

LA-UR-01-2289

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*Author(s):*

**Rod Borup, Michael Inbody, Byron Morton,  
and Lee Brown**

*Submitted to:*

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# Fuel Processing for Fuel Cells: Effects on Catalyst Durability and Carbon Formation

Rod Borup, Michael Inbody, Byron Morton, and Lee Brown

ESA-EPE, MS J580

P.O. Box 1663

Los Alamos National Laboratory

Los Alamos, NM 87545

(505) 667-2823 fax: (505) 665-6173; e-mail: [Borup@lanl.gov](mailto:Borup@lanl.gov)

## **ABSTRACT**

On-board production of hydrogen for fuel cells for automotive applications is a challenging developmental task. The fuel processor must show long term durability and under challenging conditions. Fuel processor catalysts in automotive fuel processors will be exposed to large thermal variations, vibrations, exposure to uncontrolled ambient conditions, and various impurities from ambient air and from fuel. For the commercialization of fuel processors, the delineation of effects on catalyst activity and durability are required.

We are studying fuels and fuel constituent effects on the fuel processor system as part of the DOE Fuel Cells for Transportation program. Pure fuel components are tested to delineate the fuel component effect on the fuel processor and fuel processor catalysts. Component blends are used to simulate 'real fuels', with various fuel mixtures being examined such as reformulated gasoline and naptha. The aliphatic, naphthenic, olefin and aromatic content are simulated to represent the chemical kinetics of possible detrimental reactions, such as carbon formation, during fuel testing.

Testing has examined the fuel processing performance of different fuel components to help elucidate the fuel constituent effects on fuel processing performance and upon catalyst durability. Testing has been conducted with vapor fuels, including natural gas and pure methane. The testing of pure methane and comparable testing with natural gas (97% methane) have shown some measurable differences in performance in the fuel processor. Major gasoline fuel constituents, such as aliphatic compounds, naphthenes, and aromatics have been compared for their effect on the fuel processing performance. Experiments have been conducted using high-purity compounds to observe the fuel processing properties of the individual components and to document individual fuel component performance. The relative carbon formation of different fuel constituents have been measured by monitoring carbon via *in situ* laser optics, and by monitoring carbon buildup on the catalyst surface. The fuel processing performance of the individual components is compared with the fuel processing performance of blended fuel components and the reformulated gasoline to examine synergistic or detrimental effects the fuel components have in a real fuel blend.

## **Introduction**

The goal of this research is to explore various effects on fuel processor performance and durability. Various catalysts, catalyst supports, fuel constituents and fuel impurities on the performance of on-board hydrogen generation devices and consequently on the overall performance of a PEM fuel cell system utilizing a hydrocarbon fuel is examined. A main emphasis is placed on the catalyst and fuel constituent effect on carbon formation in the fuel processor.

Fuels and fuel impurities have effects on fuel processor operation, efficiency, reformatte gas composition, transient performance, lifetime, and catalyst durability. These effects are being investigated through experiments with various fuel processor hardware in Los Alamos National Laboratories' fuel processor test facility. Fuel effects on catalyst performance and catalyst durability ultimately determine the performance and operation of the fuel cell system from the effect on the anode feed stream composition.

## **Approach: Fuel Effects on Carbon Formation Measurement and Catalyst Durability**

The fundamental tools for our research on catalyst durability and the effects of fuels and fuel impurities on on-board hydrogen generation are the reactor test beds in which the fuel effects are monitored, the gas analysis and catalyst characterization techniques employed in this work. The balance-of-plant framework, the necessary analytical instrumentation and the supervisory control to characterize operation and performance of different fuel processors and fuel components allows determination of fuel component effects on fuel processing.

An adiabatic partial oxidation (POx) reactor for use in evaluating fuel components and the fuel component tendency for carbon formation is shown in Figure 1. This reactor incorporates ease of catalyst replacement, *in situ* carbon formation monitoring, gas and temperature measurements with radial and axial profiles. Figure 2 is a schematic showing laser detection for *in situ* carbon formation. An argon ion laser is used with extinction monitoring to observe the onset of carbon formation. Scattering is also used to observe relative carbon particle size distributions, and spectral detection allows for fluorescence detection of PAHs (poly-cyclic-aromatic-hydrocarbons).



Figure 1. Partial oxidation reactor during operation with windows for carbon formation monitoring.

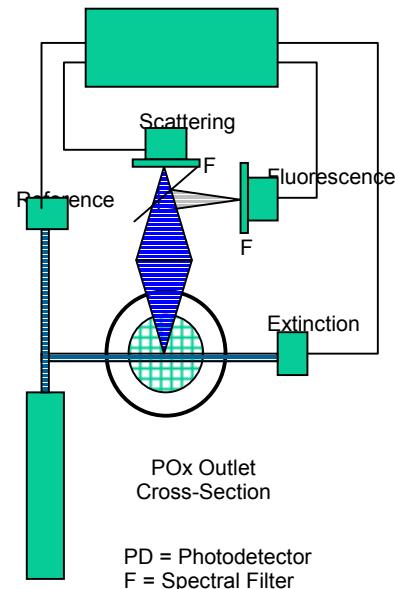


Figure 2. Schematic of carbon formation optics

## **Results: Fuel Constituent Effects on Fuel Processing Catalysts**

Differences in fuel processing of natural gas (97% methane composition) and pure 100 % methane have been measured to be the result of differences in heat of combustion of the fuels. Even though the natural gas composition included 97% methane, the heat of combustion shows significant differences at low O/C. The stoichiometric combustion of methane and natural gas have heat of combustions of 212.8 and 213.9 kJ/mol – less than a 0.5 % difference, however the heat of combustion of the fuels at O/C = 1 is 35.65 and 37.43 which is over 5 % different.

Nickel supported on alumina catalyst shows markedly different reforming characteristics between no sulfur fuels, and fuel with sulfur. Iso-octane with 100 ppm sulfur within five hours shows reduced hydrogen production, which is the result of much lower iso-octane conversion. Pure iso-octane fuel has consistent hydrogen production over the testing period of 24 hours. The sulfur effect on this catalyst appears to have greatly inhibited both the oxidation and steam reforming kinetics,

thus lowering the iso-octane conversion on nickel catalysts.

Partial oxidation of hydrocarbons over Pt catalysts has been shown to occur with fast kinetics, thus requiring low residence times of the order of 5 msec, (high space velocities  $720,000 \text{ hr}^{-1}$ ). The conversion of hydrocarbons to  $\text{H}_2$  and  $\text{CO}$ , including the complete conversion of  $\text{O}_2$ , has been monitored as a function of air/fuel ratio (O/C), residence time and pure fuel components. At ratios of  $\text{O/C} = 1$  (stoichiometric oxygen for complete hydrocarbon conversion to  $\text{H}_2$  and  $\text{CO}$ ), the partial oxidation of Iso-Octane and Iso-Octane mixtures with Xylene are nearly identical for residence times above 6 msec. However below 6 msec, the conversion of the Iso-Octane/Xylene mixture falls precipitously. This data is shown in Figure 3.

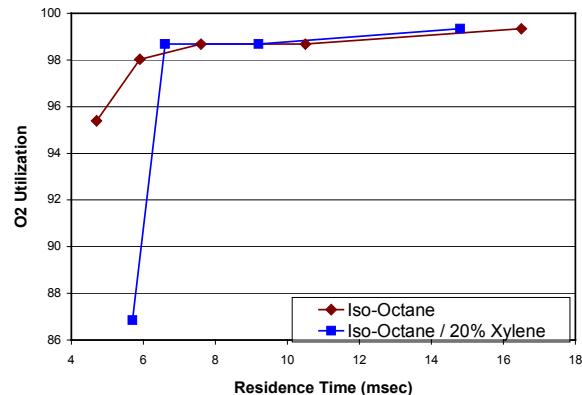


Figure 3. Partial Oxidation of Iso-Octane and Iso-Octane/20% Xylene ( $\text{O/C} = 1.0$ ,  $\text{S/C} = 1$ ) on a  $\text{Pt}/\text{Al}_2\text{O}_3$  washcoated monolith

At ratios of  $\text{O/C} = 0.8$  (lower than stoichiometric oxygen for complete conversion to  $\text{H}_2$  and  $\text{CO}$ ), the partial oxidation of Iso-Octane occurs with greater conversion than does that of Iso-Octane/Xylene mixtures. This occurs for residence times from 5 msec up to approximately 15 msec, where conversions are similar. This is shown in Figure 4. The differences in conversion with the addition of xylene to pure iso-octane show that the partial oxidation reactor operating conditions are more stringent for fuels with aromatic components than do fuels with pure aliphatic components.

Carbon formation has been monitored by the carbon buildup on the catalyst surface over time as a function of different fuel components, and measured *in situ* by laser diagnostics. Post characterization after testing of sample nickel catalysts with various fuels indicates that relative carbon buildup on the catalyst surface is much higher with aromatic and unsaturated compounds than aliphatic hydrocarbons.

## Conclusions

Test capabilities have been developed which are capable of testing fuel processors with gaseous and liquid fuels. These capabilities provide the balance-of-plant necessary to support operation of fuel processor systems including analytical instrumentation and the supervisory control required to characterize operation and performance of different fuel processors and fuel components.

These capabilities are being used to measure fuel constituent and fuel impurity effects on fuel processor technology. Differences between natural gas and pure methane have been observed which can be explained by the difference in heat of combustion at low O/C ratios. The effect of sulfur on hydrogen production has shown dramatic effects on a  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst, with hydrogen production (iso-octane conversion) decreasing by over a factor of 3 within only five hours of operation. The tendency for carbon formation has been observed to be a function of the fuel component, with the general trend for carbon formation: xylene > methyl cyclohexane > pentene > iso-octane.

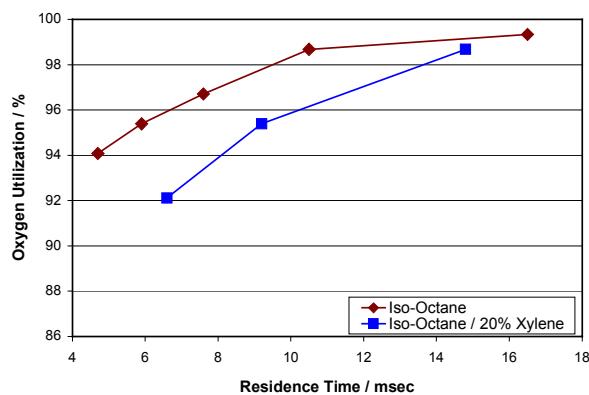


Figure 4. Partial Oxidation of Iso-Octane and Iso-Octane/20% Xylene ( $\text{O/C} = 0.8$ ,  $\text{S/C} = 1$ ) on a  $\text{Pt}/\text{Al}_2\text{O}_3$  washcoated monolith.