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CATALYST AND PROCESS DEVELOPMENT FOR THE H_2 PREPARATION FROM FUTURE FUEL CELL FEEDSTOCKS

QUARTERLY PROGRESS REPORT FOR
PERIOD APRIL 1, 1979 - JUNE 30, 1979

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RESEARCH AND DEVELOPMENT DEPARTMENT
ENGELHARD INDUSTRIES DIVISION
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MENLO PARK, EDISON, N.J. 08817

DATE PUBLISHED - JULY, 1979
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DISCLAIMER

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ABSTRACT

Phase I of this contract, which involved preliminary catalyst and process evaluations has been completed. A decision has been made to pursue the autothermal reforming process during the remainder of this contract as the most likely process for producing hydrogen for fuel cells for No. 2 oil. The basis for this decision is presented in this report.

Work on Phase II of this contract, which involves catalyst preparation and development, was started during the quarter. As part of an Engelhard cost contribution, catalyst samples were prepared for potential use in the steam reforming section of the ATR. These catalysts, after steam treatment at high temperatures, are being screened for steam reforming activity using ethane as a model compound. Those samples passing this screening test will be evaluated in an ATR catalyst screening unit which was assembled during the quarter. Preliminary work on supporting studies was started with the use of a thermogravimetric apparatus to measure coke laydown using ethylene as a model compound.

TECHNICAL SUMMARY

During this quarter work commenced on Phase II of the contract, which involves catalyst preparation and development. Catalysts for potential use in the steam reforming section of an autothermal reforming process were prepared under Task 4 of this contract as an Engelhard cost contribution. Equipment to screen these samples was set up in Task 5 (Screening and Characterization).

Task 5.1A Catalyst Screening Using a Microreactor

Catalysts prepared in Task 4 will be given a preliminary screening by measuring the activity of the sample for the steam reforming of ethane after the original catalyst sample has been deactivated by treatment in steam at 1700°F (927°C).

In a baseline run with an empty tube, thermal decomposition of ethane occured in the presence of steam at temperatures between 1100-1200°F.

A test was run with the uncatalyzed Engelhard proprietary stabilized alumina carrier. The hydrogen make, as measured by a Mine Safety Appliance Thermatron hydrogen analyzer, was similar to that of the baseline run with the empty tube.

During reduction, hydrogen uptake over United Catalysts' G90C was greater than that over Engelhard's SF-3B catalyst. No hydrogen uptake was measured on the uncatalyzed alumina support.

The water to hydrogen ratio during steam deactivation strongly affects the subsequently measured steam reforming activity of a nickel catalyst. Lower H_2O/H_2 ratios during steam deactivation favor higher activities.

Task 5.1B Catalyst Screening Using an ATR Unit

An existing Engelhard catalyst screening unit has been modified to screen steam reforming catalysts in the autothermal reforming mode. In this test rig, vaporized No. 2 oil is injected through a nozzle into a hot stream containing steam and air. The mixture is passed through a static mixer to assure good blending and then into a monolithic type catalyst where partial oxidation of the No. 2 oil will occur. The hot reaction products will then be reformed over the steam reforming catalyst under evaluation. The unit is now ready for test development.

Task 7 Supporting Studies on Catalyst Aging and Likely Catalyst Deactivation Mechanisms

Some preliminary work was started using a thermogravimetric apparatus to study the coking rate of ethylene. Ethylene was selected as a model compound since light olefinic hydrocarbons were observed in the product gas from the CPO test runs with No. 2 oil.

In a baseline run, no coke was formed on the empty platinum sample holder in the apparatus after 1 hour at 500°C with 100% ethylene.

The B.E.T. surface area of the non-stabilized alumina carrier appeared to affect coke laydown. Higher B.E.T. surface areas were associated with higher coke formation.

An Engelhard stabilized alumina carrier showed approximately one half the coke laydown as compared to the unstabilized carrier even though both had equivalent B.E.T. surface area.

REVIEW BY TASKS

PHASE I. PRELIMINARY CATALYST AND PROCESS EVALUATION

A decision has been made to study autothermal reforming as a promising process for reforming No. 2 oil and heavier stocks. This decision is based in part on the technical analysis and experimental observations made in Phase I. This analysis is presented in this section. The ATR reactor to be used in Task 5 to evaluate catalysts will use a monolithic catalytic partial oxidation preheater section before the steam reforming portion. This choice is based on good performance noted at low O_2/C molar ratios with the monolithic type catalyst. Also, it appears possible to use even higher molecular weight oils in this type of preheat. The reactor to be used will also permit us to evaluate high temperature steam reforming catalysts under conditions of severity expected later in the fuel processor.

THERMODYNAMIC APPROACH

A computer program ATR-1 (in APL) has been written to calculate the thermodynamic composition of the reformer gases, the adiabatic temperature and the thermal efficiency of the reformer. This program considers the following chemical reactions:

catalytic partial oxidation (CPO):

$$CnHm + \frac{n}{2} O_2 \rightarrow nCO + \frac{m}{2} H_2 \qquad (1)$$

steam reforming reaction:

$$CnH_m + nH_2O \rightarrow nCO + (n+\frac{m}{2}) H_2 \qquad (2)$$

methanation reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

water gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

methane cracking reaction

$$CH_4 \rightarrow C + 2H_2 \qquad (5)$$

CO disproportionation reaction

$$2CO \rightarrow C + CO_2 \qquad (6)$$

Briefly, for a given set of inlet conditions, i.e. for a given temperature, pressure, water to carbon ratio and air to fuel ratio, the hydrocarbon in the feed is first partially oxidized catalytically according to reaction (1) and, then, the reamining hydrocarbon is completely converted to carbon monoxide and hydrogen by reaction (2). The product gas obtained from these two reactions is subsequently used to calculate the equilibrium product compositions by searching for a set of concentrations for each product component to satisfy simultaneously the equilibrium constants for reactions (3) and (4). In case the set of equilibrium concentrations calculated from reactions (3) and (4) is in the carbon formation region, additional reactions (5) and (6) are included in the above equilibrium calculation.

In this computer program, only CH_4, CO, CO_2, H_2, H_2O and C are considered as the reaction products because the thermodynamic equilibrium concentrations for other components in the CHO system are relatively small. In other words, from the free energy of formation, only the above six components are thermodynamically considered to be the major products under our experimental conditions,while all other components such as alcohols and aldyhydes are minor products and, thus, can be neglected. Therefore, from the thermodynamic point of view, the equilibrium composition calculated from reactions (3) and (6) are appropriate. As shown in Table 1, the equilibrium compositions calculated from ATR-1 program agree with the data published in the literature.

From the heat balance, the adiabatic oxidation temperature after reaction (1) can be calculated from the heat released by this catalytic partial oxidation (CPO) reaction. Furthermore, from the heat and mass balance across the reformer, the final equilibrium composition and the adiabatic reforming temperature can also be calculated. Once the final equilibrium composition is obtained, the reformer thermal efficiency can be determined from the following equation:

$$\text{Reformer Thermal Efficiency} = \frac{\left(\text{Lower Value of Heat of combustion of } H_2\right)\left(\text{Total moles of CO+ } H_2 \text{ in product gas}\right)}{\left(\text{Lower Value of Heat of combustion of Hydrocarbon}\right)\left(\text{Moles of hydrocarbon}\right)}$$

To generate hydrogen from hydrocarbons (expecially from No. 2 oil) by the catalytic partial oxidation process, a stoichiometric amount of oxygen is admitted into the reactor, and all hydrocarbons in the feed will be completely converted to CO and H_2 according to reaction (1). This product gas then reaches thermodynamic equilibrium according to reactions (3) and (4), or according to reactions (3) to (6) if carbon formation is favored under the experimental conditions. Since the oxidation reaction is exothermic, the reactor temperature will be higher than the inlet feed temperature and also excess heat can be produced from this process.

For the high temperature steam reforming reaction, all the hydrocarbons will be converted to CO and H_2 according to reaction (2). The product so obtained then reaches thermodynamic equilibrium according to equations (3) and (4) (or equations (3) to (6) if condition favors carbon formation). Since steam reforming is endothermic, a net heat should be transferred into the reactor to maintain the reactor temperature above 1600°F.

For the autothermal reactor system, oxygen below the stoichiometirc amount is admitted into the reactor together with water in the feed. The hydrocarbon is first oxidized according to reaction (1) to produce heat and, thus, raise the reactant temperature above 1600°F. The remaining hydrocarbon will be adiabatically reacted with water to produce hydrogen according to reactions (2) to (4) (or reaction (2) to (6) if conditions favor carbon formation). For this autothermal reactor system, the reactor temperature is maintained by the degree of oxidation reaction and also by the inlet preheat temperature.

The ATR-1 computer program is used to illustrate thermodynamically the thermal efficiencies for each of the above three processes.

Since propane has well defined thermodynamic properties as compared to No. 2 oil, it is used here for the above comparison. As shown in Table 2, the reformer thermal efficiencies are calculated according to experimental inlet conditions given in the same table. The results indicate that the isothermal high temperature steam reforming has the highest thermal efficiency among the three processes concerned, but the net heat (224,274 Btu/lb-mole) is required to keep the reactor isothermal. For the autothermal process, the thermal efficiency is higher than that of catalytic partial oxidation process. Therefore, according to the thermodynamic analysis of thermal efficiencies given here, the fuel processor designer should consider isothermal high temperature steam reforming first, the autothermal process second, and catalytic partial oxidation last.

TABLE 1

EQUILIBRIUM COMPOSITION IN CHO SYSTEM (IN EQUILIBRIUM WITH SOLID CARBON) %

							% COMPOSITION AT EQUILIBRIUM					
ROGRAM	COMPONENT	H/O	TEMP. °F	PRESS ATM	H_2O/C	O_2 FUEL	H_2O	CH_4	CO_2	CO	H_2	C
TR-1	C_3H_8	3.0	1500	1	1.587	0.54	2.18	1.37	1.36	37.06	58.03	EXCESS
1*		3.0	1500	1			2.25	1.34	1.47	36.83	58.09	EXCESS
TR-1	C_3H_8	3.0	1250	1	1.587	0.54	11.00	4.96	7.98	22.62	53.44	EXCESS
1*		3.0	1250	1			11.15	4.94	8.27	22.04	53.58	EXCESS
TR-1	C_3H_8		1400	1	3.0	---	29.93	0.08	7.71	10.99	51.29	NO
2**	C_3H_8		1400	1	3.0	---	29.908	0.078	7.728	10.974	51.312	NO

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* R. E. Baron, J. H. Porter and O. H. Hammond " Chemical Equilibria in CHO Systems". the MIT Press 1976.

** M. J. Schlatter Report 2, NTIS AD 456740

TABLE 2

COMPARISON OF REFORMER THERMAL EFFICIENCIES (η) FOR FUEL PROCESSES

Fuel Process	Hydrocarbon	O_2 Fuel	H_2O/C	Reactor Inlet Temperature	Reactor Exit Temp (°F)	Thermal Eff. (%)
Catalytic Partial Oxidation	C_3H_8	1.5	2.0	1000	1679	82.81
		1.5	2.0	1400	2025	82.82
		1.5	2.0	1800	2393	82.82
Autothermal	C_3H_8	1.3	2.0	1000	1451	87.46
		1.3	2.0	1400	1795	87.55
		1.3	2.0	1800	2164	87.55
		1.0	2.0	1600	1585	94.62
Steam Reforming	C_3H_8	---	2.0	1800	1800	94.26(1)

(1) Isothermal reforming, i.e., net heat is provided to the system (224,247 Btu/lb-mole).

EXPERIMENTAL APPROACH

As illustrated thermodynamically in the previous section, the thermal efficiencies for each of the three processes considered have been analyzed. In this section, the advantages and disadvantages for each of the above three processes will be analyzed from the experimental point of view.

(A) HIGH TEMPERATURE STEAM REFORMING (HTSR)

Without special treatment, the No. 2 oil normally contains approximately up to 0.5% of sulfur compounds (Catalytica, Final Report EPRI EM-570 September 1977). Since the conventional steam reforming catalyst is a supported Ni catalyst, and since the reforming activity for metallic Ni is much higher than that of NiS, the reformer temperature must be kept above ∿1700°F to minimize the formation of NiS and, thus, maintain a high reforming activity for a given catalyst. Therefore, in order to do high temperature steam reforming, the No. 2 oil in the feed must be pre-heated to a temperature above 1700°F. However, it is known that No. 2 oil will be cracked when the preheat temperature reaches above ∿1200°F, and carbon will be deposited in this preheater due to these cracking reactions as well as due to the polymerization of the unsaturated hydrocarbons compounds formed by cracking. Therefore, carbon deposition can occur in the preheater before the No. 2 oil reaches the catalyst intact as oil.

To minimize the carbon deposition in the preheater, the residence time as well as the heating rate of the reactants must be considered simultaneously. The effect of the residence time on the pyrolysis of n-paraffins is shown in the following table:

RESIDENCE TIME (SEC)	FRACTIONAL $C_{14}H_{30}$ CONVERSION
0.14	0.58
0.034	0.19
0.001	0.06
0.002	0.0123
0.001	0.0062

According to Shu & Ross (71st Annual AIChE meeting, Miami Nov. 12, 1978), the pyrolysis of n-paraffins ($C_{14}H_{30}$) follows a first order kinetics and the rate constant at zero conversion (at 700°C) is 6.2 sec^{-1}. Disappearance of the paraffin molecules is a strong function of the residence time. To decrease the residence time while maintaining the same outlet preheat temperature, the heat transferred through the tubes as well as the velocity of reactant must be simultaneously increased. Therefore, factors such as residence time, heat flux, reactant velocity and pressure drop must be simultaneously considered in designing a preheater.

In our previous hydrogen assisted steam reforming experiments, a conventional type of spiral preheater was used to preheat the reactants from about 800°F to 1720°F. Briefly, the No. 2 oil at 310°F was first heated and then vaporized by the preheat mixture of hydrogen and water (at 850°F) at the injector. The reactant mixture was then passed through a spiral preheater with a residence time of 0.14 sec.. In this set up, the carbon deposition was found in the preheater and the pressure drop across the reactor was thus increased as the time on stream increased. Therefore, the experiments had to be terminated because of this carbon deposition problem.

To further reduce the residence time, the velocity would have to be increased still further. Eventually, the pressure drop would become limiting even though it may be possible to transfer heat to the gas at the desired rate. This analysis suggests that the fired tubular heater is probably not suitable for high temperature steam reforming of No. 2 oil. Adiabatic reactors where the oil is preheated rapidly by very high temperature steam is a possible alternative to the more conventional fired tubular reactor.

Several experiments for moderate temperature (1500 to 1800°F) and high temperature (1900°F) steam reforming have been tried at United Technologies Corp. (UTC), and the carbon deposition in their reactor system remains as a serious problem. In their recent report, (December, 1978) a newly improved configuration, which included a trap to remove all the carbon formed upstream of the catalyst bed, was reported to operate for 190 hours without carbon formation in the catalyst bed. However, the carbon formation in the preheating zone apparently has not been solved in their experimental rig, because a carbon trap was required in their improved configuration.

Because of the carbon deposition associated with the preheating of No. 2 oil the high temperature steam reforming should be deferred unitl a method has been found to preheat the reactants to above 1700°F without carbon formation in the preheater. A method proposed by Toyo Engineering, which preheats and partially reforms in an inactive bed of calcium aluminate pellets, may be one method for solving this problem.

(B) CATALYTIC PARTIAL OXIDATION (CPO)

The partial oxidation of No. 2 oil was carried out catalytically in the presence of steam over Pt-Pd-Rh/monolithic type catalysts. Air was used as the source of oxygen. The catalyst was made as cylinders 1" O.D. by 3 inches long; three of these cylinders were used in the 9" long reactor section. Experimental conditions for three runs with No. 2 oil are listed in Table 3.

Because of analytical equipment limitations, complete analysis of the product gas was not performed. However, these were exploratory runs made to determine process feasibility. From the results listed in Table 3 it is observed that partial oxidation did occur as evidenced by the temperature rise of about 530°C and by the formation of hydrogen as measured by gas chromatography. Not all of the oil was converted to CO and H_2 as is shown by the presence of some hydrocarbons. These were measured as total hydrocarbons by a flame ion monitor and reported as propane. In Table 4, a comparison is made between results calculated from the data of Run 6 and a hypothetical calculation for the partial oxidation ($O_2/C = 0.5$) of $-CH_2-$. The dry gas composition for this hypothetical case would be 50% N_2, 25% H_2 and 25% CO. Fair agreement is noted between the hypothetical case and the experimental results from Run 6. The presence of CO_2 and hydrocarbons in the experimental case indicate that the equivalent hydrogen (H_2 + CO) is somewhat lower than for the hypothetical partial oxidation case.

Another important observation made during these exploratory runs was that the monolithic catalyst was free of carbon as observed when the catalyst was unloaded. Thus, it appears possible to operate the CPO monolithic unit without carbon blockage at O_2/C ratios as low as 0.31.

The catalytic partial oxidation of Diesel fuel has been reported previously. (Henkel, et al., presented at the Fuel Processing Meeting in Palo Alto, April 13, 1977). A non-noble metal particulate catalyst was used at O_2/C ratios as low as 0.15 with results as listed in Table 5. An equivalent hydrogen concentration of 44.6% (H_2 + CO) was measured at 32 LHSV with about 60% Diesel fuel conversion. These results also show that heat can be generated by the CPO process and H_2 and CO produced under conditions of low O_2/C ratios.

Because of the high O_2/C ratio of the partial oxidation process ($O_2/C = 0.5$), excess heat will be generated along with the production of H_2 and CO from No. 2 oil. This heat of reaction can only be partially utilized in preheating the reactants. The bulk of the reaction heat can not be used and the anode vent gas is not required for heating in this process. The excess reaction heat and the anode vent gas (after combustion) could be used to raise steam. However, this may not be of value in some dispersed fuel cell systems. Because of this relatively low thermal efficiency as compared to the other processes, a low priority should be assigned to the catalytic partial oxidation process.

(C) AUTOTHERMAL REFORMING

The high temperature steam reforming process has high thermal efficiency but carbon is formed in the preheater due to the rapid decomposition of No. 2 oil at inlet temperatures above 1500°F. In the catalytic partial oxidation process ($O_2/C = 0.5$), the oil can be oxidized to produce heat as well as $CO + H_2$, but the thermal efficiency is low. Therefore, a compromise process is to combine the above two processes by operating a CPO section in front of the steam reforming section. In this case, the CPO section will operate at O_2/C ratios below 0.5 with enough oxygen to generate sufficient heat to preheat the reactant stream to the high temperatures required at the inlet of the adiabatic steam reforming section. Since the heat required for steam reforming is generated in-situ by the partial oxidation reaction, the process is called autothermal.

In Phase I of this contract, the CPO process has experimentally been demonstrated to be able to produce heat as well as hydrogen and CO from No. 2 oil without soot formation inside the catalyst bed, and the HASR process is capable of reforming the No.2 oil and/or its derived cracked hydrocarbon products into hydrogen and CO with some CH_4 leakage. Therefore, an ATR reactor can be designed to simulate the actual experimental conditions used previously for each stage of the reaction. Based on this design concept, a schematic flow diagram of an ATR fuel processor is shown in Figure 1. As shown in this diagram, Pt/Pd/monolith catalyst is loaded in front of a traditional steam reforming catalyst (a supported nickel catalyst). The design feed rates for this processor correspond to a O_2/C ratio of 0.3 and a H_2O/C ratio of 3.0, and the product gas would contain theoretically 40 SCFH of H_2, 32 SCFH of CO and 36 SCFH of N_2.

TABLE 3

EXPERIMENTAL RESULTS ON THE CATALYTIC PARTIAL OXIDATION OF NO. 2 OIL

	Run No.		
	6	7	8
AIR, SCFH	210	210	210
No. 2 OIL, ml/hr*	1726	2441	2739
WATER, ml/hr	3286	3286	1383
O_2/C, moles/atom	0.489	0.346	0.308
H_2O/C, moles/atom	1.733	1.226	0.460
Temp., °C Inlet	364	362	399
Temp., °C Exit[a]	895	890	962
EXIT DRY GAS ANALYSIS:			
H_2, vol % (by GC)	27.0	9.5	13.5
CO_2, vol % [b]	4.3	3.1	3.5
HC (as C_3H_8), vol % [c]	1.3	3.0	Not measured

* No. 2 oil density = 0.841 g/ml; Formula $C_{13.9}H_{24.8}$, MW = 192

[a] Maximum temperature measured

[b] Measured by non-dispersive infra-red (NDIR)

[c] Measured by a flame ion total hydrocarbon analyzer and reported as propane.

TABLE 4

CATALYST PARTIAL OXIDATION

COMPARISON BETWEEN HYPOTHETICAL AND EXPERIMENTAL RESULTS

1. HYPOTHETICAL

$-CH_2- + 1/2\ O_2 \rightarrow CO + H_2$

AIR CONTAINS ∼4 N_2/ 1 O_2

COMPONENT	INLET MOLES	INLET %	EXIT MOLES	EXIT %
$-CH_2-$	1.0	28.6	0	0
O_2	0.5	14.3	0	0
N_2	2.0	57.1	2	50
CO	---	---	1	25
H_2	---	---	1	25
TOTAL	3.5	100	4	100

2. EXPERIMENTAL (RUN 6)

OIL $C_{13.93}\ H_{24.7} = CH_{1.77}$

$O_2/C = 0.489$

$H_2O/C = 1.73$

	EXIT GAS COMPOSITION		HYPOTHETICAL
O_2	0.3		0
N_2	48.3	(BAL)	50
CO	19.1	(C BAL)	25
H_2	27.0		25
CO_2	4.0		0
C_3H_8*	1.3		0
	100.0		100

* Total hydrocarbons determined by a FID and reported as [illegible]

TABLE 5

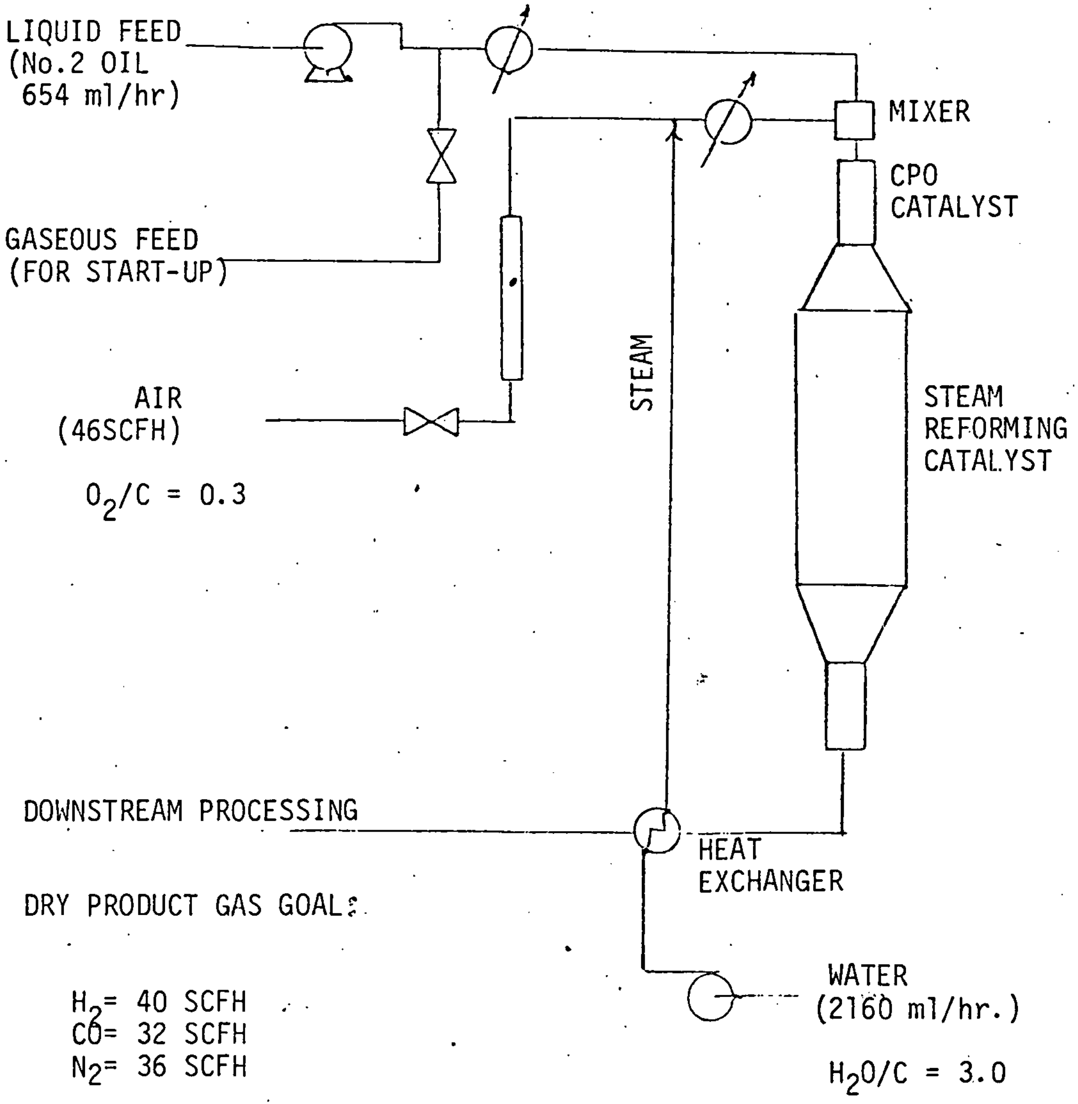
GASIFICATION OF DIESEL FUEL BY CATALYTIC PARTIAL OXIDATION[(a)]

liquid hourly space velocity hr^{-1}	H_2O/C mol/mol	air-fuel equivalence ratio	catalyst temp. °C	conversion w/o	gas composition O_2	H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4
18	0.44	0.1	801	77.1	0.6	11.0	27.6	12.6	19.5	2.7	25.9
32	0.44	0.1	799	60.7	1.8	11.3	31.4	24.6	10.7	2.1	18.7
32	0.20	0.1	797	59.7	0.5	10.5	34.1	10.6	18.7	2.4	23.3

(a) Henkel, H. J., Kostka, H., and Michel, A., "Autothermal Gasification of Liquid Hydrocarbons by Partial Oxidation", Presented at Fuel Processing Meeting, Palo Alto, April 13, 1977.

FIGURE 1

PROPOSED FLOW SCHEME OF
ATR FUEL PROCESSOR UNIT



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A similar autothermal reactor design has been developed by BASF (V.P. Schmulder, Brennstoff - Chemie 46 (4), 23 (1965)). The schematic flow diagram for this process is shown in Figure 2. Note that oxygen is used as an oxidant and a Pt catalyst (pellet type catalyst) is used in front of a traditional steam reforming catalyst. The purpose of this Pt catalyst is to "light off" the reaction at a lower temperature, so that carbon formation can be prevented in the reforming catalyst bed (Catalytica, EPRI Final Report, EM-570, Oct. 1970). As shown in Table 6, gasoline can successfully be reformed into synthesis gas (i.e., CO and H_2) at the reactor inlet temperature of 200°C, and the exit temperature of about 870°C. The product gas contains about 87.1% of total hydrogen and carbon monoxide. Therefore, this BASF autothermal process has successfully been used to generated H_2 fron gasoline.

Recently, the successful use of the autothermal reactor system to generate hydrogen from No. 2 oil has also been reported by both Jet Propulsion Laboratories (JPL) and also United Technologies Corporation (UTC). (D.O.E. Workshop on Hydrocarbon Processing and Mixing and Scale Up Problems, December 14, 1978, Washington, D. C.). Because of their initial success in this process and also because of the higher thermal efficiency associated with this process as compared to that for the CPO process, the autothermal reformer should further be developed so that, hopefully, the overall thermal efficiency can be optimized. The use of the monolithic type catalyst in the Engelhard design holds promise of operation at lower O_2/C molar ratios at low H_2O/C ratios. Also, as long as the hydrocarbon stream can be vaporized, it can be fed to this system. Thus it may be possible to use oils heavier than No. 2 in this system.

PHASE II CATALYST PREPARATION AND DEVELOPMENT

Task 5.1A Catalyst Screening Using a Microreactor

To differentiate the relative activity of catalysts prepared in Task 4, a screening test was developed. A pressure micro reactor (PMR) was designed to evaluate sample activity for steam reforming ethane. Catalysts are reduced at 932°F and steam aged at 1700°F for 16 hours in-situ prior to activity measurements. Using simple data treatment, relative activity can be calculated and the most active catalysts further evaluated in the ATR unit using No. 2 oil.

Catalysts charged in the PMR react with a feed consisting of 10 vol % ethane, 2 vol % H_2 and balance N_2 which is mixed with steam. The reactor schematic is presented in Figure 3 and the operating conditions are given in Table 7.

During steam reforming of hydrocarbons, carbon deposition occurs catalytically above 932°F and thermally above 1200°F. To evaluate the effect of thermally decomposing ethane during a screening run, a test was made using an empty reactor tube. Decomposition of the ethane was monitored by an increase in hydrogen content of the product stream. (Note, a hydrogen analyzer was being used during the initial tests while a new chromatograph was being ordered and set up. Hydrogen could be produced either by the direct thermal decomposition of ethane or by the steam reforming mechanism).

FIGURE 2

SCHEMATIC DIAGRAM OF THE BASF AUTOTHERMAL REFORMING PROCESS

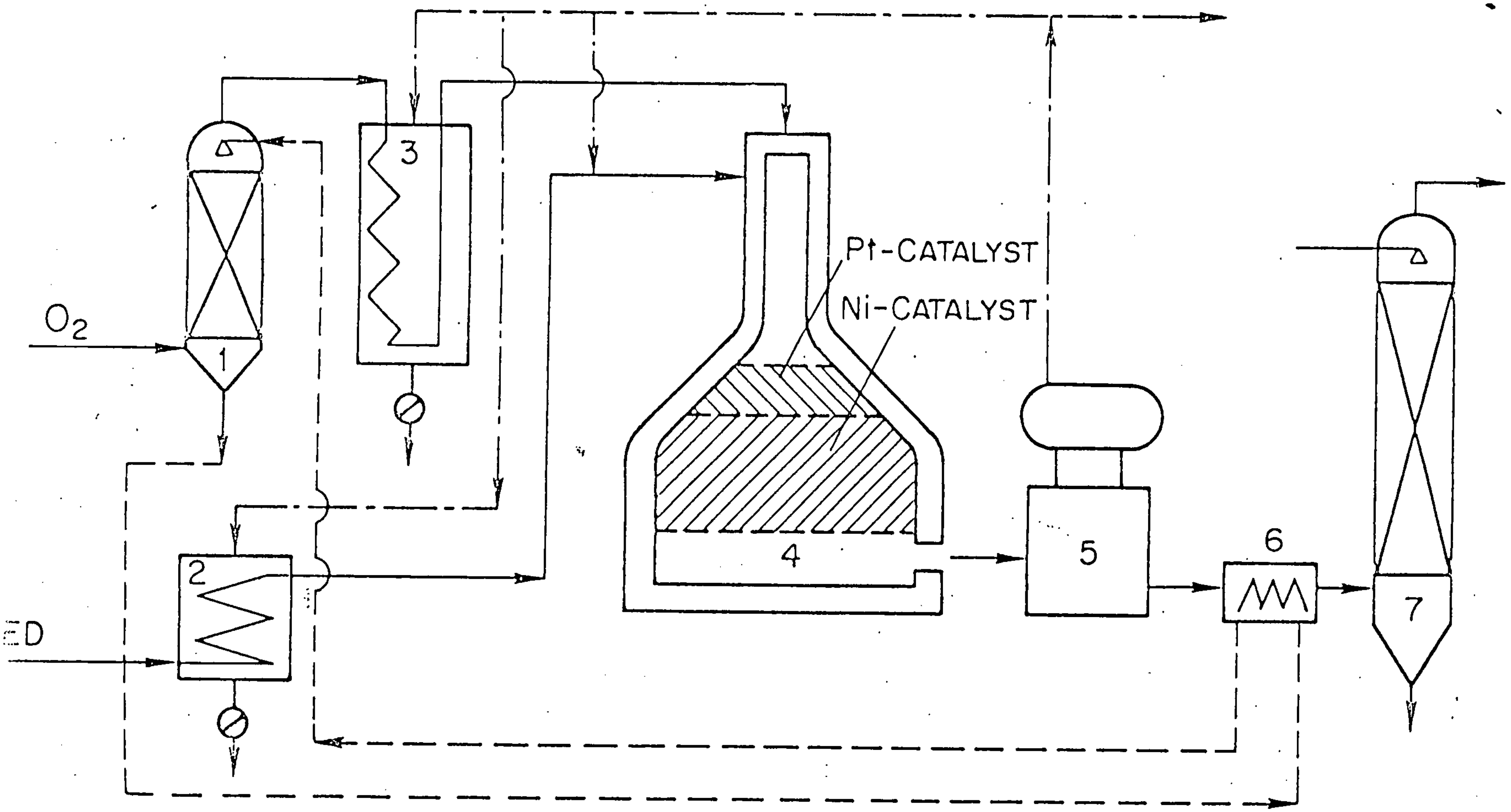


TABLE 6

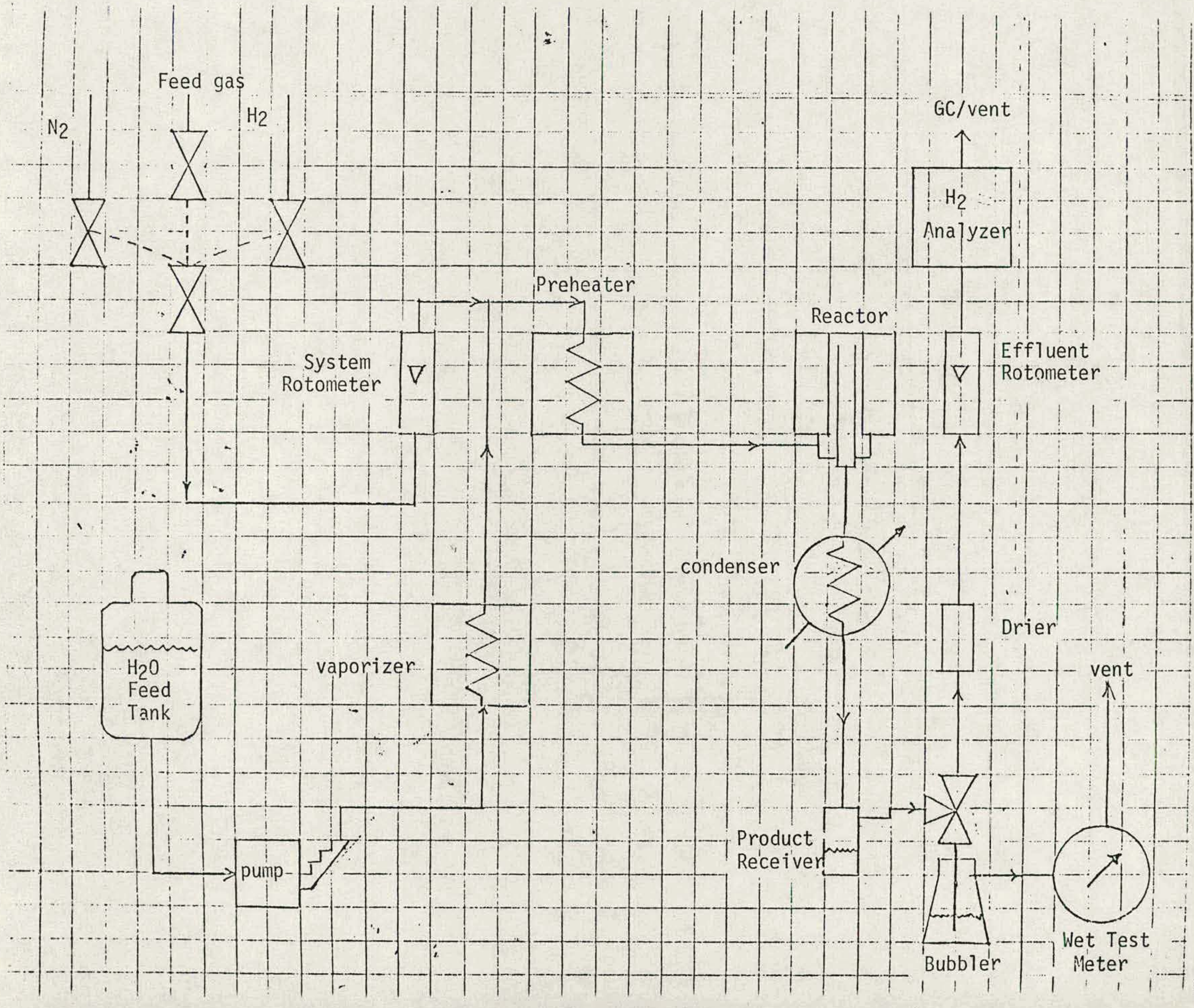
REFORMING GASOLINE FEEDSTOCKS USING THE BASF AUTOTHERMAL REFORMING PROCESS [a]

	1	2
Gasoline Characteristics		
End point, °C	115-165	41-166
C, wt.%	85.6	85.3
H, wt.%	14.4	14.7
S, wppm	450	110
Aromatics, wt.%	12.4	11.3
Naphthenes, wt.%	34.0	35.0
Density at 15°C	0.751	0.725
Feed Requirements for 1000 Nm^3 CO + H_2		
Gasoline, kg	290	285
Steam, kg	470	285
O_2, Nm^3	220	200
Conditions		
Preheat temperature, °C	200	200
Exit temperature, °C	870	810
Exit Gas Analysis, mole %		
CO_2	12.0	8.5
CO	28.1	32.5
H_2	59.0	58.1
CH_4	0.2	0.2
N_2	0.7	0.7
	100.0	100.0

[a] Von P. Schmulder, Brennstoff - Chemie 46, No. 4, p. 23 (1965)

FIGURE 3

Pressure Microreactor Apparatus for Steam Reforming Ethane



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6-19-79

TABLE 7

C_2H_6 STEAM REFORMING PROCEDURE

A. START UP

1. Purge with N_2 at 200cc/min
2. Record system and effluent flow/pressure and Thermatron set

B. REDUCTION ≃ 4 HRS.

1. N_2 off, 2% H_2/N_2 in at 200cc/min.
2. Repeat A-2
3. Leak Check
4. Set heating tape, VF (400-500°F), PHR (800°F), and RF (932°F)
5. Repeat A-2 and B-3
   Time to heat and hold at 932°F is ≃ 4 hours.

C. STEAM AGING

1. Switch on 100% H_2 turning off 2% $H_2 + N_2$
2. Pump on at 1.0cc/min. - after liquid appears in condenser reset to 0.5cc/min. - $H_2O/H_2 \simeq 3.1$
3. Repeat A-2 and record H_2O rate

D. HIGH TEMP. STEAM AGING ≃ 16 HRS.

1. Set PHF (800°F) and RF (1700°F)
2. Repeat B-3 and C-2
3. Hold at 1700°F overnight

E. COOL DOWN

1. Set RF (400°F), PH (400°F) and Repeat C-2
2. When RF reads 1000°F, turn off 100% H_2 and switch on 2% $H_2 + N_2$ (200cc/min)
3. Set Pump to 0.1cc/min.

TABLE 7 - con't

F. INITIAL ACTIVITY

1. Turn 2% H_2/N_2 off, feed gas on at 160cc/min.
2. Repeat C-2 and record effluent product via Thermatron and flow rate via WTM

G. Activity @ ≃ 1900 hr^{-1}

1. Set PH (800°F) and RF (752°F) - equilibrate at temp. for 1/2 hour.
2. Set RF (842°F) - equilibrate at temp. for 1/2 hr.
3. Set RF (932°F) - equilibrate at temp. for 1/2 hr.

Activity @ ≃ 10,000 hr^{-1}

4. Hold RF at 932°F and adjust pump to 0.54 cc/min. and feed gas flow rate to 833 cc/min. - equilibrate at temp. for 1/2 hr.
5. Set RF (842°F) - equilibrate at temp. for 1/2 hr.
6. Set RF (752°F) - equilibrate at temp. for 1/2 hr.

H. PURGE

1. Turn feed gas off, 2% H_2/N_2 in at 200cc/min.
2. Repeat C-2

I. COOL DOWN

1. Turn H_2O pump off
2. Set PHF (R.T.) and RF (R.T.)
3. Repeat C-2

J. SHUT DOWN

1. At RF (500°F) turn 2% H_2/N_2 off and N_2 on at 200cc/min.
2. Repeat A-2
3. At room temp. remove, weigh, and bottle sample.

After allowing both the preheater and reactor tubes to equilibrate at 1000°F with feed flowing, the preheater temperature was slowly increased in steps of 100°F. At 1200°F, H_2 content was measured on the MSA Thermatron Analyzer slightly above that in the feed gas. As shown in Figure 4 the hydrogen content increased until at a temperature above 1300°F the amount of hydrogen in the product stream exceeded the upper limit of detection (30%). A sample analyzed by gas chromatography showed a H_2 content of 34 vol %, CO plus N_2 at 64 vol % (these were not separated on the particular GC unit used), 0.3 vol % CO_2 and 1.7 vol % C_2 hydrocarbons.

After running 1.5 hours at 1380°F, the backpressure began to rise in the unit. Within three hours, the preheater inlet pressure equaled the delivery feed gas pressure accompanied with a sharp decrease in product gas flow. After shutting the unit down and cooling, the preheater coil contained sufficient "coke" to completely block the reactant flow.

These results limit the maximum reactor temperature to about 1200°F whereby no hydrogen will be made by the thermal decomposition of ethane.

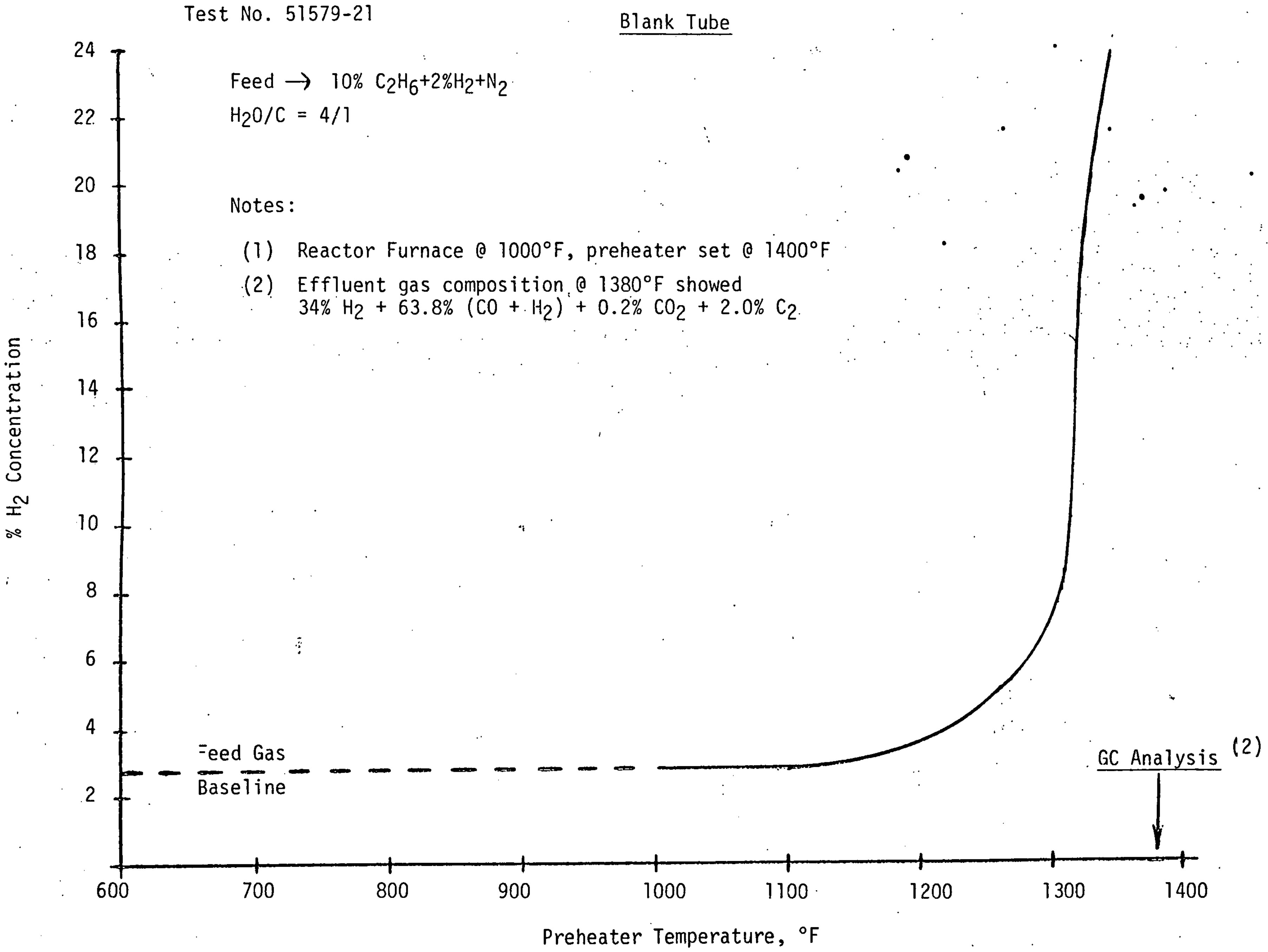
A sample of the noncatalyzed Engelhard stabilized 1/16" Al_2O_3 carrier (10984-19-3) was loaded into the microreactor and subjected to reduction and steam aging. The results of steam reforming ethane are shown in Figure 5. No appreciable hydrogen make occured until 1150°F and at 1200°F a 4% increase in hydrogen content over feed was measured. Comparison with the empty tube run at 1200°F showed that the carrier produced slightly more hydrogen. Thus, the carrier may have some catalytic activity.

United Catalyst's G90C was evaluated for high-temperature steam reforming activity of No. 2 oil during Phase I. Of the seven catalysts tested, G90C was the second most active and the highest of all the commercial samples. (E.I. SF-3 was the most active). Thus G90C was selected as a baseline commercial sample.

G90C "as received" is in a gray, 1/4" ceramic ring form. To eliminate the possibility of diffusion effects in the microreactor, G90C was crushed and a sieved portion of -14 mesh/+25 mesh retained.

The hydrogen content during reducing G90C was monitored. As shown in Figure 6, after the temperature reached 400°F hydrogen was removed from the reducing gas stream reaching a level of 0.5 volume percent (the reducing gas mixture contains approximately 2.7 vol % H_2). The reduction is allowed to continue at 932°F for four hours. During this period the H_2 content measured gradually returned to that in the reducing gas stream. Since the H_2 level during the reduction step over the noncatalyzed Al_2O_3 carrier did not change (Figure 7), the H_2 uptake over the catalyst is probably due to the

FIGURE 4



Test No. 51579-21

Blank Tube

Feed ⟶ 10% $C_2H_6+2\%H_2+N_2$

$H_2O/C = 4/1$

Notes:

(1) Reactor Furnace @ 1000°F, preheater set @ 1400°F

(2) Effluent gas composition @ 1380°F showed
34% H_2 + 63.8% $(CO + H_2)$ + 0.2% CO_2 + 2.0% C_2

C.P.M.
5/15/79

FIGURE 5

Ethane Steam Reforming of Stabilized Carrier
(10984-19-3)

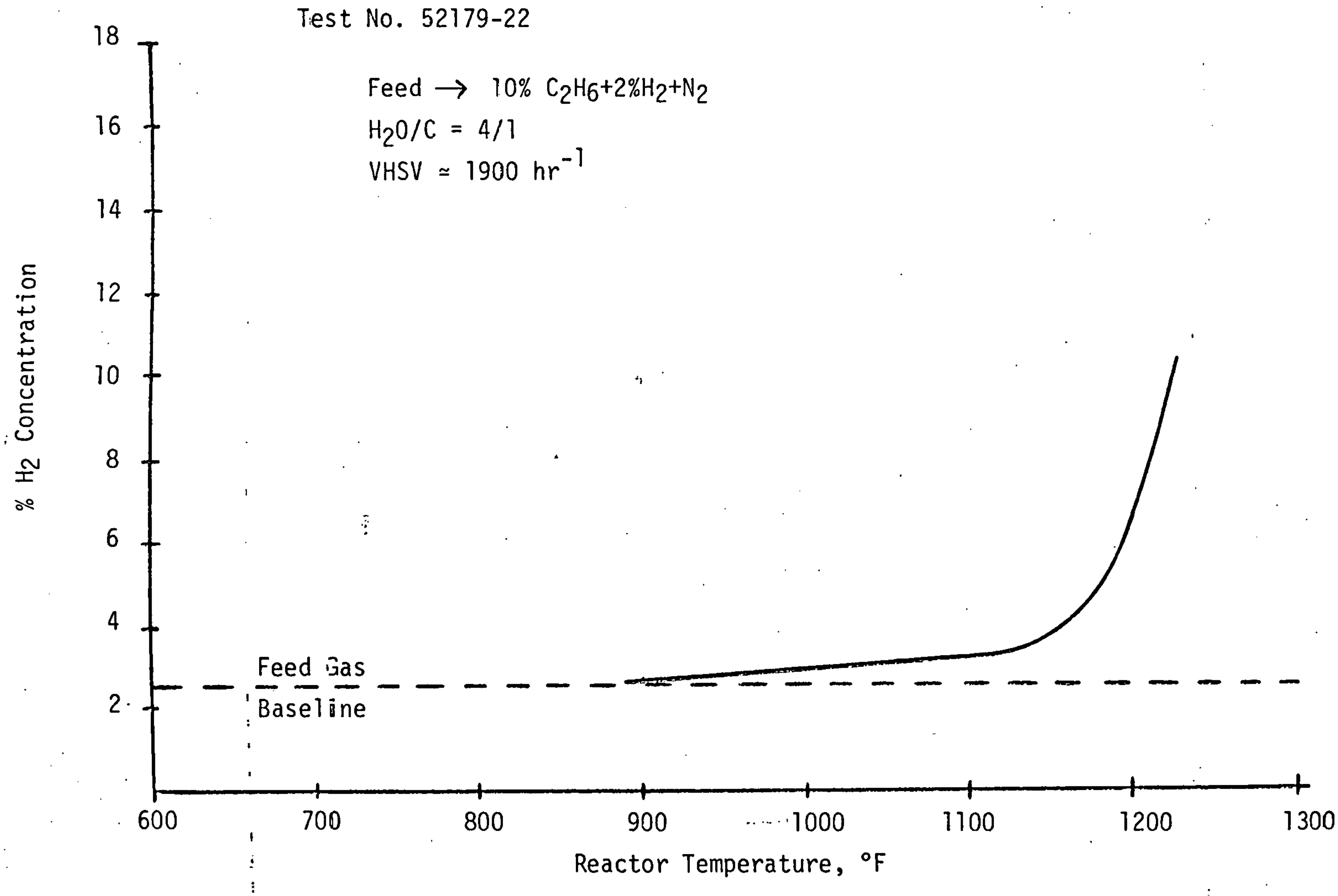


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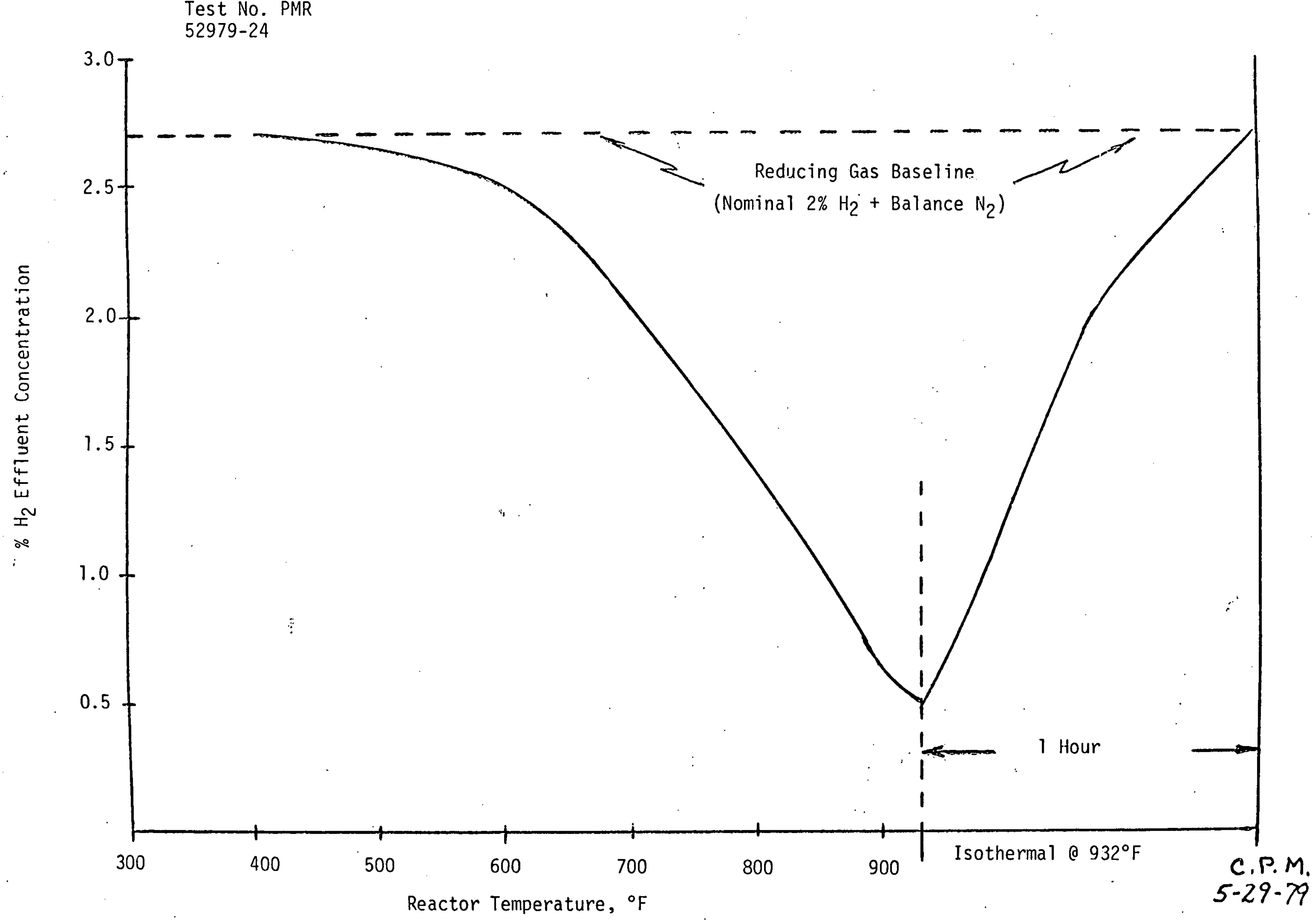
FIGURE 6

% H_2 Effluent Concentration During Reduction of G90C



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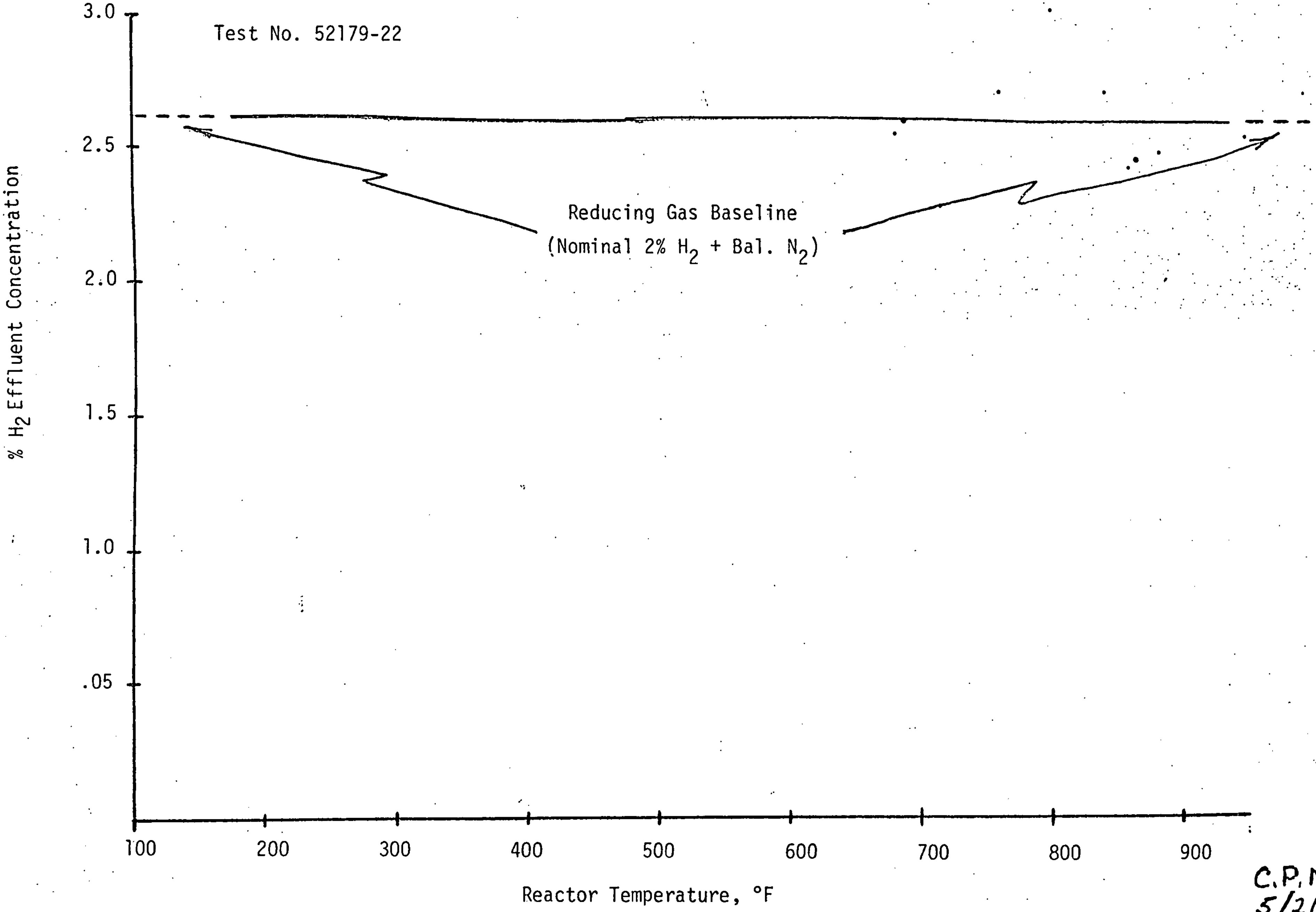
5-29-79

FIGURE 7

% of H_2 Effluent Concentration During Reduction of Stabilized Carriers

(10984-19-3)



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reduction of the NiO present. The amount of H_2 uptake may be related to the available nickel surface area and the ease which the sample reduces.

After completing the reduction step, steam was introduced into the reactor and the temperature raised slowly to 1700°F. After reaching 1700°F, the sample was aged for an additional 17 hours before cooling to 800°F. The feed mixture was substituted for the reducing gas and within 20 minutes the hydrogen content of the product gas stream reached 12%. The temperature was reduced to 500°F and the H_2 content measured was equivalent to the feed gas. The reactor temperature was then raised slowly in 100°F increments every 30 minutes and the hydrogen content of the product stream monitored. These results are shown in Figure 8.

After the last data point, the furnaces and feed were turned off and the system was allowed to cool in a stream of dry reducing gas (2.7 vol % H_2, balance N_2). At room temperature the system was purged with nitrogen and the catalyst removed for postmortem analysis. The tested sample was now light gray-blue and lost about 5.3 percent of its initial weight without any apparent volume change.

Engelhard's SF-3B (a remake of the original Engelhard sample tested in Phase I which was labeled SF-3A for clarity) was also screened in the PMR. The results for hydrogen production by steam reforming ethane after reduction and steam aging for SF-3B are shown in Figure 9. The difference in activity between SF-3B and G90C was not expected since when tested for HASR of No.2 oil (Phase I) SF-3A was more active than G90C.

SF-3B after testing in the PMR was blue in color as compared to the black color of the original sample and was also black after testing in the HASR unit. The blue coloration of nickel supported on Al_2O_3 carriers usually is associated with formation of a nickel aluminum spinel which is inactive for steam reforming hydrocarbons. Since SF-3B contains a larger amount of transitional Al_2O_3 in the carrier than G90C, more interaction between nickel and the carrier is expected thus affecting the activity of SF-3B more than G90C.

Oxidizing atmospheres such as steam favor the nickel oxide - Al_2O_3 reaction. Hydrogen is added during steam aging to prevent the reoxidation of nickel and the subsequent NiO-Al_2O_3 interaction. The water/hydrogen ratio is critical and is typically between 5 and 10 in commercial steam reforming units. Further the H_2O/H_2 ratio of the exit stream from the catalytic partial oxidation tests run during Phase I ranges between 3-5. Since the first stage is a CPO catalyst bed, steam aging at 1700°F should be done at a typical water/hydrogen ratio expected at the entrance to the first bed.

FIGURE 8

Ethane Steam Reforming of G90C

(15% Ni on Ceramic)

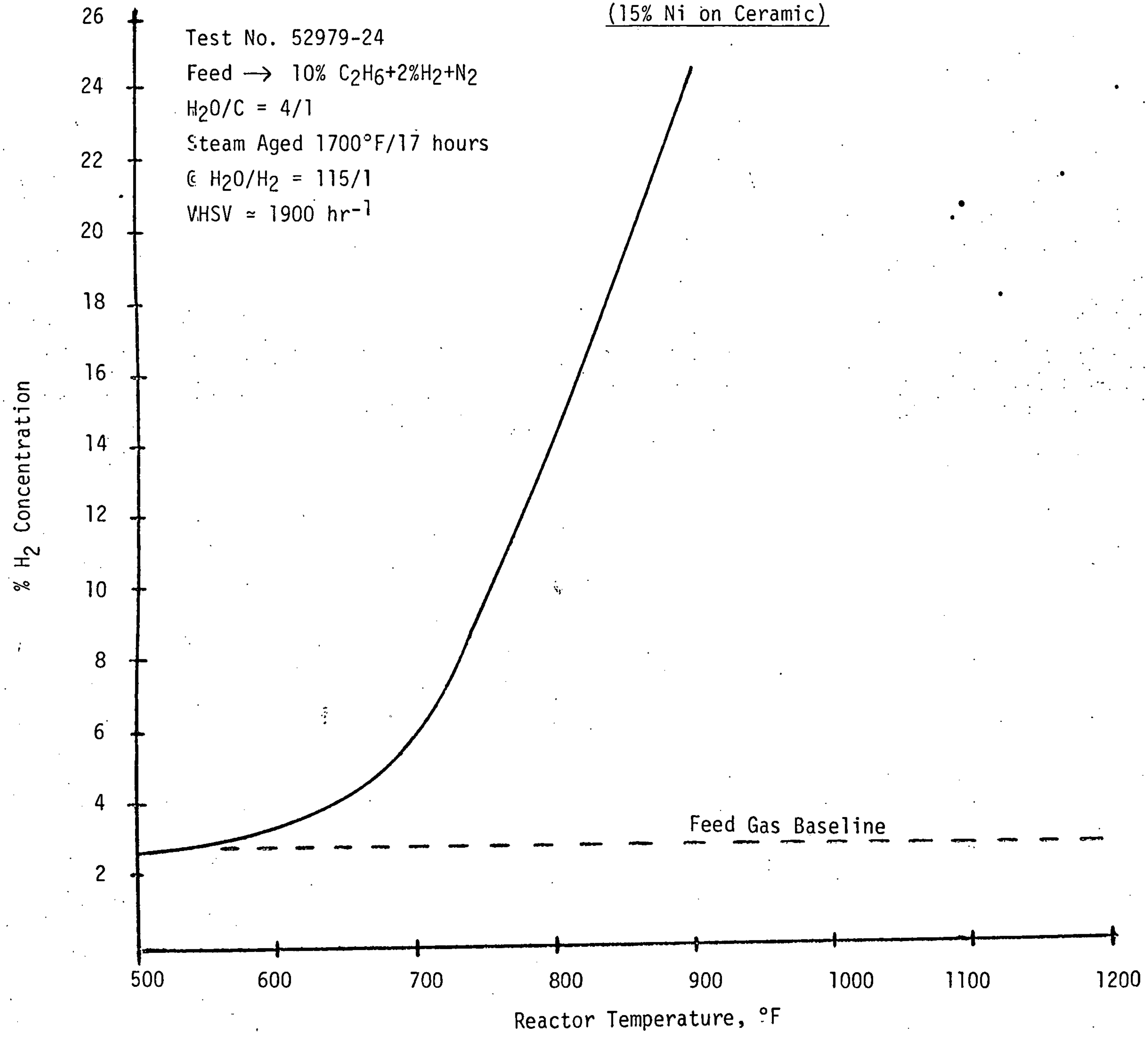

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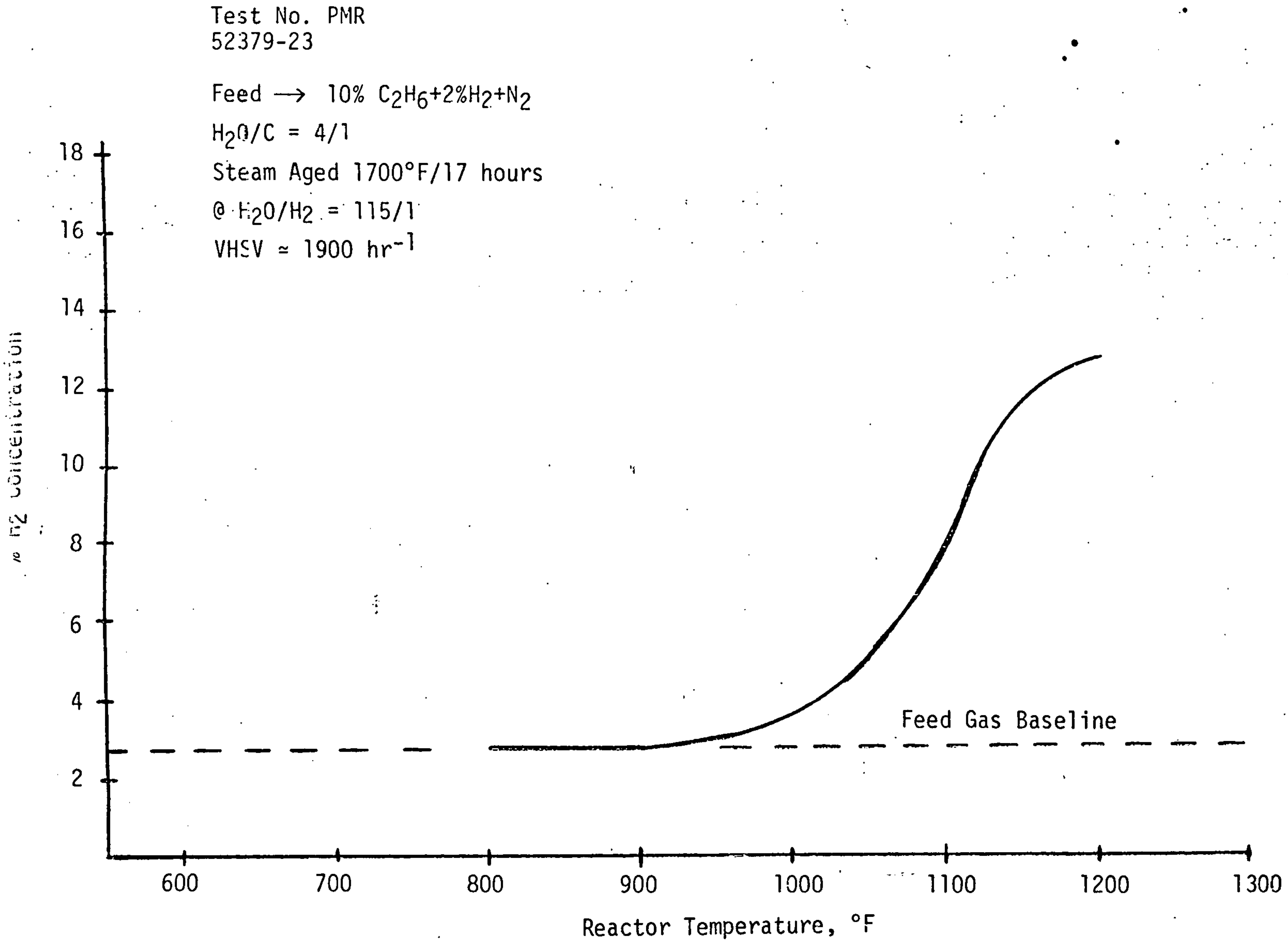
FIGURE 9

Ethane Steam Reforming of SF-3-B

(10957-36-1/15% Ni on Al_2O_3)



Test No. PMR
52379-23

Feed → 10% $C_2H_6+2\%H_2+N_2$

$H_2O/C = 4/1$

Steam Aged 1700°F/17 hours

@ $H_2O/H_2 = 115/1$

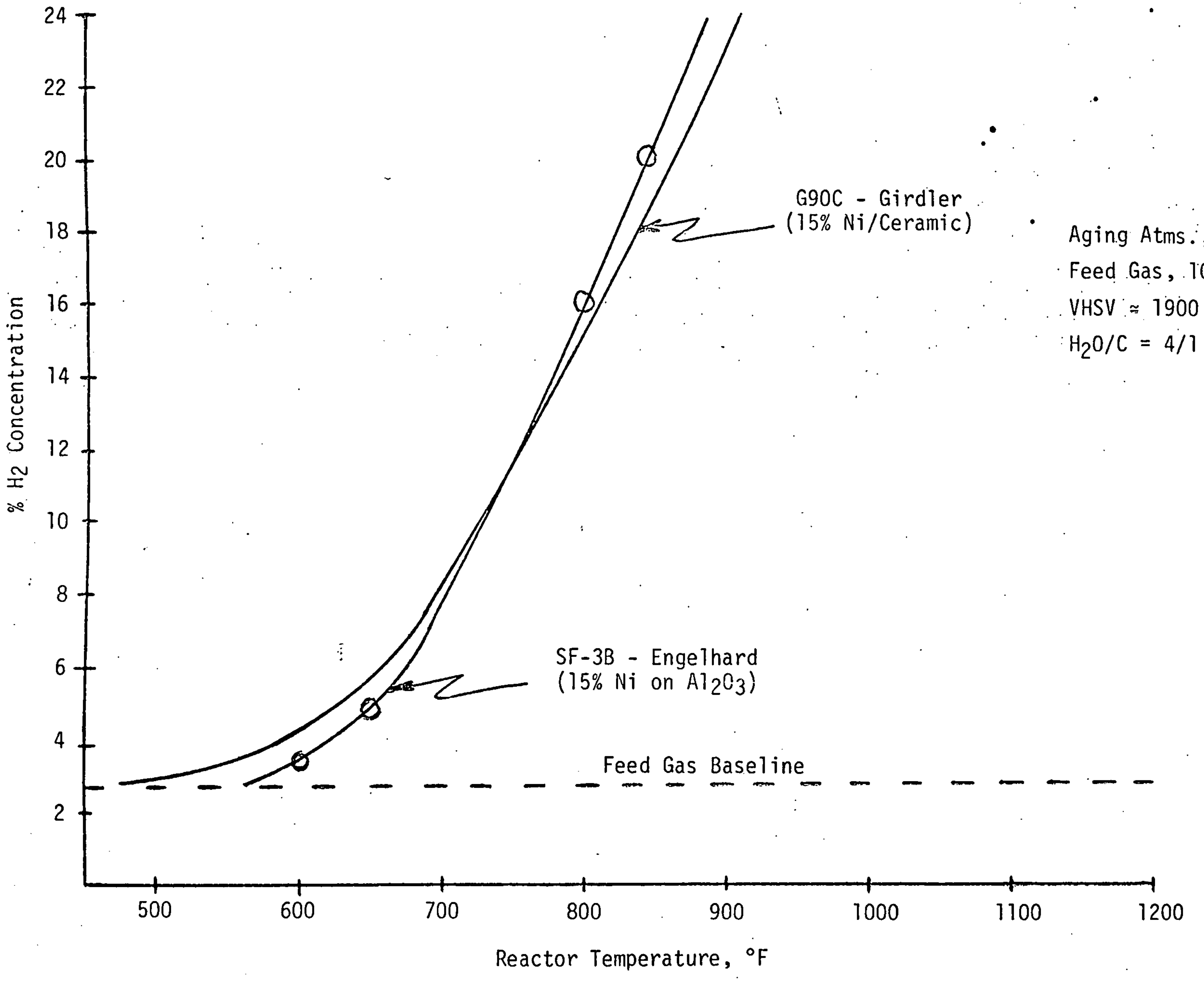
VHSV ≃ 1900 hr^{-1}

C.P.M.
5/23/79

FIGURE 10

Ethane Steam Reforming of Ni Catalysts via PMR

Steam Aged 1700°F/17 Hours



Aging Atms., $H_2O/H_2 = 3.1$
Feed Gas, $10\% C_2H_6 + 2\% H_2 + N_2$ Bal.
VHSV ≈ 1900 hr^{-1}
$H_2O/C = 4/1$

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Changing to a 100% hydrogen reducing mixture from the 2.7 vol % H_2, balance N_2 mixture decreased the H_2O/H_2 ratio to 3.1. Test results for G90C and SF-3B after reduction and steam aging at a H_2O/H_2 ratio of 3.1 are shown in Figure 10. The activity for both samples have improved compared with the previous runs (H_2O/H_2 = 115) and now both samples appear to be equivalent in activity. Both samples tested with the lower H_2O/H_2 ratio were black after being removed from the microreactor.

Task 5.1B Catalyst Screening Under ATR Conditions

Unit 5 at Delancy Street has been modified to screen catalysts in the autothermal reactor mode. The flow diagram is shown in Figure 11 and the detail description of this system has been reported previously. During the quarter the injector was redesigned and constructed as shown in Figure 12. For this new injector, a vaporized No. 2 oil (≃ 700°F) is injected through a 0.04" ID hole into a hot air and water stream (about 1000°F). This fuel is then passed through a static mixer to homogenize the mixture. After the static mixer, this homogenized feed is admitted into a monolithic catalyst, where partial oxidation of No. 2 oil with air will occur over the Pt/Pd/monolith catalyst. As a result of this oxidation reaction, CO and H_2 will be produced and the temperature of the CPO product gases will be increased to a temperature above 1700°F. The remaining No. 2 oil and/or hydrocarbons (from cracking reactions) will further be reformed into the product gas over traditional steam reforming catalysts. The location of the CPO and steam reforming catalysts inside the reactor is shown in Figure 5.

Tests with different start up procedures will soon be performed. It is intended to use propane or othe gaseous hydrocarbons to trigger the initial partial oxidation reaction, and the H_2 and CO produced from the CPO unit will be used to do in situ reduction of the downstream nickel catalyst. After reduction, No. 2 oil will be admitted in place of the propane used for start-up.

FIGURE 11

AUTOTHERMAL REACTOR CATALYST SCREENING UNIT

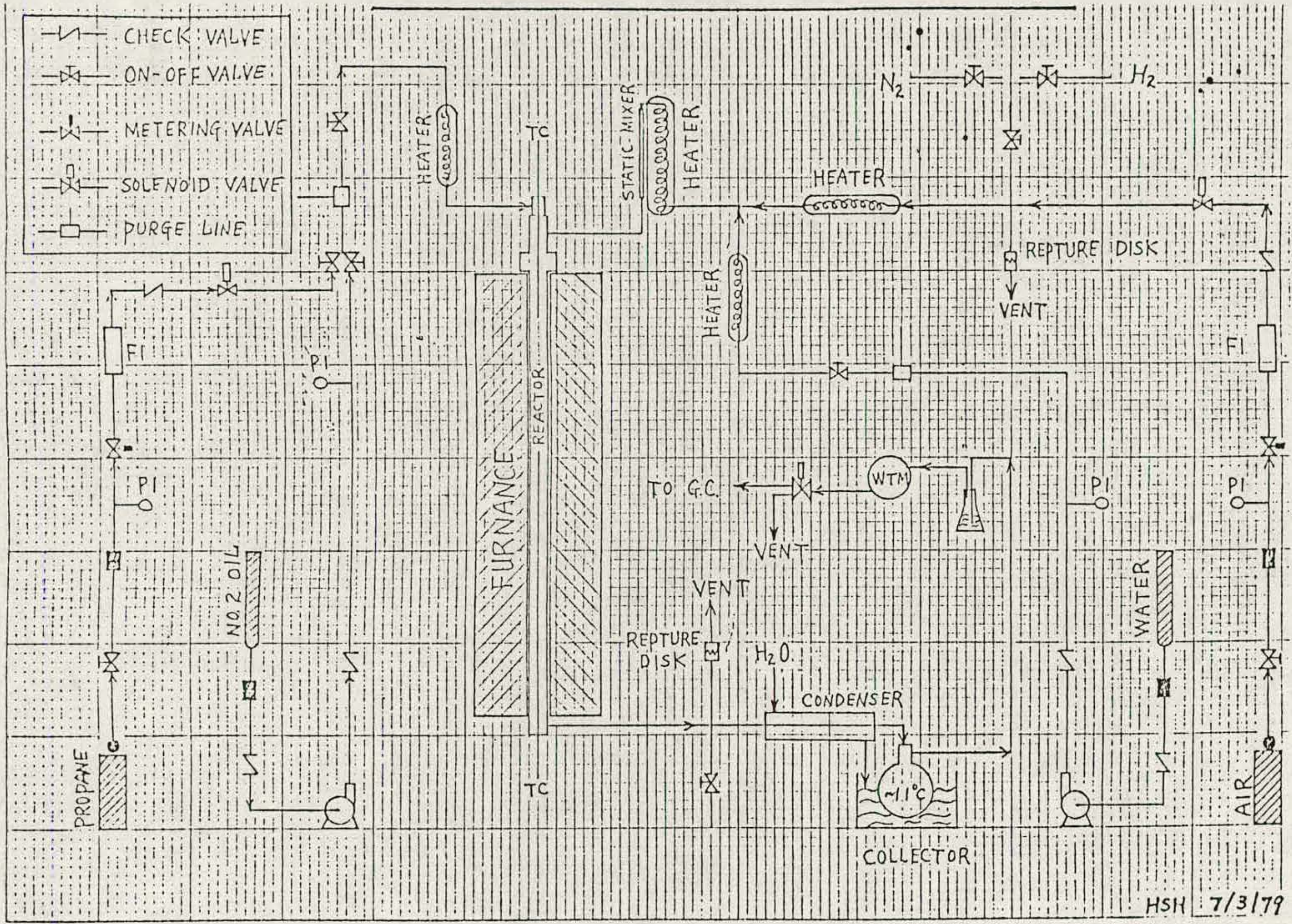

FIGURE 12

INJECTOR DESIGN

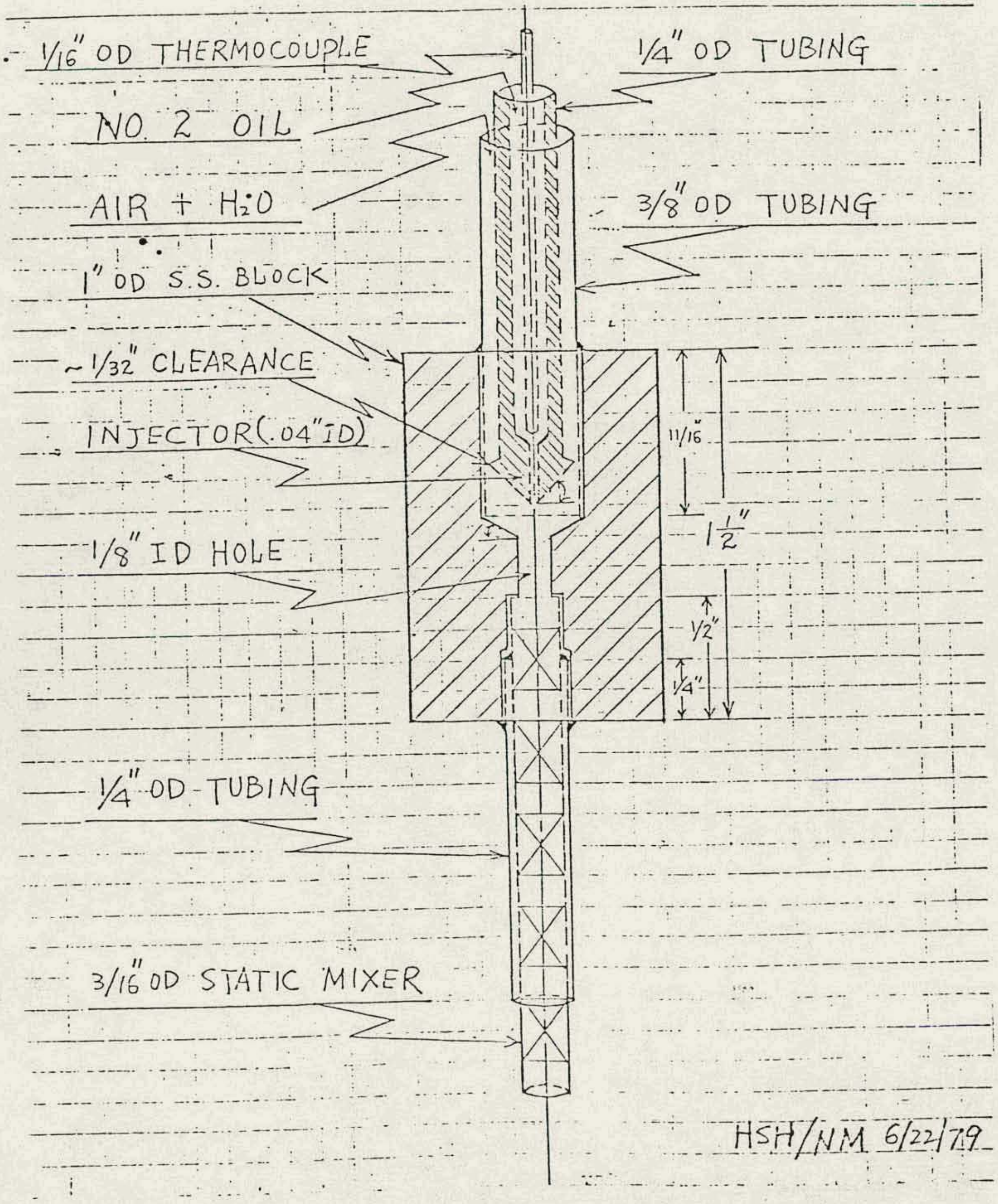

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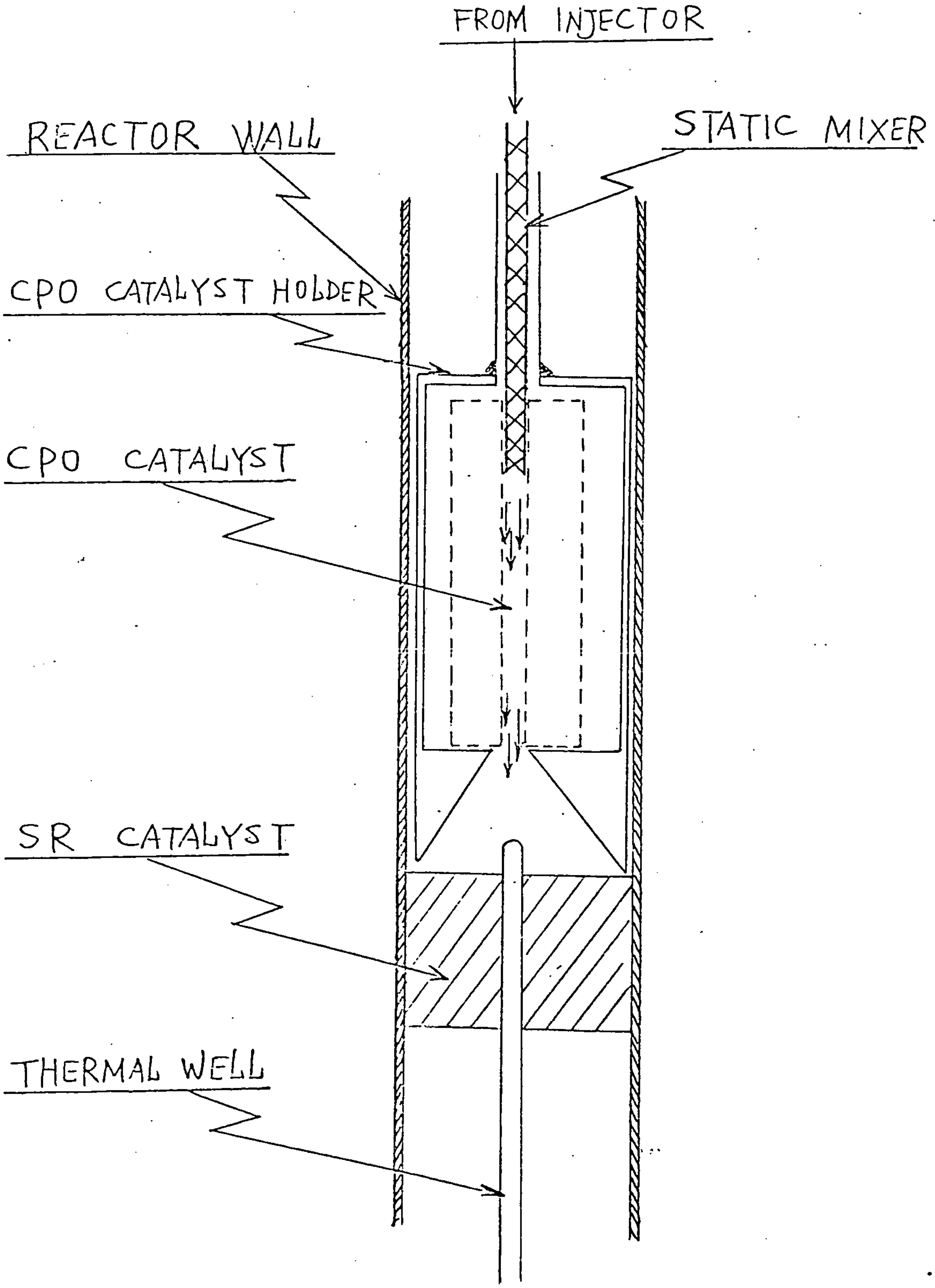
FIGURE 13

ASSEMBLY DIAGRAM OF THE AUTOTHERMAL REACTOR



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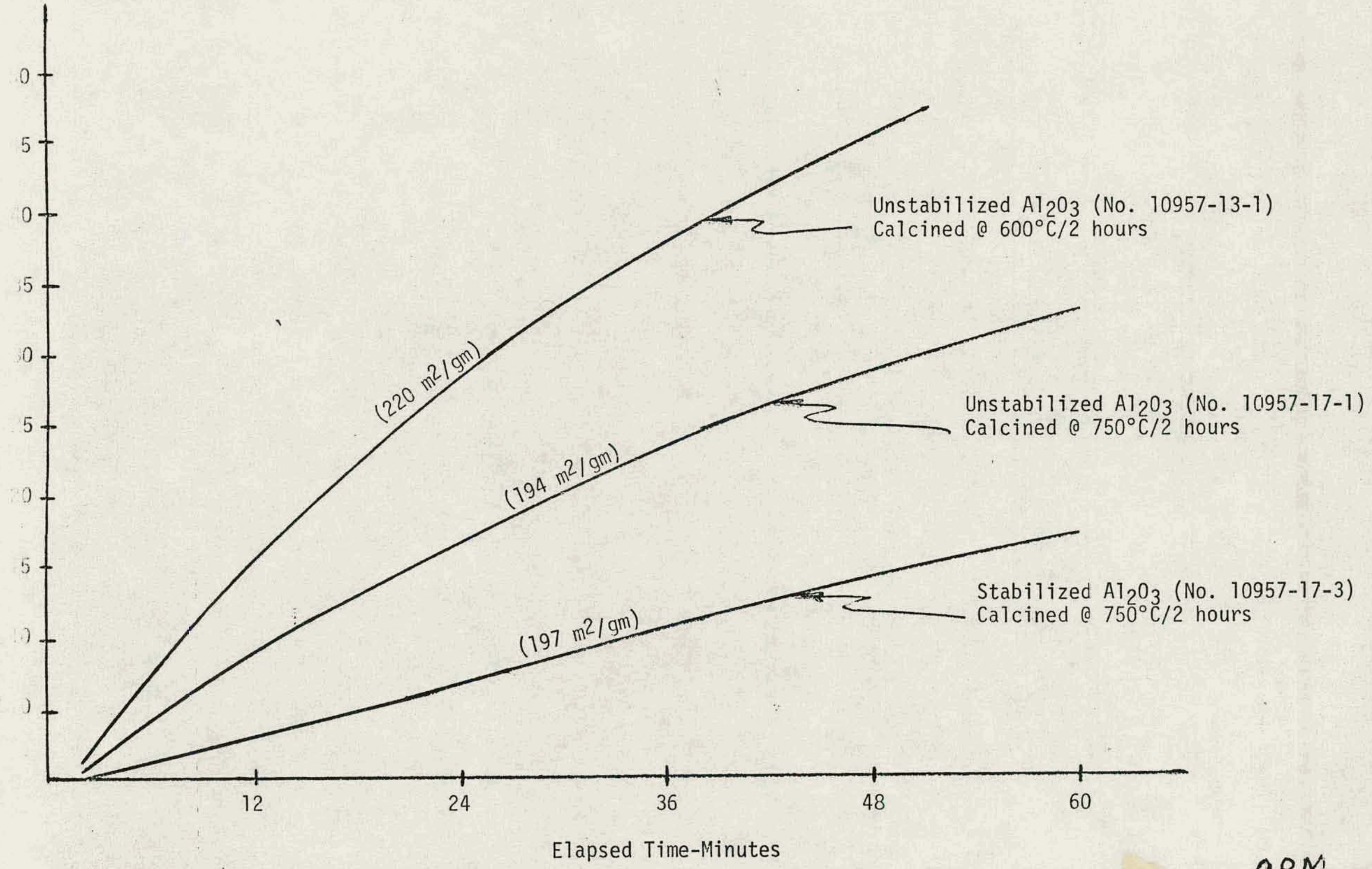
Task 7 Supporting Studies

Thermal coke formation determined gravimetrically (Perkin-Elmer Microbalance Model TGS-2) was investigated using dry ethylene to develop fundamental baseline data. No detectable coke laydown was measured on an empty Pt sample holder with flowing C_2H_4 up to 600°C. Two nonstabilized Al_2O_3 carriers with different B.E.T. surface areas (194 vs $220m^2/gm$) were evaluated using ethylene and showed that the higher surface area material picked up a greater amount of carbon after 1 hour at 500°C. A proprietary E.I. stabilized carrier having a similar B.E.T. surface area as compared to the unstabilized sample (197 vs. $194m^2/gm$) showed approximately 1/2 the amount of coke laydown after 1 hour at 500°C as shown in Figure 14.

The above experiments, scoped out an extreme coke condition, and sets the stage for use of a water saturated synthetic feed gas stream which will approximate the composition of the exit stream from the first stage CPO unit.

FIGURE 14

Coking Studies via Microbalance
With C_2H_4 @ 500°C



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