A Fuel Processor for Fuel Cell Systems

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Abstract

Argonne National Laboratory is developing a liquid fuel processor for converting hydrocarbon fuels to a hydrogen-rich feed suitable for a polymer electrolyte fuel cell stack. The processor uses an autothermal refomer to convert the feed to a mixture of hydrogen, carbon dioxide, carbon monoxide and water with trace quantities of other components. The carbon monoxide in the product gas is then converted to carbon dioxide in water-gas shift and preferential oxidation reactors. Fuels that have been tested include standard and low-sulfur gasoline and diesel fuel, and Fischer-Tropsch fuels. Iso-octane and n-hexadecane were also examined as surrogates for gasoline and diesel, respectively. Complete conversion of gasoline was achieved at 750?C in a microreactor over a novel catalyst developed at Argonne. Diesel fuel was completely converted at 850?C over this same catalyst. Product streams contained greater than 60% hydrogen on a dry, nitrogen-free basis with iso-octane, gasoline, and n-hexadecane. For a diesel fuel, product streams contained >50% hydrogen on a dry, nitrogen-free basis. The catalyst activity did not significantly decrease after >16 hours operation with the diesel fuel feed. Coke formation was not observed. The carbon monoxide fraction of the product gas could be reduced to as low as 1% on a dry, nitrogen-free basis when the water-gas shift reactors were used in tandem with the reformer.

Introduction

Hydrocarbon fuels, such as gasoline and diesel, have been considered as potential fuels for vehicles powered by a polymer-electrolyte fuel cell (PEFC) stack because of their high energy contents, low cost, and well-established infrastructure (1). However, for a fuel cell-powered vehicle, an onboard processor is required to convert these fuels to hydrogen-rich fuel gas. One option for on-board processing is autothermal reforming. In autothermal reforming, a hydrocarbon fuel is reacted with both air and steam to produce hydrogen. The heat generated in autothermal reforming can be controlled directly by adjusting the proportions of fuel, air, and steam in the feed. Consequently, external heat sources are not required, and designs for autothermal reformers (ATR) are simpler and smaller than steam reformers and demonstrate better dynamic response to transients. 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 demonstrate the processing of the reformate using in-house water-gas shift catalysts to achieve a process gas stream containing less than 1% carbon monoxide.

Experimental

The autothermal reforming catalysts were either fabricated in-house or obtained from Sud-Chemie Inc. in pellet form. Zinc oxide pellets for H_2S removal were obtained from Sud-Chemie Inc. The water-gas shift catalysts were fabricated using a proprietary formulation. Iso-octane (2,2,4 trimethylpentane, C_8H_{18}) 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, and a thermal conductivity detector 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) microreactor. The microreactor was housed in a furnace to maintain the temperature of the bed constant. Gas flow rates were controlled with mass flow controllers. The water flow rate was controlled with a high pressure 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 (reformate) 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 reformate. These components will poison the electrodes of a PEFC stack. Sulfur will be present in the reformate as H_2S. It can be removed with a ZnO sorbent bed. Carbon monoxide clean-up 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.

The current approach at ANL is to fully integrate the reformer, scrubber, and shifter into one unit. The ANL processor is based on catalytic autothermal reforming (ATR). 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.

In order to demonstrate its effectiveness, the ANL ATR catalyst has been incorporated into a bench-scale processor. In this processor, complete conversion of the fuel occurs over a single catalyst bed. Consequently, the fuel processor can be made smaller and lighter, more appropriate for power systems for transportation and remote applications. This becomes particularly important because the reformer effluent or reformate will require additional processing.

The engineering-scale integrated fuel processor (Fig. 1) is 20.3-cm (8-in) in diameter, 35.6-cm (14-in.) in height, and is rated for up to 10 kW(e) power output. It includes an autothermal reformer, a sulfur scrubber, and water-gas shifter, shown schematically in Fig. 2. The schematic illustrates the integration of the various components; it does not represent the actual arrangement of each processor segment steps. In the processor, the internal configuration super-heats the air and steam before they are combined with injected fuel and additional water at the inlet of the reformer. This thermal integration also results in 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, iso-octane, 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 essentially self-sustaining or autothermal. Autothermal reforming can be considered a melding of partial 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 reformate. With the ANL catalyst formulation, and depending on the type of fuel, the reformer operates between 450 and 900^{o}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 reformate is required. At the reformer exit the reformate typically contains 5-10% CO. Additionally, gasoline contains substantial quantities of sulfur compounds, at concentrations as high as 300ppm, equivalent to 30ppm in the process gas. This CO and sulfur must be eliminated from the reformate.

In the processor, ZnO is used to scrub the reformate of sulfur. Exiting the reformer, the sulfur in is predominantly present as H_2S. H_2S reacts with the ZnO at ~350^{o}C to form ZnS and H_2O; by this process, sulfur can be reduced to approximately 1ppm in the reformate, the equilibrium value.

CO is removed from the reformate via the WGS reaction over a catalyst; CO and water react to form to CO_2 and H_2. 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 is 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 Figure 3, we were able to achieve a CO content of <1% in the reformate using the ANL shift catalyst in the fuel processor.

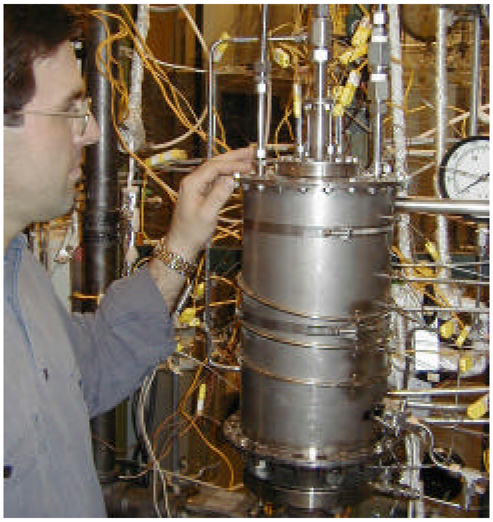

Fig. 1. ANL Integrated Fuel Processor

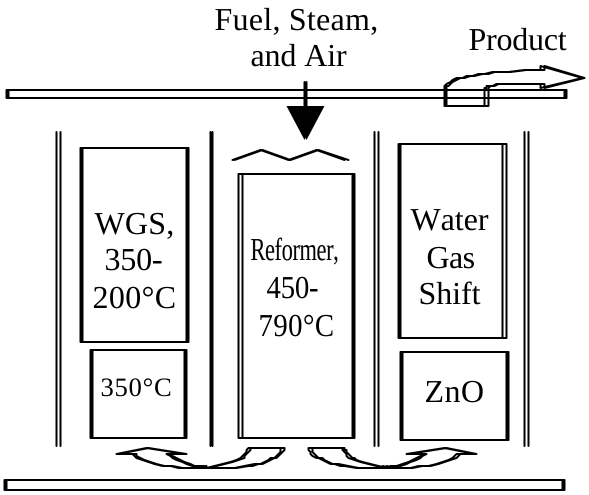

Fig. 2. Schematic of ANL Integrated Fuel Processor

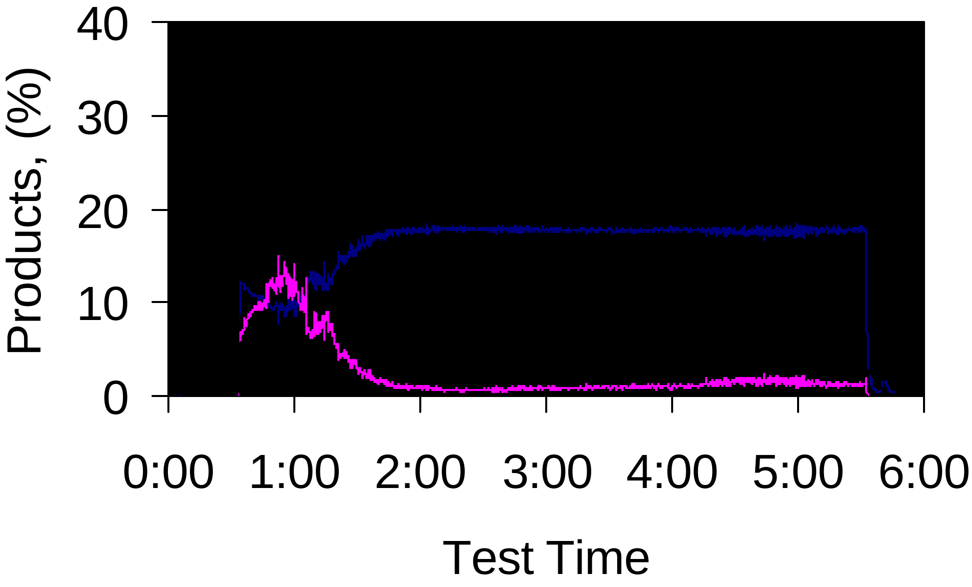

Fig. 3. Product composition from test with isooctane at fuel feed of 14 mL/min

Isooctane

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. Fig. 4 shows 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. These rates would be equivalent to 25 to 75% of the rated power. The O_2/fuel molar ratio was maintained between 3.0-3.5, and the average reformer temperature was 750-800^{o}C. The concentration of hydrogen varied from 38% to 43%, with an average value of 41%. Greater than 99% iso-octane 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 CO_2, CO, and CH_4 concentrations were17%, 4%, and 2%, respectively.

The reformer operated most effectively at 28 mL/min, equivalent to 5W(e), with maximum hydrogen yield and CO elimination. Increasing the fuel feed rate from 14 to 28mL/min, increased the hydrogen (40% to 43%) and carbon dioxide (12% to 16%) fractions, 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 operate a 4.2 kW(e) fuel cell stack.

These effects can be attributed to the temperature profiles achieved within the two reactors. The carbon monoxide 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. However, in this test, complete elimination of CO <1% was not be 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.

As the fuel feed rate was further increased to 36 mL/min, there was a reduction in hydrogen yield, a slight reduction in conversion, and an increase in CO. These latter results may be attributed to operation at unoptimized temperature profiles throughout the processor. 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 deliver rate.

The higher CO content in the reformate 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

While isooctane is a reasonable analog, gasoline places a premium on intermixing of the feeds at the inlet of the reformer. 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 breakdown. In order to determine of the relationship of these factors to the operating conditions, the 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 O_2/fuel molar ratio was 3.4-3.7 using isooctane as a reference composition for gasoline. The average reforming temperature was 780°C at lower fuel feed rate; the processor ran hotter for gasoline than for isooctane. The hydrogen fraction in the product gas varied from 30% to 38%, lower than similar tests with isooctane. The lower hydrogen yield and 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 of isooctane. The hydrocarbon products were primarily C_1-C_4 hydrocarbons; there were only trace quantities of aromatics detected.

The CO content was dropped to <2% at the lower fuel feed rate as the shift beds warmed but rose to >5% at the higher rates. As was the case for isooctane, the higher CO at high throughputs can be attributed to the lack of an ideal temperature profile within the WGS bed. The results for gasoline indicate that the operating conditions required are more stringent than for simple mixtures. Higher reforming temperatures and a more optimal WGS thermal profile are necessary to achieve high H_2 yields and low CO in the product gas. Gasoline places a premium on the establishment of a complete thermal integration between the the reformer and shift bed, between the feed and product streams, to transfer the waste heat from former to the latter more effectively.

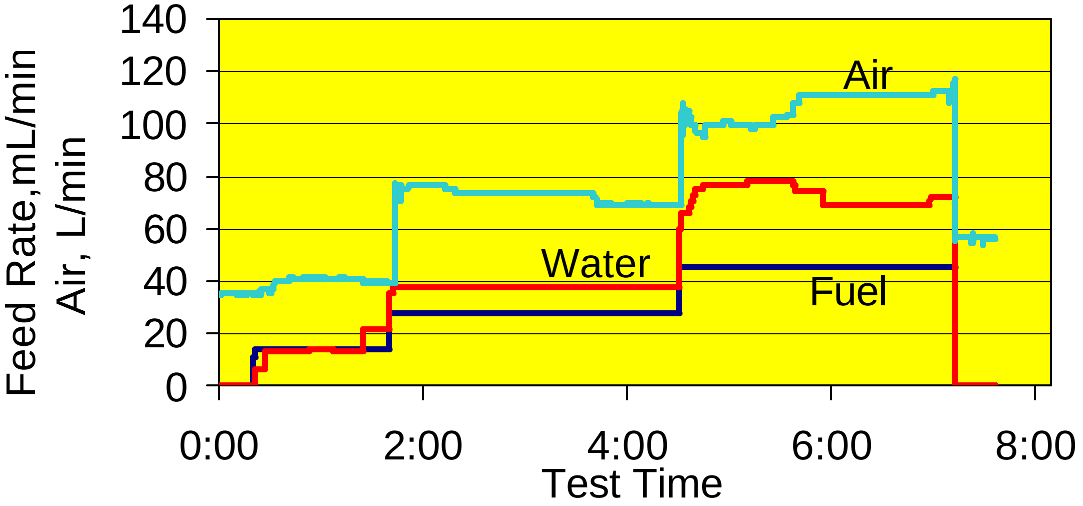

Fig. 4. Iso-octane Reforming Test: Feed Rates of Iso-octane, Air, and Water.

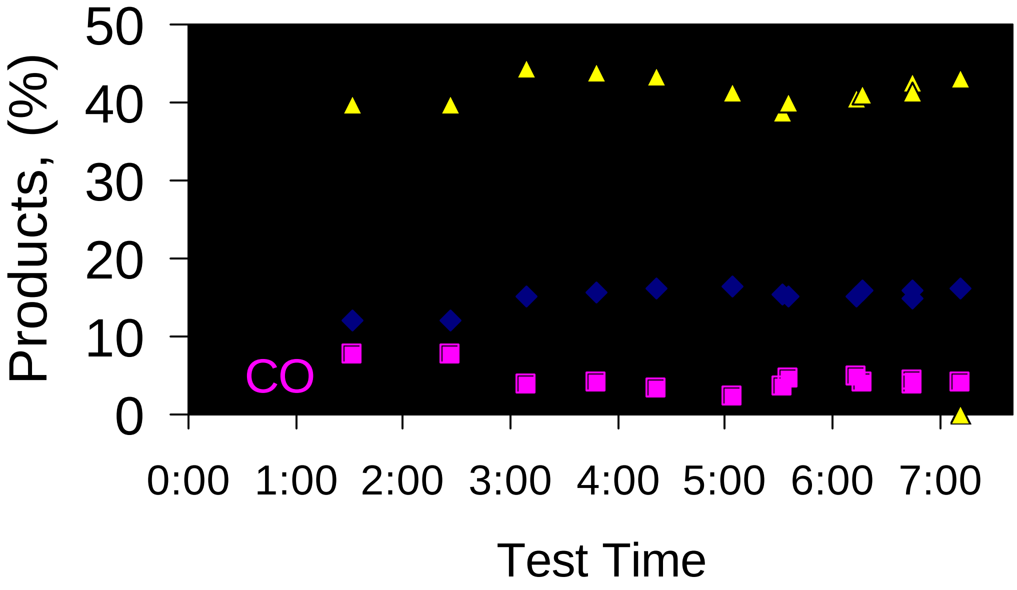

Fig. 6. Product composition for test with isooctane.

Conclusion

Argonne National Laboratory has developed a novel autothermal reforming catalyst that can achieve the conversion of hydrocarbon feeds to hydrogen at much lower temperatures and in a simpler process than conventional catalysts. This catalyst has been incorporated into a bench-scale integrated fuel processor also developed at ANL. In this paper we describe results with this processor for isooctane and gasoline. The results show that a product stream containing up to 43% hydrogen can be achieved for isooctane. Somewhat lower yields were achieved with gasoline, however, we were able to reduce the carbon monoxide content of the product gas to below 2% using ANL's air-stable WGS catalyst. These results demonstrate the feasibility of the process that combines an autothermal reforming catalyst with sulfur and carbon monoxide scrubbing technologies for fuel cell applications.

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