

Testing of Fuels in Fuel Cell Reformers

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Objectives

- Quantify fuel effects on fuel processor performance and durability
 - Measure fuel component, impurity, additive effects
 - Examine fuel effects on fuel processor start-up
- Understand parameters that affect fuel processor and stack lifetime and durability
 - Measure fuel processor catalyst stability and activity
 - Evaluate fuel effect and start-up effect on carbon formation
 - Identify chemical species limiting durability
 - Test durability to evaluate long term performance

Technical Barriers

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

- I. Fuel Processor Start-up/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency
- N. Cost

Approach

- Examine fuel effects on fuel processing by testing fuels in catalytic and gas phase oxidation and reforming reactors
 - Examine individual fuel components, component blends
 - Examine 'real' fuels (reformulated gasoline, naphtha)
 - Examine fuel additives (anti-oxidants, detergents, impurities)
- Examine fuel effect on fuel reformer light-off and start-up
 - Measure fuel light-off temperature
 - Measure carbon formation during fuel processor light-off
- Model and measure carbon formation
 - Model carbon formation equilibrium
 - Measure carbon formation during fuel vaporization

- Measure carbon formation during start-up of fuel processor
- Examine reforming of fuels at low temperatures for portable power applications

Accomplishments

- Measured carbon formation during vaporization process of hydrocarbon fuels
- Measured carbon formation during start-up of fuel processor
- Examined effect of fuel components on light-off temperature and start-up
 - Delineated straight-chained hydrocarbons vs. branched chains and aromatic compounds
 - Oxygenated fuel components
 - Additives and impurities such as detergents and sulfur
- Compared gas phase oxidation and catalytic oxidation with different fuel components
- Examined the reforming of fuels at low temperatures for portable power applications

Future Directions

- End task on Testing of Fuels in Fuel Cell Reformers
 - Summarize and publish final results
- Focus on H₂ durability of PEM Fuel Cells
 - Single cell MEA durability
 - Short stack Durability
 - Drive cycle testing of MEAs
 - MEA and GDL evaluation and characterization
 - Off-line and accelerated durability testing

Introduction

The goal of this research is to explore the effects of fuels, fuel constituents, additives and impurities on the performance of on-board hydrogen generation devices and, consequently, on the overall performance of a PEM fuel cell system using a reformed hydrocarbon fuel. Understanding the performance of fuels and their effects on the durability of PEM fuel cell systems is key for their commercial introduction and use. A fast start-up time of the fuel processor systems is crucial for their use in automotive fuel cell applications. Energy consumption, carbon formation, start-up time and limits on durability are all potential effects of fuel composition on the fuel processor during the start-up and light-off of fuel processors.

Approach

To examine the effect of fuel on hydrogen generation devices, various fuel components, mixtures, and real fuels have been tested in automotive-scale autothermal (ATR) fuel reformers. The focus of the testing is to examine fuel effects on start-up performance and factors that limit durability. Start-up time and durability are critical aspects of reformer performance for onboard vehicle operation. Carbon formation can significantly limit durability. Fuel effects on carbon formation were examined by measuring carbon formed during fuel vaporization of various fuel components and mixtures and by measuring carbon formed in the start-up of an ATR fuel reformer. The carbon formed was measured by

physical collection and by in situ laser scattering-extinction measurements in the ATR experiments.

The light-off temperature of the ATR catalyst is a significant factor in its start-up performance. Thus, light-off temperatures were measured for fuel components, component blends, and real fuels in an isothermal catalyst test reactor.

The effect of fuel composition on fuel processor operating temperature and stability was compared between a catalytic partial oxidation reactor and a gas-phase partial oxidation reactor, both automotive-scale. Fuel composition effects were delineated by matching performance of real fuels with blended component mixtures.

Results

In autothermal reforming, proper fuel/steam/air mixture preparation is critical to avoid hot/cold spots, carbon formation, and catalyst degradation and to obtain proper conversion of hydrocarbons. Vaporization is one method to introduce fuel into a reformer, however it may lead to fuel pyrolysis, thus forming particulates or carbon during vaporization. Figure 1 compares the carbon formation measured during vaporization and refluxing of fuels and fuel components. In general, pure hydrocarbons did not show carbon formation, while real fuels did show carbon formation during the vaporization. The higher hydrocarbon streams such as kerosene and diesel fuel had more carbon formation than reformulated gasoline (RFG) or kerosene and diesel fuel in which sulfur had been removed. To suppress carbon formation with these fuels that pyrolyze, direct fuel injection into the autothermal reformer may be required instead of prior fuel vaporization.

The start-up of the fuel processor system is critical for commercialization. During the start-up process, water may not be available. Without water it is impossible to light off a fuel processor at rich operating conditions and avoid regimes where carbon formation is favored by chemical equilibrium. Fuel effects on carbon formation during start-up were quantified for different fuel compositions using an ATR reactor. These measurements were made at steam/carbon ratios of 0.0 and 0.5, simulating low water light-off of the reactors. The carbon formed is

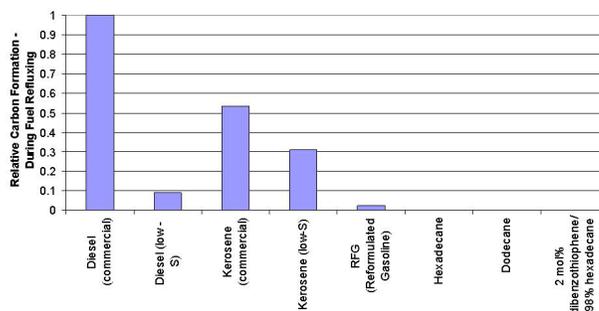


Figure 1. Carbon Formation Measured During Fuel Vaporization and Refluxing of Fuel Components

summarized in Figure 2. Ethanol addition to iso-octane and RFG helps suppress carbon formation, while the addition of aromatic compounds or longer-chained hydrocarbon (dodecane) leads to increased carbon production.

Under rich operating conditions, catalysts require pre-heating before the oxidation reaction lights off, creating a self-sustaining exothermic reaction. The amount of preheat required is a factor in the start-up time and energy. Figure 3 shows measured light-off temperatures for various hydrocarbon fuel constituents. Straight-chained hydrocarbons are observed to light off at lower temperatures than similar branched-chained hydrocarbons. Aromatics, such as xylene and methyl naphthalene, increased the light-off temperature.

Figure 4 shows the change in the light-off temperature by the addition of oxygenated hydrocarbons and sulfur-containing hydrocarbons to iso-octane. The addition of oxygenated hydrocarbons, such as ethanol or methanol, to either

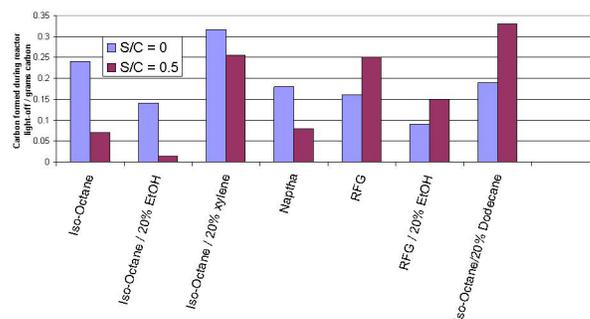


Figure 2. Fuel Composition Effect on Carbon Formation During Start-Up of ATR Reactor

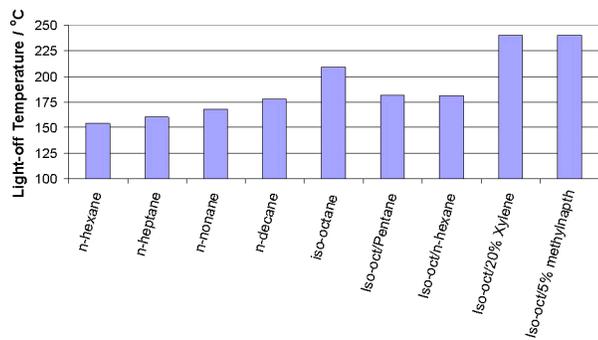


Figure 3. Fuel Composition Effect on ATR Light-Off Temperatures by Straight-Chained Aliphatic, Branched-Chained Aliphatic and Aromatic Hydrocarbons

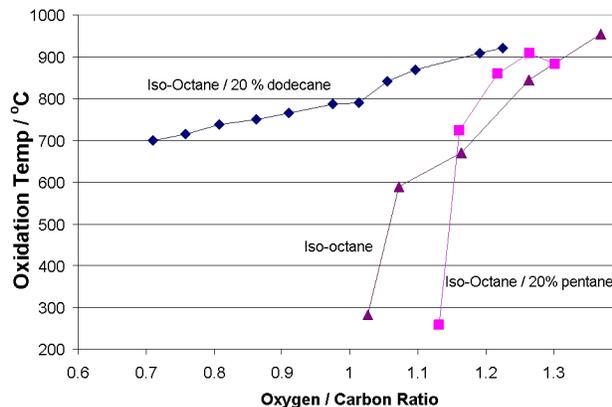


Figure 5. Comparison of Fuel Composition Effect of Heavy And Light Straight-Chained Hydrocarbon on Gas Phase Partial Oxidation

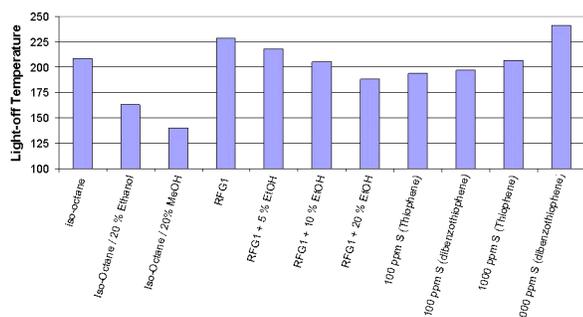


Figure 4. Fuel Composition Effect on ATR Light-Off Temperatures by Oxygenated Hydrocarbons and Sulfur Containing Hydrocarbons

iso-octane or RFG reduced the light-off temperature, with greater concentrations reducing the light-off temperature to a greater extent. The addition of sulfur-containing hydrocarbons at low concentrations (100 ppm S) reduced the light-off temperature, while higher concentrations (1000 ppm S) increased the light-off temperature.

In FY2002, we observed that during gas phase partial oxidation, real fuel blends operated stably at lower oxygen-to-carbon (O/C) ratios than pure components, such as iso-octane, opposite to the trend for catalytic partial oxidation. To delineate this effect, pentane (short-chained) and dodecane (long-chained) hydrocarbons were added to iso-octane and tested over a range of O/C ratios in the gas phase partial oxidation reactor. Figure 5 shows that the addition of dodecane increased the range of O/C ratio

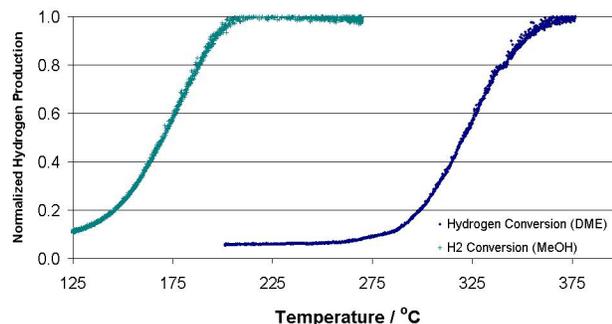


Figure 6. Comparison of Low-Temperature Reforming Fuels, Methanol And Dimethylether

at which the gas phase partial oxidation reactor could operate, while pentane did not. Thus the long-chain hydrocarbons in real fuels increase the range of O/C ratio for gas phase partial oxidation, which is reflected in the relative cetane number of the fuel, a measure of the ignition delay.

Fuels such as gasoline and diesel fuel require high temperature reforming reactions. For portable power applications, there is interest in developing lower temperature reformers. Figure 6 shows a comparison of two fuels that reform at low temperature, methanol and dimethylether (DME). Full conversion of methanol was observed by about 205°C, while 360°C was required for DME. While DME requires a higher operating temperature, it does not have the toxicity issues that methanol has, and it

still reforms at a significantly lower temperature than hydrocarbons containing carbon-carbon bonds.

Conclusions

Fuel effect on catalytic light-off has been measured for a large number of different components. Straight-chained hydrocarbons have a lower light-off temperature than similar carbon number branched-chained hydrocarbons. Aromatics require higher light-off temperatures, while oxygenated compounds lower the light-off temperatures.

Carbon formation was measured for various hydrocarbon compositions and operating conditions. Carbon formation was also measured during the fuel processor start-up transient. Aromatics show the highest tendency for carbon formation, while oxygenates help suppress carbon formation during light-off.

Fuel composition effects have been measured for their relative kinetics during catalytic and gas phase oxidation and reforming. Gas phase oxidation favors real fuel mixtures with longer-chained hydrocarbons over gasoline-sized hydrocarbons such as iso-octane. Steam concentration has a large effect on gas phase

oxidation, while its effect on catalytic oxidation is not large. Catalytic oxidation favors short-chained aliphatic hydrocarbons, while aromatics and long-chained hydrocarbons have lower catalytic kinetics.

FY 2002 Publications/Presentations

1. 2002 American Chemical Society Meeting, Boston, Massachusetts, August 18-22.
2. 2002 Fuel Cell Seminar Poster, Palm Springs, California, Nov. 17-21.
3. Department of Defense Logistic Fuel Reforming Conference, Panama City Beach, Florida, August 27.
4. Spring 2003, American Institute of Chemical Engineers, New Orleans, Louisiana, March 30-April 3.
5. Hydrogen Production and Northwest Transportation Meeting, Seattle, Washington, June 16.
6. 2003 SAE Powertrain & Fluid Systems Conference, October 27-30, Pittsburgh, Pennsylvania, SAE paper 2003-01-3271.