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. 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. This fiscal year we have focused on molecular size effects and additives that have the potential to improve reforming.

**Results**

As potential reforming enhancers, we are investigating oxygenated compounds (which should increase the octane number, increase \( p_{O_2} \) 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. 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 dimethylcarbonyl 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 \( O_2:C \) and \( H_2O:C \) 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 (\( H_2O:C \), \( O_2:C \), GHSV, temperature) affect product gas composition.
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 H\(_2\) 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 O\(_2\):C or H\(_2\):O: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 O\(_2\):C ratio has two effects: it increases the temperature in the reactor, and it increases the oxygen potential.

Oxygenated and olefinic species found in the reformate gas decreased rapidly with increasing O\(_2\):C ratio, decreasing by 3 and 2 orders of magnitude, respectively, as the O\(_2\):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 O\(_2\):C. Thus, increasing O\(_2\):C is very effective at removing olefins, but it is much less effective at removing aromatic species. Increasing H\(_2\):O: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. Methylphenanththalene, in particular, has been associated with the formation of 3-ring aromatic species and carbon deposition.
- Increasing the O$_2$:C ratio decreases olefinic species, with smaller decreases in multi-ring aromatic species.

References


FY 2004 Publications/Presentations


