Diesel Reforming
(For Solid-Oxide Fuel Cell APUs)

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Introduction

Los Alamos has been conducting research under the sponsorship of the DOE/ SECA program – Solid State Energy Conversion Alliance. This work has been to develop technology suitable for the on-board reforming of diesel fuel for SOFC (Solid-Oxide Fuel Cells) for APU (Auxiliary Power Units). This work leverages on going programs sponsored by DOE/OAAT fuel cell programs which support on-board reforming of gasoline for PEM based fuel cell systems. In addition, diesel reforming work at LANL is examining on-board formation of reductants for the reduction of NOx on lean-burn engines (diesel and lean gas). This work examines the reforming of diesel fuel to form reductants suitable to reduce NOx over lean NOx catalysts in oxygen rich environments, such as found in advanced diesel engines.

Research Sponsors – DOE

SECA

(PM: Wayne Surdoval / Norman Holcombe)

Fuel Cells for Transportation Program (OAAT)

(PM: JoAnn Milliken)

Fuels for Fuel Cells Program (OAAT)

(PM: Pete Devlin)

CIDI (OAAT)

(PM: Kathi Epping)

Objectives and Tasks

Objectives:

- Develop technology leading to reforming of diesel fuel for APU applications.
  - Examine diesel fuels and fuel components
  - Understand the parameters that affect fuel processor lifetime and durability
    - Carbon formation and catalyst durability

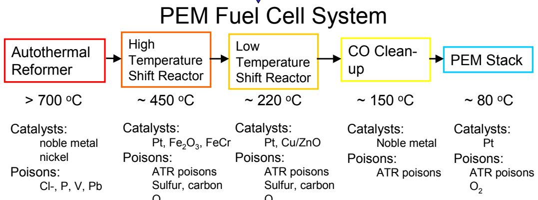
Tasks:

- Carbon Formation Measurement of Diesel Fuel(s)
  - Equilibrium and component modeling
  - Experimental carbon formation measurement
- Fuel Mixing
  - Vaporization / Fuel atomization
  - Direct liquid injection
- 'Waterless' Partial Oxidation of Diesel Fuel
- *In situ* Regeneration of Diesel Partial Oxidation Catalysts

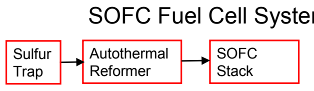
Approach to Diesel Reforming Development

- Develop technology for the reforming of diesel fuels
  - Examine diesel fuel vaporization
- Measure and identify chemical species ('known' poisons)
  - Carbon Formation
  - Hydrocarbons
- Compare fuels and reactor conditions on performance:
  - fuel components
  - Monitor performance of Fuel Processor Catalyst degradation
  - Carbon formation modeling
  - Equilibrium modeling / Thermodynamic property modeling

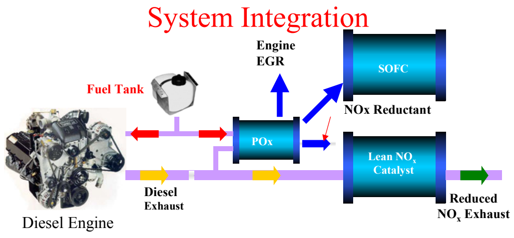
PEM Fuel Cell System



SOFC Fuel Cell System



Diesel Reformer Vehicle System Integration



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

- fuel for SOFC / APU
- reductant for NOx reduction
- fuel for engine allowing high engine EGR
- fast light-off and heating of engine / catalytic convertor

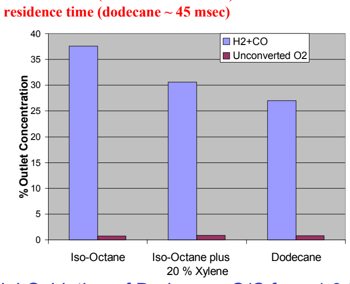
Incorporation into vehicles may require reforming to be suitable for all of the concurrent applications even though the requirements and applications can be significantly different.

Diesel Fuel Partial Oxidation

Partial Oxidation Stage Outlet Concentrations (for similar oxygen conversion)

Higher Temperatures (O/C ratio's) are required for long chained hydrocarbon conversion for similar residence times – leads to H2 dilution

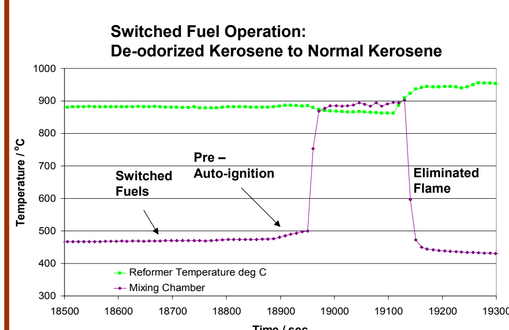
Longer residence times required for similar conversion
(same Temperature / O/C)
residence time (iso-octane ~ 10 msec)
residence time (dodecane ~ 45 msec)



Partial Oxidation of Dodecane O/C from 1.0 to 1.2
Higher O/C, S/C and residence times required than for gasoline fuel components..

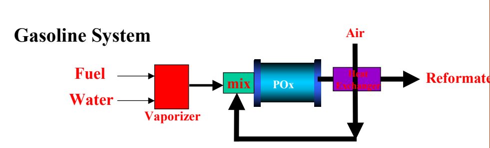
To achieve similar conversion of dodecane and kerosene fuel, compared with gasoline, a partial oxidation reactor requires ~ 4x residence time for a similar O/C

Diesel Fuel Effect on Pre-Combustion



Diesel fuels show high tendency for homogeneous pre-ignition. De-odorized kerosene shows lower tendency than commercial kerosene.

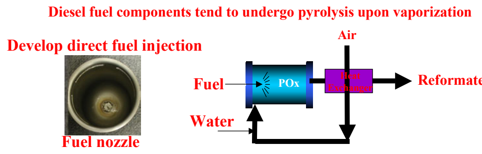
Fuel Injection to POx/SR



Diesel System

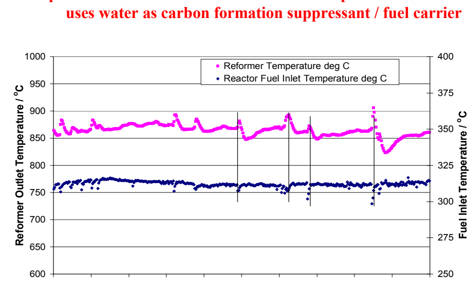
Diesel fuel components tend to undergo pyrolysis upon vaporization

Develop direct fuel injection



Fuel / Water co-vaporization Issues

Co-vaporization of water and fuel in external vaporizer uses water as carbon formation suppressant / fuel carrier



Diesel fuel feed into partial oxidation/steam reforming is more difficult than corresponding gasoline fuel processor. Diesel fuel components show high tendency for pyrolysis upon vaporization forming carbon residues. Using water to suppress carbon formation during vaporization leads to 'distillation effect' not observed with gasolines. Limited water is available in SOFC system, thus it is hard to suppress carbon formation for diesel fuel vaporization.

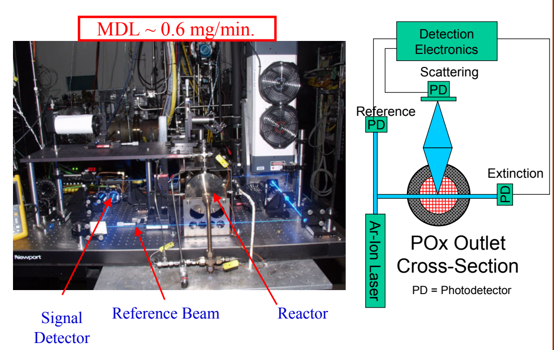
Our near term approach is to examine the direct injection of diesel fuel into reactor.

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

Carbon Formation

- Diesel fuels
  - carbon formation due to pyrolysis upon vaporization
  - pre-ignition of fuel
- 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
  - as low 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)
- Transient operation & fuel processor control

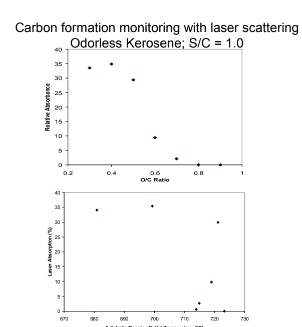
in situ Carbon Formation Laser Optics



Catalytic Partial Oxidation Reactor

Catalysts:
Pt/Al2O3, FC1
Diesel fuels & components:
Dodecane, Hexadecane
Kerosene, deodorized kerosene
Low sulfur Swedish Diesel

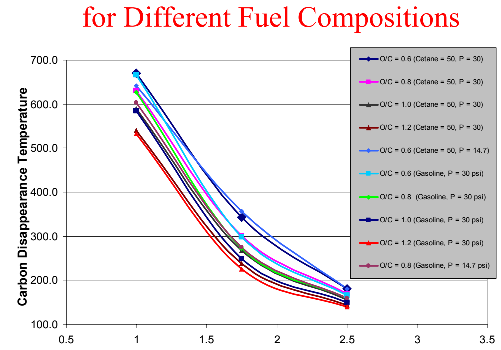
Carbon formation measurements



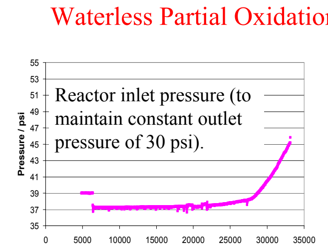
Results

- 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

Modeling of Carbon Formation Disappearance for Different Fuel Compositions



Waterless Partial Oxidation of Kerosene

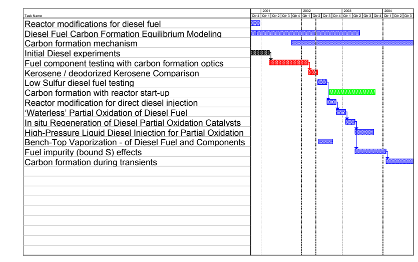


Fuel: Kerosene
S/C = 0
Light-off and operation without water feed to POx

Reactor pressure drop increases over time due to carbon formation

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

Diesel reforming for SOFC Timeline



Diesel fuel reforming work initiated in FY2001

Diesel Reforming for NOx Reduction

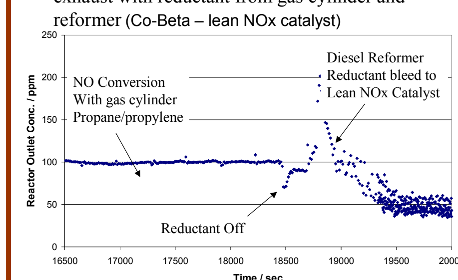
Introduction to NOx Reduction

- Direct decomposition
  - $2NO \dashrightarrow N_2 + O_2$
- SCR (Selective Catalytic Reduction):
  - $3NO + 2NH_3 \dashrightarrow 5/2\ N_2 + 3H_2O$
  - $4NO + 4\ NH_3 + O_2 \dashrightarrow 4N_2 + 6H_2O$
  - NO reduction competes with NH_3 oxidation to NO in presence of O_2
- NOx Reduction in oxygen atmosphere
  - $NO + HC + O_2 \dashrightarrow N_2 + CO_2 + H_2O$
  - Challenge lies in reducing NOx in oxidizing atmosphere
- Avoid putting NH_3, HCN, NO_2, SO_3, N_2O, RNO_2, RCHO, RCOOH, RCN, …. out the tailpipe

Approach

- Form NOx reductants by oxidation of diesel fuel
- POx - Rich fuel burn:
  - (O/C < 1)
    - $C_nH_{(2n+2)} + {}_{(m/2)}O_2 \dashrightarrow mCO + C_{(n-m)}H_{2(n-m)} + H_2$
  - POx effluent includes:
    - H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8
- Propene known to catalyze NOx reduction reaction
  - reductant for plasma, zeolites (similar to NH_3 SCR)
- H2 / CO known to reduce NOx adsorbents

NOx reduction in simulated diesel engine exhaust with reductant from gas cylinder and reformer (Co-Beta – lean NOx catalyst)



Experimental Fuel Penalty over Co-Beta Catalyst
For various assumpt.: Diesel fuel penalty is ~ 3 - 6 %
NOx reduction using Cobalt-Ferrite catalysts did not show activity with diesel reformate

Interactions

Presentations:
AIChE (multiple spring & fall presentations)
ACS
SECA review meeting (Nov. & June)
Delphi Automotive - presentation & discussions about reactor operation and testing

Technical Progress Summary/Findings

- Catalytic oxidation / reforming
  - Diesel Fuel Components (Dodecane)
    - Long chained hydrocarbons require higher residence time for conversion - ~ 4x
    - aromatics slow and inhibit overall reaction rate
- Pre-combustion
  - Diesel fuels much more likely for pre-combustion
    - Kerosene has higher pre-combustion tendencies than de-odorized kerosene
- Carbon Formation
  - Hysteresis observed after on-set of carbon formation
  - Greater carbon formation with aromatics
  - Diesel fuel shows tendency for pyrolysis

- Diesel fuel reforming shows potential to help catalyze NOx reduction in lean atmosphere
- Cobalt-beta-zeolite and Cobalt-Ferrite lean-NOx catalysts
  - drastically different results with reductant from reformer