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Development of the Adiabatic Reformer to Process No. 2 Fuel Oil and Coal-Derived Liquid Fuels

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Prepared by
United Technologies Corporation
South Windsor, Connecticut

ELECTRIC POWER RESEARCH INSTITUTE

Development of the Adiabatic Reformer to Process No. 2 Fuel Oil and Coal-Derived Liquid Fuels

EM-1701
Research Project 1041-4

Interim Report, February 1981

Prepared by

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Prepared by
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South Windsor, Connecticut

ABSTRACT

Fuel cell power plants may be required to use coal derived liquids or heavy petroleum distillates as fuels. The fuel processor in present power plants is a catalytic steam reformer which is limited to the use of fuels such as naphtha or natural gas. The overall objective of this program is to develop a second type of fuel processor, the adiabatic reformer, to process the heavier fuels. In the adiabatic reformer air is added to the process fuel and steam to provide, by combustion, the endothermic heat for reforming in the catalyst bed.

Testing was conducted primarily in a 2 inch diameter, bench scale reactor. First, the configuration of the nozzle in which fuel, steam and air were mixed before entering the catalyst bed was optimized. By varying the nozzle geometry a configuration was identified which minimized the amount of air required to prevent carbon formation on a commercial nickel catalyst. Next, holding the nozzle geometry constant the effect of variation of the catalyst was studied. A novel metal oxide catalyst was identified which further reduced the air requirement when placed in the entrance section of the reactor. The commercial nickel catalyst was unable to achieve the required conversion at the exit of the reactor and thus a high activity nickel catalyst was developed for this purpose. A bench scale reactor incorporating the optimized nozzle and improved catalysts ran stably for 450 hours. The performance met the goals for a 4.8 MW phosphoric acid fuel cell power plant at a 9300 Btu/kWh heat rate for all conditions except operating pressure which was 45 psia. Tests at the performance goal of 120 psia are planned.

Two pilot scale, 6-inch diameter adiabatic reformers were built, each with a fuel-air mixing nozzle scaled-up from the best configuration identified in the bench scale reactors. The performance of the bench and pilot scale reactors (both filled with commercial nickel catalyst) agreed within a nominal scatter which defined the ability to scale-up the design.

Brief tests in the optimized bench scale reactor gave an assessment of the capability of the adiabatic reformer to process coal-derived liquid fuels. Two hydrotreated distillates from the H-coal process and a light organic liquid from the SRC-1 process were reformed at conditions comparable to No. 2 fuel oil. Heavier coal derived liquids formed carbon.

Systems studies evaluated the performance of alternate fuel processors, the hybrid, cyclic and thermal steam reformers relative to the performance of the optimized adiabatic reformer. Over a range of heat rates the studies showed lower cost for power plants with the hybrid and cyclic reformer. However, the ability of the alternate fuel processors to operate at the design conditions remains to be demonstrated.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

RP1041 involves a group of contracts that have the objective of expanding the range of fuels which can be used efficiently and economically in fuel cell systems. The project's scope includes research pertaining to the use of distillate fuels (from oil and coal) in dispersed generators, use of coal in central station fuel cell systems, and integration of the fuel processor with the fuel cell. This interim report describes the development and testing of sulfur-tolerant catalysts to process No. 2 fuel oil and selected coal-derived distillates at conditions that are compatible with fuel cells and assesses the impact these catalysts have on power plant cost and efficiency.

PROJECT OBJECTIVE

The objective of this 18-month effort was to optimize an advanced adiabatic reforming process and to define its scaling parameters. It was determined early in the effort that reactor scale-up and other configurational changes were not showing the hoped-for improvement in process efficiency. The process was obviously catalyst-limited; thus, the scope of the project was expanded to develop higher-activity sulfur-tolerant catalysts and to verify catalyst performance by testing with No. 2 fuel oil and aromatic coal liquids.

PROJECT RESULTS

Sulfur-tolerant catalysts were found that actively promoted carbon gasification reactions. Their use in adiabatic reformers gave the improvement in process efficiency needed to meet fuel cell power plant goals and projected a power plant cost savings of nearly 5% compared to baseline commercial catalysts. The durability of these advanced catalysts was demonstrated in extended runs using high-sulfur No. 2 fuel oil. Their ability to process aromatic SRC-1 and H-Coal liquid products was also demonstrated. These catalysts can also be used in other processing concepts such as hybrid or catalytic steam reformers that can further improve power plant efficiency. Thus, further development of these catalysts is warranted.

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Energy Management and Utilization Division

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EXECUTIVE SUMMARY

The objective of this program is to develop the adiabatic steam reformer to produce hydrogen from No. 2 fuel oil and coal-derived liquids for fuel cell power plants. In this reformer, shown schematically in Figure S-1, air is added to the fuel and steam to provide, by combustion, the endothermic heat for reforming in the catalyst bed. The combustion of additional air is also necessary to raise the reactor to high temperature to compensate for deactivation of the catalyst by sulfur in the feed. Analytical studies of the reformer in 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 S-1, were selected to give minimum values for air addition (O_2/C ratio) and pre-reaction temperature while maintaining high fuel conversion.

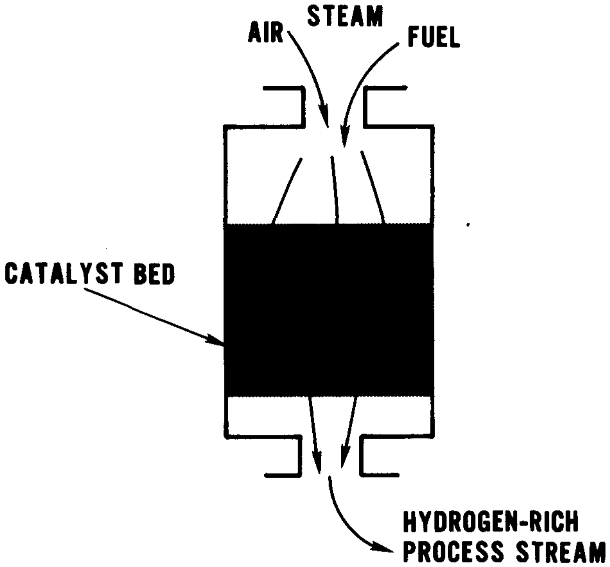


Figure S-1. Adiabatic Reformer

TABLE S-1
ADIABATIC REFORMER PERFORMANCE

		Reactor Performance	
	Design (1) Baseline	Commercial (2) Nickel Catalyst	Metal Oxide (3) Plus 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^3 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 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. A 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 S-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 S-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 S-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.

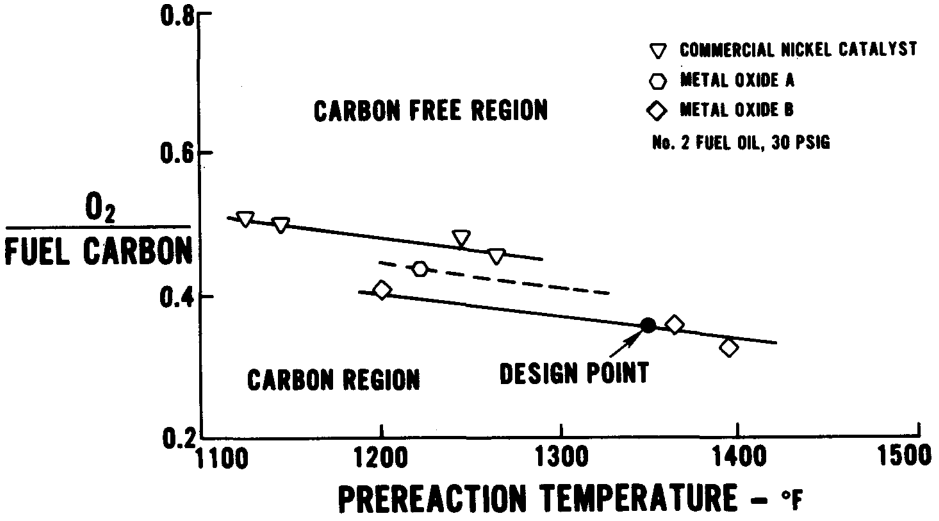


Figure S-2. Effect of Catalyst on Carbon Formation in the Adiabatic Reformer

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 S-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 S-4. The minimum space velocity which could be attained in this reactor was greater than that selected for the power plant design, therefore the experimental data were extrapolated to the power plant space velocity using a 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, in Figure S-4, showed that the conversion achieved by the advanced nickel catalyst projected to the design point.

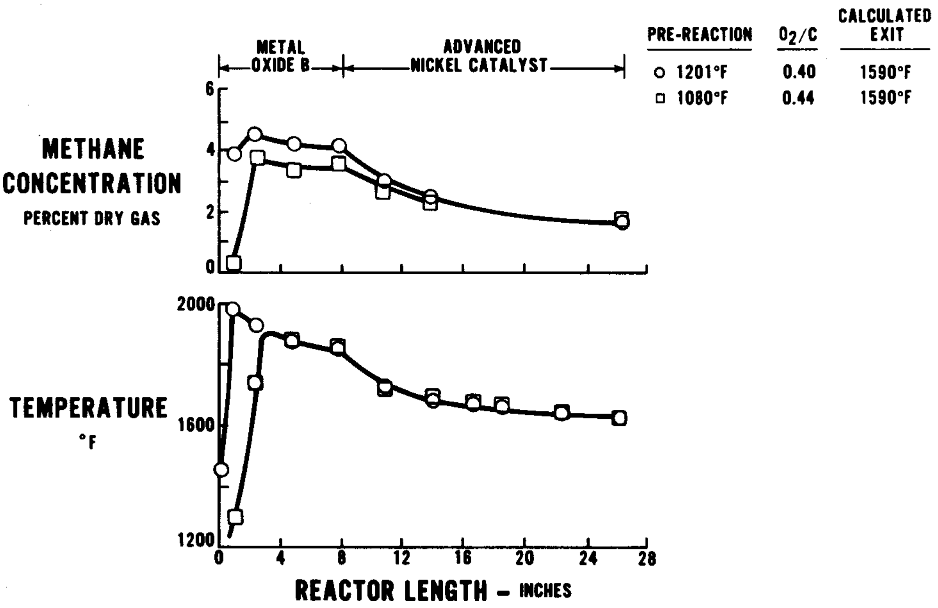


Figure S-3. Effect of O_2/C and Reaction Temperature on Fuel Conversion

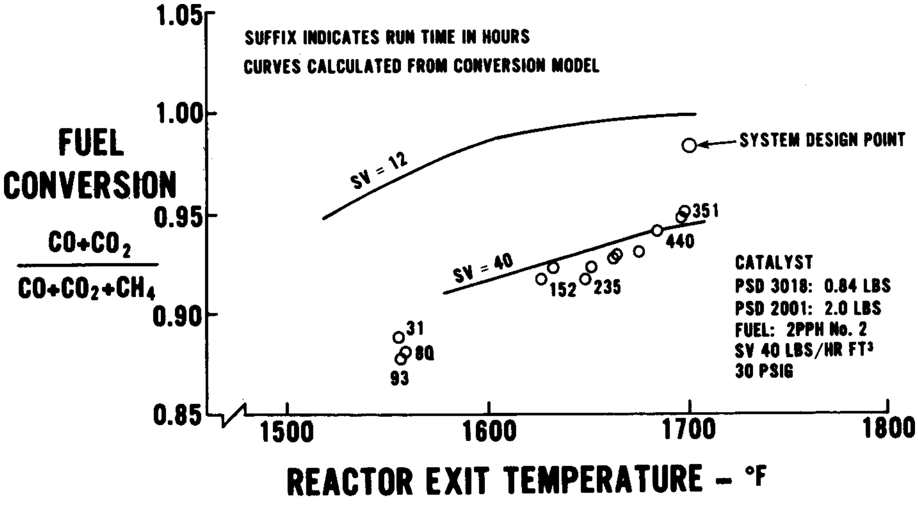


Figure S-4. Fuel Conversion on High Activity Nickel Catalyst

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 S-1. These closely matched the design requirements except in regard to pressure. Preparations are in progress to verify the reactor performance at the design pressure and 6-inch diameter scale.

The reactor development testing used No. 2 fuel oil as reference fuel. The capability of the adiabatic reformer to process coal-derived liquid fuels was established in a series of tests using fuels derived from the H-coal and SRC-1 processes. The dual catalyst loading used in the reactor varied, but in each case was shown to be effective in operating on No. 2 fuel oil for the brief, 24-50 hour, period of the test. The results of tests with coal liquids are listed in Table S-2. Carbon-free operation and performance comparable to No. 2 fuel oil were obtained with hydro-treated H-coal distillates and SRC light organic liquid. The heavier fuels, which had higher end points and aromatic contents than No. 2 fuel oil, deposited carbon in the reactor. Due to the brief nature of the test series, little attempt was made to probe for conditions at which the reactor could operate with these fuels. Table S-2, therefore, gives a preliminary assessment of the capability of the reactor to process coal-derived liquid fuels.

TABLE S-2
COAL LIQUID TEST RESULTS ON A 2-INCH ADIABATIC REFORMER

COAL LIQUID	RESULT
*2% H-Coal Distillate	Carbon Free
*1% H-Coal Distillate	Carbon Free
SRC Light Organic Liquid	Carbon Free
H-Coal Distillate	Carbon Formation
SRC Wash Solvent	Carbon Formation

*Percentage values refer to extent of hydrogen addition by hydrotreating.

Analytical system studies evaluated the performance of the alternate fuel processors relative to the optimized performance of the adiabatic reformer. The alternate systems are shown schematically in Figure S-5. The hybrid reformer has two reactors in series; a primary, tubular reformer in which partial conversion of fuel is effected, followed by a secondary, adiabatic reformer to complete conversion. The thermal reformer is simply a very high temperature tubular reformer. The cyclic reformer has two reactors in parallel, operating alternately in a reforming or regeneration mode. Heat generated in one reactor by the combustion of fuel cell anode exhaust is stored in the heat capacity of the bed to supply the endothermic heat for reforming in the subsequent cycle.

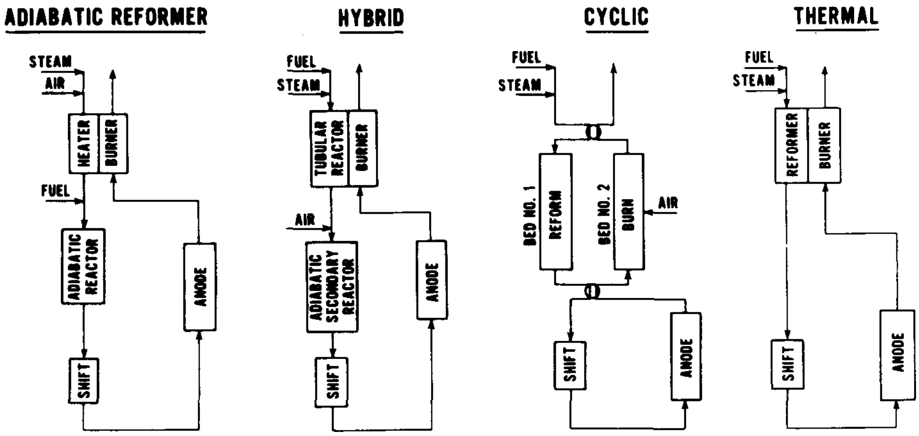


Figure S-5. Fuel Processing Systems Studied

Reactor volumes for the various alternate systems were estimated using catalytic activity data obtained in the adiabatic reformer test program. Figure S-6 compares power plant cost for the thermal, hybrid and adiabatic reformer using advanced nickel catalyst to the cost of a power plant with an adiabatic reformer using commercial nickel catalyst. Over a range of heat rates, the hybrid fuel processor showed a cost advantage. A power plant with a cyclic reformer, sized using preliminary test data, compared even more favorably. However, the ability of the alternate fuel processors to operate stably at the assumed conditions remains to be demonstrated.

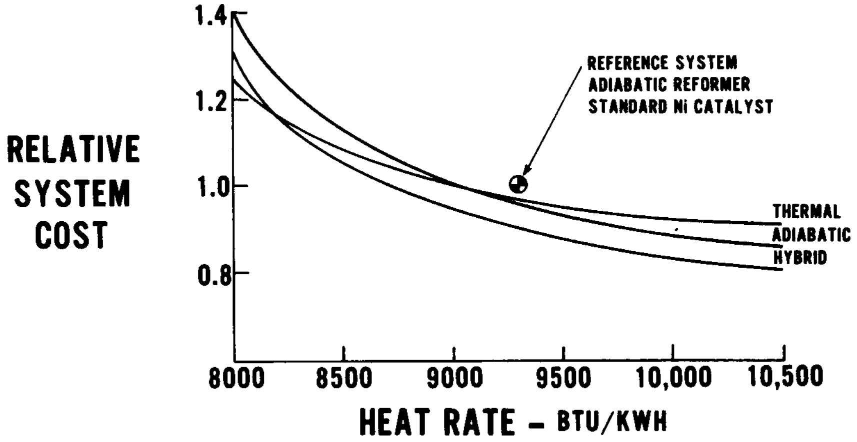


Figure S-6. Comparison of Alternate Fuel Processors

The program results hold great promise that the adiabatic reformer can significantly extend the range of fuels used in fuel cell power plants. Remaining concerns and recommendations are listed below:

- The catalysts developed for the inlet and exit sections of the adiabatic reformer are promising candidates for use in the alternate high temperature reformers. They should be evaluated for this application.
- The metal oxide reactor inlet catalysts were not exhaustively optimized. Additional development effort might yield further improvement in the ability to limit carbon formation.
- The reactor exit catalyst, PSD-2001, exhibited high and stable activity, but was physically weakened at temperatures above 1700°F. Work is required to increase its structural strength.
- The performance goals were demonstrated in the bench scale reactor at 45 psia. Verification of the performance at higher pressure as well as in pilot scale and full scale reformers is required.

Section 1

INTRODUCTION

Fuel cell power plants may be required to use coal derived liquids or heavy petroleum distillates as fuels. The fuel processor in present power plants is a catalytic steam reformer which is capable of converting natural gas or naphtha to hydrogen. To prevent deactivation of the nickel catalyst used in the catalytic steam reformer, the sulfur content of the feed to the reformer must be reduced to extremely low levels (<0.1 ppmw). For natural gas and naphtha, a hydrodesulfurizer reactor and zinc oxide adsorption bed are placed upstream of the reformer to remove sulfur. But the sulfur compounds in petroleum distillate fuels and coal derived liquids are not readily removed by this method. Therefore, for these fuels, a fuel processor is required which can operate with sulfur in the process stream.

Sulfur reduces the activity of nickel catalysts for steam reforming hydrocarbons by over three orders of magnitude. The effect is illustrated by laboratory measurements for the rate for reforming of ethane in the presence and absence of sulfur in Figure 1-1. To operate a reformer on sulfur containing fuels at a space velocity comparable to that for sulfur-free fuels would require either the development of a sulfur tolerant catalyst or catalyst temperatures in the range 1600°F to 1900°F.

One approach to high temperature operation considered by Power Systems Division, termed thermal steam reforming, merely raised the temperature of conventional, externally heated steam reforming tubular reactors into the range for significant catalytic activity. However, tests showed that the activity of presently available commercial catalysts required the reactor temperature to exceed the limits of tube wall materials.

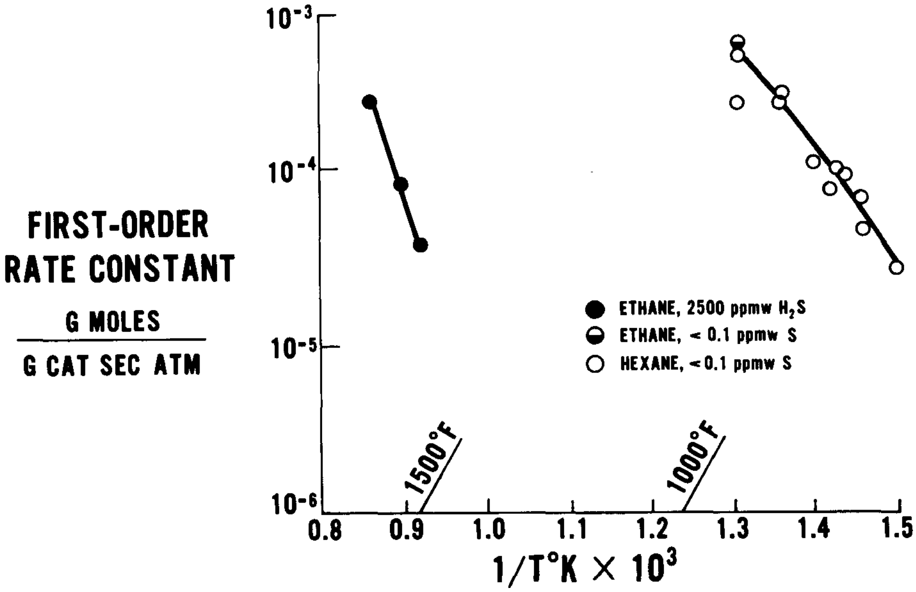


Figure 1-1. Effect of Sulfur on Steam Reforming Activity of Supported Nickel Catalyst

A second approach, adiabatic reforming, was selected for development in the present program. It achieves high temperature by the addition of air to the steam and fuel reactor feed. When combined with reactant preheat, the heat of combustion is sufficient to raise the catalyst bed into the temperature range for significant activity and to supply the endothermic heat for reforming the remaining fuel to hydrogen, i.e.,

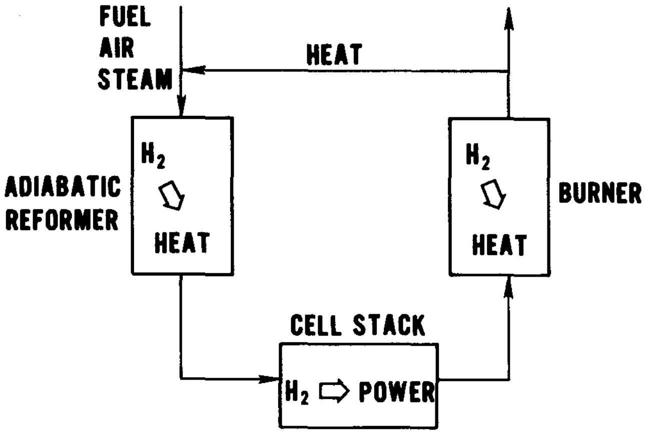
Fuel + Air → Combustion Products + Heat

Heat + Fuel + H_2O → Carbon Oxides + H_2

Since the reactor operates adiabatically, the reactor walls can be protected by ceramic insulation from exposure to high temperature. Specially strengthened tube wall materials are not required.

Adiabatic reforming of heavier fuels is also being investigated by workers at the California Institute of Technology Jet Propulsion Laboratory where the term autothermal reforming is used to describe the process. In Europe, National Industrie de l'Azote (ONIA), Haldor Topsøe A/G, Badische Aniline u. Soda Fabrike (BASF), and Lurgi Mineralöl Technik have developed versions of adiabatic reforming for industrial use. These processes do not have the high thermal efficiency required for application in fuel cell power plants(2).

When the adiabatic reformer is considered as part of a fuel cell power plant, the operating conditions for the reformer are set by the constraints of the overall system. Thus, in Figure 1-2 the reformer is shown schematically delivering hydrogen to a fuel cell stack where it is oxidized at the anode to produce electrical power. The unreacted anode vent gases are then passed to a burner-heat exchanger where the residual energy is used to preheat the reactants for the reformer. The heating value of the fuel may therefore be considered as having three parts: the hydrogen converted to power in the stack, the fuel burned in the reformer, and the anode vent gas burned in the heat exchanger. For optimum efficiency, the first should be as high as possible, while the latter two are minimized; hence, the reformer must operate with high overall fuel conversion, with low values for air addition to the process stream (O_2/C mole ratio) and minimum reactant preheating (prereaction temperature). In the detailed systems analysis, described in Section 6, additional constraints on operating conditions are imposed by the requirement for low power plant cost. Analytical studies of the reformer in a 4.8-MW phosphoric acid fuel cell power plant were initially used to define operating conditions which could minimize system cost at the design heat rate of 9300 Btu/kWH. The operating conditions set as goals for reactor development are listed in the first column of Table 1-1.



$$\eta \text{ REFORMER} = \frac{\text{LHV } H_2 \text{ STACK}}{\text{LHV FUEL}}$$

$$\text{LHV FUEL} = \text{LHV } (H_2 \text{STACK} + H_2 \text{ REFORMER} + H_2 \text{ BURNER})$$

Figure 1-2. Adiabatic Reformer in a Fuel Cell Power Plant

TABLE 1-1 ADIABATIC REFORMER PERFORMANCE

		Reactor Performance	
	Design(1) Baseline	Commercial(2) Nickel Catalyst	Metal Oxide(3) Plus Advanced Nickel
O_2/C Mole Ratio	0.36	0.42	0.36
Pre-reaction Temperature °F	1360	1360	1360
Exit Temperature °F	1700	1800	1700
Conversion %	98.2	99.0	>98.2(4)
Space Velocity, lbs fuel/ft^3 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.

The development of the adiabatic reformer at United Technologies was begun in a previous EPRI Contract, RP114-2(3). In that program, a reactor nozzle to mix fuel, steam and air was developed which showed promise for stable operation. But the performance of the reactor fell short of the design goals of Table 1-1. The work described in this report carried forward the development effort under EPRI Contract RP1041-4. The objectives were:

- To demonstrate operation of the adiabatic reformer for extended periods on No. 2 fuel oil at the design conditions required by the fuel cell power plant.
- To demonstrate the ability to scale-up the configuration of the reactor from bench to pilot scale.
- To determine the capability of the adiabatic reformer to operate on coal derived liquid fuels.
- To evaluate in a systems study the performance of the adiabatic reformer relative to other high temperature reforming processes.

Section 2

EXPERIMENTAL APPROACH

The performance goals listed in Table 1-1 required the adiabatic reformer to achieve high fuel conversion at low values for O_2/C and pre-reaction temperature. But initial tests in reactors with commercial nickel catalyst required air in excess of the design value both to achieve fuel conversion and to prevent carbon formation in the reactor. A schematic of a test reactor is shown in Figure 2-1. Pre-vaporized fuel and steam enter at A, and air with additional steam enters at B, to be mixed in the nozzle section at C. The well-mixed process stream enters the catalyst bed where a complex sequence of combustion and reforming processes occur in the entrance section. Carbon may accumulate in this section. Finally, in the exit catalyst section, the steam reforming of the residual fuel is completed. The early tests suggested that the reactor behavior could be isolated for study and development into relatively independent elements. Thus, carbon formation was affected primarily by the efficiency of mixing of reactants in the entry nozzle and by the catalyst formulation in the entry section of the reactor. Fuel conversion, on the other hand, was affected primarily by the catalyst activity and operating conditions in the exit of the reactor. The critical functional elements have been indicated in Figure 2-1. The reformer development program attempted to address each element separately. Tests focused, as far as was possible, either on the reactant mixing nozzle, on the reactor entrance catalyst or on the catalyst or the reactor exit. Three reactors of different size were used as noted in Table 2-1. Each had specific test objectives which related to the critical functional elements affecting reactor performance.

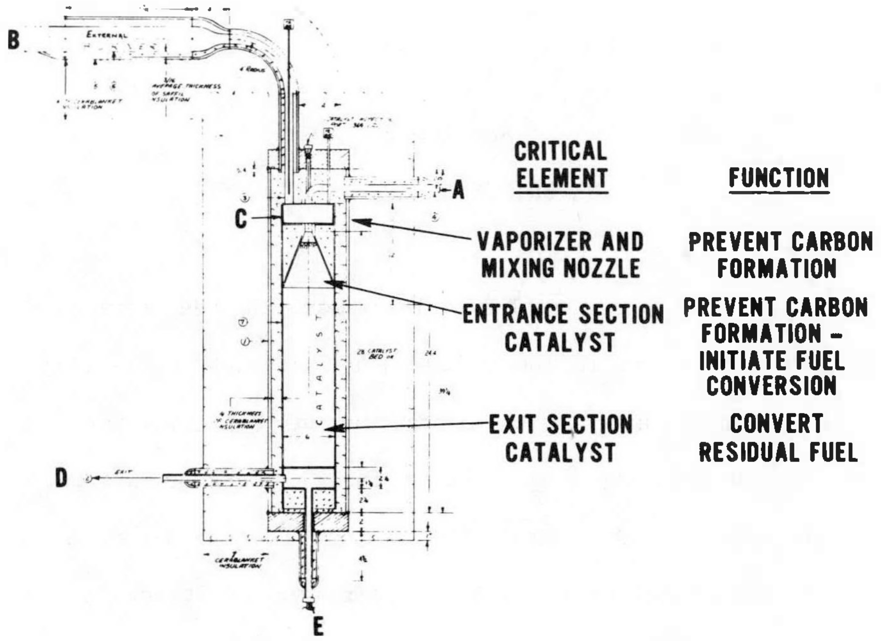


Figure 2-1. Critical Elements of an Adiabatic Reformer

TABLE 2-1 REACTORS FOR ADIABATIC REFORMER DEVELOPMENT

- 6-INCH PILOT SCALE REACTOR
    - DEMONSTRATE SCALE-UP
- 2-INCH BENCH SCALE REACTOR
    - DEVELOP NOZZLE CONFIGURATION
    - DEVELOP CATALYST FOR CARBON-FREE OPERATION
    - DEVELOP CATALYST FOR FUEL CONVERSION
    - DEMONSTRATE CAPABILITY ON COAL DERIVED LIQUIDS
- 3/8-INCH LABORATORY REACTOR
    - CATALYST DEVELOPMENT
    - FUEL CONVERSION MODELING

The electrically heated laboratory reactor was used to measure the intrinsic activity of the test catalysts. This data was used to characterize catalyts before and after test in the larger reactors and to model fuel conversion in the exit portion of the reactor. The reactor was also used in a parallel United program to develop improved catalysts. The bench scale adiabatic reformer was used for the major portion of the test program, addressing all three critical elements of the reactor. It was used to develop the reactant mixing nozzle and to test the effect of catalyst formulation both on carbon formation in the entrance to the reactor and on fuel conversion in the reactor exit. Tests with coal derived liquid fuels were also performed in this reactor. The pilot scale, 6-inch diameter adiabatic reactor processing 10 pounds of fuel per hour was constructed to establish the capability to scale-up the reactant mixing nozzle developed in the bench scale reactor.

No. 2 fuel oil was the reference fuel for the reactor development. When the program was near completion, the capability of the reactor to process coal-derived liquid fuels was determined. Data generated in the program was used in system analytical studies to further define goals for reactor performance and to compare the performance of the adiabatic reformer with other high temperature reformers.

Section 3

TEST EQUIPMENT AND PROCEDURES

The laboratory reactor was a conventional electrically heated flow reactor 3/8-inch in diameter and holding less than a gram of catalyst. Product analysis was by gas chromatography. Ethane and methane, with the addition of hydrogen sulfide, were used as fuels. No. 2 fuel oil could also be used. A novel catalyst holder shown in Figure 3-1 was assembled from swagelock fittings and discarded after each experiment since high temperature operation, up to 2000°F, froze the fittings. This design permits rapid turn-around of the test rig between experiments.

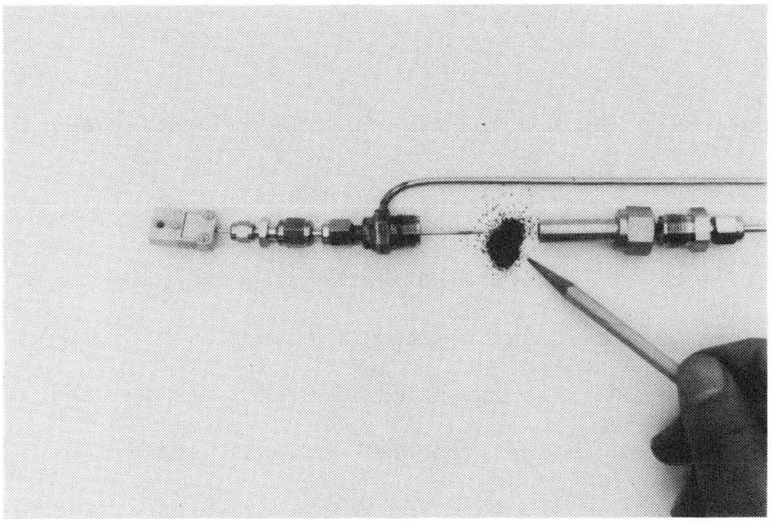


Figure 3-1. Laboratory Microreactor and Catalyst Sample

The bench scale adiabatic reformer was constructed of Inconel-601 pipe 2 inch in diameter and close to 24 inches long. The fuel flow was between 1.5 to 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 3-2.

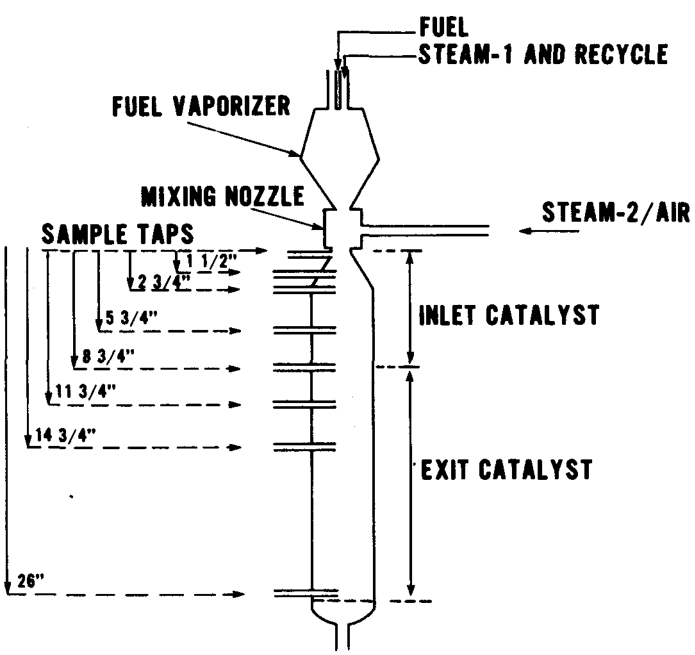
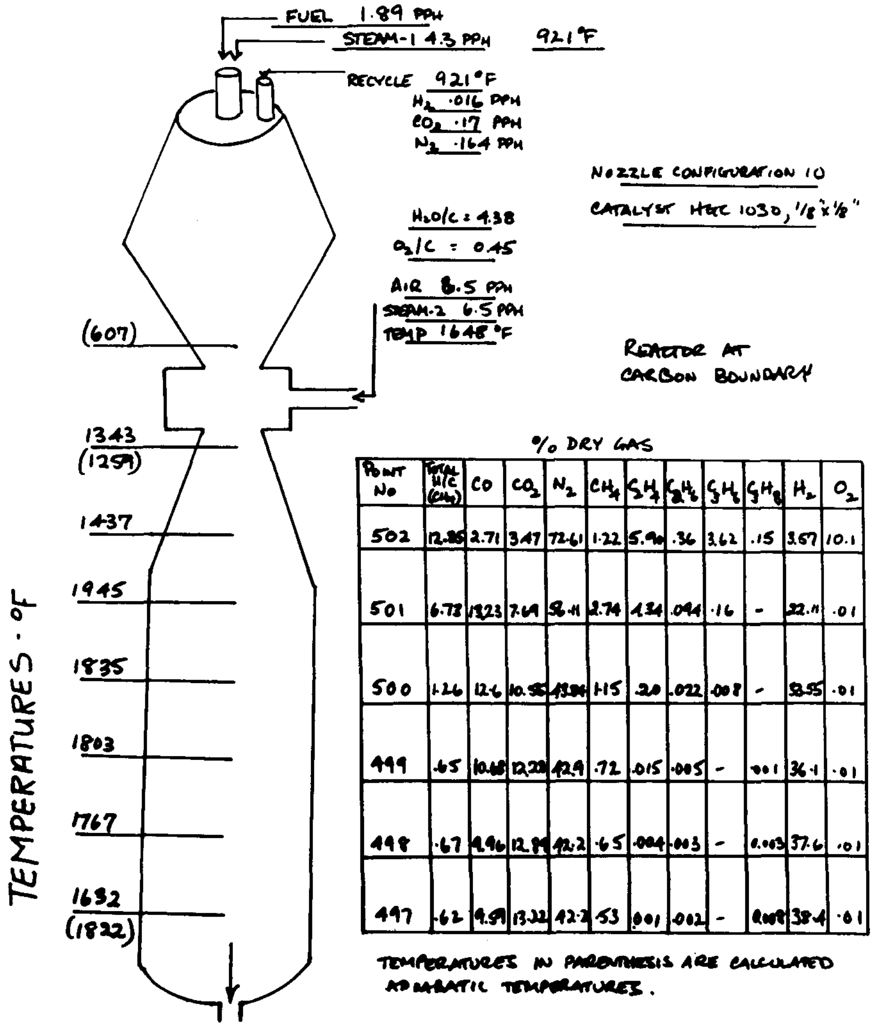


Figure 3-2. Schematic of Bench Scale Adiabatic Reformer

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 recorded by an Automatic Data Acquisition and Retrieval (ADAR) system which could automatically 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 condition. 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 15 to 45 psig.

Analyses were performed by gas chromatography on the dry gas product with thermal conductivity, flame ionization, and NDIR detection. An example of the form in which the data for each test point was tabulated is shown in Figure 3-3.



POINT No	TOTAL H/C (CH_4)	CO	CO_2	N_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	H_2	O_2
502	12.85	2.71	3.47	72.61	1.22	5.90	.36	3.62	.15	3.57	10.1
501	6.73	13.23	7.69	58.11	2.74	4.34	.094	.16	-	22.11	.01
500	1.26	12.6	10.55	43.84	1.15	.20	.022	.008	-	38.55	.01
499	.65	10.68	12.20	42.9	.72	.015	.005	-	.001	36.1	.01
498	.67	9.96	12.89	42.2	.65	.004	.003	-	0.003	37.6	.01
497	.62	9.59	13.32	42.2	.53	.001	.002	-	0.008	38.4	.01

TEMPERATURES IN PARENTHESIS ARE CALCULATED ADIABATIC TEMPERATURES.

Figure 3-3. Typical Data Sheet for Test Run With Bench Scale Adiabatic Reformer

Typically, carbon formation could be continuously monitored by observing the pressure drop across the catalyst bed; however carbon could also be observed at the end of the test by cutting open the reader and inspecting the catalyst. Catalyst could be changed either by cutting open the reactor, or more rapidly by vacuuming the pellets out through an apenture in the vaporizer section.

Two builds of the 6-inch diameter pilot scale adiabatic reformer were constructed. The first was not internally insulated and ran with hot walls. The second was intended for long term operation and was internally insulated, lowering the reactor wall temperature. The operation of both builds was similar and hence only the second, internally insulated reactor is described in detail.

A simplified diagram of the reactor was given in Figure 2-1. Figure 3-4 is a photograph of the reactor prior to its installation in the test stand. A prevaporized mixture of steam and between 8 to 12 pounds per hour of fuel was delivered to Port A of the reactor. Additional steam, and some air, sufficient to bring the overall steam/ fuel ratio and O_2/carbon ratio to desired values were added at Port B. This air and steam mixture was first heated to 1350°F by a gas-fired preheater before entering the external burner at Port B. Additional air plus a small amount of hydrogen were injected into the external burner at Port B to heat the air fuel mixture above 1600°F before entering the mixing nozzle. The steam generated in the external burner was accounted for in the overall steam-to-carbon ratio of the reactor. The steam-fuel mixture from Port A and steam-air mixture from Port B rapidly mixed in the nozzle at C. The adiabatic temperature of the process stream, prior to combustion, cracking, and reform reactions was called the prereaction temperature. The well-mixed process stream entered the catalyst bed and reacted to form H_2, CO_2, and CO before exiting at Port D. Thermocouple wells and sample taps entered the catalyst bed axially from Port E.

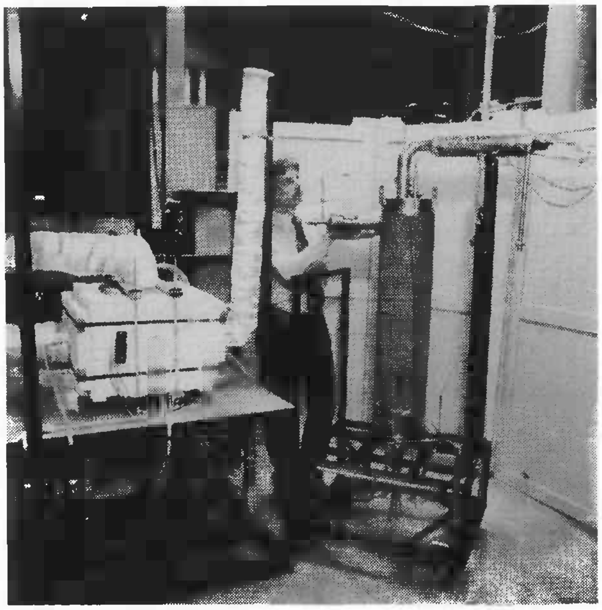


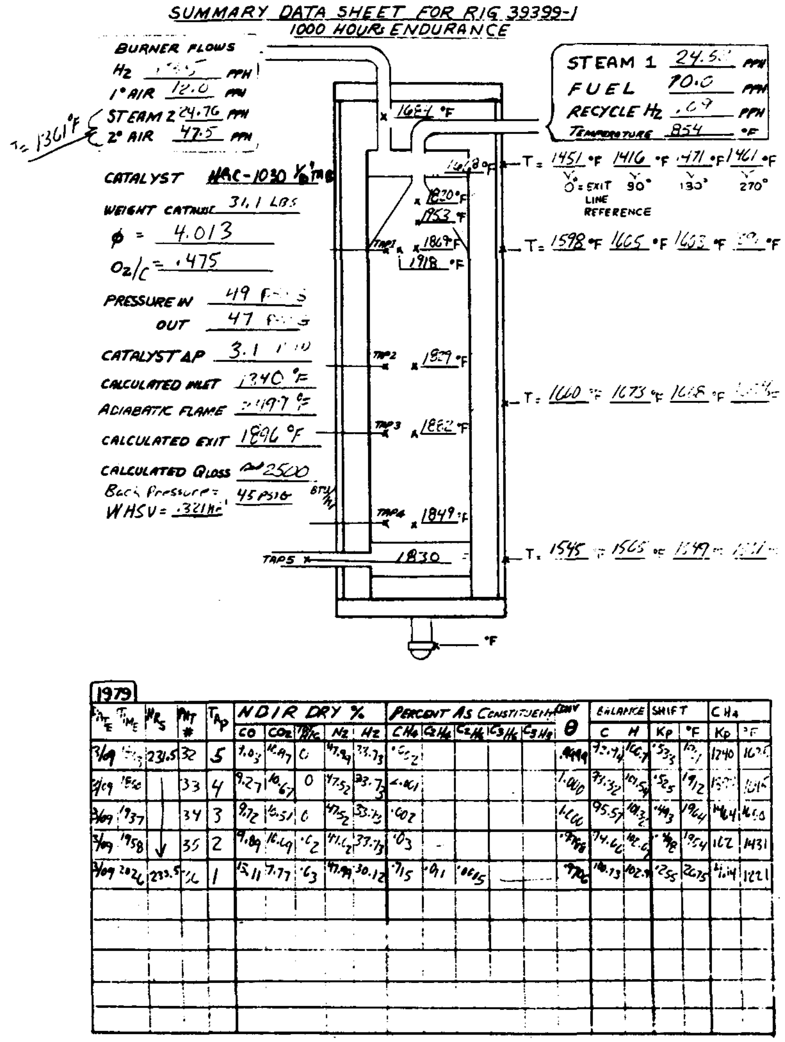
Figure 3-4. Pilot Scale Internally Insulated Adiabatic Reformer

The reactor was loaded with 31.1 lbs. of commercial 1/8 in. x 1/8 in. nickel catalyst pellets which were disposed within a 6-inch diameter by 22-inch long bed contained within a .062-inch thick Inconel 601 liner. The liner was surrounded by 1.25 inches of internal insulation (Cerablanket silica-alumina fiber), and a 9.17-inch O.D. insulated HK 40 pressure vessel. The liner was gastight to prevent possible gas bypass through the Cerablanket insulation, and possible breakdown of the insulation by leaching of the silica in the presence of flowing high temperature steam. The reactor outer retaining vessel had been designed and built to the ASME Boiler and Pressure Vessel Code and was capable of 1000 hours operation at 1630°F wall temperature and 65 psig operating pressure. There were 7 inches of external Cerablanket insulation outside the pressure vessel to minimize heat loss while operating at high temperature.

The initial reactor heat-up period was 57 hours to minimize internal thermal expansion stresses in the catalyst liner. In subsequent start-ups this time was reduced to 16 hours. The catalyst was heated in flowing N_2 and H_2 to 1000°F and then steam and hydrogen were added at a molar ratio of H_2O/H_2 = 5.6 to maintain reducing conditions for the nickel catalyst. At 1100°F bed temperatures, hydrogen and air were added and ignited within the external burner to provide sufficient energy to preheat the bed up to 1500°F. At 1500°F, excess air was brought in through the external burner and combusted directly on the adiabatic reformer catalyst with the excess hydrogen entering through the fuel-steam port of the reactor. The steam-to-hydrogen ratio was decreased to 4.1 at 1525°F and to 3.8 at 1640°F to assure reducing conditions and prevent catalyst oxidation. Fuel and air flows were established when the average bed temperature reached 1760°F. The hydrogen flow was then reduced to 0.09 pph, and normal operating conditions were established. Typical data presentation for the pilot scale reactor is shown in Figure 3-5.

No. 2 fuel oil was used in the majority of tests. One series of tests used a number of samples of coal derived liquids, obtained through EPRI from the SRC-I and H-coal processes. Fuel composition will be discussed in detail in Section 5 which describes the coal liquid tests.

In tests to optimize fuel conversion and to limit carbon formation, a variety of commercial and experimental catalysts were used. They are discussed in the pertinent sections below.



SUMMARY DATA SHEET FOR RIG 39399-1
1000 HOURS ENDURANCE

BURNER FLOWS
H_2 [illegible] PPH
1° AIR 12.0 PPH
STEAM 2 24.76 PPH
2° AIR 47.5 PPH
T = 1361°F

CATALYST HAC-1030 1/8" TAB
WEIGHT CATALYST 31.1 LBS
φ = 4.013
O_2/C = .475
PRESSURE IN 49 PSIG
OUT 47 PSIG
CATALYST ΔP 3.1 PSID
CALCULATED INLET 1340 °F
ADIABATIC FLAME 2497 °F
CALCULATED EXIT 1896 °F
CALCULATED QLOSS ~2500 BTU/HR
Back Pressure = 45 PSIG
WHSV = .321 Hr⁻¹

STEAM 1 24.5 PPH
FUEL 70.0 PPH
RECYCLE H_2 .09 PPH
TEMPERATURE 854 °F

1979

DATE	TIME	HRS	PNT #	TAP	NDIR DRY %					PERCENT AS CONSTITUENT					CONV θ	BALANCE		SHIFT		CH4	
					CO	CO_2	THC	N_2	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_3H_8		C	H	Kp	°F	Kp	°F
3/09	[illegible]	231.5	32	5	7.03	10.97	0	47.99	33.73	.052					.9999	92.74	100.7	.533	[illegible]	1240	[illegible]
3/09	1850	↓	33	4	9.27	10.67	0	47.52	33.73	<.001					1.000	93.32	101.54	.525	1912	[illegible]	[illegible]
3/09	1937		34	3	9.72	10.51	0	47.52	33.73	.002					1.000	95.57	101.32	.493	1964	1464	[illegible]
3/09	1958		35	2	9.89	10.69	.02	47.62	33.73	.03	-				.9998	94.66	102.6	.498	1954	162	1431
3/09	2026	233.5	36	1	15.11	7.77	.63	47.99	30.12	.715	.01	.0015	—	—	.9906	96.73	102.9	.255	2675	4.14	1221

Figure 3-5. Typical Data Sheet for Test Run with Pilot-Scale, Internally Insulated Adiabatic Reformer

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Section 4

TEST RESULTS - NO. 2 FUEL OIL

TYPICAL OPERATING CHARACTERISTICS OF THE ADIABATIC REFORMER

Before discussing the development of individual elements of the adiabatic reformer it will be helpful to describe typical reformer operating characteristics. Despite large variations in reactor scale, reactant mixing nozzle geometry, and catalyst formulation, the operating characteristics of the test reactors with respect to axial temperature and product composition profiles and with respect to carbon formation were very similar. Therefore, data from a test of the bench scale reformer filled with commercial nickel catalyst can be used to illustrate typical behavior. The reactor processed 2 pounds of fuel per hour, with a steam to carbon ratio of 4.25 and sufficient air added to bring the O_2/C ratio to 0.45. The pre-reaction temperature was 1189°F. In Figure 4-1, data from the test condition represented in Figure 3-3 are plotted as function of reactor length. At the entrance to the catalyst bed where combustion occurred the temperature rose rapidly to a maximum value which was less than the calculated adiabatic flame temperature, then decreased slowly as endothermic reforming processes became dominant. The measured temperature at the exit of the reactor bed was less than the value predicted assuming adiabatic reaction, due to significant heat loss from the small reactor.

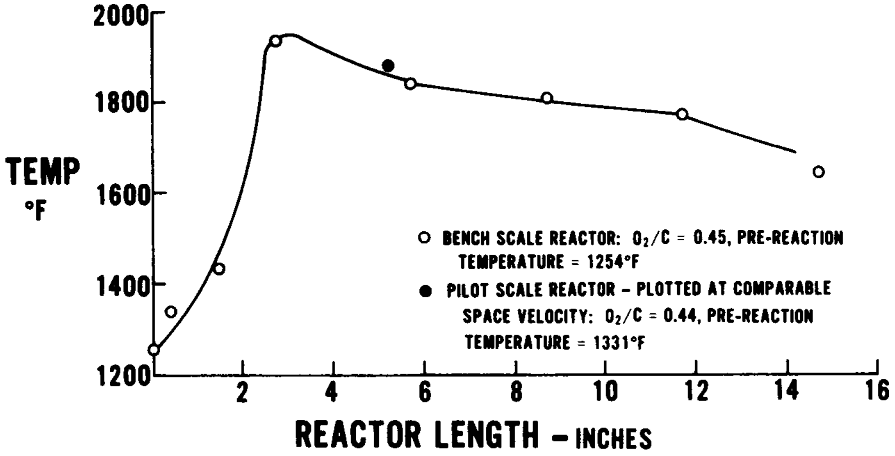


Figure 4-1. Temperature Profile in the Adiabatic Reformer

In Figure 4-2 the corresponding changes in product composition are recorded. Carbon monoxide and dioxide increased rapidly with the former initially in excess as combustion occurred. At the end of the reactor shift equilibrium was approached.

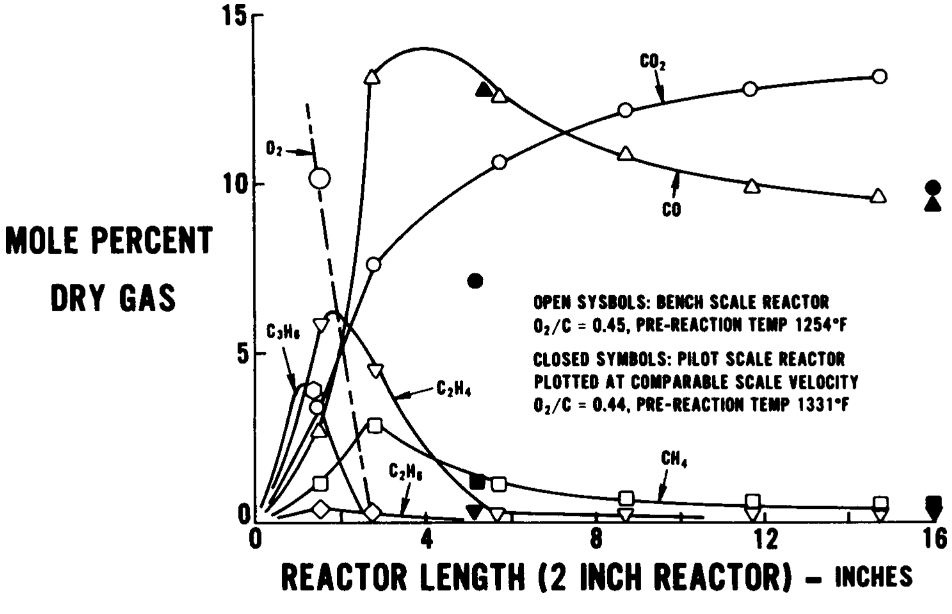


Figure 4-2. Product Distribution in the Adiabatic Reformer

Oxygen was completely consumed before the maximum in temperature was reached, and ethane, ethylene, propane, and propylene - the products of fuel cracking, passed through a concentration maximum close to this point. All the hydrocarbons other than methane disappeared shortly after the position of the temperature maximum and the carbon balance, fluctuating about the 100% value indicated that the methane and the carbon oxides were the sole products. Changes in pre-reaction temperature, O_2/C ratio and fuel flow rate brought small shifts in position but no change in the general form of the curves in Figures 4-1 and 4-2.

Carbon formed in the reactor if the mole ratio of oxygen to fuel carbon atoms (O_2/C) fell below a critical value. At fixed pre-reaction temperature the O_2/C ratio in the feed could be lowered to a point where increased pressure drop across the reactor, ΔP, indicated carbon formation; raising the O_2/C ratio from the value reversed the pressure increase. Carbon evidently could be formed and burned off by reactions which were in steady state balance at this point. The effect is illustrated in Figure 4-3. 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 as in Figure 4-4. For every reactor tested the operating line had a similar slope but different intercept on the O_2/C axis. Improvement in reactor performance was indicated by a lowering of the O_2/C intercept of the operating line. The characteristic slope of the operating line coincided closely with the slope of isotherms for the calculated adiabatic temperature of the equilibrated reactor exit stream. A given value for the adiabatic exit temperature could be achieved either by the addition of air or by increasing the pre-reaction temperature; the trade-off resulted in the isotherms indicated in Figure 4-4.

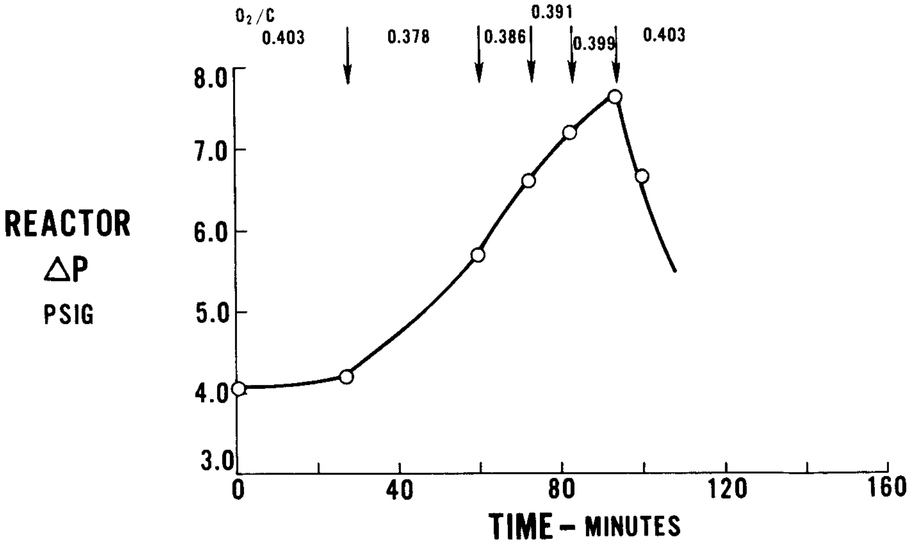


Figure 4-3. Locating the Carbon Boundary in the Adiabatic Reformer

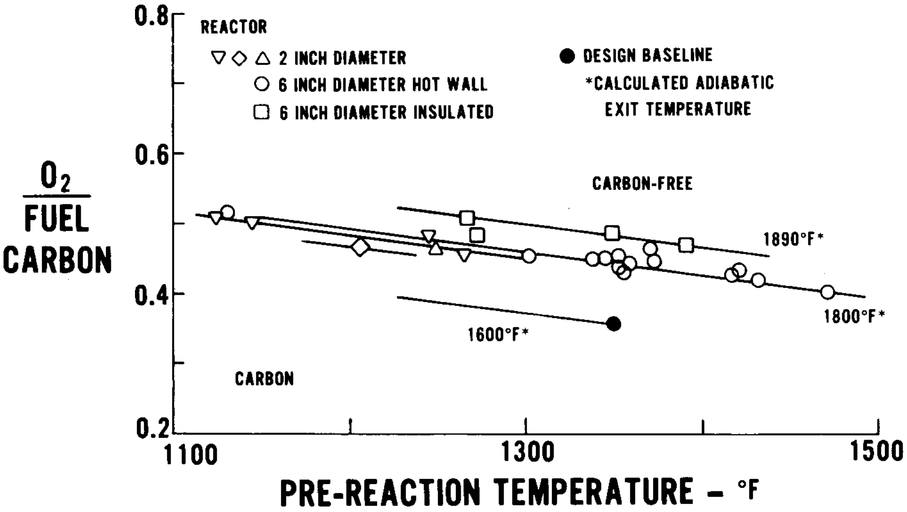


Figure 4-4. Carbon Boundary for Various Reactors

The close correspondence between the experimentally determined carbon boundary and the calculated isotherm for the adiabatic exit temperature suggested that the carbon boundary defined a critical temperature at which the steady-state rate of carbon formation matched the carbon removal rate. The steam-carbon reaction rather than the oxygen-carbon reaction appeared to be the critical removal process since carbon tended to form, as closely as could be determined, in a dense plug which filled the inter-pellet voids in the catalyst bed immediately downstream of the maximum in temperature, where the oxygen concentration was already zero. Figure 4-5 shows qualitatively where the rate for the steam carbon reaction (E_A~60 k cals) and the rate for carbon formation from paraffins (E_A~40 k cals) would intersect to give a temperature above which carbon would not form.

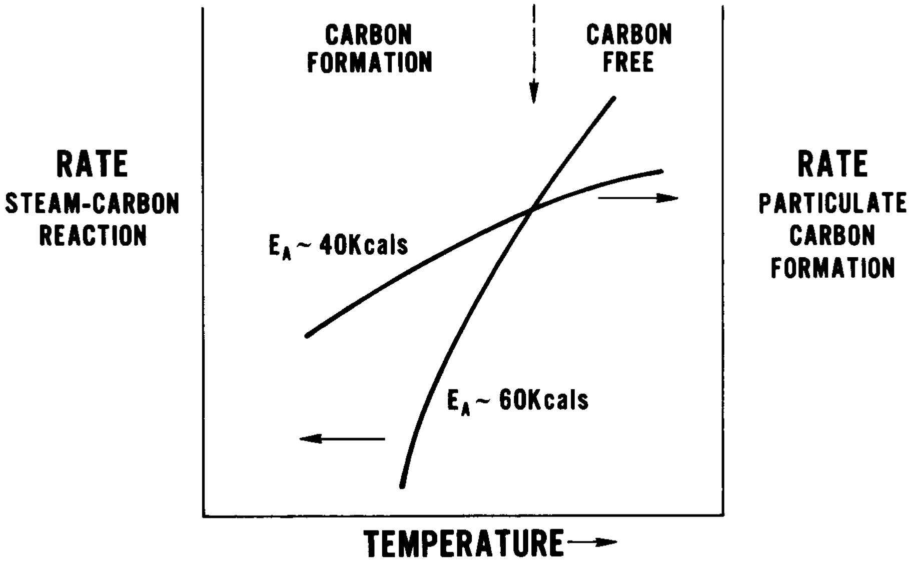


Figure 4-5. Steady-State Rates of Carbon Formation and Burn-Off in the Adiabatic Reactor

The correlation of the position of the carbon boundary with the calculated isotherm for the adiabatic exit temperature might be predicted with this hypothesis because the temperature at the location of the carbon plug was related in a regular manner by the smooth temperature profile of Figure 4-1 to the reactor exit temperature. This interpretation implies that factors which might reduce the propensity for carbon formation, such as the efficiency of mixing of the fuel and oxidant streams, and which might accelerate the removal of carbon, such as the formulation of the catalyst in the reactor entrance section, will be critical in limiting carbon accumulation.

THERMODYNAMIC CONSIDERATIONS

Operation of the adiabatic reformer at the conditions set as goals in Table 1-1 was not limited by the thermodynamic considerations. At the exit of the reformer, as illustrated in Figure 4-2, methane was the sole remaining hydrocarbon. Hence conversion was expressed by the ratio of the mole fractions:

$$\frac{CO + CO_2}{CO+CO_2+CH_4} \times 100$$

For a process stream with $O_2/C = 0.36$ and a value for H_2O/C of 4.5, typical for experiments in the bench scale reactor, equilibrium of the shift and methane steam reforming reactions, (1) and (2),

$$CO + H_2O = CO_2 + H_2 \qquad (1)$$
$$CH_4 + H_2O = CO + 3H_2 \qquad (2)$$

predicted virtually 100% conversion at 1700°F. Only at temperatures below 1400°F did the concentration of methane become significant. Table 4-1 shows that despite the high values required for fuel conversion the performance of the reformer was not limited by thermodynamic equilibrium.

TABLE 4-1

THERMODYNAMIC EQUILIBRIUM VALUES FOR FUEL CONVERSION

Temperature, °F	% Conversion (a)
1800	99.999
1700	99.997 (b)
1600	99.990
1500	99.967
1400	99.879
1300	99.513

(a) Shift and methane equilibrium for process stream with $O_2/C = .036$ and $H_2O/C = 4.5$

(b) Design requirement 98.2 at 1700°F, Table 1-1.

Carbon formation was also a kinetically controlled phenomenon. Figure 4-6 maps conditions at which carbon formation in the reactor was predicted by thermodynamics. For a given process stream composition, defined by H/C and O/C atom ratios, reactions 1, 2, 3, and 4 were brought to equilibrium at various temperatures.

$$CO + CO = CO_2 + \text{Carbon} \qquad (3)$$
$$CH_4 = H_2 + \text{Carbon} \qquad (4)$$

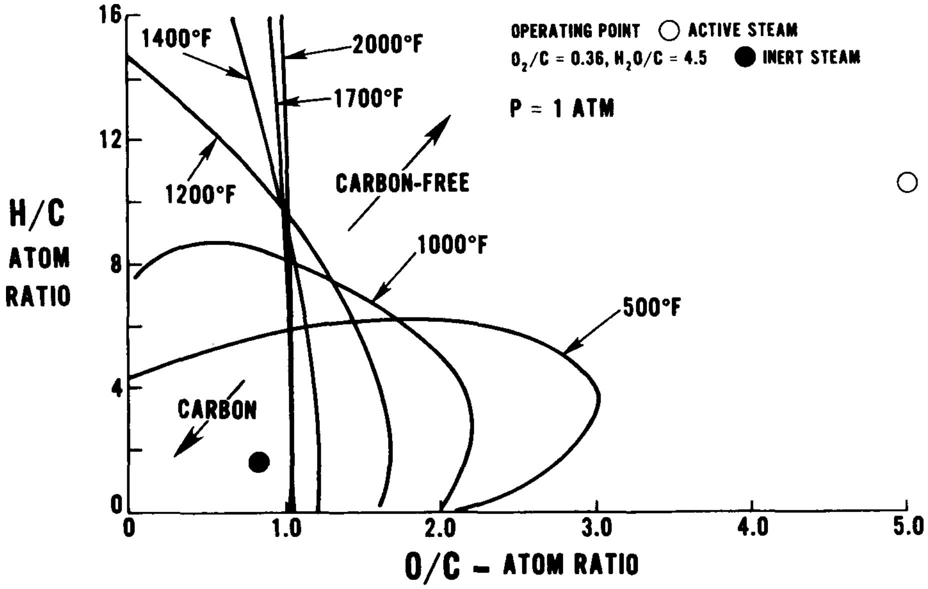


Figure 4-6. Carbon Formation Boundaries in the H-C-O System

For each temperature a regime was defined, by critical values for H/C and O/C, within which carbon formation would occur. These are shown in Figure 4-6 for a system pressure of 1 atmosphere. For the experimental pressures of up to 4 atmospheres the topography of the map was not expected to change significantly. The composition of the process stream in a reformer operating with O_2/C = 0.36 and H_2O/C = 4.5 has been entered in Figure 4-6. Evidently the conditions in the reactor were far from the regime where carbon accumulation was predicted.

Figure 4-6, however, suggests conditions under which carbon might form. Previously, steam was proposed as the oxidant which removed carbon deposited in the reactor. Certainly, at high temperature, >1700°F, and in the presence of a catalyst, the reaction would be sufficiently rapid. But if at low temperature steam acted as an inert component, the effective position on the carbon map of the process stream with No. 2 fuel oil, $CH_{1.8}$ and $O_2/C = 0.35$ would lie in a carbon formation regime. Hence, the catalyst in the entrance to the reformer might be expected to play an important role in activating the steam-carbon reaction.

OPTIMIZATION AND SCALE-UP OF THE REACTANT MIXING NOZZLE

Early reactor configurations with commercial nickel catalyst required air in excess of the design value in Table 1-1 to prevent carbon accumulation in the reactor entrance. It was recognized that rapid and efficient mixing of air and fuel was important to limit the extent of carbon - forming reactions. Therefore, a study was made of the effect on carbon formation of the configuration of the nozzle in which reactants were mixed. In the bench scale reformer the nozzle configuration was varied while fuel (No. 2 fuel oil) and the catalyst (commercial nickel catalyst) were not changed. Many configurations were tested in a program funded in part by EPRI contract RP114-2 and described in the reports of that contract. For completeness a brief summary of that work is included below.

The first test of the adiabatic reformer used a mixer in which a liquid droplet spray was injected directly into the steam - air oxidant stream. That reactor ran successfully for 1000 hours with the carbon boundary indicated in Figure 4-7. To improve the efficiency of the mixing process and hence to lower the carbon boundary a nozzle which mixed pre-vaporized fuel and air was devised. The first generation of these nozzles achieved mixing by very high shear stress on the mixing streams. A large improvement in the carbon boundary over that achieved by the liquid droplet injector was immediately effected. However stable performance of these reactors could not be maintained for extended periods (>50 hours). Invariably carbon formed in the reactor or the nozzle itself.

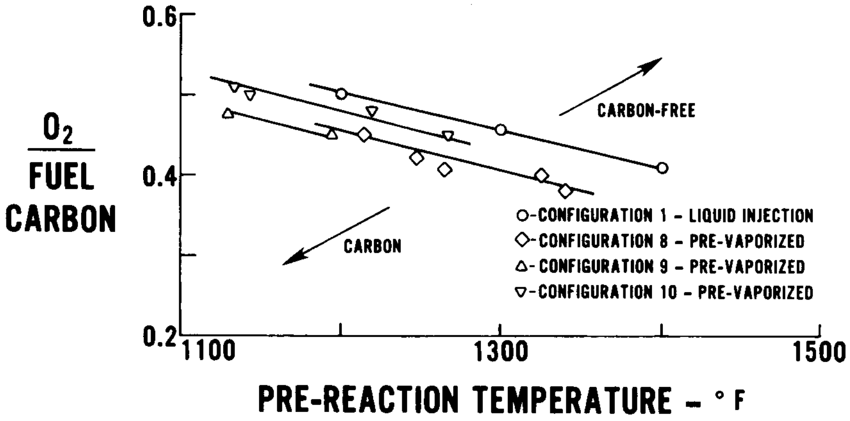


Figure 4-7. Effect of Nozzle Configuration on the Carbon Boundary

The pre-vaporized fuel approach to nozzle design was pursued through several modifications until in configurations 8, 9 and 10 a family of nozzle configurations evolved which gave less dramatic improvement in initial performance but which were able to maintain operation for extended periods without fouling or plugging with carbon. Carbon boundaries for the bench scale reactor with commercial nickel catalyst using the advanced nozzles are also shown in Figure 4-7. Although configurations 8 and 9 appeared to have superior performance to configuration 10, subsequent testing in the pilot scale, 6 inch diameter reactor showed the reverse order. The differences between the three were judged to fall within experimental ability to reproduce reactor behavior.

One of the objectives of the current program, under contract RP1041-4, was to demonstrate the ability to scale-up the design of the reformer while maintaining its performance. Nozzle configuration 10 was selected for this task. The design criteria developed in the bench scale, 2 pph fuel reactor were used to enlarge the capacity of the nozzle to 10 pph fuel, keeping the fluid dynamic properties of the nozzle constant. Cold flow tests, using CO_2 and N_2 to simulate mixing of the fuel and oxidant, indicated that the efficiency of the nozzle configuration 10 may have improved with increase in size. Two pilot scale reactors, 6 inches in diameter, processing 10 pph of fuel, were tested. They were identical in general configuration except that one was externally insulated (hot-walled) whereas the other, intended for longer term operation, was internally insulated. The reactors ran for extended periods in test programs which established their operating characteristics. The performance data for the reactors operating close to their respective carbon boundaries are shown in Table 4-2. The internally insulated reactor ran for 450 hours without significant change in performance with respect to carbon formation or fuel conversion.

TABLE 4-2 PERFORMANCE OF PILOT SCALE ADIABATIC REFORMER

	Reactor*	
	Hot Wall	Insulated
O_2/C, Mole Ratio	0.42	0.465
Pre-reaction Temperature °F	1360	1360
Exit Temperature °F	1800	1850
Conversion %	99.	99.9
Space Velocity, lbs Fuel/ft^3 Reaction hr	24	24
H_2O/C	3.85	3.85
Pressure psig	45	45
Test Duration, hrs	350	450

* 6 Inch Diameter, Nozzle Configuration 10, Commercial Nickel Catalyst.

The carbon boundaries of the pilot scale reformers were compared to those of similar bench scale reformers in Figure 4-4, which summarizes data from the two pilot scale and three of the bench scale reactors, each constructed with nozzle configuration 10 and filled with commercial nickel catalyst. The carbon boundary for all the reactors had the same characteristics slope. However, there was a variation in the O_2/C intercept of the boundary which was estimated to be ±0.025 in O_2/C. No obvious cause was identified for the variance but, within the nominal scatter, the ability to scale-up the adiabatic reformer performance was demonstrated.

In Figure 4-4 the operating point selected as the design goal for the adiabatic reformer in the fuel cell power plant is indicated. Discussion of the systems analysis will show that there is some latitude for setting this goal with respect to the particular combination of values for O_2/C and pre-reaction temperature. Hence the design goal is represented by a line having the familar slope of the adiabatic exit isotherm. It is apparent that the performance of the test reactors with nozzle configuration 10, using commercial nickel catalyst, fell far short of the design goal. O_2/C values higher than the desired values were required to prevent carbon formation.

The deficiency is emphasized in Table 1-1 where the performance parameters for the hot-wall, pilot scale reactor are compared with the power plant design requirements. Both the excess air and the high reactor exit temperatures were shown by systems analysis to result in significant increase in power plant cost over the design baseline.

Figure 4-4 represents the conclusion of an extensive program to optimize the nozzle for fuel and reactant mixing in the adiabatic reformer. To arrive at nozzle configuration 10, many different approaches to increasing the intensity of mixing had been tried without significantly improving the performance over that shown in Figure 4-4. With nozzle configuration 10, the sensitivity of the carbon boundary to fuel flow rate and process stream residence time upstream of the catalyst bed, which had been evident in earlier configurations, had disappeared. Cold flow simulation of mixing indicated that, on the macro-scale, mixing was close to complete at the entrance to the catalyst diffuser cone section. It was therefore concluded that the carbon-boundary achieved by configuration 10 could not be significantly lowered, in its O_2/C intercept, by increase in the efficiency of the gas-phase fuel mixing process alone. In further testing, nozzle configuration 10 was held constant.

EFFECT OF CATALYST FORMULATION ON THE CARBON BOUNDARY

To compare the effectiveness of various nozzle designs, the bench scale reactor had been filled consistently with commercial nickel catalyst. Following these tests the effect of the catalyst on the characteristic carbon boundary was studied by holding the nozzle configuration constant, with configuration 10, and changing the catalyst. From observations 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 only the catalyst in the inlet section of the 2-inch reactor was changed while the exit catalyst was left in place. In this way the effect of a sequence of formulation changes in the inlet catalyst could be rapidly determined.

The first objective of this part of the program was to screen a wide variety of catalyst formulations to identify those showing promise in limiting carbon formation. No. 2 fuel oil was used as the reference fuel for comparison of catalyst in tests which ran typically 25 to 50 hours. To expedite the program, in some tests which compared catalyst behavior, coal derived liquid fuels were also run. The main body of data on coal derived liquid fuels, however, is summarized under a separate heading. Later catalyst evaluation tests were different in purpose in that they examined the longer term behavior of the most promising candidate catalysts to identify any deleterious effects not evident in the shorter tests.

The catalysts evaluated in the screening program are described in Table 4-3. For reference in the discussion which follows, a summary of the test sequence, with the particular catalysts and fuels used, is given in Table 4-4. Since more than one catalyst was used in each reactor charge, the catalyst placement in each test is included.

TABLE 4-3 CATALYSTS TESTED IN THE ADIABATIC REFORMER

CATALYST	COMMENTS
HGTC 1030	A commercial nickel steam reforming catalyst, 1/8" x 1/8" pellets and 10-16 mesh granules.
SRC 32	Metal oxide A on a refractory support 1/8" x 3/16" pellets.
HGC 3020	Metal oxide B as 6-12 and 2.5-6 mesh granules
PSD 3000	Metal oxide B on a refractory support 1/8" x 3/16" pellets.
PSD 3018	A catalyst similar to PSD 3000 modified to increase resistance to carbon formation.
PSD 1033	Noble metal on a refractory support 1/8" x 3/16 pellets.
PSD 1028	Noble metal on less refractory support, 1/8" x 3/16" pellets.
PSD 2001	A high activity nickel catalyst on a refractory support, 1/8" x 3/16" pellets.

TABLE 4-4 CATALYSTS AND COAL LIQUID EVALUATION TESTS - TYPICAL CONDITIONS AND RESULTS

Run No.	Catalyst[a]	Fuel	O_2/C[b]	Prereaction Temperature	Exit Temperature	Conversion	Comments
1	HGC-1030 (14)	No. 2	0.475	1246°F	1797°F	98.9%	Baseline run.
2	HGC-1030 Ground (7) HGC-1030 1/8" (7)	No. 2	0.485	1246°F	-----	96.0%	Ground catalyst changed the temperature profile, but did not improve the carbon boundary.
3	SRC-32 (7) HGC-1030 (7)	No. 2	0.45	1230°F	1804°F	88.2%	Metal oxide catalyst does little reforming resulting in very high bed temperature. Carbon boundary stable and lower than with nickel reforming catalyst
4	PSD-1028 (8) HGC-1030 (6)	No. 2	0.215	1179°F	1363°F	54.9%	Studied lower carbon boundary only because of catalyst support stability limit.
5, 6	HGC-1030 (14)	No. 2					Repeat of baseline Run #1.
7	HGC-3020 4-10 mesh (8) HGC-1030 (6)	No. 2	0.330	1129°	1658°F	89.5%	No carbon formation.
8	HGC-3020 4-10 mesh (8) HGC-1030 (6)	2% H-coal	0.385	1172°F	1493°F	92.1%	No carbon formation.
9	HGC-3020 4-10 mesh (8) HGC-1030	SRC wash solvent	0.433	1125°F	1629°F	94.8%	Carbon formed at all conditions run.
10	PSD 1033, (26)	No. 2	0.350	1212°F	1480°F	95.6%	No carbon formation.
11	PSD 1033, (26)	H-coal	0.38	1237°F	1618°F	100.0%	Carbon formation could not be prevented.
		No. 2	0.40	------	------	-----	Carbon formation, results of run 10 could not be repeated.
12	PSD-1033 (14) PSD-1028 (8)	No. 2	0.33	1157°F	1404°F	94.7%	Catalyst was obtained from bottom of reactor from previous build (Runs 10 & 11). Carbon formed, results of run 10 could not be repeated.

TABLE 4-4 (CONT)

Run No.	Catalyst[(a)]	Fuel	O_2/C[(b)]	Prereaction Temperature	Exit Temperature	Conversion	Comments
13	HGC-3020, 2 1/2-6 mesh (8) HGC-1030, (8) PSD-1033, (5) PSD-1028, (5)	No. 2	0.35	1155°F	1417°F	88.7%	No carbon.
		1% H-coal distillate	0.35 0.40	1153°F 1259°F	1360°F 1505°F	93.9% 98.9%	No carbon, meets conversion and exit temperature goals.
		H-coal distillate	0.34	1197°F	1405°F	91.3%	Carbon formed at conditions run, but boundary search not attempted.
14	HGC-3020, 2 1/2-6 mesh (8) HGC-1030, (8) PSD-1033, (5) PSD-1028, (5)	SRC light organic liquid	0.32	1147°F	1385°F	84.6%	No carbon. Last point run in this series of tests.
15	PSD-3000 (8) PSD-1030 (6) PSD-1028 (12)	No. 2	0.35	1190°F	1385	93.4	Carbon formed after 20 hours.
16	HGC-3020 (8) PSD-1030 (6) PSD-1028 (12)	No. 2	0.35	1165°F	1370°F	86.3	Carbon formed after 150 hours. Ran 330 hours as boundary decayed.
17	PSD 3018 (8) PSD 2001 (18)	No. 2	0.35	1160°F	1526°F	90.2	Carbon boundary decayed after 150 hours to design baseline value.
18	PSD 3018 (8) PSD 2001 (18)	No. 2	0.36	1377°F	1672°F	92.6	Carbon-Free, 448 hours.

(a) Figures in parenthesis indicate bed length in inches of preceding catalyst

For each run the characteristic carbon boundary was defined by determining the value for O_2/C at which carbon formation and burn-off were in balance. In Run 1, the baseline behavior for the system was established with the commercial nickel catalyst HGC 1030 in pelleted form. After some initial decay in the boundary, which was typically observed, the carbon boundary stabilized at a value consistent with previous reactors which used configuration 10 nozzle. See Figure 4-4.

Run 2 tested the hypothesis that a catalyst which was more active for steam reforming would lower the carbon boundary. It was initially assumed that combustion was solely a homogeneous process unaffected by the catalyst. Increased catalyst activity for reforming could therefore result in a decrease in maximum temperature, in fuel cracking reactions, and hence in carbon formation. Since, for the 1/8" x 1/8" pellets of HGC 1030, diffusional limitations at high temperature reduced the catalyst effectiveness factor, it was ground to 10-16 mesh to increase activity. The resultant temperature profile for the reactor was consistent with an increase in activity both for combustion and reforming reactions. The inlet temperature gradient was steeper than for the 1/8" pellets suggesting that combustion was accelerated. See Figure 4-8. The steep temperature decrease to virtually the same value as the exit temperature indicated that the fuel was nearly completely reformed within the first 4 inches of the reformer. Surprisingly, the propensity for carbon formation, reflected in the location of the carbon boundary in Figure 4-9, was worse than for the pelleted catalyst. Evidently carbon accumulation was determined by more than a simple time-at-temperature relationship for the fuel.

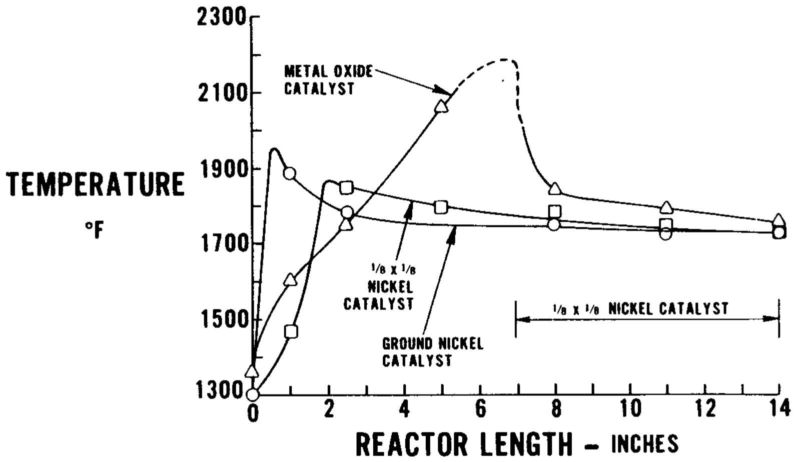


Figure 4-8. Effect of Entrance Section Catalyst on Temperature Profile

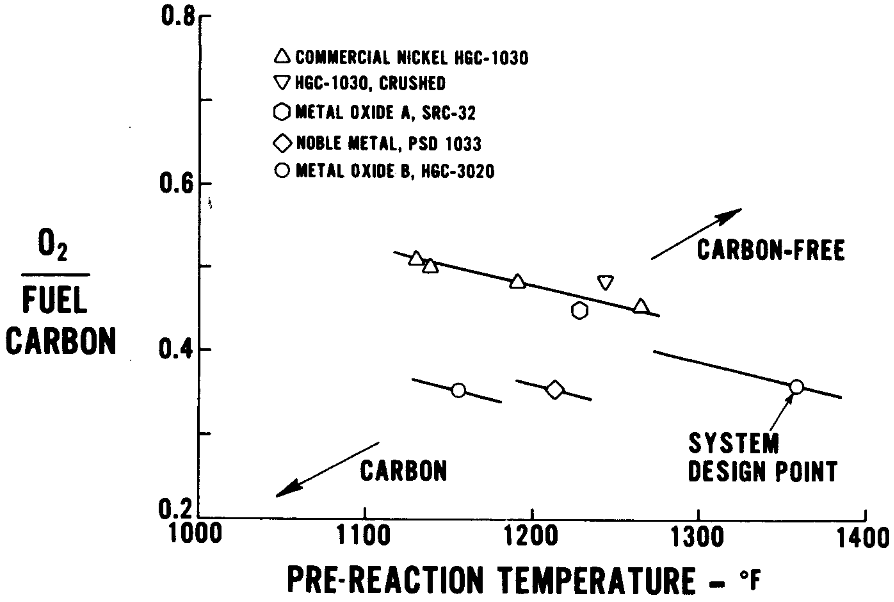


Figure 4-9. Effect of Entrance Catalyst Formulation on the Carbon Boundary

This was made more evident by Run 3 in which SRC-32, a catalyst containing metal oxide A, was placed in the entrance to the reactor. Experiments in the laboratory micro-reactor had shown that although SRC-32 was inactive for reforming, it had superior resistance to carbon formation. This catalyst effected a drastic change in the temperature profile; both combustion and reforming reactions appeared inhibited since the temperature rose less steeply but reached higher absolute values than for the nickel catalyst in the inlet section. See Figure 4-8. The rapid drop in temperature, signifying the onset of reforming, occurred only when the process stream entered the section filled with nickel catalyst. Yet, although the fuel was subjected to higher temperature throughout the metal oxide section of the catalyst bed, the carbon boundary in Figure 4-9 was improved relative to the nickel catalyst.

In Runs 7 and 13 a second oxide catalyst, metal oxide B, was tested. This catalyst, HGC 3020, ran carbon-free with no indication of carbon formation for up to 50 hours at $O_2/C = 0.35$ at 1153°F i.e. well within the system design goals. A record of the pressure drop history for this run, 13, is given in Figure 4-10 where, during operation with No. 2 fuel oil and with a coal-derived liquid fuel, no increase in pressure was observed. The earlier Run 7 with HGC-3020 had given an indication of pressure drop increase which was later identified, by examination of the catalyst after the test, as due to fusion of the catalyst pellets. In Run 13, the pellet size of HGC-3020 had been increased to minimize the effect of contact sintering with evident success.

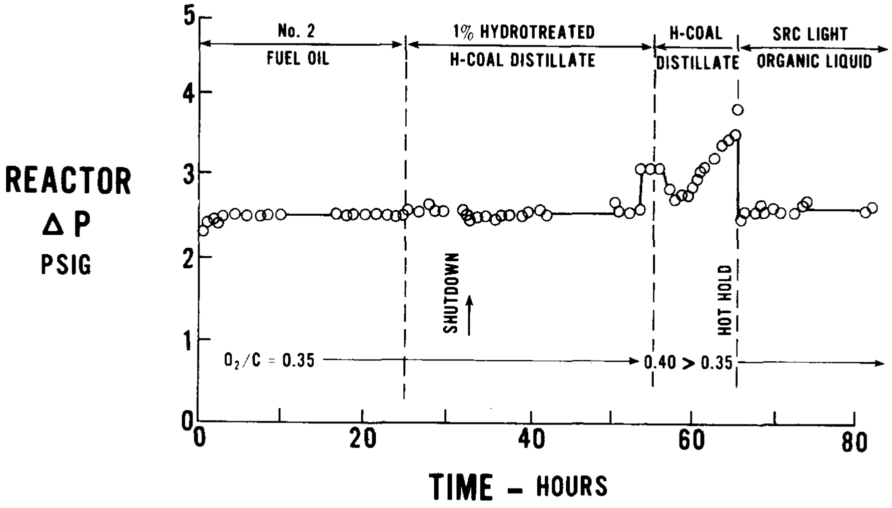


Figure 4-10. Reactor Pressure Drop History for Runs 13 and 14

HGC-3020 demonstrated unusual combustion light-off characteristics which resulted in an unexpected temperature profile. In Figure 4-11, for Runs 7 and 13, no ignition occurred in the entrance to the catalyst bed despite the presence of recycle hydrogen. Reforming or cracking appeared to occur without combustion in an induction period. One could speculate that the temperature decreased due to cracking or reforming until sufficient hydrogen was produced to initiate combustion. The decrease in temperature following the maximum indicated that HGC-3020 had significant reforming activity, but the greater activity of HGC-1030 was evident from the much more rapid drop in temperature when the process stream entered the section containing that catalyst. The induction period in Figure 4-11 decreased in length with time on stream and could be eliminated entirely by raising the pre-reaction temperature. It did not recur in subsequent start-ups of the reactor, suggesting that an irreversible change in the catalyst had occurred. Similar temperature profile characteristics were observed with HGC 3020 during the coal-liquid tests in Runs 13 and 14.

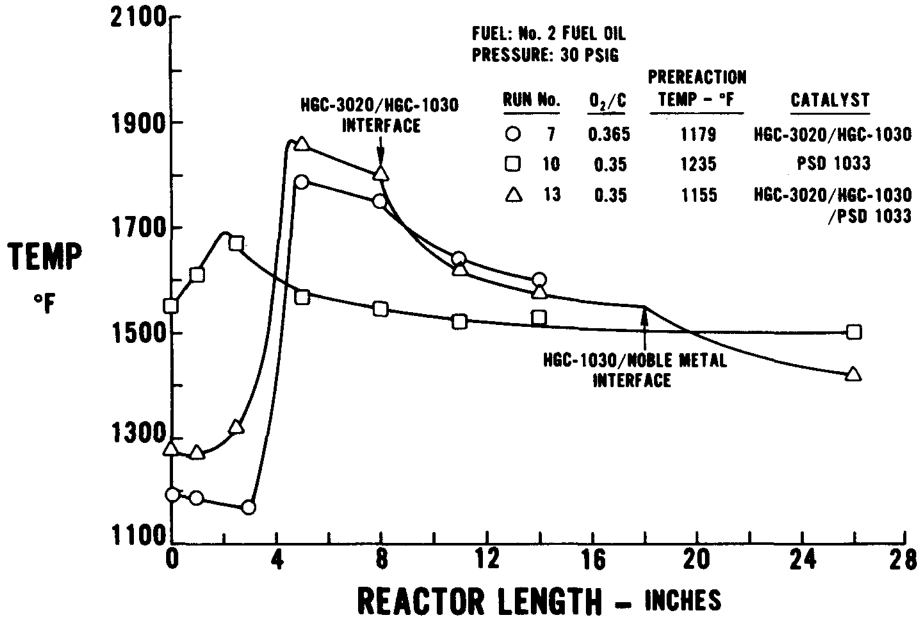


Figure 4-11. Temperature Profiles in the Bench Scale Reactor With Carbon Tolerant Catalysts

In the laboratory reactor program, catalysts containing a noble metal were developed which had very high activity for steam reforming. The first such catalyst, PSD 1028, was restricted by its thermal stability to temperatures below 1700°F. To prevent exceeding this limit in the bench scale reactor, the O_2/C ratio in Run 4 was limited to values below about 0.3. Below $O_2/C = 0.25$ a carbon-free, fuel-rich gasification region was identified. At these low values for O_2/C the reactor exit temperatures were low and consequently fuel conversion to carbon oxides did not exceed 50%.

A less active but more stable noble metal catalyst, PSD 1033, operated carbon-free on No. 2 fuel oil at $O_2/C = 0.35$ and preheat temperatures which varied between 1212°F and 1246°F in Runs 10, 11, and 12. Successful operation was indicated in Figure 4-12 by the steady value for pressure drop across the catalyst bed for over 50 hours. In Figure 4-11 the temperature profile for the reactor in Run 10 shows a rise to a maximum of only 1700°F, reflecting the high activity for reforming of the noble metal catalyst.

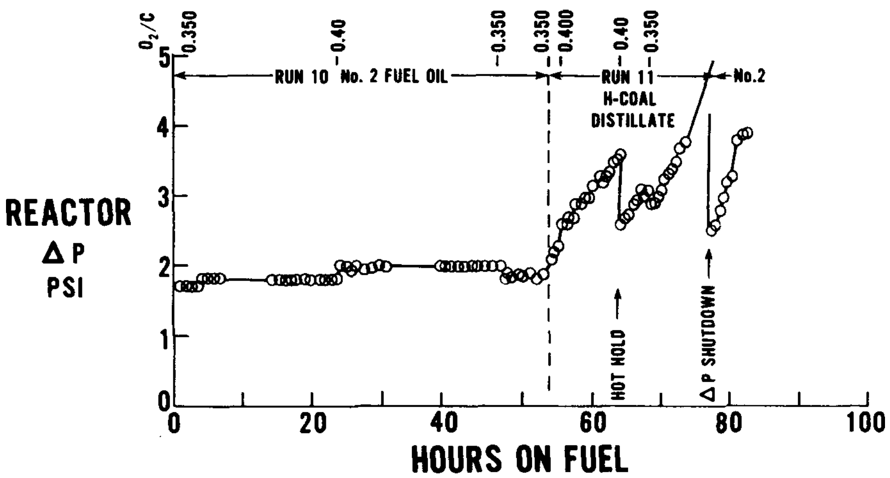


Figure 4-12. Reactor Pressure Drop History on Runs 10 and 11

As a result of the catalyst screening program through Run 14, two catalyst formulations were identified which, when placed in the entrance to the reactor, permitted operation on No. 2 fuel oil at values for O_2/C consistent with the power plant system goals. Figure 4-9 compares the reactor operating range for HGC-3020 and PSD 1033 with HGC-1030 commercial nickel catalyst. It shows that with the metal oxide B and with noble metal, significant improvement in performance was achieved.

In Runs 15 through 18 the focus of testing shifted. Catalysts based on metal oxide B were selected for longer duration runs to identify behavior characteristics not revealed in the brief screening runs. The objective was to demonstrate stable carbon-free operation at the design goal values for O_2/C for an extended period.

The pellets of metal oxide catalyst B, HGC-3020, had shown a tendency to fuse together at the extremely high temperatures experienced in the inlet to the reactor. Therefore the catalyst was modified by supporting metal oxide B on a refractory support. This catalyst, PSD 3000, gave non-reproducible behavior in Run 15. A record of the performance of PSD 3000 in Figure 4-13 charts reactor pressure drop as a function of time. The reactor operated stably at O_2/C = 0.35 and a pre-reaction temperature of 1200°F for the first 20 hours of the run, but then the amount of air added to the feed had to be progressively increased until, after 45 hours an O_2/C ratio of over 0.40 was required to burn-off carbon and prevent its accumulation in the reactor. When the catalyst was examined after the run no fusion of pellets had occurred. Because of the slow deterioration in the carbon boundary, PSD 3000 was judged unsuitable for use in the reactor inlet.

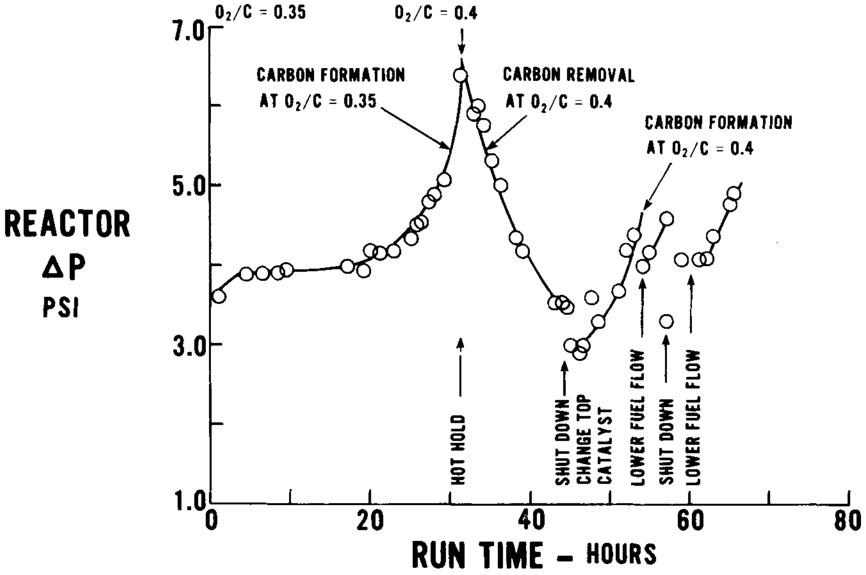


Figure 4-13. Reactor Pressure Drop History for Run 15

In an attempt to understand the cause for the deterioration of HGC 3000, in the next run, 16, the unsupported metal oxide B HGC 3020 was operated for over 350 hours. A record of the reactor pressure drop behavior is given in Figure 4-14, where the curve is formed by connecting only those data points measured at the reference conditions of $O_2/C = 0.35$. The initial data was similar to previous tests results with HGC-3020. The convex nature of the pressure drop curve to the time axis indicated that inter-pellet fusion had occurred and that the void space in the bed was stabilizing. Carbon formation in the bed would typically lead to a concave curve. Figure 4-14, therefore, shows that HGC-3020 operated carbon-free for over 150 hours at $O_2/C = 0.35$ and that at some point before 240 hours, carbon formation started to plug the reactor. At 320 hours the data point at $O_2/C = 0.32$ was also in the carbon-forming condition whereas at 145 hours this condition had been carbon-free. At 337 hours the air flow was increased to give a value of O_2/C of 0.40, but carbon could not be removed. Evidently the carbon tolerance of the system had decreased with time and the observed deterioration was judged to have occurred discontinuously after 150 hours of operation.

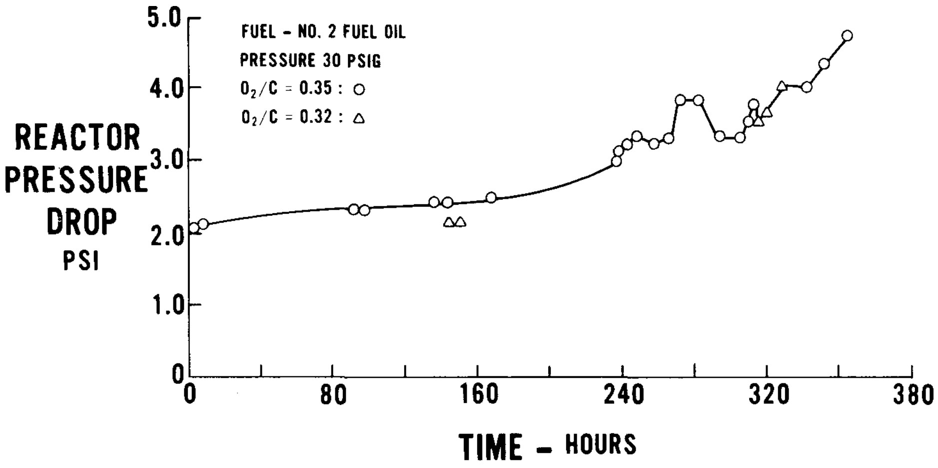


Figure 4-14. Reactor Pressure Drop History for Run 16

Post-test examination of the reactor after run 16 showed that carbon had formed in the metal oxide catalyst but that much of the carbon appeared to be associated with, or extend from, the reactor wall. The reactor wall itself appeared pitted. This led to the suspicion that the low values for O_2/C, i.e., the fuel-rich conditions at which the reactor operated with the new metal oxide catalyst, induced carburization of the reactor walls. Micrographic analysis of the wall material, I-601, confirmed the presence of precipitated carbides. Furthermore, in tests with catalysts which contained no magnetic components, the carbon in the interstices of the pellets was found to be magnetic, suggesting that it had originated from the high nickel alloy wall material. Chemical analysis of the carbon in Table 4-5 clearly showed elevated iron, chromium and nickel content in approximately constant ratio, i.e., Fe/Cr : 3/1 to 2/1 and Ni/Cr: 1/10 to 1/5 despite variation in catalyst composition. This evidence suggested that the carbon, at least in part, originated from carburization processes on the reactor walls. The reactor walls in a full-scale adiabatic reformer will be insulated from the process stream by a ceramic liner. Hence, carburization is not expected to be a problem with commercial reactors. However, since the test reactors in the development program had metal walls, carburization may have obscured the true carbon forming characteristics of the advanced metal oxide catalyst systems and may account for the erratic behavior of some tests with respect to carbon formation.

TABLE 4-5 COMPOSITION OF CARBON FORMED IN THE ADIABATIC REFORMER ENTRANCE SECTION

							Element - Wt. Percent								
Run	Entrance Section Catalyst	C	K	Fe	Si	AL	Mn	Mg	Cr	Ti	Mo	V	Ni	Ca	Co
12	Noble Metal	67.3	-	5	.1	2	.2	-	3	.05	.01	.01	.5	2	
13	Metal Oxide	85.5	-	1	.02	.02	.02	<.01	.5	.01	.03	<.01	.1	.2	<.01
15	Supported Metal Oxide	Maj.	-	6.4	.05	3.3	.05	-	2.3	.05	-	-	.2	.2	

To eliminate carburization in Run 17 the reactor walls were sand blasted to remove the carburized surface and given a protective treatment to prevent its recurrence. For this run, PSD 3018, a modified version of the supported metal oxide B catalyst, PSD 3000, was placed in the bench scale reactor inlet. It had been shown in the laboratory reactor to have superior activity, some resistance to carbon formation and no tendency for interpellet fusion. The reactor pressure drop plotted as a function of time in Figure 4-15 gives a record of the run. The reactor ran without increase in pressure at $O_2/C = 0.35$ for 50 hours, after which rapid increase in pressure drop occurred, indicating carbon deposition. After each of two shut downs, which imposed extended periods of steaming on the reactor, the ΔP returned to its original value, but additional air had to be added before carbon burn-off and stable operation was again achieved. The reactor ran at this condition, $O_2/C =$

0.40, for 140 hours before conditions were changed to investigate the location of the carbon boundary at different pre-reaction temperatures. The reactor was finally intentionally plugged at 360 hours in order to examine the carbon formed. At about 200 hours the pressure drop increased but spontaneously reversed itself indicating that this condition, $O_2/C = 0.40$, was close to the carbon boundary. It was concluded that the position of the carbon boundary had decayed from below $O_2/C = 0.35$ to about $O_2/C = 0.4$ at the constant pre-reaction temperature of 1180°F. After 300 hours of operation, carbon was deliberately formed in the reactor by lowering O_2/C to 0.35,and Run 17 was terminated. Post-test examination of the reactor indicated much reduced carburization of the reactor walls. Run 17, therefore, reflected carbon formation characteristics intrinsic to the supported metal oxide B catalyst, PSD 3018.

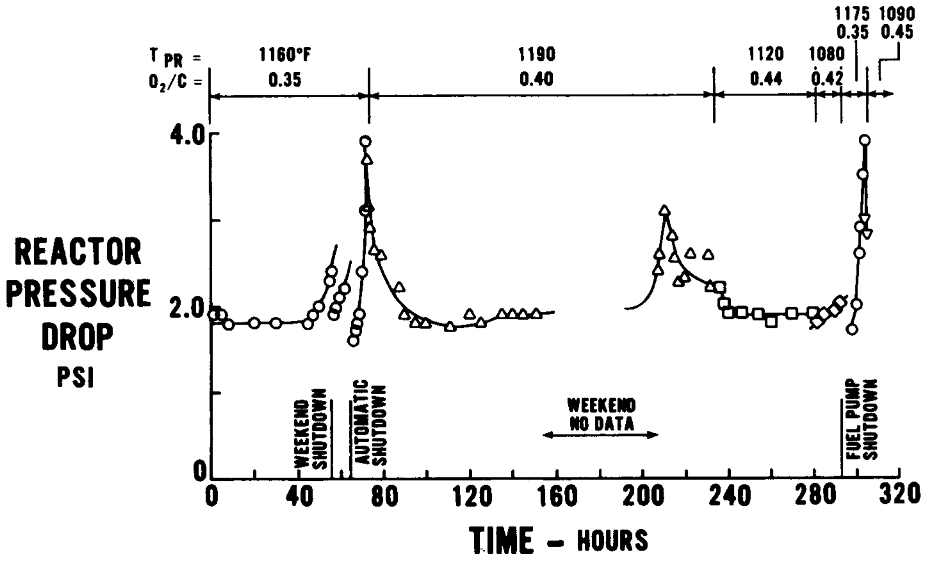


Figure 4-15. Reactor Pressure Drop History for Run 17

The position of the carbon boundary was defined as a function of pre-reaction temperature during the test. The data in Figure 4-16 showed that the carbon boundary for the reactor with metal oxide B catalyst had the same characteristic slope as had been noted for earlier reactions with commercial nickel catalyst. The maximum pre-reaction temperature which could be attained in the bench scale reactor was about 1200°F, limited by the design of the steam superheaters. Hence, the carbon boundary data for Run 17 had to be extrapolated to indicate that at the required pre-reaction temperature of 1360°F, the reactor would operate carbon-free below the design value for O_2/C of 0.35.

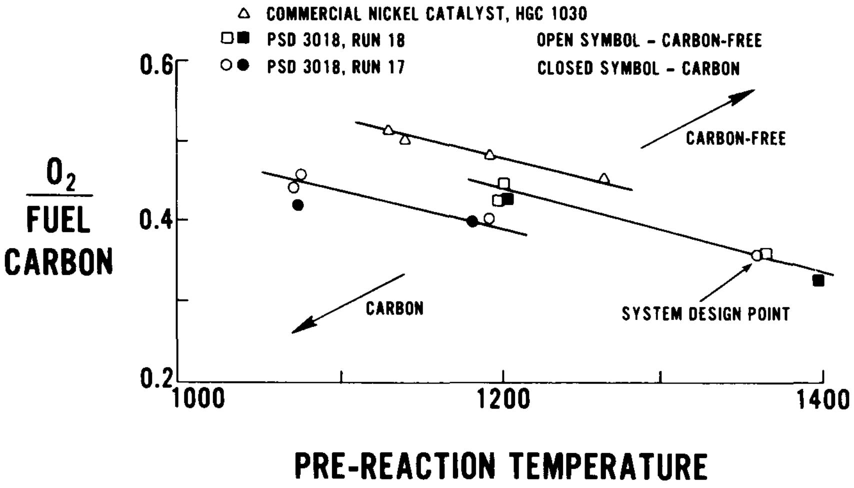


Figure 4-16. Carbon Boundary with Metal Oxide B, Catalyst PSD-3018

Run 18 was intended to give a final demonstration of the capability of PSD 3018 to operate stably at the O_2/C value required by the power plant design. For this run a second procedure was adopted to protect more effectively the reactor walls from the carburization reactions. In addition, the pre-heater for the steam-air feed was modified by inserting a small hydrogen burner prior to mixing with the vaporized fuel. By this means a pre-reaction temperature of 1360°F was achieved in test. Temperatures measured downstream of the burner indicated combustion was complete before entering the mixing zone. In reporting the data for these points therefore, the O_2/C value for the process stream was corrected for the hydrogen burned to reach temperature.

A second batch of PSD 3018 was used to fill the entrance section of the reactor. In 448 hours of testing it demonstrated operating characteristics very similar to the previous batch. The initial position of the carbon boundary at a pre-reaction temperature of 1190°F was well below the system design value for about 100 hours, but subsequently it decayed with time until after about 200 hours the boundary stabilized at a value for O_2/C close to that reqired by the design line at 1190°F. Figure 4-17 shows the changes of the boundary with time. In the period between 250 and 448 hours tests were made at higher pre-reaction temperatures, but prior to terminating the run the initial condition at 1190°F was reset and the carbon boundary had not changed. Also shown are data for Run 17, which, although it did not extend beyond 210 hours, appeared to show the same trend, perhaps stabilizing the carbon boundary at slightly lower values for O_2/C.

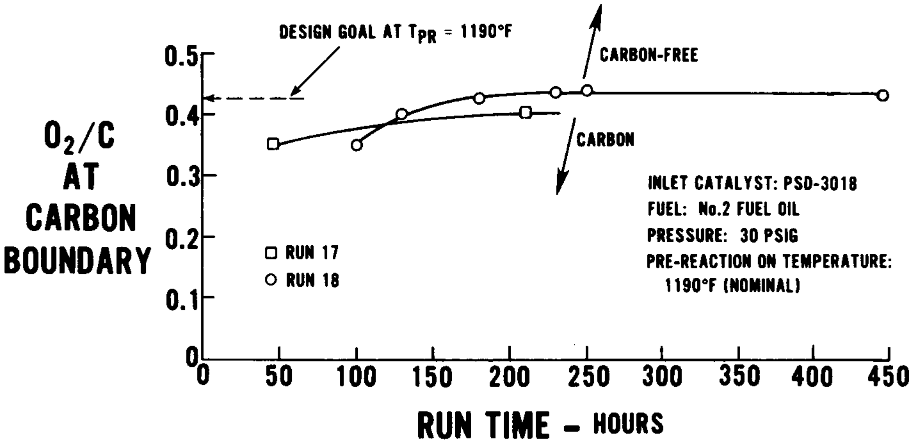


Figure 4-17. Stabilization of the Carbon Boundary in Runs 17 and 18

After the carbon boundary had stabilized, the pre-reaction temperature was raised to above 1360°F, and the carbon boundary was again located. It can be seen in Figure 4-16 that the stabilized boundary followed a slope on the plot of O_2/C versus pre-reaction temperature parallel to the system design line and to the isotherms for the adiabatic exit temperature discussed in previous reports. This confirmed the data of Run 17 which established the same slope for the boundary.

More importantly, the stabilized boundary passed close to the power plant system design point of $O_2/C = 0.35$ at 1370°F pre-reaction temperature. The bench scale reactor operated for the final 80 hours of the test at $O_2/C = 0.36$ at 1370°F pre-reaction temperature.

The reactor was shut down after 448 hours in a carbon-free condition. In the post-test examination of the reactor the catalyst poured freely from the reactor. Only traces of carbon were present, and these could be described as the residue from incomplete burn-off following one of the controlled excursions into the carbon-forming regime. The walls of the reactor were clean and unpitted. With Run 18 the development of the entrance section of the adiabatic reformer where carbon formation was of primary concern was brought to a successful conclusion. With the optimized nozzle configuration 10 and the supported metal oxide B catalyst, PSD 3018, the reactor was shown to operate stably and carbon-free. Reference to Table 1-1 will show that the initial design goals with respect to O_2/C and prereaction temperature could be met.

EFFECT OF OPERATING CONDITIONS ON THE CARBON BOUNDARY

The evaluation of mixing nozzle configuration and of catalyst formulation was performed at standard test conditions for steam to carbon (H_2O/C) mole ratio, fuel flow and pressure. In brief tests the effect of variation in these parameters on the carbon boundary was established.

In the pilot scale, hot-walled reactor with commercial nickel catalyst neither change in pressure, nor in flow rate had significant effect on the position of the carbon boundary. Thus, In Figure 4-18 from 23 to 60 psig and from 5 to 13 pounds per hour flow of fuel the location of the carbon boundary did not alter significantly.

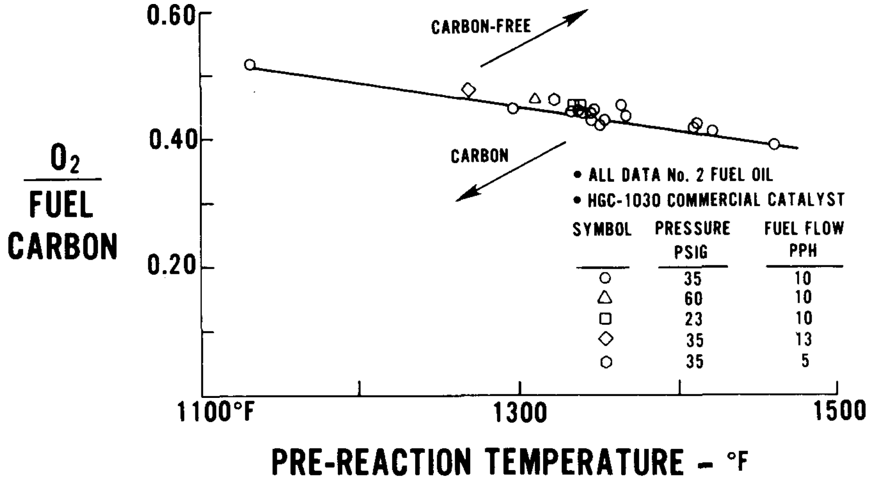


Figure 4-18. Effect of Pressure and Flow Rate on the Carbon Boundary in the Pilot Scale Reactor

Similarly, changes in the steam to carbon ratio did not significantly affect the carbon boundary. In the pilot scale insulated reactor variation in the value for H_2O/C in the feed stream from 3.85 to 6 did not alter the location of the boundary. Furthermore, systems studies of the adiabatic reformer in fuel cell power plants established that, up to a value of about 5, the H_2O/C ratio did not substantially impact the efficiency or cost of the system. Hence, the H_2O/C ratio was not identified, in Table 1-1, as a critical performance goal.

FUEL CONVERSION

The first sections of this report have focused on carbon formation rather than on the primary function of the adiabatic reformer, the conversion of fuel to hydrogen. This was a natural priority since early builds of the reactor required air significantly in excess of the design goals to prevent carbon accumulation. High temperatures generated in the exit section of the reactor by the excess air resulted in values for fuel conversion which exceeded the design requirement in this category even with commercial nickel catalyst and high space velocities. The performance data for the 6-inch pilot scale reactor listed in Table 1-1 illustrated the point.

However, the success of the optimized nozzle configuration and metal oxide catalysts in permitting carbon-free operation at lower values for O_2/C concomitantly lowered the average temperature in the exit section of the reactor. At these conditions the commercial nickel catalysts did not achieve the conversions required by the power plant system design. More active catalysts were required.

Conveniently, the phenomena affecting fuel conversion were independent of, and simpler than, those controlling carbon formation. As noted in Figure 3-3, by the time the process stream had exited the combustion zone where carbon formed, only traces of hydrocarbons other than methane remained. The exit section of the reformer was simply an adiabatic reformer for methane. Furthermore, the concentration of methane exiting the combustion zone did not vary widely over the range of nozzle configurations and catalyst formulations tested. It typically varied from 2 to 6 percent of the dry gas stream. In addition, the tendency of the exponential rate law governing the disappearance of methane was to further emphasize the importance of exit section of the reactor for fuel conversion.

For these reasons, fuel conversion could be investigated independently of the carbon forming processes. Multi-catalyst reactor charges were used. In the entrance section, comprising about 8 inches of the 26-inches long bench scale reactor, catalysts were selected which prevented carbon formation, as described above. The exit section required catalysts with high activity for methane reforming. Concurrent with the tests of the entrance catalyst the exit catalyst was also varied in the sequence listed in Table 4-4.

Because of the very gradual decrease in temperature in the final section of the catalyst bed, the temperatures measured at the bed exit bore a close relationship to the mean temperature experienced by the process stream in the all-important final portions of the catalyst. Therefore, for a given catalyst in the exit section of the reactor the conversion correlated with the temperature at the exit and was independent of whether that temperature was achieved by the addition of air or by preheating the reactants. Thus, in Figure 4-19, 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.

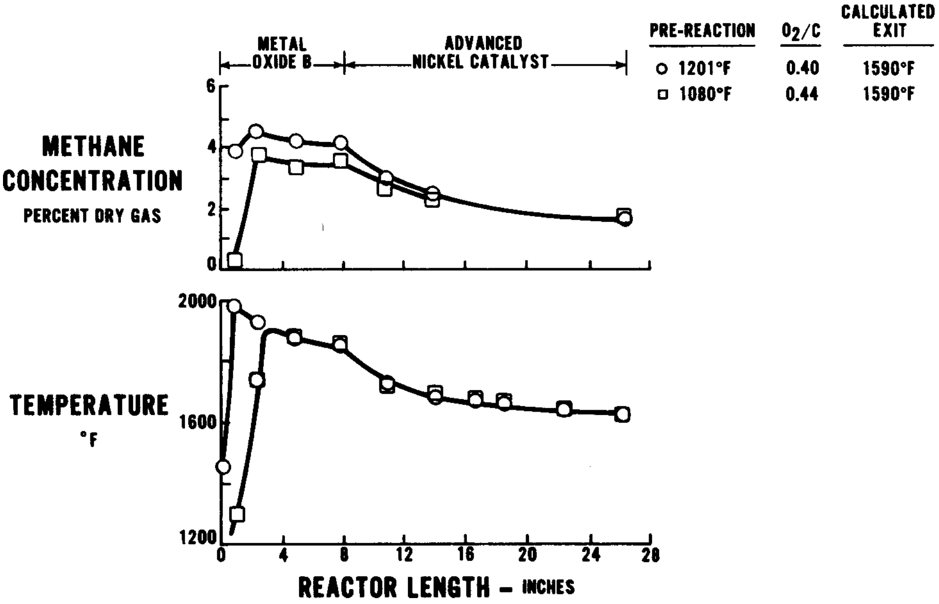


Figure 4-19. Effect of O_2/C and Pre-Reaction Temperature on Fuel Conversion

In Figure 4-20 are plotted data for early tests in which commercial nickel catalyst HGC 1030 filled the reactor. Data for the 6-inch diameter pilot scale and 2-inch diameter bench scale reactors are included. Because of its larger size and the nature of the fuel vaporizer, the pilot scale reactor could achieve lower values for space velocity than the bench scale reactor. Space velocity is expressed as pounds per hour of fuel per cubic foot of reactor volume including, where appropriate, both entrance and exit catalyst to permit easy comparison between multi-catalyst charges of varying catalyst density. Figure 4-20 shows that with commercial nickel catalyst the reactor required bed exit temperatures higher than the design value of 1700°F to achieve the fuel conversion goal at the design space velocity.

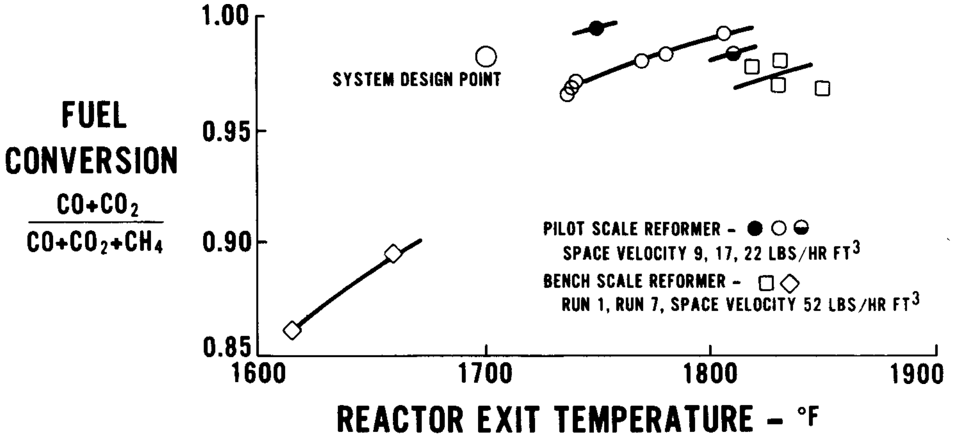


Figure 4-20. Fuel Conversion on Commercial Nickel Catalyst

In Run 7 HGC 1030 was placed downstream of HGC 3020, the metal oxide B entrance catalyst. With the metal oxide catalyst, the reactor operated at low O_2/C, reflected in the lower reactor exit temperatures; hence, the fuel conversion in the HGC 1030 catalyst, as might be expected, decreased. The extrapolation of this data to higher exit temperature, in Figure 4-20, appeared to be consistent with the runs for the reactor completely filled with HGC 1030.

A more active catalyst was required for fuel conversion in the reactor exit. The noble metal catalyst, PSD 1033, filled the whole bench scale reactor in Run 10. This catalyst had been shown in laboratory tests to have an activity for reforming methane two to three times greater than HGC 1030. With No. 2 fuel oil this catalyst charge approached the design goal. The data, however, gave some evidence for decay in catalyst activity with time.

A second noble metal catalyst, PSD 1028, with very high activity in laboratory tests, was about fifty times more active than HGC 1030 for methane steam reforming. Above about 1700°F, however, it lost physical integrity. Hence, it was loaded in the bench scale reactor, in Runs 13 and 14, in a triple charge; following the HGC 3020 metal oxide catalyst the more stable commercial nickel catalyst HGC 1030 was placed downstream of the combustion zone but upstream of HGC 1028, which was confined to the region of the reactor below 1700°F. The results of the triple loaded bed in Runs 13 and 14 with No. 2 fuel oil and with some coal derived liquids suggested that the design conversion might be achieved at exit temperatures less than 1600°F.

For Runs 15 and 16, HGC 1030 and PSD 1028 were again used in the exit portion of the reactor to determine their longer term stability. In Table 4-6 conversion data measured as a function of time at test indicated some decay in activity. Since the same charge of catalyst was used in the mid and exit portions of the reactor in both Runs 15 and 16 (only the entrance catalyst was changed), data from both runs were included. Comparison was valid since the product stream entering the mid-bed did not vary greatly from run to run and, as has been noted, the final conversion achieved in the exit portion of the bed was a function primarily of catalyst activity, volume and temperature in the exit section alone. The data points, each taken at the reference condition of $O_2/C = 0.35$ and pre-reaction temperature close to 1170°F, showed a decrease in exit conversion from 93% to about 90%, stabilizing after 150 hours. Since steam reforming is an endothermic process, the decrease in conversion was accompanied by an increase in exit temperature. The process stream leaving the metal oxide, entrance catalyst section was constant over the period covered by Table 4-6. The decay in reactor performance was therefore attributed to the mid and exit catalyst beds.

TABLE 4-6 EFFECT OF TIME ON CONVERSION AT EXIT OF THE BENCH SCALE REACTOR IN RUNS 15 AND 16

Time Hrs.	O_2/C Mole Ratio	Pre-Reaction Temperature °F	Exit Temperature °F	Conversion $\frac{CO + CO_2}{CO + CO_2 + CH_4} \times 100$
		RUN 15		
5	0.35	1190	1420	93.4
		RUN 16		
5.5	0.35	1166	1471	92.5
16	0.35	1168	1452	91.6
142	0.35	1165	1528	86.3
239	0.35	1168	1525	88.2*
312	0.35	1175	1541	90.0*
334	0.35	1178	1544	89.8

* Ethylene present and included as CH_4.

In Figure 4-21, the conversion data for Runs 15 and 16 are plotted versus reactor exit temperature. The bench scale reactor could not operate at space velocities less than about 40 pph/ft^3-hr. The adiabatic nature of the reactor, coupled with the heat losses associated with its small scale, made a simple projection of conversion data to the design space velocity of 12 pph/ft^3-hr difficult. In Figure 4-21 are plotted curves generated by a model for first order reaction of methane in the adiabatic reactor exit section. Assumptions for this calculation were that the conversion in the process steam exiting the metal oxide section of the reactor was 85%, typical for these test conditions, and that the methane in the process stream was converted in the metal catalyst exit section by a first order process with a rate constant given by the values generated for the noble metal catalyst in laboratory reactor experiments.

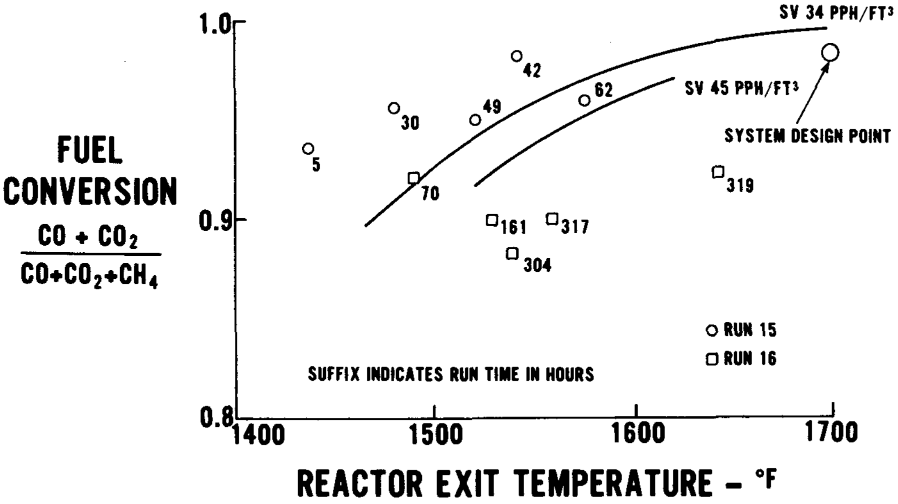


Figure 4-21. Fuel Conversion on Noble Metal Catalyst

Curves are given for two space velocities, 45 and 34 pph fuel/ft^3 reactor volume, where the reactor volume is that of the whole reactor, including the metal oxide portion. Comparable values for space velocity used in power plant design studies were about 12 pph/ft^3. Comparison of the data points for Runs 15 and 16 with the calculated curves showed that the initial conversion achieved with the exit catalyst PSD 1028 was greater than predicted by the curves (the space velocity in these runs was 42 pph/ft^3), but that the activity decayed, particularly in Run 16, to a stabilized value well below the predicted level. The calculated curve for 34 pph/ft^3 space velocity in Figure 4-21 exceeded the power plant design goal for conversion at 1700°F bed exit temperature. Since the power plant design study projected a lower space velocity (larger reactor volume) it appeared that catalyst PSD 1028 could achieve the design goal if performance could be stabilized at close to the level indicated at the end of Run 15.

In the laboratory catalyst development program a nickel catalyst, PSD 2001, was prepared which, although less active than the fresh noble metal catalyst, was still an order of magnitude more active than the commercial nickel catalyst, HGC 1030.

This catalyst filled the entire exit section of the bench scale reactor in Runs 17 and 18.

At the end of Run 17, which lasted 300 hours, the portion of catalyst, about 20%, which had experienced temperatures above about 1700°F appeared to be physically weakened and was replaced for Run 18, which lasted 448 hours. After Run 18 PSD 2001 in the high temperature regions of the reactor was again somewhat weakened, but the pellets were intact.

As with previous tests, fuel conversion at the reactor exit was a function of the bed exit temperature as shown in Figure 4-22. The conversion was very stable for the entire 748 hours operation in Runs 17 and 18, showing very little scatter and little loss in conversion. A curve calculated by the simple conversion model which used laboratory data for the activity of PSD 2001 gave a reasonable fit to the bench scale data at the test space velocity of 40 lb/ft^3-hr. Model calculation of conversion at the space velocity required by the power plant design, 12 lbs/ft^3-hr, indicated that the design requirements for conversion at 1700°F might be exceeded with PSD 2001.

The bench scale adiabatic reformer in Run 18 was built with nozzle configuration 10 and filled with the dual catalyst charge PSD3018/PSD2001 (supported metal oxide B/ high activity nickel). With this reactor the power plant design goals both for fuel conversion and for carbon-free operation at the required values for O_2/C and pre-reaction temperature were demonstrated jointly for 450 hours. Columns 1 and 3 of Table 1-1 match the reformer performance with the design goals.

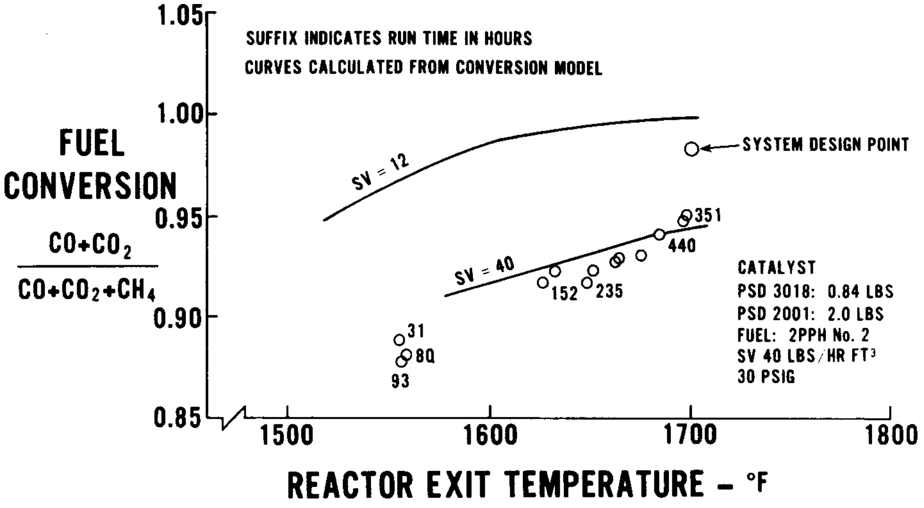


Figure 4-22. Fuel Conversion on High Activity Nickel Catalyst

Section 5

TEST RESULTS COAL DERIVED LIQUID FUELS

One of the objectives in the development of the adiabatic reformer was to assess its capability to reform coal-derived liquid fuels. For this purpose EPRI made available a number of samples of liquid fuels derived from the SRC-1 and H-Coal processes, three of which had been hydrotreated by the Conoco Coal Development Company. The properties of the coal liquid samples are listed in Table 5-1. Their composition covered a wide range of hydrogen to carbon ratios, including that of the No. 2 fuel oil used as reference fuel. None of the samples, however, had a boiling range similar to No. 2 fuel oil. The end points for the H-Coal distillates were similar to No. 1, whereas the recycle solvents were similar to gas oil.

TABLE 5-1 FUELS AVAILABLE IN THE COAL LIQUIDS PROGRAM

		H-COAL LIQUID			SOLVENT REFINED COAL LIQUID			
	No. 2 Fuel Oil	Distillate	Distillate 1% Hydro-treated	Distillate 2% Hydro-treated	Light Organic Liquid	Wash Solvent	Recycle Solvent	Recycle Solvent Hydrotreated
Gravity, °API	38.83					15.3		
Specific Gravity	0.8307	0.871	0.843	0.819		0.964	0.998	0.959
CHx	$CH_{1.78}$	$CH_{1.59}O_{0.014}$	$CH_{1.72}$	$CH_{1.86}$		$CH_{1.51}O_{0.038}$	$CH_{1.24}N_{0.0075}O_{0.03}$	$CH_{1.39}N_{0.0056}O_{0.0165}$
Hydrogen (%wt)	12.8%	11.43%	12.5%	13.41%	13.27%**	10.67%	8.96%	10.11%
Carbon (%wt)	86.8%	86.53%	87.16%	86.51%	85.05%**	84.80%	86.51%	87.36%
Sulfur (%wt)	0.322%	0.14%	0.06%	0.07%	0.14%**	0.24%**	0.33%	0.04%
Oxygen (%wt)	--	1.64	0.27%	0	0.88%**	4.31%**	3.45%	1.92%
Nitrogen (%wt)	--	0.26%	0.01%	0.01%	0.66%**	0.49%**	0.75%	0.57%
Paraffins (%v)	31.2%	38.0%*	65.3%*	84.5%*		23%	13.9%*	19.1%*
Olefins (%v)	0.8%							
Naphthenes (%v)	40.8%							
Aromatics (%v)	27.3%	62.0%	34.7%	15.5%		77%	86.1%	80.9%
Halogens (PPM)		233 PPM	58 PPM	13.42 PPM		4037 PPM	37 PPM	88 PPM
Distillate								
I B Pt	130°F	174°F	185°F	162°F	156°F**	158°F	409°F	358°F
10%	340°F	289°F	284°F	266°F	162°F**	400°F	500°F	473°F
50%	495°F	370°F	367°F	345°	217°F**	565°F	572°F	570°F
70%	545°F	408°F	408°F	381°	267°F**	638°F	662°F	653°F
90%	597°F	464°F	468°F	439°F	325°F**	74% 650°F	815°F	793°F
95%	615°F	491°F	496°F	475°F	356°F**		853°F	887°F
98%	625°F	--	522°F	509°F	363°F**		891°F	909°F

\+ Analyses Supplied By Conoco Coal Development Co.
* Total Saturates
** Typical Analysis From Southern Company Services
\++ Analysis Performed By UTRC Analytical Lab

Most of the coal liquids were either black, as-received, or turned black on exposure to air, so each drum was inerted with an N_2 blanket during use. The recycle solvent was very viscous and had a molasses-like consistency. All of the fuels except the 2% hydrotreated H-coal distillate had a very foul odor similar to creosote. The light organic liquid, being more volatile than the other coal liquids, emitted a nauseating odor whenever the fuel was exposed to the atmosphere. This made flowmeter calibration difficult despite an efficient ventilation system surrounding the test stand.

After experiencing difficulty in vaporizing the SRC wash solvent, an exact analysis showed a significant difference between the "typical" and as-received sample. The as-received sample had a much higher end point which was reported by the Southern Company Services to result from corrosion of the plates in the distillation column at the SRC plant due to the excessive chloride content of the SRC product from processing Kentucky No. 9 Coal. Subsequent modification of the SRC process was claimed to have eliminated the excess cloride.

The coal liquids were tested in the bench scale reactor with nozzle configuration 10. The catalyst loadings used in the tests listed in Table 4-4 varied but in each case were shown to be effective in operating on No. 2 fuel oil for a brief, 20-50 hour period. The fuel was then switched to the coal-derived liquid for comparison with the reference fuel.

In the first test, Run 8, the least refractory coal liquid sample, 2% H-coal distillate, was fed to the reactor containing the dual catalyst loading HGC-3020/HGC-1030 which had previously operated successfully on No. 2 fuel oil. No difficulty was encountered; the reactor operated carbon-free at $O_2/C = 0.38$ and 1170°F prereaction temperature and with fuel conversion comparable to the run with No. 2 fuel oil.

The reactor was then fed one of the more refractory fuels, the high boiling SRC wash solvent, in Run 9. There was increased scatter in the pressure drop data with this fuel, and at times it appeared that carbon burn-off was occurring. The reactor had to be shut down prematurely because of a plugged fuel filter and the carbon boundary was not fully explored. Since there appeared to be a problem in the vaporizer a heater was turned on in an attempt to fully vaporize the fuel. This resulted in large carbon deposits on the walls of the vaporizer, although no such problem had been evident with No. 2 fuel oil. Examination of the catalyst after the wash solvent test showed carbon deposits on the HGC-3020 catalyst surface. Analysis of the ash from combustion of the fuel filter indicated that it contained what appeared to be stainless steel corrosion products. Subsequent analysis of the wash solvent revealed the excess chloride content which was not predicted by the "typical" analysis of Table 5-1. No further tests were run with this fuel.

The reactor was recharged with PSD-1033, the active noble metal catalyst which also ran successfully on No. 2 fuel oil. However, with the refractory H-coal distillate, carbon formation occurred in Run 11. This is indicated in Figure 4-12 by the increasing pressure drop across the catalyst bed between hours 54 and 77. Twenty-three hours of testing were run with this fuel at an O_2/C ratio of between 0.35 to 0.50 and a pre-reaction temperature of about 1240°F (the same operating range as with the No. 2 fuel oil). The pressure drop across the catalyst increased continuously. At 64 hours the pressure drop across the catalyst bed decreased significantly when the reactor was placed in an overnight hot-hold condition which used steam and hydrogen to maintain reactor temperatures. This resulted in gasification of the carbon in the reactor. An automatic shutdown next day with hothold conditions again resulted in carbon gasification and a reduction in the reactor pressure drop. Testing with the H-coal distillate was terminated, and the fuel was switched to No. 2 fuel oil and continued. It can be seen from Figure 4-12 that the carbon-free operation with No. 2 fuel oil which had been run during the first

54 hours of testing could not be repeated. Visual examination of the catalyst pellets during reactor teardown showed some broken pellets at the reactor inlet and pellets which were "glued" together with a carbonaceous material. This aggregate was slightly magnetic. Since neither the noble metal nor the carbonaceous material are magnetic, it was assumed that the magnetic materials originated either from the H-coal liquid or from hardware corrosion.

In the final test series with coal liquids, Runs 13 and 14, the catalyst charge was selected to achieve maximum resistance to carbon formation and maximum fuel conversion. HGC-3020 metal oxide was therefore placed in the reactor inlet with high activity noble metal catalysts in the exit portion as noted in Table 4-4. This catalyst system processed 1% H-coal distillate and light organic liquid with no evidence of carbon formation at operating conditions consistent with the power plant design goal ($O_2/C = 0.35$ and 1153°F prereaction temperature). Furthermore, the fuel conversion at the exit of the reactor was 99% at a reactor exit temperature of 1500°F, i.e., it exceeded the power plant design goal.

As in Run 11, the H-coal distillate could not be processed at the same operating condition without carbon formation. Thus, in Figure 4-10, no change in pressure drop was observed with either of the less refractory fuels, but when the reactor was switched to H-coal distillate, a rapid increase in pressure occurred. In Run 14, however, there was a significant difference in response. After running on H-coal distillate, the reactor was placed on "hot-hold" conditions for the weekend, during which time the carbon was steamed off the HGC-3020 catalyst. The pressure drop returned to its initial value throughout the following run with the light organic liquid. Thus, HGC-3020 recovered from an episode of carbon deposition whereas PSD-1033, in Run 11, did not. Fuel conversion in the test with light organic liquid was similar to that with No. 2 fuel oil under comparable conditions.

The results of tests with coal liquids are summarized in Table 5-2. Carbon-free operation and conversion comparable to No. 2 fuel oil were obtained with hydrotreated H-coal distillates and SRC light organic liquid. The heavier fuels, which had higher end points and aromatic contents than No. 2 fuel oil, deposited carbon in the reactor. Due to the brief nature of the test series, little attempt was made to probe for conditions at which the reactor could operate with these fuels. Table 5-2, therefore, gives a preliminary assessment of the capability of the reactor to process coal-derived liquid fuels.

TABLE 5-2 COAL LIQUID TESTING IN THE ADIABATIC REFORMER

COAL LIQUID	RESULT
*2% H-Coal Distillate	Carbon Free
*1% H-Coal Distillate	Carbon Free
SRC Light Organic Liquid	Carbon Free
H-Coal Distillate	Carbon Formation
SRC Wash Solvent	Carbon Formation

*Percentage values refer to extent of hydrogen addition by hydrotreating.

Section 6

SYSTEM STUDIES

System studies were conducted to estimate the impact of the fuel processor performance and operating conditions on the power plant cost and heat rate. The objectives of the studies were:

- to determine the power plant sensitivity to the fuel processor characteristics and select design goals to guide the fuel processor research and development program,
- to determine the relative merits of alternate fuel processor concepts,
- to evaluate the impact of the advanced catalysts evaluated in this program.

The reference power plant for the system studies was a dispersed power plant operating at a heat rate of 9300 BTU/kWh at a rated power of 4.8 MW. The power section uses phosphoric acid fuel cells operating at a pressure of 50 psia. The fuel for the studies was No. 2 fuel oil with a H/C ratio of 1.82 and a higher heating value of 19,500 BTU/lb. For the purpose of the studies it was assumed that the nominal 2500 ppm sulfur in the fuel was removed from the fuel gas after the fuel processor by means of a regenerable metal oxide sulfur scrubber followed by a zinc oxide polisher.

The approach used in the studies was to optimize the system to maintain the power plant cost at a constant heat rate of 9300 BTU/kWh, the design goal. Similarly, the alternate fuel processors and advanced catalysts were evaluated by comparing power plant cost at the same heat rate. The general steps followed were:

1) Estimate the Fuel Processing Subsystem reactor size as a function of operating conditions and fuel conversion at a fuel flow of 2160 pounds per hour (9300 BTU/KWH @ 4.8 MW),

2) Calculate the Fuel Processing Subsystem efficiency from estimates of the energy required in the anode vent gas for the fuel process, reactant preheat, and the turbocompressor,

3) Determine the total fuel cell area required for operation at the cell voltage (power section efficiency) necessary for 9300 BTU/KWH heat rate, correcting the cell performance for fuel gas composition and hydrogen utilization effects, and

4) Estimate the relative power plant production cost based on the size of the fuel process reactor, the total cell area, and the heat exchanger sizes as determined in the previous steps.

Optimization of Power Plant with Adiabatic Reformer

The adiabatic reformer has been described in earlier sections of the report. It was the fuel processing concept which had been studied most thoroughly and was selected as the reference system for these studies. The flow schematic for the reference power plant is shown in Figure 6-1.

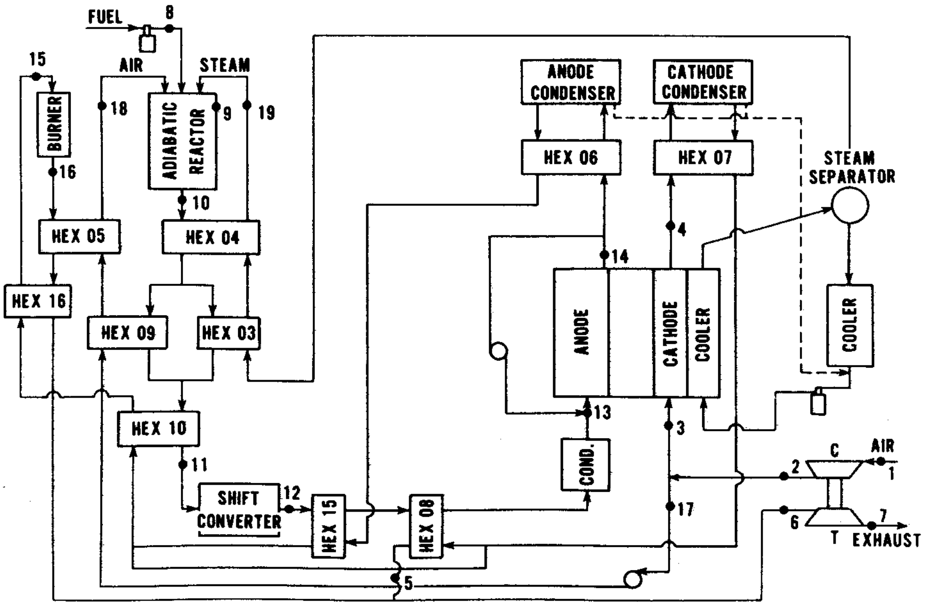


Figure 6-1. Reference Adiabatic Reformer Power Plant Schematic

The impact of the adiabatic reformer O_2/C ratio, reactor exit temperature, and fuel conversion was estimated using the adiabatic reformer model and the measured activity of the commercial nickel reform catalysts in the presence of sulfur. The activity of the commercial nickel catalyst used to size the reactant for the reference system, as well as the activity of advanced catalysts, is shown in Figure 6-2. The complete mass and energy balance throughout the system was determined by the power plant computer program and the fuel cell performance was estimated using the cell performance model. The power plant optimized at an O_2/C of 0.36, a reactor exit temperature of 1700°F, and a fuel coversion of 98.2%. These conditions were set as the initial goals for the adiabatic reformer development program which were listed in Table 1-1. Increasing the O_2/C ratio at a constant fuel conversion decreased the hydrogen produced which necessitates increasing the hydrogen utilization in the cell. Operation at utilizations above the design limit is possible by recycling gas from the anode vent. However, this was not cost effective due to the large impact on cell performance. On the other hand, operation at O_2/C ratios below the optimum was not cost effective due to the high cost of heat exchangers to preheat the reactants sufficiently to maintain a constant reactor exit temperature. The optimum reactor exit temperature and fuel conversion are a trade off between reactor size and heat exchanger requirements. The process flows and conditions for the critical locations in the powerplant are listed in Table 6-1 for the optimized conditions.

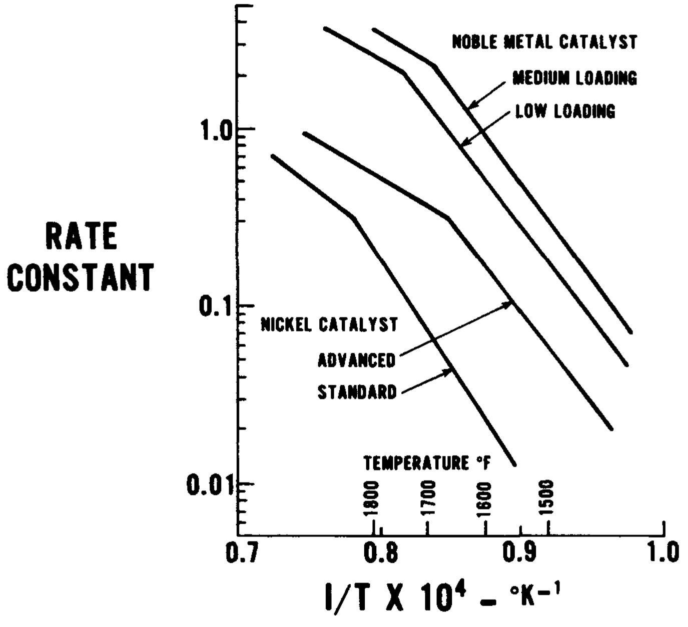


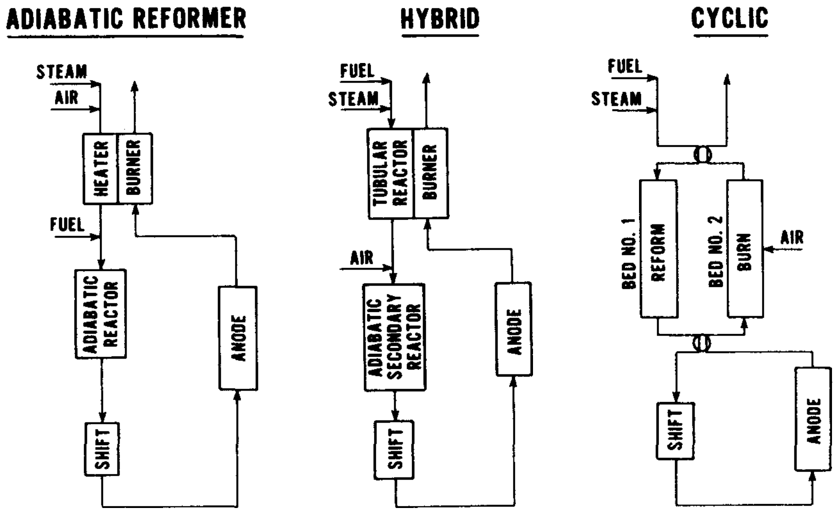
Figure 6-2. Activity of Fuel Processor Catalysts

TABLE 6-1 REFERENCE POWER PLANT PROCESS CONDITIONS

		Flows (Mols/Hr)								
Station	Temp.	H_2	H_2O	CH_4	CO	CO_2	O_2	N_2	Ar	Fuel (pph)
1	95						334.3	1242.9	15.6	
2	425						334.3	1242.9	15.6	
3	425						262.1	974.3	12.2	
4	375						104.8	974.3	12.2	
5	521						43.3	402.4	5.1	
6	689		141.9			155.9	107.5	1242.9	15.6	
7	399		141.9			155.9	107.5	1242.9	15.6	
8	95									2160
9	1363		585.6				56.4	209.8	2.6	2160
10	1700	284.7	436.4	2.7	45.4	107.9		209.8	2.6	
11	600	284.7	436.4	2.7	45.4	107.9		209.8	2.6	
12	672	323.2	397.9	2.7	6.8	146.4		209.8	2.6	
13	303	349.4	280.2	10.7	27.3	585.6		839.4	10.5	
14	375	34.9	280.2	10.7	27.3	585.6		839.4	10.5	
15	1442	8.7	88.5	2.7	6.8	146.4	77.2	839.4	10.5	
16	1760		102.6			155.9	64.1	839.4	10.5	
17	425						56.4	209.8	2.6	
18	1625						56.4	209.8	2.6	
19	1622		584.6							

Evaluation of Alternate Fuel Processors

Two alternate fuel processing systems were evaluated, the hybrid and the cyclic reformers. Very simplified diagrams illustrating the fundamental differences of the three fuel processors are shown in Figure 6-3. For the adiabatic reformer the fuel, steam and air react in an adiabatic reactor. The combustion within the reactor of part of the fuel with air provides the process heat required to be active in the presence of sulfur. The anode vent gases are burned and the heat used to preheat the reactants. This minimizes the amount of air required.


ADIABATIC REFORMER

HYBRID

CYCLIC

Figure 6-3. Fuel Processing Systems Evaluated

The hybrid fuel process has two reactors, a tubular (thermal) reformer and a secondary (adiabatic) reformer. The fuel and steam first enter the tubular reformer in which the process heat is provided by external combustion of the anode vent gases. This heat is transferred through the reactant walls to the catalyst. The requirement for the very high temperatures associated with thermal steam reforming are reduced by only partially converting the fuel. The fuel conversion is completed in the secondary reformer. The process heat provided in the thermal reformer reduces the heat and thus the air required in the adiabatic reformer.

The cyclic reformer consists of two reactors. During the make cycle fuel and steam enter the reactor and are converted to hydrogen using the heat stored in the catalyst. On the burn cycle the anode vent gases are burned in the reactor, reheating the catalyst. In this manner the process heat and high catalyst temperatures can be provided without transfer of heat through a wall or combustion of fuel upstream of the fuel cell.

The performance and size of the tubular reformer in the hybrid system were estimated as a function of reactor temperatures and fuel conversion. Estimates were made using the catalytic steam reformer tubular reactor model and the measured catalyst activity in the presence of sulfur. The secondary reformer size was estimated as a function of the inlet and exit fuel conversions and the reactor exit temperature. The fuel processor estimates were used in the system model to optimize the power plant exit temperature of 1510°F and a fuel conversion of 63%. The secondary reformer optimized at an exit temperature of 1640°F, 95% fuel conversion, and O_2/C ratio of 0.19.

Adequate models were not available to optimize the cyclic reformer reactors. The reactor size and cost were based on the results of preliminary tests with a small single bed reactor. The cyclic reformer was integrated into the powerplant system thermodynamically. The high efficiency potential of the cyclic reformer could not be fully utilized since the anode vent energy had to be increased to provide sufficient energy for the turbocompressor. The fuel conversion optimized at 94%.

The characteristics of the power plant with the three fuel processors are compared in Table 6-2. The fuel processor efficiency increases, the optimum fuel conversion decreases, and the process gas quality improves as the O_2/C ratio of the fuel processor decreases. The hybrid FPS offers the potential of reducing the power plant cost 15%, and the cyclic reformer might reduce the cost an additional 9%.

The critical factor will be the ability of these fuel processors to operate at the conditions assumed.

TABLE 6-2 COMPARISON OF POWER PLANTS WITH ALTERNATE FUEL PROCESSORS (STANDARD NICKEL CATALYSTS)

FPS	ADIABATIC	HYBRID	CYCLIC
O_2/C	0.36	0.19	0.0
Thermal Efficiency (%)	83.0	85.0	87.3
Fuel Conversion (%)	98.2	95.0	93.8
Reaction Exit Temp. (°F)	1700	1640	-
Fuel Quality * (Vol % Dry)			
H_2	19.2	57.3	72.4
CO	1.5	1.0	1.0
Power Section			
Volts/Cell	.628	.612	.595
ASF	208	293	340
Relative Power Plant Cost Cost (%)	100	85	76

* After Shift Conversion

Evaluation of Advanced Catalyst in Fuel Cell System

During this program, the technology group developed an advanced nickel and a noble metal catalyst. The activity of these catalysts is 5 to 20 times higher than the activity of the standard commercial nickel catalyst, as shown in Figure 6-2. System studies were conducted to evaluate these two advanced catalysts plus an assumed low loaded noble metal catalyst. The catalysts were evaluated for use in power plants with three different fuel processors: an adiabatic reformer, a hybrid reformer, and a thermal steam reformer.

The adiabatic reactor model was utilized to estimate the reactor size required with each catalyst to achieve a fuel conversion of 98.5% at the design fuel flow of 2160 pph. At a reactor exit temperature of 1700°F, the high activity of the noble metal catalysts reduce the adiabatic reactor size 80% compared to the size with standard nickel catalyst. The advanced nickel catalyst reduced the required reactor size 40% (Figure 6-4a). However, due to the high cost of the noble metal, the advanced nickel or the low loaded noble metal catalyst is most effective (Figure 6-4b). Either catalyst reduces the reactor cost 60%. Even the medium loaded noble metal catalyst is cost effective compared to the standard nickel catalyst. The reactor sizes were estimated assuming a metal oxide catalyst at the inlet to lower the carbon formation limit and permit operation at the design O_2/C of 0.36. Studies were conducted to investigate whether dual loading of the advanced nickel and noble metal catalysts might be more cost effective. In all cases, the advanced nickel catalyst was the optimum.

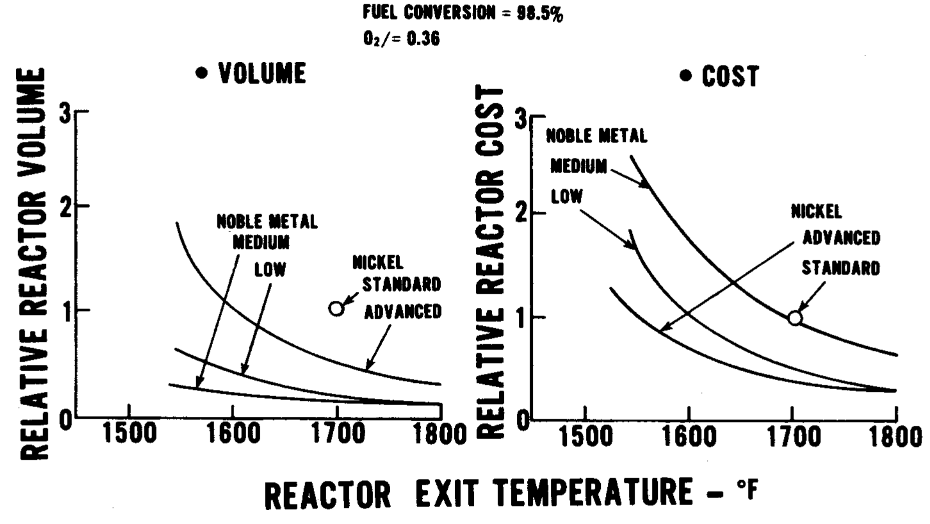


Figure 6-4. Catalyst Impact on the Adiabatic Reformer

The impact of the advanced catalysts on the power plant, including the adiabatic reformer, was estimated. At the design reactor temperature of 1700°F, the advanced nickel or low loaded noble metal catalyst reduced the power plant cost 3%. The studies showed that it was more cost effective to utilize the high catalyst activity to reduce catalyst operating temperature as well as size. Decreasing the reactor exit temperature lowers the reactant preheat required, decreasing the heat exchanger cost. Thus, with the advanced nickel catalyst, a 5% reduction of power plant cost relative to the cost of the reference power plant with standard nickel catalyst is possible at the optimum reactor exit temperature of 1600°F (Figure 6-5). The fuel conversion optimized at 98.8%.

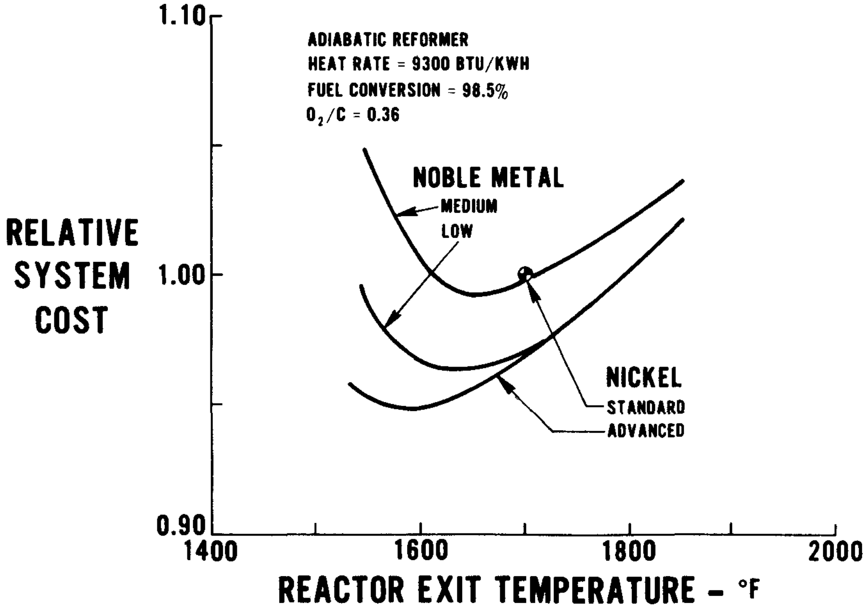


Figure 6-5. Catalyst Impact on Power Plant Cost

The impact of the higher activity of the advanced catalyst on the performance of the tubular (thermal) reactor of the hybrid Fuel Processing Subsystem was estimated using the catalyst steam reformer reactor model. The calculations showed that the higher catalyst activity had a small impact on the reactor size since its performance is limited by heat transfer as well as catalyst activity. The catalyst impact on the secondary reactor was similar to that of the adiabatic reformer Fuel Processing Subsystem. The fuel conversions and operating temperatures of the primary and secondary reformers were otimized for eight different combinations of catalysts in the primary and secondary reactors. The optimum combination was with the advanced nickel catalyst in both reactors. The optimum primary fuel conversion was 59% and the optimum secondary fuel conversion was 93.5%. At these optimum conditions, the sum of the cost of the two reactors was 28% less than the reactor cost with standard nickel catalyst. The power plant cost was reduced 3% relative to the cost of the hybrid Fuel Processing Subsystem using standard catalysts and 16% less than the reference system.

The thermal steam reformer reactor size was estimated for the advanced nickel and the medium loaded noble metal catalyst activity. The estimates were made using the catalytic steam reformer model. The reactor sizes were estimated for a fuel conversion of 87.5% at a constant wall temperature. With the advanced catalysts the reactor cost was 54% lower. Lower fuel conversions would probably optimize the power plant cost. This was not studied because the fuel cell might not be able to tolerate the higher hydrocarbons that are likely to be present in the fuel gas at lower conversion. At the fuel conversion selected, the power plant cost with the TSR fuel processor is 10% lower than the reference system and 5% less than the adiabatic reformer power plant with advanced nickel catalyst. The tubular reactor estimates for the hybrid and Thermal Steam Reformer systems were made assuming that the advanced catalysts could be loaded over the full length of the reactor. There is a good possibility that to prevent carbon formation, a low activity, carbon-tolerant catalyst will be needed at the reactor inlet, similar to that in the adiabatic reformer. The reactor model was used to estimate the increases in reactor size as a function of the tempterature at which the transition from an inlet catalyst to the advanced nickel catalyst occurs. There was no effect at transition temperatures up to 1400°F. A transition temperature of 1700°F doubled the reactor size required and increased the hybrid and Thermal Steam Reformer power plant cost 5-7%.

The effect of heat rate on the power plant cost was estimated for each of the three fuel processors loaded with the advanced nickel catalysts and operating at the optimum conditions (Figure 6-6). The tubular reformer costs in the hybrid and Thermal Steam Reformer systems are based on the 1700°F transition temperature. All of the systems could be designed with heat rates as low as 8300 BTU/KWH. The minimum cost is achieved with the power plant using a hybrid Fuel Processing Subsystem.

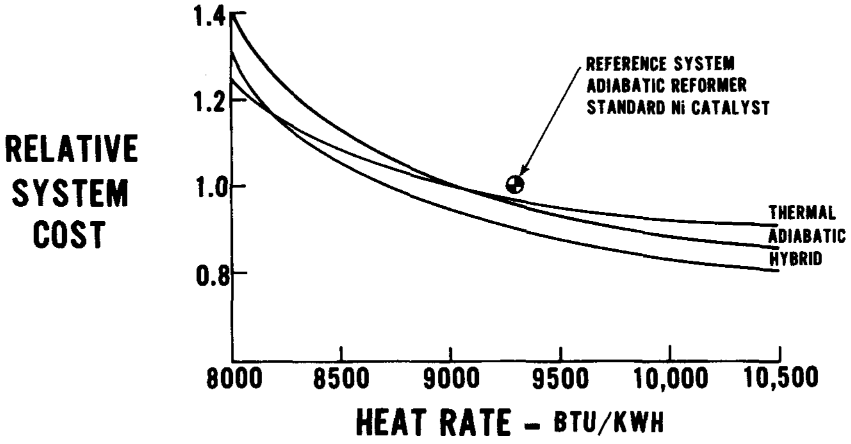


Figure 6-6. Comparison of Alternate Fuel Processors

As illustrated by the impact of transition temperature on the tubular reformer performance, the validity of the results of these systems studies are critically dependent upon the ability of the fuel processors to operate at the conditions selected. Runs 17 and 18 in the bench scale adiabatic reactor demonstrated operation at the design O_2/C and exit temperatures. The fuel conversion was less than the design value since the space velocity was much higher than design, but the conversion agreed closely with the model estimates (Figure 6-7). The model for the thermal (tubular) reformer has not been verified experimentally. The thermal reformer should be demonstrated and the transition temperature determined in order to select the optimum fuel processing system. The advanced nickel and a low loaded noble metal catalyst are equivalent. Final selection will depend upon other factors such as tolerance, strength, and life.

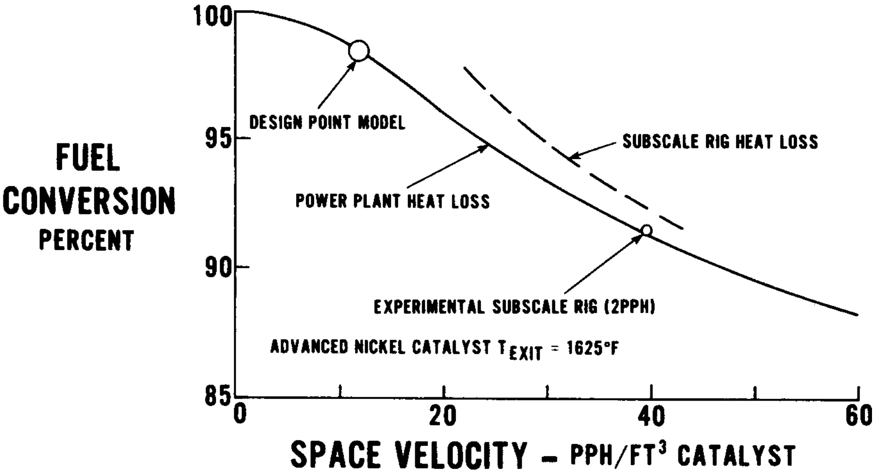


Figure 6-7. Comparison of Adiabatic Reformer Design Point and Experimental Reformer

Section 7

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