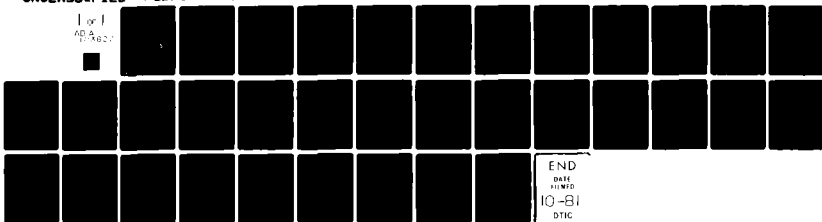


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CHARACTERIZATION OF THE PERFORMANCE  
OF ADIABATIC REFORMERS  
OPERATED WITH LOGISTIC FUELS

FINAL TECHNICAL REPORT  
(UNCLASSIFIED)

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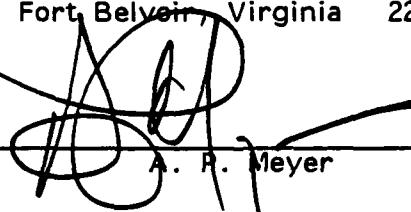
30 July 1981

Power Systems Division  
United Technologies Corporation

Prepared for

U. S. Army  
Fort Belvoir, Virginia 22060

Approved by:

  
A. R. Meyer

Project Manager

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CHARACTERIZATION OF THE PERFORMANCE OF ADIABATIC  
REFORMERS OPERATED WITH LOGISTIC FUELS

FINAL REPORT

Contract DAAK70-80-C-0115 *new*

J. A. S. Bett  
R. R. Lesieur  
A. P. Meyer  
H. J. Setzer

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## SUMMARY

United Technologies Corporation, in cooperation with the Electric Power Research Institute, has developed an adiabatic steam reformer capable of processing sulfur-containing fuels for commercial fuel cell power plants. No. 2 fuel oil and various coal-derived liquids have recently been successfully reformed to hydrogen using advanced catalyst formulations. The objective of this program is to determine the performance of the adiabatic reformer when operated with military logistic fuels. The test data will form the basis for system evaluation of the use of the adiabatic reformer in Army "SLEEP" power plants using military logistic fuels.

A two-inch diameter adiabatic reformer capable of supplying the hydrogen required for a 2.5 kW to 6 kW power plant was loaded with advanced metal oxide and nickel catalysts. It ran for over 1400 hours; 840 hours with No. 2 fuel oil as reference fuel, 350 hours on unleaded gasoline, and 216 hours on diesel fuel. The performance of the reformer on No. 2 fuel oil (for calibration against previous tests) closely matched previous tests both with respect to fuel conversion and carbon formation characteristics. After an initial decay period of about 200 hours, the performance remained stable for the remaining 1200 hours of test. The reformer operated at conditions set as design goals for a commercial fuel cell power plant.

With unleaded gasoline, the tendency for carbon formation was greatly reduced; even at the lowest values for oxygen to carbon ratio in the process steam no carbon was detected. Fuel conversion to hydrogen was a sensitive function of sulfur content; with greater than 750 ppmw sulfur content conversion was similar to No. 2 fuel, with less sulfur conversion increased. In tests using diesel fuel conversion was also similar to that obtained from No. 2 fuel oil while the carbon formation tendency was slightly improved.

Operating parameters were defined for each of the fuels. The effect of steam/carbon ratio, pressure and fuel flow rate on fuel conversion was determined. Minimum values of oxygen/carbon ratio and of preheat temperature of the process stream required to prevent carbon formation were also determined for the same variables. With both logistic fuels, performance matched or exceeded process requirements set for commercial fuel cell power plants.

Where requirements for Army SLEEP power plants might vary from commercial power plants, the performance of the adiabatic reformer was not adversely affected. Thus, fuel conversion was not significantly affected by change in pressure or by change in steam/carbon ratio between values of 2.8 and 4.38. The tendency for carbon formation was also unaffected by steam/carbon ratio and was decreased as pressure decreased from 60 to 20 psig.

→ The data in this report suggest that the adiabatic reformer may offer an attractive approach to processing military logistic fuels for Army SLEEP power plants.

## INTRODUCTION

United Technologies Corporation, in cooperation with the Electric Power Research Institute, has developed an adiabatic reformer capable of processing sulfur containing fuels for commercial fuel cell power plants. No. 2 fuel oil and various coal derived liquids have recently been successfully reformed to hydrogen using advanced catalyst formulations. The objective of this program is to evaluate the performance of the adiabatic reformer when operated with military logistic fuels. This work may be a suitable basis for extending the capabilities of the Army SLEEP power plant family to include multifuel operation on a broad range of logistic fuels.

The operation of the adiabatic reformer has been previously described (1). In the reformer, air is added to the fuel/steam process stream in sufficient quantity to supply, by combustion, the heat necessary for reforming the remaining fuel to hydrogen. For maximum efficiency, the amount of air, or the equivalent amount of heat supplied to the inlet process stream, must be reduced to a low value while achieving substantially complete conversion of fuel. However, for extended, unattended operation, carbon formation, which can readily plug the reactor, must be eliminated. With commercial nickel catalysts, the performance of the reformer is limited by the amount of air required by the process stream to prevent carbon formation. Thus, with an acceptable extent of process gas preheat, raising the prereaction temperature to about 1350°F, the minimum amount of air to avoid carbon formation gives an oxygen to carbon mole ratio of 0.45. The desired value to achieve fuel efficient operation is about 0.35. Recent programs at UTC have resulted in the development of a metal oxide catalyst which significantly improves the performance of the adiabatic reformer. With the metal oxide catalyst placed in the entrance of the reactor, i.e., the combustion zone, the reactor has been operated on No. 2 fuel oil without carbon formation at oxygen to carbon ratios as low as 0.35.

It is also important that the effluent stream from the reformer be essentially completely converted to hydrogen. Residual methane will not be oxidized at the fuel cell anode resulting in a loss in system efficiency. Again, commercial nickel catalysts have not proved sufficiently active to achieve the desired conversion of

residual methane in the adiabatic reformer. New high-activity supported metal catalysts have been developed which have achieved close to 99 percent conversion of fuel carbon to carbon oxides when placed in the exit of the reactor, downstream of the metal oxide combustion zone catalyst.

United has successfully tested a bench scale, 2.5 to 6-kW capacity, adiabatic reactor filled with a mixed catalyst bed of metal oxide and metal catalyst. No. 2 fuel oil and some coal liquids have been run at 3 atmospheres total pressure, and steam/carbon ratios in the feed of 4 to 5. The reactor was rugged in operation. It demonstrated the ability to regenerate itself while supplying hydrogen by burning-off carbon formed due to malfunction. It responded rapidly to change in feed rate. We therefore conclude that the adiabatic reformer offers an attractive approach to processing logistic fuels in the Army SLEEP power plants. With further development, it may enable the power plants to process a broad range of logistic fuels with high efficiency and to develop a fuel processor with a multifuel capability.

## TYPICAL OPERATING CHARACTERISTICS OF THE ADIABATIC REFORMER

The operation of the adiabatic reformer has been described in previous reports (1). To aid in evaluating the test results with military logistic fuel, the important features of the development of the reformer to process No. 2 fuel oil for commercial application have been summarized below.

A schematic of the bench scale test reactor is shown in Figure 1. Pre-vaporized fuel and steam are rapidly mixed with air and additional steam in the mixing nozzle. The well-mixed process stream enters the catalyst bed where a complex sequence of combustion and reforming processes occur in the inlet catalyst. Carbon may accumulate in this section. Finally, in the exit section steam reforming of the residual fuel is completed.

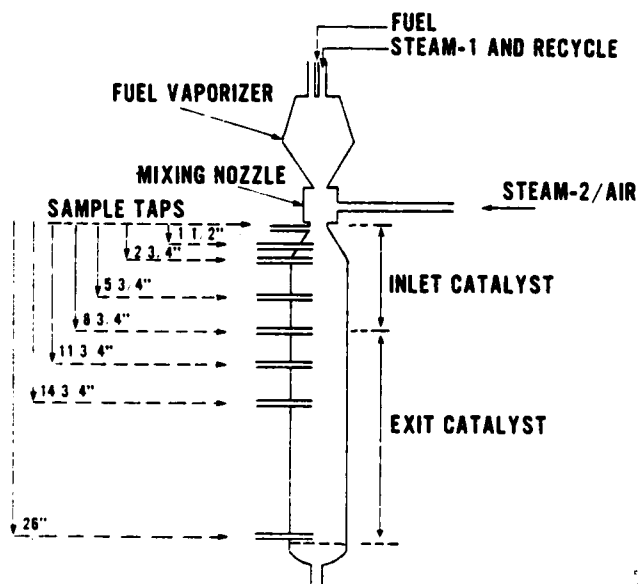


Figure 1. Schematic of Bench Scale Adiabatic Reformer

Analytical studies of the adiabatic reformer for the 4.8-MW phosphoric acid fuel cell power plant were used to define operating conditions which would minimize system cost at a design heat rate of 9300 Btu/kWh. The operating conditions which were set as goals for reactor development, shown in Table 1, were selected

to give minimum values for air addition ( $O_2/C$  ratio) and pre-reaction temperature while maintaining high fuel conversion.

TABLE 1. ADIABATIC REFORMER PERFORMANCE

|                                                        | Design(1)<br>Baseline | Reactor Performance                 |                                           |
|--------------------------------------------------------|-----------------------|-------------------------------------|-------------------------------------------|
|                                                        |                       | Commercial(2)<br>Nickel<br>Catalyst | Metal Oxide(3)<br>Plus<br>Advanced Nickel |
| $O_2/C$ Mole Ratio                                     | 0.36                  | 0.42                                | 0.36                                      |
| Pre-reaction Temperature, °F                           | 1360                  | 1360                                | 1360                                      |
| Exit Temperature, °F                                   | 1700                  | 1750                                | 1700                                      |
| Conversion                                             | 98.2                  | 99.0                                | >98.2 (4)                                 |
| Space Velocity, lbs fuel/ft <sup>3</sup><br>reactor-hr | 12                    | 24                                  | 12                                        |

(1) For 4.8 MW Phosphoric Acid Power Plant at 9300 Btu/kWh.  
 (2) 6 inch diameter reactor with optimized nozzle.  
 (3) 2 inch diameter reactor with optimized nozzle.  
 (4) Extrapolated to design space velocity.

Early reactor configurations with commercial nickel catalyst required air in excess of the design value to prevent carbon laydown in the reactor entrance. This excess air reduces the quantity of hydrogen produced and thus reduces power plant efficiency. It was recognized that rapid and efficient mixing of the air and fuel was important to limit the extent of carbon-forming reactions. Therefore, a study of the effect of reactant nozzle configuration on carbon formation was made. The 2-inch diameter bench-scale reactor processing two pounds of fuel per hour was used. The nozzle configuration was varied while the fuel (No. 2 fuel oil) and the catalyst (a commercial nickel catalyst) were not changed. After testing many configurations, an optimized nozzle geometry was defined which was subsequently scaled-up for a 6-inch diameter reactor flowing 10 pounds of fuel per hour. The ability to scale up the nozzle design was demonstrated by a close agreement in the minimum  $O_2/C$  requirement for the two reactors. However, the reactor with optimized nozzle was still limited in performance by carbon formation. As shown in Table 1, the minimum  $O_2/C$  requirement exceeded the design goal.

The effect on carbon formation of variation in catalyst formulation was therefore studied while holding the nozzle configuration fixed. From the position of the carbon deposited in the reactor and from the variation of product composition with reactor length, it was apparent that the principal function required of the catalyst depended on its position in the reactor bed; in the inlet section where combustion reactions predominated, the ability to inhibit carbon accumulation was paramount; in the exit section, the ability to reform residual methane was the only requirement. Hence, for carbon formation studies, the catalyst in the inlet of the 2-inch diameter reactor was changed while leaving the exit catalyst in place. In this way the effect of changes in the inlet catalyst could be rapidly determined.

Experiments in a laboratory microreactor had suggested that metal oxide catalysts would show superior resistance to carbon formation. When these catalysts were placed in the reactor it was clear that a major change in the rates of reaction in the combustion zone had occurred, as evidenced by a change in the temperature and product composition profiles from those observed with the commercial nickel catalyst. At the same time the minimum value for  $O_2/C$  at which the reactor would operate carbon-free was reduced.

In Figure 2, the characteristic carbon-free operating regime of the reactor is illustrated. At fixed pre-reaction temperature, it was found that the  $O_2/C$  ratio in the feed could be lowered to a point where increasing pressure drop across the reactor indicated carbon formation; raising the  $O_2/C$  ratio from this value reversed the pressure increase. Using this technique at different pre-reaction temperatures, a reactor operating line, above which the reactor could operate carbon-free, was defined. For reactors filled with commercial nickel catalyst, this line has a characteristic slope. Improvement in reactor performance was indicated by a lower value for the  $O_2/C$  intercept of the operating line. Metal oxide catalyst A can be seen in Figure 2 to have extended the carbon-free operation of the reactor below that obtained with commercial nickel catalyst while an improved formulation, catalyst B, gave even further improvement to lower values of  $O_2/C$ . The slope of the operating line for the metal oxide catalysts was similar to that of the nickel catalyst. More importantly, metal oxide B permitted operation of the reactor at the baseline design value for  $O_2/C$ .

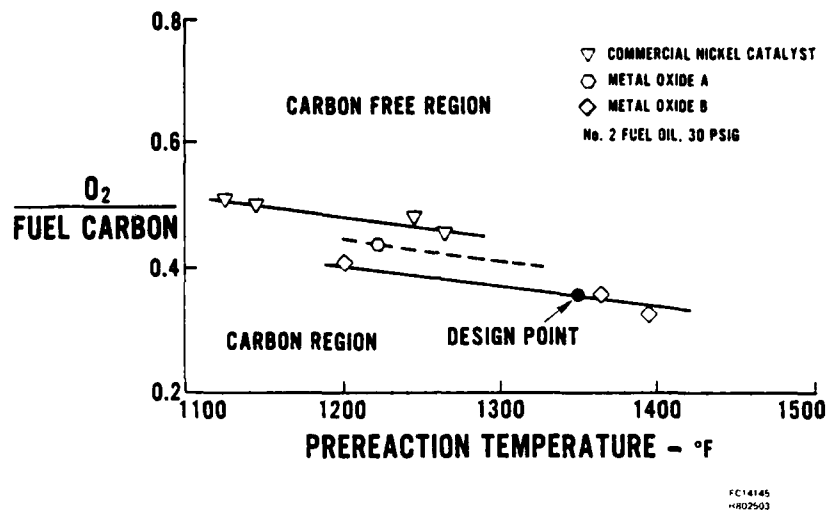


Figure 2. Effect of Catalyst on Carbon Formation in the Adiabatic Reformer

The fuel cell power plant not only requires that the reformer operate carbon-free, but also that it achieve high fuel conversion at the design conditions. For a given catalyst in the exit section of the reactor, the conversion correlated with the exit temperature and was independent of whether that temperature was achieved by the addition of air (increased  $O_2/C$ ) or by an increase in preheat temperature. Thus, in Figure 3, data are shown for two reactor conditions which represent different values for  $O_2/C$  and pre-reaction temperature, but the same adiabatic exit temperature. The temperature and methane concentration varied at the inlet to the reactor, but the conversion was the same at the reactor exit. With commercial nickel catalyst in the exit to the reactor, the required conversion could only be achieved at high temperatures. A more active nickel catalyst was developed in a parallel laboratory program which, when placed in the exit of the 2-inch diameter reactor, gave the conversions shown in Figure 4.

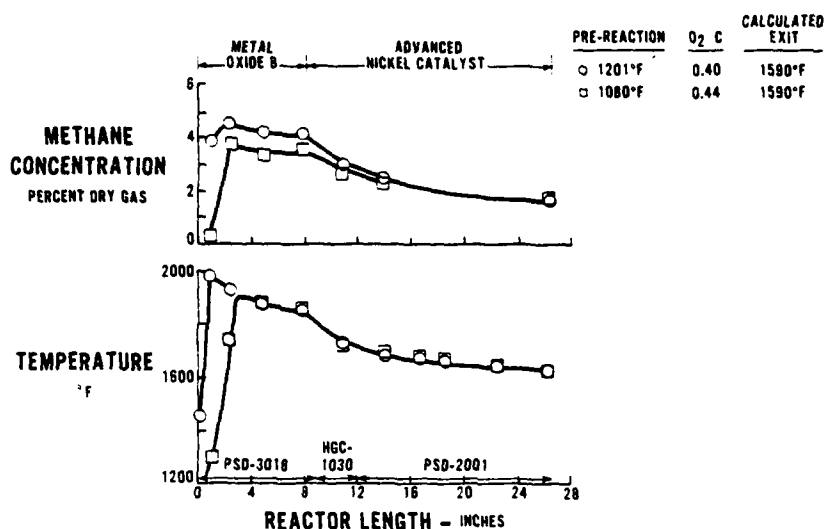
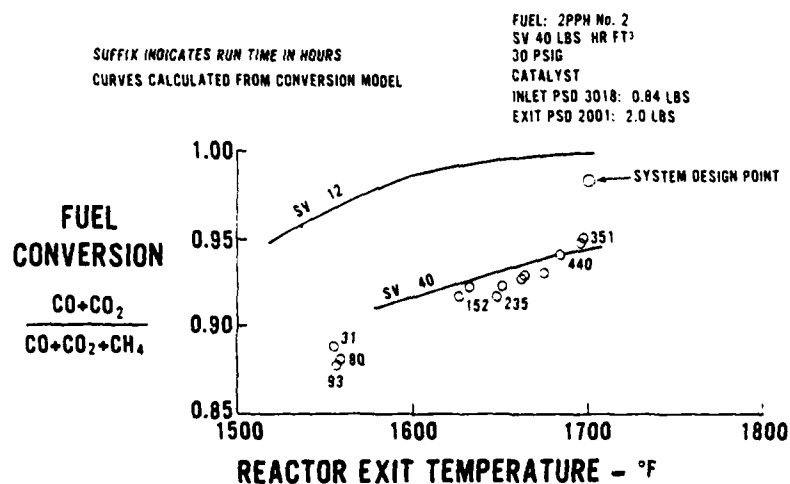
Figure 3. Effect of O<sub>2</sub>/C and Pre-reaction Temperature on Fuel Conversion

Figure 4. Fuel Conversion on High Activity Nickel Catalyst

The fuel flow rate of 2 pounds per hour corresponded to a weight hourly space velocity of approximately 0.7. Because the reactor contained catalysts of various densities, a more convenient unit was adopted, pph fuel/ft<sup>3</sup> reactor (2 pph gave a space velocity of 40 pph/ft<sup>3</sup>). Since the adiabatic reformer does not require an

external burner cavity, the catalyst volume can be commensurately higher than the catalyst volume in tubular, externally fired reformers for an equivalent overall volume. The design goal for the adiabatic reformer in Table 1 was set as 12 pph/ft<sup>3</sup>. The 2-inch diameter test reactor did not contain sufficient catalyst to give space velocities less than about 30 pph/ft<sup>3</sup>. The conversion at 12 pph/ft<sup>3</sup> was, therefore, projected from the data at 40 pph/ft<sup>3</sup> by use of a simple first order model for methane conversion in the reactor exit. A good fit to the data was obtained and the curve calculated for the design space velocity and plotted on in Figure 4 showed that the conversion achieved by the advanced nickel catalyst projected to the design point.

A 2-inch bench-scale reactor with the optimized nozzle configuration, metal oxide catalyst B in the inlet section, and the high activity nickel catalyst in the exit section was run for 450 hours on No. 2 fuel oil. The reactor performance decayed initially, but ran stably for the final 200 hours at the conditions summarized in Table 1. These closely matched the design requirements except in regard to pressure.

## PROGRAM APPROACH

The test program evaluated the performance of the bench scale, 2 pounds per hour fuel flow, adiabatic reformer containing United's advanced metal oxide and metal catalysts operated with two logistic fuels; non-leaded gasoline and diesel fuel. The reactor was initially run with No. 2 fuel oil, as reference fuel, to assure that the performance of the reactor reproduced previous tests. Unleaded gasoline and diesel fuel were then tested over a range of conditions likely to be required for Army application. This body of data established a basis for systems evaluation studies that could be conducted to determine the benefits that the adiabatic reformer may provide to the Army SLEEP program.

## TEST EQUIPMENT AND PROCEDURES

All tests run during this program were conducted in a two-inch diameter bench-scale reactor capable of operating with up to three pounds of fuel per hour. The same catalyst loading was used for the entire 1412 hours of testing. Three different fuels were utilized for determining the operating characteristics of the adiabatic reformer: No. 2 fuel oil which was used as the baseline fuel, diesel fuel and regular unleaded gasoline.

The bench scale adiabatic reformer was constructed of 2-inch schedule 40 Inconel-601 pipe approximately 24-inches long. The fuel flow was between 1.5 and 3 pounds per hour. The reactor was externally insulated. It operated adiabatically in that it was heated by internal combustion of fuel and air. There was significant heat loss amounting typically to 2000 Btu/hr or about 180°F loss from the calculated adiabatic exit temperature. A schematic of the test rig is shown in Figure 1. Fuel was vaporized by a portion of the total steam inventory, Steam 1. The mixture was delivered at about 700°F to the nozzle section where it was mixed with air and the remaining steam, Steam 2, superheated to about 1650°F. The temperature of the final mixture, before any reaction occurred, could be adjusted between 900°F and 1400°F. The reactant mixture was injected into the catalyst bed where the product gas composition was sampled and the temperature measured at intervals axially down the reactor. Reactor temperatures, pressures, and gas

flows were automatically monitored to shut down the reactor if pre-set operating limits were exceeded. The product samples passed through a condenser so that the composition of the dry gas was reported. In typical operation the reactor was started by feeding preheated steam and nitrogen to raise the catalyst temperature to about 1200°F. Hydrogen, air, and fuel were then added in sufficient flow to set the desired operating conditions. The hydrogen flow was set to simulate a condition in which some gas was recycled from the fuel cell anode vent. The pressure could be regulated from 20 to 60 psig.

Analyses were performed by gas chromatography on the dry gas product with a thermal conductivity detector. An example of the form in which the data for each test point was tabulated is shown in Figure 5.

Figure 5 also shows the placement of the three catalysts in the reactor. The inlet section was filled with PSD3018, a metal oxide on a refractory support, while the exit section contained PSD2001, a high activity nickel catalyst on a refractory support. A small section between the two catalysts contained HGC1030, a commercial nickel catalyst which had lower activity, but greater high temperature stability than PSD 2001.

POINT 12

DATA REDUCTION DRY MOLES =  $\frac{PPH N_2}{28} + (0.027 \times PPH AIR)$

$C_{IN} = \frac{PPH FUEL}{13.8} + \frac{PPH CO_2}{44} = 1.149$  FOR 2 PPM FUEL

$C_{OUT} = \sum X_{C_i}'s + C_2's \times DRY MOLES$

$C_{BAL} = \frac{C_{OUT}}{C_{IN}} \quad \theta = \frac{CO_2 + CO}{CO_2 + CO + CH_4}$

CONVERSION =  $\frac{(CO + CO_2) DRY MOLES}{C_{IN}}$

X-751 STAND, RIG 39348-7

DATE 10-13-80 TIME 1330-1615

RUN 20 ; 351 HRS ON FUEL

MID 453 LBS HGC 1030 TOP  
CATALYST BOT 1.81 LBS PSD 13 / 0.75 LBS  
PSD 3018

FUEL 2.0 PPM TYPE FUEL UNLEADED GASOLINE

STEAM 1 455 PPH 123°F

H<sub>2</sub> 0.017 PPH 80°FRECYCLE CO<sub>2</sub> 0.18 PPHN<sub>2</sub> — PPH

FUEL VAPORIZATION 480°F

PREREACTION TEMP 1307°F

ADIABATIC FLAME 2136°F

AIR 6.65 PPH 1851°F

STEAM 2 6.88 PPH + 1.21 PPM N<sub>2</sub>

## COMMENTS:

0-280 HRS 3220 PPM S N<sub>2</sub>  
280-450 HRS 134 PPM S GAS  
450-600 HRS 750 PPM S GAS  
600-630 HRS 263 PPM S GAS  
630- HRS 3220 PPM S N<sub>2</sub>

• LOWERED C<sub>2</sub>/C<sub>1</sub> RATIO  
TO 0.323.

• NO CARBON FORMATION  
INDICATED BY A  
STABLE PRESSURE DROP  
ACROSS THE REACTOR.

• AIR SHOWN (6.65) WAS  
CALCULATED BY SUBTRA.  
AIR USED IN N<sub>2</sub>  
BURNER TO RAISE  
STEAM AIR TEMP TO  
1851°F.

| BED TEMPERATURE | SAMPLE # | GAS CONCENTRATIONS IN PERCENT |      |                |                |                |                 |                               |                               |                   |                   | C <sub>BAL</sub> | CONV | θ |
|-----------------|----------|-------------------------------|------|----------------|----------------|----------------|-----------------|-------------------------------|-------------------------------|-------------------|-------------------|------------------|------|---|
|                 |          | CO <sub>2</sub>               | CO   | N <sub>2</sub> | O <sub>2</sub> | H <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> 's | C <sub>4</sub> 's |                  |      |   |
| 1677°F          | 1        |                               |      |                |                |                |                 |                               |                               |                   |                   |                  |      |   |
| 1903°F          | 2        |                               |      |                |                |                |                 |                               |                               |                   |                   |                  |      |   |
| 1941°F          | 3        | 9.4                           | 10.7 | 53.5           |                | 3.24           | 2.68            | 0.24                          |                               | 0.65              | 0.56              | 0.86             |      |   |
| 1859°F          | 4        | 13.5                          | 13.4 | 53.3           |                | 4.54           | 1.79            | 0.320                         |                               | 0.88              | 0.76              | 0.66             |      |   |
| 1738°F          | 5        | 14.3                          | 9.3  | 46.6           |                | 4.47           | 1.25            | 0.327                         |                               | 0.90              | 0.76              | 0.54             |      |   |
| 1632°F          | 6        | 15.7                          | 7.2  | 46.5           |                | 4.42           | 0.29            | 0.411                         |                               | 0.94              | 0.86              | 0.45             |      |   |
| 1549°F          | 7        | 14.6                          | 11.8 | 41.3           |                | 2.78           |                 | 0.008                         |                               | 1.06              | 0.90              | 0.50             |      |   |
| 1503°F          | 8        | 14.8                          | 11.8 | 40.1           |                | 2.66           |                 | 0.004                         |                               | 1.09              | 0.91              | 0.51             |      |   |
|                 |          | 13.9                          | 10.6 | 37.5           |                | 1.96           |                 |                               |                               | 1.05              | 0.93              | 0.93             |      |   |

ADIABATIC EXIT  
TEMP. 1500°F

\* C<sub>BAL</sub> - CARBON BALANCE ONLY REFLECTS CARBON IN GASEOUS PRODUCT  
\*\* WHERE C<sub>BAL</sub> > 100% USE CONVERSION =  $\frac{CO + CO_2}{CO + CO_2 + CH_4 + 2C_2H_6}$

Figure 5. Adiabatic Reformer Reduced Data

## FUELS TESTED

Three different fuels were tested. Diesel fuel and unleaded gasoline which were considered to be representative of the Army's logistic fuels were run and the results compared with those from tests with No. 2 fuel oil as reference. Sulfur was added to the gasoline in order to determine its effect on both the carbon boundary and the fuel conversion. A 50/50 mix (sulfur by weight) of thiophene and diphenyl sulfide was used to raise the sulfur level of the gasoline from 134 ppm to 263 ppm and 750 ppm. Properties of the fuels used are shown in Table 2. During the distillation analysis of the gasoline, 15% of the volume was lost due to its high volatility. The low initial boiling point for No. 2 fuel oil resulted from contamination by a low boiling distillate which was too small to affect the test result.

TABLE 2. FUEL PROPERTIES

|                  | No. 2 Fuel Oil | Diesel Fuel | Gasoline |
|------------------|----------------|-------------|----------|
| Specific Gravity | 0.831          | 0.853       | 0.743    |
| H/C              | 1.78           | 1.73        | -----    |
| Aromatics, %     | 27.3           | 36.0        | 47.9     |
| Sulfur, ppmw     | 3220           | 1090        | 134      |
| Distillation, °F |                |             |          |
| I.B. Pt.         | 95             | 155         | 86       |
| 10%              | 385            | 408         | 118      |
| 50%              | 532            | 540         | 226      |
| 70%              | 580            | 587         | 296      |
| 90%              | 650            | 655         | ---      |
| 95%              | 695            | 680         | 386*     |

\*15% fuel lost during distillation due to volatility.

## RESULTS

The operating characteristics of the adiabatic reformer were determined with three different fuels. The reformer ran for over 1400 hours; approximately 846 hours on No. 2 fuel oil as reference fuel, 350 hours on gasoline, and 216 hours on diesel oil. The performance with No. 2 fuel oil closely matched previous tests in which the reformer operated at conditions required to meet goals set for the fuel processor in a commercial demonstrator power plant at 9300 Btu/kW heat rate (1). The performance with diesel oil was very similar, while the performance with gasoline exceeded that with No. 2 fuel oil, both with respect to fuel conversion and resistance to carbon accumulation. Seventy-five different test points were run defining the reactor's dependence on temperature, pressure, fuel type and fuel flow rate, steam to carbon ratio ( $H_2O/C$ ) and oxygen to carbon ratio ( $O_2/C$ ). A summary of all test points with pertinent comments is listed for reference in Table 3. The tests are described in more detail below.

No. 2 Fuel Oil

The test was started with No. 2 fuel oil which was used as reference fuel to permit the reactor to "line out," and to establish that the performance was similar to previous tests using the same reactor and catalysts.

A temperature profile for the adiabatic reformer operating with No. 2 fuel oil, typical also for the other fuels, is shown in Figure 6. The temperature rose rapidly at the reactor inlet as combustion occurred then dropped as the unreacted fuel and cracked products reformed to carbon oxides and hydrogen. All of the combustion and about 80% of the reforming occurred in the metal oxide catalyst. Due to the endothermic processes, the maximum temperatures never reached the calculated 2136°F adiabatic flame temperature. The metal oxide catalyst had little activity for steam reforming below about 1800°F. Consequently, a more active nickel catalyst was installed downstream of the potential carbon formation region. In Figure 6 the increased rate of decrease in temperature signalled transition to nickel catalyst.

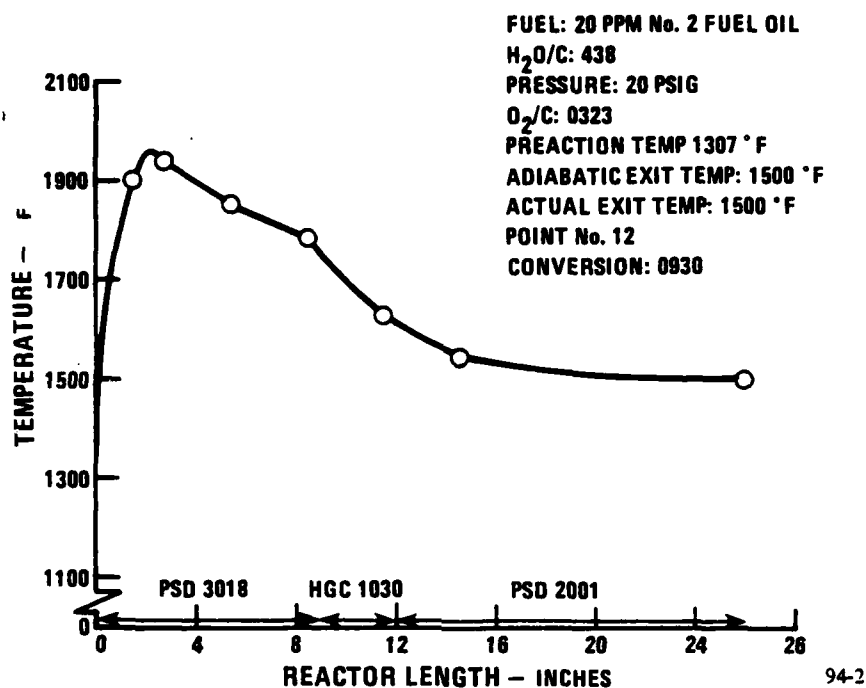


Figure 6. Typical Reactor Temperature Profile

In Figure 7 the corresponding changes in product composition are recorded. Carbon monoxide and carbon dioxide increased rapidly as combustion occurred. Ethane, ethylene, and methane, the products of fuel cracking pass through a concentration maximum close to the point where the maximum in temperature was reached. Ethylene decreased rapidly due to reforming in the metal oxide catalyst, but the less reactive methane required the nickel catalyst for significant decrease in concentration to occur. In the nickel catalyst the carbon balance, fluctuating about 100%, indicated that methane and the carbon oxides were the sole products. Changes in pre-reaction temperature, O<sub>2</sub>/C ratio, fuel type and flow rate brought small shifts in position, but no change in the general form of the conversion shown in Figures 6 and 7.

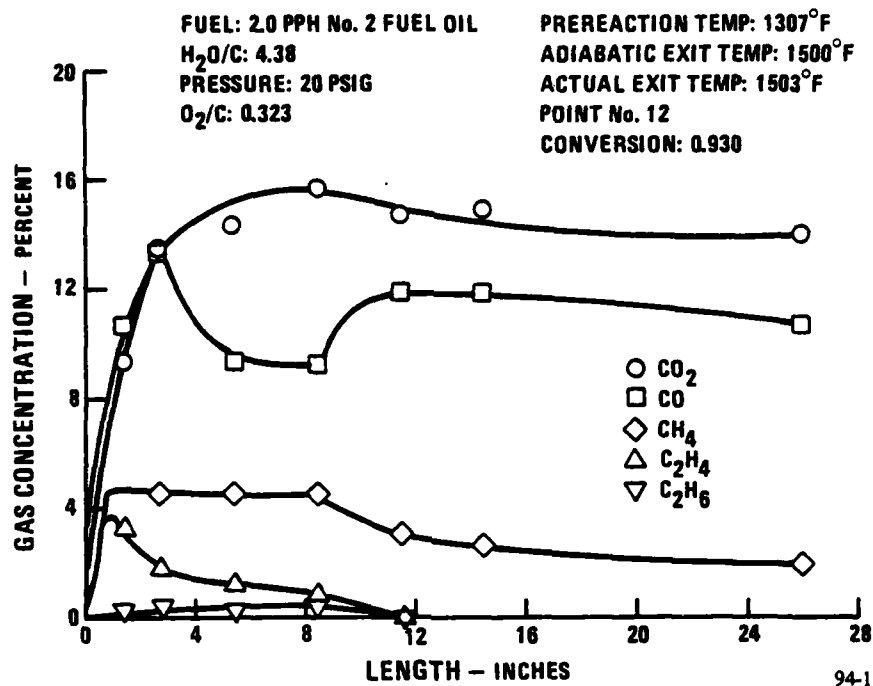
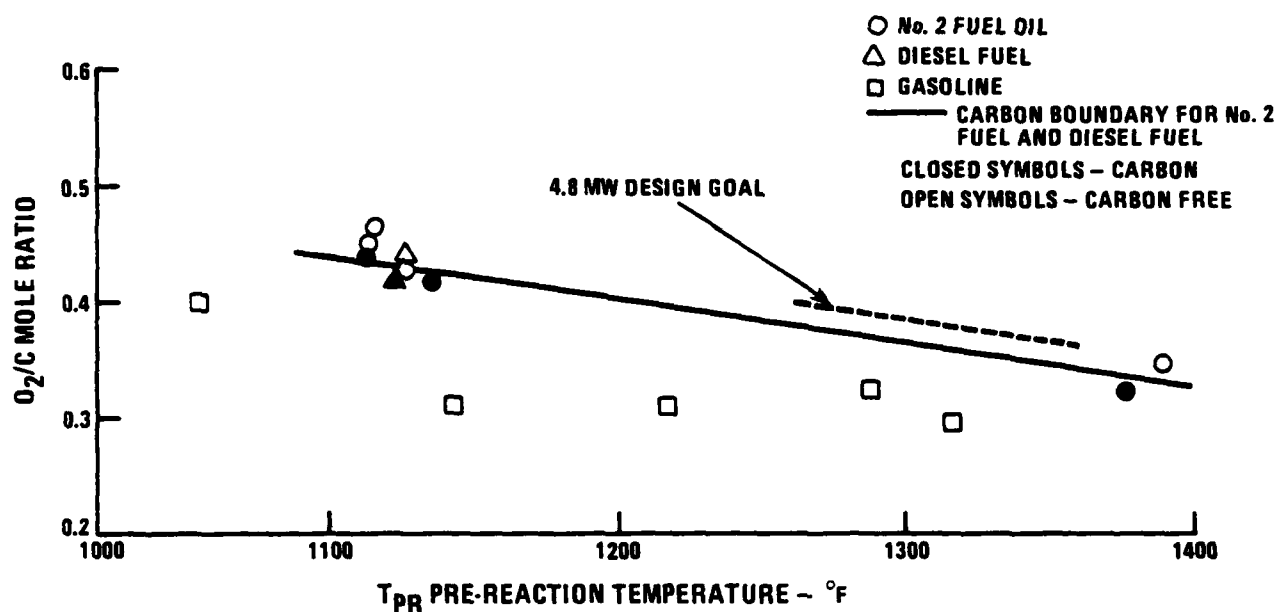


Figure 7. Typical Process Stream Composition

For fuel cell power plant application, the performance of the reformer is judged on two capabilities: the ability to achieve high fuel conversion to hydrogen and the ability to resist accumulation of carbon in the reactor with minimum energy input either as air or as reactant preheat. Critical operating parameters, listed in Table 1, were set as design goals for a commercial phosphoric acid power plant. These served as a reference for the present program. In previous programs the reactor loaded with the same catalysts operated with No. 2 fuel oil at the design conditions for over 500 hours.

It was important to establish that the reactor could operate carbon-free at the desired operating conditions. Carbon formed in the reactor if the mole ratio of oxygen to carbon ( $O_2/C$ ) fell below a critical value. At fixed pre-reaction temperatures the  $O_2/C$  ratio in the fuel could be lowered to the point where increasing pressure drop across the reactor indicated carbon formation; raising the  $O_2/C$  ratio from this value reversed the previous increase. Using this technique at different pre-reaction temperatures, a reactor operating line or carbon boundary,

above which the reactor could operate carbon free, was defined. (See Figure 8). In previous tests this line had been shown to have the same characteristic slope for every reactor. Improvement in reactor performance was indicated by a lower value for the  $O_2/C$  intercept of the operating line. Figure 8 shows that the present reactor with No. 2 fuel oil operated carbon-free slightly below the design point of Table 1, and with the same slope for the carbon boundary.



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Figure 8. Carbon Boundary in the Adiabatic Reformer for Various Fuels

In previous tests the position of the carbon boundary had initially deteriorated with time, stabilizing at the design line indicated in Figure 8. Figure 9 shows test points defining the carbon boundary for No. 2 fuel oil and diesel fuel as a function of time for the present tests. The decay in the boundary closely follows the curve defined by previous tests and shows that for the final 1200 hours of the present test, the carbon formation characteristics of the reactor had stabilized.

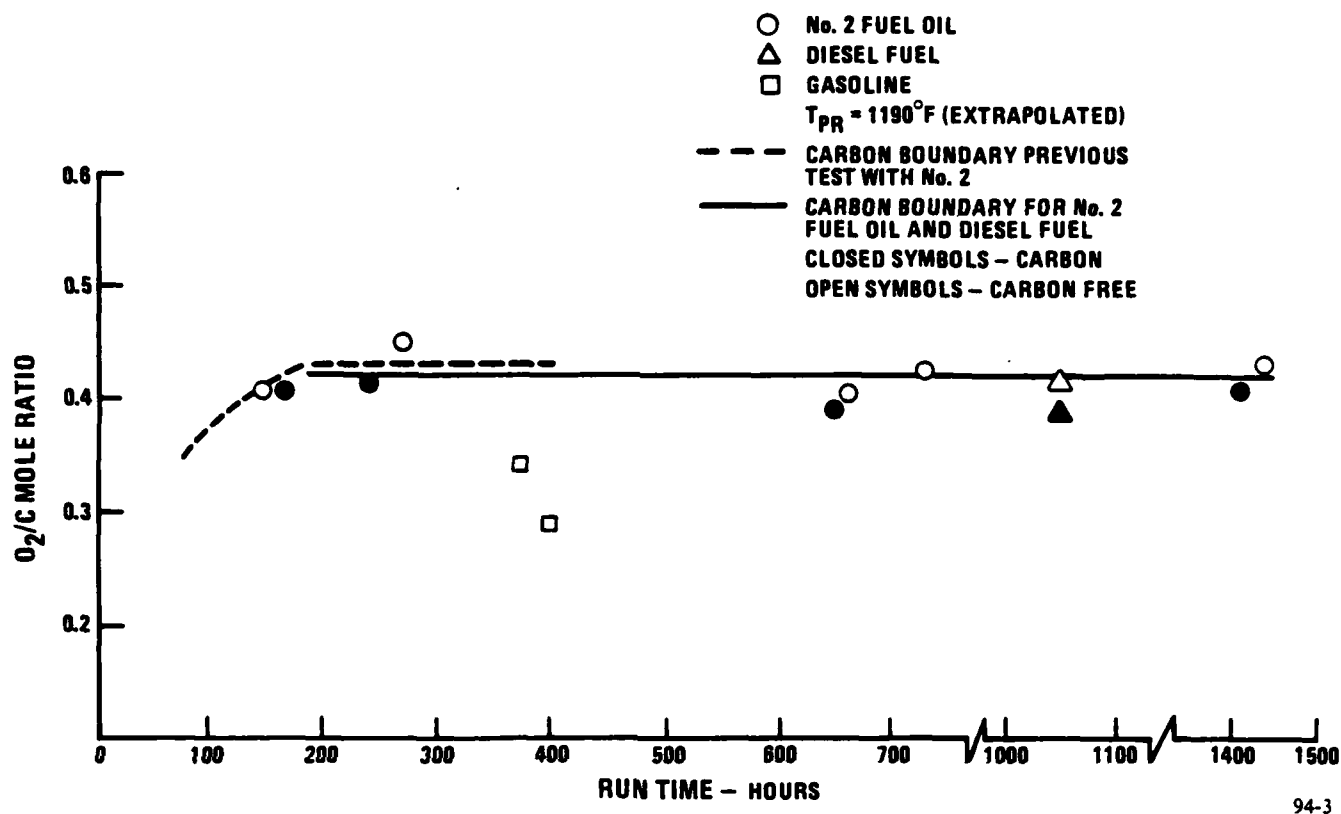


Figure 9. Position of Carbon Boundary as Function of Time

The fuel cell power plant not only requires that the reformer operate carbon-free, but also that it achieve high fuel conversion at the design conditions. It has been shown that for a given catalyst in the exit section of the reactor the conversion correlated with the exit temperature and was independent of whether that temperature was achieved by the addition of air (increased  $\text{O}_2/\text{C}$ ) or by an increase in preheat temperature. Figure 10 shows this correlation for No. 2 fuel oil in the present tests. The data closely matched conversions achieved in previous tests at comparable conditions.

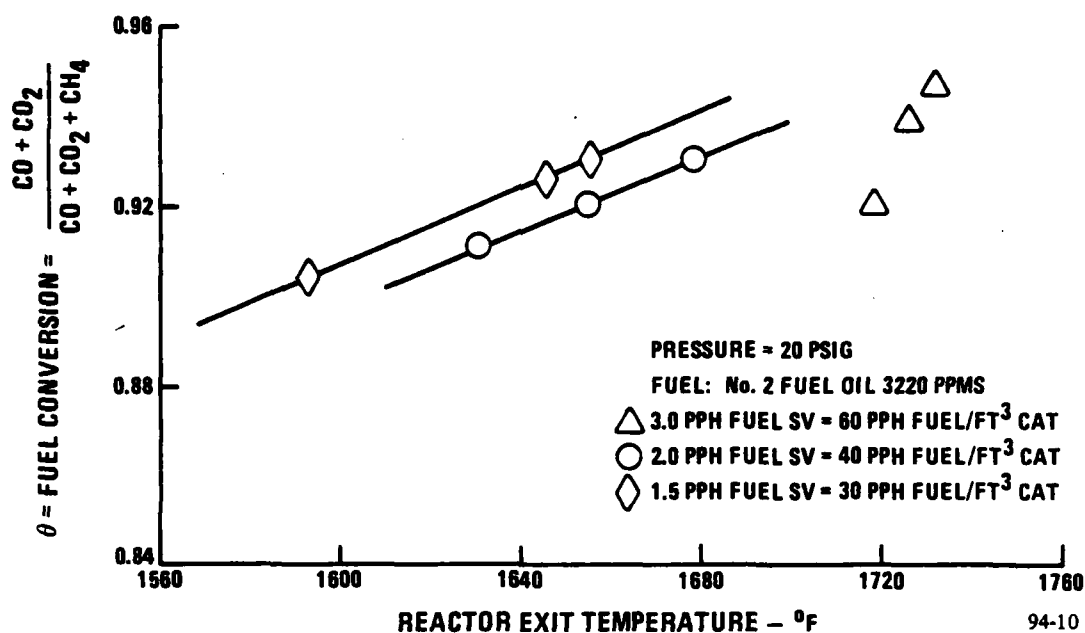


Figure 10. Fuel Conversion vs. Reactor Fuel Flow

### Gasoline

After 280 hours operation with No. 2 fuel oil the reactor feed was switched to gasoline. The first data points (11-18, Table 3) attempted to establish a carbon boundary and measure fuel conversion for the reactor with gasoline containing 134 ppm sulfur. Even at the lowest values for  $\text{O}_2/\text{C}$  and  $\text{H}_2\text{O}/\text{C}$  (0.315 and 3.28, respectively) no carbon accumulation could be identified. Plotted on Figure 8 the data points show that with gasoline the reactor could operate carbon-free at values for  $\text{O}_2/\text{C}$  well below the carbon boundary for No. 2 fuel oil. Fuel conversion was high even at low reactor exit temperatures. See Figure 11. There appeared to be an inflection in the curve correlating conversion and exit temperature at very low temperatures.

TABLE 3. DATA SUMMARY

| Point | Time<br>(Hours) | Temperatures (°F) |                 | O <sub>2</sub> /C | H <sub>2</sub> O/C | Fuel             | Fuel<br>Conv. | Press.<br>(PSIG) | Comments                                                              |
|-------|-----------------|-------------------|-----------------|-------------------|--------------------|------------------|---------------|------------------|-----------------------------------------------------------------------|
|       |                 | Pre-reaction      | Adiabatic Flame | Calculated        | Exit               |                  |               |                  |                                                                       |
| 1     | 5.0             | 1142              | 2161            | 1565              | 1552               | No. 2, 3220 ppmS | 0.954         | 20               | Initial point                                                         |
| 2     | 74.0            | 1158              | 2188            | 1593              | 1616               | " " " "          | 0.930         | 20               | Point check after weekend running.                                    |
| 3     | 102.7           | 1167              | 2197            | 1601              | 1622               | " " " "          | 0.911         | 20               | Some conversion decay evident, carbon-free.                           |
| 4     | 145.7           | 1169              | 2199            | 1600              | 1624               | " " " "          | 0.93          | 20               | Conversion back to Point 3                                            |
| 5     | 170             | 1156              | 2093            | 1475              | 1561               | " " " "          | 0.889         | 20               | Possible carbon form.                                                 |
| 6     | 178             | 1386              | 2156            | 1517              | 1707               | " " " "          | "             | "                | Carbon region.                                                        |
| 7     | 242             | 1167              | 2186            | 1586              | 1620               | " " " "          | 0.922         | 20               | Point check after weekend.                                            |
| 8     | 246             | 1378              | 2169            | 1535              | 1589               | " " " "          | 0.896         | 20               | Carbon region.                                                        |
| 9     | 270             | 1390              | 2235            | 1611              | 1635               | " " " "          | 0.926         | 20               | Carbon-free.                                                          |
| 10    | 282             | 1095              | 2114            | 1525              | 1522               | " " " "          | 0.950         | 20               | Check point before fuel change.                                       |
| 11    | 349             | 1105              | 2153            | 1569              | 1558               | Gas, 134 ppmS    | 0.958         | 20               | 1st gasoline point carbon-free.                                       |
| 12    | 351             | 1301              | 2136            | 1500              | 1503               | " " " "          | 0.930         | 20               | Carbon-free.                                                          |
| 13    | 378             | 1296              | 2053            | 1400              | 1458               | " " " "          | 0.891         | 20               | Carbon-free.                                                          |
| 14    | 398             | 1156              | 2192            | 1425              | 1485               | " " " "          | 0.910         | 20               | Lower H <sub>2</sub> O/C, still carbon-free.                          |
| 15    | 400             | 1144              | 2091            | 1317              | 1426               | " " " "          | 0.88          | 20               | Lower O <sub>2</sub> /C at low H <sub>2</sub> O/C, still carbon-free. |
| 16    | 404             | 953               | 2211            | 1469              | 1496               | " " " "          | 0.92          | 20               | Raised exit temp. to check conversion.                                |
| 17    | 424             | 1211              | 2152            | 1379              | 1474               | " " " "          | 0.893         | 20               | Raised preheat to compare conversion profile.                         |
| 18    | 444             | 1216              | 2157            | 1381              | 1483               | " " " "          | 0.900         | 20               | Repeat of above point, C <sub>2</sub> 's found in exit.               |
| 19    | 478             | 962               | 2195            | 1445              | 1551               | Gas, 750 ppmS    | 0.879         | 20               | High S decreases conv., but no carbon.                                |
| 20    | 482             | 951               | 2185            | 1437              | 1563               | " " " "          | 0.879         | 20               | Repeat of above point.                                                |
| 21    | 488             | 945               | 2279            | 1557              | 1609               | " " " "          | 0.921         | 20               | Raised exit temp. to check conversion.                                |
| 22    | 500             | 1246              | 2269            | 1517              | 1593               | " " " "          | 0.906         | 20               | Raised preheat to compare with PT.21. No C.                           |
| 23    | 510             | 1268              | 2058            | 1437              | 1537               | " " " "          | 0.875         | 20               | Lowered temp. to compare conv. Still no C.                            |

TABLE 3. DATA SUMMARY  
(Continued)

| Point | Time<br>(Hours) | Pre-reaction | Temperatures (°F)  |                    | O <sub>2</sub> /C | H <sub>2</sub> O/C | Fuel             | Fuel<br>Conv. | Press.<br>(PSIG) | Comments                                                                                                              |
|-------|-----------------|--------------|--------------------|--------------------|-------------------|--------------------|------------------|---------------|------------------|-----------------------------------------------------------------------------------------------------------------------|
|       |                 |              | Adiabatic<br>Flame | Exit<br>Calculated |                   |                    |                  |               |                  |                                                                                                                       |
| 24    | 572             | 1058         | 2061               | 1467               | 0.400             | 4.38               | Gas, 750 ppmS    | 0.895         | 20               | Check point after weekend.<br>Intermediate 5 affects<br>conversion.                                                   |
| 25    | 609             | 1057         | 2060               | 1467               | 0.400             | 4.38               | Gas, 263 ppmS    | 0.905         | 20               |                                                                                                                       |
| 26    | 624             | 1248         | 2086               | 1461               | 0.338             | 4.38               | "                | "             | 20               | Increase preheat,<br>no carbon.                                                                                       |
| 27    | 629             | 1258         | 2168               | 1559               | 0.378             | 4.38               | "                | "             | 20               | Raise O <sub>2</sub> /C to check<br>conversion.                                                                       |
| 28    | 647             | 1138         | 2157               | 1563               | 0.41              | 4.38               | No. 2, 3220 ppmS | 0.911         | 20               | Switched to No. 2 carbon<br>region.                                                                                   |
| 29    | 652             | 1128         | 2177               | 1591               | 0.425             | 4.38               | "                | "             | 20               | Carbon boundary.                                                                                                      |
| 30    | 654             | 1086         | 2134               | 1550               | 0.425             | 4.40               | "                | "             | 20               | Lower fuel flow from 2.0<br>to 1.5 pph.                                                                               |
| 31    | 658             | 1108         | 2237               | 1673               | 0.467             | 4.40               | "                | "             | 20               | Increased exit temp. by<br>raising O <sub>2</sub> /C.                                                                 |
| 32    | 669             | 1149         | 2195               | 1609               | 0.424             | 4.38               | "                | "             | 20               | Raised fuel flow to 3.0<br>pph. Carbon formed.                                                                        |
| 33    | 676             | 1184         | 2233               | 1643               | 0.424             | 4.38               | "                | "             | 20               | Raised exit temp.<br>(preheat). Carbon-free.                                                                          |
| 34    | 681             | 1123         | 2321               | 1635               | 0.430             | 3.61               | "                | "             | 20               | Lowered HO/C at 2.0 pph,<br>carbon-free.                                                                              |
| 35    | 719             | 1183         | 2291               | 1725               | 0.460             | 4.38               | "                | "             | 20               | Poor conversion after H <sub>2</sub> -<br>free start-up. Carbon<br>boundary between O <sub>2</sub> /C =<br>0.41-0.46. |
| 36    | 732             | 1155         | 2204               | 1615               | 0.425             | 4.38               | "                | "             | 20               | Boundary between O <sub>2</sub> /C<br>0.425-0.44.                                                                     |
| 37    | 755             | 1118         | 2231               | 1600               | 0.425             | 4.00               | "                | "             | 20               | Lowered H <sub>2</sub> O/C carbon.                                                                                    |
| 38    | 765             | 1141         | 2286               | 1670               | 0.44              | 4.00               | "                | "             | 20               | Raised O <sub>2</sub> /C, carbon-free.                                                                                |
| 39    | 780             | 1094         | 2172               | 1595               | 0.44              | 4.40               | "                | "             | 20               | Lowered fuel flow to 1.5<br>pph. Carbon region.                                                                       |
| 40    | 786             | 1103         | 2231               | 1667               | 0.467             | 4.40               | "                | "             | 20               | Raised exit temp. with<br>O <sub>2</sub> /C. Carbon-free.                                                             |
| 41    | 800             | 1100         | 2229               | 1665               | 0.467             | 4.40               | "                | "             | 20               | Repeat of 40.                                                                                                         |
| 42    | 807             | 1160         | 2208               | 1630               | 0.425             | 4.38               | "                | "             | 20               | Raised fuel flow to 3.0<br>pph. Carbon.                                                                               |

TABLE 3. DATA SUMMARY  
(Continued)

| Point | Time<br>(Hours) | Temperatures (°F) |                    |            |      | O <sub>2</sub> /C | H <sub>2</sub> O/C | Fuel              | Fuel<br>Conv. | Press.<br>(PSIG) | Comments                                                                                                                |
|-------|-----------------|-------------------|--------------------|------------|------|-------------------|--------------------|-------------------|---------------|------------------|-------------------------------------------------------------------------------------------------------------------------|
|       |                 | Pre-reaction      | Adiabatic<br>Flame | Calculated | Exit |                   |                    |                   |               |                  |                                                                                                                         |
| 43    | ---             | ---               | ---                | ---        | ---  | ---               | ---                | ---               | ---           | 20               | Manifold leak rendered<br>this point invalid.                                                                           |
| 44    | 838             | 1226              | 2127               | 1540       | 1655 | 0.378             | 4.53               | No. 2, 3220 ppms  | 0.903         | 30               | C-free, fuel flow = 2.0<br>pph, react. p = 30<br>psig. High C's found<br>in 44 series points.<br>G.C. being questioned. |
| 44A   | 842             | 1121              | 2226               | 1660       | 1677 | 0.455             | 4.38               | " " "             | 0.913         | 30               | C-free at lower pre-<br>react temp. Manifold<br>leak did not change<br>carbon boundary.                                 |
| 44B   | 852             | 1158              | 2227               | 1640       | 1678 | 0.435             | 4.38               | " " "             | 0.90          | 30               | Reactor ΔP holding,<br>must be on carbon<br>boundary.                                                                   |
| 44C   | 866             | 1156              | 2226               | 1640       | 1690 | 0.435             | 4.38               | " " "             | 0.916         | 30               | Carbon slowly forming.                                                                                                  |
| 44D   | 917             | 1204              | 2264               | 1670       | 1692 | 0.430             | 4.38               | " " "             | 0.918         | 30               | Carbon free condition.                                                                                                  |
| 44E   | 940             | 1095              | 2439               | 1713       | 1703 | 0.455             | 3.20               | " " "             | 0.936         | 30               | Carbon boundary at<br>lower H <sub>2</sub> O/C.                                                                         |
| 44F   | 976             | 1053              | 2525               | 1737       | 1694 | 0.465             | 2.80               | " " "             | 0.930         | 30               | Carbon forming slowly.<br>H <sub>2</sub> O/C does not seem<br>to affect carbon<br>boundary.                             |
| 45    | 982             | 1150              | 2284               | 1693       | 1714 | 0.455             | 4.23               | Diesel, 1090 ppms | 0.947         | 30               | Changed to diesel<br>fuel. Conversion<br>improved.                                                                      |
| 46    | 986             | 1147              | 2271               | 1677       | 1639 | 0.45              | 4.23               | " " "             | 0.934         | 30               | Carbon free.                                                                                                            |
| 47    | 996             | 1141              | 2226               | 1623       | 1675 | 0.43              | 4.23               | " " "             | 0.920         | 30               | Carbon free.                                                                                                            |
| 48    | 1016            | 1139              | 2224               | 1621       | 1669 | 0.43              | 4.23               | " " "             | 0.924         | 30               | Carbon free.                                                                                                            |
| 49    | 1018            | 1138              | 2202               | 1595       | 1660 | 0.42              | 4.23               | " " "             | 0.916         | 30               | Lowering air to find<br>carbon boundary.                                                                                |
| 50    | 1022            | 1136              | 2179               | 1567       | 1629 | 0.41              | 4.23               | " " "             | 0.902         | 30               | No indication of carbon<br>after 3 hours.<br>Carbon formation may<br>have started.                                      |
| 51    | 1023            | 1134              | 2157               | 1539       | 1614 | 0.40              | 4.23               | " " "             | 0.906         | 30               |                                                                                                                         |
| 52    | 1022            | 1132              | 2133               | 1511       | 1617 | 0.39              | 4.23               | " " "             | 0.905         | 30               |                                                                                                                         |
| 53    | 1039            | 1131              | 2111               | 1485       | 1595 | 0.36              | 4.23               | " " "             | 0.887         | 30               |                                                                                                                         |

TABLE 3. DATA SUMMARY  
(Continued)

| Point | Time<br>(Hours) | Temperatures (°F) |                    |                    | O <sub>2</sub> /C | H <sub>2</sub> O/C | Fuel   | Diesel,<br>1090 ppm | Fuel<br>Conv. | Press.<br>(PSIG) | Comments                                                                                                    |
|-------|-----------------|-------------------|--------------------|--------------------|-------------------|--------------------|--------|---------------------|---------------|------------------|-------------------------------------------------------------------------------------------------------------|
|       |                 | Pre-reaction      | Adiabatic<br>Flame | Exit<br>Calculated |                   |                    |        |                     |               |                  |                                                                                                             |
| 54    | 1044            | 1115              | 2016               | 1365               | 0.34              | 4.23               | Diesel | 1090 ppm            | 0.887         | 30               | Reactor definitely<br>plugging from carbon<br>formation.                                                    |
| 55    | 1047            | 1116              | 2058               | 1419               | 0.36              | 4.23               | "      | "                   | "             | 30               | Carbon formed.                                                                                              |
| 56    | 1050            | 1129              | 2236               | 1639               | 0.44              | 4.23               | "      | "                   | 0.879         | 30               | Carbon free.                                                                                                |
| 57    | 1074            | 1129              | 2250               | 1663               | 0.45              | 4.23               | No. 2  | "                   | 0.940         | 30               | Changed fuel. Carbon<br>initially gasified, then<br>accumulated.                                            |
| 58    | 1038.5          | 1126              | 2259               | 1671               | 0.455             | 4.23               | "      | "                   | 0.923         | 30               | Carbon free.                                                                                                |
| 59    | 1148            | 1126              | 2210               | 1609               | 0.43              | 4.23               | Diesel | "                   | 0.926         | 30               | Changed fuels. Carbon<br>free.                                                                              |
| 60    | 1165            | 1123              | 2197               | 1595               | 0.425             | 4.23               | "      | "                   | 0.921         | 30               | Carbon free, appeared<br>to be the carbon boundary.                                                         |
| 61    | 1171            | 1127              | 2272               | 1687               | 0.460             | 4.23               | "      | "                   | 0.944         | 30               | Raised exit temp. (O <sub>2</sub> /C)<br>to study conversion.                                               |
| 62    | 1185            | 1061              | 2139               | 1540               | 0.425             | 4.23               | "      | "                   | 0.919         | 30               | Repeat Pt. 60 at 1.5 pph<br>fuel flow. Carbon free.                                                         |
| 63    | 1190            | 1075              | 2259               | 1685               | 0.48              | 4.23               | "      | "                   | 0.954         | 30               | Raised exit temp. (O <sub>2</sub> /C)<br>at 1.5 pph to study<br>conversion.                                 |
| 64    | 1208            | 1135              | 2156               | 1690               | 0.487             | 5.35               | "      | "                   | 0.935         | 50               | Raised fuel flow to 3.0<br>pph. Carbon free.                                                                |
| 64A   | 1209            | 1135              | 2185               | 1685               | 0.493             | 5.21               | "      | "                   | 0.936         | 50               | Same as point 64, but<br>conditions more steady.                                                            |
| 65    | 1215.5          | 1106              | 2214               | 1625               | 0.442             | 4.20               | "      | "                   | 0.915         | 30               | Lowered exit temp. (O <sub>2</sub> /C).                                                                     |
| 66    | 1218            | 1115              | 2124               | 1510               | 0.393             | 4.20               | "      | "                   | 0.886         | 30               | Carbon free.                                                                                                |
| 67    | 1220            |                   |                    | 1723               | 0.500             | 6.29               | "      | "                   | -----         | 30               | Lowered exit temp. (O <sub>2</sub> /C),<br>still 3.0 pph. Carbon<br>formed.                                 |
| 68    | 1235.5          | 1115              | 2241               | 1653               | 0.450             | 4.23               | "      | "                   | 0.909         | 30               | Ran overnight (12 hrs.)<br>to gasify carbon at 2.0<br>pph fuel flow. Maintained<br>2.0 pph for rest of run. |
| 68A   | 1238            | 1116              | 2242               | 1653               | 0.450             | 4.23               | "      | "                   | 0.895         | 30               | 0.029 pph CH added to<br>Tap 4.<br>0.083 pph CH <sub>4</sub> added to<br>Tap 4.                             |

TABLE 3. DATA SUMMARY  
(Continued)

| Point | Time<br>(Hours) | Temperatures (°F) |                    |                    | O <sub>2</sub> /C | H <sub>2</sub> O/C | Fuel            | Fuel<br>Conv. | Press.<br>(PSIG) | Comments                                                           |
|-------|-----------------|-------------------|--------------------|--------------------|-------------------|--------------------|-----------------|---------------|------------------|--------------------------------------------------------------------|
|       |                 | Pre-reaction      | Adiabatic<br>Flame | Exit<br>Calculated |                   |                    |                 |               |                  |                                                                    |
| 69    | 1308.5          | 1117              | 2279               | 1700               | 0.47              | 4.23               | No. 2, 3220 ppm | 0.92          | 60               | Rig pressure raised to 60 psig.                                    |
| 69A   | 1329            | 1118              | 2280               | 1701               | 0.47              | 4.23               | " " "           | 0.931         | 60               | Repeat of Pt. 69 exit T and conv. slightly higher. Carbon forming. |
| 70    | 1359            | 1120              | 2282               | 1703               | 0.47              | 4.23               | " " "           | 0.935         | 30               | Lowered pressure to 30 psig. Carbon gasified.                      |
| 71    | 1365            | 1135              | 2298               | 1717               | 0.47              | 4.23               | Diesel          | 0.956         | 60               | Raised pressure to 60 psig. Carbon gasif. continued.               |
| 71A   | 1376            | 1134              | 2297               | 1715               | 0.47              | 4.23               | " " "           | 0.958         | 60               | Carbon may have started forming again.                             |
| 72    | 1385            | 1252              | 2339               | 1720               | 0.43              | 4.23               | " " "           | -----         | 60               | Carbon formed.                                                     |
| 73    | 1400            | 1113              | 2237               | 1649               | 0.45              | 4.23               | No. 2           | -----         | 22               | Lowered press. to 22 psig. Carbon gasifying.                       |
| 74    | 1403            | 1113              | 2217               | 1623               | 0.44              | 4.23               | " " "           | -----         | 22               | Carbon forming.                                                    |
| 75    | 1412            | 1116              | 2250               | 1663               | 0.465             | 4.23               | " " "           | -----         | 22               | Carbon gasifying. Rig shut down.                                   |

\*Fuel Flow = 2.0 pph unless otherwise noted.

$$\theta = \frac{\text{CO} + \text{CO}_2}{\text{CO} + \text{CO}_2 + \text{CH}_4}$$

To investigate the effect of sulfur content on the performance of the reactor with gasoline, the as-received gasoline was doped with thiophene and diphenyl sulfide to give concentrations of 263 ppm and 750 ppm. Figure 11 shows that this addition brought a marked decrease in conversion until, at 750 ppm, the conversion closely matched that achieved with No. 2 fuel oil containing 3220 ppm sulfur. No conditions were found with either 263 ppm or 750 ppm sulfur at which carbon accumulation occurred in the reactor.

The reactor operated for 350 hours on gasoline. The reactor was then switched back to No. 2 fuel oil since with this feed the carbon boundary could be identified and, hence, the stability of the reactor with respect to resistance to carbon formation could be established.

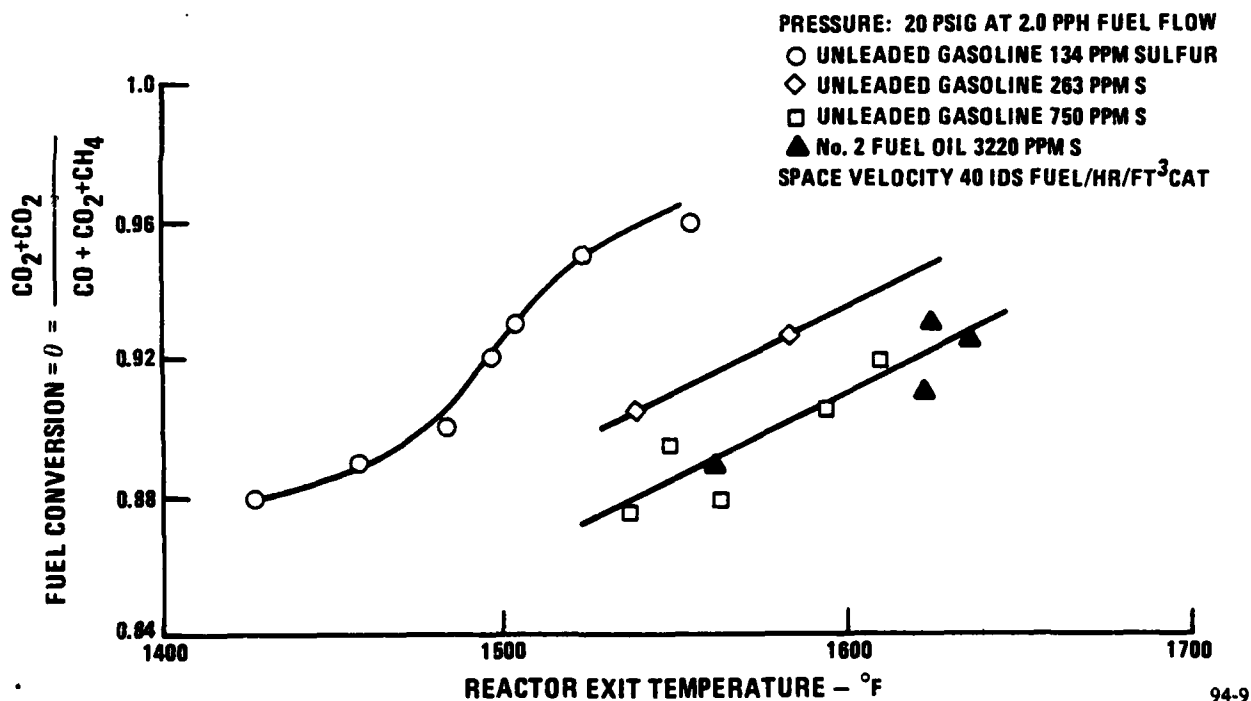


Figure 11. Effect of Sulfur on Fuel Conversion

### Diesel Fuel

After 982 hours on stream the feed was switched to diesel fuel. Again, both the characteristic carbon boundary and the fuel conversion were determined. Test conditions defining the location of the carbon boundary are included in Figure 8 which shows diesel fuel to be slightly better than No. 2 fuel oil with respect to tendency for carbon formation.

The results of a series of tests to map the effect of fuel flow and exit temperature on conversion are shown in Figure 12. As space velocity decreased, conversion increased. At the reference condition of 2 pph fuel flow, the conversions were slightly below those for No. 2, but this was the result of catalyst decay resulting from equipment failures during the start-up of points 35 and 43.

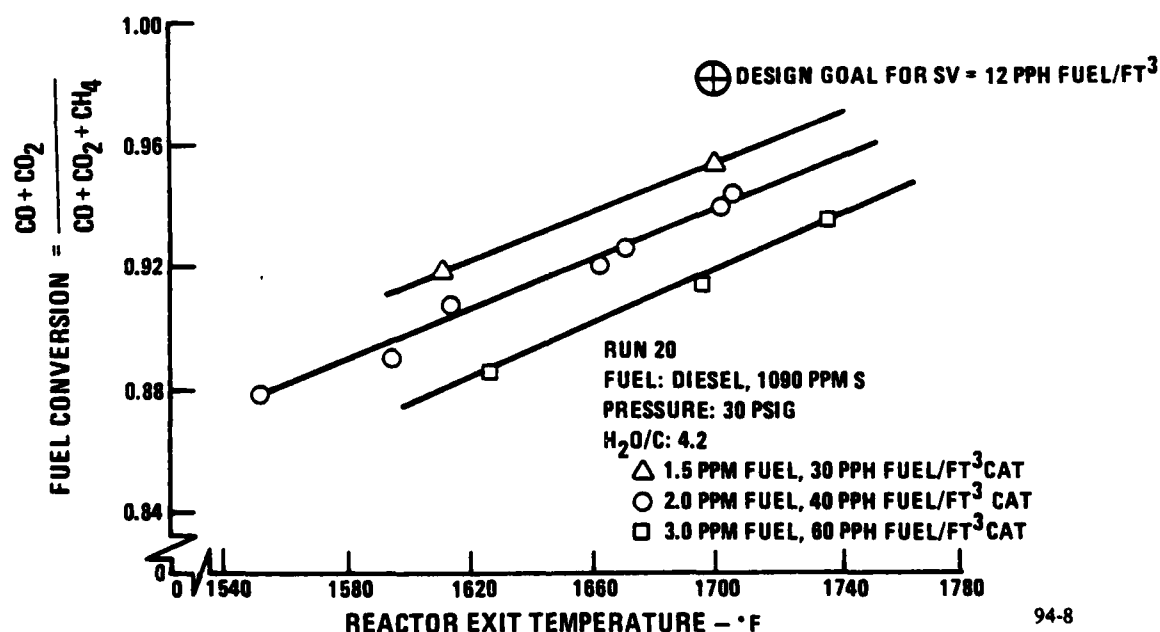


Figure 12. Fuel Conversion vs. Reactor Fuel Flow

The 2-inch diameter, bench scale reactor did not contain sufficient catalyst volume to give experimentally the space velocity required for the commercial power plant goal (12 pph/ft<sup>3</sup>). Therefore, a simple crossplot of the data from Figure 12 was

used to show that the conversions achieved in the test of diesel fuel might reasonably be extrapolated to show that the design conversion could be achieved. This is shown in Figure 13.

After 216 hours on diesel fuel the reactor feed was returned to No. 2 fuel to determine, by operation at reference conditions, that the reactor had operated stably for the duration of the 1400 hours of test.

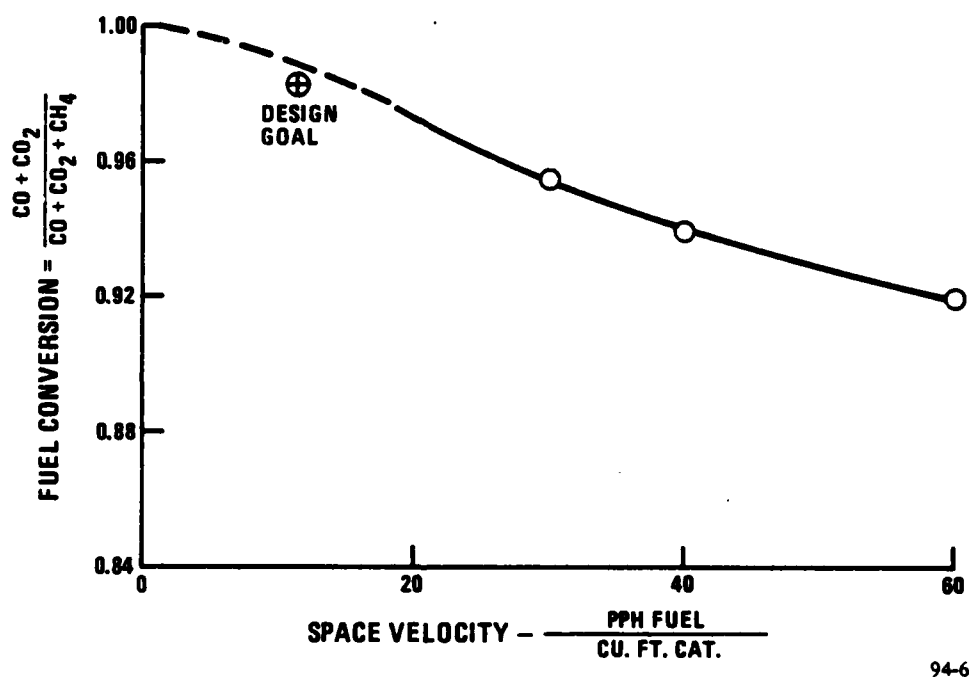


Figure 13. Fuel Conversion as Function of Space Velocity at 1700°F Exit Temperature

## DISCUSSION

During the course of the tests with the three fuels, individual test points established the effects of various reactor operating parameters on carbon formation behavior and on fuel conversion. These can be summarized as follows:

- o The carbon boundary location for each fuel matched or exceeded goals set for a commercial power plant. This can be seen by reference to Figure 8.
- o The carbon boundary location was dependent on fuel type. The minimum  $O_2/C$  ratio required to prevent carbon formation was in the order No. 2 Fuel Oil > Diesel Oil >> Gasoline. Figure 8 also shows this effect.
- o The carbon boundary location was stable for 1400 hours. Figure 9 establishes this point.
- o The carbon boundary location was not significantly affected by the  $H_2O/C$  ratio. In tests with No. 2 fuel oil the  $H_2O/C$  ratio was varied from 2.8 to 4.38 without moving the location of the boundary. See Figure 14. The reason for this surprising effect was thought to be the result of the increased reactor temperature which accompanies a decrease in steam flow.
- o The carbon boundary location was adversely affected by increase in pressure from 22 to 60 psig. Figure 15 shows the pressure drop increasing in a reactor operating on No. 2 fuel oil at 60 psig. When the pressure was decreased to 30 psig, the pressure drop decreased, indicating carbon gasification occurred.
- o Fuel conversion was not significantly affected by change in pressure. This can be established by comparison of the test points listed in Table 4.
- o Fuel conversion was not significantly affected by variation in  $H_2O/C$  ratio between 2.8 and 3.8. This can be established by comparison of test points listed in Table 5.
- o Fuel conversion increased when the sulfur content of the fuel fell below 750 ppmw. This was shown in Figure 11.
- o Fuel conversion increased with decreasing space velocity. Extrapolation of the data in Figure 13 indicated that goals set for reactor volume in a commercial power plant could be achieved.

The objective of the program was to determine the capability of the adiabatic reformer to process diesel fuel and unleaded gasoline for Army SLEEP power plants.

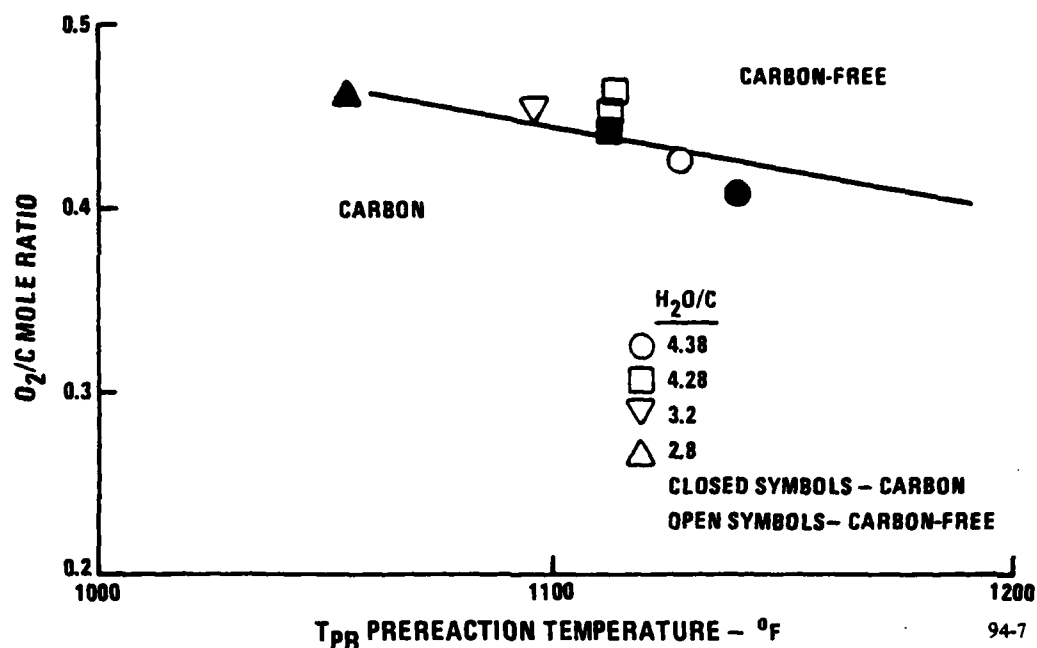
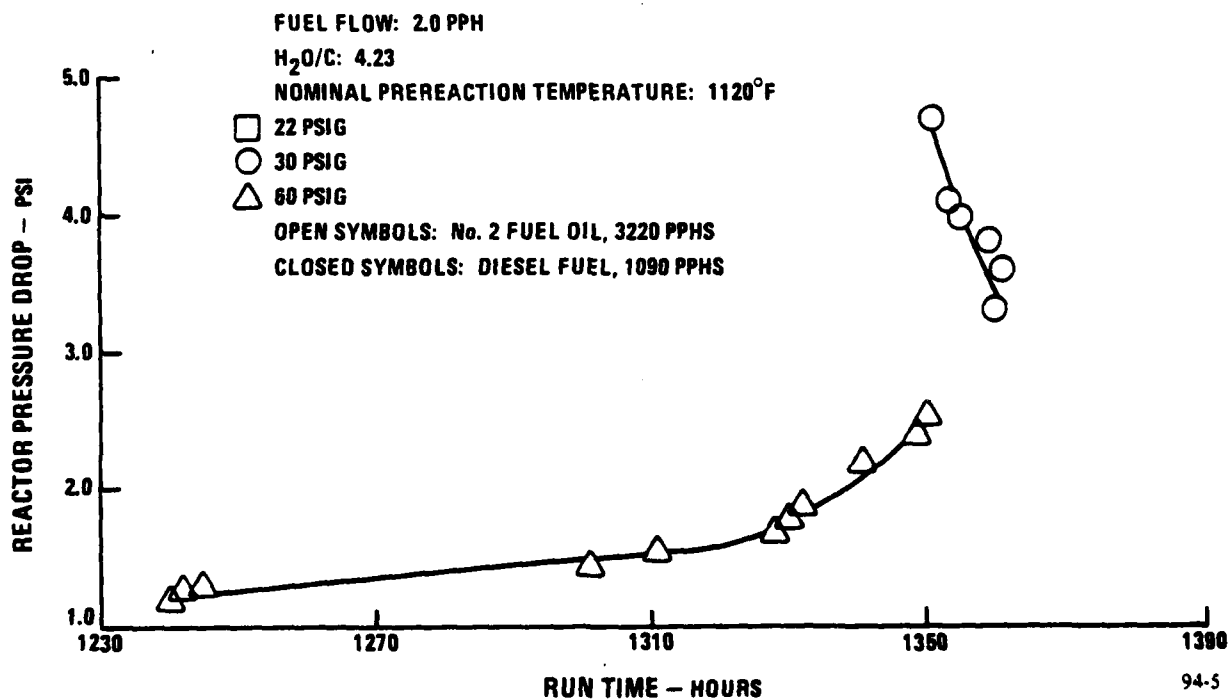
Figure 14. Effect of H<sub>2</sub>O/C Mole Ratio on Location of Carbon Boundary

Figure 15. Effect of Fuel and Pressure on Carbon Boundary

TABLE 4. FUEL CONVERSION NOT AFFECTED BY PRESSURE

| Point No.             | T <sub>PR</sub> °F | T <sub>EXIT</sub> °F | O <sub>2</sub> /C | H <sub>2</sub> O/C | Press.,<br>PSIG | FUEL<br>CONVERSION |
|-----------------------|--------------------|----------------------|-------------------|--------------------|-----------------|--------------------|
| <u>Diesel</u>         |                    |                      |                   |                    |                 |                    |
| 56                    | 1129               | 1702                 | 0.44              | 4.23               | 30              | 0.940              |
| 71                    | 1135               | 1705                 | 0.47              | 4.23               | 60              | 0.956              |
| <u>No. 2 Fuel Oil</u> |                    |                      |                   |                    |                 |                    |
| 70                    | 1120               | 1718                 | 0.47              | 4.23               | 30              | 0.935              |
| 69A                   | 1118               | 1702                 | 0.47              | 4.23               | 60              | 0.931              |

TABLE 5. FUEL CONVERSION NOT AFFECTED BY H<sub>2</sub>O/C RATIO

| Point No.             | T <sub>PR</sub> °F | T <sub>EXIT</sub> °F | O <sub>2</sub> /C | H <sub>2</sub> O/C | FUEL<br>CONVERSION |
|-----------------------|--------------------|----------------------|-------------------|--------------------|--------------------|
| <u>Gasoline</u>       |                    |                      |                   |                    |                    |
| 20                    | 951                | 1563                 | 0.40              | 3.28               | 0.879              |
| 24                    | 1058               | 1551                 | 0.40              | 4.38               | 0.895              |
| <u>No. 2 Fuel Oil</u> |                    |                      |                   |                    |                    |
| 44F                   | 976                | 1694                 | 0.465             | 2.80               | 0.930              |
| 44C                   | 866                | 1690                 | 0.435             | 4.38               | 0.916              |

The results summarized above form the basis for an evaluation of this capability. With both fuels, the performance of the adiabatic reformer matched or exceeded process requirements set as goals for commercial fuel cell power plants in Table 1. Where requirements for Army SLEEP power plants might vary from commercial power plants, the performance of the adiabatic reformer was not adversely affected. Thus, for SLEEP application the adiabatic reformer might operate close to atmospheric pressure. In these tests a lower limit on system pressure was set at 20 psig by pressure drop in tubing and absorption traps downstream of the reactor, not by the reactor itself. However, tests of the effect of pressure above this point showed little effect on fuel conversion and a favorable effect on the carbon boundary as pressure was lowered. With respect to the process water requirement also, neither fuel conversion nor carbon boundary location were significantly affected by changes in  $H_2O/C$  ratio between 2.8 and 4.38. The results of the test program, therefore, support the conclusion that the adiabatic reformer offers an attractive alternative for processing logistic fuels for Army SLEEP power plants. Further development may enable the power plants to process a broad range of logistic fuels with high efficiency.

#### RECOMMENDATIONS

A more detailed systems analysis is required, using the data of this report, to evaluate system concerns peculiar to SLEEP power plants; for example, heat loss and water management. Following this analysis further testing will be required to reduce the system to practice. Specifically, a reactor should be tested with internally insulated reactor walls and with reduced length/diameter ratio to establish heat loss and pressure drop requirements. In addition, work is required to develop a fuel vaporizer system with turn-down capability in the fuel flow range suitable for SLEEP application. The present vaporizer developed for commercial use is limited in this respect.

#### REFERENCES

- (1) (a) Bett, J.A.S., Buswell, R.F., Lesieur, R.R., and Setzer, H.J., "Development of the Adiabatic Reformer to Process No. 2 Fuel Oil and Coal Derived Liquids," National Fuel Cell Seminar, San Diego, CA, 1980. (b) Reports to the Electric Power Research Institute under Contract No. RP1041-4.

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