# SECA Fuel Processing

## Fossil Energy Fuel Cell Program

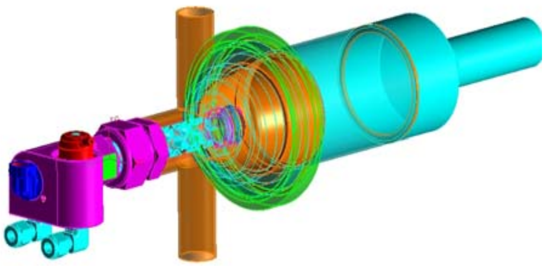

Wayne Surdoval, SECA Coordinator


June 3, 2003

**National Energy Technology Laboratory**
**Office of Fossil Energy**

# REFORMING

- **Focus**
  - Heavy hydrocarbons
  - Minimal use of water
  - Simplified system
  - Reduced cost
  - Sulfur tolerance with conversion to hydrogen sulfide
- **Challenges**
  - Carbon deposition
  - Sulfur poisoning
  - Thermal gradients
  - Vaporization
- **Approaches**
  - Metal oxide catalysts
  - Nobal metal cPox or ATR
  - Decorated nickel surface
  - Complete system interactions



**Tubular cPox Reformer**

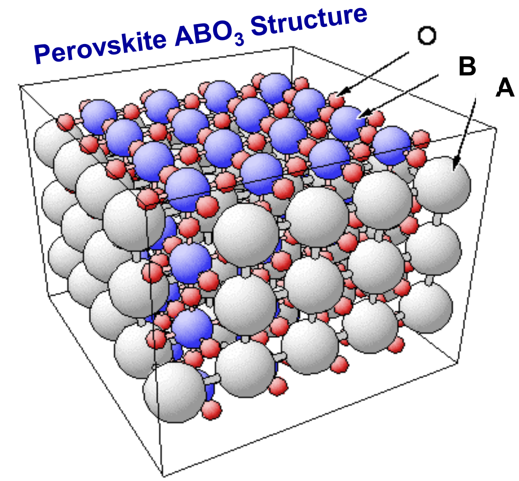
# NETL Fuel Processing Budget Summary

| Proj. # | PROJECT | PERSONNEL | KEY TASKS | COST EST. |
|---|---|---|---|---|
| 1 | Diesel Reforming Kinetic Fundamentals | *Shekhawat<br>Gardner<br>Berry | 1.) Bring Reforming Lab Online 2.) Conduct Diesel Compound Interaction Study 3.) Level 1 Kinetic Determination with Benchmark Diesel | $350 |
| 2 | Fuel Desulfurization of Diesel & NG | *Gardner<br>Shekhawat<br>Berry | 1.) Evaluate Process & Cat.Parameters on SCOHS NG Desulf. 2.) Evaluate Potential of High T. Desulfurization Sorbents | $275 |
| 3 | Fundamental Reforming Studies - Role of Catalytic O2 Supports on Fuel Reforming and Alternate Reforming Catalysts | *Berry<br>Gardner<br>Shekhawat | 1.) Identify Techniques for Determining Role of O2 Supports 2.) Conduct Experimental Study 3.) Evaluate Alternate Reforming Catalysts | $350 |
| 4 | SECA Fuel Processor Component Test Stands | *Lyons<br>Berry | 1.) Develop Design Spec for 2-Article Test Bay for 10-kW Reformers 2.) Conduct Facility Shakedown | $395 |
| 5 | Fuel Processing Data Base - Ref. & Desulf. | *Berry<br>*Shekhawat<br>Gardner | 1.) Develop Fuel Reforming Database & Report 2.) Develop Fuel Desulfurization Database and Report | $75 |
| 6 | Evaluation of Fuel Processor APU's | *Rogers<br>*Berry<br>James | 1.) Develop Model for APU Reformer & Conduct Concept Evaluations 2.) Conduct System Analysis Tradeoff Studies | $175 |
| | | | **TOTAL FUEL PROCESSING BUDGET** | $1,620 |

# Technology Advantages & Critical Issues in Diesel Reforming for SOFC Applications

- **The diesel advantages**
  - Highest volumetric and gravimetric density for hydrogen content.
  - Available distribution network
  - Preferred fuel for heavy vehicle, remote site power generation, and military applications.
- **Key challenges for diesel reforming catalyst development**
  - Carbonaceous Deposit Formation.
    - Coke formation – High molecular weight and aromatics result in more C-deposit.
  - Catalyst Durability
    - Sulfur tolerance – S poisoning to metal deactivates the catalyst.
    - Metal stability – Metal vaporization and agglomeration causes the loss of active site.
    - Support stability – Extreme operating temperature and chemical environment destruct catalyst surface area and morphology.
  - Reforming Efficiency To Hydrogen And Carbon Monoxide.
    - Reaction temperature – High fuel conversion requires higher reforming temperature.
    - Steam usage – Onboard water storage needs to be reduced or removed.

# Argonne's approaches to address diesel reforming catalyst issues




- **New ATR Catalyst Development**
  - Develop new parasite type catalyst with improved thermal and chemical stability at high operating temperature.
  - Selectively substitute transition metal to A & B site to enhance reforming activity.
  - Characterize catalyst to establish structure-property relationship.
- **Catalyst Performance Evaluation**
  - Investigate catalyst activity and reforming efficiency under different operating conditions ($O_2$/C, $H_2O$/C, space velocity, etc) with diesel surrogate fuels.
  - Study catalyst deactivation mechanism under elevate temperature & in presence of sulfur.
- **Investigation of Alternative Catalytic Operating Mode**
  - Reduce or remove steam content from ATR to POX.
  - Reform fuel with recycled SOFC emission stream.
  - Use alternative catalyst substrate to improve ATR thermal management.

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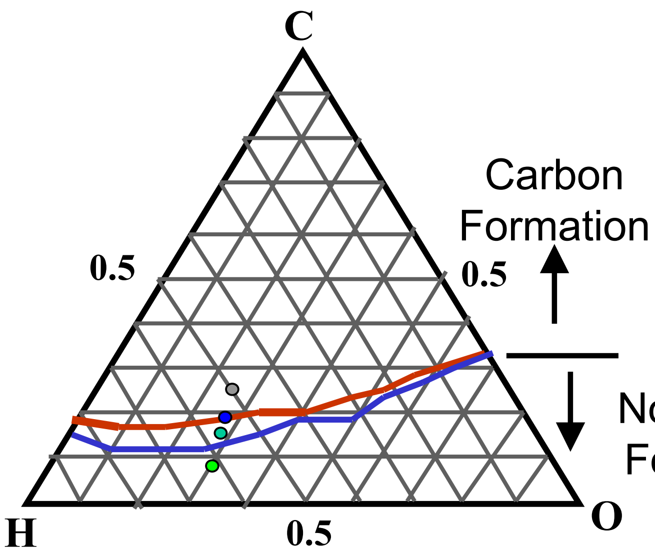
# Examination of Carbon Formation During Fuel Reformation

- Approach: Examine the conversion of diesel fuel to syn. gas ($H_2$ + CO)
  - Examine fundamentals of reforming of diesel fuel
    - Evaluate methodology (ATR, CPOx, Gas-Phase Oxidation)
    - System water balance and fuel/water feed methods
  - Model, measure and control carbon formation
  - Develop carbon removal-catalyst regeneration techniques
- Tasks: Model and Measure Carbon Formation
  - Equilibrium and component modeling
  - Measure carbon formation via *in situ* techniques
  - Examine/develop reformer operation that limits carbon formation
    - Fuel/Air/Steam Mixing
      - Fuel vaporization/fuel atomization
      - Direct liquid injection
      - Steam as fuel carrier gas
      - Simulate SOFC anode recycle (water addition by anode recycle)
  - Catalyst regeneration by oxidative carbon removal

# Carbon Formation During Diesel Refoming

## Carbon Formation Modeling




Temperature 450 °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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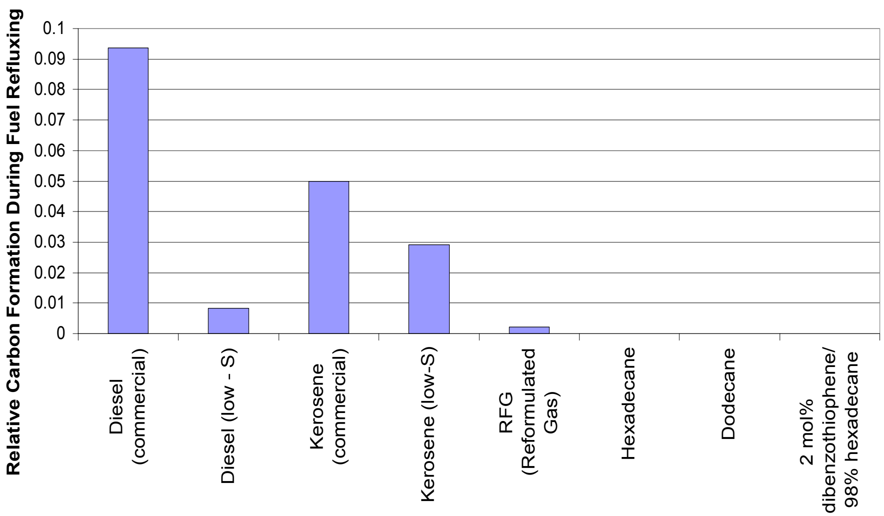
## Carbon Formation in Vaporization




- Saturated pure diesel components and lower hydrocarbons do not show pyrolysis
  - added sulfur (dibenzothiophene) does not show carbon formation
- Diesel fuels, kerosenes show pyrolysis (carbon formation) upon vaporization
- Diesel fuel reformers require:
  - Direct fuel injection
  - Water to suppress carbon formation

# Current Work and Results

- Carbon Formation Measurements and Modeling
  - Measured diesel fuels and components for vaporization pyrolysis
    - Sulfur removal decreases carbon formation from pyrolysis
    - Pure components do not show pyrolysis
  - Equilibrium carbon formation modeling
    - Defined carbon disappearance equilibrium temperature
    - Equilibrium varies greatly with air/steam, slightly with pressure, cetane #.
    - Equilibrium calculations for various carbon types
  - Hysteresis observed after on-set of carbon formation
- Demonstrated diesel fuel reforming with direct fuel injection via fuel nozzle
  - Control of fuel temperature is critical to:
    - Prevent fuel vaporization
    - Prevent fuel pyrolysis / clogging of nozzle
- Regeneration of catalysts by oxidative removal of carbon
  - Carbon/oxygen content control required to prevent ‘catastrophic’ temperature rise

# Programs Initiating in Fuel Reformation at PNNL SECA Core Technology: Carbon Minimization

- Carbon formation during reformation of gasoline and diesel fuels limits catalyst options
  - Especially problematic with nickel catalysts
  - Precious metals commonly used despite high expense
- Surface alloying of nickel catalysts show promise in reducing carbon formation and catalyst cost
  - Low concentrations of gold atoms form surface alloys
  - Most active sites for carbon formation are blocked
  - Activity of neighboring nickel sites is affected
- Stability of nickel-gold and other surface alloys will be investigated for performance and stability with heavy liquid hydrocarbons

# Programs Initiating in Fuel Reformation at PNNL SECA Core Technology: Sulfur Tolerance

- Liquid hydrocarbon feedstocks contain organosulfur compounds
  - Sulfur deposits on catalytically active sites
  - Performance of reformer catalysts and fuel cell anode drastically reduced
- Use of precious metal catalysts and high temperatures is current method to minimize effects of sulfur
  - Expensive catalysts
  - Expensive materials of construction for reactors
- Program will evaluate performance of several classes of catalysts for activity and stability with sulfur-bearing fuels
  - Catalysts identified from patent and open literature
  - Limited or no precious metal content
- Program will also evaluate mode of reforming (SMR, ATR, CPOX) on resistance to deactivation by sulfur