Diesel Reforming and Carbon Formation Measurements

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Technical Issues

Fuel Processing for Fuel Cells – Hydrogen Production

- Fuel cells operate on hydrogen rich mixtures best
  - Hydrogen rich leads to highest power density in fuel cell
  - Cost of SOFC is high, lower cost SOFC system is potentially highest power density SOFC stack
- Partial Oxidation / steam reforming
  - Steam reforming requires water
  - Partial oxidation less efficient that SR
  - Combination of POx/SR leads to ATR (autothermal reforming)
- Durability
  - Carbon formation
  - Sulfur tolerance
  - Repeated cycling
  - Operational hours (400,000(?))
- Cost
- Understand parameters that affect fuel processor lifetime and durability.

Fuel Processing Systems

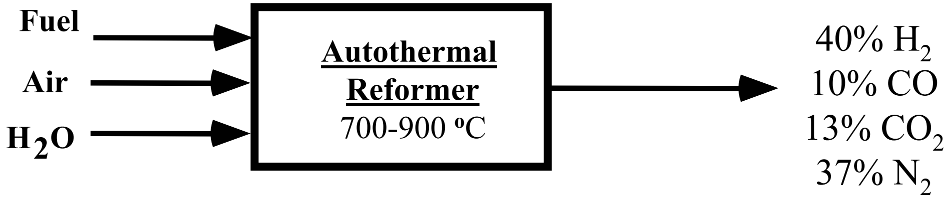
PEM Fuel Cell System

Autothermal Reformer	High Temperature Shift Reactor	Low Temperature Shift Reactor	CO Clean-up	PEM Stack
> 700 ^{o}C	~ 450 ^{o}C	~ 220 ^{o}C	~ 150 ^{o}C	~ 80 ^{o}C
Catalysts: noble metal / Ni	Catalysts: Pt, Fe_2O_3, FeCr	Catalysts: Pt, Cu/ZnO	Catalysts: Noble metal	Catalysts: Pt
40% H_2 10% CO 0.4 - 1% CH_4	4% CO	1% CO	10 ppm CO	

SOFC Fuel Cell System

Sulfur Trap	Autothermal Reformer	SOFC Stack
	> 700 ^{o}C	> 700 ^{o}C

ATR Reactions



Partial Oxidation (POx) - Rich fuel burn (exothermic):

oxygen / carbon ratio (oxygen from air only) **(O/C = 1)**

$C_nH_{(2n+2)} + {}_{(n/2)}O_2 \text{ --> } nCO + {}_{(n+1)}H_2$

(O/C < 1)

$C_nH_{(2n+2)} + {}_{(m/2)}O_2 \text{ --> } mCO + C_{(n-m)}H_{2(n-m)} + H_2$

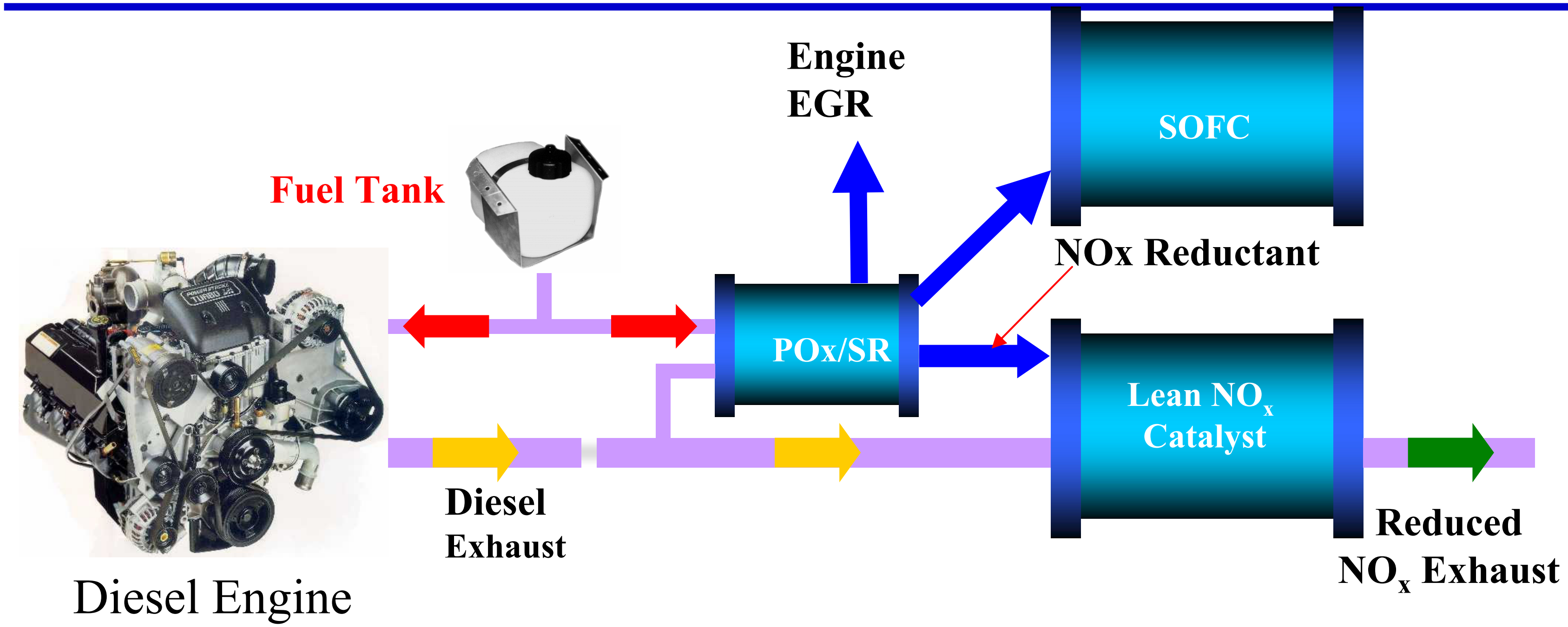
Steam Reforming (endothermic):

Steam / carbon ratio (S/C = 1)

$C_nH_{(2n+2)} + nH_2O \rightarrow nCO + (2n+1)H_2$

Couple POx (exotherm) and Steam Reforming (endotherm) for ATR (Autothermal reforming)

Potential Applications of Diesel Refomers in Transportation Systems



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

- fuel for SOFC / APU
- reductant for lean-burn engines catalyzing NOx reduction
- Hydrogen addition to the fuel charge allowing high engine EGR
- fast light-off and heating of engine / catalytic convertor

Incorporation into vehicles may require reforming to be suitable for all of the concurrent applications even though the requirements and applications can be significantly different.

Objectives and Tasks

Objectives:

- Develop technology for reforming of diesel fuel for APU applications.
  - Fuel/air mixing, catalytic partial oxidation / steam reforming
- Understand parameters that affect fuel processor lifetime and durability.
  - Catalyst durability
  - Carbon formation and system durability

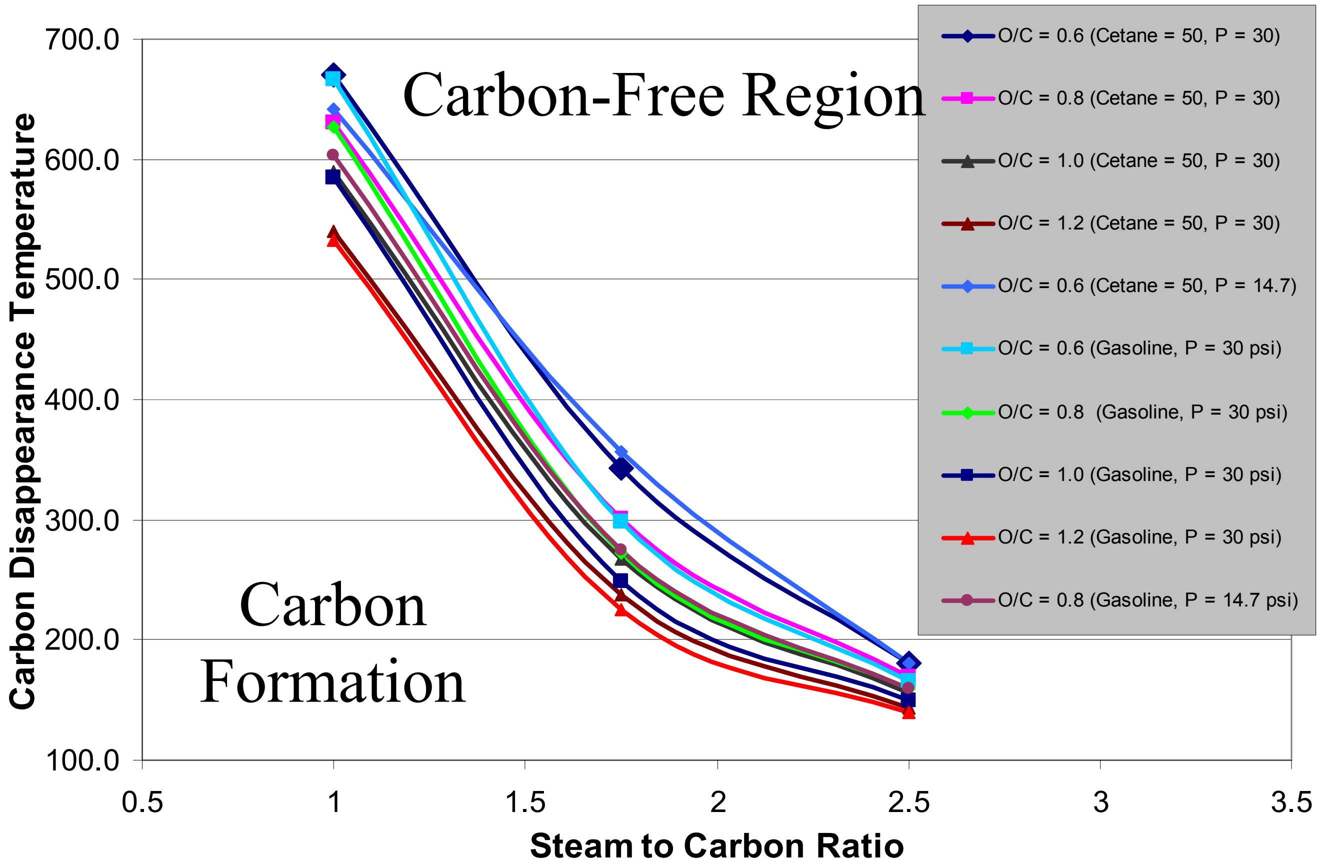
Tasks:

- Measurement of Carbon Formation in Diesel Fuel Processing
  - Equilibrium and component modeling
  - Experimental carbon formation measurement
- Fuel Mixing
  - Vaporization / Fuel atomization
  - Direct liquid injection
- 'Waterless' Partial Oxidation of Diesel Fuel
  - Start-up
  - SOFC anode recycle (water addition to reformer)

Carbon Formation Issues

- Avoid Fuel Processor Degradation due to Carbon Formation
  - Operation in non-equilibrium Carbon formation regions
    - High temperatures / Steam Content – limits efficiency (80 %)
    - Promoted catalysts
- Operation for maximum efficiency
  - minimization of O/C and S/C as possible (CH_4, C limits)
  - 100 % fuel conversion
- Start-up
  - Rich start-up
    - Cannot avoid favorable carbon equilibrium regions
  - Water-less (Water not expected to be available at start-up)
- Diesel fuels
  - carbon formation due to pyrolysis upon vaporization
  - pre-ignition of fuel
- Transient operation & fuel processor control

Modeling of Carbon Formation Disappearance for Different Fuel Compositions



- Carbon formation varies greatly with steam content, only slightly with pressure and cetane #.

Ternary Diagrams

- **Equilibrium Calculations**
  - **Pressure Dependence**
  - **Temperature Dependence**
  - **Fuel composition**
  - **Steam Content**
  - **Air content**
  - **Carbon product**

● = diesel fuel

● = steam (H_2O)

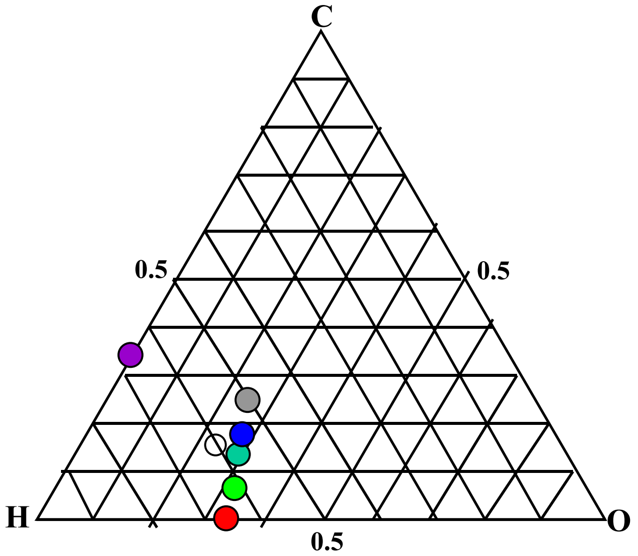
● = diesel, steam, air mixture (O/C = 1.0, S/C = 2.5)

● = diesel mix (O/C = 1.0, S/C = 1.0)

● = diesel mix (O/C = 1.0, S/C = 0.5)

● = diesel mix (O/C = 1.0, S/C = 0.0)

Pure C



Pure H

Pure O

Lower O/C more efficient fuel reformation

Carbon Equilibrium (450 ^{o}C)

Pressure 14.7 to 30 psi

Temperature 450 ^{o}C

--x-- = amorphous carbon

--x-- = graphite

● = (O/C = 1.0, S/C = 2.5)

● = (O/C = 1.0, S/C = 1.0)

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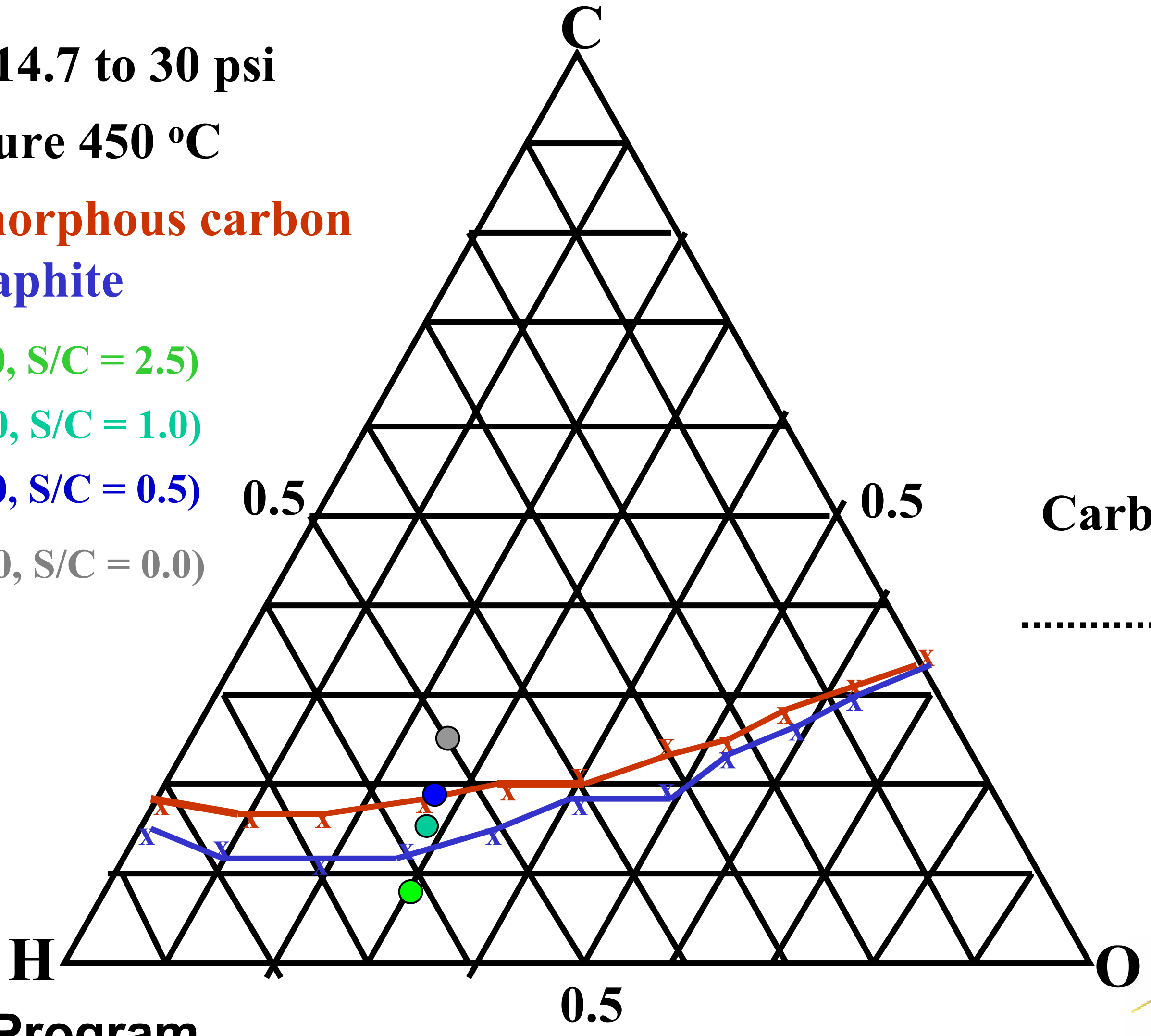

Carbon formation

No Carbon formation

Carbon Equilibrium (270 °C)

Pressure 14.7 to 30 psi

Temperature 270 °C

--x-- = amorphous carbon

--x-- = graphite

● = (O/C = 1.0, S/C = 2.5)

● = (O/C = 1.0, S/C = 1.0)

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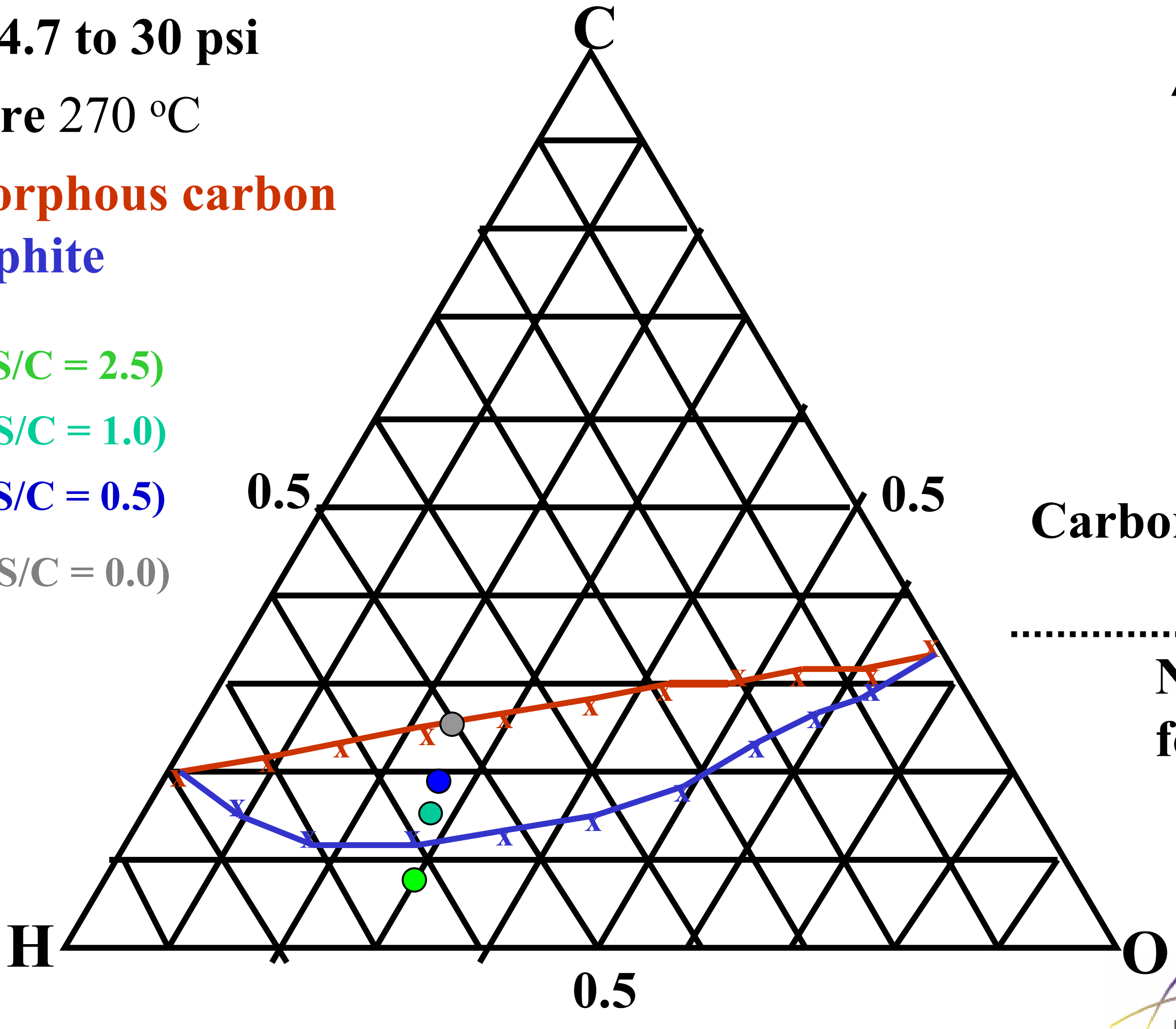
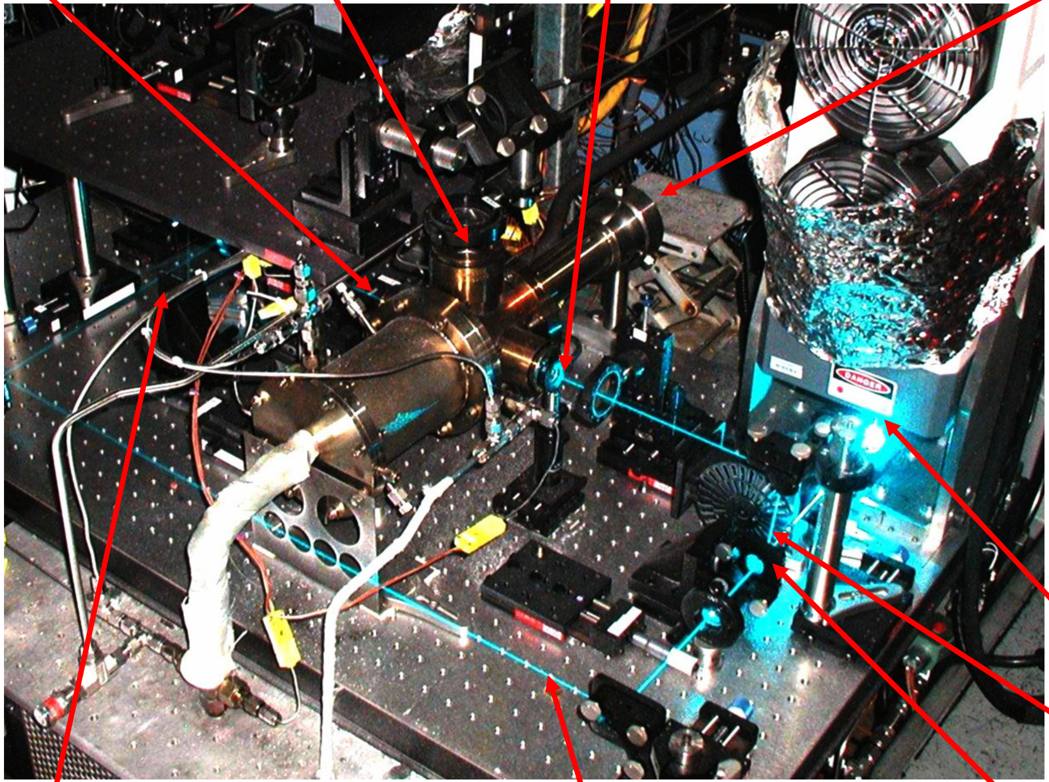


Carbon formation

No Carbon formation

Carbon Formation Monitoring Laser Optics

(adiabatic POx/SR reactor)



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

Carbon Formations Diagnostics

MDL ~ 0.6 mg/min.

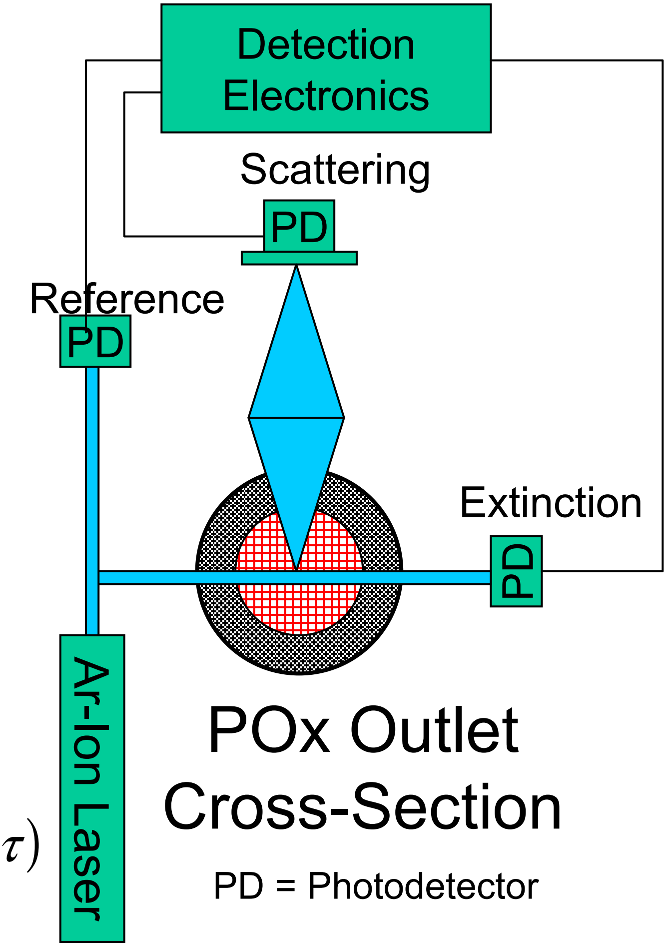
$$\tau = \frac{I_t}{I_0} = \exp(-K_{ext} \cdot L) \quad = \text{Laser Transmission}$$

I_t = Transmitted Intensity
I_o = Incident Intensity
L = Path Length

$$K_{ext} = \frac{1}{L}\ln(\tau)$$

$$f_v = -\frac{\lambda}{6\pi}\left[\mathrm{Im}\left\{\frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2}\right\}\right] \cdot K_{ext} = -\frac{\lambda}{6\pi L}\left[\mathrm{Im}\left\{\frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2}\right\}\right] \cdot \ln(\tau)$$

$\tilde{m}^2 \equiv$ Complex Index of Refraction

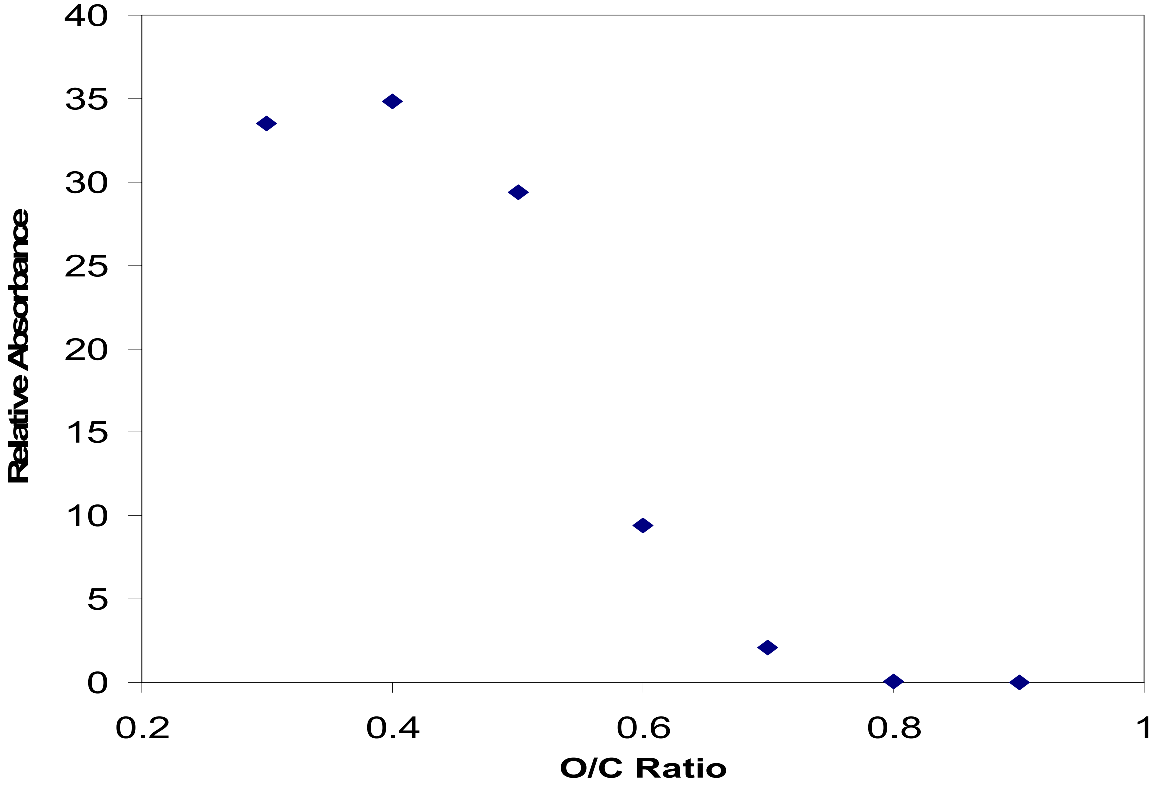


POx Outlet Cross-Section

PD = Photodetector

Technical Results:
Carbon formation measurements

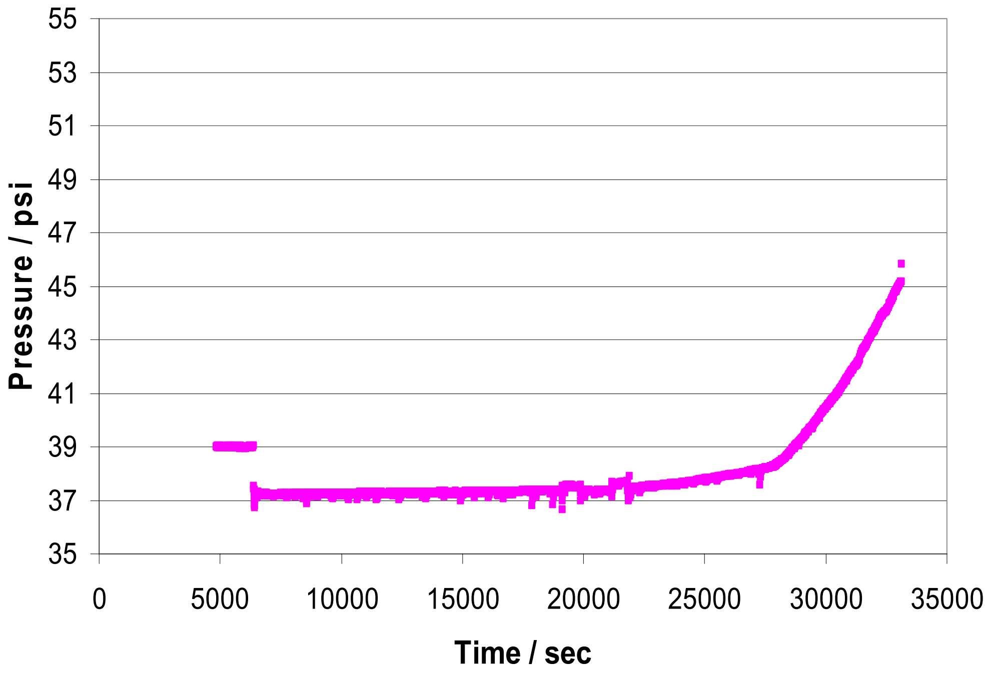
Carbon formation monitoring with laser scattering
Odorless Kerosene; S/C = 1.0



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

Carbon Formation: Pressure Drop

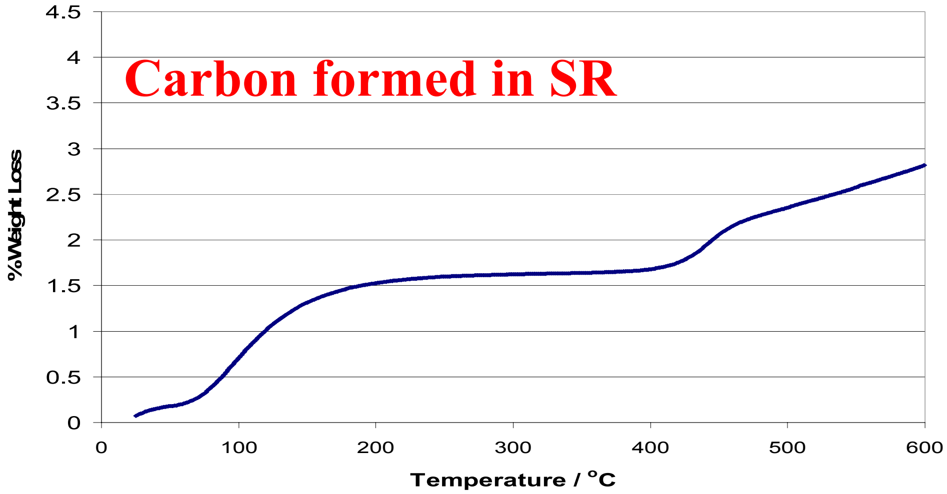


Fuel: Kerosene
S/C = 0
Light-off and operation without water feed to POx

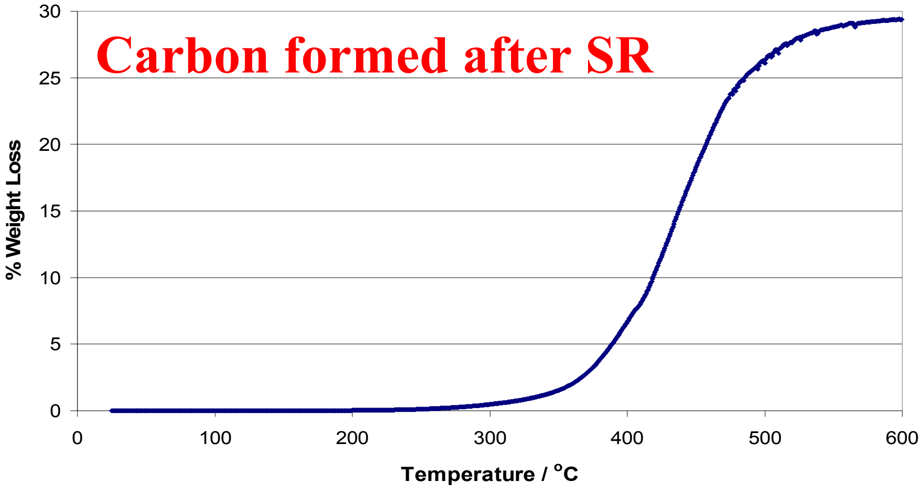
Reactor pressure drop increases over time due to carbon formation

- Carbon formation observed upon vaporization of diesel fuel due to fuel pyrolysis.
- Partial oxidation of diesel fuels without water has been demonstrated, however carbon formation occurs rapidly - in ~7 – 8 hours a prohibitive pressure drop resulted.
- Laser optics being used to observe the onset of carbon formation.

Carbon Analysis



Initial weight loss of 1.7%
Estimate amorphous carbon as:
$C_1H_{0.2}$



30 % by weight Hydrocarbons
Material is solidified
hydrocarbon compounds
No initial weight loss

TGA-thermogravimetric analysis

Catalyst Regeneration:
oxidative removal of carbon

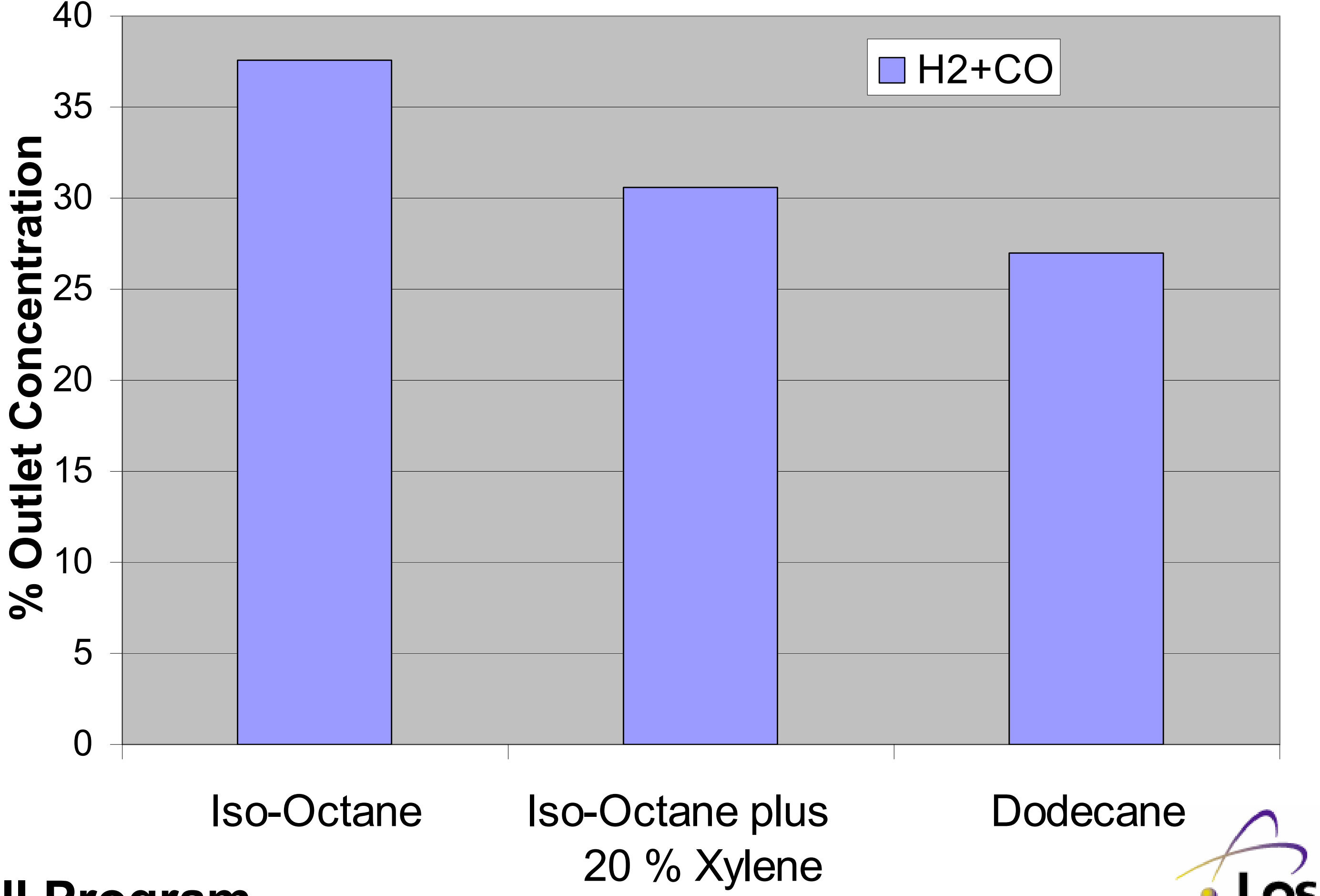
- Post-carbon formation experiments:
  - Regeneration of catalyst/reactor by carbon oxidation
  - Air feed to reactor at 500 – 600 °C
  - Similar to regenerative particulate filters
- Successful about ~5 times in succession
  - Control of the reactor temperature could be difficult.
  - For large carbon build-up:
    - Subsequent oxidation of the carbon yielded high adiabatic temperatures
- Eventually disables light-off of the partial oxidation stage
  - Due to catalyst sintering - loss of catalyst surface area.

- Catalyst regeneration
  - Potential solution to carbon formation
  - Need to control oxidation temperature/rate of oxidation

Partial Oxidation Stage Outlet Concentrations

(for similar conversions)

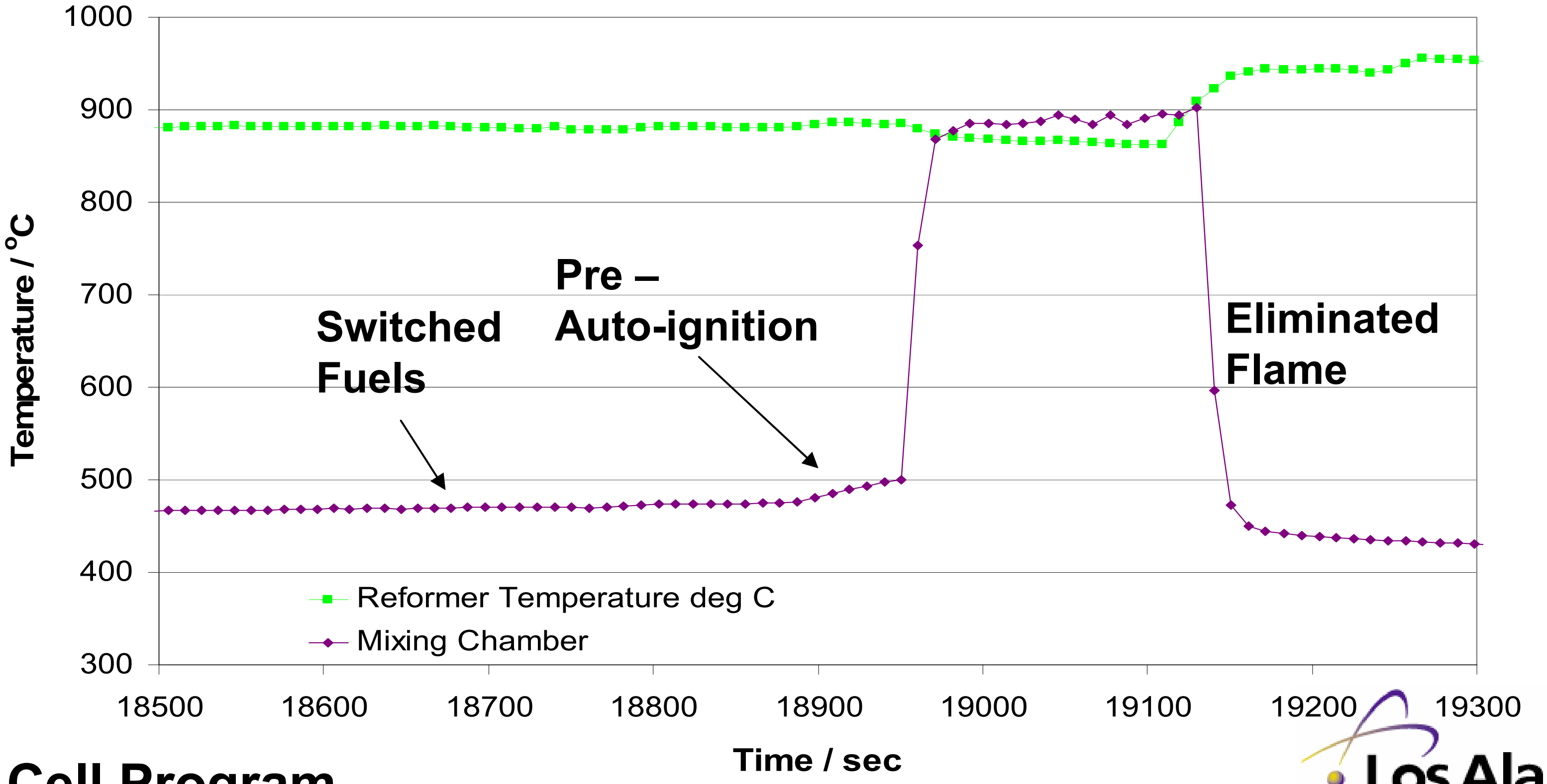
Higher O/C (temperature) required for Dodecane conversion yields diluted H_2/CO fuel mixture



Fuel Effect on Auto – Ignition (Pre-Combustion)

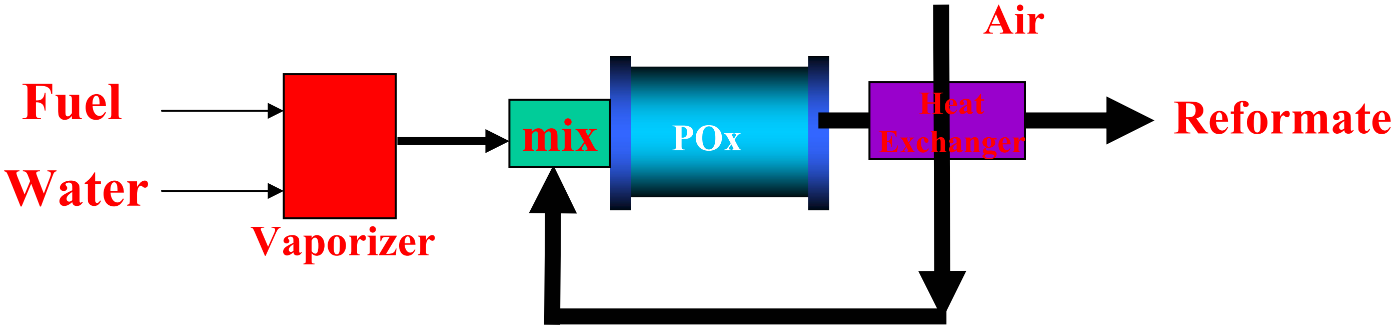
- Diesel fuels show high tendency for pre-combustion
- Show fuel effect on pre-combustion
- Potential design impacts of seasonal diesel fuels

Switched Fuel Operation: De-odorized Kerosene to Normal Kerosene



Fuel Injection to POx/SR

Gasoline System



Fuel

Water

Vaporizer

mix

POx

Air

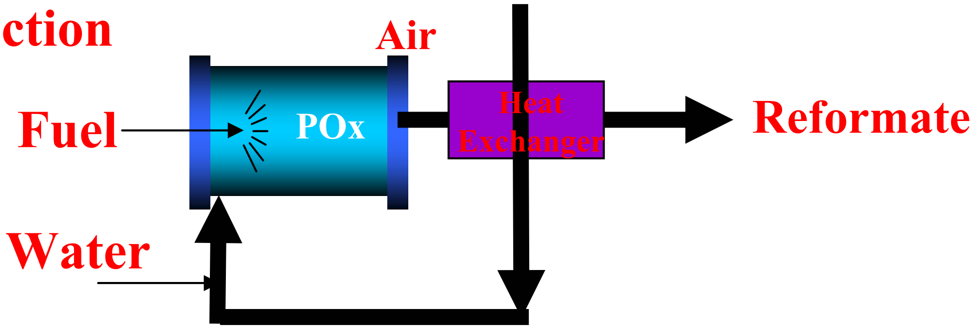
Heat Exchanger

Reformate

Diesel System

Direct fuel injection

Fuel nozzle



Air

Fuel

POx

Heat Exchanger

Reformate

Water

Diesel fuel components tend pyrolyse upon vaporization

Our approach is to examine the direct injection of diesel fuel into reactor.

- Fuel nozzle for direct fuel injection
- High pressure / flash vaporization
- Reduce residence time before fuel is oxidized

Technical Progress Summary/Findings

- Catalytic oxidation / reforming
  - Diesel Fuel Components (Dodecane)
    - Long chained hydrocarbons require higher residence time for conversion
    - aromatics slow and inhibit overall reaction rate
- Pre-combustion
  - Diesel fuels much more likely for pre-combustion
    - Differences in pre-combustion with fuel components (kerosene)
- Carbon Formation
  - Equilibrium carbon formation modeling
    - Equilibrium varies greatly with air/steam content, slightly with pressure and cetane #.
  - Diesel fuels show high tendency for pyrolysis
  - Hysteresis observed after on-set of carbon formation
  - Greater carbon formation with aromatics
- Regeneration of catalysis for limited number of cycles
  - Carbon content / oxygen content control to prevent ‘catastropic’ temperature rise

On-Going / Future Work

- Diesel fuel/air mixing
    - Durability testing of fuel processing components
    - Carbon formation during start-up and reactor transients
- Carbon formation fundamentals:
    - Sulfur effect on carbon formation
    - Delineate carbon formation mechanisms
    - Kinetic expressions for carbon formation
- Catalyst Regeneration
    - Oxidative regeneration of reforming catalysts
- Expand equilibrium modeling to incorporate other carbon species
    - carbon with H/C ratio ~ 0.2
    - PAHC (poly aromatic hydrocarbons)