

Integrated Fuel Processor Development*

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ABSTRACT

The Department of Energy's Office of Advanced Automotive Technologies has been supporting the development of fuel-flexible fuel processors at Argonne National Laboratory. These fuel processors will enable fuel cell vehicles to operate on fuels available through the existing infrastructure. The constraints of on-board space and weight require that these fuel processors be designed to be compact and lightweight, while meeting the performance targets for efficiency and gas quality needed for the fuel cell. This paper discusses the performance of a prototype fuel processor that has been designed and fabricated to operate with liquid fuels, such as gasoline, ethanol, methanol, etc. Rated for a capacity of 10 kWe (one-fifth of that needed for a car), the prototype fuel processor integrates the unit operations (vaporization, heat exchange, etc.) and processes (reforming, water-gas shift, preferential oxidation reactions, etc.) necessary to produce the hydrogen-rich gas (reformate) that will fuel the polymer electrolyte fuel cell stacks. The fuel processor work is being complemented by analytical and fundamental research. With the ultimate objective of meeting on-board fuel processor goals, these studies include: modeling fuel cell systems to identify design and operating features; evaluating alternative fuel processing options; and developing appropriate catalysts and materials. Issues and outstanding challenges that need to be overcome in order to develop practical, on-board devices are discussed.

INTRODUCTION

Hydrocarbon fuels, such as gasoline and diesel, have been considered as potential fuels for vehicles powered by a polymer-electrolyte fuel cell (PEFC) because of their high energy content, low cost, and well-established infrastructure (1). However, for a fuel cell-powered vehicle, an on-board processor is required to convert these fuels to a hydrogen-rich fuel gas. One option for on-board processing is autothermal reforming, in which the hydrocarbon fuel is reacted with both air and steam to produce hydrogen. The heat generated in autothermal reforming can be controlled by adjusting the proportions of fuel, air, and steam in the feed. External heat sources are not required; therefore, autothermal reformers (ATR) are

simpler and smaller than steam reformers and demonstrate better dynamic response to transients. Furthermore, they operate at lower temperatures than partial oxidation systems. Argonne National Laboratory (ANL) has developed a fuel processor based on catalytic autothermal reforming of hydrocarbon fuels that incorporates a novel catalyst.

In this work, we present results for the catalytic reforming and processing of isooctane and gasoline with a bench-scale fuel processor incorporating autothermal reforming. We were able to demonstrate complete conversion of isooctane, a surrogate for gasoline, to lower hydrocarbons and hydrogen. We demonstrated the processing of the reformate by using in-house water-gas shift catalysts to obtain a process gas stream containing less than 1% carbon monoxide (CO).

EXPERIMENTAL PROCEDURE

The autothermal reforming catalysts were either fabricated in-house or obtained from Sud-Chemie, Inc., in pellet form. Zinc oxide pellets for H₂S removal were obtained from Sud-Chemie, Inc. The water-gas shift catalysts were fabricated using a proprietary formulation. Isooctane (2,2,4 trimethylpentane, C₈H₁₈) was obtained from Sigma-Aldrich, Inc., and was used without further purification. A premium gasoline blend was obtained from the ANL motor-pool.

The processor product gases were analyzed continuously with on-line infrared analyzers for carbon dioxide and carbon monoxide; a thermal conductivity detector was used for hydrogen. Batch samples of product gases were analyzed for hydrocarbons with a gas chromatograph/mass spectrometer (GC/MS).

Selected experiments were carried out in a 1-cm (0.41-in) diameter microreactor. The microreactor was housed in a furnace to maintain a constant bed temperature. Gas flow rates were controlled with mass flow controllers. The water flow rate was controlled with a high-performance liquid chromatography (HPLC) pump. Water could be fed into the reactor as a liquid, or vaporized prior to injection.

INTEGRATED FUEL PROCESSOR

A fuel processor consists of several components: reformer, sulfur scrubber, water-gas shifter, and preferential oxidizer. These units may be separate components, or they may be integrated. The reformer breaks down the fuel, producing a gas (reformat) rich in hydrogen but containing other reaction products. Before it is a suitable fuel for a PEFC, carbon monoxide or sulfur compounds must be removed from the reformat. These components poison the electrodes of a PEFC stack. Sulfur is present in the reformat as H_2S . It can be removed with a ZnO sorbent bed. Carbon monoxide cleanup is achieved with water-gas shift (WGS) reactors that convert CO and water to CO_2 and hydrogen (2). Any residual CO is removed with a preferential oxidizer, where CO is reacted with oxygen to form CO_2 . As part of the fuel processor development effort at ANL, we are developing more robust WGS catalysts that will work better under transient operating conditions than current catalysts developed for process plant service. We are also working to optimize sulfur scrubber configurations for use within the processor.

This paper reports on a bench-scale fuel processor that has integrated the autothermal reformer, the sulfur scrubber, and water-gas shift reactor into a single piece of hardware. The ANL processor is based on catalytic autothermal reforming. A catalytic process should significantly reduce the operating temperature, leading to faster start-up, greater efficiencies, and a wider choice of materials for construction. An appropriate ATR catalyst will promote reactions that produce H_2 and minimize undesirable components, such as CO, CH_4 , and coke. ANL has developed an ATR catalyst that achieves complete conversion of isooctane, methanol, and other fuels.

The bench-scale integrated fuel processor (Fig. 1) is 20.3 cm (8 in.) in diameter and 35.6 cm (14 in.) in height, and it is rated for up to 10 kWe power output. It includes an autothermal reformer, a sulfur scrubber, and a water-gas shifter, shown schematically in Fig. 2. In the processor, the internal configuration superheats the air and steam before they are combined with injected fuel and additional water at the inlet of the reformer. The thermal integration is also designed to achieve a declining temperature profile within the shift bed, minimizing the size of that reactor. A similar configuration has been successfully tested with methanol, ethanol, methane, isooctane, and gasoline (3).

During start-up, a mixture of fuel and air is ignited by a small, electrically heated coil or "igniter." Once the fuel-air mixture has ignited, the igniter is turned off, and the system becomes self-sustaining. Autothermal reforming can be considered a melding of partial

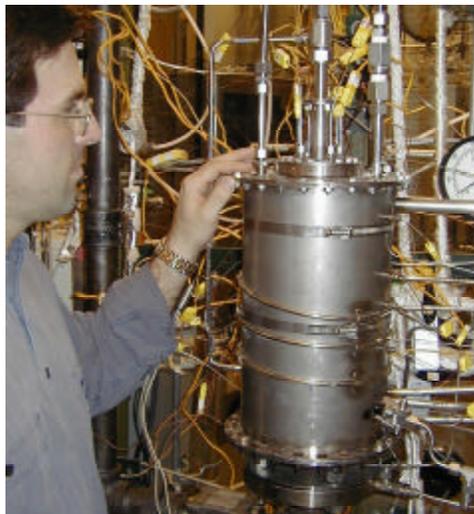


Fig. 1. Integrated fuel processor.

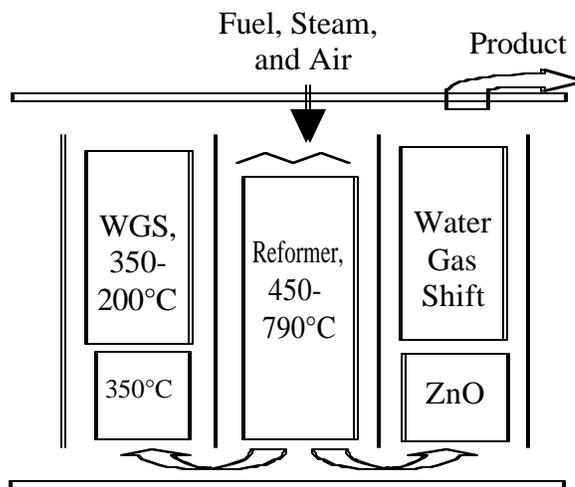


Fig. 2. Schematic of the integrated fuel processor.

oxidation ($CH_x + 1/2O_2 = CO + x/2H_2$) with steam reforming ($CH_x + 2H_2O = CO_2 + (2+x/2)H_2$) over a catalyst to produce a hydrogen-rich reformat. With the ANL catalyst formulation, and depending on the type of fuel, the reformer operates at between 450 and 900°C, up to several hundred degrees lower than non-catalytic processes. Because conversion to CO_2 is thermodynamically limited at these elevated temperatures, further processing of the reformat is required. At the exit from the ATR catalyst bed, the reformat typically contains 5–10% CO. Additionally, gasoline contains substantial quantities of sulfur compounds at concentrations as high as 300 ppm, which is equivalent to 30 ppm in the process gas. This CO and sulfur must be eliminated from the reformat.

In the processor, ZnO is used to scrub the reformat of sulfur. Exiting the reformer, the sulfur is predominantly present as H₂S, which reacts with the ZnO at ~350°C to form ZnS and H₂O; by this process, sulfur can be reduced to approximately 1 ppm in the reformat, the equilibrium value.

CO is removed from the reformat via the WGS reaction over a catalyst; CO and water react to form CO₂ and H₂. This reaction is moderately exothermic but conversion is limited by equilibrium. Complete conversion to the low parts-per-million range requires low temperatures (<200°C), where the kinetics of the reaction are very slow and the reactor would become prohibitively large. To minimize the size of the WGS bed, the largest component of the processor, a declining temperature profile is set up within the bed. If the experimental profile shows a much steeper drop in temperature than is desired, poorer conversions will result, particularly at higher fuel feed rates.

The WGS catalyst in the processor tests described here is a formulation developed at ANL. The major advantage of ANL's formulation over standard commercial catalysts is that it is air-stable. The trade-off is a moderate reduction in activity (2). Air-stability is particularly important for systems that go through many start-up and shut-down cycles, as is the case for automobiles. As shown in Fig. 3, we were able to achieve a CO content of <1% in the final dry reformat by using the ANL shift catalyst in the fuel processor.

ISOCTANE - Isooctane was used as a surrogate for gasoline. Isooctane provides a fixed reference composition, eliminating one process variable. Small changes to the water and air feeds were used to modulate the reformer temperature, to maximize hydrogen yield without overheating the reactor components. Figure 4 shows the feed rates of isooctane, air, and water into the processor for a test with isooctane, while Fig. 5 shows the composition of product gases produced by the processor. In this test, the power output of the reactor was raised in stages. The fuel feed rate was gradually increased from 14 to 42 mL/min, equivalent to 25 to 75% of the rated power. The O₂/fuel molar ratio was maintained 3.0-3.5, and the average reformer temperature was 750-800°C. The concentration of hydrogen varied from 38 to 43%, with an average value of 41%. Greater than 99% isooctane conversion was achieved. The theoretical maximum after complete conversion of CO in the shift beds for the feed ratios used was 46.4%. The average CO₂, CO, and CH₄ concentrations were 17%, 4%, and 2%, respectively.

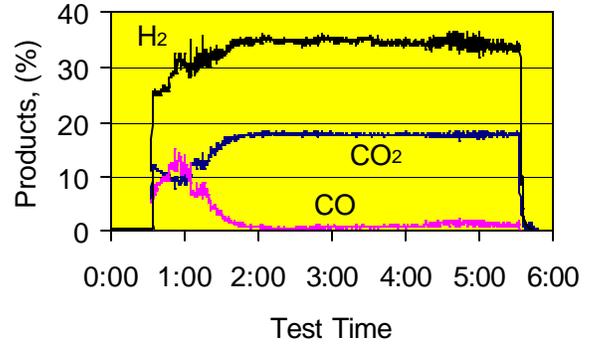
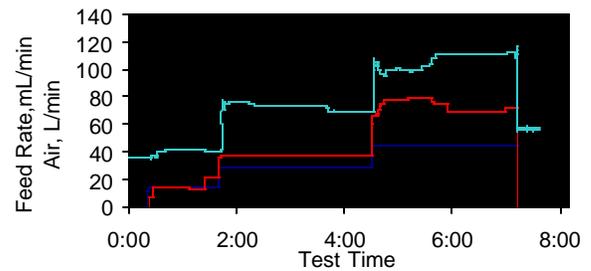


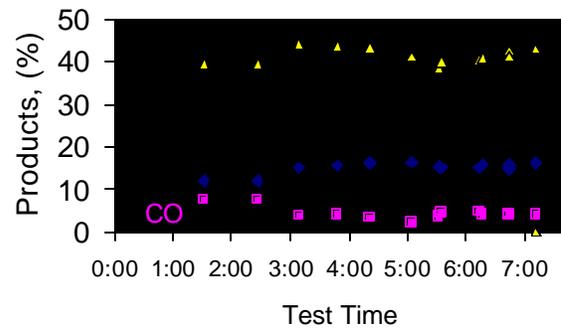
Fig. 3. Product composition from test with isooctane at fuel feed of 14 mL/min (equivalent to 2.5 kWe).

Fig. 4. Isooctane reforming test: feed rates of isooctane,



air, and water.

Fig. 5. Product composition for test with isooctane.



The fuel processor operated most effectively at 28 mL/min, equivalent to 5 kWe, with maximum hydrogen yield and CO elimination. Increasing the fuel feed rate from 14 to 28 mL/min increased the hydrogen (40 to 43%, dry) and carbon dioxide (12 to 16%, dry) concentrations, with a significant reduction in carbon monoxide from 7 to 3%. At this feed rate, the processor produced 75 L/min of hydrogen, sufficient to generate 4.2 kWe in a fuel cell stack.

These changes in product concentrations can be attributed to the temperature profiles achieved within the

ATR and WGS reactors. The CO concentration is strongly dependent on WGS temperature. The WGS bed was at a uniformly higher temperature at the higher fuel feed rate, improving the CO conversion. In this test, however, CO level reduction to less than 1% was not accomplished, because the WGS temperatures were still too low. Within the autothermal reformer, temperatures were more stable at the higher fuel feed rates, apparently because fuel delivery was more stable at the higher flow rate. There was some pulsing of the fuel and water feeds, especially at low feed rates, with the pumps that were used.

When the fuel feed rate was increased further to 36 mL/min, there was a reduction in hydrogen concentration, a slight reduction in isooctane conversion, and an increase in CO concentration. This reduced performance of the fuel processor was caused by a change in the reactor temperature profiles to less than the optimum. At the higher feed rate, the average reformer temperature tended to oscillate over a wider range, 750–850°C; the peak temperature was higher as well. The greater oscillations were likely related to fluctuations in the fuel delivery or to a flow that was somewhat below the expected fuel delivery rate.

The higher CO content in the reformat is again attributed to a non-ideal temperature profile and too low temperatures within the WGS bed. Temperatures within the WGS were between 200 and 350°C. At the lower flow rate, the lower gas-hourly space velocity somewhat compensated for the non-ideal profile. However, at the higher fuel feed rates, CO conversion was more strongly affected.

GASOLINE – Premium gasoline is a complex mixture with a substantial aromatic fraction. The boiling points vary, making uniform vaporization difficult. Larger aromatic components require higher temperatures to break down. To determine the relationship of these factors to the operating conditions, the fuel processor was run with a premium gasoline. As in the isooctane tests, the gasoline feed rates were 14 and 28 ml/min. In this run, the nominal O₂/fuel molar ratio was 3.4–3.7, using isooctane as a reference composition for gasoline. The average reforming temperature was 780°C at the lower fuel feed rate; the processor ran hotter for gasoline than for isooctane. The hydrogen concentration in the product gas varied from 30 to 38%, lower than in similar tests with isooctane. The lower hydrogen concentration and the higher operating temperatures can be partially attributed to the deviation between the assumed fuel composition and the actual composition. The hydrogen-to-carbon ratio for gasoline, typically 2–2.1, is lower than that for isooctane. The hydrocarbon products were primarily C₁–C₄ hydrocarbons; only trace quantities of aromatics were detected.

The CO content dropped to <2% at the lower fuel feed rate as the shift beds warmed up, but it rose to >5% at the higher processing rates. As was the case for isooctane, the higher CO at high throughputs could be

attributed to a less than desirable temperature profile within the WGS bed. The results for gasoline indicate that the operating conditions required are more stringent than for single paraffins. Higher reforming temperatures and an appropriate WGS thermal profile are necessary to achieve high H₂ and low CO in the product gas. Gasoline puts a premium on establishing a complete thermal integration between the reformer and shift bed, and between the feed and product streams, to transfer the waste heat from the former to the latter more effectively.

CONCLUSION

We have developed a novel autothermal reforming catalyst that can achieve the conversion of hydrocarbon fuels to hydrogen at much lower temperatures and in a simpler process than can conventional catalysts. This catalyst has been incorporated into a bench-scale integrated fuel processor. Tests were conducted with isooctane and gasoline. The results showed that a product gas containing up to 43% hydrogen on a dry basis could be achieved for isooctane. Somewhat lower yields were achieved with gasoline. However, CO content in the product gas could be reduced to below 2% using ANL's air-stable WGS catalyst. These results demonstrate the feasibility of a process that combines an autothermal reforming catalyst with carbon monoxide scrubbing technologies for fuel cell applications.

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