Effects of Fuel Composition on Fuel Processing

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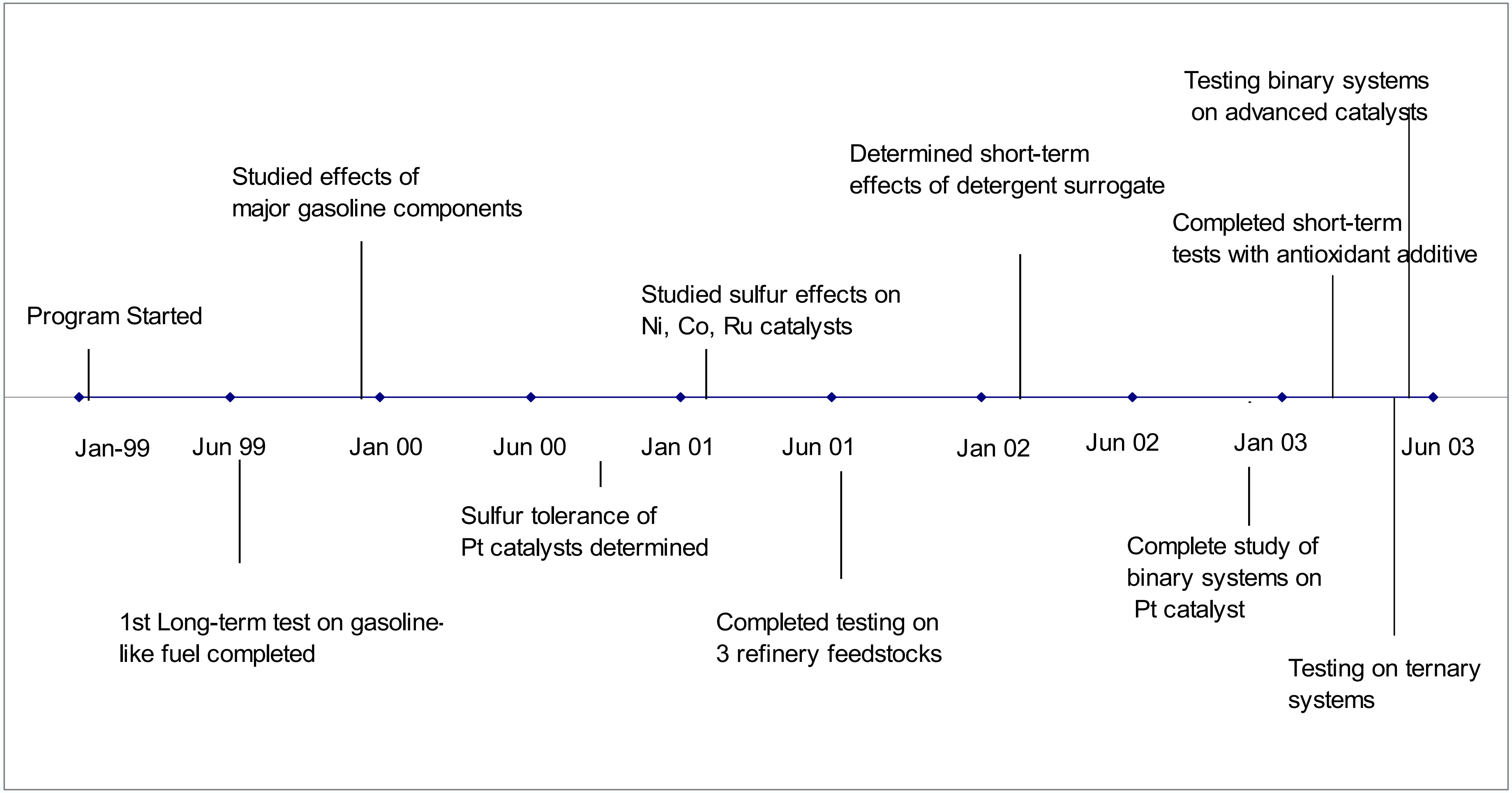
Objective: Evaluate effect of the fuel composition on H_2 yield

- Determine effects of major constituents, additives, and impurities in petroleum fuels on fuel processor performance and durability
- Collaborate with major oil companies for development of future fuels for fuel cells

Fuel composition affects many technical targets/barriers

- Fuel processor efficiency (barrier M)
- Processor durability (barrier J)
- Power density
  - Catalyst volume
  - Catalyst weight
- Costs (barrier N)
- Emissions (barrier K)

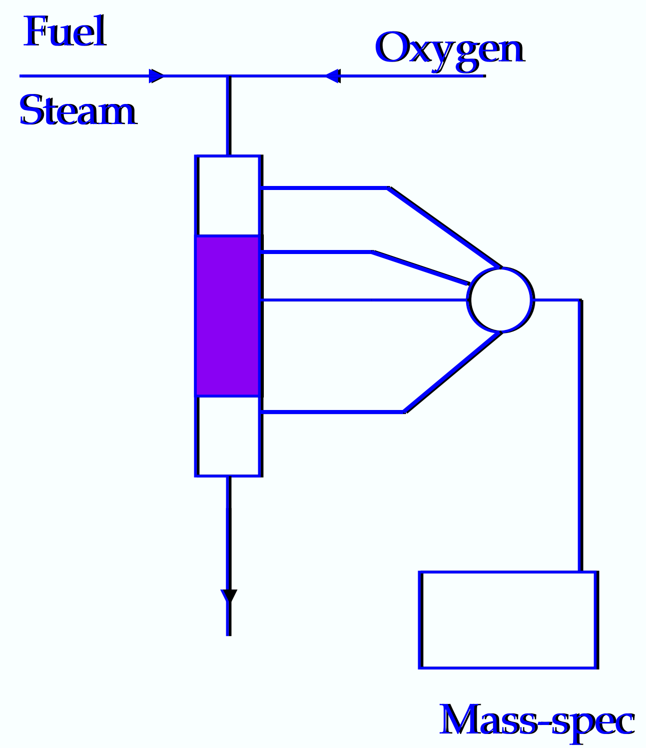
Timeline



Testing binary systems
on advanced catalysts
Determined short-term
effects of detergent surrogate
Studied effects of
major gasoline components
Completed short-term
tests with antioxidant additive
Studied sulfur effects on
Ni, Co, Ru catalysts
Program Started
Jan-99
Jun 99
Jan 00
Jun 00
Jan 01
Jun 01
Jan 02
Jun 02
Jan 03
Jun 03
Sulfur tolerance of
Pt catalysts determined
Complete study of
binary systems on
Pt catalyst
1st Long-term test on gasoline-
like fuel completed
Completed testing on
3 refinery feedstocks
Testing on ternary
systems

Experimental approach

- Determine product gas composition dependence on temperature and space velocity using a microreactor
  (relates to targets for reforming efficiency, and GHSV)
  - test minor components, additives, and impurities as isooctane solutions
  - test blends of fuel components
  - test real-world fuels from refineries



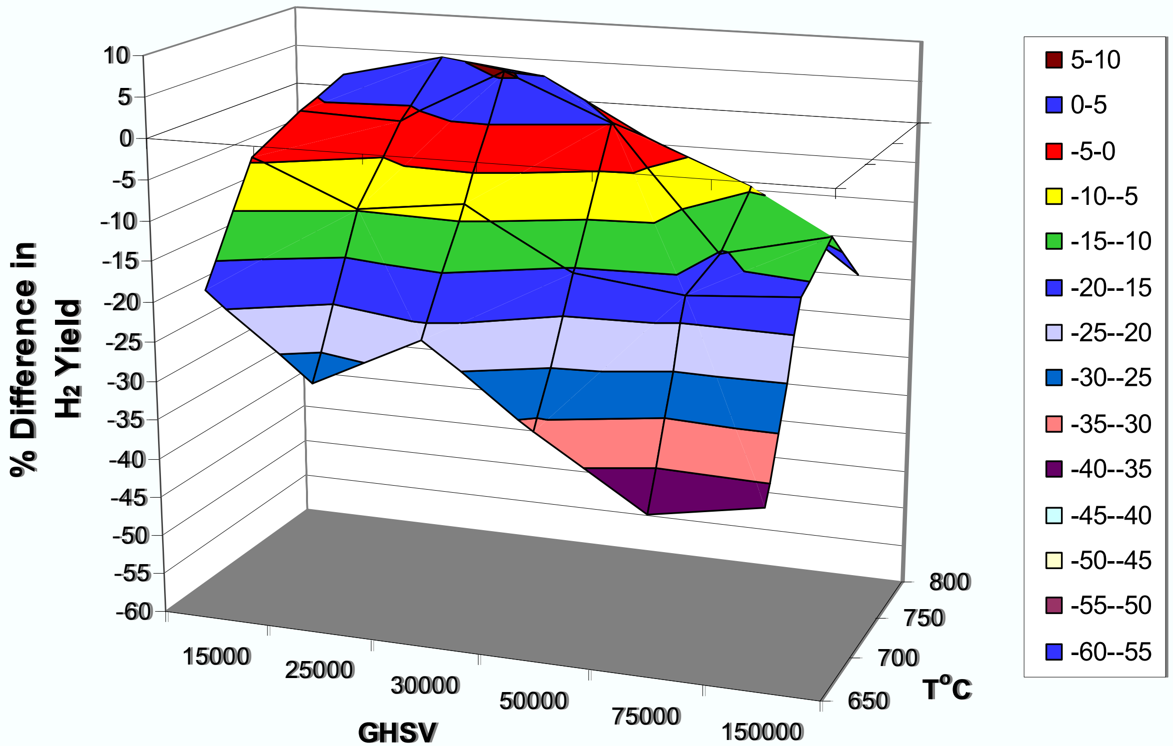
- Long-term testing (1000h)
  - determine poisoning, long-term degradation effects

Additive and impurity studies

- Phenol used as surrogate for hindered-phenol class of antioxidants
- Ethanol used as oxygenate additive
- Pyridine used to investigate effects of N-containing heterocyclic impurities
- Benzothiophene used to investigate S effects
- Held O_2:C ratios constant at 0.42
- Held H_2O:C ratios constant at 1.4
- Varied temperature and GHSV

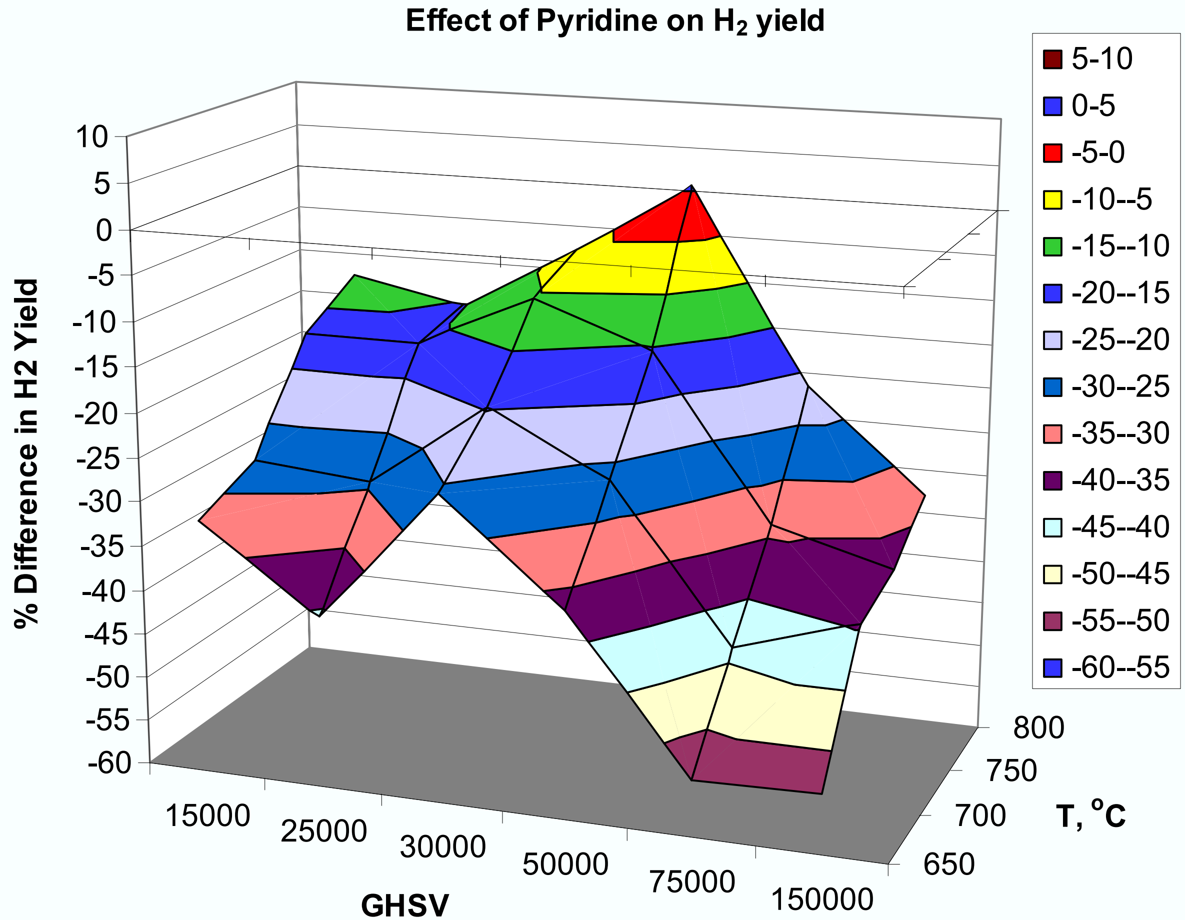
Antioxidant had little effect on H_2 yield from isooctane reforming at high temperature and GHSV < 50,000 h^{-1}

- H_2 yields decreased at high GHSV or low temperature
- Poorer H_2 yields due to increased breakthrough of heavier cracking products



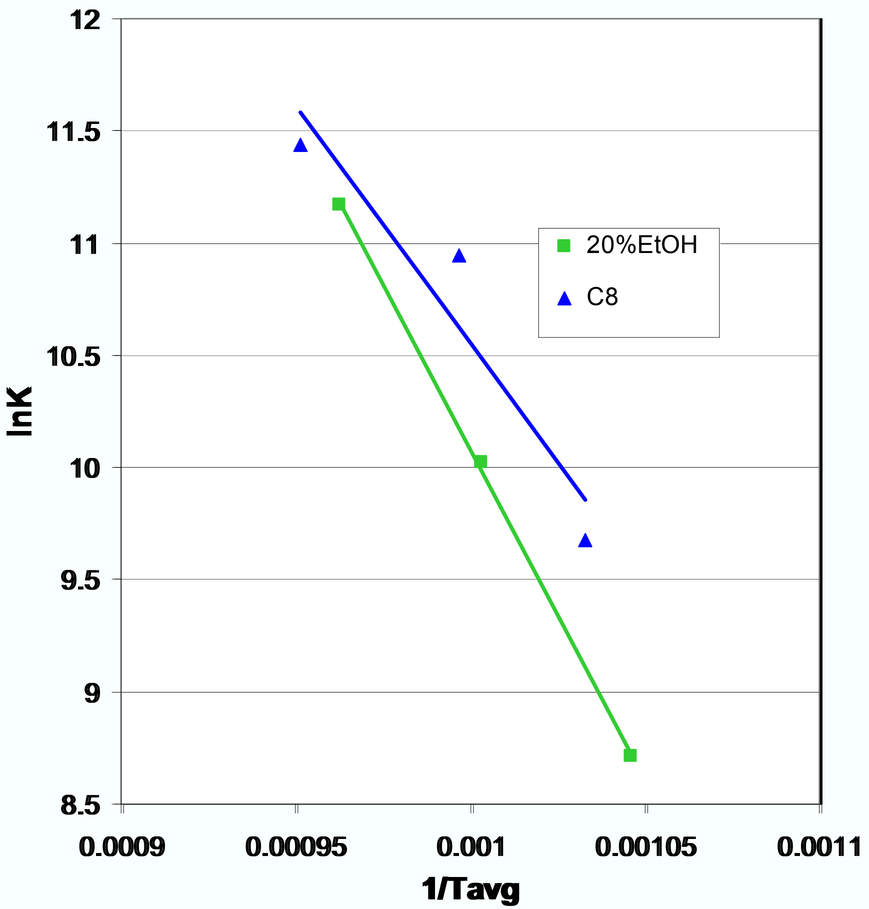
Pyridine decreased H_2 yields substantially under most conditions

- 50 ppm pyridine decreased H_2 yield from isooctane by >10% over most of the parameter space investigated



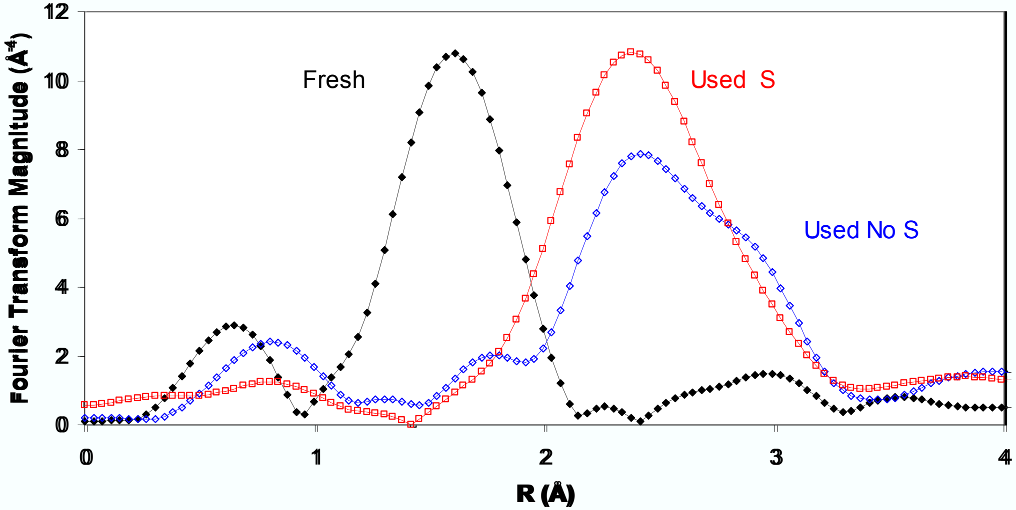
Ethanol decreased the rate of reforming of isooctane at low temperature

- First-order rate constants for decay of C4 species for isooctane-ethanol mixtures are less than those for pure isooctane when corrected to the average catalyst temperature



Long-term tests suggest sulfur affects Pt sintering

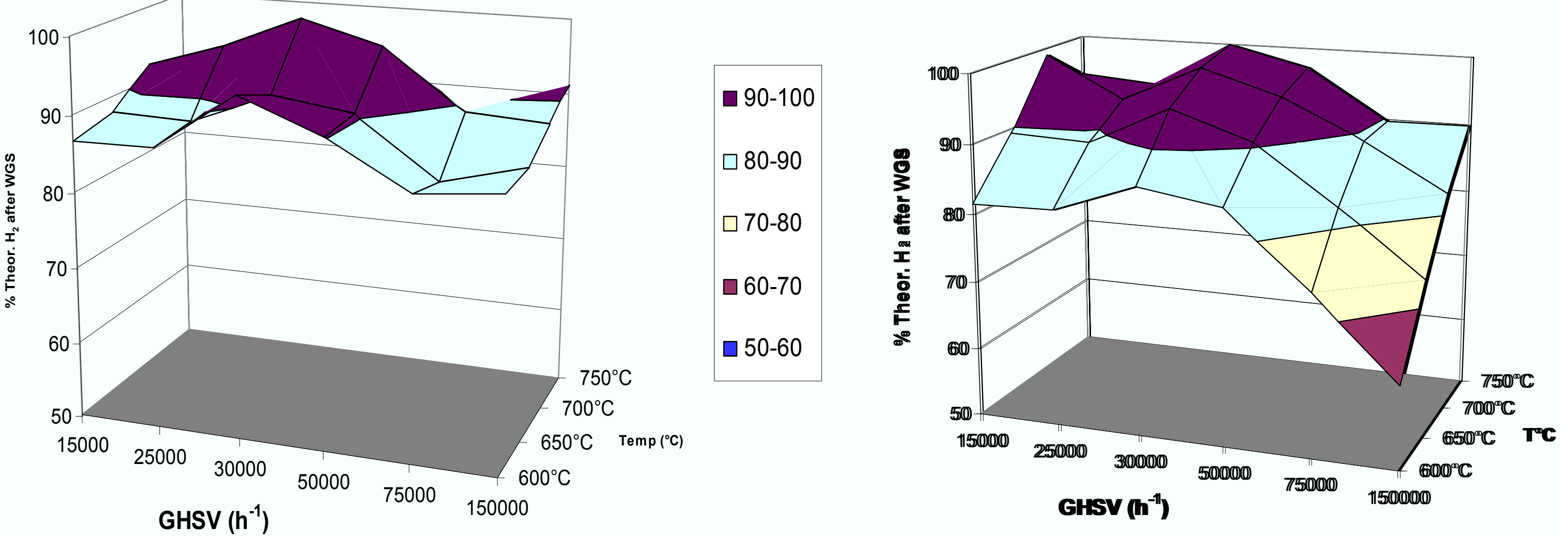
- EXAFS analysis of catalysts after reforming suggests sintering is more prevalent when S is present
  - Fresh sample Pt-O distance and adsorption energy match that for PtO_2
  - Large shift in adsorption energy and Pt-O distance for sample with S indicates no PtO_2 present.
  - Sample with S indicates larger Pt-Pt coordination number



Sample	Shell	N	R (Å)	ΔE (eV)
Fresh	Pt-O	6.0	2.07	0.1
Used - no S	Pt-O	1.0	2.14	0.4
	Pt-Pt	9.6	2.78	0.0
Used - S	Pt-O	1.4	2.29	10.8
	Pt-Pt	12.0	2.76	0.2

Aromatic or naphthenic components decreased H_2 production at high GHSV or low temperature regardless of catalyst

% Theoretical H_2 Yield after WGS from Reforming over Bimetallic Catalyst

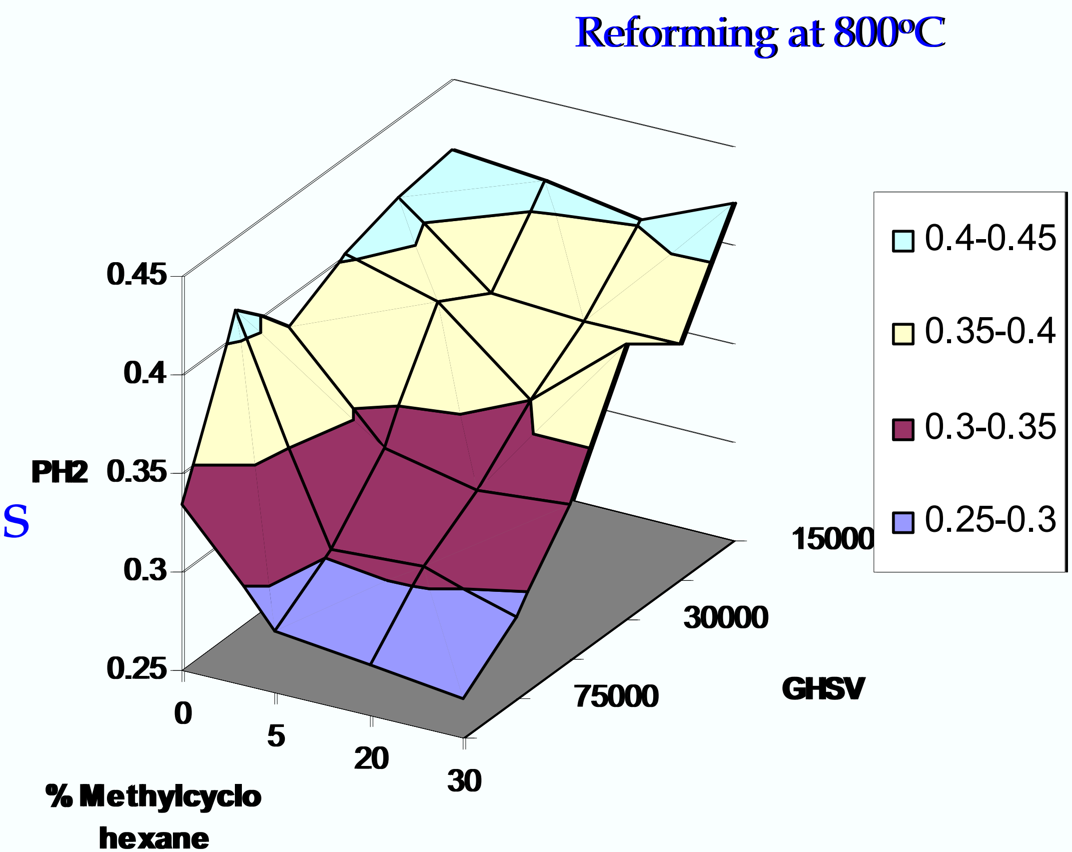


Isooctane **Isooctane+20% Xylene**

- Observe decreased H_2 production at low temperature and high GHSV due to slower kinetics for paraffin reforming with mixtures for Pt catalyst and bimetallic catalyst
- Effects are reduced in magnitude and shifted to lower temperature for more active catalysts

Ternary blends indicate complex relationship between composition and performance

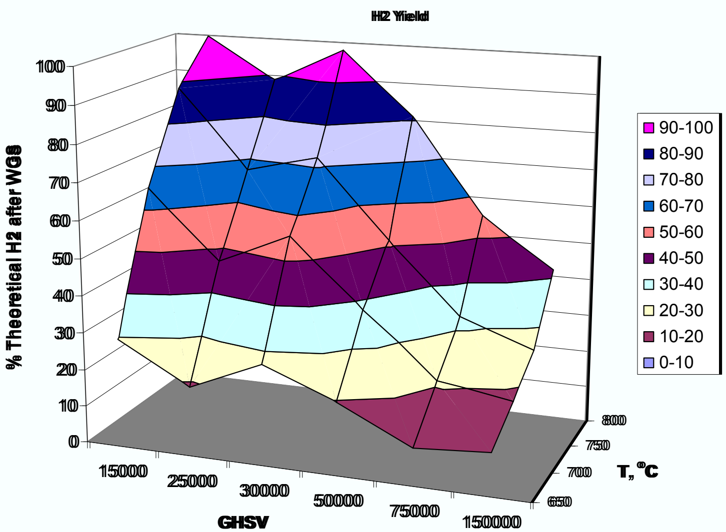
- Dependence of hydrogen yield on methylcyclohexane content in blends of isooctane, xylene, and methylcyclohexane was found to be highly nonlinear



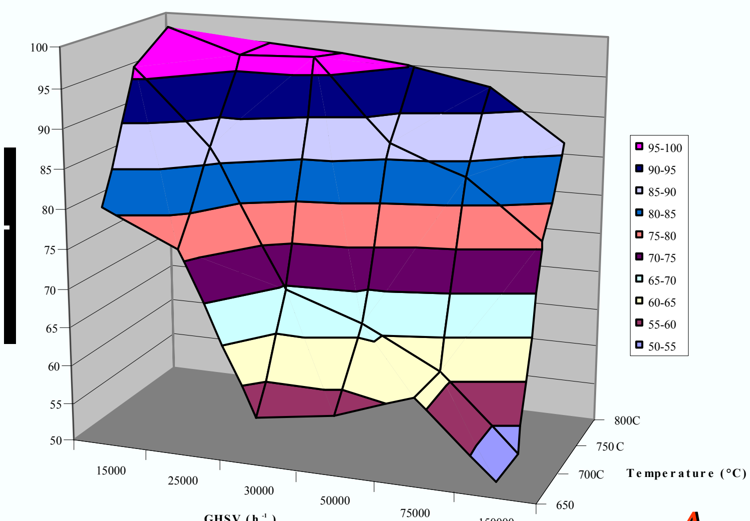
Refinery streams high in naphthenic components reformed poorly

- Naphthenic fuel reforms poorly except at high temperature and low GHSV

Naphthenic Fuel

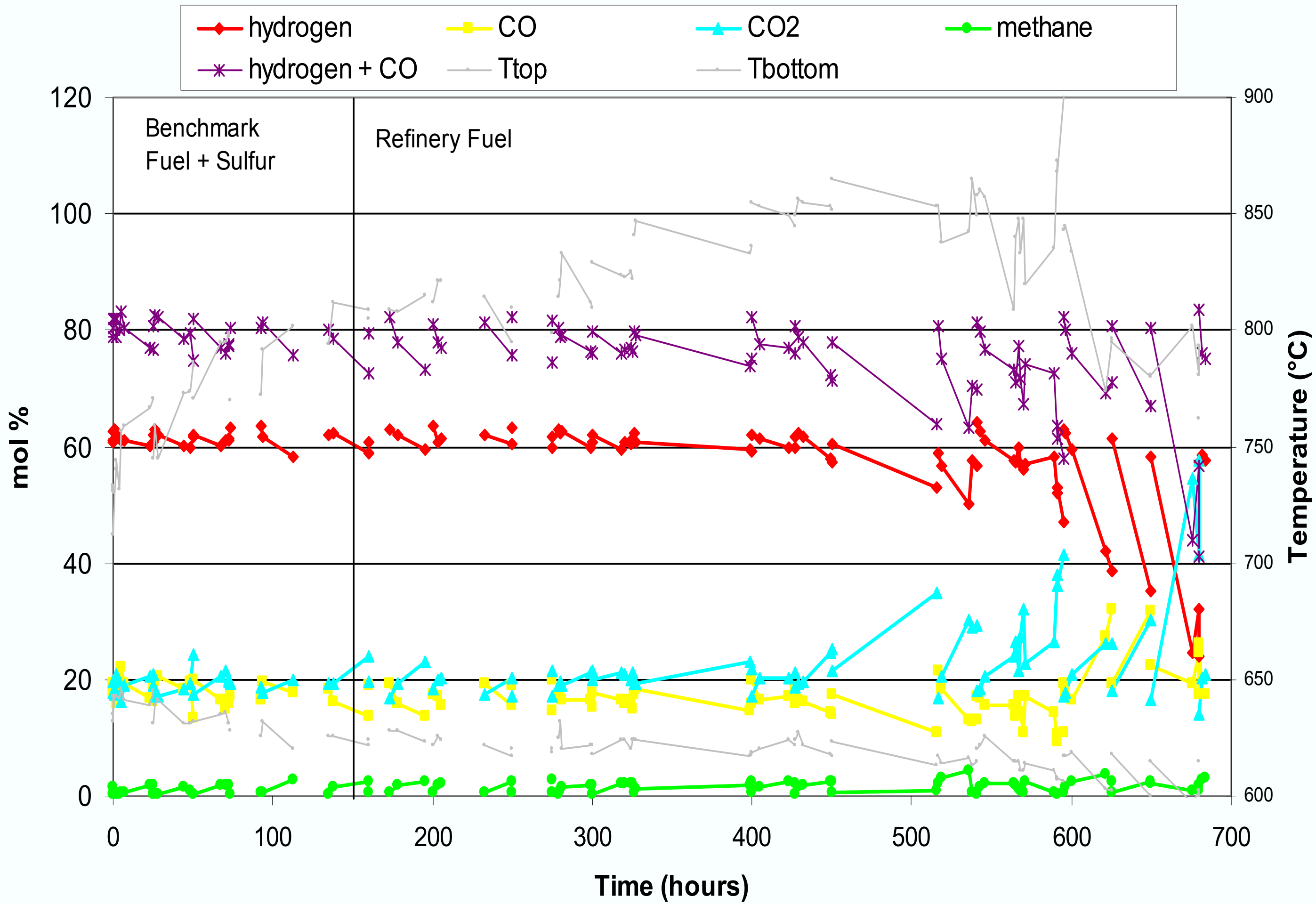


Paraffinic Fuel

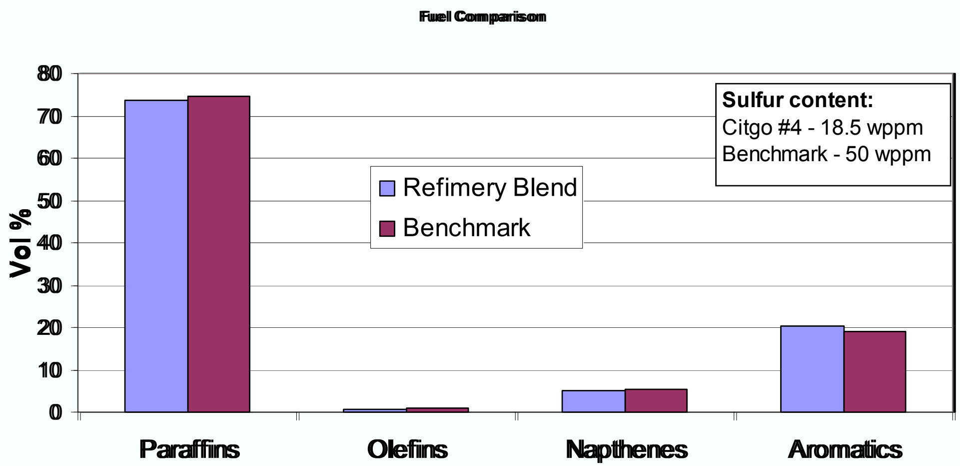


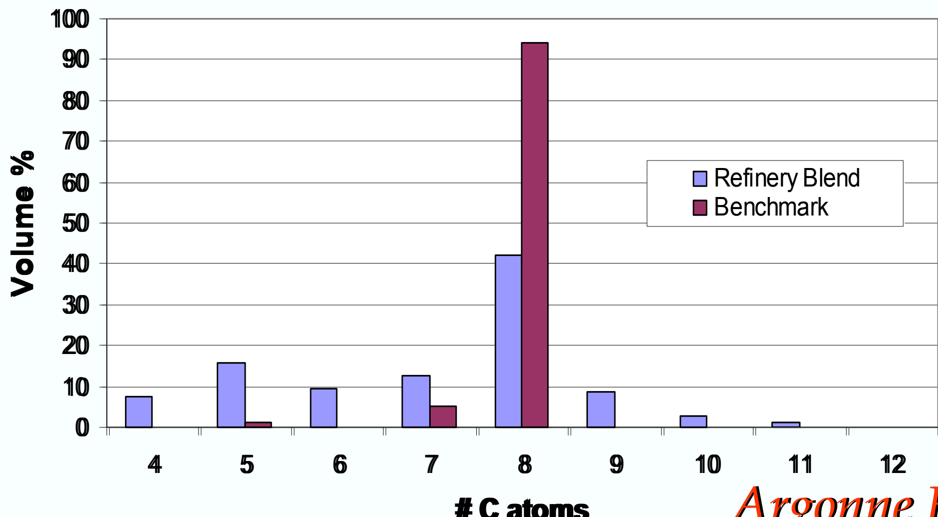
Paraffinic fuel provides good H_2 yield over a wider range of temperature and GHSV

Long-term testing of gasoline shows problems developed after ~600h on-line



Main difference between Refinery blend and benchmark fuel is the size of the chains/rings





Results suggests chain length may affect reforming

Size also impacts transport properties

We are investigating mass transfer effects

Conclusions

- Fuel composition can have substantial effects on reforming
- Fuel components compete for reaction at catalyst sites
- Kinetic rates decreased when more strongly adsorbing species are present

Future Work

- Have initiated testing of gasoline plus commercial additives in engineering scale reactor
  - Liquid injection capability which allows for delivery of high molecular weight polymeric additives
- Investigate reforming of binary/ternary mixtures with advanced catalysts
- Investigate effects of additives with advanced catalysts
- Investigate long-term effects of antioxidant additives and heterocyclic impurities
- Modeling reforming of complex fuel mixtures

Milestones

- Complete long-term testing on detergent surrogates 12/02
  - Completed long-term test using secbutyl amine
- Complete short-term testing of oxygenate and antioxidant additive/surrogate 2/03
  - Completed testing using phenol as antioxidant surrogate
  - Completed testing using ethanol as oxygenate
- Complete testing of binary mixtures on 2 different catalysts 6/03
  - Completed testing on Pt based catalyst
  - Testing on bimetallic catalyst underway

Reviewers Comments

- … final resolution of the detergent issue will require real chemistry and direct injection of liquid fuel into the fuel processor to prevent fractionation and gum formation within vaporizer
  - Have initiated tests in reactor with direct liquid injection capability to test commercial detergent additive package
- Focus on development of fuel additives/compositions that can enhance fuel processor performance
  - We are investigating optimizing fuel composition with our industrial collaborators

Collaborations

- Industrial collaborations with major oil companies
  - PDVSA/Citgo
  - Shell
- Collaborations with catalyst producers
  - Süd-Chemie
- University collaborations
  - Royal Military College of Canada