

LA-UR- 02-5696


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Title: Fuels for Fuel Cells: Fuel and Catalyst Effects on Carbon Formation

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Submitted to: Fuel Cell Seminar



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Fuels for Fuel Cells: Fuel and Catalyst Effects on Carbon Formation

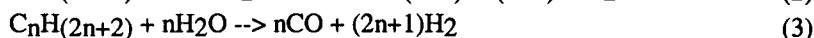
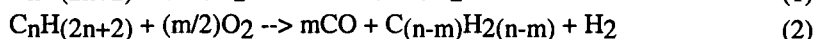
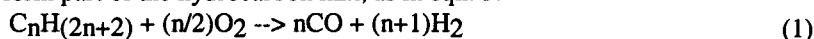
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Introduction

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 fuel cell systems using reformed hydrocarbon fuels. Different fuels and components have been tested in automotive scale, adiabatic autothermal reactors to observe their relative reforming characteristics with various operating conditions. Carbon formation has been modeled and was experimentally monitored *in situ* during operation by laser measurements of the effluent reformat. Ammonia formation was monitored, and conditions varied to observe under what conditions NH₃ is made.

Autothermal Reforming of Gasoline and Diesel Fuels

Fuel partial oxidation and reforming are being explored for onboard production of hydrogen. For the chemical conversion of fuel hydrocarbons, air is combusted with fuel, typically over a catalyst to produce hydrogen and carbon monoxide. Eqn. 1 shows the partial oxidation of a generic hydrocarbon for an air stoichiometry exactly correct (O/C = 1) for the production of hydrogen and carbon monoxide. If the oxygen-fuel ratio is more fuel rich (O/C < 1) such as in eqn 2, without sufficient residence time and water content, unconverted hydrocarbons will be present in the reformat stream. These hydrocarbons include small hydrocarbons such as methane and ethane. Since the oxidation reaction is exothermic, it is common to use water to steam reform part of the hydrocarbon mix, as in eqn. 3.



To understand the fundamentals underlying hydrocarbon reforming technology, we are employing both experimental measurements and chemical modeling of the systems. To experimentally measure fuel reformation, we have developed partial oxidation (POx) reactors with the supporting test equipment to test the feasibility of generating reformat. Carbon formation for different operating conditions and fuel components was monitored by *in situ* laser scattering. Mapping of the onset of carbon formation for different fuel components as a function of operating conditions has been conducted with these techniques. Modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends. Modeling is conducted using commercial codes, such as ASPEN to model equilibrium concentrations of expected outlet species of the fuel reformer. Other codes have been developed, specifically to model different carbon species and the formation thereof. In particular, modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends

Carbon Formation Modeling Results

Solid carbon formation equilibrium was determined using thermodynamic data to determine the equilibrium composition of reactions at various temperatures, pressures and feed composition. Figure 1 displays the temperature at which carbon formation is no longer observed, for a specific operating condition and fuel blend for various steam/carbon ratios. Depending upon the relative oxygen content, the carbon disappearance temperature can vary by up to 150 °C. The relative effect of increasing the steam content of the fuel mixture greatly reduces the tendency for carbon formation. Ternary, or triangular diagrams have also been used to present the carbon formation modeling with the each corner representing an atom fraction of 1.0 for each one of the atoms, C-H-O, to define regions where carbon will form. The apex of the triangle represents a composition of 100% carbon. The left bottom corner represents a composition of 100%

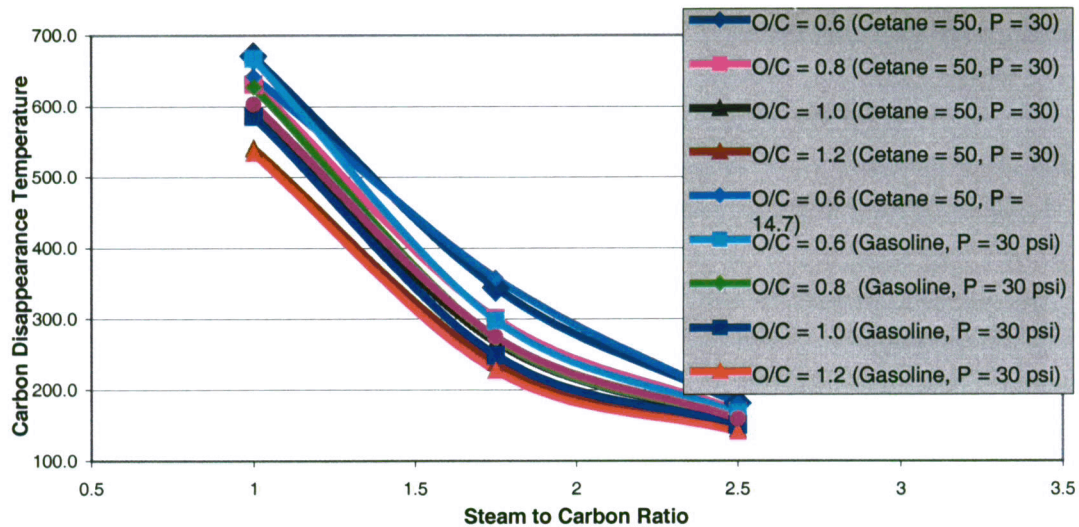


Figure 1. Carbon disappearance temperature for various fuels and operation conditions

hydrogen and the right bottom corner represents a composition of 100% oxygen. For any given temperature and pressure we can determine a locus of composition points on this diagram that represent the equilibrium composition at which solid carbon will begin to form. Equilibrium compositions were from Gibb's energy of formation data that can be found in the literature as a function of temperature. Figure 2. shows the carbon forming regions for 600 °C and any system pressure between 14.7 and 30.0 psi. In figure 2, we have plotted the carbon formation locus for both amorphous and graphite carbon. The area above the blue line represents all compositions that should form (but probably won't) solid graphite. The area above the red line represents all compositions that should (and probably will) form solid amorphous carbon.

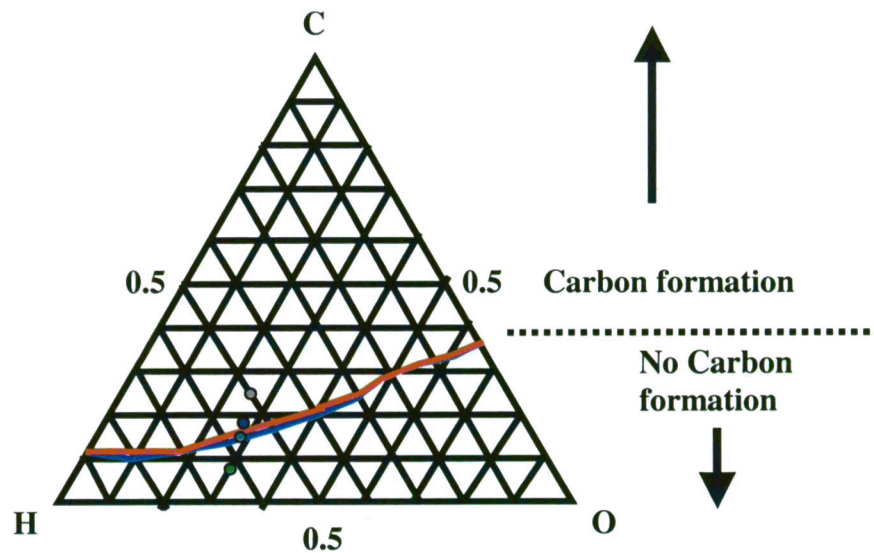


Figure 2. Carbon forming regions for 600 °C and low pressures. The dots correspond to the following fuel/reactor operating conditions: green: O/C = 1.0, S/C = 2.5, aqua: O/C = 1.0, S/C = 1.0, blue: O/C = 1.0, S/C = 0.5, gray O/C = 1.0, S/C = 0.0. The red line (top) corresponds to amorphous carbon, while the blue line (bottom) corresponds to graphite.

These calculations show that as the temperature increases the amorphous carbon starts to behave more like graphite. It also shows that the graphite formation requires a higher carbon content in the feed. This means one can use less steam in the feed at higher temperatures in order to inhibit solid carbon formation. At temperatures above 700 °C, there is essentially no difference between amorphous carbon and graphitic carbon equilibrium formation conditions.

Fuel Effects Comparisons in Catalytic Partial Oxidation

The relative rates for catalytic partial oxidation for different fuels have been measured for various operating conditions. Figure 3 shows relative reaction rate for various fuel components, mixtures and a Phillips Petroleum Hydrotreated Naptha stream at a S/C of 1.0. The relative reaction rates vary as the O/C ratio varies due to temperature changes. At lower O/C ratios, the adiabatic temperature rise is lower, thus the overall reaction rate is lower. The reaction rate for all components are higher at higher O/C, and subsequently, higher temperatures. The oxidation rates for O/C's of 0.7 and 0.8 are fastest for iso-octane. The addition of aromatics such as xylene slows the kinetics and conversion. Real fuel composition mixtures such as the Phillips Naptha and CA reformulated gasoline show an oxidation rate faster than that of iso-octane/xylene mixtures even though the relative aromatic concentration is approximately the same. At high O/C ratios (O/C = 1.0), the real fuel mixtures show an equal or faster oxidation rate compared with pure iso-octane. The resulting decrease in reaction rate due to the presences of aromatic hydrocarbons indicate that the fuel composition will have an effect on the required size (and cost due to catalyst loading) of the fuel processor. The reforming of diesel fuel components indicates that higher residence times are required for similar conversion compared to that of gasoline components by approximately 4x residence time. In addition, sulfur poisoning has been shown to greatly inhibit non-noble metal catalysts such as nickel. In addition, diesel fuel components have more stringent requirements to prevent equilibrium carbon formation conditions. These results indicate that as the hydrocarbon chain length is increased, higher O/C ratios are required to get similar fuel conversion in the reactor.

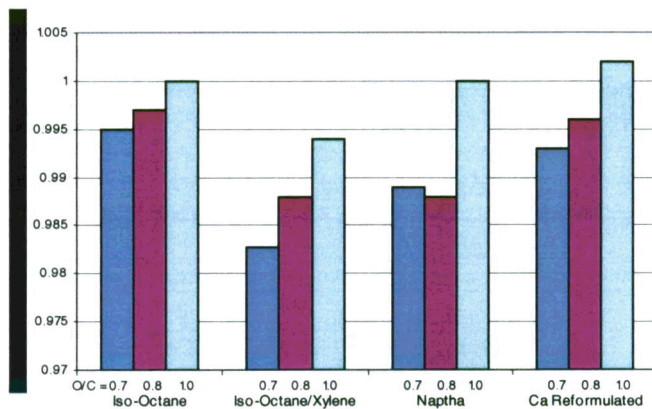


Figure 3. Relative oxidation rates of iso-octane, iso-octane/20% xylene, Phillips Naptha and reformulated gasoline.

Ammonia Formation

Ammonia (NH_3) formation in the fuel processor is a concern as NH_3 is a poison to PEM fuel cells membranes and ionomer. The normal catalytic partial oxidation of fuel components does not show a measureable NH_3 concentration. To examine NH_3 formation, the operating conditions were varied, and over the conditions studied, with operating conditions from 600 °C to 1150 °C, no ammonia formation was observed under normal catalytic operation with simple hydrocarbon fuels. However, precombustion can occur in a reformer due to mixing air/fuel at high temperatures; this is essentially homogeneous combustion before the catalyst surface and typically an operation mode which is avoided. When pre-combustion of fuels occurs (homogeneous combustion upstream of the catalyst), NH_3 is observed, at concentrations of about 10 ppm.

Nitrogen-containing hydrocarbons are also present in gasoline fuels, and to a greater extent in diesel fuel. To determine the conversion products of nitrogen-containing hydrocarbons, 50 ppm of anti-oxidant was added to MCH to observe potential NH_3 formation. In addition, pyridine was added to a pure fuel to observe whether NH_3 formation would occur at higher concentrations of nitrogen-containing hydrocarbons. With the addition of 10 % pyridine measured NH_3 in the reformat was 414 ppm NH_3 . When 1% pyridine was added to MCH, the reformat analysis measured 54 ppm NH_3 . When 50 ppm of the nitrogen containing anti-oxidant was added, no NH_3 was observed.

Carbon Formation

Carbon formation is recognized to be a potential limiter of fuel processor ATR durability. Equilibrium calculations can identify proper operating conditions to prevent carbon formation, however during the start-up of the fuel processor, avoiding non-zero carbon equilibrium is difficult. Laser extinction measurements have been conducted to observe carbon formation for different fuel components. An example of this is shown in Figure 4. The residence time of this reactor was short, about 10 msec. As the S/C ratio is decreased, carbon formation is detected by a decrease in the laser extinction signal, which is converted to a mass flow rate of carbon formed. Little measurable carbon was formed until equilibrium conditions predicted carbon formation. Aliphatic hydrocarbons such as iso-octane could be reformed without significant carbon formation even when equilibrium predicted carbon formation. However the addition of aromatic hydrocarbons caused significant carbon formation. The addition of anti-oxidants to the fuel stream did not make any measurable difference in carbon formation.

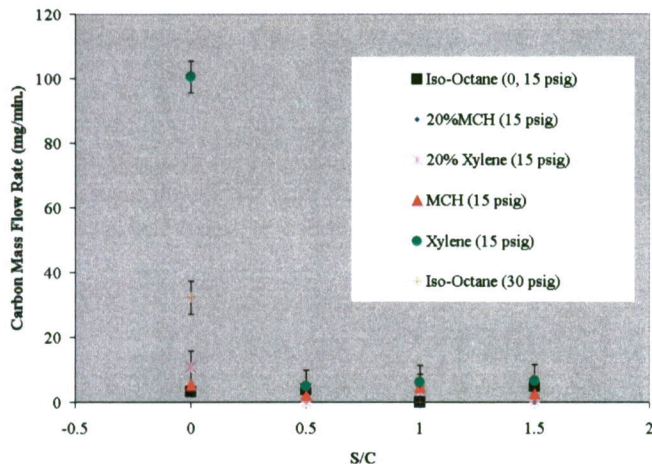


Figure 4. Mass flow rate of carbon formation for various fuel components, and component blends. Shown for O/C = 0.65

Conclusions

Measurements show that the fuel composition does effect the design and operation of the fuel reformer, and fuel blends low in aromatic content show higher reforming kinetics, which result in a reduced fuel processor size (and thus cost). The fuel composition effect also effects the relative carbon formation, which will effect the fuel processor durability. The addition of aromatics slows the overall reaction rate for catalytic oxidation. Real fuels have similar oxidation rates at high O/C compared with iso-octane, but lower oxidation rates at O/C < 1.0. Diesel fuels and diesel fuel components (such as dodecane) have been found to require higher residence times for similar conversions than comparable gasoline components. The pre-ignition tendencies for diesel fuel are higher than comparable gasoline. Ammonia formation was not observed at a measurable concentration for normal operating conditions with expected fuel compositions. Precombustion of fuels lead to the formation of NH₃ measured at 11 ppm NH₃. Large concentrations of nitrogen-containing hydrocarbons lead to higher amounts of NH₃ formation. Laser extinction measurements mapping the onset of carbon formation have been conducted. Carbon formation was quantified by the laser extinction measurement. Post analysis of carbon formed indicates the method and cause of carbon formation lead to different carbonaceous species. Carbon formed in the steam reformer was mostly carbonaceous carbon with an approximate H/C ratio of 0.2, while carbon formed downstream from the reformer consisted of high amounts of solidified hydrocarbons. Modeling has shown that fuel effects on the temperature for equilibrium onset of carbon formation can vary up to 150°C with varying O/C ratios, and the reformer temperature most likely will need to be kept above 700 °C for low S/C reactor feeds.

Acknowledgments

This research was supported by the DOE: Office of Hydrogen, Fuel Cells, and Infrastructure Technologies: Program Managers: Peter Devlin, JoAnn Milliken and Nancy Garland
Solid State Energy Conversion Alliance: Managers: Norman Holcombe and Wayne Surdoval
We also thank Fred Cornforth of Philips Petroleum for the fuels and anti-oxidants tested.