MASTER

CATALYST AND PROCESS DEVELOPMENT FOR HYDROGEN
PREPARATION FROM FUTURE FUEL CELL FEEDSTOCKS

QUARTERLY REPORT

APRIL 1 TO JUNE 30, 1980

PREPARED BY:

R. M. YARRINGTON

I. R. FEINS

H. S. HWANG

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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

DATE PUBLISHED - JULY 1980
DIVISION OF FOSSIL FUEL UTILIZATION
UNITED STATES DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AC-03-79-ET15383

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Phase II of the contract, which involved catalyst preparation and evaluation, was nearly completed this quarter. Phase III, which calls for the design and construction of a fuel processor, was started.

During the quarter, four types of tests were run on the small scale catalyst screening unit. The operating line for coke-free operations was found to be approximately between 0.41 to 0.44 O_2/C level. Screening at lower O_2/C levels lead to problems with plugging. In other tests, increased severity for screening steam reforming catalysts was obtained by doubling the space velocity. Another series of tests were run to determine the gas composition from the catalytic partial oxidation (CPO) section and to evaluate two CPO catalysts. In the other series of tests, catalysts were aged for about 20 hours using a propane, steam, and air mixture before testing with No. 2 oil for another five hours.

This latter test has been used to study Pt/Rh catalysts made with various supports. Differences were readily determined for Pt/Rh supported on alpha alumina and Pt/Rh supported on stabilized alumina. This test method will find continued use in evaluating metal-support interactions. Several samples must be evaluated by this method before aging runs are made in the larger unit.

After leaching alumina from a used Pt/Rh catalyst, the XRD pattern showed the presence of a Pt-Rh alloy in the metal residue. Experiments were run to show that the alloy was formed in the reactor during testing and not during catalyst preparation.

A larger version of the ATR reactor has been designed and major components are on order. Completion of the construction phase is scheduled for the next quarter.

REVIEW BY TASKSTask 5.2 Catalyst Screening Using an ATR Reactor

During the quarter, four types of tests were run using the small catalyst screening unit. The objective of these tests was to learn more about the Engelhard autothermal reformer while exploring more severe testing procedures for catalyst evaluation. Previous testing had eliminated most of the catalysts under consideration but several precious metal catalysts appeared comparable under previous test conditions. Results from each type of test are described in detail below.

A. Runs to Determine the Coke-Free Operating Line

To screen catalysts in a more realistic manner it would be desirable to operate at lower oxygen/carbon ratios. However, the test unit itself has a characteristic operating line related to its size and construction of the mixing zones. Runs 7369 and 7379 were made to establish this coke-free operating line for this small test unit. For these runs, fresh monolithic CPO-1 catalyst (6" long) and fresh FP-1 (Pt/Rh) steam reforming catalyst (30ml) were loaded into the reactor. The standard start-up and testing procedures were used. The results are listed in Tables I, II and III and are further compared with previous runs as follows:

<u>Run No.</u>	<u>O₂/C</u>	<u>H₂O/C</u>	<u>Mid-Bed Temp., °F</u>	<u>Temp. Drop in SR Bed, °F</u>	<u>Equivalent H₂</u>	<u>Coke Observed</u>
7369	0.363	2.57	1463	229	1.84	Yes
7379	0.40	2.59	1429	195	1.84	Yes
7251	0.41	2.67	1463	116	1.91	No
7238	0.44	2.72	1483	77	1.99	No

For runs 7369 and 7379, coke was found on the surface of the steam reforming catalyst, FP-1. It was not observed in the previous runs with FP-1 at higher O₂/C ratios. It may be concluded that under the current test conditions (1 atm, 1450°F mid-bed temperature, WHSV = 4.0, and H₂O/C = 2.6) the coke-free operating line lies approximately between 0.41 and 0.44. Thus, it appears that catalyst screening at lower O₂/C ratios would not be possible with this unit. The increase in temperature drop through the steam reforming bed as the O₂/C ratio is lowered indicates the increased burden placed on the steam reforming section when the unit operates at these desired lower levels. Tests designed to determine the gas composition after the CPO section at various O₂/C levels will be described later.

B. Increasing the Space Velocity for Screening Steam Reforming Catalysts

In run 7382, the space velocity was doubled by charging in 15ml of FP-13 (2% Rh) catalyst. The weight hourly spaced velocity based on oil feed rate divided by the weight of catalyst was 7.5 hrs⁻¹. The experimental results are listed in Tables I and IV. Further comparisons with a test on the same catalyst but with 30ml of material are listed below:

<u>Volume of SR Cat, ml</u>	<u>O₂/C</u>	<u>H₂O/C</u>	<u>Mid-Bed Temp., °F</u>	<u>Temp. Drop in SR Bed, °F</u>	<u>HC Conv. %</u>	<u>Equivalent H₂</u>
30	0.41	2.59	1443	123	96.0	1.93
15	0.38	2.60	1481	135	84.0	1.40

Some coke was observed on FP-13 after the high space velocity run with 15ml of catalyst. This is probably related to the low O₂/C ratio (0.38) used. The results show that as space velocity is increased, the hydrocarbon conversion is decreased as expected. In fact, the conversions are about as expected for a first order reaction. Thus, higher space velocities offer a means of more severe screening of promising steam reforming catalysts.

C. Gaseous Products from the CPO Section and Evaluation of CPO Catalysts

Several experiments were run with only the CPO catalyst in place. These were designed to provide information about the type and quantity of compounds emerging from the CPO section which must be subsequently reformed. The effect of residence time during sampling was also investigated. Also, the effect of the composition of the CPO catalyst upon the gas composition was determined.

In these experiments, air and water rates were held constant and oil feed rate was adjusted to vary O₂/C and H₂O/C ratios. Previous results had indicated that almost no steam reforming occurs in this section, thus the presence or absence of steam is not critical in terms of gas composition.

The effect of O₂/C ratio was determined in a series of experiments. One set of conditions was held constant for each days run of 5 hours duration. The results of Run No. 7429 at the 3 hour period are summarized in Table V to observe the effect of O₂/C. In making these observations the H₂O/C ratio varied from 1.9 to 2.5 in direct relation to O₂/C level. This variation effects the residence time in the sampling tube slightly; that is, the time for the gas to travel from the exit of the CPO section to the condenser where the reactions would be quenched. Results are as listed below:

Conversion of No. 2 Oil, %

<u>O₂/C</u>	<u>H₂O/C</u>	<u>to C₄⁻</u>	<u>To (CO + CO₂)</u>
.292	1.92	83.4	35.1
.324	2.18	84.5	43.2
.332	2.18	87.0	38.1
.380	2.52	88.6	44.7
.386	2.51	90.7	49.4

The unconverted oil was observed to be more dense than the feedstock. This implies that paraffins and olefins were oxidized preferentially leaving behind the more dense aromatic fraction. In the larger ATR unit having higher inlet temperatures, higher conversion of oil in the CPO section is expected. In Table V we notice that about 5-6% hydrogen is produced in the CPO section. Thus, hydrogen assisted steam reforming is occurring in the subsequent catalyst zone. The results versus O₂/C ratio are plotted in Figure 1.

Sampling residence time could be varied in these experiments by collecting samples either after the gases passed through the remaining portion of the one inch diameter reactor or by using the thermowell as a sampling probe which has a shorter residence time. Run No. 7443 was designed to demonstrate the effect of residence time in sampling and also to check the reproducibility of the previous run (No. 7429). Once again, CPO-2 catalyst was used in this catalytic partial oxidation run. The results are summarized in Table VI. The results as listed in Table VI are plotted in Figure 2 and show that methane and propane content change considerably with sampling residence time; methane increases whereas propane decreases. Good agreement was noted with the previous run when sampling was done at 19 milliseconds. The results suggest that further thermal cracking occurs during the period of sampling before the products are quenched to room temperature in the condenser.

In our work to date, we have used a monolithic CPO catalyst which use Pt and Pd as the active metals. In CPO-1 and CPO-2, the ratio of Pd to Pt was 1:1. To determine the effect of Pd in this section, catalyst CPO-3 was prepared with a Pd to Pt ratio of 4:1. This sample of CPO-3 was evaluated using the procedures reported above. The results are listed in Table VII after three hours on stream. Also, to compare results, the effect of O₂/C ratio is shown for CPO-3 in Figure 3. This can be compared with Figure 1 where results for CPO-2 are shown. The results of the two tests indicate no difference in selectivity. The effect of aging on activity and selectivity must be determined later. For the larger ATR reactor, CPO-2 will be used initially.

D. Evaluating Steam Reforming Catalysts After Aging

Four catalysts have been evaluated after a period of aging. The standard start-up procedure was used but the samples were kept under propane, water, and air for about 20 hours before switching to No. 2 oil. The results after 3 hours on No. 2 oil are summarized in Table VIII.

ENGELHARD

During the period on propane, approximately constant product gas composition were observed as listed in Table IX. The results also show that propane can be readily reformed in the ATR unit without methane slippage.

The four catalysts tested are listed below:

<u>Catalyst No.</u>	<u>Metal(s)</u>	<u>Support</u>	<u>Virgin Surface Area, m²/g</u>
FP-13	Rh	Stabilized Alumina	114
FP-30	Pt/Rh	"	140
FP-31	Pt/Rh	"	137
FP-33	Pt/Rh	Alpha Alumina	13

The results versus time on stream are listed in Tables X, XI, and XII for FP-13, FP-33 and FP-31, respectively. In all of these runs, some unconverted oil or wax was observed in the condensate throughout the run. Conversions were lower even after one hour on No. 2 oil than was observed in previous runs. The production of H₂ plus CO was observed to decline with age. Hydrocarbon slippage increased as shown in Figure 4. This may be due to the accumulation of sulfur and coke. It must be remembered that these tests are at high space velocities and relatively low preheat temperatures.

The effect of metal-support interaction is also observed in these runs. With FP-33, Pt/Rh is supported on alpha alumina. Rapid aging is observed.

This rapid aging test provides a method of quality control for samples before they are charged to the larger ATR unit now under construction.

Task 5.3 Catalyst Characterization

A. Hydrogen Chemisorption of Used Nickel Catalysts

One proposed catalytic deactivation mode is the loss of active metal surface area. This metal surface area can be decreased by either sintering of the active metal resulting in larger metal crystallites or by a reaction of the active metal with the carrier resulting in a metal-carrier compound.

One method of measuring the metal surface area is by chemisorption of an active gas. For the precious metal catalysts, CO can be used but Rh has multisorption sites so that the ratio of CO molecules sorbed to Rh surface atoms is not known accurately. For nickel containing catalysts, CO chemisorption measurements usually result in the formation of $\text{Ni}(\text{CO})_4$ which is undesirable. Therefore, hydrogen chemisorption is to be used to measure metal surface area.

Although the H_2 chemisorption measurement is straightforward, a problem occurs when the metal surface area of a used sample is to be determined. The used sample contains some deposited coke which will reduce the amount of gas sorbed leading to a lower measure of H_2 sorbed, thereby giving a false indication of metal area. Removal of this deposited coke by controlled burning in a slight partial pressure of O_2 in nitrogen or steam results in the thermal sintering of the nickel from the heat of combustion of the coke.

As an alternative method, a LFE low temperature asher, model LTA-504, was used to remove coke. After loading the samples into the unit and evacuating, the system is recharged with 1 to 4mm of O_2 . Energy is supplied via a radio frequency generator and the temperature does not exceed 250°C . Samples of FP-27, 25 wt % Ni on stabilized Al_2O_3 , were dry ashed for 48 hours. The samples and results are listed below.

<u>Sample of FP-27</u>	<u>wt % Coke</u>	<u>wt % Ashed</u>	<u>H_2 Sorbed cc/gm</u>
Virgin	None	Not Treated	3.85
Virgin	None	2.3%	3.80
Used (Run 7351)	5.3	Not Treated	0.0
Used (Run 7351)	4.0	2.5	0.0

Thus, the dry ashing technique did remove some coke but did not give a measurable metal surface area. The ashed used sample appears to have a metallic nickel plating on the surface.

ENGELHARD

In speaking with Dr. Adir Jacob of LFE Process Control Division (the manufacturer of the low temperature asher), he feels that the use of pure O_2 lead to the formation of non-reducible NiO_2 . He suggests we use a mixture of 4 vol % N_2 in oxygen to remove the coke. He used this gas mixture to remove organic from metallic nickel mesh in a low temperature asher without oxidizing the nickel surface.

The hydrogen chemisorption was also measured for a used 14.5 wt % Ni - 0.5 wt % Rh sample (FP-22). Both the ashed used and "as received" used samples had zero H_2 sorption although the carbon content was around 0.1 wt % for each. These samples have been submitted for X-ray diffraction analysis to determine if the nickel is present as massive crystallites which would explain the zero hydrogen chemisorption.

B. Unexpected Poor Activity of FP-31

FP-31, a new batch of FP-1, failed to give good performance in Run 7471. Below are some properties of FP-1 and FP-31 for comparison.

<u>Sample</u>	<u>BET Surface Area</u>	<u>CO Chem.</u>
Virgin FP-1	131.2	2.32
Used FP-1	116.5	0.34
Virgin FP-31	137.7	2.46
Used FP-31	119.3	0.20

From the above data, there is no apparent reason for the poor performance of FP-31.

To increase the severity of the screening test, the time the unit runs using propane as a feed was increased from 2 to 20 hours. The effect of the additional time on propane can be seen below by comparing an earlier run using FP-13 (Run No. 7331 ... a typical screening run similar to that under which FP-1 was tested) to the aging run using FP-13, Run No. 7403 (similar conditions used to test FP-31).

Run #	7331	7403
Time on Stream	3 hrs. oil	24 hrs. (21 hrs. propane + 3 hrs. oil)
Inlet to Steam Reforming Bed	1581°F	1607°F
ΔT Inlet to Top SR Bed	82°F	27°F
ΔT Inlet to Mid SR Bed	138°F	144°F
ΔT Inlet to Bottom SR Bed	123°F	171°F
% Coke on Catalyst	0.25	0.62
Used Sample	102	103.5
BET SA, m ² /gm		

ENGELHARD

The cold-spot in Run 7403 occurs further down the steam reforming bed than in Run 7331 indicating greater deactivation of the steam reforming catalyst. Also in Run 7403 it appears that the top portion of the steam reforming bed has totally deactivated. This test is extreme, but does give the rapid aging necessary to screen catalysts.

Even though the aging test is more severe than the original screening test, FP-31 appears to be less active than FP-1. As of this writing, however, no explanation is meaningful until more aging runs are made.

C. Post Run Assay (With J. Sciarriello)

Since a change in the CO chemisorption of FP-1 after testing was measured, an X-ray powder diffraction method was used to identify phases and to determine the average crystallite size of the precious metals. While the XRD pattern of the virgin FP-1 showed only peaks for $\gamma\text{-Al}_2\text{O}_3$, the used sample showed a broad overlapping Pt and Rh XRD peak along with those of $\gamma\text{-Al}_2\text{O}_3$ as given in Figure 5a.

To resolve the pattern, the used sample was leached with a 50% aqueous solution of HBF_4 . This solution dissolved away the alumina leaving behind a residue of Pt and Rh. The XRD pattern for the Pt/Rh residue showed good agreement with data listed on the JCPDS reference card No. 27-504 for a Pt-Rh alloy, indicating a possible interaction between the two metals (Figure 5b).

To show that this Pt-Rh interaction occurs only during testing and not as a result of preparation, the following experiments were done and their XRD patterns examined.

- 1a. Pt black and Rh powder were mixed to give a ratio of Pt and Rh similar to that found in FP-1. The XRD pattern showed peaks characteristic for each metal but no alloy peaks.
- b. This mixture was heated to 340°C in Argon and held 25 hours. Again the XRD pattern showed only characteristic metal peaks with those due to Pt sharpened indicating an increase in the Pt crystallite size.
- c. The heated mixture after treating with HBF_4 solution showed only separate Pt and Rh XRD peaks but no indication of a Pt/Rh alloy.
2. A mechanical mixture of Pt, Rh and pulverized carrier in the same weight proportions as FP-1 (1.5 wt % Pt - 0.6 wt % Rh - 98 wt % carrier) was prepared and treated in the same manner as the Pt-Rh mixture.
 - a. The XRD pattern showed peaks of $\gamma\text{-Al}_2\text{O}_3$. The Pt and Rh peaks overlap with those of $\gamma\text{-Al}_2\text{O}_3$ and cannot be seen clearly.
 - b. Heating the Pt-Rh- Al_2O_3 mixture for 20 hours at 340°C in Argon yielded an XRD pattern of $\gamma\text{-Al}_2\text{O}_3$, Rh and Pt. The Pt peaks are more intense than in the non-heat treated mixture since heating has caused sintering of the Pt resulting in a larger crystallite size. Again no indication of a Pt/Rh alloy could be seen.

ENGELHARD

- c. The residue obtained by extracting the heated mixture with HBF_4 solution showed XRD peaks assignable to metallic Pt and Rh only. No $\gamma\text{-Al}_2\text{O}_3$ or Pt/Rh peaks can be observed.
3. The virgin catalyst was treated similarly to the two mixtures.
 - a. Virgin FP-1 shows XRD peaks characteristic of $\gamma\text{-Al}_2\text{O}_3$ only.
 - b. FP-1 heated at 340°C in Argon for 25 hours showed an XRD pattern typical of $\gamma\text{-Al}_2\text{O}_3$ only.
 - c. Extracting the heated FP-1 with HBF_4 solution yielded a residue whose XRD pattern was very weak (essentially amorphous) with no identifiable peaks.
4. XRD pattern for used catalyst FP-1 indicated a mixture of $\gamma\text{-Al}_2\text{O}_3$ with minor amounts of $\delta\text{-Al}_2\text{O}_3$ present. Rh and Pt peaks cannot be seen clearly possibly because of overlap with Al_2O_3 peaks.
5. The residue from treating FP-1 with HBF_4 to dissolve the Al_2O_3 yielded a XRD pattern with peaks at d-spacings $2.230\text{\AA}$, $1.931\text{\AA}$, $1.372\text{\AA}$ and $1.167\text{\AA}$ which are in agreement with peaks listed on JCPDS reference card #27-504 for a platinum-rhodium intermetallic.

From this background work we have concluded:

1. The Pt/Rh alloy does not form during the catalyst preparation.
2. Leaching samples with HBF_4 solution does not cause Pt and Rh to alloy but does remove most of the $\gamma\text{-Al}_2\text{O}_3$.
3. The Pt/Rh alloy forms during testing. Work is underway to determine whether changes in the carrier stabilizers affect the Pt/Rh interaction.

ENGELHARD

Task 8 Design and Build a Demonstration Unit

The small unit that has been used for the last year to evaluate catalysts has several limitations. The unit is not adiabatic and heat is added to maintain a reasonable bed temperature. This is not realistic for evaluating the process and also tends to mask any deterioration of the CPO catalyst. The current test unit is also limited to about 900°F preheat temperature. Higher preheat temperatures may be desirable to increase the conversion of oil in the preheat section and as a means of controlling the exit temperature from the steam reforming bed. This latter item is important as a means of preventing sulfur poisoning of the steam reforming catalysts.

Other items considered in designing a larger unit were:

- (a) Operations at higher pressures. Some fuel cell systems are being designed to operate at 120 psig. The processor would have to operate slightly above this pressure level.
- (b) Capable of operating over the following range of variables:

O ₂	0.30 - 0.45
H ₂ O/C	1 - 3
Preheat Temperature	900-1300°F

- (c) Unit must have sampling probes to analyze the gas at various elevations in the bed. This is needed since more than one catalyst may be used in the bed.

The flow diagram for the new unit is shown in Figure 6. This is similar to the flow diagram of the current unit. Improved instrumentation will allow precise control of the O₂/C ratio and will allow monitoring of the pressure drop in the bed.

Figure 7 is a schematic drawing of the new reactor. The outside shell is constructed of 6" Inconel 601 steel. This high temperature alloy was selected for this first rig since the shell temperatures can only be determined by experimentation. A lower grade steel could be used in future designs if the shell temperatures are sufficiently low for the pressures selected.

The injector has been scaled up from the current design which has been used successfully for about one year without flashback or coke deposition.

The catalysts will be contained in a ceramic insert which will be molded from Alfrax 66, an alumina cement used commercially in second stage reformers. Between the ceramic insert and the steel shell will be a layer of insulation (Fiberfrax).

ENGELHARD

The steam reforming catalyst is supported on a section of honeycomb ceramic. The hot exit gasses are cooled to below 1000°F with a heat exchanger below the catalyst bed. A condenser section is outside the reactor as shown in the detailed drawing of Figure 7.

Long delivery items were ordered during the quarter and construction work was started in July 1980. This is scheduled for completion during the third quarter of 1980.

TABLE I

CATALYST SCREENING SUMMARY

Steam Reforming Catalysts in the ATR Mode
(CPO Catalyst = Pt/Pd/Monolith)

RUN NO.	7369	7379	7382*
SR CATALYST	FP-1	FP-1	FP-13
ACTIVE METAL(S)	Pt/Rh	Pt/Rh	Rh
CONDITIONS:			
H ₂ O/C	2.57	2.59	2.60
O ₂ /C	0.363	0.40	0.38
TEMPERATURES, °F			
OIL PREHEAT	835	855	840
AFTER CPO	1652	1620	1517
SR BED TOP	1614	1553	1520
" " MID	1463	1429	1481
" " BOTTOM	1423	1425	1382
BELOW SR BED			
SR FURNACE	1517	1517	1517
DRY GAS COMPOSITION, MOLE%			
H ₂	37.18	36.17	31.03
CO	11.84	10.56	10.57
CO ₂	12.85	13.33	12.43
N ₂	36.33	38.26	42.51
CH ₄	1.19	1.05	1.61
C ₂ H ₆	0.02	0.01	0.10
C ₂ H ₄	-	-	0.63
C ₃ H ₆	-	-	0.28
OTHER HC	-	-	0.13
HYDROCARBON CONV, %	95.3	95.7	84.0
EQUIVALENT HYDROGEN	1.84	1.84	1.40

* Only 15ml of SR Catalyst was used.

TABLE II

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run 7369; $H_2O/C = 2.57$; $O_2/C = 0.363$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													
		H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₆	C ₅ ⁺
1		37.57	11.11	13.53		36.08	1.10	0.02							
2		37.46	11.52	13.13		36.14	1.14	0.01							
3		37.18	11.84	12.85		36.33	1.19	0.02							
4		36.85	11.87	12.79		36.63	1.23	0.02							
5		36.55	12.06	12.60		37.34	1.30	0.03			0.03	0.09			
6		35.65	12.20	12.30		37.70	1.35	0.03			0.07	0.07			

Catalysts: CPO-1+FP-1 (1.4% Pt - 0.6% Rh/Al₂O₃, 30ml)

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run 7379; $H_2O/C = 2.59$; $O_2/C = 0.400$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													
		H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₆	C ₅ ⁺
1		36.79	10.29	13.62		37.78	0.92	-	-		-	-		-	
2		36.39	10.58	13.38		38.09	0.94	-	-		-	-		-	
3		36.17	10.56	13.33		38.26	1.05	0.01	-		-	-		-	
4		35.80	10.57	13.14		38.73	1.10	0.03	-		-	-		-	
5		35.03	10.61	12.89		39.51	1.20	0.04	-		0.02	0.07		-	
6		33.85	11.01	12.56		40.34	1.38	0.06	-		0.09	0.09		-	
7		32.00	11.38	11.92		41.88	1.50	0.08	0.05		0.14	0.14		0.02	

* Catalysts: CPO-1 + FP-1 (30 ml Pt-Rh/Al₂O₃)

TABLE IV

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run 7382; $H_2O/C = 2.60$; $O_2/C = 0.38$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													
		H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₆	C ₅ ⁺
1		33.81	10.63	12.97		39.90	1.57	0.08	0.06	-	0.19	0.14	-	-	
2		32.41	10.70	12.68		41.18	1.62	0.09	0.06	-	0.39	0.18	-	0.02	
3		31.03	10.57	12.43		42.51	1.61	0.10	0.06	0.02	0.63	0.28	-	0.05	
4		29.05	10.59	12.22		44.18	1.69	0.12	0.06	-	0.94	0.32	0.02	0.08	
5		27.16	10.51	12.04		45.75	1.79	0.14	0.05	-	1.27	0.40	0.03	0.11	

* Catalysts: CP0-1 + FP-13 (15ml of 2% Rh/Al₂O₃)

TABLE V

 CATALYST SCREENING SUMMARY
 CATALYTIC PARTIAL OXIDATION OF NO. 2 OIL

RUN NO.	#7429	#7429	#7429	#7429	#7429
CPO CATALYST	CPO-2	CPO-2	CPO-2	CPO-2	CPO-2
ACTIVE METALS	Pt/Pd	Pt/Pd	Pt/Pd	Pt/Pd	Pt/Pd
CONDITION(S)					
O ₂ /C	0.324	0.386	0.292	0.332	0.380
H ₂ O/C	2.18	2.51	1.92	2.18	2.52
OIL PREHEAT (°F)	825				
S.R. FURNACE (°F)	1472	1472	1472	1472	1472
τ (X10 ⁻³ SEC)	19	19	19	19	19
DRY GAS COMPOSITION (%)					
H ₂	6.92	7.83	5.02	4.78	5.28
CO	11.45	12.57	8.56	9.08	10.39
CO ₂	6.90	6.63	7.96	7.84	7.47
N ₂	61.23	62.17	62.73	63.80	64.66
CH ₄	3.68	2.31	3.16	2.88	2.46
C ₂ H ₆	0.33	0.28	0.38	0.35	0.29
C ₂ H ₄	5.81	4.57	6.82	6.24	5.15
C ₃ H ₆	1.57	1.39	2.26	2.00	1.60
OTHER HC					
CARBON BALANCE, %	84.5	90.7	83.4	87.0	88.6
HC CONVERSION, %	43.2	49.4	35.1	38.1	44.7
EQUIV. H ₂	0.37	0.48	0.24	0.27	0.35

TABLE VI
 CATALYST SCREENING SUMMARY

RUN NO.	#7443	#7443	#7443	#7443	#7443
CPO CATALYST	CPO-2	CPO-2	CPO-2	CPO-2	CPO-2
ACTIVE METALS	Pt/Pd	Pt/Pd	Pt/Pd	Pt/Pd	Pt/Pd
CONDITION(S)					
O ₂ /C	0.400	0.340	0.33	0.387	0.297
H ₂ O/C	2.56	2.18	2.18	2.53	1.92
OIL PREHEAT (°F)	820	825	820	820	820
S.R. FURNACE (°F)	1472	1472	1472	1472	1472
τ (X10 ⁻³ SEC)	340	340	19	19	19
DRY GAS COMPOSITION (%)					
H ₂	6.71	4.88	4.68	4.50	4.07
CO	10.72	12.71	8.15	8.70	6.91
CO ₂	8.34	5.92	8.99	8.86	9.25
N ₂	62.50	62.73	64.80	66.01	64.02
CH ₄	4.33	5.83	2.56	2.22	3.19
C ₂ H ₆	0.29	0.37	0.33	0.29	0.36
C ₂ H ₄	4.94	5.53	5.76	5.03	6.76
C ₃ H ₆	0.87	0.80	1.97	1.65	2.37
OTHER HC					
CARBON BALANCE, %	90.0	81.0	83.0	88.0	82.2
HC CONVERSION, %	50.4	46.9	39.6	44.0	34.3
EQUIV. H ₂	0.42	0.36	0.24	0.29	0.19

ENGELHARD MINERALS & CHEMICALS
CALCULATIONS

SHEET NO. _____ OF _____

FILE _____

SUBJECT _____

DATE _____

BY _____

Table VII : Catalyst Screening Summary
Catalytic Partial Oxidation
of No. 2 Oil

Run No. CPO Catalyst Active Metals	# 7458 CPO-3 Pt/Pd	# 7458 CPO-3 Pt/Pd	# 7458 CPO-3 Pt/Pd	# 7458 CPO-3 Pt/Pd	
Condition(s)					
O ₂ /C	0.374	0.326	0.287	0.379	
H ₂ O/C	2.50	2.16	1.86	2.50	
Oil Preheat (°F)	845	850	845	850	
S. R. Furnance (°F)	1472	1472	1472	1472	
τ ($\times 10^{-3}$ sec)	19	19	19	19	
Dry Gas Composition (%)					
H ₂	5.45	3.98	3.84	4.19	
CO	11.44	8.86	7.82	9.64	
CO ₂	7.14	7.97	8.17	7.85	
N ₂	64.09	65.07	64.45	66.14	
CH ₄	2.89	2.59	2.85	2.23	
C ₂ H ₆	0.28	0.33	0.36	0.28	
C ₂ H ₄	5.11	5.91	6.44	5.03	
C ₃ H ₆	1.39	1.97	2.27	1.63	
Other HC					
Carbon Balance, %	87.1	81.8	76.6	85.5	
HC Conversion, %	46.8	38.8	35.0	44.1	
Equiv. H ₂	0.37	0.24	0.20	0.30	

HSH 6/29/80

TABLE VIII

CATALYST SCREENING SUMMARY*

Steam Reforming Catalysts in the ATR Mode

(CPO Catalyst = Pt/Pd/Monolith)

RUN NO.	7331**	7403	7466	7471	7478***
SR CATALYST	FP-13	FP-13	FP-33	FP-31	FP-30
ACTIVE METAL(S)	Rh	Rh	Pt/Rh	Pt/Rh	Pt/Rh
MODE	Screening	Aging	Aging	Aging	Aging
CONDITIONS:					
H ₂ O/C	2.59	2.59	2.54	2.53	
O ₂ /C	0.41	0.41	0.41	0.40	
TEMPERATURES, °F					
OIL PREHEAT	840	850	845	850	
AFTER CPO	1581	1607	1490	1562	
SR BED TOP	1499	1580	1490	1544	
" " MID	1443	1463	1483	1512	
" " BOTTOM	1458	1436	1463	1416	
BELOW SR BED					
SR FURNACE	1517	1517	1517	1517	
DRY GAS COMPOSITION, MOLE%					
H ₂	37.20	34.43	11.91	24.74	
CO	10.55	9.75	12.03	9.81	
CO ₂	13.33	14.12	8.31	12.48	
N ₂	37.77	39.45	58.77	47.81	
CH ₄	0.97	1.55	2.72	2.51	
C ₂ H ₆	0.01	0.02	0.24	0.14	
C ₂ H ₄	-	-	3.79	1.62	
C ₃ H ₆	-	-	0.93	0.50	
OTHER HC	No	Wax	Yes	Yes	
HYDROCARBON CONV, %	96.0	95.6	57.3	93.7	
EQUIVALENT HYDROGEN	1.93	1.72	0.63	1.06	
COKE OBSERVED ?	No	No	Yes	Yes	

* Results reported are those after 3 hours on oil feed.

** Usual run conditions, i.e., 2 hour propane run.

*** This run was terminated in the first hour on stream due to pressure increase.

TABLE IX

DRY GAS COMPOSITION

(Run 7403; C₃H₈ ATR (CPO-1 + FP-13))

Hours on Stream	% DRY GAS COMPOSITION							
	H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄ C ₃ H ₆
1	36.32	6.24	14.27	42.49				
3	35.27	5.70	14.45	43.88				
5	35.37	5.80	14.47	43.63				
8	35.09	5.85	14.58	43.74				
11	36.31	6.28	14.46	42.23				
14	35.23	6.23	14.00	43.36				
16	36.36	6.36	14.47	42.09				
19	35.43	5.94	14.65	43.24				
21	35.43	5.84	14.47	43.47				

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run 7403; $H_2O/C = 2.59$; $O_2/C = 0.41$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													
		H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₆	C ₅ ⁺
1		35.67	9.67	14.33		38.29	1.40								
2		35.21	9.75	14.22		38.60	1.55	0.01							
3		34.43	9.75	14.12		39.45	1.55	0.02							
4		34.55	9.87	13.87		39.36	1.58	0.03			0.02				
5		33.97	9.99	13.75		39.85	1.65	0.03			0.05	0.09			
6		33.47	10.01	13.61		40.29	1.66	0.04			0.10	0.12			
7		32.88	10.09	13.44		40.85	1.70	0.05		0.30	0.18	0.15			
8		32.24	10.14	13.21		41.49	1.79	0.06			0.29	0.12			
9		31.08	10.36	12.96		42.32	1.88	0.07		0.03	0.44	0.20		0.01	

* Catalysts: CPO-1 + 30ml FP-13

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run #7466; $H_2O/C = 2.54$; $O_2/C = 0.41$)

Hours on Stream	Temp.	% DRY GAS COMPOSITION													
	(°C)	H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₅	C ₅ ⁺
1		27.02	10.14	12.28		46.15	1.91	0.15	0.07		1.16	0.35	0.01	0.07	
2		16.07	11.64	9.33		55.38	2.40	0.21	0.07	0.01	3.04	0.76	0.06	0.22	
3		11.91	12.03	8.31		58.77	2.72	0.24	0.07	0.02	3.79	0.93	0.07	0.26	
4		11.91	11.99	7.85		59.03	2.86	0.25	0.06	0.01	3.96	0.88	0.07	0.26	
5		9.86	12.09	7.97		60.43	3.05	0.26	0.03	0.01	4.16	0.88	0.06	0.26	

* CPO-2 and FP-33 Catalysts

HSB 7/8/80

TABLE XII

Dry Gas Composition for Autothermal Reaction of No. 2 Oil.

(Run #7471; $H_2O/C = 2.53$; $O_2/C = 0.40$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													
		H ₂	CO	CO ₂	O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₂ H ₄	C ₃ H ₆	C ₄ ⁼	C ₄ H ₆	C ₅ ⁺
1		31.15	8.17	14.62		42.34	3.01	0.08							
2		28.50	10.24	12.33		43.86	2.85	0.15			0.16	0.11			
3		24.74	9.81	12.48		47.81	2.51	0.14	0.07	0.01	1.00	0.36		0.04	
4		22.09	9.47	12.18		49.95	2.61	0.16	0.07	0.01	1.62	0.50		0.09	
5		20.11	9.35	11.98		51.82	2.58	0.16	0.07		2.32	0.58	0.02	0.15	
											2.60	0.71	0.01	0.16	

* CPO-2 and FP-31 Catalysts

* CP0-2 and FP-31 Catalysts

HSB 7/8/80

SUBJECT _____

FILE _____

DATE 5/19/80

BY HSH

FIGURE 1 : GAS COMPOSITION AFTER
CPO CATALYST (CPO-2)

SUBJECT _____

FIGURE 2 : GAS COMPOSITION AFTER
CPO CATALYST - EFFECT
OF SAMPLING RESIDENCE TIME.

SUBJECT _____

FILE _____

DATE 6/29/80

BY HSH

FIGURE 3 : GAS COMPOSITION AFTER
CPO CATALYST
(CPO-3 Pt/Pd/MONOLITH)

FIGURE 4

AGING EFFECT ON
STEAM REFORMING
CATALYSTS

FIRST 20 HOURS
ON PROPANE, AIR
AND STEAM.

Figure 5: XRD Patterns of Used FP-1 Catalyst

a. "as received"

b. Residue after leaching with 50% aq. HBF_4

Rhodium and Platinum major peaks also marked

FIGURE 6. FLOW SHEET FOR NEW ATR UNIT

HSH 2/25/80

FIGURE 7

SCHEMATIC DRAWING
OF THE NEW ATR REACTOR

HSH 3/14/80

FIGURE 8

DETAILED DRAWING AUTOTHERMAL REACTOR

ENGELHARD
INDUSTRIES