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[98e]-Catalytic Reforming of Gasoline and Diesel Fuel[†]

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Abstract

Argonne National Laboratory is developing a fuel processor for converting liquid hydrocarbon fuels to a hydrogen-rich product suitable for a polymer electrolyte fuel cell stack. The processor uses an autothermal reformer 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 over >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

In autothermal reforming a hydrocarbon fuel is reacted with both air and steam to produce hydrogen. The heat generated by 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 are simpler, smaller, and lighter. Argonne National Laboratory has developed a new process that achieves the autothermal reforming of hydrocarbon fuels with a novel catalyst.(1) In this catalytic process the conversion occurs in a single catalyst bed and enables the reactor to operate much cooler than the non-catalytic process. The catalytic process leads to a smaller and lighter fuel processor that is more appropriate for remote fuel cell power systems. The catalyst has been demonstrated to work with several different fuels including methanol, ethanol, natural gas, gasoline, and diesel fuel.

Because carbon monoxide and sulfur compounds in the effluent from the fuel processor will poison the electrodes of a polymer electrolyte fuel cell stack, the reformate must be treated further to remove these components. Sulfur is present in the reformate as H_2S which can be removed with a ZnO sorbent bed. Carbon monoxide clean-up is achieved with a series of water-gas shift reactors that convert CO and water to CO_2 and hydrogen.(2) Residual CO is removed with a preferential oxidizer, where CO is reacted with oxygen to form CO_2. We are developing more robust water-gas shift catalysts that will work better under transient operating conditions than current catalysts developed for process plant service. In addition, we are testing catalysts for preferential oxidation of CO and adsorbents for selective removal of trace CO.

In this work we present results for the catalytic reforming and processing of gasoline and diesel feeds. We were able to demonstrate complete conversion of isoactane, a surrogate for gasoline, to lower hydrocarbons and hydrogen. We demonstrate the production of hydrogen from hexdecane and low-sulfur diesel fuels by autocatalytic reforming at lower temperatures than is used in traditional reforming processes. We demonstrate the processing of a simulated reformate using in-house water-gas shift and preferential oxidation catalysts to achieve a process gas stream containing less than 100 PPM carbon monoxide.

Experimental

The autothermal catalysts were fabricated using a proprietary formulation. Two water-gas shift catalysts were used. Iron-chromium oxide catalyst was obtained from United Catalyst Inc. in the form of pellets; the catalyst was coarsely ground prior to placement in the reactor. Before the reactor was placed on-line, the catalyst was reduced with wet simulated process gas following the manufacturer's procedure. The second shift catalyst was developed by our group and used as a low temperature shift catalyst. It was produced by depositing an active metal and a active oxide layer on an inert substrate. This catalyst was not pre-treated prior to introduction of process gas. Zinc oxide pellets for H_2S removal were obtained from United Catalysts Inc. These pellets were coarsely ground before use. A metal oxide catalyst developed at Argonne was used for preferential oxidation.

Experiments were carried out in microreactors. The microreactors were tubular reactors from 0.4 to 1-in ID. In the reformer a "dead-man" was used to minimize volume between the top of the catalyst bed and the fuel injectors. The reactors were housed in furnaces that were used to maintain the temperatures of the beds. Gas flow rates were controlled with mass flow controllers. Liquid flow rates were controlled with high pressure liquid chromatography (HPLC) pumps. Fuel and water could be fed into the reactor as liquids or vaporized prior to injection.

Iso-octane (2,2,4 trimethylpentane, C_8H_{18}) and n-hexadecane ($C_{16}H_{34}$) were used as surrogates for gasoline and diesel fuel, respectively. Tests were also conducted with two actual diesel fuels: a certified low-sulfur diesel fuel and a standard diesel fuel taken from the Argonne motorpool. In addition to the hydrocarbon feeds, a simulated reformate containing 46% H_2, 13% CO_2, 10% CO, 2% CH_4, and 29% N_2 was used for tests conducted with the process train when the reformer was off-line.

Results

Equilibrium Calculations

The equilibrium compositions of the reaction products for the autocatalytic reforming of iso-octane, hexadecane, and a simulated diesel fuel were calculated to determine the feasibility of hydrogen production. The surrogates were used in microreactor tests to determine the initial operating conditions and expected product distributions for tests with actual fuels. Figure 1 shows the equilibrium product gas distribution obtained as a function of temperature for the autothermal reforming of iso-octane. The equilibrium product distributions as a function of temperature were similar for all three feeds examined.(3,4) For all three, the hydrogen percentage is maximized near 700°C, with a small decrease as the temperature is raised due to the reverse water-gas shift reaction. Complete conversion, as manifest by the absence of methane is also achieved at 700°C.

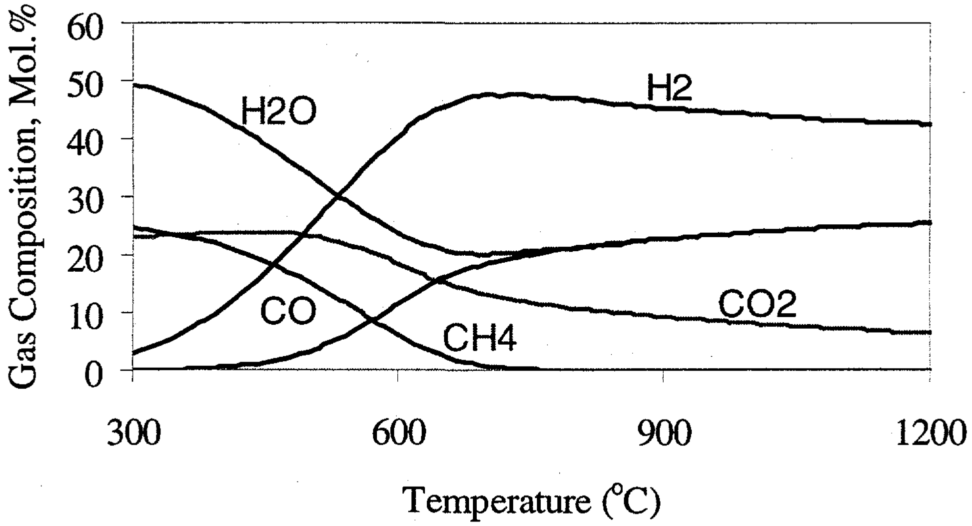

Figure 1: Equilibrium product composition vs. temperature for iso-octane. Molar feed ratios are water:fuel = 8; oxygen:fuel = 4

Iso-octane

The conversion of iso-octane as a function of temperature is shown in Figure 2. The product distribution is very similar to that of the equilibrium calculation. Hydrogen production is at a maximum at a somewhat higher temperature than predicted by the equilibrium calculation. Complete conversion of iso-octane was achieved at 750°C, while conversion at 700°C was 98.9%. The primary hydrocarbon products were methane and ethene. The slope of the methane curve does not decrease significantly with temperature.

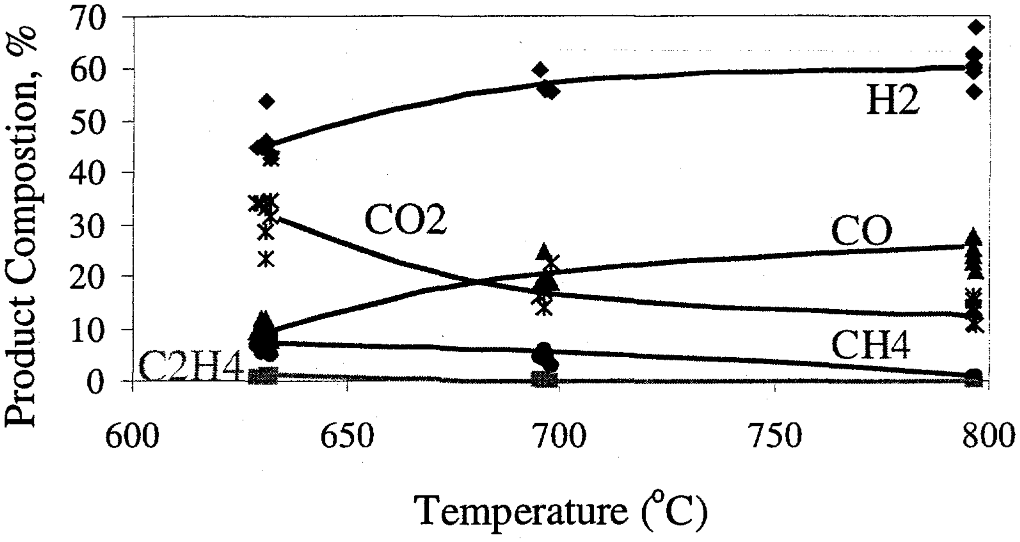

Figure 2: Product composition vs. temperature for iso-octane. Molar feed ratios are water:fuel = 8; oxygen:fuel = 4.

The effect of space velocity on the reaction products from the autothermal reforming of iso-octane is shown in Figure 3. There was a significant reduction in the hydrogen fraction in the product as the space velocity is increased from 2,000 h^{-1} to 10,000 h^{-1}. The hydrogen fraction in the product gas falls from 50% to less than 40%. Further increases have little effect on the product gas composition until a space velocity of 40,000 h^{-1} is reached at which point another significant drop in the hydrogen fraction is observed. The results suggest that an autothermal reformer can operate at very high space velocities with a small cost in the amount of hydrogen produced.

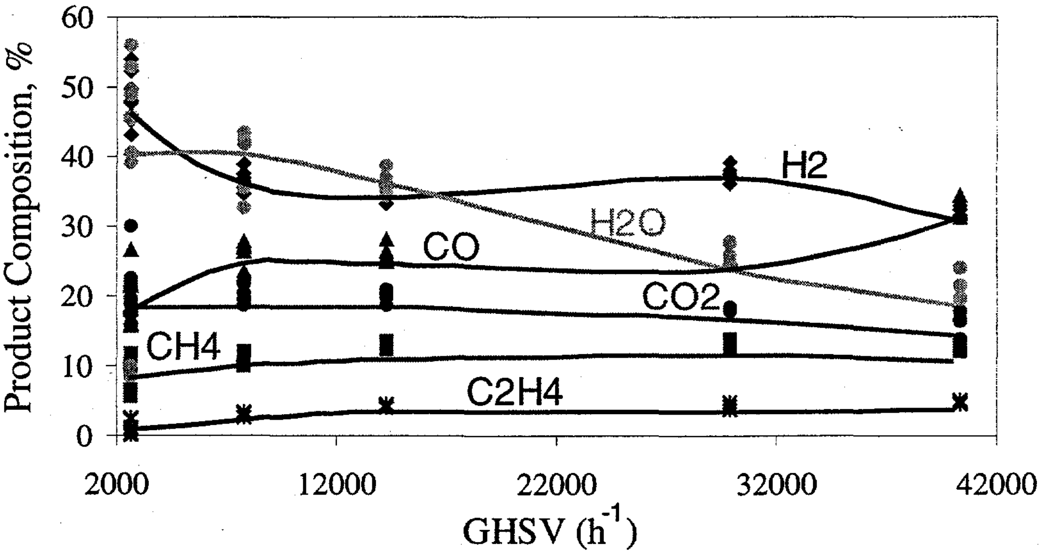

Figure 2: Product composition vs. gas hourly space velocity for iso-octane. Molar feed ratios are water:fuel = 8; oxygen:fuel = 4.

Hexadecane and Diesel Fuel

Figure 4 shows the effect of temperature on the product distribution from the partial oxidation reforming of hexadecane. The feed corresponds to an O_2-to-fuel molar ratio of 8, and a water-to-fuel molar ratio of 16.2. The gas hourly space velocity was 3,700 h^{-1}. As with iso-octane, the trends are similar to the equilibrium product distributions in Figure 1. However, the maximum in hydrogen production is shifted to a much higher temperature. As can be seen in Figure 4, the hydrogen and carbon monoxide levels increase as the temperature is raised, while the carbon dioxide and methane levels decrease. Above 725°C, the hydrogen percentage in the product begins to level off at 60%. Raising the reactor temperature leads to a greater conversion of methane. The measured product composition for the autothermal reforming of hexadecane contains slightly more H_2 and CO_2, but less CO than that predicted by equilibrium. This suggests that the selectivity of the catalyst favors the formation of hydrogen. The CO:CO_2 ratio increases with temperature due to the reverse water-gas shift reaction, which is favored at high temperatures. At 800°C, undesirable byproducts such as ethane and ethylene are present in trace quantities. Although methane remains a significant product, the slope of the methane curve indicates that it is not reduced significantly at higher temperatures.

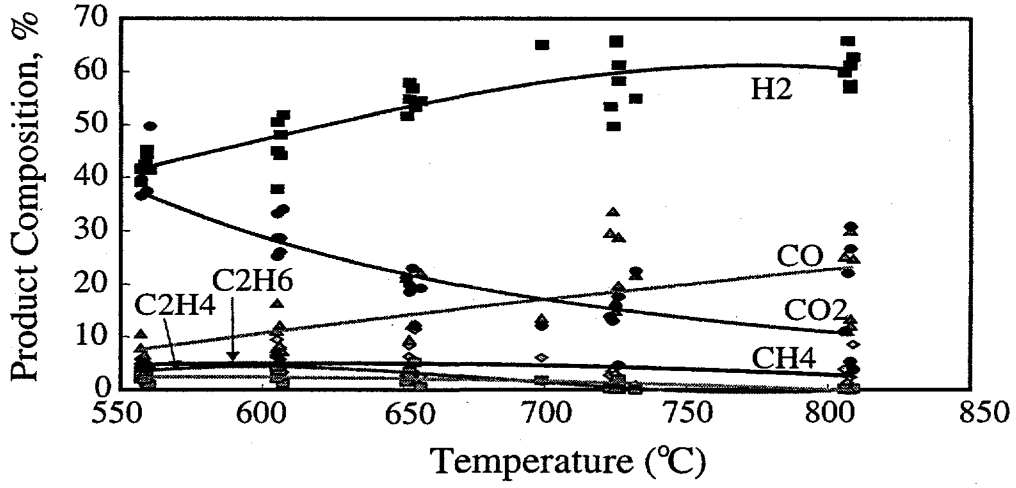

Figure 4: Product composition vs. temperature for hexadecane. Molar feed ratios are water:fuel = 16; oxygen:fuel = 8

The amount of H_2 dropped slightly with increasing space velocity, while the percentage of CH_4, CO and CO_2 increased. Increasing the space velocity reduced the contact time between the catalyst and the reactants, which limited the extents of the various reactions. However, the observed decrease of the hydrogen amount was small – even at the highest space velocity of 24,000 h^{-1}, the product still contained 55% hydrogen. Additionally, the conversion of hexadecane remained close to 100% for all space velocities, indicating that the reduced contact time affected the secondary reactions rather than the initial reactions involving hexadecane. Consequently, hexadecane was converted to a hydrogen-rich reformate gas, that is feasible for use with a fuel cell.(3)

Figure 5 shows the product composition as a function of temperature for certified low-sulfur diesel fuel for a water-to-fuel ratio of 20 and oxygen-to-fuel ratio of 8. In Figure 5, hydrogen production is maximized at 875°C. This temperature is higher than the maximum observed at 800°C with hexadecane. For the certified fuel, the average hydrogen fraction in the product at 840°C is 46%, while at 875°C it is 50%. Similar results were obtained for grade 2 diesel fuel, but a higher hydrogen product yield of 52% was obtained at 850°C.(3) As was the case for hexadecane, the hydrogen and carbon monoxide levels increase as the temperature is raised, while the carbon dioxide and methane levels decrease. However, conversion to hydrogen is significantly lower at similar reaction temperatures. Hydrogen production was unaffected for space velocities between 2,000 h^{-1} to 10,000 h^{-1}.

The diesel fuel reformate contains less hydrogen than the hexadecane reformate, which is due in part to the lower H/C ratio of the grade 2 diesel (H/C =) vs. 2.1 for hexadecane. In addition, diesel reforming requires a slightly higher reforming temperature. Based on these preliminary data, it appears that the Argonne catalyst can reform the complex

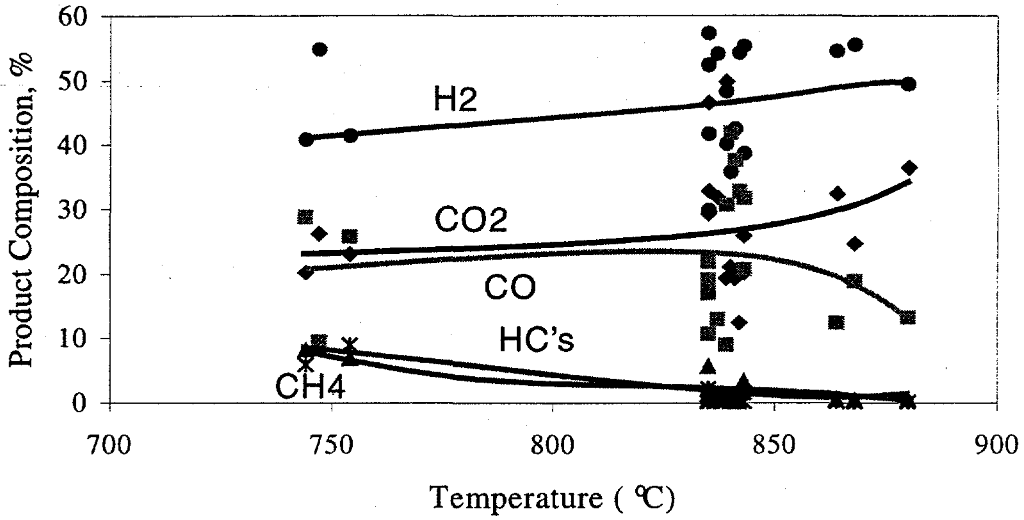

Figure 5: Product composition vs. temperature for certified diesel fuel. Molar feed ratios are water:fuel = 20; oxygen:fuel = 8.

hydrocarbons present in diesel at the relatively low temperatures of 850°C. This is significant because non-catalyzed partial oxidation-reforming requires temperatures in excess of 1200°C to achieve similar conversions.

Fuel Processing

We are investigating the integration of the individual process units required to convert a hydrocarbon fuel to hydrogen (and benign byproducts) to serve as a feed for a fuel cell stack. The system or "process train" includes a reformer microreactor, a sulfur removal bed, high and low temperature water-gas shift units, and a CO scrubber. The fuel process train was run with a simulated reformate, iso-octane feed, and diesel fuel. The tests with simulated reformate and iso-octane were conducted with the preferential oxidizer on-line. The diesel test did not include the preferential oxidizer.

Iso-octane, water, air, and nitrogen were fed to reformer with the bed maintained at 735°C. The CO concentration in the effluent from the preferential oxidizer, the last reactor in the train, is shown in Figure 6 as a function of time. The CO concentration in the effluent remained below 100 ppm for the majority of the test. As the test proceeded, there was a steady rise in CO baseline from 10 ppm to nearly 100 ppm with spikes approaching 200 ppm. The spikes increase in intensity as the test proceeds, following the trend in the baseline CO concentration. Spikes in the CO content were not as prevalent for tests with synthetic reformate suggesting that the observed spiking may be related to variations in the reformer effluent composition rather in the operation of the other components of the train. With the synthetic reformate the baseline did not rise progressively as with a liquid fuel. Rather, the CO concentration curve was flat once a relatively once a steady state was attained consistent with the observed effects being related to an unsteady CO concentration or product feed.

With a diesel fuel feed to the reformer, only a portion of the effluent was passed through the process train to prevent the CO from overwhelming the in-line detector. For the same reason, the preferential oxidizer was left off-line. However, the carbon monoxide content of the reformate was reduced from approximately 20% to less than 2% on a dry basis with the two water-gas shift reactors. As was the case for iso-octane, there was some variability in the baseline CO concentration, which varied between 1.2 and 1.8 Vol.%. There was no evidence of the sharp spiking observed in the test with iso-octane, however, the variation observed in the GC data for the reformer effluent indicates that a constant CO level would not be expected.

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. In this paper we describe results for partial oxidation-reforming of iso-octane, hexadecane, and a low sulfur diesel fuel. The results show that a product stream containing up to 60% hydrogen on a dry, nitrogen-free basis can be achieved for iso-octane or hexadecane feeds at 750°C. Somewhat lower yields were achieved with diesel fuel. However, we were able to achieve greater than 50% hydrogen in the product stream at 800°C. The carbon monoxide content of the product gas could be reduced

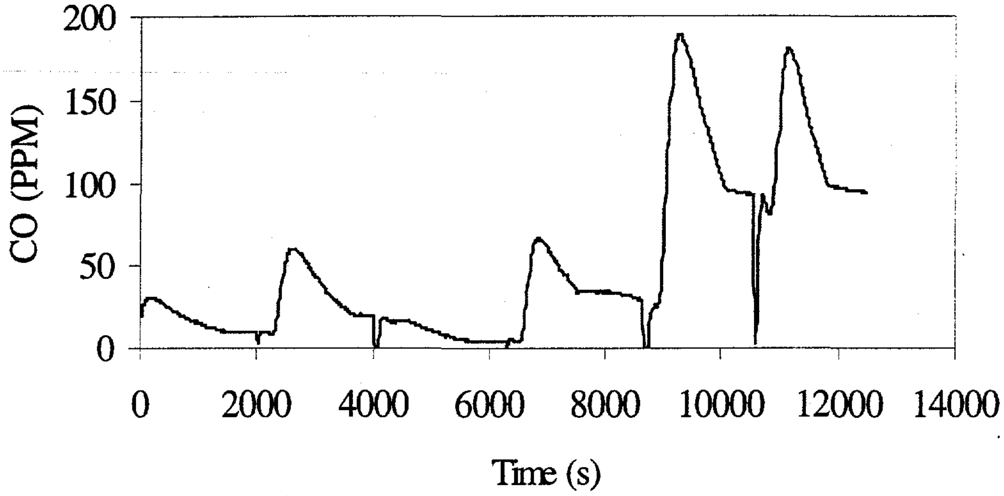

Figure 6: CO concentration in process train effluent with time.

to less than 100 ppm for an iso-octane feed with water-gas shift and preferential oxidation reactors. For diesel, we were able to lower the CO content of the effluent to less than 2% using two shift beds. 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.

Acknowledgements
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