# Fuel Processing Development

## SECA Core Technology Program

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# Objectives and Tasks

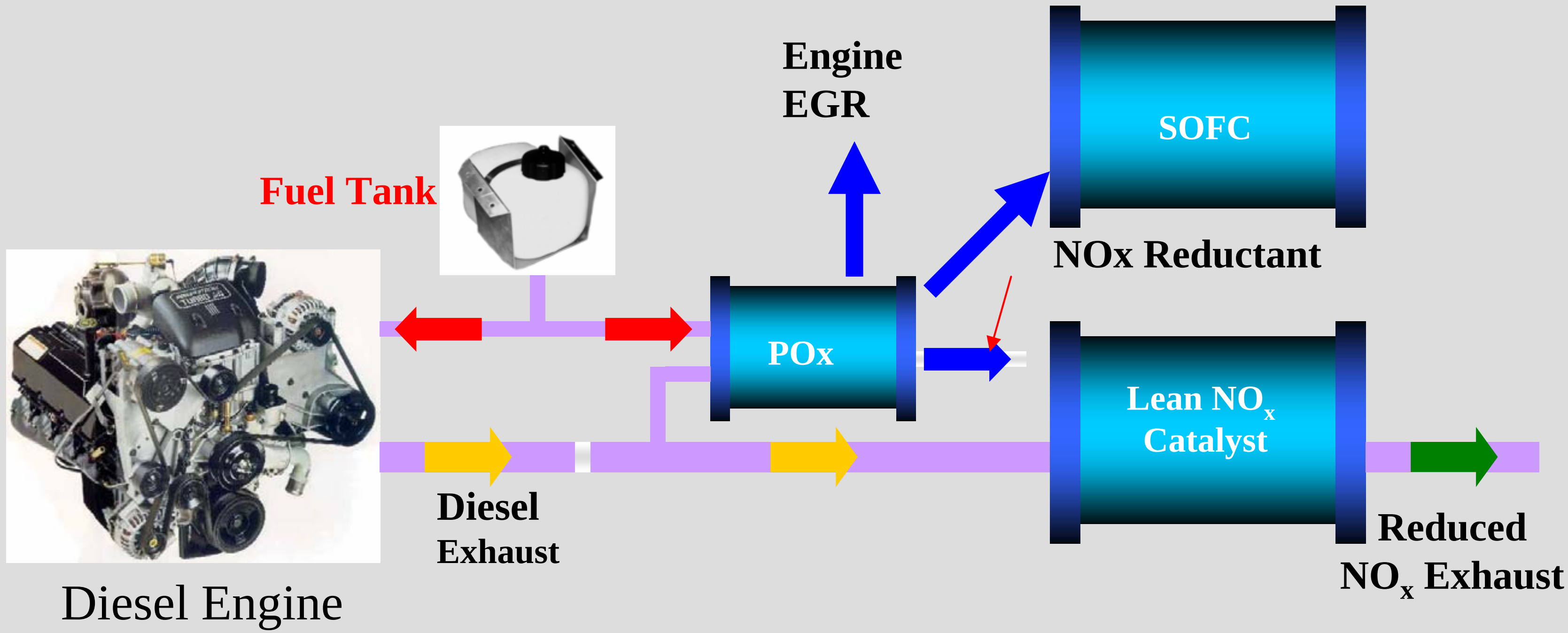
## Objectives:

- Develop technology for on-board reforming diesel fuel for APU applications.
- Understand parameters that affect fuel processor performance, lifetime and durability.

## Tasks:

- Carbon Formation Measurement of Diesel Fuel
    - Equilibrium and component modeling
    - Experimental carbon formation measurement
- Fuel Mixing
    - Vaporization
    - Direct liquid injection & fuel atomization
- Low water ‘Waterless’ Partial Oxidation of Diesel Fuel
    - Start-up
    - SOFC anode recycle

# Diesel Reformer Vehicle System Integration




**Integration Issues:**

- **Expect multiple uses for Diesel reformate: (SOFC, de-NOx, EGR)**
- **Oxidant (Air or Engine Exhaust [12 – 17 % $O_2$])**
- **On-board water (low water operation, zero water start-up)**
- **SOFC Anode recycle/Engine exhaust add water**

# Fuel Processing Catalysts & Poisons

## PEM Fuel Cell System

Sulfur Trap(?) → Autothermal Reformer → High Temperature Shift Reactor → Low Temperature Shift Reactor → CO Clean-up → PEM Stack

| Autothermal Reformer | High Temperature Shift Reactor | Low Temperature Shift Reactor | CO Clean-up | PEM Stack |
|---|---|---|---|---|
| > 700 $^oC$ | ~ 450 $^oC$ | ~ 220 $^oC$ | ~ 150 $^oC$ | ~ 80 $^oC$ |
| Catalysts:<br>noble metal<br>nickel<br>Poisons:<br>Cl-, P, V, Pb | Catalysts:<br>NM, $Fe_2O_3$, FeCr<br>Poisons:<br>ATR poisons<br>Sulfur, carbon<br>$O_2$ | Catalysts:<br>NM, Cu/ZnO<br>Poisons:<br>ATR poisons<br>Sulfur, carbon<br>$O_2$ | Catalysts:<br>NM<br>Poisons:<br>ATR poisons<br>Sulfur | |

## SOFC Fuel Cell System

Sulfur Trap(?) → Autothermal Reformer or POx → SOFC Stack

Autothermal Reformer or POx: > 700 $^oC$

SOFC Stack: > 700 $^oC$

# Diesel Reforming System Integration Issues

- BOP - Balance of plant
  - Air Feed
    - air compressor air
    - engine exhaust
  - Water
    - Operation without water
    - System water balance
- Reactor fuel feed
  - vaporization (without carbon formation)
  - direct injection / atomization
- Reactor start-up / light-off
  - Time
  - Carbon formation
- Catalyst durability and activity / fuel sulfur
- Carbon formation

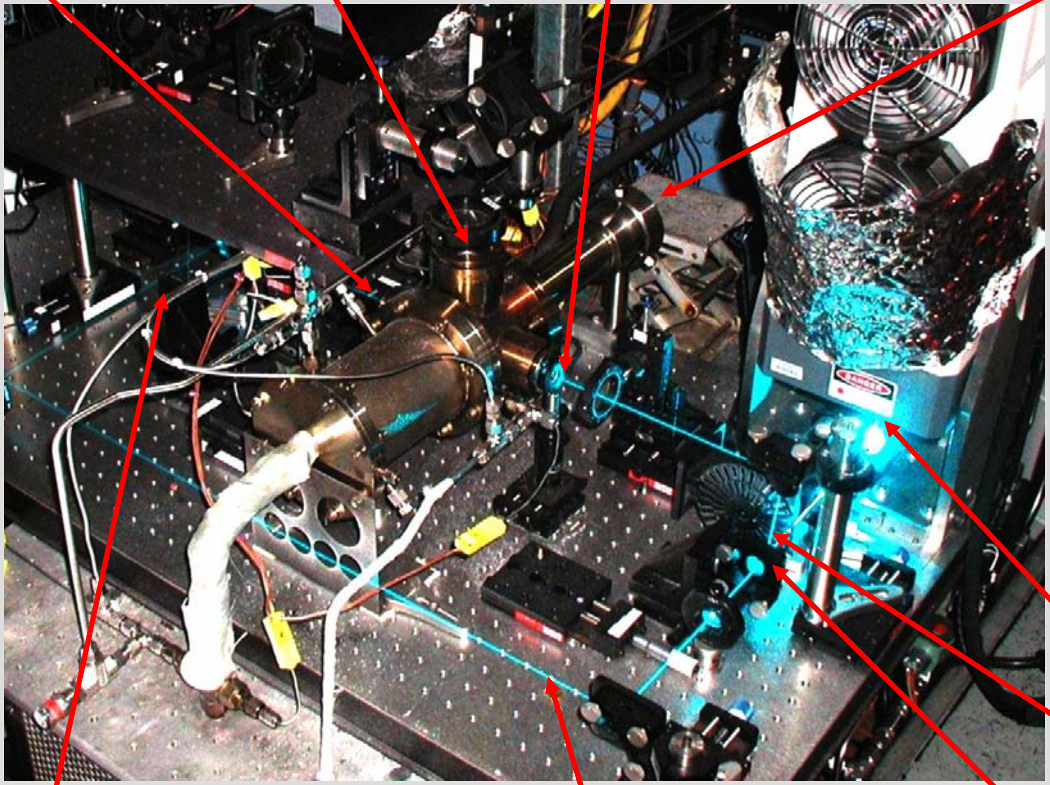
# Carbon Formation Laser Optics

Extinction

Fluorescence - Scattering

Reactor Window

Catalyst Window



Signal Detector

Reference Beam

Beam Splitter

Laser Chopper

Ar Ion Laser

- Laser extinction measurements monitor on-set of carbon
- Laser scattering quantifies carbon formation
- Fluorescence indicates PAHCs

# Gasoline/Diesel
# Partial Oxidation / Reformers

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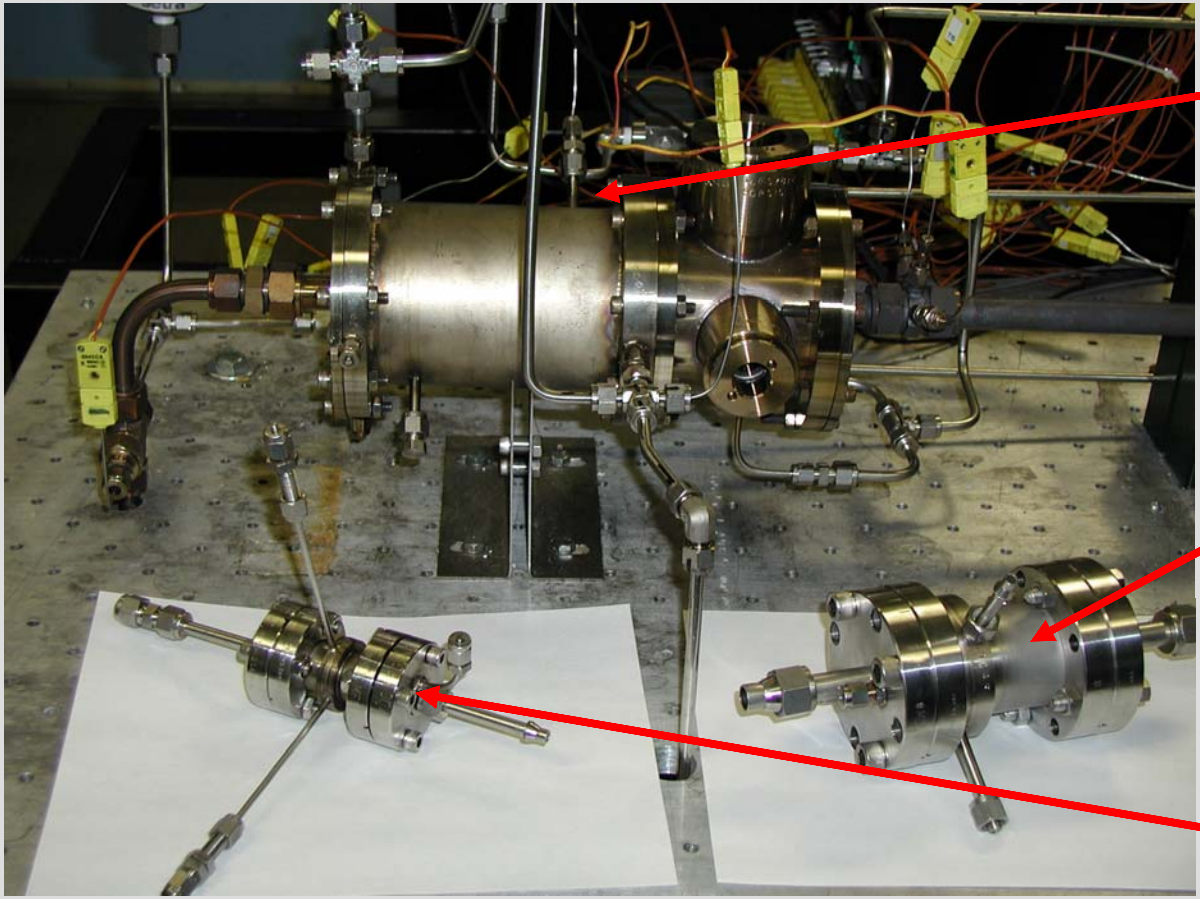
## Adiabatic Reactors – ‘real’ operating conditions



Gasoline/diesel Reformer - *in situ* carbon formation measurements

Reformer for APU/SOFC (Solid-Oxide Fuel Cell / Auxiliary Power Unit – 5 kW)

Reformer (1 kW)

# Fuel Injection/Vaporization

- Fuel injection techniques into the reformer
  - Pre-vaporization
    - fuel pyrolysis and carbon formation
  - Liquid injection
    - limit residence time of fuel under carbon forming condition
      - fuel atomization and distribution
      - flash vaporization
      - potential catalyst degradation
  - Steam vaporization of fuel
    - steam suppresses carbon formation
    - requires steam – still can have feed issues

# Carbon Formation Issues

- Avoid Fuel Processor Degradation due to Carbon Formation
  - Operation in non-equilibrium Carbon formation regions
    - Requires high temperatures / steam Content – limits efficiency (80 %)
    - Promoted catalysts
  - Start-up
    - Rich start-up cannot avoid favorable carbon equilibrium regions
    - Stoichiometric has high adiabatic temperature rise
    - Water-less (Water not expected to be available at start-up)
- Operation for maximum efficiency
  - low of O/C and S/C as possible (C limits)
  - fuel conversion
- Diesel fuels
  - carbon formation due to pyrolysis upon vaporization
  - pre-ignition of fuel

# Limiting Carbon Formation

- Mapping Carbon Equilibrium and Carbon Formation
  - Temperature / Steam Content / Oxygen Content
- Fuel / Steam / Water mixing
  - Fuel vaporization
  - Direct fuel injection to oxidation

- Carbon Formation Mechanisms
  - Hydrocarbon decomposition
  - Accumulation of hydrocarbon on surface with polymer formation (polyaromatics)
  - Pyrolytic carbon formed from olefins

## Carbon (Soot) Formation

**$2CO \Leftrightarrow C + CO_2$ (Boudart Reaction)**

**$CH_4 \Leftrightarrow C + 2H_2$ ($CH_4$ Decomposition)**

**$CH_4 \rightarrow C_2H_6 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \rightarrow \text{aromatics} + H_2 \rightarrow \text{soot}$**

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

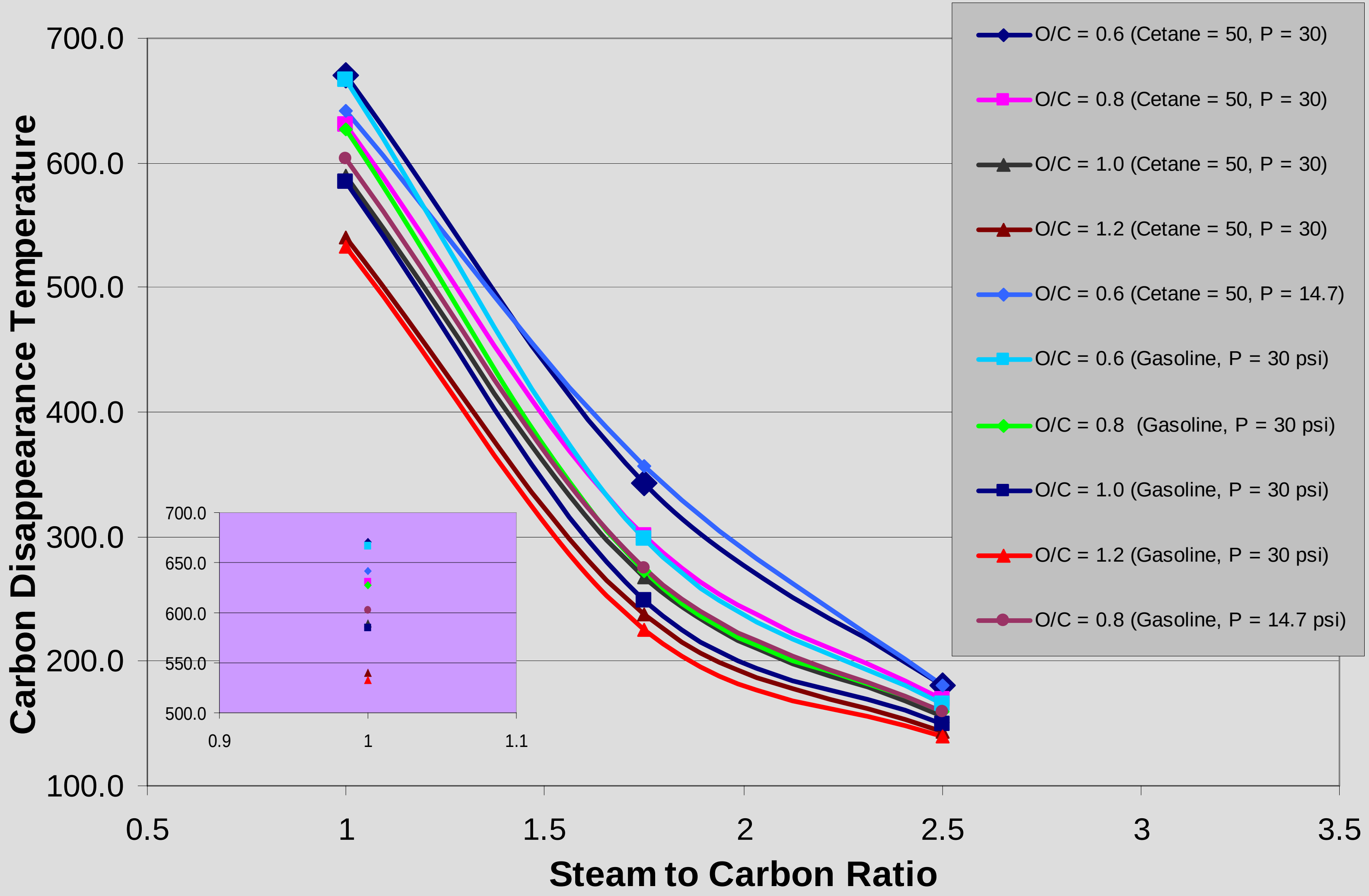
# Catalyst Interaction with Carbon Formation

- Catalysts Compositions
  - Catalyst
    - Pd >> Pt > Rh > Re > Ru, Ir (Methane decomposition studies)
  - Support
    - Oxygen donation
      - YSZ, Ceria, La
      - Pt/YSZ -Pt/Ceria
      - Alkali promoters (K etc.)
    - Bimetalics
      - Pt/Re/$Al_2O_3$

        (Re must be reduced - operation with $H_2O$)

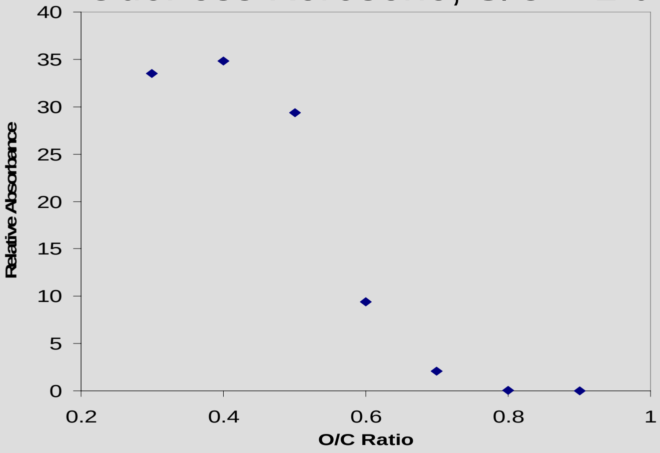
        [Pt/Re/YSZ shows poor performance with $H_2O$, good dry]

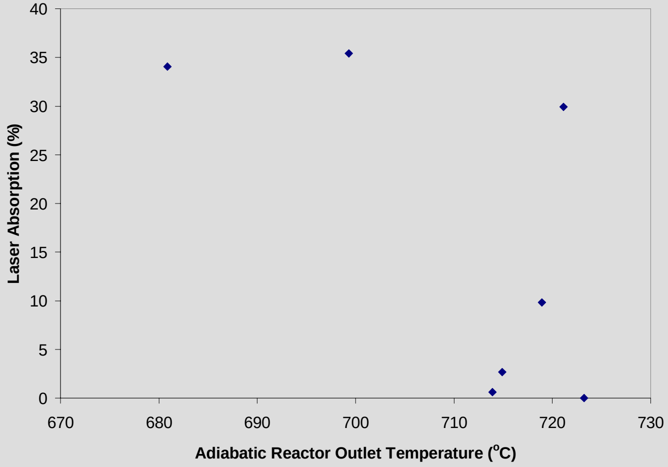
# Modeling of Carbon Formation Disappearance for Different Fuel Compositions



# Technical Results:
## Carbon formation measurements

Carbon formation monitoring with laser scattering
Odorless Kerosene; S/C = 1.0



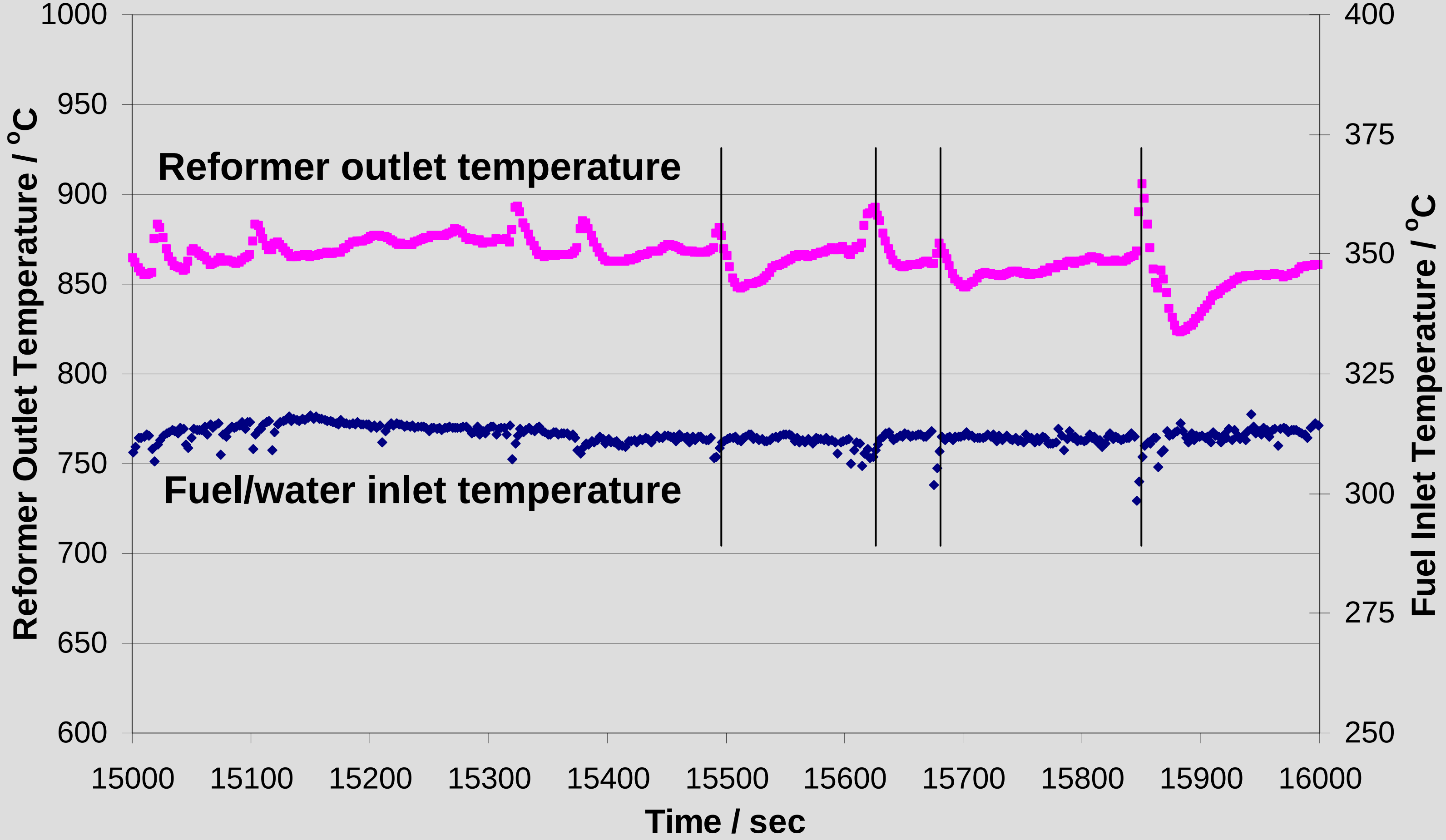




## Results

- Partial oxidation of
  - odorless kerosene
  - kerosene
  - dodecane
  - hexadecane
- Carbon formation monitoring by laser optics
- Carbon formation shown at low relative O/C ratios and temperature with kerosene (left)
- Demonstrated start-up with no water – carbon formation observed after ~ 100 hrs of operation

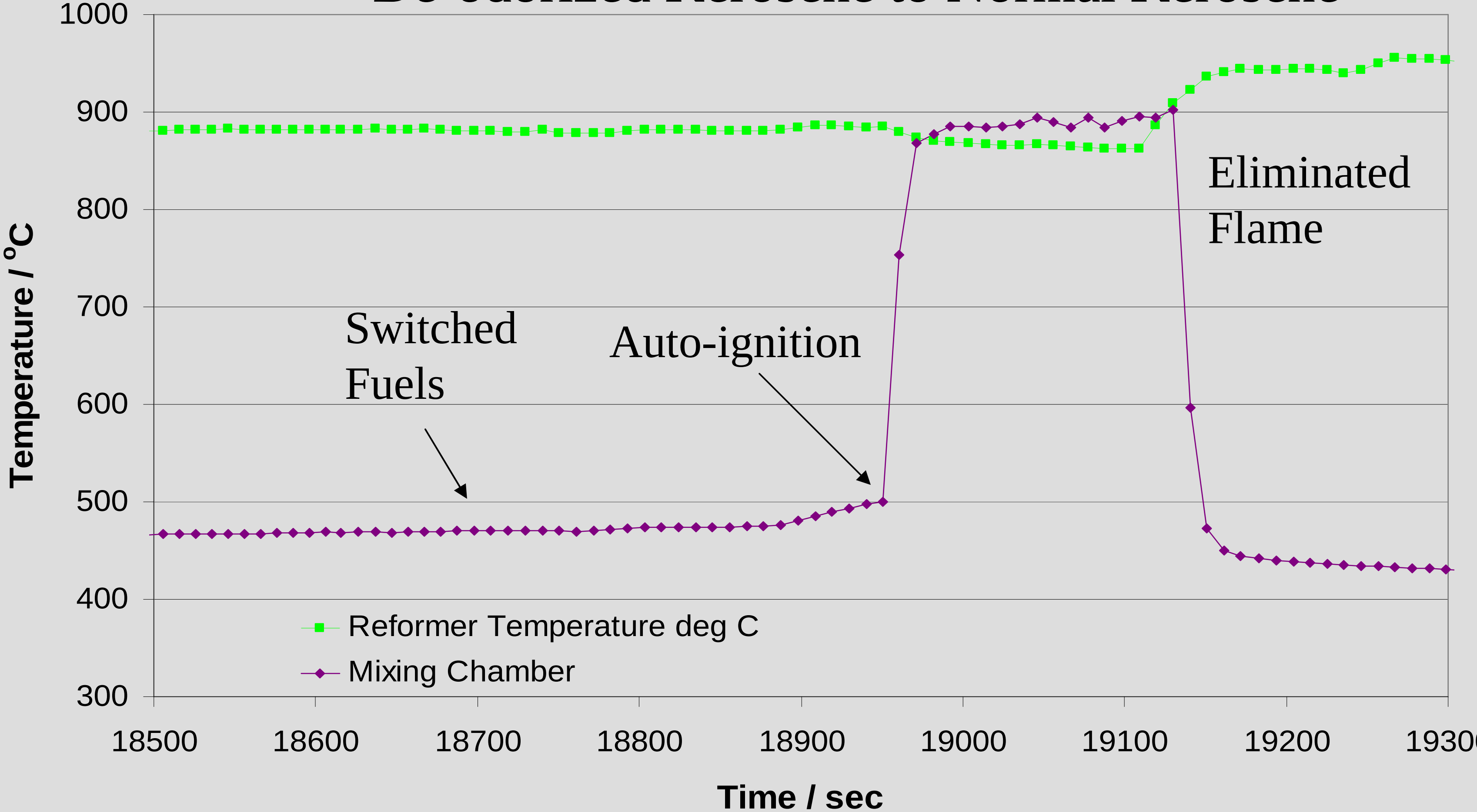
# Fuel / Water co-vaporization Issues

Decrease in fuel/$H_2O$ inlet temperature (pool boiling or condensation) corresponds with increase in adiabatic temperature rise



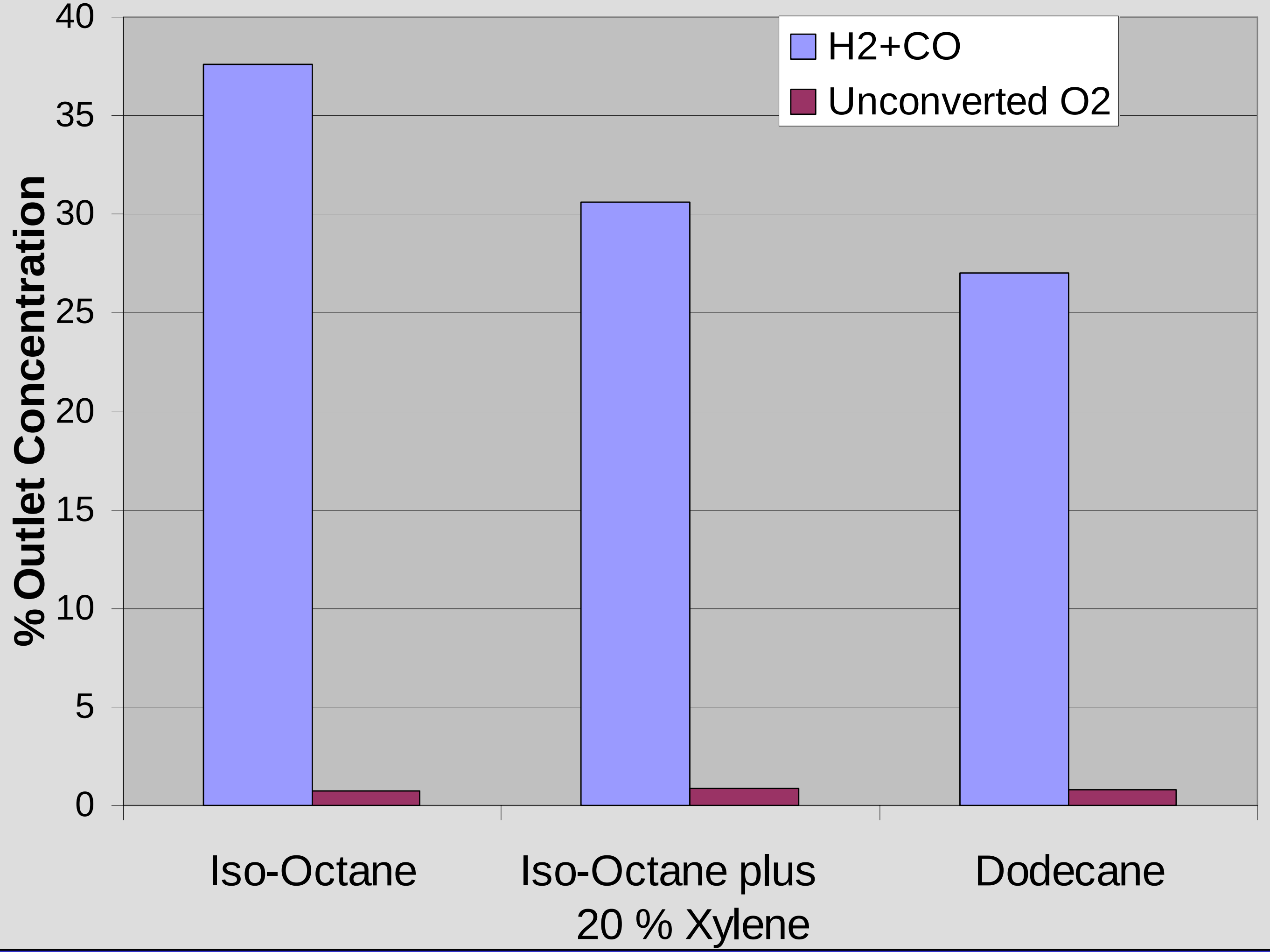
# Fuel Effect on Auto - ignition

## Switched Fuel Operation:
## De-odorized Kerosene to Normal Kerosene



# Partial Oxidation Stage Outlet Concentrations

(for similar oxygen conversion)



# Technical Progress Summary/Findings

- Demonstrated start-up with no water – carbon formation observed after ~ 100 hrs of operation
- Catalytic oxidation
  - diesel components kinetically slower than gasoline components
- Carbon Formation
  - Greater carbon formation with aromatics
- Diesel Fuel Components (Dodecane)
  - Lower conversion / higher residence time required for conversion
- Laser & visual monitoring of carbon formation
- Fuel testing: Dodecane, hexadecane, kerosene, de-odorized kerosene
- Modeling: equilibrium, carbon formation, thermodynamic properties
- Pre-combustion
  - Diesel fuels much more likely for pre-combustion
    - kerosene has higher pre-combustion tendancies than de-odorized kerosene