PARTICLE SIZE DEPENDENCE IN FISCHER-TROPSCH SYNTHESIS

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COAL LIQUEFACTION AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

Title: Particle Size Dependence in Fischer-Tropsch Synthesis

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ABSTRACT

The use of ultrafine particle (UFP) iron catalysts in slurry-phase Fischer-Tropsch (F-T) synthesis was investigated. Two systems were selected: 1) NANOCAT™ or MACH-1, a commercially available unsupported Fe_2O_3 material with mean particle diameter (MPD) of 3 nm (surface area (SA) = 255 $m^2.g^{-1}$; density (d) = 0.05 $g.mL^{-1}$), and 2) an unsupported Fe_2O_3 material from BASF with MPD of 20-80 nm (SA = 16-20 $m^2.g^{-1}$; d = 5.25 $g.mL^{-1}$). For reference, the UCI catalyst with MPD of 32.5 μm SA = 232 $m^2.g^{-1}$; d = 0.80 $g.mL^{-1}$; composition (wt%): Fe_2O_3 = 69.6, K_2O = 5.1, SiO_2 = 8.3, CuO = 2.6; loss on ignition (LOI) = 14.8) was also included. A low catalyst loading, ~ 5 wt% in ethylflopolyolefin-164 solvent, was selected. After slurried catalyst reduction with CO at 280°C, F-T activity data were collected at 240°C and 0.78 MPa with balanced gas (H_2/CO ~ 2/1). A run was also completed with MACH-1 at 260°C and 2.77 MPa. At 240°C, 0.78 MPa, and gas-hourly-space-velocity (GHSV) of 4.5-4.7 $NL.gFe^{-1}.h^{-1}$, space-time-yields (STY) of hydrocarbon products were 0.36, 0.26, and 0.54 $kg.kgFe^{-1}.h^{-1}$ for BASF, MACH-1, and UCI respectively. The corresponding α values obtained from Anderson-Schulz-Flory (ASF) plots (in the C_3-C_7 range) were 0.60, 0.57, and 0.50.

A Mössbauer study on a MACH-1 sample, quenched after 199 hours at 260°C, indicated that MACH-1 was in the magnetite phase. EXAFS and Mössbauer measurements on several unreduced, freshly reduced, and quenched UFP samples are in progress.

The H_2/CO stoichiometry used is relevant to natural gas-derived syngas. Future runs will utilize these data for development of UFP catalysts for oxygenates synthesis with CO_2-rich syngas.

INTRODUCTION

Though coal and natural gas can be transformed to hydrocarbon liquid fuels via catalytic conversion of synthesis gas, only two economical but site-specific commercial plants are presently operating that utilize this "indirect" approach: 1) a coal-based Fischer-Tropsch (F-T) technology in Sasol, South Africa and 2) a recent natural gas-based process patented by Shell to produce middle distillates in Malaysia. The use of abundant coal to produce liquid fuels is still of interest but the process economics is adversely affected by sensitivity of the preferred Fe-based catalyst to sulfur and the overall low space-time-yield (STY). To overcome these drawbacks, the use of ultrafine particle (UFP) catalysts has been investigated (1,2). The present task was specifically undertaken to test the performance of two Fe UFP catalysts for F-T synthesis. Some of these data have been reported in a recent communication (3).

EXPERIMENTAL

F-T Unit.

A flow-diagram of the BNL F-T test unit is shown in Figure 1. The core of the unit was a 1L stirred reactor rated at 40 MPa at 343°C commercially available from Autoclave Engineers (AE). To ensure that all liquids exiting the reactor were condensed, both receiver tanks No. 1 and No. 2 were cooled to 5°C and -45°C respectively.

Analytical.

All gaseous samples and collected liquid were analyzed on Gow Mac 580 or Perkin Elmer 8500 gas chromatographs. EXAFS analysis were done at the National Synchrotron Light Source (NSLS), BNL and Mössbauer analyses were carried out at CFFLS, University of Kentucky. A full mass balance was performed on each run.

Materials.

Samples of MACH-1 (α-Fe_2O_3; mean particle diameter (MPD) = 3 nm; surface area (SA) = 255 $m^2.g^{-1}$; d (bulk) = 0.05 $g.mL^{-1}$), from MACH-1, Inc., Ethylflopolyolefin-164 solvent, a dec-1-ene homopolymer (composition: 84.4% trimer, 14.5% tetramer; b.pt. = 518°C; d = 0.818 $g.mL^{-1}$; mol. wt. = 437) from Ethyl Corporation, and UCI catalyst (Fe_2O_3 = 69.6, K_2O = 5.1, SiO_2 = 8.3, CuO = 2.6, loss on ignition (LOI) = 14.8, all in wt%; MPD = 32.5 μm; SA = 232 $m^2.g^{-1}$ from Air Products and Chemicals, Inc. were obtained. Gases were purchased in aluminum cylinders from Scott Specialty Gases and purified before use.

Catalyst Reduction.

Of the typical reductants, CO, H_2, and synthesis gas, utilized for catalyst reduction, CO was used for *in situ* reduction before F-T operation. In a typical procedure, a 4.6 wt% starting material in 330 g ethylflopolyolefin-164 solvent was loaded under argon into the 1L AE reactor. The vessel was flushed twice with 0.6 MPa CO before pressurizing to 1.43 MPa. The slurry temperature was slowly raised to 280°C under a 0.2 L/min CO flow. The CO_2 concentration in the exit gas was followed as function of time (Figure 2). For MACH-1, CO_2 concentration maximized at 3.7 vol% in 2.2 hours and then slowly decreased to 0.5

vol% in 44 hours. The plots for UCI and BASF reduction are also shown in Figure 2. Typically, the reduction period was limited to 24 hours.
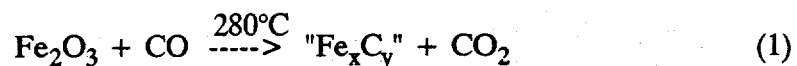
<u>F-T Synthesis.</u>

After catalyst reduction, the temperature was lowered to a desired value, CO replaced with preblended syngas, and the reactor maintained at a set pressure. Typical reaction conditions were: P = 0.78 MPa; syngas: H_2/CO = 65%/35%; gas hourly space velocity (GHSV) = 4.4-5.8 normal liters (NL).g $Fe^{-1}.h^{-1}$; stirring speed = 750 rpm. Gas and liquid samples were periodically taken and analyzed.

RESULTS AND DISCUSSION

A 1 lb sample of MACH-1 obtained by BNL was certified to be anhydrous α-Fe_2O_3 by the manufacturer. Since a recent EXAFS/XANES study (4) described this material to be iron oxyhydroxide, the acquired sample was further dried overnight at 120°C *in vacuo* before each run. No water was collected and no loss in weight of the dried sample was noted. Similarly, BASF catalyst was dried. The UCI catalyst was used as received.

The catalyst reduction step proceeds according to Equation (1):

$$Fe_2O_3 + CO \xrightarrow{280°C} \text{"}Fe_xC_y\text{"} + CO_2 \quad\quad (1)$$

The CO_2 evolution peaked in < 5 hours for all three samples. But the F-T synthesis was typically initiated after 24 hours. For establishing the Fe_2O_3/CO_2 relationship, it was assumed that Fe_2O_3 converted mainly to Fe_5C_2 during reduction.

For the production of pure hydrocarbon products, the following stoichiometry prevails during F-T synthesis with syngas of H_2/CO = 2/1:

$$nCO + 2nH_2 \longrightarrow (CH_2)_n + nH_2O \quad\quad (2)$$
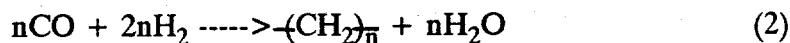
But this reaction is further complicated by the water-gas-shift (WGS) reaction:

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad\quad (3)$$
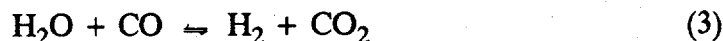
Therefore, both H_2O and CO_2 appear as byproducts in the temperature regime where F-T reaction is carried out.

Since the commercial F-T synthesis, catalyzed by Fe-based systems, is carried out at $T \geq 260$°C (5), MACH-1 was initially tested at 260°C and 277 MPa. Under the selected F-T synthesis conditions, CO and H_2 conversions dropped to 61 and 52% (50 h) from the initial high of 91 and 62% (1 h) and then to 44 and 43% at 200 hours (Figure 3). The H_2/CO consumption ratio steadily increased from 1.3 (1 h) to 1.8 (200 h). From the plot of hydrocarbon distribution during this run (Figure 4), CH_4 and C_1-C_4 were 16 and 54 wt%

respectively at 174 hours. An overall mass balance yielded hydrocarbons, CO_2, H_2O at 32, 30, 38 wt% respectively (Figure 5). The F-T data are summarized in Table 1. Though high boiling liquids were retained in the reactor, the total decrease in gas conversions in 200 hours was too steep to be attributed solely to a steady increase in the liquid volume in the reactor during the above run. Considering that highly dispersed catalysts tend to agglomerate in the absence of a support or other agglomeration inhibitors especially at higher temperatures, the temperature used (260°C) might have been too high for effective utilization of unsupported UFP catalyst systems. It is surprising that generally the UFP systems were tested at T $\geq$ 260°C ($\underline{1,2}$). This reasoning prompted us to test the selected UFP systems at lower temperatures.

With MACH-1 loading of 4.6 wt% in ethylflo-164 solvent (330 g), the catalyst was reduced as per procedure described earlier. The carbided MACH-1 system was then evaluated for F-T synthesis at 240°C. The selected reaction conditions were: P = 0.78 MPa, syngas: H_2/CO = 1.86, SV = 4.6 $NL.gFe^{-1}.h^{-1}$. CO and H_2 conversions exhibited maxima at 77% and 49% at 24 hours and then steadily decreased to 43% and 35% at 120 hours while the H_2/CO consumption ratio followed: 2.04 (0 h), 1.3 (24 h), 1.84 (96 h), 1.65 (120 h) (Figure 6). CH_4 and C_1-C_4 were 12.8% and 45.6% at 120 hours (Figure 7, Table 1). The data in Table 1 and Figure 8 also show that the overall product distribution (hydrocarbons, CO_2, H_2O) did not change appreciably with temperature (260 and 240°C data) but STY decreased from 0.37 at 260°C to 0.26 $Kg.KgFe.h^{-1}$ at 240°C (Table 1). The decrease in CO and H_2 conversions were less pronounced at 240°C than at 260°C (Figures 3 and 6). In the run at 240°C, the temperature was raised to 260°C at 120 hours. As expected, CO and H_2 conversions, CH_4, CO_2, and STY values increased to 63%, 45.3%, 14.5%, 46.6%, 0.39 kg.kg $Fe^{-1}.h^{-1}$ (Figures 6, 7, and 8). The hydrocarbon distribution data from Figure 7 were plotted. From the plot in Figure 9, α was calculated from the slope to be 0.57 (in the C_3-C_7 range).

The next evaluated Fe UFP catalyst was obtained from BASF with MPD = 20-80 nm but small surface area of 16-20 $m^2.g^{-1}$. At 240°C, CO and H_2 conversions peaked at 78% and 48% in 24 hours and then declined steadily to 55% and 42% in 144 hours (Figure 10). The H_2/CO consumption ratio decreased from 1.56 (2.5 h) to 1.27 (29 h) but then increased to 1.53 (144 h). At 144 hours, CH_4, C_1-C_4 and CO_2 were 10.1%, 41.2%, 42.7% respectively.

With BASF, the hydrocarbon and overall produced distribution as a function of time are shown in Figures 11 and 12. A data summary from this run is shown in Table 1.

For reference, a run with UCI (MPD = 32,500 nm) a supported iron catalyst, was also carried out at 240°C. The data from this run are included in Figure 13, 14, 15 and Table 1. For these data, it is noteworthy that the unsupported and unpromoted BASF Fe catalyst with intermediate particle size (20-80 nm) and the lowest surface area (16-20 $m^2.g^{-1}$) outperformed both MACH-1 and UCI catalysts at 240°C with the highest STY. But Figure 13 clearly shows that the UCI catalyst was more attrition resistant exhibiting steady-state CO and H_2 conversions of 64 $\pm$ 2% and 37 $\pm$ 1% between 54 and 198 hours. The corresponding CO and H_2 values with the BASF catalyst showed steady decline (Figure 10).

Of the three catalysts tested, the activity order was: BASF (20-80 nm) > MACH-1 (3 nm) > UCI (32,500 nm). Though caution should be exercised while drawing this conclusion because the indicated MPD values were those of the unreduced catalysts. Whether carbided catalysts after reduction with CO at 280°C retained the same particle size is to be considered. Mössbauer and EXAFS studies (6) are presently under way to confirm these findings.

With UCI reference at 240°C, the C_1-C_{10} hydrocarbon fraction accounted for 39%. With both UFP catalysts, this fraction increased to ~ 70%. This value increased to 84% with MACH-1 at 260°C. The α values, extracted from slopes of the Andesrson-Schulz-Flory (ASF) plots, are listed in Table 2 for all three catalysts.

In addition to hydrocarbons, a small amount of oxygenates were also produced during these runs. Of the aqueous phase, oxygenates accounted for 6.0, 7.0, 2.3, 5.2 wt% with MACH-1 at 260°C and MACH-1, BASF, and UCI at 240°C respectively. The utilization of UFP catalysts to enhance oxygenates synthesis is the subject of follow-up work presently ongoing at BNL.

CONCLUSIONS

From the above data, the following conclusions are noteworthy:

- Both unsupported Fe UFP catalysts, MACH-1, and BASF were effective catalysts for F-T synthesis.

- During reduction with CO at 280°C, it took longer to carbide the UFP catalysts.

- The BASF catalyst showed higher CO and total (H_2 + CO) conversions at 55.9% and 48.5% compared to those obtained with MACH-1 (42.9% and 40.5%).

- At 240°C, BASF yielded lower CH_4 (10.7%) but higher CO_2 (39.0%) compared to that with MACH-1 (12.8% and 31.7%). The corresponding values for UCI were 7.0% and 46.6%. In the C_3-C_7 range, α values were 0.60, 0.57, and 0.50 respectively.

- With MACH-1, at 4.6 wt% catalyst loading and SV of 5.8 (260°C) and 4.6 (240°C) NL.gFe^{-1}.h^{-1}, STY was higher at higher temperature. But the rate of catalyst deactivation was also higher.

- At 240°C, the C_{11+} fraction was comparable for BASF and MACH-1 (27.8% and 30.7%) but higher for the reference UCI (60.6%).

- STY was higher with BASF on both weight and volumetric basis. Both UFP catalysts performed better as compared to the reference UCI catalyst.

- The overall data show that BASF performed better than both MACH-1 as well as UCI reference. But time dependent CO conversion plots show that BASF and MACH-1 deactivated faster than UCI over 120 hours test period. This aspect needs to be further evaluated.

- The presented results do not follow the expected pattern with smaller particles necessarily enhancing activity.

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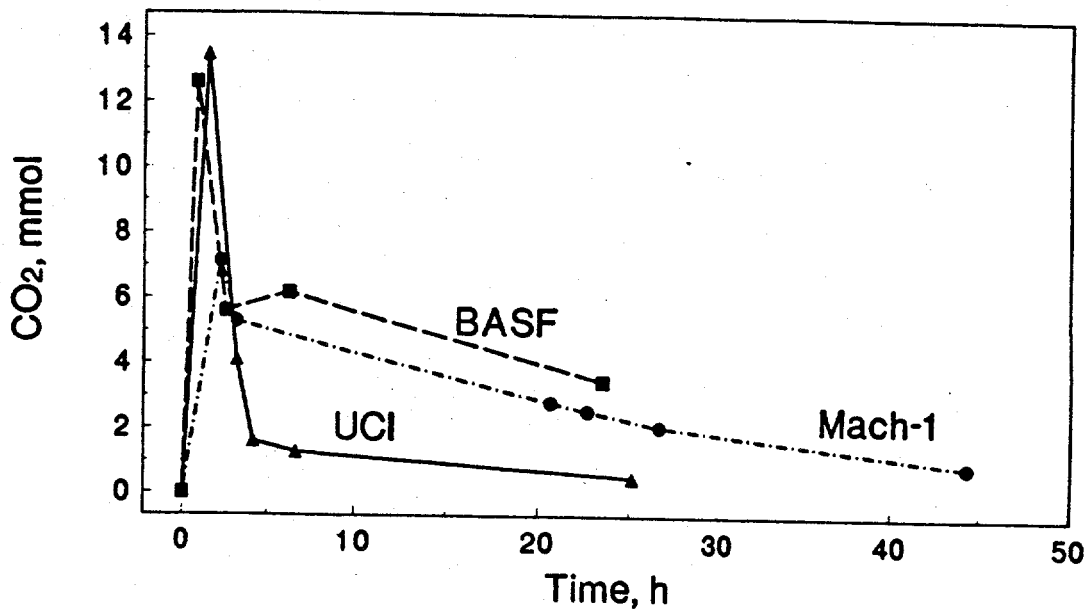
ACKNOWLEDGEMENTS
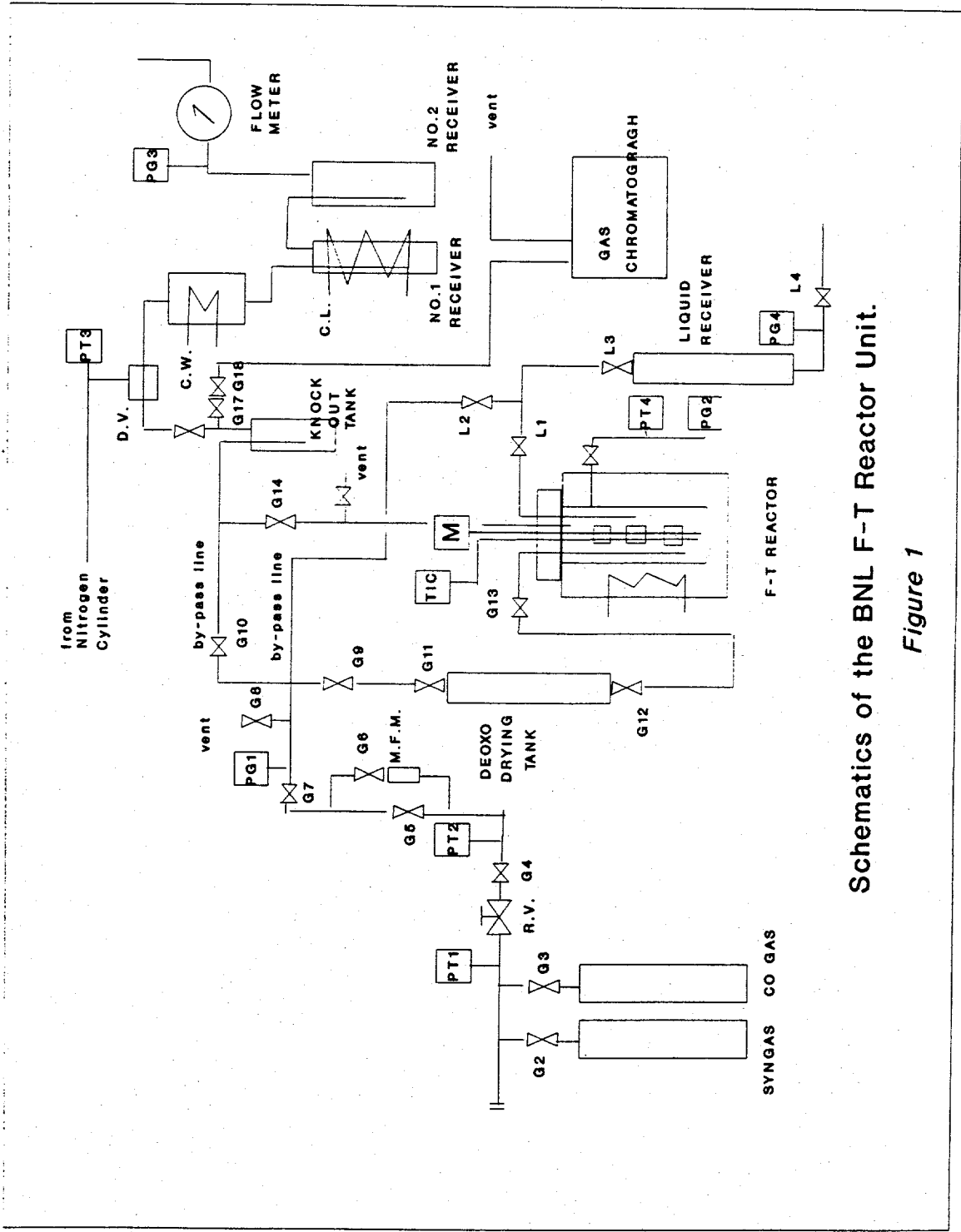
Schematics of the BNL F-T Reactor Unit.
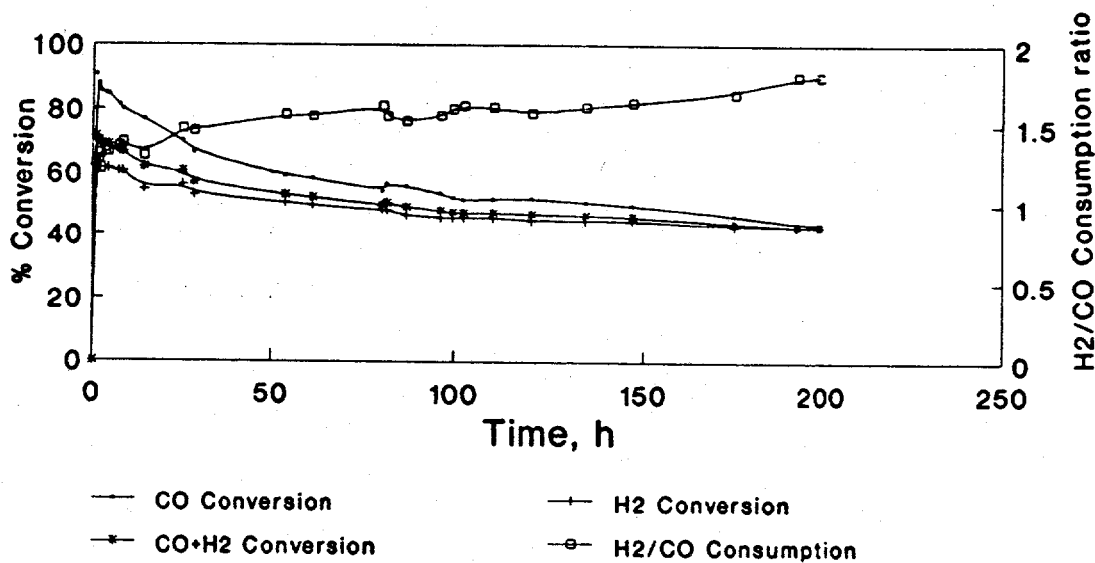
Figure 1

Figure 2
### Time Profile of CO_2 Evolution during Catalyst Reduction

T: 280 °C; P: 1.45 MPa
Reductant: CO; 750 rpm
Solvent: Ethylflo-164

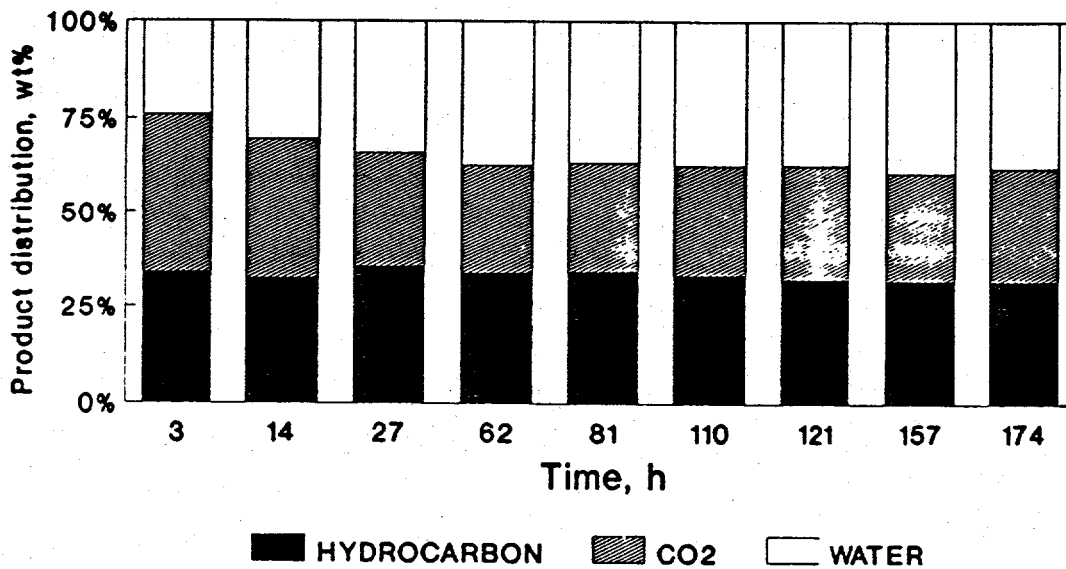## Figure 3
H2, CO Conversions and Consumption
Data with Mach-1

—— CO Conversion	—+— H2 Conversion
—*— CO+H2 Conversion	—◦— H2/CO Consumption

T: 260 °C; P: 2.77 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 5.8 NL/g-Fe/h; 250rpm

Figure 4
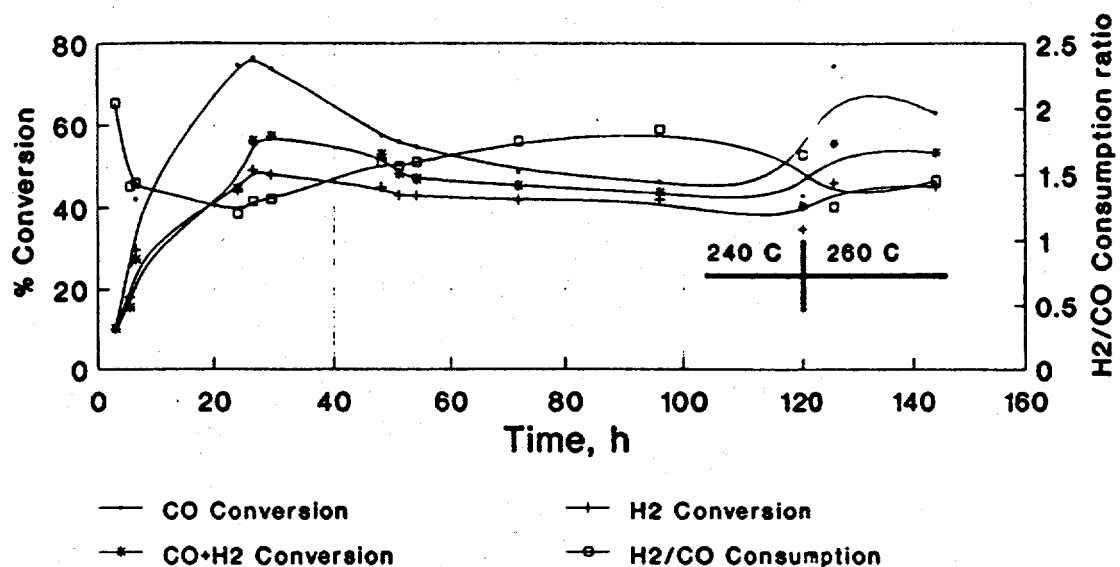## Hydrocarbon Distribution as a Function
of Time with Mach-1
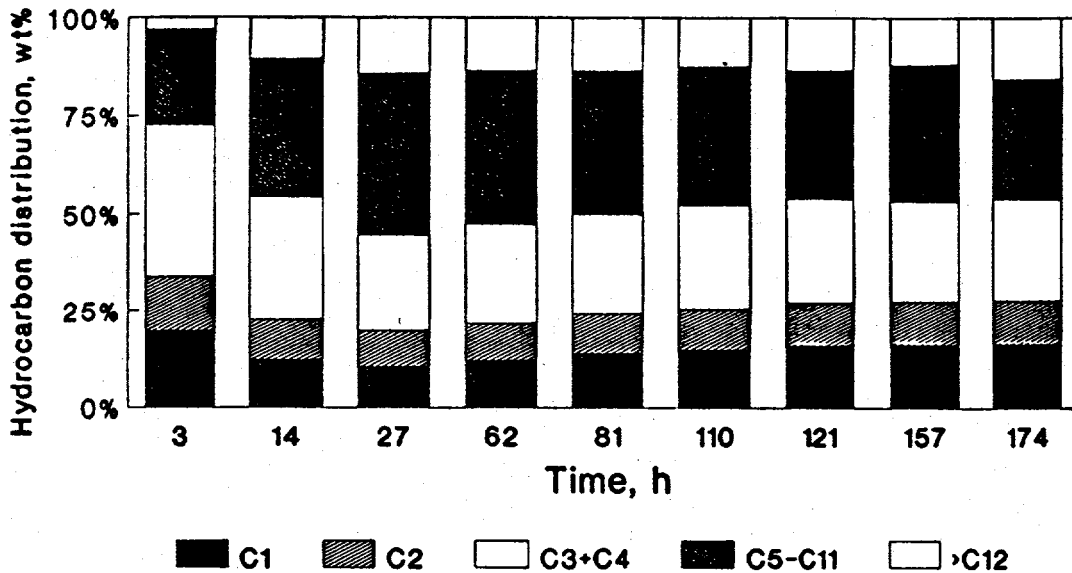
T: 260 °C; P: 2.77 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 5.8 NL/g-Fe/h; 250 rpm

Figure 5
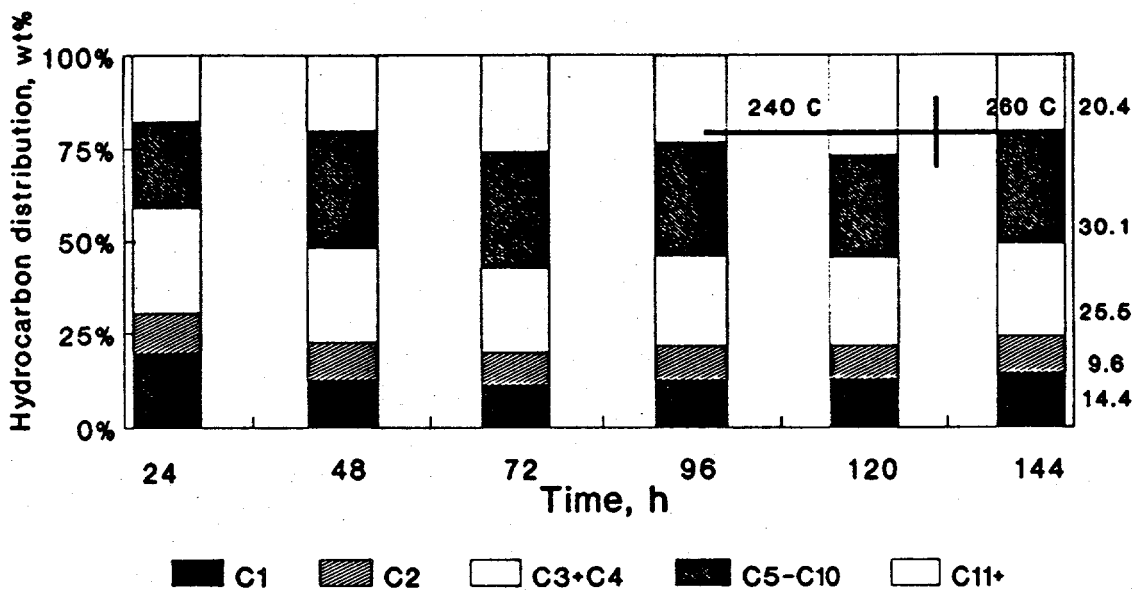## Overall Product Distribution as a
Function of Time with Mach-1

T: 260 °C; P: 2.77 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 5.8 NL/g-Fe/h; 250 rpm

Figure 6
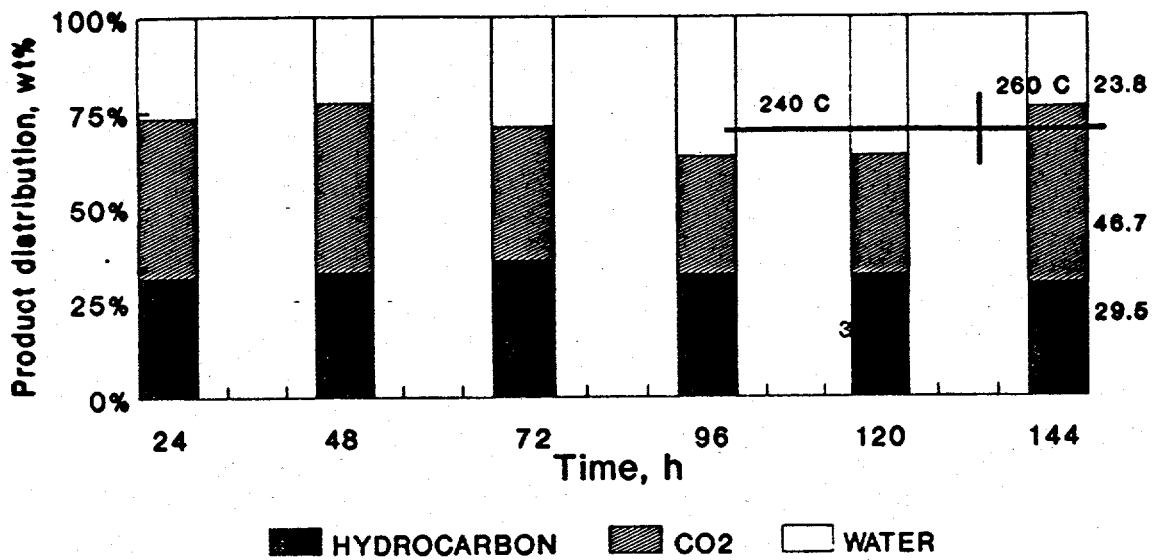## H2, CO Conversions and Consumption
Data with Mach-1

T: 240, 260 °C; P: 0.78 MPa
Solvent: Ethlflo-164; H2/CO: 2/1
SV: 4.6 NL/g-Fe/h; 750 rpm

Figure 7
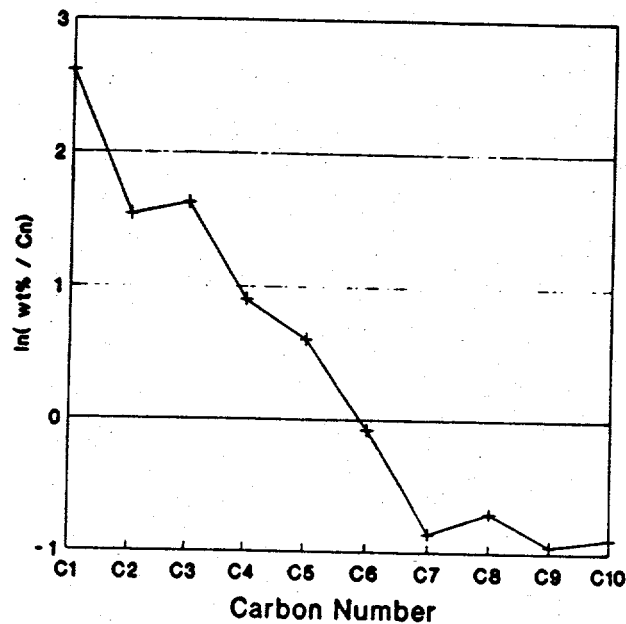## Hydrocarbon Distribution as a Function
of Time with Mach-1

T: 240, 260 °C; P: 0.78 MPa
Solvent:Ethylflo-164; H2/CO: 2/1
SV: 4.6 NL/g-Fe/h; 750 rpm

Figure 8
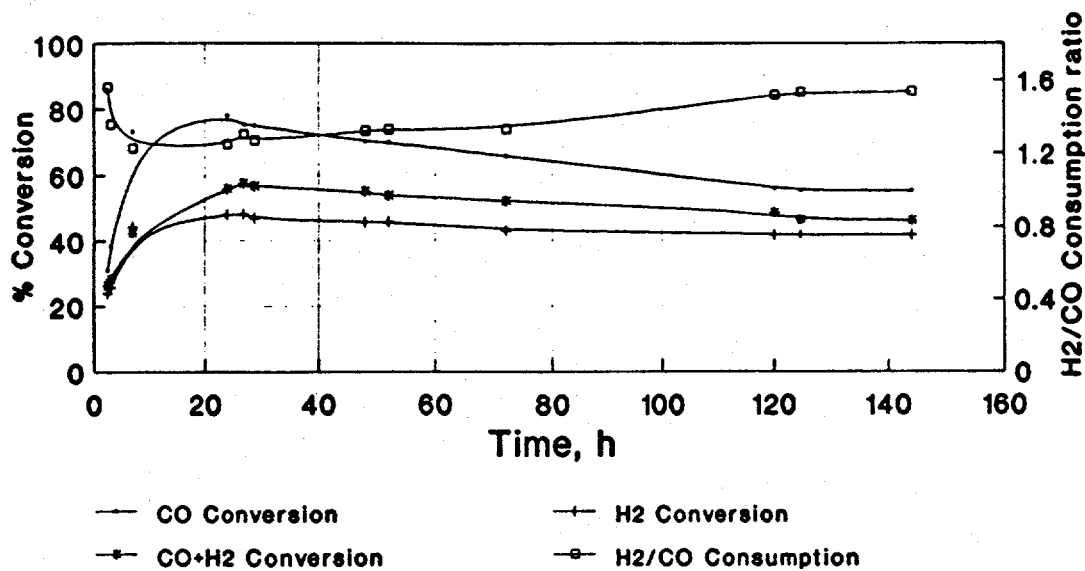## Overall Product Distribution as a
Function of Time with Mach-1

T: 240, 260 °C; P: 0.78 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 4.6 NL/g-Fe/h; 750 rpm

Figure 9
A ASF Plot of the Data From Mach-1
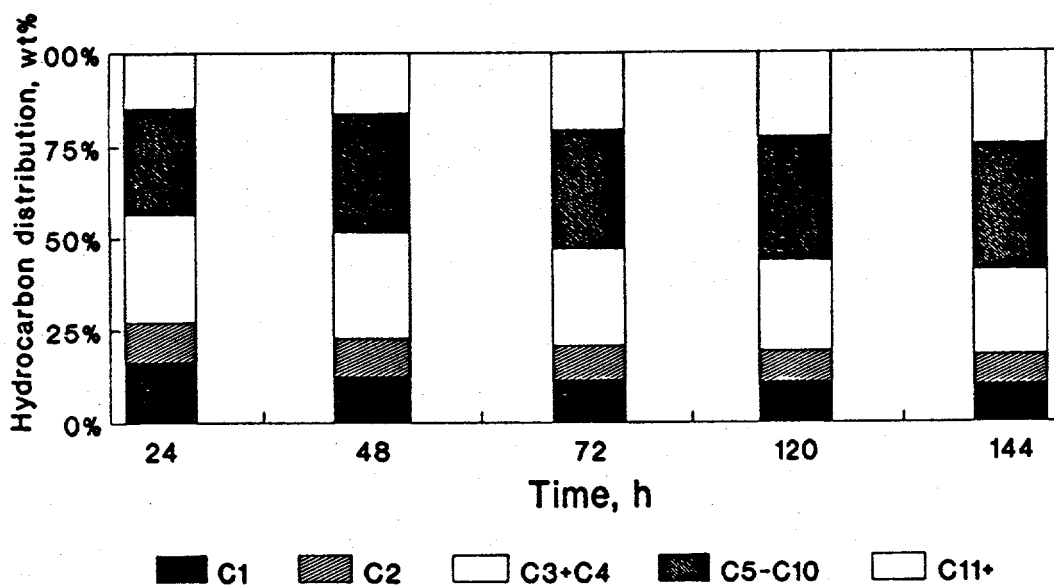### Catalyzed F-T Synthesis

T: 240°C; P: 0.78 MPa
Solvent:Ethylflo-164; H2/CO: 2/1
SV: 4.6 NL/g-Fe/h; 750 rpm

Figure 10
H2, CO Conversions and Consumption
Data with BASF

- ── CO Conversion
- ─+─ H2 Conversion
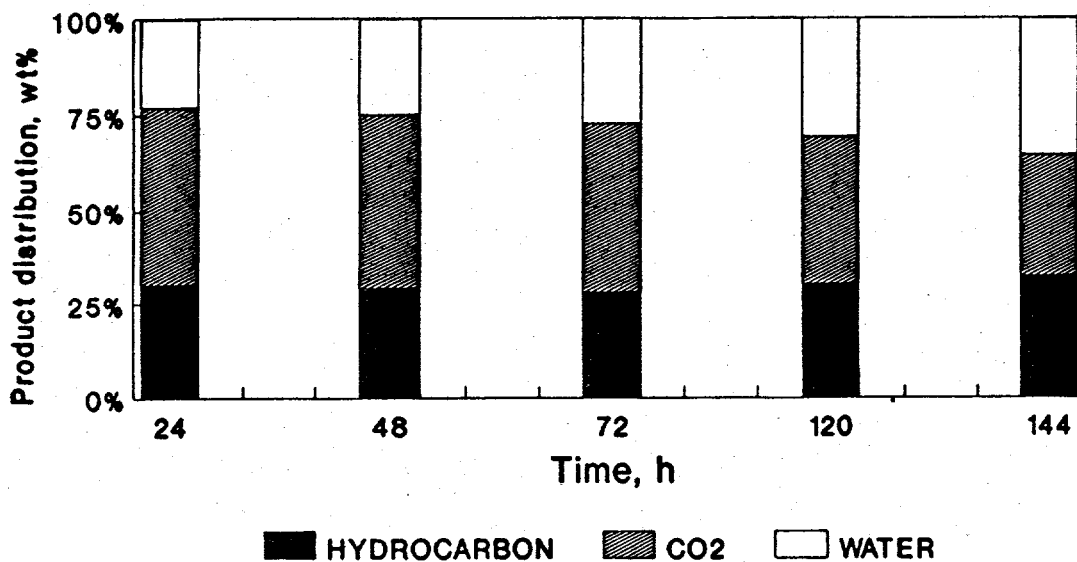- ─*─ CO+H2 Conversion
- ─□─ H2/CO Consumption

T: 240 °C; P: 0.78 MPa
Solvent: Ethlflo-164; H2/CO: 2/1
SV: 4.5 NL/g-Fe/h; 750 rpm

Figure 11
Hydrocarbon Distribution as a Function
of Time with BASF

- ■ C1
- ▨ C2
- ☐ C3+C4
- ▨ C5-C10
- ☐ C11+

T: 240 °C; P: 0.78 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 4.5 NL/g-Fe/h; 750 rpm

Figure 12
Overall Product Distribution as a
Function of Time with BASF

T: 240 °C; P: 0.78 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 4.5 NL/g-Fe/h; 750 rpm

Figure 13
H2 and CO Conversions and Consumption
Data with UCI

T: 240 °C; P: 0.78 MPa
Solvent: Ethlflo-164; H2/CO: 2/1
SV: 4.7 NL/g-Fe/h; 750 rpm

Figure 14
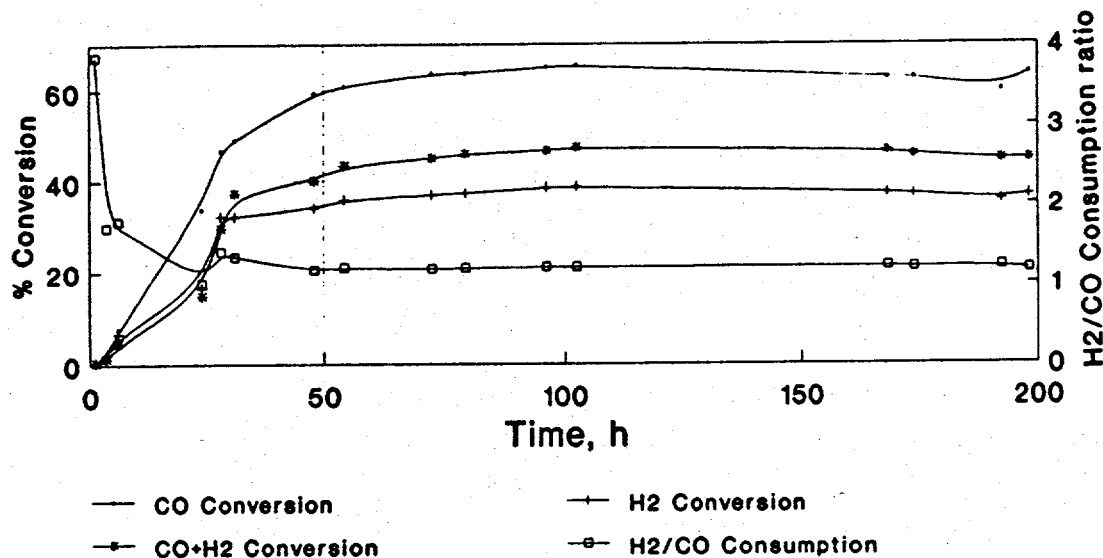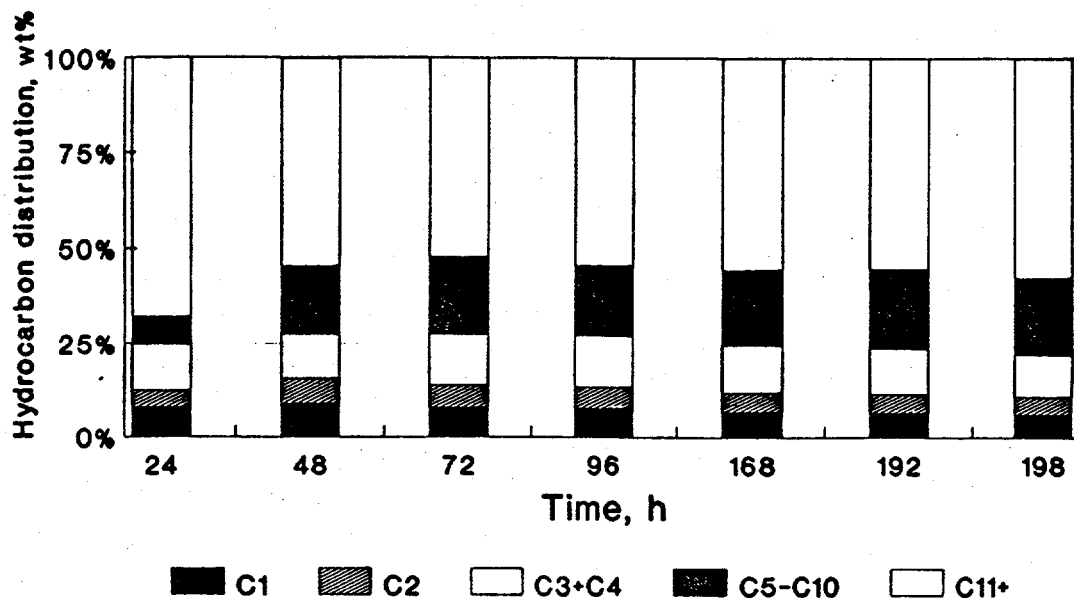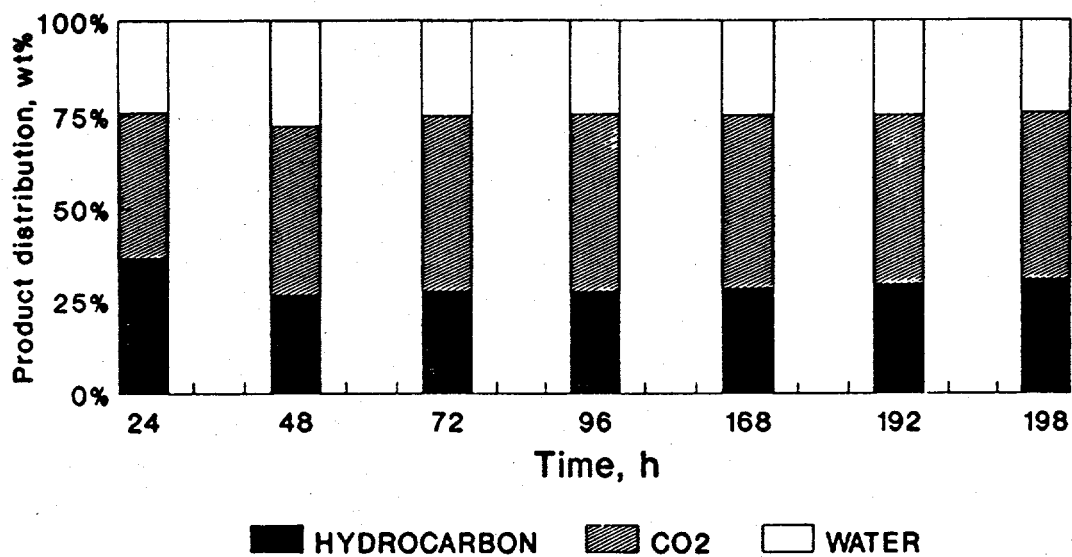## Hydrocarbon Distribution as a Function
of Time with UCI

T: 240°C; P: 0.78 MPa
Solvent: Ethylflo-164; H2/CO: 2/1 ·
SV: 4.7 NL/g-Fe/h; 750 rpm

Figure 15
Overall Product Distribution as a
Function of Time with UCI

T: 240°C; P: 0.78 MPa
Solvent: Ethylflo-164; H2/CO: 2/1
SV: 4.7 NL/g-Fe/h; 750 rpm

Table 1

Data[1] Summary of F-T Synthesis Runs Catalyzed by Unsupported Fe UFP (MACH-1 and BASF) and Supported UCI Systems

Reaction Conditions: Catalyst loading = 4.6 wt%; Ethylflo-164 = 330 g; P = 0.78 MPa; SV = 4.5-4.7 NL gFe^{-1}.h^{-1}.

Catalyst:	MACH-1 260°C[2]	MACH-1 240°C	BASF 240°C	UCI 240°C
% Conversion				
H_2	44.7	34.8	41.7	38.7
CO	52.1	42.9	55.9	65.4
H_2 + CO	46.8	40.5	48.5	47.4
Hydrocarbon Product Distribution (wt%)				
C_1	16.0	12.8	10.7	7.0
C_2	11.2	8.9	8.5	5.2
C_3	15.4	14.6	15.2	.6
C_4	11.4	9.3	9.6	5.1
C_5-C_{10}	30.0	23.7	28.2	14.5
C_{11+}	16.0	30.7	27.8	60.6
Overall Product Distribution				
Hydrocarbons	32.3	31.8	30.5	28.4
H_2O	37.2	36.5	30.5	25.0
CO_2	30.5	31.7	39.0	46.6
STY, Kg.KgFe^{-1}.h^{-1} (Kg.Lcat^{-1}.h^{-1})				
C_1-C_4	0.37 (0.051)	0.26 (0.036)	0.36 (0.010)	0.22 (0.006)
C_{5+}	0.17 (0.023)	0.14 (0.019)	0.20 (0.005)	0.16 (0.004)

1. At 120 h.
2. At P = 2.77 MPa; SV = 5.78 NL.gFe^{-1}.h^{-1}

Table 2

α Values[1] for MACH-1, BASF, and UCI Catalysts.

Catalyst	T,°C	α
MACH-1	260	0.63
MACH-1	240	0.57
BASF	240	0.60
UCI	240	0.50

1. Data extracted from ASF plots in the C_3-C_7 range.