

Diesel Reforming for Solid Oxide Fuel Cell Auxiliary Power Units (APUs)

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Objectives

- Develop technology leading to reforming of diesel fuel.
 - Examine diesel reforming in fuel processors by testing fuels in adiabatic reactors.
 - Examine diesel fuel components.
 - Examine ‘real’ fuels (kerosene, low-sulfur diesel, diesel fuel).
- Quantify fuel processor operation and outlet compositions.
- Examine diesel fuels and fuel components.
- Optimize fuel processor outlet composition.
- Develop suitable techniques for diesel fuel/air/steam mixing.
- Conduct *in situ* regeneration of diesel partial oxidation catalysts.
- Understand the parameters that affect fuel processor operation lifetime and durability.
- Measure carbon formation.
- Model carbon formation equilibrium.
- Measure catalyst durability and degradation.

Key Milestones

- Model carbon formation and equilibrium compositions (FY2002).
- Demonstrate staged pressurized liquid fuel injection (FY2002).
- Demonstrate of catalytic regeneration (FY2002).
- Quantify carbon formation kinetics (FY2003).

Introduction

This report describes technical progress in developing onboard fuel reforming from diesel fuel suitable for a solid-oxide fuel cell (SOFC) for an auxiliary power unit (APU). The technology being developed uses partial oxidation and steam reforming of onboard fuel (diesel fuel) to produce reformat suitable for use in the solid oxide fuel cell anode, having constituents of H₂, CO, CO₂, N₂ and small amounts of hydrocarbons, such as methane. The onboard reformation of diesel fuel to produce this reformat stream will allow the operation of SOFCs at optimal power densities (high power density of the fuel cell equates to low mass and volume of the system, and low cost of the SOFC).

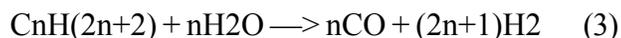
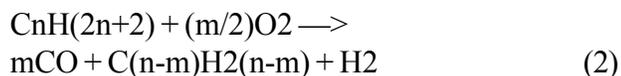
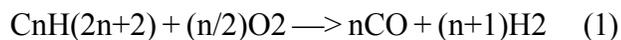
Our project is working to develop reaction fundamentals for onboard reforming of diesel fuel for SOFC/APU applications. This includes understanding the parameters that affect fuel processor performance, lifetime and durability. Specific technical objectives include the study of carbon formation in fuel processors, including experimental measurements and theoretical modeling, examining fuel vaporization, and fuel/air/steam mixing, low steam content reforming operations, direct fuel injection into partial oxidation reactors, and reformer start-up issues.

The formation of carbon in the oxidation/reforming stage of a fuel processor inevitably leads to catalyst deactivation and fouling in all stages of the system. Therefore, understanding the effect of typical fuels and operating conditions on carbon formation and catalyst performance aids in the overall goals of fuel processor development. To this end, we have examined the effect

of diesel fuels and diesel fuel components on the formation of carbon in the gas phase and on the surface of reforming catalysts. Absolute carbon formation was measured by monitoring carbon via *in situ* laser absorption and scattering measurements. TGA measurements provided a measure of carbon deposition on the catalyst. Also, we compared carbon formation from pure components to fuel component mixtures and real fuels to observe synergistic or detrimental effects that may occur. The kinetics of diesel fuel reformation and oxidation are being examined for different diesel fuel components and compositions with different reforming catalysts.

Approach

Fuel partial oxidation and reforming is technology being explored for onboard production of hydrogen for applications such as fuel cells. For the chemical conversion of fuel hydrocarbons, air is combusted with fuel, typically over a catalyst to produce hydrogen and carbon monoxide. Equation 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 Equation 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 Equation 3.



To understand the fundamentals underlying diesel reformation technology, we are employing both experimental measurements and chemical modeling of the systems. To experimentally measure diesel reformation, we have developed partial oxidation (POx) reactors with the supporting test equipment to test the feasibility of generating reformat suitable for a SOFC. The reactor reacts fuel with air (or simulated engine exhaust) in a fuel-rich mixture to generate a gas stream containing

H_2 , CO, CO_2 , N_2 , CH_4 and small amounts of other hydrocarbons. One of our research reactors has optical access windows for analysis of the effluent stream by a laser to observe conditions under which carbon formation occurs. Carbon formation is an important consideration of operation, as it will inhibit durability of the system. This work varies operating conditions to map the outlet gas composition as a function of operating conditions and allows for subsequent optimization of the production of the desired reformat stream. Carbon formation is monitored as a function of fuel component and operating condition. The oxidant feed can be simulated for operation from ambient air or from engine exhaust. Initial operating conditions of the reactor were determined by modeling equilibrium gas compositions for the expected range of S/C and O/C.

The relative distribution of the catalytic conversion has been observed with various fuel components with different catalyst substrates (monoliths and reticulated foams). The onset of carbon formation for different fuel components is mapped as a function of operating with these techniques. The reactor with catalyst observation windows, laser extinction, and scattering facilities is shown in Figure 1.

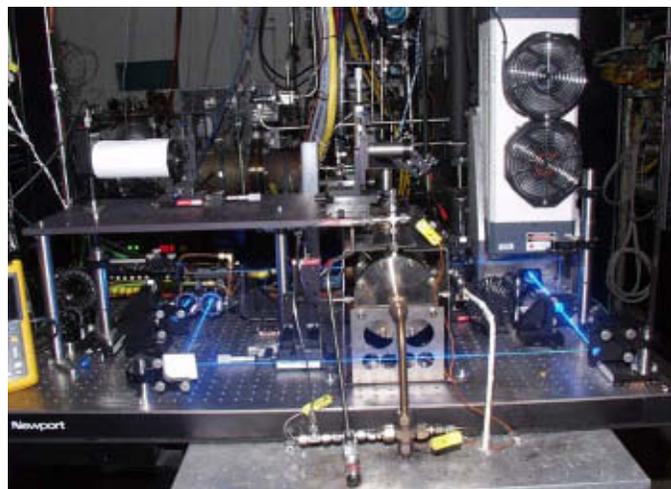


Figure 1. *in situ Carbon Formation Laser Optics*

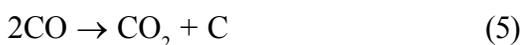
Modeling is conducted using commercial codes, such as ASPEN, to model equilibrium concentrations of expected outlet species of the fuel reformer. Other codes have been developed specifically to model different carbon species and the formation thereof. In particular, modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends.

Modeling Results

Solid carbon formation equilibrium was determined using thermodynamic data to establish the equilibrium composition of reactions at various temperatures, pressures and feed composition. We have used a ternary, or triangular, diagram with each corner representing an atom fraction of 1.0 for each 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% 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 can be found in Gibb's energy of formation data in the literature, as a function of temperature.

Even though the thermodynamics are favorable for the formation of solid graphite, many experimentalists [1, 2] have determined that solid graphite does not actually form, even when the conditions are favorable for that formation. This is probably due to the fact that most catalysts used for C-H-O reactions do not favor, or participate in, the graphite-forming reaction. Dent [1] and other researchers [2, 3] have determined, however, that other forms of solid carbon can be formed during these reactions. These forms are loosely termed amorphous carbon to distinguish them from graphite. There seem to be at least three amorphous forms that are all slightly different and all have slightly different thermodynamic functions. These functions and the conditions under which the solid carbons form are all different from graphite carbon.

The different forms of carbon were isolated by isolating and running the three chemical reactions separately, as shown in Equations 4, 5, and 6, over various catalysts:



The carbon formed by Equations 4 and 5 tend to be whisker-like or tubular [2]. Thermodynamic functions or excess free energies were determined for these carbon types from experiments. The carbon produced from Equation 4 tends to be more ideal, or graphite like, than that produced by Equation 5. Thermodynamic functions tend to be weakly dependent upon the types of catalysts used in the experiments, so it is important to keep in mind that the results presented here are only approximate. Only one data point is available from Equation 6, so the thermodynamic functions for this carbon type are really an interpolation of those carbon types from Equations 4 and 5.

In order to make the results of this study meaningful, we have presented results from the carbon formation modeling in two methods by displaying the carbon formation disappearance temperature for various fuel compositions and operating conditions, and by using the ternary diagrams in the context of the operating conditions. Figure 2 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.

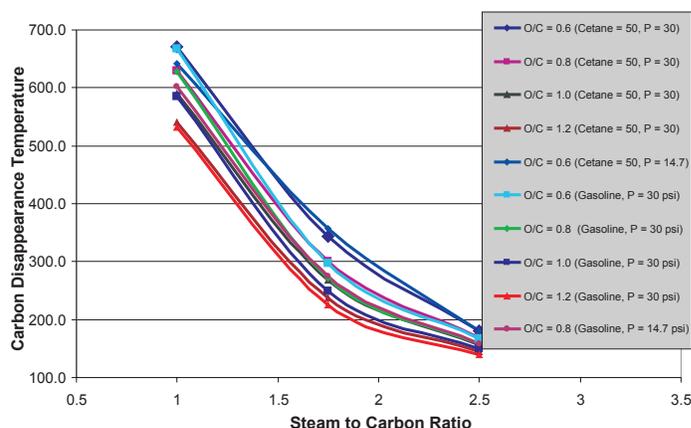


Figure 2. Carbon disappearance temperature for various fuels and operation conditions.

To create C-H-O ternary equilibrium diagrams, the temperatures used for the calculations were 270, 600, 700, and 800 °C. Two pressures were examined, 30 psi and 14.7 psi, or atmospheric. In these calculations

there was only a slight difference in the results, due to the differences in pressure. The differences were so small that they couldn't be detected on the ternary diagram. The temperature differences are more significant and it appears that the higher the temperature, the closer the similarity between the amorphous carbons and the graphite. Figure 3 shows the carbon forming regions for 270 °C and any system pressure between 14.7 and 30.0 psi.

In Figure 3 we have plotted the carbon formation locus for both amorphous and graphite carbon. The area above the blue line represents all compositions that should (but probably won't) form solid graphite. The area above the red line represents all compositions that should (and probably will) form solid amorphous carbon. Figures 4 and 5 represent similar carbon formation calculations for 600 °C and 800 °C respectively.

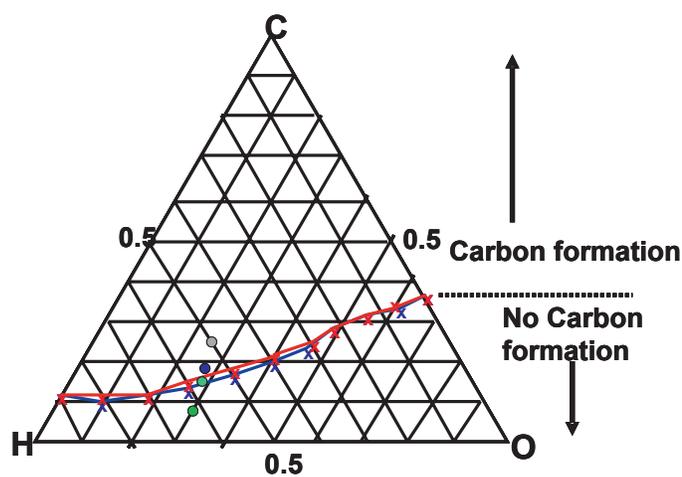


Figure 3. Carbon forming regions for 270 °C and low pressures. The dots correspond to the following fuel/reactor operating conditions: green: $O/C = 1.0$, $S/C = 2.5$, aqua: $O/C = 1.0$, $S/C = 1.0$, blue: $O/C = 1.0$, $S/C = 0.5$, gray $O/C = 1.0$, $S/C = 0.0$. The red line (top) corresponds to amorphous carbon, while the blue line (bottom) corresponds to graphite.

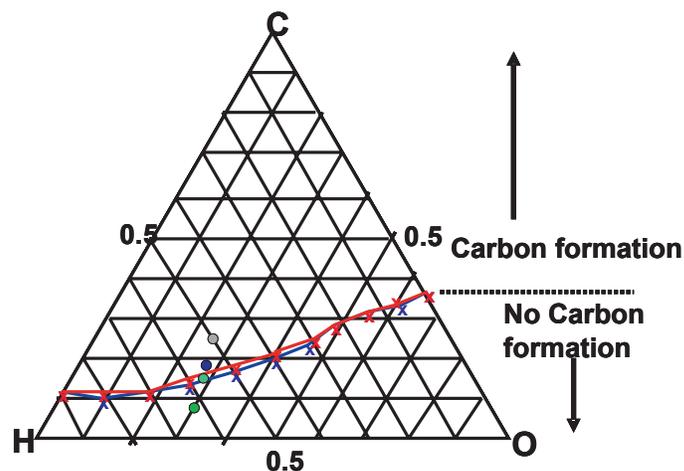


Figure 4. Carbon forming regions for 600 °C and low pressures. The dots correspond to the following fuel/reactor operating conditions: green: $O/C = 1.0$, $S/C = 2.5$, aqua: $O/C = 1.0$, $S/C = 1.0$, blue: $O/C = 1.0$, $S/C = 0.5$, gray $O/C = 1.0$, $S/C = 0.0$. The red line (top) corresponds to amorphous carbon, while the blue line (bottom) corresponds to graphite.

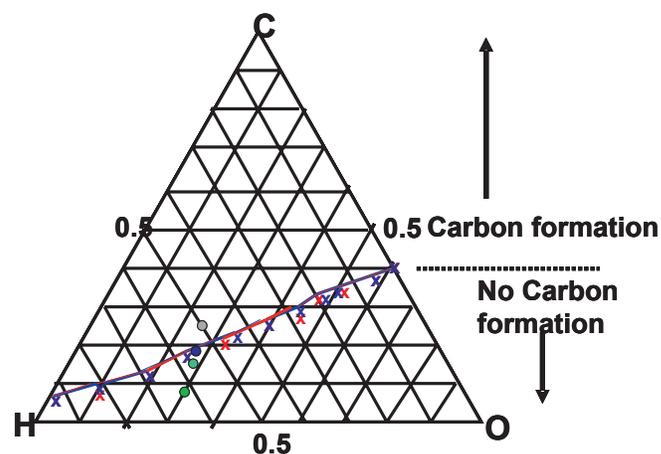


Figure 5. Carbon forming regions for 800 °C and low pressures. The dots correspond to the following fuel/reactor operating conditions: green: $O/C = 1.0$, $S/C = 2.5$, aqua: $O/C = 1.0$, $S/C = 1.0$, blue: $O/C = 1.0$, $S/C = 0.5$, gray $O/C = 1.0$, $S/C = 0.0$. The red line (top) corresponds to amorphous carbon, while the blue line (bottom) corresponds to graphite.

Experimental Results

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. 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.

Carbon formation has been monitored experimentally and is shown in Figure 6 for odorless kerosene. This was conducted for constant S/C, with decreasing O/C. As the O/C (O from air only) was decreased, carbon formation was observed to initiate at an O/C of about 0.7, with large amounts of carbon observed at O/C < 0.7. Note that the temperature also decreases as the O/C is decreased. The catalyst used for this experiment was a catalyzed reticulated foam with catalyst FCR1 from Sud Chemie. Nickel based reforming catalysts show significantly higher carbon formation than do noble metal-based catalysts.

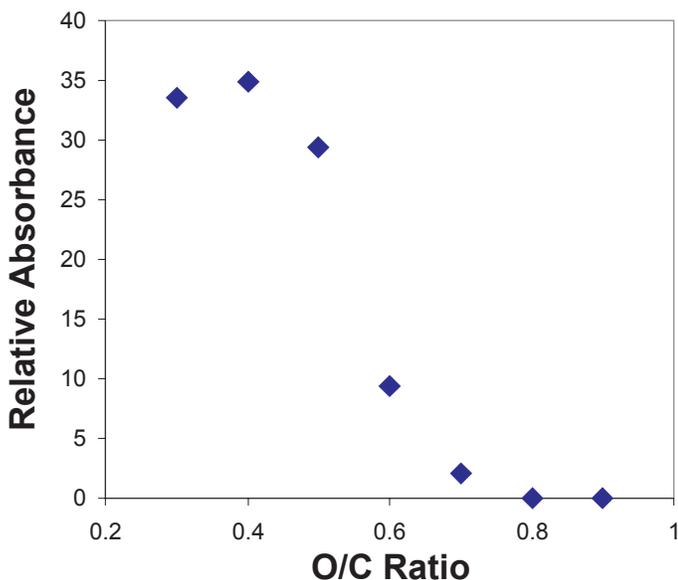


Figure 6. Carbon formation monitoring with laser scattering, fuel was odorless kerosene; S/C = 1.0, shown for various O/C ratios.

Low water content in a diesel reforming SOFC/APU is critical to commercialization. In particular, water may not be available for reactor system start-up. To examine operation that might be expected during system start-up—high temperatures but low water content—we operated for about 8 hours with no water content with an O/C ~ 1.0. Figure 7 shows the inlet pressure to a partial oxidation reactor operating with kerosene, with outlet pressure of 30 psig.

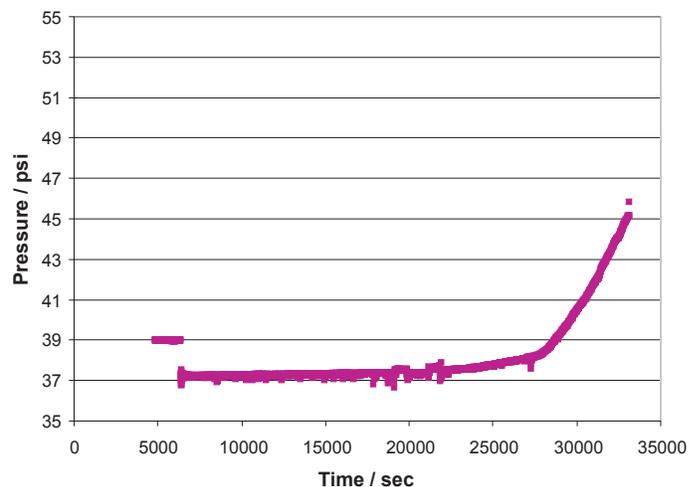


Figure 7. Inlet pressure of partial oxidation reactor operation with kerosene and S/C = 0.0.

This demonstrated that the partial oxidation of a diesel fuel without water can be accomplished, however carbon formation occurs rapidly where in ~7 to 8 hours a prohibitive pressure drop resulted from the formation of carbon.

Beside differences described in fuel reformation from gasoline, we observed that diesel fuel components much more easily pre-ignite. Figure 8 shows operation of a partial oxidation reactor with de-odorized kerosene switched to a normal kerosene during operation. While operation with the de-odorized kerosene occurred smoothly, the normal kerosene pre-ignited before the oxidation catalyst at the same operating conditions. This is potentially an important result, as diesel fuel characteristics have seasonal changes, and these characteristics may be important to diesel reformer operation and design.

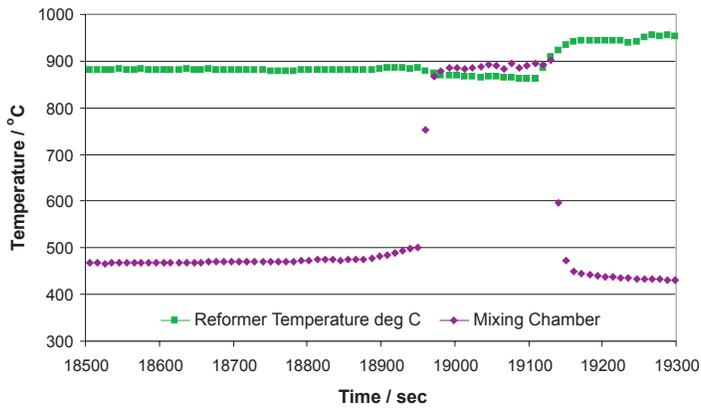


Figure 8. Fuel effect on auto – ignition (pre-combustion). During operation of partial oxidation, the fuel was switched from de-odorized kerosene to normal kerosene.

Conclusions

Various fuel components and fuels have been tested with various O/C and S/C ratios in catalytic fuel reformer reactors. The outlet gas composition has been measured to help determine optimum operating conditions for these reactors. Diesel fuels and diesel fuel components (such as dodecane) were found to require higher residence times for similar conversions than comparable gasoline components. Partial oxidation of kerosene was demonstrated for a period of time, however, carbon formation was occurring. The pre-ignition tendencies for diesel fuel are higher than comparable gasoline.

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 should be kept above 700 °C for low S/C reactor feeds. Ternary equilibrium charts are based on the results generated by a thermodynamic computer code, designed specifically to produce results for ternary diagrams.

References

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3. Colton, J. W., *Hydrocarbon Processing*, January 1981, pp 177-184.