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HYDROCARBON FUELS***

S. Ahmed, M. Krumpelt, R. Kumar, S.H.D. Lee, J.D. Carter, R. Wilkenhoener,
and C. Marshall

Electrochemical Technology Program
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439

Introduction

The polymer electrolyte fuel cell (PEFC) is the primary candidate as the power source for light-duty transportation systems. On-board conversion of fuels (reforming) to supply the required hydrogen has the potential to provide the driving range that is typical of today's automobiles. Petroleum-derived fuels, gasoline or some distillate similar to it, are attractive because of their existing production, distribution, and retailing infrastructure. The fuel may be either petroleum-derived or other alternative fuels such as methanol, ethanol, natural gas, etc. [1]. The ability to use a variety of fuels is also attractive for stationary distributed power generation [2], such as in buildings, or for portable power in remote locations.

Argonne National Laboratory has developed a catalytic reactor based on partial oxidation reforming that is suitable for use in light-duty vehicles powered by fuel cells. The reactor has shown the ability to convert a wide variety of fuels to a hydrogen-rich gas at less than 800°C, temperatures that are several hundreds of degrees lower than alternative noncatalytic processes. The fuel may be methanol, ethanol, natural gas, or petroleum-derived fuels that are blends of various hydrocarbons such as paraffins, olefins, aromatics, etc., as in gasoline. This paper will discuss the results obtained from a bench-scale (3-kWe) reactor, where the reforming of gasoline and natural gas generated a product gas that contained 38% and 42% hydrogen on a dry basis at the reformer exit, respectively.

Partial Oxidation Reforming of Hydrocarbons

An idealized equation for the partial oxidation reforming of a hydrocarbon can be written as $C_nH_mO_p + x(O_2 + 3.76N_2) + (2n - 2x - p)H_2O = nCO_2 + (2n - 2x - p + m/2)H_2 + 3.76xN_2$ (1) where x is the oxygen-to-fuel molar ratio [3]. This ratio is a very important parameter because it determines (a) the amount of water required to convert the carbon to carbon dioxide, (b) the hydrogen yield (moles), (c) the concentration (mol%) of hydrogen in the product, and (d) the heat of reaction. When $x=0$, equation (1) reduces to the endothermic steam reforming reaction; when $x=12.5$, equation (1) is the combustion reaction. The partial oxidation reactor should be operated in a manner that the overall reaction is exothermic, but at a low value of x where the higher hydrogen yields and concentrations are favored.

The desired reaction can be achieved with or without a catalyst. Noncatalytic processes for gasoline reforming require temperatures in excess of 1000°C. These high temperatures necessitate the use of special materials of construction and significant preheating and thermal integration of process streams. The presence of a suitable catalyst substantially reduces the operating temperature, allowing the use of more common reactor materials, such as steel. Lower temperature reforming leads to less carbon monoxide in the raw reformat – which means that the water-gas shift reactor can be considerably smaller. Also, analysis of fuel cell power systems has shown that the effect of temperature on the system efficiency can be quite drastic [4]. Argonne National Laboratory has developed a family of such catalysts that has proven effective for reforming a wide range of conventional and alternative fuels.

Catalysts for Partial Oxidation of Hydrocarbon Fuels

Argonne National Laboratory's catalyst consists of a substrate and a promoter, where it is estimated that the substrate participates in the oxidation of the carbon, while the promoter dehydrogenates the hydrocarbon. This catalytic activity has been found in various combinations of materials with certain characteristic properties needed for either the substrate or promoter [5].

Micro-Reactor Studies: The catalysts have been evaluated in a micro-reactor with 2 g of catalyst in a 12-mm diameter tube. The desired temperature was attained by placing the reactor in a tube

furnace. The vaporized fuel and water were mixed with oxygen and passed over the heated catalyst zone, and the products were analyzed with a gas chromatograph.

Petroleum-derived fuels such as gasoline are blends of different types of hydrocarbons, such as paraffins, olefins, naphthenes, etc. The catalyst evaluation was, therefore, conducted initially with surrogates for the different types of hydrocarbons, e.g., iso-octane for paraffins, toluene for aromatics, etc. In these experiments, the oxygen feed rate was adjusted so that $O/C=1$, while the water rate was maintained to provide $H_2O/C \geq 1$. Table 1 presents some results from these experiments. The first column lists the hydrocarbon components, and the second column shows the reactor temperature at which complete conversion was achieved. The next three columns list the percentages of hydrogen, carbon monoxide, and carbon dioxide measured in the product gas. The last three columns list the percentages of the gases that would exist at equilibrium at those temperatures.

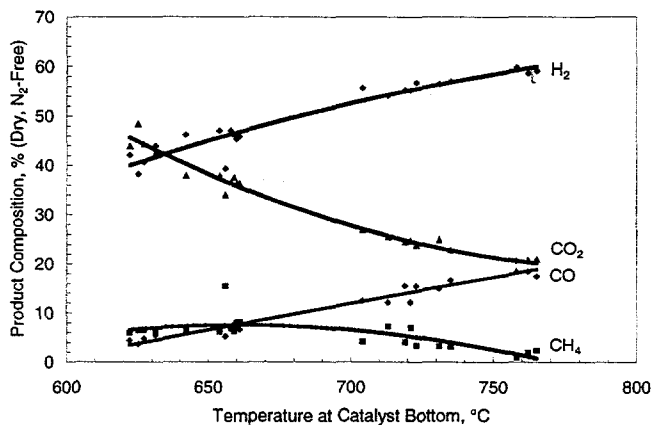
Fuel	Temperature	Experimental (% dry, N ₂ -free)			Equilibrium (% dry, N ₂ -free)		
	°C	H ₂	CO	CO ₂	H ₂	CO	CO ₂
<i>Iso-Octane</i>	630	60	16	20	57	20	19
<i>Toluene</i>	655	50	8	42	49	23	26
<i>2-Pentene</i>	670	60	18	22	56	21	21
<i>Ethanol</i>	580	62	15	18	62	18	16
<i>Methanol</i>	450	60	18	20	60	19	17

Table 1. Experimental product gas composition compared with equilibrium compositions calculated for the given feed mixture and experimental temperature.

Using our catalyst we were able to convert the different hydrocarbons at less than 700°C, indicating that this catalyst has promise for a fuel-flexible reformer. Comparison between the experimental and equilibrium percentages shows that the experimental values for hydrogen and carbon monoxide are more favorable (i.e., higher hydrogen and lower carbon monoxide) than what might be achieved at equilibrium.

Figure 1 shows the composition of the product gas obtained from the partial oxidation reforming of retail gasoline. The curve for hydrogen shows that nearly 60% (on a dry and nitrogen-free basis) hydrogen was produced at 760°C. Based on the composition of the gasoline and the oxygen-to-fuel ratio, we estimated that the maximum hydrogen percentage achievable is 67%. The experiments were conducted intermittently for over 40 hours, during which time no deactivation was noticed; this finding indicates that the catalyst has some sulfur tolerance.

Figure 1. Product gas composition obtained from the partial oxidation reforming of gasoline in a micro-reactor. Fuel(*I*)=0.04 mL/min; water(*I*)=0.04 mL/min; oxygen=24.7 mL/min.



Similar experiments have also been performed with other fuels such as natural gas and diesel. Natural gas reforming was possible at below 800°C, with similarly high selectivity for hydrogen. Limited studies with diesel fuel have also shown that it fuels can be processed at or around 800°C.

Bench Reactor Studies: In order to study the catalysts under more realistic operating conditions, further evaluations are being conducted in an engineering scale reactor. This larger reactor is a cylindrical tube (8.6-cm diameter) filled with 1.7 L of the catalyst (pellets, 6.4-mm dia., 3.2-mm high). Vaporized fuel, steam, and preheated air enter the top of the reactor. A small, electrically heated coil ensures immediate ignition. The gases then flow down through the catalyst bed and emerge at the bottom. The product gases are then analyzed with a gas chromatograph.

The bench reactor has been used to reform iso-octane, gasoline, and natural gas. Figure 2 shows the feed rates of iso-octane, water, and air into the reactor and the composition of the product gas coming out of the reactor. Near the start of the experiment when the fuel flow rate was low (16 mL/min), the hydrogen percentage in the product was over 45%. The carbon dioxide and carbon monoxide were at 16% and 6%, respectively. As the processing rate and the air-to-fuel ratio were increased, a small drop in hydrogen and carbon dioxide levels was accompanied by a commensurate increase in carbon monoxide level. This behavior was a result of the combination of higher air-to-fuel ratios and reduced residence time in the catalyst. The level of methane remained essentially constant at ~0.6%. The ratio of carbon dioxide to carbon monoxide dropped from ~3 at the start to ~2 near the end of the day's experiment....

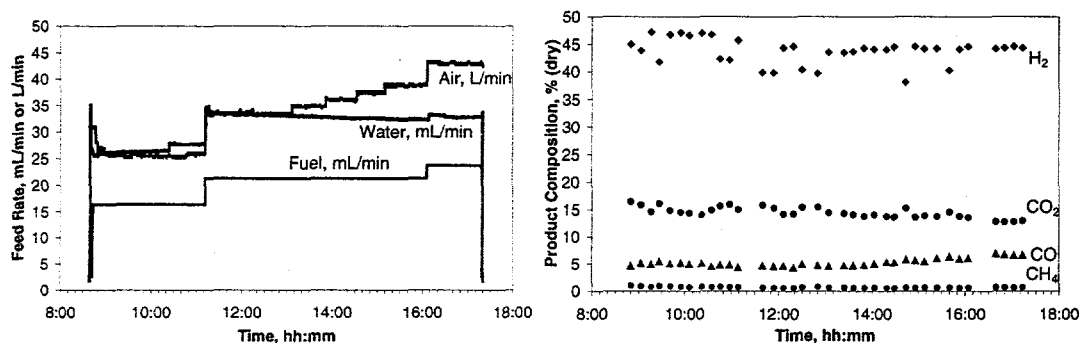


Figure 2. Feed rates of iso-octane, water, and air into the bench reactor, and the product gas composition measured at the reformer exit.

The composition of the product gas obtained from the reforming of retail gasoline is shown in Fig. 3. The fuel (gasoline), water, and air feed rates were maintained at 22 mL/min, 24 mL/min, and 45 L/min, respectively. The product gas contained 38% hydrogen, 12% carbon dioxide, and 10% carbon monoxide. After the water-gas shift reaction, the hydrogen percentage can be expected to increase to 43%. Compared with the gas compositions from iso-octane (Fig. 2), the hydrogen percentage and the ratio of CO₂/CO were lower with gasoline. This is partly due to the lower H/C ratio in gasoline. The reformer produced 40 L/min of hydrogen at its exit, sufficient to operate a 3 kW fuel cell stack.

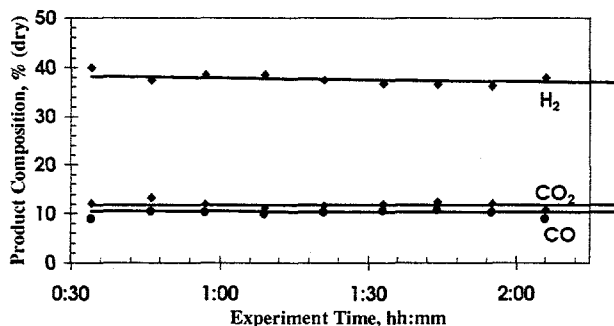


Figure 3. Percent of hydrogen, carbon monoxide, and carbon dioxide measured in the product gas from the partial oxidation reforming of gasoline.

Figure 4 shows the product gas composition obtained from the partial oxidation reforming of natural gas. The fuel (natural gas) feed rate was maintained at 6 L/min, the water feed rate was held at 8 mL/min, while the air flow rate was 14-17 L/min, as shown in the figure. At the beginning, operating at a low oxygen-to-fuel ratio, there was 45% hydrogen, 6% carbon monoxide, 14% carbon dioxide, and nearly 5% unreacted methane in the

product. When the air rate was subsequently increased, it resulted in higher reactor temperatures, which, in turn, improved the methane conversion.

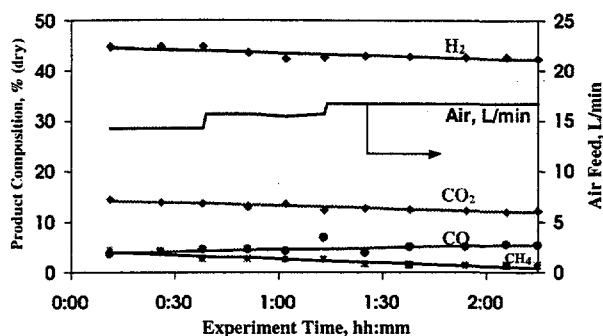


Figure 4. Air feed rate during the partial oxidation reforming of natural gas and the resulting product gas composition (natural gas = 6 L/min, water = 8 mL/min).

The net effect as seen in the figure is that there was a small drop (from 45% to 42%) in hydrogen, the carbon dioxide decreased, and the carbon monoxide

increased. These net effects are the result of a combination of the following factors. (1) The higher air flow rate increased the bed temperature, which increased the methane conversion, leading to higher yields (moles) of H₂, CO, and CO₂. (2) The higher temperature and lower residence time resulting from the increased air feed favored higher concentrations of carbon monoxide and less hydrogen and carbon dioxide. (3) The larger nitrogen presence in the product gas resulted in greater dilution of all of the product gases: viz. hydrogen, carbon monoxide, and carbon dioxide.

Conclusions

Fuel processors for fuel-cell systems that are based on partial oxidation reforming have distinct advantages over steam reformers by not requiring any indirect (through a wall) heat transfer. These compact and lightweight fuel processors are suitable for power systems that require quick-starting and load-following capabilities, which range from automotive to distributed and portable systems. Due to their simplicity, these fuel processors would appear to be manufacturable at low cost.

Argonne National Laboratory has developed a fuel-flexible fuel processor that is based on a novel catalyst. The catalyst has demonstrated the ability to process different types of hydrocarbons and alcohols in a micro-reactor – achieving the conversions at temperatures that are several hundreds of degrees (centigrade) below those required for noncatalytic systems. The catalyst has successfully converted fuels such as methanol, ethanol, natural gas, gasoline, and diesel.

The catalyst performance has been verified in an engineering-scale reactor with gasoline and natural gas. The 1.7 L of catalyst in the reactor converted retail gasoline and was able to produce a reformat containing 38% hydrogen, in quantities sufficient to power a 3-kW fuel-cell stack. Modifications in reformer design and enhancements in catalyst activity will make the reformer lighter and smaller.

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