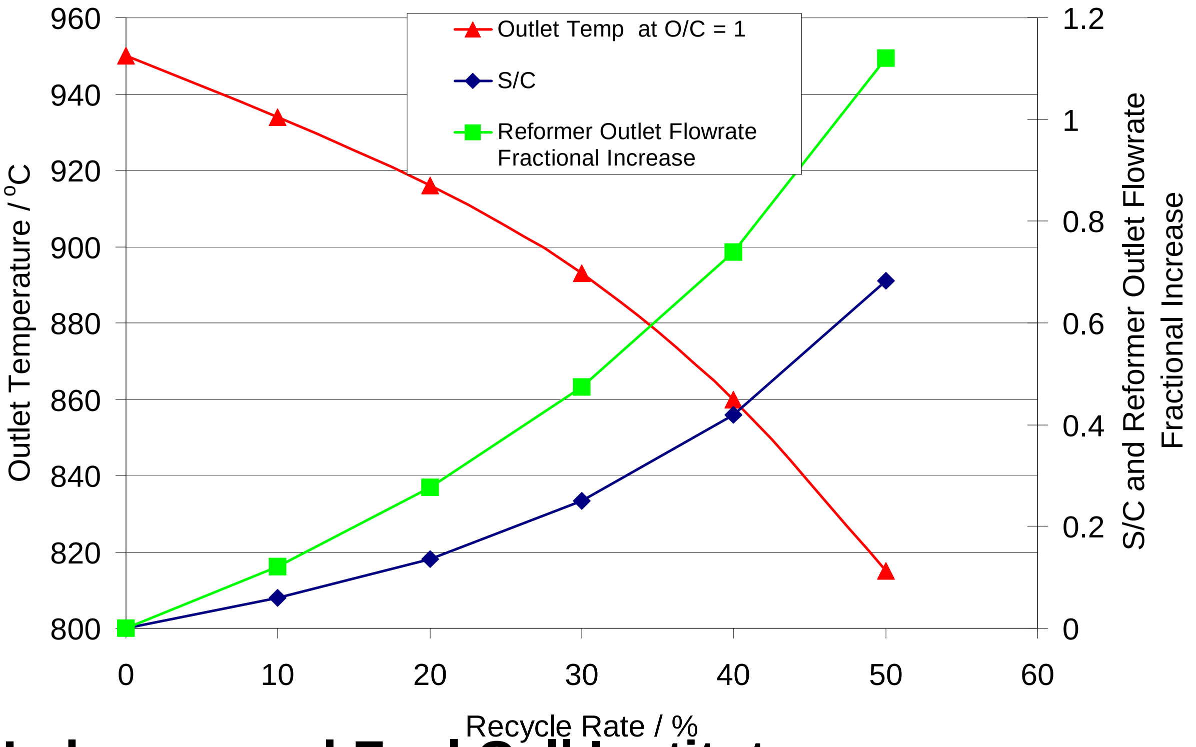
- **To avoid carbon formation during vaporization requires direct fuel injection**
- **Directly inject fuel to reforming catalyst**
  - Commercial nozzle, control fuel pressure for fuel flow (~ 80 psi)
  - Air / anode recycle (H_2 / N_2) distribute in annulus around fuel line / nozzle
- **Experimental results**
  - Operated successfully at steady state
    - Minimum fuel flow dictated by fuel distribution from nozzle
  - Requires control of fuel/air preheat, limiting preheat (~ < 180 °C)
    - Prevents fuel vaporization/particulate formation





SOFC Anode Recycle Modeling



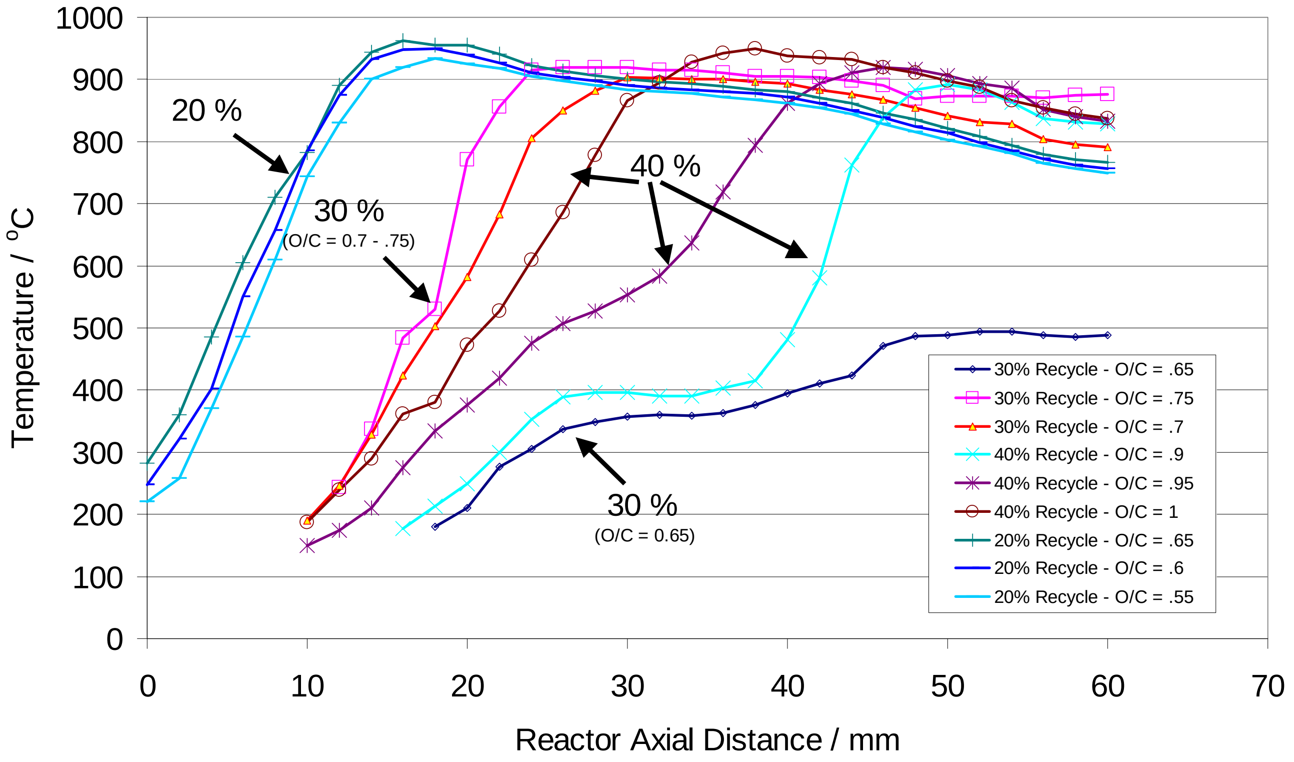


Recycling of 50% SOFC Anode Flow, S/C = 0.7

Model assumes 50% anode fuel conversion

Axial Temperature Profiles during Diesel Reforming

Low-S Swedish diesel fuel



Adjusted O/C for similar operating temperatures

Pt / Rh supported catalyst

Residence time ~ 50 msec

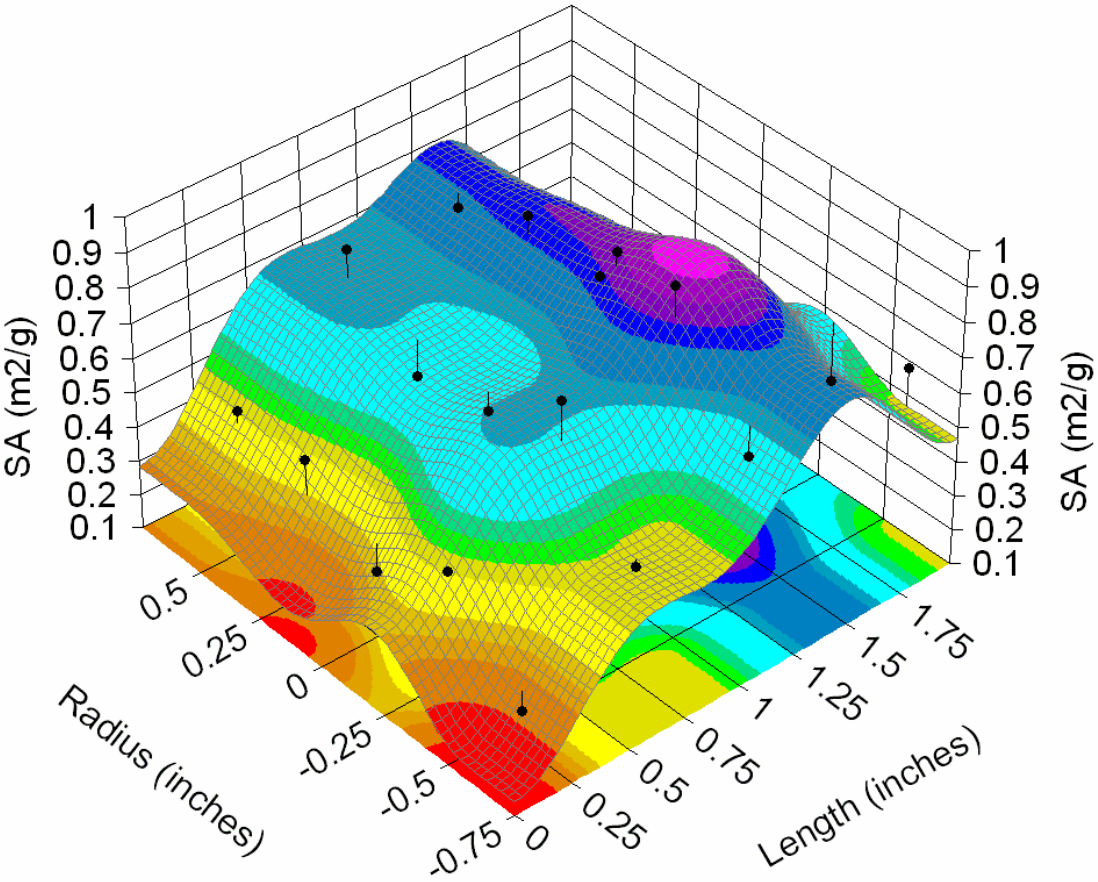
Anode recycle simulated with H_2, N_2, H_2O

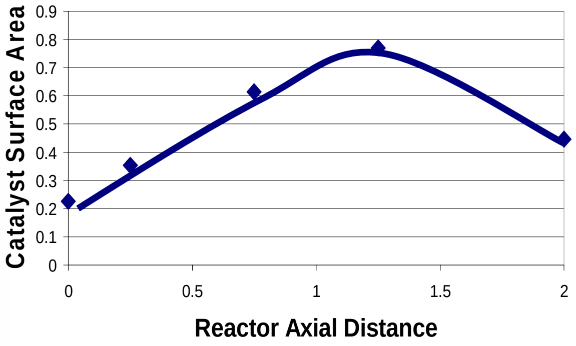
Higher recycle ratios move oxidation downstream in reformer

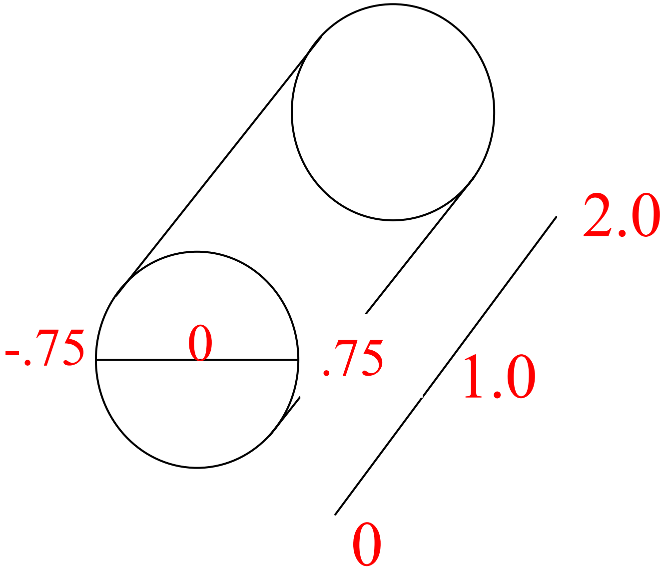
Lower recycle ratios require low O/C for similar adiabatic temperature rise

Adiabatic Reformer Catalyst Surface Area Axial and Radial Profile

BET Surface Area Distribution



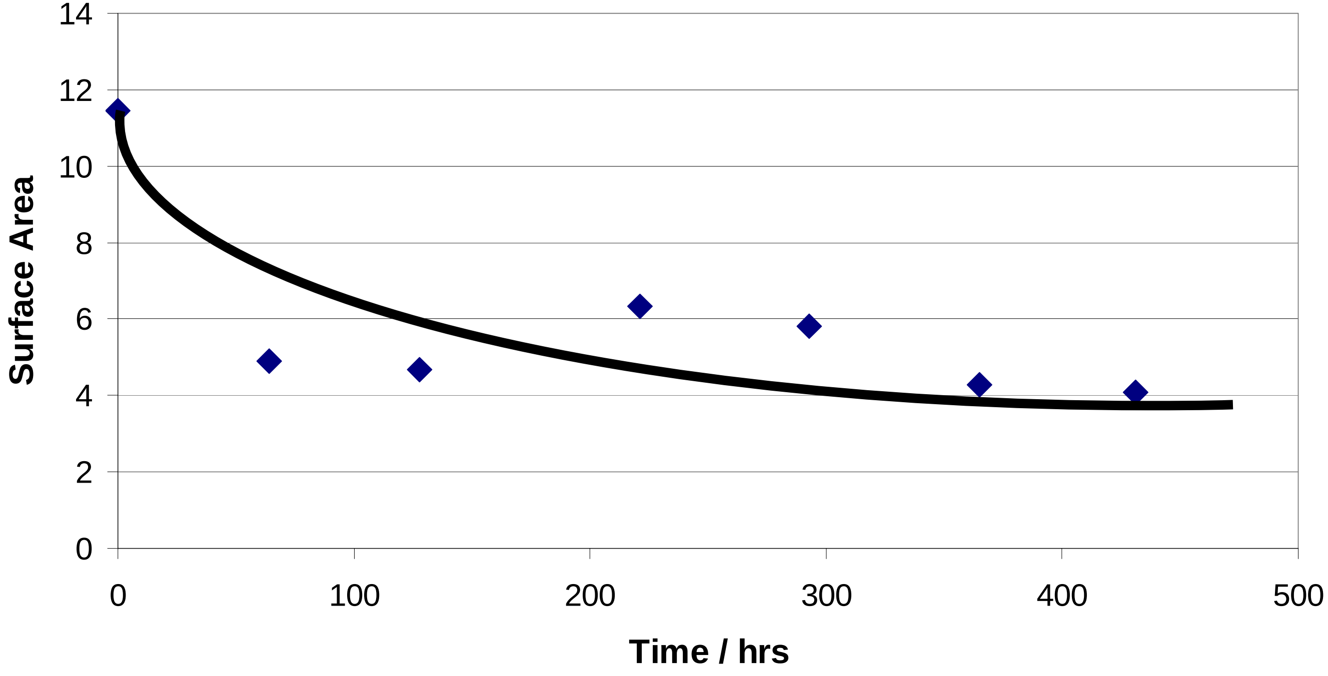




Original Surface Area ~ 4.3

Catalyst Sintering Measurements

Catalyst surface area with exposure at 900 °C
(inert atmosphere)



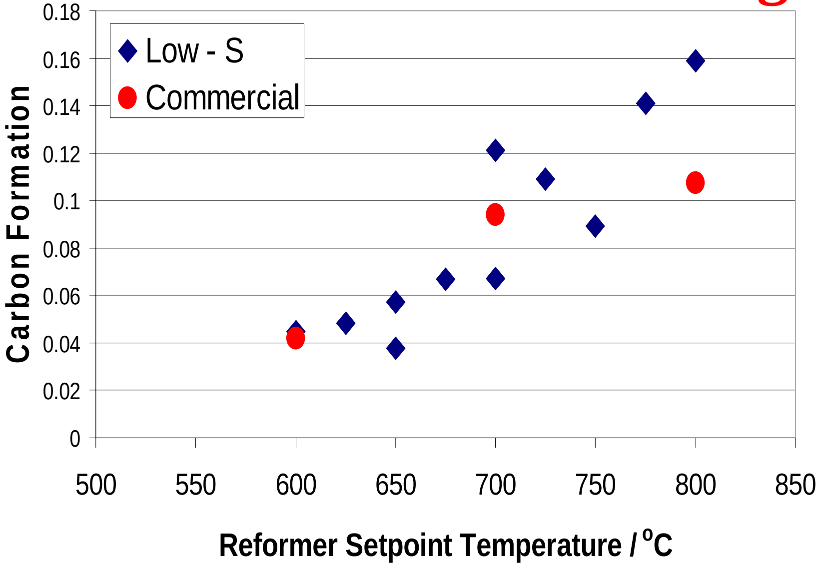
Initial catalyst sintering tests to determine effects on catalyst surface area loss (temperature, chemical environment, poisoning)

Carbon Formation Issues

- Avoid fuel processor degradation due to carbon formation
  - Carbon formation can reduce catalyst activity, system pressure drop
  - Operation in non-equilibrium carbon formation regions
  - Low water content available for transportation diesel reforming
  - Rich operation - Cannot avoid favorable carbon equilibrium regions
- Catalysts
  - Various catalysts more/less prone to carbon formation
- Diesel fuels
  - Carbon formation due to pyrolysis upon vaporization

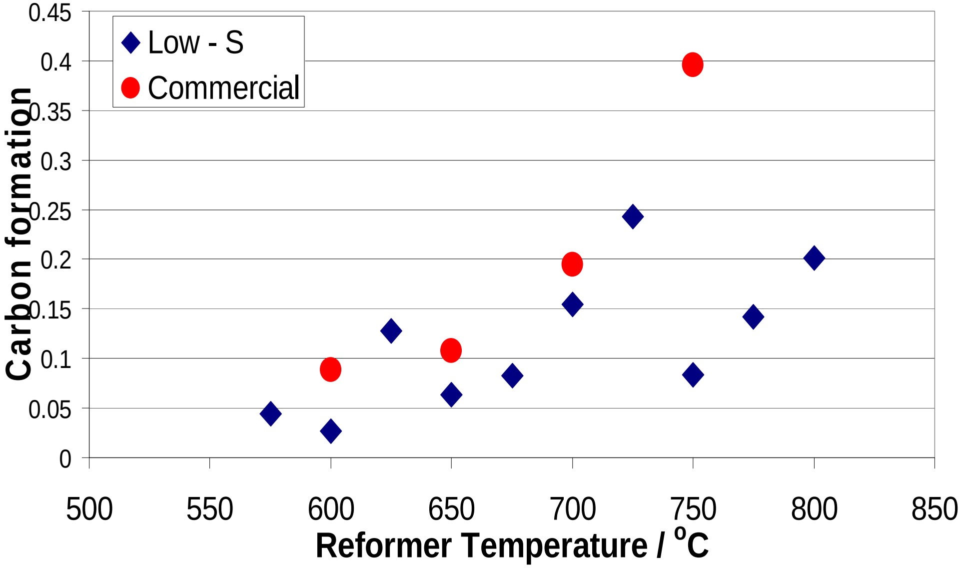
Carbon Formation from Low-Sulfur Swedish and Commercial Diesel Fuel (iso-thermal)

AutoThermal Reforming



O/C = 1.0
S/C = 0.34

Steam Reforming

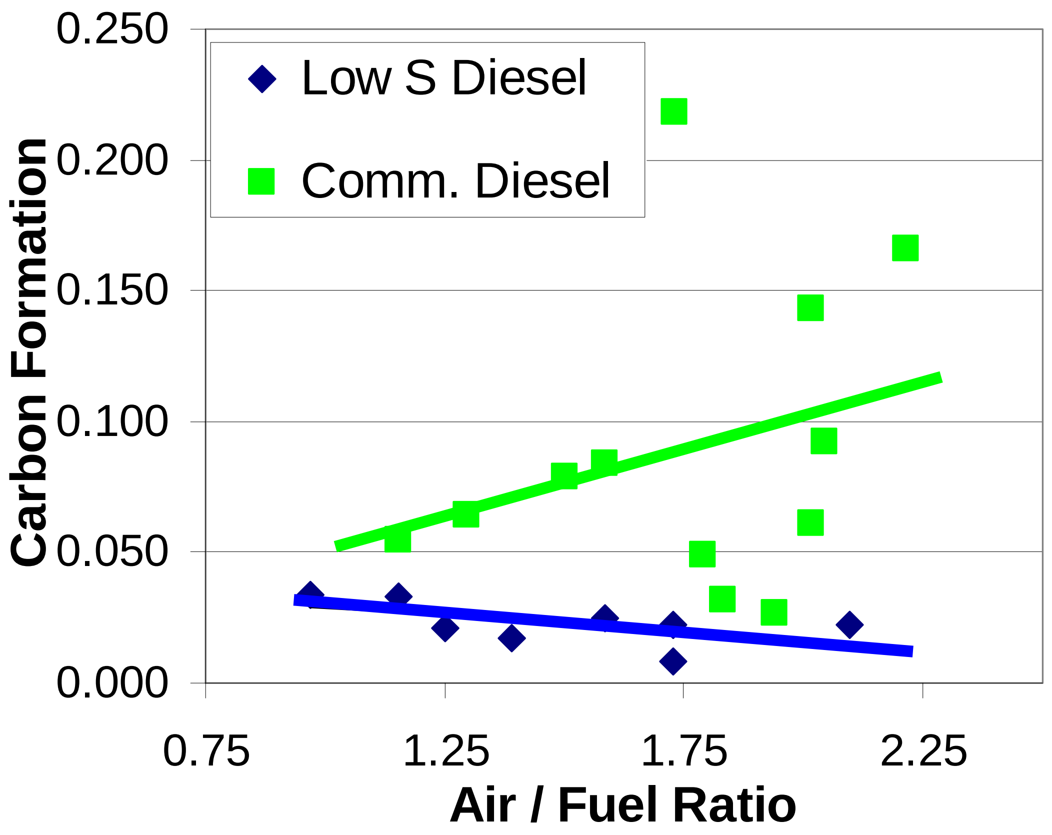


S/C = 1.34

Increased carbon formation with increasing temperature during both ATR and SR

Adiabatic Reactor
Carbon Formation Measurements

AutoThermal Reforming

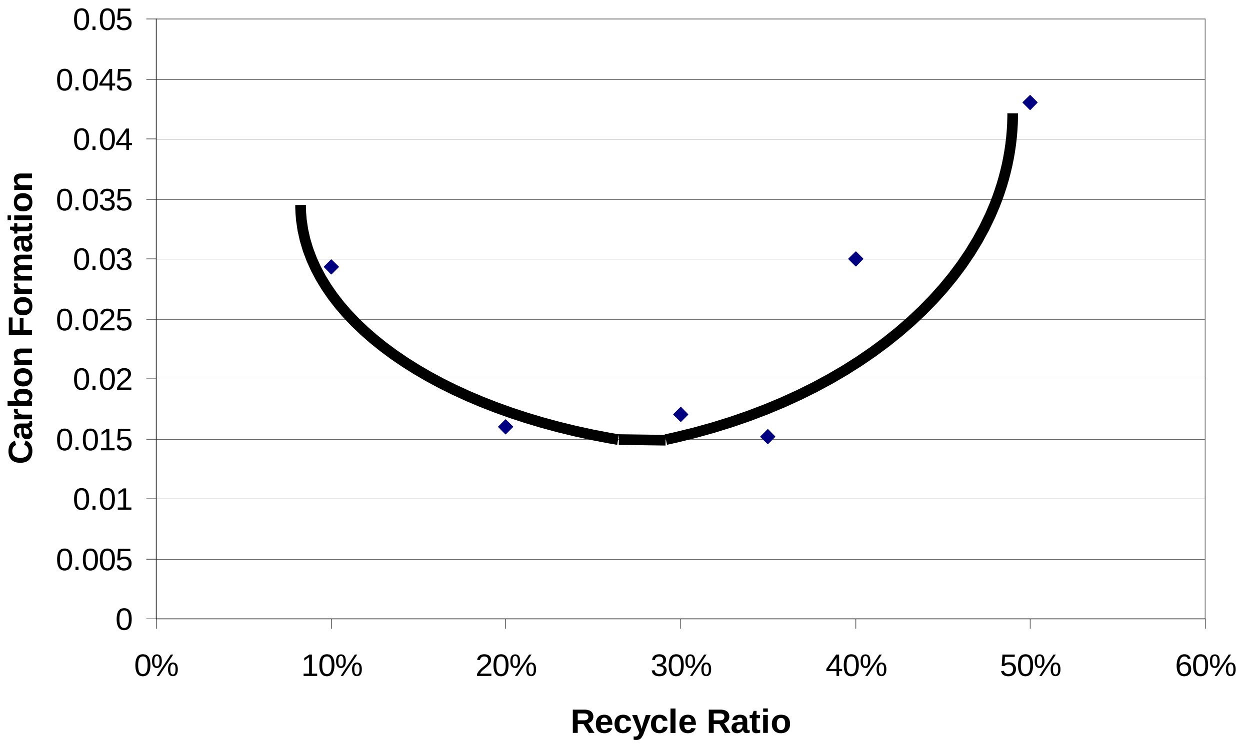


Air (SLPM) / Fuel (ml/min)

- Simulates 35% SOFC anode recycle
  - S/C ~ 0.34
- Average 3x higher carbon with commercial fuel than Low-S
- Carbon formation increases with increasing air (T) for commercial
- Carbon formation decreases with increasing air flow (T) for Low–S

Carbon Formation vs. recycle ratio

(adiabatic ATR reforming)



Constant air/fuel ratio: O/C = 0.7

Fuel: Swedish Diesel Fuel

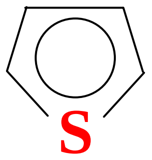
Sulfur Effect on Diesel Reforming

Sufur content in tested fuels	
Odorless Kerosene	N.D.
Commercial Diesel	314 ± 17
Swedish Diesel	N.D.
Kerosene	149 ± 16

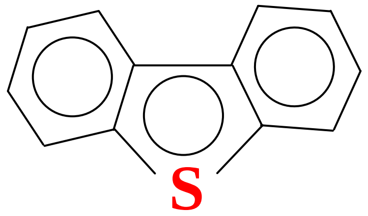
Added 300 ppm S (by wt% S) From Thiophene and DiBenzoThiophene (DBT) to Low-Sulfur Swedish diesel and dodecane to examine effect on reforming fuel conversion and carbon formation.

Sulfur compounds

Thiophene

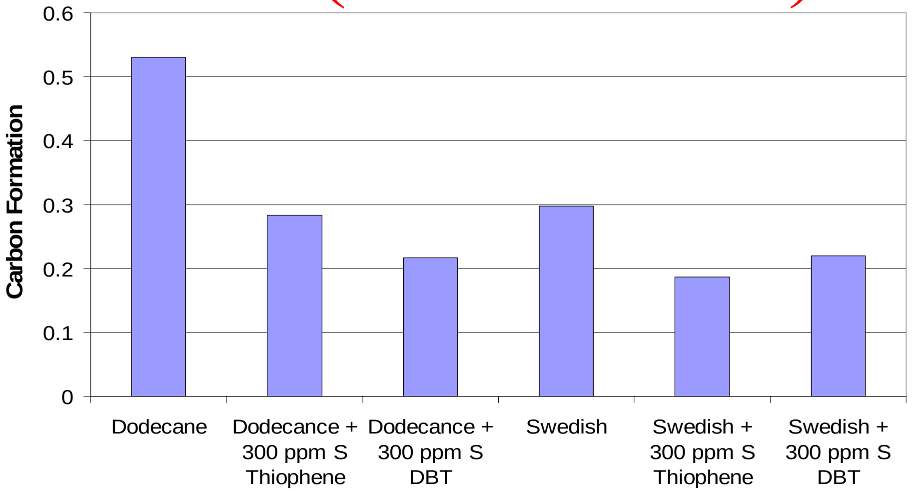


Dibenzothiophene

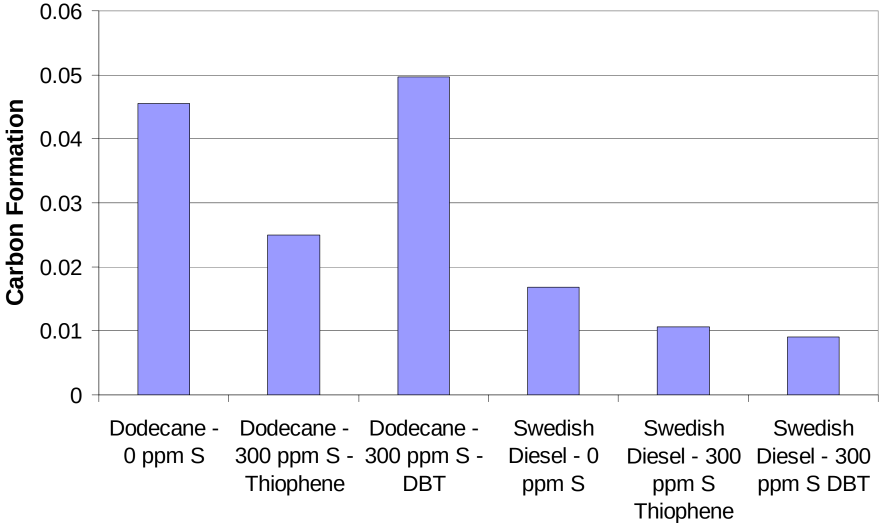


Sulfur effect on Carbon formation

(Iso-thermal)



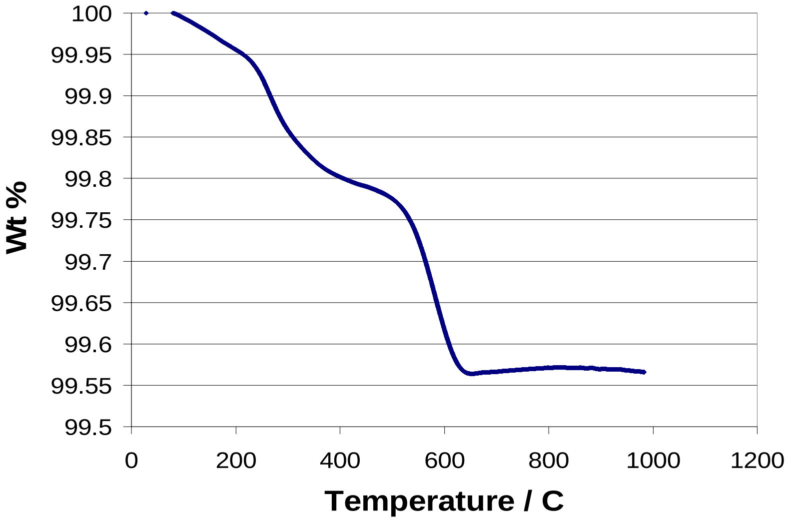
(Adiabatic)



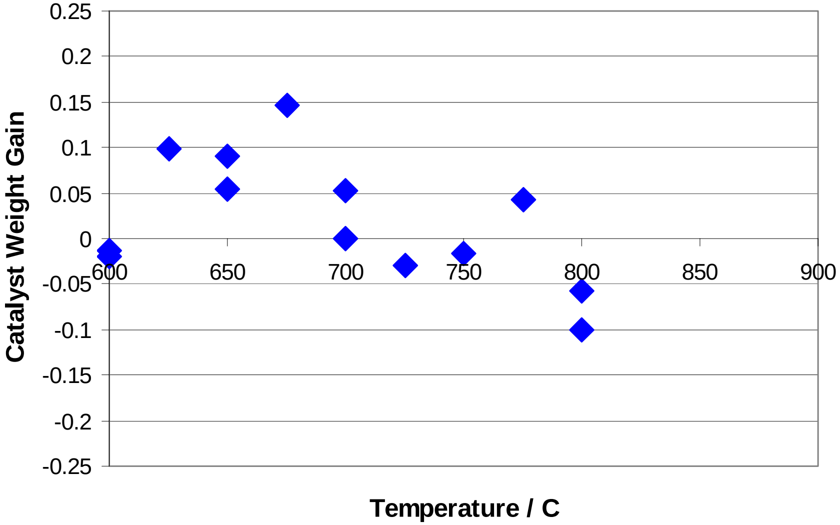
- Addition of Sulfur compounds (thiophene and DBT) does not increase carbon formation
- Higher carbon formation from pure dodecane than from Swedish diesel
- No detectable carbon (by XRF) in carbon samples regardless of sulfur content in fuel (Dodecane and Low-S Swedish Diesel Fuel)

Carbon Formation Analysis and Location

(TGA) Thermal Gravimetric Analysis of catalyst after carbon formation measurements in isothermal reactor



Catalyst weight change after carbon formation measurements in the isothermal reactor



Carbon removal is about 0.4 % catalyst weight

Carbon is not typically 'bound' to catalyst surface (for noble metal catalysts / with oxide supports)

Carbon Formation Rate

Activation energy for carbon formation:

$$r_{carbon} = k \exp(-Ea/RT)$$

Isothermal steam reforming (S/C = 1.0)

commercial diesel	86.8 kJ/mol
low-S diesel	134.2 kJ/mol

Isothermal ATR (O/C = 1.0, S/C = 0.34)
(Simulating 35% recycle)

commercial diesel	97.9 kJ/mol
low-S diesel	72.4 kJ/mol

Literature values for carbon formation of 118 kJ/mol (CO_2 reforming of CH_4 over Ni/Al_2O_3 catalysts)
Wang, S., Lu, G., Energy & Fuels **1998**, 12, 1235.

Carbon from fuel that ends up as carbon particulate

Iso-thermal ATR	
0.13%	Low-S Diesel
0.12%	Commercial Diesel
Iso-thermal SR	
0.22%	Low-S Diesel
0.21%	Commercial Diesel
Adiabatic ATR	
0.03%	Low-S Diesel
0.09%	Commercial Diesel

Low –S Diesel ATR scales to
3.1 kg Carbon (10,000 hrs)
12.4 kg Carbon (40,000 hrs)

Nanocomposite Ni Catalyst Work

- Initial success usingNi/YSZ and Ni/ZrO2 nanocomposite catalysts (separate project)

- Freeze-drying process to prepare nanocomposites:
- Ultrasonic nozzle makes aerosol of liquid droplets
- Liquid droplets frozen in LN_2 and collected
- Solvent removed by sublimation
- Obtain low density reactive precursor powder
- Catalyst activated by calcining and reduction

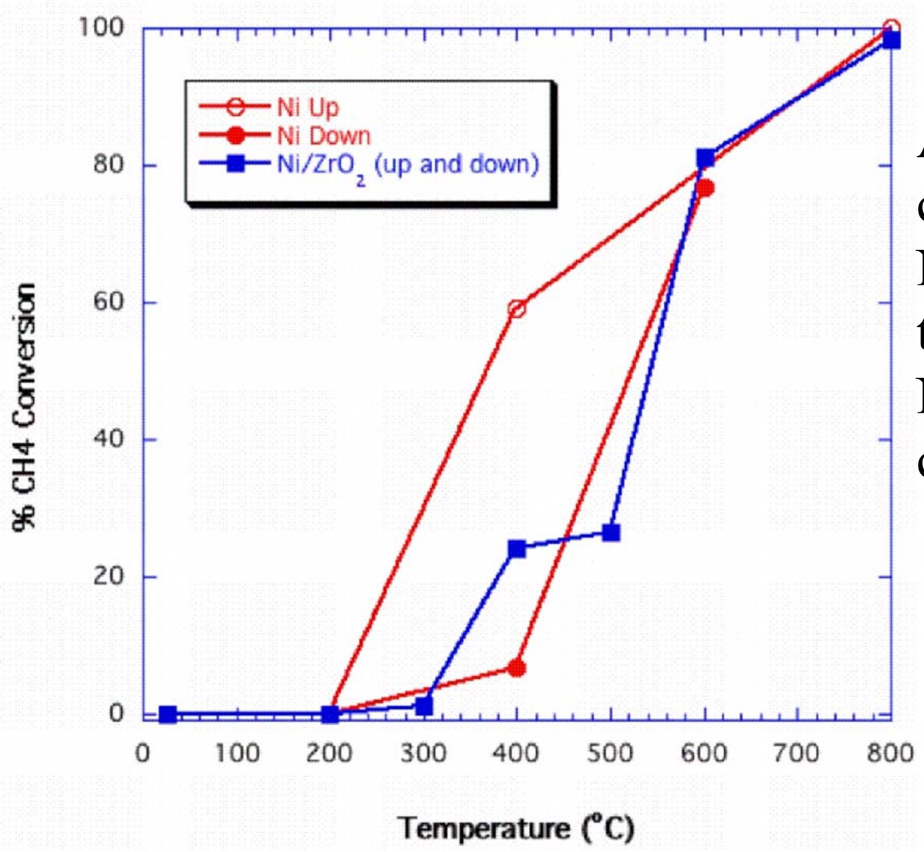
After activation 0.10 g/ml

Initial Catalyst Precursor 0.018 g/ml

Particle Sizes by XRD
42 nm. Ni/ZrO_2
Black Ni/ZrO_2 141 Å
Grey Ni/ZrO_2 206 Å
Ni/YSZ 60 Å

Initial development of this work funded by LANL LDRD

Ni Nano-composite Stability During CH_4 Reforming



Activity of Ni/ZrO_2 nanocomposite is comparable to that of Ni

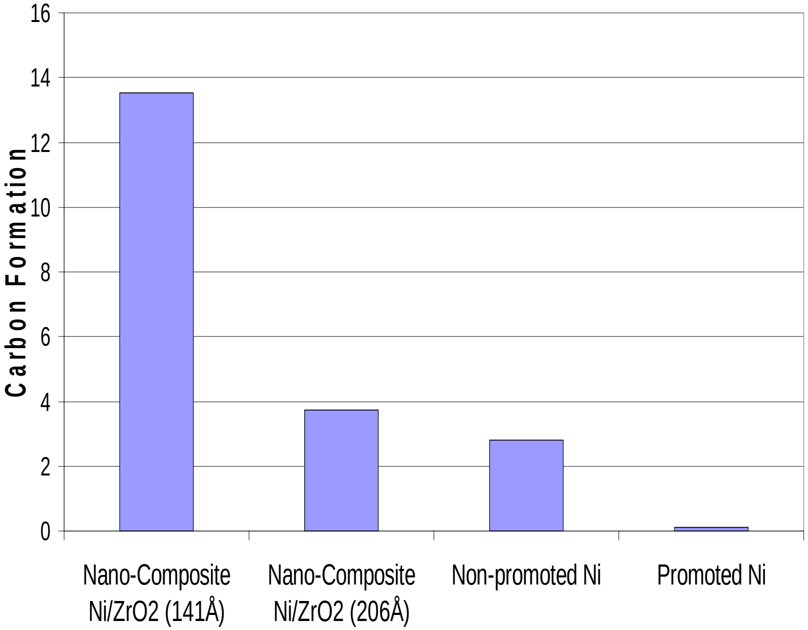
Nanocomposite Ni/ZrO_2 is stable over time during CH_4 Reforming

Ni degraded rapidly at 800 °C due to carbon deposition

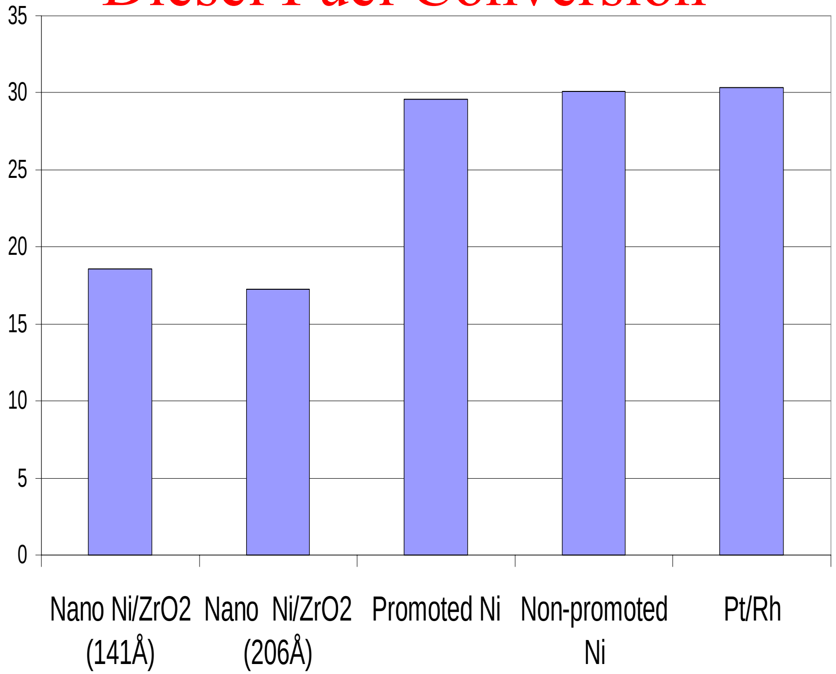
Nanocomposite nickel catalysts showed better durability than nickel during CH_4 Reforming

Carbon Formation During Diesel Reforming over Nickel Catalysts

Carbon Formation



Diesel Fuel Conversion

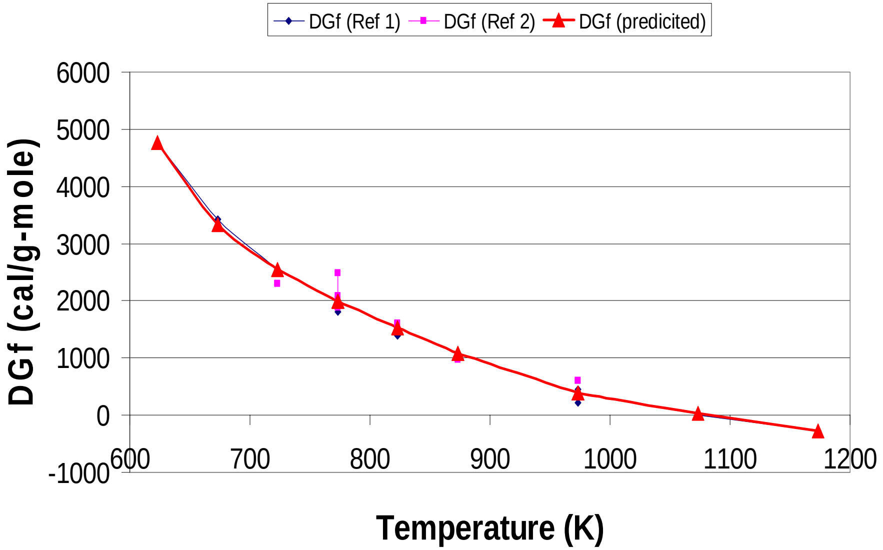


Nanocomposite nickel catalysts (Ni/ZrO_2) show worse carbon formation

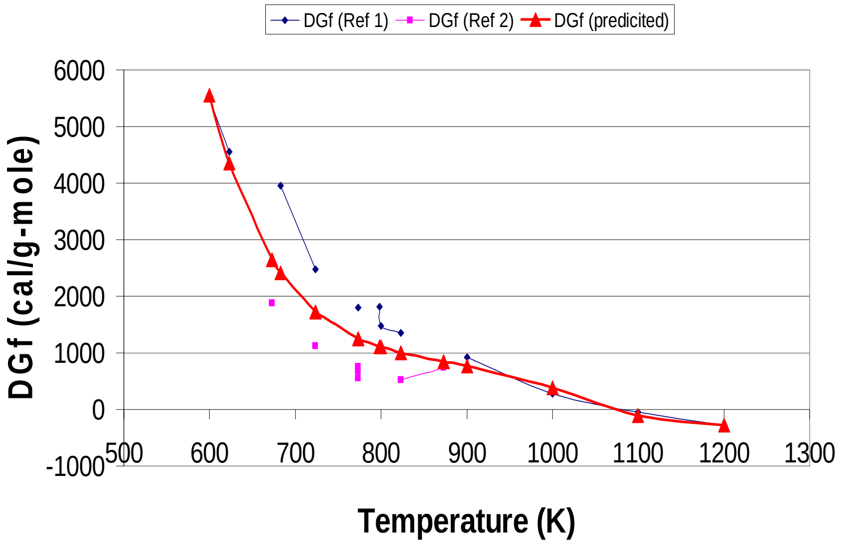
- Nanocomposite nickel catalysts (Ni/ZrO_2) do not show good reforming activity with diesel fuel
- Examine nano - Ni/YSZ composite
- Potentially better application for catalyst is SOFC anode for CH_4

Amorphous Carbon Formation Modeling Carbon Gibb's Free Energies

Computed data with Least Squares fit for C_2^* amorphous carbon



Computed data with Least Squares fit for C_1^* amorphous carbon

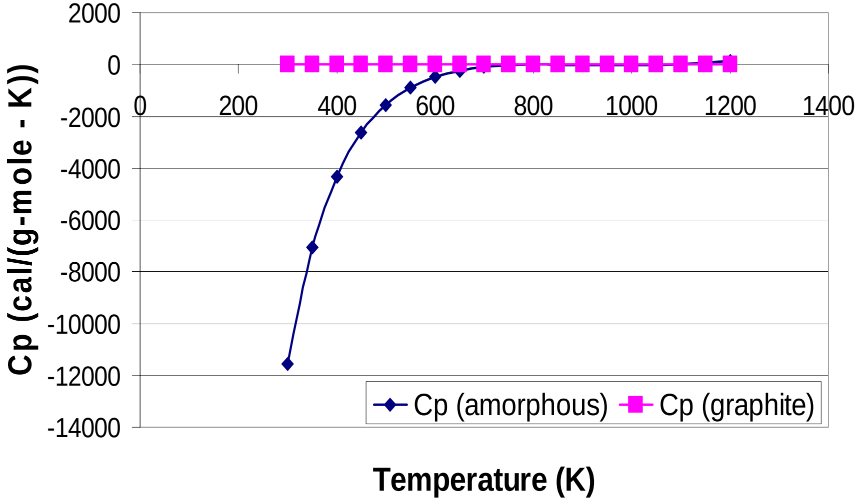


The Gibb's Free Energies Plotted were computed from measured K-values from carbon formation, with the definition:

$$\Delta G = -RT\ln(K)$$

Carbon Heat Capacity Determination

Heat capacities for C_2^* amorphous carbon from
Gibb’s Free Energy data



Heat capacities for C_1^* amorphous carbon from
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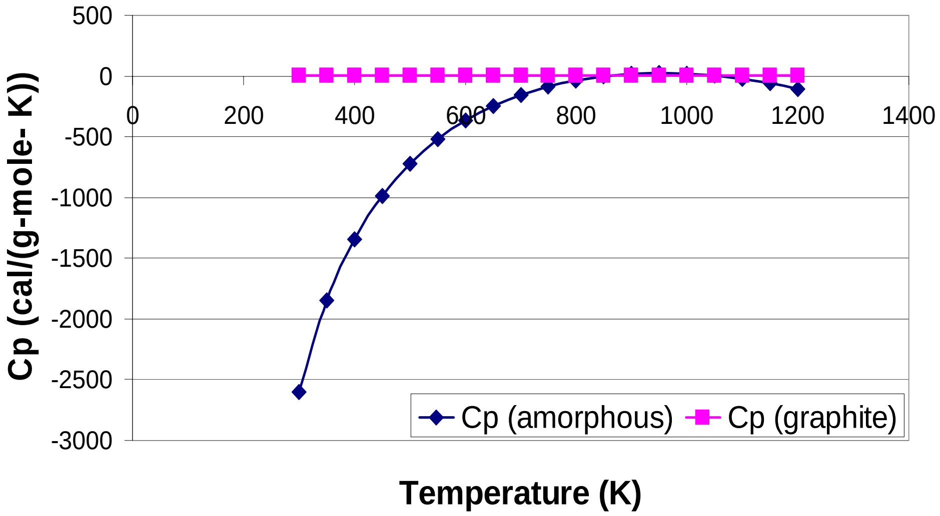


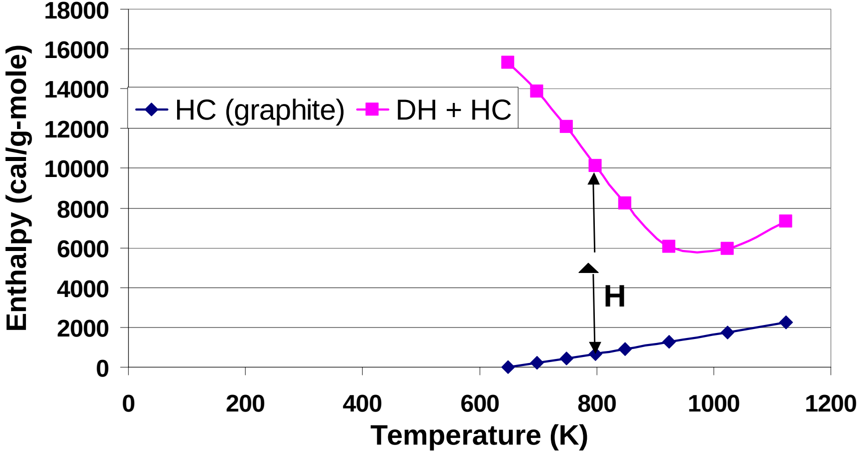
$$\Delta G = \Delta H - T\Delta S$$

$$Cp = a + bT + cT^2 + d/T^2$$

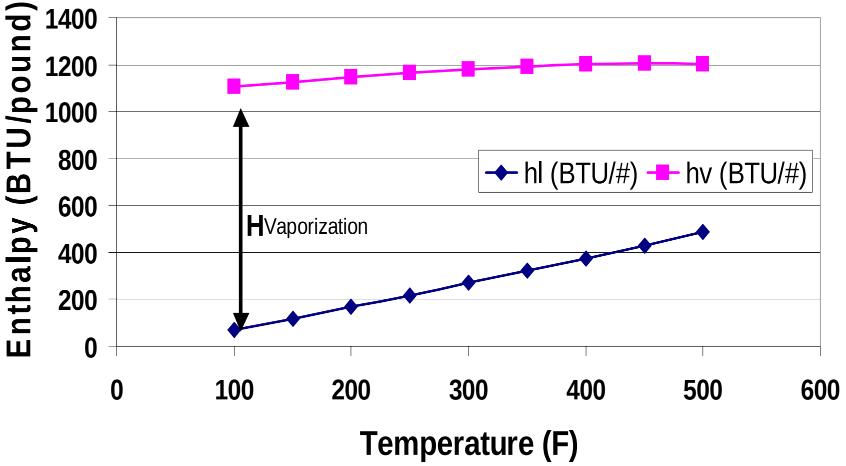
$$\Delta H = \int CpdT - and - \Delta S = \int \frac{Cp}{T} dT$$

$$\Delta G = A + BT - \Delta aT\ln T - \frac{\Delta b}{2}T^2 - \frac{\Delta c}{6}T^3 - \frac{\Delta d}{2T}$$

Carbon Enthalpy with Temperature



Enthalpy for C_2^* carbon, referenced to graphite, with 0 enthalpy at 648 K



Enthalpy-Temperature diagram for liquid water to steam.

- **Carbon Enthalpies show carbon thermodynamics not consistent**
- **Different thermodynamic carbon species are formed**

Summary/Findings

- Direct fuel injection via fuel nozzle
  - Control of fuel temperature critical (Prevent fuel vaporization, fuel pyrolysis)
  - Turndown can be limited by the nozzle fuel distribution
- Reformer operation with SOFC anode recycle
  - High adiabatic temperatures at low recycle rates (Leads to catalyst sintering)
  - Increasing recycle rates moves oxidation downstream in reformer
  - Operation at 30 – 40 % recycle rate has shown most reasonable results
- Nanocomposite nickel catalysts
  - Showed promising results during CH_4 reforming
  - Ni/ZrO_2 not as promising for diesel reforming
- Carbon Formation
  - Addition of Sulfur (thiophene and DBT) do no increase carbon formation
  - Carbon formation modeling shows at least two different thermodynamic types of carbon
  - Higher carbon formation with commercial diesel than low-S diesel (adiabatic)
  - Carbon formation primarily not adherent to catalyst surface
- Catalyst Durability
  - Catalyst loss in surface area during reforming and with temperature

Future Activities

- ➢ Carbon formation
  - Define diesel components contributing to high carbon formation rates
  - Examine additive effects on carbon formation (EtOH)
  - Stand-alone startup & consideration to avoid C formation
  - Develop carbon removal/catalyst regeneration schemes
- ➢ Catalyst sintering and deactivation
  - Characterize durability – catalyst sintering
  - Develop reformer operational profiles that limit catalyst sintering
  - Stabilize active catalyst particles
- ➢ Durability and hydrocarbon breakthrough on SOFC
- ➢ Modeling (Improve carbon formation model)
    - – Improve robustness of code, develop 'user-friendly' interface
  - Examine system effects of anode recycle