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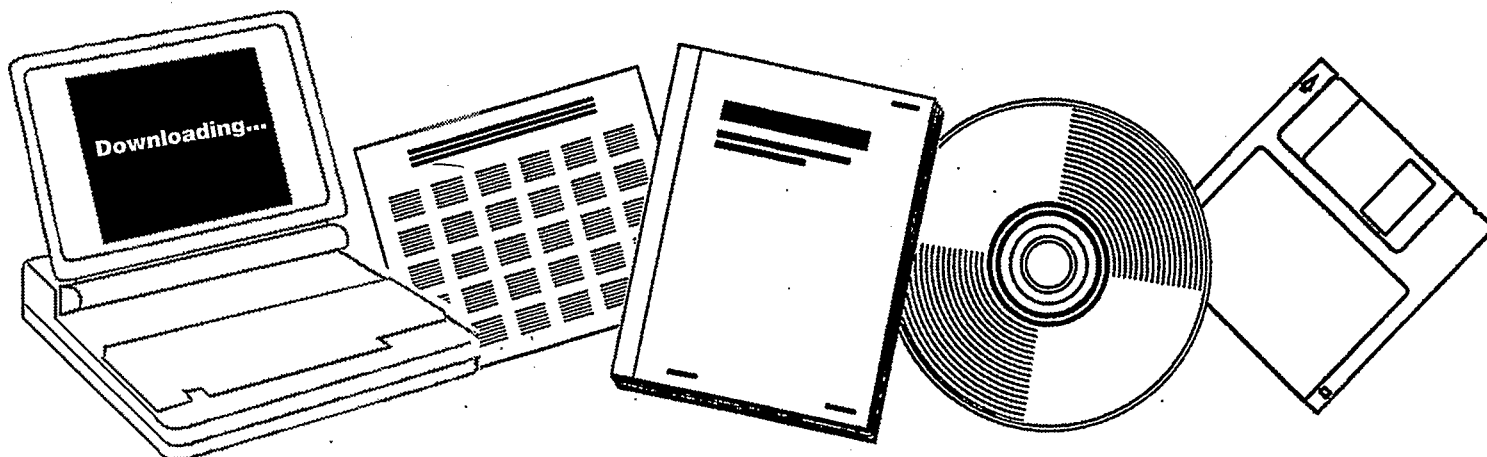
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**TWO-STAGE PROCESS FOR CONVERSION OF
SYNTHESIS GAS TO HIGH QUALITY
TRANSPORTATION FUELS. QUARTERLY REPORT,
APRIL 1-JUNE 30, 1984**

**MOBIL RESEARCH AND DEVELOPMENT CORP.
PAULSBORO, NJ**

AUG 1984



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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS
TO HIGH QUALITY TRANSPORTATION FUELS

QUARTERLY REPORT FOR THE PERIOD
1 APRIL - 30 JUNE, 1984

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I. Abstract

This quarter, the sixth run of the two-stage BSU was completed and the seventh started. Many of the new features of the pilot plant were successfully tested, and low methane + ethane yields were achieved in both runs. Run CT-256-7 is the first to use an orifice-type feed-gas distributor. The 10.2 cm ID tall hot-flow column was shaken down, while further scoping hydrodynamic studies were performed in our short hot-flow bubble-columns. An improved chromatographic technique was developed for analyzing reactor-wax and some results are reported here. Proprietary wax-upgrading studies are reported in the Mobil Proprietary Appendix.

II. Objective and Scope of Work

The general objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H₂/CO ratio synthesis gas, of the type produced in a coal gasification system, into maximum yield of transportation fuels. To accomplish this objective, the following tasks will be undertaken.

Task 1 - Process Studies in Two-Stage Bench-Scale Unit

Operation of the bench-scale unit will be directed toward production of hydrocarbons containing less than 8 wt % of methane plus ethane with high throughput, high conversion, and good catalyst stability. Together with Task 2, high quality liquid fuels, particularly the distillate, will be maximized. At least two tests shall be conducted using at least two different catalysts. One of these catalysts may be provided by DOE's alternate catalyst development projects.

Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

The methods for upgrading the reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated. These methods should include conventional refinery processes, such as Fluidized Catalytic Cracking, Hydrocracking, Catalytic Selective Cracking, Thermal Cracking, and Hydrodewaxing. Proprietary mathematical models and open literature information will be used to the extent possible for these process evaluations.

Means for separating the reactor-wax from the catalyst fines, if such a separation is needed prior to reactor-wax upgrading, shall be investigated.

Task 3 - Product Evaluation

The quality of the hydrocarbon liquid products from the two-stage unit and the reactor-wax upgrading processes shall be evaluated. Gasoline octane and distillate cetane quality, as well as pour points should also be determined.

Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

The effect of different feed-gas distributor designs on the slurry Fischer-Tropsch reactor performance will be investigated. Tests will be conducted in the BSU slurry reactor, or other bubble-column reactors, to provide guidance for subsequent runs in Task 1 as well as for design and operation of the non-reacting models. For hydrodynamic studies, the design, construction, and operation of hot, non-reacting bubble-column

models will be required.

Task 5 - Development of Conceptual Process Schemes

A conceptual process scheme to maximize gasoline and distillate yield using a combined system of slurry Fischer-Tropsch/ZSM-5 reactor plus reactor-wax upgrading will be developed. Scoping costs of the plant will be estimated.

III. Summary of Progress to Date

The sixth run of the two-stage Fischer-Tropsch/ZSM-5 bench-scale unit ended after thirty-three days of operation. Highlights include:

- The catalyst I-D (Fe/Cu/K₂CO₃) was activated in only two hours.
- Methane + ethane yield was only 1.7-3.8 wt % of hydrocarbons produced.
- Fresh catalyst was activated in-situ without a separate pretreatment.
- Successfully tested the following systems for the slurry F-T bubble-column:
 - A new catalyst/reactor-wax separation system.
 - A new DP-system for monitoring the slurry level in the reactor.
 - A new steam co-feed system.

The seventh run of the BSU was then started up, using catalyst I-B at high pressure, as was done in Run CT-256-4. A 1 mm orifice feed-gas distributor was used for the first time in the pilot plant. Pretreatment and start of synthesis operations went smoothly, indicating no adverse distributor effects. By the end of this reporting period, the run had accumulated thirty-one days on-stream, with excellent conversion and selectivity results.

Our ability to analyze reactor-waxes was enhanced greatly by the development of a modified Gas Chromatographic method, enabling estimation of the fraction heavier than C₆₀. New Schulz-Flory distributions from Runs CT-256-4 and -5 are presented here based on this.

The 10.2 cm ID x 9.1 m tall hot-flow bubble-column was shaken down in preparation for hydrodynamic studies. Meanwhile, scoping studies continued, using short hot-flow bubble-columns. Results show that dynamically similar gas distributors give similar holdups in both a 3.2 and 5.3 cm ID columns.

IV. Detailed Description of Technical Progress

A. Task 1 - Process Studies In Two-Stage Bench-Scale Unit

1. Run CT-256-6 - Conclusion

The sixth run of the two-stage BSU, designated as Run CT-256-6, using catalyst I-D (containing Fe/Cu/K₂CO₃) in the first stage F-T bubble-column reactor and catalyst II-B (a ZSM-5 class catalyst) in a second-stage fixed-bed reactor, was smoothly started up on March 21, 1984. The major objectives of the run were to evaluate the performance of catalyst I-D for low methane + ethane operation, and to test many new features of the F-T slurry bubble-column, including an on-line slurry catalyst/reactor-wax separation system, a purgeless DP-system and a steam co-feed system.

Major highlights from this run are:

- The catalyst was activated in two hours in a high temperature (280°C) pretreatment step.
- Initial catalyst activity was equivalent to that of the most active F-T catalysts evaluated so far. The ranges of the first-stage slurry F-T reactor operating conditions and performance during the 33-day run were:

H ₂ +CO Flow Rate, Nm ³ /hr	0.5-3.4
Temperature, °C	250
Pressure, MPa	1.14-2.18
H ₂ /CO Feed Molar Ratio	0.7
Superficial Feed-Gas Velocity, cm/s	1.1-4.0
Space Velocity, NL/gFe-hr	0.4-4.1
Catalyst Loading, wt % (Average)	8-20
H ₂ +CO Conversion, mol %	37-75
Methane + Ethane Yield, wt % of HC	1.7-3.8
Reactor-Wax Yield, wt % of HC	30-80
Hydrocarbon Production, gHC/gFe	250

- The low methane + ethane yield over 33 days of operation demonstrates the stability of catalyst I-D for maximum liquid fuels production.
- The second-stage fixed-bed reactor was operated for only two days (due to end zone heater burnout) at:

Inlet Temperature, °C
GHSV, 1/hr

288
2419-5067

- Increased pressure (from 1.14 to 2.18 MPa) significantly decreased the H₂+CO conversion (e.g., at 9 DOS conversion dropped from 63 to 42 mol %). This contradicts previous experience with other catalysts (e.g., catalyst I-B, Run CT-256-3) and requires further investigation.
- Two minor and one major interruptions occurred in the F-T operation. Significant loss in activity and increased methane + ethane yield resulted only after a major upset at 26 DOS. This upset was caused by a faulty surge check valve on the CO feed line. N₂ was fed to the slurry reactor for 76 hours. After this upset, the activity was very low and the run was terminated, even though the methane + ethane yield was a low 3.8 wt %.
- Demonstrated addition of fresh catalyst I-D and in-situ activation without separate (high temperature) pretreatment.
- Demonstrated reliable operation of an on-line slurry catalyst/reactor-wax separation system and of a purgeless differential pressure (DP) system.
- Tested for the first time a steam co-feed system for in-situ shift of very low (0.43) H₂/CO ratio feeds.

a. First-Stage Fischer-Tropsch Reactor Operation

The last quarterly report (January-March, 1984) contained details of the startup and pretreatment of Run CT-256-6. These will not be repeated here. A brief discussion of the synthesis operation was also given. A detailed description and discussion of the entire run is given here. The run lasted thirty-three days and was successful in establishing low methane + ethane operation, with a new catalyst (Fe/Cu/K₂CO₃, designated as I-D). In addition, it provided a great deal of new information on slurry F-T bubble-column operation.

Immediately after catalyst pretreatment, at which point the CO conversion reached 75%, the slurry reactor temperature was lowered to 250°C. Twelve hours later, when the H₂+CO conversion gradually increased back to about 68 mol %, the pressure was increased to 2.18 MPa for increased throughput, and the on-line catalyst/reactor-wax separation system was started up to remove the reactor-wax accumulated in the reactor. The major events are

listed in Table 1.

Figure 1 shows the conversion and methane + ethane selectivities, as well as the temperature, pressure, superficial gas velocity and space velocity for the entire run. The range of synthesis conditions and performance of the first-stage F-T reactor were:

H ₂ +CO Flow Rate, NM ³ /hr	0.5-3.4
Temperature, °C	250
Pressure, MPa	1.14-2.18
H ₂ /CO Feed Ratio, Molar	0.7
Superficial Feed Gas Velocity, cm/s	1.1-4.0
Space Velocity, NL/gFe-hr	0.4-4.1
H ₂ +CO Conversion, mol %	35-75
Methane + Ethane Yield, wt %	1.7-3.8
Reactor-Wax Yield, wt %	30-80

The synthesis operation was interrupted three times. The first interruption was due to a slurry leak in the on-line slurry catalyst/reactor-wax separation system, which resulted in the loss of about 480 g of catalyst. The second interruption was caused by a faulty surge check valve on the CO feed line. N₂ was fed to the slurry reactor for 9 hours, while the surge check valve was replaced. This upset had no detrimental effect on reactor performance.

The third interruption was again due to the surge check valve on the CO line. The system was then modified to include two surge check valves in parallel. This allows replacement of one valve without interrupting CO supply to the unit. During this last interruption, leaks were found on the pancake valves which activate the H₂ and CO glycol systems used for feed flow rate measurement. While these were being fixed, N₂ was fed to the slurry reactor over a total of 76 hours. This last upset seemed to have a detrimental effect on both H₂+CO conversion and methane + ethane yield. It is not clear whether the interruption itself or the four-day operation at very low gas superficial velocity (about 1 cm/s) preceding the interruption caused the drop in H₂+CO conversion and the increased methane + ethane yield. Such low velocity operation had caused problems before (e.g., Run CT-256-3, Kuo 1983).

The initial catalyst activity was found to be comparable to that of the most active F-T catalysts used. This is shown in Figure 2, as H₂+CO conversion versus space velocity. Except for the low velocity data, all data fall on the same curve.

During the run, fresh I-D catalyst was added twice, to bring the catalyst content to the initial level, and to test in-situ activation without separate pretreatment. The results

are shown in Figure 3. Volume contraction is proportional to H_2+CO conversion, and was used to determine the extent of catalyst activation. It is seen that, in two cases, the catalyst reached 95 and 75% of the full expected activity, respectively, within ~10-20 hours, indicating the capability of on-line catalyst makeup without separate high temperature pretreatment.

Increased pressure had a detrimental effect on the H_2+CO conversion, without affecting the methane + ethane yield. For instance, increasing the pressure from 1.14 to 2.18 MPa reduced the H_2+CO conversion at 9 DOS from 63 to 42 mol %. This contradicts previous experience, (e.g., catalyst I-B in Run CT-256-3, Kuo, 1983) and requires further investigation.

Although the H_2+CO conversion varied significantly throughout the run, mostly the result of upsets and pressure variation (between 1.14 and 2.18 MPa), the methane + ethane yield was a low 1.7-3.8 wt % over the whole run (33 days). This indicates that catalyst I-D has good stability for low methane + ethane operation. The run was terminated because of the very low activity after the last upset even though the methane + ethane yield was still low (3.8 wt %).

Note that the conversion drops every time the on-line slurry catalyst/reactor-wax separation system is on. The reason for this is that the separation system has a slurry holdup of about 2,000 cm^3 , and the catalyst in this slurry does not participate in the reaction, being removed from the reactor during separation.

Material balances were performed daily. Table A-1 summarizes the operating conditions and results for this run. Detailed analytical breakdowns of the first-stage product are given in Table A-2. No breakdown of the reactor-wax and no oxygenates breakdown is available at the present time.

F-T reactor-wax was removed regularly (to keep the level in the slurry reactor at 762 cm) by using the new on-line slurry catalyst/reactor-wax separation system. The slurry inventory in the slurry reactor was monitored by the new purgeless DP-system described in the previous quarterly report. Figure 4 shows the cumulative reactor-wax production versus time-on-stream. The reactor-wax production rate is estimated from the slope of the least squares fit of the data, shown as the continuous curves in Figure 4.

The purgeless DP-system was also used to estimate the gas holdup in the reactor. Table 2 shows the average gas holdup at two superficial gas velocities. The gas holdup at 3 cm/s velocity is substantially higher than that measured at the end of Run CT-256-5 (8.6 vol % at 4 cm/s velocity). The reason for this may be that Run CT-256-5 and -6 waxes are different. This will be further investigated as soon as analysis of Run CT-256-6 wax

is available.

Table 2 also shows the predicted gas holdup from Deckwer's correlation (Deckwer et al., 1980). At low velocity, the agreement is good; however, at high velocity, the actual gas holdup is substantially higher than that predicted by Deckwer.

Figure 5 shows catalyst concentration profiles obtained by sampling of the reactor slurries at 30, 152, 305, and 610 cm levels. The flatter profile at 29.4 DOS is due to the somewhat higher superficial gas velocity (3.8 vs 3.0 cm/s). The increased catalyst loading between 15.1 and 19.7, and 19.7 and 29.4 DOS is the result of the two catalyst additions at 16.1 and 21.6 DOS. Good agreement exists between the measured catalyst loading (straight line fit of the data) and the catalyst loading estimated from the initial loading and from the estimated catalyst loss through leaks and reactor-wax removal.

b. Second-Stage Fixed-Bed ZSM-5 Reactor Operation

The second-stage reactor, containing 215 g of fresh II-B ZSM-5 catalyst was brought on-stream at 14 DOS, using a start-of-cycle inlet temperature of 288°C. After 39 hours, the second-stage had to be shut down because of burnout of its end zone heater. Since 39 hours are not sufficient to equilibrate the liquid product receivers, no liquid product analysis is available.

2. Run CT-256-7 - Startup

The seventh run of the two-stage BSU, designated as Run CT-256-7, was started successfully on May 31, 1984. The main objectives of the run were:

- Demonstrate long-term low methane + ethane operation using catalyst I-B at high pressure, as was done in Run CT-256-4.
- Evaluate for the first time in the two-stage unit a single-orifice feed-gas distributor (1 mm in diameter).

As of the end of this quarter, 31 days on-stream had been accumulated. Methane + ethane yields have ranged from 2.4 to 4.8 wt % of hydrocarbons produced, and H₂+CO conversions have been 50-86 mol %. No adverse effects of the orifice distributor on reactor performance have been detected.

A detailed account of this run will be presented upon completion of the run.

a. Fischer-Tropsch Slurry-Catalyst Loading and Pretreatment

2,200 g of catalyst I-B were loaded at the start of Run CT-256-7, which corresponds to an initial loading of 23.5 wt % catalyst. Pretreatment was then started at the following conditions:

Temperature, °C	280
Pressure, MPa	1.14
H ₂ /CO Feed Ratio, Molar	0.67
Superficial Feed-Gas Velocity, cm/s	6
Space Velocity, NL/gFe-hr	1.76

These conditions are identical to those used in Run CT-256-4 except that the space velocity there was 1.56 NL/gFe-hr. A plot of the volume contraction of this run is shown in Figure 6. It can be seen that the pretreatment resulted in a high volume contraction at the end. This was our first indication that the orifice feed-gas distributor would not inhibit the slurry reactor performance.

b. Brief Description of Fischer-Tropsch Reactor Synthesis Operation

Following pretreatment, the temperature was lowered to 257°C and the pressure was increased to 2.17 MPa. The H₂+CO conversion lined out at 86 mol %, and the methane + ethane yield was 2.4 wt % of hydrocarbons produced. Also, the reactor-wax removal system was started, and it easily handled the wax yield of 60-80 wt % of the hydrocarbon produced.

During the first 21 days on-stream, conversion remained steady, while the methane + ethane yield rose to about 4.0 wt %. After that, however, the H₂+CO conversion dropped to 50 mol % over the next eight days. The reasons for this decline are presently under investigation. The rate of increase in the methane + ethane yield, however, remained small.

The second-stage fixed-bed reactor has been on-stream for 23 days thus far, converting first-stage overhead product into gasoline. No product analyses are yet available.

3. Future Work

- Continue Run CT-256-7 to achieve low methane + ethane mode operation.

B. Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

1. Thermal Cracking, Hydrocracking, Fluid Catalytic Cracking, and Hydrodewaxing

Preliminary results from proprietary hydrocracking, fluid catalytic cracking, hydrodewaxing, and thermal cracking studies to upgrade F-T reactor-wax are described in the Mobil Proprietary Appendix.

2. Future Work

- Continue scoping studies for F-T reactor-wax upgrading using conventional refinery processes.

C. Task 3 - Product Evaluation

1. Improved Fischer-Tropsch Reactor-Wax Analysis

Based on the results of the vacuum-fractionation of Run CT-256-4 reactor-wax, it was shown that the reactor-wax contained a large fraction of hydrocarbons heavier than C₆₀. The GC method used so far was limited to hydrocarbons up to C₆₀.

A modified Gas Chromatographic (GC) method was, hence, developed to obtain "boiling point" profiles (carbon number distribution) and to estimate the fraction of reactor-wax boiling above 596°C (C₅₅⁺). As described below, two major improvements were done to the existing method.

A suitable solvent is not available to completely dissolve the heavy reactor-wax sample prior to injection into the GC. To circumvent the solubility problem, the reactor-wax was injected as solids by employing a packed, cool-on-column injection port. The second improvement was the addition of a small but known amount of n-C₁₁, n-C₁₂ and n-C₁₃ hydrocarbons as internal standards. These standards were used to prorate the amount of reactor-wax which was not eluted from the GC column (i.e., the C₅₅⁺ hydrocarbons). Figure 7 shows a typical chromatogram for Run CT-256-4 reactor-wax.

The reactor-waxes from Runs CT-256-3, -4 and -5 were reanalyzed by the improved method and the results are reported in the Table 3. Reactor-wax from Run CT-256-3, which gave a low yield of reactor-wax (4-30 wt % of total hydrocarbons), contained only 2 wt % of C₅₅⁺. This is consistent with the earlier analysis using the older GC method without internal standards. On the other hand, the reactor-waxes from Runs CT-256-4 and -5 (the high reactor-wax yield operation) contained 64.8 and 74.8 wt % of C₅₅⁺ hydrocarbons, respectively.

Table 4 compares the improved GC analysis with the vacuum fractionation results and shows the good agreement between them.

In view of the above results, it is interesting to compare the Schulz-Flory distribution (Flory, 1967) of Run CT-256-3 (Figure 21, Kuo, 1983) with that of Runs CT-256-4 and -5 (Figures 8 and 9). In all cases there is a distinct break in the slope at C₂₀, coinciding approximately with the inclusion of the reactor-wax. In addition, another break in the slope occurs for Runs CT-256-4 and -5 at C₆. Such a break was not observed with Run CT-256-3 data. As expected, the probability of chain growth for the C₂₀⁺ fraction increases from Run 3 to 4 to 5, i.e., with increasing wax yield and/or increasing molecular weight of the wax.

A possible explanation for the break in the Schulz-Flory distribution is the readsorption of large molecules on the catalyst active sites and further chain-growth.

2. Product Analyses

Product analyses to support other tasks were carried out.

3. Future Work

- Evaluate Field-Ionization-Mass-Spectrometer (FIMS) to analyze F-T reactor-waxes.
- Continue providing product analyses to support other tasks.

D. Task 4 -Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

1. Scoping Hydrodynamic Studies Using Short Hot-Flow Columns

Scoping hydrodynamic studies were carried out to determine whether dynamically similar feed-gas distributors give rise to the same gas holdups in two different diameter columns.

To accomplish this, it was decided to use previously reported data from a 3.2 cm ID x 1.9 m tall hot-flow bubble-column (see June-September, 1983 Quarterly Report). That data was taken with FT-200⁽¹⁾ and a 0.25 mm single-orifice distributor, among others.

Using a 5.3 cm ID x 1.9 m tall hot-flow bubble-column, we then measured the gas holdup in FT-200 over two other gas distributors, a 0.41 mm orifice and a 0.25 mm 3-hole. Both of these produce roughly the same gas jet velocity through the holes as the 0.25 mm orifice did in the 3.2 cm ID column, making them dynamically similar (see January-March, 1984 Quarterly Report).

The results are shown in Figure 10. The two gas distributors used in the 5.3 cm ID bubble-column produced identical holdups.

The flow pattern was very violent in both cases, with very small bubbles swirling rapidly and occasional large bubbles rising through. No slugging was visible, however, as was the case with the 3.2 cm ID column.

These results lend support to the jet-velocity criterion for similarity. The 3.2 cm column, however, shows a higher holdup at superficial velocities above 2.0 cm/s, though not dramatically so. This may be attributed to the presence of foam, which was more prominent in the smaller column. It may be that the foam is stabilized by the walls of the narrower column. This difference probably would not be present in a non-foaming medium.

(1) A F-T paraffin wax with an average molecular weight of 600.

2. Hydrodynamic Studies Using a Tall Hot-Flow Bubble-Column

a. Shakedown of 10.2 cm ID x 9.1 m Tall Hot-Flow Bubble-Column

While the 5.1 cm ID tall hot-flow bubble-column was undergoing modifications, the 10.2 cm ID bubble-column was shaken down. A partial shakedown was carried out earlier (January 1984) along with the 5.1 cm ID column. However, it was never heated at that time. The shakedown consisted mainly of pressure-testing the bubble-column with 239 kPa N₂ at 138°C. Also, the pressure controller was checked out. The shakedown was carried out very smoothly without any problems.

3. Future Work

- Conduct hydrodynamic studies in 10.2 cm ID tall hot-flow bubble-column.
- Continue evaluation of a series of CSTR's as an alternative to the slurry bubble-column reactors.

V. Nomenclature

Acronyms

BSU	Bench-Scale Unit
DOS	Days on Stream
DP	Differential Pressure
FIMS	Field-Ionization-Mass-Spectrometry
F-T	Fischer-Tropsch
GC	Gas Chromatography
ID	Inside Diameter

VI. Literature

Deckwer, W.-D., Louisi, Y., Zaidi, A., and Ralek, M.,
Ind. Eng. Chem. Process Des. Dev., 19, 699 (1980).

Flory, P. J., Principles of Polymer Chemistry, Cornell
University Press, Ithaca, NY (1967).

Kuo, J. C. W., "Slurry Fischer-Tropsch/Mobil Two-Stage
Process of Converting Syngas to High Octane Gasoline",
Mobil Research and Development Corporation, Final
Report, DOE Contract No. DE-AC22-80PC30022, June, 1983.

TABLE 1
MAJOR EVENTS IN RUN CT-256-6
 (Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
-0.1- 0	Pretreatment
0 - 0.8	1.14 MPa; 250°C; 4 cm/s; 0.7 H ₂ /CO
0.8- 2.0	1.14 ---> 2.18 MPa
1.1 separation system.	Upset: Slurry leak at on-line catalyst/wax
2.0- 9.1	2.18 ---> 1.14 MPa, 4 ---> 3 cm/s
9.1-11.8	1.14 ---> 2.18 MPa
11.8-14.6	2.18 ---> 1.14 MPa
14.2	2nd-Stage on at 288°C
14.6-22.6	1.14 ---> 2.18 MPa
15.8	2nd-Stage off: end zone heater burnout
16.1	350 g of fresh catalyst added
19.3 hours	Upset: CO leak caused syngas cut off for 10
21.6	400 g of fresh catalyst added
22.6-25.9	2.18 ---> 1.14 MPa; 3 -> 1.1 cm/s
25.9 valve	Upset: No CO flow due to safety surge check shut off -- no syngas to unit for 3 days
25.9-33.1	1.14 MPa; 250°C; 3 cm/s; 0.7 H ₂ /CO
32.1 cofeed	0.7 ---> 0.4 H ₂ /CO and stoichiometric steam to the slurry reactor for 4 hours
33.1	End of Run CT-256-6

TABLE 2
 AVERAGE GAS HOLDUP
 FROM PURGELESS DP SYSTEM(1)

 (Run CT-256-6)

DOS	17.0	20.4	23.6	24.3
Gas Sup. Vel., cm/s	3	3	1.2	1.2
Contraction, Vol %	33.7	35.5	61.3	60.5
Avg. Gas Sup. Vel., cm/s	2.5	2.5	.8	.8
Avg. Gas Holdup, Vol %	23.0	21.4	3.5	4.8
Avg. Gas Holdup, (2) Vol %	14.5	14.5	4.2	4.2

(1) 250°C, 0.7 H₂/CO

(2) Deckwer, et al., 1980

TABLE 3
 COMPOSITION OF
 FISCHER-TROPSCH REACTOR-WAXES

<u>Carbon Number</u>	<u>Run CT-256-3</u>	<u>Run CT-256-4</u>	<u>Run CT-256-5</u>
10-20	7.7	1.9	1.5
21-25	15.1	3.9	3.1
26-30	19.8	6.2	3.9
31-35	17.9	6.6	4.3
36-40	13.2	5.3	3.5
41-45	9.7	4.6	3.3
46-50	6.7	4.1	3.1
51-55	3.9	2.6	2.6
55+	<u>6.0</u>	<u>*64.8</u>	<u>74.7</u>
Total	100.0	100.0	100.0

Unit: Wt %

TABLE 4
 COMPOSITION OF A
 FISCHER-TROPSCH REACTOR-WAX

 (Run CT-256-4)

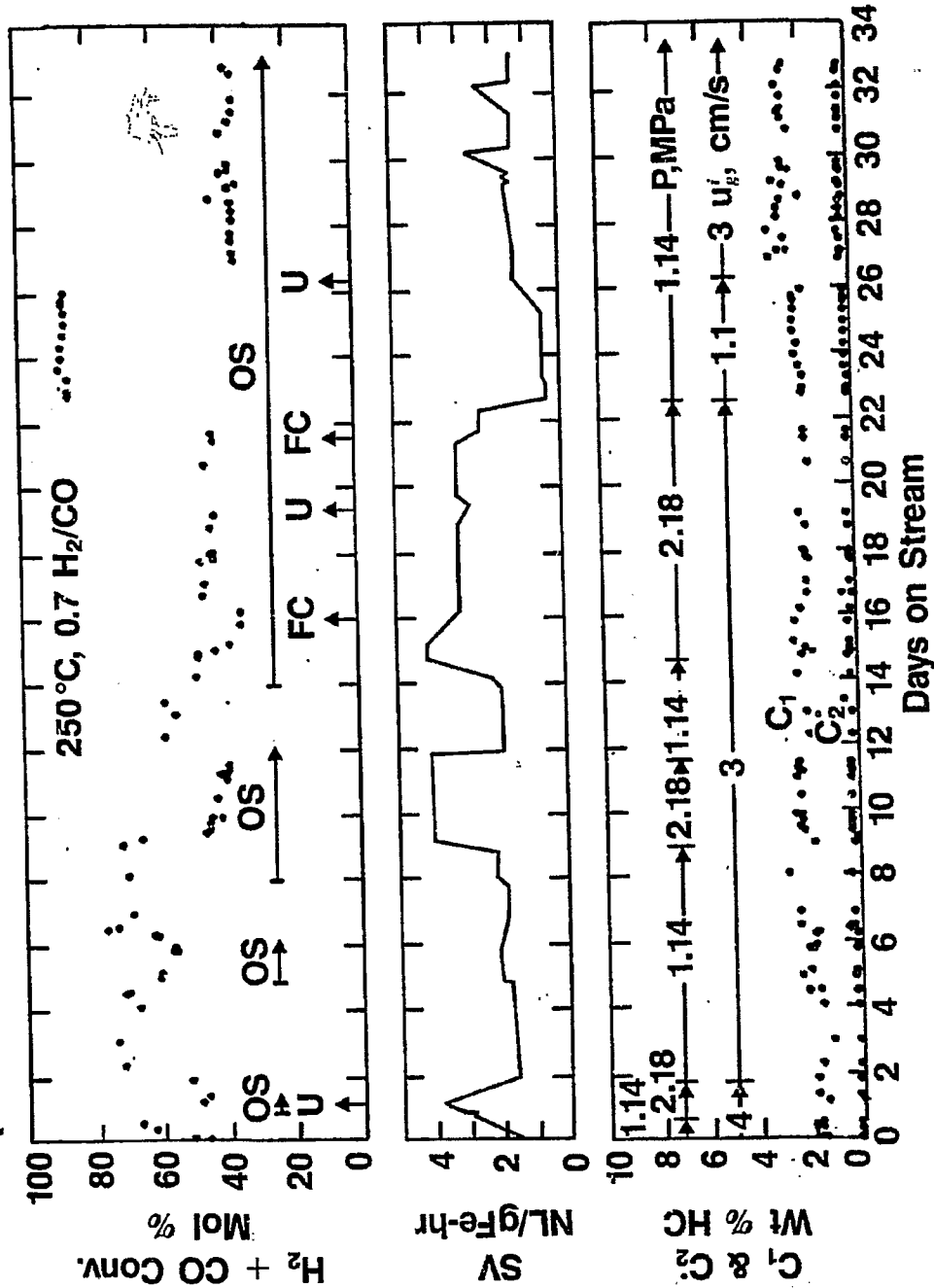
<u>TBP Fraction (°C)</u>	<u>Distillation</u>	<u>New GC Analysis</u>
343-	1.1	1.9
343-399	2.5	3.9
399-454	7.0	6.2
454-461	6.3	1.9
461+	<u>83.1</u>	<u>86.1</u>
Total	100.0	100.0

Unit: Wt %

FIGURE 1

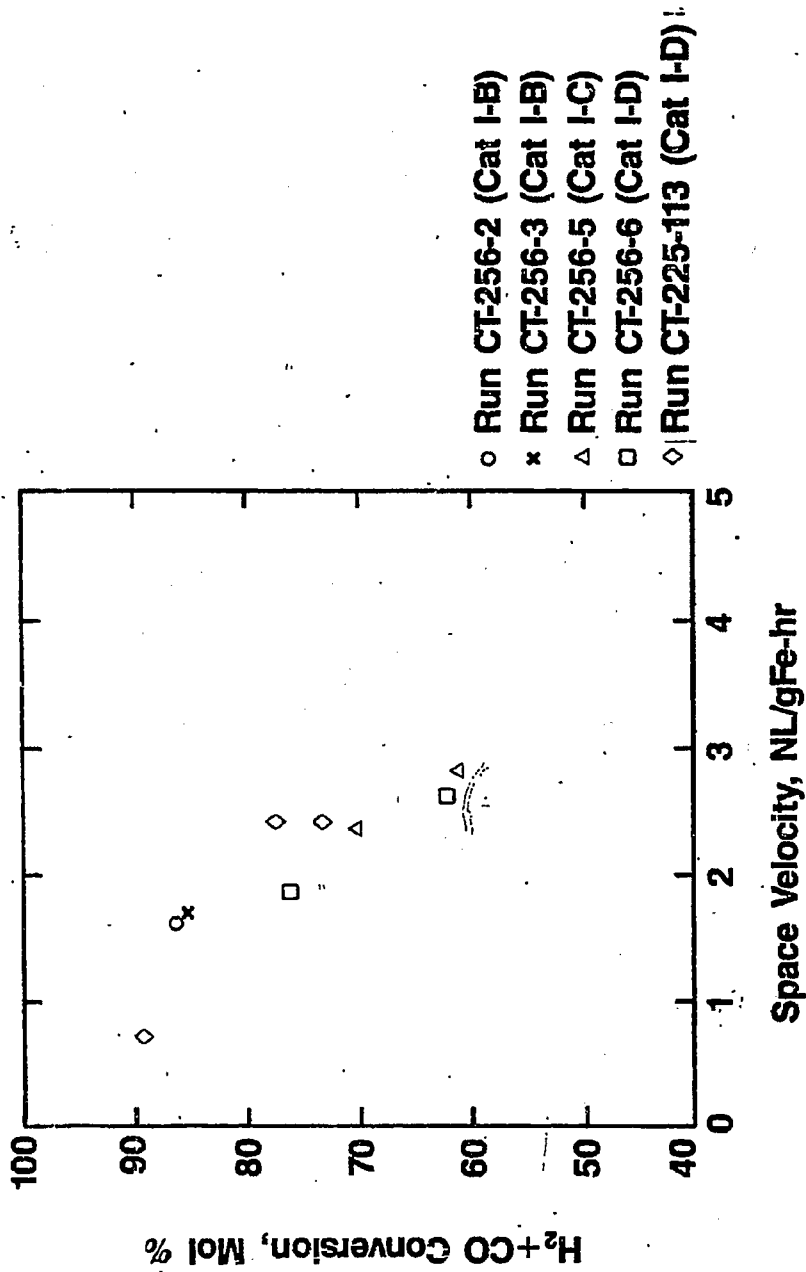
**SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD**

(RUN CT-256-6; 1ST-STAGE CATALYST I-D:PPTD Fe/Cu/K₂CO₃)



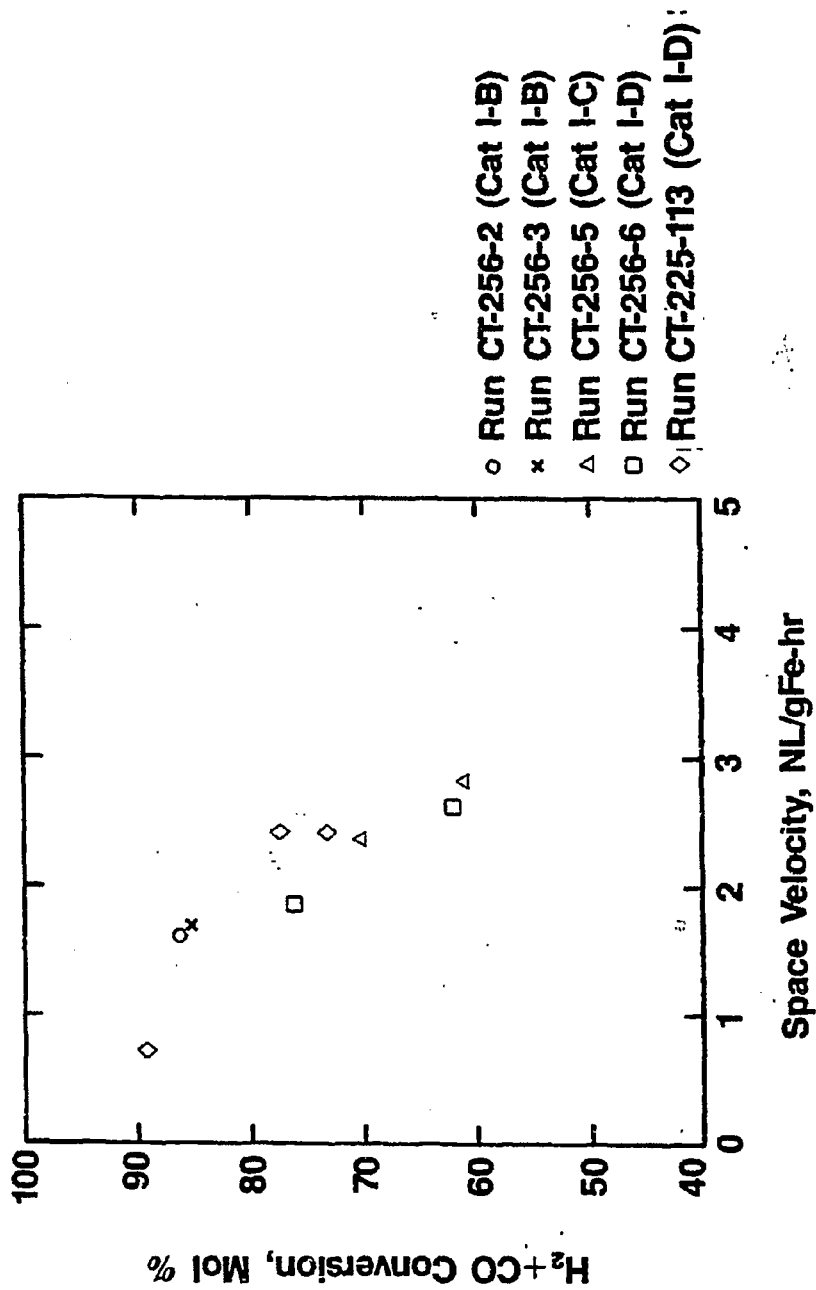
U - Upset FC - Fresh Catalyst Added OS - On-line Catalyst/Wax Separation

FIGURE 2
COMPARISON OF INITIAL FISCHER-TROPSCH CATALYST ACTIVITIES



All data corrected to 1.48 MPa, 250 °C

FIGURE 2
COMPARISON OF INITIAL FISCHER-TROPSCH CATALYST ACTIVITIES



All data corrected to 1.48 MPa, 250 °C

FIGURE 3

FRESH FISCHER-TROPSCH CATALYST ADDITION

(Run CT-256-6)

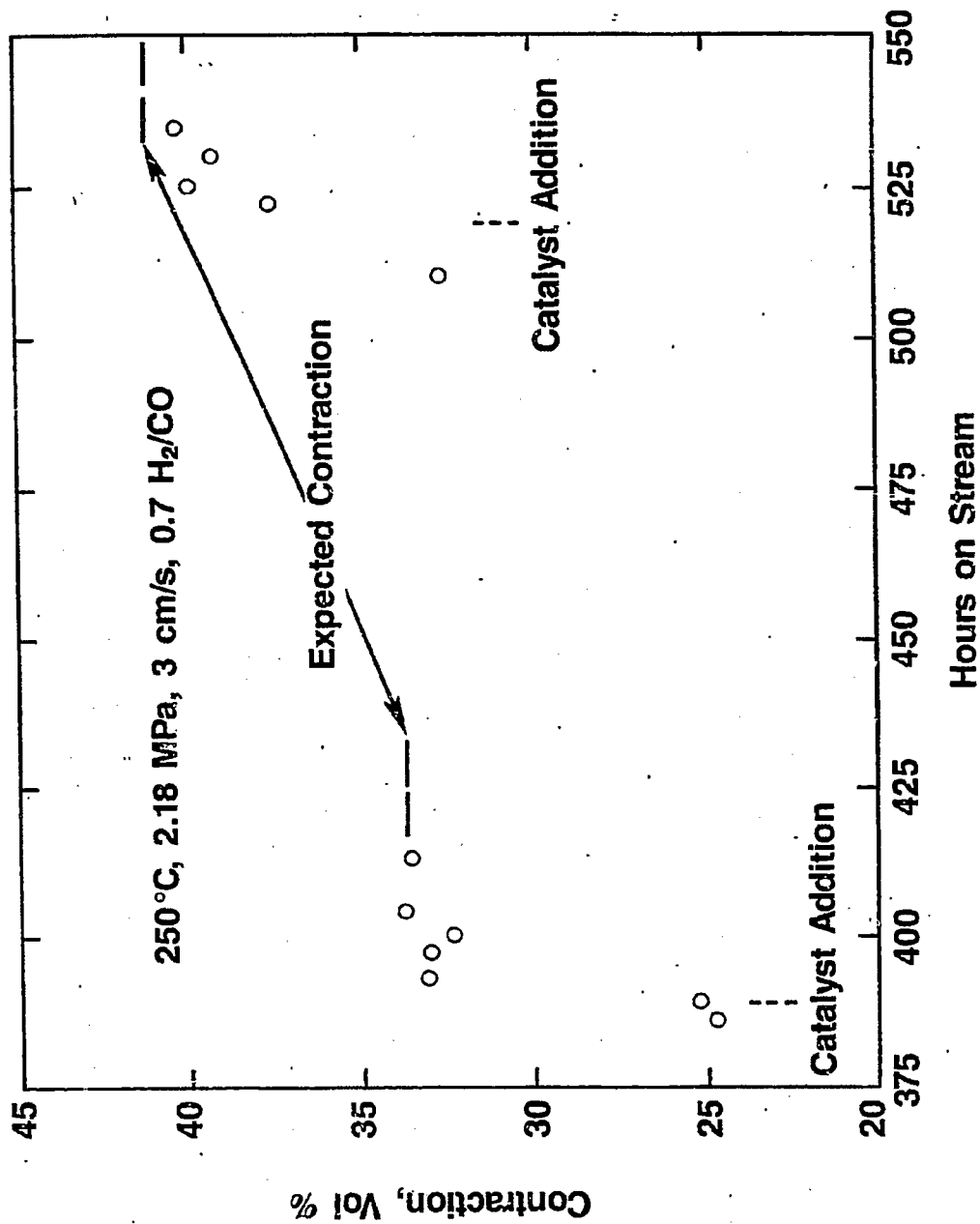


FIGURE 4
CUMULATIVE FISCHER - TROPSCH REACTOR-WAX PRODUCTION
(Run CT-256-6)

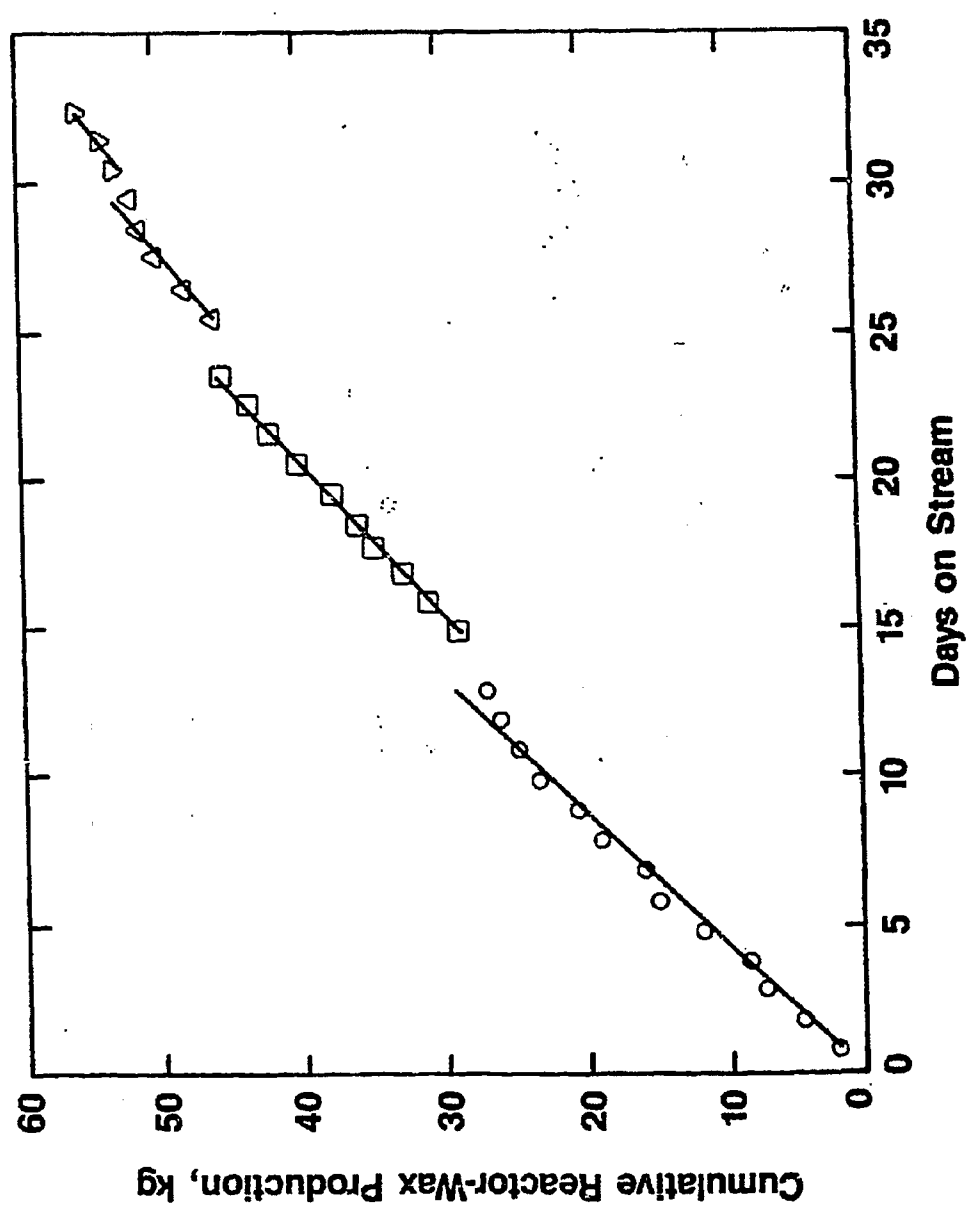


FIGURE 5

**SLURRY FISCHER-TROPSCH BUBBLE-COLUMN
CATALYST CONCENTRATION PROFILES**

(Run CT-256-6)

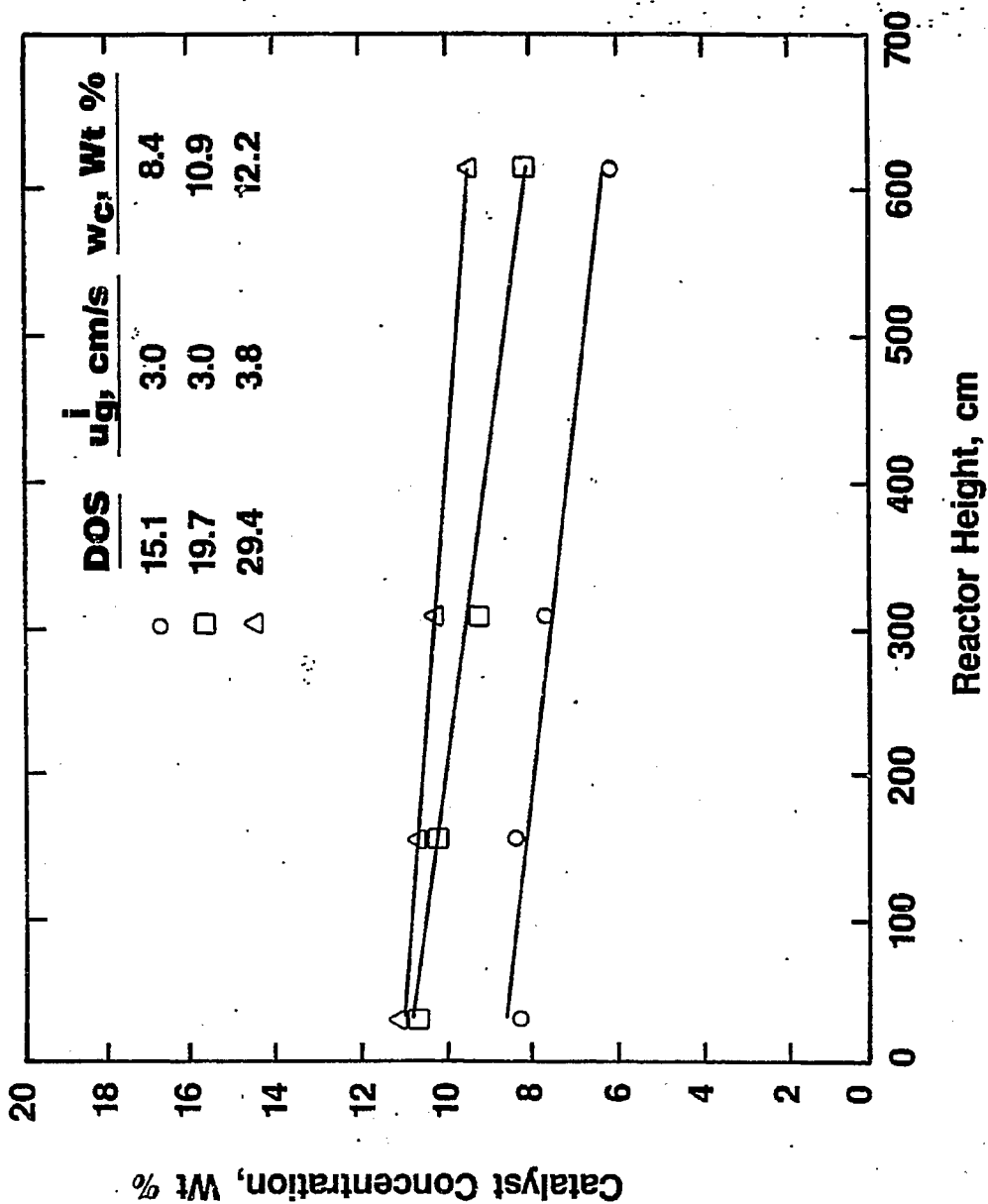


FIGURE 6

PRETREATMENT OF FISCHER-TROPSCH CATALYST I-B
(Runs CT-256-7 and -4)

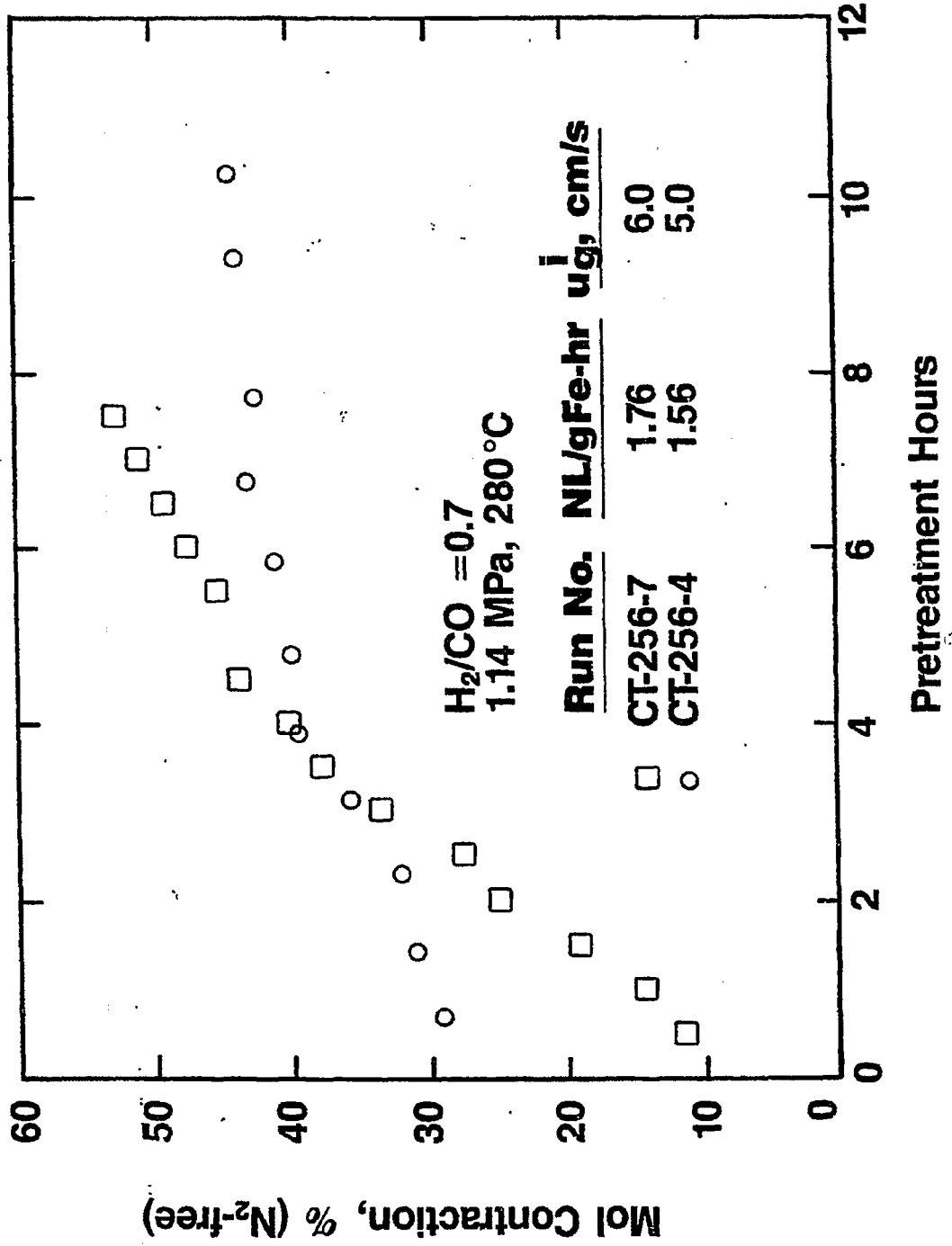


FIGURE 7
GAS CHROMATOGRAM OF RUN CT-256-4 REACTOR-WAX

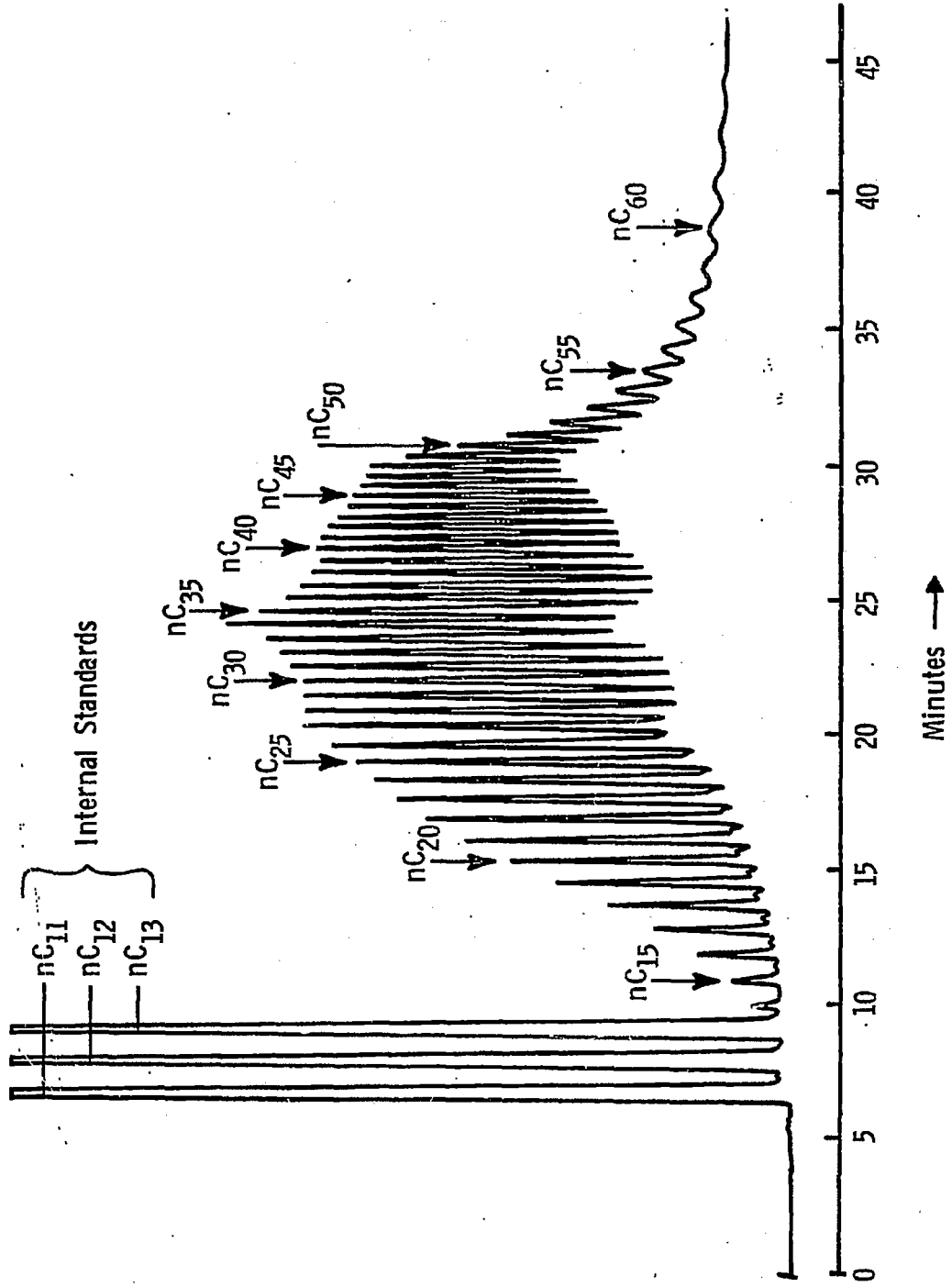


FIGURE 8

**SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE
FISCHER-TROPSCH PRODUCTS**

(Run CT-256-4, 26.3 DOS
Reactor-Wax Yield — 46 Wt%)

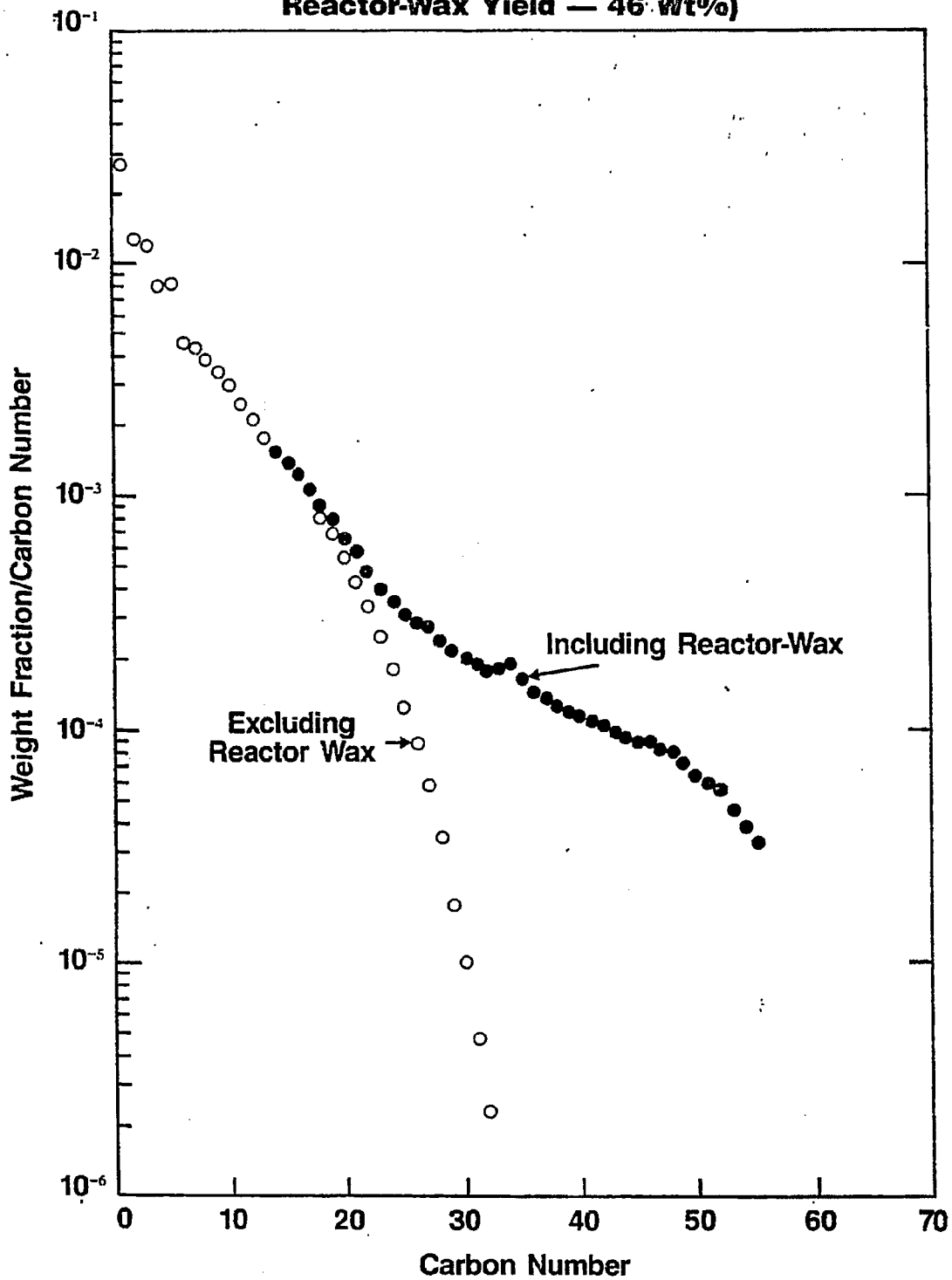


FIGURE 9

**SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE
FISCHER-TROPSCH PRODUCTS**

(Run CT-256-5, 5.8 DOS
Reactor-Wax Yield — 77 Wt%)

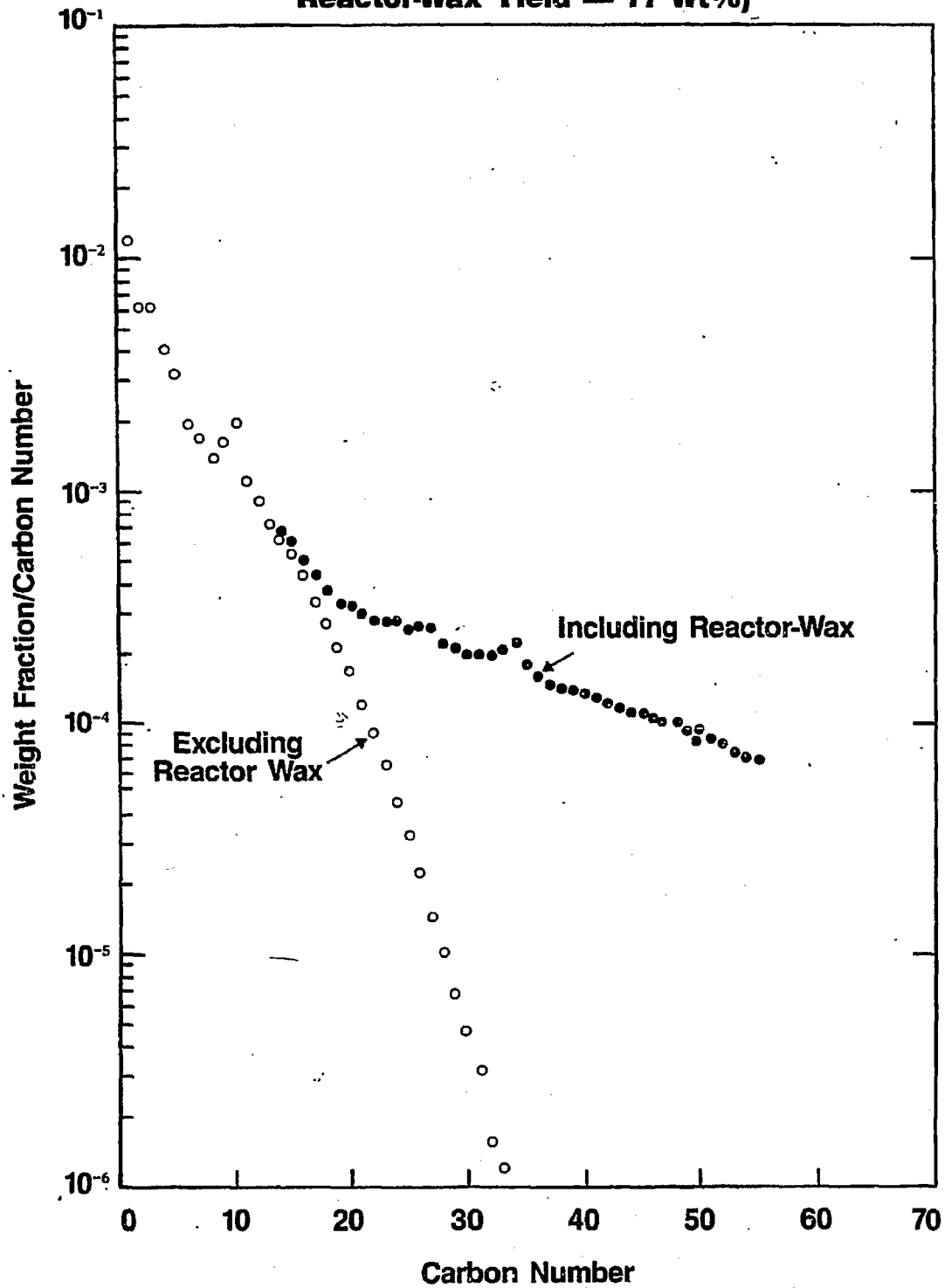
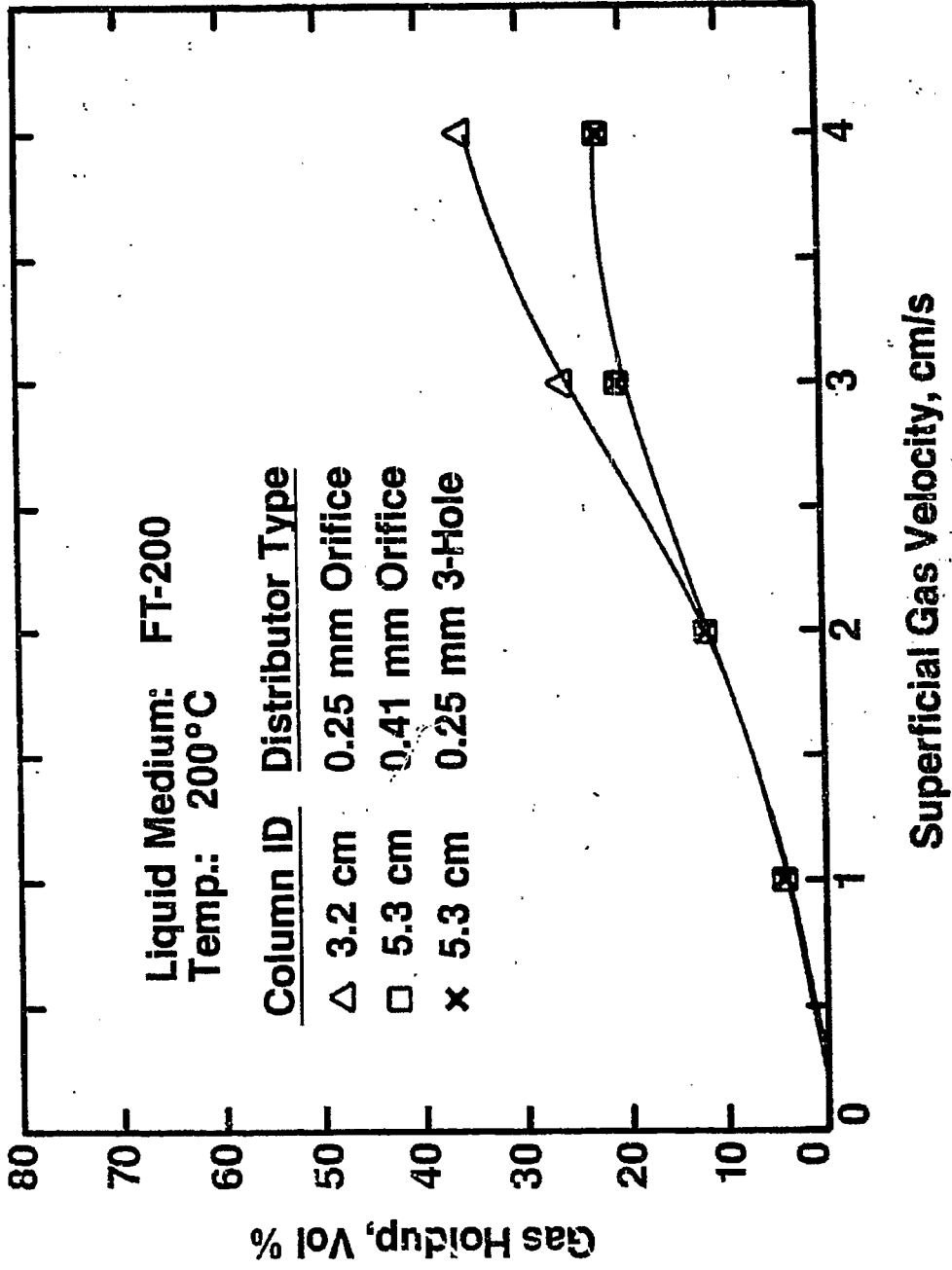


FIGURE 10

EFFECT OF COLUMN DIAMETER ON GAS HOLDUP



APPENDIX A

SUMMARY OF DATA FROM RUN CT-256-6

Table A-1
 First Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances
 (Second-Stage Not Operative)
 (Run CT-256-6)

(Nitrogen-Free Basis)	6-3	6-4	6-5	6-6	6-10	6-11	6-14
M.B. No.	8.2	9.2	10.2	12.5	16.2	17.2	20.8
Days On-stream							
Charge H ₂ /CO (Molar)	0.706	0.714	0.714	0.720	0.684	0.706	0.644
Temperature, °C	250	249	249	249	249	249	249
Pressure, MPa	1.170	2.184	2.184	2.184	2.197	2.197	2.197
Feed Sup. Vel., cm/s	2.926	2.984	2.984	3.010	3.081	3.012	2.825
Space Vel., NL/gFe-hr	2.113	3.968	3.988	4.036	3.098	3.047	2.934
N ₂ in Feed, Mol %	1.2	0.7	0.7	0.7	3.2	2.9	1.2
Conversions, Mol % :							
H ₂	56.05	43.82	42.22	38.84	30.43	36.17	35.17
CO	61.11	45.25	43.82	37.68	25.60	34.40	44.51
H ₂ +CO	59.02	44.65	43.15	38.14	27.56	35.13	40.85
Yields, Wt % of Products :							
Hydrocarbons (1)	16.92	9.85	9.87	9.59	7.92	8.15	9.58
CO ₂	41.30	31.36	28.43	25.65	18.18	29.00	24.68
H ₂ O (1)	0.71	1.56	1.21	1.60	1.32	1.25	0.65
H ₂	2.24	2.87	3.04	3.06	3.20	2.91	3.25
CO	38.84	54.36	57.45	60.09	69.38	58.69	61.74
Total	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	95.22	95.73	92.94	98.53	102.14	106.29	85.84
gHC/Nm ³ (H ₂ +CO) conv.:	209	161	162	188	227	189	159
(H/C) Atomic Ratio in HC :	2.12	2.12	2.12	2.12	2.11	2.13	2.12
Selectivities, Wt % of HC :							
Methane	2.83	2.45	2.31	2.19	2.15	2.64	2.09
Ethane	2.15	2.13	1.95	1.84	1.36	1.84	1.74
Ethane	0.46	0.45	0.41	0.38	0.31	0.40	0.38
Propene	2.80	2.64	2.43	2.28	1.77	2.35	2.19
Propene	0.53	0.61	0.58	0.54	0.43	0.62	0.58
Butenes	2.26	2.11	1.94	1.83	1.51	2.00	1.80
i-Butane	0.14	0.24	0.23	0.24	0.16	0.37	0.24
n-Butane	0.54	0.63	0.60	0.56	0.48	0.72	0.67
C ₅ - C ₁₁ (2)	7.00	6.95	6.40	5.65	3.36	6.48	5.86
Light Hydrocarbons (3)	13.56	18.18	19.65	15.52	23.56	19.41	17.56
Heavy Hydrocarbons (4)	10.88	12.59	11.05	18.28	15.42	15.49	15.97
Slurry Rx.-Wax	56.83	51.00	52.46	50.68	49.18	47.28	50.56
Total	100	100	100	100	100	100	100

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condensers

(4) Collected in Hot Condenser

Table A-1(cont'd)
 First Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances
 (Second-Stage Not Operative)
 (Run CT-256-6)

	6-17	6-18	6-19	6-20	6-23	6-24
(Nitrogen-Free Basis)						
M.B. No.	23.8	24.8	25.8	27.6	30.6	31.6
Days On-stream						
First-Stage Conditions:						
Charge H ₂ /CO (Molar)	0.676	0.679	0.690	0.721	0.684	0.651
Temperature, °C	249	249	249	249	249	249
Pressure, MPa	1.156	1.156	1.156	1.177	1.163	1.170
Feed Sup. Vel., cm/s	1.198	1.214	1.205	2.899	3.114	3.059
Space Vel., NL/gFe-hr	0.509	0.512	0.507	1.293	1.317	1.299
N ₂ in Feed, Mol %	3.1	4.1	4.2	1.9	7.1	7.4
Conversions, Mol % :						
H ₂	83.43	82.19	81.85	76.68	41.07	40.16
CO	91.35	90.09	90.07	84.68	34.18	31.52
H ₂ +CO	88.16	86.90	86.71	35.52	36.98	34.93
Yields, Wt % of Products :						
Hydrocarbons (1)	24.62	22.41	22.55	10.84	8.39	7.86
CO ₂	64.25	63.55	64.24	26.26	25.25	24.53
H ₂ O (1)	0.60	2.08	1.23	0.18	0.69	0.28
H ₂	0.90	0.97	1.00	3.01	2.78	2.65
CO	9.62	10.99	10.99	59.72	62.89	64.63
Total	100	100	100	100	100	100
Ball Recovery, Wt % of Charge:	85.33	85.56	85.76	103.54	99.32	100.76
SHC/Nm ³ (H ₂ +CO) conv.:	187	172	173	241	175	179
(H/C) Atomic Ratio in HC :	2.11	2.11	2.11	2.12	2.12	2.12
Selectivities, Wt % of HC :						
Methane	2.28	2.52	2.12	2.39	2.39	2.40
Ethene	1.21	1.36	1.37	1.83	1.95	1.98
Ethane	0.27	0.30	0.33	0.39	0.38	0.38
Propene	1.70	1.90	1.94	2.33	2.46	2.50
Propane	0.36	0.39	0.46	0.51	0.53	0.53
Butenes	1.52	1.73	1.74	1.95	2.11	2.14
i-Butane	0.08	0.07	0.07	0.24	0.27	0.31
n-Butane	0.43	0.48	0.49	0.98	0.62	0.63
C ₅ - C ₁₁ (2)	3.75	4.24	4.93	6.65	7.46	7.80
Light Hydrocarbons (3)	19.51	19.15	16.32	27.06	23.08	28.04
Heavy Hydrocarbons (4)	13.68	12.56	14.87	3.12	7.28	2.84
Slurry Rx.-Max	55.00	55.00	55.00	52.49	50.98	50.00
Total	100	100	100	100	100	100

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condensers

(4) Collected in Hot Condenser

Table A-2
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor
(Run CT-256-6)

M.B.No.	6-3	6-4	6-5	6-6	6-10	6-11	6-14
Days On-stream	8.2	9.2	10.2	12.5	16.2	17.2	20.8
METHANE	2.83	2.45	2.31	2.19	2.15	2.64	2.09
ETHENE	2.15	2.13	1.95	1.84	1.36	1.84	1.74
ETHANE	0.46	0.45	0.41	0.38	0.31	0.40	0.38
PROPENE	2.80	2.64	2.43	2.28	1.77	2.35	2.19
PROPANE	0.53	0.61	0.58	0.54	0.43	0.62	0.58
1-BUTANE	0.14	0.24	0.23	0.24	0.16	0.37	0.24
1-BUTENE+2-METHYLPROPENE	2.21	2.08	1.94	1.83	1.51	2.00	1.80
N-BUTANE	0.54	0.63	0.60	0.56	0.48	0.72	0.67
TRANS-2-BUTENE	0.03	0.00	0.00	0.00	0.00	0.00	0.00
CIS-2-BUTENE	0.03	0.03	0.00	0.00	0.00	0.00	0.00
3-METHYL-1-BUTENE	0.44	0.16	0.14	0.13	0.08	0.00	0.00
1-PENTANE	0.25	0.30	0.27	0.28	0.04	0.07	0.07
1-PENTENE	1.69	1.54	1.46	1.40	1.13	1.67	1.45
2-METHYL-1-BUTENE	0.08	0.07	0.06	0.06	0.06	0.06	0.06
N-PENTANE	0.43	0.50	0.48	0.46	0.11	0.62	0.54
TRANS-2-PENTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CIS-2-PENTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEXENES + ISO-HEXANES	0.00	0.06	0.05	0.06	0.00	0.07	0.10
2,3-DIMETHYLBUTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-METHYLPENTANE	0.22	0.17	0.16	0.14	0.04	0.13	0.13
3-METHYLPENTANE	0.03	0.07	0.07	0.07	0.00	0.11	0.12
1-HEXENE	1.37	1.16	1.14	1.08	0.68	1.35	1.17
N-HEXANE	0.39	0.39	0.38	0.37	0.21	0.50	0.46
HEPTENES + ISO-HEPTANES	0.24	0.09	0.09	0.04	0.00	0.13	0.13
1-HEPTENE	0.86	0.72	0.73	0.70	0.30	0.84	0.77
N-HEPTANE	0.24	0.25	0.24	0.24	0.09	0.31	0.30
1-OCTENE	0.44	0.39	0.37	0.33	0.11	0.40	0.35
ISO-C8-P + O + N5 + N6	0.06	0.06	0.05	0.00	0.00	0.00	0.00
N-OCTANE	0.11	0.13	0.12	0.10	0.05	0.14	0.11
C9-OLEFINS + ISO-P	0.15	0.91	0.59	0.19	0.16	0.10	0.08
ACETONE	0.00	0.00	0.00	0.00	0.17	0.11	0.11
I-PROPANOL	0.00	0.00	0.00	0.00	0.14	0.29	0.25
UNKNOWN LITE HYDRO-CARB LIQ (1)	13.56	18.18	19.65	15.52	23.56	19.41	17.56
UNKNOWN HVY HYDRO-CARB LIQ (2)	10.88	12.59	11.05	18.28	15.42	15.49	15.97
SLURRY REACTOR WAX	56.83	51.00	52.46	50.68	49.18	47.28	50.56

(1) Collected in Ambient and Chilled Condensers

(2) Collected in Hot Condenser

Table A-2(cont'd)
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor
(Run CT-256-6)

M.B.No.	6-17	6-18	6-19	6-20	6-23	6-24
Days On-stream	23.8	24.8	25.8	27.6	30.6	31.6
METHANE	2.28	2.52	2.12	2.39	2.39	2.40
ETHENE	1.21	1.36	1.37	1.83	1.95	1.98
ETHANE	0.27	0.30	0.33	0.39	0.38	0.38
PROPENE	1.70	1.90	1.94	2.33	2.46	2.50
PROPANE	0.36	0.39	0.46	0.51	0.53	0.53
1-BUTANE	0.08	0.07	0.07	0.24	0.27	0.31
1-BUTENE+2-METHYLPROPENE	1.52	1.70	1.74	1.95	2.11	2.14
N-BUTANE	0.43	0.48	0.49	0.58	0.62	0.63
TRANS-2-BUTENE	0.00	0.01	0.00	0.00	0.00	0.00
CIS-2-BUTENE	0.00	0.02	0.00	0.00	0.00	0.00
3-METHYL-1-BUTENE	0.02	0.07	0.09	0.13	0.14	0.15
1-PENTANE	0.10	0.00	0.00	0.05	0.00	0.00
1-PENTENE	1.27	1.44	1.49	1.62	1.76	1.84
2-METHYL-1-BUTENE	0.03	0.04	0.07	0.06	0.00	0.00
N-PENTANE	0.35	0.40	0.44	0.50	0.54	0.54
TRANS-2-PENTENE	0.01	0.01	0.02	0.00	0.00	0.00
CIS-2-PENTENE	0.01	0.01	0.04	0.00	0.00	0.00
HEXENES + ISO-HEXANES	0.10	0.12	0.20	0.25	0.19	0.21
2,3-DIMETHYLBUTANE	0.01	0.00	0.00	0.00	0.00	0.00
2-METHYLPENTANE	0.02	0.01	0.06	0.09	0.13	0.13
3-METHYLPENTANE	0.01	0.03	0.05	0.00	0.00	0.03
1-HEXENE	0.83	1.00	1.06	1.39	1.49	1.57
N-HEXANE	0.24	0.28	0.32	0.44	0.47	0.48
HEPTENES + ISO-HEPTANES	0.09	0.08	0.16	0.00	0.12	0.11
1-HEPTENE	0.38	0.44	0.50	1.00	1.18	1.19
N-HEPTANE	0.11	0.13	0.17	0.32	0.38	0.37
1-OCTENE	0.11	0.13	0.16	0.51	0.67	0.70
ISO-C9-P + O + N5 + N6	0.00	0.00	0.00	0.00	0.00	0.00
N-OCTANE	0.03	0.04	0.07	0.14	0.19	0.19
C9-OLEFINS + ISO-P	0.02	0.02	0.04	0.14	0.21	0.23
ACETONE	0.06	0.12	0.14	0.23	0.22	0.22
I-PROPANOL	0.15	0.18	0.23	0.25	0.24	0.22
UNKNOWN LITE HYDRO-CARB LIQ (1)	19.51	19.15	16.32	27.06	23.08	28.04
UNKNOWN HVY HYDRO-CARB LIQ (2)	13.68	12.56	14.87	3.12	7.28	2.84
SLURRY REACTOR WAX	55.00	55.00	55.00	52.49	50.98	50.00

(1) Collected in Ambient and Chilled Condensers

(2) Collected in Hot Condenser

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