

Effects of Fuel Constituents on Fuel Processing Catalysts

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Objectives

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

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- E. Durability
- K. Emissions and Environmental Issues
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Investigate reforming the major components of gasoline under controlled conditions in a microreactor.
- Determine the dependence of product gas composition on temperature and space velocity.
- Test simple mixtures of components, impurities, and additives to determine their synergistic or poisoning effects.
- Test complex refinery blends to determine which streams are most attractive for on-board reforming.
- Conduct long-term (1000-h) tests to determine catalyst poisoning and other degradation effects over time.

Accomplishments

- Determined that antioxidant additives have little or no effect on reforming at temperatures $\geq 750^\circ\text{C}$ and gas-hourly space velocities (GHSVs) $\leq 50,000 \text{ h}^{-1}$; however, they can decrease hydrogen yield at lower temperatures or higher GHSVs.
- Discovered that pyridine decreases the rate of isooctane reforming, even at 800°C .
- Examined reforming refinery streams and refinery blends supplied by major oil companies.
- Investigated the long-term effects of detergent additives on reforming.
- Developed an understanding of reforming binary mixtures in terms of the effects of competition for the limited number of active sites on the catalyst.
- Demonstrated that aromatics and naphthenes decrease the rate of reforming of isooctane on advanced bimetallic catalysts, as well as on Pt-based catalysts.

Future Directions

- Investigate the long-term effects of antioxidant additives and heterocyclic impurities.
- Develop a reforming model that can predict the performance of complex fuel mixtures.
- Investigate reforming binary/ternary mixtures and additives with advanced catalysts.

Introduction

Fuel cell vehicles offer the potential for very low emissions and high fuel economies. Efficiency and emissions, however, are affected by the fuel used. With hydrogen as the on-board fuel, the lowest vehicle emissions (zero) and the highest fuel economy can be obtained. In the absence of a hydrogen production, delivery, and marketing infrastructure, on-board reforming of hydrocarbon fuels (e.g., gasoline) is a potential transitional solution for the near-term introduction of fuel cell vehicles. The goals of this project are to identify the desirable and undesirable constituents of gasoline and develop specifications for a hydrocarbon fuel especially suitable for fuel cell vehicles.

Our previous work indicated that there are significant differences in how readily the major types of hydrocarbons in gasoline (paraffinic, aromatic, naphthenic, and olefinic) can be reformed.^{1,2} Tests on refinery blends indicated that fuels high in aromatic content were more difficult to reform and that aromatics affected the rate at which paraffinic species could be reformed.² We have expanded our study to investigate the effects of gasoline additives and impurities on reformer performance.

Approach

The reformability of various fuel mixtures was measured at Argonne National Laboratory (ANL) under autothermal reforming conditions. These studies were conducted at 600-800°C and GHSVs between 15,000 and 150,000 h⁻¹ (corresponding to reactor residence times of approximately 200 to 20 milliseconds) and involved various blends of isooctane with aromatic, naphthenic, N-containing heterocycle, and oxygenate compounds, as well as surrogates for the additives used in gasoline.

Results

Antioxidants. We investigated the reforming of isooctane-phenol solutions over a Pt-ceria-based catalyst to determine the effects of phenol-based antioxidants. The phenol concentration was ~100 ppm, an order of magnitude higher than in gasoline, to accelerate catalyst degradation. A comparison of the product gas compositions from reforming these solutions at 800°C and various space velocities is shown in Figure 1. The hydrogen content of the product gas decreased with the addition of phenol for GHSV >50,000 h⁻¹. In addition, CO levels decreased throughout the GHSV range. Hydrogen yields for pure isooctane and isooctane + phenol were close to the theoretical maximum yields at 750 and 800°C and GHSVs below 50,000 h⁻¹, but dropped off with decreasing temperature. The decrease accelerated with the phenol additive.

A plot of the difference in the H₂ yield between isooctane and isooctane + phenol as a function of

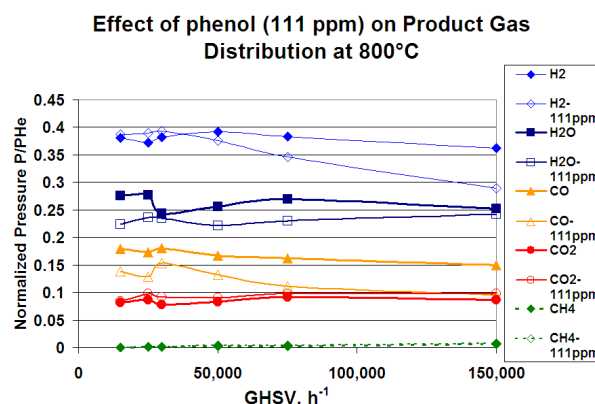


Figure 1. Product Gas Compositions from Reforming Isooctane and Isooctane + 111-ppm Phenol over a Pt Catalyst at 800°C for Various Space Velocities

temperature and GHSV is shown in Figure 2 (% difference = $(P_{H_2(C8+phenol)} - P_{H_2(C8)})/P_{H_2(C8)} \times 100$).

This plot shows that the additive had no effect on hydrogen yield at 750 to 800°C and 15,000 to 50,000 h^{-1} GHSV. However, the phenol additive decreased the hydrogen yield at higher space velocities or lower temperatures. This is partly due to a decrease in the rates of feed hydrocarbon breakdown. With pure isooctane, no hydrocarbons higher than C6 were observed in the product gas, whereas with phenol present, fragments as large as C₇H₁₅ were observed.

Heterocyclic impurities. The effect of pyridine, a nitrogen heterocyclic impurity in gasoline, was investigated by reforming mixtures containing 50-ppm pyridine in isooctane. The difference in hydrogen yield with and without pyridine is shown in Figure 3. The hydrogen yield decreased substantially over most of the operating space, even at high temperatures and low space velocities.

Fuel composition. Our previous work had shown that aromatic and naphthenic constituents decreased the rate of reforming isooctane over a Pt-ceria-based catalyst.^{2,3,4} To determine if this is true for autothermal reforming in general, we investigated the reforming of isooctane-xylene and isooctane-methylcyclohexane mixtures over a bimetallic Pt-Rh catalyst. This bimetallic catalyst has substantially higher activity than the Pt catalyst, yielding 80–90% of the theoretical maximum hydrogen yield at 600°C and 150,000 h^{-1} GHSV. In comparison, the Pt catalyst yielded less than 60% of the theoretical

maximum hydrogen at 650°C and the same GHSV. The bimetallic catalyst was tested for reforming isooctane, isooctane + xylene (20%), and isooctane + methylcyclohexane (20%).

The addition of xylene decreased the hydrogen yield at high GHSVs ($\geq 75,000 h^{-1}$) and low temperatures, as shown in Figures 4(a) and 4(b). Hydrogen yields fall below 90% of the theoretical maximum at 750°C and a GHSV of 150,000 h^{-1} . This decrease is believed to be due to competitive reactions at the catalyst sites. Aromatics interact more strongly with the metal centers and decrease the number of available reaction sites for the less strongly adsorbing paraffins. The naphthenes dehydrogenate to form aromatics, which then compete with the paraffins for the catalytic sites.

Conclusions

- Antioxidant additives in gasoline have been found to decrease hydrogen yield in the reformat, but only at high GHSVs and/or low reforming temperatures.
- Pyridine decreased hydrogen yield, even at low GHSV and high temperature.
- Aromatic and naphthenic components decreased the rate of paraffin reforming, even when using advanced bimetallic catalysts.

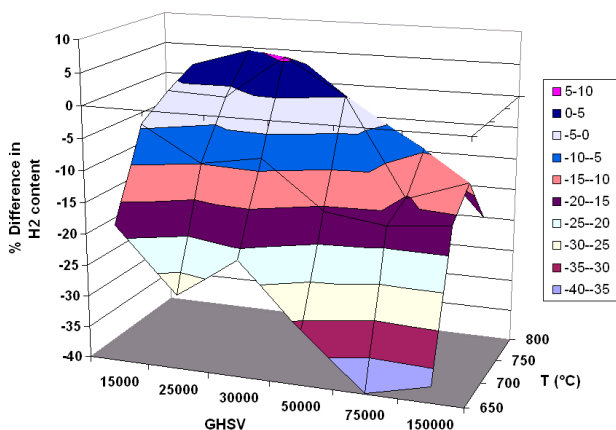


Figure 2. Difference in the H₂ Yield between Isooctane and Isooctane + Phenol as a Function of Temperature and GHSV

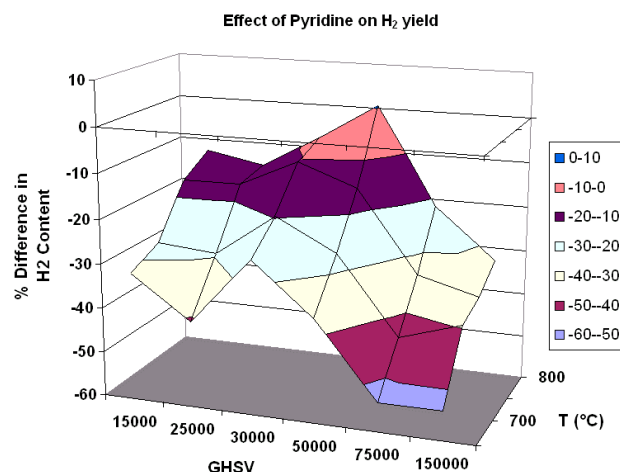


Figure 3. Difference in the H₂ Yield between Isooctane and Isooctane + 50-ppm Pyridine as a Function of Temperature and GHSV

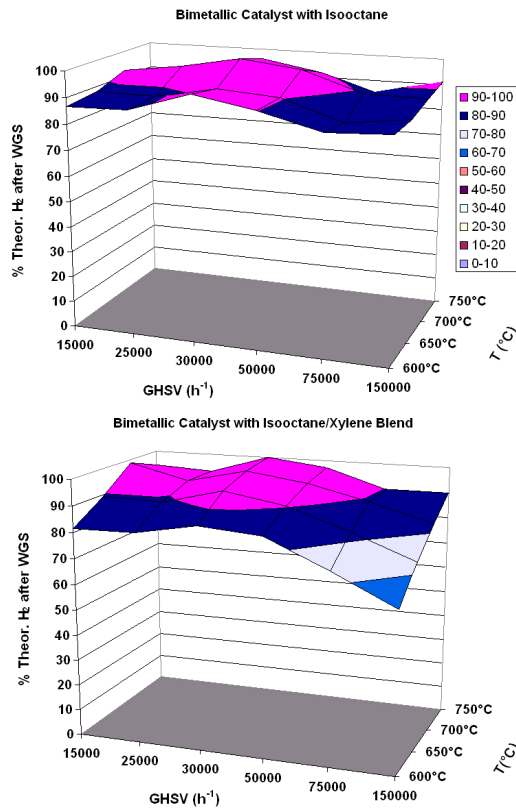


Figure 4. Hydrogen Yield as a Percentage of the Maximum Theoretical Hydrogen Yield Obtainable from Reforming (a) Isooctane and (b) Isooctane + 20% xylene over an Advanced Bimetallic Catalyst

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4. J. P. Kopasz, L. E. Miller, and D. V. Applegate, "Effects of Multicomponent Fuels, Fuel Additives, and Fuel Impurities on Fuel Reforming," SAE Future Transportation Technology Conference (2003).
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