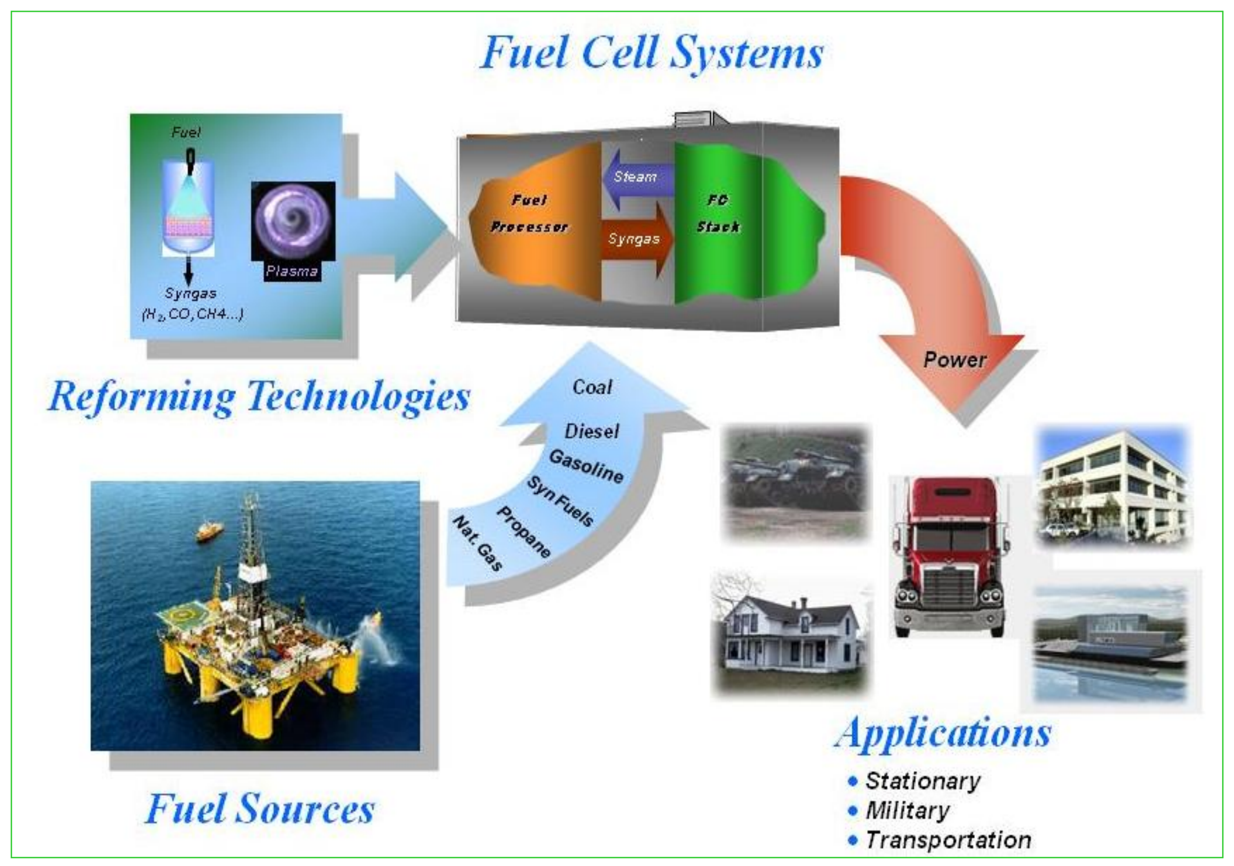
Fuel Processing R&D at NETL

NETL-RUA Regional University Alliance

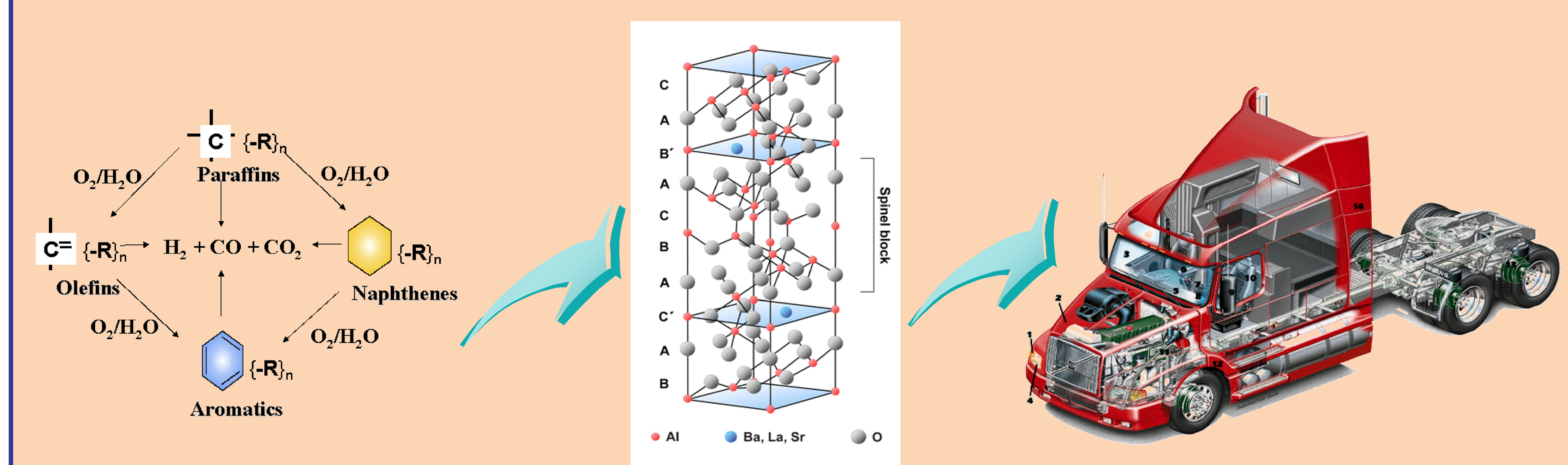
U.S. DEPARTMENT OF ENERGY

Fuel Reforming for Solid Oxide Fuel Cells



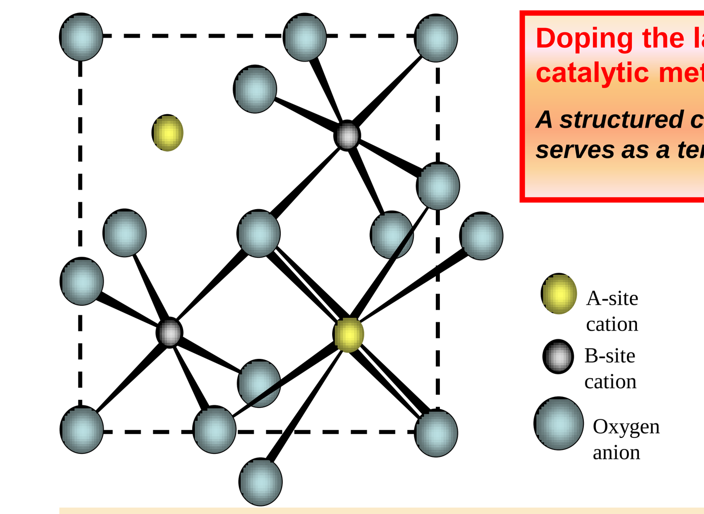
Primary Goal

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)

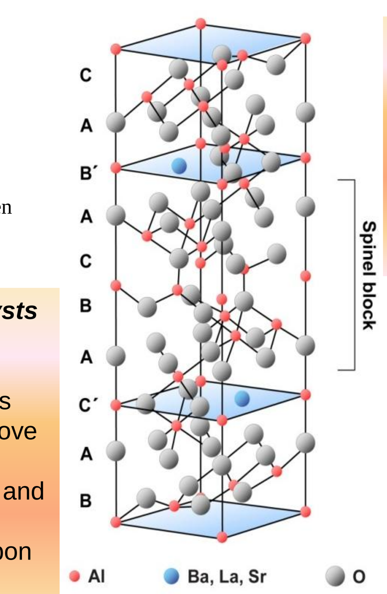


Doping the lattice of certain oxide-based compounds with catalytic metals results in…

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.

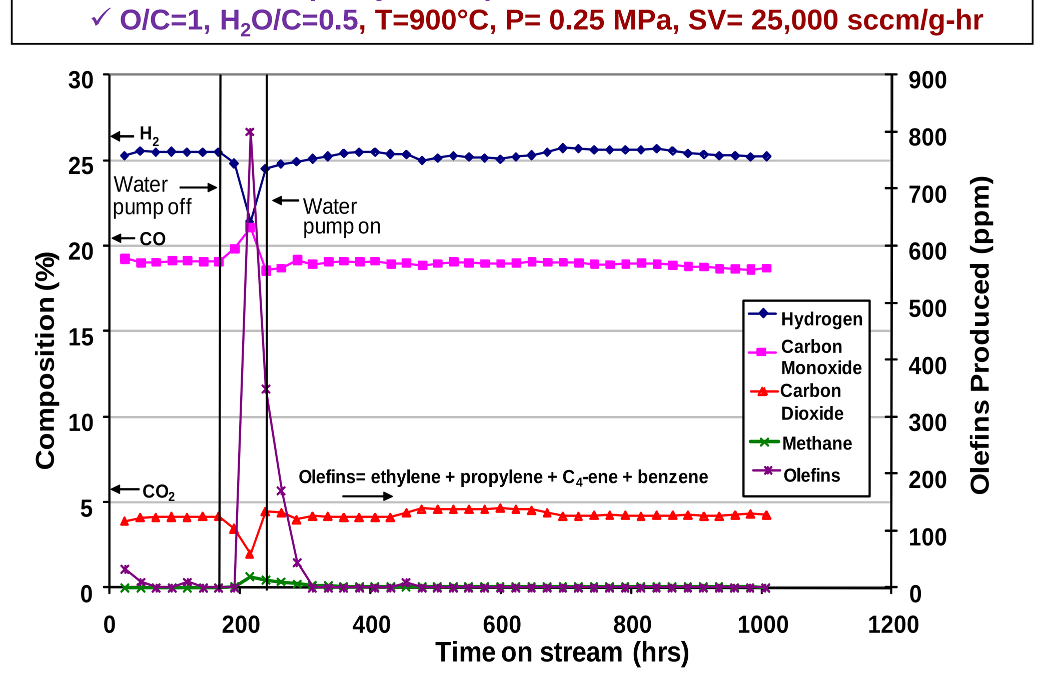


Hexaaluminates ($AAl_{12}O_{19}$):

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

1000-hr Demonstration of Pyrochlore Catalyst for Oxidative Steam Reforming of Pump Diesel

- ✓ Fully reformed local pump diesel
- ✓ Equilibrium syngas yields achieved
- ✓ Survived multiple system upsets
- ✓ O/C=1, H_2O/C=0.5, T=900°C, P= 0.25 MPa, SV= 25,000 sccm/g-hr

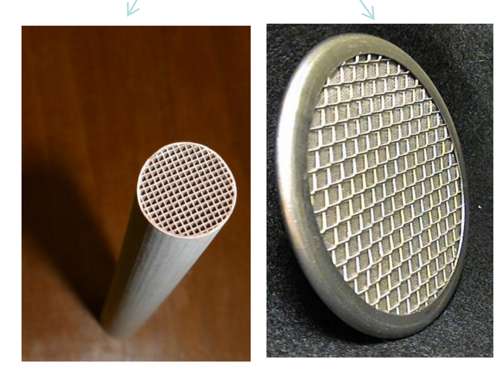


Diesel Fuel Reforming using Pyrochlore Catalyst

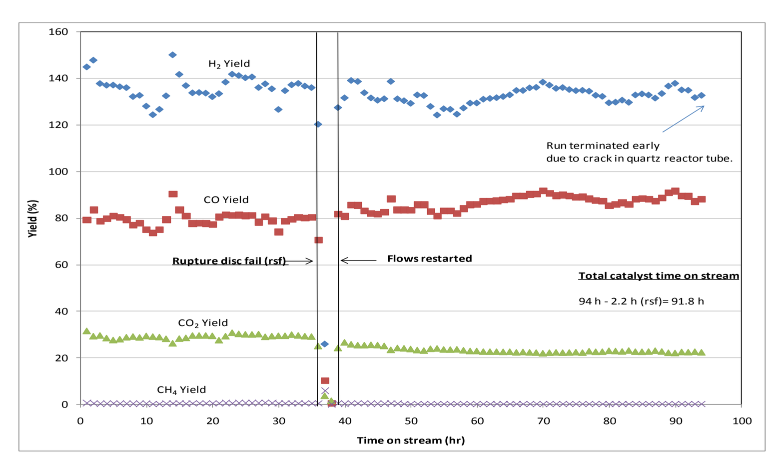
Collaboration with Industrial Partner

NETL's Pyrochlore Catalyst in Powder Form

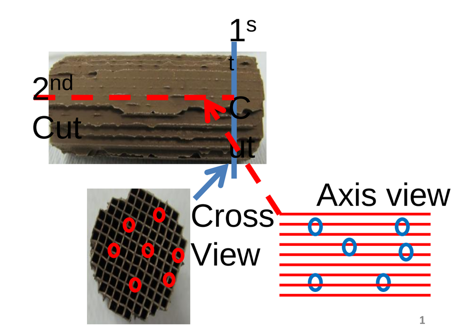
- Fabrication of Catalyst into a Commercially Viable Structure
- Powder Catalyst Validation:
  - Activity tests; TPO (carbon formation)
  - Bulk characterization – ICP, XRD
  - Surface characterization – XPS, TPR, H2-chemisorption
- Preliminary Tests on Coated Monolith



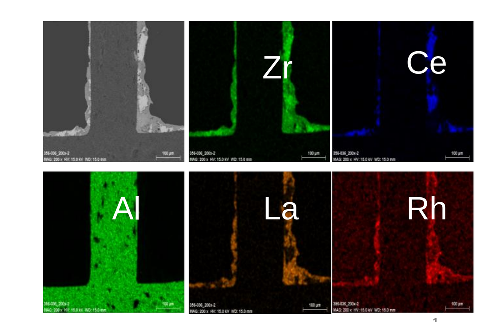
Monolith Coated by NexTech | *Microlith® Technology by PCI*



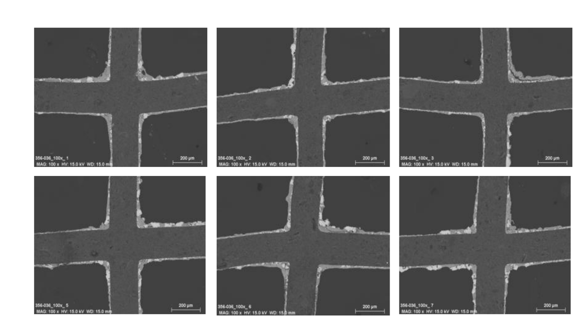
Monolith Characterization

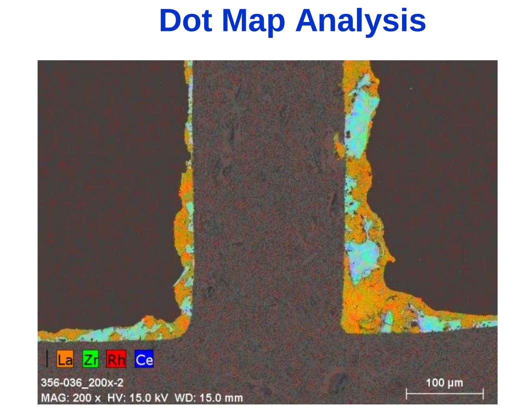


Monolith Cutting



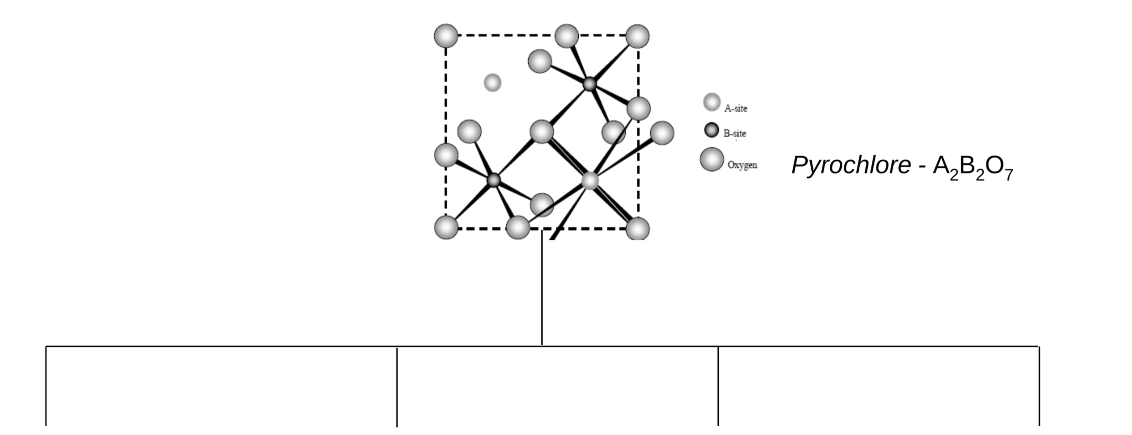
Dot Map Analysis





Corner coating thickness: 53 ± 13 microns

Pyrochlore Synthesis Methods



Pechini (NETL)

- Good for small scale (lab)
- Results in well-mixed, uniform catalyst
- Most active material (1000 hr catalyst)
- Economic scale-up?

Hydrothermal

- Can produce larger batch size.
- Not able to get Rh into pyrochlore structure.
- Activity not as good as Pechini.

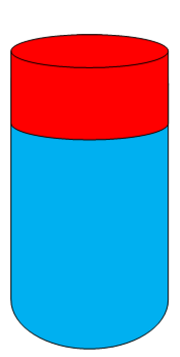
Solid State Mixing

- Economical for large batches.
- Requires high temperatures and long firing times to form pyrochlore.
- Catalyst uniformity a potential issue.

Combustion Method

- Potential for continuous high throughput.
- Material produced should be similar to Pechini.
- Under development

Graded-Bed Approach



$$CH_4 + O_2 \rightarrow xCO_2 + 2xH_2O + (1-x)CH_4; \Delta H < 0$$

Total Oxidation

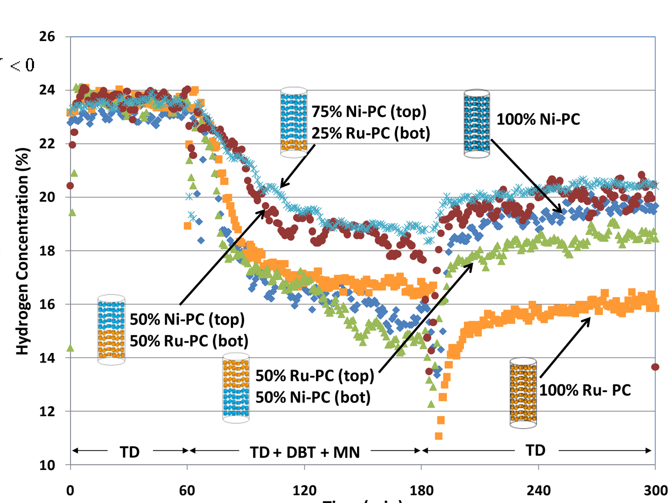
$$CH_4 + H_2O \rightarrow CO + 3H_2; \Delta H > 0$$

Steam Reforming

$$CH_4 + CO_2 \rightarrow CO + H_2; \Delta H > 0$$

CO₂ Reforming

M.W. Smith, D. Shekhawat, Catalytic partial oxidation, Fuel Cells: Technologies for Fuel Processing, Chapter 5, p. 73-128, Elsevier, Amsterdam, June 2011.



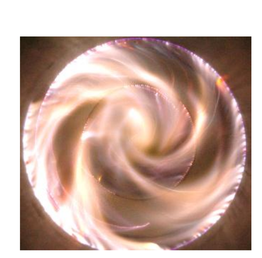
- **Partial oxidation of *n*-tetradecane (TD) in presence of sulfur and aromatics**
  - 2hrs pure TD
  - 2hrs TD + 50ppmw S as DBT + 5,10%wt. 1-MN
  - 1hr pure TD
- **Total bed carbon (TBC) formation study**
  - Temperature Programmed Oxidation (TPO)
  - 200 C to 900 C at ramp of 1 C/min

Top (%) / Bottom (%)	Total Carbon (g)	Predicted* Carbon (g)
100% Ni3-PC	1.12	--
100% Ru1-PC	0.59	--
50% Ru1-PC/ 50% Ni3-PC	0.75	0.86
50% Ni3-PC/ 50% Ru1-PC	0.82	0.86
75% Ni3-PC/ 25% Ru1-PC	0.72	0.99

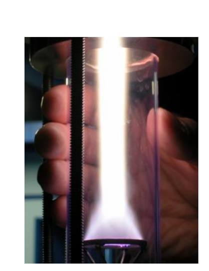
*Calculated from Total Carbon measured for 100%Ni-PC and Ru-PC

Low-temperature plasma capability at NETL

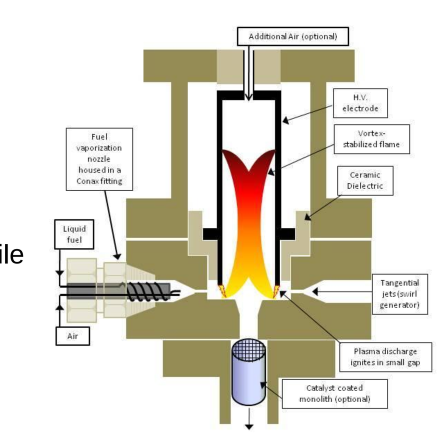
- Low-temperature plasmas create high energy free electrons that can excite internal energy states of reactants (vibrational, electronic) and stimulate non-thermodynamically favorable reactions at low gas temperatures
- Plasmas also create aggressive chemical radicals & charged species that can accelerate the kinetics of a chemical reaction while reducing the activation energy cost for the reaction to proceed
- NETL capabilities: 15-30kV AC/DC (0-400W) plasmas, two continuous flow plasma reactors, Spectroscopic tools to study of populations of excited particles



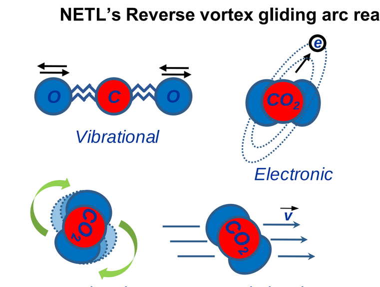
Gliding arc plasma (top view)



Reverse vortex stabilized gliding arc plasma



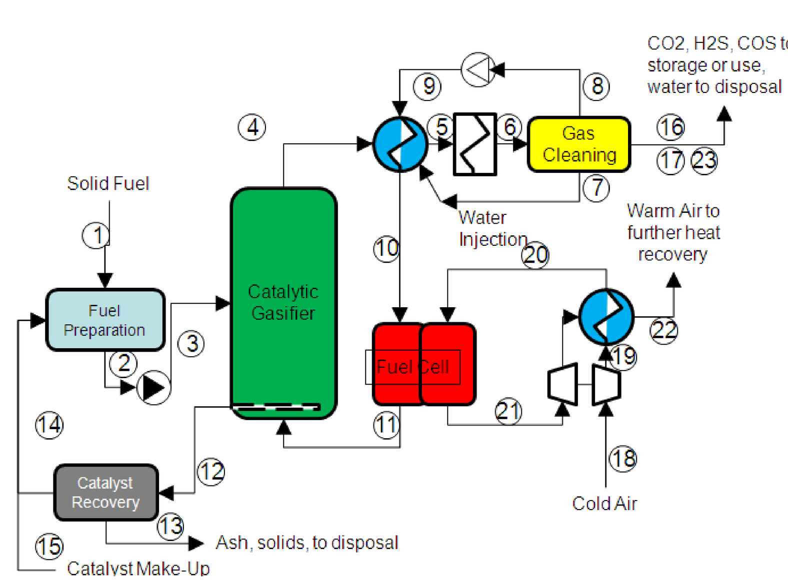
NETL's Reverse vortex gliding arc reactor



Excited molecular states stimulated by plasma

Integrating SOFCs with Catalytic Coal Gasifier

Anode Tail Gas Recycling[1]



- 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
- CO_2 removed from N_2-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

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

NETL | Carnegie Mellon | PENNSTATE 1855 | University of Pittsburgh | VirginiaTech | WestVirginiaUniversity | URS

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Albany, OR • Fairbanks, AK • Morgantown, WV • Pittsburgh, PA • Sugar Land, TX

12th Annual SECA Workshop, Pittsburgh, PA
July 26-28, 2011

Dushyant Shekhawat, Dave Berry, Nick Siefert, Dan Haynes, Mark Smith, Mike Gallagher, Don Floyd, Mike Bergen, and James Spivey (LSU)