
IV.B.2 Reformer for Conversion of Diesel Fuel into CO and Hydrogen

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Objectives

- Develop a fuel reformer for converting pump-grade diesel fuel with 15 ppmw sulfur into a mixture of H₂ and CO suitable for use in solid oxide fuel cells (SOFC).
- Demonstrate the use of a self-cleaning reactor wall, which diffuses and effuses oxygen to prevent the formation of carbonaceous layers that could otherwise plug a reformer.
- Synthesize and evaluate low-cost, sulfur tolerant, perovskite-based catalysts for use on the reformer wall and in the hot zone.

Accomplishments

- Designed and built laboratory scale reformer system for testing catalysts and design parameters.
- Commissioned laboratory reactor components (fuel handling lines, air input, seals and fittings, gas chromatograph, etc.).
- Measured permeability of air through porous yttria-stabilized zirconia (YSZ) and found it to meet or exceed minimum design specification.
- Designed and fabricated porous YSZ tubes according to design specifications.
- Analyzed pump-grade low-sulfur diesel fuel for sulfur content and carbon-hydrogen ratio.

Introduction

A fuel reformer is under development for the conversion of pump-grade diesel fuel into a mixture of hydrogen and carbon monoxide which can be utilized in solid oxide fuel cells. The design of the reformer is being driven by the following considerations. Thermodynamic

analysis indicates that the desired products will be maximized and overwhelmingly favored if one atom of oxygen is added for each carbon atom in the fuel and if the mixture is brought to equilibrium above about 950°C, and preferentially above 1,000°C [1, 2]. Such temperatures place severe stability requirements on catalysts and reformer wall materials. Components must not melt or significantly evaporate, or form volatile compounds which potentially could contaminate fuel cells downstream. In the strongly reducing, high-temperature environment of the reformer, many common ceramics and oxide catalyst supports are reduced, and these must be avoided. Most common catalysts are sintered and deactivated at such high temperatures. Sulfur in the diesel fuel can also poison common catalysts. The reactor must be almost perfectly insulating if maximum efficiency is to be achieved, because the heat released by the partial oxidation of diesel fuel is just sufficient to heat fuel and air to the reaction temperature.

Thermodynamic and kinetic analyses indicate that formation of elemental carbon is favored in the range of 300–900°C. A major challenge is to bring the diesel fuel from room temperature to the catalytic hot zone without deposition of carbon onto reactor walls. Deposition of carbon is autocatalytic and can rapidly plug reactors. Infrared radiation from the catalyst hot zone can heat reactor walls in cool zones or heat the fuel injector nozzle, cracking diesel fuel to carbon and clogging reactors. Deposition of carbon at lower temperatures is suppressed by addition of extra oxygen, but usually at the expense of efficiency due to formation of deep oxidation products, carbon dioxide and steam. Thermodynamics also indicates that if the reformat is cooled, some hydrogen and carbon monoxide could be lost due to formation of carbon, water, methane and carbon dioxide, which become thermodynamically favored and could form in the exhaust if exhaust line surfaces are catalytic.

Approach

A catalytic membrane reactor is being developed. In such a reactor, oxygen is brought into the system through the reactor walls (see Figure 1). A goal is to form self-cleaning walls which prevent formation of carbon. High local concentration of oxygen near the inner walls, combined with oxidation catalysts having good bulk transport properties for atomic oxygen, suppresses deposition of carbon. Porous yttria-stabilized zirconia is being used as one reactor wall material because of its good thermal and chemical stability, its ability to transport oxygen through the bulk, and because of its good thermal insulating properties. Silver,

is being investigated as an oxidation catalyst on the inner walls of the cool zones of the reactor and at the fuel injector nozzle. Silver has the advantage of high oxygen diffusivity through its bulk, allowing oxygen to attack deposited carbon from beneath. Silver also has the highest reflectivity for infra-red radiation of any element, allowing reflection of radiation, especially from the fuel nozzle, back to the hot zone. Perovskite-based catalysts are being investigated as oxidation catalysts on the walls of the hot zones of the reactor. These materials also readily transport oxygen through their bulk, allowing attack of carbon from beneath. Oxygen transported through the porous zirconia and high local concentration of oxygen near the walls helps stabilize the perovskites and inhibit reduction of these oxides.

Perovskites containing cobalt and iron are being investigated as oxidation catalysts in the hot zone. Such catalysts act as reverse Fischer-Tropsch type catalysts, converting hydrocarbons back into hydrogen and carbon monoxide. These less expensive catalysts are being

compared to a platinum-rhodium wire gauze. Molecular oxygen adsorbs and dissociates on the Pt-Rh surface into atomic oxygen. Atomic oxygen is especially reactive with hydrocarbons and is desired for oxidation of the more refractory aromatic compounds in the diesel fuel. Unlike Pt-Rh bimetallic catalysts supported by zirconia, the Pt-Rh gauze does not suffer from sintering. At high temperatures, the gauze is not poisoned by sulfur at levels in commercial diesel fuel (15 ppmw). The high cost of the noble metals will prevent their use in all but military applications but is providing a good baseline for comparison of activity of the less expensive perovskite-based catalysts.

Results

Most of the activity in this reporting period involved the design, construction and commissioning of a laboratory apparatus (Figure 2) for testing of the various components of the catalytic membrane reactor. A schematic of the catalytic membrane reactor is shown in Figure 1. Inner walls are all of yttria-stabilized zirconium

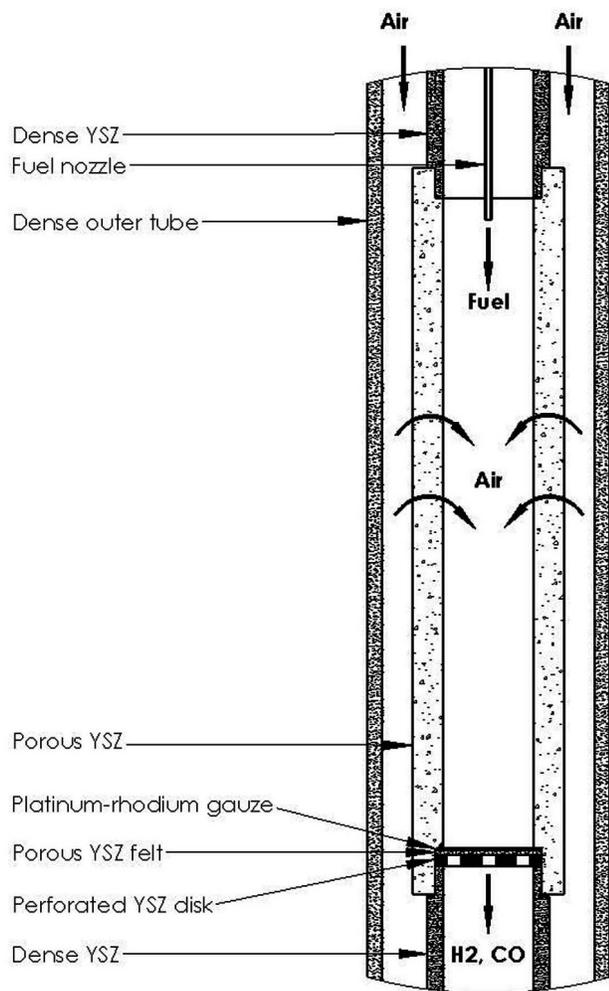


FIGURE 1. Schematic of Catalytic Membrane Reactor Employing Porous Yttria-stabilized Zirconia Inner Walls

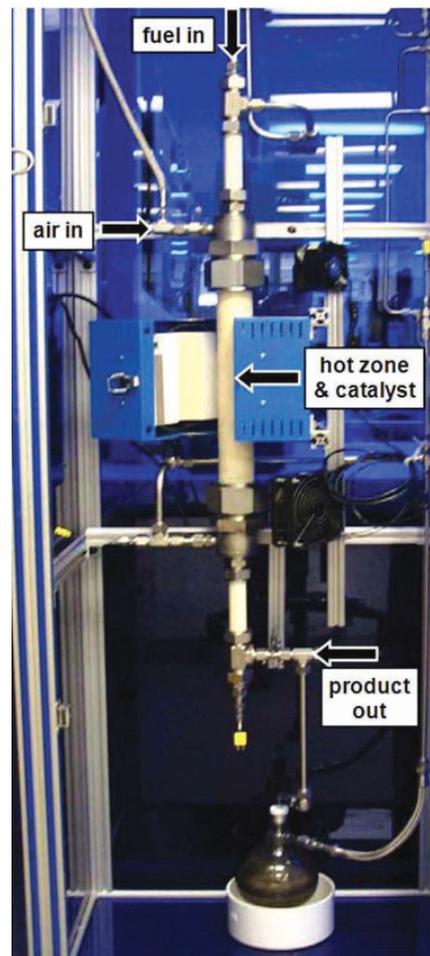


FIGURE 2. Laboratory Test Apparatus

oxide. Dense cylinders of yttria-stabilized zirconia are used surrounding the fuel injector nozzle and in the exhaust. In the exhaust tube, it is desired to use a catalytically inert inner wall material to avoid reaction between H_2 and CO to form H_2O , CH_4 , CO_2 and C, which have a significant thermodynamic driving force for formation at temperatures below about $900^\circ C$ [1].

Air is brought into the system through the walls of a porous yttria-stabilized cylinder (Figure 1). Figure 3 shows one end the porous cylinder, which is $\frac{1}{4}$ inch (0.635 cm) thick to provide mechanical support and insulation. Flow of air through the porous material is more than adequate for the partial oxidation of the fuel.

The present configuration employs a platinum-rhodium wire gauze as reforming catalyst in the reactor hot zone. The wire gauze is placed atop a porous felt of yttria-stabilized zirconia. The purpose of the porous felt is to promote turbulence and allow longer residence time of the reactive gases near the wire gauze. Figure 4a shows a scanning electron microscope image of the wire gauze. Figure 4b shows an image of the zirconia felt.

Most of the zirconia employs yttria-stabilized material containing quantities of yttria near that of the Nernst Mass (8.8 mole % = 15 mass % Y_2O_3), which maximizes oxygen flux. In the hot zones, however, yttria concentrations above about 9.5 mole % are being considered to ensure that the material remains completely within the cubic fluorite phase of the ZrO_2 - Y_2O_3 phase diagram [3] to avoid potential phase transformations at elevated temperatures.

Perovskite catalysts containing cobalt and iron as the catalytic metal [1] have been synthesized. The goal

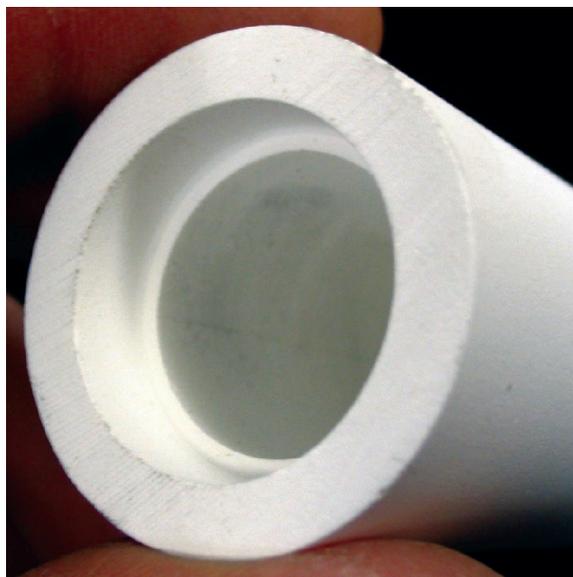


FIGURE 3. Photograph of porous yttria-stabilized zirconia tube used in the catalytic membrane reactor. Walls are $\frac{1}{4}$ inch (0.635 cm) thick.

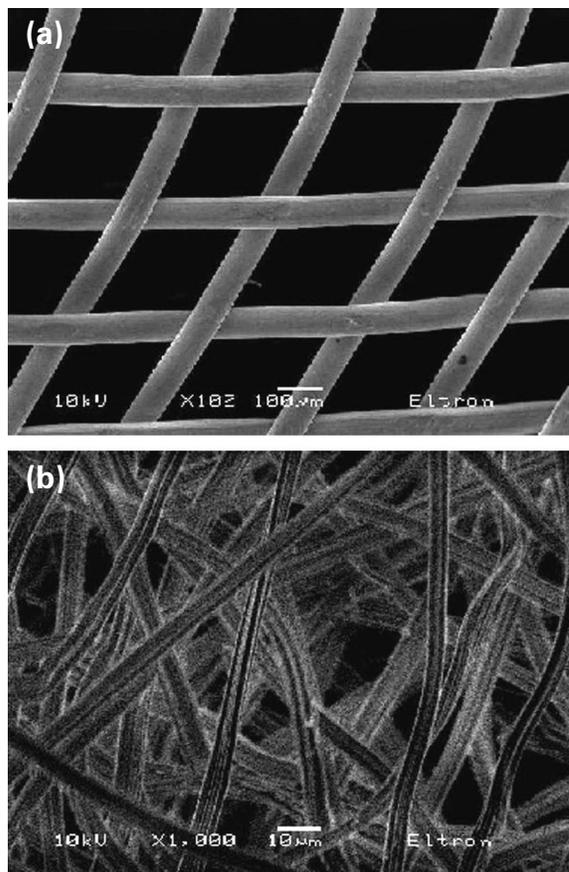


FIGURE 4. (a) Scanning electron microscope image of platinum-rhodium wire gauze used as a diesel fuel reforming catalyst. (b) Image of yttria-stabilized zirconia felt.

is to replace the expensive Pt-Rh wire gauze with less expensive pellets of perovskite catalysts [4].

Conclusions and Future Directions

- A laboratory test apparatus has been completed and commissioned.
- A catalytic membrane reactor using inner walls of porous zirconia has been fabricated and tested with commercial diesel fuel containing ~ 15 ppmw sulfur using a Pt-Rh wire gauze as the ideal test catalyst.
- Perovskite catalysts have been synthesized and will be tested.
- Considerable laboratory tests and engineering design remain to produce a viable prototype design with low cost. Considerable effort remains to control carbon deposition on all components.
- Stability of catalysts and components under repeated temperature cycling must be demonstrated. Insulation and thermal efficiency must be improved. Fuel ignition sources must be improved. Parasitic power consumption must be reduced.

Special Recognitions & Awards/Patents Issued

1. Michael V. Mundschau, *Catalytic Membrane Reactor and Method for Production of Synthesis Gas*, U.S. Provisional Patent Application Filed September 8, 2006.

FY 2007 Publications/Presentations

1. M.V. Mundschau and J.A. Benjamin, *Liquid Fuel Processing Using Catalytic Membrane Reactors*, SECA Core Program – Fuel Processing, 7th Annual SECA Workshop and Peer Review, Philadelphia, Pennsylvania, September 13, 2006.
2. D.S. Jack, J.H. White, J.A. Trimboli, C.G. Burk, S.L. Rolfe, D.H. Anderson, M.V. Mundschau, *Liquid Fuel Reforming Using Catalytic Membrane Reactors*, Submitted to and accepted by the Division of Fuel Chemistry for the 234th ACS National Meeting, Boston, MA, August 19–34, 2007.

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3. H. G. Scott, Phase Relationships in the Zirconia-Yttria System, *J. Mat. Sci.* **10** (1975) 1527–35.
4. Di-Jia Liu and Michael Krumpelt, Activity and Structure of Perovskites as Diesel-Reforming Catalysts for Solid Oxide Fuel Cells, *Int. J. Appl. Ceram. Technol.* **2** [4] (2005) 301–307.