Effects of Fuels/Contaminants on Reforming Catalyst Performance and Durability

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Argonne Electrochemical Technology Program

Program Objectives

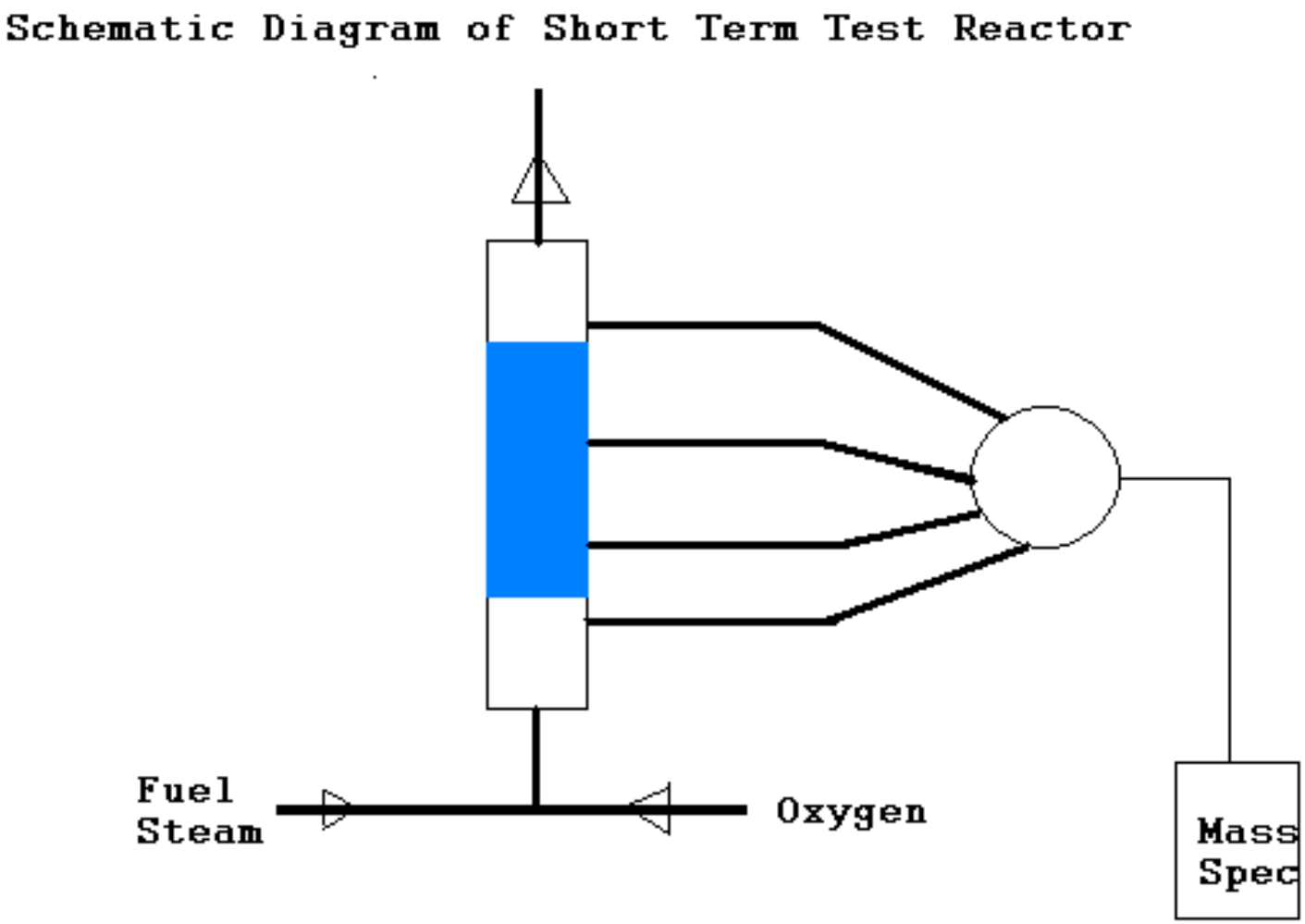
- Investigate differences in reforming of gasoline components to
  - identify problem compounds
  - identify beneficial compounds
- Evaluate the effects of fuel constituents and impurities (sulfur) on catalyst stability

Experimental Approach

- Determine product gas composition dependence on temperature, space velocity
  - test major fuel components individually
  - test minor components, additives, and impurities as isooctane solutions

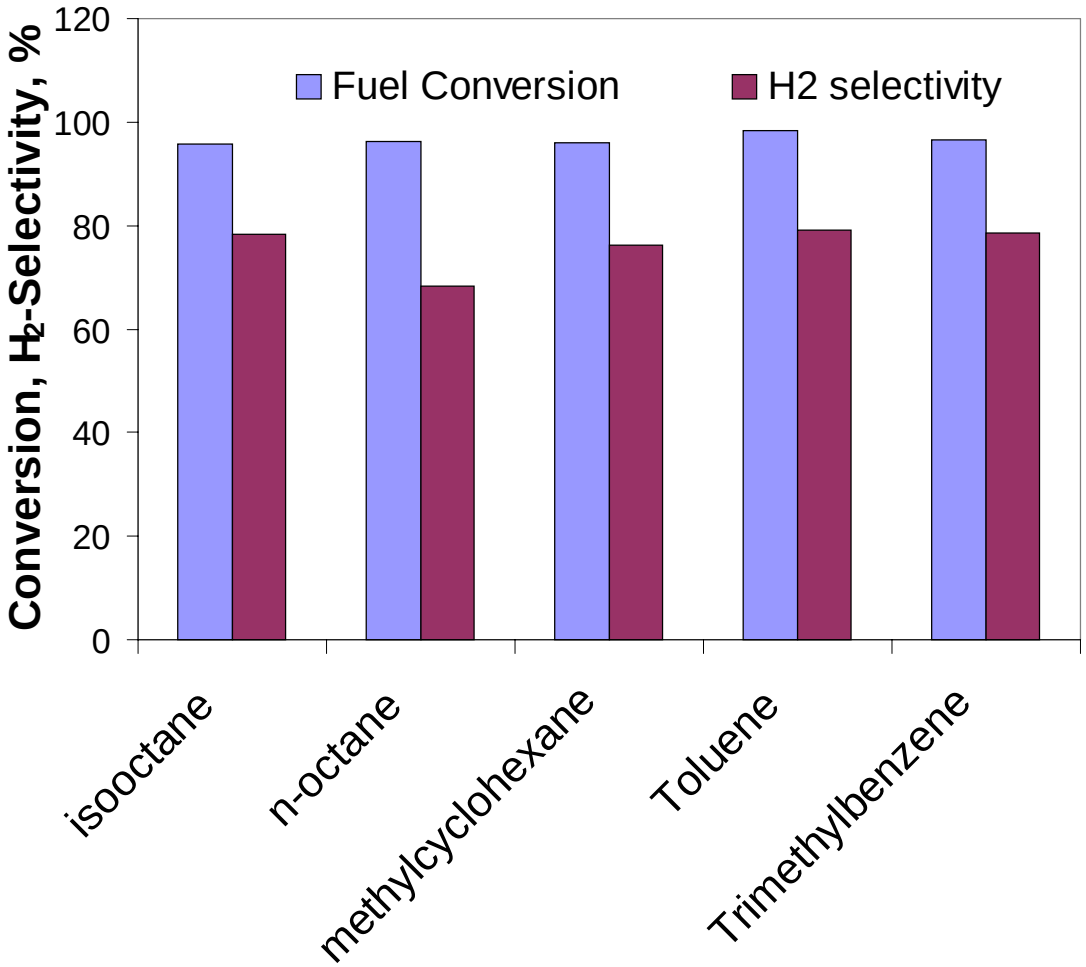
- Long-term testing (1000h)
  - determine poisoning, long-term degradation effects

The short-term test reactor is capable of sampling at various points



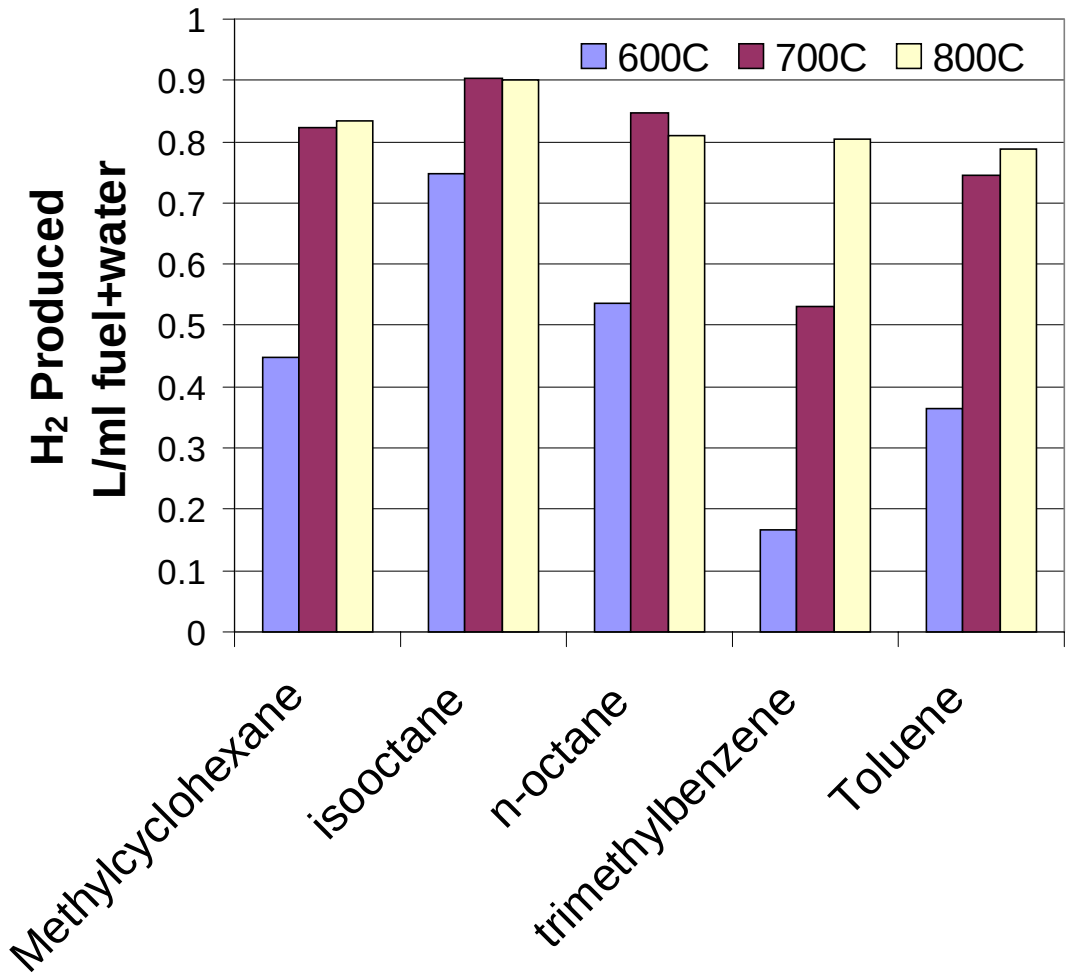
ATR unit can reform all major gasoline substituents at 800°C

- Conversion of all major substituents is >95%
- Hydrogen selectivity is lower for n-octane

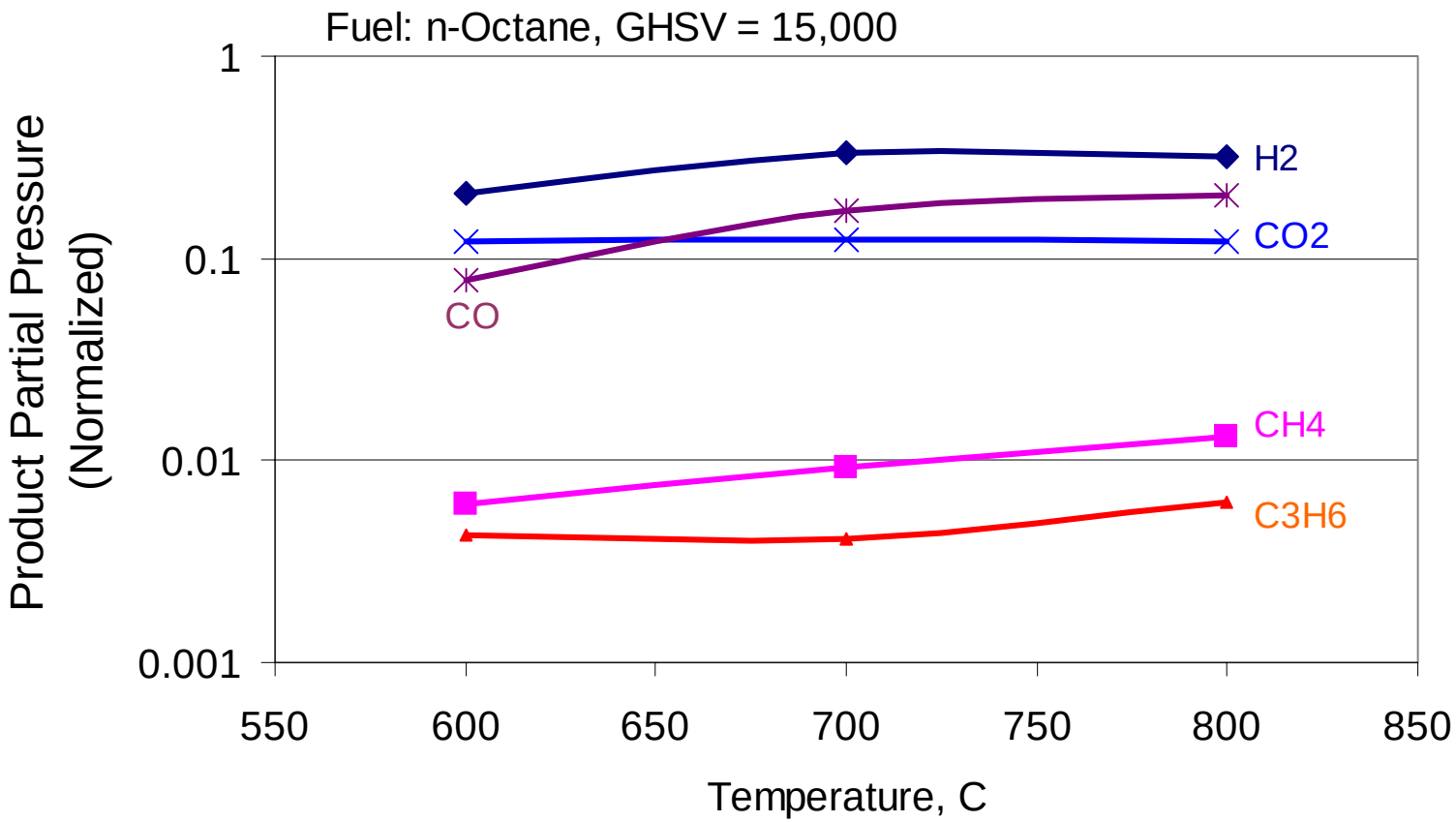


H_2 yield from trimethylbenzene is most sensitive to temperature

- Trimethylbenzene must be reformed at high temperature
- Isooctane reforms better than other components at low temperature

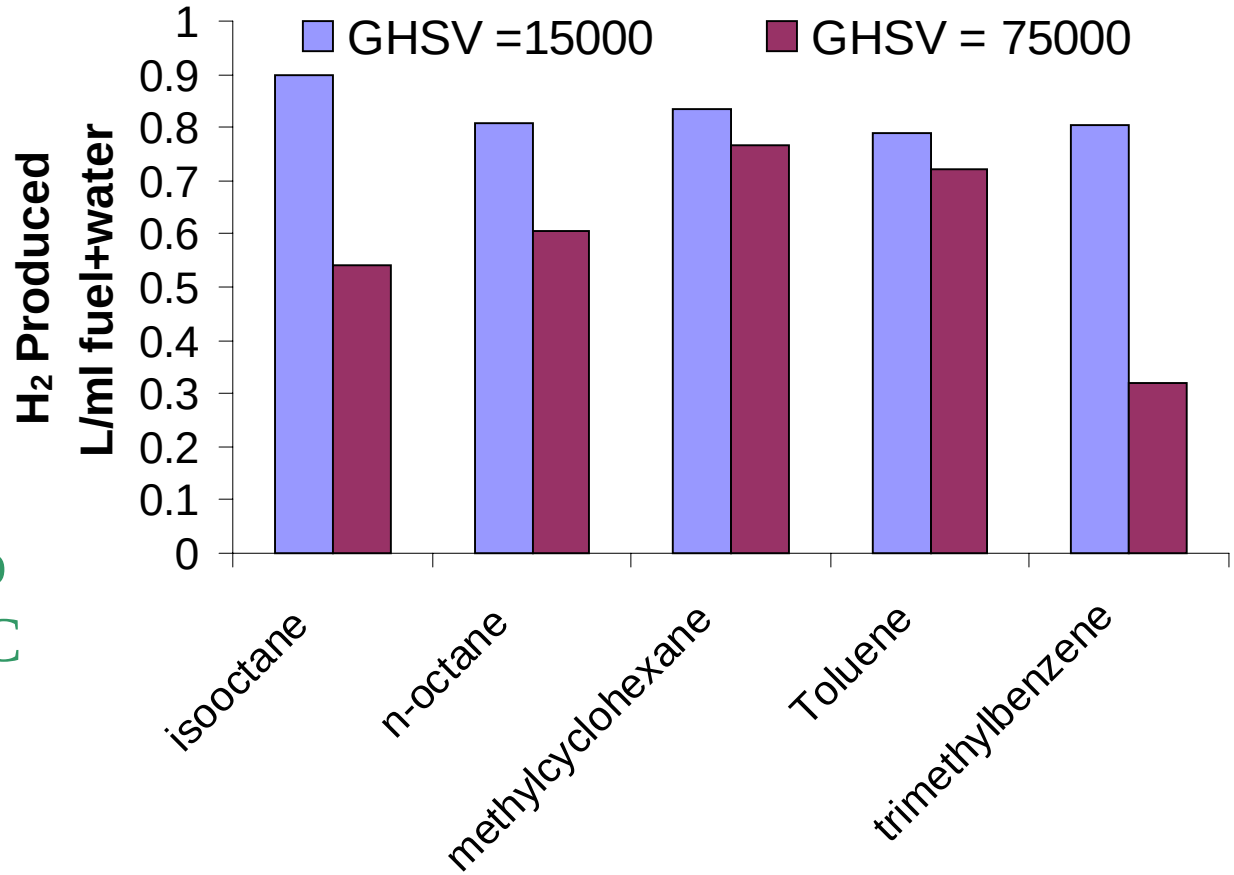


H_2 selectivity from n-octane decreases with increasing temperature

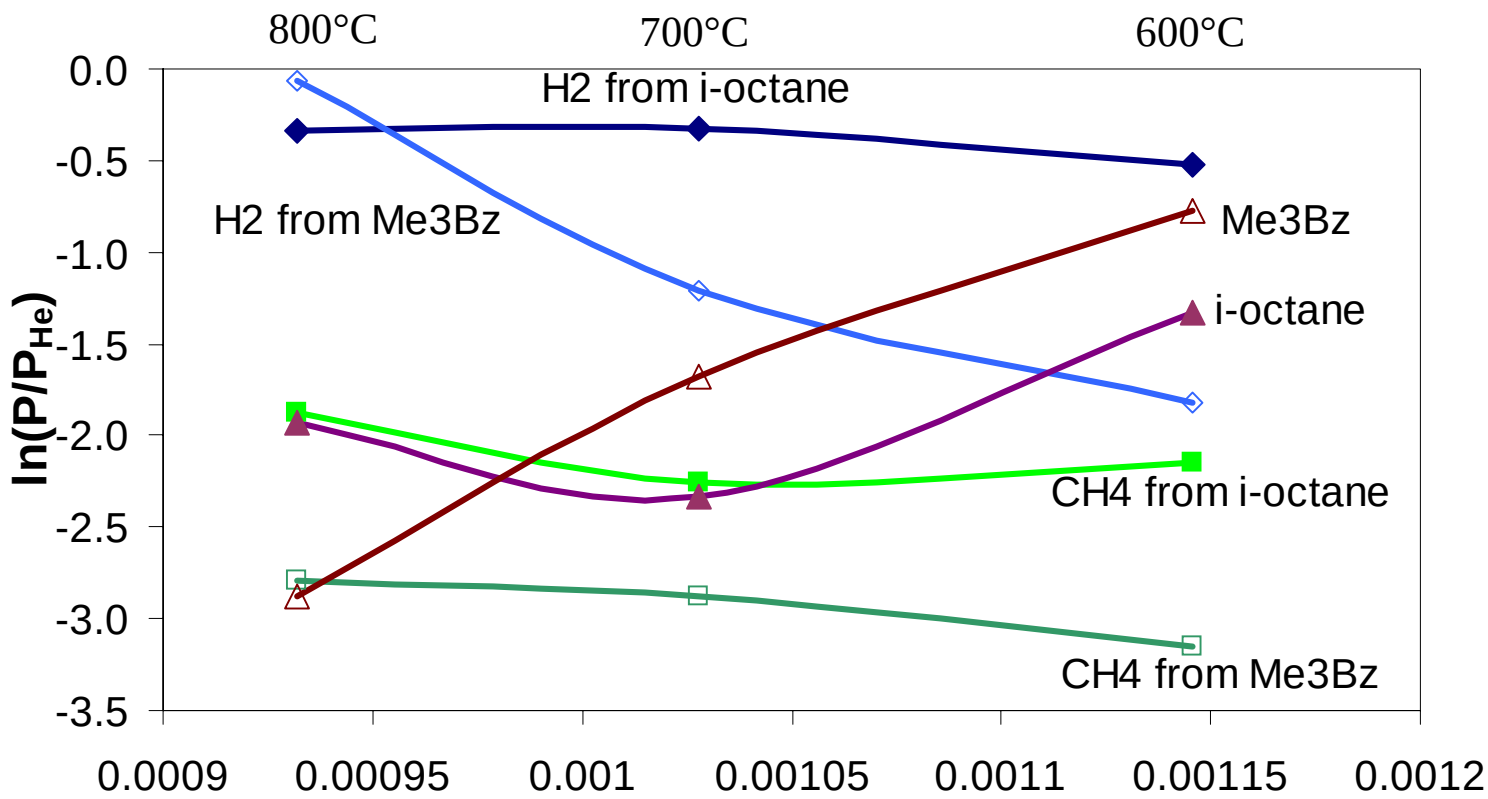


Hydrogen yield is highest from branched paraffins at low space velocities

- Rate of reforming of trimethylbenzene appears to be slower than that for other components
- methylcyclohexane and toluene appear to react rapidly at 800°C



Trimethylbenzene reforming decreases rapidly with decreasing temperature

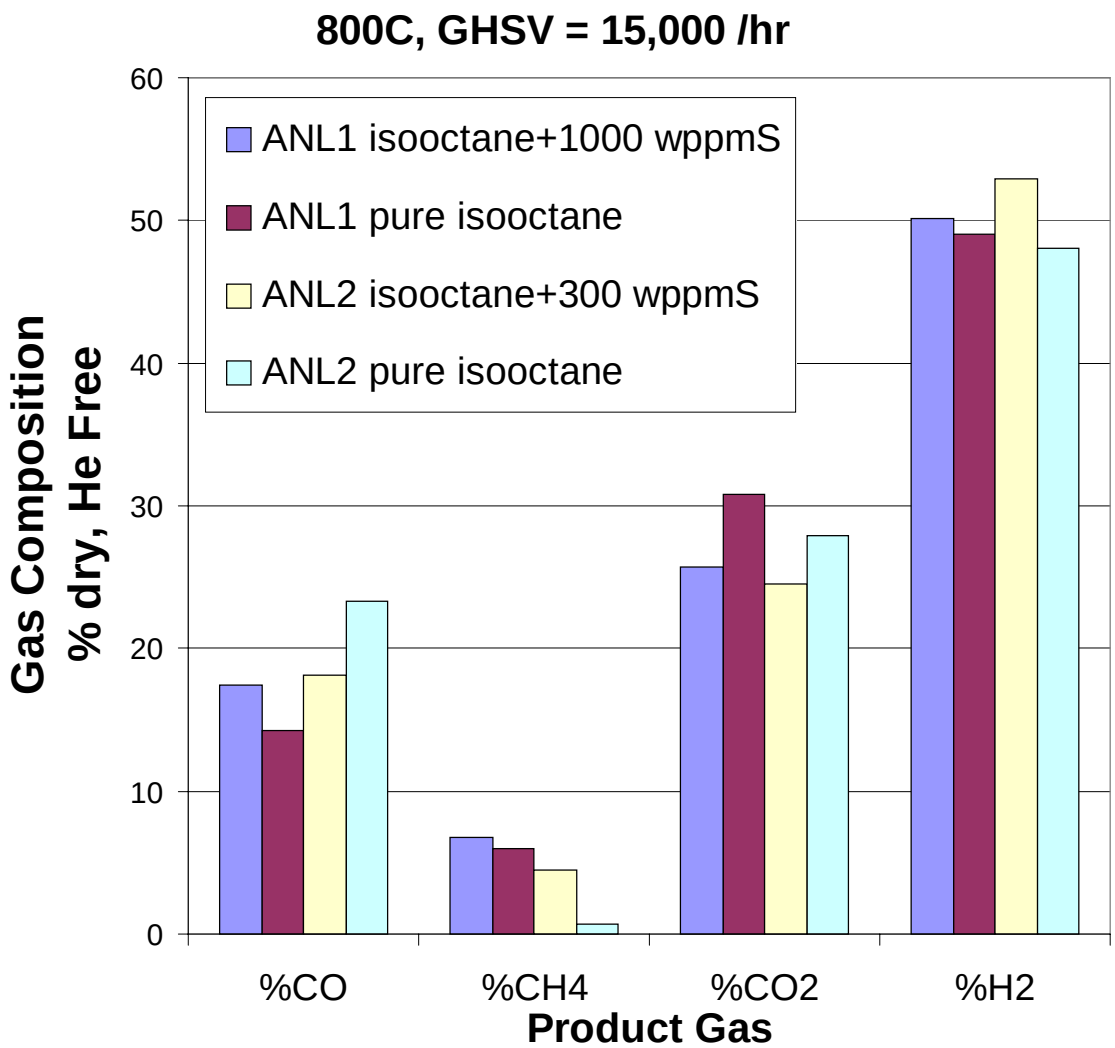


GHSV = 15000 /hr

Autothermal reforming of major gasoline components have been studied

- All major substituents can be reformed at 800°C
- Trimethylbenzene reforming requires high temperatures and low space velocities
- Methylcyclohexane and toluene can be reformed at high space velocity at 800°C
- Isooctane reforms better than other components at low temperature

Sulfur impurities increased hydrogen yield from ANL catalysts

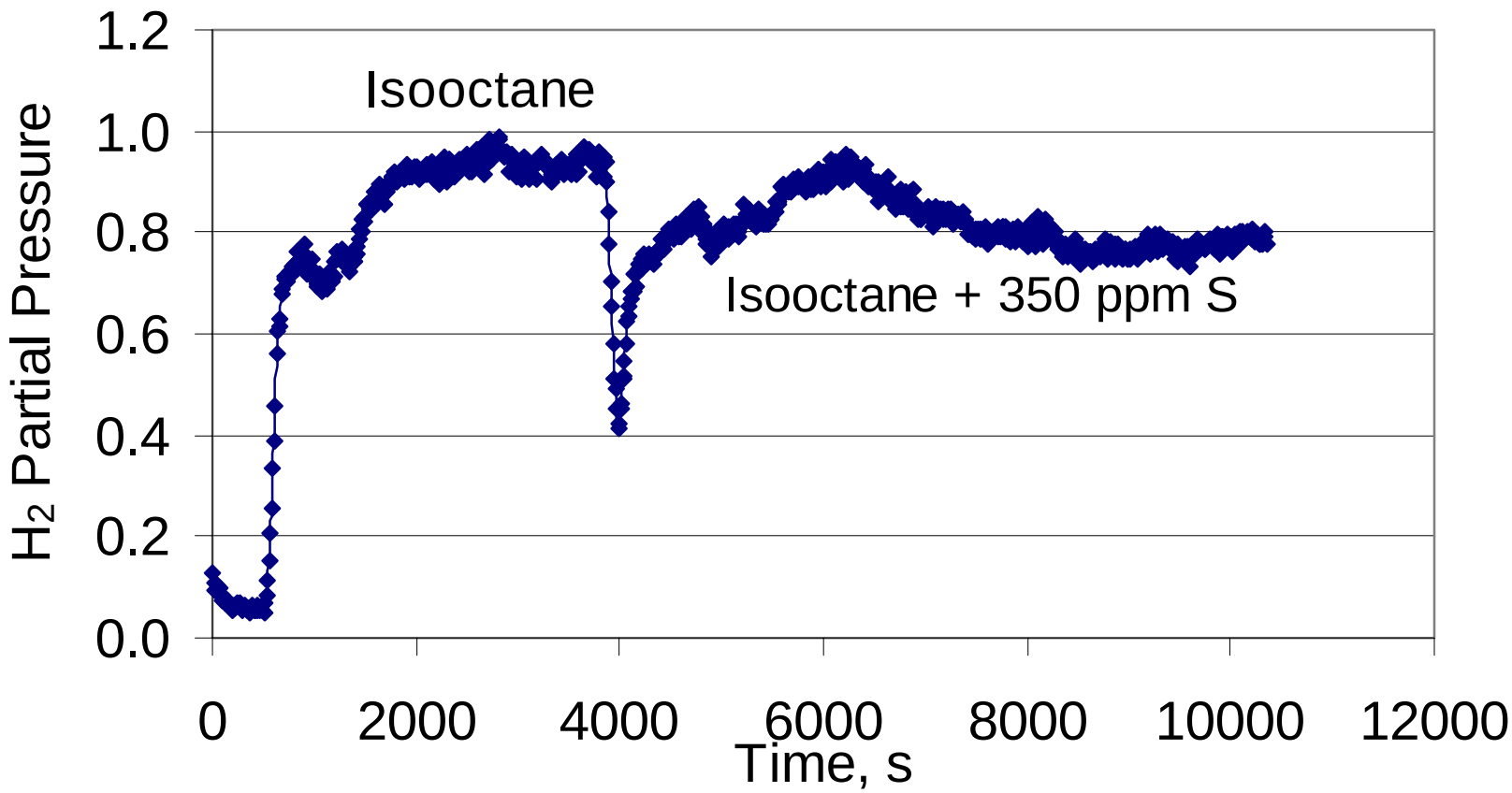


Some sulfur remains on the catalyst

Sulfur in Fuel (wppm)	*S on catalyst after reaction (wt.%)*
300	0.02
1000	0.04

- Sulfur found in reformate gas as H_2S

Short term tests with sulfur containing fuels show some loss in activity of Ni ATR catalyst

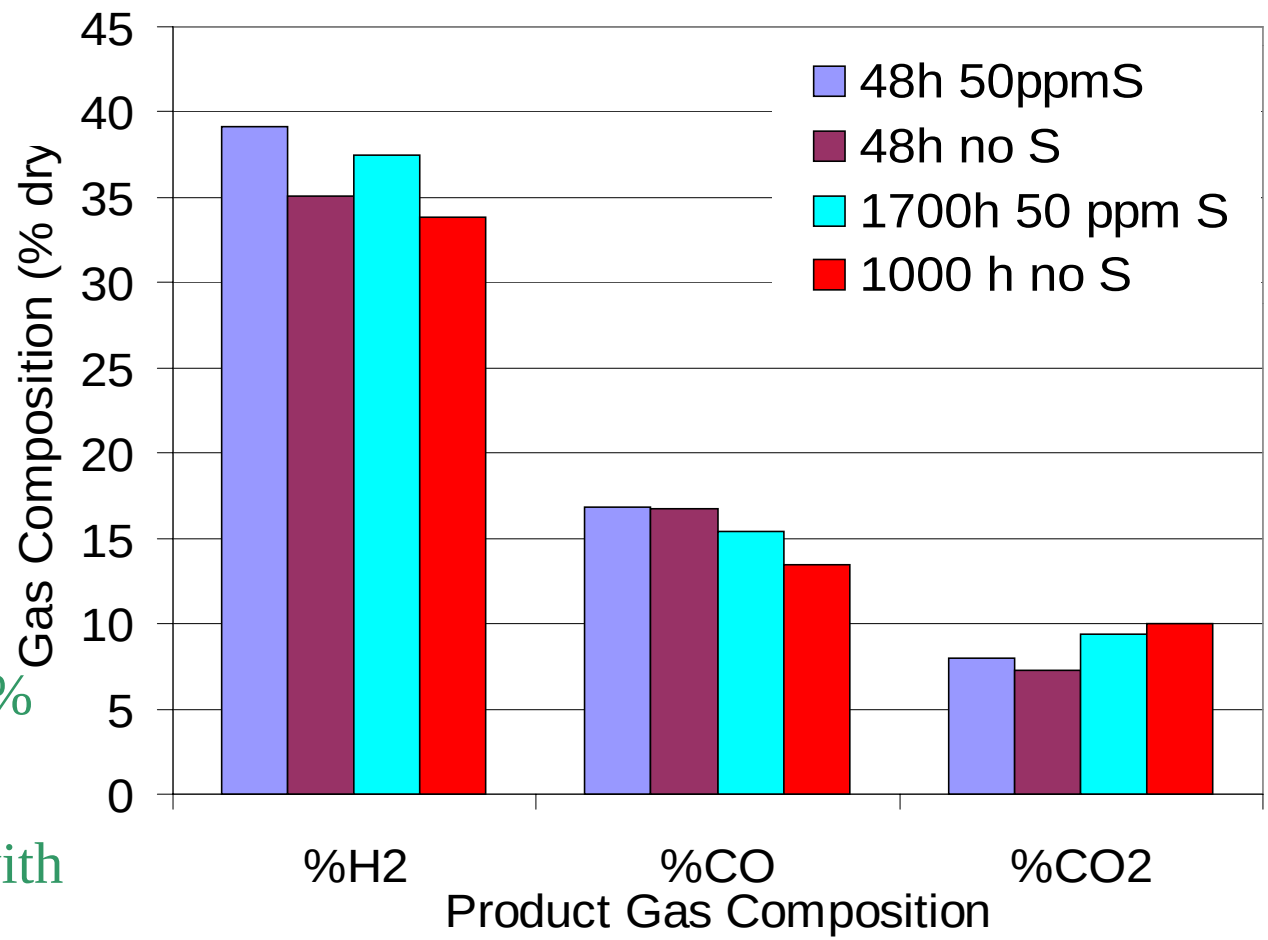


Sulfur containing fuel showed 5% loss in H_2 yield after 1700 hrs

- 750-790°C
- GHSV= 5169/h
- Benchmark Fuel + S
  - (50 wppm)
- 1700h

Results

- No decline in CO_x
- ~5% decline in H_2
- H_2 selectivity: 88-85%
  - (40-38% H_2 dry)
- More H_2 from fuels with sulfur



Effects of S impurities are dependent on catalyst

- Sulfur improved hydrogen production from Pt-containing ATR catalyst
- Sulfur poisoned Ni-containing ATR catalyst
- Long-term tests with S impurities indicate little degradation of Argonne Catalyst

Future Work

- Investigate sulfur effects further
  - Sulfur XANES investigation of catalyst at University of Louisiana
  - Investigate kinetics of sulfur effects
- Investigate effects of additives
- Continue collaboration with petroleum companies on future fuel-cell gasoline
- Synergistic effects

Conclusions

- Trimethylbenzene is undesirable in a fuel cell gasoline
  - has lower hydrogen density, requires high temperature, long contact times
- Sulfur effects are dependent on catalyst
  - improves H_2 production from Pt-containing ANL catalyst

Industry Collaborations

- Syntroleum
  - Evaluated reformability of Fischer-Tropsch fuels

    [S. Ahmed, J.P. Kopasz, B.J. Russell, H.L. Tomlinson Proceedings of the 3rd International Fuel Cell Conference, Nagoya, Japan, 1999]
- UOP, BP-Amoco, Exxon-Mobil
  - Continuing discussions on fuel chemistry, future fuels for fuel cells

Responses to Previous Reviewers

- Several reviewers indicated need for further interaction with petroleum industry
  - We now interact with BP-Amoco, Exxon-Mobil, Syntroleum, and UOP on fuels issues
- Too much emphasis on fuels analysis
  - Fuels analyses were needed to identify principal gasoline constituents for current work

Timeline/Milestones

- Program initiated - 5/99
- Completed first 1000h test - 9/99
- Recommended reference benchmark fuel - 10/99
- Completed second long-term test reactor - 2/00
- Tests completed on 5 gasoline components - 4/00

Timeline/Milestones

- Define alternative fuel blend(s) as standard reformer "gasoline(s)" -7/00
- Test 3 major gasoline additives -7/00
- Complete 1000h tests on four catalysts -7/00
- Identify problem contaminants and constituents in FTP gasoline - 9/00