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Title:

Diesel Reforming For SOFC Auxiliary Power Units

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Introduction

The use of a solid-oxide fuel cell (SOFC) to provide auxiliary power for heavy duty trucks can increase fuel efficiency and reduce emissions by reducing engine idling time. The logical fuel of choice for a truck SOFC APU is diesel fuel, as diesel is the fuel of choice for these vehicles. SOFC's that directly oxidize hydrocarbon fuels have lower power densities than do SOFC's that operate from hydrocarbon reformate, and since the SOFC is a costly component, maximizing the fuel cell power density provides benefits in reducing the overall APU system cost. Thus current SOFC APU systems require the reformation of higher hydrocarbons for the most efficient and cost effect fuel cell system. The objective of this research is to develop the technology to enable diesel reforming for SOFC truck APU applications.

Diesel fuel can be reformed into a H_2 and CO –rich fuel feed stream for a SOFC by autothermal reforming (ATR), a combination of catalytic partial oxidation (CPOx), and steam reforming (SR). The typical autothermal reformer is an adiabatic, heterogeneous catalytic reactor and the challenges in its design, operation and durability on diesel fuel are manifold. These challenges begin with the vaporization and mixing of diesel fuel with air and steam where fuel pyrolysis can occur and improper mixing leads to hot and cold spots, which contribute to carbon formation and incomplete fuel conversion. The exotherm of the partial oxidation reaction can generate temperatures in excess of 800 °C [1], a temperature at which catalysts rapidly sinter, thus reducing their lifetime. The temperature rise can be reduced by the steam reforming endotherm, but this requires the addition of water along with proper design to balance the kinetic rates. Carbon formation during operation and startup can lead to catalyst deactivation and fouling of downstream components, thus reducing durability of the fuel processor. Water addition helps to reduce carbon formation, but a key issue is the source of the water onboard a vehicle. Additionally, changes in diesel fuel composition, such as seasonal changes affect the reactor operation and design considerations. Our research addresses these issues through an experimental and modeling examination of the fundamentals of these processes.

Experimental

Experimental measurements of diesel reforming are made in heterogeneous catalytic reactors simulating SOFC APU diesel reformer operation. The results from two reactor designs will be discussed; one reactor operating iso-thermally under controlled operating temperatures, and one reactor operating adiabatically which operates with a temperature profile defined by the autothermal reforming reactions. The adiabatic reactor was used to investigate and develop direct diesel fuel injection for effective fuel vaporization and mixing with air and steam, and was also instrumented to measure axial profiles through the catalyst volume. The isothermal reactor was used to map carbon formation as a function of operating conditions (S/C, O/C) for both partial oxidation and steam reforming and quantity of SOFC anode recycle.

Following the experiments, the catalyst surface area was measured using BET and carbonaceous deposits characterized with TGA. The fuel reforming reactions were performed over noble metal based catalysts (platinum and rhodium). The catalysts are supported on a substrate of reticulated YSZ (Yttria Stabilized Zirconia) foam.

Results

The successful operation of a diesel reformer requires effective mixing of fuel, air and steam. This is especially challenging with diesel fuel because of it's propensity to pyrolyze upon vaporization. This problem was solved in the adiabatic reactor by using direct fuel injection through a commercial (BETE PJ8) nozzle. The air, steam, and SOFC anode recycle components were injected through an annulus around the fuel nozzle and mixed with the diesel fuel prior to introduction to the catalyst. Good mixing of the fuel and air streams was verified by thermal imaging of the outlet catalyst face. Proper fuel distribution was observed at flow rates greater than 24 g/min fuel flow, thus, the reactor turndown is limited by the fuel flow distribution from the nozzle. Fuel/steam/air preheat was also limited to below 180 °C to prevent either clogging of the fuel nozzle by pyrolysis or unsteady fuel flow caused by fuel vapor lock.

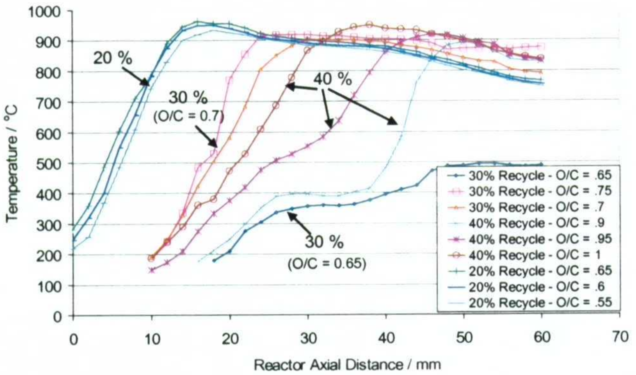

Figure 1. Axial temperature profiles measured during diesel reforming for simulated anode exhaust recycle ratios of 20 % (O/C = 0.55, 0.60, 0.65), 30 % (O/C = 0.65, 0.70, 0.75) and 40% (O/C = 0.90, 0.95, 1.00). Adjusted O/C with recycle ratio to obtain similar operating temperatures. Fuel was Low-S Swedish diesel fuel. Pt / Rh supported catalyst, 1.5" diameter. Residence time ~ 50 msec.

Water availability on-board a transportation vehicle such as a truck is a non-trivial issue. The simplest method to make water available for the diesel ATR is by recycling the SOFC anode exhaust. However, this also recycles other diluents such as nitrogen and carbon dioxide and unconverted hydrogen and carbon monoxide. The effect of SOFC anode exhaust recycle on diesel reforming was investigated by injecting a $H_2/N_2/H_2O$ mixture into the operating adiabatic reactor. Figure 1 shows axial temperature profiles measured through a Pt/Rh catalyst supported on a YSZ reticulated foam during diesel reforming of low-sulfur Swedish diesel fuel with simulated SOFC anode exhaust recycle rates of 20%, 30%, and 40%. The O/C ratio was increased as the recycle flow was increased in order to maintain the reformer outlet temperatures between 750 and 850 °C. The temperature profiles at 20% recycle show a temperature rise from the oxidation reactions starting at the catalyst inlet and peaking about 10 mm downstream. The temperature profiles at 30% and 40% recycle rates show the temperature rise from oxidation moves downstream to about 10-20 mm from the catalyst inlet. This is most likely due to the diluent effect of the SOFC recycle, and the resulting decrease in

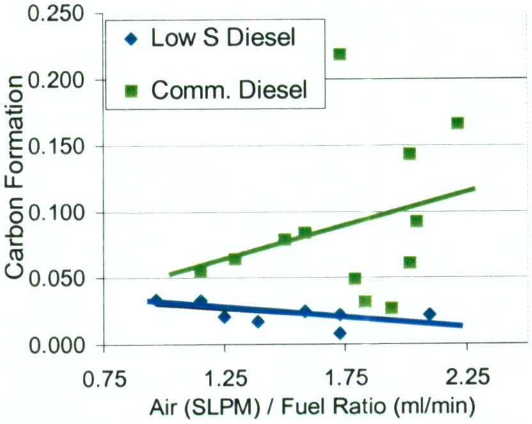

Figure 2. Carbon formation as a function of air/fuel ratio measured during adiabatic diesel reforming at 35% SOFC anode exhaust recycle ratio.

reactor residence time. Higher recycle ratios require also an increase in the O/C to achieve a similar adiabatic temperature because of the increased flow of inert species.

Carbon formation has been identified as a main durability concern during the autothermal reforming of diesel fuel. Figure 2 shows measured carbon formation during adiabatic diesel reforming of low-S Swedish and commercial diesel fuels as a function of air-fuel ratio. The measured carbon formation with commercial diesel fuel was an average three times higher than that for the low-S Swedish diesel fuel. Carbon formation increased with increasing air flow (and temperature) for commercial diesel fuel, while carbon formation decreased with increasing air flow (and temperature) for low-S Swedish diesel fuel.

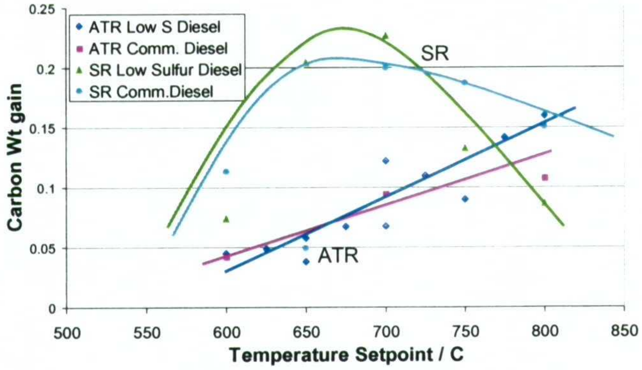

Figure 3. Carbon formation measured as a function of temperature in the isothermal microcatalyst reactor for autothermal reforming (ATR) conditions (O/C = 1.0, S/C = 0.34) simulating 35% SOFC anode exhaust recycle ratio and for steam reforming conditions (O/C = 0.0, S/C = 1.0).

Experiments were conducted using an isothermal microscale reactor to clarify the effects of temperature and specific operating conditions on carbon formation rates. Figure 3 shows carbon formation as a function of temperature for autothermal reforming (ATR - O/C = 1.0, S/C = 0.34) and for pure steam reforming (SR - O/C = 0.0, S/C = 1.0) of low-S Swedish and commercial diesel fuels. The ATR conditions simulate measurements for a SOFC anode recycle of 35%. Under these ATR conditions, carbon formation increases linearly with temperature, contrary to equilibrium predictions. Carbon formation during steam reforming appears to be limited by kinetic rates as the temperature increases to a carbon formation maximum at 700 °C, then, at higher temperatures, carbon formation decreases with increasing temperature as predicted by equilibrium. During these experiments, the carbon formed during reforming was collected downstream of the catalyst and did not adhere to the Pt/Rh catalyst surface. However, carbon has been observed on the surface of Pt/Al_2O_3 catalysts in other diesel reforming measurements [10].

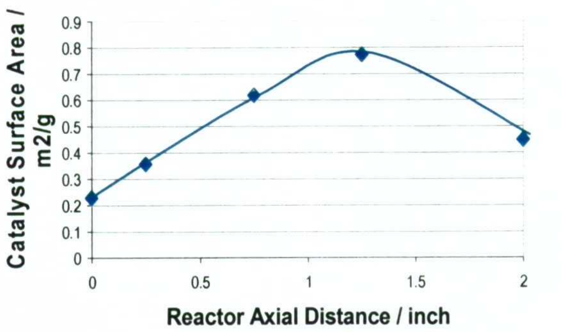

Figure 4. Axial profile of catalyst surface area (radially averaged) after adiabatic diesel reforming at 35% anode recycle by BET.

For optimal efficiency, a diesel reformer should convert all of the diesel fuel to CO, CO_2, and H_2. In practice, hydrocarbon breakthrough is observed after 500 to 1000 hours of operation and is ascribed to loss of catalyst surface area [2,3]. To investigate the effect of operation during ATR on the catalyst surface area, a cylindrical catalyst was sectioned axially and radially and the catalyst surface area measured using BET. Little difference in catalyst surface area was measured in the radial direction.

The axial profile (radially averaged) of the catalyst surface area after testing is shown in figure 4. The fresh surface area of ~ 4.3 m^2/g. Catalyst surface areas are smaller at the inlet than at longer axial distances. This is an indication that the high temperatures observed from the oxidation reaction are sintering the catalyst at the reactor inlet, in correspondence with the axial temperature distribution observed in Figure 1.

Conclusions

Diesel fuel reforming has been conducted under isothermal and adiabatic conditions to examine the oxidation and reforming reactions, operational conditions, catalyst activity, durability, and carbon formation. Diesel reforming with adiabatic operation has simulated SOFC anode recycle, without additional water, with operation at about 30 – 40 % recycle reasonably successful in terms of diesel conversion, carbon formation and catalyst temperature control. Temperature profiles inside the catalyst have been measured for a number of recycle rates and oxygen/carbon ratios and for various fuels, including commercial diesel and low-sulfur diesel. Increasing recycle rates moves oxidation downstream in the reformer as does commercial diesel fuel compared with low-sulfur diesel fuel. High adiabatic temperatures (> 800 °C) are generally observed at low recycle rates (20 %). Operation with 30 – 40% recycle rate appears to be good trade-off between high adiabatic temperatures and larger reactor volume.

Carbon formation has been modeled for equilibrium conditions for formation and has been measured during isothermal and adiabatic diesel reforming operation. Isothermal carbon formation measurements from steam reforming appear to show both kinetic and equilibrium effects, with a maximum amount of carbon formation at about 700 °C, for both commercial and low sulfur diesel fuels. Autothermal reforming measurements made isothermally show increasing carbon formation with increasing temperature, in contrast to equilibrium predictions. Adiabatic operation shows lower carbon formation for higher operating temperatures for low sulfur diesel fuel, but higher carbon formation for higher operating temperatures for commercial diesel fuel.

References

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Acknowledgments

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