

IV.F.11 Effects of Fuel Composition on Fuel Processing

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Objectives

- Determine how infrastructure fuel composition affects reformer performance
- Determine how to tailor fuel composition to improve performance

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 Research, Development and Demonstration Plan:

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

Approach

- Evaluate fuel composition effects on reforming
- Start with simple components and build up to complex fuels
- Investigate reforming in microscale and bench-scale reactors
- Perform short-term and long-term testing

Accomplishments

- Determined that ethanol addition to gasoline leads to higher methane slip
- Determined that addition of dimethylcarbonate improves hydrogen yield from isooctane-xylene mixtures [improved by 13% at 650°C at a gas hourly space velocity (GHSV) of 150,000 h⁻¹]
- Identified sensitivity of different types of hydrocarbons (in a mixture) to H₂O:C and O₂:C ratios [olefins decreased as (O₂:C)¹⁷ while aromatics decreased as (O₂:C)⁵]
- Identified formation of aromatics and growth of multi-ring species (from 2- to 3-ring complexes) during reforming

Future Directions

- Evaluate effects of renewable fuels such as biodiesel and ethanol
- Develop models to assess effects of molecular size on the reforming process

Introduction

In the absence of a hydrogen production, delivery, and marketing infrastructure, and with the limitations of current hydrogen storage technologies, on-board reforming of hydrocarbon fuels is a potential solution to aid the near-term introduction of fuel cell vehicles. Reforming of gasoline or gasoline-like fuels using the existing refueling infrastructure with little or no modification is an attractive strategy for this purpose. The goals of this project are to identify the desirable and undesirable constituents of gasoline for use in fuel cell systems and to develop specifications for hydrocarbon fuels especially suitable for fuel cell vehicles.

Previous work has indicated that there are significant differences in how readily the major types of hydrocarbons in gasoline (paraffinic, aromatic, naphthenic, and olefinic) can be reformed.^{1,2,3} 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. The effects of gasoline additives and impurities on reformer performance have also been investigated.^{4,5} This fiscal year we have focused on molecular size effects and additives that have the potential to improve reforming.

Approach

In order to determine the effects of fuel composition on fuel reformer performance, we start with the reforming of single components, then progress to simplified multi-component blends and ultimately to real-world multi-component fuels. This approach allows us to determine the effects of different species and also determine synergistic effects, if any. We are investigating the effects of molecular size by reforming homologues of different sizes (C8, C10, C12 and C16), as well as mixtures of paraffins and aromatics of different sizes (such as isooctane-xylene and dodecane-methylnaphthalene). Reforming tests are conducted in externally heated microreactors, where conditions can be closely controlled, and in adiabatic engineering-scale reactors, where heat effects can be observed. Commercially available noble metal on doped ceria type catalysts are used. Steam and air flows are adjusted so that reforming is performed at the same

O₂:C and H₂O:C ratios. Fuel flow rates are adjusted to provide identical heat content from the fuel. The product gas composition is analyzed using a combination of mass spectrometry, gas chromatography (GC)-mass spectrometry, and solid-phase extraction GC-mass spectrometry to provide detailed information on how the fuel composition and reforming parameters (H₂O:C, O₂:C, GHSV, temperature) affect product gas composition.

Results

As potential reforming enhancers, we are investigating oxygenated compounds (which should increase the octane number, increase p_{O₂} in the reactor and decrease water recovery issues) and radical initiators (which have been used to stimulate the combustion of diesel).

Long-term effects of ethanol addition to gasoline have been investigated. Ethanol addition to benchmark fuel led to increased methane in the product gas, as compared to the benchmark fuel without ethanol. There was little evidence of dehydrogenation or dehydration of the ethanol, as no increased formation of ethylene or acetaldehyde was observed under the conditions studied. However, the addition of ethanol to the benchmark fuel did accelerate catalyst degradation.

Dimethylcarbonate (DMC) has been considered as an additive to meet the Environmental Protection Agency oxygenate requirements in gasoline.⁵ DMC also has a high octane rating, which suggests it may be possible to replace some high-octane aromatics, which are difficult to reform, with DMC, which should be easier to reform. We have investigated the reforming of isooctane-dimethylcarbonate and isooctane-dimethylcarbonate-xylene mixtures over a temperature range of 650-800°C and GHSVs from 15,000 to 150,000 h⁻¹. Additions of 5 vol.% dimethylcarbonate had little to no effect on the temperature profile in the catalyst bed, with the inlet and outlet temperatures varying by less than 5°C upon addition. The dimethylcarbonate improved reforming, increasing the fraction of theoretically available hydrogen in the fuel mixture that is observed as hydrogen in the product gas at low temperatures and high GHSV (Figure 1). Hydrogen yield was increased by 13% at a GHSV of

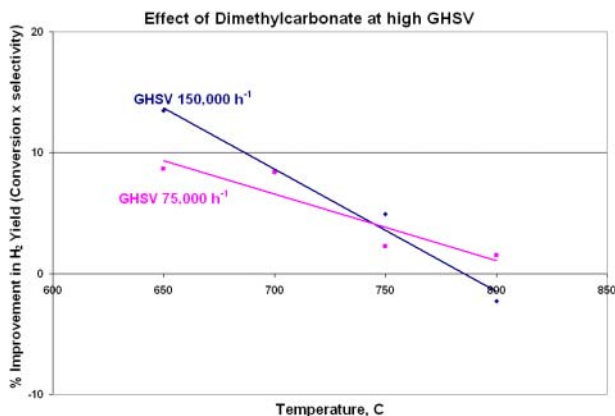


Figure 1. Improvement in Hydrogen Yield with Addition of DMC

150,000 h⁻¹ at 650°C. Dimethylcarbonate addition was less effective at higher temperatures and at lower GHSVs.

We have also investigated the effects of molecular size on reforming. Experiments have been performed with C8, C10, C12, and C16 straight chain paraffins, using monoliths with 600, 900 and 1200 cpsi. Reforming of hexadecane with the 1200-cpsi monolith produced volatile aromatics (benzene and toluene) at a rate more than twice that obtained during decane reforming. In the reforming of mixtures, increasing from a C7-C8 range mixture of paraffins and aromatics to a C11-C12 mixture decreased H₂ yield by ~33% when using 900-cpsi catalyst monoliths, and by ~44% with the 1200-cpsi catalyst monoliths (see Figure 2). Increasing the molecular size increased the sensitivity to the catalyst support dimensions. Methylnaphthalene was found to have a strong negative effect on reforming. When methylnaphthalene was present, we observed an increase in the complexity of aromatic species with increasing reaction time. One-, two- and three-ring aromatic species were observed, along with carbon deposits. In practice, carbon formation is reduced by increasing O₂:C or H₂O:C ratios. Experiments were performed in the adiabatic engineering-scale reactor to determine how these changes affect reforming of a dodecane–methylnaphthalene–decalin mixture. The results are shown in Figure 3. Increasing the O₂:C ratio has two effects: it increases the temperature in the reactor, and it increases the oxygen potential.

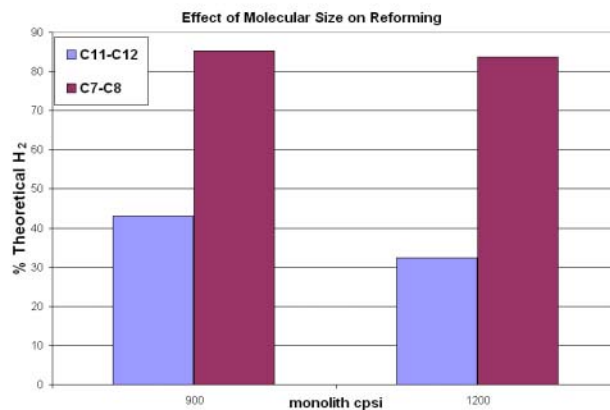


Figure 2. Effect of Molecular Size and Catalyst Structure on Reforming

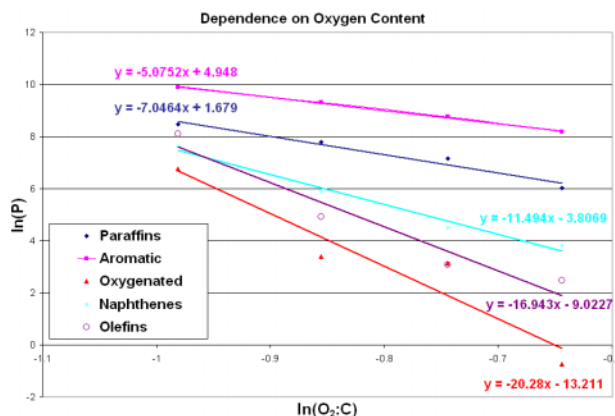


Figure 3. Effect of O₂:C Ratio on Different Classes of Hydrocarbons Formed During Reforming of Dodecane + 10% Methylnaphthalene + 10% Decalin

Oxygenated and olefinic species found in the reformate gas decreased rapidly with increasing O₂:C ratio, decreasing by 3 and 2 orders of magnitude, respectively, as the O₂:C was increased from 0.375 to 0.525. Aromatics, on the other hand, decreased by only a factor of 5.5 over the same range of O₂:C. Thus, increasing O₂:C is very effective at removing olefins, but it is much less effective at removing aromatic species. Increasing H₂O:C ratio was less effective in reducing hydrocarbon content in the product gas.

Conclusions

- Addition of ethanol to benchmark fuel (a gasoline-like blend) increased the rate of catalyst deactivation and led to increased methane content in the product gas.
- Dimethylcarbonate addition resulted in improved reforming of a mixture of isooctane and xylene at low temperature and high GHSV, but the improvement was less at higher temperatures.
- Multi-ring aromatic species are formed during autothermal reforming of larger molecules over noble metal-doped ceria catalysts. Methyl-naphthalene, in particular, has been associated with the formation of 3-ring aromatic species and carbon deposition.
- Increasing the O₂:C ratio decreases olefinic species, with smaller decreases in multi-ring aromatic species.

References

1. J. P. Kopasz, S. Ahmed, M. Krumpelt and P. Devlin, "Challenges in Reforming Gasoline: All Components Are Not Created Equal," SAE Technical Paper Series, 2001-01-1915, 2001.
2. J. P. Kopasz, L. E. Miller, S. Ahmed, P. Devlin and M. Pacheco, "Reforming Petroleum-based Fuels for Fuel Cell Vehicles: Composition-Performance Relationships," SAE Technical Paper Series, 2002-01-1885, 2002.
3. R. Borup, M. Inbody, L. Brown, B. Morton, T. Semelsberger, L. Perry, and J. Parkinson, "Testing of Fuels in Fuel Cell Reformers," p. 110–115 in 2001 Annual Progress Report for Fuels for Advanced CIDI Engines and Fuel Cells, Energy Efficiency and Renewable Energy, Office of Transportation Technologies, U.S. Department of Energy, Washington, DC, November 2001.
4. J. P. Kopasz, L. E. Miller, D. Applegate, "Effects of Multicomponent Fuels, Fuel Additives and Fuel Impurities on Fuel Reforming," SAE Technical Paper Series, 2003-FTT-56.
5. J. P. Kopasz, D. Applegate, L. Miller, C. Rossignol, "Effects of Fuel Constituents on Fuel Processing Catalysts," Annual Progress Report, Hydrogen, Fuel Cells and Infrastructure Technologies Program, 2003, IV-138.
6. M. Pacheco, C. Marshall, *Energy & Fuels*, 1997, 11, 2.

FY 2004 Publications/Presentations

1. "Unraveling the maze: building an understanding of diesel reforming through the use of simplified systems," J. P. Kopasz, D. Applegate, L. Miller, H. K. Liao, and S. Ahmed, presented at the AIChE Spring National Meeting, April 25-29, 2004.
2. "How fuel composition affects on-board reforming for fuel cell vehicles," J. P. Kopasz, L. E. Miller, and D. V. Applegate, presented at SAE Powertrain and Fluid Systems Conference, October 27-20, 2003.
3. "Autothermal reforming of diesel type hydrocarbons," J. P. Kopasz, L. Miller, D. Applegate, H. K. Liao, and S. Ahmed, presented at the DOD Logistic Fuels Reforming Conference, October 22-23, 2003.
4. "Perovskite catalysts for the autothermal reforming of liquid hydrocarbon fuels," J. Mawdsley, T. Krause, J. Ralph, J. Critchfield, D. J. Liu, L. Miller, H. K. Liao, J. Kopasz, and S. Ahmed, presented at the 2003 Fuel Cell Seminar, November 3-7, 2003.
5. "How fuel composition affects on-board reforming for fuel cell vehicles," J. P. Kopasz, L. E. Miller, and D. V. Applegate, SAE Technical Paper Series, 2003-01-3272.