Diesel Reforming for Fuel Cell Auxiliary Power Units

SECA Core Technology Program Review

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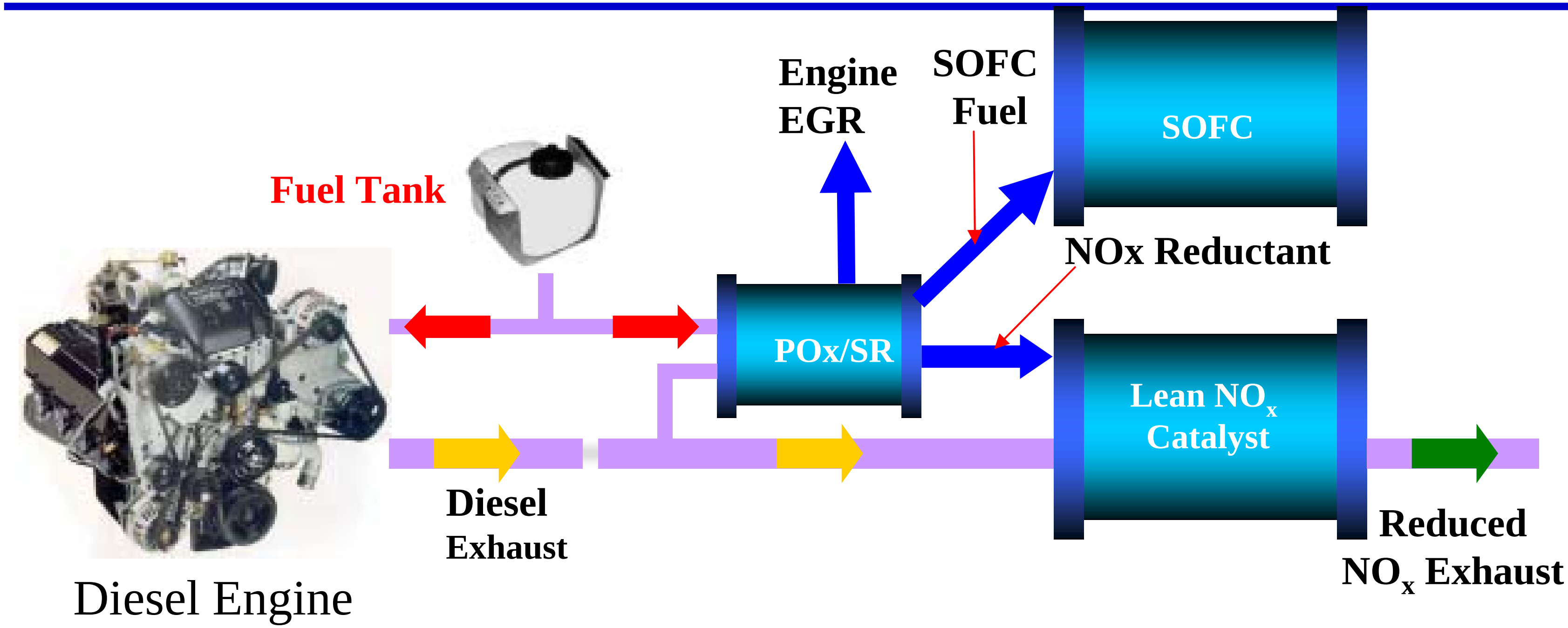
Potential Applications of Diesel Reformers in Transportation Systems



The reforming of diesel fuel potentially has simultaneous on-board vehicle applications:

- **SECA application: reforming of diesel fuel for SOFC / APU**
- reductant to catalyze NOx reduction
- Hydrogen addition for high engine EGR
- fast light-off of catalytic convertor

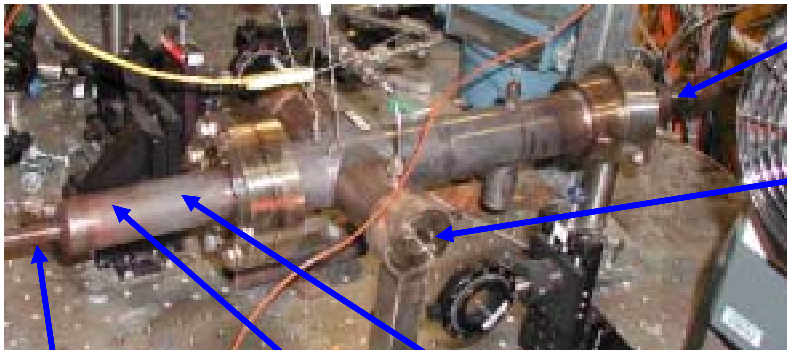
Diesel Reforming Tasks and Activities

- Objectives: Develop technology suitable for on-board reforming of diesel fuel for transportation SOFC auxiliary power units
    - Develop fundamentals (kinetics ….), models, examine components
- Approach: Examine Catalytic partial oxidation and steam reforming
- Modeling
    - Carbon formation equilibrium modeling
    - Reformer operation with anode recycle
- Experimental
    - Development of direct diesel fuel injection
    - Adiabatic reformer operation
        - Catalyst evaluation, activity measurements
            - Hydrocarbon breakthrough speciation
        - Anode recycle simulation
    - Iso-thermal reforming and carbon formation measurements
        - Carbon formation rate development
        - Catalyst regeneration due to carbon formation

Diesel Reforming Measurements

Adiabatic Reactor with nozzle

Window for Catalyst Reaction Zone Observation



Windows for laser diagnostics

Air / anode recycle

Nozzle

Catalyst (Pt/Rh)

Furnace

Iso-thermal Microcatalyst

Iso-thermal system
- Measure kinetics
- Steam reforming / POx
- Light-off
- Carbon formation

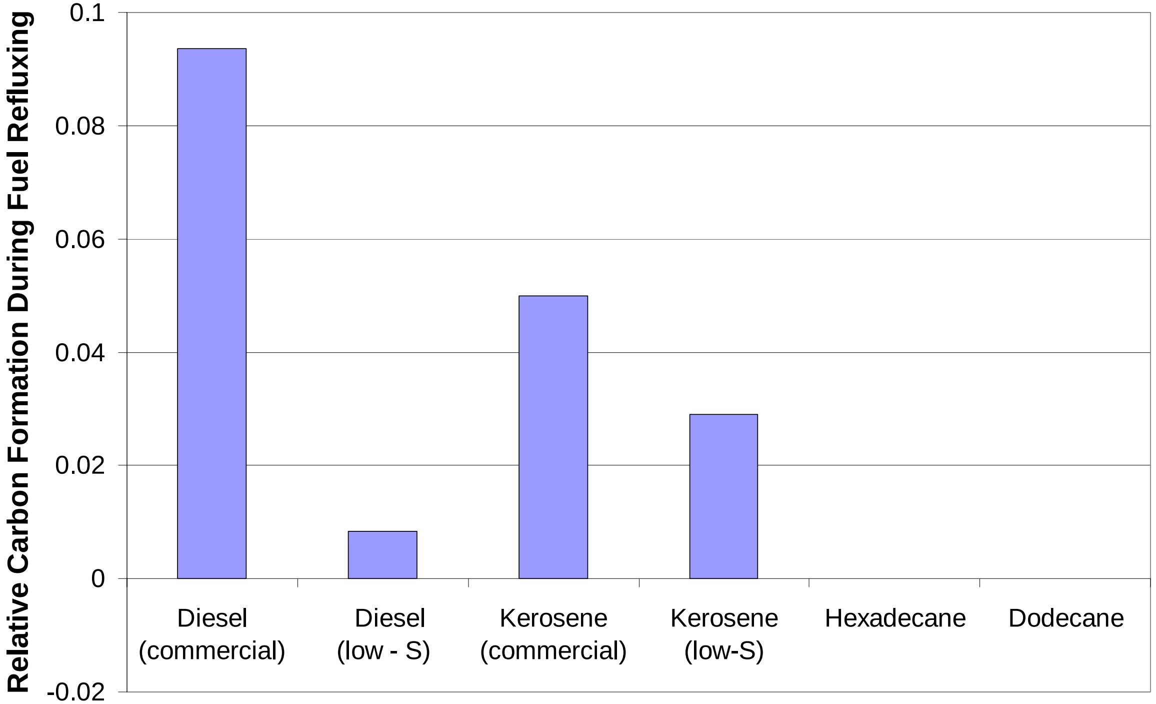
Modeling

Equilibrium

Kinetic

Composition

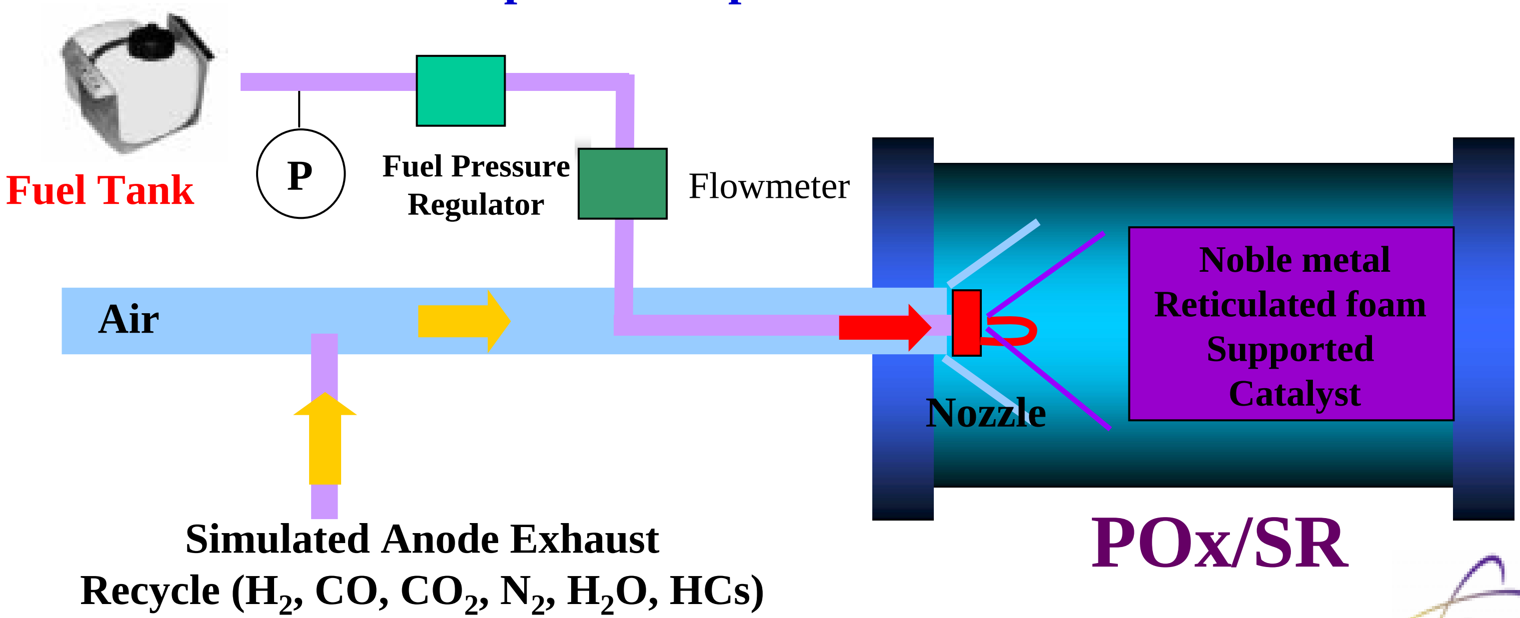
Relative Carbon Formation from Fuel Vaporization



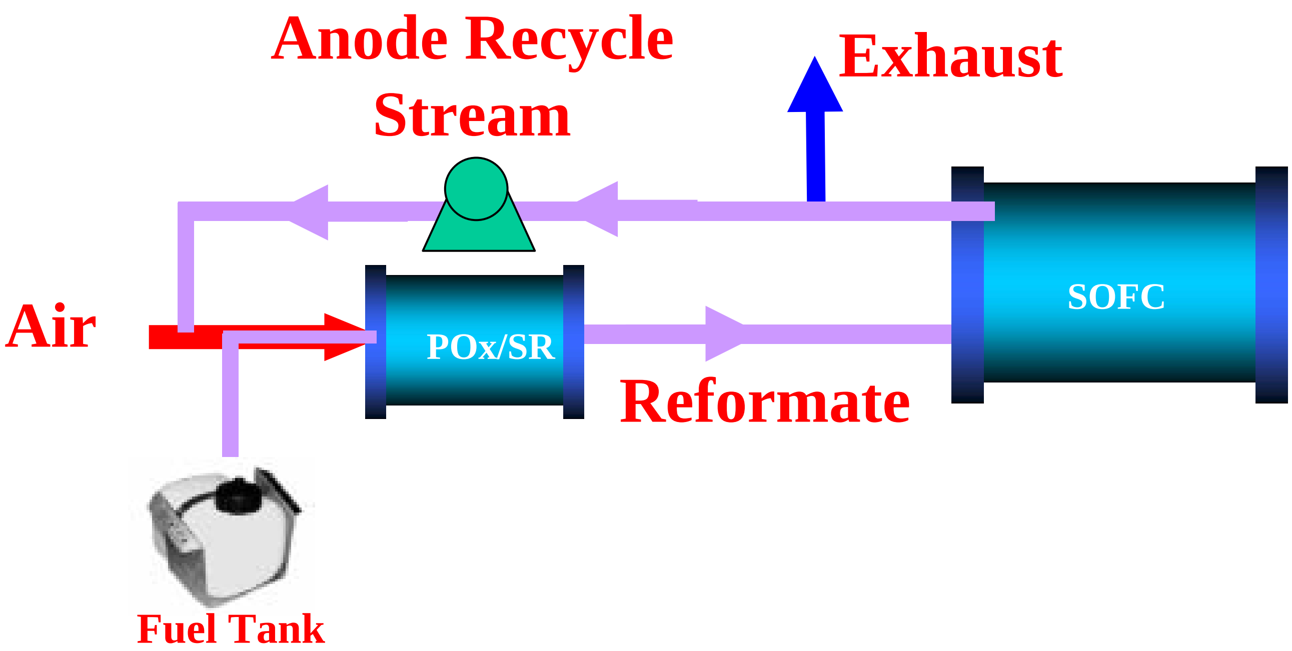
- Saturated pure diesel components do not show pyrolysis
- S removal, decreases carbon formation (removes PAHCs)
- Diesel fuel injection require technology to avoid carbon formation during vaporization

Direct Fuel Nozzle Operation

- **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**



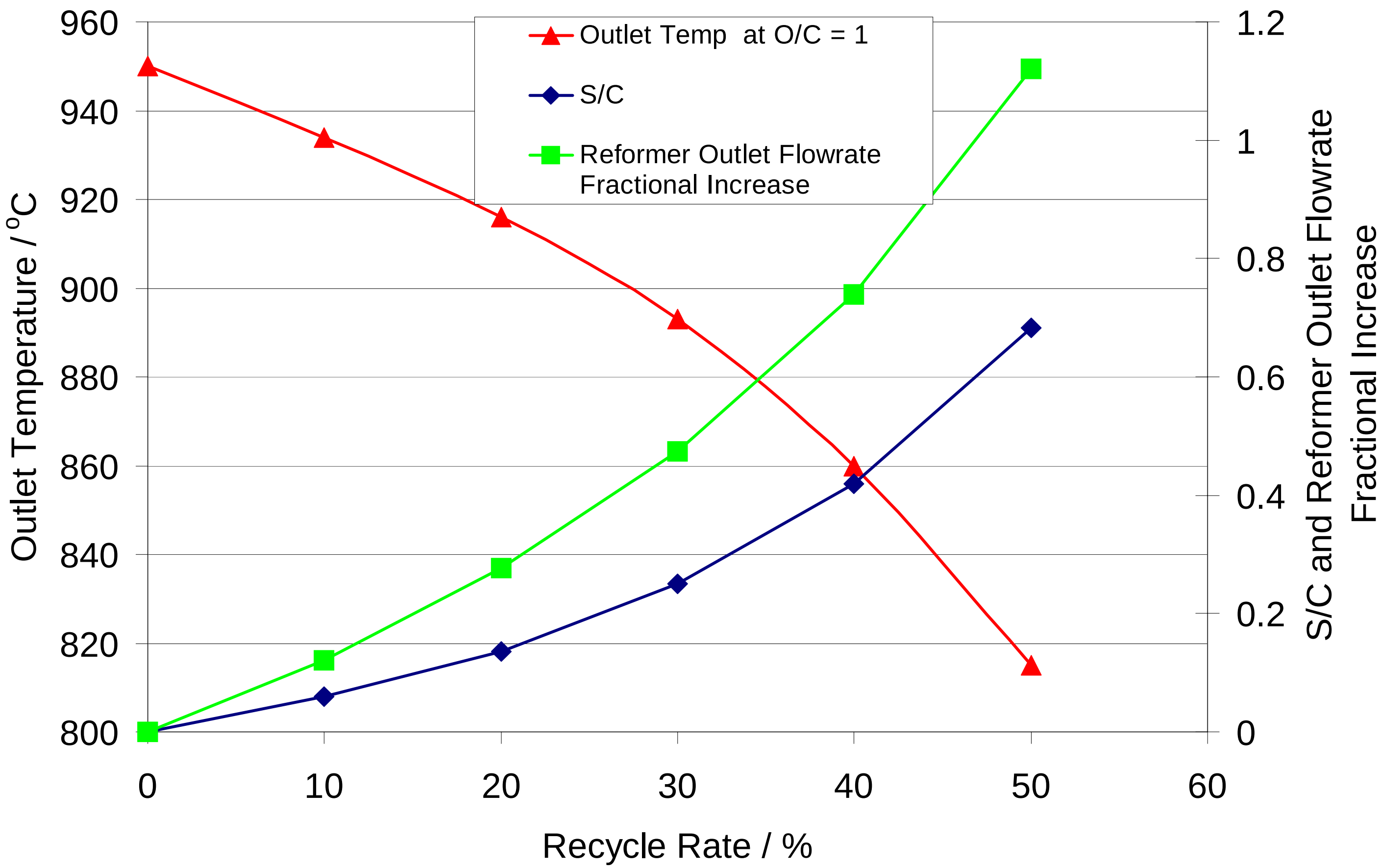
SOFC Anode Recycle to Reformer → Water Addition



- Methods for water introduction and availability:
  - Separate water tank (tank, freezing)
  - Anode water recovery by condensation (heat ex., cond., tank, pump freezing)
  - **Anode recycle to reformer (blower)**

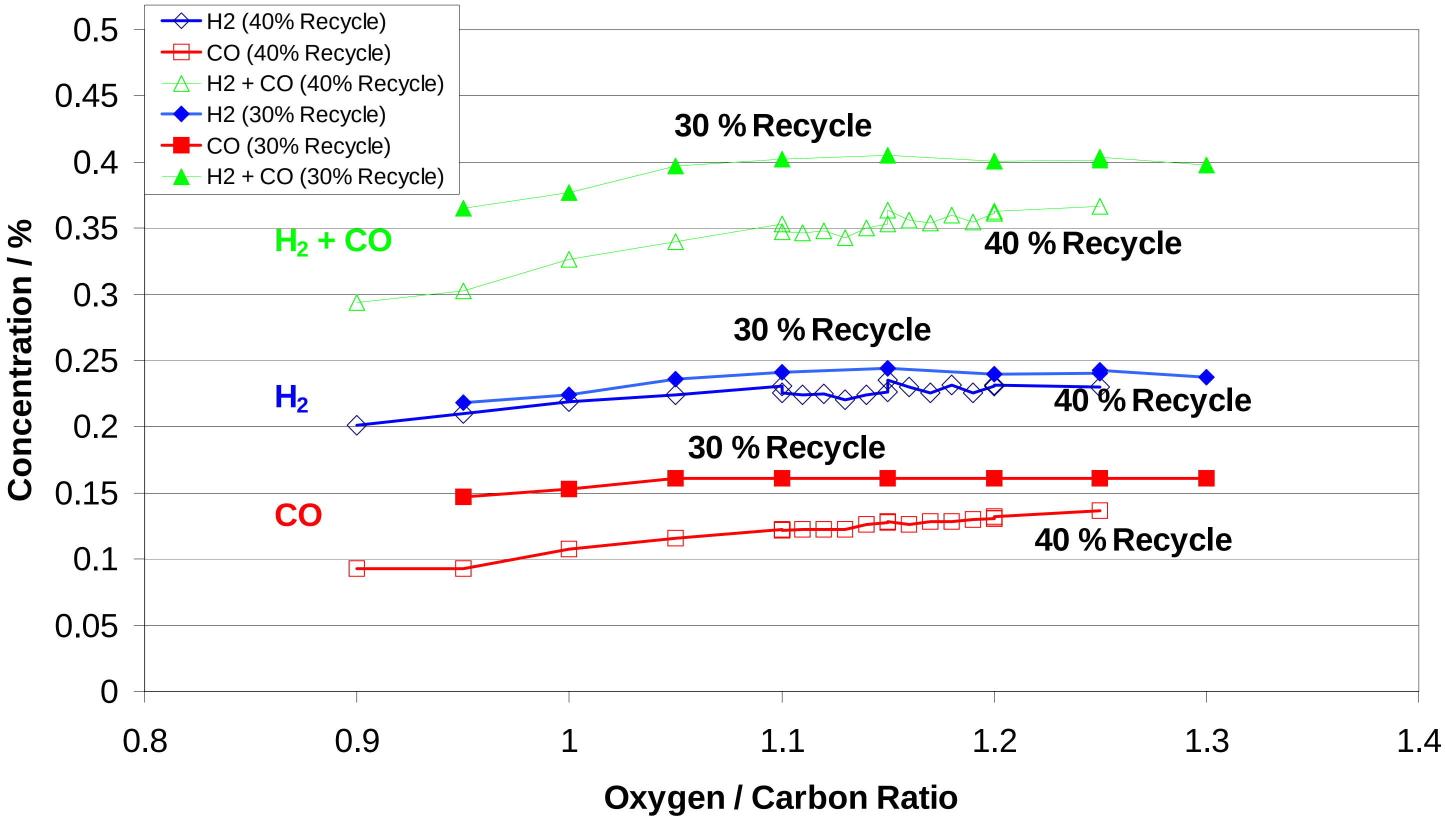
Currently simulating anode recycle with N_2/H_2 mixture

SOFC Anode Recycle Modeling



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

Hydrogen / CO production

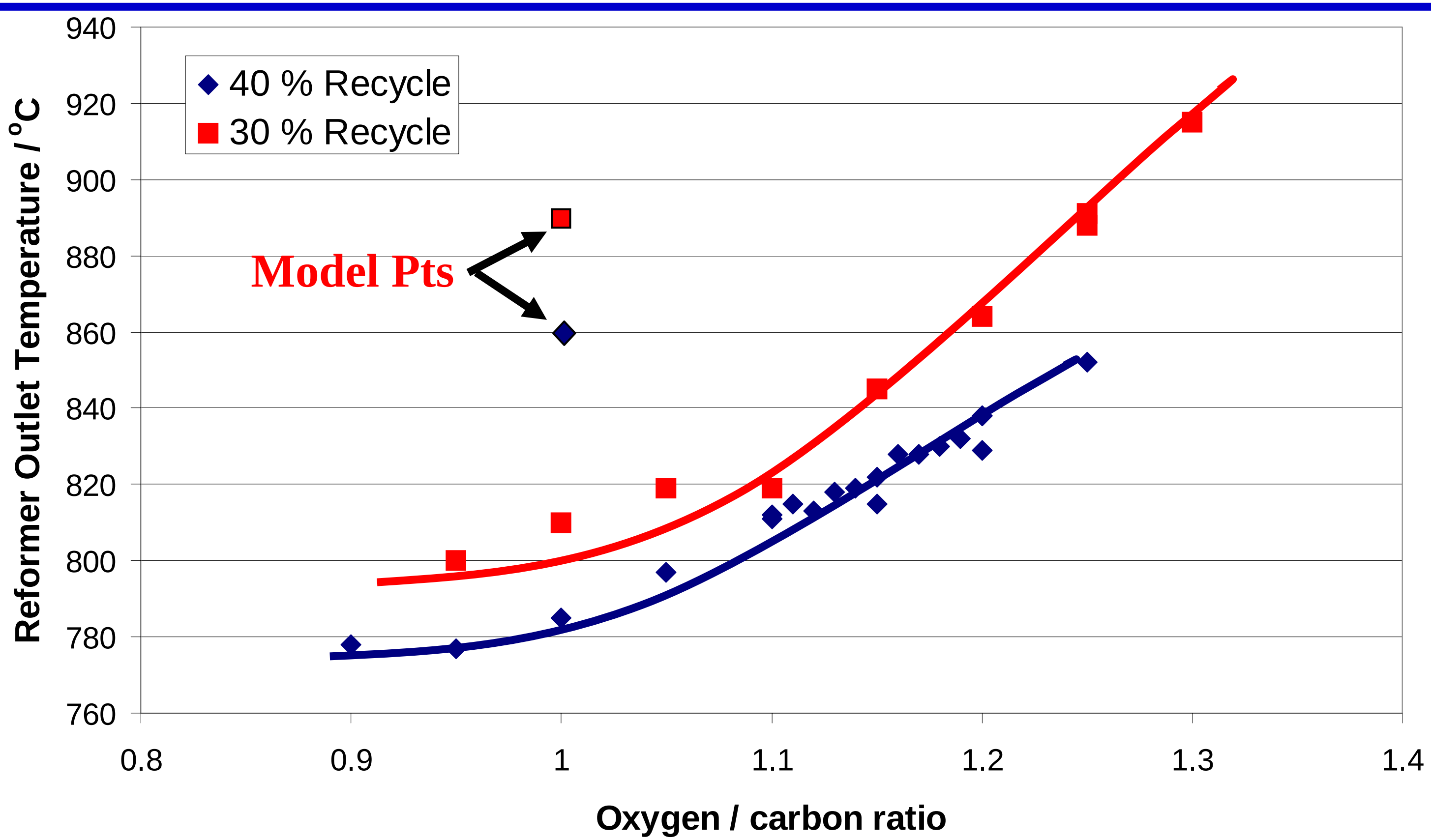


Pt / Rh supported catalyst

Residence time ~ 20 msec

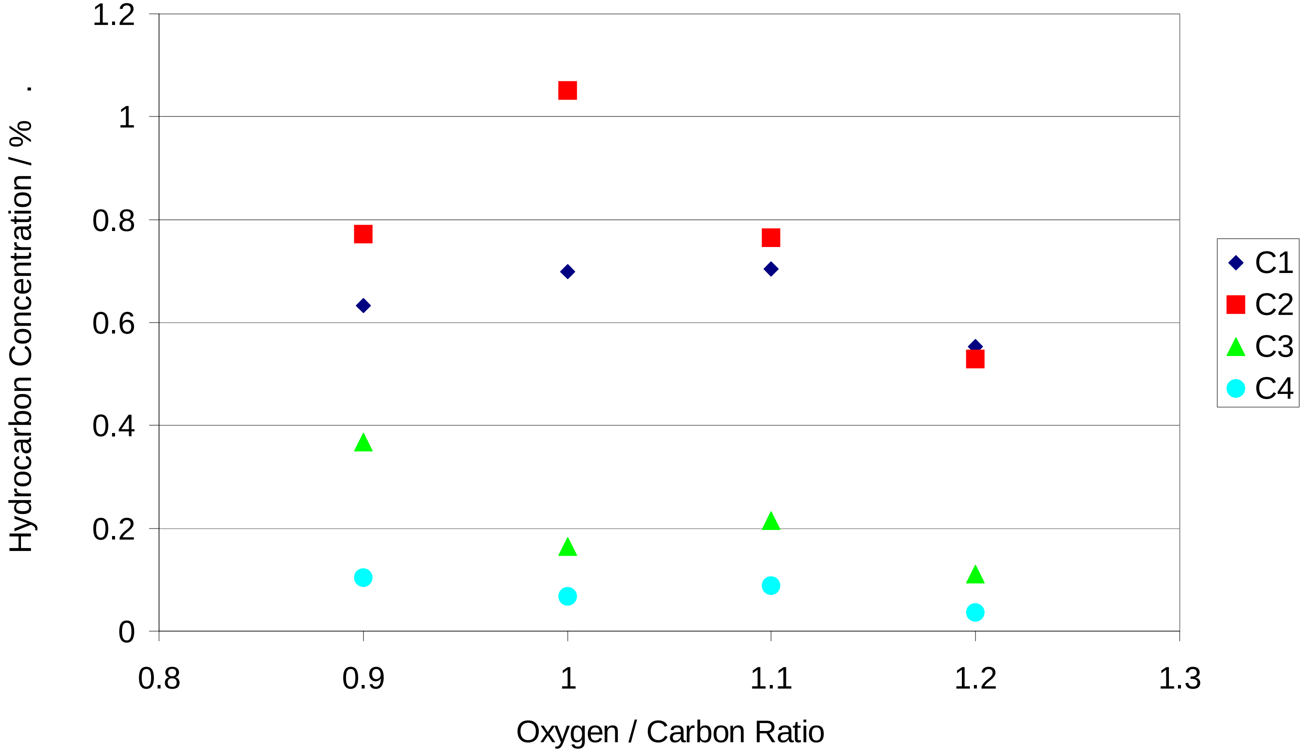
Anode recycle simulated with H_2, N_2, H_2O

Reformer temperature during diesel reforming



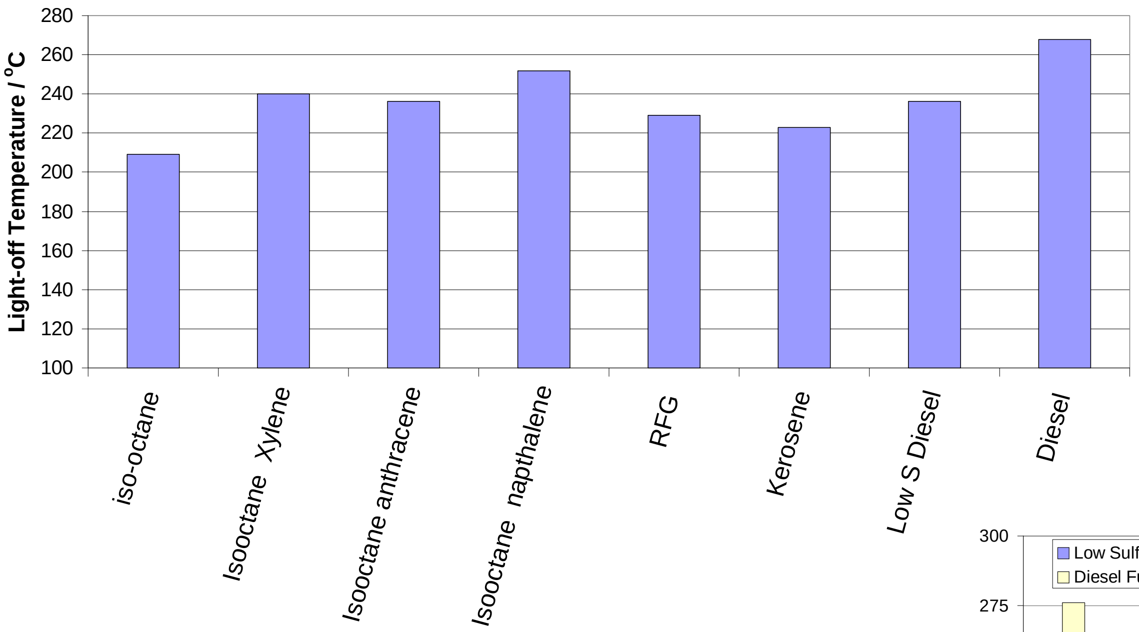
- **Higher recycle reduces operating temperature**
- **Operation with recycle < 30 % difficult due to high operating temperatures and catalyst sintering**

Reformer Outlet Hydrocarbon Speciation

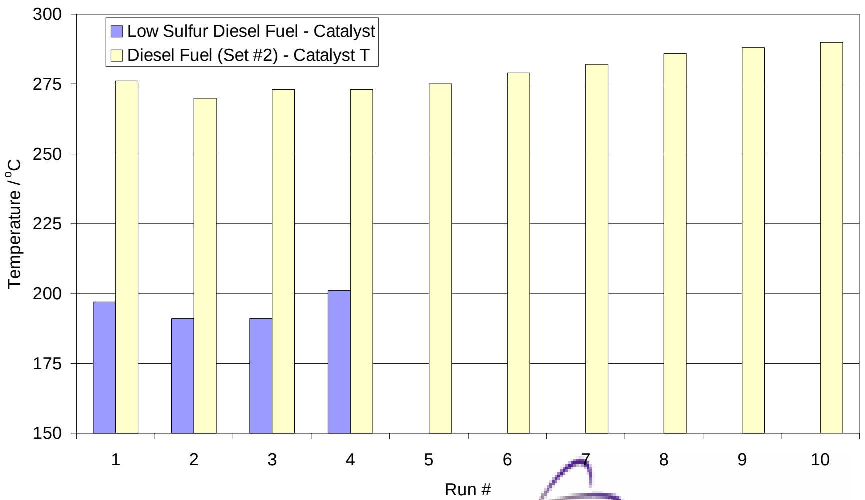


- **Complete hydrocarbon conversion:**
  - **Higher O/C reduces HCs**
  - **Higher residence and catalyst loading reduces HCs**
- **Gasoline/PEM reforming durability work shows HC breakthrough at ~ 500 – 750 hours**

Light-off of Reformer with Diesel



Repeated light-offs show an increase in temperature required to achieve light-off



- Light-off requires preheating of catalyst
- Degree of preheat depends upon fuel
- Higher HCs and aromatics require higher Preheat temperatures for light-off

Carbon Formation Equilibrium Modeling

- Various forms of carbon exist
  - (different forms of carbon exist in the literature, and different forms have been observed during reforming)
  - Commercial codes handle vapor, liquids
    - Difficult to deal with solids as 3rd phase
    - Difficult to input of thermodynamics components
  - Different carbon forms have different thermodynamic characteristics

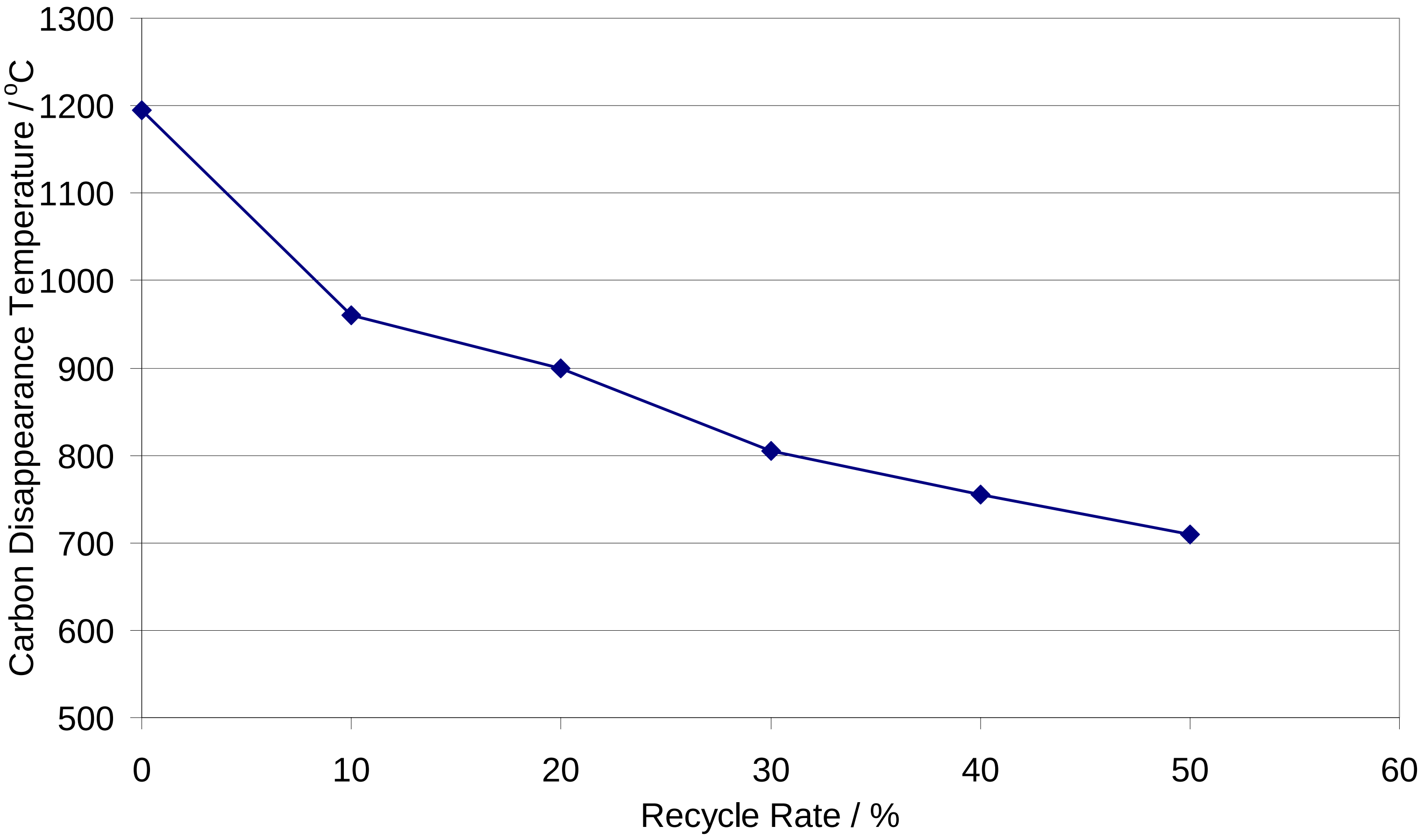
- Developed chemical equilibria code to analyze conditions for carbon formation
  - Includes 3 types of amorphous carbon
    - Dent Carbon (C1)
    - Boudart Carbon (C2)
    - Water gas carbon (C3) – (limited thermodynamic data)
  - Operation of model in iso-thermal modes (adding adiabatic)
  - C++ Code operates on Windows PC

Model Operation & Availability

- Specify:
  - 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)

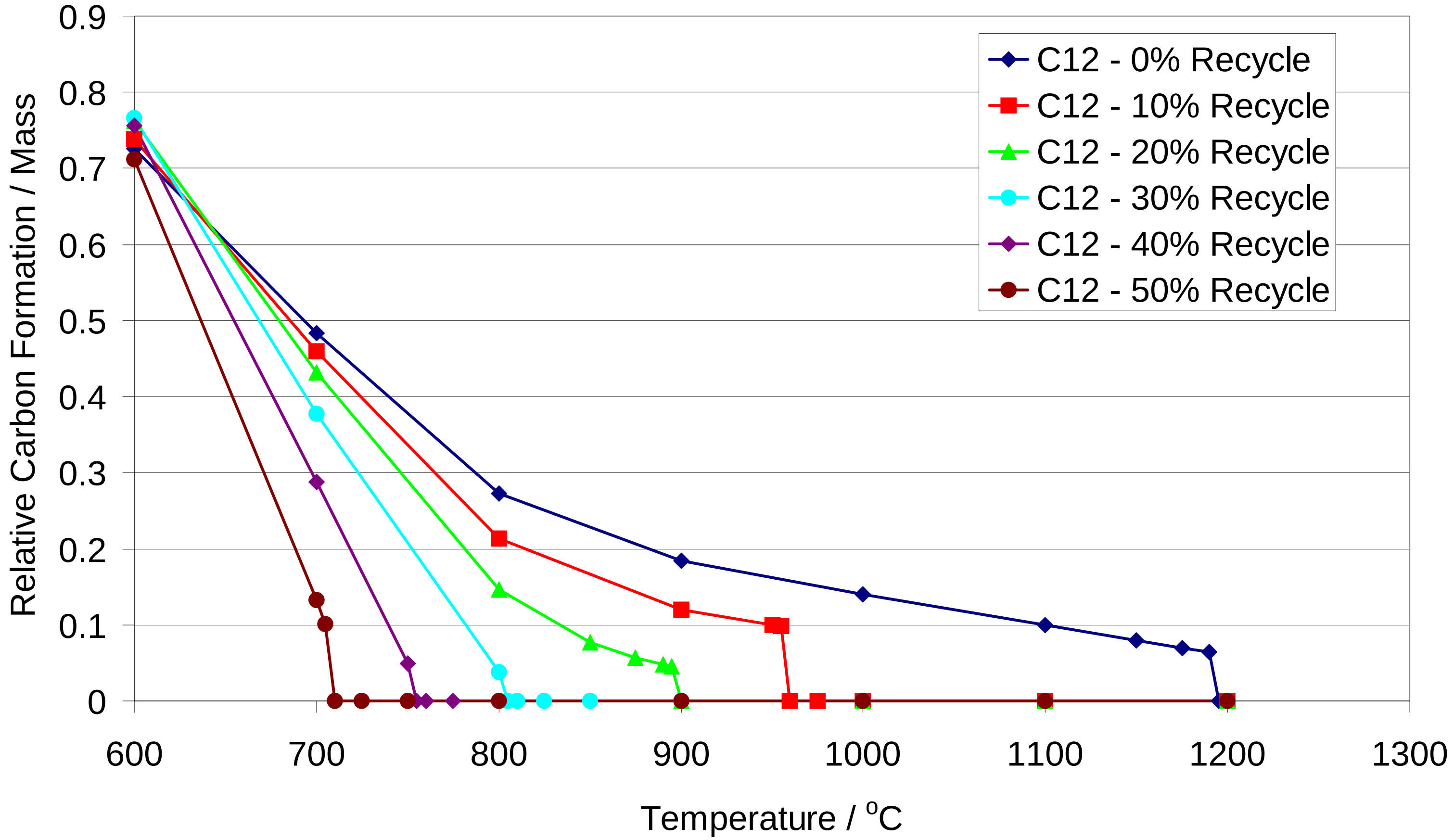
- Model is (will be) available
  - no-cost (or nominal), non-exclusive to SECA industry teams

Carbon Disappearance Temperature with Recycle Ratio



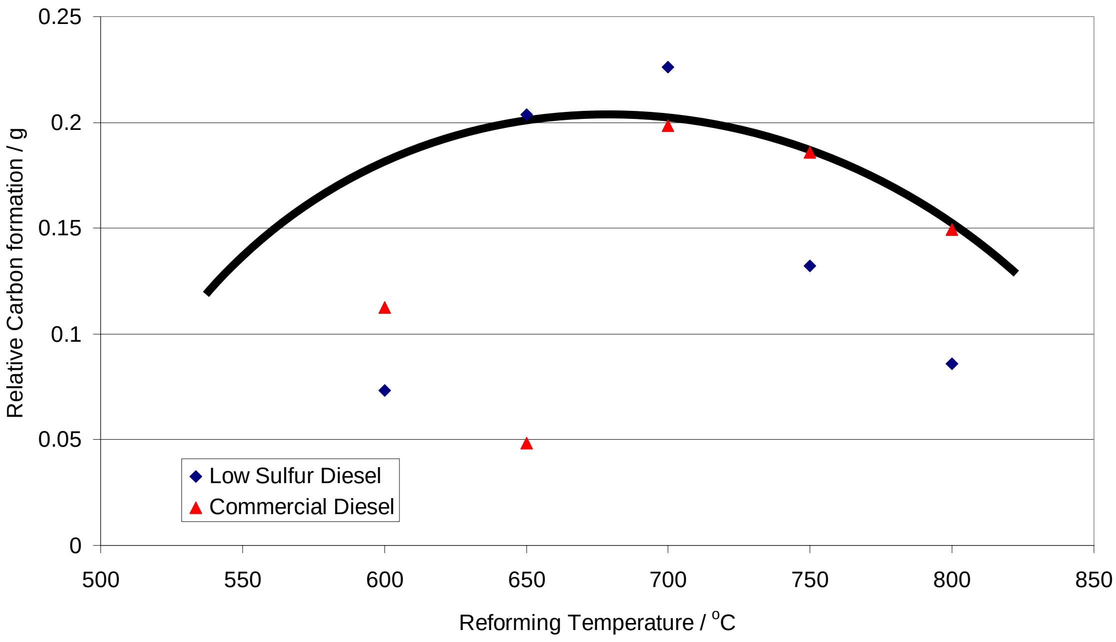
Disappearance of all types of amorphous carbon

Carbon Formation Dependence on Recycle Ratio



- Dent Carbon (C1)
- Boudart Carbon (C2)

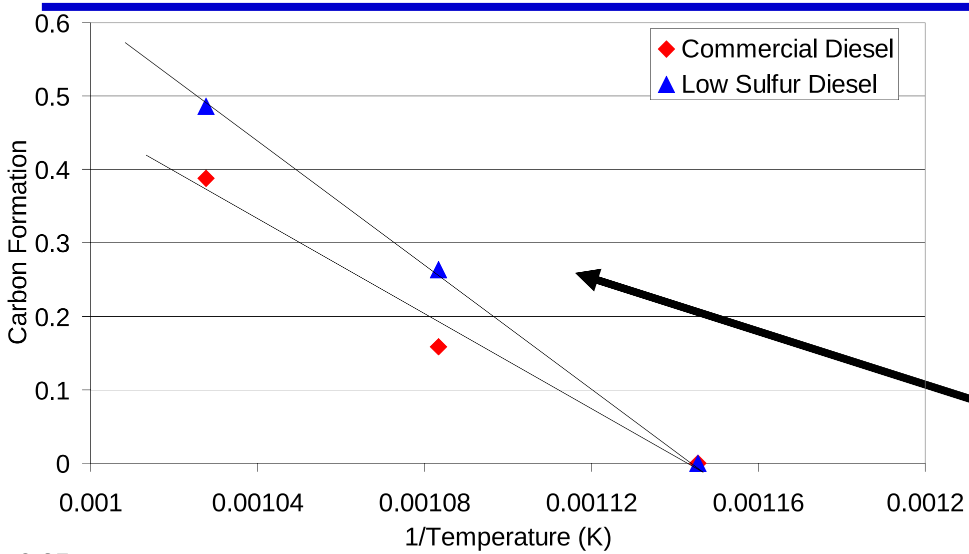
Carbon Formation:
Competing effects kinetics vs. equilibrium



<u>Conditions:</u>
Iso-thermal operation
Total O/C = 1.0
Pt/Rh support catalyst
Residence Time = ~ 30 msec

Low temperature – high equilibrium / low kinetics
High temperature – low equilibrium / high kinetics

Carbon Formation Measurements

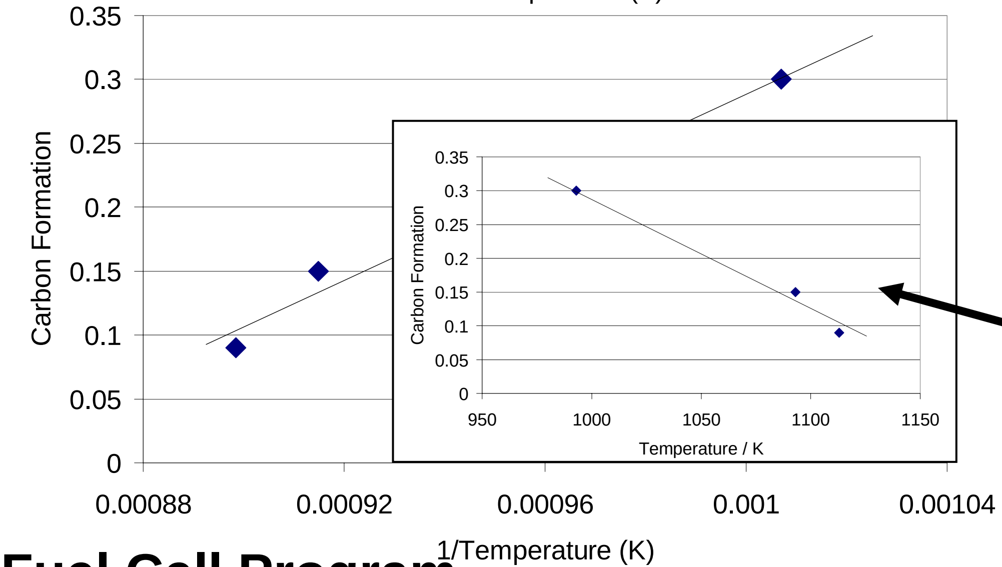


Iso-thermal operation

Carbon formation trends with equilibrium at high temperatures

Trends with T (kinetic effect) at lower temperatures

Carbon Formation linear vs. 1/T



Adiabatic operation

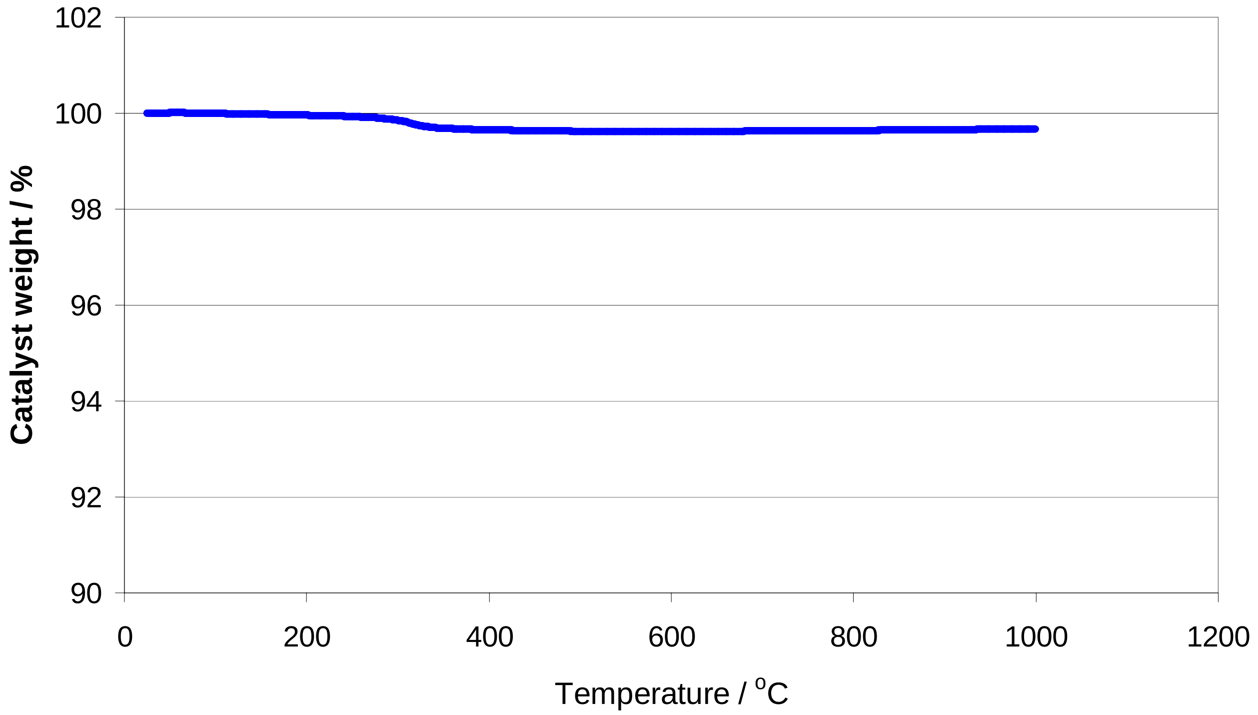
Carbon formation trends with equilibrium

Carbon decreases with increasing temperature

Carbon Formation linear vs. T

Carbon Analysis

Thermal Gravimetric analysis of catalyst post-carbon forming measurements



Carbon removal is about 0.4 % catalyst weight

Carbon is not typically 'bound' to catalyst surface (for noble metal catalysts)

Summary/Findings

- Direct fuel injection via fuel nozzle
  - Control of fuel temperature critical
    - Prevent fuel vaporization, fuel pyrolysis / clogging of nozzle
    - Potentially limited turn-down with nozzle
- Reformer operation with SOFC anode recycle
  - High adiabatic temperatures at low recycle rates
    - Leads to catalyst sintering
    - Limits light-off of reformer
  - High recycle increases reformer size, parasitic losses
  - Operation at 30 – 40 % recycle rate reasonably successful
    - Limited success at lower (<20 % recycle rates due to high adiabatic T)
- Carbon Formation
  - Equilibrium carbon formation modeling
    - Equilibrium code available for iso-thermal carbon formation cases
  - Experimental carbon formation measurements show kinetic effects and equilibrium effects

Future Activities - Modeling

- Modeling
  - Make model available for SECA industrial teams (Beta version)
    - (no or nominal cost , non-exclusive license)
  - Model improvements
    - Incorporate other carbon species enthalpies ($CH_{0.2}$)
    - Incorporate sulfur into equilibrium code
    - Improve code robustness & make ‘user friendly’
  - Examine system effects of anode recycle (efficiency and parasitics)

Future Activities - Experimental

- Experimental
  - Examine reformate effect on SOFC
    - Effect of hydrocarbon ‘breakthrough’ on SOFC
      - incorporate SOFC ‘button’ cell operating on reformate
    - Sulfur effect on reforming kinetics
    - Carbon formation as function of catalyst, recycle ratio
  - Reformer design considerations
    - Durability – catalyst sintering
    - Turndown – fuel / air feed preparation
    - Stand-alone start-up & consideration to avoid C formation
    - Recycle ratios – evaluate various anode recycle ratios
      - ‘real’ recycle – incorporate major/minor constituents