Diesel Reforming for Fuel Cell Auxiliary Power Units

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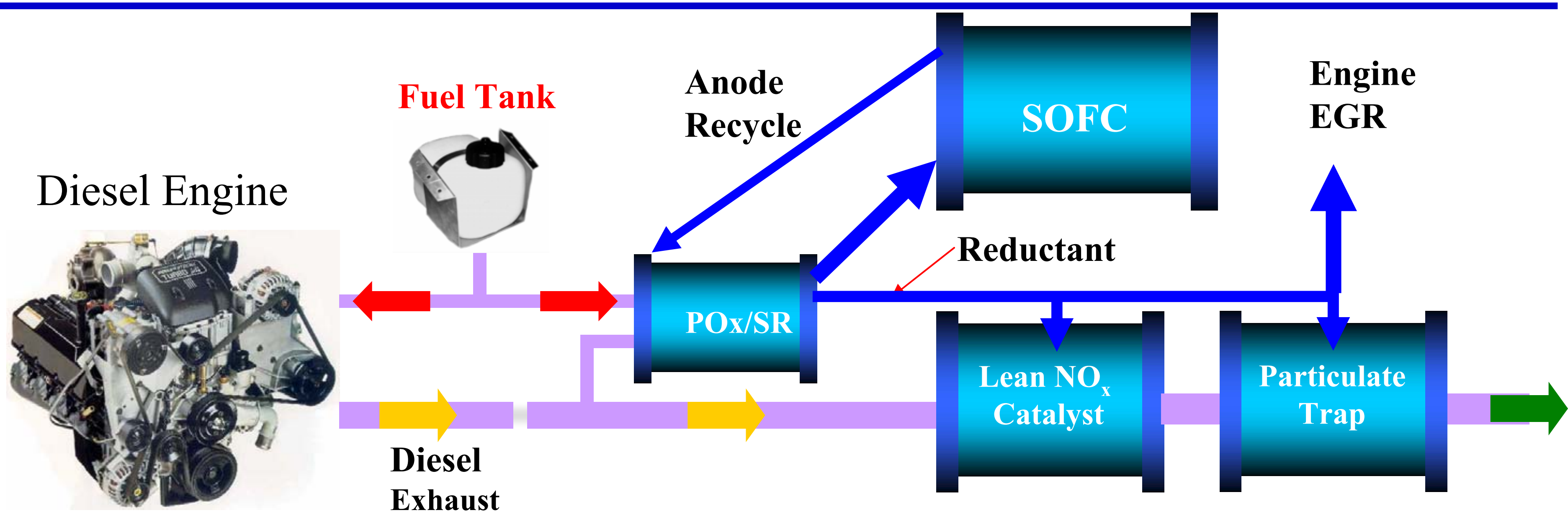
Applications of Diesel Reformers in Transportation Systems



Reforming of diesel fuel can have simultaneous vehicle applications:

- **SECA application: reforming of diesel fuel for 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

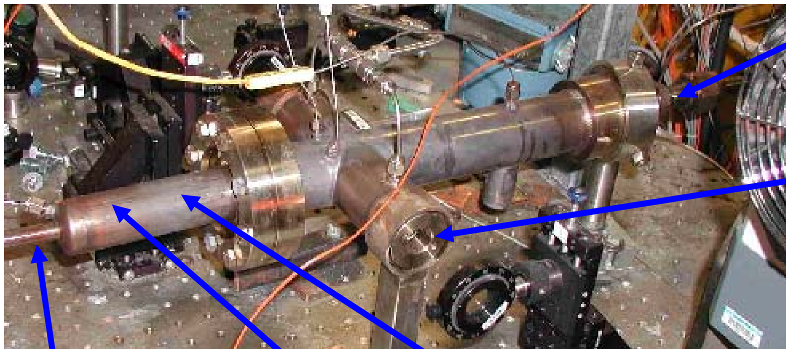
- Diesel fuel is prone to pyrolysis upon vaporization
  - Fuel/Air/Steam mixing
  - Direct fuel injection
    - Nozzle turndown and atomization quality
- Diesel fuel is difficult to reform
  - Reforming kinetics slow
  - Catalyst deactivation
    - Fuel sulfur content
    - Minimal hydrocarbon slip
    - 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 - reformer start-up an issue

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

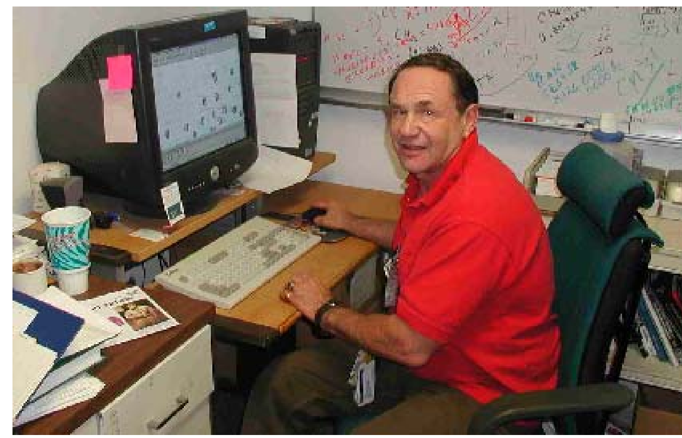
Catalyst (Pt/Rh)

Furnace

Iso-thermal system

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

Iso-thermal Microcatalyst



Modeling

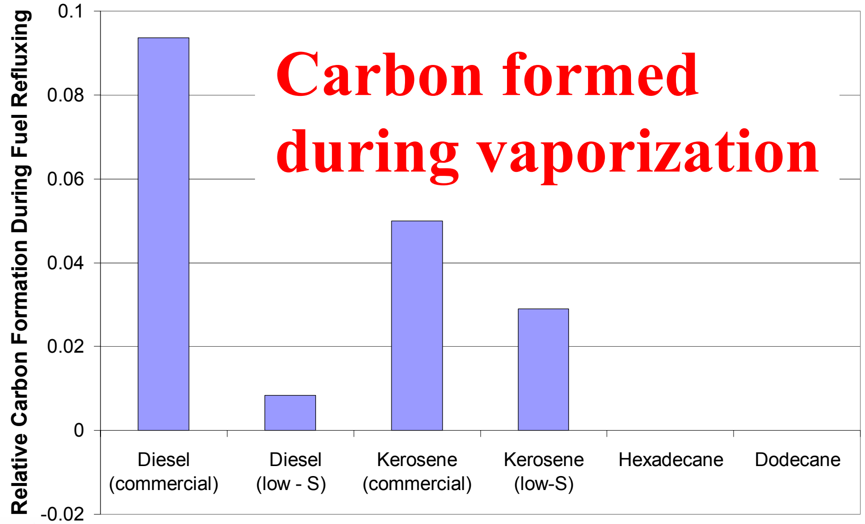
Equilibrium

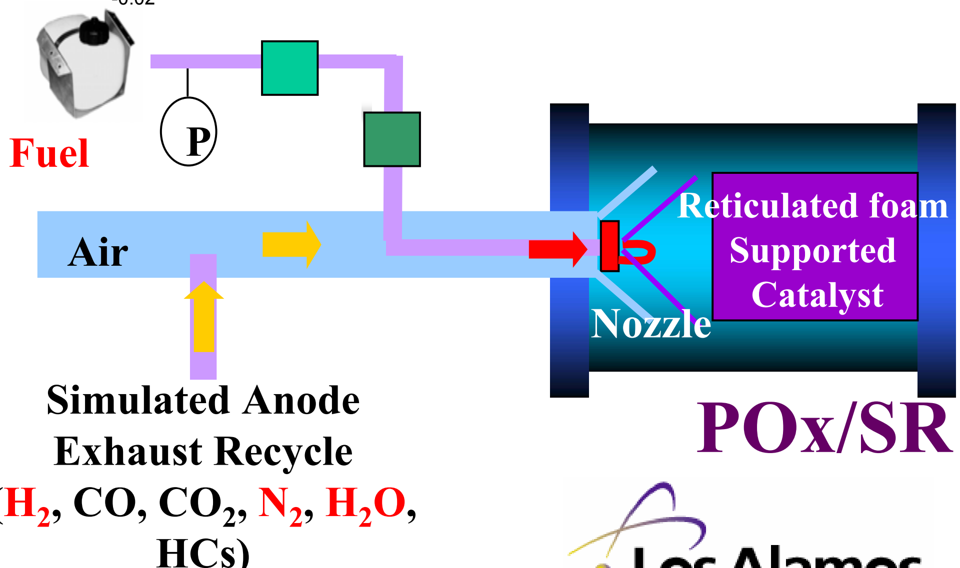
Kinetic

Composition

Direct Injection Fuel Nozzle Operation

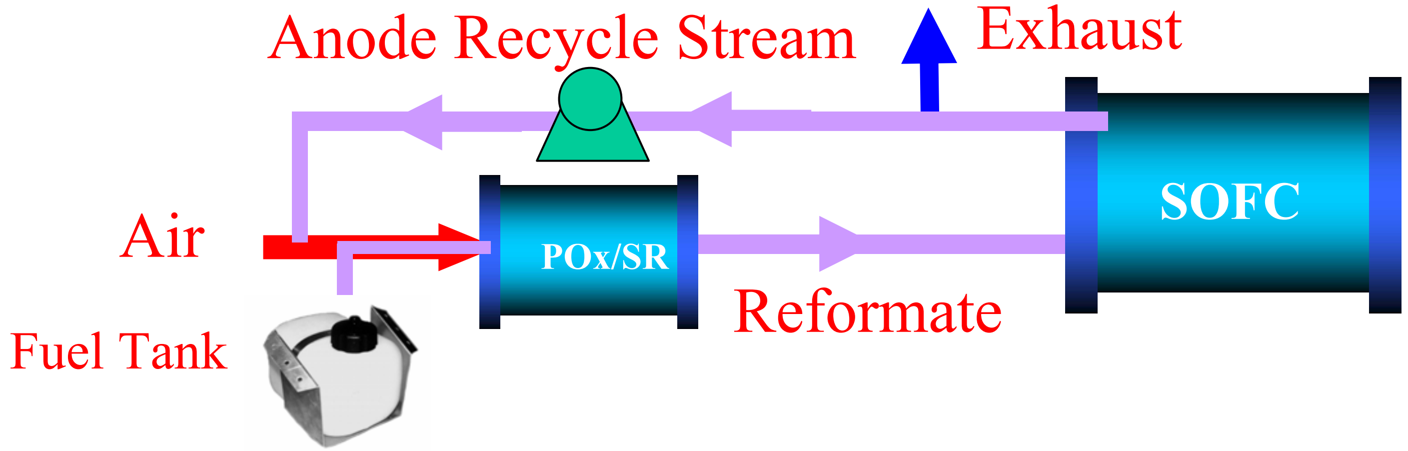
- To avoid carbon formation during vaporization requires direct fuel injection
- **Directly inject fuel to reforming catalyst**
  - Commercial nozzle, control fuel pressure for fuel flow (~ 80 psi)
  - Air / anode recycle (H_2 / N_2) distribute in annulus around fuel line / nozzle
- **Experimental results**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





Los Alamos

Water Addition for Steam Reforming →SOFC Anode Recycle to Reformer

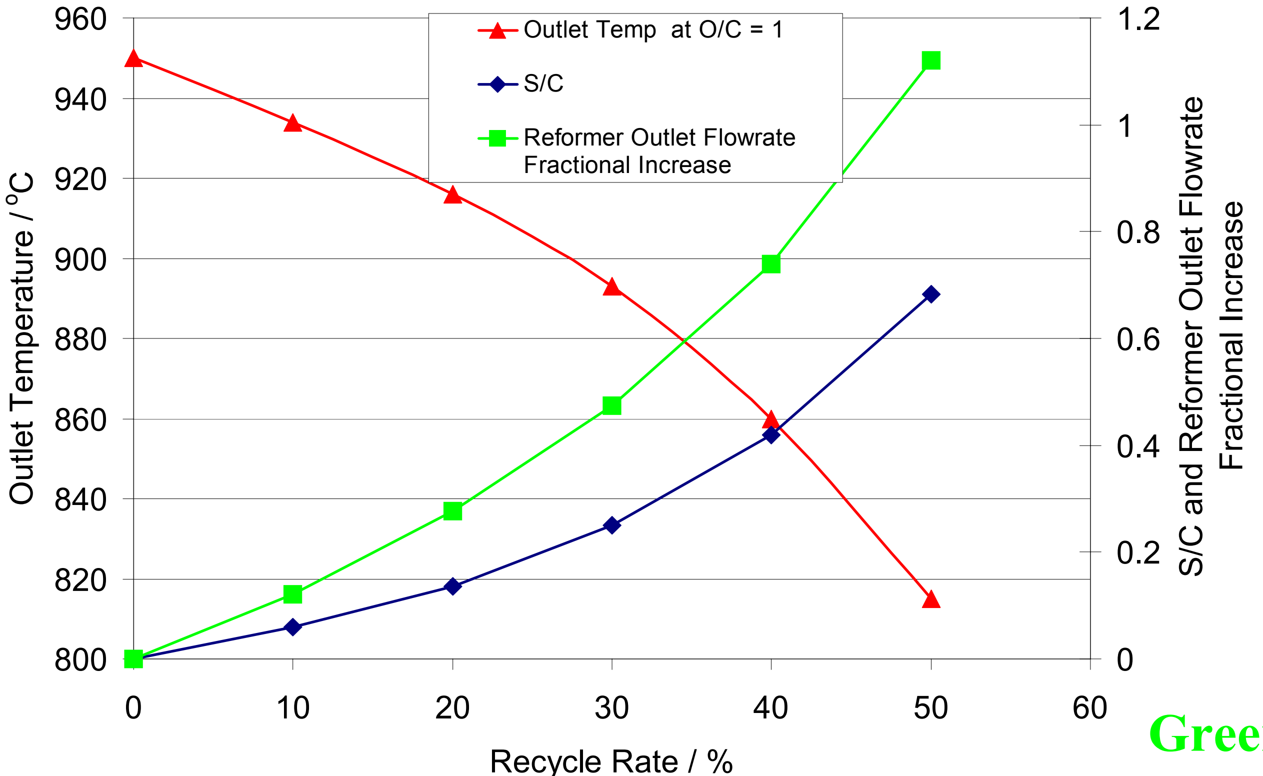


- Water required for:
  - steam reforming of fuel
  - carbon suppression
- Methods for water introduction and availability:
  - Separate water tank (tank, freezing, refilling)
  - Anode water recovery by condensation (heat ex., cond., tank, pump freezing)
  - **Anode recycle to reformer** **(blower)**

Preferred systems are water neutral

Simplest method is anode recycle to reformer

SOFC Anode Recycle Modeling



Anode Recycling Model Assumptions	
Fuel - Diesel (C12H26)	
Power - LHV Fuel In	16
O/C = 1	1
SOFC Conversion	50%

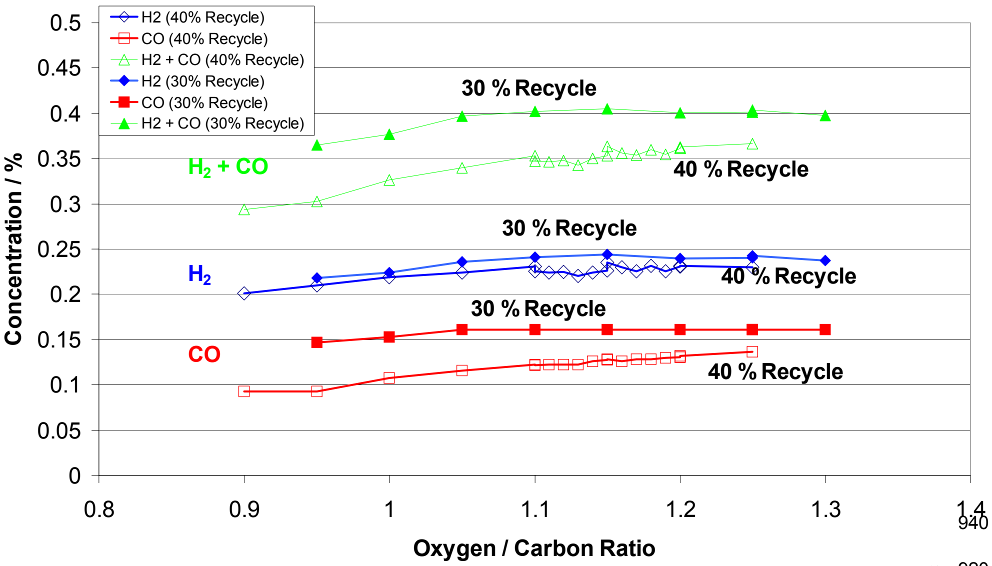
Recycling of 50% SOFC Anode Flow, S/C = 0.7

Most data presented simulates 35% recycle

Green – Fractional increase in flow caused by increasing gas volume due to recycle ratio, leads to larger reformer

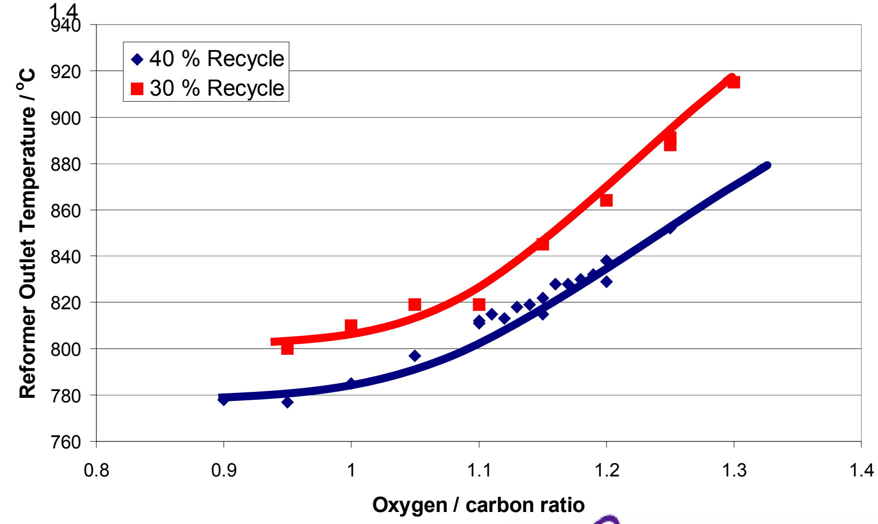
Reforming of Diesel with SOFC Recycle

Temperature and Hydrogen / CO production



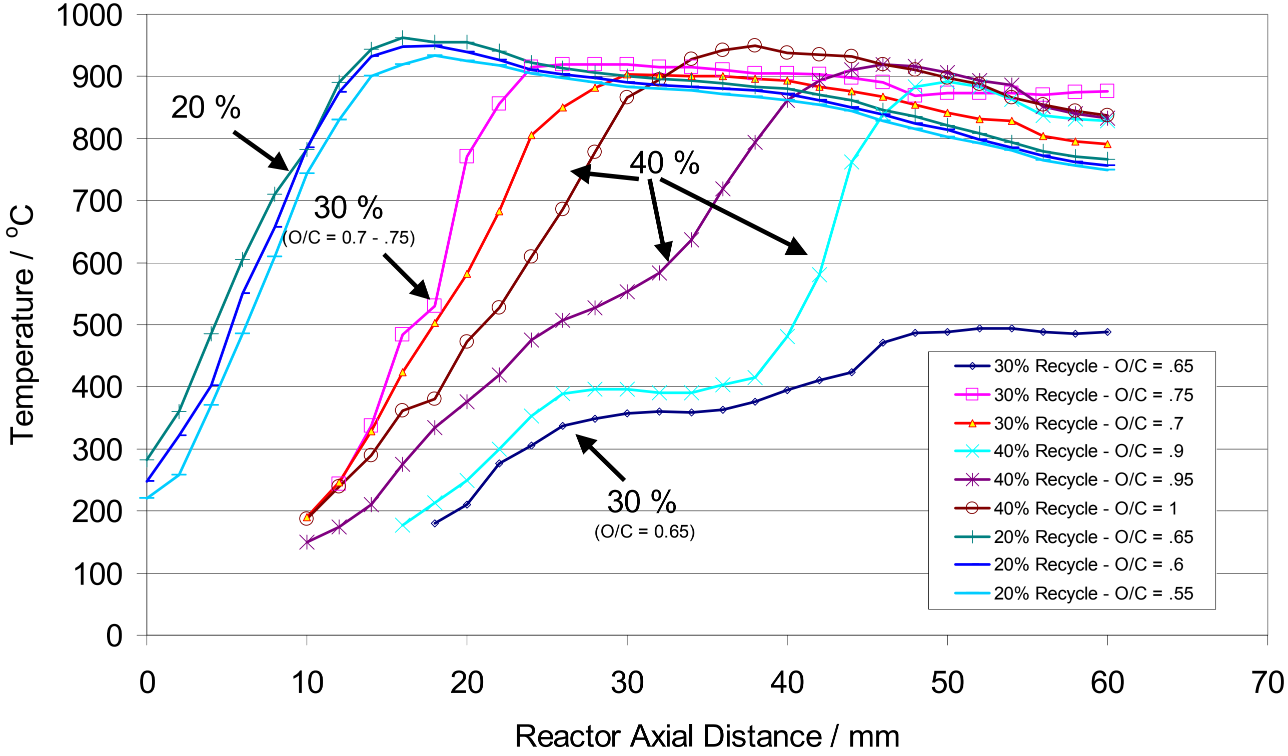
- **Higher recycle reduces operating temperature**
- **Operation with recycle < 30 % difficult due to high operating temperatures and catalyst sintering**

Pt / Rh supported catalyst
Residence time ~ 20 msec
Anode recycle simulated with
H_2, N_2, H_2O



Axial Temperature Profiles during Diesel Reforming

Low-S Swedish diesel fuel



Adjusted O/C for similar operating temperatures

Pt / Rh supported catalyst

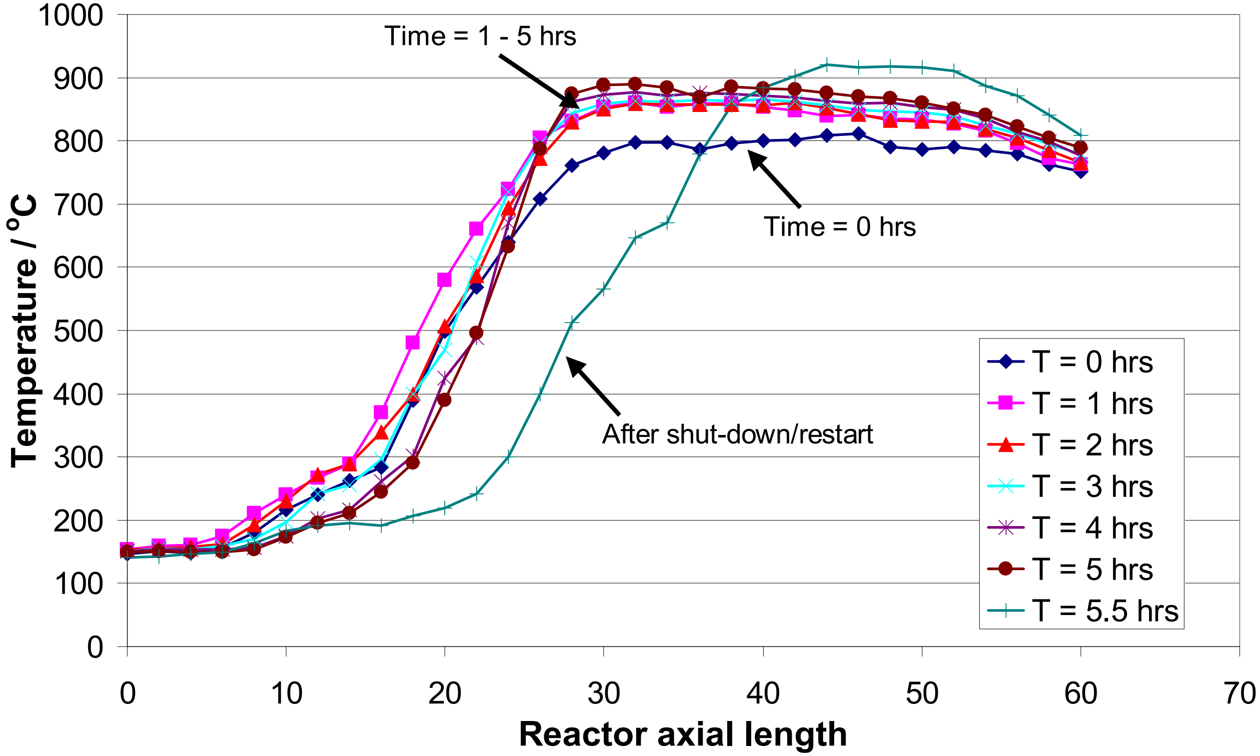
Residence time ~ 50 msec

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

Reactor Axial Profile with Time
(Commercial diesel fuel)

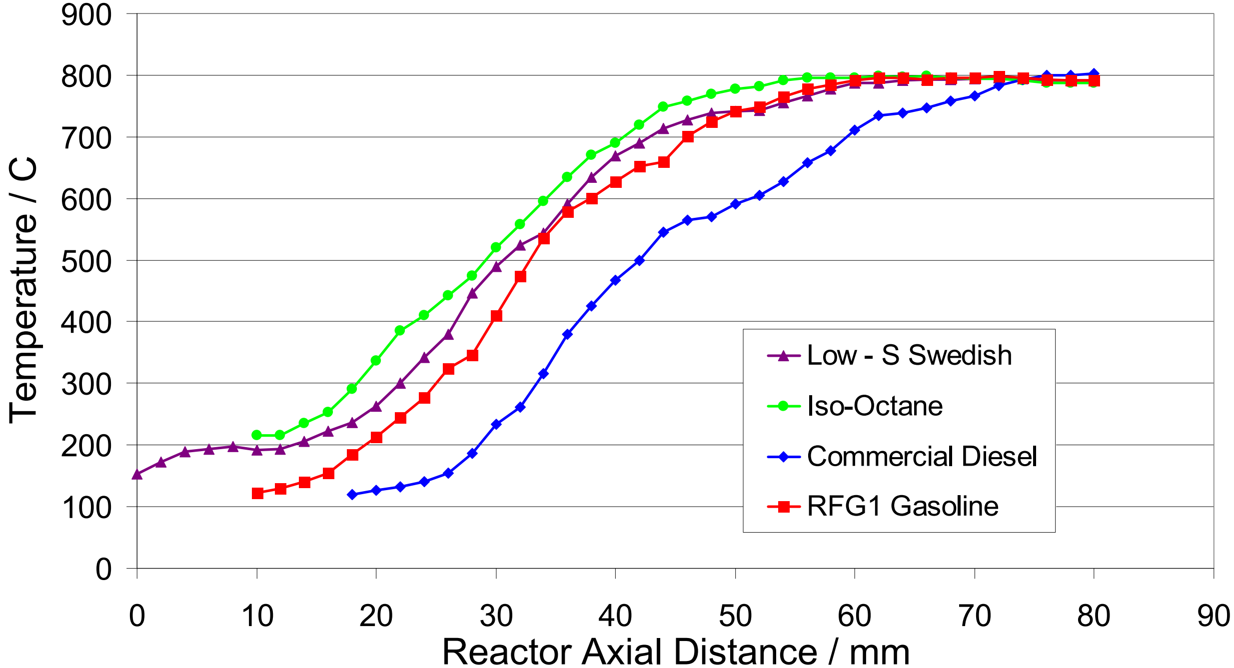


Initial temperature profile flattens out at ~ 800 °C

Subsequent temperature profiles peak at > 850 °C and then decrease to outlet

Temperature (oxidation) profile shifts downstream following shutdown/restart cycle

Fuel Effect on Reactor Temperature Profile



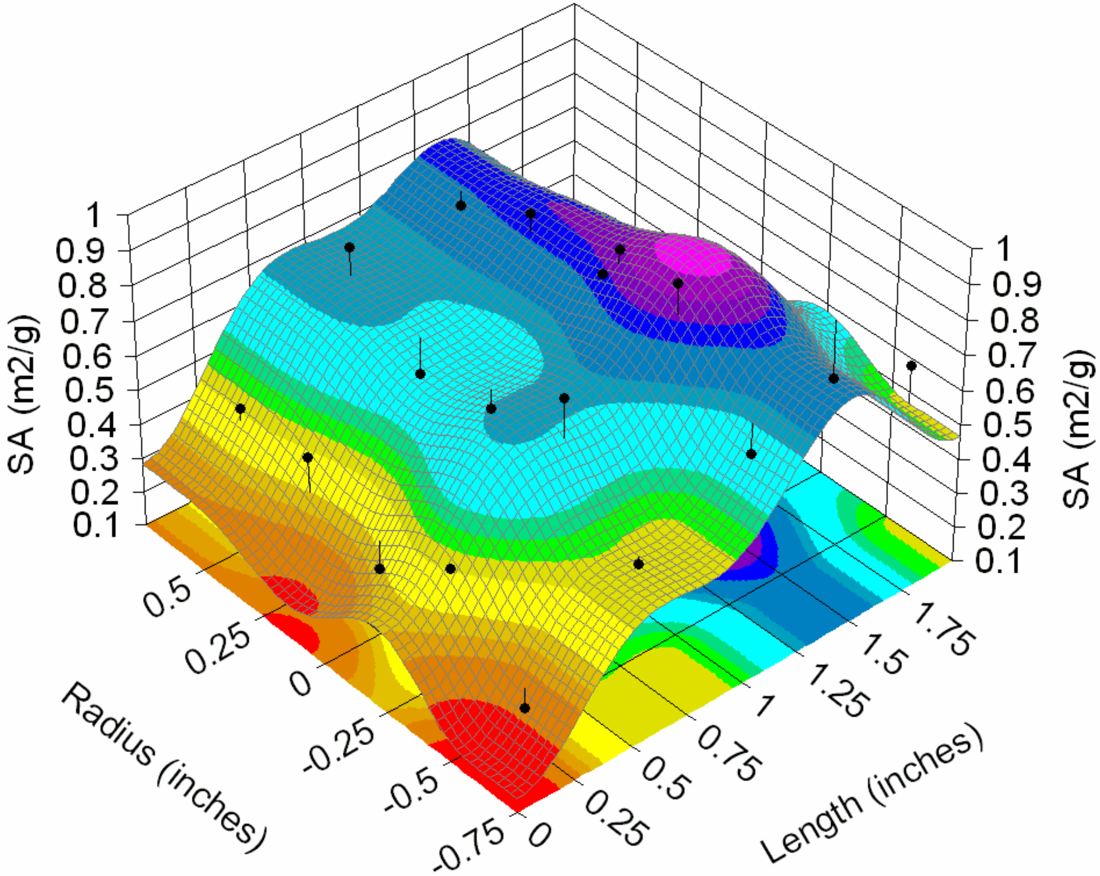
35% recycle ratio
Adjusted O/C for similar reformer outlet temperature

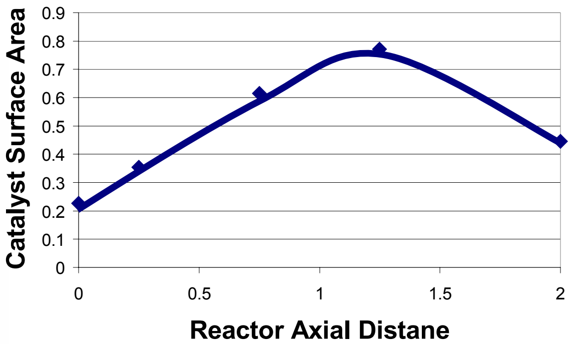
Fuel composition affects the reactor front end light-off

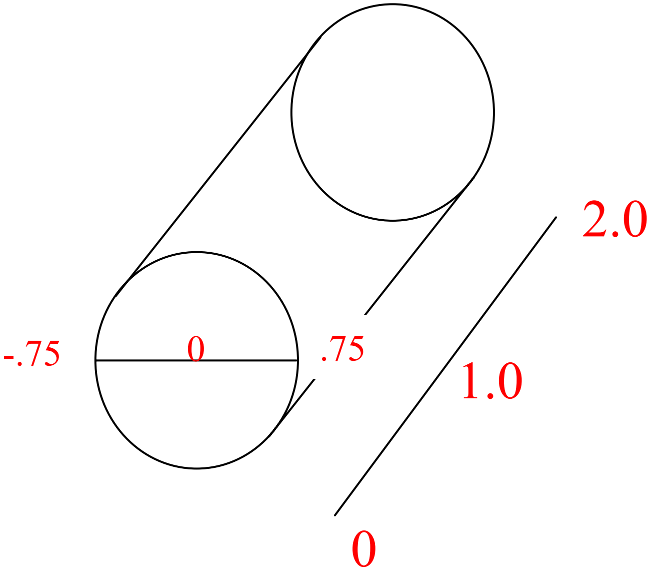
Sulfur content and aromatic content highest in
Diesel > Gasoline > Swedish Diesel > Iso-Octane

Adiabatic Reformer Catalyst Surface Area Axial and Radial Profile

BET Surface Area Distribution

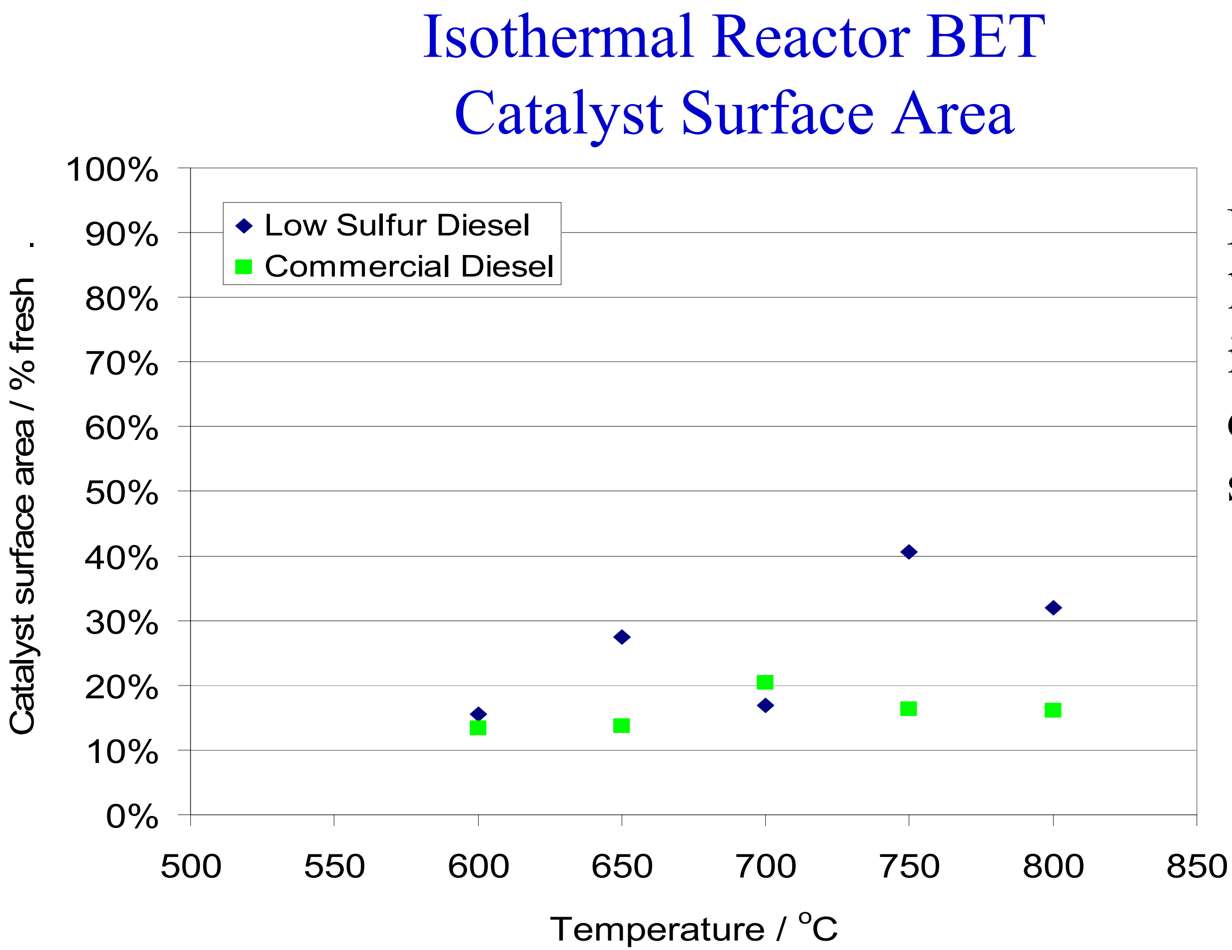






Original Surface Area ~ 4.3

Isothermal Reformer Catalyst Surface Area



Large catalyst surface area loss after testing, mostly independent of temperature during isothermal diesel steam reforming

Greater catalyst surface area loss after testing with commercial diesel fuel

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 start-up - Cannot avoid favorable carbon equilibrium regions
    - Water-less (Water not expected to be available at start-up)
- Catalysts
  - Various catalysts more/less prone to carbon formation
- Diesel fuels
  - Carbon formation due to pyrolysis upon vaporization

<u>Carbon Formation Reactions</u>

$$2CO \Leftrightarrow C + CO_2 \quad \text{(Boudart Reaction)}$$

$$CH_4 \Leftrightarrow C + 2H_2 \quad (CH_4 \text{ Decomposition})$$

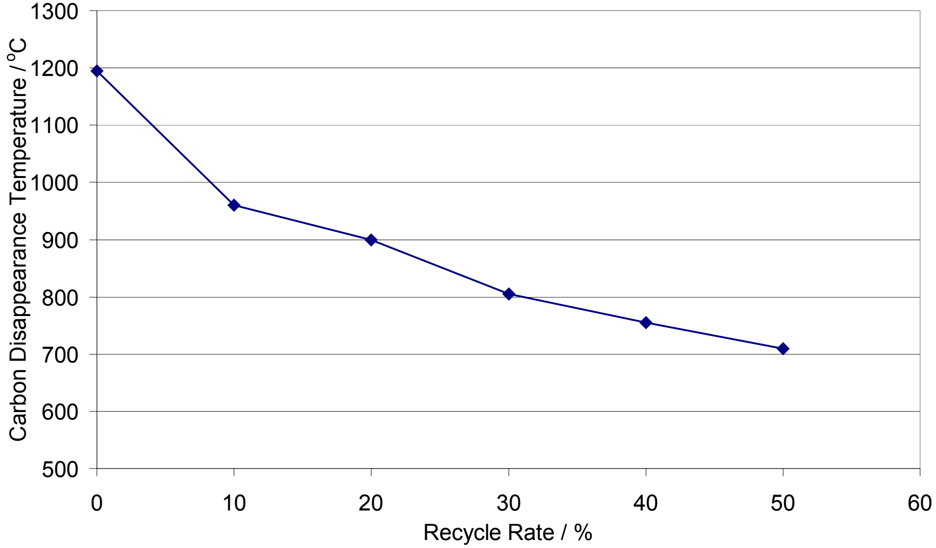
$$C_nH_{2n} \rightarrow C_n + nH_2$$

$$\text{Fuel pyrolysis} \rightarrow \text{aromatics} \rightarrow \text{PAH} \rightarrow C$$

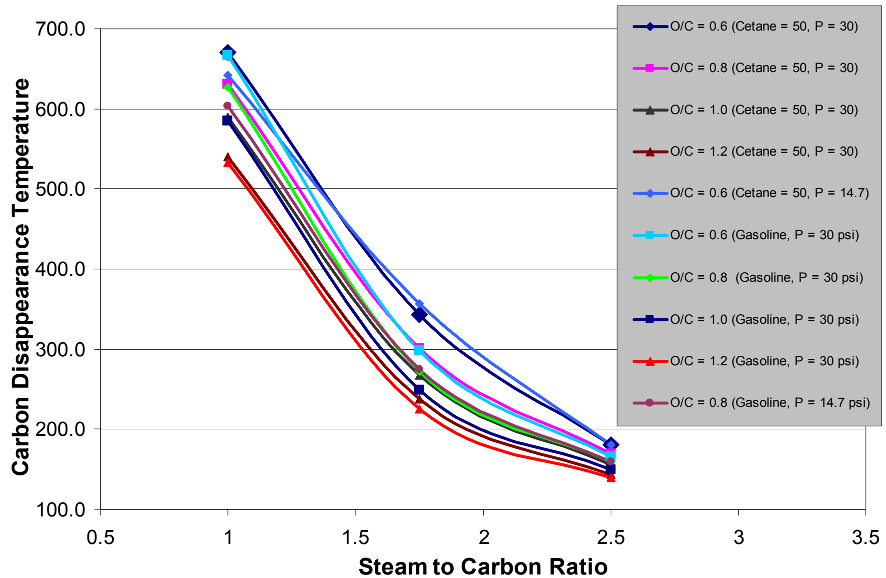
Carbon Formation Equilibrium Modeling

- Various forms of carbon exist
  - Different carbon forms have different thermodynamic properties
- Developed chemical equilibrium code to analyze conditions for carbon formation
  - Includes 3 types of amorphous carbon
    - Operation of model in isothermal modes (adding adiabatic)
  - C++ code operates on Windows PC
- Input:
  - Isothermal /Adiabatic (needs improvement for amorphous Carbon)
  - Gas phase components & concentrations
  - Equilibrium temperature, pressure, types of solid phase
- Output yields (code works where carbon formation is observed)
  - Gas phase concentration, solid phase quantities
  - (Delta H reaction, outlet temperature – for adiabatic case)
- Model is (will be / maybe??) available
  - no-cost, non-exclusive license

Modeling Carbon Formation Dependence for SOFC APU Recycle Ratio

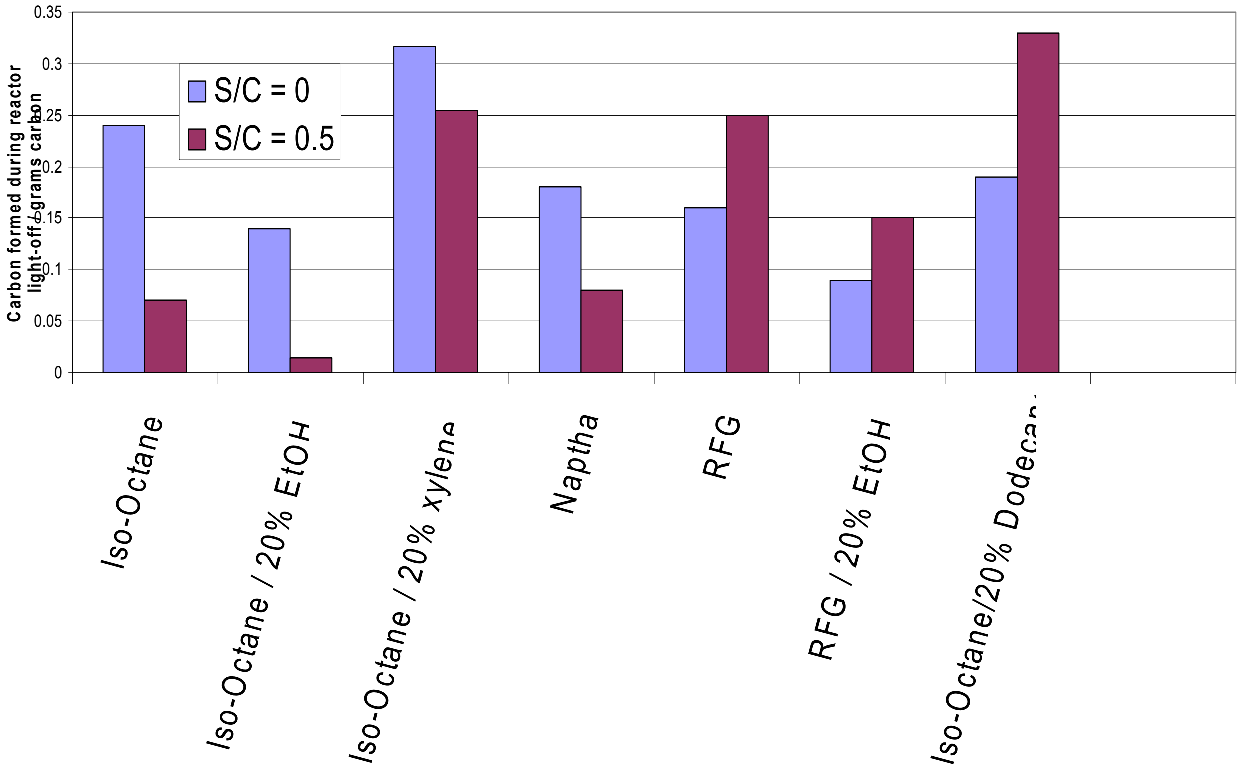


Temperature for disappearance of all types of amorphous carbon as a function of SOFC anode recycle ratio



Carbon disappearance temperature as a function of steam to carbon ratio

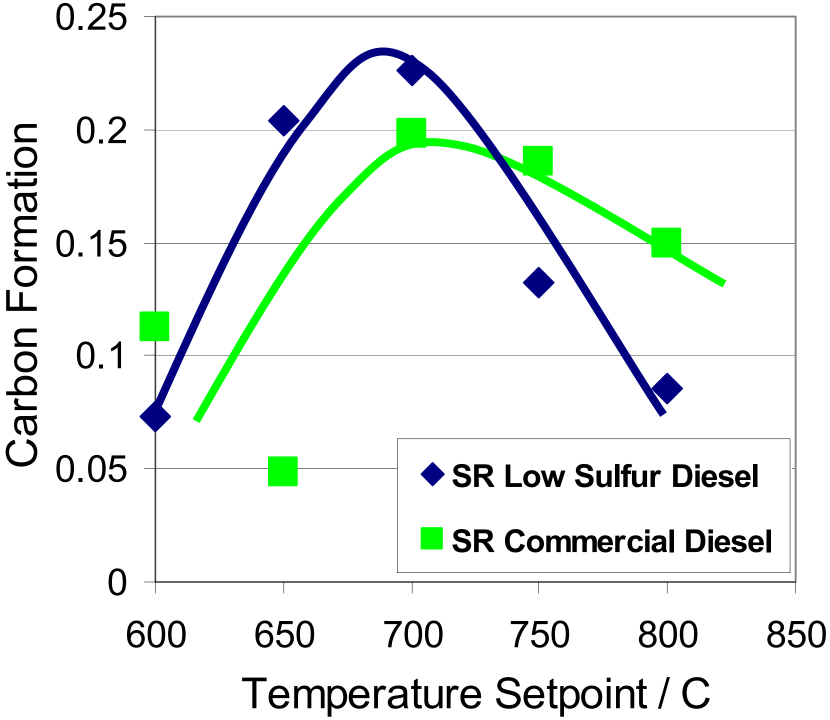
Carbon Formation during light-off:
Quantitative carbon measurements



- Quantitative carbon measurements indicate carbon made during start-up for all fuels.
- Water during start-up suppresses some carbon formation, but carbon is still formed, in smaller quantities.
- Ethanol suppresses carbon formation, while aromatics show higher carbon formation.

Isothermal Reactor
Carbon Formation Measurements

Steam Reforming

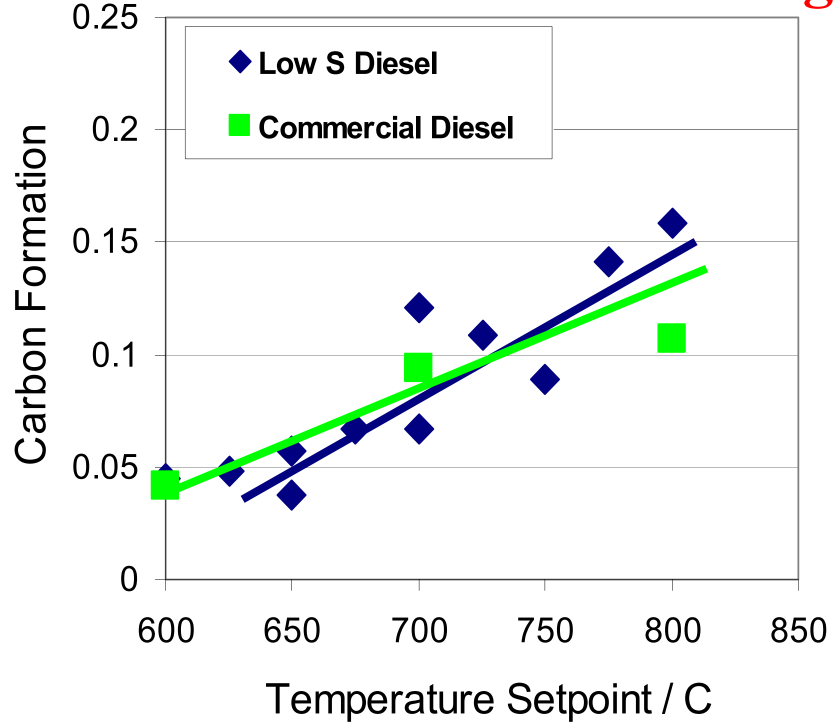


$O/C = 0.0$, $S/C = 1.0$

Peak carbon formation ~ 650 – 700 ^{o}C

Equilibrium and kinetics effects

AutoThermal Reforming



$O/C = 1.0$, $S/C = .34$

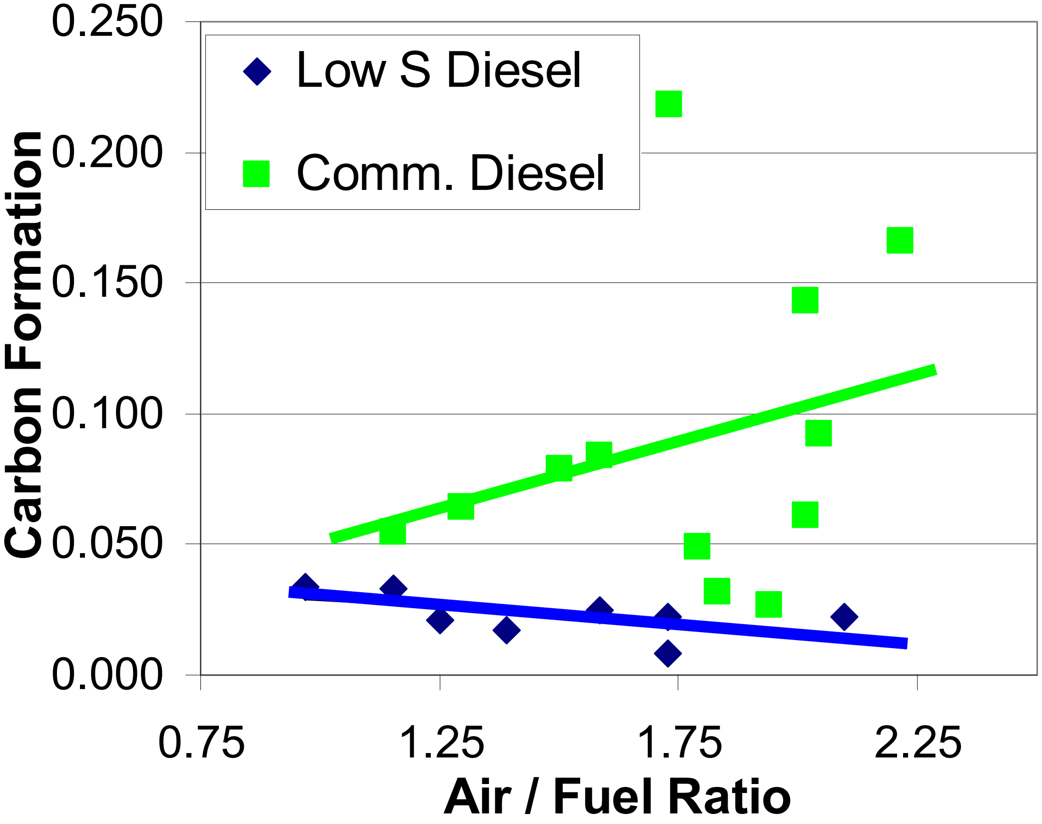
(35% Anode Recycle)

Carbon formation increases with temperature

5 hour operation

Adiabatic Reactor
Carbon Formation Measurements

AutoThermal Reforming

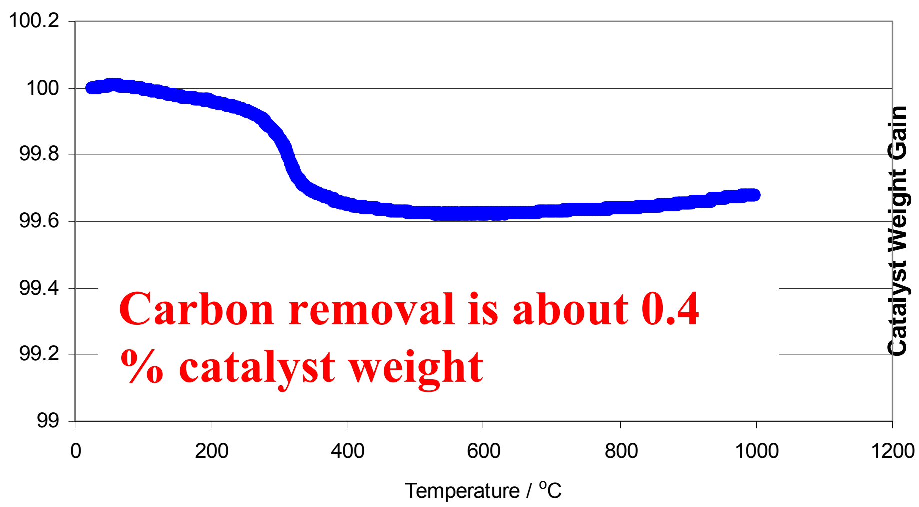


Air (SLPM) / Fuel (ml/min)

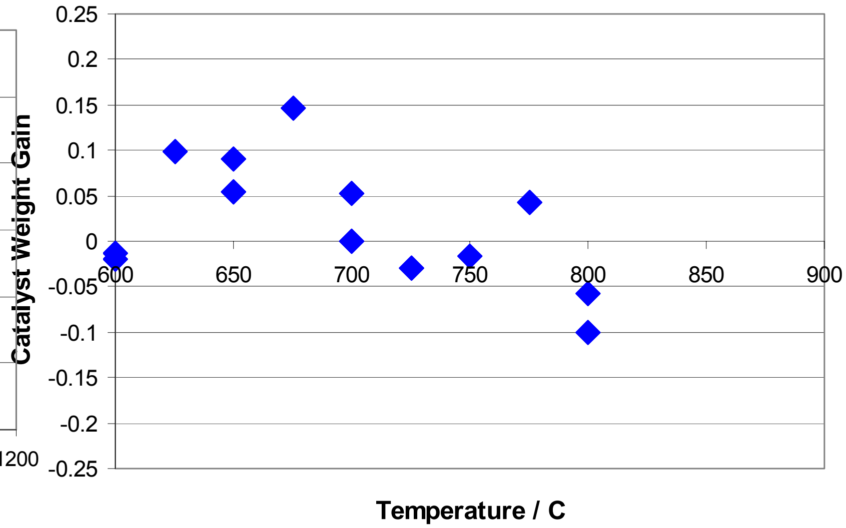
- Simulates 35% SOFC anode recycle
  - S/C ~ 0.34
- Average 3x higher carbon with commercial fuel than Low-S
- Carbon formation increases with increasing air (T) for commercial
- Carbon formation decreases with increasing air flow (T) for Low–S
- Carbon Formed (% fuel flow):

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

Carbon Formation Rate

Activation energy for carbon formation:

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

Iso-thermal steam reforming (S/C = 1.0)

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

Iso-thermal ATR (O/C = 1.0, S/C = 0.34)
(Simulating 35% recycle)

commercial diesel	97.9 kJ/mol
low-S diesel fuel	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

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 ATR scales to
3.1 kg Carbon (10,000 hrs)
12.4 kg Carbon (40,000 hrs)

Summary/Findings

- Direct fuel injection via fuel nozzle
  - Control of fuel temperature critical
    - Prevent fuel vaporization, fuel pyrolysis / clogging of nozzle
  - 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
    - Limits light-off of reformer
  - Increasing recycle rates moves oxidation downstream in reformer
  - High recycle increases reformer size, parasitic losses
  - Operation at 30 – 40 % recycle rate
- Carbon Formation
  - Equilibrium carbon formation modeling
  - Carbon formation measurements show kinetic and equilibrium effects
  - Higher carbon formation during adiabatic operation with commercial diesel compared with low-S diesel
  - Carbon formation primarily not adherent to catalyst surface

Future Activities
Experimental

- Carbon formation
  - Quantify as a function of catalyst, recycle ratio
  - 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
  - Incorporate SOFC 'button' cell operating on reformate
- Sulfur effect on reforming kinetics and carbon formation

Future Activities
Modeling & Technology Transfer

- Modeling
  - Improve carbon formation model
    - Incorporate enthalpies of other carbon species ($CH_{0.2}$) and sulfur
    - Improve robustness of code
    - Develop 'user-friendly' interface
  - Examine system effects of anode recycle
    - Efficiency and parasitics
- Technology Transfer
  - Dissemination of results via publications and presentations
    - AIChE, ACS, SECA meetings and reports
  - Make carbon formation model available for SECA teams
    - (effort ongoing for 6 months)