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ABSTRACT

The objective was a fuel processing system that would use No. 2 fuel oil or other heavy sulfur-containing fuels to provide hydrogen for fuel cell power plants. Two approaches were considered, adiabatic and hybrid steam reforming.

In the adiabatic reformer, air is added to the inlet fuel and steam to provide, by combustion, the endothermic heat for reforming. A fuel mixing nozzle and a system of two catalysts were developed which permitted a bench scale (3 kW) adiabatic reformer to operate for 800 hours on No. 2 fuel oil and some coal liquids at design conditions for a 4.8 MW phosphoric acid fuel cell power plant.

The hybrid reformer consists of a primary catalytic, tubular reformer followed by an adiabatic reformer in series. Various catalysts for the primary reformer were tested with No. 2 fuel oil in an electrically heated bench-scale reformer. Catalyst T-12 (Toyo Engineering Company) operated carbon-free at conditions suitable for the hybrid reformer for over 300 hours.

At the design heat rate for the 4.8 MW phosphoric acid fuel cell power plant, the cost of the power plant with the hybrid fuel processor was estimated to be 8% less than with the adiabatic reformer.



EPRI PERSPECTIVE

PROJECT DESCRIPTION

RP1041 involves a group of contracts that have the objective of expanding the range of fuels that can be used efficiently and economically in fuel cell systems. This final report, which was preceded by EPRI Interim Report EM-1701, describes the development of fuel processors that could utilize middle-distillate fuels in dispersed fuel cell generators. Since the interim report, activities have focused on developing what is referred to as the hybrid process. This consists of a high-temperature catalytic reformer followed by a secondary, internally fired adiabatic reformer. The hybrid process was also evaluated by Kinetics Technology International Corporation (KTI) under a complementary project, with results described in EPRI Interim Reports EM-1010 and EM-1487 and EPRI Final Report EM-2096.

PROJECT OBJECTIVE

When RP1041 was initiated in 1978, the objective was to demonstrate the feasibility of adiabatic reformers, using high-sulfur middle-distillate fuels, to operate at the conditions required for dispersed generator applications. This involved evaluation of alternative catalyst systems, scale-up of the reactor, and testing of petroleum and coal-derived liquid fuels. While improvements in catalyst performance were demonstrated, the scaled-up adiabatic reforming process was only marginal in meeting dispersed generator goals; therefore, the effort was redirected in 1980 toward evaluating catalysts in the hybrid process.

PROJECT RESULTS

It is believed that the results described in this report and in the KTI reports confirm the technical feasibility of the hybrid fuel processor to use high-sulfur middle-distillate fuels in dispersed fuel cells. Furthermore, the hybrid process promises lower capital costs than alternative single-stage processes, and it is shown to be insensitive over a wide range to the degree of fuel conversion in its primary (thermocatalytic reforming) stage. This could have important implications in the operability of the hybrid process and its control requirements in dispersed generator service.

The hybrid fuel processor, however, will be physically larger and thus more expensive than a conventional steam reformer using light, low-sulfur fuels such as natural gas or naphtha. Thus, further engineering studies are required to determine if the hybrid processor is cost effective, and this will be very sensitive to many factors including the price and/or availability of No. 2 fuel oil in relation to natural gas or naphtha. In view of current projections showing little real differences in the availability or price of such fuels as No. 2 fuel oil, naphtha, and natural gas, it is believed that the hybrid processor technology can be shelved for now and picked up for engineering development whenever there is interest in its application by specific utilities.

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At United, in addition to the authors, significant technical input was given by D. R. McVay, B. Dec, L. Karavolis and W. Wnuck.



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SUMMARY

The objective of this project, which began in 1978, was to develop a fuel processing system that would use No. 2 fuel oil or other heavy sulfur-containing fuels to provide hydrogen for fuel cell power plants. The fuel processor in present plants, such as the 4.8-MW FCG-1 Demonstrator installed in the Consolidated Edison system in New York City, is a catalytic steam reformer capable of converting natural gas or naphtha to hydrogen for use in fuel cells. The sulfur content of the feed to catalytic steam reformers must be very low (< 0.1 ppmw) to prevent deactivation of the reformer's nickel catalyst. 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 of reforming of ethane in the presence and absence of sulfur as shown in Figure S-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 .

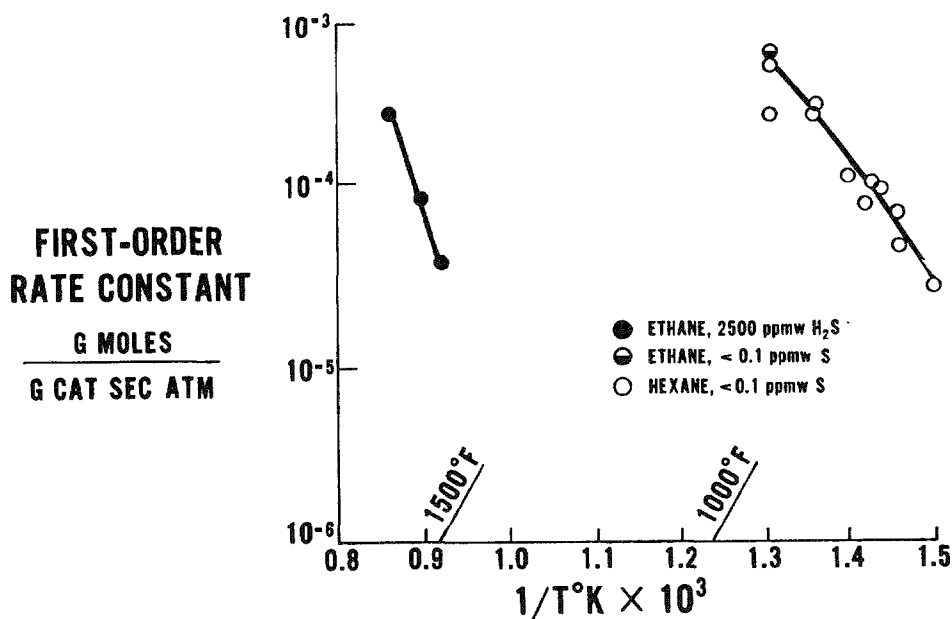


Figure S-1. Effect of Sulfur on Steam Reforming Activity of Supported Nickel Catalyst

For natural gas and naphtha, a hydrosulfurizer reactor and zinc oxide absorption bed placed upstream of the reformer effectively remove sulfur compounds to the required low level. But the sulfur compounds in heavier petroleum distillate fuels and coal-derived liquids are more complex compounds that are not effectively removed by this method. Therefore, the purpose of this project was to develop a fuel processing system which would convert these heavier fuels directly to hydrogen without upstream sulfur removal.

Four sulfur-tolerant fuel processing systems, shown schematically in Figure S-2, were considered in this project. The thermal steam reformer is simply a very high temperature tubular reformer heated externally by combusting anode vent gas. In the adiabatic reformer, air is added to the fuel and steam to provide, by combustion, the endothermic heat for reforming. 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. The hybrid reformer has two reactors in series; a tubular (primary) reformer in which only partial conversion of fuel is effected hence requiring lower operating temperatures, followed by an adiabatic (secondary) reformer to which air is added, to complete the conversion. The cyclic reformer has two reactors in parallel, operating alternately in a reforming or regenerator mode. Heat generated in one reactor by combustion is stored in the heat capacity of the bed to supply the endothermic heat for reforming in the subsequent cycle.

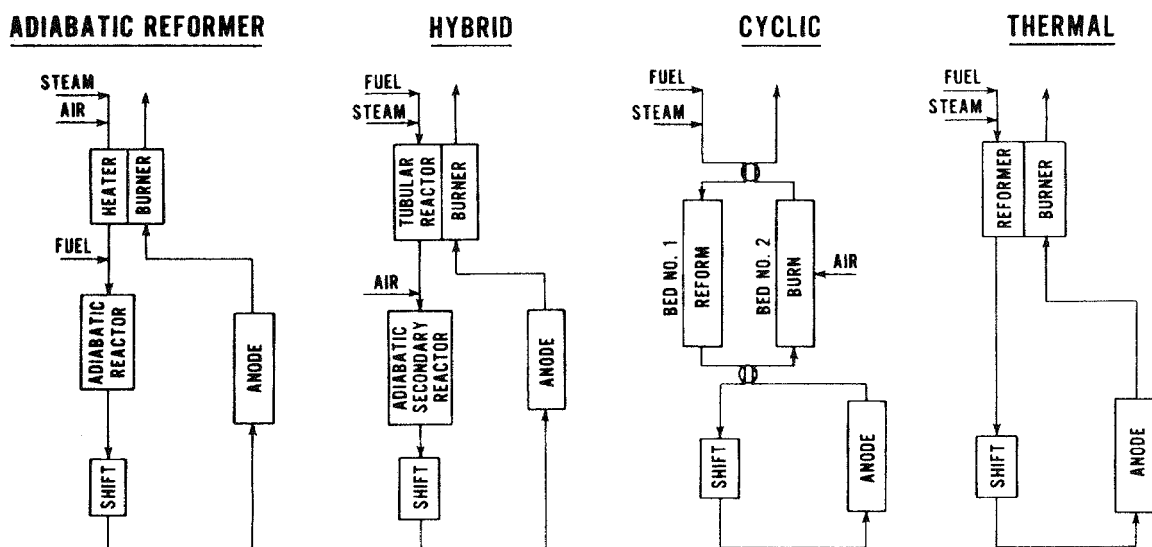


Figure S-2. Fuel Processing Systems Studies

The early work in this project focused on the adiabatic reformer. Analytical studies defined operating conditions for the reformer in a 4.8-MW phosphoric acid fuel cell power plant. Early tests with commercial nickel catalysts in various reactor configurations were unable to operate at these conditions without forming carbon. With specially developed catalysts and a fuel mixing nozzle, a bench scale (5-kW) reformer operated for 800 hours on No. 2 fuel oil and some coal liquid fuels at design conditions, as shown in Table S-1. Recently, a scaled-up (30-kW) reformer verified this operation. The development and evaluation of the adiabatic reformer have been described at length in an interim report (1).

Table S-1
ADIABATIC REFORMER PERFORMANCE

	Design ¹ Baseline	Reactor Performance	
		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, lb. fuel/ ft ³ reactor-hr	12	24	12

¹ For 4.8 MW Phosphoric Acid Power Plant at 9300 Btu/kWh.

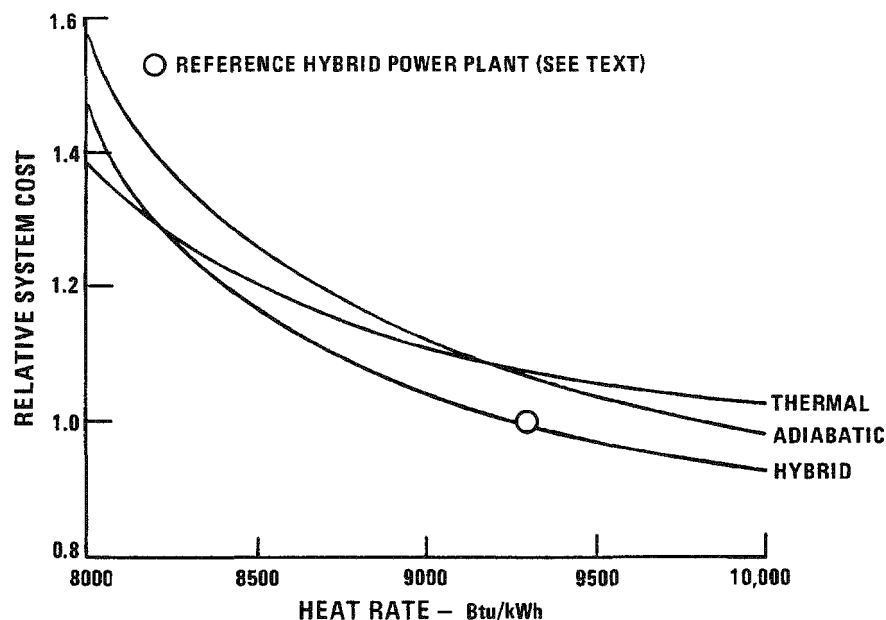
² Six inch diameter reactor with optimized nozzle.

³ Two inch diameter reactor with optimized nozzle.

⁴ Extrapolated to design space velocity.

In that report, a preliminary analytical study compared the performance of the hybrid, cyclic and thermal steam reformers to that achieved by the adiabatic reformer. The size and cost for the cyclic reformer were based on the results of brief tests with a small single-bed reactor. The operating conditions for the thermal and hybrid reformers were estimated by assuming, without verification at that time, that the primary reformer could reform No. 2 fuel oil using metal oxide and nickel catalysts developed for the adiabatic reformer. The power plants were compared by estimating the cost of a power plant capable of operating at a given heat rate. In the preliminary study, the cyclic reformer had the potential for achieving lowest cost; however the ability of the parallel switching reactors to operate stably at the assumed conditions was not demonstrated.

Of the remaining fuel processing approaches, compared in Figure S-3, the hybrid reformer appeared most cost-effective. The projected performance, however, was highly contingent upon the ability of the primary tubular reformer to partially convert fuel at suitable temperatures and without formation of carbon.



(REPRODUCED FROM EPRI EM-1701, FEBRUARY 1981)

Figure S-3. Comparison of Alternate Fuel Processors

Tests at Toyo Engineering Company (TEC) in conjunction with Kinetics Technology International Corporation showed that a tubular reformer charged with TEC nickel-free catalyst, T-12, followed by high activity nickel catalyst, T-48 downstream, could reform No. 2 fuel oil at conditions suitable for a hybrid fuel processor (2). Later tests at United Technologies confirmed this result although they also indicated that very high reformer bed temperatures ($>1800^{\circ}$) were required to prevent carbon accumulation in the T-48 catalyst (3).

In the latest phase of the project, described in this report, metal oxide and noble metal catalysts developed by United were evaluated for duty in the primary reformer of the hybrid fuel processor. The goal was to reduce tube wall temperatures and sensitivity to carbon formation. However, these catalysts were rapidly deactivated by No. 2 fuel oil and accumulated carbon. Finally, therefore, the performance of a reformer filled entirely with TEC T-12, the nickel-free TEC catalyst, was evaluated.

Tests were run in an electrically-heated tubular reformer which was fed from 1 to 3 pounds per hour of No. 2 fuel oil. At temperatures and space velocities suitable for the hybrid reformer, the conversion of fuel to carbon oxides was low, but the reformer operated carbon-free for over 300 hours. Moreover, the partially converted fuel did not deposit carbon in the exit lines provided the temperature of the process steam did not fall below about 1000°F. This assured that in the hybrid system, the product of the primary reformer could be transferred to the secondary reformer.

Analytical studies were made of a 4.8-MW phosphoric acid fuel cell power plant with a hybrid fuel processor, shown schematically in Figure S-4. It was evaluated by optimizing the system to obtain minimum power plant cost at a constant heat rate of 9300 Btu/kWh, the design goal. This heat rate was maintained by changing the power section efficiency (fuel cell voltage) to offset any change in fuel processor efficiency. An existing cell performance model was used to adjust the total cell area required for the different cell voltage, fuel gas quality and hydrogen utilizations. A computer program determined mass and energy balances, process temperatures, pressures, flow rates and gas compositions throughout the system. The primary and secondary reformer sizes in the hybrid fuel processor were estimated using catalyst activities determined for the T-12 catalyst in the tubular reactor, and for the metal oxide and nickel catalysts in the adiabatic reformer.

The system cost proved to be relatively insensitive to the fuel conversion achieved in the primary reformer. There was an optimum at 53.5%, as shown in Figure S-5, but conversions of 40 - 60% had only 2% impact on plant capital cost. The process gas temperatures, composition and flows at stations throughout the power plant at 53.5% fuel conversion are shown in Table S-2. The estimated cost of the power plant with the hybrid fuel processor was 8% less than that with the adiabatic reformer, compared at the design heat rate in Table S-3. By increasing the cell area the heat rate can be reduced, with some increase in cost. Thus, the heat rate could be reduced to 8300 Btu/kWh with a 20% increase in power plant cost as shown in Figure S-6. At this heat rate, the power plant cost with the hybrid fuel processor is 15% lower than with the adiabatic reformer.

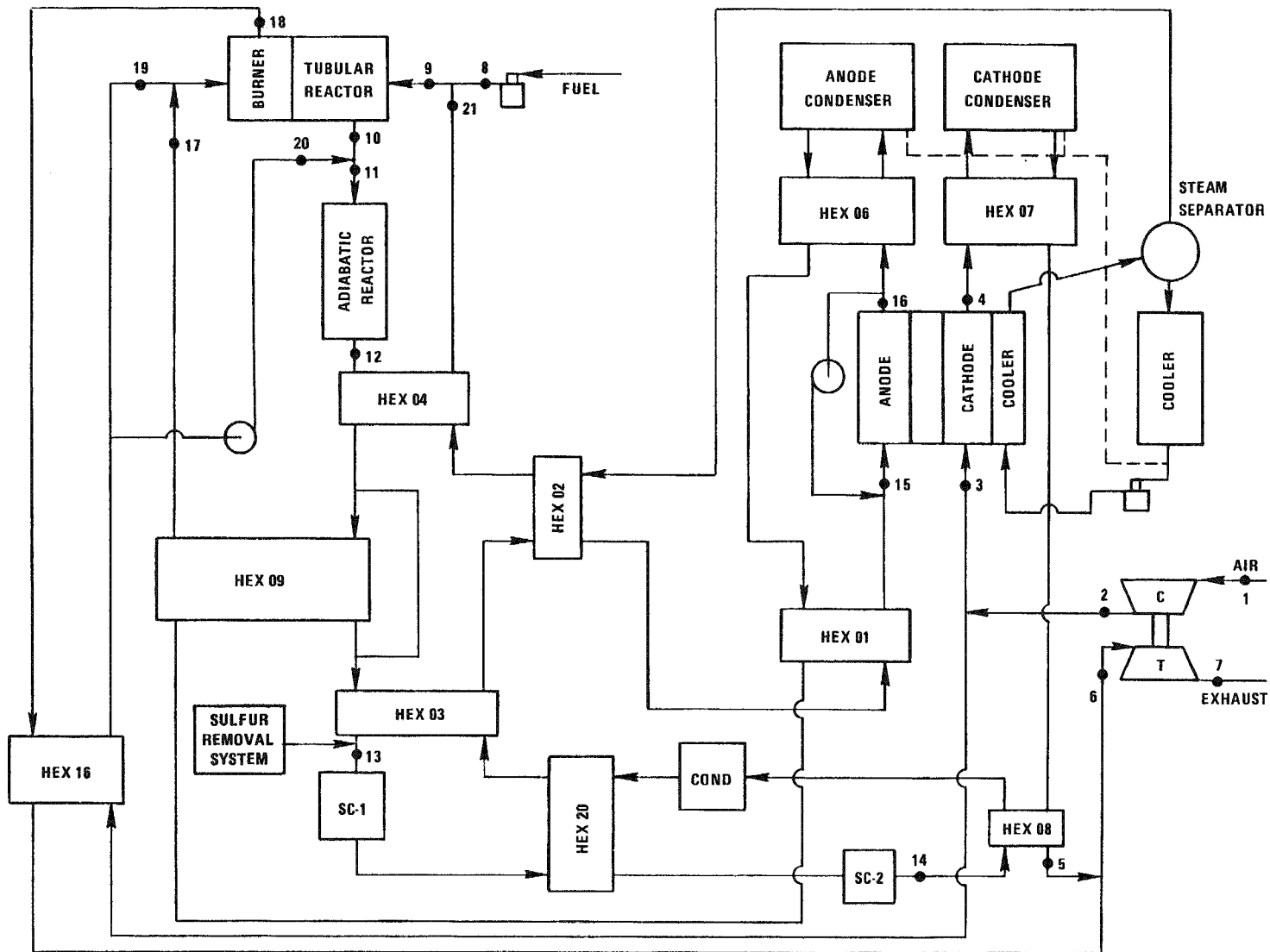


Figure S-4. Hybrid Reformer Power Plant Schematic

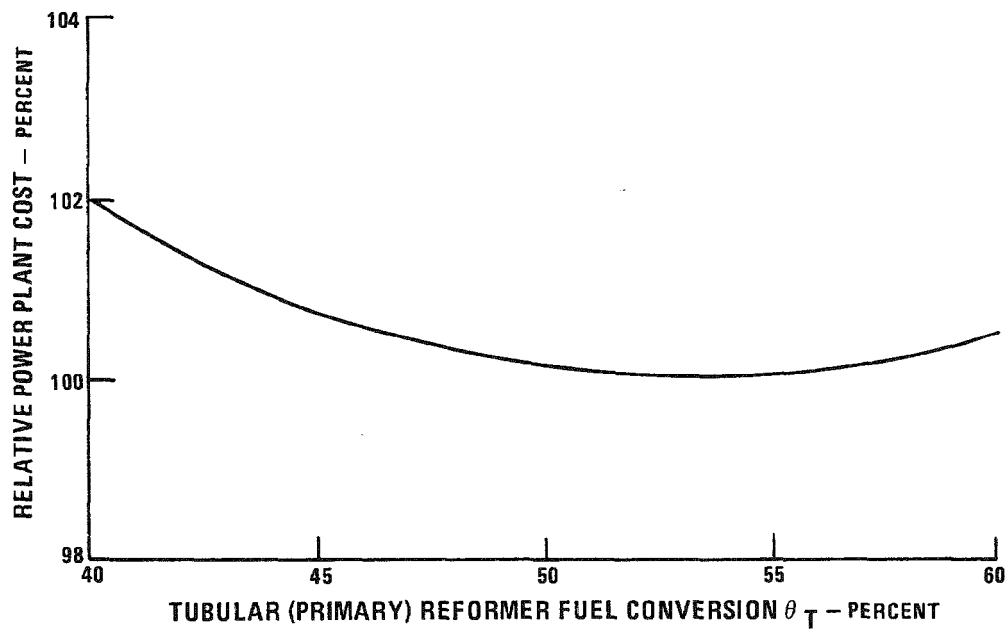


Figure S-5. Hybrid Power Plant Optimization

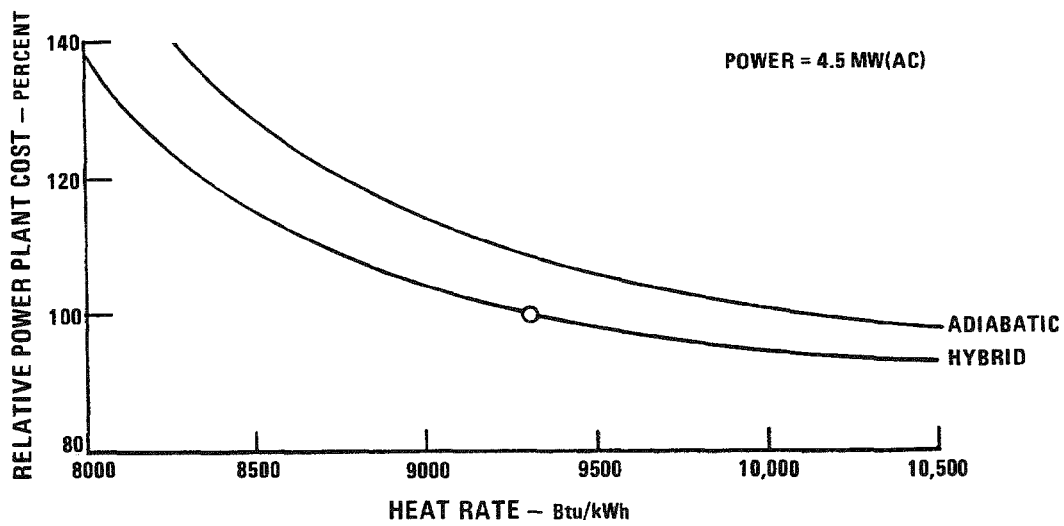


Figure S-6. Impact of Heat Rate on Power Plant Cost

Table S-2
HYBRID POWER PLANT PROCESS CONDITIONS

Station	Temp.	Flows (Mols/Hr)								Fuel (ppm)
		H ₂	H ₂ O	CH ₄	CO	CO ₂	O ₂	N ₂	Air	
1	95						339.2	1261.0	15.8	
2	432						339.2	1621.0	15.8	
3	432						258.8	961.9	12.1	
4	375		310.5				103.5	961.9	12.1	
5	482		61.8				103.5	961.9	12.1	
6	698		141.2			156.3	111.9	1261.0	15.8	
7	400		141.2			156.3	111.9	1261.0	15.8	
8	95									2160
9	950		468.9							2160
10	1745	132.3	333.4	72.7	31.8	51.8				
11	1572	132.3	333.4	72.7	31.8	51.8	30.5	113.5	1.4	
12	1638	287.7	307.8	7.8	74.8	73.6		113.5	1.4	
13	620	287.7	307.8	7.8	74.8	73.6		113.5	1.4	
14	539	356.2	239.3	7.8	6.3	142.2		113.5	1.4	
15	533	365.3	175.2	9.4	7.5	170.9		136.4	1.7	
16	375	54.8	175.2	9.4	7.5	170.9		136.4	1.7	
17	1342	45.6	18.2	7.8	6.3	142.2		113.5	1.4	
18	1113		79.4			156.3	8.3	298.9	3.8	
19	528						49.9	185.4	2.4	
20	528						30.5	113.5	1.4	
21	1256		468.9							

Table S-3
SYSTEM COMPARISON

Fuel Processing System	Adiabatic	Hybrid
Power Output (MW-Net AC)	4.5	4.5
Heat Rate (Btu/kWh)	9300	9300
<u>Tubular (Primary) Reformer</u>		
Specific Area (lb/hr-ft ²)	--	2.1
Fuel Conversion (%)	--	53.5
Steam/Carbon	--	3.0
Inlet Temperature (°F)	--	950
Exit Temperature (°F)	--	1745
Maximum Wall Temperature (°F)	--	1900
<u>Adiabatic (Secondary) Reformer</u>		
Space Velocity (lb/ft ³ -Hr)	9.0	10.3
Fuel Conversion (%)	98.5	95
Oxygen/Carbon (O ₂ /C)	0.35	0.195
Inlet Temperature (°F)	1300	1572
Exit Temperature (°F)	1625	1638
<u>Power Section</u>		
Cell Voltage (Volts)	.616	.636
Current Density (Amps/Ft ²)	231	245
Relative Power Plant Cost	1.08	1.0



Section 1

INTRODUCTION

The ultimate objective of this program was to develop a fuel processor which would reform No. 2 fuel oil, or other heavy, sulfur-containing fuels, to provide hydrogen for fuel cell power plants. Several systems were considered and two were evaluated in depth, the adiabatic and the hybrid steam reformers. Very simplified diagrams illustrating fundamental differences are shown in Figure 1-1. In the first phase of the program, work focused on the adiabatic reformer, in which fuel, steam and air react in an adiabatic catalytic reactor. The combustion of part of the fuel within the reactor provides the process heat required for reforming and for raising the reactor to temperatures where the catalyst has significant activity in the presence of sulfur. The anode vent gases are burned and the heat is used to preheat the reactants. This reduces the amount of air required which must be a minimum since it consumes hydrogen otherwise used in the cell. With a specially developed fuel mixing nozzle and catalyst, a bench scale adiabatic reformer operated on No. 2 fuel oil at conditions suitable for fuel cell power plants for over 800 hours. The development and evaluation of the adiabatic reformer have been described at length in an interim report on the first phase of this program (1), the Executive Summary of which is included for convenient reference in Appendix A.

A second fuel processor system, a hybrid, was proposed which might further reduce the amount of air required, and hence offer potentially higher reformer efficiency than the adiabatic reformer. In the hybrid fuel processor, fuel and steam first enter a tubular reformer which is heated by external combustion of the anode vent gases. This heat is transferred through the reactor walls to the catalyst. The very high temperatures required to activate the sulfur-poisoned catalyst in the tubular reformer are reduced by only partially converting the fuel. Fuel conversion is completed in a secondary, adiabatic reformer. The process heat provided in the primary, tubular reformer reduces the heat and thus the air required in the adiabatic reformer.

Preliminary assessments of the hybrid reformer suggested that it had the potential to achieve higher efficiencies than the adiabatic reformer. This resulted in reduced overall power plant cost when compared at fixed heat rate. The projected performance, however, was highly contingent upon the ability of the primary tubular reformer to partially convert fuel at suitable temperatures and without formation of carbon. Tests at the Toyo Engineering Company in conjunction with Kinetics Technology International Corporation (KTI), showed that their T-12 and T-48 catalysts could perform this function (2). Tests at United Technologies confirmed the result (3), although they also showed that very high reformer bed temperatures were required to prevent carbon accumulation in the T-48 catalyst.

In the final phase of the present program (RP1041-4), the objective was to reduce the tube wall temperatures and sensitivity to carbon formation of the primary reformer and to complete the evaluation of the fuel cell power plant with a hybrid fuel processor. In an electrically-heated reactor, several metal oxide and noble metal catalysts were evaluated for duty in the primary reformer. None except the TEC T-12 catalyst was able to prevent accumulation of carbon in the reformer for extended times. Consequently, in a final analytical system evaluation, a fuel cell power plant with a hybrid fuel processor containing T-12 catalyst in the primary reformer was compared to a similar power plant with an adiabatic reformer operating at conditions demonstrated in test reactors.

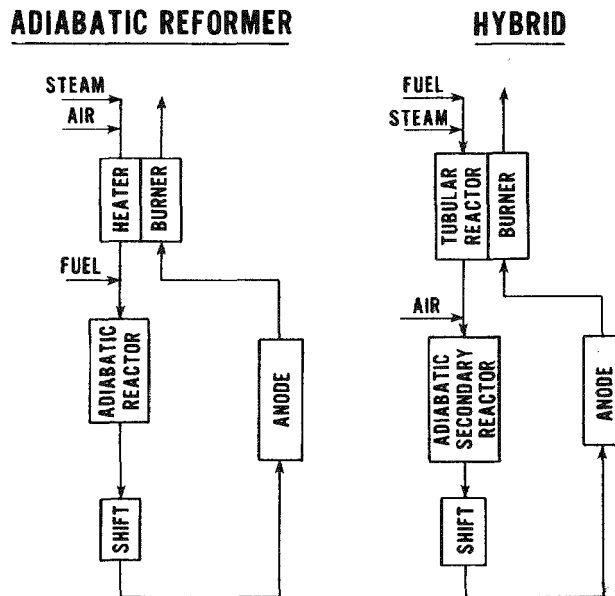


Figure 1-1. Fuel Processing Systems Evaluated

Section 2

PROGRAM PLAN

To evaluate the hybrid fuel processing system, the following tasks were performed:

- An electrically-heated tubular reactor, 4 feet long and 1.33 inches in diameter was constructed in which heat and mass transfer characteristics approached those found in full scale reformers.
- The performance of metal oxide, noble metal and TEC T-12 catalysts was measured at conditions suitable for the primary reformer of the hybrid.
- At conditions of low fuel conversion in the tubular reformer, the capability for transferring the exiting process stream to the secondary reformer was established.
- In an analytical system study, a 4.8 MW phosphoric acid fuel cell power plant with a hybrid fuel processor was optimized with a T-12 catalyst in the primary reformer. Its cost was compared at fixed heat rate with a power plant in which the fuel processor was an adiabatic reformer.



Section 3

TEST STAND AND PROCEDURES

A reactor was constructed to evaluate catalysts for the primary reformer of a hybrid fuel processor. It was a conventional packed bed reactor, 1.38 inches in diameter and 4 feet long. A vaporizer of novel design fed steam from 1.5 to 3 pounds per hour of vaporized No. 2 fuel oil in a down-flow configuration. The reactor was heated by a Lindberg furnace, with four heating zones so that an axial temperature profile could be imposed on the tube, simulating heat and mass transfer characteristics expected in the primary reformer of a hybrid system.

A photograph of the test stand is shown in Figure 3-1. The cylindrical vessel on the left is a superheater which heats steam to the calibration temperature of the steam metering orifices. The four zone 30-kW Lindberg furnace is shown in the center. Five sample taps from the reactor lead to separate condensers and liquid condensate traps seen on the right-hand wall, before passing to a gas chromatograph for analysis.

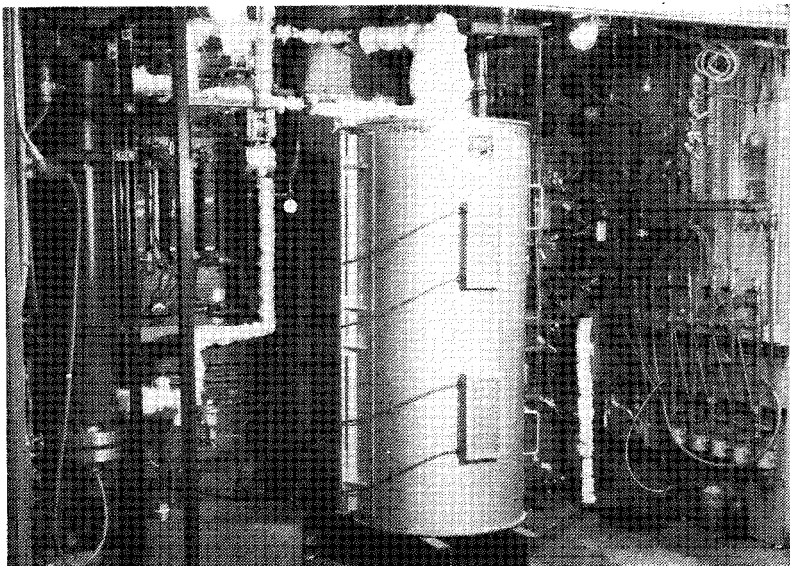


Figure 3-1. Test Stand

Figure 3-2 is a more detailed view of the reactor installed in the furnace with the furnace door open. A six-inch scale is taped on top of the furnace door as a dimension reference. The five sample taps are shown insulated to minimize coking of the sample stream as it is withdrawn for analysis.

The sample tubes exited the furnace through the heated furnace wall. There was concern that measured conversions might be in error due to reaction in this section of the tube. Tests proved that this was the case at low flow rates of gas through the sample tube but that as flow rate increased, the effect became insignificant.

The sample taps projected one-quarter of an inch into the catalyst bed to assure sampling representative of the bulk process stream composition. Thermocouple leads exited with the sample lines. Thermocouples were placed at the center of the catalyst bed, one-eighth inch from the reactor wall and on the exterior reactor wall so that radial as well as axial temperature profiles could be recorded. The insulated body above the reactor is the fuel vaporizer. A rough schematic of the reactor is shown in Figure 3-3, which is a typical data record sheet.

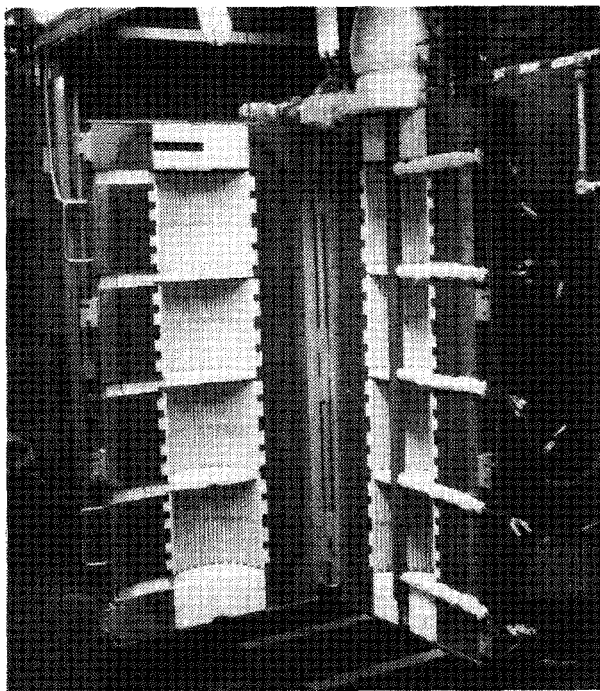


Figure 3-2. Test Reactor

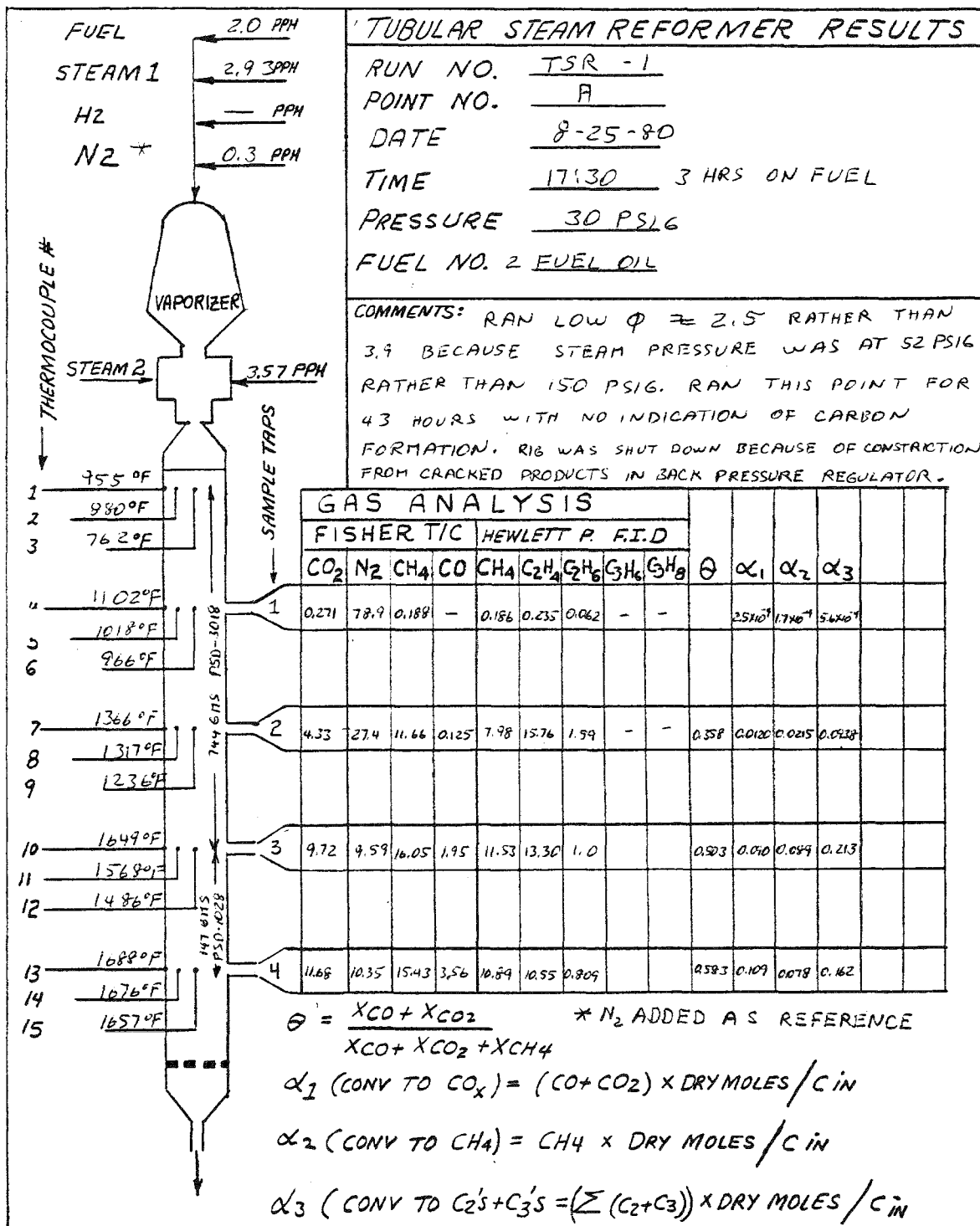


Figure 3-3. Results of First Test Point

The composition of No. 2 fuel oil used as fuel is shown in Table 3-1. A test was also run with a liquid product of the H-coal process which had been hydrotreated to increase its hydrogen content by 1% weight. H-coal liquid analysis is included in Table 3-1.

Various catalysts used in the test program are described in Table 3-2.

Table 3-1
COMPOSITION OF FUELS TESTED

NO. 2 FUEL OIL		1% HYDROTREATED H - COAL LIQUID
Gravity, *API	38.83	
Specific Gravity	0.8307	0.843
CH _x	Ch _{1.78}	CH _{1.78}
Hydrogen (%wt)	12.8%	12.5%
Carbon (%wt)	86.8%	87.16%
Sulfur (%wt)	0.322%	0.06%
Oxygen (%wt)	--	0.27%
Nitrogen (%wt)	--	0.01%
Paraffins (%v)	31.2%	65.3%*
Olefins (%v)	0.8%	
Naphthenes (%v)	40.8%	
Aromatics (%v)	27.3%	34.7%
Halogens (PPM)		58 PPM
Distillates		
1 B Pt	130°F	185°F
10%	340°F	284°F
50%	495°F	367°F
70%	545°F	408°F
90%	597°F	468°F
95%	615°F	496°F
98%	625°F	522°F

Table 3-2
CATALYST TESTED

PSD 3018	A metal oxide on a refractory support, prepared at United 1/8" x 1/16" pallets
PSD 3019	A high surface area form of 3018
PSD 1028	Noble metal on a refractory support, prepared at United, 1/8" x 3/16" pallets
PSD 1042	Noble metal catalyst similar to PSD 1028
PSD 1043	More carbon resistant form of 1042
T-12	A calcium aluminate catalyst with a high loading of calcium, 5 mm diameter spheres. (Toyo Engineering Co.)
T-48	A nickel catalyst with calcium oxide and alumina, 5 mm diameter spheres (Toyo Engineering Co.)



Section 4

TEST RESULTS

The performance of the catalyst was established in a series of test runs which are summarized for reference in Table 4-1. In each run, test points were set at various conditions of temperature, pressure, fuel flow rate and process stream composition. Measurements were made of process stream composition along the reactor length and observations of pressure drop increase on carbon formation were noted. The results are summarized in abbreviated form in Tables 4-2 through 4-9. They are discussed in more detail below.

Table 4-1
SUMMARY OF TEST RUNS

RUN	CATALYST CHARGE	DURATION HOURS	COMMENTS
1	PSD 3018/PSD 1028	138	Metal oxide active Noble metal inactive
2	PSD 3019/PSD 3018	150	Low activity, some carbon
3	T-12	77	* For KTI, reported in (3)
4	T-12/T-48	43	* For KTI, reported in (3)
5	T-12/T-48	158	* For KTI, reported in (3)
6	PSD 3018	203	Attempt to duplicate Run 1 but similar to Run 2
7	PSD 1042	80	Rapid decay - Carbon
8	PSD 1043	270	Rapid decay - Carbon
9	PSD 3018	290	Attempt to duplicate Run 1 but similar to Run 2
10	T-12	213	To map low conversion region
11	T-12	315	To demonstrate endurance and examine exit lines

* Source: EPRI Report EM-2596, Project RP1041-1, June 1981. Prepared by Kinetics Technology International Corporation (3).

Table 4-2
SUMMARY OF TSR RUN 1

Point	Time (Hrs)	Temperature (°F)				PSD 1028	Fuel Flow (pph)	H ₂ O/C	Press. (psig)	Conversion		Comments	
		Inlet		PSD 3018						To C. Oxides			
		Bed	Wall	Bed	Wall					PSD 3018	PSD 1028		
A	3	762	955	1486	1649	1657	1688	2.0	2.50	30	0.090	0.109	Low, Ø, low conversion, no increase in ΔP
B	50	830	978	1553	1765	1656	1727	2.0	3.60	32	0.304	0.423	ΔP seemed to be increasing
C	65	809	977	1572	1741	1650	1757	2.0	3.60	34	0.293	0.378	Continued Pt, B ΔP still increasing
D	71	817	980	1577	1744	1632	1754	2.0	3.60	34	0.289	0.458	Continued Pt. B, ΔP may be dropping
E	75	817	980	1577	1744	1632	1754	1.5	4.80	34	0.241	0.288	Lowered fuel flow ΔP dropping slowly
F	80	787	973	1544	1762	1549	1742	2.0	3.9	37	0.321	0.575	Restarted at Pt. B, ΔP high but steady
G	88	785	972	1575	1773	1620	1749	2.0	3.9	90	0.368	0.483	Raised P insignificant change in conv.
H	105	767	974	1500	1766	1602	1730	3.0	3.9	90	0.194	0.242	Raised flow conversion down
I	110	768	958	1615	1777	1587	1724	1.5	3.9	90	0.468	0.615	Lowered flow conversion high
J	128	776	971	1739	1897	1648	1795	1.5	3.9	90	0.748	0.809	Raised Temps. conversion increased
K	133	715	932	1597	1762	1600	1738	2.0	2.5	90	0.375	0.490	Lowered Ø no apparent effect
L	137	737	957	1525	1759	1613	1724	2.0	5.0	90	0.419	0.548	Raised Ø no apparent effect
* Catalyst Fuel		744 g PSD 3018, 147 g PSD 1028 No. 2 Fuel Oil											

* Catalyst 744 g PSD 3018, 147 g PSD 1028
Fuel No. 2 Fuel Oil

Table 4-3
SUMMARY OF TSR RUN 2

Point	Time (Hrs)	Inlet		Temperatures (°F)				Fuel Flow PPH	H ₂ O/C	Press. (PSIG)	Conversion to C ₁ Oxides		Comments
		Bed	Wall	1st Bed	Exit(a) Wall	Exit Bed	Wall				1st Bed	Exit	
A	6	697	907	1249	1373	1634	1702	2.0	3.9	30	N/A	0.412	Initial pt. conv. <than Run 1.
B	23	695	896	1248	1363	1635	1701	2.0	3.9	30	0.020	0.357	Continue A. Some decay.
C	43	750	940	1254	1363	1637	1699	2.0	3.9	30	0.115	0.359	Continue A. ΔP increasing
D	47	777	948	1263	1366	1652	1701	1.5	5.0	30	0.017	0.403	Lower fuel flow in- crease φ
E	70	777	941	1257	1363	1663	1704	1.5	5.0	30	0.003	0.341	Continue D. ΔP still incre. slightly. Gas analysis questionable.
F	80	791	953	1340	1492	1773	1804	1.5	5.0	30	N/A	N/A	Raised temp., esp. in 3rd quarter. Max. wall 1900° F w/1736° F bed.
G	100	790	1003	1403	1563	1814	1902	1.5	5.0	30	0.010	0.660	Raised inlet T. Signi- ficantly. Looks like significant decay in 1st bed.
H	105	684	914	1241	1365	1634	1702	2.0	3.9	30	0.002	N/A	Repeat A, 1st bed looks badly decayed.
I	108	733	957	1361	1514	1785	1810	1.5	5.7	30	N/A	N/A	Repeat F, slightly higher.
J	120	789	958	1339	1500	1765	1800	1.5	5.0	30	N/A	0.575	Repeat F for gas analysis.
K	135	762	944	1334	1505	1754	1801	2.0	3.9	30	N/A	0.489	Increase S.V. at pt. F. Temps.
L	250	779	953	1259	1365	1675	1708	1.5	5.0	30	N/A	0.262	Repeat of D. PSD-3018 decayed.

TOTAL RUN TIME: 158 hours

(a) 1st bed 551 g PSD 3019, Exit 543 g PSD 3018
Fuel No. 2 Fuel Oil

Table 4-4
SUMMARY OF TSR RUN 6

Point	Time (Hrs)	Temperatures (°F)								Fuel Flow (PPM)	H ₂ O/C	Press (psig)	Conversion to Carbon Oxides		Comments
		Inlet Bed	Wall	2nd Tap Bed	Wall	3rd Tap Bed	Wall	Exit Bed	Wall				3rd Tap	Exit	
A	8.0	663	765	1271	1370	1981	1601	1691	1803	1.5	3.9	30	0.088	N/A	Initial Low temp. point low conv. tap 4 plugged.
B	10.5	664	766	1271	1373	1558	1705	1784	1907	1.5	3.9	30	0.189	N/A	Raised temp. to determine effect of temp on conv.
C	12.5	657	750	1261	1372	1530	1700	1755	1900	2.0	3.9	30	0.109	N/A	Increased reactant flows to determine effect of S.V.
D	29	674	778	1364	1502	1661	1799	1778	1850	1.5	3.9	30	0.336	0.627	Lowered flow and changed temp profile.
E	35	687	786	1364	1495	1714	1818	1817	1865	1.5	3.9	30	0.165	N/A	Rechecked Pt. D after placing on hot hold to unplug tap 3.
F	51	668	763	1366	1507	1650	1803	1771	1855	2.0	3.9	30	0.303	0.528	Raise reactant flows conversion relatively high.
G	57	661	768	1376	1503	1674	1804	1783	1850	1.5	3.9	30	0.351	0.435	Recheck point D tap 3 conversion high, tap 4 low.
H	71	688	786	1374	1498	1667	1796	1780	1849	1.5	3.9	30	0.329	0.551	Repeat Pt 6 after 11 hrs on H ₂ + fuel + steam. conv. similar.
I	75	665	816	1412	1523	1695	1805	1789	1853	1.5	3.9	30	0.318	0.448	Repeat Pt. 6 after 7 hrs on H ₂ /N ₂ tap 4 conv. slightly low.
J	85	686	781	1376	1505	1721	1804	1787	1851	1.5	3.9	30	0.294	0.461	Repeat Pt 6 after weekend shutdown
K	100	682	773	1389	1504	1713	1803	1784	1850	1.5	3.9	30	0.246	0.478	0.06 PPH H ₂ (~15%) conv. slightly lower than expected.
L	108	676	774	1376	1498	1700	1800	1779	1850	1.5	3.9	30	0.257	0.511	No. N ₂ , steamed cat. for 2 hours between Pts K and L.
M	133	619	740	1370	1498	1684	1800	1758	1850	2.0	2.5	30	0.223	0.559	Low H ₂ O/C improves conversion.
N	153	598	724	1390	1498	1709	1801	1765	1851	1.5	2.5	30	N/A	N/A	Tried to compare conversion with Pt. 6, but gas analysis wasn't taken.
O	157	690	787	1385	1498	1697	1803	1768	1851	1.5	3.9	30	0.272	0.500	Repeat of Pt L after low H ₂ O/C point. conv. similar. Shut rig down after this point.

* Catalyst 1027 gm. (1.13 liter) PSD-3018
Fuel No. 2 Fuel Oil

Table 4-5
SUMMARY OF TSR RUN 7

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O C φ	Rig Press. (psig)	Conversion		Comments
			$\frac{1}{2}$ Inlet		2nd Tap		3rd Tap		Exit					Carbon to 3rd Tap	Oxide Exit	
			Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed						
A	0	0	1118	966	1282	1147	1402	1259	1564	1312	-	-	30	-	-	Started point on No. 2 fuel (3220 P.P.M.S.)
	4	4	1123	980	1289	1173	1443	1340	1613	1413	1.5	5.0	30	-	0.23	
	8	8	1245	1067	1465	1324	1622	1517	1702	1646	1.5	5.0	31	-	0.071	
	25	25	1205	1060	1471	1337	1620	1510	1695	1598	1.5	5.0	30	-	0.193	
B	26.5	0	1166	1076	1502	1398	1649	1587	1716	1681	-	-	30	-	-	Point B run after 1.5 Hrs. on steam & H ₂ only
	27.0	0.5	1202	1058	1469	1334	1584	1423	1642	1420	1.5	5.0	30	-	0.722	
	27.5	1.0	1204	1056	1471	1336	1596	1453	1644	1417	1.5	5.0	30	-	0.665	
	28.5	1.5	1204	1060	1473	1338	1625	1496	1710	1530	1.5	5.0	33	-	0.318	
	29.5	3.0	1199	1057	1469	1332	1626	1502	1706	1588	1.5	5.0	30	-	.268	
	30.5	4.0	1200	1059	1471	1336	1625	1499	1703	1597	1.5	5.0	31	-	0.227	
	31.0	4.5	1199	1059	1471	1336	1626	1499	1709	1597	1.5	5.0	30	-	0.244	
C	34.0	0	1315	1159	1479	1446	1634	1599	1703	1687	-	-	30	-	-	Point C started at end of 3 Hrs H ₂ S exposure (0.011 lbs. sulfur into reactor)
	35.0	1	1228	1070	1465	1328	1623	1491	1694	1427	1.5	5.0	30	-	0.663	
	38.0	4	1205	1062	1471	1329	1629	1506	1706	1594	1.5	5.0	30	-	0.202	
	41.0	7	1202	1057	1473	1330	1631	1512	1710	1620	1.5	5.0	30	-	0.179	
	45.0	9	1214	1047	1475	1320	1628	1499	1702	1607	1.5	7.5	36	-	0.155	Raised φ to 7.5
	56.5	22.5	1194	1025	1470	1312	1627	1491	1701	1571	1.5	7.5	30	-	0.246	
	59.0	25	1195	1029	1472	1314	1627	1494	1698	1570	1.5	7.5	30	-	-	
D	59.0	0	1191	1088	1469	1363	1598	1538	1698	1653	-	-	30	-	-	Started on diesel fuel (1090 P.P.M.S.)
	60.5	1.5	1201	1057	1470	1328	1602	1468	1699	1427	1.5	5.0	30	0	0.426	
	64.0	5	1199	1061	1468	1327	1604	1486	1720	1596	1.5	5.0	30	-	0.219	
	67.0	8	1198	1061	1466	1326	1603	1488	1705	1605	1.5	5.0	33	-	0.203	
	70.5	11.5	1196	1058	1465	1324	1603	1487	1705	1610	1.5	5.0	30	-	0.118	
	80.0	21	1198	1063	1466	1326	1605	1489	1700	1598	1.5	5.0	30	-	0.217	
	80.5	21.5	1197	1062	1469	1326	1602	1487	1697	1591	1.5	5.0	31	-	-	Shut down

* Reactor inlet wall temp <1000°F, inlet center bed temp <850°F for all points.
Catalyst 700 g PSD 1042
Fuel As noted

Table 4-6
SUMMARY OF TSR RUN 8

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O C φ	Rig Press. (psig)	Conversion to Carbon Oxides			Comments
			½L		2nd Tap		3rd Tap		Exit								
			Into Wall	Bed** Bed	Wall	Bed	Wall	Bed	Wall	Bed							
A	0	0	1140	1014	1376	1253	1705	1637	1707	1530	2.0	3.75	33	-	-	.395	Steam for 5.5 hrs. + .12 PPH H ₂ recycle Fuel: No. 2 fuel oil with 3220 PPM sulfur Catalyst is decaying
	4	4	1138	1007	1380	1277	1703	1640	1701	1552	2.0	3.75	33	.02	.09	.342	
	8	8	1140	1006	1375	1278	1715	1664	1707	1562	2.0	3.75	36	0.016	0.06	.018	
B	20	0	1137	986	1371	1240	1707	1531	1709	1501	-	-	36	-	-	-	Steam for 2.5 hours with .12 PPH H ₂ recycle Increased φ from Point A Catalyst still decays at high φ
	21	1	1141	983	1371	1245	1707	1549	1720	1537	2.0	5.0	34	0.01	0.16	0.44	
	26.5	7	1145	989	1378	1249	1706	1556	1710	1568	2.0	5.0	41	0.01	0.07	0.27	
C	28	0	1052	828	1501	1339	1778	1706	1841	1785	-	-	31	-	-	-	Steam for 0.5 hours with 0.06 PPH H ₂ recycle Raised exit temp.
	31.5	3.5	1143	929	1550	1343	1816	1626	1837	1585	2.0	5.0	30	0.0004	.001	.724	
	33	5	1102	822	1506	1313	1790	1765	1850	1585	2.0	5.0	30	-	-	.621	
D	33	0	1102	822	1506	1313	1790	1713	1850	1600	-	-	31	-	-	-	Steam for 1 hour with 0.06 PPH H ₂ recycle Repeat of Point C
	35	2	1109	912	1542	1323	1802	1577	1839	1603	2.0	5.0	31	0.02	0.24	0.83	
	43	10	1118	907	1549	1336	1806	1629	1856	1605	2.0	5.0	31	0.017	0.213	0.76	
	55	17	1113	901	1543	1338	1807	1640	1860	1661	2.0	5.0	29	0.01	0.15	0.47	Sample may not have been purged adequately for a good exit analysis.
E	58	0	1124	971	1548	1377	1802	1725	1856	1602	-	-	31	-	-	-	Steam for 3 hrs with 0.12 PPH H ₂ recycle Conversion increased gradually over 4 hours
	59+62	1+4	1050	874	1557	1319	1847	1657	1851	1605	2.0	5.0	31	0.013	0.24	.14+.74	
	79	22	1052	872	1551	1329	1806	1633	1847	1682	2.0	5.0	33	0.006	0.13	.49	

Table 4-6
SUMMARY OF TSR RUN 8
(Continued)

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	HO C φ	Rig Press. (psig)	Conversion to Carbon Oxides			Comments
			½L		2nd Wall	Tap Bed	3rd Wall	Tap Bed	Exit					2nd Tap	3rd Tap	Exit	
			Into Wall	Bed** Bed					Wall	Bed							
F	84	0	1106	946	1200	1427	1840	1756	1891	1815	-	-	33	-	-	-	Steam for 2 hours with 0.06 PPH H ₂ recycle Faulty T/C at Tap 2 resulted in an over- temperature of Zone 2 and very high con- version
	84.5	0.5	1119	905	1507	1564	1814	1657	1851	1688	2.0	5.0	32	.114	.52	.82	
	88	4	1120	906	1520	1615	1811	1691	1845	1672	2.0	5.0	33	.125	.52	.89	
	100	15	1116	899	2007*	1592	1811	1686	1842	1648	2.0	5.0	34	.242	.48	.88	
	105	20	1115	900	1973*	1565	1805	1691	1836	1643	2.0	5.0	34	.38	-	.80	
G	106	0	1160	965	1379	1743	1850	1829	1901	1831	-	-	34	-	-	-	Steam for 2 hours with 0.06 PPH H ₂ recycle Tap 3 is plugged
	107	1	1112	905	1554	1327	1807	1587	1840	1611	2.0	5.0	32	-	-	.84	
	110	4	1114	909	1559	1336	1829	1773	1831	1586	2.0	5.0	32	-	-	.715	
	121.5	15.5	1113	905	1556	1338	1805	1638	1876	1704	2.0	5.0	32	0.01	.132	.61	
	129	23	1108	904	1554	1337	1802	1638	1842	1688	2.0	5.0	33	-	-	0.52	
H	130	0	1115	911	1555	1333	1824	1611	1844	1624	-	-	30	-	-	-	Steam for 2 hours + .06 PPH H ₂ Fuel: Varsol ~ 1000 PPM sulfur
	131	1	1115	911	1555	1333	1824	1611	1844	1624	2.0	5.0	32	.01	-	.76	
	143	13	1115	912	1554	1336	1847	1676	1863	1702	2.0	5.0	33	.005	-	.61	
	151	21	1118	915	1548	1337	1851	1683	1853	1718	2.0	5.0	34	.006	-	.42	
I	152	0	1117	914	1547	1337	1853	1685	1854	1719	-	-	32	-	-	-	Steam for 2 hours + 0.06 PPH H ₂ ~ repeat Point H Catalyst decay more rapid than with No. 2 fuel oil
	155	3	1127	894	1543	1330	1824	1663	1841	1569	2.0	5.0	32	.009	-	.793	
	161	9	1126	894	1541	1329	1802	1670	1856	1649	2.0	5.0	32	.008	-	.70	
	171.5	19.5	1125	892	1547	1329	1793	1642	1844	1698	2.0	5.0	37	-	-	.31	
J	175	0	1187	990	1594	1427	1838	1775	1874	1798	-	-	32	-	-	-	Steam for 2 hours + 0.06 PPH H ₂ Fuel: Varsol ~ 3200 PPM sulfur
	177.3	2.3	1128	897	1554	1334	1814	1656	1842	1590	2.0	5.0	33	-	-	.69	
	181.0	6.0	1126	894	1551	1332	1806	1669	1854	1586	2.0	5.0	33	-	-	.61	
	184.2	9.2	1125	894	1551	1331	1807	1674	1846	1643	2.0	5.0	33	-	-	.45	
	193.0	17	1124	891	1551	1330	1804	1658	1853	1705	2.0	5.0	34	-	-	.256	

Table 4-6
SUMMARY OF TSR RUN 8
(Continued)

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O C φ	Rig Press. (psig)	Conversion to Carbon Oxides			Comments
			½L		2nd Tap		3rd Tap		Exit					2nd Tap	3rd Tap	Exit	
			Into Wall	Bed** Bed	Wall	Bed	Wall	Bed	Wall	Bed							
K	194.5	0	1181	979	1593	1423	1846	1778	1883	1792	-	-	33	-	-	-	Steam for 2 hours + 0.06 PPH H ₂ ~ repeat Point J
	196	1.5	1124	892	1554	1330	1802	1581	1851	1615	2.0	5.0	34	-	-	.73	Fuel: Varsol N 3200 PPM sulfur
	203.5	9.0	1126	894	1554	1331	1823	1670	1834	1570	2.0	5.0	33	-	-	.66	Catalyst decay similar
	206	11.5	1125	893	1553	1331	1826	1678	1838	1575	2.0	5.0	33	-	-	.63	to Point H. The last 4
	215	20.5	1121	888	1551	1328	1818	1666	1855	1691	2.0	5.0	33	-	-	.32	points may not have had the sulfur well mixed with the fuel. Varsol appeared to cause more rapid decay than No. 2. But data is too scattered to br quantitative.
L	215.3	0	1184	984	1594	1422	1856	1781	1891	1797	-	-	33	-	-	-	Steam for 2 hours + 0.06 PPH H ₂
	216.5	1.5	1123	891	1549	1323	1760	1501	1812	1561	2.0	5.0	33	-	-	.87	Fuel: Varsol N 100 PPM sulfur
	219	4.1	1125	892	1551	1326	1782	1538	1827	1575	2.0	5.0	33	-	.36	.83	
	226	11.4	1126	896	1551	1325	1807	1645	1844	1506	2.0	5.0	33	-	.19	.825	
	237	22.4	1124	892	1550	1323	1814	1664	1837	1482	2.0	5.0	34	-	.13	.72	
	246	31.5	1138	901	1550	1325	1799	1643	1848	1484	2.0	5.0	34	-	.12	.78	
M	250	0	1136	914	1555	1333	1807	1662	1851	1530	-	-	34	-	-	-	Steam for 2 hours, No. 2 fuel oil ~ ³ 3220 ppms
	252.5	2.5	1125	921	1549	1321	1805	1628	1847	1560	2.0	5.0	30	-	.18	.81	
	256	6	1126	929	1549	1325	1806	1657	1875	1632	2.0	5.0	31	-	-	.57	
	262	12	1118	926	1550	1326	1808	1663	1857	1676	2.0	5.0	31	-	-	.35	
	273	23	1114	920	1547	1323	1806	1656	1852	1639	2.0	5.0	34	-	-	.356	Shut down at 274 hours

**Reactor inlet wall temp. <1000°F, inlet center bed temp. <850°F for all points

* Corrected temperature
Catalyst 853 g PSD 1043
Fuel No. 2 fuel oil

Table 4-7

SUMMARY OF TSR RUN 9

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O/C φ	Press. (psig)	Conversion to Carbon Oxides			Comments
			½ L		2nd Wall Bed	Tap Bed	3rd Wall Bed	Tap Bed	Exit					2nd Tap	3rd Tap	Exit	
			Into Wall	Bed** Bed					Wall	Bed							
A	3	3	1129	982	1344	1232	1700	1497	1699	1631	2.0	2.5	31	-	.12	.337	Initial point duplication of TSR 1.
B	30		1131	982	1359	1243	1762	1545	1761	1688	2.0	2.5	32	-	.11	.373	Raised 3rd tap & exit temperatures.
B	61		1129	978	1361	1246	1765	1543	1765	1693	2.0	2.5	32	-	.10	.367	
B	70		1131	981	1361	1248	1764	1544	1764	1691	2.0	3.6	32	-	.10	.367	Raised φ, no effect on conversion.
C	77		1212	1048	1582	1400	1904	1718	1924	1848	1.5	5.0	33	-	.47	.687	0.05 PPH H ₂ , raised temp. and lowered flow to improve conversion.
D	86		1130	978	1360	1251	1763	1565	1765	1713	2.0	3.6	32	-		.25	0.2 PPH H ₂ , repeat 70 hour point at high H ₂ , conversion low.
E	97		1248	1088	1649	1480	1902	1758	1925	1871	1.5	5.0	32	-	.401	.562	0.2 PPH H ₂ , repeat Point C at high H ₂ , conversion low.
F	110		1220	1062	1648	1455	1901	1730	1924	1864	1.5	5.0	33	-	.642*	.610	
F	116		1212	1062	1648	1454	1901	1725	1925	1864	1.5	5.0	32	-	.409	.643	0.0 PPH H ₂ . Turned off H ₂ . Conv. up slightly. Tap 3 data incorrect because of low sample flow.
G	119		1229	1052	1648	1436	1902	1695	1924	1847	2.0	5.0	35	-	.570*	.582	
G	131		1215	1039	1647	1429	1898	1684	1922	1838	2.0	5.0	36	-	.483	.590	Raised flow. Conversion decreased slightly.
H	135		1266	1103	1653	1464	1901	1705	1928	1844	2.0	2.5	29.5	.265	.510	.62	Lowered φ
I	143.5		1220	1064	1650	1461	1903	1715	1928	1862	1.5	5.0	32	-	.764*	.669	
I	156.5		1215	1061	1649	1459	1901	1716	1926	1862	1.5	5.0	32	-	.605*	.627	Repeat of Point F. Conversion slightly higher. Conversion similar to F.

Table 4-7
SUMMARY OF TSR RUN 9
(Continued)

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O/C φ	Press. (psig)	Conversion to Carbon Oxides			Comments
			$\frac{1}{2}$ L		2nd Tap		3rd Tap		Exit					2nd Tap	3rd Tap	Exit	
			Into Wall	Bed** Bed	2nd Wall	Tap Bed	3rd Wall	Tap Bed	Exit Wall	Exit Bed							
J	165.5		1213	1067	1648	1461	1900	1715	1926	1860	1.5	5.0	31	-	.565*	.582	Lowered N ₂ tracer flow from 0.3 to 0.15 PPH to determine effect on N ₂ tracer flow on conversion.
K	169		1215	1069	1652	1467	1902	1722	1929	1867	1.5	5.0	31	-	.666*	.605	Raised tracer N flow to 0.4 PPH.
K	178		1217	1062	1646	1458	1899	1713	1926	1861	1.5	5.0	33	-	.614*	.642	No strong effect on N ₂ tracer on conversion.
L	188		1214	1059	1797	1564	1898	1753	1927	1871	1.5	5.0	31	-	.721*	.698	Raised tap 2 temp. to duplicate Point N of TSR 5, no H ₂ .
M	196		1188	1029	1800	1526	1899	1743	1926	1861	2.0	5.0	32	-	.673*	.641	
N	199		1192	1031	1083	1532	1899	1748	1922	1857	2.0	5.0	32	-	.73*	.63	0.05 PPH H ₂ used
N	205		1192	1033	1804	1534	1899	1750	1926	1860	2.0	5.0	32	-	.77*	.66	through Point S.
O	201		1194	1034	1803	1532	1899	1749	1926	1860	2.0	5.0	32	-	-	-	No tracer shut ~ gas analysis showed no N ₂ in effluent.
P	216		1262	1049	1805	1515	1900	1721	1921	1834	3.0	4.1	33	-	.668*	.56	Raised fuel flow to 3.0 PPH, steam to max. calibration flow.
Q	232		1171	993	1796	1462	1902	1691	1926	1819	3.0	4.1	40	-	.23	.48	Cleaned out tap 3 to allow a greater sample flow.

Table 4-7
SUMMARY OF TSR RUN 9
(Continued)

Point	Time on Fuel (Hrs)	Time at Point (Hrs)	Temperatures								Fuel Flow (PPH)	H ₂ O/C φ	Press. (psig)	Conversion to Carbon Oxides			Comments
			$\frac{1}{2}$ L	Into Bed**		2nd	Tap	3rd	Tap	Exit				2nd Tap	3rd Tap	Exit	
			Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed							
R	239		1163	1013	1796	1496	1897	1711	1924	1842	2.0	5.0	32	-	.36	.64	Maintain tempera-
S	242		1164	1042	1802	1548	1900	1742	1924	1864	1.5	5.0	30	-	.50	.69	tures. Lower flow.
																	Duplicate Point L with
																	0.05 PPH H ₂ , same
																	temps. as R but lower
																	flow.
S	256		1147	1029	1795	1538	1898	1738	1929	1870	1.5	5.0	30	-	.44	.65	
S	264		1148	1030	1795	1535	1899	1736	1923	1865	1.5	5.0	30	-	.54	.70	Analysis at 66 ml/min
																	flow (3 ball sample).
S	264		1148	1030	1795	1535	1899	1736	1923	1865	1.5	5.0	30	-	.475	.70	Analysis at 582 ml/
																	min flow (8 ball).
S	264		1148	1030	1795	1535	1899	1736	1923	1865	1.5	5.0	30	-	.47	-	Analysis at 994 ml/
																	min flow (12 ball).
T	302		1123	994	1352	1233	1778	1538	1794	1697	2.0	3.9	30	-	.09	.35	Repeat point F TSR-1,
																	conversion signifi-
																	cantly lower than
																	Run 1.
U	317		1118	989	1497	1323	1780	1577	1780	1699	2.0	3.9	30	-	.11	.29	Raised temp. at Tap 2.
																	No change in conver-
																	sion. Reactor may be
																	plugging.
V	322		1120	991	1501	1325	1901	1652	1925	1786	2.0	3.9	30	-	.12	.47	Raised temp. at Tap 3
																	& 4 duplicate of TSR-3
																	Point E. Exit con-
																	version slightly bet-
																	ter than with Toyo
																	T-12.
W	344		1122	992	1501	1324	1901	1609	1926	1757	2.0	5.0	30	-	-	.47	Raised φ, no effect
																	on conversion, reactor
																	plugging.
W	356		1119	977	1478	1303	1873	1629	1916	1787	2.0	5.0	30	-	-	.42	Shut reactor down
																	at 358.5 hours due
																	to a plug between
																	tap 2 & 4.

** Reactor inlet wall temp. <1000°F, inlet center bed temp. <850°F for all points

* Tap 3 data incorrect because of low sample flow

Catalyst 1065 g PSD 3018 (3031)

Fuel No. 2 fuel oil

Table 4-8
SUMMARY OF TSR RUN 10

Point	Time on Fuel (Hrs)	Temperatures										Fuel Flow (PPH)	H ₂ O C φ	Press. (psig)	H ₂ Recycle PPH	Conversion to Carbon Oxides			5th Tap	Comments
		Inlet		Into Bed		2nd Tap		3rd Tap		Exit						2nd Tap	3rd Tap	Exit		
		Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed									
A	4	770	630	1112	952	1315	1260	1517	1407	1674	1601	1.5	2.5	30	0	.01	.057	.12	Initial low temperature point. Conversion is low. Increased H ₂ O/C to 3.0. Increased H ₂ O/C to 3.5. Raised reactor temperature profile. Raised reactor temperature profile again.	
B	15	724	571	1111	914	1375	1256	1527	1416	1678	1614	1.5	3.0	30	0	.01	.045	.118		
C	21	788	669	1120	949	1377	1264	1519	1403	1671	1588	1.5	3.5	30	0	.008	.043	.103		
D	40	784	651	1145	974	1499	1339	1649	1556	1799	1741	1.5	3.0	30	0	.025	.085	.244		
E	45	802	656	1199	1015	1624	1419	1796	1732	1920	1865	1.5	3.0	30	0	.042	.15	.44		
F	59	796	663	1200	999	1626	1398	1799	1698	1919	1843	2.0	3.0	31	0	.035	.127	.356	Raised reactant flow rate.	
G	65	803	695	1197	967	1625	1363	1798	1628	1918	1808	2.9	3.1	30	0	.02	.093	.293	Raised reactant flow rate. Conversion decrease was slight.	
H	69	797	677	1145	971	1509	1337	1901	1757	1927	1873	1.5	3.9	30	0	0.018	.323	.407	Repeat of Point 3C. Conversion about 20% less than 3C.	
I	85	792	666	1145	996	1501	1342	1651	1560	1799	1738	1.5	3.0	30	0	.043	.095	.242	Repeat of D. Increased Pressure. Sample flow too low from 3rd tap. Raised H ₂ O/C	
J	89	794	666	1147	1000	1501	1335	1662	1583	1806	1757	1.5	3.0	75	0	.038	.157	.275		
K	93	804	686	1145	994	1500	1340	1649	1542	1799	1735	1.5	3.5	30	0	.016	.105	.232		

Table 4-8
SUMMARY OF TSR RUN 10
(Continued)

Point	Time on Fuel (Hrs)	Temperatures										Fuel Flow (PPH)	H ₂ O C φ	Press. (psig)	H ₂ Recycle PPH	Conversion to		Exit	5th Tap	Comments
		Inlet		1/2 Into Bed		2nd Tap		3rd Tap		Exit						Carbon Oxides				
		Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed					2nd Tap	3rd Tap			
L	108	766	621	1145	992	1497	1338	1654	1569	1804	1751	1.5	2.5	29	0	.02	.097	.27		Lower H ₂ O/C looking for effect of φ at high temp. After shut down found carbon on inlet catalyst and in exit line.
N	115	768	632	1144	984	1498	1338	1648	1542	1801	1733	1.5	3.0	30	0	.016	.076	.244		Repeat of I and D after re- start.
O	120	776	650	1144	988	1499	1328	1649	1561	1806	1754	1.5	3.0	75	0	.022	.11	.286		Repeat of J, note correct con- version at 3rd tap.
P	123	771	653	1142	988	1501	1344	1649	1559	1799	1735	1.5	3.0	30	.06	.013	.063	.193		Added H to Point N. Conversion decreased.
Q	135	766	659	1143	987	1497	1342	1649	1565	1798	1731	1.5	3.0	31	.12	.01	.03	.17		Increased H ₂ recycle. Conversion decreased further.
R	144	796	686	1238	995	1576	1350	1751	1566	1864	1746	3.0	3.0	30	0	.012	.049	.197		High space velocity at same bed temps. as Point I.
S	147	800	681	1277	1017	1696	1415	1902	1731	1987	1869	3.0	3.0	31	0	.02	.115	.33		High space velocity at same bed temps. as Point E.

Table 4-8
SUMMARY OF TSR RUN 10
(Continued)

Point	Time on Fuel (Hrs)	Temperatures										Fuel Flow (PPH)	H ₂ O C φ	Press. (psig)	H ₂ Recycle PPH	Conversion to Carbon Oxides			Exit	5th Tap	Comments
		Inlet		Into Bed		2nd Tap		3rd Tap		Exit						2nd Tap	3rd Tap	Exit			
		Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed										
M	164	768	630	1149	994	1505	1354	1646	1552	1797	1722	1.5	3.0	29	0	.014	.076	.337		Point I con- ditions with 1% hydro- treated H- coal fuel N 700 PPM sul- fur. On coal fuel at 162 hours.	
M ₁	176	763	632	1131	961	1496	1336	1649	1533	1797	1713	1.5	3.0	30	0	.018	-	.37		After 14 hours on coal fuel.	
M ₂	193	780	642	1149	989	1501	1345	1651	1551	1803	1725	1.5	3.0	30	0	.03	-	.344		After 31 hours on coal fuel.	
T	198	778	619	1201	1020	1525	1428	1802	1729	1927	1839	1.5	3.0	30	0	.056	-	.49		Raised temp. N repeat of Point E after 36 hrs. on coal fuel.	
T	202	778	619	1201	1020	1625	1428	1802	1729	1937	1839	1.5	3.0	30	0	.055	-	.512		After 40 hrs. on coal fuel.	
T	212	777	619	1201	1018	1624	1429	1800	1726	1924	1837	1.5	3.0	30	0	.059	-	.513		After 50 hrs. on coal fuel.	
	213	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		Shut down after 51 hrs. on coal fuel.	
Catalyst	1067 g TOYO T-12																				
Fuel	No. 2 fuel oil																				

Table 4-9
SUMMARY OF TSR RUN 11

Point	Time on Fuel (Hrs)	Temperatures										Fuel Flow (PPH)	H ₂ O C φ	Press. (psig)	H ₂ Recycle PPH	Conversion to Carbon Oxides			5th Tap	Comments
		Inlet		1/2 Into Bed		2nd Tap		3rd Tap		Exit						2nd Tap	3rd Tap	Exit		
		Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed	Wall	Bed									
A	12	903	663	1116	956	1441	1272	1601	1485	1742	1671	1.5	3.0	31	0	--	.06	.173	--	
A	28	897	656	1115	950	1438	1269	1600	1480	1738	1662	1.5	3.0	30	0	.01	.06	.17	--	
A	35	899	658	1117	955	1441	1272	1600	1480	1739	1665	1.5	3.0	31	0	.01	.06	.165	--	
A	50	903	621	1115	953	1437	1276	1598	1474	1732	1656	1.5	3.0	31	0	--	--	.173	--	
	51																			Shut down, examined exit lines
B	56	879	696	1151	931	1524	1323	1716	1539	1821	1721	3.0	3.0	30	0	.006	.048	.166	--	
B	61	874	694	1140	922	1524	1318	1711	1529	1815	1713	3.0	3.0	30	0	.007	.040	.152	--	
B	74	866	688	1119	908	1525	1307	1718	1532	1822	1718	3.0	3.0	30	0	.005	.04	.16	--	
B	84	874	691	1144	924	1526	1312	1720	1529	1816	1716	3.0	3.0	30	0	.006	.04	--	.173	
B	99	871	690	1147	927	1530	1312	1719	1535	1821	1722	3.0	3.0	30	0	.006	.04	--	.178	
B	109	879	700	1150	931	1524	1315	1712	1534	1821	1725	3.0	3.0	30	0	.005	.036	--	.168	
B	122	880	711	1134	928	1524	1312	1719	1524	1824	1714	3.0	3.0	30	0	.006	.038	--	.172	
	125.5																			Shut down examined exit lines
C	132	933	712	1273	1012	1678	1433	1901	1764	1986	1856	3.0	3.0	30	0	.02	.108	--	.31	
C	195	925	708	1275	1014	1693	1453	1904	1756	1990	1920	3.0	3.0	30	0	.02	.104	--	.332	
																				After week-end run
C	206	932	709	1285	1020	1695	1454	1903	1756	1989	1920	3.0	3.0	30	0	.022	.112	.32	--	
	222																			Shut down to repair exit line from B/P regulator
D	233	940	674	1278	1101	1699	1463	1898	1812	1987	1891	1.5	3.0	30	0	.044	--	.41	--	
D	243	936	675	1279	1097	1696	1461	1899	1816	1985	1892	1.5	3.0	30	0	.037	.191	.423	--	
																				@ 24B hours stand shut down on auto
D	251	940	678	1283	1100	1701	1471	1900	1812	1982	1889	1.5	3.0	30	0	.04	.19	.38	.45	
D	273	940	675	1282	1101	1703	1477	1899	1812	1987	1887	1.5	3.0	30	0	.04	.191	.42	.442	
	275																			
E	280	930	703	1280	1018	1698	1475	1899	1752	1988	1843	3.0	3.0	30	0	--	--	.306		
	311																			Shut down examine exit line

Catalyst 1021 g TOYO T-12
Fuel No. 2 Fuel Oil

METAL OXIDE CATALYSTS

The metal oxide catalyst, PSD-3018, was developed for use in the adiabatic reformer. It showed significantly more resistance to carbon accumulation than a nickel catalyst when placed in the inlet combustion zone of that reactor and it also had some activity for steam reforming. Figure 4-1 shows the results of measurements made in a laboratory microreactor of its activity for steam reforming methane in the presence of sufficient sulfur to be equivalent to 3000 ppmw in No. 2 fuel oil.

PSD-3018 was tested on No. 2 fuel oil in the 4 foot long reactor in runs 1, 2, 6 and 9. Initially promising performance in run 1 could not be duplicated in subsequent tests.

In the first test, run 1, the inlet, three-quarters of the reactor, was filled with PSD-3018. The exit section was filled with more active PSD-1028 noble metal catalyst which was intended to increase fuel conversion and to minimize fouling of the exit lines. Its performance will be discussed in detail later.

Using the analyses from Tap 3, the conversion in the section of reactor containing PSD-3018 could be determined. The effects on conversion of pressure, temperature, flow rate and steam to carbon ratio were measured. For comparison with the Toyo T-12 catalyst, a rate expression derived by KTI (2) was used to correlate data where

$$k = \frac{\theta \ln (C_2/100)}{(S/C)^2}$$

$C_2 = 100 (1 - \text{fractional conversion})$
 $S/C = \text{steam to carbon ratio}$
 $\theta = \text{space time } \frac{\text{liter catalyst-hour}}{\text{Kg (fuel + steam)}}$
 $k = \text{rate constant}$

and the correlating temperature was taken as that at the exit of the reactor. Since the tests showed the effect of S/C on conversion to be small for PSD-3018, whereas the rate expression implies great sensitivity to S/C, the comparison could only be made at similar process conditions. This comparison in Figure 4-2, showed PSD-3018 to be significantly more active than T-12 and to have stable activity for the duration of the run.

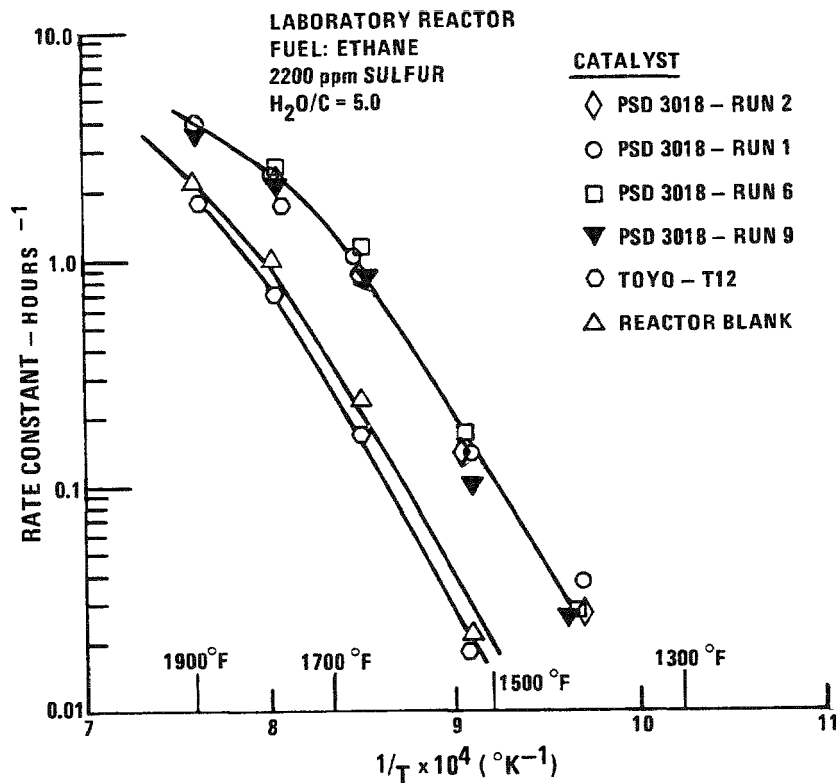


Figure 4-1. Activity of Various Catalysts for Steam Reforming Ethane with H_2S Present

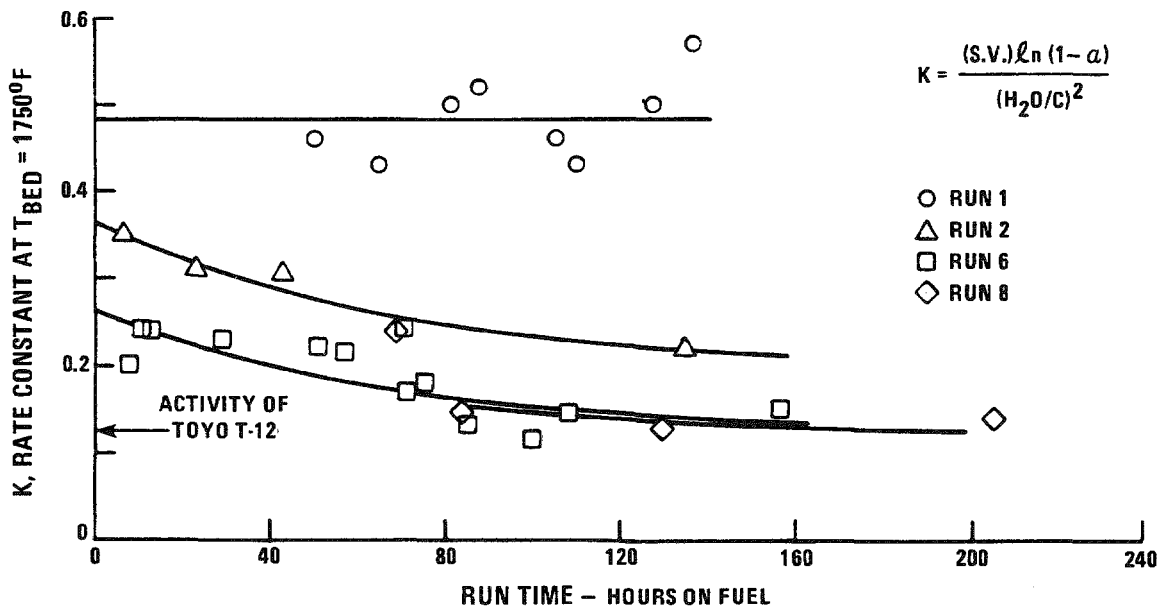


Figure 4-2. Change in Activity with Time of Metal Oxide Catalysts

No pressure drop increase was measured in the PSD-3018 section of the reactor, an indication that no significant carbon accumulation had occurred. When the reactor was opened at the end of the test some shiny, graphitic carbon was formed on the pellets of PSD-3018 which had been at highest temperature.

Run 1 suggested that a reactor filled entirely with metal oxide catalyst might give sufficient conversion for the primary reformer of the hybrid system. Run 2 was planned to achieve increased overall conversion in the reactor by placing a high surface area modification of the metal oxide catalyst, PSD-3019, in the inlet half of the reactor where, due to the lower temperature, great physical stability was not required. This was followed in the exit, high temperature half of the reactor by the more stable PSD-3018.

In Run 2, the reactor ran 150 hours on No. 2 fuel oil. The modified catalyst, PSD-3019, did not improve conversion in the inlet section of the reactor while PSD-3018 in the exit section had an initial activity approximately half that shown in the previous test and which decreased with time. Post-test inspection showed both PSD-3018 and PSD-3019 to be visibly altered, being covered with a deposit which proved to have resulted from improper application of a protective coating applied to the reactor walls. This may have caused the observed decay in activity. Post-test examination showed some carbon formation in the PSD-3019 catalysts.

In Run 6, an attempt to duplicate the high activity observed in run 1 was made by filling the reactor with a fresh batch of PSD-3018. The initial points A to F (Table 4-4) were run to study the effect of temperature profile and flow rate on fuel conversion. When it became obvious that conversion was significantly lower than expected from the results of run 1, attempts were made to activate the catalyst both with hydrogen and with steam. Point H was analyzed after operating the catalyst for 11 hours with 0.06 PPH hydrogen in addition to the normal reactant flows. Point I was analyzed after pretreating the catalyst for 7 hours with hydrogen and nitrogen gas. Point K was analyzed while 0.06 PPH hydrogen was added to the reactant gases, and point L was run after steaming the catalyst for 2 hours. None of these procedures improved the catalyst activity.

Not only was the initial activity for this batch of PSD-3018 low but it decreased with time until it became close to that obtained with T-12 catalyst. X-ray analysis of PSD-3018 showed no significant difference in phase composition between the two batches, and their activities for reforming methane was identical, see Figure 4-1. However, a close review of manufacturing steps showed slight variation in procedure, therefore for Run 9, a third batch of PSD-3018 was prepared which duplicated in every respect the batch used in Run 1. The methane reforming activity of this batch was again identical to that of Run 1.

The start-up procedures for Run 9 followed those used in run 1 in every respect including a brief period of operation initially at low steam/carbon ratio (2.5). It was suspected that these conditions might have altered the composition of the catalyst in Run 1. The activity of the catalyst was low. Fuel conversion was similar to that seen in Runs 2 and 6 rather than Run 1. Figure 4-2 shows the activity of the catalyst compared to previous tests using the rate constant used for the Toyo catalyst system. The activity lined-out at values close to those obtained in Runs 2 and 6 and was similar to that measured for the Toyo T-12 catalyst at comparable conditions.

No increase in pressure drop across the reactor and hence no indication of carbon formation was observed during the first 290 hours of the test. This was consistent with previous tests with this catalyst which had been terminated at shorter times. After about 300 hours, the pressure drop in the reactor increased steadily and the reactor was shut down with a carbon plug formed in the exit (high temperature) section of the reactor after 350 hours.

In Runs 2, 6 and 9, three attempts were made to duplicate the behavior given by PSD-3018 in Run 1. No obvious reason was found for the change in activity between the first and later runs. One experimental difference between the two sets of data was the presence of the noble metal catalyst in the exit section of the reactor in Run 1. This may have affected the analysis in the metal oxide section of the reactor bed despite the fact that the metal oxide catalyst was placed downstream.

NOBLE METAL CATALYSTS

In Run 1, a noble metal catalyst PSD-1028 was placed in the exit section of the reactor to increase fuel conversion and to minimize fouling of the exit lines. It had proved active and resistant to carbon formation in adiabatic reformer tests with No. 2 fuel oil. But in Run 1, it appeared to be virtually inactive. After the test, PSD-1028 was badly weakened from the high operating temperatures and many of the pellets had powdered. Carbon had deposited between the pellets. The conclusion was that an unreacted fraction of No. 2 fuel oil had passed to the noble metal catalyst and at high temperature formed carbon which deactivated the metal surface. A more active catalyst was required in the inlet section of the reactor to reform the fuel to light gases before the process steam reached temperatures where carbon formed.

To test this hypothesis, in Runs 7 and 8, the reactor was filled entirely with noble metal catalyst. The catalyst in Run 7, PSD-1042, contained a noble metal deposited on a stabilized high surface area support. The activity of this catalyst for reforming ethane in the presence of sulfur had been shown in the laboratory microreactor to be significantly greater than the activity of a reference commercial nickel catalyst. See Figure 4-3. When tested in the 4 foot long electrically heated tubular reformer, in Run 7, PSD-1042 gave high initial activity for reforming No. 2 fuel oil but the activity decayed rapidly with time, see Figure 4-4. The initial activity could be recovered by regeneration with steam and hydrogen.

Before the next test point, a mixture of steam, hydrogen and hydrogen sulfide was passed over the catalyst until it had been exposed to sufficient hydrogen sulfide to form more than a monolayer. A subsequent test with No. 2 fuel oil, shown in Figure 4-4, decayed in a similar manner to the first test. This suggested that decay was due to poisoning or coking by the higher molecular weight components of No. 2 fuel oil rather than to the sulfur poisoning. Confirmation of this hypothesis was made by running a test with diesel fuel containing only 1000 ppm sulfur rather than the 3220 ppm in No. 2. The decay rate was again similar to the first run on No. 2 fuel oil.

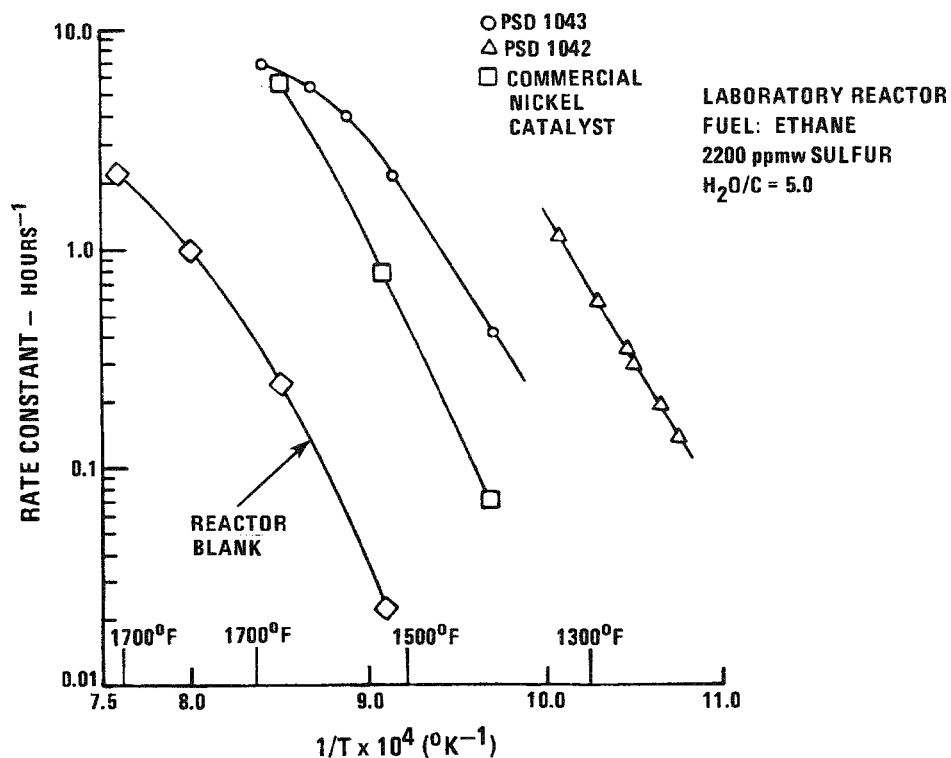


Figure 4-3. Activity of Noble Metal Catalysts for Steam Reforming Ethane with H_2S Present

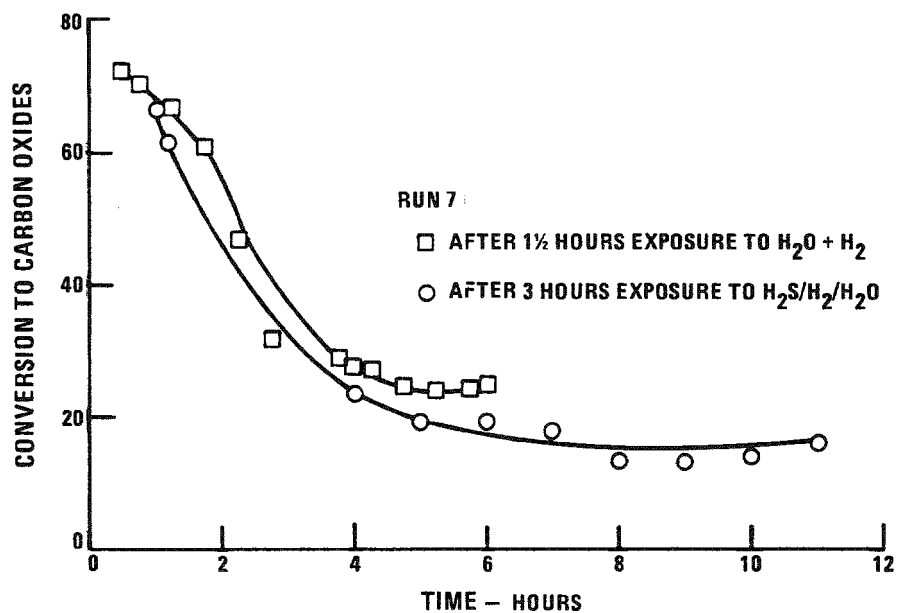


Figure 4-4. Decrease in Activity of PSD 1042 Noble Metal Catalyst with Time on Fuel

Since carbon formation on the surface of the catalyst appeared to be the cause for the decrease in activity, a second catalyst, PSD-1043, was tested. This contained the same noble metal but now deposited on a support which had increased resistance to carbon formation. PSD-1043, in the microreactor, had shown lower activity than PSD-1042, but higher activity than the reference nickel catalyst. See Figure 4-3.

In Run 8, PSD-1043 showed decay in activity for reforming No. 2 fuel oil, as had PSD-1042. No condition was found at which it would maintain its initial activity. To explore the cause of decay, the catalyst was run on a less refractory fuel, Varsol, with various levels of sulfur added. It was expected that, having a lower end point and aromatic content, this fuel would not form carbon and hence would not deactivate, even when its sulfur content was the same as No. 2 fuel oil. However, the decrease in activity was very similar to No. 2 fuel oil. Only when the sulfur content was reduced to 100 ppm did the rate of decay in activity decrease. See Figure 4-5.

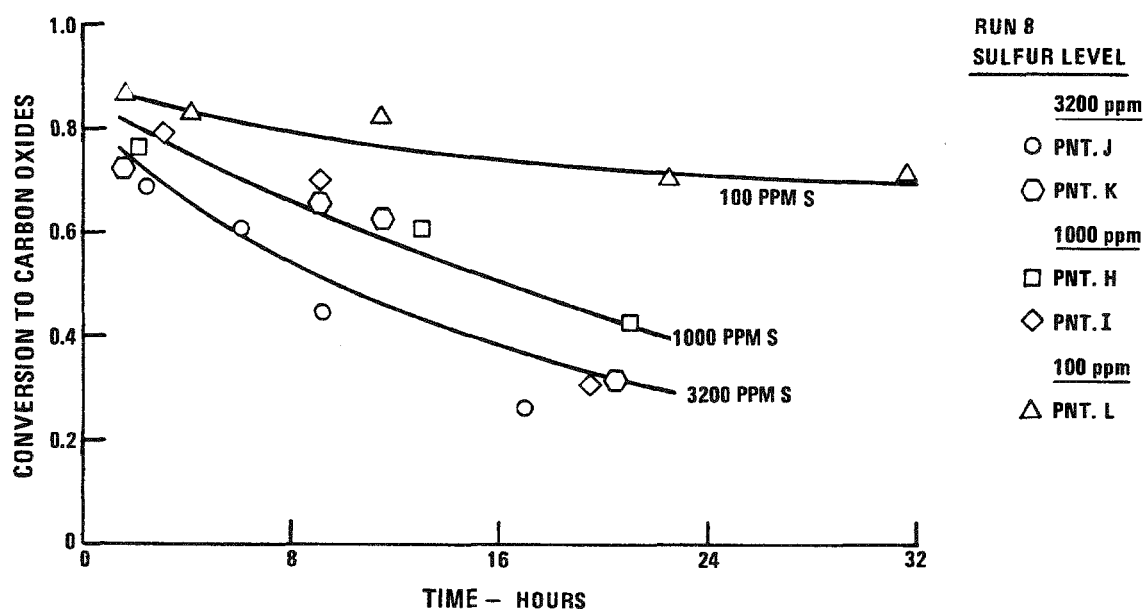


Figure 4-5. Steam Reforming Varsol on PSD 1043 Noble Metal Catalyst - Effect of Added Sulfur

In both Runs 7 and 8, reactor pressure drop measurements during the run and post-test examination showed that carbon had formed on the catalyst.

Apparently the decay caused by surface carbon formation was dependent on the sulfur level in the process stream. One mechanism consistent with the test result would require that the carbon form on the catalyst when unreacted fuel penetrated the high temperature region of the reactor where it could polymerize. With increasing sulfur content, the catalyst would deactivate, more fuel would pass to the high temperature zone and increased decay in activity would occur. Evidently more sulfur tolerant and more carbon tolerant catalyst formulations would be required to stabilize activity at levels exhibited initially by PSD-1042 and PSD-1043.

Thus, with both metal oxide and noble metal catalysts, attempts to increase steam reforming activity in the inlet section of the reformer by introducing an active element led to carbon laydown.

TOYO ENGINEERING COMPANY T-12 CATALYST

Catalysts T-12 and T-48, used in the Toyo Engineering Company's THR process, were considered for use in fuel cell power plants by Kinetics Technology International Corporation. A tubular reactor filled with a mixed charge of T-12 and T-48 was evaluated both as a single reactor generating hydrogen at high fuel conversion and in a hybrid system operating at lower conversion, followed by a secondary reformer. KTI concluded that a hybrid system in which the high temperature reformer had a regenerator tube which transferred heat from the effluent stream to the inlet of the reformer was the most desirable fuel processor. UTC confirmed the performance of the reactor with mixed catalyst charge and analyzed a hybrid system in which the primary reformer was a simple tube without a regenerator.

Both KTI and UTC studies assumed the hybrid required T-48, the nickel containing catalyst, downstream of T-12 in order to achieve significant conversion in the primary reformer. UTC experimental studies showed that a very high temperature, about 1800°F, was required at the transition point between the T-12 and T-48 sections of catalyst in order to prevent carbon formation in the reformer at space velocities required for fuel cell power plants.

In this study, it became evident that the T-12 catalyst, although relatively inactive, was the only catalyst to achieve carbon-free gasification of No. 2 fuel oil. Further consideration of the hybrid system suggested that it might be optimized at the low conversions achieved by T-12. Therefore some additional experiments were performed to provide data for this optimization. The objectives of the test were:

- To obtain detailed performance data at low temperatures and conversions
- To demonstrate that the product mixture at low fuel conversion could be transferred from the primary to the secondary adiabatic reformer.

In Run 10, the electrically heated, tubular reformer was filled with 2.35 pounds (0.04 cu. ft.) of TOYO T-12 catalyst. Table 4-8 is a summary of the test points and results.

The initial Points A, B and C showed the conversion to carbon oxides at low reactor exit temperature to be insensitive to change in steam/carbon ratio (ϕ). Points, L, I and K, run at higher exit temperature also showed that the effect of ϕ on conversion was small. See Figures 4-6 and 4-7.

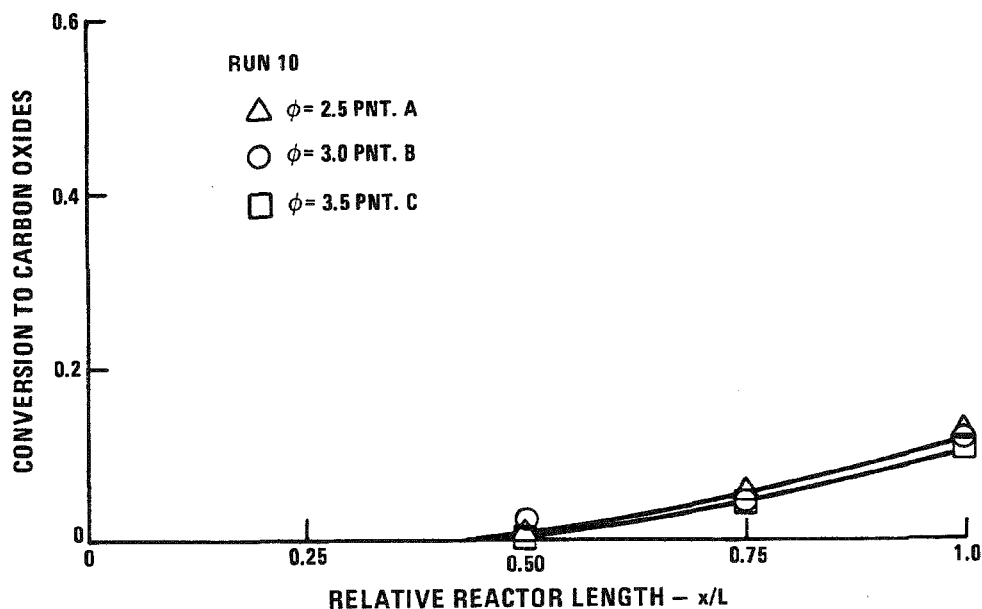


Figure 4-6. Effect of Steam/Carbon Ratio on the Activity of T-12 Catalyst

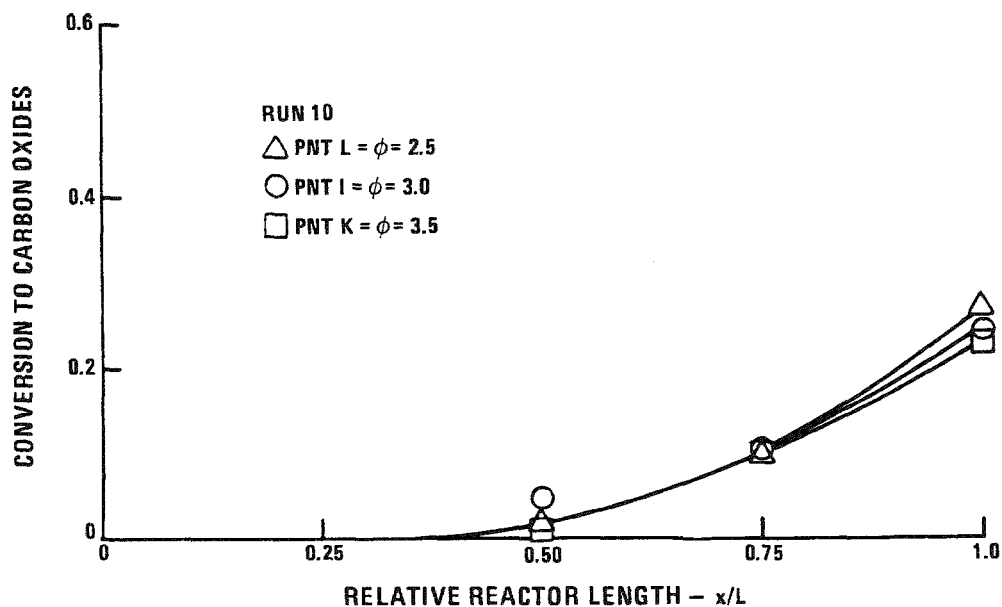


Figure 4-7. Effect of Steam/Carbon Ratio on the Activity of T-12 Catalyst

The effect of space velocity was established in two ways. In Figure 4-8 (Points E, F and G) the reactor wall temperature was maintained constant, allowing the catalyst bed temperature to vary with change in space velocity. In Figure 4-9, (Points E and S) the bed temperature was held constant, by varying the wall temperatures.

Figure 4-10 shows that the addition of hydrogen to the process stream, to simulate recycle had a slight depressant effect on conversion to carbon oxides. There was no significant change in the concentration of cracking intermediates, CH_4 and C_2H_4 , in the same tests.

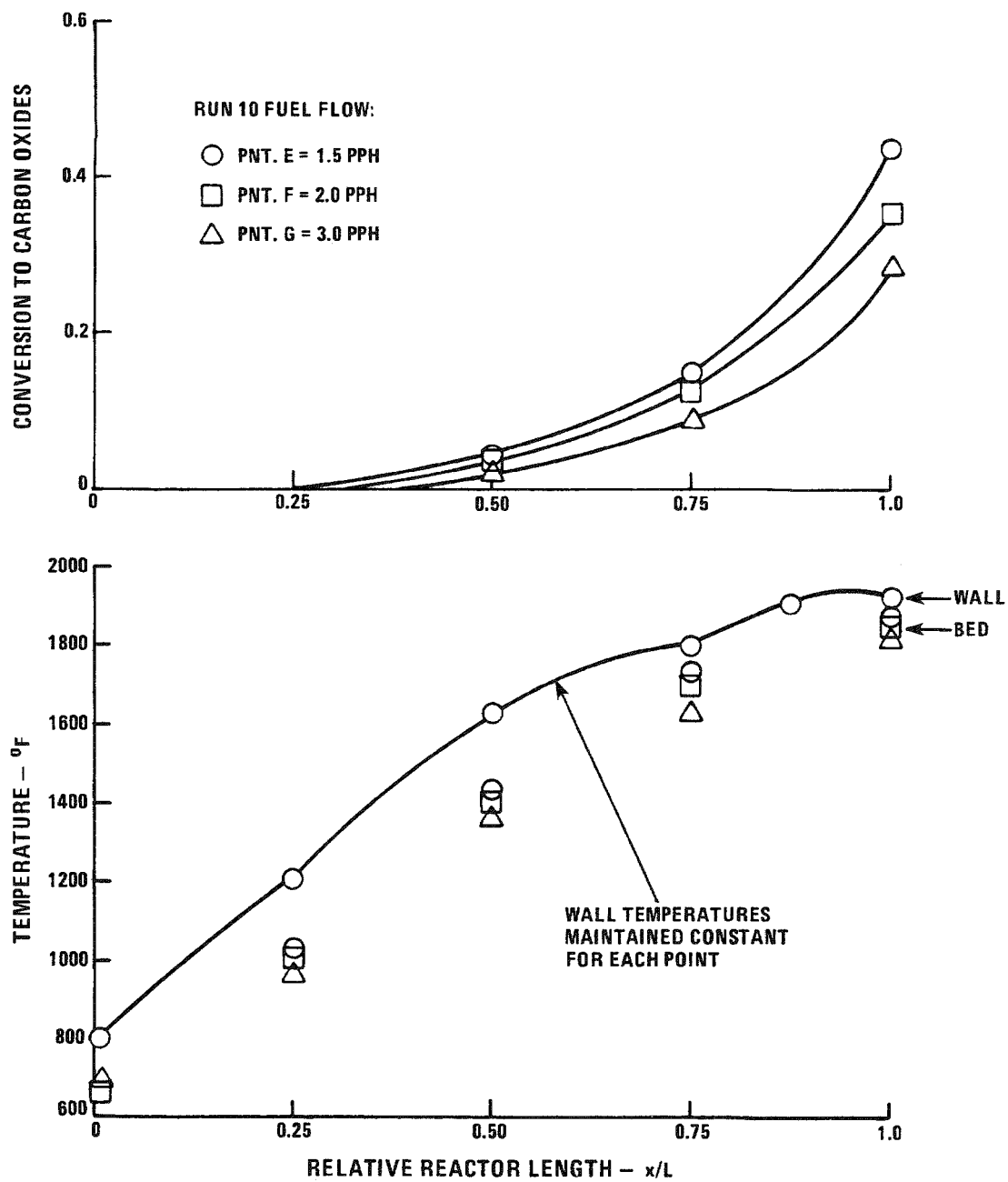


Figure 4-8. Effect of Space Velocity on Activity of T-12 Catalyst (Reactor Wall Temperatures Maintained Constant)

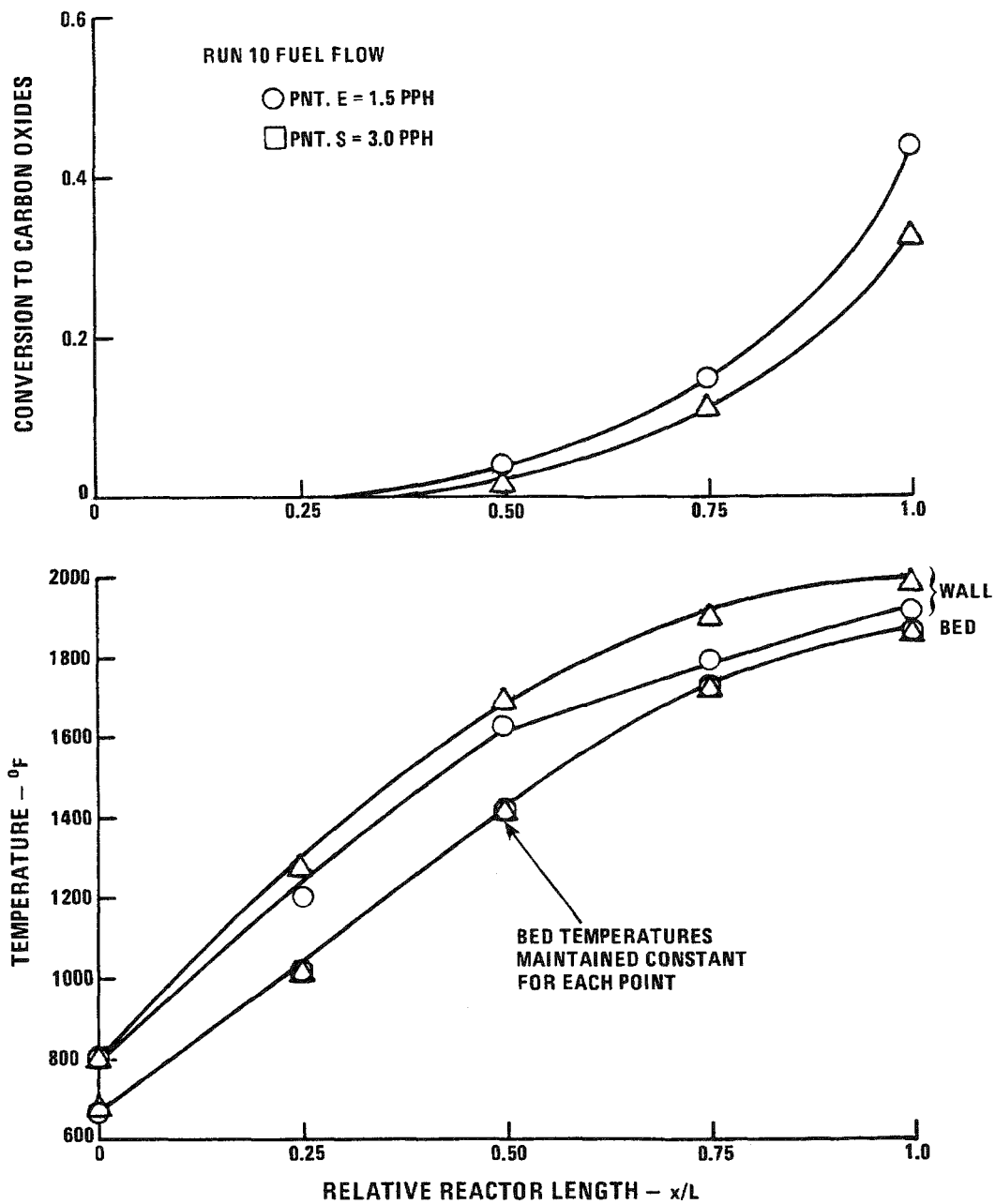


Figure 4-9. Effect of Space Velocity on Activity of T-12 Catalyst (Reactor Bed Temperature Maintained Constant)

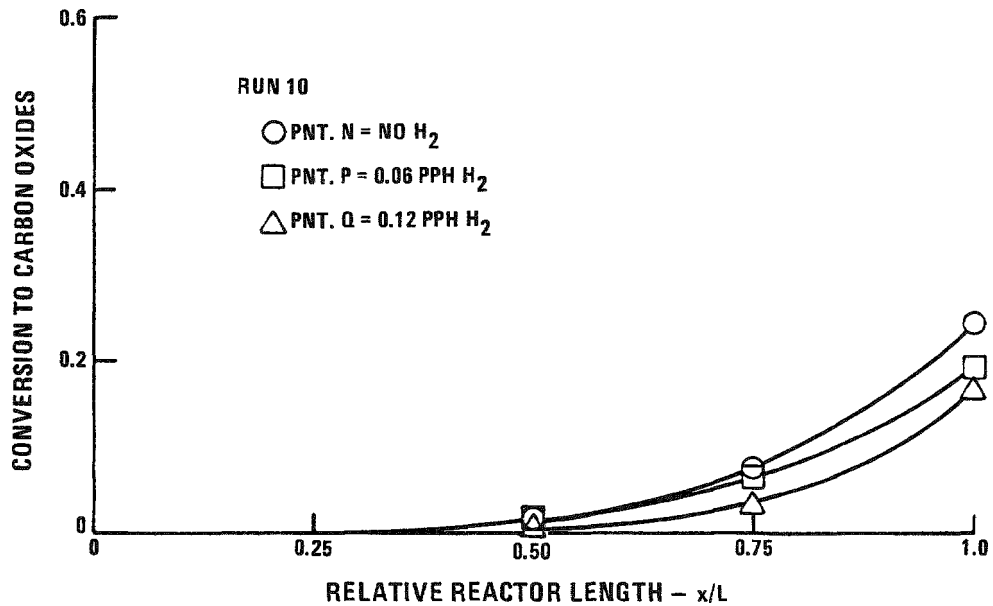


Figure 4-10. Effect of Hydrogen Recycle on Performance of T-12 Catalyst

Finally, Figures 4-11 and 4-12 show the results of tests in which total reactor pressure and reactor wall temperatures were changed. These completed the test sequence which defined performance parameters for the reformer in the range likely to be required by a primary reformer of a hybrid fuel processing system.

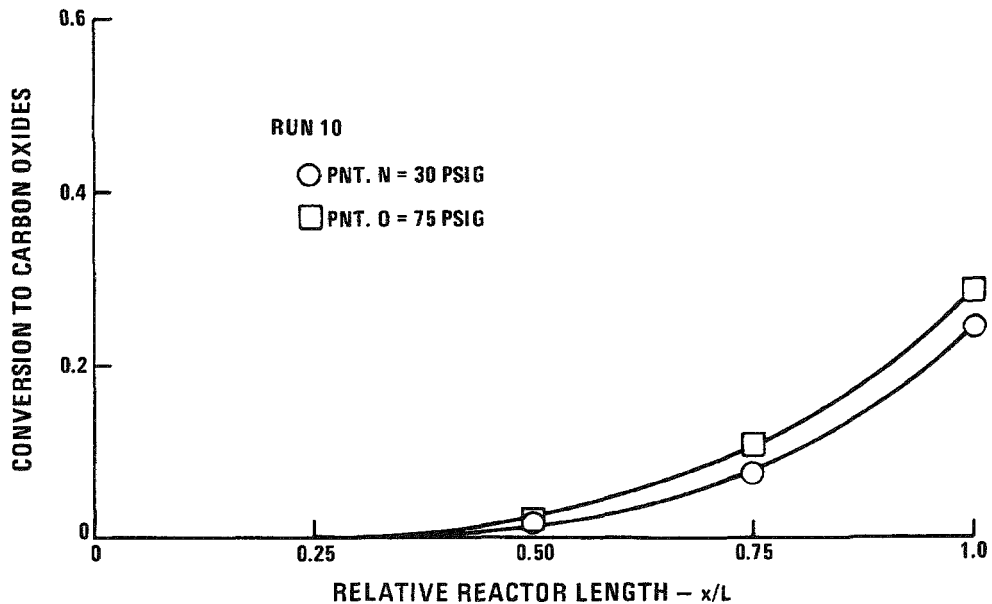


Figure 4-11. Effect of Pressure on Performance of T-12 Catalyst

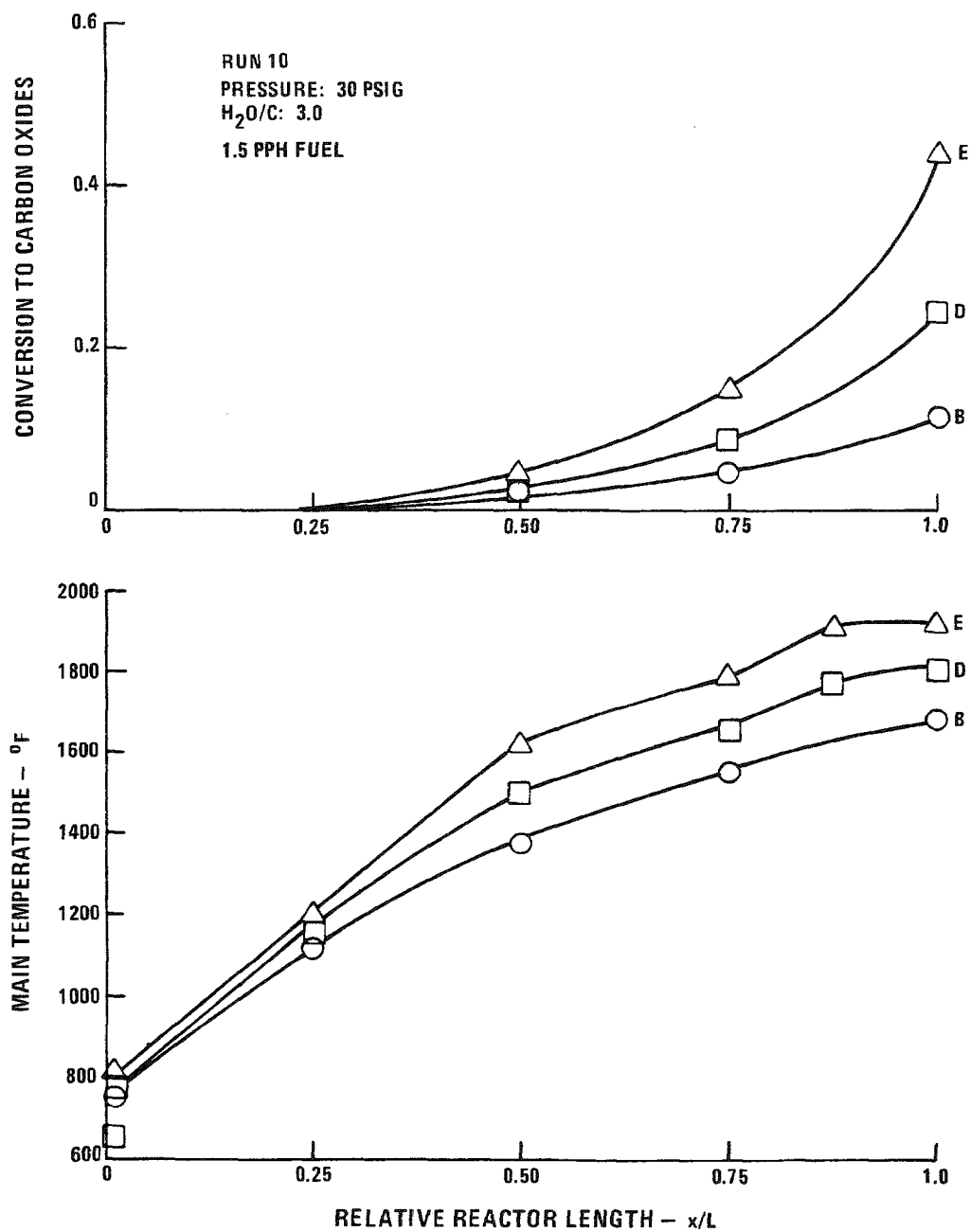


Figure 4-12. Effect of Temperature on Performance of T-12 Catalyst

A demonstration of the performance of the reformer using a hydrotreated coal liquid was included in Run 10. The fuel was a product of the H-coal process which had been hydrogenated to an extent which increased the hydrogen content of the raw liquid fuel by 1 weight percent. The fuel properties were compared to No. 2 fuel oil in Table 2. The reformer operated on the H-coal liquid for 51 hours with slightly increased conversion over that achieved with No. 2 fuel oil. See Figure 4-13.

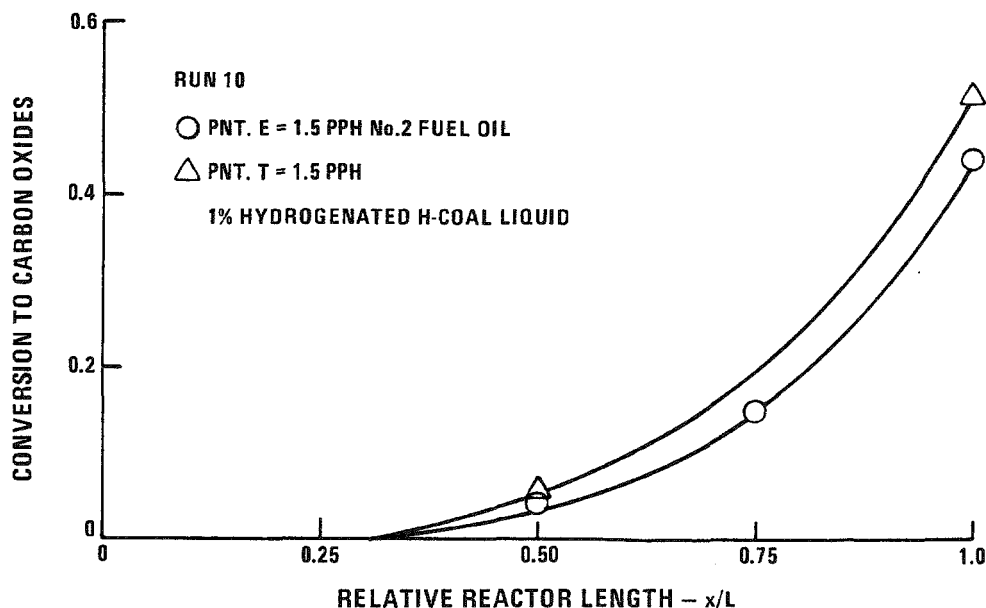


Figure 4-13. Steam Reforming of No. 2 Fuel Oil and H-Coal Liquid on T-12 Catalyst

The reactor was shut down after point L (112 hours) to examine the exit lines of the reactor and the appearance of the catalyst at the inlet of the reactor. The inlet catalyst was blackened by a light coating of carbon. The exit line was fouled by a tarry deposit at a point where the line had cooled to 850°F. The test was restarted to complete 213 hours on fuel. No increase in pressure drop across the reactor occurred during this time. After the intermediate shutdown at Point L, the exit line was insulated in the region of the tarry deposit. On reopening the exit lines at the end of the test, the tarry deposit had been cleaned from the line where the temperature now had reached approximately 1000°F.

The reactor was emptied at the end of the test. The catalyst in the inlet was again blackened with carbon, both on the inside and outside of the pellets.

Blackened catalyst pellets appeared only in the first quarter of the bed; beyond that point, the pellets were clean. No increase in pressure drop was associated with this carbon over 200 hours of test. It was ascribed to imperfect mixing of fuel and steam since the UTC mixing system was recognized to be less efficient at the lowest fuel flow rate, 1.5 lbs. per hour. Since TEC tests operated at similar conditions without observing carbon on the T-12 catalyst, it was judged not to be a problem intrinsic to the catalyst. At the exit of the reactor, some catalyst pellets, though clean, had spalled. This was subsequently explained by an inadvertent dumping of condensed water on the catalyst in this section during the shutdown procedure. Spalling was not seen in the subsequent test.

In Run 11, the reformer was again run with T-12 catalyst for an extended period to demonstrate stable fuel conversion and to define more closely the conditions under which the product gas, at low fuel conversion, could be transferred without fouling the exit lines. The reformer was operated on No. 2 fuel oil at several conversion levels for over 300 hours. Comparison in Table 4-9, of analyses taken at the exit of the reformer at 12 and 50 hours, at 84 and 122 hours and finally at 132 and 280 hours show no change in conversion with time.

The exit lines in Run 11 were insulated and instrumented with thermocouples. At 50, 122 and 311 hours, the exit lines were removed from the reactor and cut open for inspection. In every case, the interior tube walls were clean with no evidence of carbon deposition except where the temperature of the tube wall fell below about 1000°F. These observations, therefore, were consistent with those made during Run 10. It was concluded that the product gases from the primary reformer operating at low fuel conversions could be transferred to the secondary reformer, provided the transfer lines were maintained above 1000°F.



Section 5

KINETIC ANALYSIS OF FUEL CONVERSION DATA

Catalyst performance was described previously in terms of conversion of fuel to carbon oxides since fuel must be completely converted to hydrogen and carbon oxides for the fuel cell power plant. However, at partial conversions achieved in the proposed primary reformer, in addition to carbon oxides, a considerable fraction of the initial No. 2 fuel oil is converted to methane, olefins and other products of cracking reactions.

Figure 5-1 shows a typical product distribution through the reformer containing T-12 catalyst. In the inlet section of the reactor, methane and C_2 and C_3 hydrocarbons exceeded the carbon oxides in concentration. Only with high reactor exit temperatures did the carbon oxides become the major product. Figure 5-2 collates product distribution data from all points run with T-12 catalyst by plotting conversion to methane and to C_2 and C_3 compounds versus conversion to carbon oxides. For completeness, data sheets from each run are included in Appendix B.

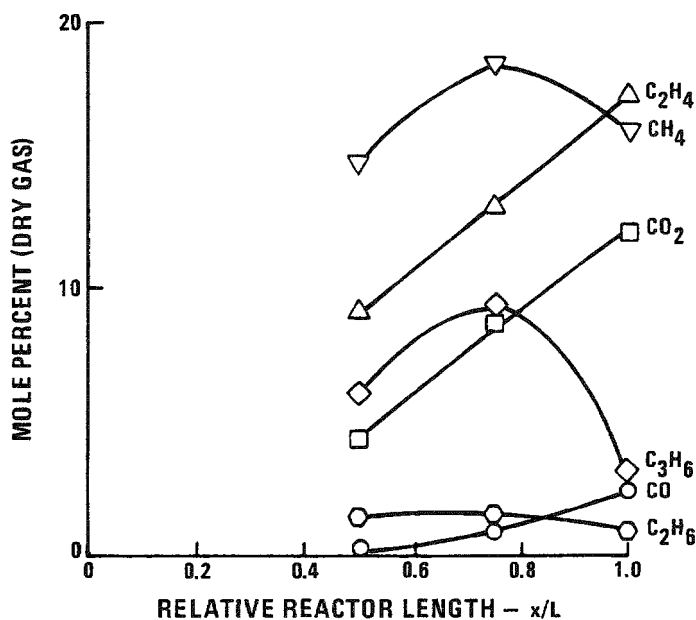


Figure 5-1. Process Steam Composition - Run 10, Point A

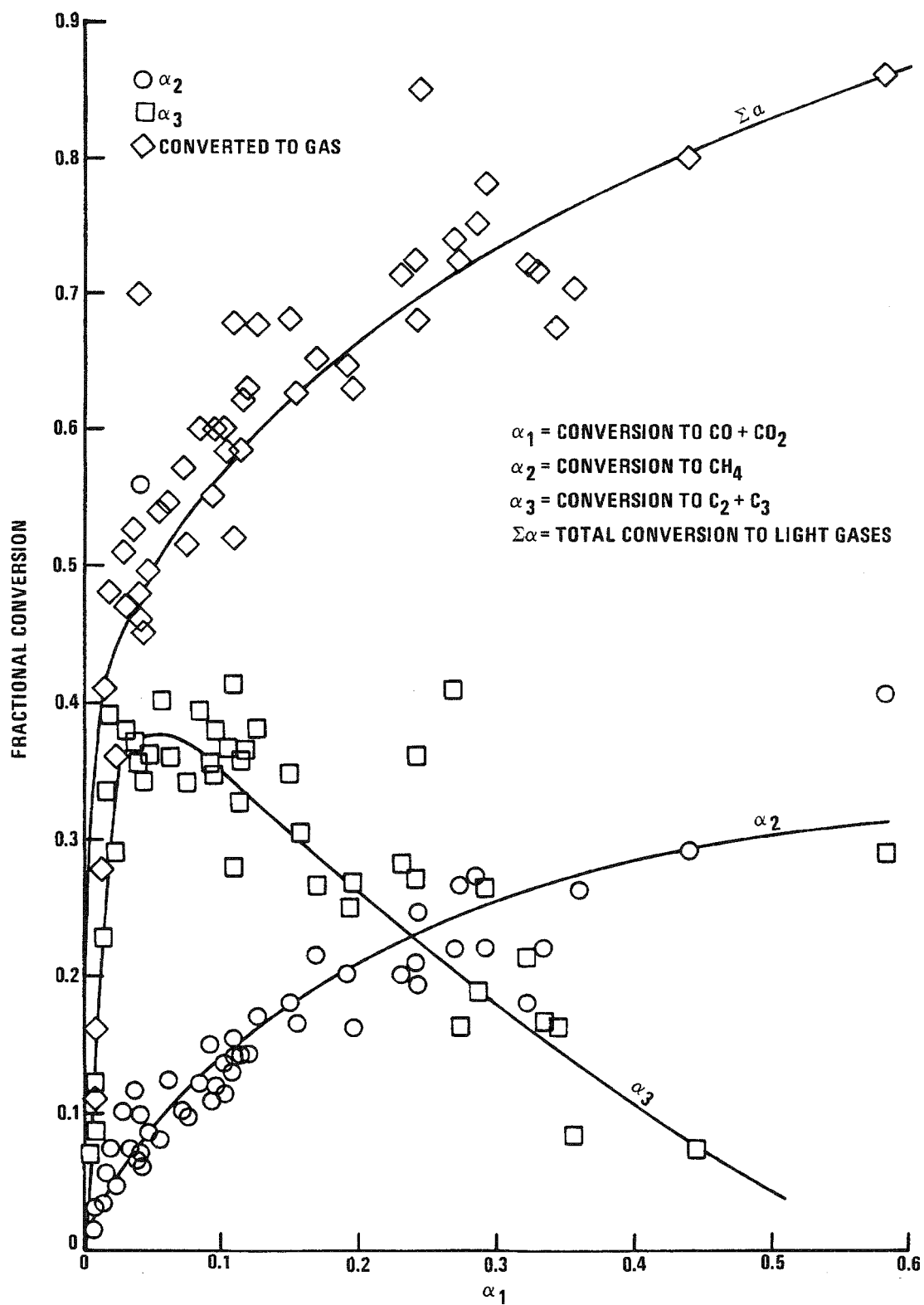


Figure 5-2. Selectivity of Fuel Conversion to Light Gas Products on T-12 Catalyst

To select operating conditions for the primary reformer in a hybrid fuel processor, a correlation of data is required for interpolation and extrapolation. We initially used a simple kinetic expression, first order in No. 2 fuel oil and zero order in steam to describe the reaction of virgin No. 2 fuel oil to form carbon oxides and hydrogen. A computer model which included heat and mass transfer effects integrated the test reactor to fit experimental temperatures and carbon oxide concentrations. By trial and error, best values for the frequency factor and activation energy in rate constant were established. The data could be satisfactorily fitted, for example in Figure 5-3, with an activation energy of 30 k cal/mole.

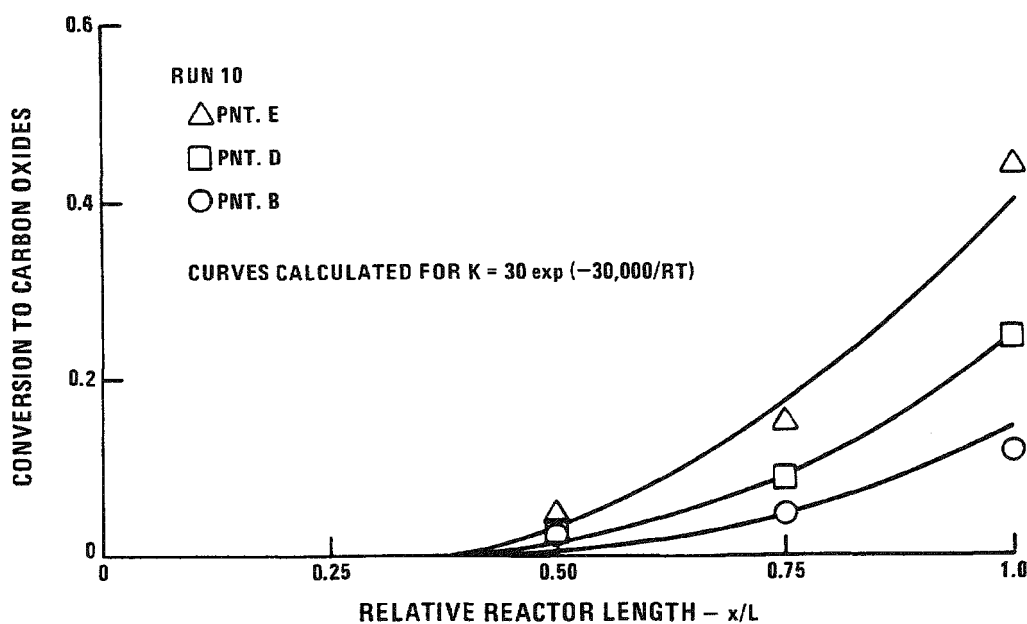


Figure 5-3. Fit of First Order Rate Expression for Steam Reforming No. 2 Fuel Oil to Test Data

A critical factor, however, in the design of the power plant is the amount of heat transferred to the reformer tube from the burner. To be correct, therefore, the model should predict not just the formation of carbon oxides but also the intermediate production of cracked fuel products which significantly alter the energy balance of reaction. Our reactor model did not have this capability, so, to predict the heat duty of the reformer more closely, a second measure of conversion, α_T , was used. α_T was a calculated value for conversion of fuel to carbon oxides which gave an enthalpy change equivalent to that associated with

the experimentally-measured product mix. The relationship between α , the measured conversion to carbon oxides and α_T , for the data points in run 10, is given in Figure 5-4. The reactor model fit was adjusted to match values for α_T at the exit of the reformer.

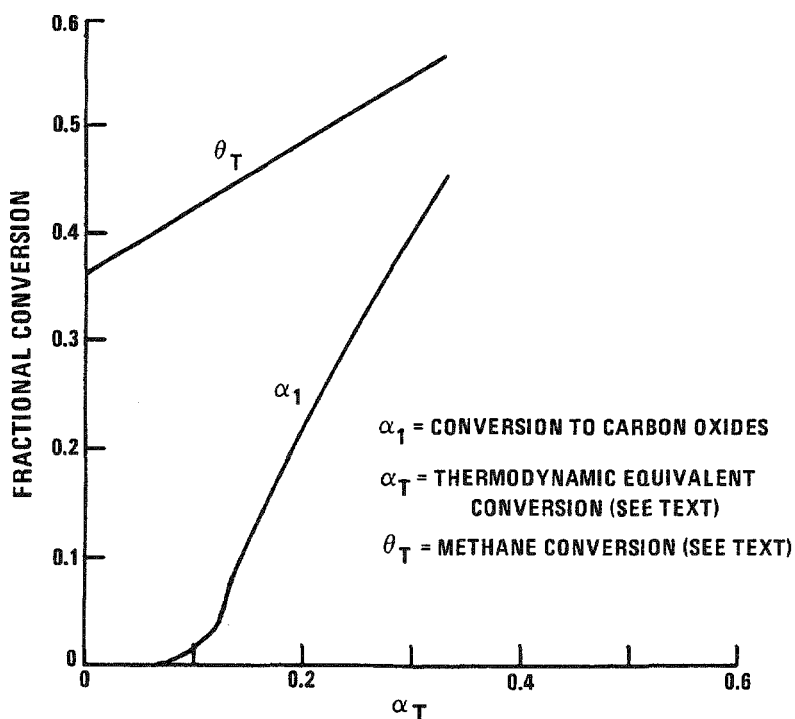


Figure 5-4. Thermodynamically Equivalent Conversions for Run 10

On further consideration of the energy balances for the reformer, it was apparent that errors due to incorrect assignment of the product mix did not introduce significant error to the reformer simulation because at low conversion, the major energy input to the process stream was the sensible heat. In Figure 5-5, the enthalpy of the process stream, calculated from analyses at various points in the reformer, is plotted against the temperature of the reactor at that point. Also included are lines indicating the enthalpy for the process stream if the thermodynamic conversion, α_T , were 0% and 100%. The figure shows that errors in estimating the enthalpy of reaction would not significantly affect estimates of heat duty for the reformer since the enthalpy of reaction represents only a small increment over the input sensible heat.

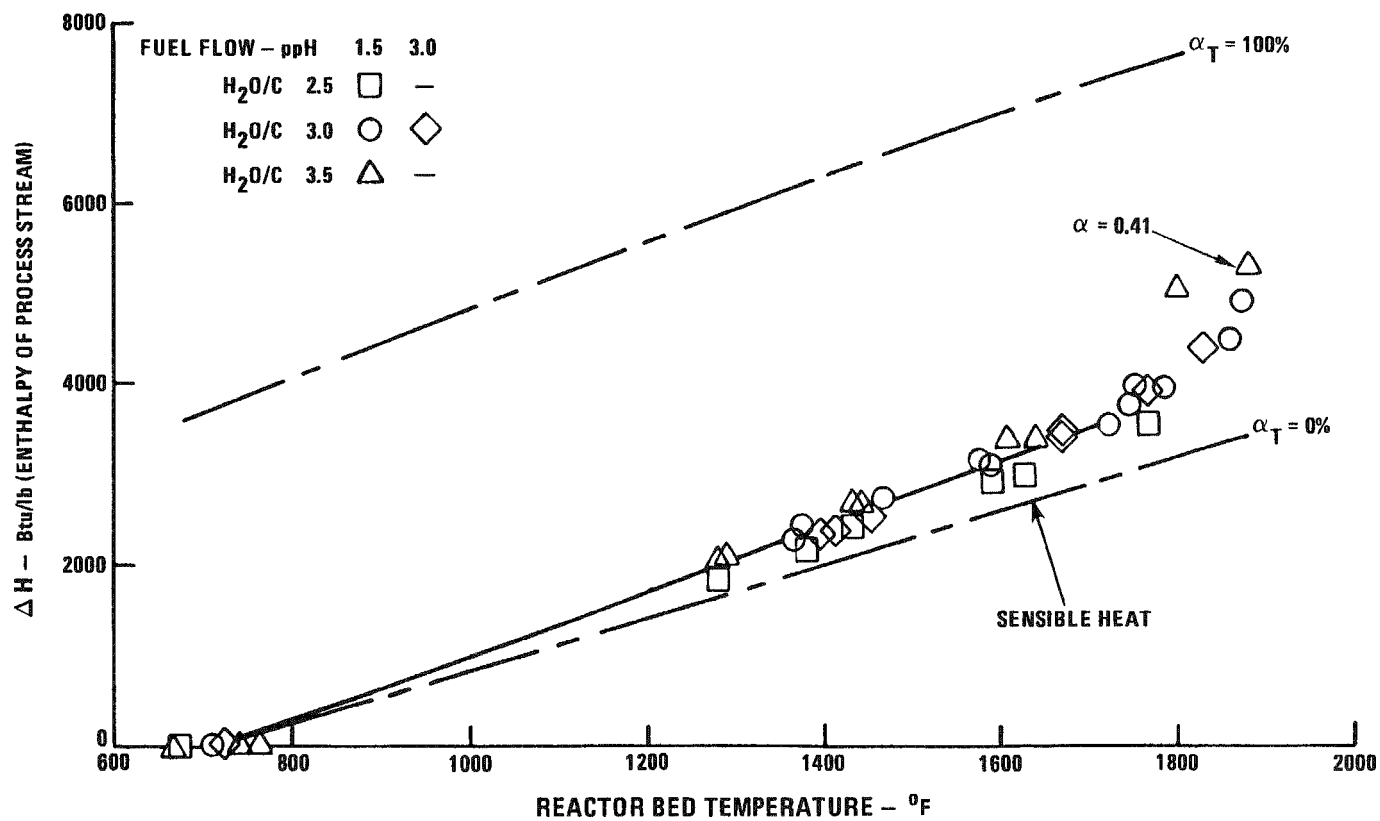


Figure 5-5. Enthalpy of the Process Stream in Run 10

Therefore, the rate expression generated by fitting the reactor model to α_T , as in Figure 5-5, i.e.,

$$- d \text{ Fuel}/dt = 2.4 \exp (-25000/RT) P_{\text{Fuel}} \\ \text{g moles/g cat sec}$$

was used with confidence in the final reformer model simulation which included heat transfer from an externally-fixed burner to the reformer tubes. This model generated reformer size and operating conditions required to achieve fuel conversions suitable for the primary reformer of a hybrid system.

In the system studies described below, a computer program determined mass and energy balance, process temperatures, pressures, flow rates and gas compositions throughout the fuel cell power plant. This program, for convenience, used a third measure of fuel conversion, θ_T , which was the calculation assuming all residual hydrocarbon was present as methane, i.e.

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

The relationship between θ_T and α and α_T is included in Figure 5-4.

Section 6

SYSTEM STUDIES

In the initial phase of this program, system studies were made of fuel cell power plants with four alternate fuel processors; the adiabatic, thermal, hybrid and cyclic reformers, EPRI EM-1701 (1). Operating conditions for the adiabatic reformer were selected using data from bench scale reactors run in a concurrent development program. A bench scale adiabatic reformer operated on No. 2 fuel oil at conditions required by the power plant for over 800 hours. The size and cost for the cyclic reformer in the system study were based on the results of preliminary tests with a small single bed reactor. The operating conditions for the thermal and hybrid reformers were estimated by assuming, without verification at that time, that the primary reformer could reform No. 2 fuel oil using the metal oxide and nickel catalysts developed for the adiabatic reformer. The power plants were evaluated by estimating the cost of a power plant capable of operating at a given heat rate. In the preliminary study, the cyclic reformer appeared capable of achieving lowest cost; however the ability of the parallel switching reactors to operate stably at the assumed conditions remains to be demonstrated. Of the remaining fuel processing approaches, the study showed that the hybrid reformer appeared most cost-effective. In the final phase of this program, the objective of the systems' study was to update the evaluation of the fuel cell power plant with the hybrid fuel processor based on the test results described in previous sections.

The optimistic objective was a steam reforming process which could treat No. 2 fuel oil in a single reactor at temperatures and space velocities compatible with fuel cell power plant design. Test experience showed, however, that catalysts which were active for steam reforming, i.e., the noble metal, active metal oxide and nickel catalysts, when placed in the inlet of the reformer, rapidly deactivated and accumulated carbon. Evidence suggested that deactivation of the catalysts by sulfur allowed unreacted No. 2 fuel oil to penetrate to high temperature portions of the reformer where refractory residues and cracking intermediates formed carbon causing further deactivation. Only Toyo T-12 remained carbon-free.

A mixed catalyst bed was proposed by the Toyo Engineering Company to eliminate deactivation and carbon accumulation. Nickel-free T-12 catalyst was placed in the inlet to the reformer to gasify the No. 2 fuel oil to a product mix which could be reformed without carbon accumulation in a nickel T-48 catalyst placed downstream. This concept was validated by both TEC and UTC (2) (3), but the temperature at the inlet of the T-48 catalyst bed had to be close to 1800°F to assure carbon-free operation.

The hybrid reformer approach was introduced to alleviate the high temperature requirement. Only partial conversion was achieved in a primary, tubular reformer. A secondary adiabatic reformer completed the conversion of fuel to hydrogen downstream. Preliminary systems studies suggested that the hybrid fuel processor in a fuel cell power plant might find an optimum operating condition at relatively low conversion in the primary reformer achievable with T-12 catalyst alone. This would greatly reduce concern for carbon formation, therefore, this was the option considered in the analytical study of the fuel cell power plant.

For this study, a dispersed power plant with a rated output of 4.8-MW dc (4.5-MW net ac) power was considered. The power section utilized phosphoric acid fuel cells operating at 50 psia. The power plant with the hybrid fuel processor has been described in previous reports (1). For convenience, a schematic diagram is shown in Figure 6-1 and a brief description of the system follows.

In the hybrid fuel processor, the fuel is mixed and vaporized by steam, and partially converted in a tubular (primary) reactor. The process heat required by this reactor is provided by heat transferred to the tubes from the hot burner gases. A small amount of air is then added to the partially converted fuel gas and the fuel conversion completed in the adiabatic (secondary) reactor. The process heat required is provided within the reactor by the oxidation of part of the fuel by the air. The process fuel gas is then cooled and the CO converted to CO₂ in two sulfur tolerant shift converters. Cooling between the shift converters is utilized to stay within the catalyst's operating limits and reduce the CO to the desired level. The processed fuel then flows to the power section where most of the hydrogen is consumed to produce electricity. The residual hydrogen in the anode vent gas, and any unconverted CH₄ or CO are burned in the tubular reformer to provide the process heat. The energy in the reformer

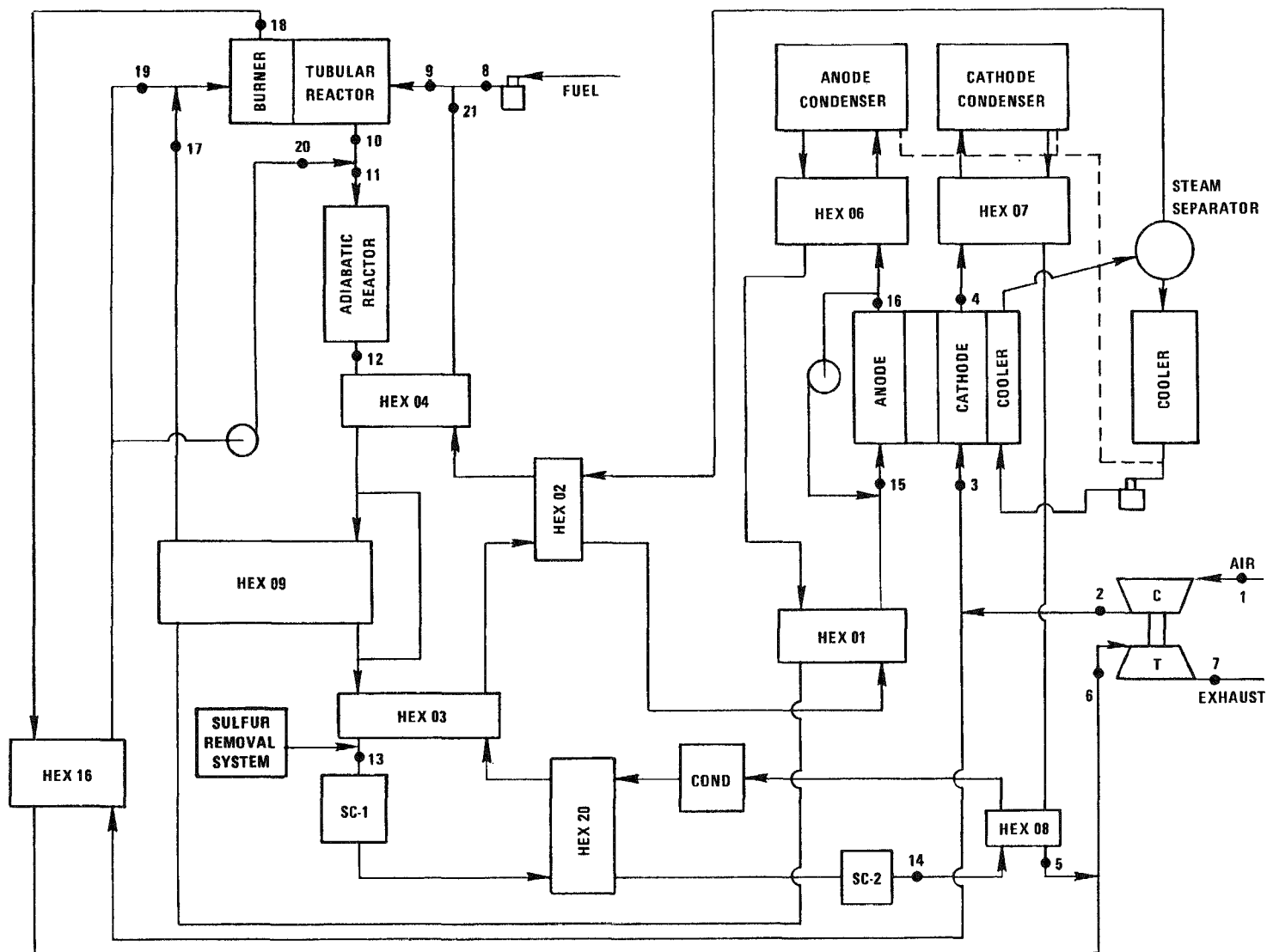


Figure 6-1. Hybrid Reformer Power Plant Schematic

burner exhaust gases is utilized to drive the turbocompressor which pressurizes the system and provides the air for the fuel cells and fuel processor. Heat exchangers are used to recover heat to preheat the process fuel gas and maintain the proper temperatures throughout the system. Water for the steam required by the fuel processor is recovered from the vent gases from the power section by means of condensers. For the hybrid system, the primary reformer does not include an internal regenerator as used in a thermal steam reformer. This eliminates the need for a heat exchanger and reduces the probability of plugging in the transfer line.

The fuel utilized in the study 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 study, it was assumed that the nominal 3220 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. This requirement was common to all the power plants and hence was not included in the comparison of systems.

The impact of the catalyst activity on total power plant cost was evaluated by optimizing the system to obtain the minimum power plant cost at a constant heat rate of 9300 Btu/kWh, the design goal. The 9300 Btu/kWh heat rate was maintained by changing the power section efficiency (cell voltage) to offset any change in the fuel processor efficiency. An existing cell performance model was used to adjust the total cell area required for the different cell voltage, fuel gas quality, and hydrogen utilizations.

A computer program determined the mass and energy balance, process temperatures, pressures, flow rates, and gas compositions throughout the system. The tubular and adiabatic reactor sizes were estimated using existing reactor models with the catalyst activity adjusted to the value determined from the test results.

Power plant costs were estimated using the same approach and dollars (1979) as in the previous study (1). For the present evaluation, power plant costs were adjusted for any changes in the reactor size, total cell area and heat exchanger requirements and were expressed in values relative to the original study.

In the earlier study, the power plant with the hybrid fuel processor was optimized by estimating the power plant cost as a function of fuel conversion both in the tubular (primary) and adiabatic (secondary) reformer. For this study, the overall fuel conversion from the adiabatic (secondary) reformer was held constant at 95%. This was the optimum from the previous study which showed there was almost no effect on power plant cost at overall fuel conversions of 92 to 98%. TOYO T-12 catalyst was used in the tubular reformer, and the PSD metal oxide and advanced nickel catalyst in the secondary reformer, with performance estimated from the data of the experimental program.

A maximum tube temperature of 1900°F was selected for the tubular reformer to stay within limits for conventional tube materials. To increase the tubular reformer fuel conversion, the process gas temperature at the exit of the tubular (primary) reformer must be increased. This requires a large increase in the tubular reactor size (Figure 6-2A) and thus cost, to maintain the maximum wall temperature selected. Increasing the primary reformer fuel conversion decreases the amount of conversion in the secondary reformer. Thus, the secondary reformer size (Figure 6-2B) and cost decrease as the primary reformer fuel conversion is increased. Increased primary fuel conversion decreases the amount of process heat and thus the air required for the secondary reformer. This improves the fuel quality and reduces the hydrogen utilization. Both factors improve the cell performance, which results in a decrease in the total cell area (Figure 6-2C) and power section cost as the primary fuel conversion increases. The net effect of these trends is an optimum fuel conversion which minimizes the power plant cost. The optimum primary fuel conversion is 53.5%, as shown in Figure 6-3. Operation at primary fuel conversion as low as 46% or as high as 60% would increase power plant cost only half a percent. The process gas temperatures, composition, and flows at stations throughout the power plant are listed in Table 6-1 for the optimum condition.

The optimum fuel conversion of 53.5% is expressed in terms of θ_T , equivalent to a conversion to oxides of carbon, α , of only 37.5%. As was evident in Figure 5-5, the primary reformer is primarily a means of heating the fuel and steam to a high temperature without fouling. The sensible heat added to the process gas by this means reduces the heat, and thus the oxygen, required in the secondary reformer.

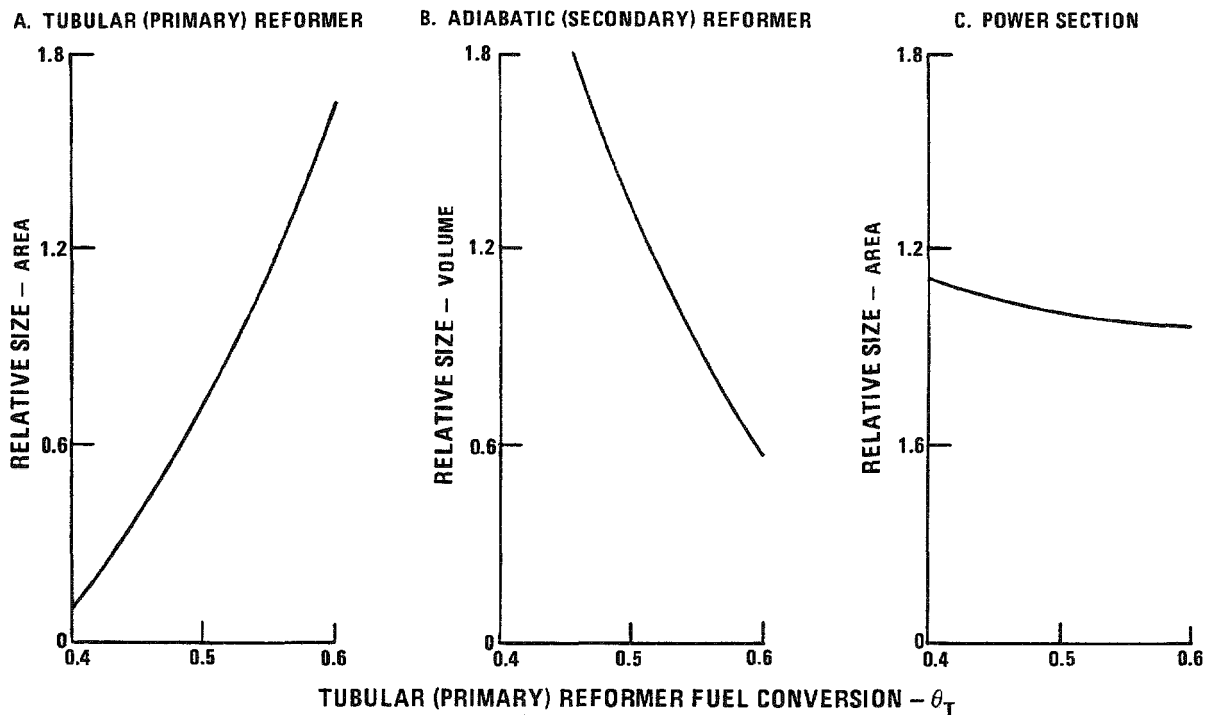


Figure 6-2. Impact of Tubular Reformer Fuel Conversion on Hybrid System Components

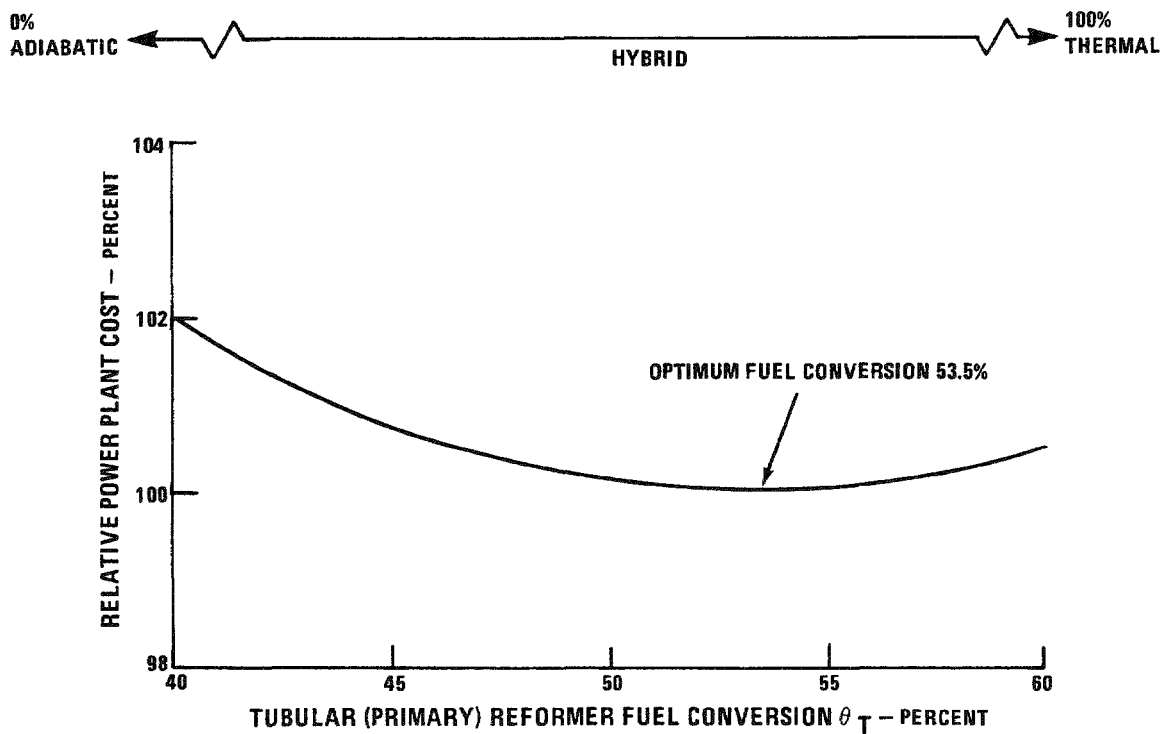


Figure 6-3. Hybrid Power Plant Optimization

Table 6-1
HYBRID POWER PLANT PROCESS CONDITIONS

Station	Temp.	Flows (Mols/Hr)								Fuel (pph)
		H ₂	H ₂ O	CH ₄	CO	CO ₂	O ₂	N ₂	Air	
1	95						339.2	1261.0	15.8	
2	432						339.2	1621.0	15.8	
3	432						258.8	961.9	12.1	
4	375		310.5				103.5	961.9	12.1	
5	482		61.8				103.5	961.9	12.1	
6	698		141.2			156.3	111.9	1261.0	15.8	
7	400		141.2			156.3	111.9	1261.0	15.8	
8	95									2160
9	950		468.9							2160
10	1745	132.3	333.4	72.7	31.8	51.8				
11	1572	132.3	333.4	72.7	31.8	51.8	30.5	113.5	1.4	
12	1638	287.7	307.8	7.8	74.8	73.6		113.5	1.4	
13	620	287.7	307.8	7.8	74.8	73.6		113.5	1.4	
14	539	356.2	239.3	7.8	6.3	142.2		113.5	1.4	
15	533	365.3	175.2	9.4	7.5	170.9		136.4	1.7	
16	375	54.8	175.2	9.4	7.5	170.9		136.4	1.7	
17	1342	45.6	18.2	7.8	6.3	142.2		113.5	1.4	
18	1113		79.4			156.3	8.3	298.9	3.8	
19	528						49.9	185.4	2.4	
20	528						30.5	113.5	1.4	
21	1256		468.9							

In the hybrid system, as the primary reformer fuel conversion is decreased, its size decreases until, in the limit, it disappears and the fuel processing system becomes an adiabatic reformer. As the primary fuel conversion is increased to 95%, the secondary reformer disappears and the system becomes a thermal steam reformer fuel processor. Thus, the optimization curve (Figure 6-3) confirms that the hybrid system is superior to either the adiabatic reformer or the thermal steam reformer.

In the previous study, a metal oxide and advanced nickel catalyst were assumed to operate in the primary reactor of the hybrid system. The activity of this advanced nickel catalyst is an order of magnitude higher than the TOYO T-12 catalyst in the present study. But, operating at a lower conversion and higher process temperature, the size of the primary reactor is only 30% larger than with the TOYO T-12 catalyst. This is offset by a 35% reduction in the size of the secondary reformer due to the higher inlet temperature to give a final system cost not significantly different from that of the reference system, as shown in Table 6-2. The significance of the present study therefore is that catalyst activity is not critical. The system conditions can be adjusted so the impact on power plant cost is negligible.

The estimated cost of the power plant with the hybrid fuel processor is 8% less than that with the adiabatic reformer fuel processor. By increasing the cell area, the heat rate can be reduced. The heat rate could be reduced to 8300 Btu/kWh with a 20% increase in power plant cost, as shown in Figure 6-4. At this heat rate, the power plant cost with the hybrid fuel processor is 15% lower than with the adiabatic reformer.

Table 6-2
SYSTEM COMPARISON

Study Fuel Processing System	Previous * Adiabatic	Previous Hybrid	Present Hybrid
Power Output (MW-Net AC)	4.8	4.8	4.8
Heat Rate (Btu/kWh)	9300	9300	9300
<u>Tubular (Primary) Reformer</u>			
Specific Area (lb/hr-ft ²)	--	2.7	2.1
Fuel Conversion (%)	--	62.7	53.5
Steam/Carbon	--	3.0	3.0
Inlet Temperature (°F)	--	950	950
Exit Temperature (°F)	--	1563	1745
Maximum Wall Temperature (°F)	--	1880	1900
<u>Adiabatic (Secondary) Reformer</u>			
Space Velocity (lb/ft ³ -Hr)	9.0	6.6	10.3
Fuel Conversion (%)	98.5	95	95
Oxygen/Carbon (O ₂ /C)	0.35	0.19	0.195
Inlet Temperature (°F)	1300	1473	1572
Exit Temperature (°F)	1625	1638	1638
<u>Power Section</u>			
Cell Voltage (Volts)	.616	.635	.636
Current Density (Amps/Ft ²)	231	250	245
Relative Power Plant Cost	1.08	1.0	1.0

* REFERENCE (1).

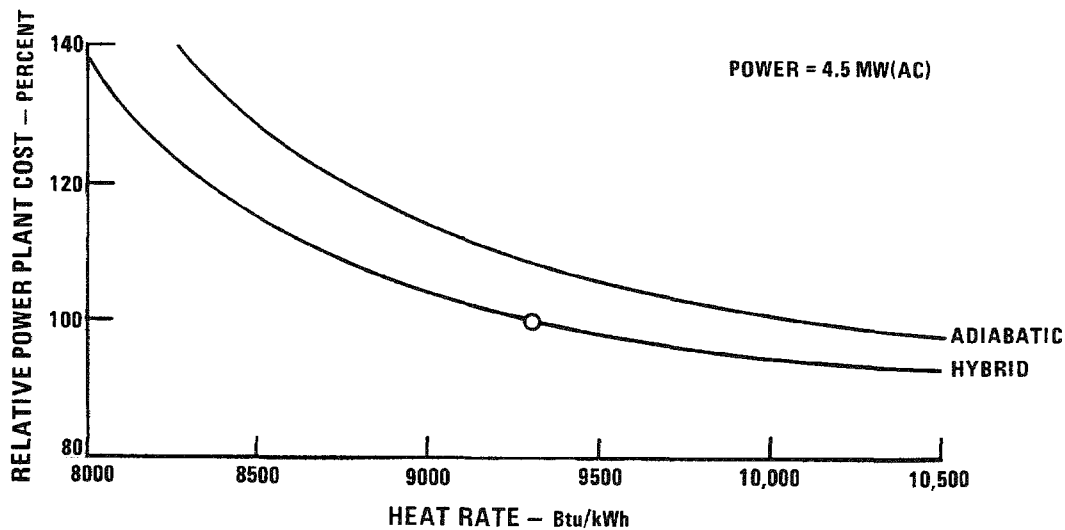


Figure 6-4. Impact of Heat Rate on Power Plant Cost



Section 7

CONCLUSIONS AND RECOMMENDATIONS

At the end of the program, the status of sulfur tolerant fuel processors for fuel cell power plants could be summarized as follows:

- The adiabatic fuel processor demonstrated the capability for reforming No. 2 fuel oil at conditions suitable for fuel cell power plants in bench-scale (3 kW) and pilot-scale (20 kW) reactors.
- The adiabatic fuel processor demonstrated performance comparable to No. 2 fuel oil with hydro-treated H-coal distillates and SRC light organic liquid. Heavier coal derived liquid fuels, which had higher end points and aromatics than No. 2 fuel oil, deposited carbon in the reactor.
- Of catalysts tested for the primary reformer of a hybrid fuel processor, only the Toyo Engineering Company T-12 catalyst could operate on No. 2 fuel oil at conditions suitable for fuel cell power plants.
- A bench-scale test of over 300 hours demonstrated that the primary reformer filled with T-12 catalyst could operate carbon-free and that the partially converted product would not deposit carbon in the transfer lines.
- Systems analysis showed that the performance of a fuel cell power plant with a hybrid fuel processor was insensitive to the conversion achieved in the primary reformer.
- A comparison, by systems analysis, of the adiabatic and hybrid fuel processors showed that a 4.8 MW phosphoric acid fuel cell power plant with a hybrid fuel processor had a lower cost at comparable design heat rate.

To bring the development of the hybrid fuel processor to the point of engineering design, the following additional tasks are recommended.

- Demonstrate at the bench scale that a secondary reformer can operate at the low primary fuel conversions, O/C ratio and high inlet temperatures of the optimized hybrid fuel processor power plant.

- Identify an approach for internal insulation of the secondary reformer which is compatible with the temperature transient requirements peculiar to fuel cell power plant operation.
- Verify operation of the primary and secondary reformers, in series, at the pilot scale.
- Develop a sulfur removal system to eliminate sulfur from the process stream before it enters the fuel cell stack.

Section 8

REFERENCES

1. United Technologies Corporation, "Development of the Adiabatic Reformer to Process No. 2 Fuel Oil and Coal-Derived Liquid Fuels", Electric Power Research Institute Report, EM-1701, Project 1041-4, February 1981.
2. Kinetics Technology International Corporation, "Assessment of Fuel Processing Systems for Dispersed Fuel Cell Power Plants", Electric Power Research Institute Report, EM-1487, Project 1041-1, March 1980.
3. Kinetics Technology International Corporation, "Evaluation of Hybrid THR-ATR Fuel Processor", Electric Power Research Institute Report, EM-2596, Project 1041-1, June 1981.



2



Appendix A

DEVELOPMENT OF THE ADIABATIC REFORMER TO
PROCESS NO. 2 FUEL OIL AND
COAL-DERIVED LIQUIDS

EM-1701
RESEARCH PROJECT 1041-4
INTERIM REPORT, FEBRUARY 1981

EXECUTIVE SUMMARY

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 A-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 A-1, were selected to give minimum values for air addition (O_2/C ratio) and pre-reaction temperature while maintaining high fuel conversion.

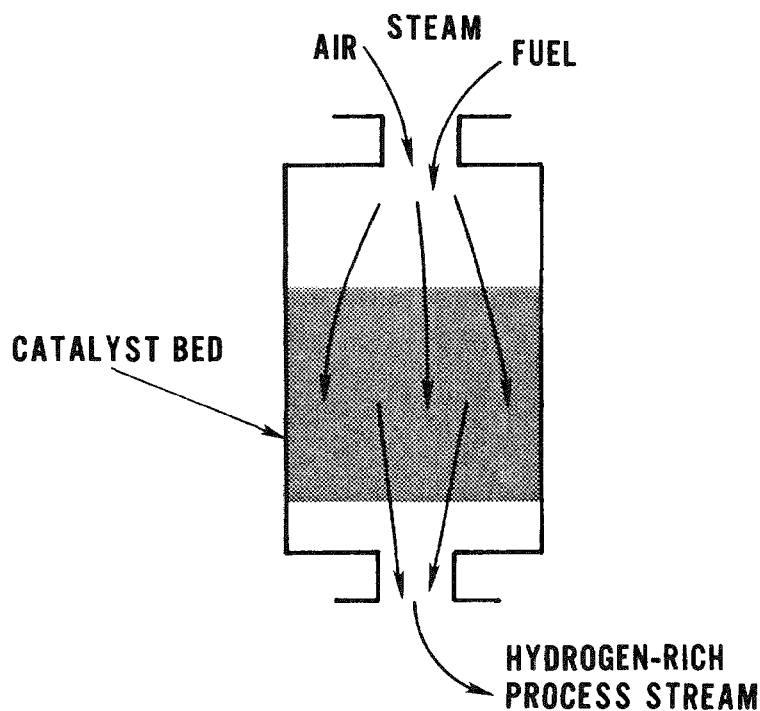


Figure A-1. Adiabatic Reformer

Table A-1
ADIABATIC REFORMER PERFORMANCE

	Design (1) Baseline	Reactor Performance	
		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 reaction. 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 O₂/C requirement for the two reactors. However, the reactor with optimized nozzle was still limited in performance by carbon formation. As shown in Table A-1, the minimum O₂/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 A-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,

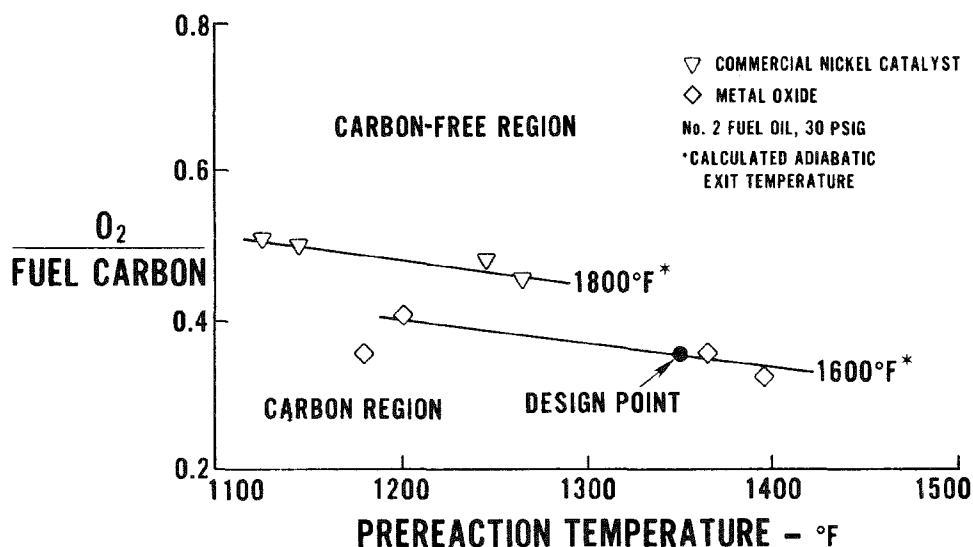


Figure A-2. Effect of Catalyst on Carbon Formation in the Adiabatic Reformer

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 A-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 .

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 A-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 A-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 A-4, showed that the conversion achieved by the advanced nickel catalyst projected to the design point.

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

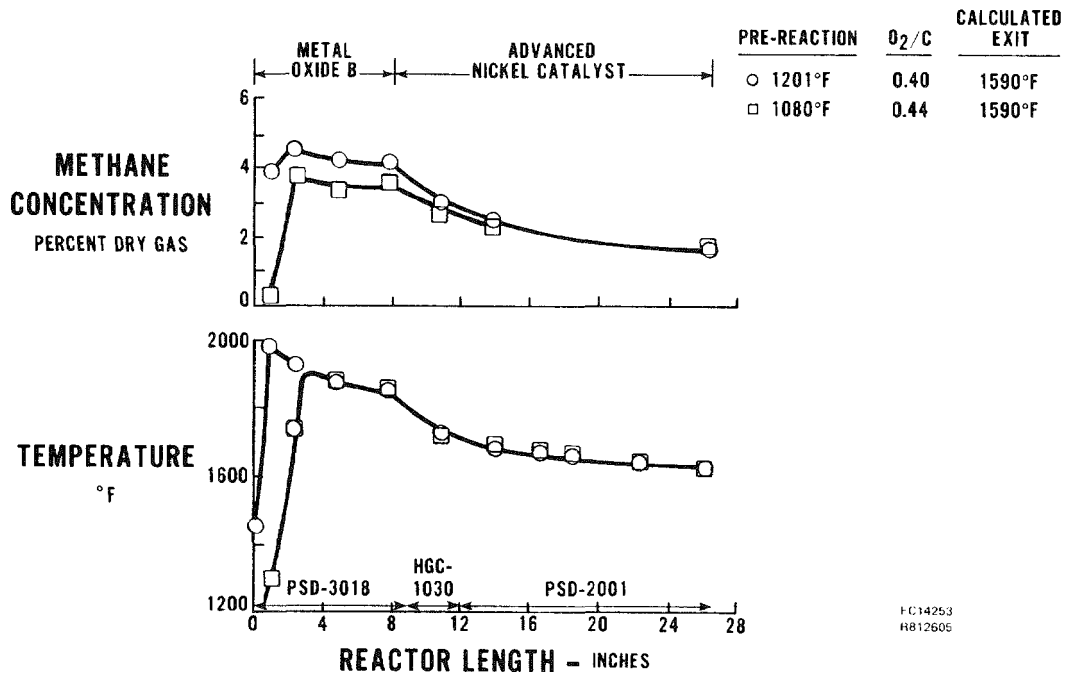


Figure A-3. Effect of O₂/C and Reaction Temperature on Fuel Conversion

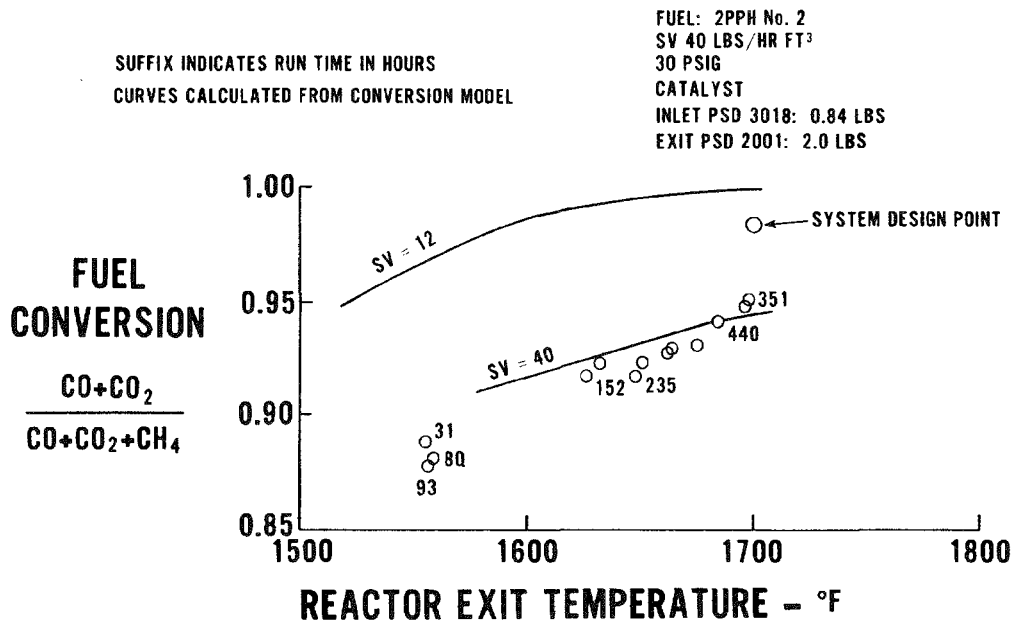


Figure A-4. Fuel Conversion on High Activity Nickel Catalyst

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 A-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 A-2, therefore, gives a preliminary assessment of the capability of the reactor to process coal-derived liquid fuels.

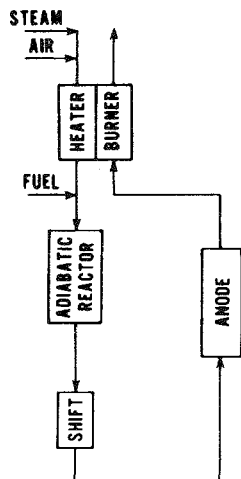
Table A-2
COAL LIQUID TEST RESULTS IN THE 2-INCH ADIABATIC REFORMER

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

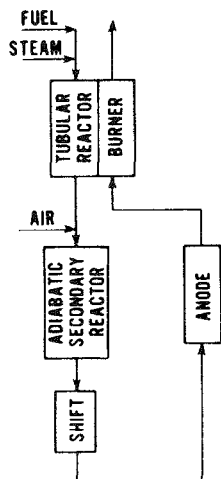
*Percentage values refer to extent of hydrogen addition by hydrotreating.

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 A-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.

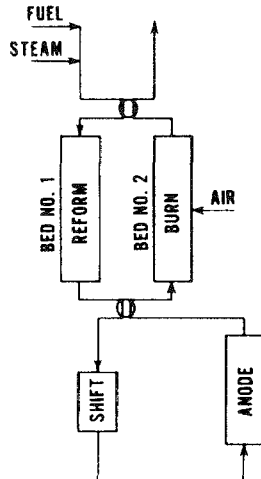
ADIABATIC REFORMER



HYBRID



CYCLIC



THERMAL

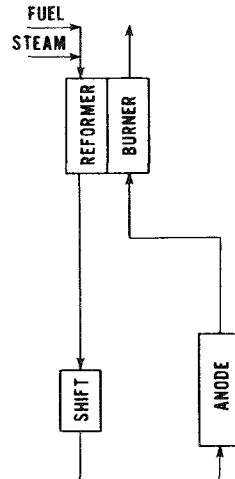


Figure A-5. Fuel Processing Systems Studied

Reactor volumes for the various alternate systems were estimated using catalytic activity data obtained in the adiabatic reformer test program. Figure A-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.

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.

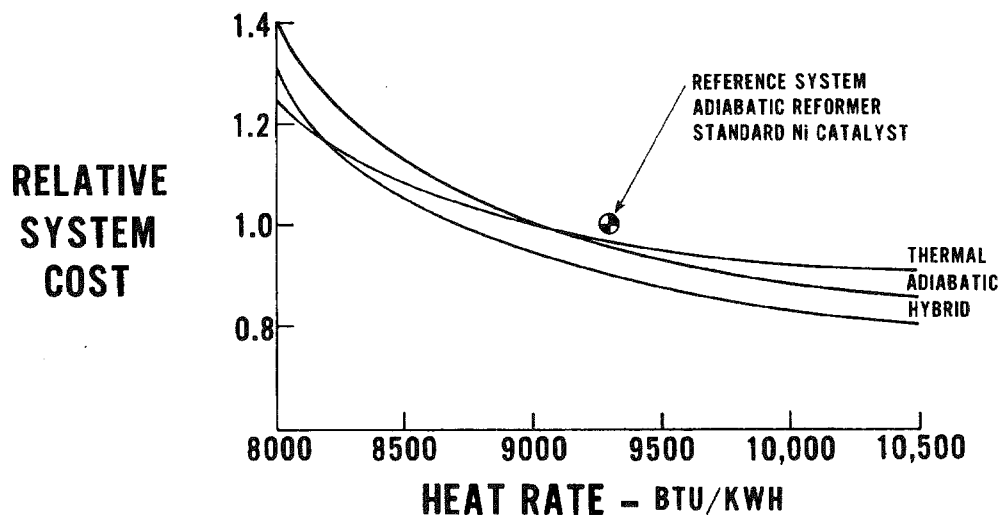
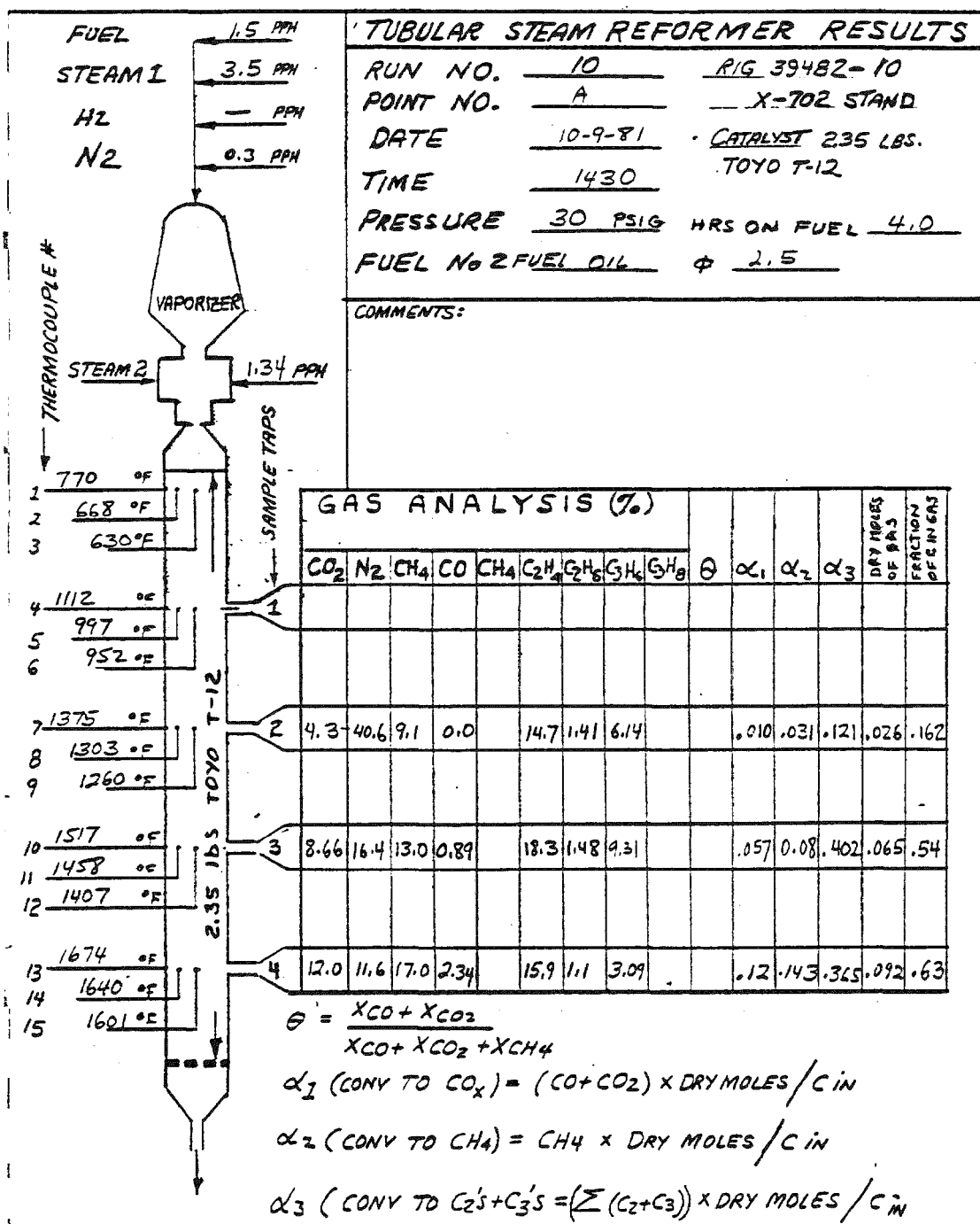


Figure A-6. Comparison of Alternative Fuel Processors

Appendix B

DATA FROM RUNS 10 AND 11





FUEL 1.5 PPH
STEAM 1 3.5 PPH
H₂ — PPH
N₂ 0.3 PPH

VAPORIZER

STEAM 2 2.38 PPH

THERMOCOUPLE #

1 724 °F
2 619 °F
3 571 °F
4 1111 °F
5 980 °F
6 914 °F
7 1375 °F
8 1307 °F
9 1256 °F
10 1527 °F
11 1471 °F
12 1416 °F
13 1678 °F
14 1645 °F
15 1614 °F

SAMPLE TAPS

2.35 LBS TOYO T-12

TUBULAR STEAM REFORMER RESULTS

RUN NO. 10 RIG 39482-10
POINT NO. B X-702 STAND
DATE 10-12-81 CATALYST 2.35 LBS.
TIME 1500 TOYO T-12
PRESSURE 30 PSIG HRS ON FUEL 15.0
FUEL No 2 FUEL OIL φ 3.0

COMMENTS:

GAS ANALYSIS (%)											θ	α ₁	α ₂	α ₃	DRY MOLES OF GAS	FRACTION OF C ₂ 'S
CO ₂	N ₂	CH ₄	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄						
4.43	47.2	6.06	—		11.2	1.16	5.42				.01	.013	.086	.023	.11	
7.83	17.7	11.2	0.43		18.2	1.33	7.75				.045	.062	.343	.06	.45	
11.7	11.7	16.9	2.37		16.2	0.87	2.88				.118	.142	.36	.091	.62	

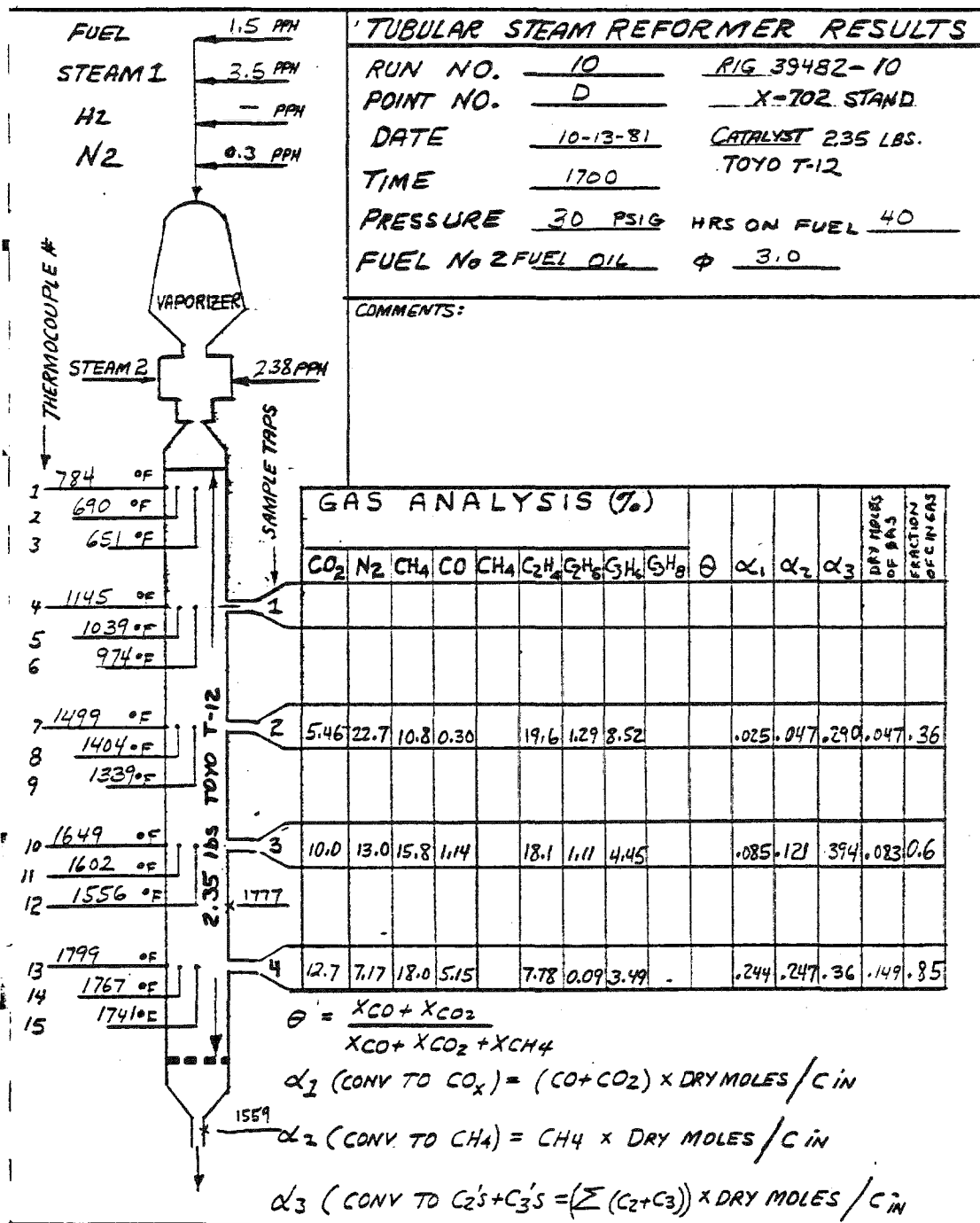
$$\theta = \frac{X_{CO} + X_{CO_2}}{X_{CO} + X_{CO_2} + X_{CH_4}}$$

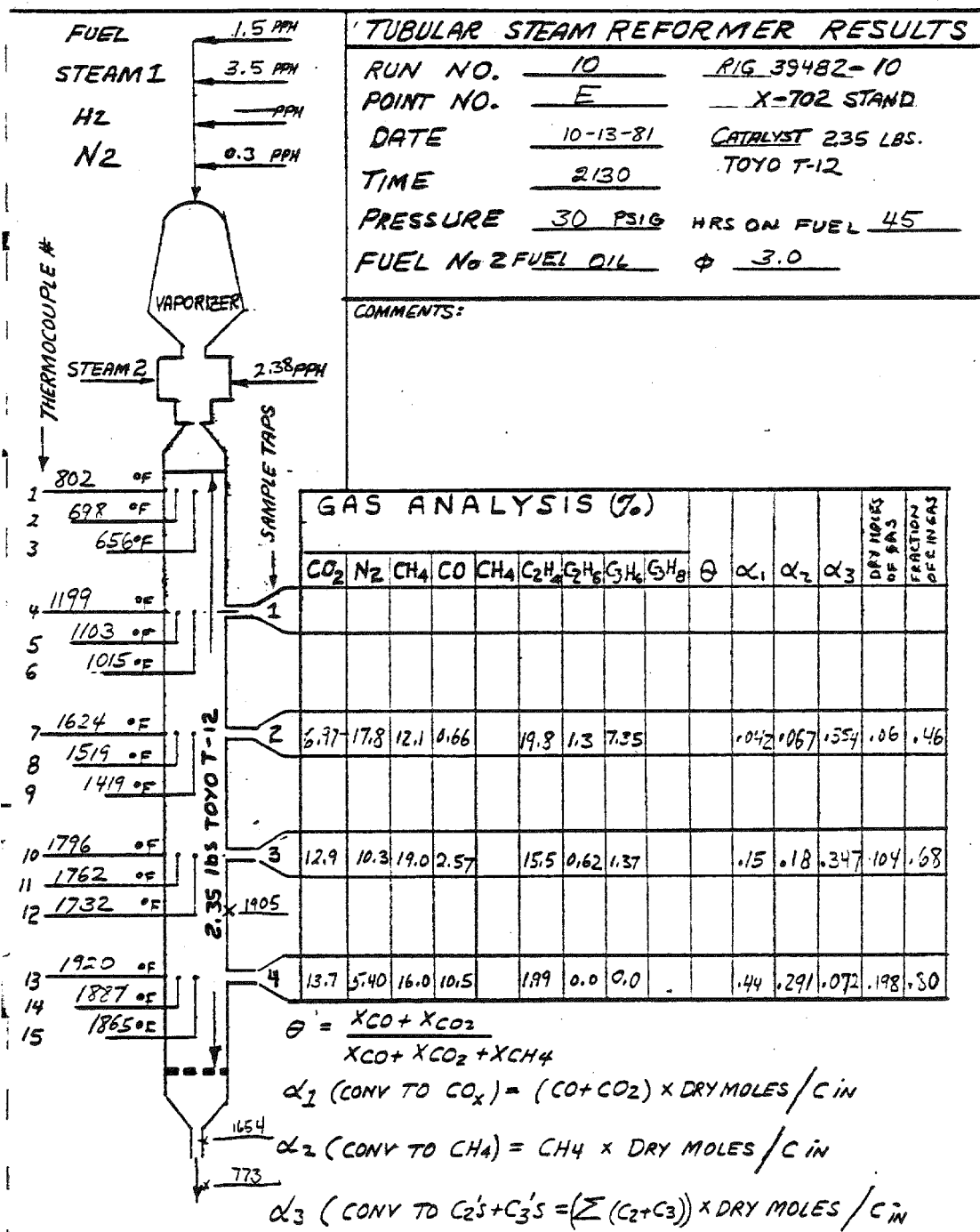
$$\alpha_1 \text{ (CONV TO CO}_x\text{)} = (CO + CO_2) \times \text{DRY MOLES / C in}$$

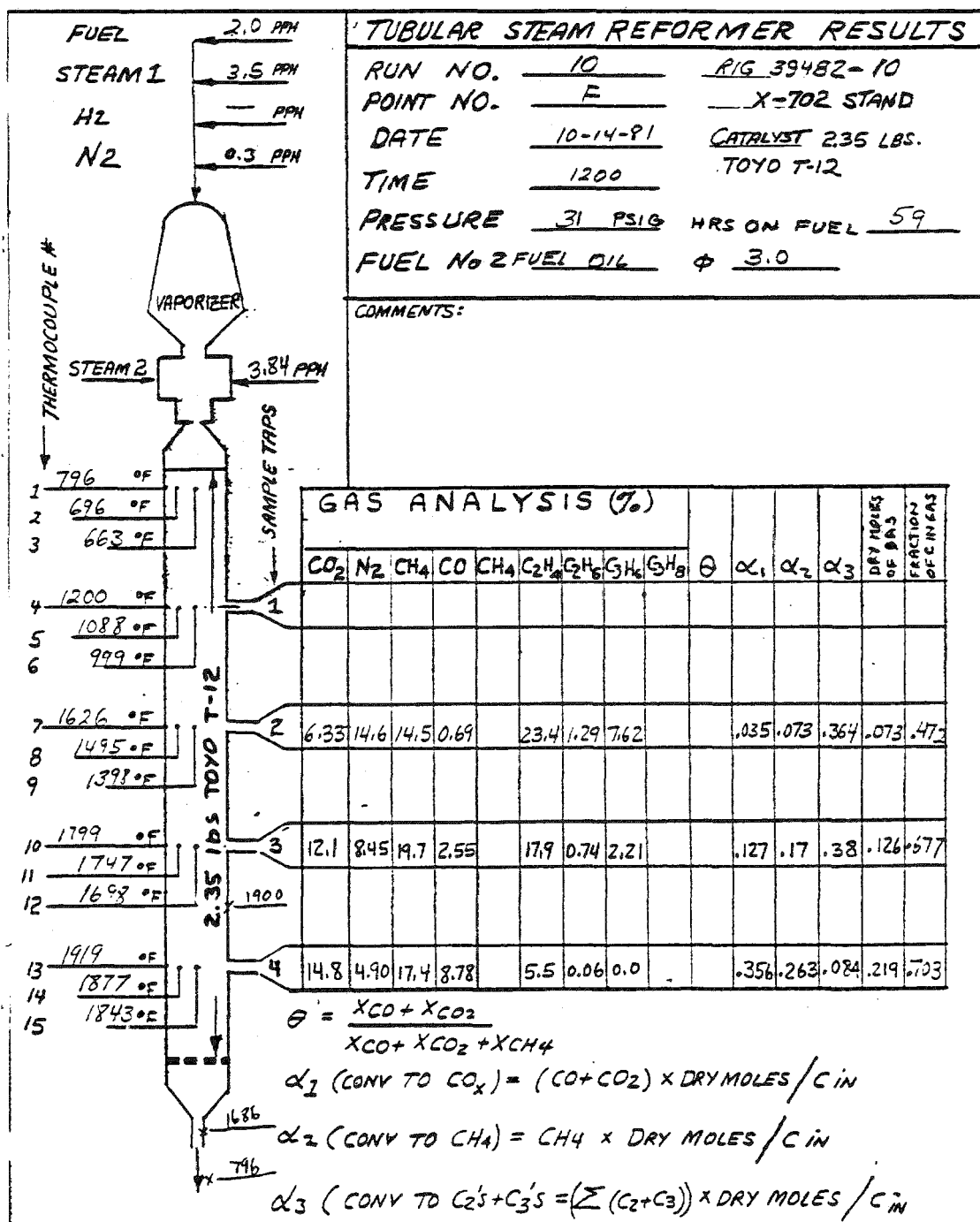
$$\alpha_2 \text{ (CONV TO CH}_4\text{)} = CH_4 \times \text{DRY MOLES / C in}$$

$$\alpha_3 \text{ (CONV TO C}_2\text{'S + C}_3\text{'S)} = (\sum (C_2 + C_3)) \times \text{DRY MOLES / C in}$$



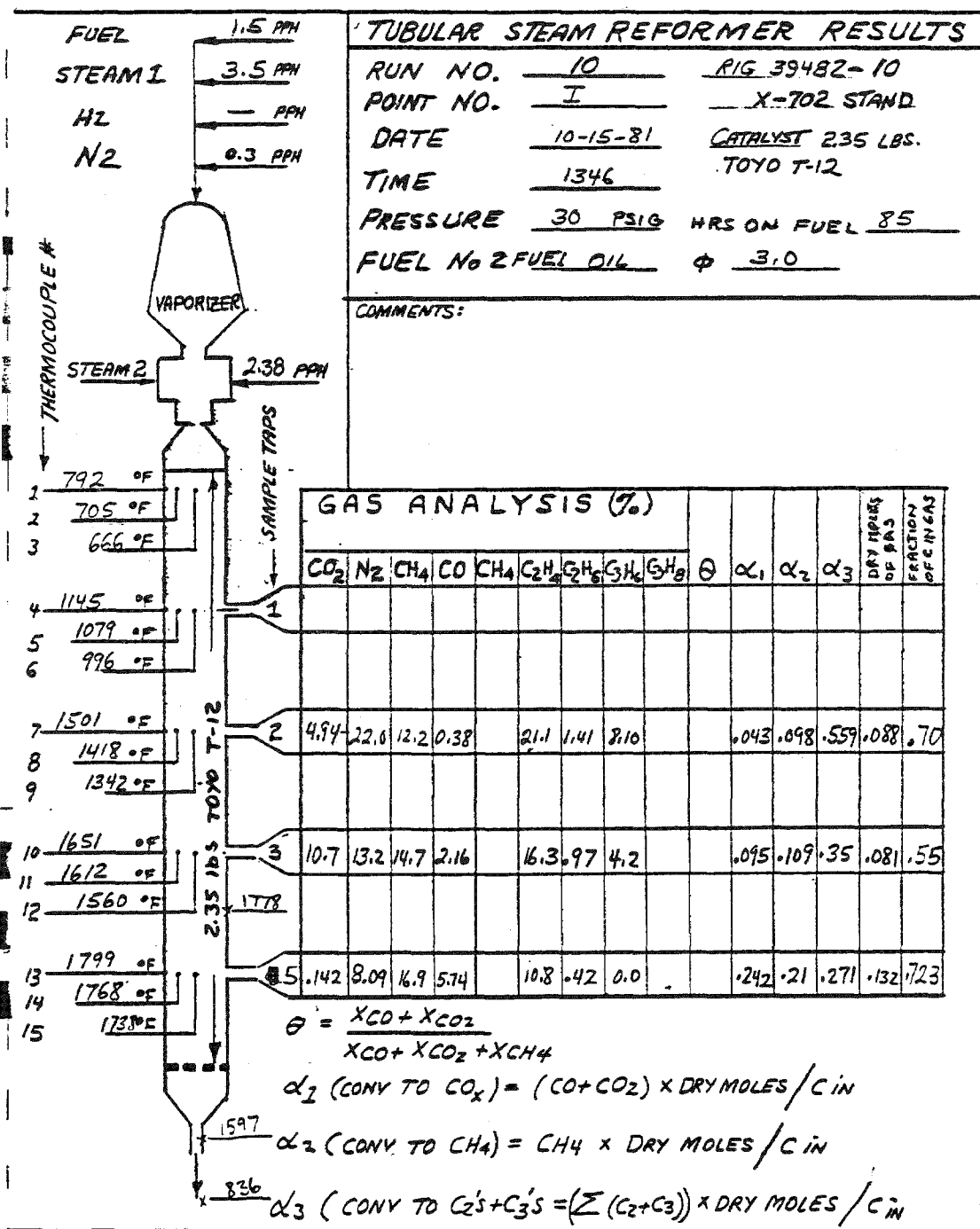




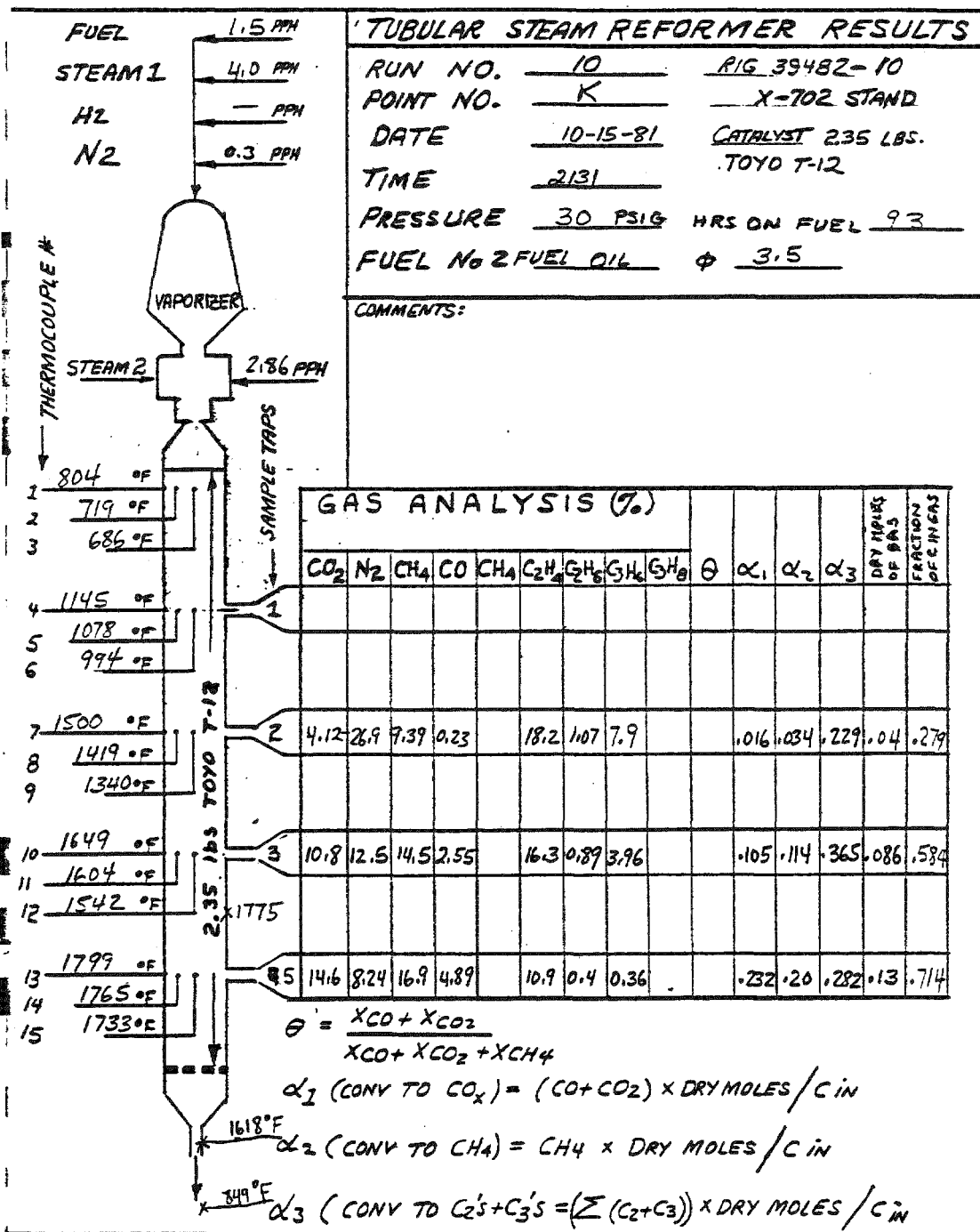


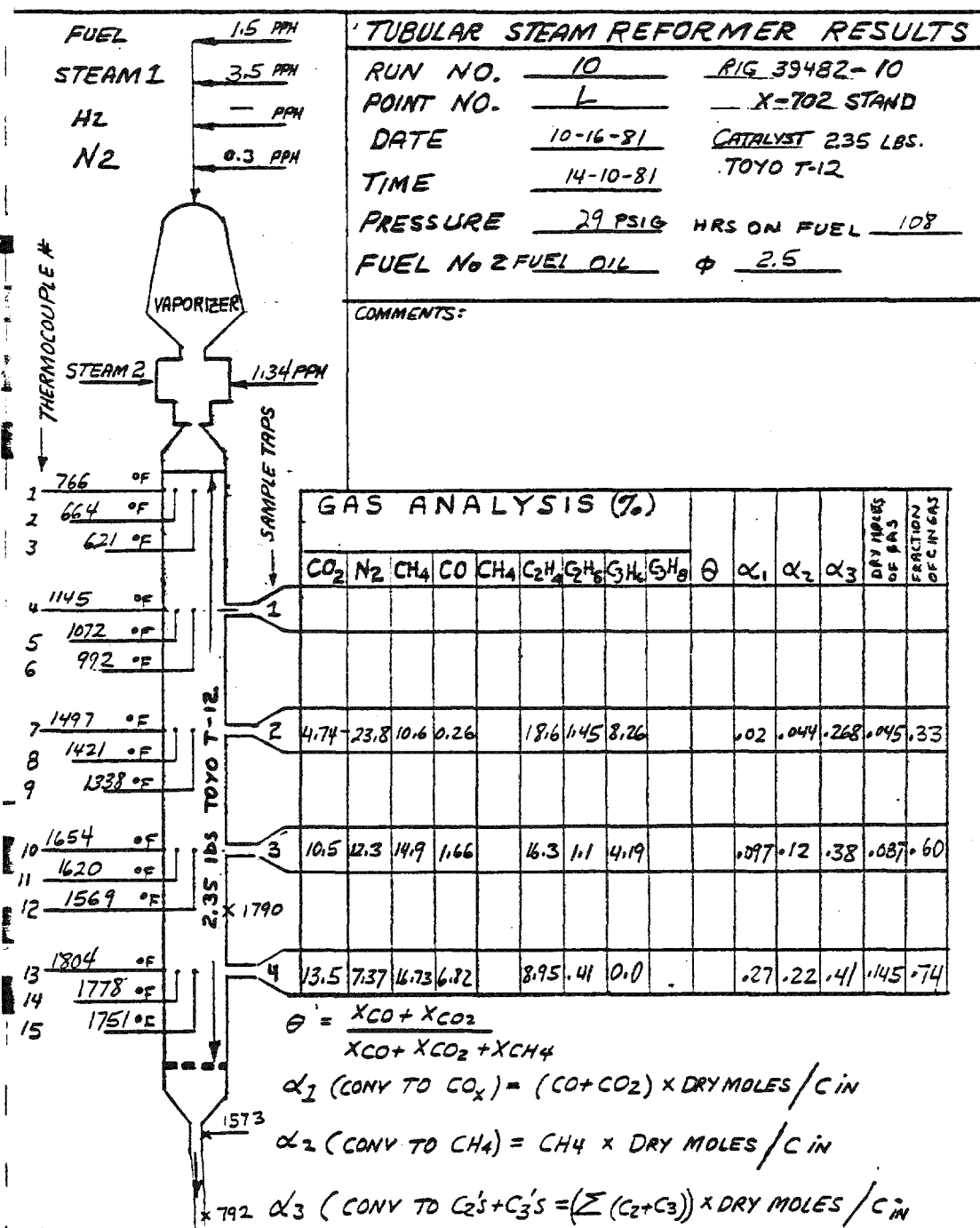












FUEL 1.5 PPH
STEAM 1 3.5 PPH
H₂ 0.0 PPH
N₂ 0.3 PPH

VAPORIZER

STEAM 2 238 PPH

THERMOCOUPLE #

SAMPLE TAPS

1 768 °F
2 670 °F
3 632 °F
4 1144 °F
5 1062 °F
6 984 °F
7 1498 °F
8 1421 °F
9 1338 °F
10 1648 °F
11 1604 °F
12 1542 °F
13 1801 °F
14 1764 °F
15 1733 °F

2.35 LBS TOYO T-12

TUBULAR STEAM REFORMER RESULTS

RUN NO. 10 RIG 39482-10
POINT NO. N X-702 STAND
DATE 10-20-81 CATALYST 2.35 LBS.
TIME 1207 TOYO T-12
PRESSURE 30 PSIG HRS ON FUEL 115
FUEL NO 2 FUEL OIL Φ 3.0

COMMENTS:

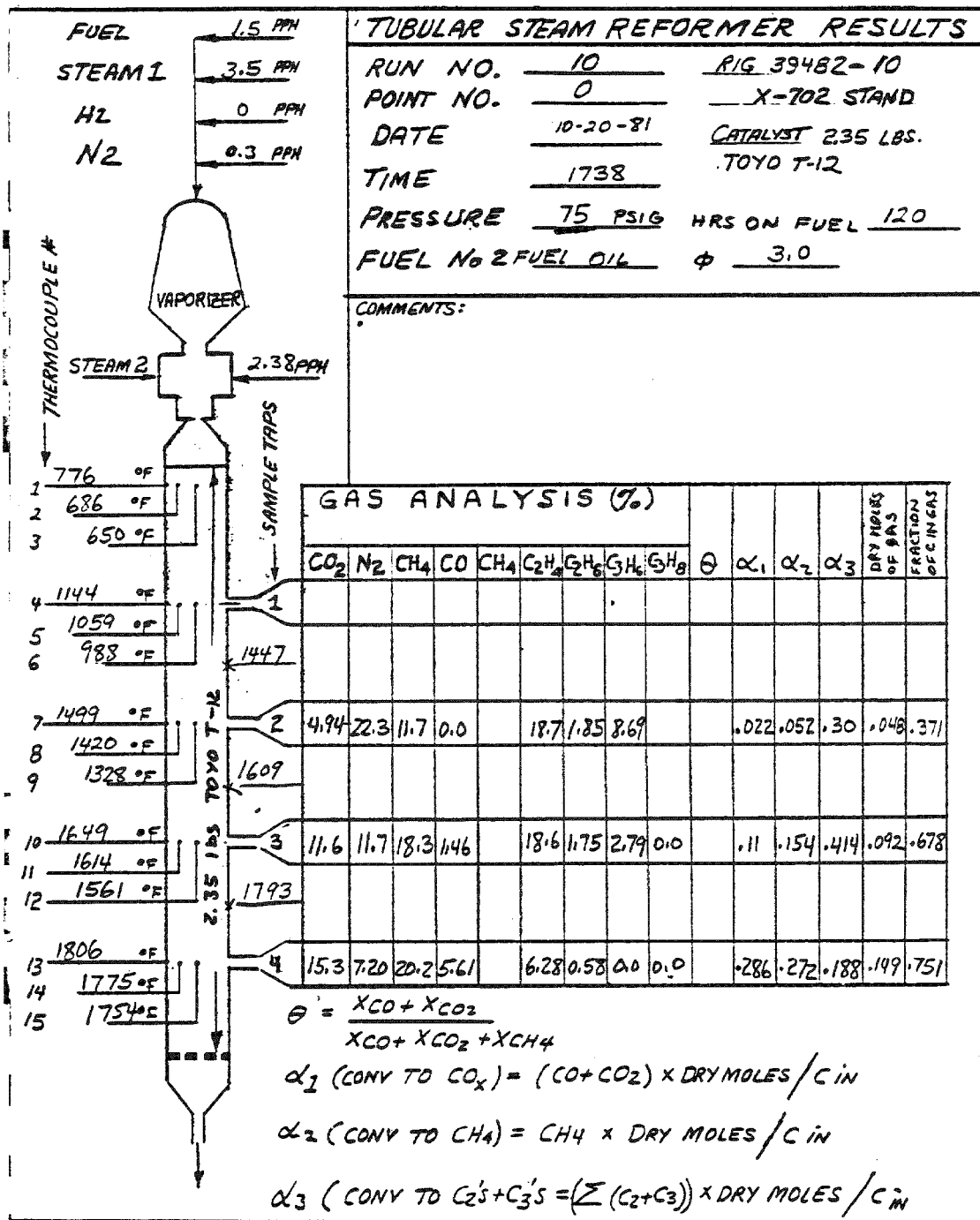
GAS ANALYSIS (%)											θ	α ₁	α ₂	α ₃	DRY MOLES OF GAS	FRACTION OF C IN GAS
CO ₂	N ₂	CH ₄	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂							
4.40	26.7	9.49	0.0		18.3	1.15	7.84	0.0			0.16	0.35	0.229	0.04	0.28	
10.1	14.8	14.8	1.34		17.7	1.15	4.69				0.076	0.098	0.34	0.072	0.515	
14.7	8.37	16.5	6.04		10.2	0.31	0.0	0.0			0.244	0.193	0.246	0.128	0.68	

$$\theta = \frac{X_{CO} + X_{CO_2}}{X_{CO} + X_{CO_2} + X_{CH_4}}$$

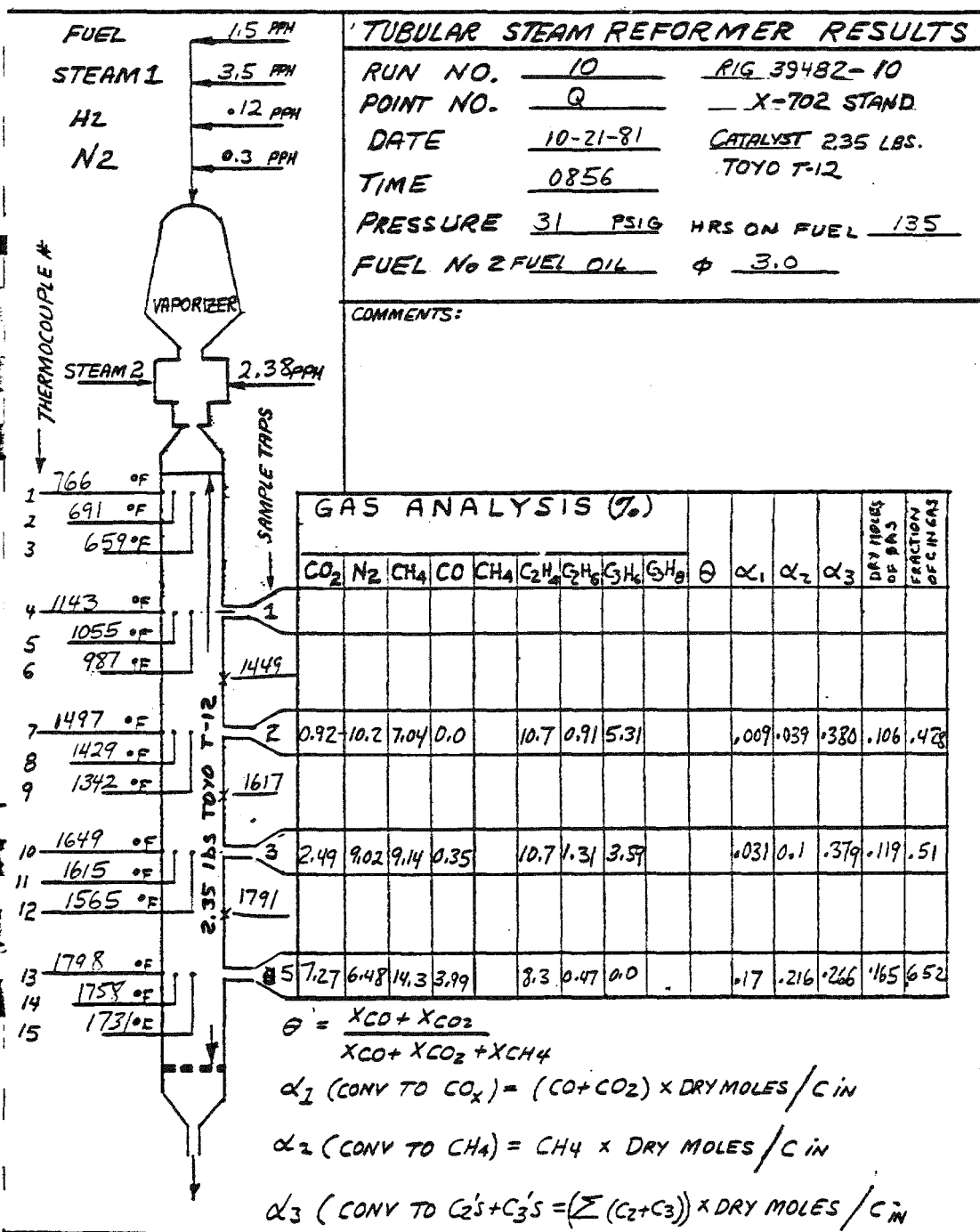
$$\alpha_1 \text{ (CONV TO CO}_x\text{)} = (CO + CO_2) \times \text{DRY MOLES} / C \text{ in}$$

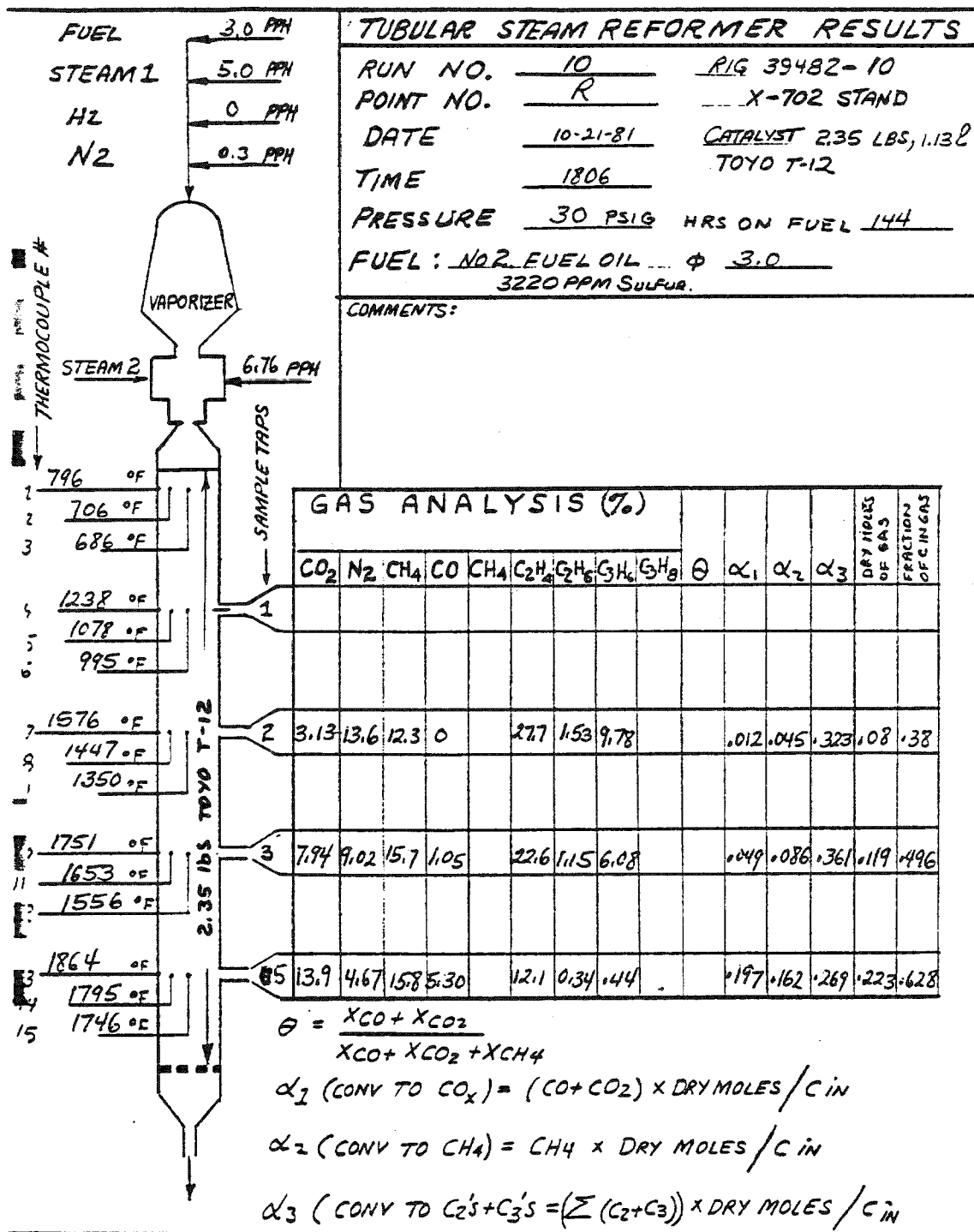
$$\alpha_2 \text{ (CONV TO CH}_4\text{)} = CH_4 \times \text{DRY MOLES} / C \text{ in}$$

$$\alpha_3 \text{ (CONV TO C}_2\text{'S + C}_3\text{'S)} = (\sum (C_2 + C_3)) \times \text{DRY MOLES} / C \text{ in}$$









FUEL		3.0 PPM		TUBULAR STEAM REFORMER RESULTS	
STEAM 1		5.0 PPM		RUN NO. <u>10</u> RIG <u>39482-10</u>	
H ₂		0 PPM		POINT NO. <u>5</u> X-702 STAND	
N ₂		0.3 PPM		DATE <u>10-21-81</u> CATALYST <u>2.35 LBS.</u>	
				TIME <u>2130</u> TOYO T-12	
				PRESSURE <u>31 PSIG</u> HRS ON FUEL <u>147</u>	
				FUEL NO 2 FUEL OIL <u>φ</u> <u>3.0</u>	
COMMENTS:					

VAPORIZER

STEAM 2 676 PPM

THERMOCOUPLE #

SAMPLE TAPS

TOYO T-12

2.35 LBS

1539 °F

1869 °F

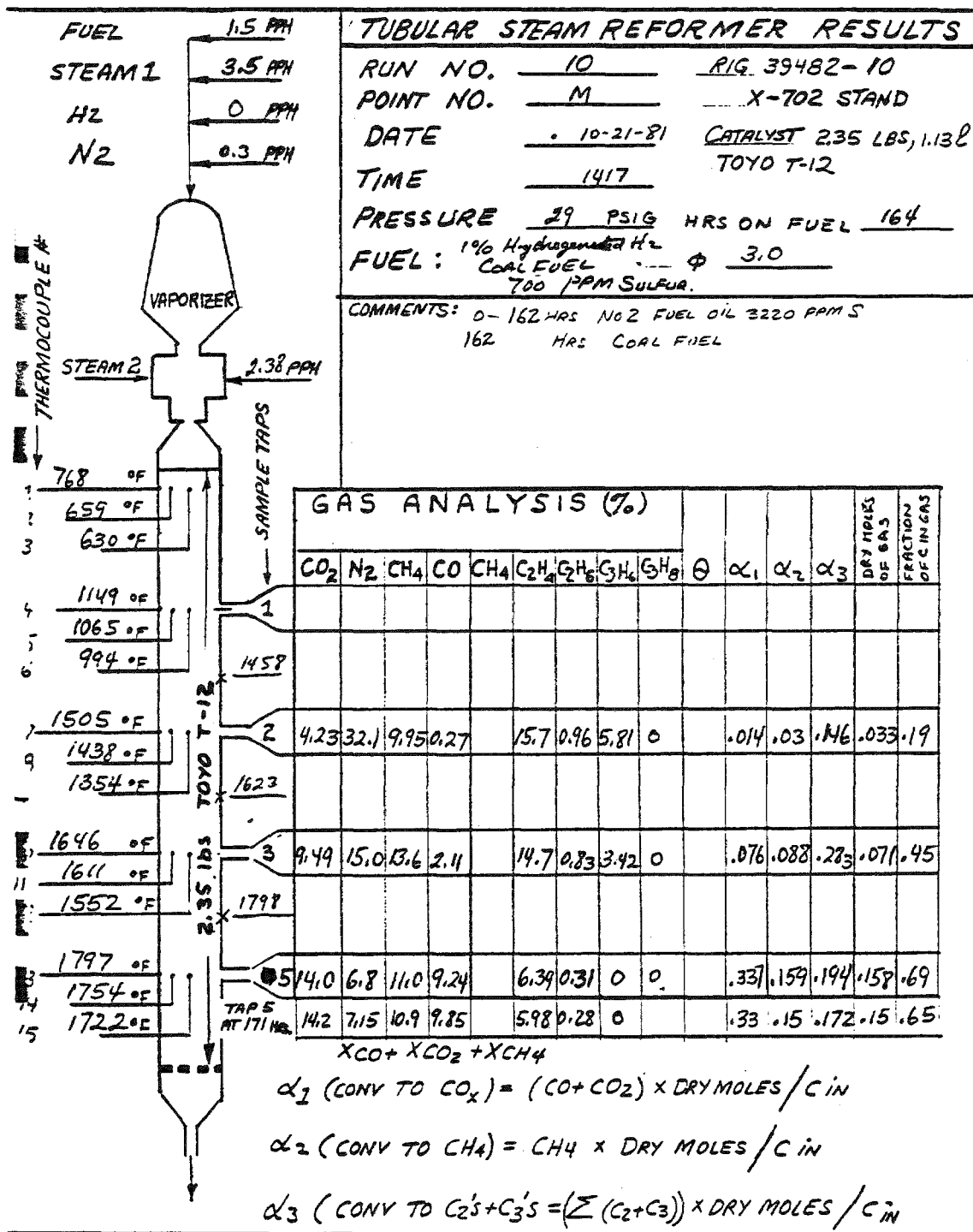
GAS ANALYSIS (%)												θ	α ₁	α ₂	α ₃	DRY MOLES OF GAS	FRACTION OF C ₂ 'S
CO ₂	N ₂	CH ₄	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆						
1	800 °F																
2	706 °F																
3	681 °F																
4	1277 °F																
5	1109 °F																
6	1017 °F																
7	1696 °F																
8	1539 °F																
9	1415 °F																
10	1902 °F																
11	1827 °F																
12	1731 °F																
13	1987 °F																
14	1919 °F																
15	1869 °F																

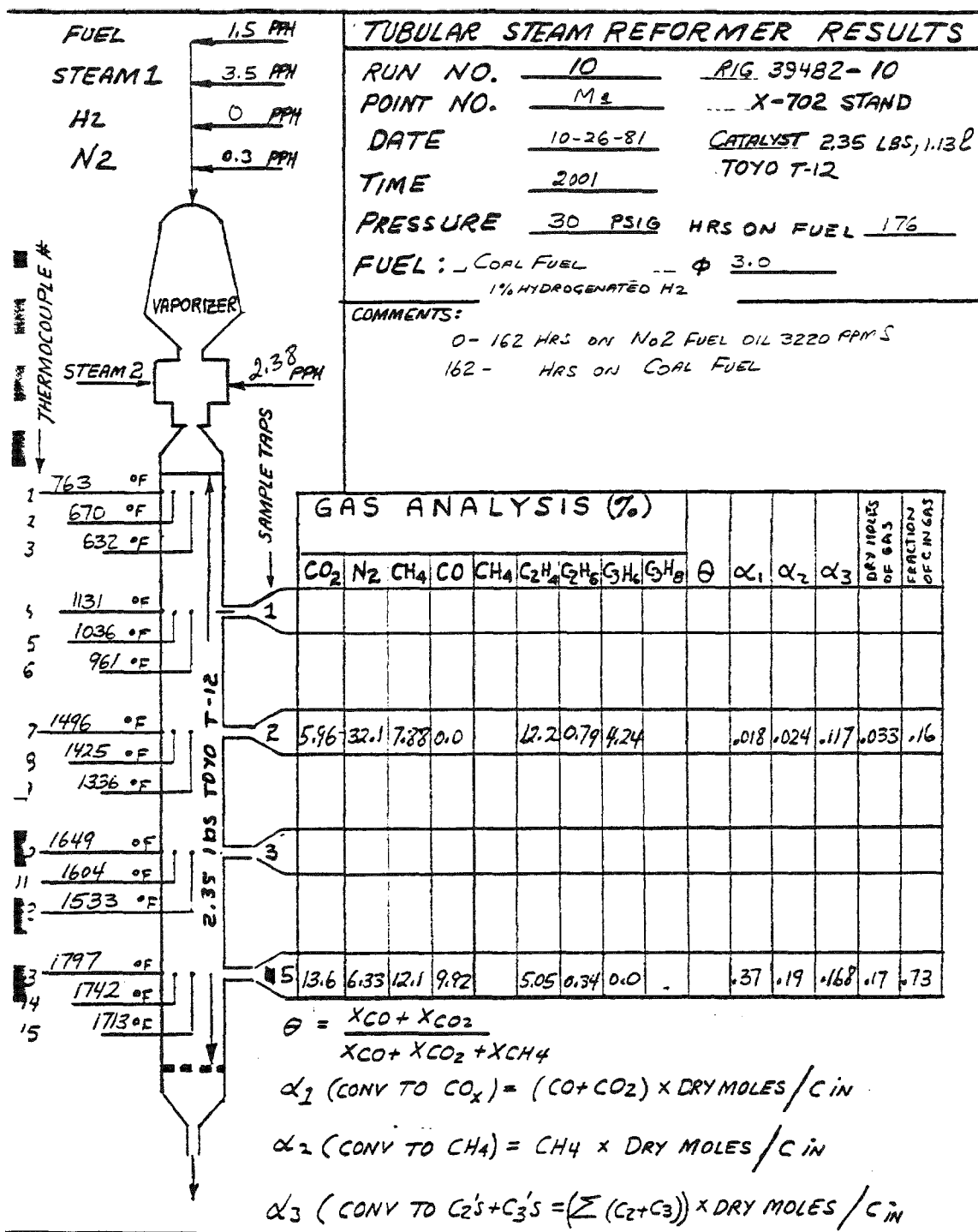
θ = $\frac{X_{CO} + X_{CO_2}}{X_{CO} + X_{CO_2} + X_{CH_4}}$

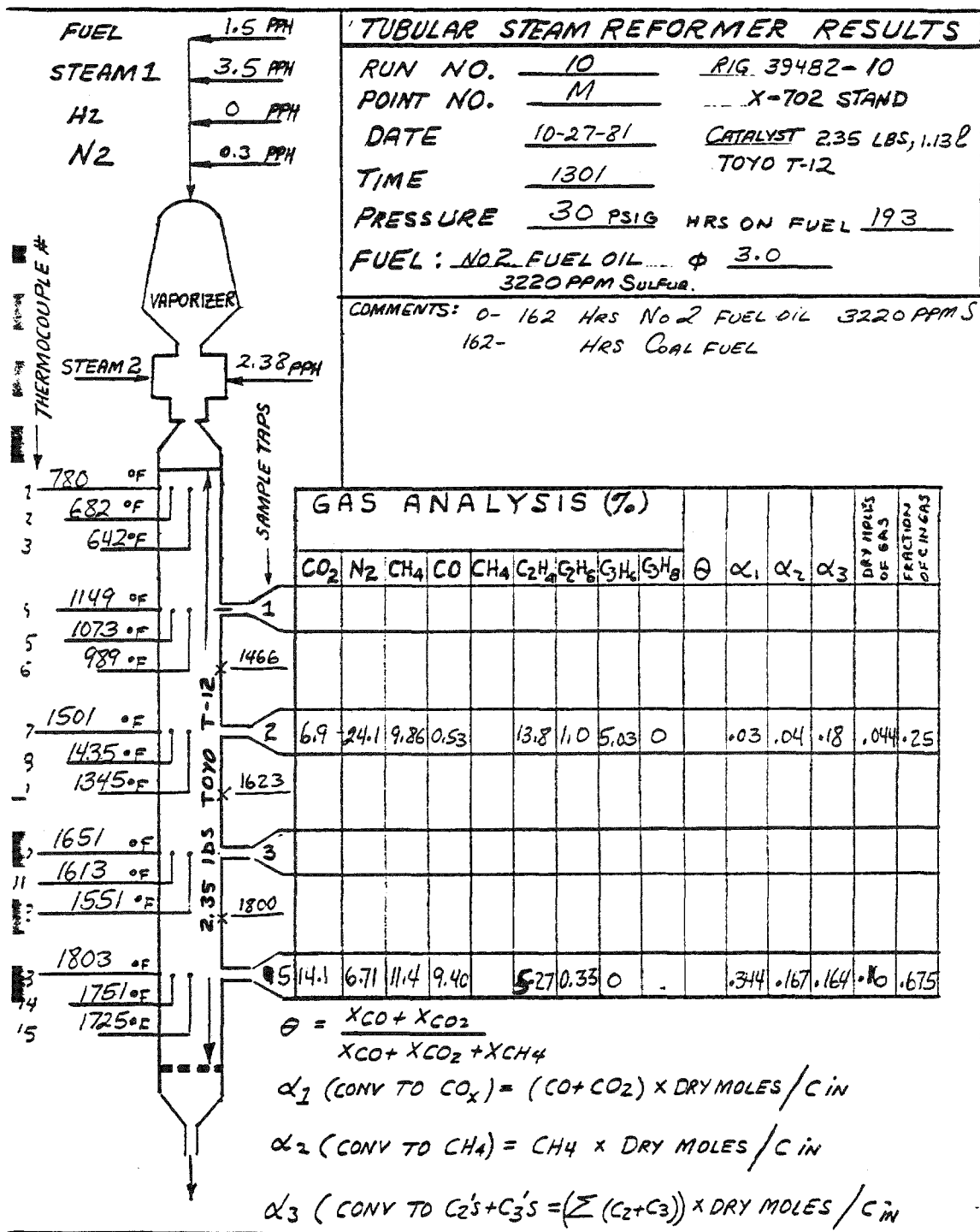
α₁ (CONV TO CO_x) = $(CO + CO_2) \times \text{DRY MOLES} / C \text{ in}$

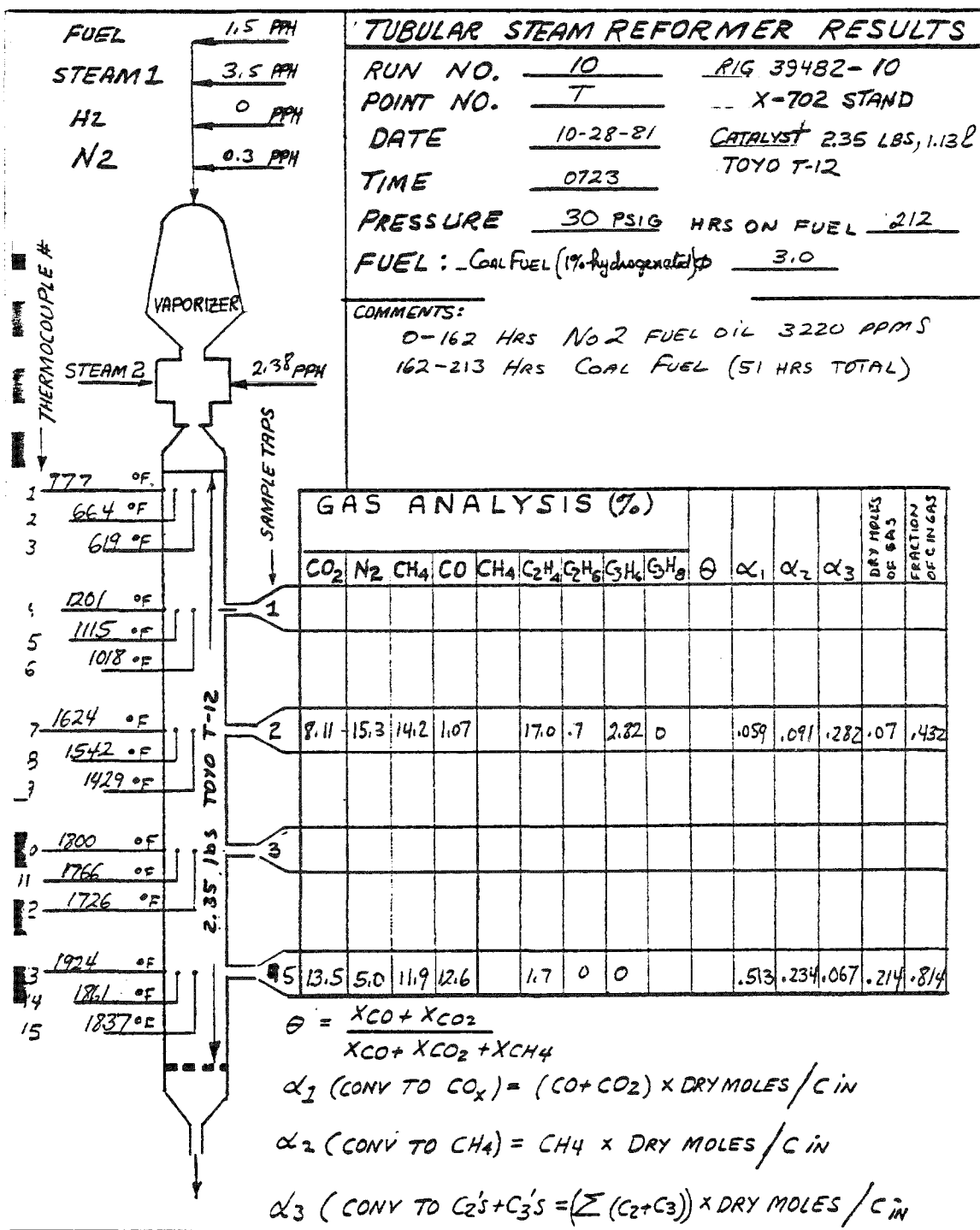
α₂ (CONV TO CH₄) = $CH_4 \times \text{DRY MOLES} / C \text{ in}$

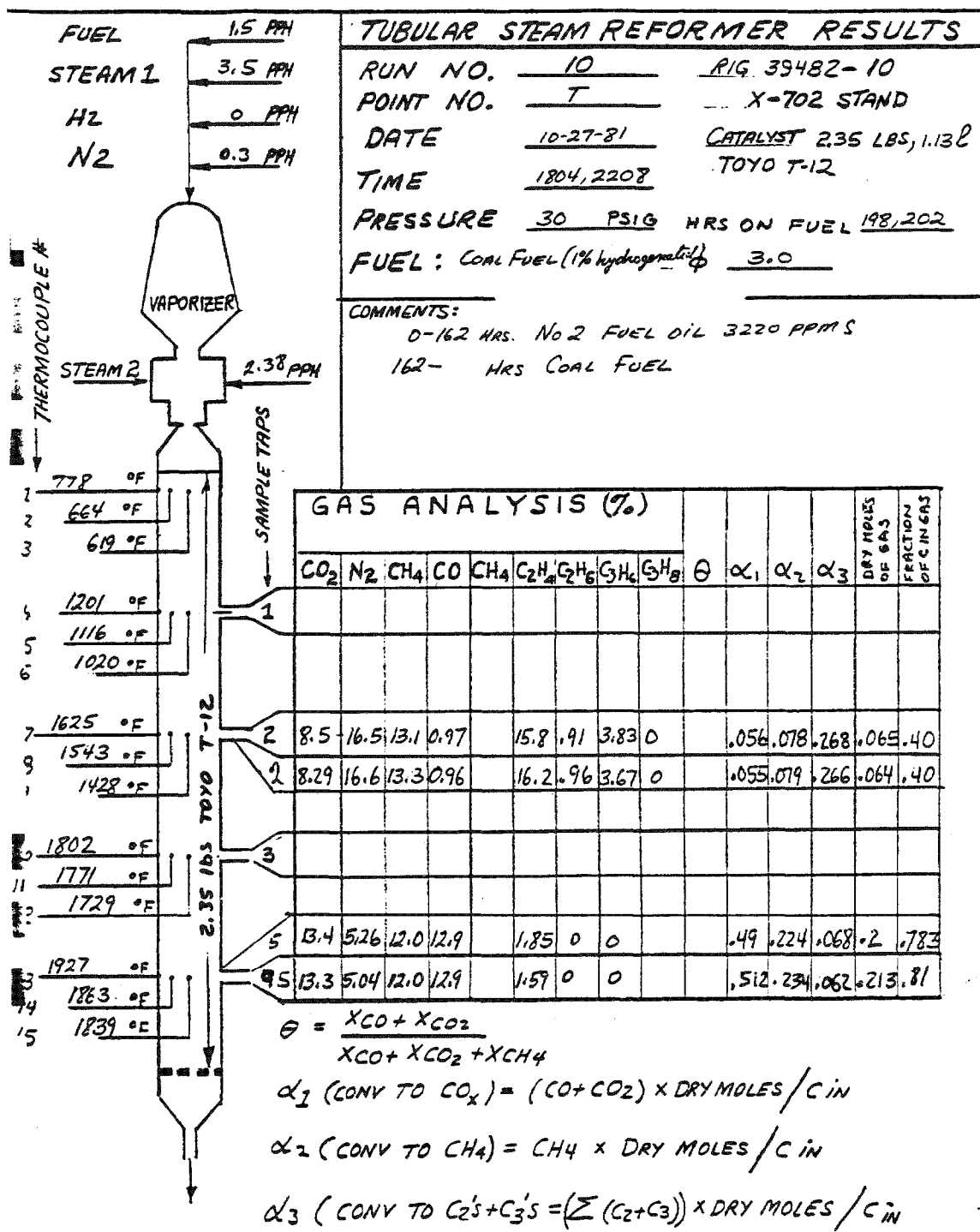
α₃ (CONV TO C₂'S + C₃'S) = $(\sum (C_2 + C_3)) \times \text{DRY MOLES} / C \text{ in}$

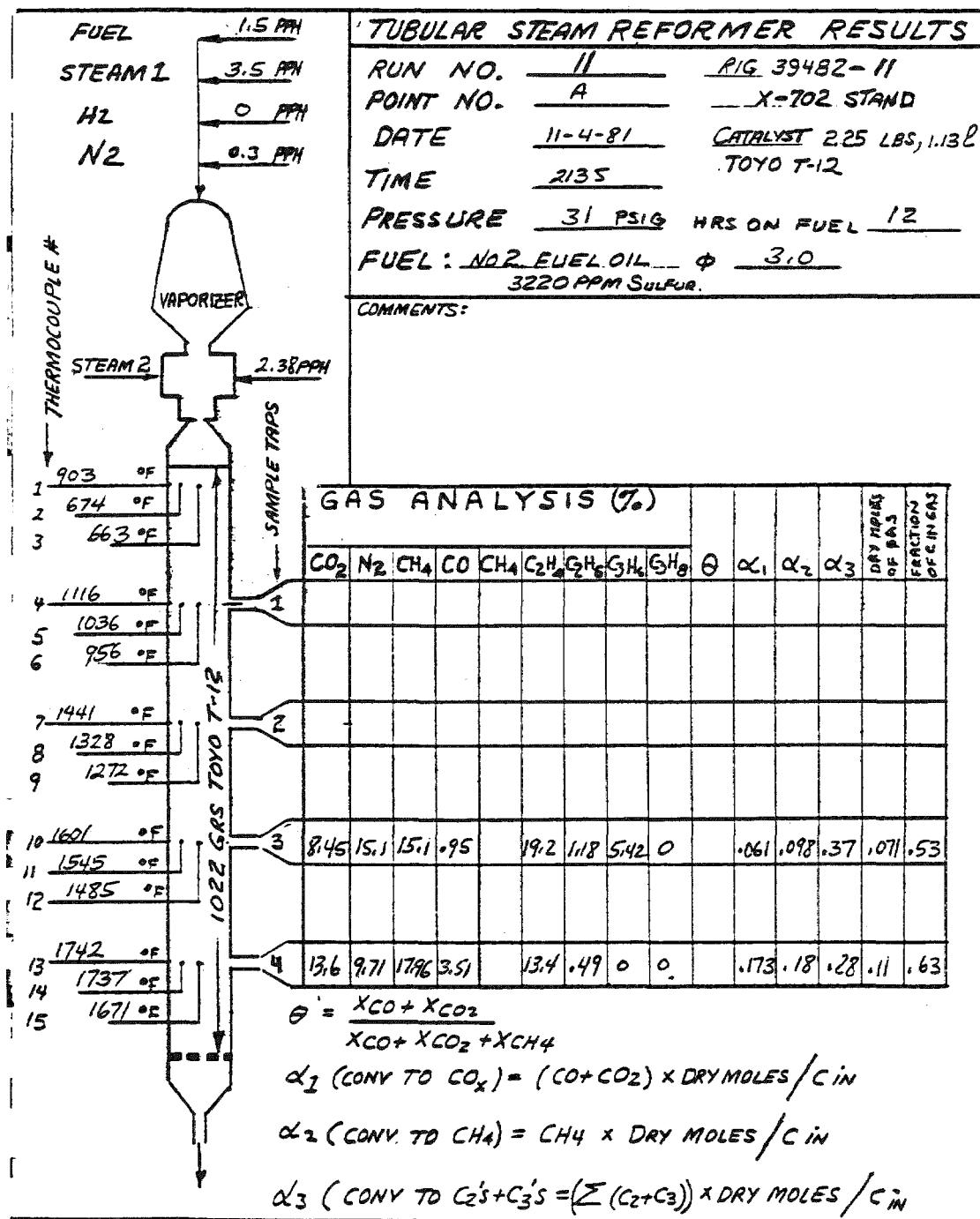














FUEL		PPH		TUBULAR STEAM REFORMER RESULTS	
STEAM 1		PPH		RUN NO. <u>11</u>	RIG <u>39482-11</u>
H ₂		PPH		POINT NO. <u>A</u>	<u>X-702 STAND</u>
N ₂		0.3 PPH		DATE <u>11-5-81</u>	CATALYST <u>2.25 LBS, 1.132</u>
				TIME <u>2054</u>	TOYO T-12
				PRESSURE <u>31</u> PSIG	HRS ON FUEL <u>35</u>
				FUEL: <u>NO. 2 FUEL OIL</u>	ϕ <u>3.0</u>
				3220 PPM SULFUR.	
VAPORIZER				COMMENTS:	

THERMOCOUPLE #

STEAM 2

PPH

SAMPLE TAPS

1022 GAS TOYO T-12

15

GAS ANALYSIS (%)														θ	α_1	α_2	α_3	DRY MOLES OF GAS	FRACTION OF GAS
CO ₂	N ₂	CH ₄	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈	C ₉ H ₂₀						
1	899 °F																		
2	670 °F																		
3	658 °F																		
4	1117 °F																		
5	1034 °F																		
6	955 °F																		
7	1441 °F																		
8	1327 °F																		
9	1272 °F																		
10	1600 °F																		
11	1540 °F																		
12	1480 °F																		
13	1739 °F																		
14	1730 °F																		
15	1665 °F																		

$$\theta = \frac{X_{CO} + X_{CO_2}}{X_{CO} + X_{CO_2} + X_{CH_4}}$$

$$\alpha_1 \text{ (CONV TO CO}_x\text{)} = (CO + CO_2) \times \text{DRY MOLES / C in}$$

$$\alpha_2 \text{ (CONV TO CH}_4\text{)} = CH_4 \times \text{DRY MOLES / C in}$$

$$\alpha_3 \text{ (CONV TO C}_2\text{'S + C}_3\text{'S)} = (\sum (C_2 + C_3)) \times \text{DRY MOLES / C in}$$

