

SLURRY-PHASE FISCHER-TROPSCH CATALYSIS

by

Robert J. Gormley and Michael F. Zarochak
Pittsburgh Energy Technology Center
U.S. Department of Energy
P.O. Box 10940
Pittsburgh, Pa. 15236

ABSTRACT

The purpose of this research project is to evaluate a particular precipitated iron, copper, potassium catalyst, prepared at PETC, in a stirred slurry reactor against the objectives set forth by the DOE project management group. These goals for fiscal year 1991 (FY91) involve using a 0.7:1 H₂/CO to achieve a H₂+CO conversion of 88%. The allowed deactivation of the conversion is <1%/week. The selectivity to methane, ethane plus ethylene (C1+C2) should be <7% wt. The syngas feed should be ≥3.4 NL/g Fe hr. In experiments lasting two weeks, many of the stated goals were achieved. A new porous metal filtering system allowed daily draining of the reactor wax without significant loss of catalyst, even with a heavier catalyst loading. Two liquid medium were tested: Humphrey n-octacosane and EthylFlo poly-alpha-olefin. The effect of reactor internals on the bubble size was studied. A catalyst with cobalt present in addition to the other components was tested in hopes of gaining some improvement in stability. The main focus of this work was the stability of the catalyst.

INTRODUCTION

The Department of Energy at the Pittsburgh Energy Technology Center (PETC) has had an in-house research program of Fischer-Tropsch catalysis for many years [1,2,3,4,5,6,7,8,9,10,11,12]. In the past the Indirect Liquefaction division has conducted extensive testing of a precipitated iron, copper, potassium (Fe,Cu,K) catalyst in a slurry-phase reactor. The effect of catalyst pretreatment was investigated [2,5]. The activation gas was varied from H₂ to syngas to CO at various temperatures and important effects on the activity were observed. Also the effect of the feed syngas ratio was evaluated [6]. As the feed ratio was varied from 1:1 to 0.65:1 the decline in H₂+CO conversion was more rapid. Mossbauer experiments showed different carbide phases were produced with different activations [2]. Variations in the weight % K and the weight % Cu have been tested [2,5] for their effects on the activity of the precipitated Fe,Cu,K catalyst. A particular composition was chosen to work with at this time: 65.8% Fe, 2.9% Cu, 0.2% K.

Goals for the FT slurry reactor work were set out by DOE project management and are shown in Figure 1 for 1990 and 1991. Although the conversion goal is 88%, this is for a slurry bubble column. One would have to extrapolate to find what results would be needed in a stirred slurry reactor. One could aim for a lower conversion or a smaller feed rate in a stirred slurry reactor.

EXPERIMENTAL

The catalyst prepared at PETC was made by mixing ferric nitrate and copper nitrate in water with ammonium hydroxide at 80°C in a glass continuous precipitation unit [1]. The precipitation was done at pH7, followed by an 80°C washing. The filter cake was dried at 110°C in N₂ and vacuum, then crushed to -140 mesh. The different columns in Figure 2 show catalysts prepared from 1988 through 1991. Three batches, which had surface areas of 206,247 and 248 M²/g, were mixed together to make "MB6 before potassium addition". An incipient wetness technique was used to add potassium carbonate, followed by drying with stirring at 100°C, then by a N₂ and vacuum drying at 110°C. The catalyst was calcined in air at 350°C, then crushed and sieved to -325 mesh. The mean particle diameter of the catalyst, MB6, which was tested during this report period, was 20 microns. The final catalyst had 129 M²/g and 65.8% Fe, 2.9% Cu and 0.2% K.

All the experiments discussed in this report had the same start-up procedure, as shown in Figure 3. This involved loading catalyst and purified n-octacosane (Humphrey Chemical Co.) or poly-alpha-olefin 164 (Ethyl Corp.) into the 1 liter reactor. The reactor was then brought to a temperature of 280°C in helium with 1000 rpm stirring. The activation was carried out in CO at 280°C and 200 psig for 24 hours. The next day the temperature was decreased to 260°C, the stirring was stopped and the liquid level was dropped to the starting height. H₂/CO of 0.65:1 was introduced at 260°C and 200 psig. Every 24 hours, the stirring was stopped while the full flow was maintained. Then the valve connecting the internal filter with the liquid level trap was opened and closed several times with a pressure drop of 50 psi. This method of draining, developed at Texas A&M, gave a clear wax, relatively free of catalyst. The experimental reactor system is described in detail in reference [1].

This report provides data from two different one liter autoclaves with different internals. Slurry 1 (S1) was manufactured by Pressure Products Industries. Slurry 2 (S2) was manufactured by Autoclave Engineers. S2 consistently gave poorer conversion results than S1 until some changes were made.

RESULTS

A test with 4 weight% catalyst and purified n-octacosane, called S2-45, is shown in Figure 4. The H₂+CO conversion is plotted versus time on stream. The drop in conversion was

undesirably rapid during this test. In this and older tests, the wax liquid level was drained through several 325 mesh screens every 24 hours. The weight of catalyst loaded was 13g. During the collection of wax throughout the first 10 days the total weight of catalyst which left the reactor was 1.57 g. This was measured by reheating, stirring and sampling the hot wax with catalyst. This catalyst-wax mixture was ashed at 900°C leaving only oxidized catalyst. It was analyzed by atomic absorption and contained the correct percentage of iron. The last several days a total of 0.49 g of catalyst left the reactor. A not very careful cleaning of the reactor yielded 7.08g of catalyst. This does not add up to the 13 g loaded but does show the very least that left the reactor. Later on in other tests, with a sintered filter draining system, only 0.1 g of catalyst was lost during the first 15 days. Also, 10.0 g was recovered at the end of that run. The drop in conversion is too high during this test. Figure 5 shows the product distribution for test S2-45. The average methane plus ethane plus ethylene, C1+C2, was 8.5% for this test at 4.1 NL/g Fe hr.

Figure 6 shows some modifications made to S2 after test S2-45. The draining tube with screens was removed and replaced with a 3/4" diameter horizontal filter. This succeeded, as mentioned previously, in keeping most of the catalyst in the reactor. More importantly, a plexiglas reactor body was made to simulate the reactor. Gas was bubbled in through the gas inlet tube into a liquid paraffin wax. The bubbles observed with the old 1 1/4" diameter impeller on S2 were too large, at >2 mm, and they had a short residence time in the liquid. Both reactors use a hollow shaft with two holes in the top of the shaft to draw gas down in to be recirculated through the impeller. By changing the S2 impeller to 2" diameter, the bubbles decreased to < 0.5 mm size and had a longer residence time in the liquid. In fact, there were so many bubbles that the internal parts could not be seen at 1000 rpm. At < 700 rpm bubble size was poor. S1 always had the 2" diameter impeller and a good small bubble size. There are possibly other ways to achieve small bubble size than by adjusting the size of the impeller. One might be to have the impeller closer to the bottom of the reactor as the researchers at UOP have found.

Also it was found that the external zone 1 heat on S2 had been operated at a lower external temperature than on S1 for the last several tests. This could have led to less preheating of the incoming gases. So in future S2 tests the zone 1 temperature was kept higher at the expense of the temperature profile at the top of the reactor. Another thermowell was added that reached to the bottom of the reactor to ensure that the liquid profile was uniform.

Figure 7 shows the improvement obtained on test S2-48 by making several hardware changes including: an in-line sintered 0.5 micron filter, a 2" diameter impeller, three baffles instead of 2 and keeping the external zone 1 temperature as hot as zone

2. The conversion held stable for a longer time but there was then another problem that the filter plugged. By the tenth day, the draining took about an hour, unlike the case with the screen draining system. This upset the conversion because the stirring had to be stopped for that hour to drain. U.O.P. has gotten around this problem by keeping the stirring going and raising the height of the filter close to the top of the reactor so too much wax is not drained out. They also drain every eight hours. Without having technicians working overnight, this is not an option for our testing. In the future, a reactor will be built with two filters so that once one becomes plugged, the other will be used. In test S2-48, after the fourteenth day the zone 3 heater burned out and was off for five hours at night. This probably also adversely affected the conversion near the end of the test. There was some improvement in this test over S2-45, which was probably mainly due to the larger impeller size and therefore improved bubble hydrodynamics.

The hydrocarbon product distribution is shown in Figure 8 and the C1+C2 averaged 7% which meets the FY91 goals. This is however with an average H_2+CO conversion of 70%. This was at 4.1NL/g Fe hr which exceeded the goal of syngas flow of ≥ 3.4 NL/g Fe hr.

Figure 9 shows the results in S1-110 with 4 wt% catalyst and purified n-octacosane. A sintered 0.5 micron filter of smaller (1/2") diameter but greater (2") length was used. In this test, the catalyst and wax filtered very well and draining was fast even until the end of the test. This met the FY 90 goal of a drop in H_2+CO conversion of $\leq 1\%$ /day. The average H_2+CO conversion was around 73%.

Figure 10 shows the hydrocarbon product distribution for S1-110. The C1+C2 averaged 9.5% which is higher than the FY 91 goal and therefore not at a satisfactory level.

Figure 11 shows the results from S1-111. Three parameters were changed in this test. First, a higher weight loading of catalyst in wax, 10 wt%, was used. Eventually 20 wt% will be used since the slurry bubble column can handle this weight loading. Also, a new wax medium was used: EthylFlo poly-alpha-olefin 164. It is a hydrogenated paraffin centered around a carbon number of 30. It is a liquid at room temperature because of the degree of branching. This wax was not made by the Wurtz reaction so it did not have to be purified of bromine. It is also less expensive than n-octacosane. Also the flow was dropped from 4.1 to 3.1 NL/g Fe hr to ensure a high conversion. This is still close to the FY91 goal of 3.4 NL/g Fe hr and gave an average H_2+CO conversion of 81% over the first 11 days. The drop in conversion of 1%/day met the FY90 goal but not the FY91 goal. This time, with a higher catalyst loading and the 2" long sintered 0.5 micron filter there was a long draining time beginning at 10 days. This again meant the stirrer was off for over an hour. It sometimes took more than one additional hour

for the CO_2 produced to come back up to normal. This upset was probably not good for the catalyst as seen by comparing this test with S1-110 when the draining went quickly. The hydrocarbon product distribution is shown in Figure 12 for S1-111, yielding an average C1+C2 of 10.5 wt%. There is a trend that at this higher average H_2 +CO conversion of 81%, too much C1+C2 is produced. At least with this particular catalyst formulation, one can only achieve 7% C1+C2 at $\leq 70\%$ H_2 +CO conversion.

One other type of catalyst was prepared which contained 5 wt% cobalt in with the Fe,Cu,K catalyst. It was hoped that cobalt would give potentially less carbon formation since cobalt carbide is not believed to be the active species. This might have lead to a more stable catalyst with time on stream. The H_2 +CO conversion results in Figure 13 show a lower conversion of 67% was attained for S1-108. Many details of this preparation were different from the usual catalyst. Cobalt nitrate does not precipitate completely with ammonium hydroxide so potassium carbonate was used, along with a lower precipitation temperature of 50°C . A slower flow rate into the precipitator was used to prevent excessive bubbling by the CO_2 produced. The final catalyst had 55.2% Fe, 4.8% Co, 3.1% Cu, and 0.3% K.

Figure 14 shows period N from an Fe,Cu,K catalyst with 65.5% H_2 +CO conversion compared with period I from the Fe,Co,Cu,K catalyst with 66.5% H_2 +CO conversion. The C1+C2 for the Fe,Cu,K was 9.7 wt% while for the Fe,Co,Cu,K it was 17.2 wt%. So, either the cobalt's presence or the difference in preparative technique caused a lighter product to be made. The apparent shift constant is shown as being slightly lower for the Fe,Co,Cu,K. Also, the H_2/CO seen in the outlet is lower at 0.75 for the Fe,Co,Cu,K probably because more H_2 was used to make the lighter alkanes. The CO_2 made was similar for these two catalysts at similar conversions. In summary, the addition of cobalt did not seem to improve the test results and no further improvement was attempted.

CONCLUSIONS

The conclusions are shown in Figure 15. A stable H_2 +CO conversion of 70% to 80% was achieved for at least 300 hours at 260°C and 200 psig. The flow used was at 4.1 or 3.1 NL/g Fe hr which is near the FY 91 goal. The C1+C2 selectivity reached the goal of ≤ 7 wt% when conversion was $\leq 70\%$. At higher conversions, higher C1+C2's were obtained. One problem encountered was that halting the stirring for greater than one hour during wax draining decreased conversion. The one attempt at using a new EthylFlo poly-alpha-olefin wax produced good results. Also, it was discovered that bubble size decreases as the impeller diameter increases. The conversion is higher and can be maintained at a higher level over 15 days with this smaller bubble size.

FUTURE

Future plans are to: build a new slurry unit in another building, test 20 wt% catalyst loading, use a dual filter system to decrease draining time, and prepare a new master batch of catalyst for testing. Later plans are to conduct a round robin test with other labs and vary the catalyst preparation to achieve better activity.

ACKNOWLEDGEMENTS

The authors wish to thank John Boff and Fred Harke for the technical help provided.

DISCLAIMER

Reference in this paper to any specific commercial product, process or service is to facilitate understanding, and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

- 1 H.W.Pennline, M.F.Zarochak, R.E.Tischer and R.R.Schehl, Appl.Catal., 21 (1986) 313.
- 2 M.A.McDonald and M.F.Zarochak, Proc. of the 6th DOE Indirect Liquefaction Contractors' Review Meeting, Pgh., Pa, 1986, p.58.
- 3 H.W.Pennline, M.F.Zarochak, J.M.Stencel and R.J.Diehl, Ind. Eng. Chem. Res., 26 (1987) 595.
- 4 J.M.Stencel, J.R.Diehl, S.R.Miller, R.A.Anderson, M.F.Zarochak and H.W.Pennline, Appl. Catal., 33 (1987) 129.
- 5 M.F.Zarochak and M.A.McDonald, Proc. of the 7th DOE Indirect Liquefaction Contractors' Review Meeting, Pgh., Pa., 1987, p.96.
- 6 M.A.McDonald and M.F.Zarochak, Proc. of the 8th DOE Indirect Liquefaction Contractors' Review Meeting, Pgh., Pa., 1988, p.483.
- 7 J.P.Hackett and G.A.Gibbon, Automated Stream Analysis for Process Control, Vol.1, Academic Press, New York, 1982, p.95.
- 8 J.P.Hackett, G.A.Gibbon and J.A.Feldman, J.Chromatogr. Sci., 23 (1985) 285.
- 9 J.P.Hackett and G.A.Gibbon, J.Chromatogr. Sci., 27 (1989) 405.
- 10 R.A.Diffenbach and D.J.Fauth, J.Catal., 100 (1986) 466.
- 11 M.F.Zarochak, H.W.Pennline and R.R.Schehl, DOE/PETC/TR-84/5, U.S.Dept. of Energy, 1984.
- 12 J.P.Baltrus, J.R.Diehl, M.A.McDonald and M.F.Zarochak, Appl. Catal., 48(1989)199.

Figure 1

GOALS OF FISCHER-TROPSCH

SLURRY WORK FOR DOE

- To chose a catalyst, an activation technique, and perform synthesis with a ~0.7/1.0 H₂/CO gas that gives the listed results and is reproducible.

	<u>FY 90</u>	<u>FY 91</u>
- H ₂ + CO	88%	88%
CONVERSION		
- DEACTIVATION (H ₂ +CO CONV.)	≤ 1% / DAY	≤ 1% / WEEK
- C1 + C2	≤ 7% CH ₄ +	≤ 7% CH ₄ +
SELECTIVITY	ETHANE	C ₂ H ₆ +C ₂ H ₄
- SYN GAS FEED	≥ 2	≥ 3.4
ML/g-Fe, h		

Figure 2

Fe(NO₃)₃, Cu(NO₃)₂ plus NH₄OH YIELDS: 65.8% Fe, 2.9% Cu, 0.2% K

	M ² /G			
	MB4	MB5	FH003	MB6
	<u>Low Cu</u>			
80 ⁰ C Precipitation at pH 7				
80 ⁰ C Washing				
110 ⁰ C N ₂ and Vacuum Drying	145,163	?	?	206,247,248
Crush and Sieve, -140 Mesh				
20 ⁰ Impregnation with K ₂ CO ₃ /H ₂ O				
100 ⁰ C Stir-Drying in Air				222
110 ⁰ C N ₂ and Vacuum Drying				
350 ⁰ C Air Calcination				
Crush and Sieve, -325 Mesh	38,42	94,98	128	129

Figure 3

Run Procedures

- Bring reactor to temperature
 - 200 psig He
 - 1000 rpm
 - Room T to 280 °C

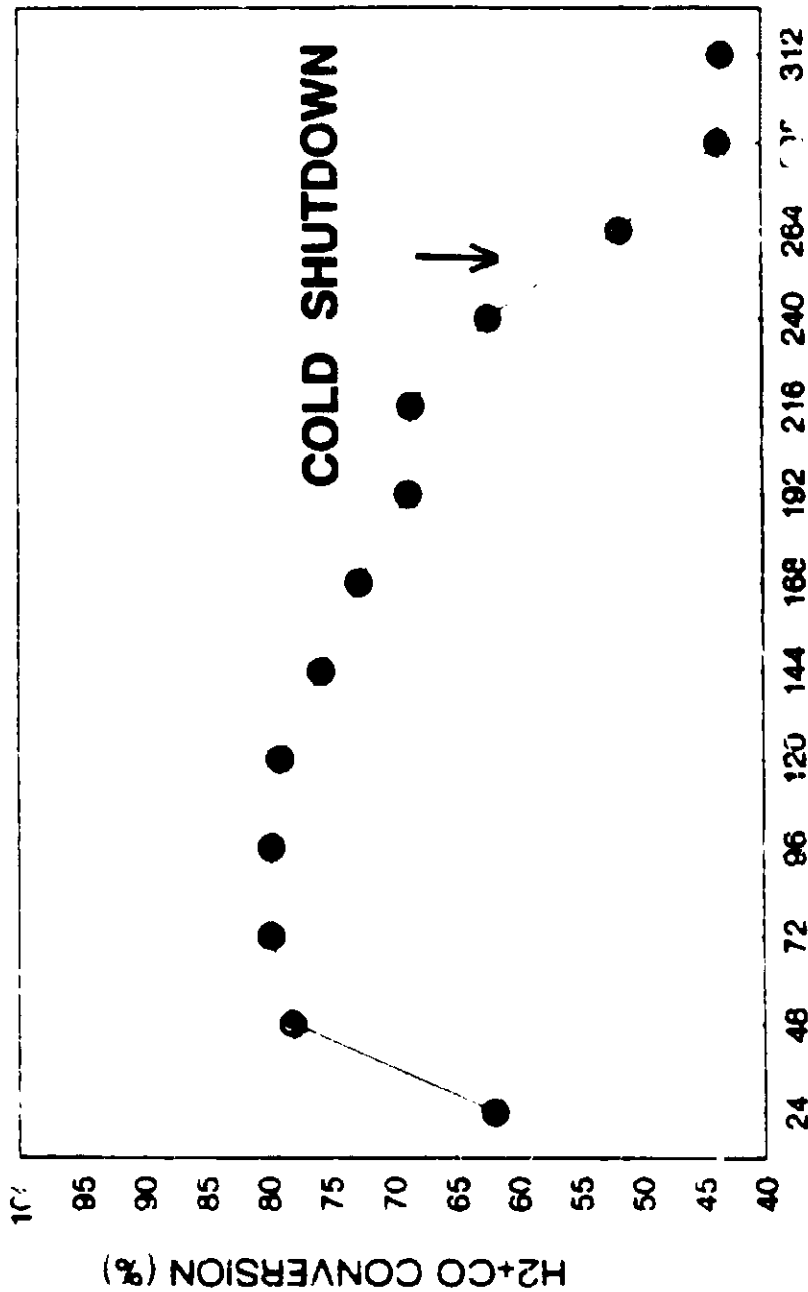
- Pretreatment
 - CO
 - 200 psig
 - 280 °C
 - 24 h

- Decrease to 260 °C, drain liquid with no stirring

- Introduce syngas
 - 0.65 H₂/CO
 - 200 psig
 - 260 °C

- Draining liquid during run:
 - Stop stirring while maintaining flow
 - Open/close valve from internal filter to liquid level trap while maintaining $\Delta P = 50$ psig

Figure
4 WT% CATALYST, PURE OCTADECANE
HYDROGEN PLUS CARBON MONOXIDE
CONVERSION LEVELS S2-45
CATALYST MB6-ABC



7.08g cat. Remains
 0.49g cat.
 1.57g cat.

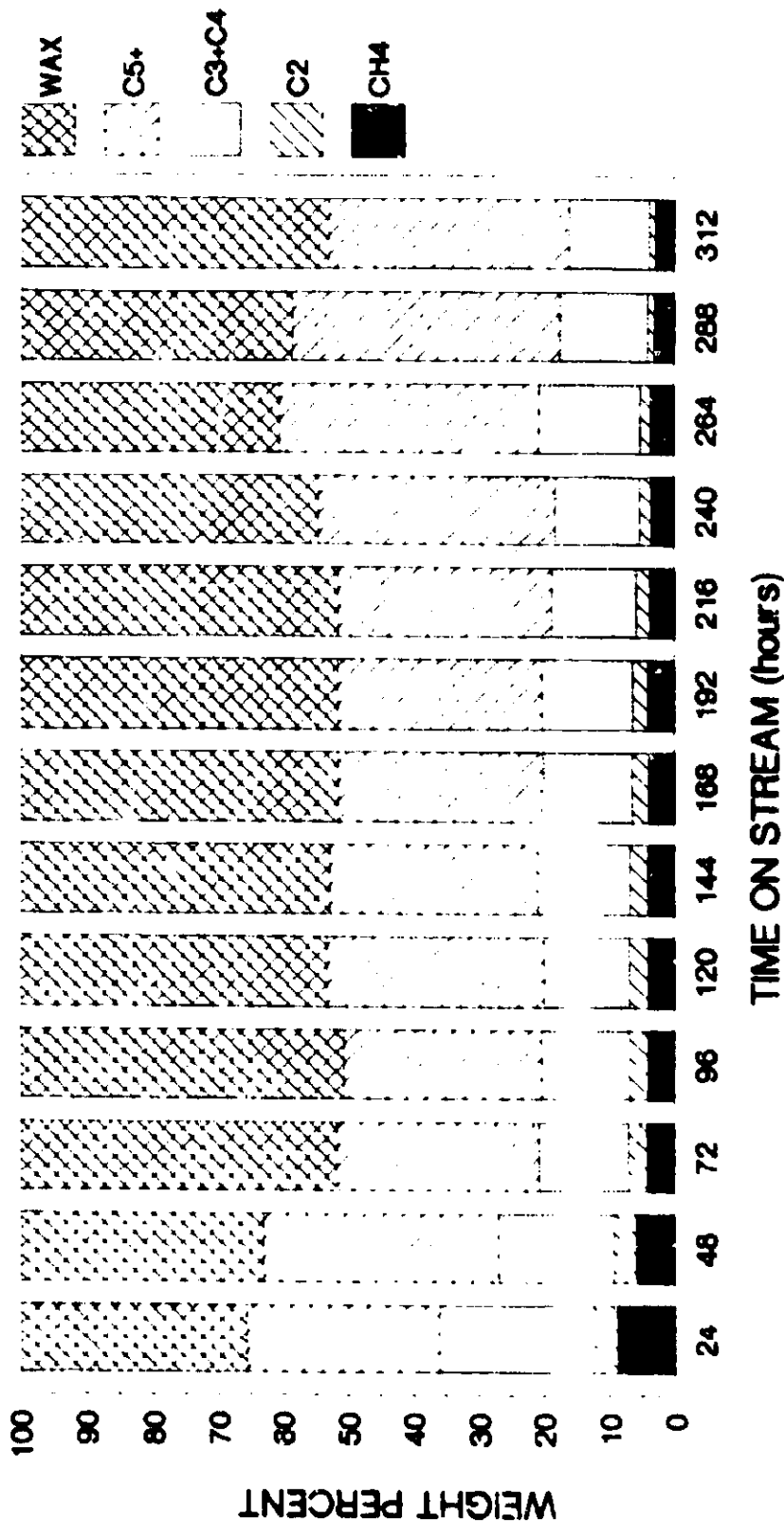
Activation CO, 280 C, 200 psig, 24 h
 Synthesis H₂/CO=0.65, 255 C, 200 psig
 4 NL/g-Fe. h

13.0g Catalyst at Start
DRAINING WAX THROUGH 325 MESH SCREENS

Figure 5

4 WT% CATALYST, PURE OCTACOSANE HYDROCARBON DISTRIBUTION EXPERIMENT S2-45

CATALYST MB6-ABC



Activation: CO, 280 C, 200 psig, 24 h
Synthesis: H₂/CO=0.65, 255 C, 200 psig
4.1 NL/g-Fe. h

Figure 6

SLURRY #2 WITH MODIFICATIONS

HEAT ZONE 3

HEAT ZONE 2

HEAT ZONE 1

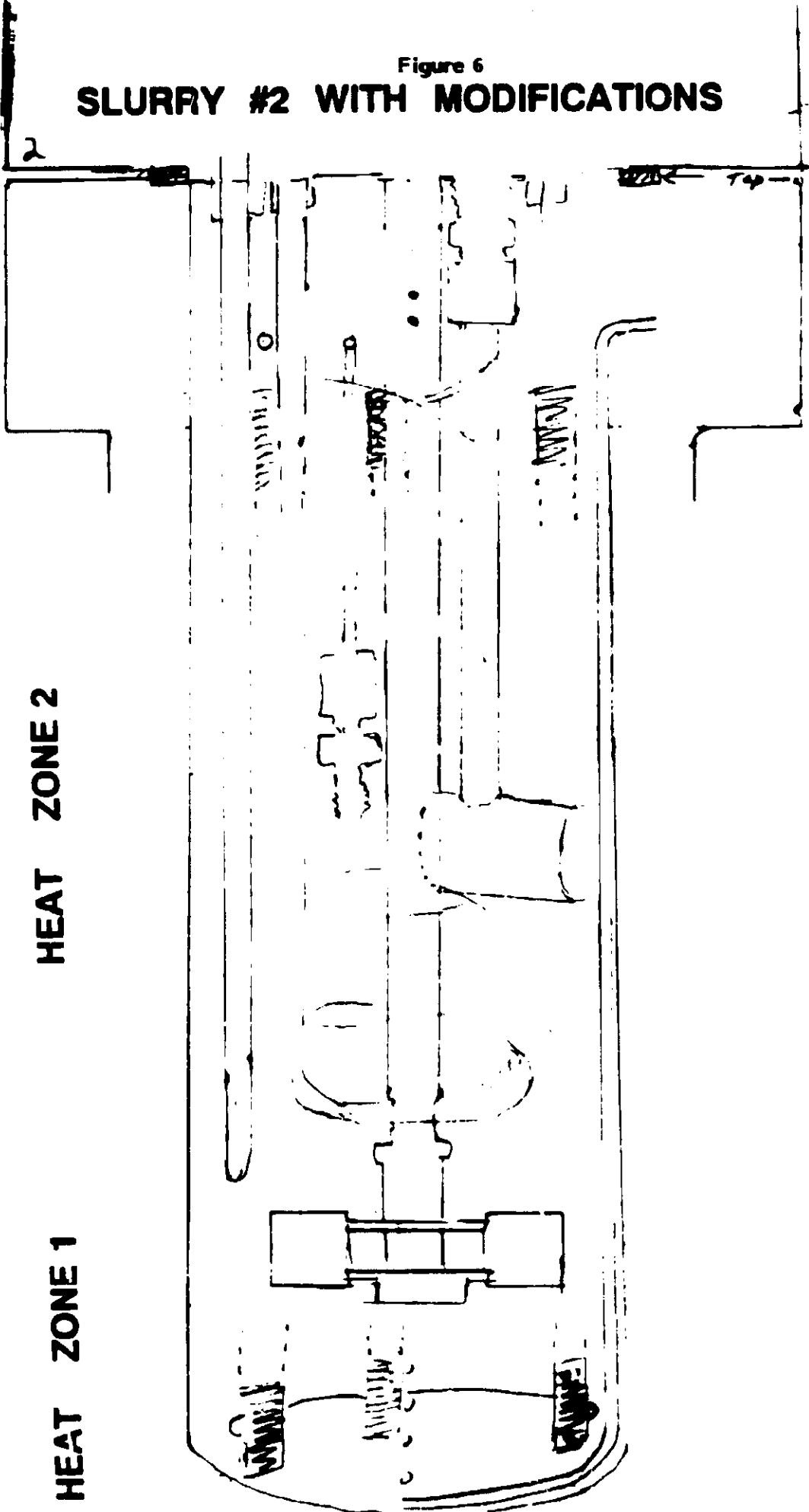
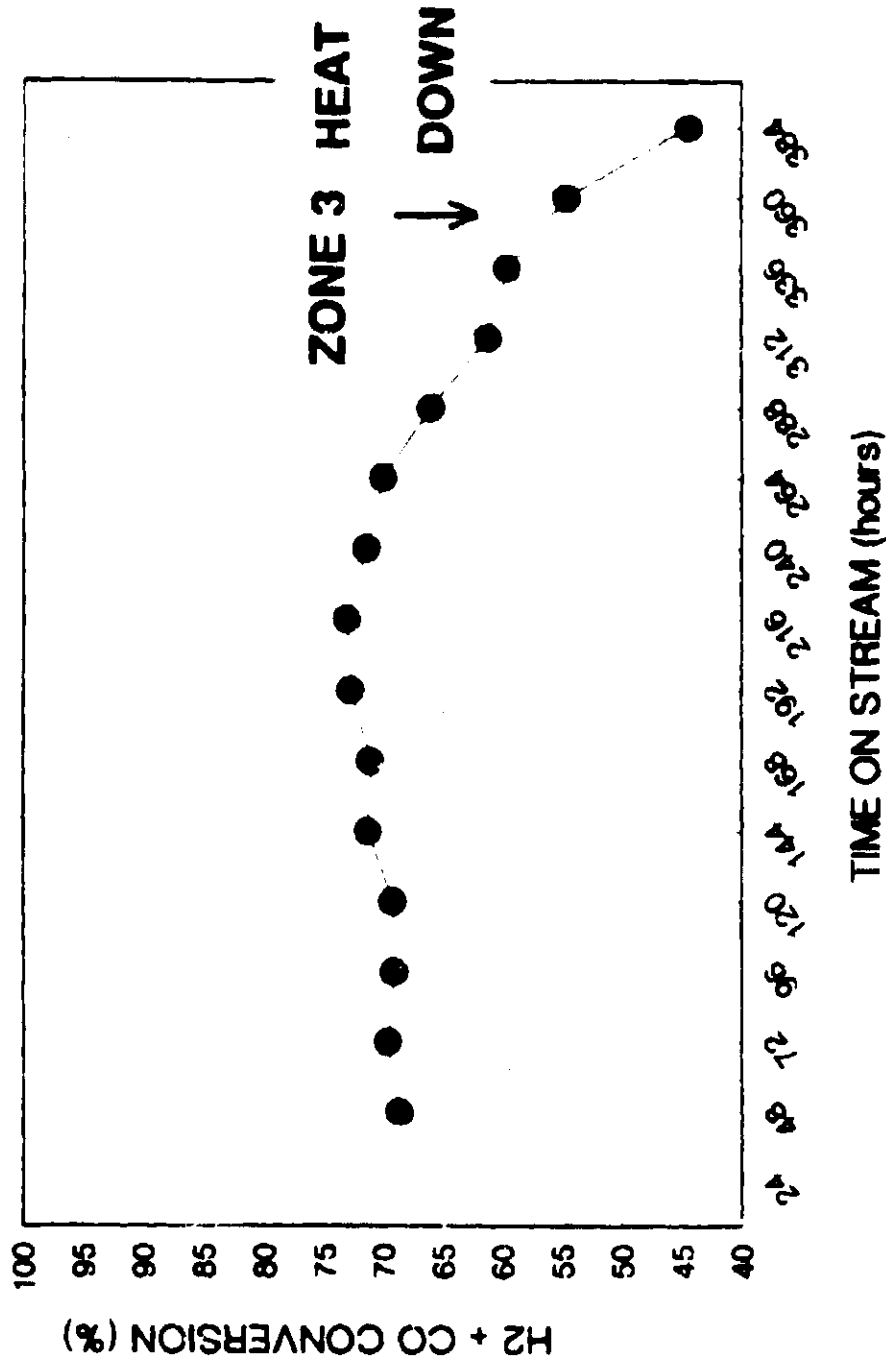


Figure 7

**4 WT% CATALYST, PURE OCTACOSANE
HYDROGEN PLUS CARBON MONOXIDE
CONVERSION LEVELS S2-48**

CATALYST: MB6-ABC

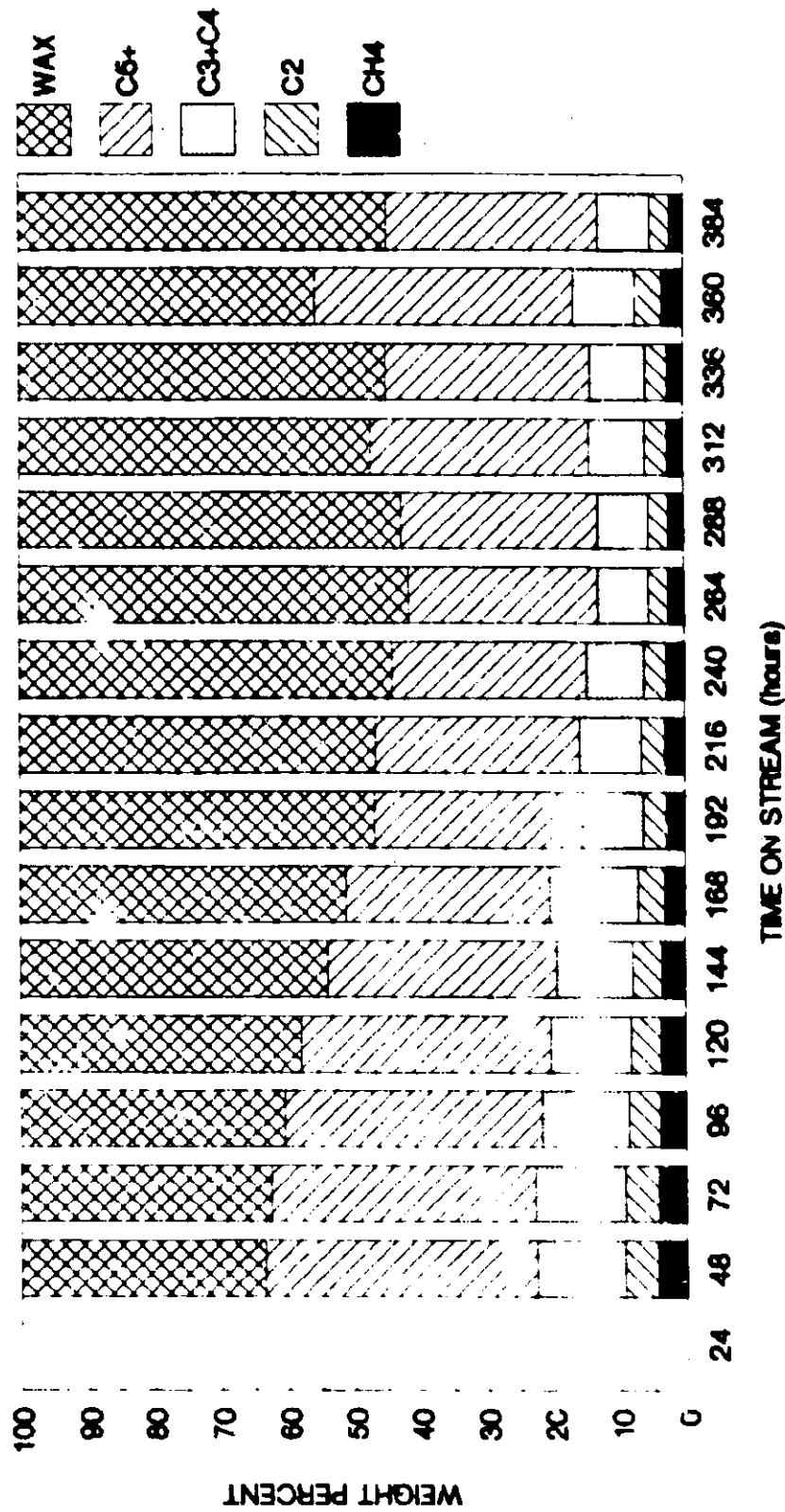


Activation CO, 280 C., 200 psig, 24 h
Synthesis H₂/CO=0.65, 258 C., 200 psig
4 NL/g-Fe. h

↑ DRAINING TOOK
1 HR.

Figure 8

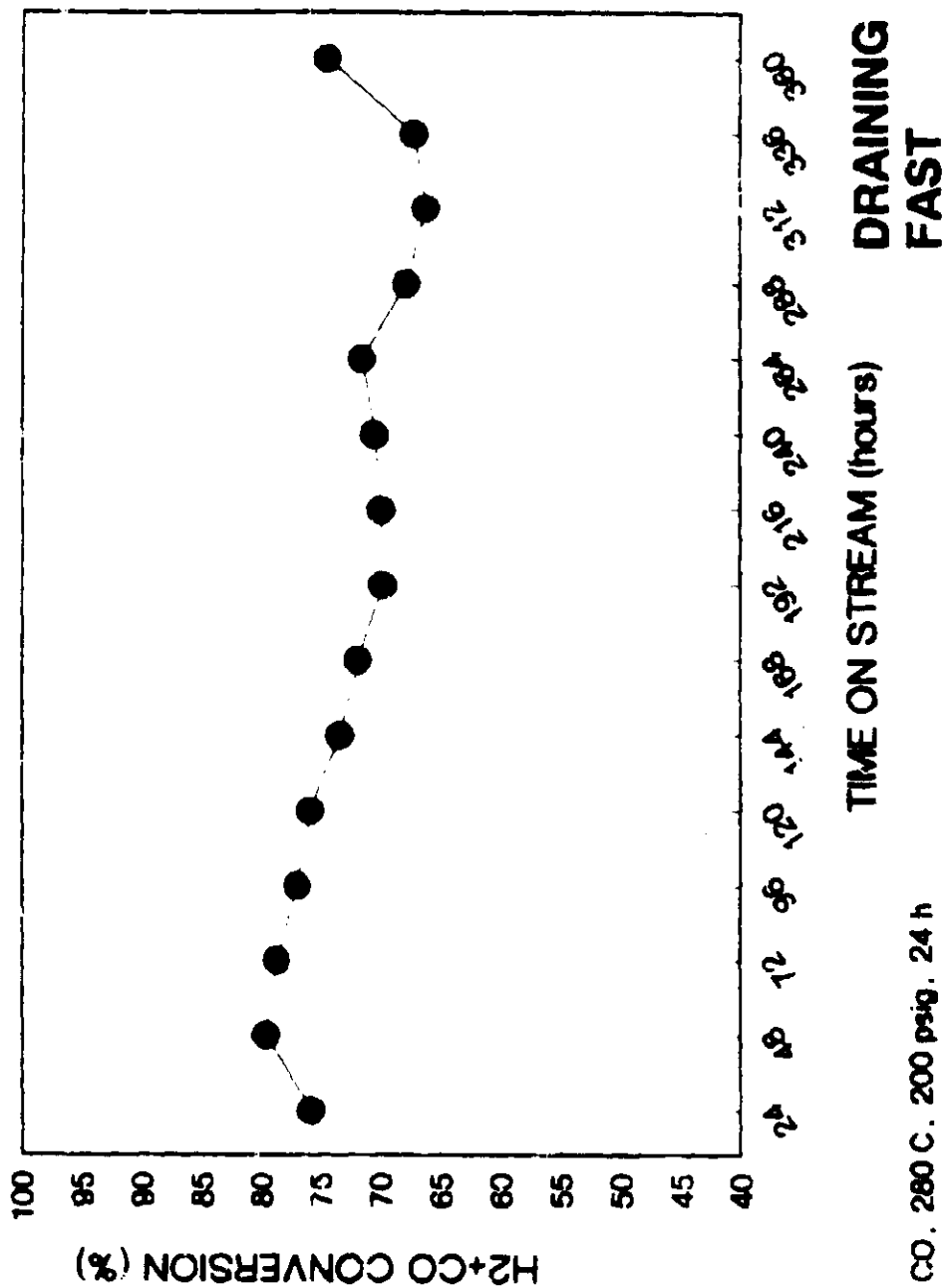
4 WT% CATALYST, PURE OCTACOSANE HYDROCARBON DISTRIBUTION EXPERIMENT S2-48 CATALYST MB6-ABC



Activation: CO, 280 C, 200 psig, 24 h
Synthesis: H₂/CO=0.65, 258 C, 200 psig
4.1 NL/g-Fe. h

Figure 9

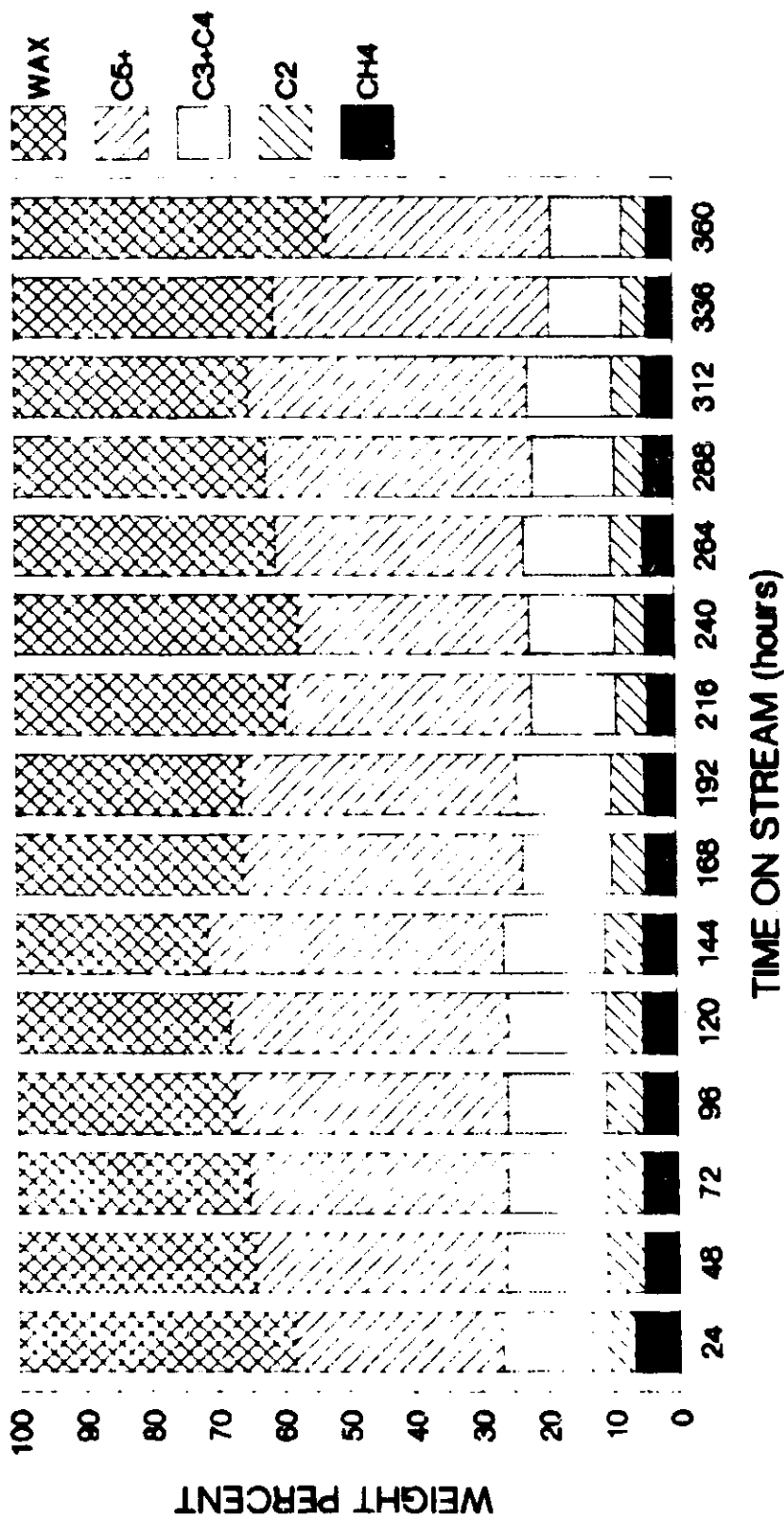
**4 WT% CATALYST, PURE OCTACOSANE
HYDROGEN PLUS CARBON MONOXIDE
CONVERSION LEVELS S1-110
CATALYST MB6-ABC**



Activation: CO, 280 C., 200 psig, 24 h
Synthesis: H₂/CO=0.65, 255 C., 200 psig,
4.1 NL/g-Fe. h

Figure 10

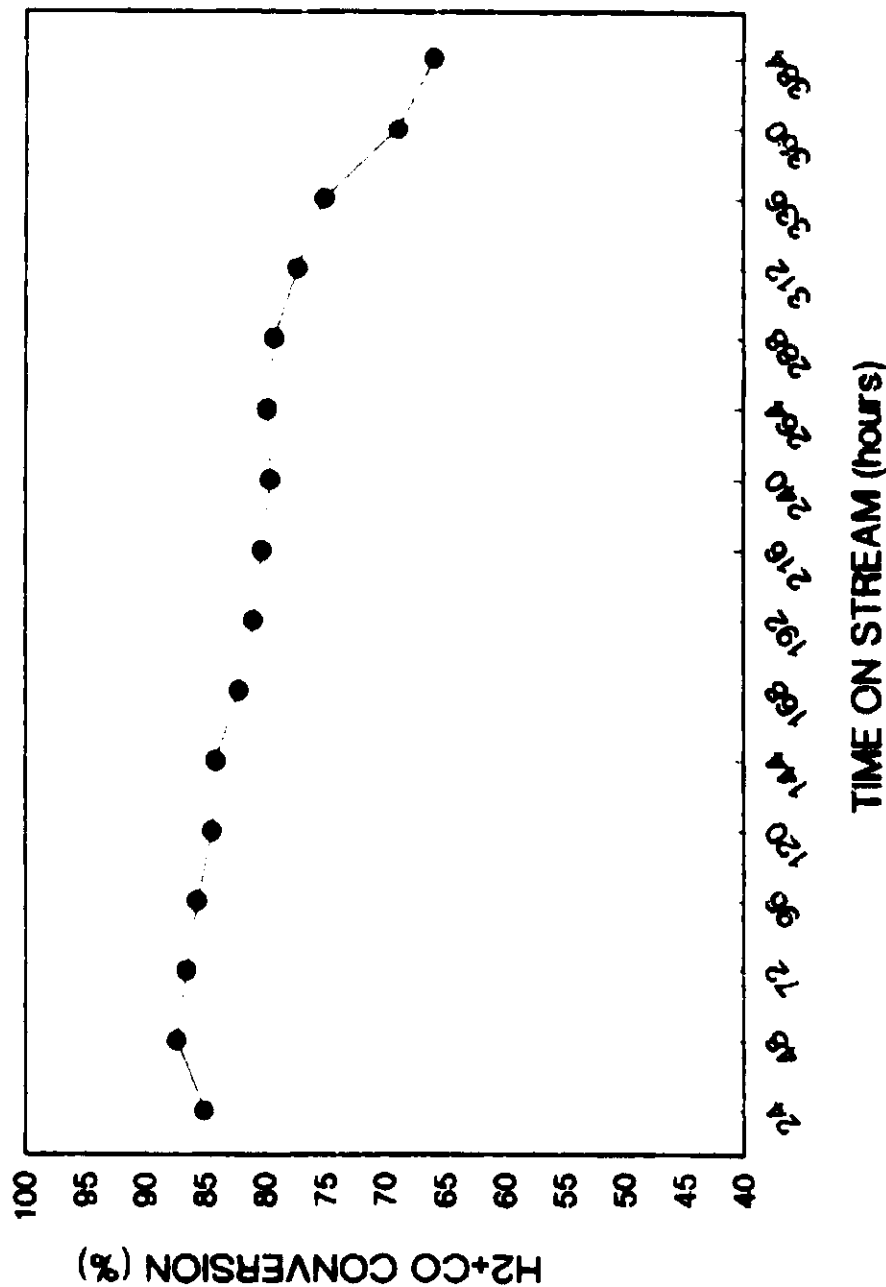
**4 WT% CATALYST, PURE OCTACOSANE
HYDROCARBON DISTRIBUTION
EXPERIMENT S1-110
CATALYST MB6-ABC**



Activation: CO, 280 C, 200 psig, 24 h
Synthesis: H₂/CO=0.65, 255 C, 200 psig,
4.1 NL/g-Fe, h

Figure 11

**10 WT% CATALYST ETHYLFLU WAX
HYDROGEN PLUS CARBON MONOXIDE
CONVERSION LEVELS S1-111
CATALYST MB6-ABC**



Activation: CO, 280 C, 200 psig, 24 h
Synthesis: H₂/CO=0.65, 260 C, 200 psig,
3.1 NL/g-Fe, h

↑ DRAINING TOOK
≥ 1 HR.

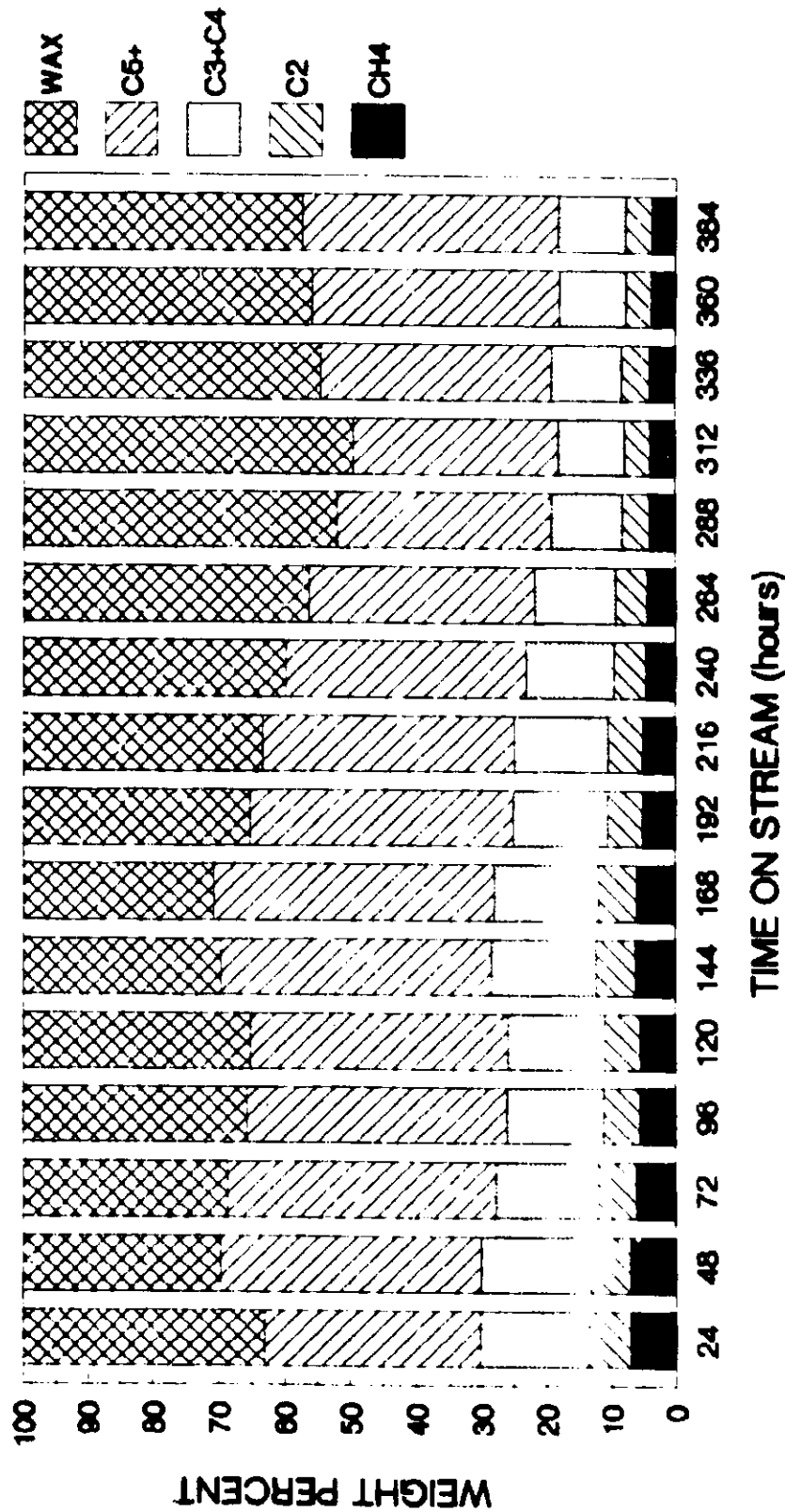
Figure 12

10 WT% CATALYST ETHYLFLU WAX

HYDROCARBON DISTRIBUTION

EXPERIMENT S1-111

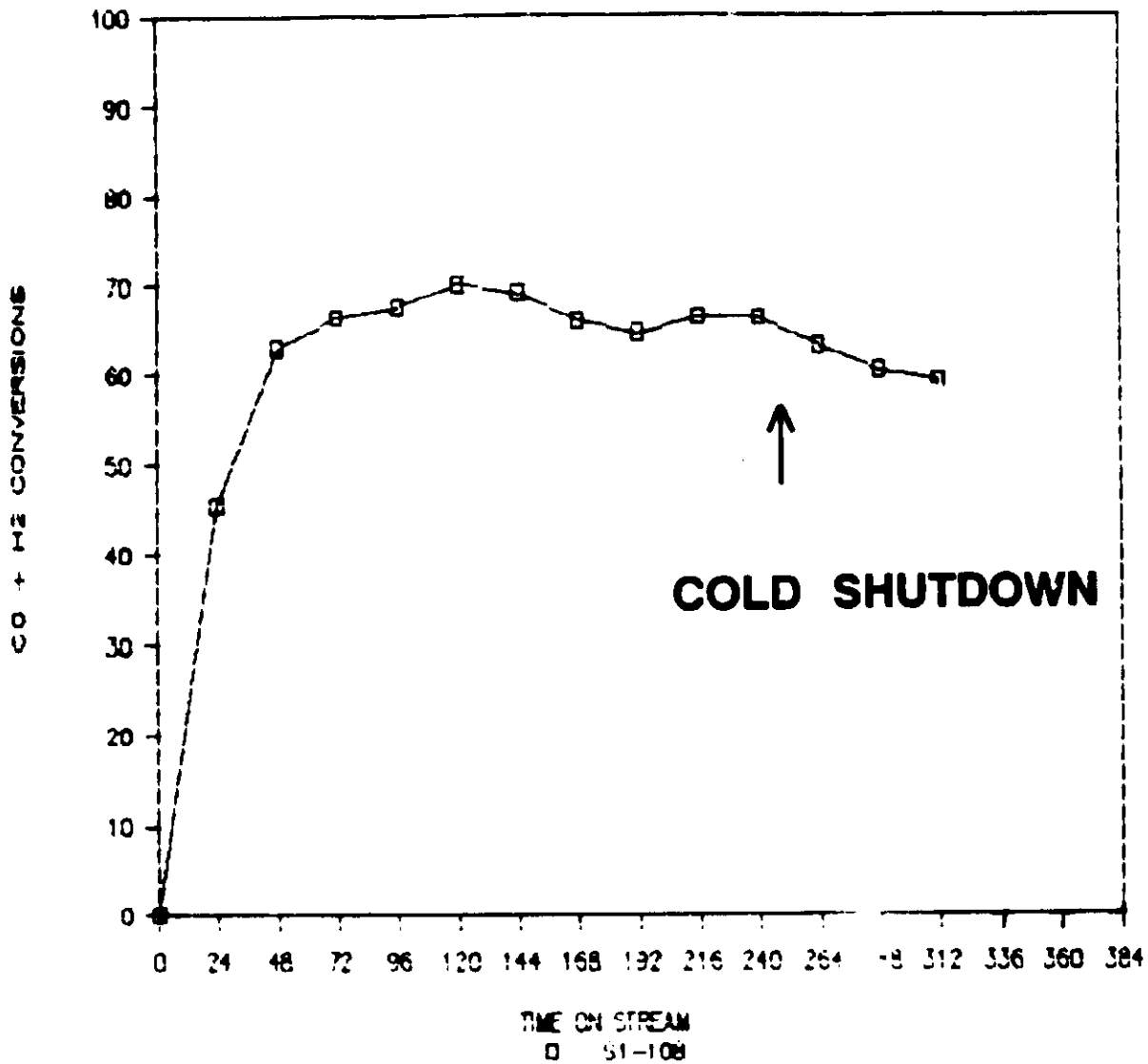
CATALYST MB6-ABC



Activation: CO, 280 C, 200 psig, 24 h
 Synthesis: H₂/CO=0.65, 280 C, 200 psig,
 3.1 NL/g-Fe, h

Figure 13

S1-108



Fe-Cobalt-Cu-K Catalyst

**13g
Catalyst
at Start**

1.77g cat.

?g cat.

**3.49g cat.
Remains**

DRAINING WAX THROUGH 325 MESH SCREENS

Figure 14

SLURRY REACTOR RESULTS

PROCESS CONDITIONS: H₂/CO = 0.68, P = 200 psig.

T = 260 C, WHSV = 2.1/h

	Fe-Cu-K	Fe-Co-Cu-K
HOURS ON STREAM	308-328	191-215
CONVERSIONS %		
H ₂	58.8	61.0
CO	69.9	70.2
H ₂ + CO	65.5	66.5
PRODUCT COMPOSITION		
CO ₂	74.1	73.5
H ₂ O	1.4	2.4
CH _n	24.5	24.1
CH _n COMPOSITION %		
CH ₄	4.7	9.1
C ₂ H ₄	2.4	2.4
C ₂ H ₆	2.6	5.7
C ₃ H ₆	6.4	7.8
C ₃ H ₈	1.2	2.4
C ₄ H ₈	4.6	5.1
C ₄ H ₁₀	1.2	1.9
C ₅ + MINUS WAX TRAP	40.3	38.7
WAX TRAP	36.6	26.9
K(APPARENT SHIFT)	20.3	10.8
RUN #	S1-107-N	S1-108-I
CAT #	MB6-1-81	FH09-1-101
H ₂ /CO OUTLET	0.92	0.75

Figure 15

Conclusions

- PETC catalyst approached conversion goal
 - Stable 70-80 % ($H_2 + CO$) conversion for 300 hr at 260 °C, 200 psig
 - Near goal of 3.4 NL/(g Fe)/ hr
- PETC catalyst achieved selectivity goal
 - $C_1 + C_2 \leq 7$ wt% when ($H_2 + CO$) conversion ≤ 70 %
 - $C_1 + C_2 = 11$ wt% when ($H_2 + CO$) conversions = 70-86 %
- Halting stirring for > 1 hr during wax draining decreases conversion
- EthylFlo wax gave conversions comparable to purified Humphrey n-octacosane
- Bubble size decreases as impeller diameter increases
 - Conversion higher with smaller bubble size
 - Conversion maintained better with smaller bubble size