Fuel Processing R&D at NETL

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Fuel Reforming for Solid Oxide Fuel Cells

Fuel Sources

Reforming Technologies

Fuel Cell Systems

Applications
- Stationary
- Military
- Transportation
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.
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
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, H₂O/C=0.5

![Graph showing composition over time](image)

- **Composition (%)**
  - Hydrogen
  - Carbon Monoxide
  - Carbon Dioxide
  - Methane
  - Olefins (ethylene + propylene + C₄-ene + benzene)

- **Produced (ppm)**
  - Water pump off
  - Water pump on

- **Time on stream (hrs)**
  - 0 to 1200 hours

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Olefins: ethylene + propylene + C₄-ene + benzene
Diesel Fuel Reforming using Pyrochlore Catalyst
Collaboration with Industrial Partners

- 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

NETL’s Pyrochlore Catalyst in Powder Form

Monolith Coated by NexTech

Microlith® Technology by PCI

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

![Biodiesel Reformer]
Graded Bed Approach

Combustion
Steam Reforming + CO2 Reforming
SR + WGS

~1100°C
High Aromatic Concentration

~900°C

~700°C
Low Temp Sulfur Poison

Rh-Pyrochlore
Ni, Pt, Ru-Pyrochlore/Ni-HxAl

Combustion Catalyst (LSMn-HxAl)
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

Fuel & Air (in)

T=900°C

Catalyst bed

RF Antenna

H₂ & CO (out)

Furnace
Alternative Reforming Concepts

Plasma: Thermal vs. Non-thermal

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

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

**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 torches** – used in cutting applications, gas temperatures > 10,000K
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
Integrating SOFCs with Catalytic Coal Gasifier

Anode Tail Gas Recycling

- 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%¹²
- CAPEX: <$2000 / kW (2007 basis)¹²

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

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.