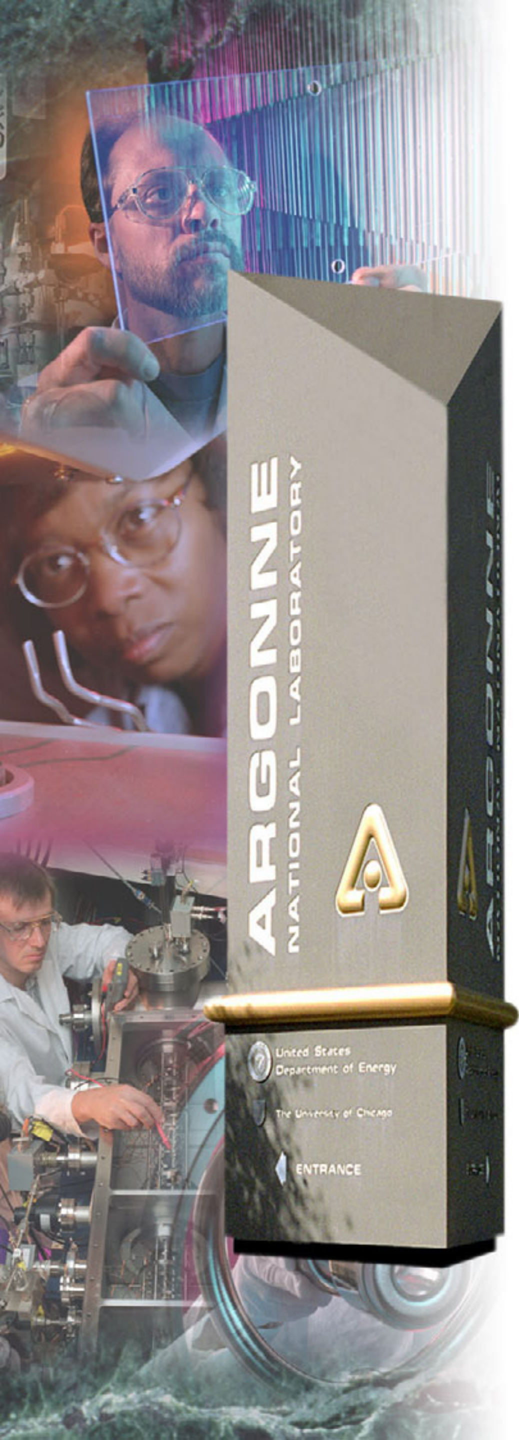

Effects of Fuel Composition on Fuel Processing

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The 2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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This presentation does not contain any proprietary or confidential information.

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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Objective

- Determine how fuel composition affects reformer performance
  - Determine how changes/variations in composition affect performance
  - Determine how we can tailor composition to increase performance

Goals for 2004

- Find additives that can increase performance
- Determine how molecular size affects reforming
- Study reforming of two renewable fuels

Technical Barriers and Targets

- Fuel composition directly and indirectly affects many technical targets/barriers for the fuel processor, including
- Barrier J, Processor durability, 2005 target 4000 h
- Barrier K, emissions, 2005 target <Tier 2 Bin 5
- Barrier M, Fuel processor efficiency, 2005 Target 78%
- Barrier N, costs, 2005 Target $25/kWe

- *FY 2004 Budget $300K*

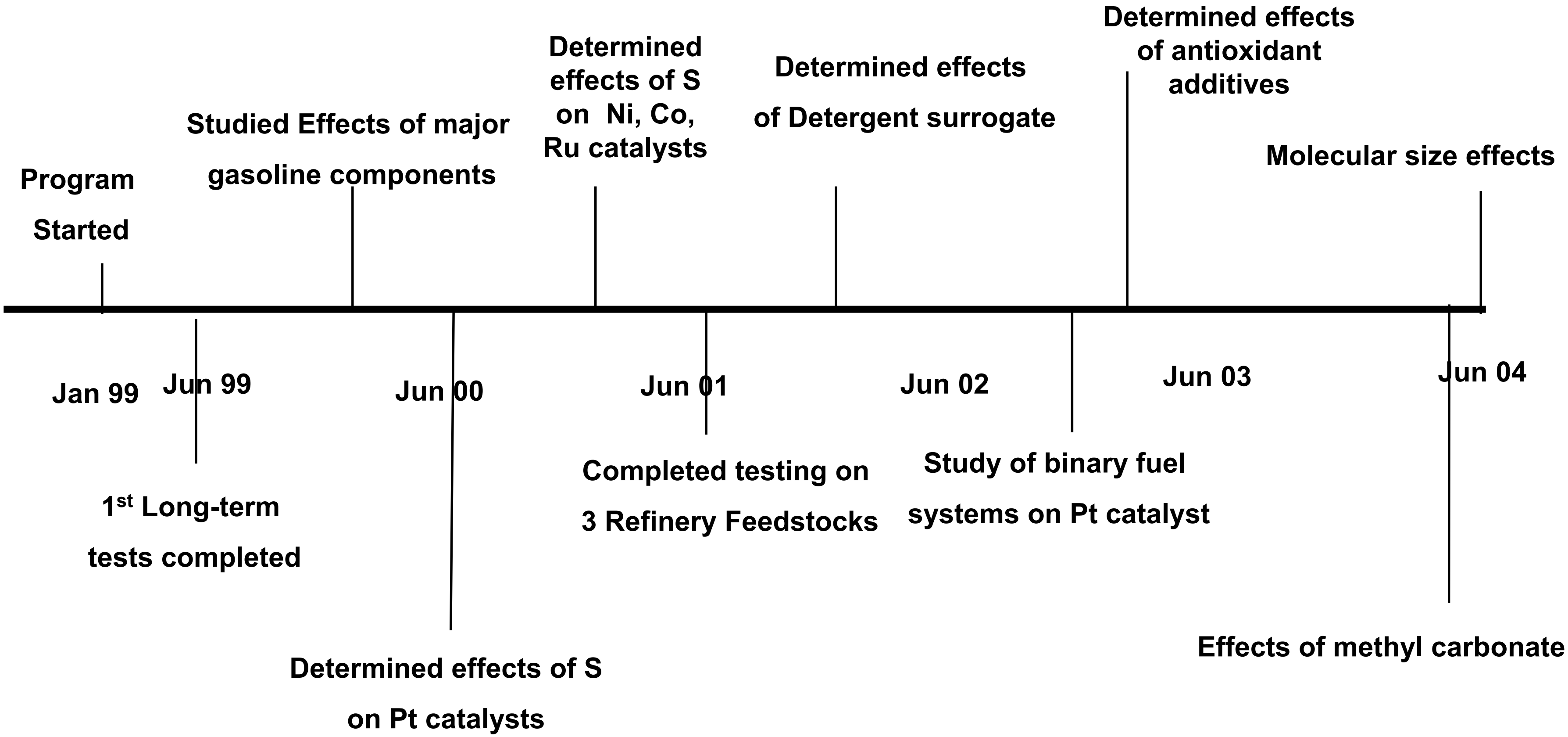
Approach

- **Investigate reforming of simplified systems and real world fuels in microscale and bench scale reactors**
  - Perform short-term and long-term testing
  - Start with simple components and build up to complex fuels
  - Evaluate composition effects on hydrogen production, intermediates formed, side products, and reactant breakthrough
  - Determine how compositional changes affect reaction path and kinetics

Project Safety

- Safety reviews held before initiation of work and revisited yearly
- Reactors located in hoods with dedicated exhaust lines
- Integrated safety switches which automatically shut down reactor and place it in a safe mode when extreme temperature or pressure detected
- Hydrogen sensors placed in fan loft which trip emergency shutdown of reactors

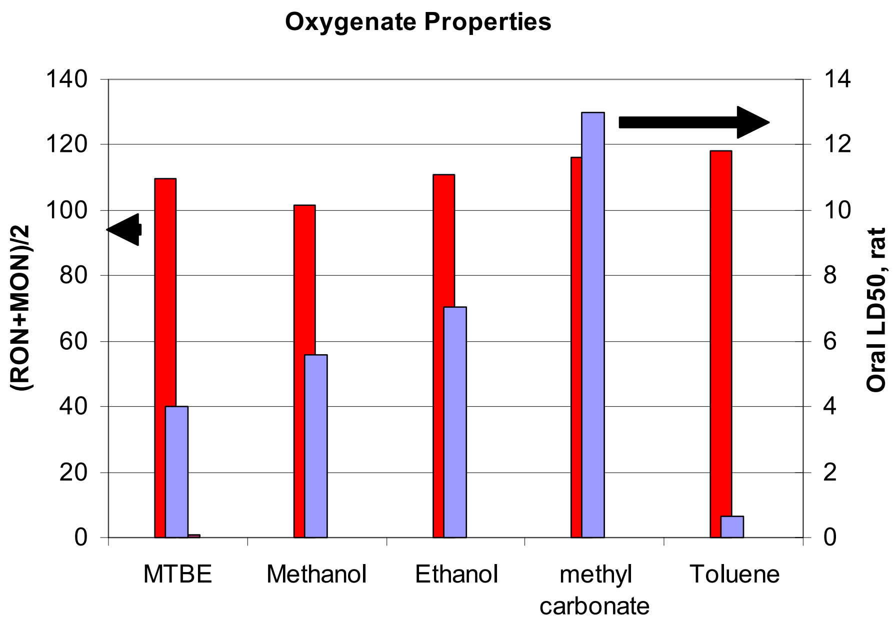
Timeline



Program Started
Studied Effects of major gasoline components
Determined effects of S on Ni, Co, Ru catalysts
Determined effects of Detergent surrogate
Determined effects of antioxidant additives
Molecular size effects
Jan 99
Jun 99
Jun 00
Jun 01
Jun 02
Jun 03
Jun 04
1st Long-term tests completed
Determined effects of S on Pt catalysts
Completed testing on 3 Refinery Feedstocks
Study of binary fuel systems on Pt catalyst
Effects of methyl carbonate

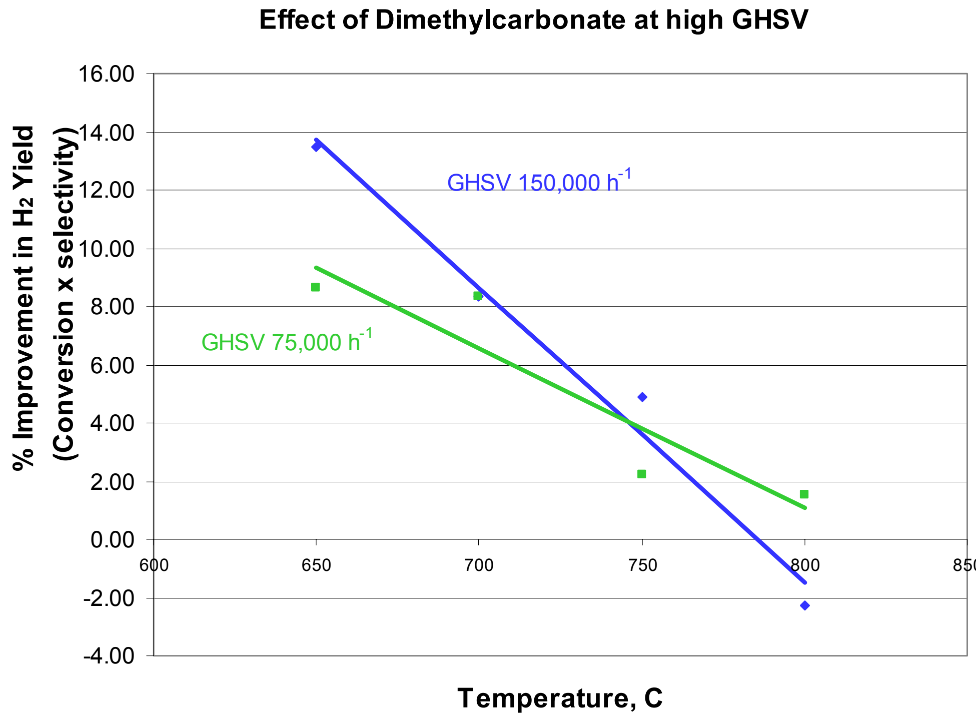
Technical Accomplishments-Additives to improve reforming

- Oxygenates may improve reformability by increasing P_{O2} in reactor
- Oxygenates also act as octane enhancers
- Oxygenates reduce water recovery issues
- Problems with toxicity of some oxygenates
- May be able to replace aromatics with oxygenates



Dimethylcarbonate as a Reforming Enhancer

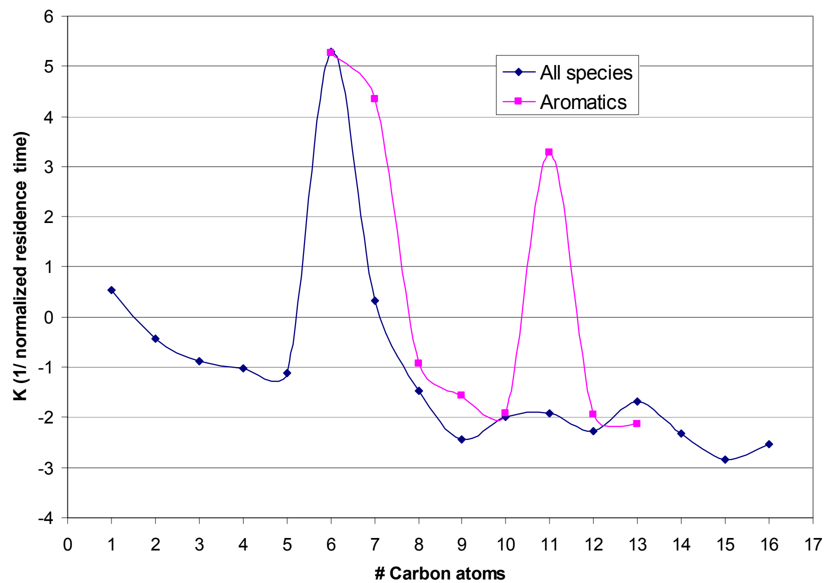
- Dimethylcarbonate improved hydrogen yield from isooctane-xylene mixture by 13% at GHSV of 150,000 h^{-1} at 650˚C.
- H_2 yield still below acceptable values at these conditions
- Dimethylcarbonate less effective at higher temperatures
- Started testing on radical intitiator additives



Technical Accomplishments-Molecular weight

- Testing of gasoline showed problems after ~600h on-line while testing with benchmark fuel did not show problems up to 1000 h. Major difference between fuels is that gasoline contains a substantial fraction of larger molecules.
- **Determined effects of higher molecular weight components**
  - Form more complex aromatic species during reforming, with complexity increasing with heavier components and leading to 2 and 3-ring aromatic species

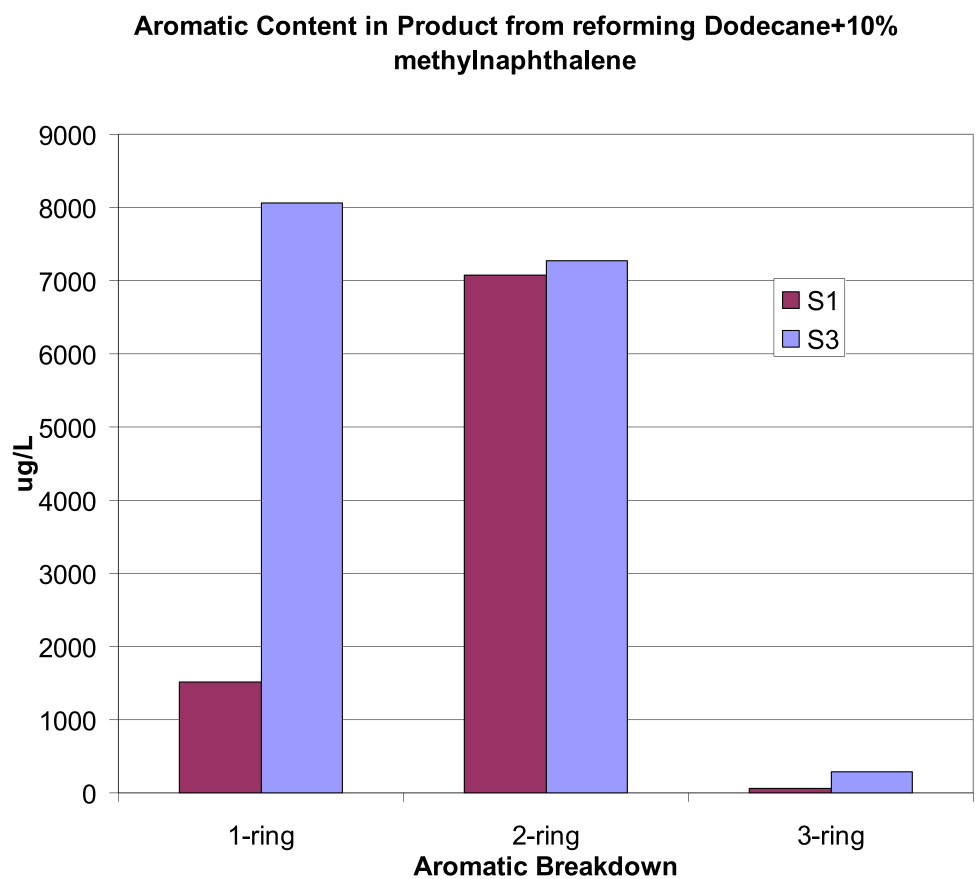
C6, C7, and C11 aromatic species are formed in the reactor during reforming of heavier fuels



Psuedo –first order rate constants determined during reforming, Positive values indicate species being formed, negative values indicate species being destroyed

Technical accomplishments- Effects of multi-ring aromatics

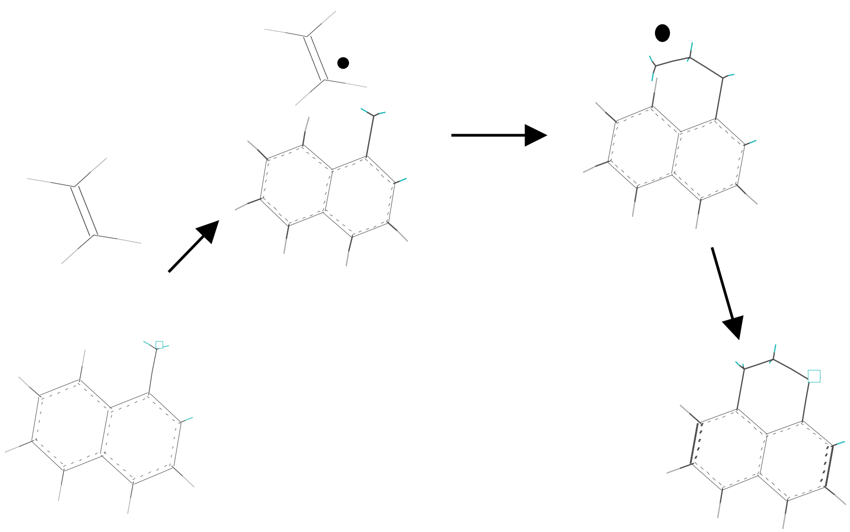
- When 2-ring aromatic present, complexity of aromatic species increased with increasing reaction time.
- H_2 content in product gas decreased by 20% and efficiency to H_2+CO decreased by 30%

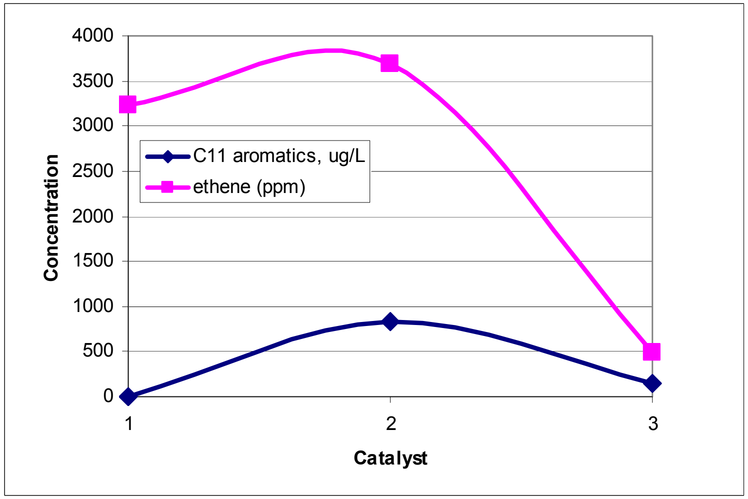


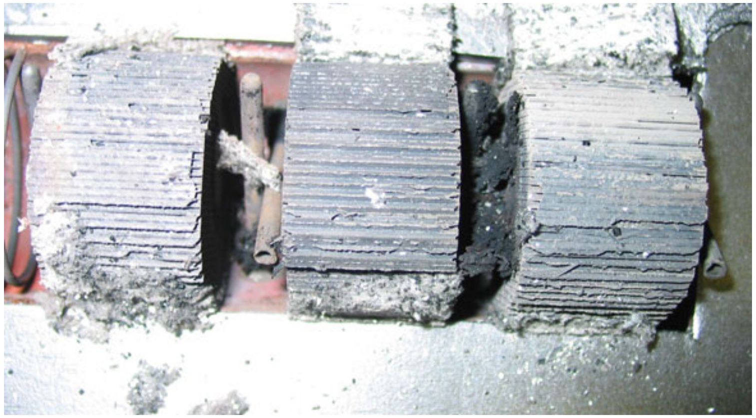
Aromatic content and complexity increases from S1 (after the first monolith) to S3 (after the 3rd monolith)

Technical Accomplishments/Progress

When reforming fuels with higher molecular weight components ethylene and methylnaphthalene content were observed to correlate with carbon formation

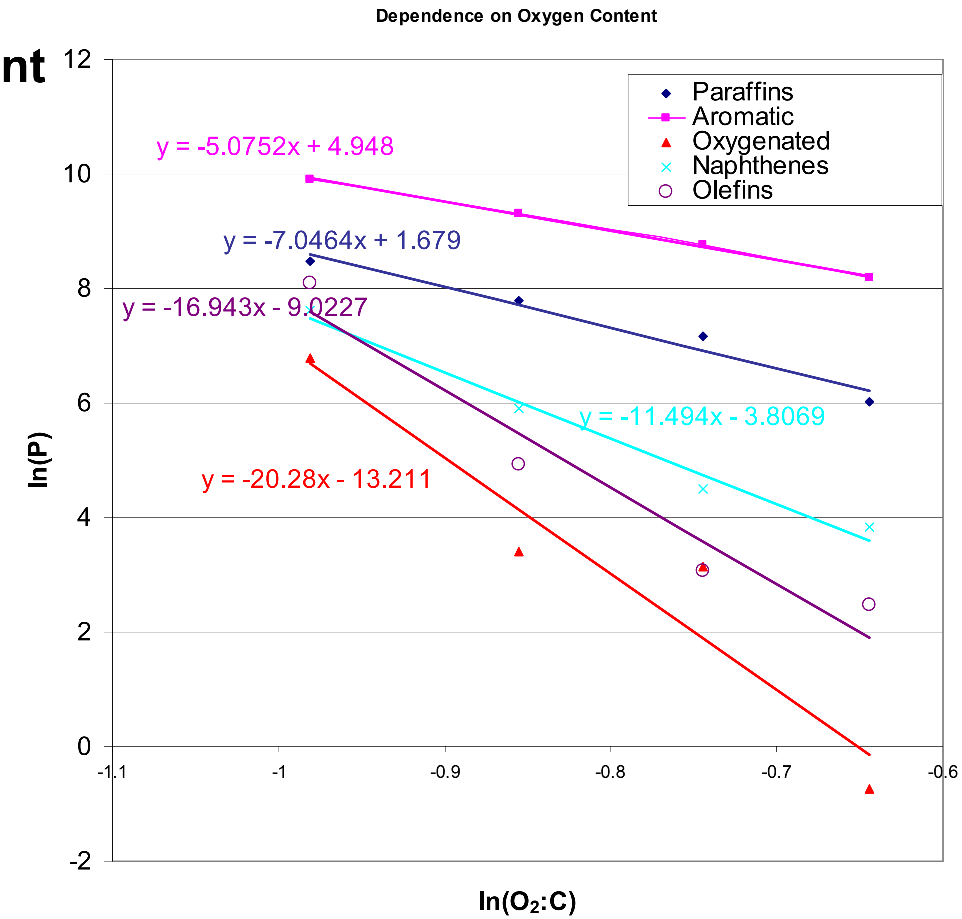






Technical Accomplishments/Progress

- **Identified sensitivity of different types of species to O_2:C ratio**
  - olefins and oxygenated species most sensitive, aromatics least sensitive
  - Increasing O_2:C effective at reducing olefins, not very effective at reducing aromatics



Technical accomplishments- Renewable Fuels

- **Looking at ethanol as an additive in gasoline and as a fuel**
  - Challenge is preventing dehydration to form ethene (problems with coking)
- **Ethanol as an additive has minor effects**
  - Observe slightly higher methane slip with ethanol after 450 h
  - No evidence for dehydration of the ethanol
- **Ethanol as a fuel**
  - Co catalysts show promise for reforming ethanol at decreased temperature
- **Biodiesel**
  - Tests will be initiated on autothermal reforming of biodiesel in May 04

Interactions and Collaborations

- Catalyst development groups at ANL and Süd-Chemie
- Shell/ Shell Hydrogen on fuel composition effects
- Dr. Chia-fon Lee, University of Illinois, Urbana Champaign
- Provided data to modeling efforts at NETL and Royal Military College of Canada
- Investigating collaboration with Renewable Solutions on Biodiesel Reforming

Response to Previous Year Reviewers' Comments

Comment: De-emphasize conventional gas additives. Increase focus on new performance enhancers.

Response: Added work investigating oxygenated and radical initiating performance enhancing additives

Future Work

This FY:

Complete study varying molecular size and catalyst geometry to elucidate size/mass transfer effects

Complete study of at least one radical initiator additive

Autothermal reforming of biodiesel

Next FY:

Investigate composition effects on reformability of gaseous fuels (Natural gas, LPG) looking at effects of minor components (ethylene, propylene) and impurities (sulfur species)

Continue testing additives to improve reforming