



NATIONAL ENERGY TECHNOLOGY LABORATORY



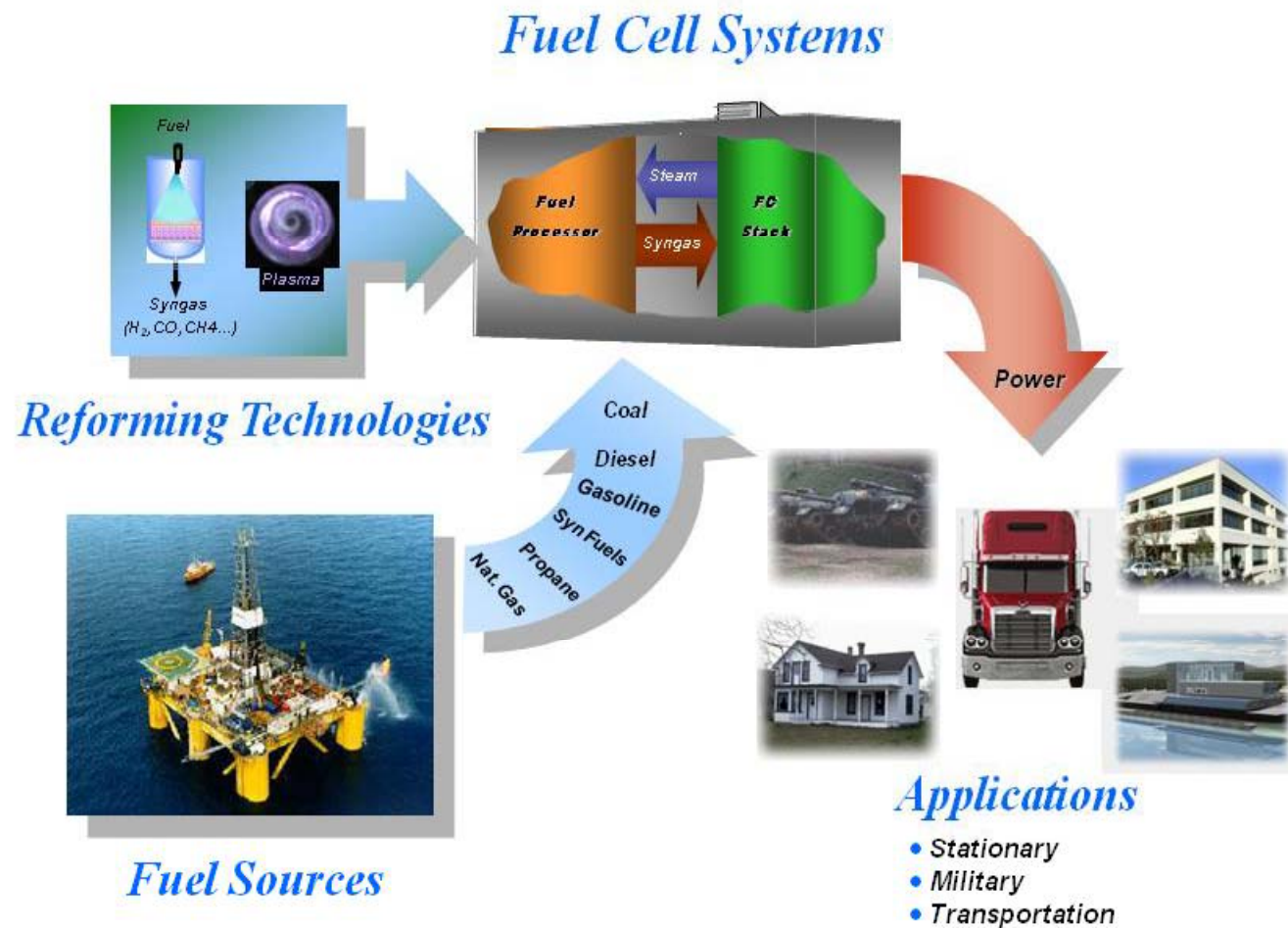
Fuel Processing R&D at NETL

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**11th Annual SECA Workshop, Pittsburgh, PA
July 27-29, 2010**

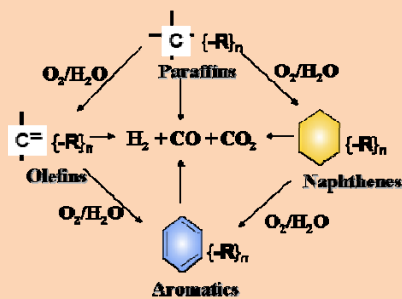


Fuel Reforming for Solid Oxide Fuel Cells

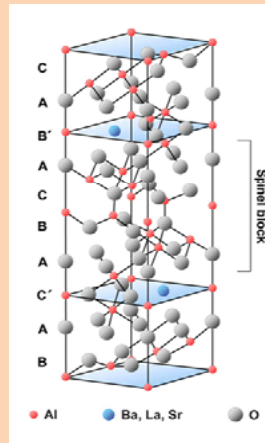


Primary Goal

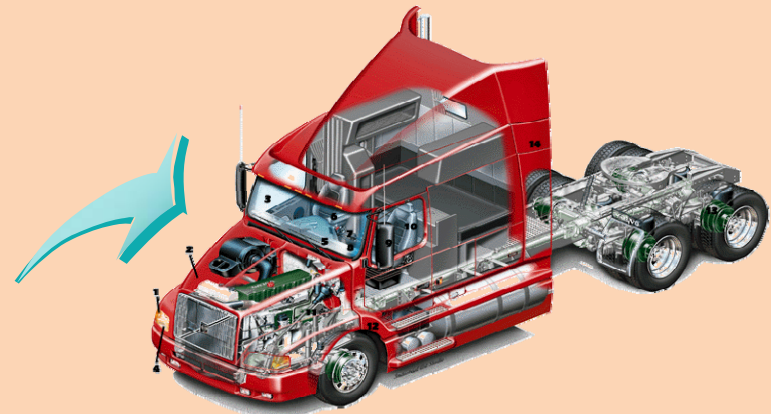
Identify, evaluate and/or develop viable hydrocarbon fuel processing technologies for high temperature solid oxide fuel cells being supported in the NETL SECA program through fundamental understanding, research, and technology demonstration.



Fuel

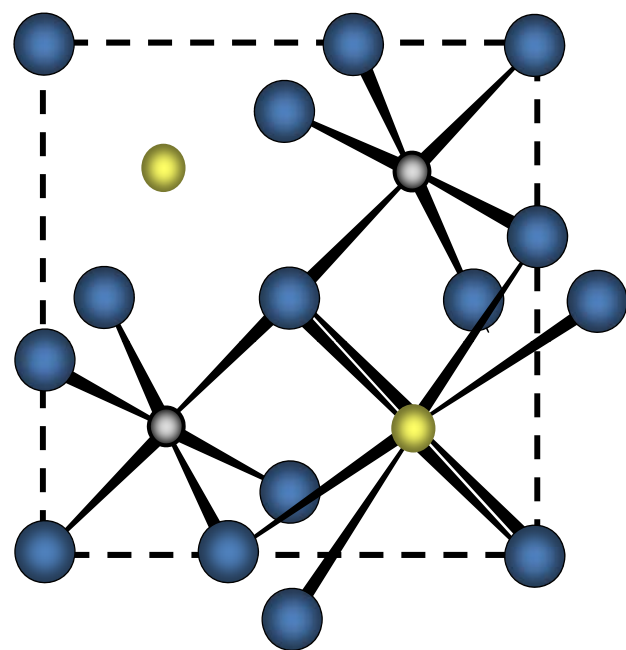


Technology



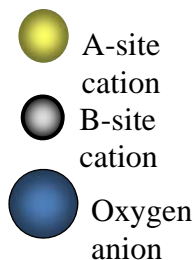
End Use

Oxide-based Catalyst Systems (ABO)



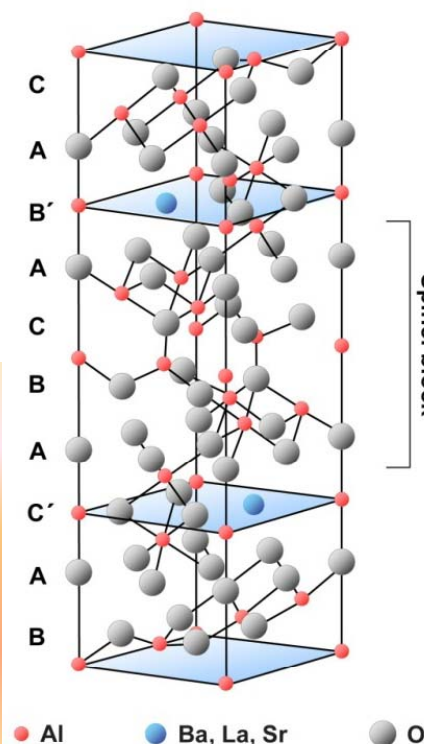
Doping the lattice of certain oxide-based compounds with catalytic metals results in...

A structured catalytic surface with nano-sized metallic crystallites that serves as a template to control metallic crystallite size and dispersion.



Pyrochlores ($A_2B_2O_7$) are viable reforming catalysts because they exhibit:

- High chemical and thermal stability
- Mechanical strength to accommodate substitutions
- Active metal can be substituted into B-site to improve catalytic activity
- Substitution with lower valence elements in A-site and B-site can create oxygen vacancies, which may increase lattice oxygen-ion mobility to reduce carbon formation.



Hexaaluminates ($AA1_2O_{19}$):

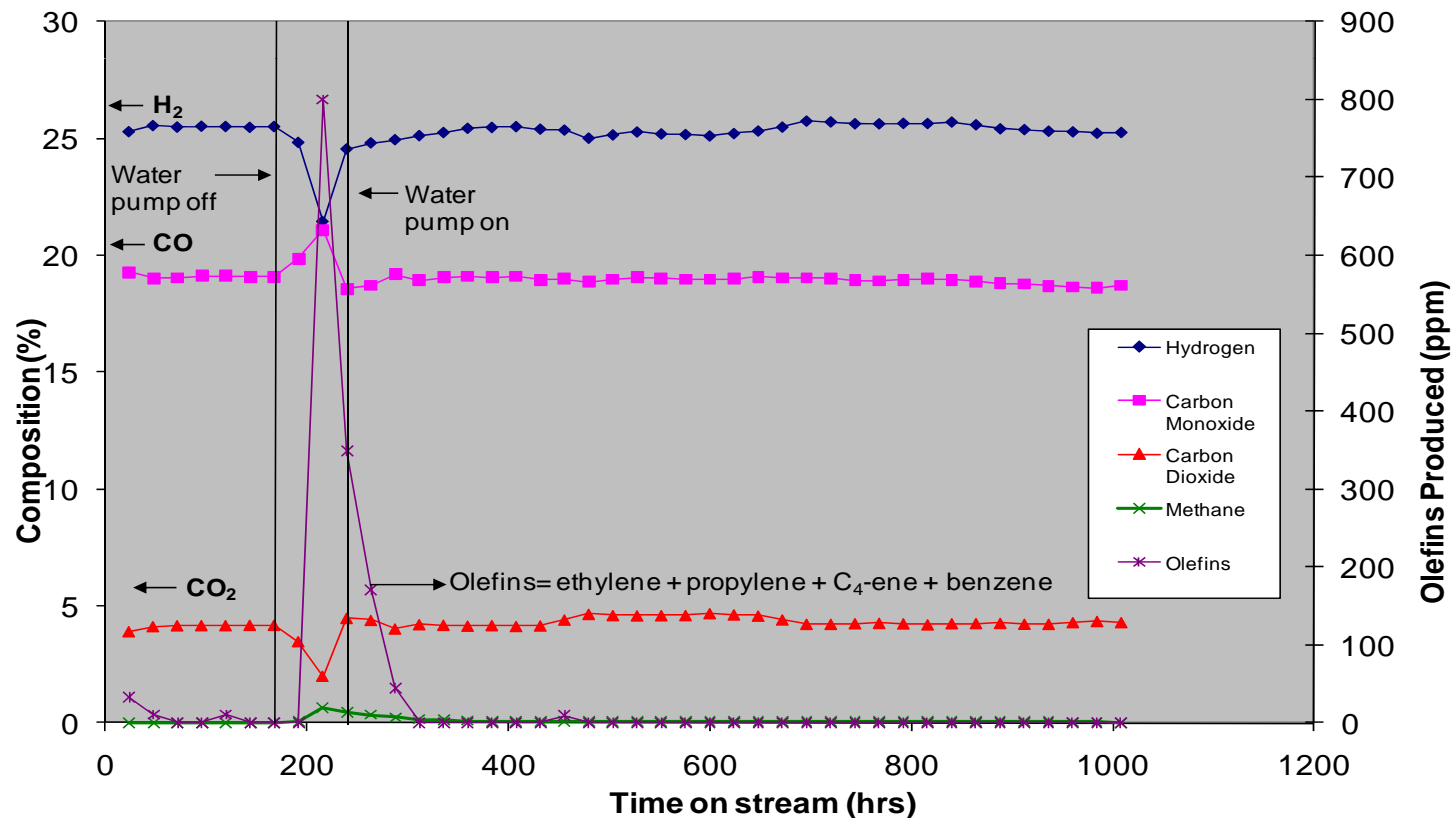
- High chemical and thermal stability
- Mechanical strength to accommodate substitutions
- Active metal can be substituted into Al-site

Diesel Fuel Reforming using Pyrochlore Catalyst

Long-Term Testing

➤ 1000 hour Endurance Test

- ✓ Fully reformed local pump diesel
- ✓ Equilibrium syngas yields achieved
- ✓ Survived multiple system upsets
- ✓ $O/C=1$, $H_2O/C=0.5$

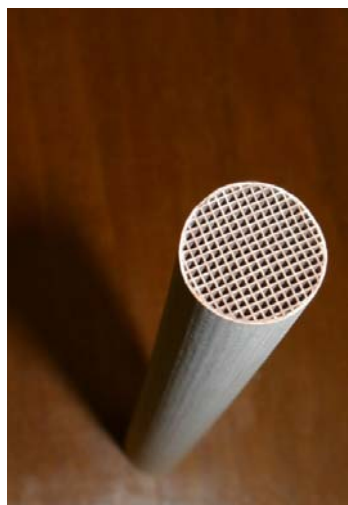


Diesel Fuel Reforming using Pyrochlore Catalyst

Collaboration with Industrial Partners



**NETL's Pyrochlore
Catalyst in Powder Form**



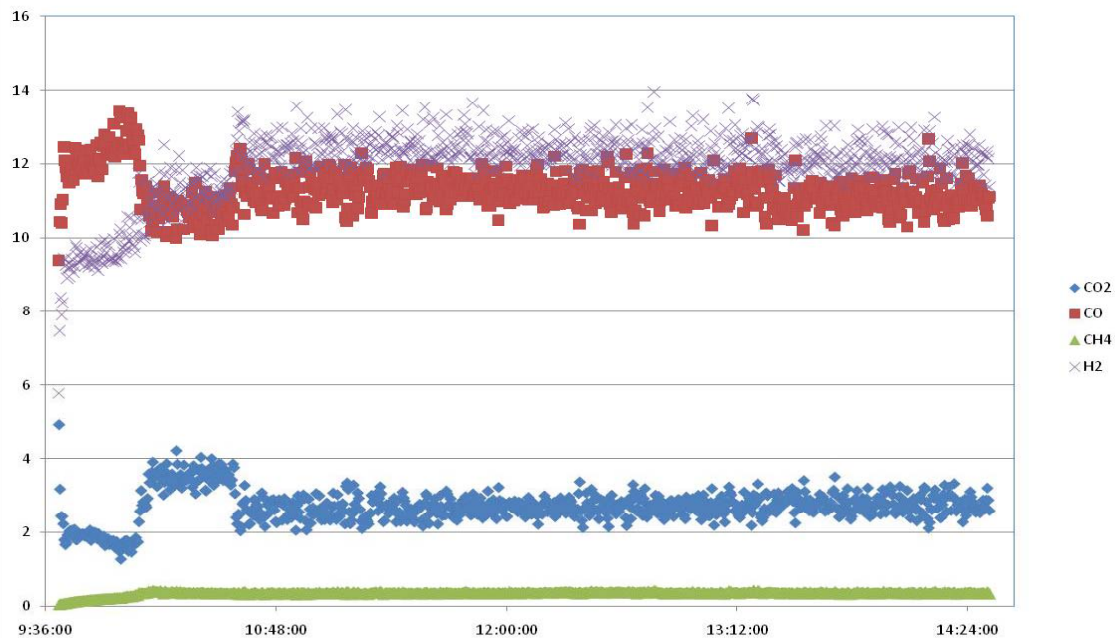
**Monolith Coated
by NexTech**



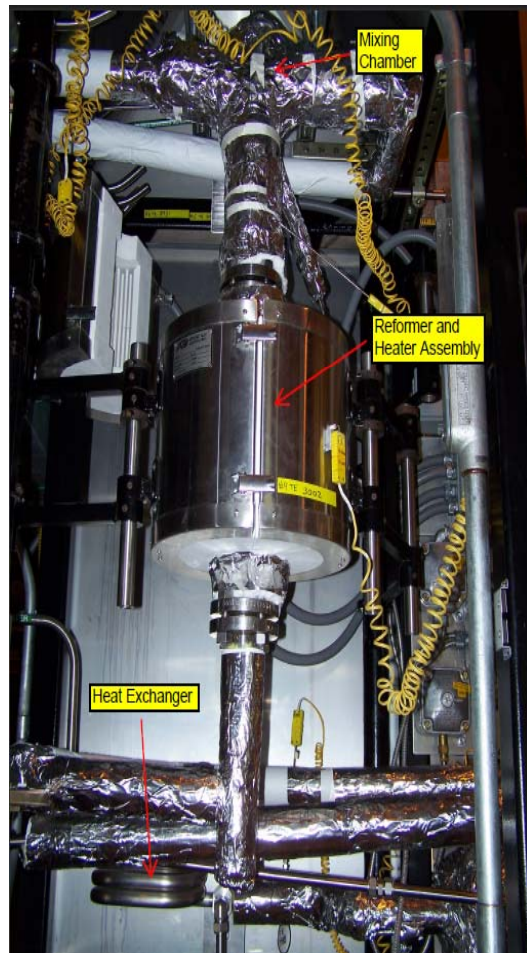
**Microlith®
Technology by PCI**

- **Fabrication of Catalyst into a Commercially Viable Structure**
- **Powder Catalyst Validation:**
 - Activity tests; TPO (carbon formation)
 - Bulk characterization – ICP, XRD
 - Surface characterization – XPS, TPR, H₂-chemisorption
- **Preliminary Tests on Coated Monolith**

Monolith C10003-12.3(900 C, 0.065 cc/min diesel, 0.036 cc/min H₂O,
O/C = 1.0, S/C = 0.5, air 215 sccm, N₂ 355 sccm)

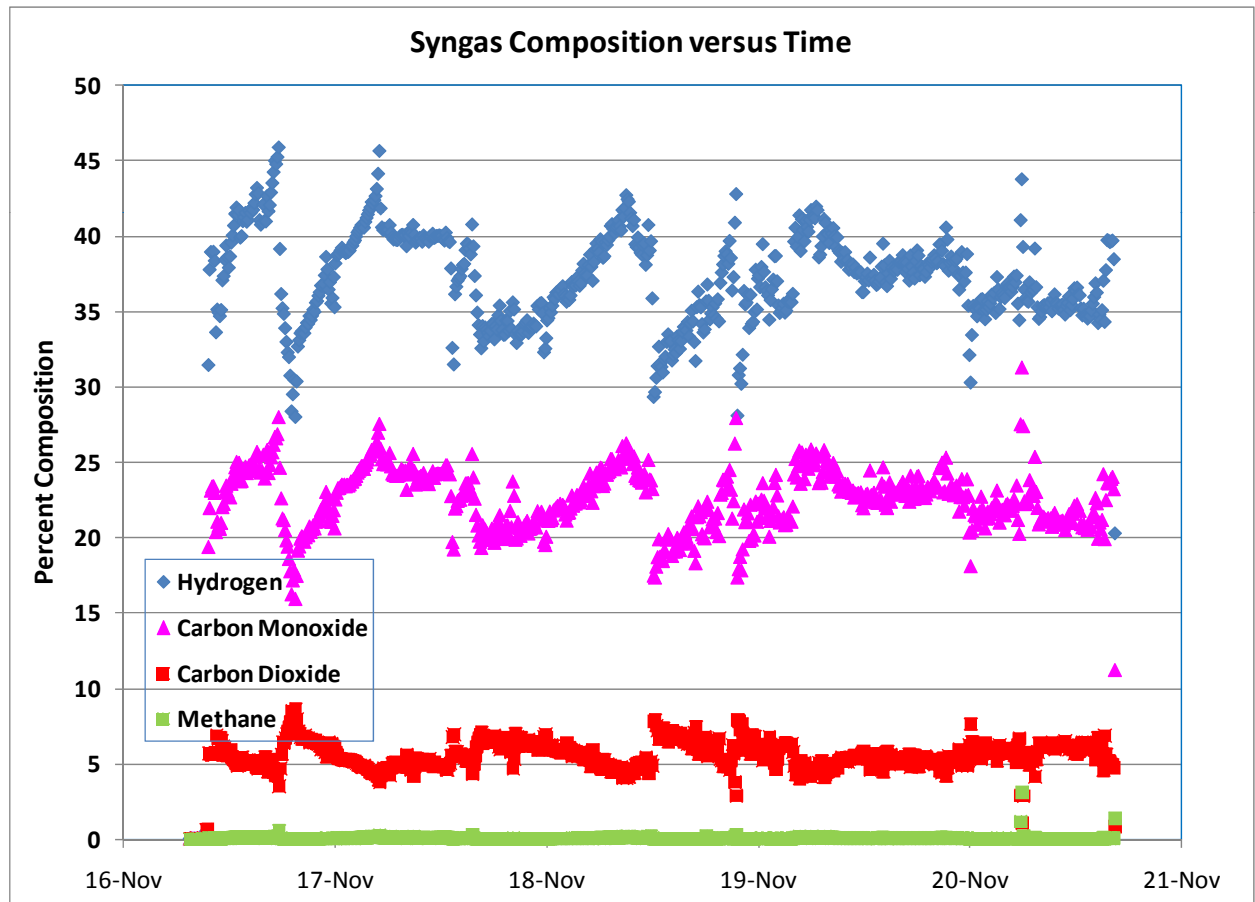


Successful Operation of a Solid Oxide Fuel Cell Fueled with Syngas from Biodiesel Reforming

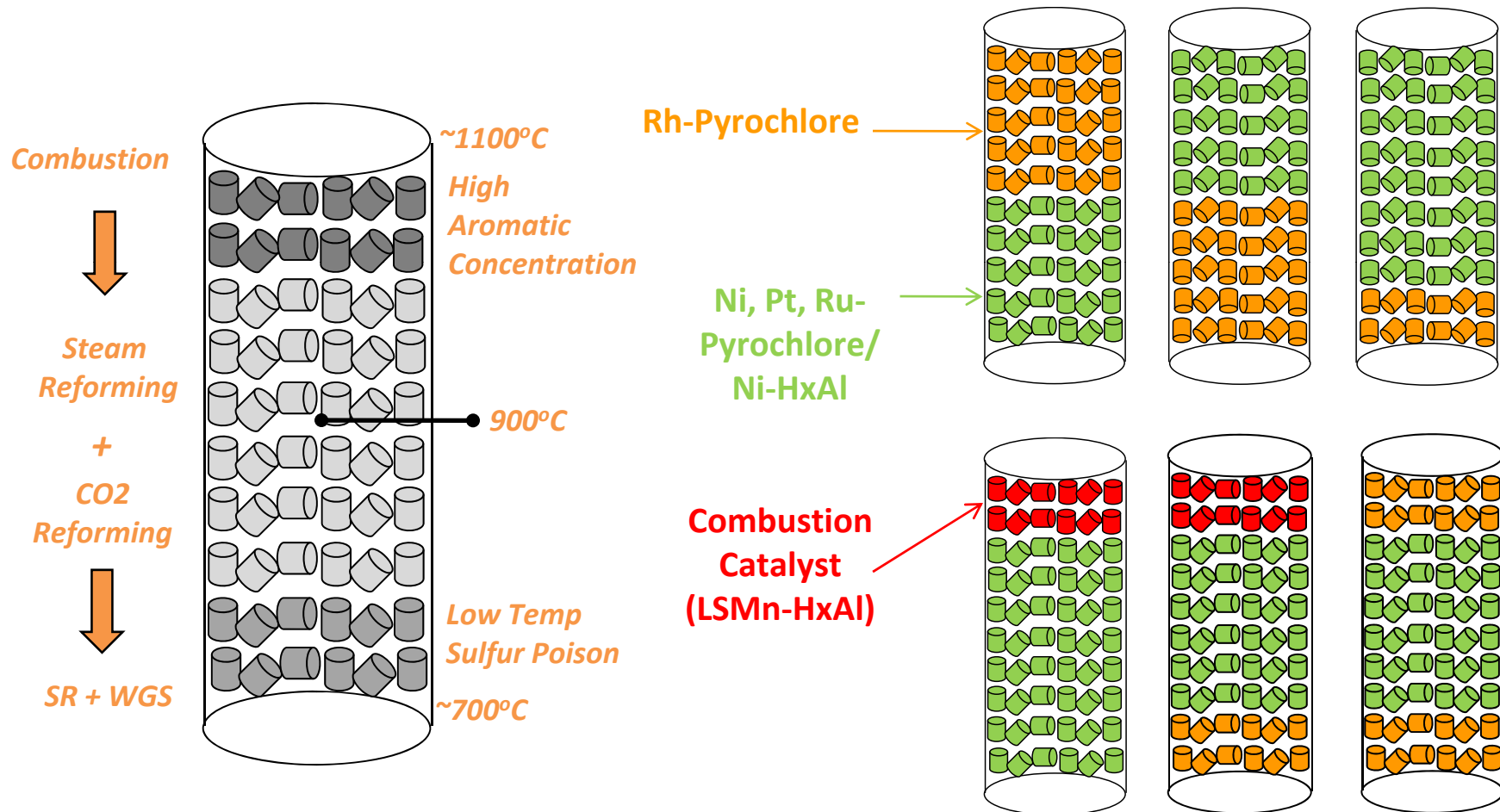


Biodiesel Reformer

- Biodiesel was reformed for 100 hrs on a pyrochlore catalyst supported on a monolith



Graded Bed Approach



Alternative Reforming Concepts

Radio-Frequency Enhanced Reaction Concept

Energy bands of atoms or molecules absorb the RF energy



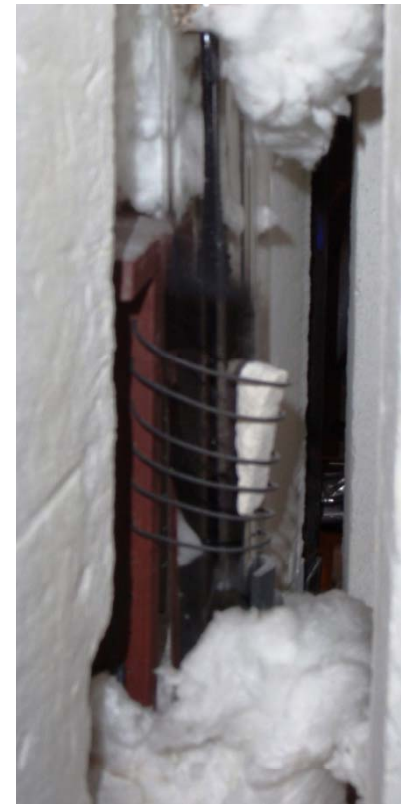
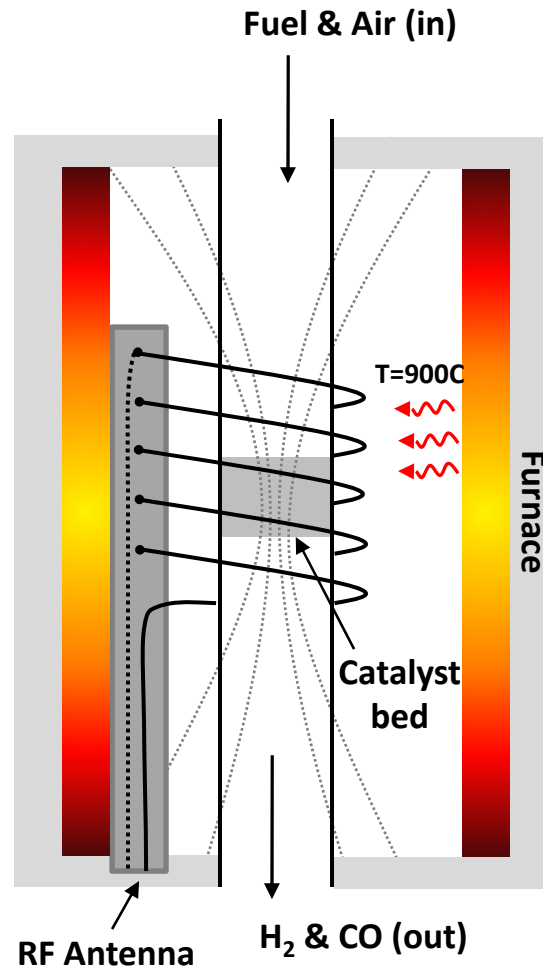
Localized heating of the material at the rxn site with higher dielectric loss index and excitation of valence electrons



Lowers the activation energy required for desired chemical reactions



Functions as an enhanced catalyst

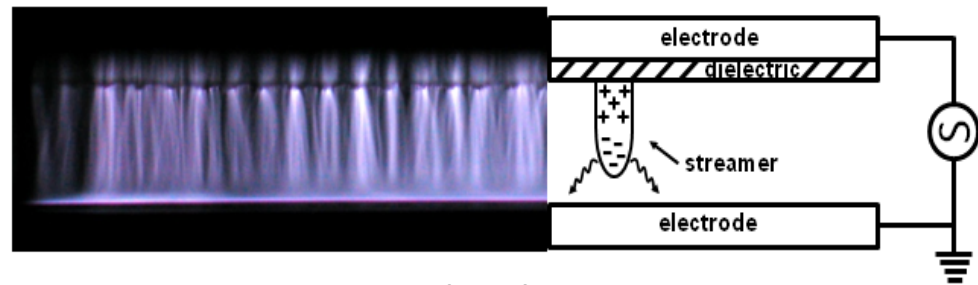


Alternative Reforming Concepts

Plasma: Thermal vs. Non-thermal

Non-thermal plasma

- Very high electron temperature but low gas temperature ($T_g=300\text{K}$)
- High chemical selectivity possible because high electron energy stimulates the creation of active chemical agents (radicals, excited species)
- Low power density



Dielectric Barrier Discharge (DBD) plasma – has lower power density compared to thermal plasma, but higher energy electrons, which induce formation of active chemical agents

Thermal Plasma – conventional technology

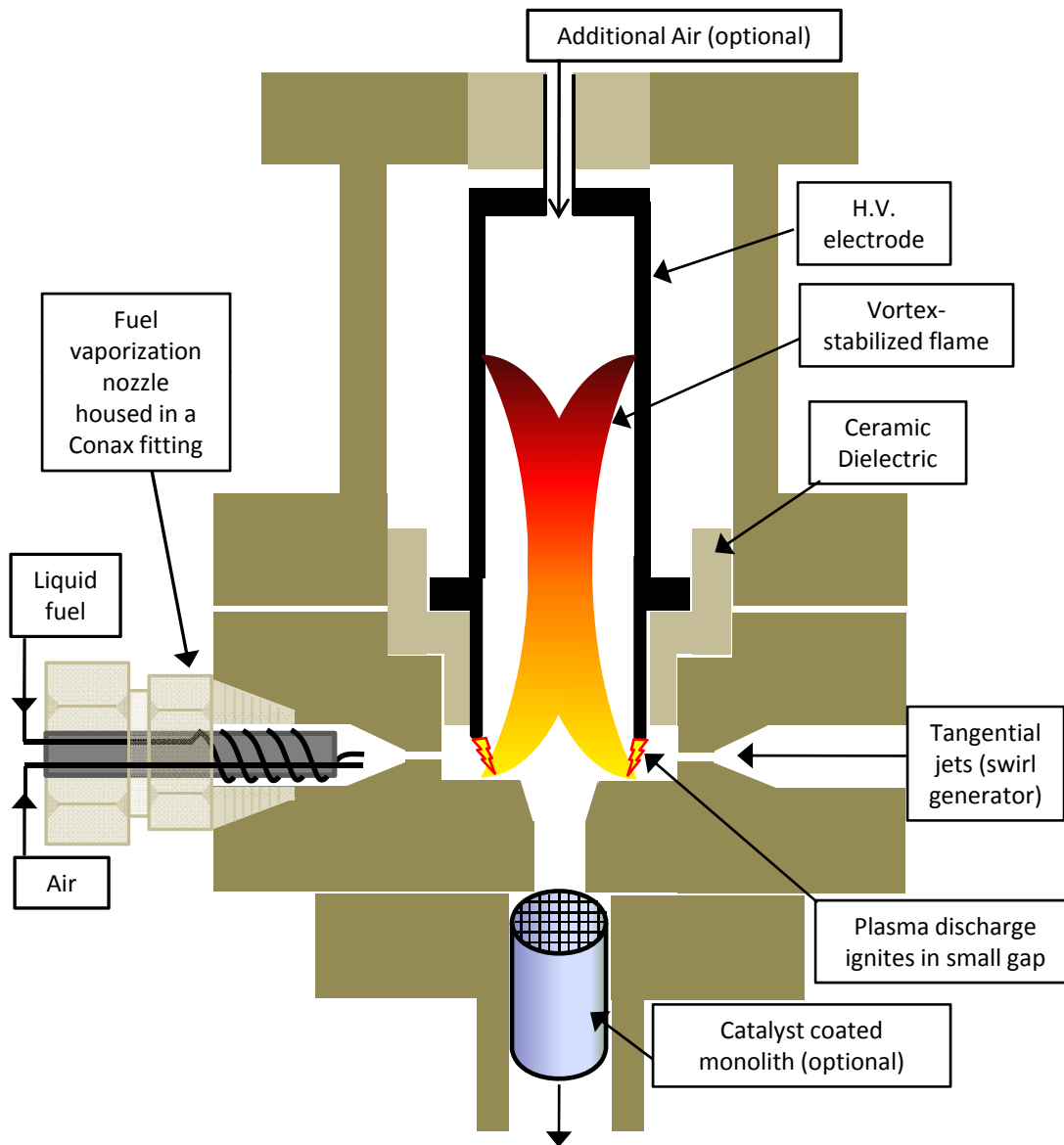
- All species are in thermal equilibrium – high gas temperature ($T_g=10,000\text{K}$)
- Very high plasma power and density
- Little chemical selectivity can be obtained, energy is only spent for gas heating (including inert nitrogen)



Thermal plasma torches – used in cutting applications, gas temperatures $> 10,000\text{K}$

Alternative Reforming Concepts

Gliding Arc Plasma Reformer



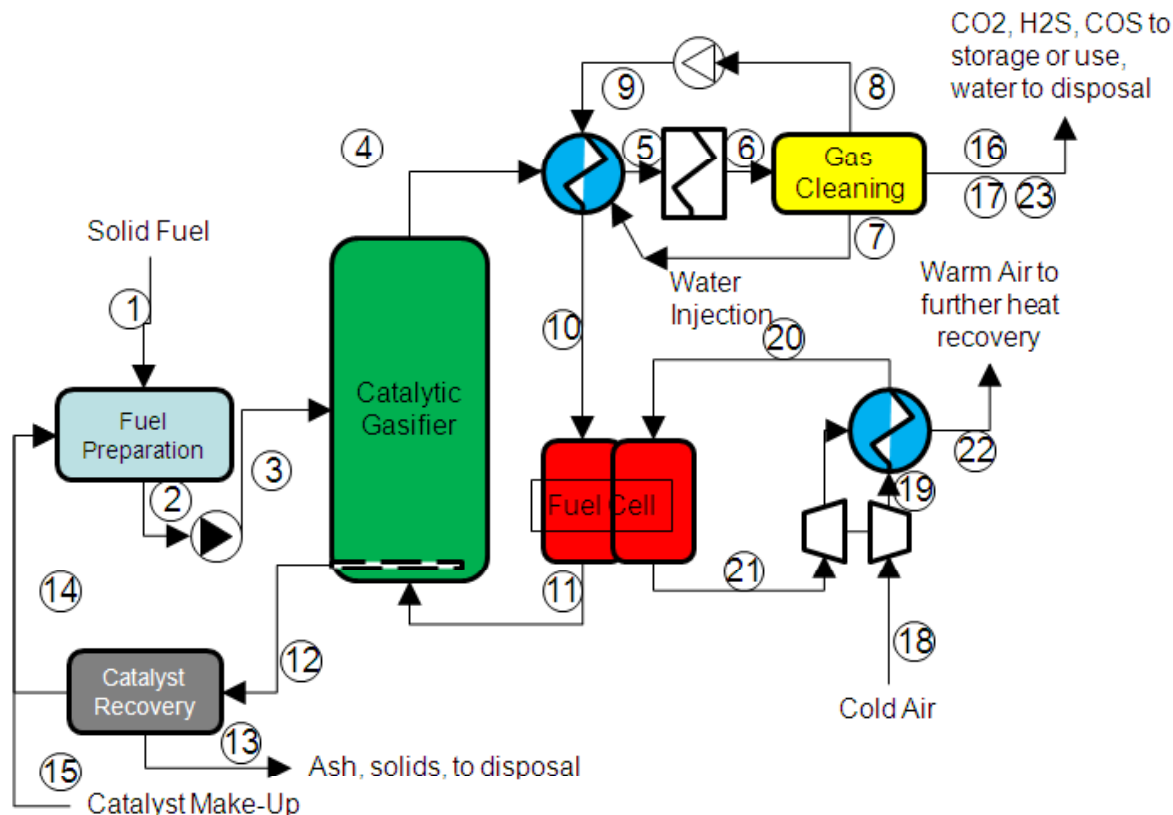
- DC Gliding Arc plasma stabilized in reverse vortex (tornado) flow – to convert diesel/JP-8 into syngas
- Utilizes new prototype fuel vaporization nozzle
 - Provides accurate control of reactant temperatures
 - Avoids fuel cracking prior to exposure to plasma
- Reactor has capability to attach a catalytic monolith to exhaust to investigate synergistic combination of plasma + catalytic reforming



Gliding arc
Plasma discharge
(top view)

Integrating SOFCs with Catalytic Coal Gasifier

Anode Tail Gas Recycling¹



- **Catalytic gasifier creates a syngas stream with ~20% methane**
- **Methane reduces the amount of waste heat generated in the SOFC**
- **Catalyst: Potassium carbonate or mixed alkali carbonates**
- **CO₂ removed from N₂-free syngas stream at elevated pressure**
- **No oxygen separation from air**
- **System Efficiency ~62%^{1,2}**
- **CAPEX: <\$2000 / kW (2007 basis)^{1,2}**

Areas for Future Research include:

- **Process studies to optimize overall system efficiency**
- **Catalyst regeneration to minimize catalyst replacement costs**
- **Use of potassium hydroxide for combined methanation and carbon dioxide capture, with regeneration of KOH**

¹Thijssen, J., "IGFC With Catalytic Hydro-Gasification Using Anode Exhaust," Presentation at NETL, July 13, 2009.

²Includes cost of 20% catalyst loss and replacement

Conclusions

- SOFC-based APUs for commercial diesel trucks is an excellent market entry technology
- Reforming catalyst with long-term stability and performance is critical for successful demonstration of transportation application
- Pyrochlore catalyst has high thermal stability and other enhanced properties that make it effective reforming catalyst
- Pyrochlore catalyst on oxygen-conducting support successfully reformed pump diesel for 1000-hr
- Optimized pyrochlore catalyst applied to commercially representative structured supports
- Preliminary performance of catalyst monolith demonstrated on pump diesel and biodiesel fuels under oxidative steam reforming
- Preliminary experiments have shown some evidence of reduced carbon formation, however a detailed analysis is currently underway to repeat these findings and understand the mechanisms of RF-assisted reforming at various frequencies and power levels.
- Non-thermal plasma reforming technology has shown promising results for reforming of complex fuels such as diesel
- Evaluating molten salt coal gasifier to generate high methane content syngas at lower pressures and temperatures