2003 SECA CORE REVIEW

Fuel Processing Core Program: Overview & Status

David A. Berry

National Energy Technology Laboratory

&

Rod Borup

Los Alamos National Laboratory

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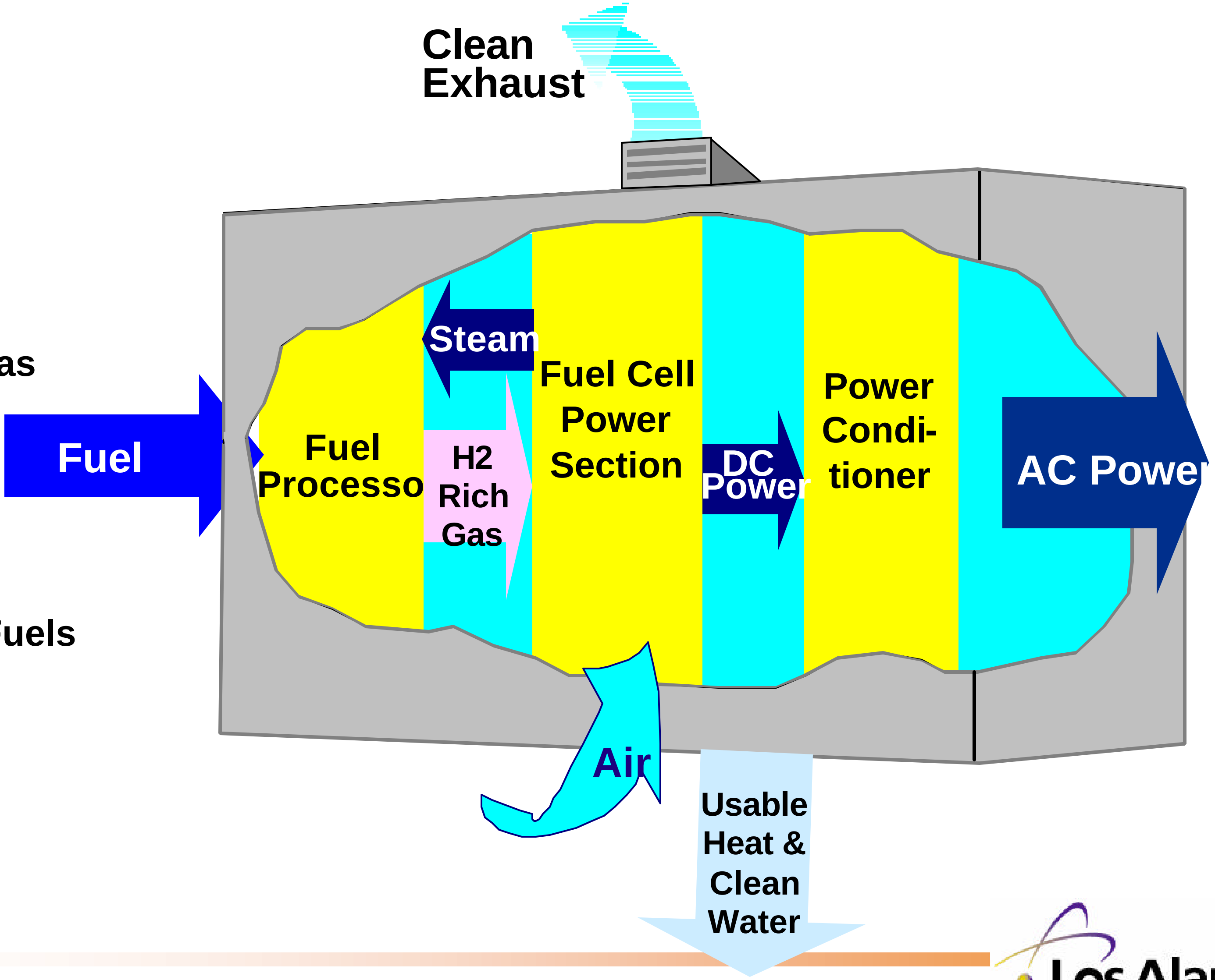
Fuel Processing

How Do We Get Suitable Fuel to the Stack?

- Hydrogen
- Natural Gas
- Propane
- Gasoline
- Diesel
- Logistic Fuels



Fuel Processing for SECA

A variety of development issues

Sulfur poisoning

Coke formation

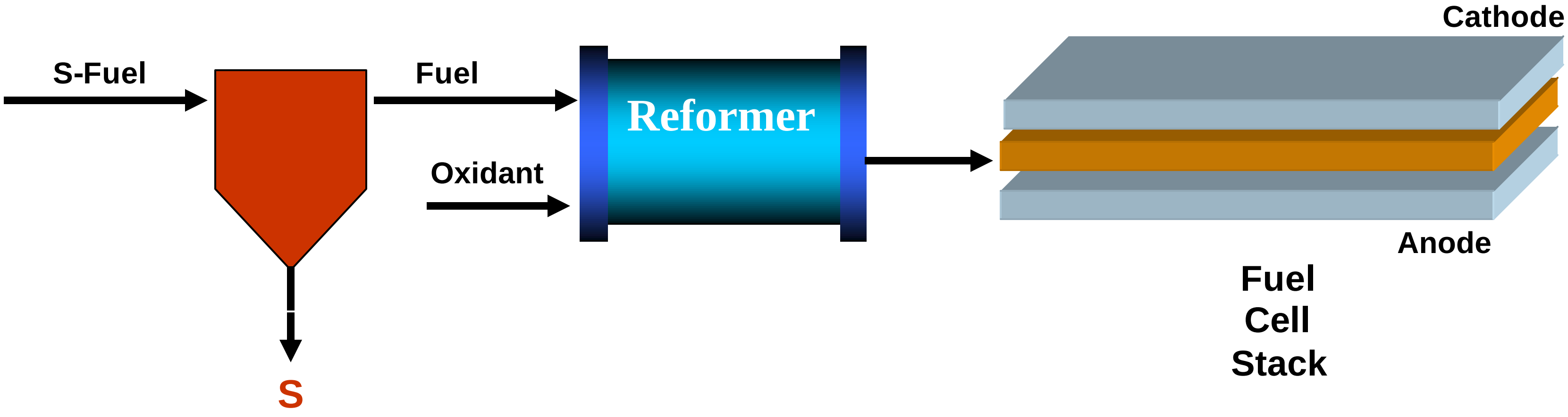
High efficiency & thermal integration

Quick startup and transient response

Fuel Processing for SECA

General Approaches

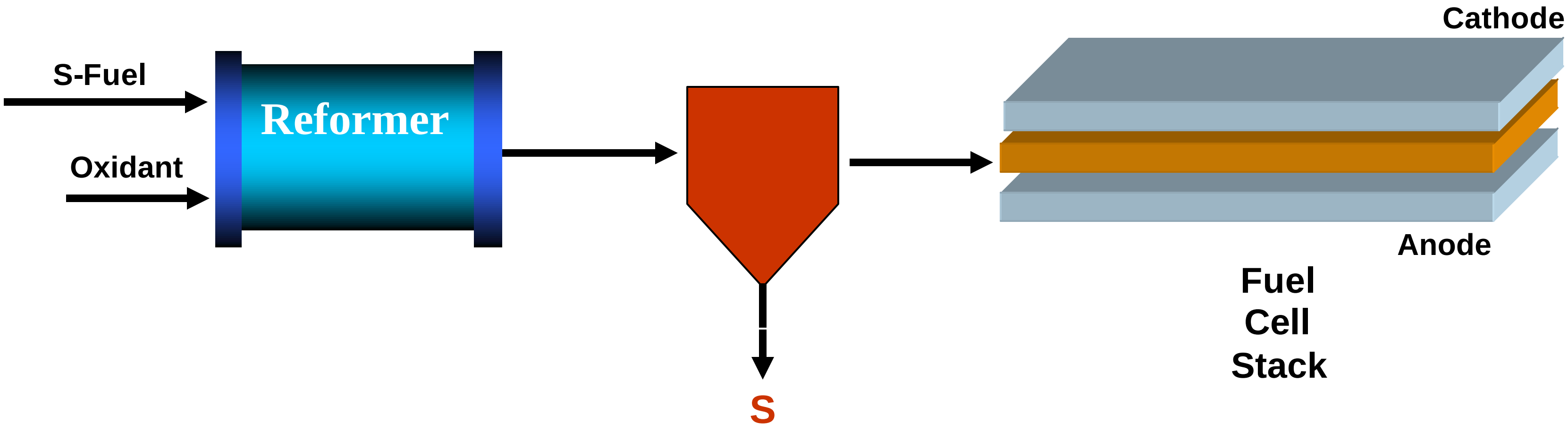
Conventional Technology:



Fuel Processing for SECA

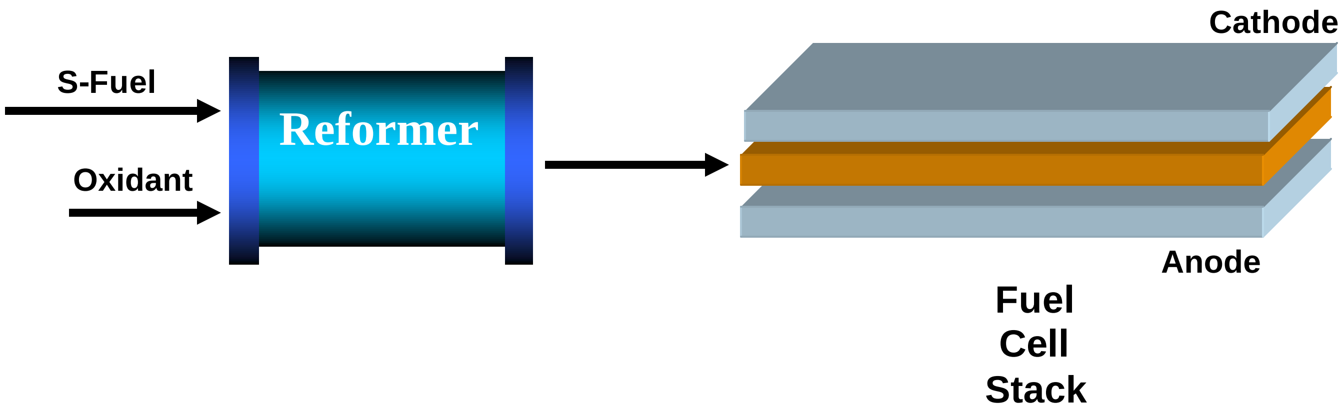
General Approaches

S-Tolerant Reforming Catalysts:



Fuel Processing for SECA
General Approaches

S-Tolerant Reformer & FC Anode:

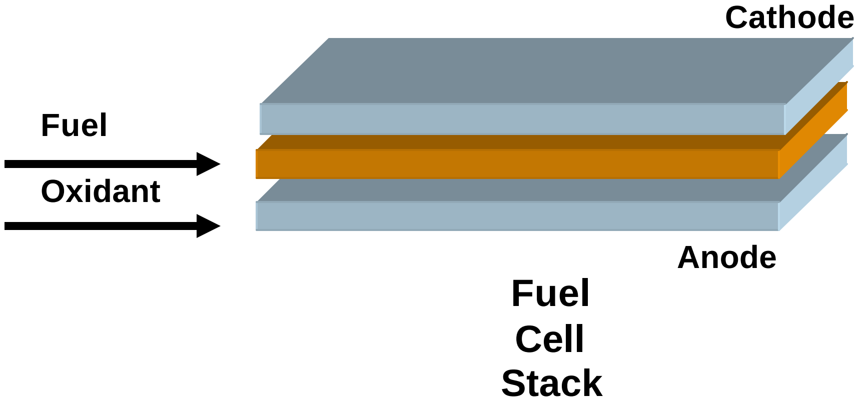


Fuel Processing for SECA

General Approaches

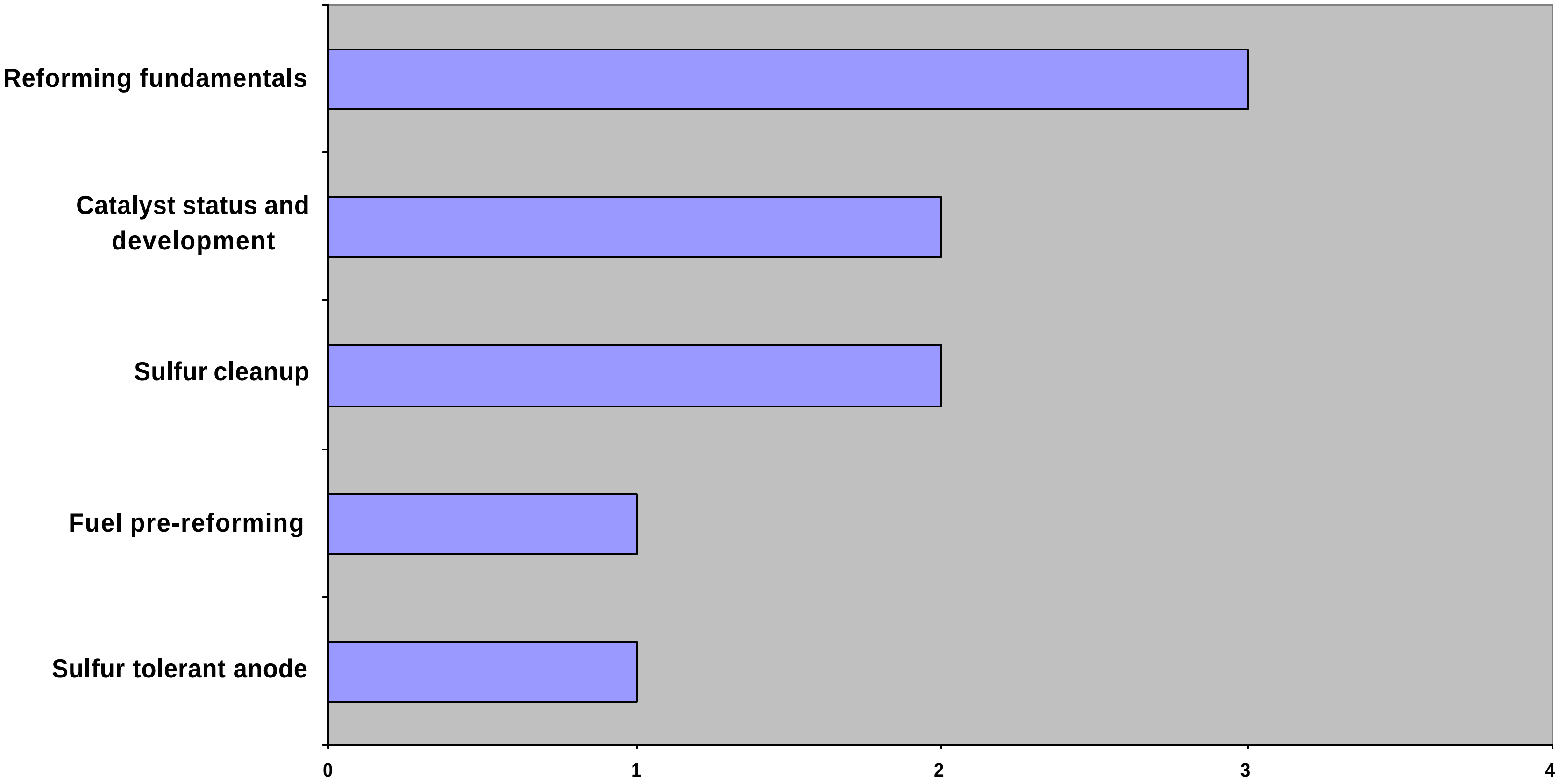
Direct Oxidation

S-Tolerant FC:



Fuel Processing for SECA

Reforming Needs Based on Vertical Team Feedback



Fuel Processing for SECA

Fuel Reforming Fundamentals

The following is of interest for the major reforming approaches (SMR, ATR, CPOX)

- Catalyst activity, cost
- Kinetics, mechanisms
- Effects of fuel type on performance
- Deactivation by sulfur, carbon
- Reaction/reactor models

Fuel Processing for SECA

Catalyst Status and Development

- **Need for improved catalysts in the following areas**
  - Dual function catalysts for CPOX, ATR
  - Dry reforming catalysts to reduce H2O
  - Multi-fuel catalysts
  - Assistance with catalyst characterization, especially post-mortem
  - Faster light-off times for CPOX
- **Identify state-of the-art in fuel reformation, especially diesel reformation**

Fuel Processing for SECA

Sulfur Cleanup

Broad-based needs to handle several sulfur issues

- Desulfurization of liquid fuels
- High temperature H_2S removal (between sulfur tolerant reformer, anode)
- Identify sulfur tolerance limits for reformer, anode
- Higher capacity, more effective natural gas desulfurization
- Develop sulfur tolerant anodes

SECA Solicitation Addressed Some Core Technology Needs

- **High temperature sulfur removal**
  - Sulfur tolerant reforming catalysts create sulfur contamination of fuel cell anode
  - High temperature H2S removal obviates energy losses from lower temperature absorbents (ZnO)
- **Contaminant-resistant fuel cell anodes and reforming catalysts**
  - Sulfur
  - Carbon
  - Other impurities

Current Core Technology Efforts to Address Vertical Teams Needs in Fuel Processing

- **Two contracts awarded under 1st Core Solicitation for sulfur-tolerant / direct oxidation anodes**
  - Northwestern University
  - Gas Technology Institute
- **Current efforts at NETL**
  - Kinetic studies and modeling of diesel fuel reforming
  - Assessment studies for reforming and desulfurization
- **Current efforts at LANL**
  - Target diesel reforming
  - Study parameters/rates for carbon formation

Diesel Reforming for Fuel Cell Auxiliary Power Units

Rod Borup, Michael Inbody, Jose Tafoya, Will J. Vigil, and W. Jerry Parkinson

Los Alamos National Laboratory

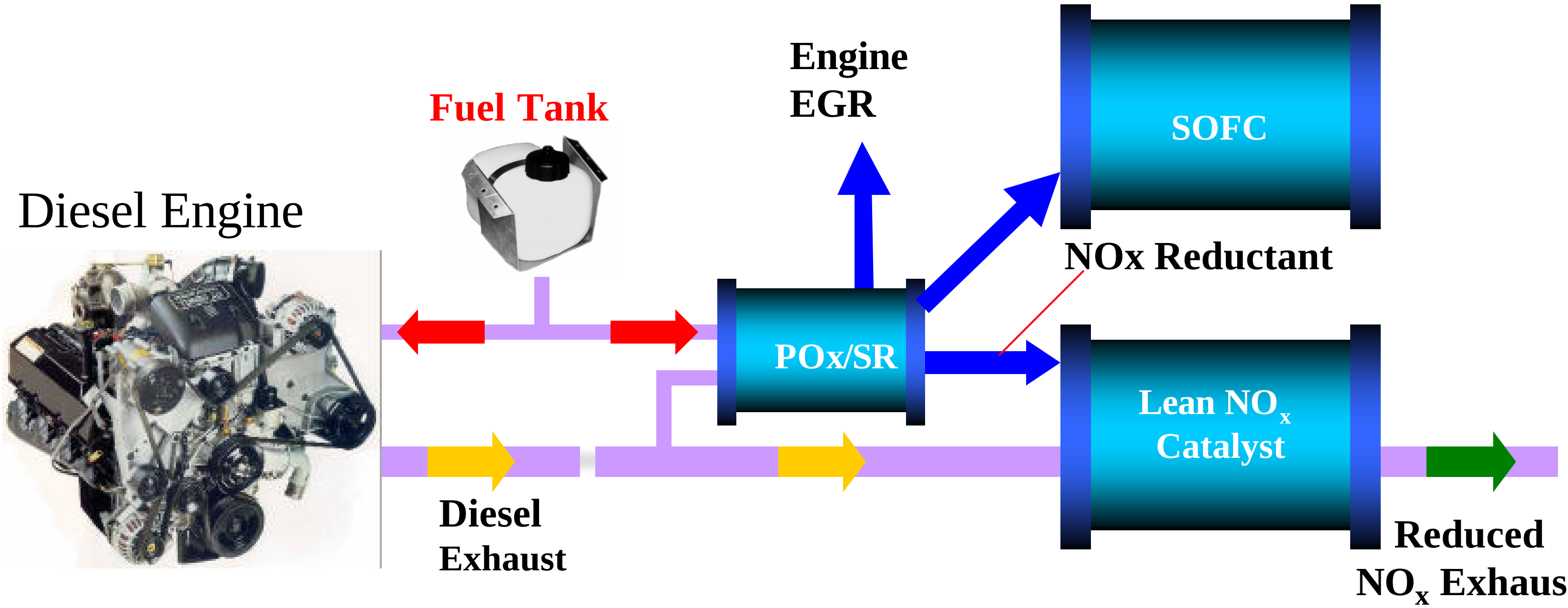
DOE Program Managers

SECA – Norman Holcombe/Wayne Surdoval

H_2, Fuel Cells & Infrastructure Technologies – Nancy Garland / JoAnn Milliken

POC: Rod Borup:Borup@lanl.gov - (505) 667 - 2823

Potential Applications of Diesel Reformers in Transportation Systems



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

- fuel for SOFC / APU
- reductant for lean-burn engines catalyzing NOx reduction
- Hydrogen addition to the fuel charge 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.

Technical Issues:

Hydrogen Production from Diesel Reforming

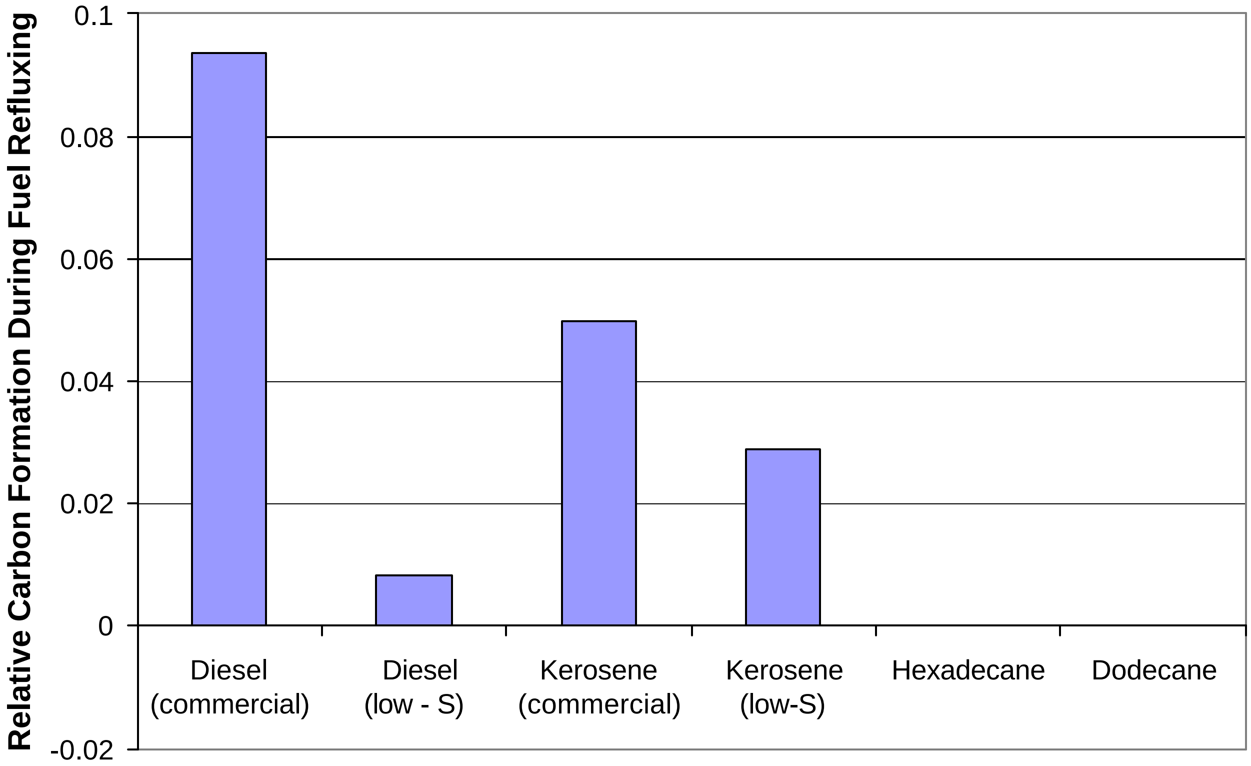
Approach:

- Examine Partial Oxidation and Steam Reforming for the conversion of diesel fuel to syn. gas (H_2 + CO).

Tasks:

- Carbon Formation in Diesel Fuel Processing
  - Equilibrium and component modeling
  - Experimental carbon formation measurement
- Fuel/Air/Steam Mixing
  - Vaporization / Fuel atomization
  - Direct liquid injection
  - Steam as fuel carrier gas
  - SOFC anode recycle (water addition to reformer by recycling of the anode-off gas)
- Catalyst regeneration
  - Oxidation of carbon from catalyst/reformer
- Reduction of NOx from lean-burn Engines

Relative Carbon Formation from Fuel Vaporization

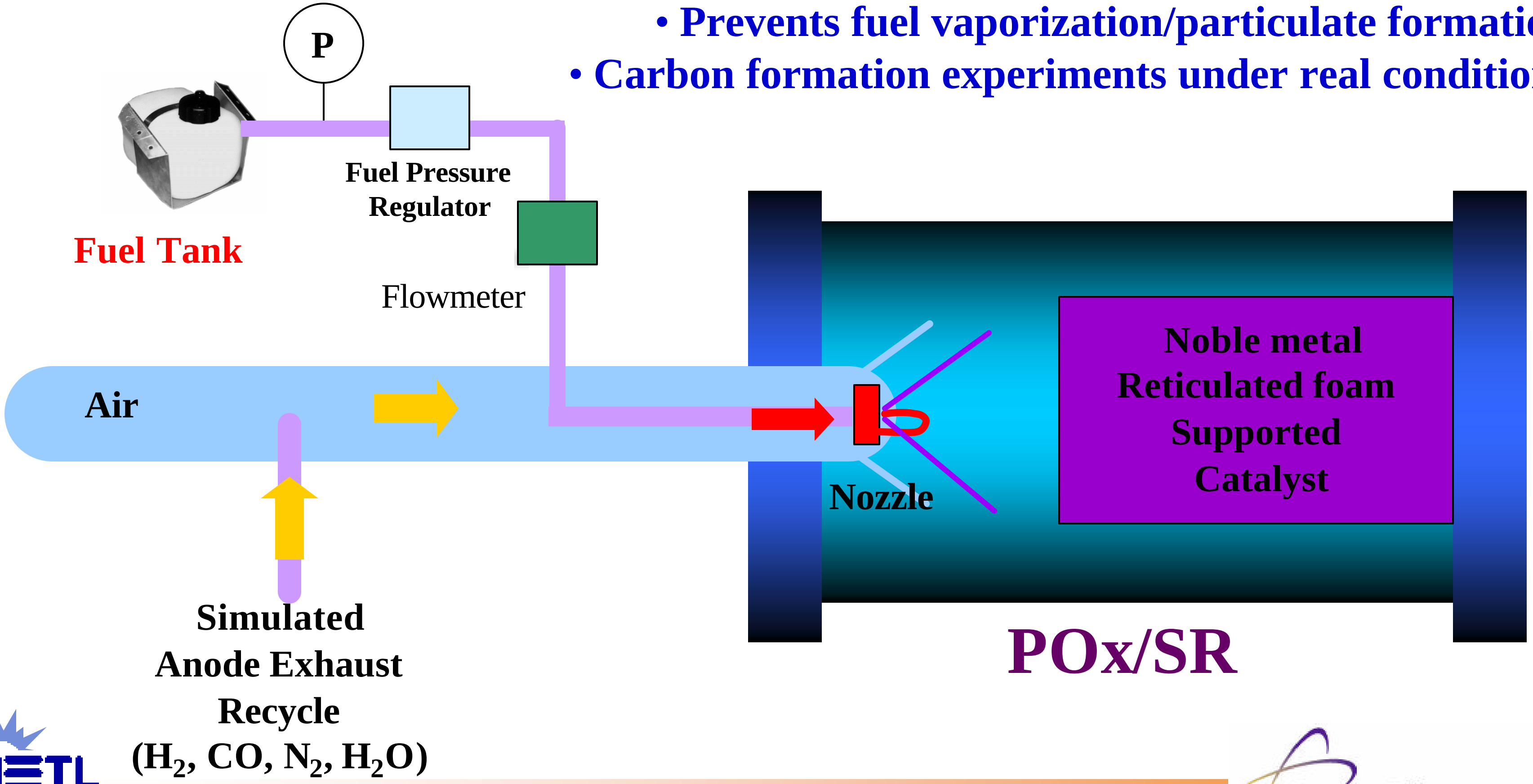


S enhances carbon formation of fuels

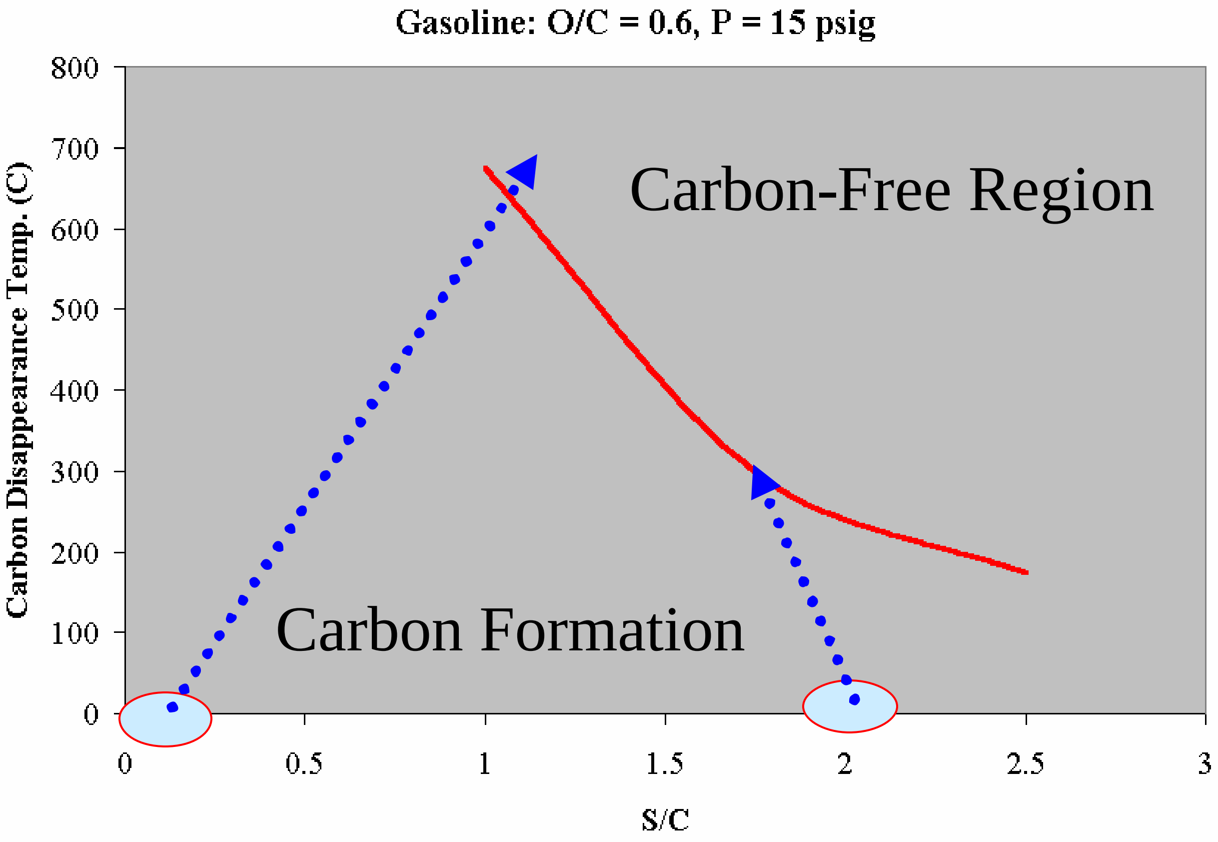
Saturated pure diesel components (low MW) do not show pyrolysis

Direct Fuel Nozzle Operation

- Directly inject fuel to reforming catalyst
  - Commercial fuel nozzle
  - No preheating of fuel/air
    - Prevents fuel vaporization/particulate formation
  - Carbon formation experiments under real conditions



Equilibrium Modeling



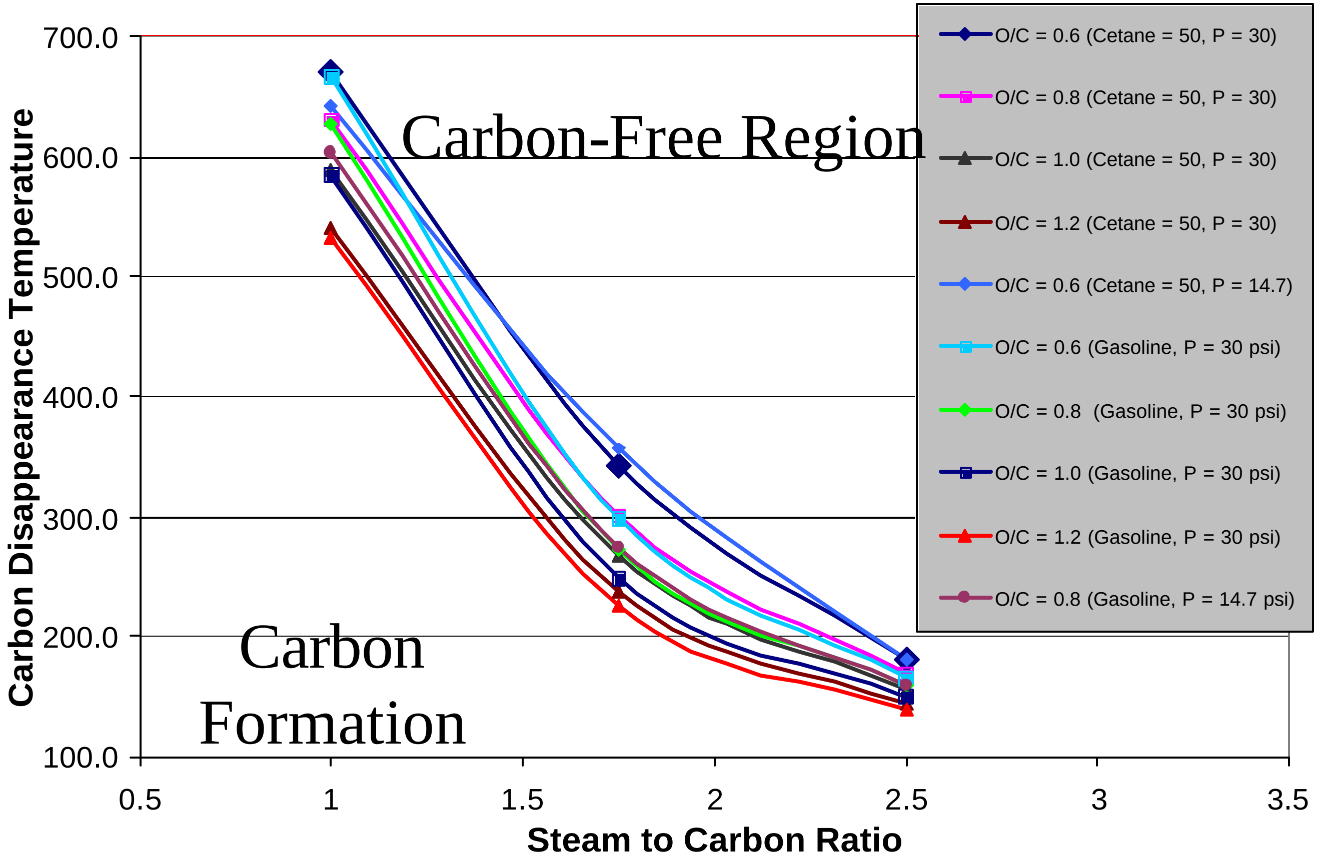
Equilibrium defines fuel processor operating conditions

At start-up of fuel processor, water availability is questionable (freezing conditions)

Avoiding zero equilibrium carbon will be difficult whether water is available or not.

At high S/C during start-up, during transition to carbon-free region - carbon formation kinetics appear low

Modeling of Carbon Formation Disappearance for Different Fuel Compositions



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

Carbon Equilibrium (450 ºC)

Pressure 14.7 to 30 psi

Temperature 450 ºC

--x-- = amorphous carbon

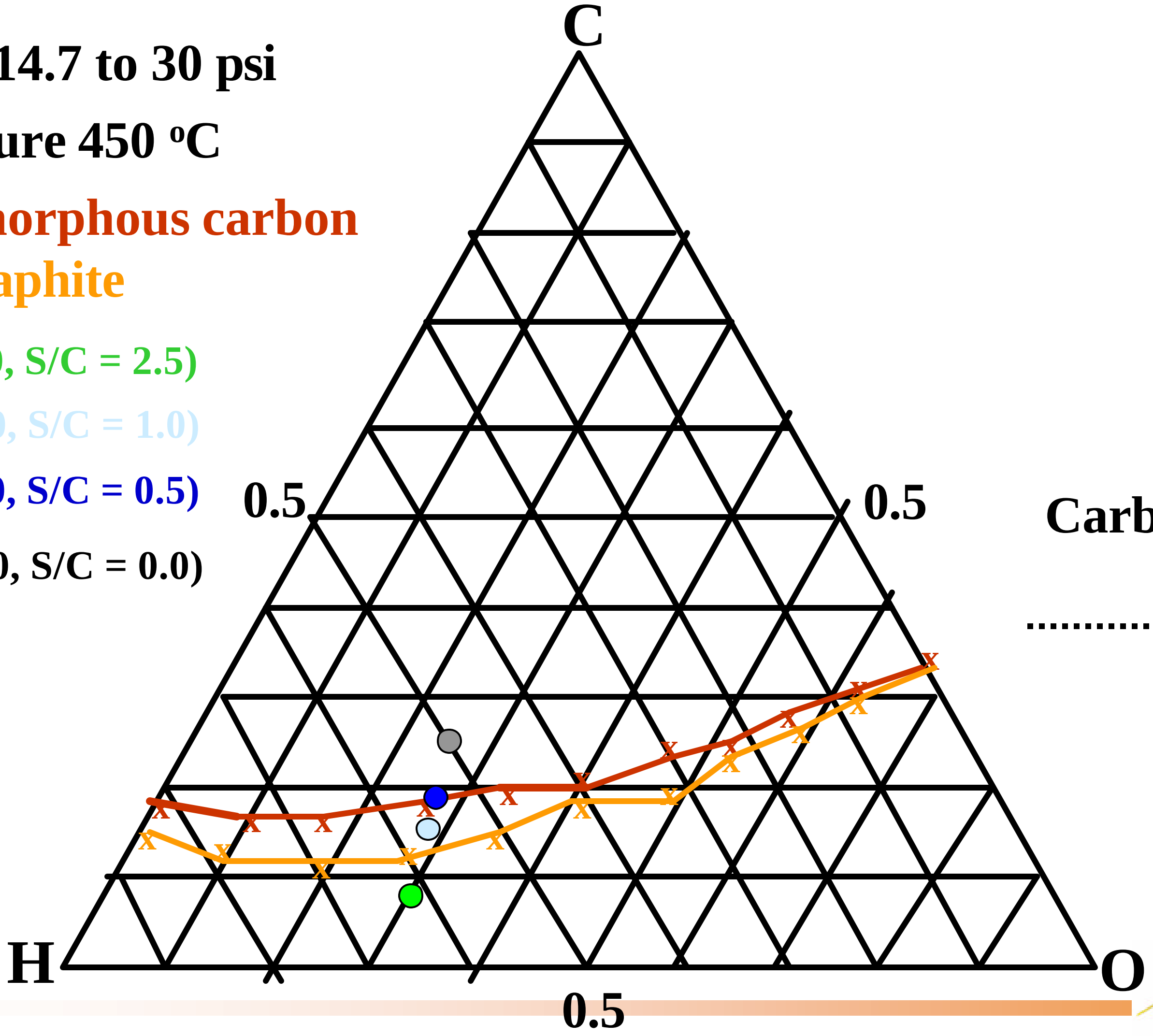
--x-- = graphite

● = (O/C = 1.0, S/C = 2.5)

○ = (O/C = 1.0, S/C = 1.0)

● = (O/C = 1.0, S/C = 0.5)

● = (O/C = 1.0, S/C = 0.0)



Carbon formation

No Carbon formation

Carbon Equilibrium (700 °C)

Pressure 14.7 to 30 psi

Temperature 1292 F (700C)

Legend

--x-- = amorphous carbon

--x-- = graphite

● = (O/C = 1.0, S/C = 2.5)

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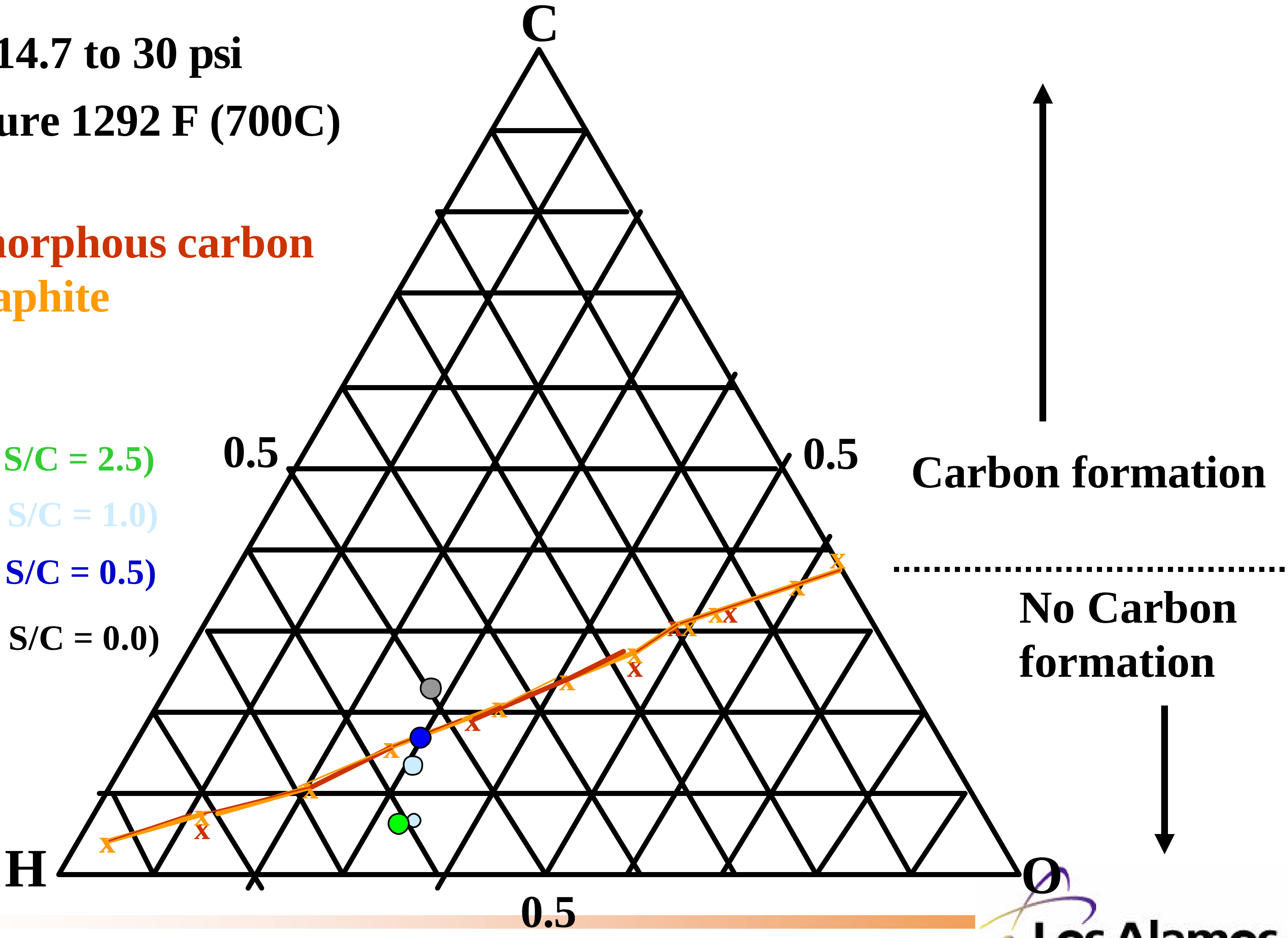

Carbon formation

No Carbon formation

Carbon Equilibrium (800 ^{o}C)

Pressure 14.7 to 30 psi

Temperature 1472 F (800 C)

Legend

--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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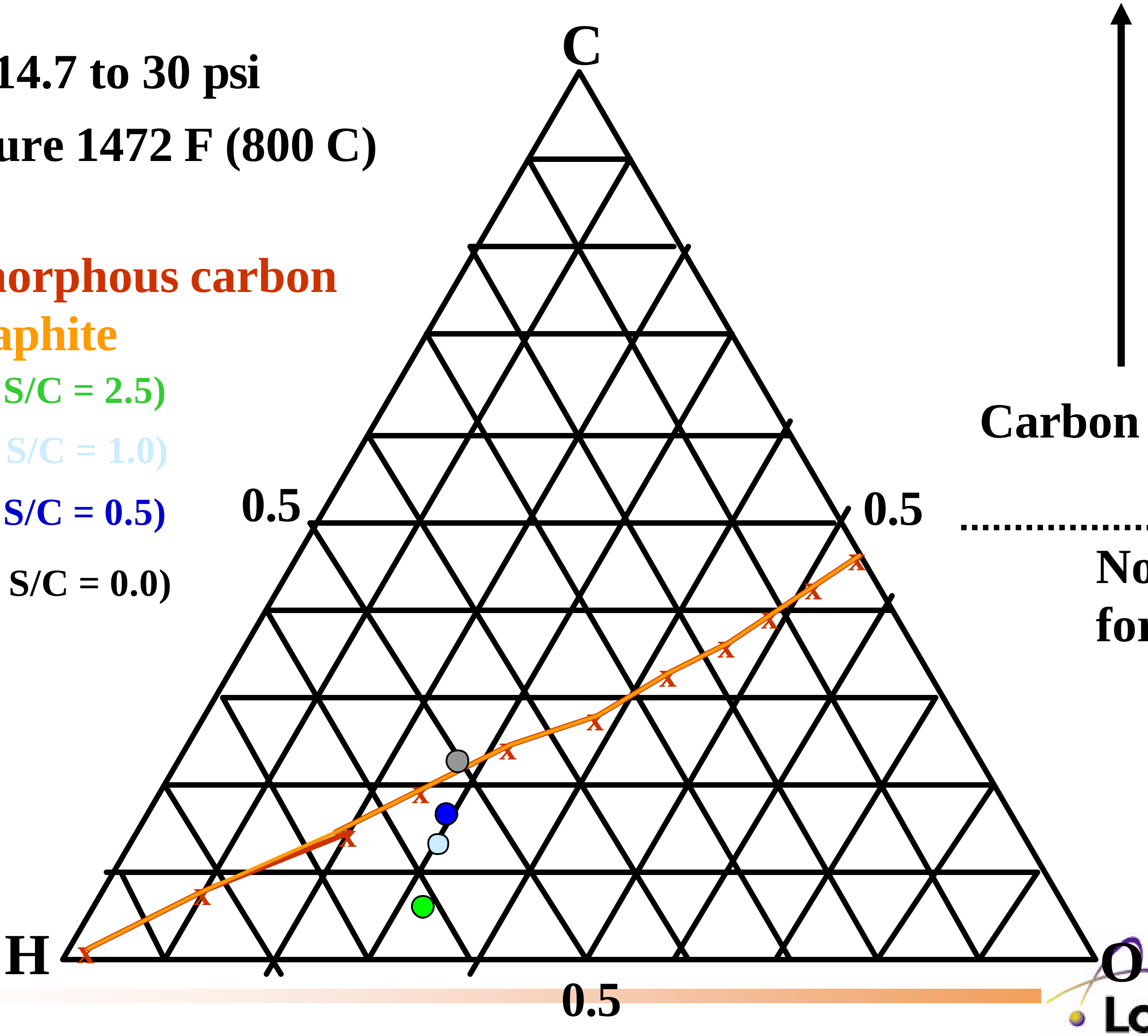


Carbon formation

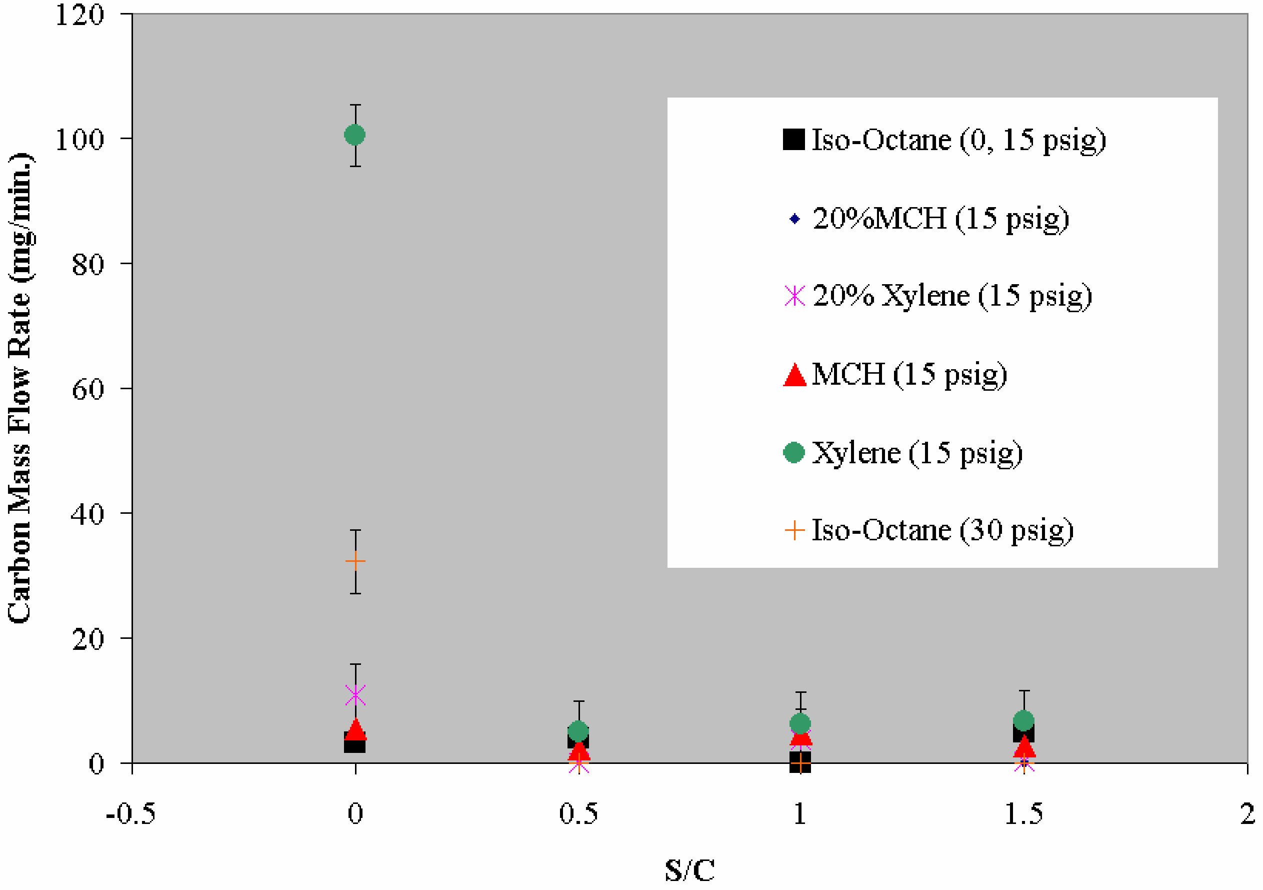
....

No Carbon formation

Carbon Mass Flow Rate

O/C = 0.65

30 kW, 15 psig



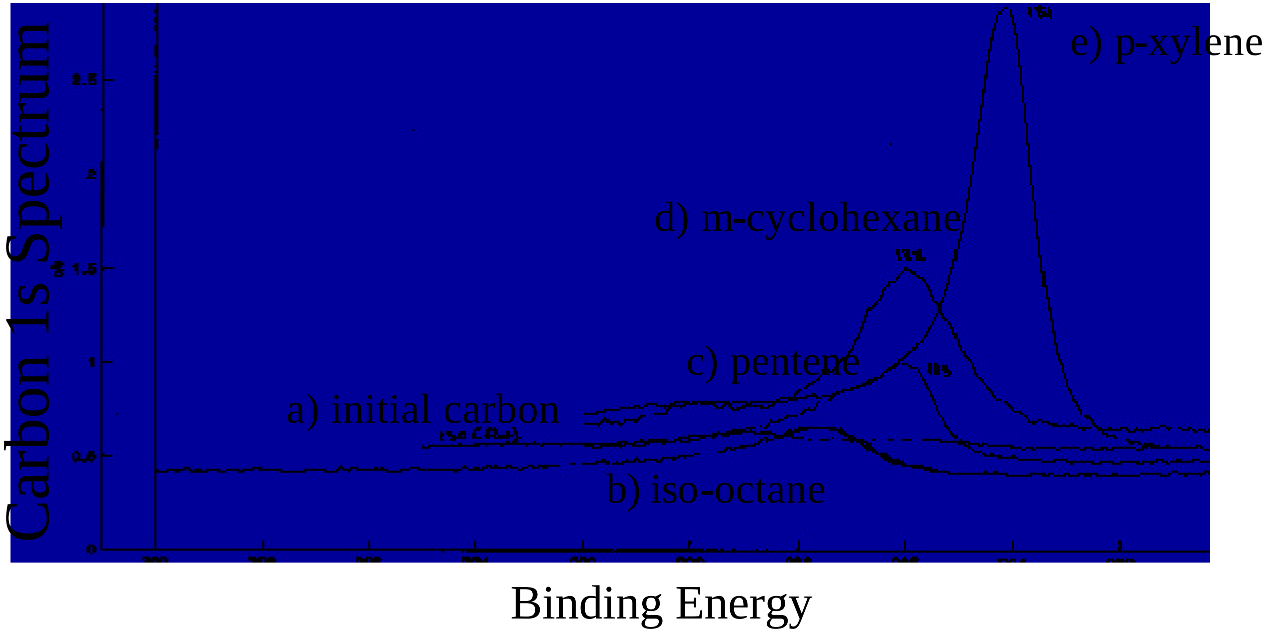
Saturated hydrocarbons with noble metal catalysts, and short residence times show little (no) carbon formation, even when carbon formation is predicted.

Fuel, catalyst and residence time have all been noted to have effects on carbon formation.

No change detected with 50 ppm N,N' – di-sec-butyl-p-phenylene diamine

XPS Post-Characterization of Catalysts

Carbon 1s Spectrum for Ni/Al_2O_3 Catalysts



- **Elemental Analysis / Chemical Shift**
  - large amounts of carbon formation:
    - p-xylene >> methylcyclohexane > 1-pentene >> iso-octane
  - NiC (nickel carbide) was formed with p-xylene
  - Carbon shifting to lower binding energies with increasing quantity
    - different carbon species?

Catalyst Regeneration:
oxidative removal of carbon

- Post-carbon formation experiments:
  - Regeneration of catalyst/reactor by carbon oxidation
  - Air feed to reactor at 500 – 600 °C
  - Similar to regenerative particulate filters
- Successful about ~5 times in succession
  - Control of the reactor temperature could be difficult.
  - For large carbon build-up:
    - Subsequent oxidation of the carbon yielded high adiabatic temperatures
- Eventually disables light-off of the partial oxidation stage
  - Due to catalyst sintering - loss of catalyst surface area.

- Catalyst regeneration
  - Potential solution to carbon formation
  - Need to control oxidation temperature/rate of oxidation

Summary/Findings

- Direct fuel injection via fuel nozzle
    - Control of fuel temperature critical
        - Prevent fuel vaporization
        - Prevent fuel pyrolysis / clogging of nozzle
- Carbon Formation
    - Equilibrium carbon formation modeling
        - Equilibrium varies greatly with air/steam, slightly with pressure and cetane #.
    - Diesel fuels show high tendency for pyrolysis
        - S enhances carbon formation
        - Pure components (dodecane/hexadecane) do not show pyrolysis
    - Hysteresis observed after on-set of carbon formation
    - Greater carbon formation with aromatics
- Regeneration of catalysis for limited number of cycles
    - Carbon / oxygen content control to prevent ‘catastrophic’ temperature rise

On-Going / Future Work

- Direct Fuel Injection/Air Mixing
- Refinement of Carbon formation modeling & comparison with measurements
- Carbon Formation Kinetics Rate Expression Development
- Regeneration Cycles Removing Carbon From Catalytic Partial Oxidation
- Investigate diesel SOFC / ATR operating conditions for anode recycle operation
    - Survey
    - Modeling
- Operation simulating SOFC anode recycle