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Advanced Turbine Systems Program
Conceptual Design and Product Development
Task 8.3 -- Autothermal Fuel Reformer (ATR)

Topical Report

November 1996

Work Performed Under Contract No.: DE-AC21-93MC30246

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Solar Turbines Incorporated
San Diego, California

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EXECUTIVE SUMMARY

Autothermal fuel reforming (ATR) consists of reacting a hydrocarbon fuel such as natural gas or diesel with steam to produce a hydrogen-rich "reformed" fuel. The ATR task work has been designed to investigate the fuel reformation and the product gas combustion under gas turbine conditions. The hydrogen-rich gas has a high flammability with a wide range of combustion stability. Being lighter and more reactive than methane, the hydrogen-rich gas mixes readily with air and can be burned at low fuel/air ratios producing inherently low emissions. The hydrogen-rich reformed fuel also has a low ignition temperature which makes low temperature catalytic combustion possible – another factor contributing to low NOx emissions. ATR can be designed for use with a variety of alternative fuels including heavy crudes, biomass and coal-derived fuels. When the steam required for fuel reforming is raised by using energy from the gas turbine exhaust, cycle efficiency is improved because of the steam and fuel chemically recuperating.

Reformation of natural gas or diesel fuels to a homogeneous hydrogen-rich fuel has been demonstrated. Performance tests on screening various reforming catalysts and operating conditions were conducted on a batch-tube reactor. Producing over 70 percent of hydrogen (on a dry basis) in the product stream was obtained using natural gas as a feedstock. Hydrogen concentration is seen to increase with temperature but less rapidly above 1300°F. The percent reforming increases as the steam to carbon ratio is increased. Two basic groups of reforming catalysts, nickel- and platinum-basis, have been tested for the reforming activity. The test results indicated that the reactant conversion and product distribution remained about constant for both nickel and platinum catalysts. However, the nickel-basis with lanthanum promoted catalyst converted natural gas to more CO instead of CO_2 and yielded a higher heating value of product gas than other catalysts.

Autothermal fuel reformation system durability tests were conducted to investigate the catalyst life and the effect of acidic compounds (e.g., H_2S, HCl) found in raw natural gas on the reforming performance. An absorbent consisting of zinc and calcium dual-oxides was selected for removing these acidic species and served as a polishing step to ensure a consistent fuel quality. The durability tests with an absorber bed resulted in obtaining high hydrogen (65 to 75 percent on a dry basis) product gases under the steady-state operation. No catalyst deactivity was found after the extended testing when using a fuel mixed with hydrogen sulfide (H_2S) at a concentration of 200 times higher than that in the local natural gas. Analyses of the used catalyst by electronic diffraction X-ray showed no accumulation of sulfur on the catalyst. The results also indicated that the catalyst activity can be regenerated by steaming the used catalyst after duration testing.

Tests of liquid (diesel) fuel reformation using the ATR batch-tube reactor have confirmed thegeneration of 60 to 65 percent hydrogen (on a dry basis) in the product stream. The tests also demonstrated the system tolerance for high sulfur content in the liquid fuel. Meanwhile, the product gas ignition can be achieved without torch ignitor assistance at low temperatures (approximately 800°F). A comparison of the ignition behavior of reformed product gases showed that the ignition energy of the hydrogen rich gas is much less than that of natural gas. Unlike the natural gas, the product streams with hydrogen above 37 percent (on a dry basis) were ignited easily without torch assistance when using either diesel fuel or natural gas as the feedstock. This low ignition energy requirement is one of the benefits of reforming conventional fuels to a hydrogen-rich product gas for combustion in a gas turbine.

The ATR test rig has been designed for investigation of fuel reformation and product gas combustion under gas turbine conditions. The rig design utilizes an injector for premixing of fuel and steam. A pilot combustor was included which partially combusts the fuel to provide the heat required for raising the steam/fuel mixture to the reformation temperature. In the rig design, the heated steam/fuel mixture passing through the reforming catalyst produces a hydrogen-rich reformed fuel which is delivered to a lean-burn post-combustor where its heat content and emissions characteristics are determined.

Initial ATR rig tests were conducted at reforming temperatures of 1300° to 1600°F under operating pressures of 60 to 120 psig. Steam was injected at steam-to-fuel ratios in the 0.3 to 1.0:1 range and passed through a nickel-based reforming catalyst coated on a ceramic monolith. Results from the tests are positive in that a stable burning of product gas was maintained and controlled with an easy ignition, stable flame, moderate pressure drops and burning without the assistance of a torch ignitor and auxiliary fuel. Further tests are needed to demonstrate the low emissions and high thermal efficiency as steam and fuel chemically recuperate.

Results of the test work suggest that fuel reformation is a promising approach to the clean combustion for gaseous and liquid fuels. The unusual fuels that normally present problems with meeting clean air requirements could be handled via fuel reforming to generate hydrogen-rich gases prior to combustion. Fuel reformation would allow a single fuel injector and combustion system to be employed in a gas turbine regardless of the parent fuel to meet customer specified requirements. A fully developed autothermal reformer would bring fundamental benefits to the advanced turbine system (ATS) on reducing emissions, increasing thermal efficiencies and improving fuel flexibility.

SECTION 1

INTRODUCTION

Fuel reformation rearranges and reforms a primary fuel such as natural gas or diesel with water, as steam, to produce a hydrogen-rich gaseous secondary fuel. The reformed fuel has a heating value (on a mass flow basis) greater than that of the parent fuel. The secondary fuels reformed from paraffinic materials have high hydrogen contents and this makes them desirable from an ease of combustion viewpoint. A hydrogen-rich gas has a wide flammability limit which contribute significantly to the stability of the combustion process. A wide flammability limit will benefit combustor light off, turbine cold/hot flameout and combustion efficiency during light off and acceleration. The wide range of combustion stability provided by the high hydrogen reformed fuel would also allow the operation of most combustion systems at low fuel/air ratios where low NOx is produced. Solid fuels such as coal, biomass, or other carbonaceous materials can also be reformed via gasification.

A fuel with a high hydrogen content is lighter and more reactive than the original fuel and it mixes better with the combustor air. The hydrogen in the combustible stream enhances the flame stability and speeds the burn rate through the combustion zone. Hydrogen would lower the lean flammability limit and draw the flame towards the head end of the combustor, allowing greater residence time for CO burnout to reduce CO emissions. It can also be burned at much leaner conditions (low flame temperatures) producing lower NOx in exhausts. The ignition energy of the hydrogen rich gas is much less than that of natural gas, a major factor in making low temperature catalytic combustion possible.

The fuel reformation with steam may formally be depicted by the following equations:

$$C_nH_m + n\,H_2O = n\,CO + (n + m/2)\,H_2 \qquad [1]$$

$$CO + H_2O = CO_2 + H_2 \qquad [2]$$

$$CO + 3\,H_2 = CH_4 + H_2O \qquad [3]$$

When hydrocarbons (CnHm) in the fuel and steam (H_2O) are heated together to a temperature of approximately 1250 - 1500°F, the hydrocarbons begin to decompose and react with the steam to form hydrogen (H_2) and CO. Equation [1] is endothermic and is generally considered to be irreversible. The product distribution of steam reforming is governed by the water-gas shift [2] and methanation [3] reactions. In the fuel reforming, the rate-determining step appears to be the catalytic surface reactions between adsorbed CHx and OH species. It is generally agreed that the fuel reforming activity will be dependent on the accessibility of catalyst surface area where the surface being covered with adsorbed OH groups for reactions with the hydrocarbon fragments.

Steam reforming requires a thermal input to raise the reactant temperature for proceeding the reforming reactions. In autothermal reforming, this energy is internally supplied by partial oxidation of a portion of the parent fuel,

$$C_nH_m + n/2\,(O_2 + 3.76\,N_2) = m/2\,H_2 + n\,CO + 1.88n\,N_2 \qquad [4]$$

In autothermal reforming, air ($O_2 + 3.76\ N_2$) reacts with parts of the fuel to provide heat. Then, when the bulk of fuel is heated by absorbing thermal energy, it dissociates into smaller fragments. The partial combustion reaction [4] is exothermic providing the energy for the intra-bed steam reforming reaction [1]. In practice a small quantity of fuel and air is burned separately and the products mixed with the heated steam and fuel, resulting in simplified hardware and enhanced load-following ability.

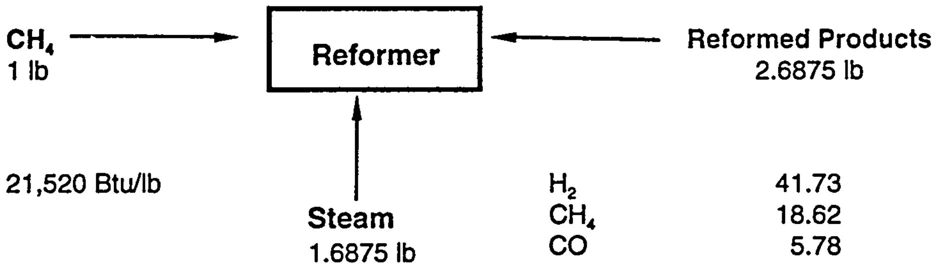
The steam reformation of fuel in gas turbines utilizes the heat removed from the intercooling and the engine exhaust. Recovering the waste thermal energy in the form of steam and then converting it to hydrogen which chemically recuperates a gas turbine engine enhances the system efficiency. The reforming of fuels would produce the same primary constituents (albeit in differing proportions) regardless of the parent fuels, thereby allowing a single fuel injection and combustion system to be employed. This is particularly important with catalytic combustion systems, which usually require separate catalysts of differing compositions for each fuel. Therefore, the fuel reformation permits the use of a single catalyst composition for the reactor section, thus making the system fuel independent for the ATS and is capable of being adapted to a wide range of fuels to meet customer specified requirements.

SECTION 2

FUEL REFORMING - CHEMICAL RECUPERATION

In the reformation process, the steam and fuel are heated via a heat exchanger which utilizes the engine exhaust heat. The heated fuel stream is then passed through a catalytic reformer where steam reacts endothermically with the fuel to produce a hydrogen-rich product gas. Because the endothermic heat required for the fuel reformation would be added/transferred to the product stream internally and chemically, this heat could be converted into the final total heating value of product gas at near 100 percent efficiency. The sensible and latent heat of the steam will be incorporated into the secondary fuel as chemical energy. That is to say, the final heating value of the product gas (on a mass basis) would exceed the heating value of the reactants by an amount equal to the endothermic heat of reactions. Therefore, when the steam used for the reformation is raised from the turbine exhaust, cycle efficiency would be improved leading to the term "chemical recuperation". Chemical recuperation via fuel reformation recovers the engine exhaust heat while minimizing the losses from combustion interfection and superfluous air. Chemical recuperation is applicable to most turbine cycles including simple cycle, recuperated, and intercooled/recuperated.

Under equilibrium conditions, the reformation of natural gas (methane) with steam yields the product stream as listed in Table 1 where the operation temperatures are varied but the steam-to-carbon molar ratios of feed are kept at one and at one-and-half. The steam/carbon molar ratio of 1.5:1 would translate to a steam/methane mass ratio of 1.6875. Thus for each pound of methane that comes into the system there would be 2.6875 pounds of the steam/methane mixture enter the reformer and 2.6875 pounds of the reformed product leaving it as follows:



LHV 21,520 Btu/lb

Available Energy Flow 21,520 Btu/unit time

H_2	41.73
CH_4	18.62
CO	5.78
CO_2	6.10
H_2O	27.77
LHV	8737 Btu/lb

Available Energy Flow 23,481 Btu/unit time

With the appropriate product distribution as listed in Table 1 for the 1300°F case, the product stream has a lower heating value of 8737 Btu/lb that when multiplied by 2.6875 provides an "available" energy flow of 23,481 Btu/unit time. The 1 lb/unit time of methane entering the system has a lower heating value of 21,520 Btu/lb and this provides a chemical energy flow of 21,520 Btu/unit time.

Table 1. Steam Reforming Products*

Steam / Carbon = 1.5				
Temperature (°F)	**1200**	**1250**	**1300**	**1500**
Composition (vol%)				
H_2	33.95	37.84	41.73	55.85
CH_4	23.32	21.04	18.62	9.05
CO	3.05	4.29	5.78	12.92
CO_2	6.20	6.24	6.10	4.27
H_2O	33.45	30.59	27.77	17.91
LHV (Btu/lb)*	8523	8623	8737	9299
(Btu/ft^3)	316	310	303	278
Steam / Carbon = 1.0				
Temperature (°F)	**1200**	**1250**	**1300**	**1500**
Compositon (vol%)				
H_2	33.10	36.97	40.90	55.64
CH_4	31.71	29.08	26.23	15.01
CO	3.49	4.88	6.54	14.34
CO_2	5.66	5.58	5.32	3.15
H_2O	26.05	23.49	20.96	11.86
LHV (Btu/lb)*	10,648	10,753	10,874	11,389
(Btu/ft^3)	392	383	374	336

*Product distributions and heating values on a wet basis.

The ratio of the energy flow leaving the reactor to that entering is thus 1.091 (obtained from dividing 23,481 by 21,520). This means that the product gases leaving the reactor have an increase in chemical energy flow of 9.1 percent. For a constant energy input into the engine the fuel reformation process would allow the methane input to be reduced by 9.1percent and thus the overall efficiency to be increased by a factor of 1.091. This calculation ignores any parasitic losses and assumes that the heat flows in the recuperator flowing the reactor are constant and are not affected by the reformation heat exchanger. If a similar calculation is performed for the 1500°F case it will be found that the efficiency improvement multiplier is approximately 1.161 which represents a significant gain in efficiency. Figure 1 plots the thermal efficiency increment as a function of temperature for fuel reformation at a steam-to-carbon ratio of 1:1 and 1.5:1.

The steam reformation of fuel utilizing the heat removed from the engine exhaust is shown schematically in Figure 2. Recovering the waste thermal energy in the form of steam and then converting it to a hydrogen-rich reformed gas which chemically recuperates a gas turbine fuel enhances the system efficiency. In operation, the steam for the reformer can be raised from the engine hot exhaust. The fuel reformation would generate a mixture of hydrogen and carbon monoxide to be burned in a lean condition.

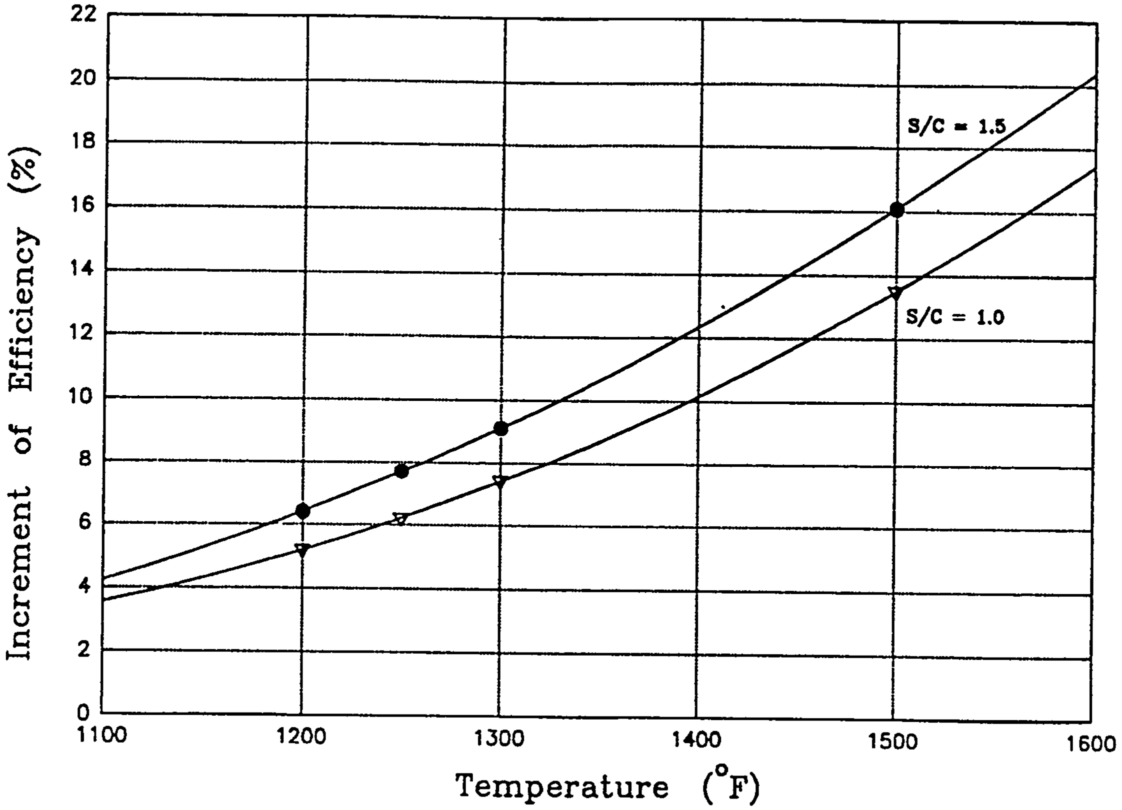


Figure 1. Thermal Efficiency Increment as Chemical Recuperation by Fuel/Steam Reforming

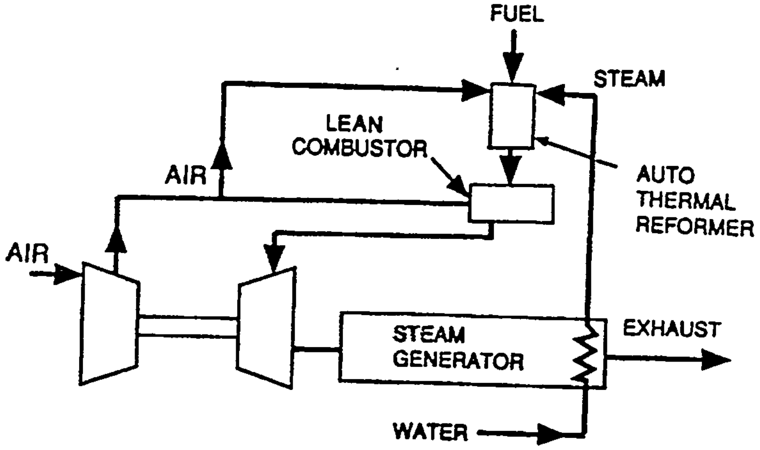


Figure 2. Integrated Steam/Fuel Reformer

Liquid fuels will require vaporization and cracking of fuel macro-molecules before the resulting secondary fuel can be reformed. Similarly, solid fuels (i.e., biomass, coals) and undesirable heavy crudes can be readily used by gas turbines, if they are first gasified or hydrocracked. Although the ATS is primarily designed to utilize natural gas as a fuel source, with a fuel reformer the system would be adaptable to a wide range of fuels. Dual fuel or even multi-fuel capability are options available with fuel reformation that will broaden the ATS market applicability.

SECTION 3

REFORMING CATALYST/PARAMETER SCREENING

An effective fuel reforming catalyst requires the maintenance of a desired activity over its lifetime. Care must be taken in the proper catalyst selection and reformer design in order for the reformer to perform effectively. Any known catalyst poisons or deactivators need to be carefully identified. Sulfur poisoning, catalyst migration, and substrate durability are contriibutors to the problems of catalyst life. Sulfur in natural gas is known to poison the commercial steam/methane reformation catalyst. The selection of a sulfur-tolerant catalyst is one of the critical material requirements for the processing of autothermal reforming. This section centers on screening reforming catalysts and determining the effect of reformer operating conditions upon catalyst performance. Sulfur-tolerance duration tests, liquid fuel reformation, and reformed fuel combustion are also included and discussed.

3.1 REFORMING OPERATION CONDITIONS

The operating conditions of inlet temperature and steam/methane ratio are varied to optimize the catalyst activity. In the tests, a bench scale tube reactor is used to screen the reforming catalyst. The bench reactor (Figure 3) contains a one-inch diameter stainless steel tube heated with an electric furnace. The reactor furnace is 36 inches long with three temperature control zones. The temperature in each zone can be controlled and programmed at specified rates. The screening tests have been run using a 1-inch diameter of monolith or foam which is coated with reforming catalysts to 1) determine the catalyst activity and 2) select an optimal operating condition. Preheated natural gas and steam are mixed before entering the catalytic conversion zone. The fuel used in the test was pipeline quality natural gas, containing about 1 ppmv of H_2S (hydrogen sulfide). Typical compositions are:

	Composition (mol %)
Methane	92.79
Ehane	4.16
propane	0.84
Butane	0.18
Penane	0.04
C_6 +	0.04
Carbon Dioxide	0.44
Nitrogen	1.51
Hydrogen Sulfide	1. ppm

During a test run, the product gas samples are taken at various time intervals. Once collected the samples are analyzed for hydrogen and other gas components with a fast, high sensitive gas analyzer (Microsensor Technology Inc., Model M200). The MTI analyzer is equipped with two 0.32 mm (i.d.) and 4 m (length) capillary columns, packed either with molsieve or Poraplot U, for product gas analyses. The MTI analyzer has been calibrated with standard gases (H_2, CH_4, CO, CO_2, etc.) in the range of the measurements being made. Figure 4 shows a typical chromatogram of reforming product gas in which a hydrogen peak dominates. Trace amounts of O_2, N_2, CH_4, and CO only can be seen after zooming the chromatogram at a very high sensitivity level (from 10.00 to 0.45 volts in the scale as indicated in Figure 4).

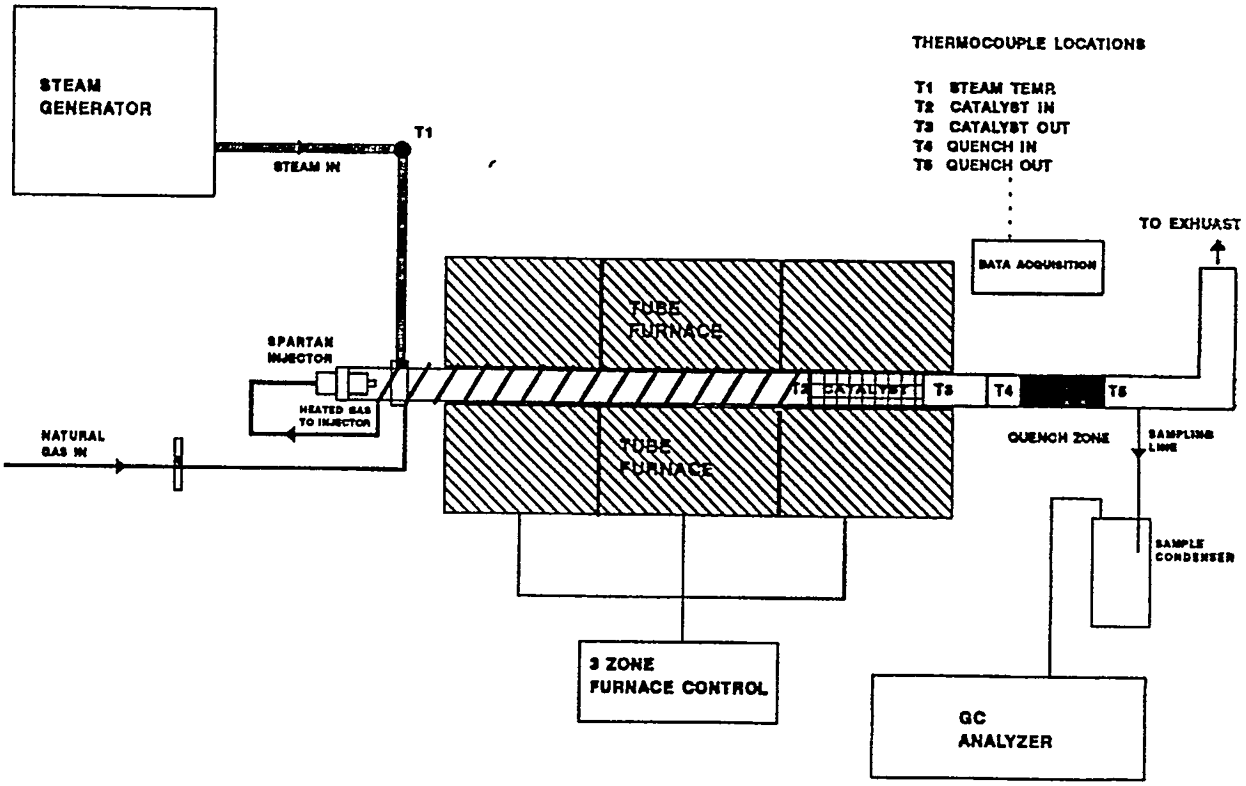


Figure 3. Tube Reactor for Reforming Catalyst Screening Tests

Several catalyst candidates and operating conditions are prescreened to select a primary catalyst and operating conditions for the autothermal reforming rig testing. Figure 5 shows the test results on producing hydrogen in the product stream as functions of temperature and steam to carbon ratio (S/C, carbon in natural gas). Hydrogen concentration increases remarkably with temperature below 1300°F but beyond this point the advantage of higher temperature is less pronounced. The equilibria of the reactions involved in steam reformation depend largely on the operating temperature and steam-to-carbon ratio. The percent reforming increases as the temperature and the steam-to-carbon ratio are increased.

The equilibria of the reactions between steam and natural gas (methane) depend also strongly on the operation pressure of the reactor. The reactions of steam-natural gas reforming can be depicted by the following equations:

$$CH_4 + H_2O = CO + 3H_2 \qquad [5]$$

$$CO + H_2O = CO_2 + H_2 \qquad [6]$$

Using mole fractions or partial pressures, the relationship between the pressure, gas composition, and equilibrium constant at any temperature can be expressed by the equation for the reaction [5]:

$$K_1 = \frac{(P_{H_2})^3 \ (P_{CO})}{(P_{CH_4}) \ (P_{H_2O})} = \frac{(X_{H_2})^3 \ (X_{CO}) \ (P_T)^2}{(X_{CH_4}) \ (X_{H_2O})}$$

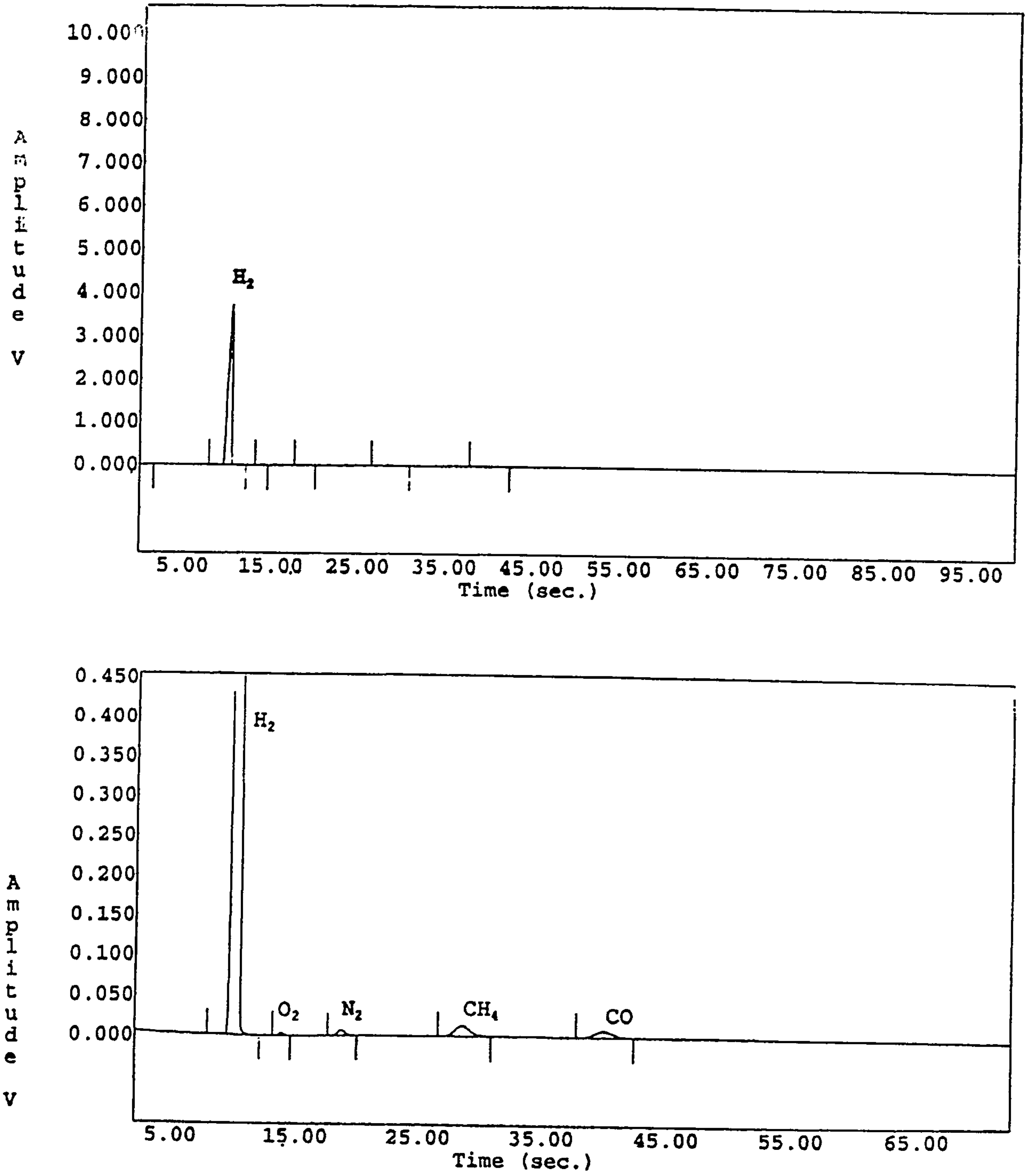


Figure 4. Typical Chromatographic Analyses of Reforming Products

where

K = equilibrium constant of the reaction
P = partial pressure of a component in the gas stream
X = mole fraction of a component in the gas stream
P_T = total pressure of gas in atmospheres

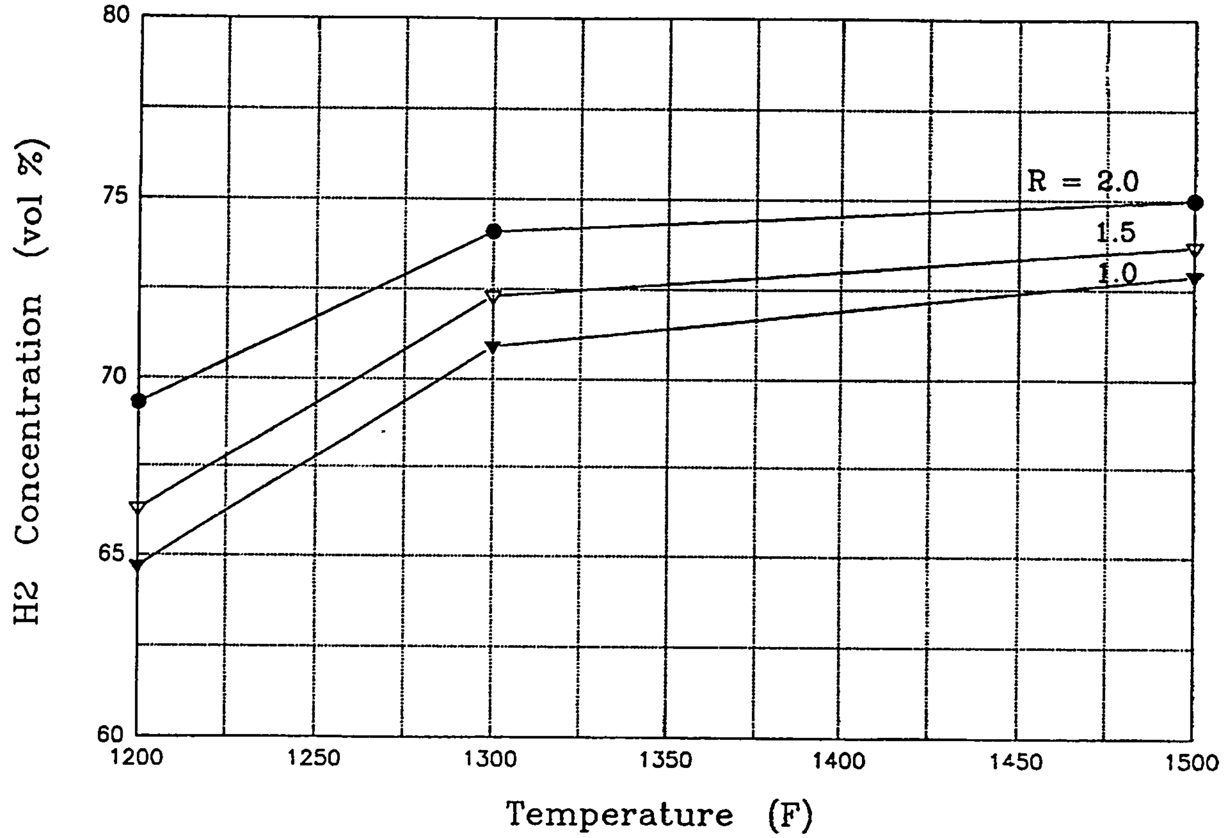


Figure 5. Test Results of Hydrogen Produced as Functions of Temperature and Steam to Carbon Ratio (R)

From the expression for K_1, it is apparent that the quantity of hydrogen produced at equilibrium varies with the pressure. Since another equilibrium also exists from the reaction [6], the yield of hydrogen from the steam and natural gas must also satisfy the equation:

$$K_2 = \frac{(X_{CO_2})\ (X_{H_2})}{(X_{CO})\ (X_{H_2O})}$$

From the above expression, pressure does not affect the value for equilibrium constant (K_2) of reaction [6].

The maximum possible reforming of methane to hydrogen is limited by equilibrium at given conditions of temperature, pressure and steam-to-carbon ratio. Conversion efficiency (expressed as hydrogen concentration in product gases on a dry basis) as functions of the temperature and pressure at various steam to carbon ratios are shown in Figures 6 through 8. The percent reforming with the hydrogen production increases as the temperature and steam to carbon ratio are increased and decreases as the pressure is increased. At higher operating temperatures the reformation reactions are less dependant on pressure. Autothermal reformation burns some of the methane fuel for raising the temperature to accelerate the reactions and to gain a higher level of reforming (more hydrogen production).

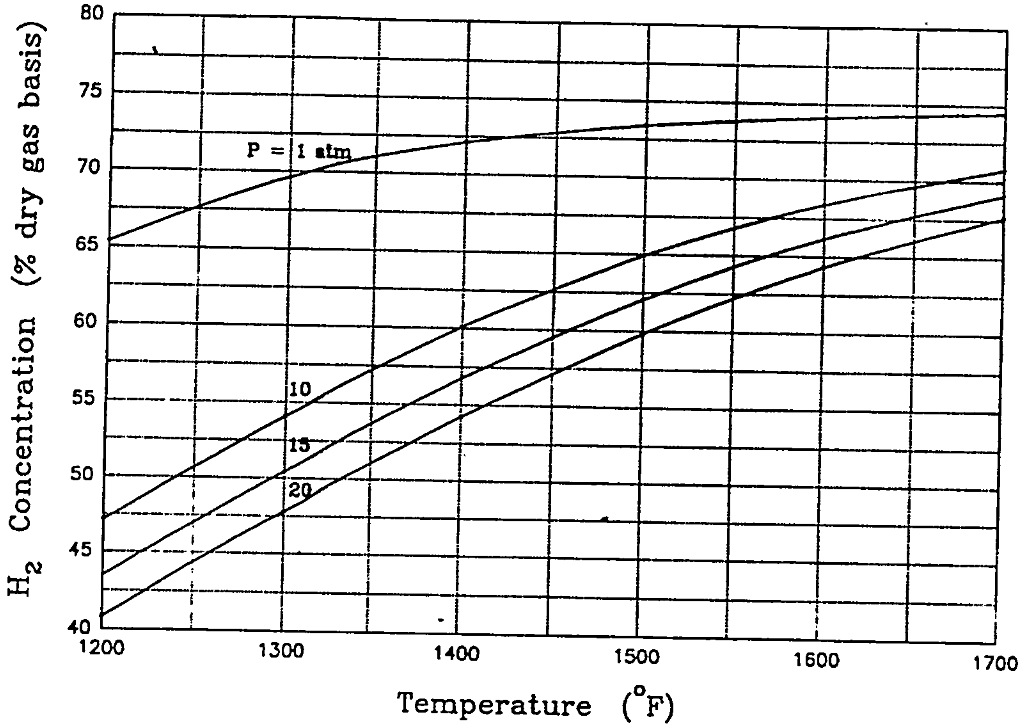


Figure 6. Reforming Efficiency (expressed as hydrogen concentration in product gas) as Functions of Temperature and Pressure at R (Steam to Carbon Ratio) = 1.0

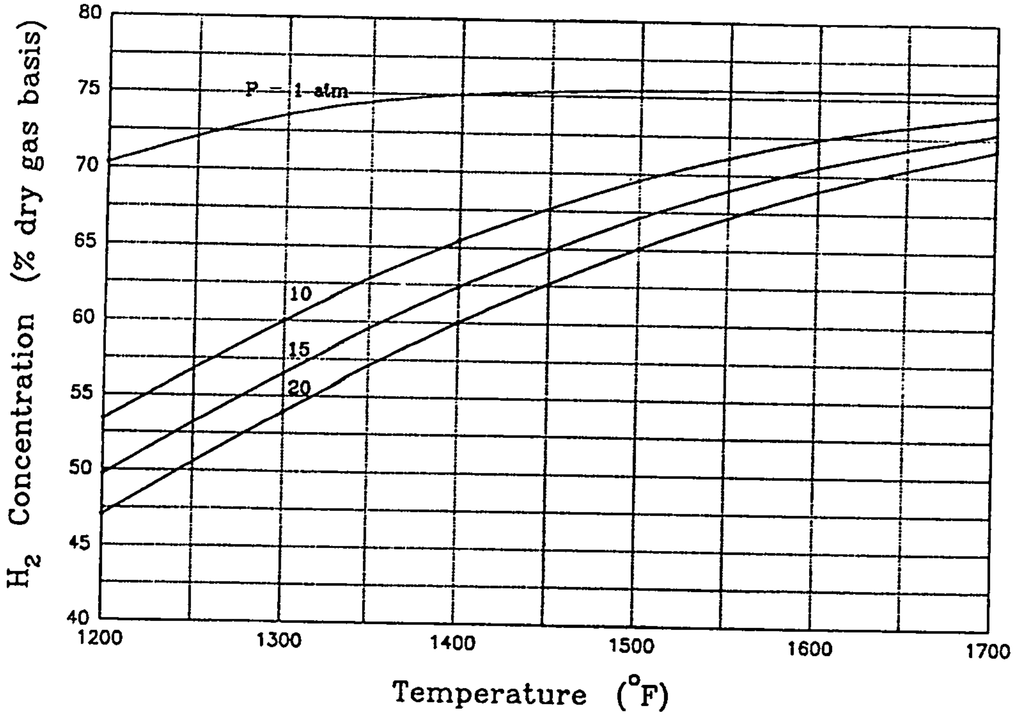


Figure 7. Reforming Efficiency (expressed as hydrogen concentration in product gas) as Functions of Temperature and Pressure at R (Steam to Carbon Ratio) = 1.5

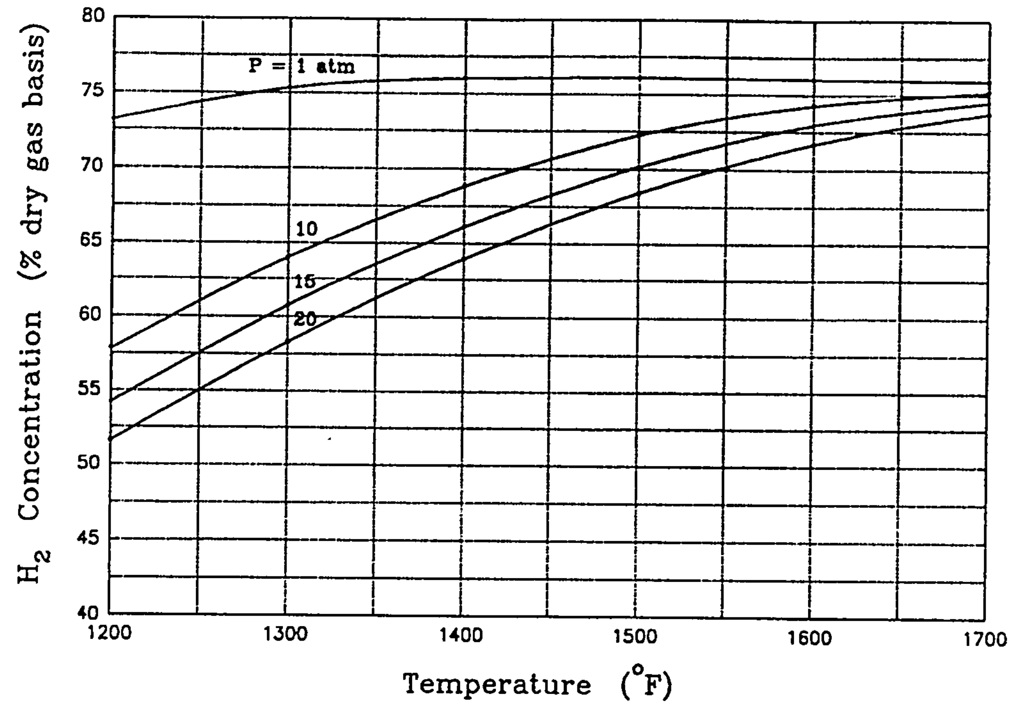


Figure 8. **Reforming Efficiency (expressed as hydrogen concentration in product gas) as Functions of Temperatuare and Pressure at R (Steam to Carbon Ratio) = 2.0**

The water usage sometime limits the applicability of steam reforming in the gas turbine engine. Figure 9 shows the natural gas reformation producing near 50 percent hydrogen (on a dry basis) in the product stream without steam injection. Although producing high hydrogen is desirable, a satisfactory amount of hydrogen generated in the reformed product could be more important on the improvement of ignition and flame stability. If the reformer would be run without or with a low steam rate, a reforming catalyst needs to be developed to overcome the carbon build-up problem.

3.2 CATALYST SCREENING

Catalysts suitable for use in reforming must meet the dual requirements of high catalytic activity and sulfur poison tolerance. The level of catalytic activity dictates the hydrogen yield in the product stream. Candidate catalysts must meet these requirements with strong thermal stability. Two basic groups of reforming catalysts, nickel- and platinum-basis, have been selected for the preliminary testing of the reforming activity. The tests are conducted at 1500°F and steam to carbon ratio of 1.34 under atmospheric pressure. Table 2 lists the catalyst type as well as the normalized product distribution of the test results on a dry gas basis. These experimental data given in Table 2 were carried out over a period of 4 to 10 hours. All catalysts resulted in producing about 70 percent hydrogen (on a dry basis) in the product stream.

Figures 10 through 13 plot the product concentrations as a function of testing time for individual tested catalysts. Reactant conversion and product distribution remained about constant during the 4-to- 10 hours testing for both the nickel and platinum catalysts. No significant change in catalyst performance has been observed. Differences in activity of the nickel and platinum catalysts have been observed on the CO and CO_2 yields. The lanthanum promoted, nickel-based catalyst (DYCAT foam) converts natural gas to more CO instead of CO_2 and yields a higher heating value of product gas than other catalysts. Analyses of the used catalysts by EDX (electronic diffraction X-ray) show

Table 2. Catalyst Type and Test Product Distribution*

Catalyst Supplier	DYCAT		Engelhard			Prototech		Met-Pro	
Type Content Bed Dimension	Foam Ni + La on Alumina 1" dia x 5"		Monolith (200 CPI) Pt + Rh on Cordierite 1" dia x 6"			Monolith (400 CPI) Ni on Cordierite 1" dia x 6"		Monolith (300 CPI) Pt + Pd on Cordierite 1" dia x 4"	
Testing Time (min)	**60**	**210**	**60**	**240**	**600**	**60**	**240**	**250**	**270**
Composition (vol %)									
H_2	73.0	69.9	70.9	71.9	69.3	71.2	70.7	71.6	72.2
CO	24.0	23.7	19.6	18.1	15.9	18.0	18.1	15.1	14.6
CH_4	1.0	4.8	3.2	3.9	7.4	4.9	5.4	3.9	3.9
CO_2	2.0	1.6	6.3	6.1	7.4	5.9	5.8	9.4	9.3
Heating Value (Btu/lb) (LHV, dry basis)	11,716	12,365	10,606	11,177	11,323	11,407	11,479	10,147	10,318

* Product distributions and heating values on a dry basis.

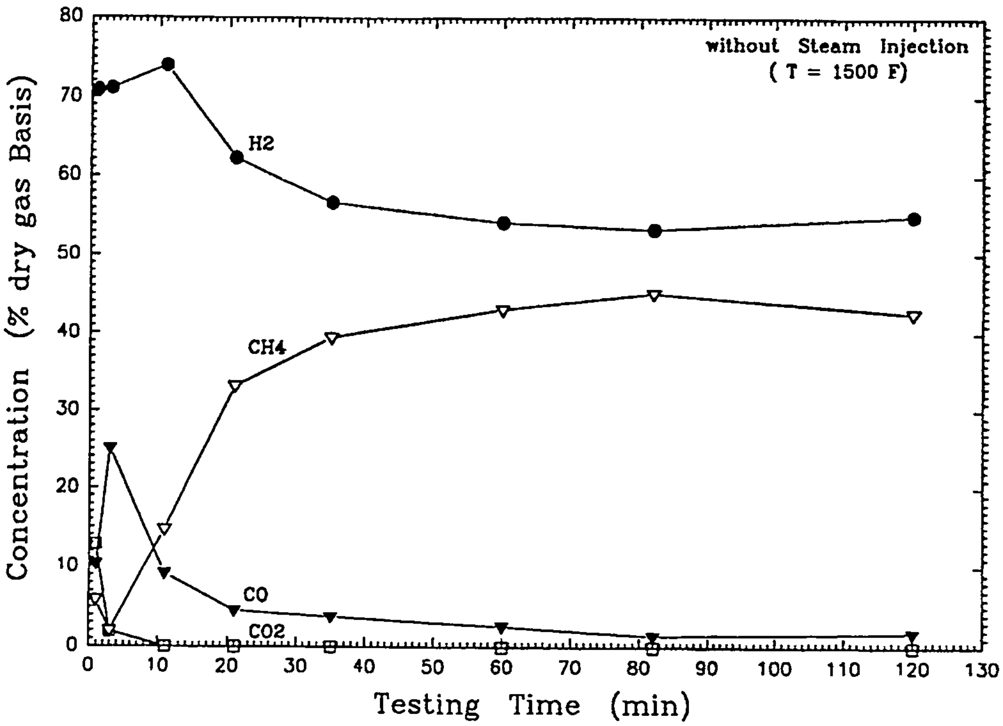


Figure 9. Product Distribution of Fuel Reformation Without Steam Injection

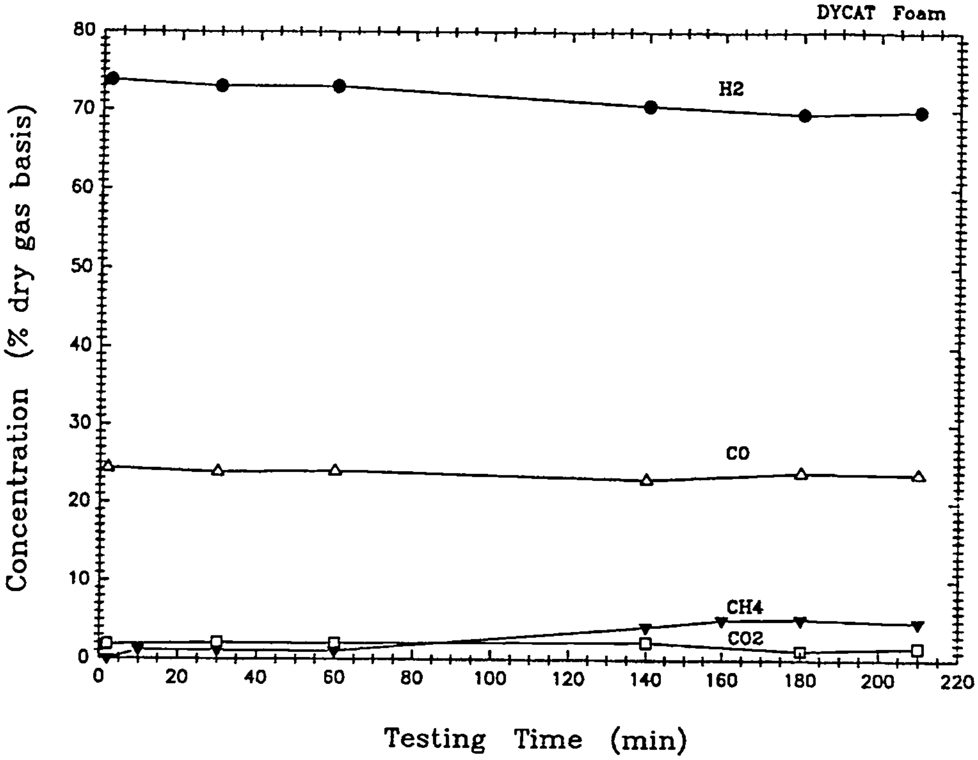


Figure 10. Product Distribution of Reforming Test With DYCAT Foam Catalyst

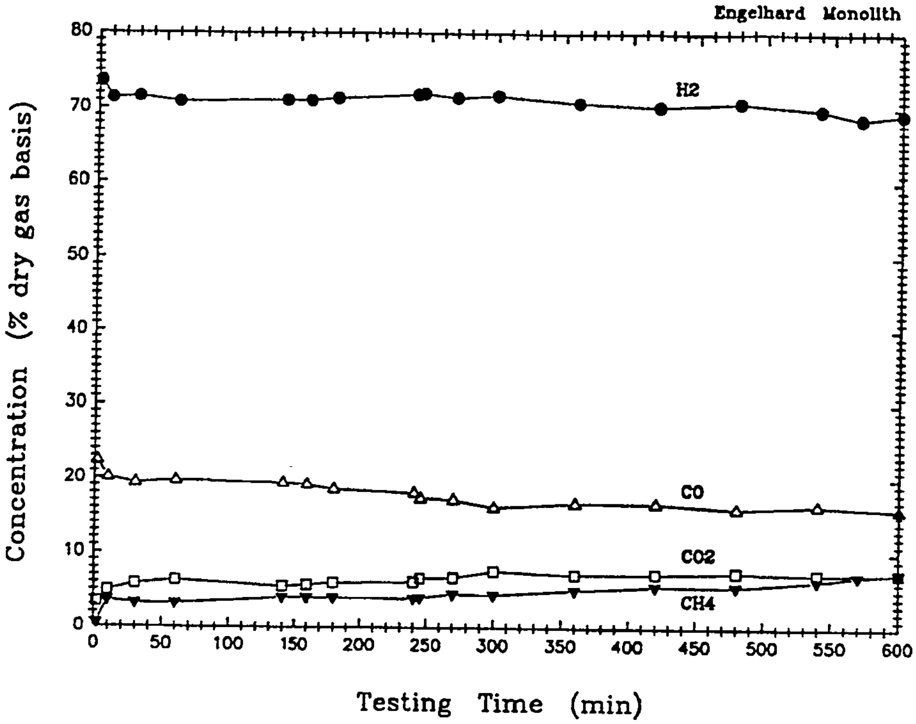


Figure 11. Product Distribution of Reforming Test With Englehard Monolithic Catalyst

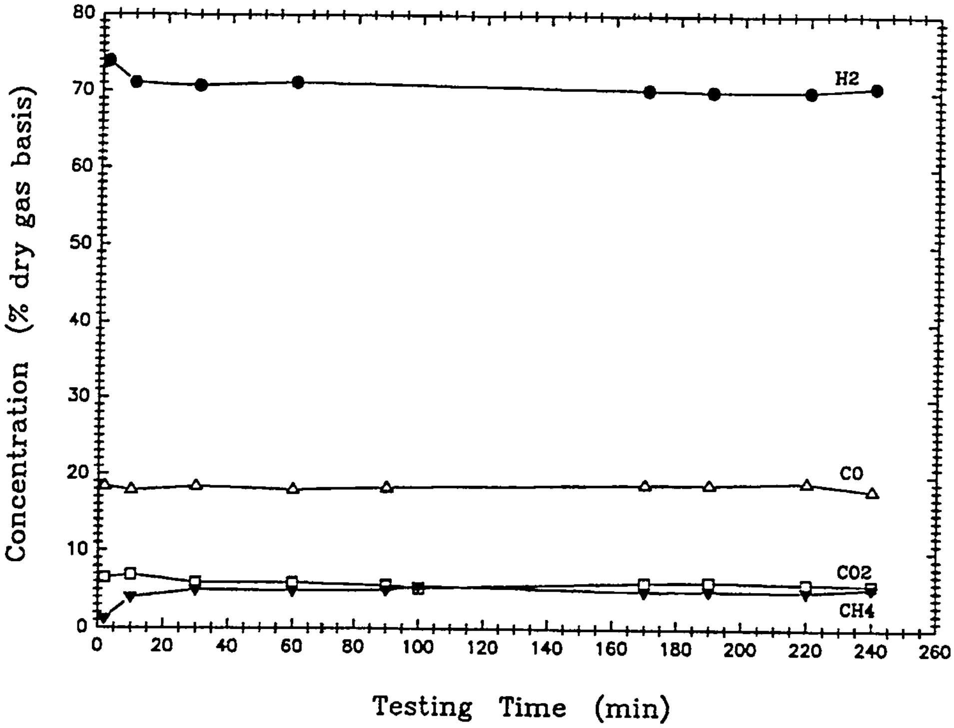


Figure 12. Product Distribution of Reforming Test With Prototech Monolithic Catalyst

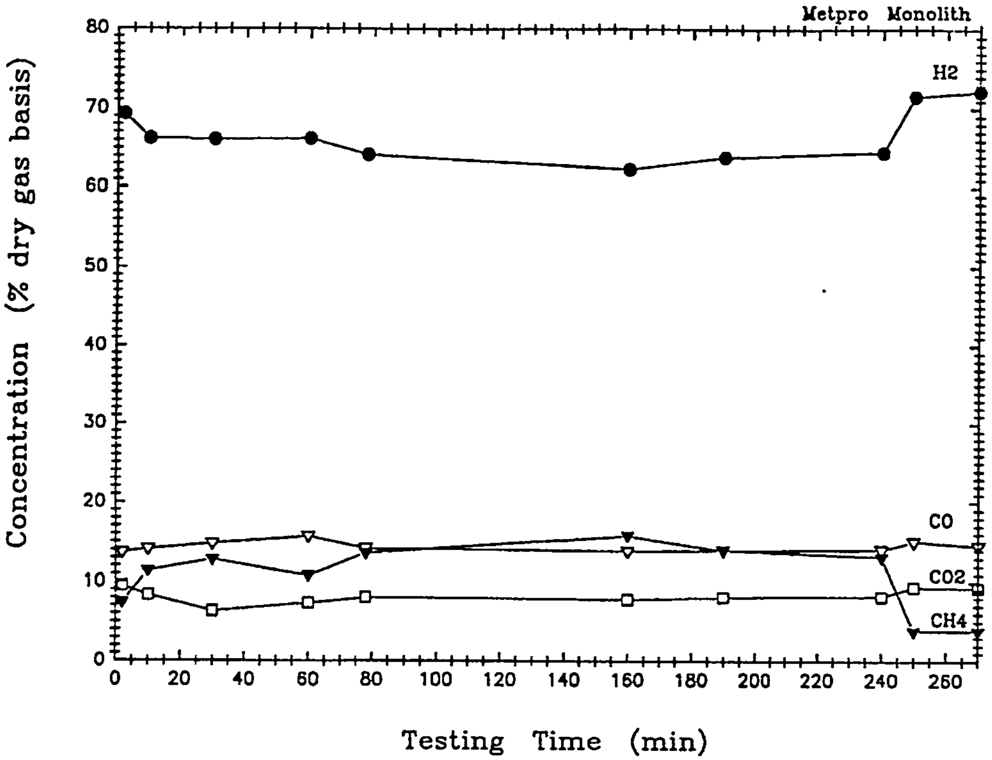


Figure 13. Product Distribution of Reforming Test With Metpro Monolithic Catalyst

no significant difference between the original and the used catalyst (Figure 14). Neither sulfur accumulation nor pore/channel blocking was observed in the used catalysts. Several decolorized spots on used catalysts were observed and found later to be due to contaminants of potassium in the water used to generate steam for the test.

3.3 DURATION TESTING

Catalyst poisoning is of primary concern in autothermal reforming. Sulfur is known to poison the catalysts used for the commercial reformation processes[1-3]. A zinc oxide based absorbent can effectively remove all of the sulfur compounds likely to be found in the hot vaporized fuel stream. An absorbent bed could be added in the vaporized fuel delivery line or it could be integrated into the catalytic reformer. In addition, sulfur poisoning is largely reversible. The bulk of the sulfur can be removed from the used catalyst by steaming.

Duration tests were performed to evaluate sulfur tolerance of the autothermal fuel reforming catalyst. Methane dipped with 200 ppm of hydrogen sulfide (H_2S) was used as the testing fuel, compared to 1 ppm H_2S contained in the local natural gas. The test results (Figure 15) indicated over 70 percent of hydrogen (on a dry basis) produced in the product stream with no deactivity on the reforming catalyst over 17 hours of testing. This would be equivalent to an exposure of sulfur on catalyst over 3300 hours if based on a fuel with 200 times high sulfur concentration than that in the local natural gas. The results also showed that the catalyst activity can be restored by steaming the used catalyst after extended testing under sulfur exposure. The tested catalyst has been steam-cleaned twice at 300 min and 800 min.

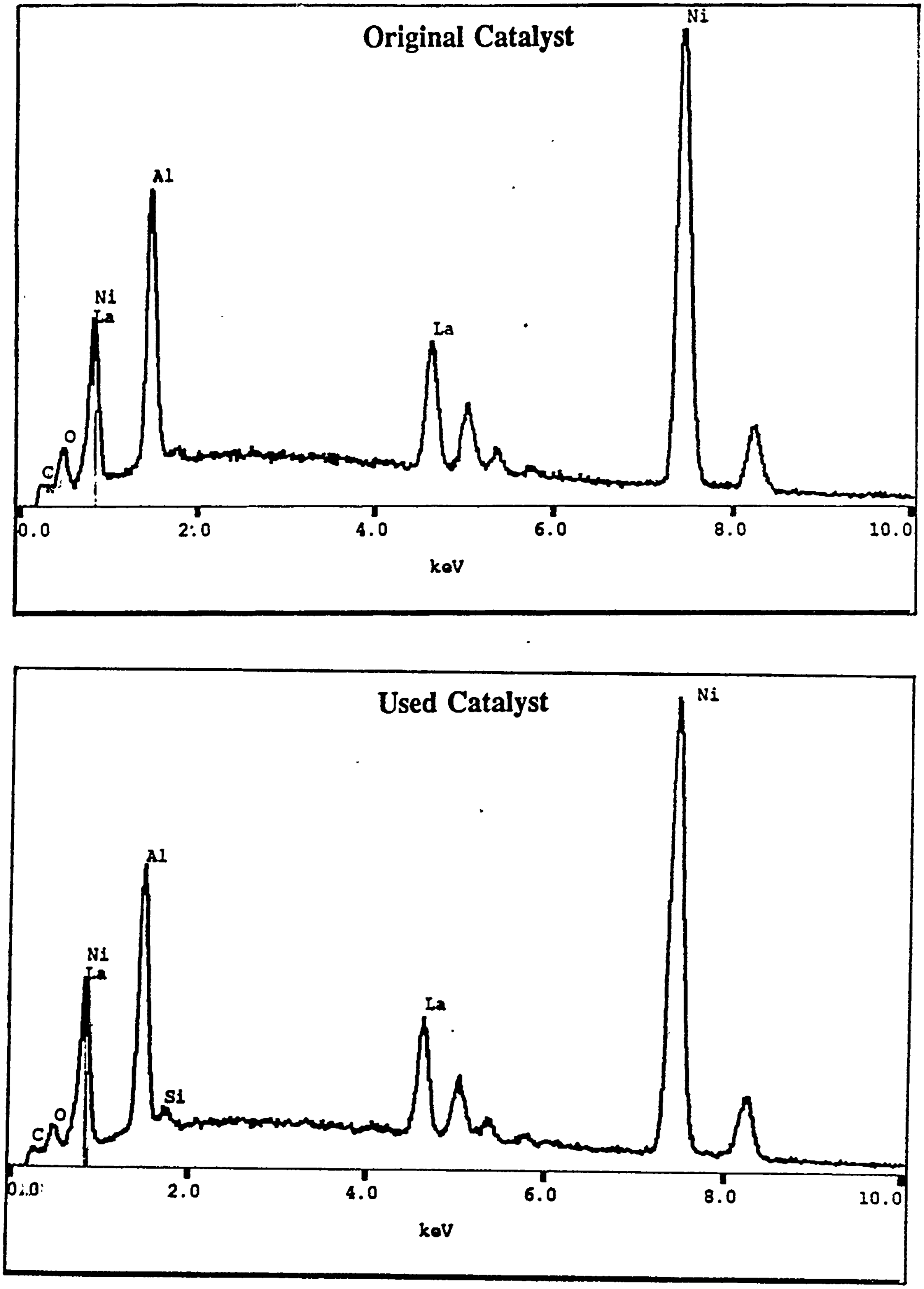


Figure 14. EDX Analyses of Original and Used DYCAT Foam Catalysts

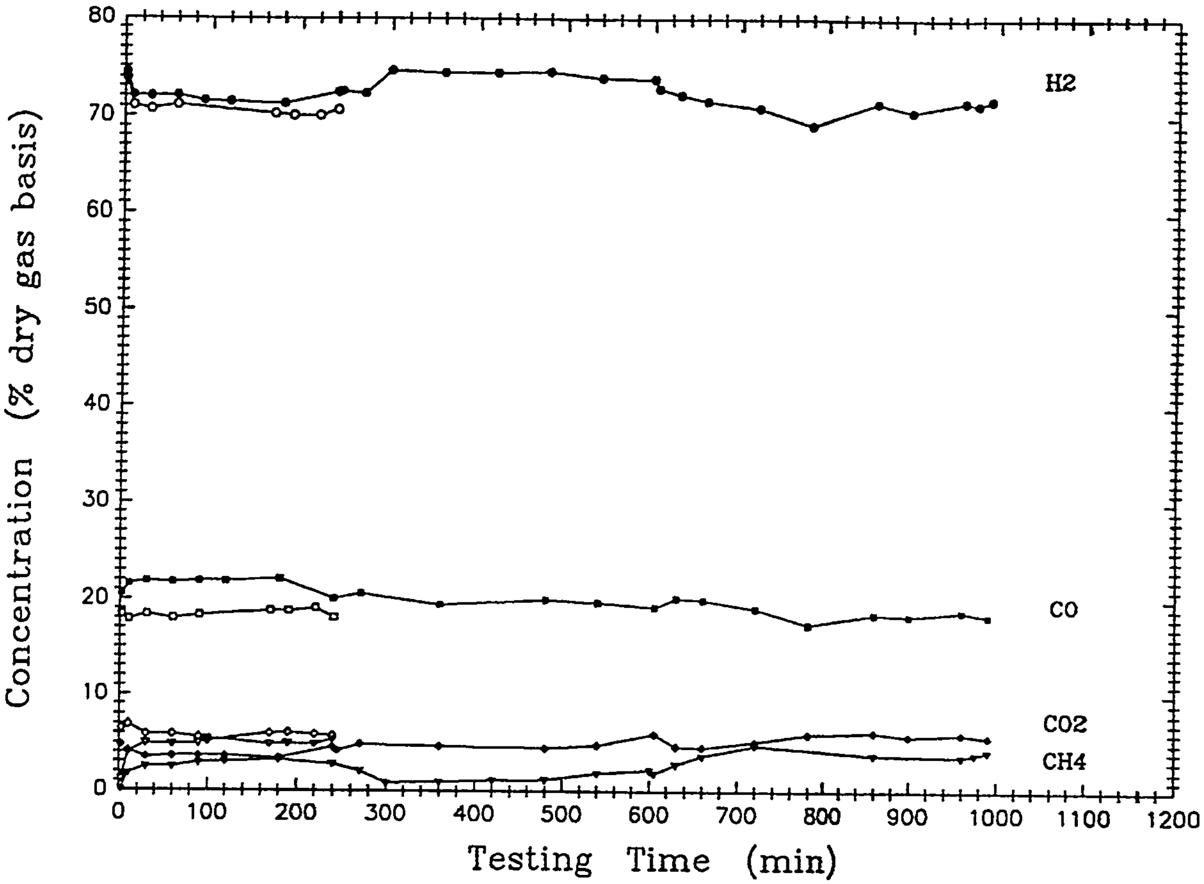


Figure 15. Product Concentrations From Prototech's Reforming Catalyst Testing (open data points using local natural gas as fuel and filled data points using 200 ppm H_2S mixed with methane)

The effect of a dual-oxide absorbent on the performance of the reforming catalyst was investigated to control the sulfur poisoning and improve the catalyst active life. An absorbent consisting of zinc and calcium oxides was selected for removing acidic species (H_2S, HCl, etc.) in the raw natural gas and serving as a polishing step to ensure a constant quality of fuel. The test results (Figure 16) indicate 65 to 70 percent of hydrogen (on a dry basis) produced with no deactivity of the reforming catalyst after over 80 hours of testing when used either the local natural gas or the high-sulfur fuel. Analyses of the used catalyst by electronic diffraction X-ray (Figure 17) show no accumulation of sulfur on the catalyst. An absorbent serving as a polishing step would ensure a constant quality of inlet fuel for autothermal reforming.

3.4 LIQUID FUEL

Use of a broad range of liquid fuels for industrial gas turbine operation has become an important requirement in power generation, marine service, and as back-up fuels for normally gaseous fuelled installations. There is an increasing worldwide customer interest in the use of the more cost effective liquid fuels. However, the use of liquid fuels has a great impact on gas turbine combustion and fuel systems. The liquid fuel's chemical composition, heating value, physical properties, and contaminations all must be addressed in order to meet specific system design requirements to ensure reliable operation. Small and medium size gas turbines having a relatively small nozzle throat area typically restrict any use of heavy liquid fuels. Even for large gas turbines, the engine must be shut down and washed from time to time to remove deposits when running liquid fuel.

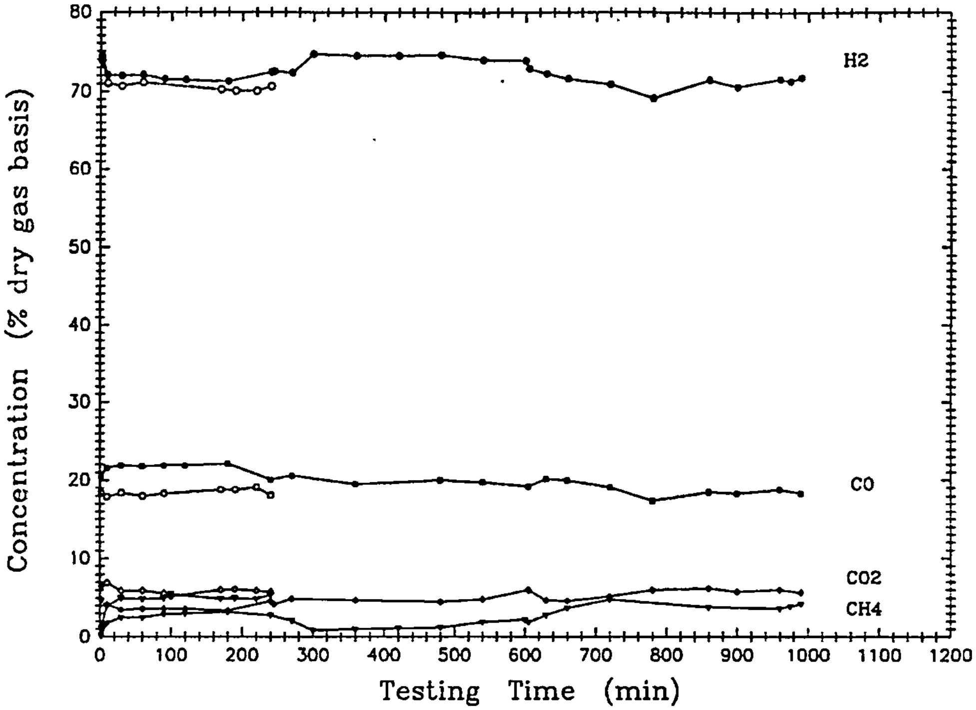


Figure 16. Hydrogen Concentration in Product Gas From Duration Test

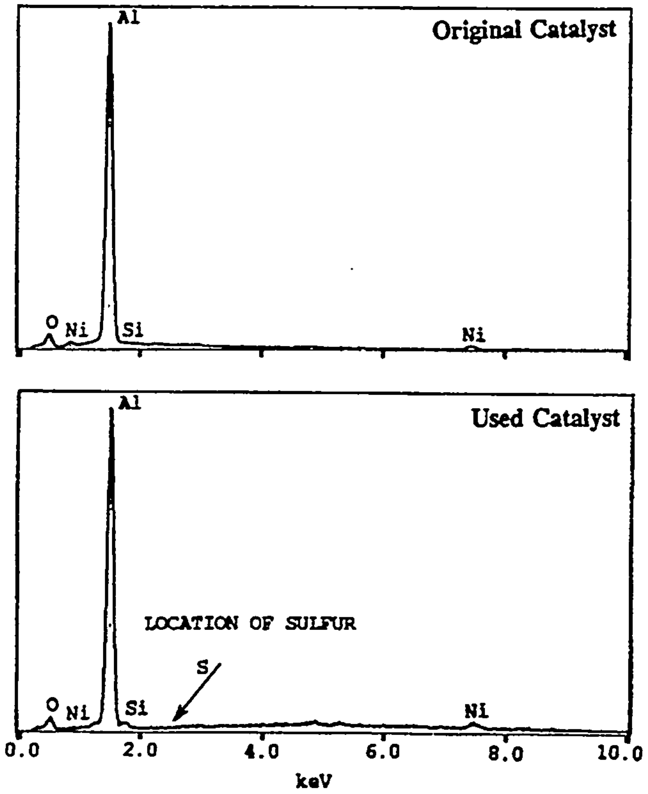


Figure 17. EDX Analyses of Original and Used Catalyst

The reforming of either gaseous or liquid fuels would produce the same primary constituents (with different proportions) regardless of the parent fuels. This would allow a single fuel injection and combustion system to be employed, thus making the system fuel independent to meet customer specified requirements. Dual fuel or even multi-fuel capability under the fuel reformation would broaden the market of the advanced turbine system applicability.

The ATR batch-tube reactor has been modified and fitted with a liquid fuel pumping and pre-treatment system as illustrated in Figure 18. No. 2 diesel from petroleum distillates was used as the feed stock for the liquid fuel reforming tests. Table 3 lists the general properties of No. 2 diesel in which shows a 90 percent distillation cut at 605°F and a lower heating value of 18,370 Btu/lb. Sulfur content in the diesel reaches 0.04 wt% along with nitrogen content of 245 ppmw and aromatics content of 18.3 vol%. Fuel-bound nitrogen (245 ppm by weight) will contribute some NOx emissions; while the aromaticity in the liquid fuel is generally accused of the soot formation during combustion and will accumulate carbon deposition.

Tests using liquid (diesel) fuel were conducted at 1500°F and steam-to-fuel (mass) ratio of 2:1 with an absorber bed under atmospheric pressure. Table 4 lists the normalized product distribution of the test results on a dry gas basis using either nickel- or platinum-based catalyst. The tests resulted in generating 60 to 65 percent hydrogen in the product stream. A slightly higher concentration of hydrogen was obtained in the reforming run using platinum-basis catalyst than that of using nickel basis. CO concentrations were in the range of 18 to 23 vol% and decreased with the testing time, while methane contents in the product gases were about 4 to 6 percent. CO and methane concentrations seem independent of the type of catalyst being tested.

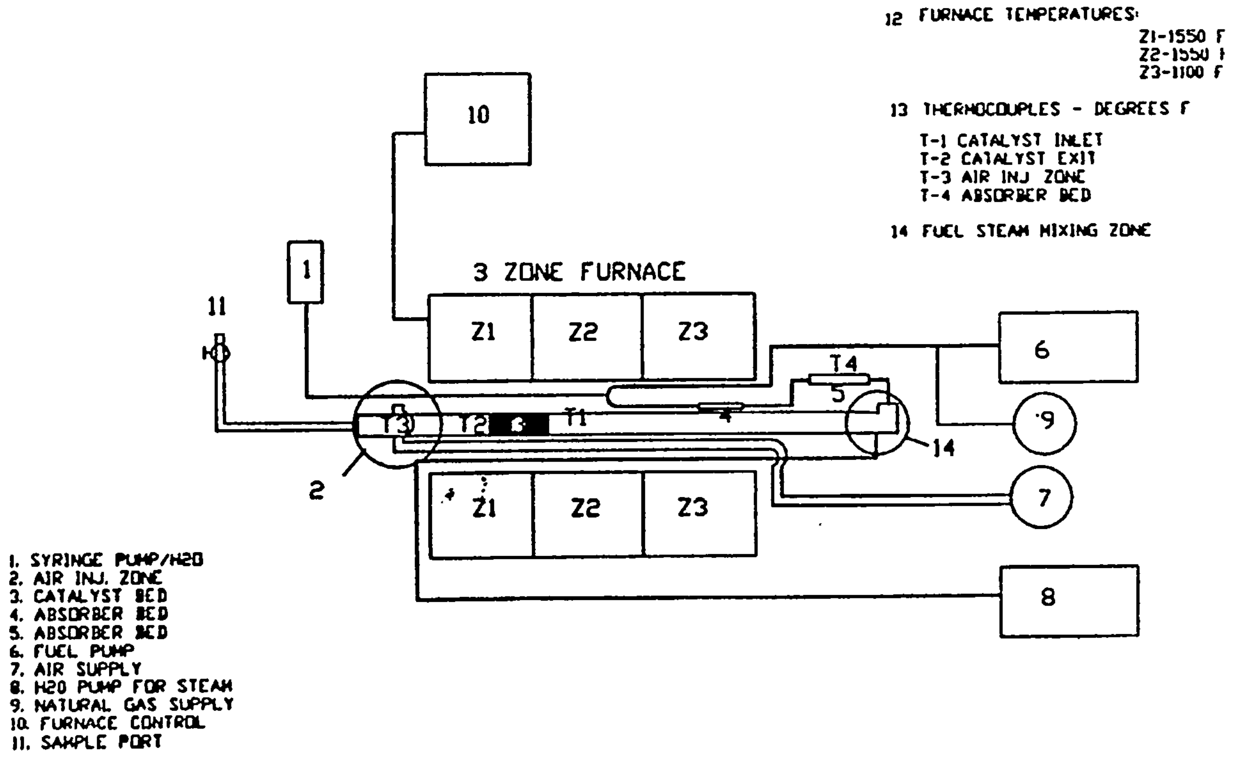


Figure 18. Tube Reactor Modified for Liquid Fuel Reforming Tests

Table 3. Properties of No. 2 Diesel Fuel*

Property	ASTM Method	Data
Flash Point (°F)	D 56	161
Gravity (API @ 60°F) (sp. gr. @ 60/60°F)	D 1298 D 287	34.5 0.8448
Cetane Number	D 6137	61.2
Aromatics (vol%)	D 5186	18.3
Distillation (°F)	D 86	
50% Recovered		546
90% Recovered		605
End Point		656
Viscosity, Kin. (CST @ 40°F)	D 445	3.7
Cloud Point (°F)	D 2500	14
Pour Point (°F)	D 97	10
Sulfur (% wt)	D 129	0.04
Nitrogen (ppmw)	D 4629	245
Carbon Residue, 10% Btms. (% wt)	D 524	0.13
Ash (%wt)	D 2709	0.002
Lower Heating Value (Btu/lb)	D 240	18,370

*Obtained from Chevron (El Segundo and Solar's Chemical Lab.

Table 4. Results of Liquid (Diesel) Fuel Reformation*

Reforming Catalyst Type	**Nickel Basis**			**Platinum Basis**		
Testing Time	**5 min**	**314 min**	**405 min**	**15 min**	**380 min**	**522 min**
Composition (vol %)						
H_2	62.2	63.0	60.9	65.2	64.3	64.7
CO	22.8	18.3	18.2	20.1	18.7	20.7
CH_4	5.6	5.6	6.5	4.6	6.2	5.1
CO_2	8.2	10.9	11.6	7.9	8.8	7.2
C_2+	1.2	2.2	2.8	2.2	2.0	2.3
Heating Value (Btu/lb) (LHV, dry basis)	9,495	9,429	9,368	10,260	10,242	10,511

*Reforming conditions: temperatures at 1500°F and steam-to-fuel (mass) ratio at 1.2.

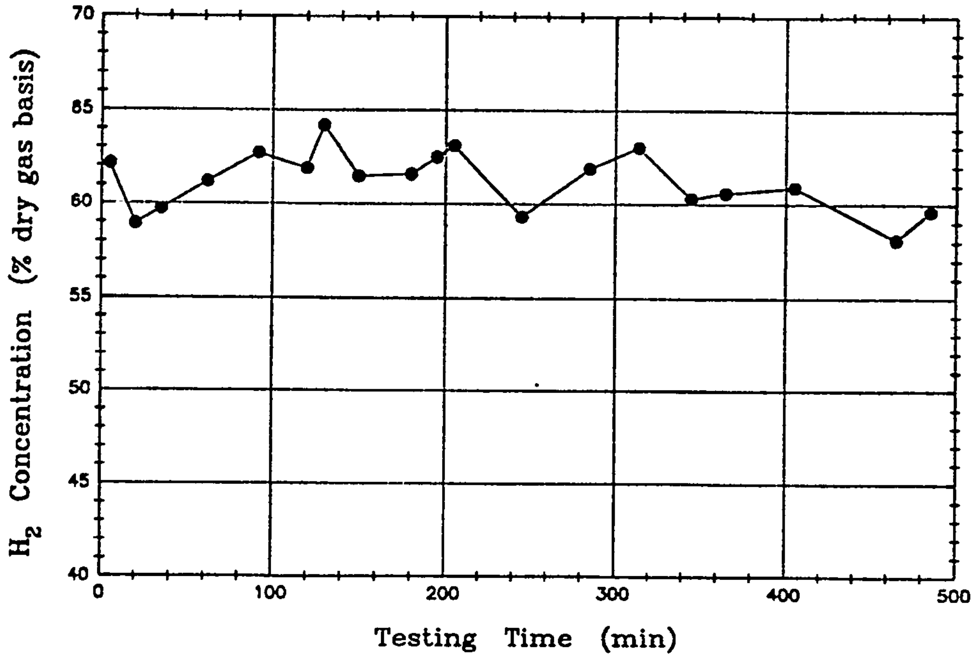


Figure 19. Hydrogen Concentration in Product Gas From Liquid (diesel) Fuel Reforming Using Nickel-basis Catalyst

Figures 19 and 20 plot the product concentrations of hydrogen as functions of testing time for nickel- and platinum-based catalysts being tested. A higher hydrogen yield was maintained when using platinum-based catalyst as compared to those generated by using nickel-based catalyst. Hydrogen yields dropped significantly when carbon deposition built up on the Ni-basis catalyst. Carbon deposition on the nickel-based catalyst takes place at conditions much milder than that on platinum catalyst. The platinum-based catalyst seems to more effective to suppress soot and carbon formation for liquid fuel reformation. The sulfur content of 0.04 percent in diesel is undesirable for the reforming catalyst. By passing diesel fuel with a dual-oxide absorber bed, the impact of sulfur poisoning has been minimized. Analyses of the spent absorbents by EDX (Figure 21) indicate the removal of sulfur and chlorine acidic species from the diesel fuel and some deposition of carbon on the absorbent.

Table 5 compares the results of a set of tests by varying the steam-to-fuel ratio. The hydrogen yield (reforming activity) differs only slightly as the steam-to-fuel ratio above 2:1. A decrease of CO and an increase of CO_2 were observed with increasing the steam ratio. CO_2 concentrations increase more significantly when the tests were run at a high steam ratio due partially to more water oxygen available for the carbon dioxide to form. In Table 5 (the last column), liquid diesel was heated and passed through the tube reactor without the reforming catalyst, showing a generation of about 31 volume percent of hydrogen in the product gas along with large amounts of methane (~24 %) and carbon dioxide (~33 %). The heating value of product stream decreases as more CO_2 was present in the product.

3.5 REFORMED FUEL (HYDROGEN-RICH) COMBUSTION

Hydrogen gas has the highest flammability ratio of 18.75 as compared to 3.0 for natural gas (methane) or 4.52 for propane (as listed in Table 6). The flammability ratio of the fuel is defined as the upper flammability limit (UFL) divided by the lower flammability limit (LFL) which affects the range of combustor operation[4]. Flammability limits directly influence combustor light-off, turbine cold/hot

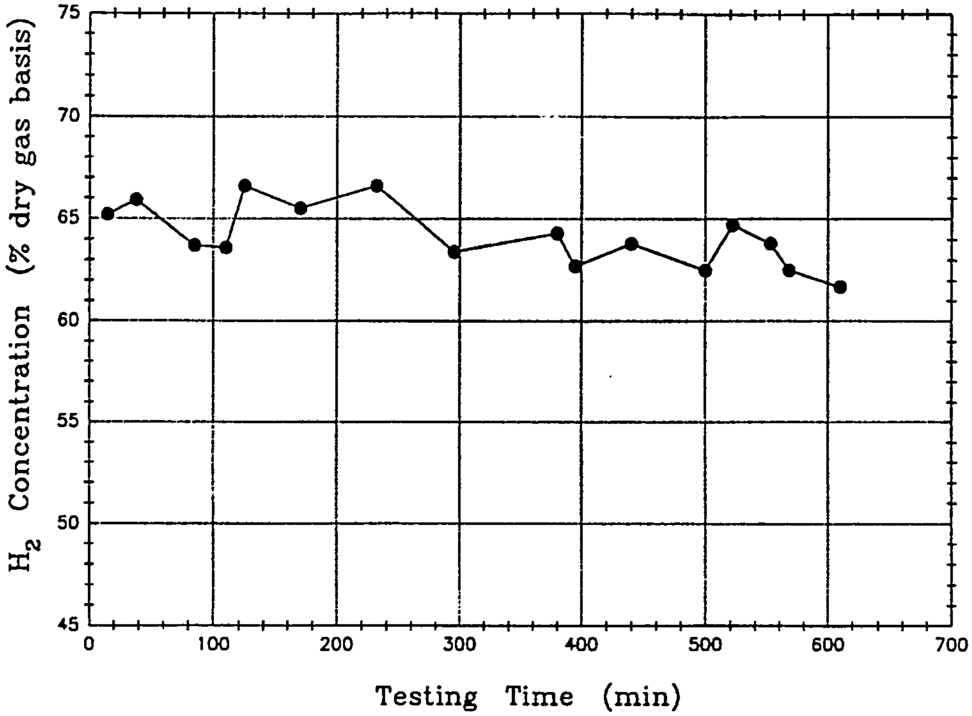


Figure 20. Hydrogen Concentraton in Product Gas From Liquid (Diesel) Fuel Reforming Using Platinum-basis Catalyst

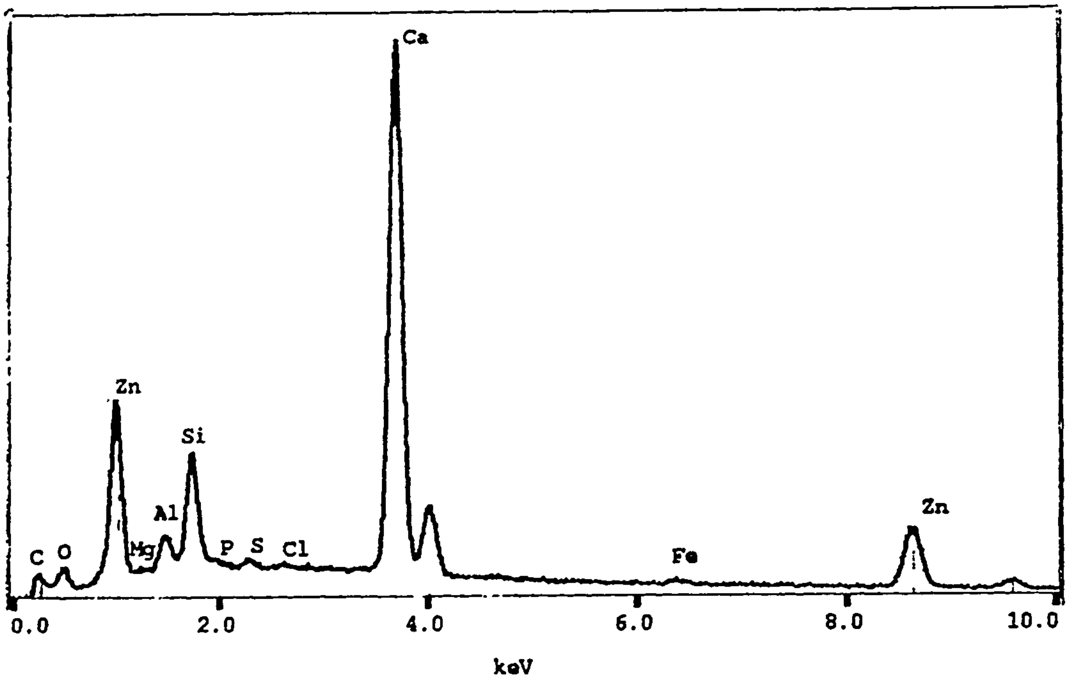


Figure 21. EDX Analyses of Used Absorbent

Table 5. Liquid (Diesel) Fuel Reformation as Function of Steam-to-Fuel Ratio*

Steam/Fuel Ratio (mass)	0.8	1.2	1.8	3.6	1.8
Reformer	yes	yes	yes	yes	no
Sampling @ Testing Time (min)	63	92	85	95	10
Composition (vol%)					
H_2	57.8	62.7	62.1	61.6	31.1
CO	25.6	21.8	22.8	18.5	7.8
CH_4	6.9	5.9	5.7	5.5	23.5
CO_2	6.9	8.3	9.2	14.2	33.0
C_2+	2.8	1.3	0.2	0.2	4.6

* Reforming with nickel-basis catalyst at 1500°F.

Table 6. Flammability Limits and Flammability Ratio*

Gas	Limits of Flammability Lower	Limits of Flammability Upper	Flammability Ratio
Hydrogen (H_2)	4.0	75.0	18.75
Methane (CH_4)	5.0	15.0	3.00
Propane (C_3H_8)	2.1	9.5	4.52
Carbon Monoxide (CO)	12.5	74.0	5.92
Natural Gas (92.8% CH_4, 4.2% C_2H_6, 0.8% C_3H_8,)	4.9	15.1	3.08
Landfill Digester Gas (55% CH_4, 45% CO_2)	10.1	20.6	2.04
Blue Water Gas (49% H_2, 41% CO, 4.7% CO_2)	6.4	70.0	11.00
Coal Gas (oxygen-blown Winkler fluidized bed)	7.5	66.7	8.92
Coal Gas (oxygen-blown Lurgi fixed bed)	7.5	45.9	6.12
Coal Gas (oxygen-blown Texaco)	7.9	71.6	9.10
Coal Gas (air-blown Winkler fluidized bed)	20.5	71.2	3.47
Coal Gas (air-blown Lurgi fixed bed)	12.6	51.8	4.11
Coal Gas (air-blown IGT/U-Gas fluidized bed)	17.7	59.0	3.33
Shale Oil Gas (In-situ retorting)	12.5	36.1	2.88
Coke Oven Gas (51.2% H_2, 30.6% CH_4, 4.0 %CO_2)	4.9	30.2	6.21

* Referred from [9].

flameout and combustion efficiency during light-off and acceleration. Based on experimental and empirical data, a higher flammability ratio gives satisfactory gas turbine operation from start-up to full load, including load transients. The flammability ratio of the fuel depends primarily on the type and concentration of the individual constituents in the fuel. Hydrogen-rich gas generated via fuel reforming can help handle the engine start-up, especially for fuel gases derived from biomass which have flammability ratios around 2.0. The low flammability ratio of methane, combined with the quenching effects of carbon dioxide, usually increases the level of difficulty when burning landfill and digester gases.

The hydrogen-rich reformed gas can extend the lean extinction limit to lower temperatures. This would allow the combustor to be operated in lean conditions for low NOx emissions. As shown in Figure 22, the limits of hydrogen flammability[5] in air diluted with an inert gas (hydrogen/inert/air mixture) is extended to the peninsula-shaped areas. No flame occurs only when the percentage of N_2 in air exceeds 75 percent or O_2 in the mixture is below 5.0 percent. For comparison, Figure 23 shows the limits of flammability of methane mixture[5] in which the flammability range of methane is restricted below 38 percent N_2 or above 13 percent O_2.

Flammable gases may ignite and combust when they reach the temperature at which more heat is generated by combustion than is lost to the surroundings so that the combustion process becomes self-sustaining. The lowest temperature that can cause ignition for combustible substances varies greatly. The minimum ignition temperature[6-8] for hydrogen or hydrogen mixtures is much lower than

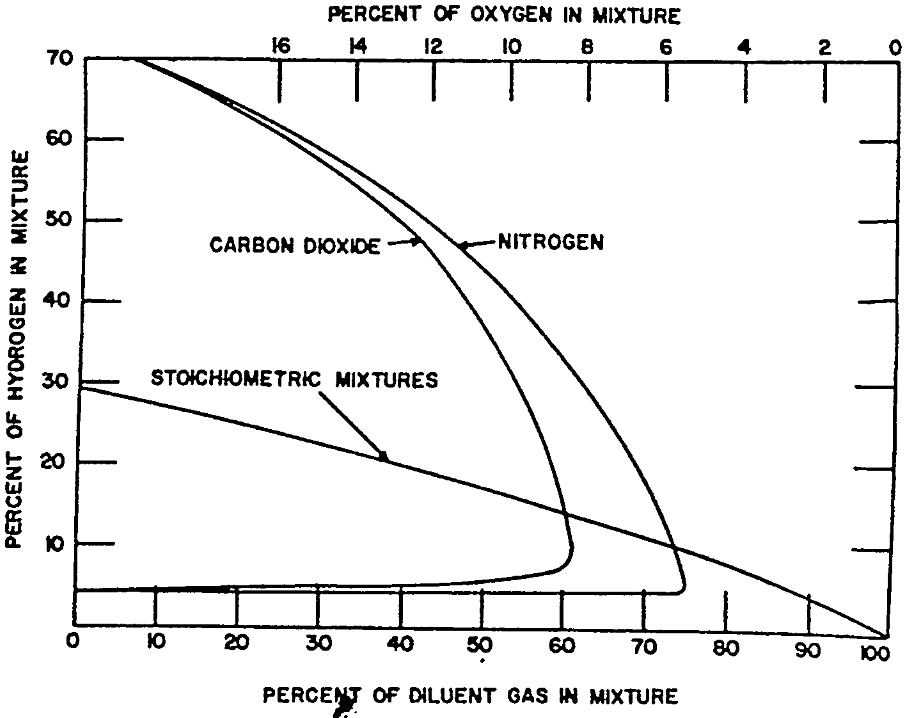


Figure 22. Limits of Flammability of Hydrogen in Air Diluted With CO_2 and N_2 [5]

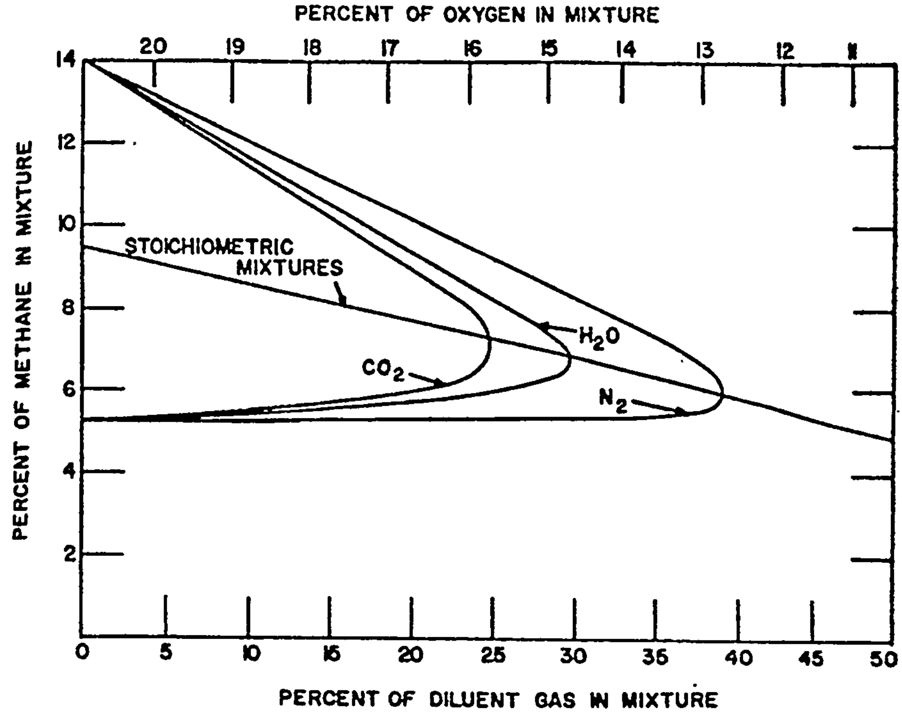


Figure 23. Limits of Flammability of Methane in Air Diluted With CO_2, H_2O and N_2 [5]

other gases. Light-off of the hydrogen-rich gas is relatively straightforward and requires no assistance of ignitor or pilot fuel. This reduction of system hardware is an important advantage of the hydrogen-rich gas combustion. The ignition energy of hydrogen (Table 7) is about 0.02 milijoule[6], which is less than 4 percent of the ignitioin energy required for natural gas (methane), a major factor in making low temperature catalytic combustion possible.

In our tests, attempts were made to compare the ignition behavior of reformer product streams using the ATR batch-tube reactor. Temperature readouts monitored by thermocouples are illustrated in Figure 24 where a controlled air flow was introduced downstream of the reformer to burn the product gas. As shown, the product streams with hydrogen above 37 percent were ignited easily without torch assistance for both diesel fuel and natural gas as the feedstock. Under the same conditions natural gas heated through the tube reactor without reforming raised the temperatures only about 100°F. The low ignition energy requirement is one of the benefits for reformation of conventional fuels to a hydrogen-rich gas for combustion in a gas turbine.

Hydrogen is an attractive fuel resulting in its relatively short ignition delay times, high specific energy and huge capacity for cooling. Autoignition is characterized by an induction period or delay time during which reaction is slowly gaining momentum, followed by a sudden and large rise in temperature with complete combustion of reactants. The temperature dependence for hydrogen ignition delay times[9] is illustrated in Figure 25. The ignition delay measured for hydrogen approaches 0.2 msec at 1 atm and increases with decreasing temperatures. Meantime, ignition delay is seen to increase with decreasing pressure for low temperatures. Figure 26 displays the effect of added water on ignition delay times for stoichiometric H_2-Air mixture at 1 atm. Addition of H_2O was found to lengthen the delay time at low temperatures. No clear effect of water is seen on high temperature ignition.

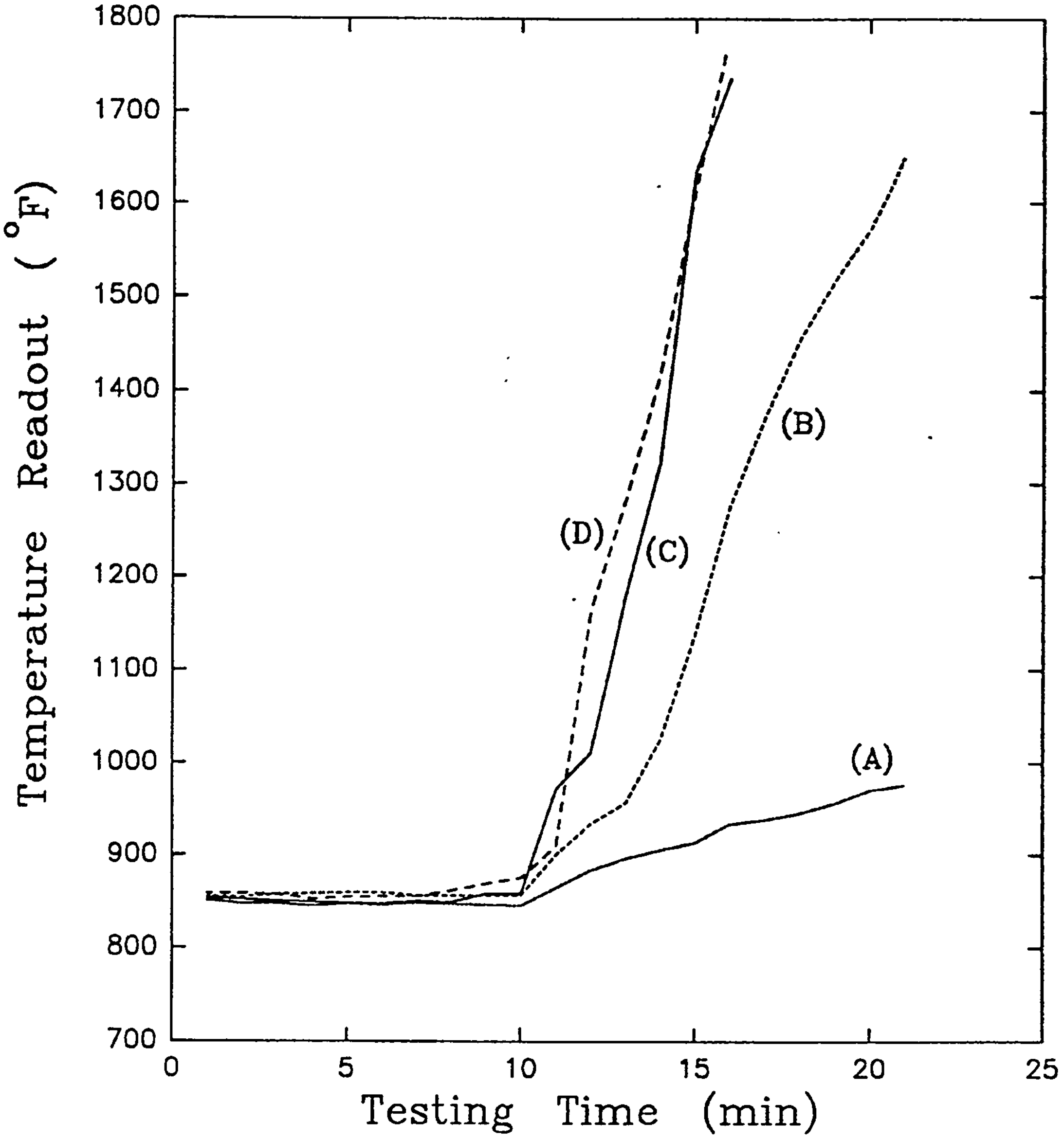
Table 7. Minimum Ignition Energy for Stoichiometric Mixtures with Air*

Fuel	Formula	Ignition Energy (10^{-3} J)		
		0°C	25°C	100°C
Hydrogen	H_2	0.0315	0.028	0.018
Acetylene	C_2H_2	0.030	0.029	0.021
Methane	CH_4	--	0.75	0.46
Propane	C_3H_8	0.67	0.55	0.35
n-Pentane	C_5H_{12}	1.01	0.78	0.42
n-Hepane	C_7H_{16}	--	1.45	0.67
Isooctane	C_8H_{18}	--	2.7	1.1
Propylene oxide	C_3H_6O	--	0.24	0.15
Carbon disulfide	CS_2	0.086	0.070	0.049

*Referred from [12]

Because hydrogen is easily dispersed in air, less fuel preparation or mixing is necessary. Combustion time for hydrogen-rich gas is short once ignition temperature is reached. Hydrogen-air mixtures burn with high speed (~ 8.3 ft/sec) over a very wide range of fuel-air ratios[10,11] as compared to other gaseous-air mixtures (Figure 27). In general, the rate of flame propagation must be sufficient to assure that ignition cannot travel back (flashback) into the burner. Hydrogen flame speed may be sufficiently high to avoid undesired disturbances of the combustion process due to the flashback. Quenching the H_2 flame can avoid its flashback. The quenching diameter for the H_2 flame[12] is around 0.024 inch that decreases with increasing the temperature and pressure. The quenching diameter is the minimum diameter of a tube through which a flame can propagate indefinitely without flashback.

When methane is used as a fuel, the combustion reactions proceed via the methyl radical[8]. Oxidation of methyl is quite slow, except in flame. This low reactivity distinguishes it from other alkyl radicals and largely explains why methane is harder to detonate or ignite than hydrogen or heavy hydrocarbons. Unlike methane, hydrogen ignition is characterized as an isothermal chain branching process. The hydrogen combustion proceeds[10] mainly via the hydrogen atom and OH radical. As the temperatures increase toward autoignition, the hydrogen atom generated by collision radical reacts directly with O_2, $H + O_2 = OH + O$, to form OH radical and O atom. The OH radical in turn reacts with hydrogen molecules, $OH + H_2 = H_2O + H$, forming water and regenerating the H atom which repeats the combustion process. Meantime, the O atom also can react with hydrogen molecules to form OH radical and H atom, $O + H_2 = OH + H$. The reaction rate of hydrogen combustion increases exponentially via chain-branching when reaches the ignition temperature and its delay time.



	A	B	C	D
FUEL	N. Gas	N. Gas	N. Gas	Diesel
STEAM	yes	yes	yes	yes
REFORMER	no	partial	yes	yes

GAS STREAM COMPOSITION (after heated tube-reactor):
(dry, vol%)

H2	3.36	37.11	62.55	62.14
CH4	90.66	49.28	13.78	5.64
CO	1.43	5.15	22.21	22.82
CO2	1.60	8.46	1.46	9.17
C2+	2.95	-	-	0.23

Figure 24. Ignition Temperature Readouts Monitored for Fuel Reformed Products

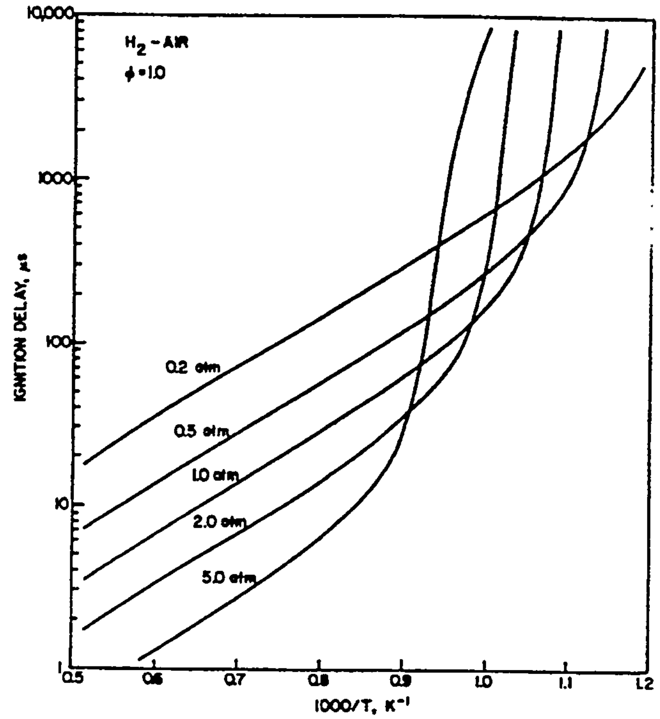


Figure 25. Hydrogen Ignition Delay Time for Stoichiometric H_2-Air as Function of Temperature and Pressure[9]

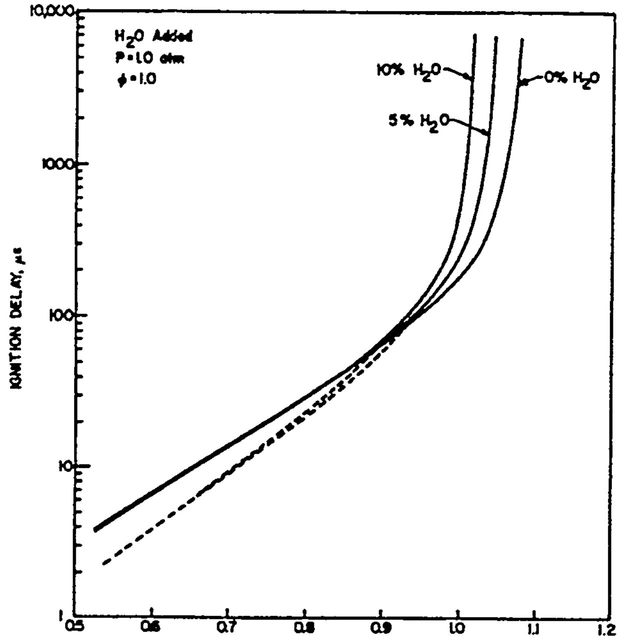


Figure 26. Hydrogen Ignition Delay Time for Stoichiometric H_2-Air at 1 atm as Function of Temperature for Various Amounts of Added Water[9]

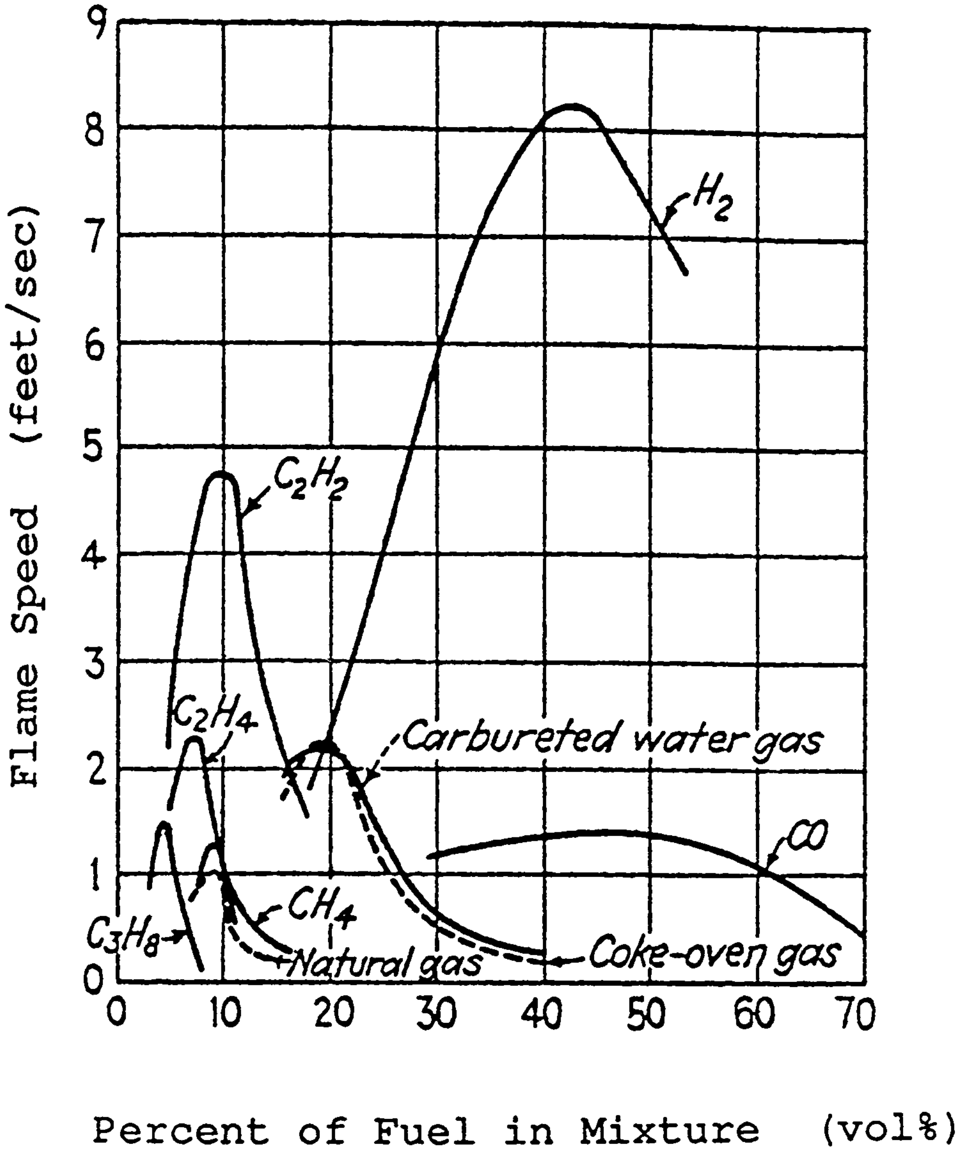


Figure 27. Flame Speeds of Hydrogen and Various Gas Air Mixtures

4.0 RIG DESIGN AND TESTING

The autothermal reforming system can be integrated with gas turbine cycles, using an intercooler to raise the steam and the engine exhaust to increase the steam temperature[13]. The energy usually lost in the cooling process would be recovered and returned to the system. The low exhaust temperature allows a considerable portion of the water present in the gas stream to be easily condensed. This would improve the efficiency and provide the desirable emissions. It is anticipated that all of the water needed for autothermal reforming will be available from the exhaust condensate. In addition, the steam produced from the combustion of hydrogen would increase the power available from the cycle due to increased mass flow when compared to the combustion of the parent fuel. This is equi-valent to the injection of steam into the turbine section at the equivalent combustor exit temperature.

Figure 28 shows a schematic representation of a fuel reformer integrated with an intercooled/recuperated engine system. In general the hot water or steam raised in the intercooler will be heated further either in the exhaust leaving the recuperator or the gas stream leaving the power turbine. The mixture of steam and fuel after heated will be injected into the preheat mixing section of the reformer. A small pilot combustor is arranged to provide the additional heat for the fuel-steam mixture. The hot exhaust gases from the pilot combustor will mix with the steam and vaporized fuel to heat them further to the desired reforming temperature. The mixed gases would be constrained to pass through a catalytic reformer constructed as a multi-channel monolith.

The gases leaving the catalytic reformer will exit into a lean-burn low NO_x combustor where they will

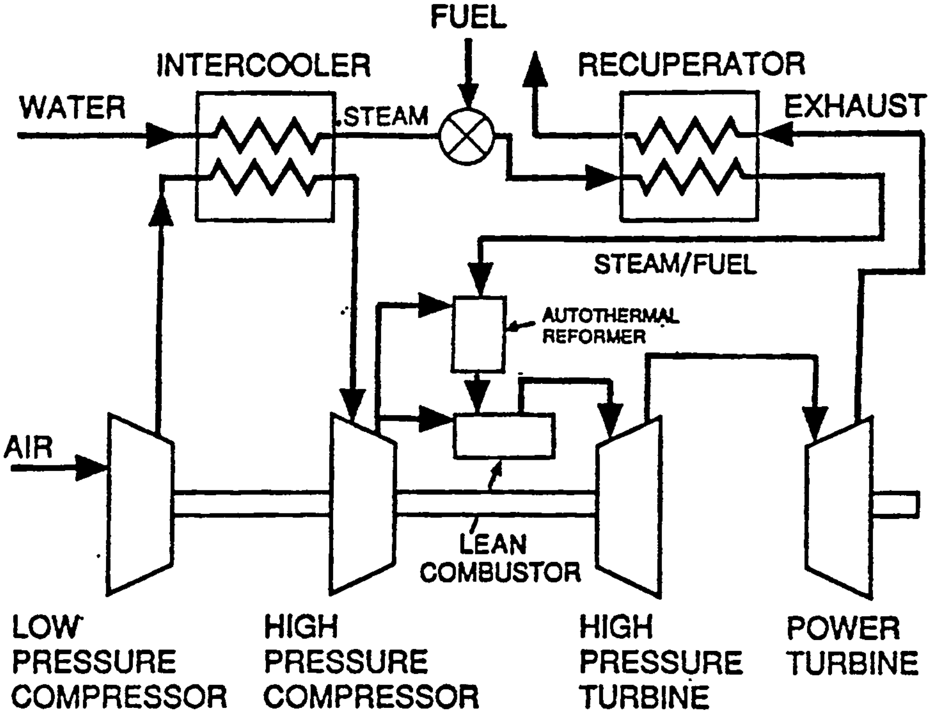


Figure 28. Integration of Fuel Reformer With Intercooled and Recuperated Gas Turbine

combustion. The post combustor would operate with a high excess air at which low emissions can be obtained. The hot combusted gas after exiting the combustor is expanded across a turbine to produce shaft work to drive the compressor. Burning a lighter, more reactive hydrogen-rich fuel with wider flammability limits than those available from the parent fuel permits combustion at a low equivalence ratio and improve its flame stability. With the steam-fuel reforming, the system can improve the thermal efficiency and fuel flexibility with low emissions.

Steam required for the fuel reforming could also be raised in the engine exhaust, in much the same manner as a heat recovery steam generator is used today in a gas turbine. If steam is available at the site such as at industrial power stations, a free-standing ATR could be the economical choice. If steam is not available, as is the case with most remote gas turbine compressor stations, the integrated reformer system with its inherent steam generation capability from a recuperated engine will probably more economical. The steam generator could be part of a heat recovery system. The steam raised for the autothermal reformer could also be diverted for cogeneration uses and emissions control in a more conventional mode.

However, before the efficiency and emission advantages of fuel reformation can be realized in existing gas turbine systems, a number of catalyst and system design criteria must be addressed. Catalyst life and poisoning, substrate structural strength, product stream ignition, emission levels, and flame stability and flashback are all needed to be investigated in ATR rig tests. Concepts for integration of reformer with combustor and other gas turbine components also have to be developed.

4.1 ATR RIG DESIGN

Autothermal reforming rig tests were conducted with a subscale, staged rich-lean combustor consisting of the reformer and the selected catalyst. The detailed drawing of rig design is shown in Figure 29. The design features a fuel injection premixer, catalytic reformer, and dilution lean combustor. The injector design goal is to achieve good premixing of steam and natural gas. The drawing also indicates a pilot combustor that partially oxidizes the fuel and supplies heat required for preheating the steam-fuel mixture to desirable reforming temperature. The pilot combustor is operated at rich conditions with an equivalence ratio around 2.3:1. The exhaust leaving the pilot combustor enters a mixing section where the combustion products contact with the incoming steam and fuel.

Fuel and steam are injected into the mixing zone via a modified Saturn injector equipped with a fuel/steam mixture swirler (Figure 30). It consists of a central fuel passage with exit area of 0.0057 in^2, and a surrounding annular passage for steam flow with an exit area of 0.012 in^2. The nozzle ends at the plane of the swirler vanes, before the extended venturi. The swirler and fuel nozzle exit into a venturi device which serves as a mixing section. The steam and fuel would be preheated prior to the mixing section. The mixed gases are constrained to pass through a catalytic reactor constructing as a multichannel monolith where the high hydrogen content secondary fuel is generated. The hydrogen produced from the steam-fuel reforming creates energy from non-combustible steam and increases the thermal efficiency.

The monolith material of construction is cordierile ceramic. The active catalytic materials are deposited on the inner surface of the monolith channels thus exposing the reacting gases to a large catalytic surface area. A rapid quenching zone consisting of an uncoated metal honeycomb is also included as indicated in Figure 29. The channel diameter of metal honeycomb was selected to meet the quenching diameter (0.024 inch) of hydrogen flame to prevent the flame flashback. After the

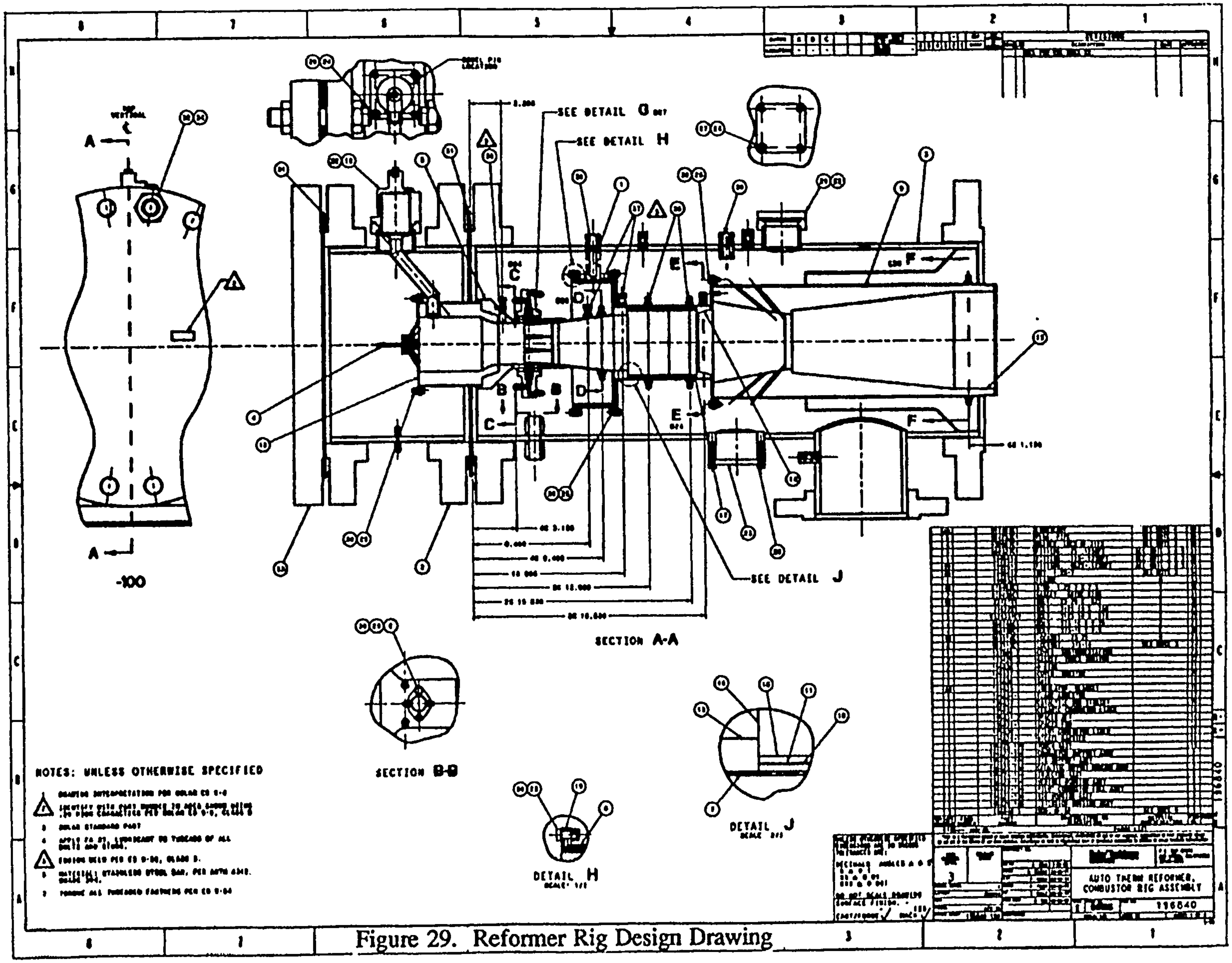


Figure 29. Reformer Rig Design Drawing

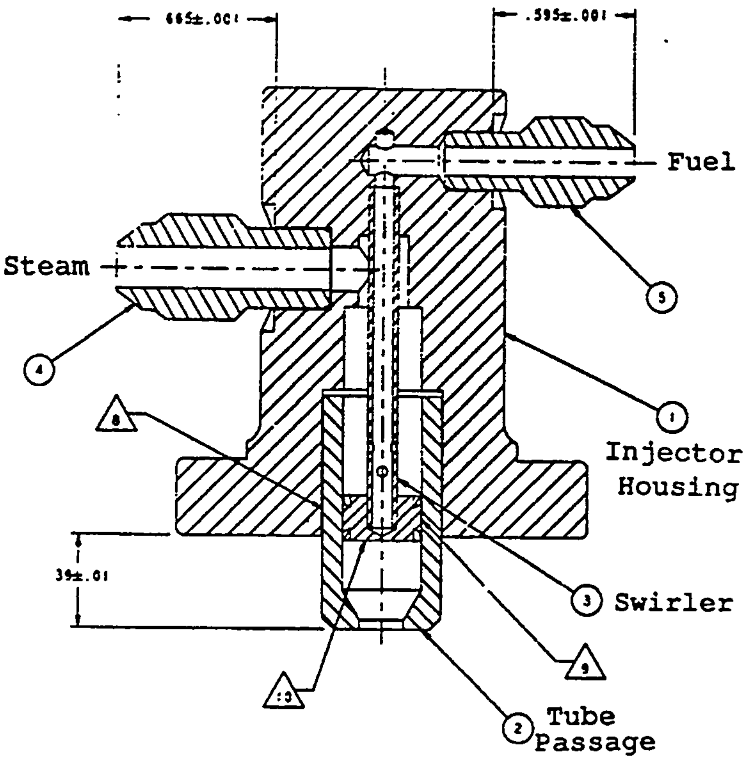


Figure 30. Design of Fuel and Steam Mixture Injector

quenching zone, sufficient air is brought angularly through air holes to mix rapidly with the reforming product which leads to autoignition. There is no need for an auxiliary fuel or the torch assistance for the combustion of the reformed fuel.

The rapid mixing is crucial to prevent local hot spots and ensure low NOx emissions. The equivalence ratio in the post combustor is designed to be around 0.25. A large amount of air is quenched and used to further burn the reformed hydrogen-rich product gas. The final burn-out of H_2, CO and/or unconverted methane takes place in the post combustor where combustion is completed. The flame temperature calculated by Stanjan[14] is around 2450°F to ensure low emissions. The pilot combustor and post combustor are all refractory lined to reduce any heat loss. A composite picture of the reforming test rig with its housing configuration is illustrated in Figure 31.

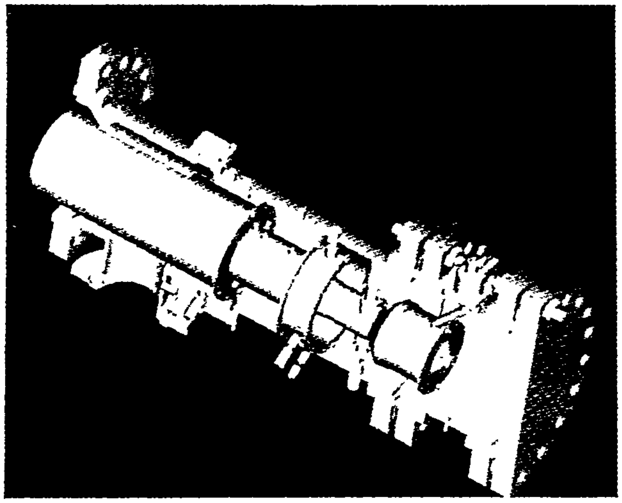


Figure 31. Composed Picture of Reforming Test Rig with its Housing Configuration

4.2 ATR RIG TESTING

Combustion integration and operation problems are foreseen due to the high-hydrogen-content secondary fuel that is produced. Rig tests are designed to resolve some of these problems. Tests were conducted using heated pressurized air and natural gas with steam injection to assess the likelihood of the exhaust waste heat recovery. A primary catalyst and the best operating condition were employed for the rig testing based on the test results and the selection from the previous tube reactor testing.

Two initial rig tests have been conducted to investigate the fuel reformation and the reformed product gas combustion. The first test was a system shakedown run to see all the rig components being connected properly including the thermocouples and the control valves. Steam is supplied from an electric steam generator to produce saturated steam. The steam flow rate is metered with a McCrometer V-Cone Flowmeter and controlled with an electrically-actuated transmitter and control valve. Testing was completed at 40 psig and stable flame was maintained over a 2 hour period with several ignition sequences demonstrated without any auxiliary fuel burning downstream of the post combustor. The reforming bed temperature was increased from 1200°-to-1500°F and held around 1400° to 1550°F during the test. Burning the hydrogen-rich product gas under steady-state flame temperatures has been achieved with a controlled inlet air flow. Ignition with the reformed product gas was much smoother than with natural gas. Furthermore, once ignition was obtained the reformed gas burns with remarkable stability. Lightoff and steady-state operation were easily controlled.

The second test was oriented toward obtaining baseline performance data with a completed set of reforming component over the full range of operating conditions. The test (Table 8) was conducted at reforming temperatures of 1300° to 1600°F and under operating pressures of 60 to 120 psig. Steam was injected at steam-to-fuel ratios in the 0.3 to 1.0 range. The successful light-off was easily achieved with stable flame operation. The pilot combustor was tested at fuel rich conditions. The rig post-combustor operated in a stable manner with the exit temperatures ranging from 2000°-to-2500°F (Figure 32). The combustor was operated for over two and half hours with the last 30 minutes running the pilot combustor at high fuel-to-air ratios. At this rich burning condition in the pilot combustor, the pressure became unstable, indicating a rich extinctioin occurred when the methane exceeded its flammability limits.

Table 8. Initial Test Results of ATR Rig Testing

• **Reformer Temperature (°F)**	1300 - 1600
• **Pressure (psig)**	60 - 120
• **Steam-to-Fuel Ratio (:1)**	0.3 - 1.0
• **Combustor Temperature (°F)**	2000 - 2500
• **Pressure Drop (%ΔP / P)**	3.5 - 5.6

Results from the tests were positive in that a stable burning of product gas was maintained and controlled with an easy ignition, moderate pressure drops and without the assistance of auxiliary fuel and torch. As shown in Table 8, the pressure drops, expressed as percent, for the entire testing were held within 5.6 percent of the total pressures. Observation of the flame by a TV monitor through the rig vessel window showed the flame color difference between the hydrogen-rich product gas and natural gas. The flame color of reformed product gas is pale white and burned slightly brighter compared to a light orange flame for natural gas, indicating a striking change in flame character when burned the refomed hydrogen-rich product gas. Burning the reformed product gas produced. Rig tests are designed to resolve some of these problems. Tests were conducted using heated, pressurized air and natural gas with steam injection to assess the likelihood of the exhaust waste heat recovery. A primary catalyst and the best operating condition were employed for the rig testing based on the test results and the selection from the previous tube reactor testing.

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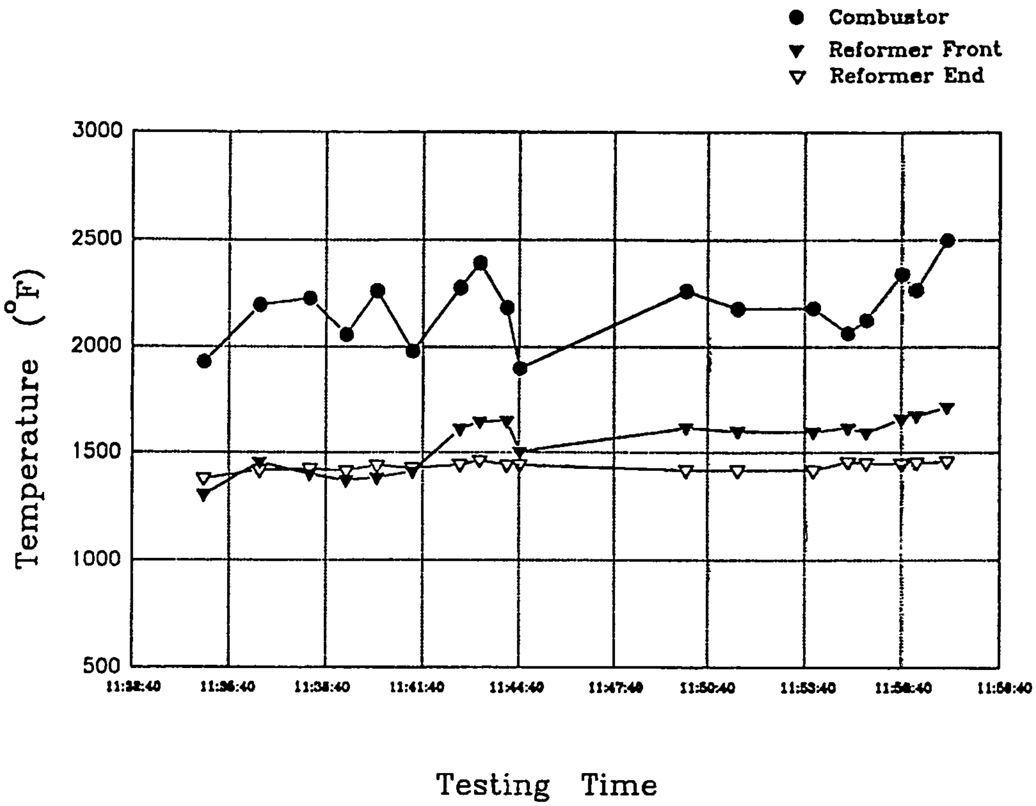

Figure 32. Temperatures of Reformed Bed and Post Combustor From ATR Rig Test

improves stability because of the wide flammability limits of hydrogen content. In this test run, the temperatures of reformer bed were stable in the range around 1300 - 1600°F (as shown in Figure 32).

This second test was designed for a view of a constant combustion of the reformed product gas. Without optimizing the conditions for the exhaust emissions, the CO concentrations obtained from the test were consistently below 15 ppm (Figure 33). The HC emissions stayed high due to the rich burning of pilot combustor. The NOx emissions remained between 25 to 55 ppm due to the high stoichiometric flame temperature of hydrogen. NOx emissions are generated primarily in the preheat and pilot combustors (Table 9), those will not be required or can be operated at lower temperatures for the recuperated advanced turbine system. Additional tests will be required to run at much optimized conditions to investigate the low NOx emissions.

During post-test inspection the venturi mixing zone was deformed and some of the structure material was missing. The cause of this failure could be a hot spot, the bed temperature exceeded 2700°F, that developed during periods of higher fuel-air ratios in the last half-hour testing of the pilot combustor. Meanwhile, inspection of the used reforming catalyst revealed that small sections of the ceramic support were burned out and warped in several places. Small sections of ceramic had also been melted away, due to the high exit temperatures from the pilot combustor in the last thirty-minutes of operation.

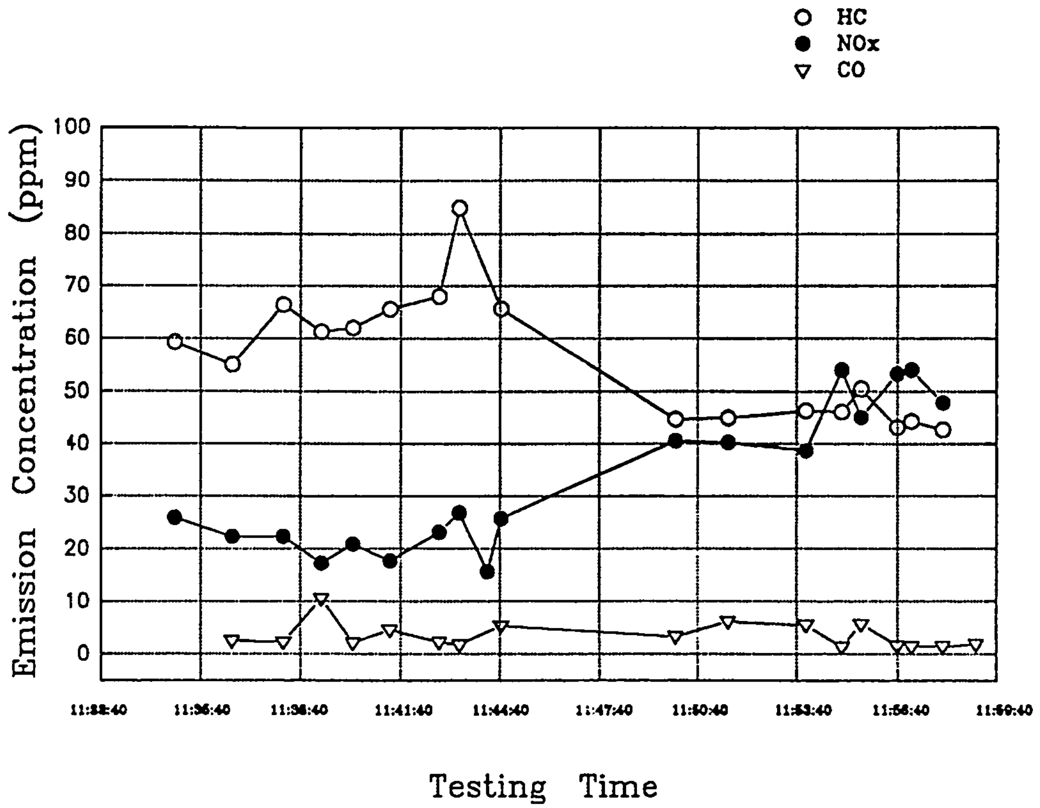

Figure 33. Emissions of ATR Rig Test

Table 9. Emissions of Initial ATR Rig Testing (ppmv)

• **NOx Emissions**	25 - 55
(NOx from pilot combustor)	(15 - 30)
• **CO Emissions**	5 - 15
• **UHC Emissions**	40 - 90

5.0 CONCLUSIONS AND SUGGESTIONS

The fuel reforming tests have demonstrated the ability to produce a hydrogen-rich reformed fuel for combustion. Reacting a hydrocarbon fuel such as natural gas or diesel with steam generates 60 to 75 percent of hydrogen (on a dry basis) in the product gas. A hydrogen-rich reformed fuel is considered an excellent, promising source of alternative gaseous fuel from the standpoint of combustion. Initial combustion testing of reformed fuel shows an easy ignition, stable flame, moderate pressure drops, and burning without the assistance of torch and auxiliary fuel. Lower emissions and higher combustion efficiencies are waiting for further proof testing. The potential for lower thermal and fuel-bound NOx emissions when burning reformed fuels is great because hydrogen can be burned in much leaner mixtures due to its mixing ability and wider flammability limits than natural gas. Because a hydrogen-rich reformed fuel has a low carbon content, the reformed fuel will have inherently low CO and unburnt hydrocarbon emissions. A combustor with a built-in fuel reformer has the potential for low overall emissions.

A fuel reformer can be designed for use with a wide range of fuels to meet customer specified requirements. Fuel reformation produces the same primary constituents regardless of the parent fuel. This would allow a single fuel injection and combustion system to be employed and make the system fuel independent. Whether the reforming is applied for hydrocarbons, biomass, or coal-derived fuels, the fuel to be burned would be hydrogen-rich and independent from the parent fuels. Solid fuels and heavy oils can be readily used by gas turbines, if they are reformed properly. Heavy crudes or solid fuels can be gasified or hydrocracked prior to reforming, then a clean, homogeneous gaseous product could be produced and burned at low emission levels. When the steam required for the reforming is recovered from the turbine exhaust, the thermal efficiency is increased leading to a chemical recuperation of steam and fuel. A reformer in the advanced turbine system would improve the efficiency and provide a low emission combustion for utilizing a wide range of fuels.

Based on the encouraging results of this task, the future studies needed to be conducted for the development of fuel reforming have been identified and are outlined below:

- Demonstrate the low emissions and high thermal efficiency as steam and fuel chemically recuperate. The initial series of the rig testing could involve a short parametric test to optimize the reforming and lean combustion conditions for target levels of emission and efficiency. Operation at the selected conditions for long time testing would then be conducted to assess long-term durability effects on the system operations. The durability tests would include the investigation of a more thermally stable monolithic material for improving catalyst life and substrate structure strength.

- Reform alternate fuels such as heavy crudes and low-grade fuels derived from coal and,biomass. Catalyst selection and criteria for alternate fuels reforming along with catalyst life, carbon built-up, and poisoning are needed to be tested. In selection of a gasifier integrated with solid fuel reformation, the considerations have to be based on the product gas requirements and the process constraints. Ash particulate carryover and clean-up in the exit gas stream, high carbon conversion, thermal efficiency, and turndown ratio are the few among the major concerns in the gasifier selection. Indirect firing with solid fuel partial oxidation to generate desirable hydrogen for improving flammability of coal-derived medium-Btu gas needs also to be investigated.

- Explore a multi-stage catalyst bed for integrating fuel reformation with catalytic combustion. A reformer coupled to a catalytic combustor would produce the favorable reformed fuel for a low-temperature, low emission catalytic combustion. Different stages of catalysts and operating conditions can be selected and tested using our existing batch-tube reactor which is currently being modified to be able to operate under pressure (up to 250 psi). A section of CO oxidation catalyst could be included to overcome the high CO emissions usually generated from the catalytic combustion. A CO endothermic reaction catalyst could also be coated on the engine hot sections or turbine blades for cooling and CO reduction. This would allow the catalytic combustion to be operated with low CO and HC along with low NOx for achieving the overall lower emission targets.

- Estimate reformer system cost with integration of gas turbine engines. A cost estimate needs to be conducted before the efficiency and emission advantages of fuel reformation can be realized. The component development is required to address a number of integration design criteria including system startup, loading, and operation management. Safety concerns with hydrogen leakage and flashback are also required to be detected. A fuel reformer can be added to an advanced turbine system whenever marketplace economics and preferences look favorable.

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