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

MASTER

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

ABSTRACT

Catalysts are being screened to steam reform hydrocarbons in an autothermal reformer. Twenty-one samples have been screened in a one inch diameter reactor using No. 2 oil as the hydrocarbon feed. A series of platinum-rhodium catalysts were evaluated to study the effect of varying compositions. A sample containing 1.7% Pt/0.3% Rh was most active but the difference among the samples was within the range of test variability.

Development of a more realistic test has been started. The effect of O_2/C level on the gas composition leaving the CPO section has been determined. The amount of unreacted oil increases as O_2/C level decreases. The unreacted oil is more aromatic than the feedstock. The gas composition contains considerably more olefins as the O_2/C level decreases.

Post-run catalyst characterization indicates that the catalyst carrier does not deteriorate in the ATR test. A drastic decrease in CO chemisorption is noted on the Pt/Rh samples. This decline in CO chemisorption could either be due to metal sintering or to carbon deposition on the metal. Other analysis are required to determine which is causing the decline in CO chemisorption. Very low coke levels were found on Pt, Rh, and Pt/Rh samples. Addition of Rh to nickel reduces the coke level over that observed for nickel catalysts.

REVIEW BY TASKSTask 5.1 Catalyst Screening Using an ATR Test Unit

Catalyst screening continued throughout this quarter with major emphasis on evaluating Pt/Rh catalysts of varying composition. Other samples were tested to round out this first pass screening. These included a sample containing Pd, another sample with 25% nickel, a Rh/Re sample, and a Ni/Rh catalyst. At the end of the quarter, tests were made to study the effect of O₂/C ratio on the gas composition exiting the CPO section. Details of these tests will be presented below.

A. Platinum-Rhodium Catalysts of Varying Metal Ratios

The catalysts were prepared with a total precious metal content of 2% with the following compositions:

<u>Catalyst No.</u>	<u>Active Metal(s)</u>	<u>Metal Content, wt %</u>
FP-18	Pt	2.0 Pt
FP-16	Pt/Rh	1.7 Pt/0.3 Rh
FP-20	Pt/Rh	1.4 Pt/0.6 Rh
FP-14	Pt/Rh	1.0 Pt/1.0 Rh
FP-13	Rh	2.0 Rh

The catalysts were tested in the ATR unit described previously under the following conditions:

Preheat Temperature	:	840°F (449°C)
H ₂ O/C	:	2.6
O ₂ /C	:	.41-.43
Feedstock	:	No. 2 oil

The unit is started using propane, air, and water under fuel rich conditions as a means of heating the steam reforming catalyst bed to operating temperatures. This requires about 1.5 to 2 hours. When the steam reforming catalyst is at operating temperature, the oil feed is started and the propane is stopped. Each test lasted about six hours on oil feed.

Results after 3 hours on No. 2 oil feed are listed in Table II. Methane breakthrough decreases with increasing Pt content. Although Pt alone is a good steam reforming catalyst, it is not as selective to the olefins as is rhodium. In Figure 1, the total hydrocarbon breakthrough is plotted against the ratio of Pt to total metal, i.e., $Pt/(Pt + Rh)$. These results show advantages for the sample containing 1.7% Pt and 0.3% Rh. However, since the results are very close together for all of these precious metal samples, further testing under more demanding conditions will be required to distinguish among these samples. Some coke was observed on sample FP-16 which gave the highest hydrocarbon conversion. This needs to be checked in the next series of tests.

B. Other Samples

The test results for other samples tested this quarter are listed in Table III. The Pd sample was essentially inert for steam reforming. In addition, it produced more coke than any other catalyst tested (16.3% coke on catalyst after 4 hours on No. 2 oil feed).

A catalyst containing 25% nickel was prepared to follow up on a lead from earlier testing that suggested better performance for high nickel content catalysts. However, this sample was considerably less active than the other nickel catalysts tested previously. Analysis of the metal crystallite size of this sample may help to explain its poor activity.

Another sample using rhodium and nickel was prepared. Compared to previous Ni/Rh catalysts, it was less active and further analysis is required to explain the differences. In FP-25, 1.4% rhenium is combined with 0.6% rhodium. Although this is not as active as the Ni/Rh samples, it has considerable activity for the amount of metal present. It was also coke free after the test. These last two samples are further compared in Figures 2 and 3 where the exit hydrocarbon concentration is plotted as a function of time on stream. Although the Re/Rh sample is less active than nickel/rhodium, the stability of the two samples are comparable as shown by the slope of the curves.

More detailed comparisons among these samples can be obtained from the data in Tables IV-XII which list the gas composition observed throughout the test runs.

C. The Effect of O₂/C Ratio on the Gas Composition from the CPO Section

So far in this contract catalysts have been screened under similar test conditions. The catalysts can be ranked in groups as listed in Table I with some very active catalysts such as Pt/Rh and some very inactive samples such as Pd. However, even for the best samples these results indicate fresh activity only. The next task in this work is to revise the test procedure such that a choice can be made among the more active samples. There are several methods of increasing severity with the existing test equipment. Lowering O₂/C ratio and further increasing the space velocity are two methods of interest.

In previous reports the composition of the material entering the steam reforming section was determined for an O₂/C ratio of 0.47. The composition at lower O₂/C ratios would be of more interest for realistic testing. In Run 7388 the composition of the gas from the CPO section was measured at three levels of O₂/C. Inert alumina was packed in the steam reforming catalyst section. It was assumed that no further reaction occurred after the gas left the CPO section.

Results are listed in Table XIII and some of the components are plotted versus O₂/C level in Figure 4. The GC used measures components through C₅. Surprisingly, no C₅ compounds were observed but heavier material was condensed out. Preliminary results indicate that the unconverted oil was heavier than the feedstock indicating that it was more aromatic than the feed. Carbon accountability, that is, carbon in gaseous product versus carbon in the feedstock varied with O₂/C ratio:

<u>O₂/C</u>	<u>Carbon Accountability, %</u>
0.47	96.5
0.43	92.9
0.39	86.9

In these runs the H₂O/C ratio was constant at about 2.6 and the inlet temperature to the CPO section was constant at about 450°C. The exit temperature from the CPO section was about 840°C and decreased slightly with O₂/C level as expected. It was not possible to increase the preheat temperature in this small unit. Higher preheat temperatures should be beneficial by increasing the oil conversion in the CPO section.

Task 5.3 Catalyst Characterization

The data summarizing the post-run catalyst characterizations is presented in Table XIV. Four modes of catalyst deactivation had been postulated which we hoped could be identified using the data in Table XIV. These deactivation modes along with the type of measurement used to identify these deactivation modes are listed in Table XV.

In reviewing the BET surface area data, the surface area loss after the run has been minimized to about 10% for sample FP-1 when compared to samples SF-3B (51% loss) and FP-6 and FP-3 (35% loss). Since the difference between these samples is in the stabilizer system used, the surface area loss can be best minimized by using the stabilizer for FP-1.

A further indication of deterioration of the catalyst carrier is loss in crush strength. For FP-1 the average crush strength before and after use remained the same (10.6 average before, 11.2 average after). Further the shift in pore size distribution for the carrier is minor after steaming in 80% H₂O-20% N₂ at 1700°F for 16 hours. The pore size distribution as measured by nitrogen desorption and calculated via the BJH technique shows a shift in average pore diameter from 170 Å before steaming to 190 Å after steaming.

From this preliminary data, we may conclude that since the BET SA and crush strength losses are small and there is only a slight shift to larger pores, the carrier is not degrading and, therefore, not occluding the active metals.

To measure changes in the dispersion of active metals, chemisorption of an active gas is used. For the precious metal catalysts, CO chemisorption was used. From the available data, a very large decrease for the used samples is measured. Since occlusion by the carrier does not appear to be playing a major role, the decrease in chemisorption may indicate a rapid sintering of the active metals. As the active metals at the surface sinter, the crystallite sizes increase, thus lowering the surface to volume ratio of the metal site resulting in less metal area being available at the surface to chemisorb (or react) with gases. We plan X-ray diffraction work to confirm this increase crystallite size effect.

The third mode of deactivation proposed is coke deposition. In Table XVI, some selected values for the coke deposited after use are listed. In general the amount of coke deposited is very low for Pt, Rh and Pt/Rh catalysts but higher for nickel containing samples. (Samples with very low activity like FP-9 (Ni) and FP-4 (Ni/Co) also have very low coke deposited). However, addition of either Rh or Pt to our nickel catalyst substantially reduces the coke make while increasing the conversion. Nickel-rhodium combinations are particularly attractive since these also give very low ethylene breakthrough.

The only sample which can be rejected because of excessive coke make is FP-21 (Pd) which yielded 16.3 weight percent coke while giving a conversion lower than that of FP-4 which was essentially non-active.

The fourth mode of deactivation was sulfur poisoning. However, for the short runs of 6 hours, the sulfur picked up by the catalysts are all similar. A longer aging test will be necessary to differentiate between catalysts.

Our preliminary conclusions based on post-run catalyst characterizations are:

- ° The carrier does not deteriorate as indicated by slight changes in BET SA, Crush Strength and PSD Measurements.
- ° Metal sintering for Pt/Rh samples may have occurred since there is a drastic loss in CO chemisorbed. However, this loss in CO chemisorption could be caused by carbon or sulfur covering the metal surface.
- ° Assays for coke deposited on used catalysts show coke deactivation only for a Pd sample. Addition of Rh to Ni samples reduces the coke level substantially. Very low coke levels were found for Pt, Rh and Pt/Rh samples.
- ° Sulfur content for all used samples was similar. Longer aging runs are required to determine effect of both sulfur and coke as deactivating agents.

TABLE I
STEAM REFORMING CATALYST

TEST RESULTS RANKED BY HYDROCARBON CONVERSION

<u>CATALYST NO.</u>	<u>ACTIVE METAL(S)</u>	<u>METAL CONTENT, %</u>	<u>HYDROCARBON CONVERSION, %</u>
FP-16	Pt/Rh	1.7/0.3	97.8
FP-1	Pt/Rh	1.4/0.6	96.9
FP-14	Pt/Rh	1.0/1.0	96.6
FP-13	Rh	2.0	96.0
FP-18	Pt	2.0	95.4
FP-3	Pt/Rh	1.4/0.6	95.3
FP-20	Pt/Rh	1.4/0.6	95.1
FP-7	Ni/Rh	14.5/0.5	93.5
FP-12	Ni/Pt/Rh	14.5/0.35/0.15	91.6
FP-19	Ni/Rh	15.0/0.5	91.3
FP-22	Ni/Rh	14.5/0.5	91.0

RMV
7/17/80

TABLE I - (Con't)
STEAM REFORMING CATALYST

TEST RESULTS RANKED BY HYDROCARBON CONVERSION

<u>CATALYST NO.</u>	<u>ACTIVE METAL(S)</u>	<u>METAL CONTENT, %</u>	<u>HYDROCARBON CONVERSION, %</u>
G90C	Ni	15	90.7
SF3B	Ni	15	89.7
FP-5	Ni/Ru	14.5/0.5	88.2
FP-6	Ni	15	87.8
FP-8	Ni/Pt	14.5/0.5	87.3
FP-25	Re/Rh	1.4/0.6	84.6
FP-9	Ni/La	10/5	83.0
FP-4	Ni/Co	7.5/7.5	79.6
FP-27	Ni	25	72.5
FP-21	Pd	2.0	61.0

Rmy
4/14/80

TABLE II
CATALYST SCREENING SUMMARY

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

RUN NO.	7344	7340	7348	7328	7331
SR CATALYST	FP-14	FP-20	FP-16	FP-18	FP-13
ACTIVE METAL(S)	Pt/Rh 1.0/1.0	Pt/Rh 1.4/0.6	Pt/Rh 1.7/0.3	Pt 2%	Rh 2%
CONDITIONS:					
H ₂ O/C	2.58	2.58	2.58	2.60	2.59
O ₂ /C	0.414	0.41	0.41	0.41	0.41
TEMPERATURES, °F					
OIL PREHEAT	840	840	840	845	840
AFTER CPO	1589	1589	1627	1562	1581
SR BED TOP	1551	1539	1533	1526	1499
" " MID	1449	1438	1447	1463	1443
" " BOTTOM	1447	1440	1447	1445	1458
BELOW SR BED					
SR FURNACE	1517	1517	1517	1517	1517
DRY GAS COMPOSITION, MOLE%					
H ₂	36.44	37.04	36.38	36.28	37.20
CO	10.96	10.16	11.03	10.47	10.55
CO ₂	13.27	13.33	13.33	13.09	13.33
N ₂	37.87	38.70	38.05	39.37	37.77
CH ₄	0.84	0.65	0.56	0.56	0.97
C ₂ H ₆	0.01	-	-	0.02	0.01
C ₂ H ₄	-	-	-	0.09	-
C ₃ H ₆	-	-	-	0.07	-
OTHER HC	-	-	-	0.05	-
HYDROCARBON CONV, %	96.6	95.1	97.8	95.4	96.0
EQUIVALENT HYDROGEN	1.95	1.86	1.93	1.81	1.93
COKE OBSERVED?	No	No	Yes	No	No

TABLE III

CATALYST SCREENING SUMMARY

Steam Reforming Catalysts in the ATR Mode

(CPO Catalyst = Pt/Pd/Monolith)

RUN NO.	7357	7365	7351	7325
SR CATALYST	FP-25	FP-22	FP-27	FP-21
ACTIVE METAL(S)	Rh/Re	Ni/Rh	Ni 25%	Pd
CONDITIONS:				
H ₂ O/C	2.61	2.57	2.57	2.61
O ₂ /C	0.41	0.42	0.42	0.43
TEMPERATURES, °F				
OIL PREHEAT	835	840	845	840
AFTER CPO	1566	1580	1544	1530
SR BED TOP	1553	1562	1547	1533
" " MID	1508	1483	1522	1528
" " BOTTOM	1481	1454	1497	1512
BELOW SR BED				
SR FURNACE	1517	1517	1517	1517
DRY GAS COMPOSITION, MOLE%				
H ₂	30.04	33.76	23.96	17.38
CO	9.41	9.73	10.03	10.08
CO ₂	13.47	40.01	11.72	9.48
N ₂	43.64	40.02	48.96	56.29
CH ₄	1.60	1.40	2.04	2.45
C ₂ H ₆	0.12	0.07	0.17	0.19
C ₂ H ₄	0.67	0.20	1.76	3.00
C ₃ H ₆	0.22	0.09	0.50	0.77
OTHER HC	0.10	0.05	0.23	0.37
HYDROCARBON CONV, %	84.6	91.0	72.5	61
EQUIVALENT HYDROGEN	1.41	1.70	1.10	0.8
COKE OBSERVED?	No	No	Yes	Yes

TABLE IV

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-14

(Run #7344; $H_2O/C = 2.58$; $O_2/C = 0.414$)

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 ⁺
1		37.25	10.97	13.50		37.51	0.77							
2		36.68	10.92	13.35		37.63	0.81							
3		36.44	10.96	13.27		37.87	0.84	0.01						
4		36.14	11.07	13.21		38.08	0.87	0.01						
5		36.13	10.98	13.20		38.16	0.88	0.11						
6		35.42	11.05	13.17		38.80	0.90	0.01						

Catalysts: CPO + FP-14 (1% Pt - 1% Rh/Al₂O₃)

Dry Gas Composition for Autothermal Reaction of N. 2 Oil Using FP-20

 (Run #7340; $H_2O/C = 2.58$; $O_2/C = 0.41$)

Hours on Stream	Temp.	% DRY GAS COMPOSITION													C ₅ ⁺
	(°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	
1		37.75	10.50	13.17		37.91	0.53								
2		37.22	10.21	13.30		38.53	0.61								
3		37.04	10.16	13.33		38.70	0.65								
4		36.56	10.33	13.22		39.07	0.67	0.01							
5		36.45	10.26	13.23		39.20	0.72	0.01							

 Catalysts: CPO + FP-20 (1.4%Pt - 0.6%Rh/Al₂O₃)

Table VI

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-16

(Run #7348; $H_2O/C = 2.58$; $O_2/C = 0.41$)**ENGELHARD**
INDUSTRIES

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 ⁺	C ₅ ⁺
1		36.91	10.96	13.51		37.48	0.51								
2		36.33	11.05	13.39		38.02	0.59								
3		36.38	11.03	13.33		38.05	0.56								
4		36.28	11.08	13.31		38.12	0.57								
5		36.28	11.06	13.24		38.19	0.60								
6															

Catalysts: CPO + FP-16 (1.7% Pt - 0.3% Rh on stabilized Al₂O₃)

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-18

(Run #7328; $H_2O/C = 2.60$; $O_2/C = 0.41$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													C ₅ ⁺
		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 ⁺	
1		36.86	10.51	13.11	-	38.88	0.51	-	0.05		-	0.04			
2		36.68	10.49	13.17	-	38.94	0.57	-	0.05		0.05	0.06			
3		36.28	10.47	13.09	-	39.37	0.56	0.02	0.05		0.09	0.07			
4		35.63	10.75	12.76	-	39.92	0.61	0.03	0.05		0.14	0.10			
5		35.32	10.47	12.95	-	40.33	0.58	0.03	0.05		0.17	0.10			
6															

Catalysts: CPO + FP-18 (2% Pt/Al₂O₃)

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-13
 (Run #7331; $H_2O/C = 2.59$; $O_2/C = 0.41$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													C ₅ ⁺
		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 ⁺	
1		37.64	10.49	13.21	-	37.71	0.90	-	-			-			
2		37.37	10.45	13.24		37.88	0.99	-	-			-			
3		37.20	10.55	13.30		37.77	0.97	0.01	-			-			
4		36.83	10.84	13.22		37.85	1.04	0.01	-			-			
5		37.07	10.71	13.18		37.84	0.99	0.01	-			-			
5															

Catalysts: CPO + FP-13 (2% Rh/Al₂O₃)

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run #7357; $H_2O/C = 2.61$; $O_2/C = 0.41$)

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 I	C ₁ -C ₄ **
1		31.36	9.13	13.94		42.53	1.53	0.10	0.06	-	0.45	0.17		0.02	2.33
2		30.64	13.73	13.73		43.02	1.58	0.10	0.06	0.01	0.58	0.24		0.03	2.60
3		30.04	13.47	13.47		43.64	1.60	0.12	0.06	-	0.67	0.22		0.04	2.71
4		29.79	13.45	13.45		43.86	1.62	0.12	0.06		0.77	0.26		0.04	2.87

* Catalysts: CPO + FP-25 (1.4% Re - 0.6% Rh)

** Total C₁ to C₄ hydrocarbons

Dry Gas Composition for Autothermal Reaction of No. 2 Oil

(Run #7365; $H_2O/C = 2.57$; $O_2/C = 0.42$)

Hours on Stream	Temp.	% DRY GAS COMPOSITION													C ₁ -C ₄ **
	(°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 ₂	
1		35.51	10.31	14.03		38.40	0.89	0.04	-		0.09	0.08			1.10
2		34.00	9.82	14.08		39.68	1.42	0.07	-		0.17	0.10			1.76
3		33.76	9.73	14.01		40.02	1.40	0.07	0.05		0.20	0.09			1.81
4		33.46	9.81	13.95		40.21	1.43	0.08	0.05		0.24	0.10			1.90

* Catalysts: CPO + FP-22 (14.5%Ni - 0.5%Rh)

** Total C₁ to C₄ hydrocarbons

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-2

 (Run #7351; $H_2O/C = 2.57$; $O_2/C = 0.42$)

Hours on Stream	Temp. (°C)	% DRY GAS COMPOSITION													C_5^+	ΣHC
		H_2	CO	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	$C_4^=$	C_4^+		
1		27.00	9.32	12.69		46.54	1.91	0.15	0.10	0.02	1.33	0.42	0.06	0.05		4.0
2		25.46	9.41	12.25		48.12	2.01	0.17	0.11	0.17	1.63	0.57	0.02	0.10		4.7
3		23.96	10.03	11.72		48.96	2.04	0.17	0.09	0.01	1.76	0.50	0.02	0.11		4.7
4		22.60	10.09	11.37		49.84	2.09	0.21	0.09	0.15	2.00	0.66	0.13	0.14		5.4
5																
6																

 Catalysts: CPO + FP-27 (25% Ni on Stabilized Al_2O_3)

Dry Gas Composition for Autothermal Reaction of No. 2 Oil Using FP-21

(Run #7325; $H_2O = 2.61$; $O_2/C = 0.43$)

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 ^{II}	C ₅ ⁺
1		20.98	8.71	11.47	-	53.23	2.41	0.17	0.06	-	2.16	0.62	0.03	0.17	
2		17.70	9.95	10.08	-	55.87	2.45	0.20	0.05	0.01	2.72	0.71	0.05	0.22	
3		17.38	10.08	9.48	-	56.29	2.45	0.19	0.06	0.02	3.00	0.77	0.05	0.24	
4		16.19	10.14	9.24	-	57.37	2.43	0.20	0.05	0.02	3.26	0.81	0.06	0.25	
5															

Catalysts: CPO + FP-21 (2% Pd/Al₂O₃)

TABLE XIII

DRY GAS COMPOSITION AFTER CPO REACTION OF NO. 2 OIL

 (Run #7388; $H_2O/C = \approx 2.6$)

Hours on Stream	$O_2/C^{(a)}$	% DRY GAS COMPOSITION ^(b)													
		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	ΣHC
1	0.47	12.46	15.23	6.49		59.94	2.04	0.17	0.03	-	2.84	0.56	0.06	0.17	5.87
2		11.00	15.50	6.20		60.26	2.08	0.17	0.04	-	2.92	0.62	0.07	0.19	6.09
3½	0.43	9.77	13.66	6.57		61.43	2.33	0.19	0.04	-	3.78	0.88	0.12	0.26	7.62
4½		9.22	13.53	6.64		61.76	2.43	0.20	0.04	0.03	3.91	0.88	0.09	0.28	7.86
6	0.39	7.40	11.88	7.28		63.05	2.74	0.23	0.04	0.03	4.70	1.11	0.14	0.37	9.36
7		6.76	11.91	7.31		63.51	2.84	0.23	0.05	0.03	4.74	1.09	0.13	0.35	9.46

 (a) O_2/C ratios are calculated from the product gas and the oil feed rate.

(b) Unconverted oil was observed throughout the run.

 (c) Coke was observed on downstream $\alpha-Al_2O_3$.

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TABLE XIV

SUMMARY OF POST-RUN CATALYST CHARACTERIZATION

Run #	Catalyst #	Composition	BET m ² /g		Porosity Hg cc/gm		Sorption* cc/gm		%C	%S
			Virgin	Used	Virgin	Used	Virgin	Used		
7238	FP-1	Pt-Rh	131	117		.4740	2.32	.34	0.47	0.03
7251	FP-1			117		.5131				
7242	FP-3	Pt-Rh	215	139		.5073	1.92	.44	0.33	0.02
7233	SF-3B	Ni	140	68	0.4368	.3620	4.45		5.30	0.10
7244	FP-6	Ni		117		.379			1.70	0.06
7255	FP-12	Ni-Pt		102		.422			0.09;1.2	0.06
7266	FP-9	Ni							0.22	0.07
7271	FP-7	Ni-Rh		102		.4428			0.15;0.24	0.01;0.02
7275	FP-4	Ni-Co							0.56	0.06
7277	FP-5	Ni-Ru							0.73	0.06
7283	FP-8	Ni-Pt		107		.5779			0.26	.041
7293	G90C	Ni	16.2	8.8	.215	.2892			0.08	.036
7302	G90C			5.0		.2425			0.20	.03
7198	FP-19	Ni-Rh		4.6		.2629			16.7	0.05
7325	FP-21	Pd	111		.3568		1.02	.03	.05	.01
7328	FP-18	Pt	109				1.81		.07	0.05
7331	FP-13	Rh	114				3.16		.07	0.03
7340	FP-20	Pt-Rh	111		.3545				.07	0.03
7344	FP-14	Pt-Rh	113				2.0		.07	0.03
7348	FP-16	Pt-Rh	111			.3511	2.04	.38	0.0	.004
7351	FP-27	Ni							4.9	.05
7365	FP-22	Ni-Rh							.05	.095

* Sorption data obtained by CO chemisorption except for those compositions containing Ni where H₂ chemisorption is used.

TABLE XV

Deactivation Modes Based Upon Post-Run Catalyst Characterizations
- Preliminary -

- Deterioration of Carrier Resulting in Occlusion of Active Metal(s)

- Indicated by:
- Loss of BET Surface Area
 - Decrease in Crush Strength
 - Shift in Pore Size Distribution

- Sintering of Active Metal(s)

- Indicated by:
- Decrease in Chemisorption
 - Changes in XRD Pattern

- Coke Deposition

- Measured by:
- Combustion Analysis

- Sulfur Poisoning

- Measured by:
- Combustion Analysis

TABLE XVI

COKE DEPOSITION

<u>Catalyst #</u>	<u>Run #</u>	<u>% C on Used Sample</u>	<u>% Conv.</u>	<u>Equiv. H₂</u>	<u>% C₂H₄</u>
G90C (Ni)	7302	0.04	89.0	1.59	0.54
SF-3B (Ni)	7233	5.30	89.7	1.67	0.31
FP-6 (Ni)	7244	1.70	87.8	1.65	1.70
FP-21 (Pd)	7325	16.3	61.0	0.8	3.00
FP-13 (Rh)	7331	0.06	96.0	1.93	ND*
FP-18 (Pt)	7328	0.05	95.4	1.81	0.09
FP-1 (Pt/Rh)	7238	0.47	96.9	1.99	ND*
FP-16 (Pt/Rh)	7348	ND*	97.8	1.93	ND*
FP-7 (Ni/Rh)	7271	0.17	93.5	1.83	0.05
FP-8 (Ni/Pt)	7283	0.26	87.3	1.64	0.26
FP-22 (Ni/Rh)	7365	0.01	91.0	1.70	0.20

*ND = Non detectable

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Figure 1 : Effect of Pt/Rh Ratios
On The Hydrocarbon
Breakthrough From The
ATR Unit

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FIGURE 2 : CH_4 And C_2H_4 Breakthrough
From the ATR Screening Unit

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Figure 3 : Total C₁ to C₄ Hydrocarbon Break-through From the ATR screening Unit

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FIGURE 4 : GAS COMPOSITION AFTER
C P O CATALYST

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