

**Liquid Fuel Reformer Development:
Autothermal Reforming of Diesel Fuel[†]**

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LIQUID FUEL REFORMER DEVELOPMENT: AUTOTHERMAL REFORMING OF DIESEL FUEL

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Abstract

Argonne National Laboratory is developing a process to convert hydrocarbon fuels to clean hydrogen feeds for a polymer electrolyte fuel cell. The process incorporates an autothermal reforming catalyst that can process hydrocarbon feeds at lower temperatures than existing commercial catalysts. We have tested the catalyst with three diesel-type fuels: hexadecane, certified low-sulfur grade 1 diesel, and a standard grade 2 diesel. Hexadecane yielded products containing 60% hydrogen on a dry, nitrogen-free basis at 850°C, while maximum hydrogen product yields for the two diesel fuels were near 50%. Residual products in all cases included CO, CO₂, ethane, and methane. Further studies with grade 1 diesel showed improved conversion as the water:fuel ratio was increased from 1 to 2 at 850°C. Soot formation was reduced when the oxygen:carbon ratio was maintained at 1 at 850°C. There were no significant changes in hydrogen yield as the space velocity and the oxygen:fuel ratio were varied. Tests with a microchannel monolithic catalyst yielded similar or improved hydrogen levels at higher space velocities than with extruded pellets in a packed bed.

Introduction

The Department of Energy's Hydrogen Program is sponsoring the development of remote power generation in the Arctic circle. Because the fuel available is diesel, the traditional means of power generation in these remote locations has been internal combustion engines. Recent developments in fuel cell power systems, which are more efficient and produce cleaner emissions, suggest that these systems, if adapted to operate with diesel fuels, can be used in the Arctic. Since fuel cells operate on hydrogen, the operation of fuel cells with a diesel feed requires that the fuel be efficiently converted into a hydrogen-rich, sulfur-free gas.

In the chemical process industries, hydrogen is produced in large quantity by the steam reforming process – where the hydrocarbon fuel, typically methane, is reacted with steam. Because this reaction is endothermic, an efficient heat exchanger is required to transfer heat from another source, such as a fuel burner, to the reformer. Consequently, steam reforming is best suited for large chemical plants, which normally have excess heat available from other processes. At a smaller scale, an attractive alternative is autothermal reforming, where the hydrocarbon fuel is reacted with both air and steam to produce hydrogen. The heat generated by this reaction can be controlled directly by adjusting the proportions of fuel, air, and steam in the feed. With an appropriate feed, external heat is not required, making autothermal reformers simpler, smaller, and lighter than steam reformers. Autothermal reforming in the petrochemical industry is typically done in a two-step process – a high-temperature (1200°C) step where the complex hydrocarbons are broken down into simpler molecules (methane and oxides of carbon), followed by (catalytic) steam reforming of methane.

At Argonne National Laboratory, we are developing a process to convert hydrocarbon fuels to clean hydrogen feeds for polymer electrolyte fuel cells (PEFC). The process incorporates an autothermal reforming catalyst that can process hydrocarbon feeds at lower temperatures than existing commercial catalysts. We have developed an autothermal reforming catalyst that converts gasoline to hydrogen, carbon monoxide, and carbon dioxide at temperatures as low as 650-900°C. We have also demonstrated complete conversion of these feeds, producing enough hydrogen to power a 5-kW fuel cell stack (Ahmed, 1998).

The effluent from the reformer requires further treatment before it can be fed to a PEFC stack. Carbon monoxide and sulfur poison the fuel cell electrodes when present above a few parts per million. To address this problem Argonne National Laboratory is optimizing sulfur scrubbers for compact systems like autothermal reformers, developing more robust water-gas shift catalysts that will work better under transient operating conditions than current catalysts (Kumar, 1999), and testing catalysts for preferential oxidation of CO and CO sorbents to treat the product stream.

Reforming diesel fuel requires that several problems be overcome. These problems are related to degradation of catalysts over time because of the nature of the fuel. Causes of degradation include poisoning of catalysts by sulfur; diesel typically has a higher fraction of sulfur than other fuels. Thermal cycling, particularly on startup and shutdown, leads to thermal shock. Because of the low H:C ratio and high molecular weight of diesel, extensive coke formation deactivates catalysts. High temperatures improve conversion, resulting in better system efficiency, but reduce material stability.

In a previous paper (Pereira, 1999) we reported preliminary results on autothermal reforming of three fuels: hexadecane, grade 1 diesel, and grade 2 diesel. This paper reports the effect of operating conditions on the performance of the catalyst and on reforming of the diesel fuel. Results of diesel reforming over a new monolithic microchannel catalyst show improved conversion at higher fuel throughputs. Finally, results of fuel tests run with reformer in tandem with water-gas shift reactors show

reduction of carbon monoxide to less than 2%. These results show that autothermal reforming appears promising as an alternative to steam reforming for remote applications, and that Argonne's autothermal reforming catalyst shows superior performance.

Experimental

Certified low-sulfur diesel fuel, grade no. 1, was obtained from Phillips Petroleum Co. Standard diesel fuel, grade no. 2, was obtained from a local service station (nomenclature according to ASTM D975-97). The fuels were not treated further; fuel properties are provided in the previous report (Pereira, 1999). The autothermal catalyst was prepared in-house as extrudates and in a monolithic form. The catalyst was placed in a 0.41 cm ID tubular reactor within a tube furnace. The bed height was approximately 2.5 cm for the extrudates, and either 1 or 2 cm for the monolith. The temperatures at the top and bottom of the bed were monitored with thermocouples. Water-gas shift catalysts were fabricated as extrudates. Commercial zinc oxide and iron-chromium oxide catalysts were obtained from United Catalysts, Inc., for sulfur removal and high temperature shift, respectively.

The fuel and water were fed at the top of the reactor, where they were vaporized and mixed with the incoming oxygen and nitrogen; the nitrogen was used as an internal standard. The liquid feed rates were controlled with high pressure liquid chromatography (HPLC) pumps; the gas flow rates were maintained with mass flow controllers. The reactant stream was passed over the catalyst, and the products analyzed with a gas chromatograph. Pure oxygen was used in the reactant stream to improve detection of any hydrocarbons that may be present in the product. The gas chromatograph (GC) could not be used to quantify water and heavy hydrocarbons. Therefore, we used the hydrogen-to-carbon (H/C) ratio to obtain an atom balance and approximate a mass balance. In addition to the GC, an infrared detector was used to continuously measure the CO concentration in the effluent from the water-gas shift beds.

Results and Discussion

Compositional Analysis

In previous feasibility studies, hexadecane ($C_{16}H_{34}$) was used as a surrogate for diesel fuel (Pereira, 1999). The initial operating conditions used for diesel fuel were set based on the results obtained for hexadecane. In this study, we have refined our operating conditions based on a more detailed analysis of the composition of diesel fuel in order to determine suitable operating conditions for the ANL catalyst. We examined more closely the composition of the two diesel fuels that were used in our tests with the autothermal reforming catalyst. The two fuels were a certified low-sulfur grade 1 fuel and a standard grade 2 fuel obtained from the ANL motor-pool. The two fuels were analyzed by two analytical methods. The analysis of the certified diesel used in the microreactor tests described in this report is discussed below.

Because of the complex nature of diesel fuel (several hundred separate components have been identified), a complete chemical breakdown of the fuel was not feasible. However, we have obtained elemental and compositional data based on chemical structure. Using

this breakdown and assigning a reference compound for each grouping, we obtained an "average" chemical composition to further refine the operating parameters for the fuels. This analysis is shown in Table 3 for the certified fuel. The elemental composition derived from this analysis matches the measured elemental composition well. These results were used to set the ranges of oxygen and water feed rates.

Table 3: Compositional analysis of certified grade 1 diesel fuel

Compound Type	Wt. %	Avg. or Ref. Compd.	Avg. Mol. Wt.	Wt% C	Wt% H	Est. mol %
Saturates	83.7	$C_{14.2}H_{29.4}$	199.6	0.853	0.147	0.726
Paraffins	38.7	$C_{16}H_{34}$	226	0.850	0.150	0.2965
Cycloparaffins	29.6	$C_{10}H_{21}$	141	0.851	0.149	0.3635
2-ring cycloparaffins	11.5	$C_{16}H_{32}$	224	0.857	0.143	0.0889
3-ring cycloparaffins	4	$C_{22}H_{38}$	302	0.874	0.126	0.0229
Aromatics	16.3	$C_{9.5}H_{11}$	125.6	0.912	0.088	0.2248
<u>Mono-aromatics</u>	10.5	$C_{9.2}H_{10.4}$	121.1	0.914	0.086	0.1502
Benzenes	7.3	C_8H_8	104	0.923	0.077	0.1215
Naphthene benzenes	3.2	$C_{12}H_{16}$	160	0.900	0.100	0.0346
Dinaphthene benzenes	0	NA	NA	NA	NA	NA
<u>Di-aromatics</u>	5.7	$C_{10.3}H_{12.3}$	136.1	0.910	0.090	0.0725
Naphthalenes	1.8	$C_{13}H_{14}$	170	0.918	0.082	0.0183
Acenaphthenes	3.5	C_9H_{12}	120	0.900	0.100	0.0505
Fluorenes	0.3	$C_{13}H_{10}$	166	0.940	0.060	0.0031
<u>Tri-aromatics</u>	0	NA	NA	NA	NA	NA
<u>Tetra-aromatics</u>	0	NA	NA	NA	NA	NA
Total	100	$C_{13.4}H_{26.3}$	187.5	0.859	0.141	1.000

NA = not available, i.e. concentration of compound type is below detection limits.

Based on the results of the analyses, grade 1 diesel was determined to be significantly richer in alkanes than the grade 2 diesel. Grade 2 is significantly richer in aromatic compounds, particularly naphthalenes and naphthene benzenes. These differences in composition lead to differences in the hydrogen yield obtained with the reforming catalyst. Grade 2, although having a lower H:C and thus being relatively hydrogen poor, yielded a greater fraction of hydrogen in the product. This finding indicates that aromatics may be more easily reformed than cyclic aliphatics.

Effect of Operating Conditions on Hydrogen Yield

The reference compounds used to determine an "average" composition for the diesel fuel were used to calculate the equilibrium composition versus temperature, as shown in Figure 1. An $H_2O:C$ ratio of 1.25 and an $O:C$ of 1 were used for most tests and in this

calculation. The curves in Figure 1 show that at thermodynamic equilibrium hydrogen formation is maximized near 700°C. These results are very similar to those obtained for hexadecane. The hydrogen fraction in the product at this temperature is 57% on a dry, nitrogen-free basis. As the temperature is reduced, the methane fraction increases, and the hydrogen yield decreases commensurately.

Figure 2 shows the product composition as a function of temperature for reforming a certified low-sulfur diesel fuel at a water:fuel ratio of 20 and oxygen:fuel ratio of 8. In Figure 2, hydrogen production is maximized at 875°C. This temperature is higher than obtained with hexadecane, where, with similar oxygen- and water-to-fuel ratios, hydrogen production was maximized at 800°C with a hydrogen fraction (on a dry, nitrogen-free basis) of 60% in the products. For the certified fuel, the average hydrogen fraction in the product at 840°C is 46%, while at 880°C it is 50%. These values are somewhat higher than previous data with this same fuel (Pereira, 1999), but still somewhat lower than the results obtained for grade 2 diesel, where 52% hydrogen was obtained in the product at 850°C.

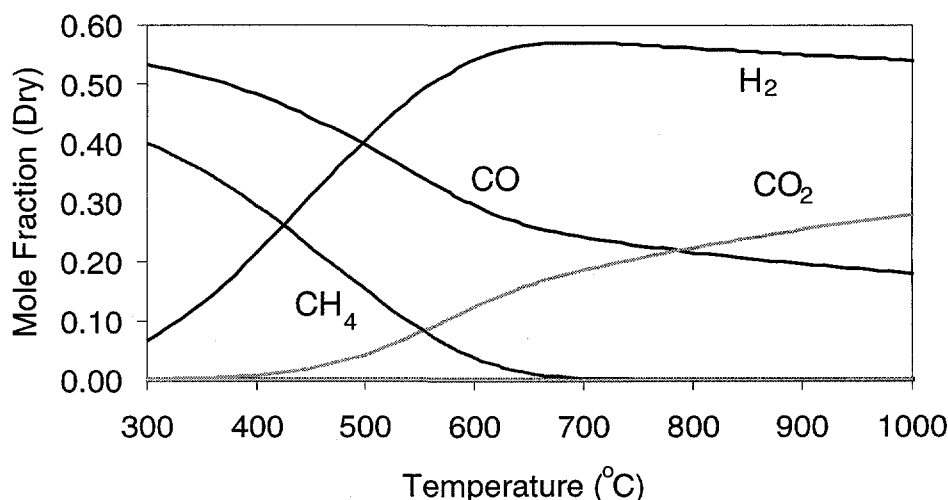


Figure 1: Equilibrium composition vs. temperature for diesel.
Oxygen:fuel = 8; water:fuel = 20.

There was a large amount of scatter in all of the data obtained with diesel fuel. The scatter was related to liquid injection of the fuel and water. We also examined the effect on hydrogen production of direct injection of steam into the reactor in place of water. This change reduced the amount of scatter somewhat, but separating the fuel and water streams led to increased soot formation above the bed. A reduction in scatter should be achieved with improvements to the design of the liquid injectors.

The product composition from diesel reforming was examined as a function of gas hourly space velocity (GHSV), oxygen:fuel ratio, and water:fuel ratio. Although apparent trends were present for some variables, the large scatter precluded any firm conclusions on their effect on hydrogen production. Some qualitative conclusions, however, can be made. Reducing the oxygen feed rate from 8 to 6 O₂ per mole of fuel, with a water:fuel ratio of

20, resulted in a much greater variety and larger fraction of hydrocarbons in the product stream; aromatics, especially, were much more prevalent. Apparently, a greater fraction of the fuel components, notably the aromatics, was not being cracked or oxidized effectively with less oxygen in the feed. There was also an increase in pressure drop across the reactor, as would be expected with an increase in coke or soot formation. At an oxygen:fuel ratio of 8 and a water:fuel ratio of 20, methane was the predominant hydrocarbon present at 840°C, and no increase in pressure drop was observed.

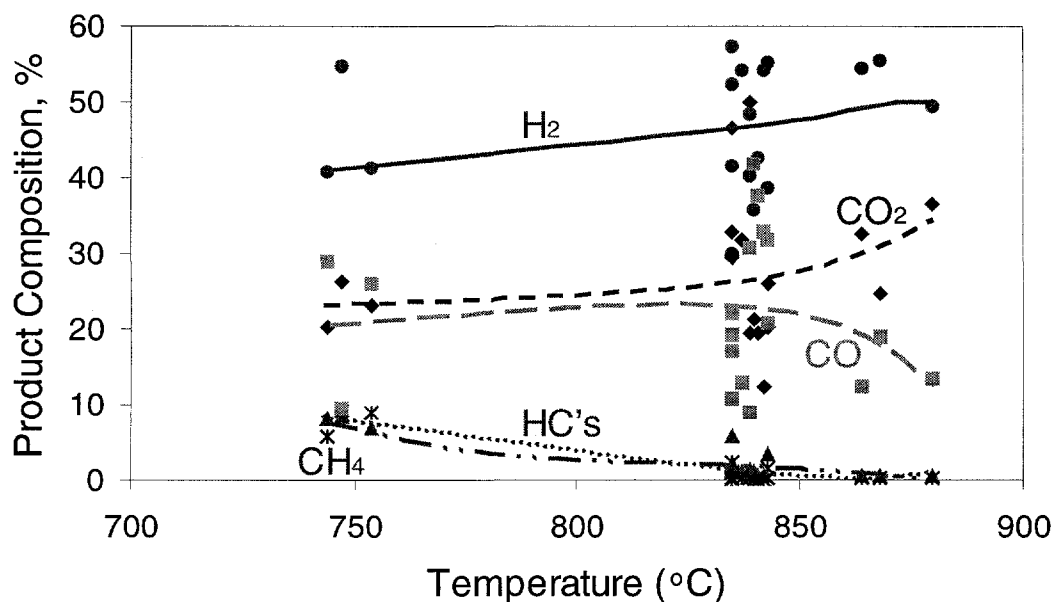


Figure 2: Composition vs. temperature for Grade 1 diesel.
Oxygen:fuel = 8; water:fuel = 20.

The GHSV was varied from 2000 to 10,000 h⁻¹ at 840°C and from 2000 to 4000 h⁻¹ at 880°C. The curves obtained were flat, with no trends evident. No significant changes were detected in the product distribution over the range of space velocities tested; no effect of GHSV on hydrogen production could be measured. Therefore, the reformer hydrogen yield in the product gas should be relatively uniform over a range of diesel fuel feed rates.

Figure 3 shows the results for the effect of water:carbon ratio, which does show an upward trend in hydrogen yield with excess water. As the water:carbon ratio was increased from 1 to 2, at a constant O₂:C ratio of 1 (oxygen:fuel ratio = 8), hydrogen yield steadily increased. As was observed with oxygen, low water:fuel ratios, resulted in increased coke or soot formation, evidenced by an increase in the pressure drop across the reactor. Soot deposits were observed in the reactor above the catalyst bed, though the catalyst did not show evidence of coke formation. As observed for low oxygen:fuel ratios, gas chromatograms showed a greater fraction and variety of hydrocarbon products at lower reaction temperatures; however, simple aromatics were not as prevalent.

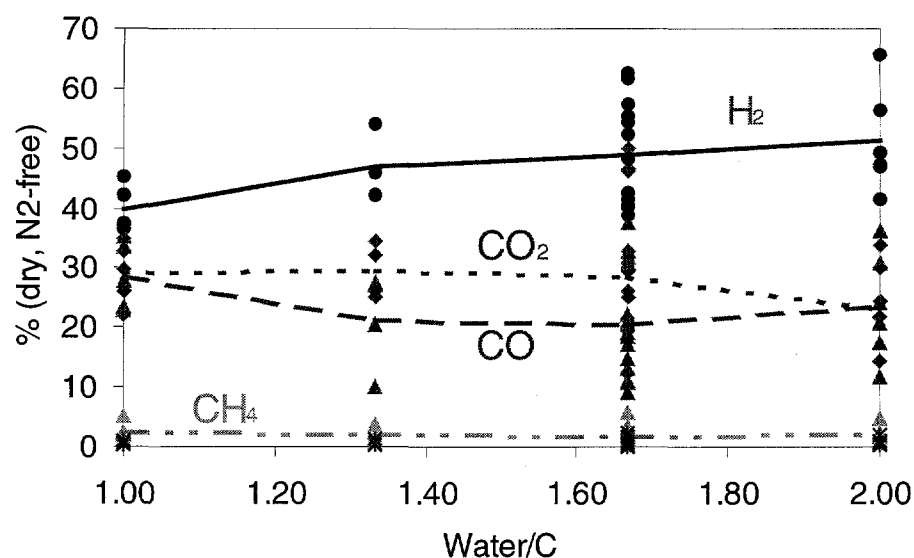


Figure 3: Product composition as a function of water:carbon ratio.
Oxygen:fuel = 8 Temperature = 850°C

We have recently developed a monolithic catalyst of a composition similar to the extruded form, but with a microchannel form. The channel diameters range in size from 30 to 300 μm . The product yield for a diesel feed over the monolithic catalyst is shown as a function of space velocity in Figure 4. Included also are average values for the extrudates. As can be seen in the figure, there is no change in yield as the space velocity is increased from 10,000 to 20,000 h^{-1} in going from extrudates to monoliths, there is no reduction in hydrogen yield. Furthermore, when the temperature was increased from 850 to 900°C at 10,000 h^{-1} , the hydrogen yield increased from 50 to 55% with the monoliths. These results show that the microchannel monolith can maintain or improve the hydrogen yield over a packed bed while reducing the size of the diesel reformer.

Diesel Fuel Processing

As part of the fuel processor development, we are tying the catalytic reforming of diesel fuel with the processing of the product gas. At the large scale, this will be done with the 5 kW(e) processor discussed later. However, because microreactor tests are much more rapid and allow us to better determine operating conditions for a large-scale unit, we are examining the entire diesel fuel process by connecting the reformer microreactor with a series of sulfur and carbon monoxide scrubbers. The scrubbers consist of a sulfur removal bed, high- and low-temperature shift beds, and a preferential oxidizer. This process train is nearly identical in configuration with the 5 kW(e) unit. However, it is much more flexible, allowing changes to materials, reactor configuration, or feeds to be made quickly.

As a test of the processing of diesel we sent a portion of the effluent from the reformer microreactor through a sulfur scrubber and the high- and low-temperature shift beds.

Because the conditions were not yet optimized for operation with a reformat produced by diesel, only a portion of the effluent was passed through the process train.

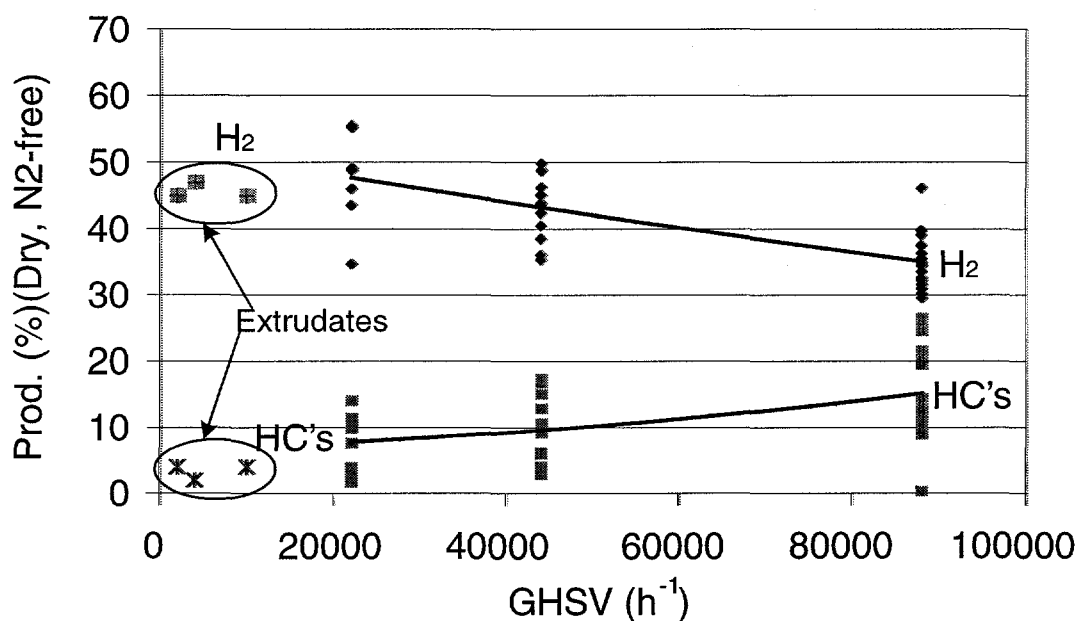


Figure 4: Results of test with monolithic microchannel catalyst.
Temperature = 850°C; water:fuel ratio = 20; oxygen:fuel ratio = 8

With this process we were able to reduce the carbon monoxide content of the reformat from 20% to less than 2% on a dry basis with the two water-gas shift reactors. Figure 5 shows the carbon monoxide level of the effluent, as a function of time, after it had dropped below 2%. There is a slight upward trend in the middle segment of data shown. However, the variation in reformer effluent composition observed above suggests that a constant CO level should not be expected for this test. Indeed the system may be reacting to a CO concentration spike. In the final segment of data, the upward trend stops, and the CO concentration drops closer to the initial level. Sulfur, as H₂S could not be measured with the on-line instruments.

Fabrication of 5 kW(e) Fuel Processor

As mentioned earlier, Argonne National Laboratory has developed an autothermal reforming catalyst that can convert diesel fuel to a hydrogen-rich stream. The reformat must be further processed to remove carbon monoxide and sulfur. To demonstrate this process, a large-scale unit is being fabricated by Dais Analytic Inc. This unit will incorporate the autothermal reforming catalyst with sulfur removal, water-gas shift, and preferential oxidization reactors.

Fabrication and assembly of the 5 kW(e) fuel processor are underway at Dais Analytic. All of the major components of the fuel processor have been procured or fabricated. The processor is being readied for final assembly. Recently, 5 kg of the reforming catalyst

(approximately 5 L total volume) was shipped to Dais Analytic for inclusion in this processor. After assembly, a series of tests will be run on the unit to assure successful operation.

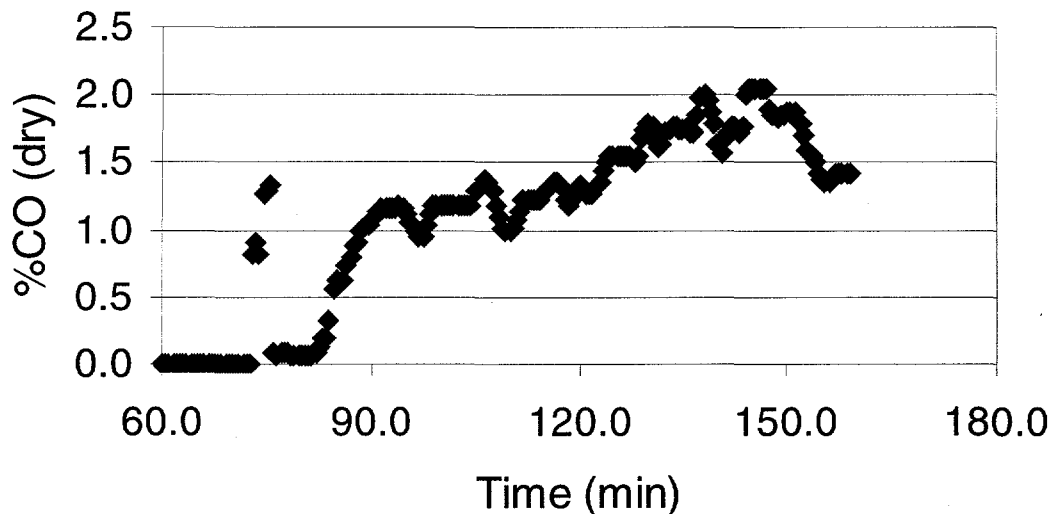


Figure 5: Carbon monoxide vs. time

Conclusions

Experiments were conducted to study the effects of temperature, water:fuel, oxygen:fuel, steam injection, and space velocity on the product composition for a certified diesel. We demonstrated improved hydrogen production from the certified diesel than was obtained previously; however, hydrogen production was still somewhat less than was obtained for grade 2 diesel. There was no clear effect due to $O_2:C$ ratio or space velocity on the hydrogen yield. Steam injection appeared to reduce scatter but increase soot formation over liquid water injection. Increasing the $H_2O:C$ ratio increased hydrogen yield. A five-fold increase in GHSV did not affect the hydrogen yield. Microchannel monolithic catalysts produced hydrogen yields comparable to extrudates at low space velocities for a diesel feed. There was a reduction in hydrogen yield at very high space velocities. As the temperature was raised, yields were well above those obtained for the extrudates.

The diesel reformat was further processed to remove carbon monoxide and sulfur using a train of reactors consisting of a sulfur scrubber and two water-gas shift beds. The carbon monoxide content of the process gas was reduced from approximately 20% to 2% on a dry basis using this process train. The process train is similar to the arrangement of reactors in the 5kW(e) diesel fuel processor.

All of the tests performed to date have been of less than 40 hours duration. We are preparing to run longer-term tests with diesel fuel. Such longer-term tests will allow us to better evaluate the effect of sulfur on catalyst activity, the long-term effects of coke formation, and the thermal stability of the catalyst to thermal cycling. Once fabrication of the 5 kW(e) diesel fuel processor is complete, it will be tested by Dais Analytic under the guidance of Argonne using the operating conditions established by the microreactor tests with diesel fuel.

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