DOE/PC/70023--T3

84-34202-TPR2

TECHNICAL PROGRESS REPORT

CONTRACT IDENTIFICATION:	REPORTING PERIOD:	CONTRACT NUMBER:
Micelle-Derived Catalysts for Extended Schulz-Flory	1/1/85-3/31/85	DE-AC22-84PC70023
CONTRACTOR: Signal UOP Research Center, UOP Inc. 50 UOP Plaza Des Plaines, IL 60016		CONTRACT START DATE: October 1, 1984
		CONTRACT COMPLETION DATE: March 31, 1987

DOE/PC/70023--T3

DE93 003291

DISCLAIMER

ABSTRACT

The reduced C-73-1-101 iron catalyst was retested in Run 10, under the third set of reference conditions: 208°C, 500 psig, 0.9 (molar) H_2/CO feed ratio, ~35% initial CO conversion. The analysis of the products collected during the entire 252-hour run, including the wax recovered from the catalyst, resulted in $\alpha = 0.78$ for carbon numbers 1 to 15 and $\alpha = 0.88$ for carbon numbers 16 to 45. The results of Run 10 are satisfactory and will be used in the future as reference performance. No further tests with the reference catalyst are going to be conducted until a method for testing experimental catalysts is established and new reference performance under different conditions is necessitated.

Ruthenium particles, mostly in the 40 to 60 Å size range, were prepared on γ-alumina by using a micelle technique. The narrow size distribution of ruthenium particles was not maintained and some very large particles up to 1000 Å resulted when the catalyst preparation was upscaled from 2 g to ~30 g. The causes of the maldistribution that occurred during the scaling up of the catalyst preparation are under investigation. The catalyst which showed broad size distribution of ruthenium particles showed rapid deactivation during a test in Plant 700. Investigations are under way to improve the catalytic stability.

Small angle X-ray scattering was used to characterize the reversed micelle solution used in the preparation of ruthenium catalysts. The volume averaged diameter of the water core for the reversed micelles is between 75 and 90 Å.

OBJECTIVES

The wax extracted from the used catalyst was not included in calculating the overall product distributions in Runs 3, 6, 7 and 8 and unique α's were obtained up to a carbon number of 35 (Technical Progress Report for 10/1/84-12/31/84). It was assumed that this wax was mostly made during the early part of the runs before switching to the material balance periods. Calculations were also done by assuming that the wax on the catalyst accumulated linearly with time during the whole course of the run. These new plots all showed two different α's, a smaller one at carbon numbers less than 20 and a larger one at carbon numbers greater than 20. The first objective of the present work was, therefore, to establish reliable reference performance with the reduced C-73-1-101 iron catalyst by analyzing all of the products made during the run, including the wax extracted from the used catalyst, in the calculation of the overall product distribution.

A 0.8% Ru on γ-Al_2O_3 catalyst (4956-12) was prepared by using a micelle technique. This catalyst was examined with the Scanning Transmission Electron Microscope (STEM) and was found to have a broad size distribution of ruthenium particles (Technical Progress Report for 10/1/84-12/31/84). The second objective of the present work was to establish a micelle method by which narrow size distribution ruthenium particles can be prepared on γ-alumina.

The third objective was to evaluate a ruthenium catalyst prepared by a variation of the micelle technique in the Fischer-Tropsch fixed bed plant.

EXPERIMENTAL

Catalyst Testing Plant

All catalyst testing runs were conducted in Plant 700. In Run 9 and 10, the $H_2/CO/Ar$ feed blend (from Matheson) was first brought to 2500 psig by using two Whitey compressors in series. The gas was then metered and then fed downflow to a stainless steel 7/8" I.D. reactor that was placed in an electric furnace maintained at uniform temperature. The catalyst temperature was controlled 2" and 4" above catalyst inlet in Runs 9 and 10, respectively. The catalyst section in the reactor was 1/2" I.D., and the catalyst was held in place by two stainless steel screens and with quartz wool. The bed length in Runs 9 and 10 were 17 1/2" and 11 3/4", respectively. The reactor inner diameter, past the catalyst section, was reduced to 3/16" to achieve high linear velocities and to minimize product loss via adherence to inner walls. The reactor outlet was collected to a box that was maintained at 115°C by circulating hot air. The hot box contained two identical alternate 1" I.D. x 12" long stainless steel product recovery vessels that were kept at plant pressure. The vessels each had a removable glass sleeve where the C_8~C_{35} hydrocarbons, and some of the water were collected. All connecting lines, past the reactor, in the product recovery system were 1/8" O.D. stainless steel. The outlets from the hot box were connected to a freon-cooled box maintained at ~-2°C. The cold box contained two alternate Fischer Porter cylinders, kept at 50 psig, and where the C_5~C_{20} hydrocarbons and the rest of the aqueous phase were collected. The outlets from the cold box were followed by two alternate traps kept at atmospherical pressure in dry ice-acetone baths. Here, most of the C_3-C_{10} hydrocarbons were collected. Gas samples for analysis by gas chromatography (GC) were taken after the dry ice-acetone traps. The effluent gas was then passed through a water saturator and metered by a wet test meter.

Catalyst Testing Procedure

The premixed catalyst and the α-Al_2O_3 diluent in Run 10 or the catalyst in Run 9 were loaded to the reactor at room temperature in a N_2 glove bag. The reactor was then filled with H_2 for pressure testing at 200 psig above testing pressure. After a successful pressure test in Run 9, the pressure was reduced to 500 psig and the reactor heated to testing temperature under H_2 flow; the H_2 then was cut off, and the feed was introduced. Pressure was then raised to testing pressure of 1500 psig. In Run 10, the pressure was reduced to 0 psig after a successful pressure test at room temperature, heated under H_2 to reaction temperature. The H_2 was cut off, helium was introduced, and the pressure was raised to 500 psig with helium. The feed was then introduced and helium cut off.

For the two runs, the initial feed rates were maintained throughout the run, and all products were collected in the same product recovery system.

Run Analysis Procedure

The run analysis procedure is described in detail in Figure 1. The liquid and solids products collected during various periods in each of the three separators were first separated to their respective hydrocarbon and aqueous phases, then weighed, and then analyzed separately by GC. The overall product distributions were calculated based on the GC analysis of the products recovered in the separators, products recovered from the used catalyst, and the analysis of the effluent gas.

Argon was used as an internal standard to determine the conversion of the feed gas, i.e.:

$$\% \text{ CO Conversion} = \frac{\left(\frac{CO}{Ar}\right)_{feed} - \left(\frac{CO}{Ar}\right)_{product}}{\left(\frac{CO}{Ar}\right)_{feed}} \times 100$$

$$\% \text{ CO Conversion to } CO_2 = \frac{\left(\frac{CO_2}{Ar}\right)_{product}}{\left(\frac{CO}{Ar}\right)_{feed} - \left(\frac{CO}{Ar}\right)_{product}} \times 100$$

UOP Method 734 developed for water and C_1-C_4 alcohols was previously used for the GC analysis of the aqueous layer in Runs 3, 6, 7 and 8. Some experimental difficulties were encountered, however, during several of these measurements, i.e, base line shift, very long elution times, unknown peaks. An alternate GC technique is presently being evaluated and was used in Runs 9 and 10 to analyze the aqueous products. The analysis is performed on a boiling point column using an internal standard and an FID detector. Retention times and response factors were determined for C_1-C_9 alcohols and aldehydes by using calibration blends. The fraction of the sample that was not detected by the FID detector was taken to be water. Results for the amount of water calculated in this manner were later found to be in agreement (within 2%) with independent quantitative determination of water via Karl Fischer analysis.

C_3-C_{55} hydrocarbons are analyzed by the ASTMD 2887 chromatographic boiling point method, as previously described in the Technical Progress Report for 10/1/84-12/31/84. However, since in the presence of oxygenates the boiling point distribution of products does not correspond to the carbon number distribution, the new GC technique described above is being used as a supplement for quantitative determination of C_1-C_{10} oxygenates in the hydrocarbon layers. The carbon number distribution for paraffins and olefins is then determined by

subtracting from the total boiling point chromatogram the peaks that correspond to the oxygenates.

An on-line GC was installed at the reactor outlet to analyze the gas composition using UOP Method 539. An additional GC method is also used off-line to analyze the hydrocarbons in the gas with high precision.

LIST OF FIGURES

RESULTS

Tests in the Fixed-Bed Pilot Plant

One run was carried out in the fixed bed pilot plant with the reduced C-73-1-101 iron reference catalyst and one with a micelle-derived ruthenium catalyst. The operating conditions for these runs are summarized in Figure 2. Some of the key results, like the total weight of hydrocarbons, oxygenates, water made during the runs, weight recoveries, amount of wax extracted from the used catalyst, percent coke on the used catalyst, outlet H_2/CO ratio, olefin to paraffin ratios and α, the growth probability, are also summarized in the same figure.

Testing of the Reduced C-73-1-101 Iron Reference Catalyst in the Fixed Bed Pilot Plant (Task 2.2)

The same batch of reduced C-73-1-101 iron reference catalyst that was used in Runs 1 through 8 was used in Run 10 also. The reduction procedure for this catalyst was described in the Technical Progress Report for 10/1/84-12/31/84. The operating conditions were: 208°C inlet temperature, 500 psig, 0.9 (molar) inlet H_2/CO, 950 hr^{-1} GHSV, 252 hours. The results are described in Figures 2 through 9. During the run, the catalyst temperature increase over the inlet temperature was 1~2°C.. The total material recovery was 92.7%. The material balance became 99.5% after correcting the feed rates by the ratio of recovered-to-fed argon.

The CO conversion was initially 30~50% and then leveled off to ~30%. CO conversion to CO_2 was steady at 7~8% throughout the run. Two different Anderson-Schultz-Flory distributions, one based on hydrocarbons only and one based on hydrocarbons plus oxygenates, were calculated. The distributions gave

α = 0.78 between carbon numbers 1 to 15 and α = 0.88 between carbon numbers of 16 to 45.

Testing of a Ruthenium Catalyst Prepared by a Micelle Method (Task 3.1.2)

A ruthenium catalyst (4956-23) prepared on γ-alumina by a micelle method showed a broad size distribution of ruthenium particles between 40 to 1000 Å in the STEM examination. This catalyst was nevertheless tested in the fixed-bed pilot plant in Run 9 to determine the catalytic activity and stability. The operating conditions were: 207°C inlet temperature, 1500 psig, 0.9 (molar) inlet H_2/CO, 75 hr^{-1} GHSV, 81 hours. The results are described in Figures 10 through 16. The catalyst temperature increase over the inlet was initially ~6°C and then decreased to 1~3°C. The total material recovery was 94.2%. The material balance became 99.2% after correcting the feed rates by the ratio of recovered-to-fed argon. The initial CO and CO + H_2 conversions were very high and then decreased rapidly to 5~10% and 10~15%, respectively, in ~30 hours. Initially, CO conversion to CO_2 was very low, <13%. Virtually no CO_2 was obtained in the products after 18 hours.

Two different Anderson-Schultz-Flory distributions, one for hydrocarbons only and one for hydrocarbons plus oxygenates, were calculated. These distributions gave α = 0.78 between carbon numbers 8 to 21 and α = 0.93 between carbon numbers 21 to 40.

Some of the products in Run 9 were also analyzed by GC/MS and IR and were found to contain iron and ruthenium carbonyls. The amount of iron and ruthenium in the liquid products were determined by Atomic Absorption Spectroscopy (AAS) to be 0.41 g and 0.0068 g, respectively. AAS analysis done on the used catalyst indicated that there was no significant ruthenium loss from the catalyst, while there was about 0.35 wt.% iron. Also, 4.93 wt.% coke was analyzed on the used catalyst.

Presently, H_2 and CO/Ar are separately being fed to the reactor, and an iron carbonyl trap installed on the CO/Ar line at the reactor inlet is being evaluated to determine its effectiveness.

Establishing a Preparation Procedure for Alumina-Supported Ruthenium Catalysts by Using Micelle Methods (Task 3.1.1)

Some of the ruthenium catalysts prepared by using micelle methods under the present program are listed in Figure 17. Some of these catalysts were examined by STEM.

Results of STEM examination of catalyst 4956-19 (~1.7% Ru by wt.) prepared in 2 g quantity is shown in Figures 18 through 20. A high proportion of the particles in the 40-60 Å, was observed with some few large particles of 110 to 130 Å size range. Two-thirds of the alumina particles that were examined were found to contain ruthenium.

Similar ruthenium particle size distributions were obtained with catalyst 4956-21 (~1.1% Ru by wt.) prepared in 2 g quantity by variation of the micelle technique used for catalyst 4956-19 (Figures 21 and 22). For this catalyst, all of the alumina particles that were examined contained ruthenium.

Catalyst 4956-23 was prepared in a similar manner to 4956-21 but in 30 g quantity instead of 2 g. The particle sizes varied from 40 to 1000 Å. Another catalyst (4956-27) prepared by a variation of the micelle technique in ~30 g quantities also showed broad size distribution of ruthenium particles.

Characterization of the Reversed Micelle Solution by Small Angle X-ray Scattering

Small angle X-ray scattering (SAXS) was used to characterize the reversed micelle solution used in the preparation of ruthenium catalysts. SAXS occurs because of the difference in electron density between the water core of the reversed micelles and the organic phase (surfactant plus organic solvent).

The radius of gyration of the water core of the reversed micelles, R_G, is determined from the scattering at very low angles, in the so-called Guinier region. R_G is determined from a plot of ln I vs. h^2, where I is the scattered intensity, $h = 4\pi \sin\theta/\lambda$, θ is one-half the scattering angle, and λ is the X-ray wavelength in Angstroms. This plot is linear in the Guinier region and its slope is equal to $-R_G^{2/3}$. For a single particle or for a monodisperse system, R_G is related to more conventional dimensions. For exmaple, for a sphere of radius r, $R_G = r(3/5)^{1/2}$. For a polydisperse system, R_G becomes the volume averaged radius of gyration. The diameter distributions were calculated by an algorithm due to Vonk.[1] It was here assumed that the reversed micelles were spherical in shape.

The SAXS curve (I vs. h) for the reversed micelle solution is shown in Figure 23. The inflection point near 0.04 A^{-1} indicates that the number of reversed micelles per unit volume is large enough to cause interactions between individual reversed micelles, and therefore the size distribution of the reversed micelles cannot be accurately calculated. An approximate radius of gyration of 29 A was calculated for the water core from the slope of the Guinier plot (Figure 24). The reversed micelle solution was then diluted with an equal volume of the organic solvent. The SAXS curve for the diluted system (Figure 25) did not show an inflection point, indicating the absence of interactions between individual reversed micelles. The radius of gyration calculated from the slope of the Guinier plot was then 35 A, resulting in a volume averaged sphere diameter of 75 to 90 A. The radius of gyration of the water core of the reversed micelles actually used in the catalyst preparations seems to be then between 29 and 35 A. Figure 27 shows the diameter distribution for the diluted reversed micelle solution. The distribution was between 40 to 110 A with a peak near 55 A.

[1] C. G. Vonk, J. Appl. Cryst., 9 433 (1976).

DISCUSSION AND FUTURE PLAN

Establishment of Reference Performance

The reduced C-73-1-101 catalyst was previously tested in Run 7 under the third set of operating conditions: 208°C, 500 psig, 0.9 H_2/CO feed ratio, ~35% initial CO conversion (Figure 28) The Anderson-Schultz-Flory distribution for the products made between 52 to 116 hours in Run 7, excluding the wax recovered from the catalyst, is shown in Figure 29. The same figure also shows, with the same catalyst and under the same conditions, the distribution obtained in Run 10 for products made during the entire 252-hour test, including the wax recovered from the catalyst. Between carbon numbers 1 to 15, the data in both runs was reproducible. The higher α, at carbon numbers greater than 15 in Run 10, may indicate the assumption that wax recovered form the catalyst in Run 7 was made during the first 52 hours is not correct. Since virtually the same amount of wax was recovered over 116 hours in Run 7 and over 252 hours in Run 10 (Figure 30), the steady state wax production rate should have been reached somewhere between 52 and 116 hours.

In order to determine whether an increase in α with run time for the Fischer-Tropsch liquid retained in the catalyst pores may explain the higher α observed in Run 10 at carbon numbers greater 15, the composition of the wax recovered from catalyst in Runs 7 and 10 were compared in Figure 31. The results indicate that the wax recovered from the catalyst at the end of the longer test did not have a higher molecular weight, indicating that α for the Fischer-Tropsch liquid retained in catalyst pores did not increase with run time. It is not presently clear why the wax recovered at the end of the longer test showed apparently lower average molecular weight.

Results of Run 10 are satisfactory and will be used in the future as reference performance. No further tests are going to be conducted with the reference catalyst until a method for testing experimental catalysts is established, and new reference performance under different conditions is necessitated.

Characterization of the Reverse Micelle Solutions by SAXS

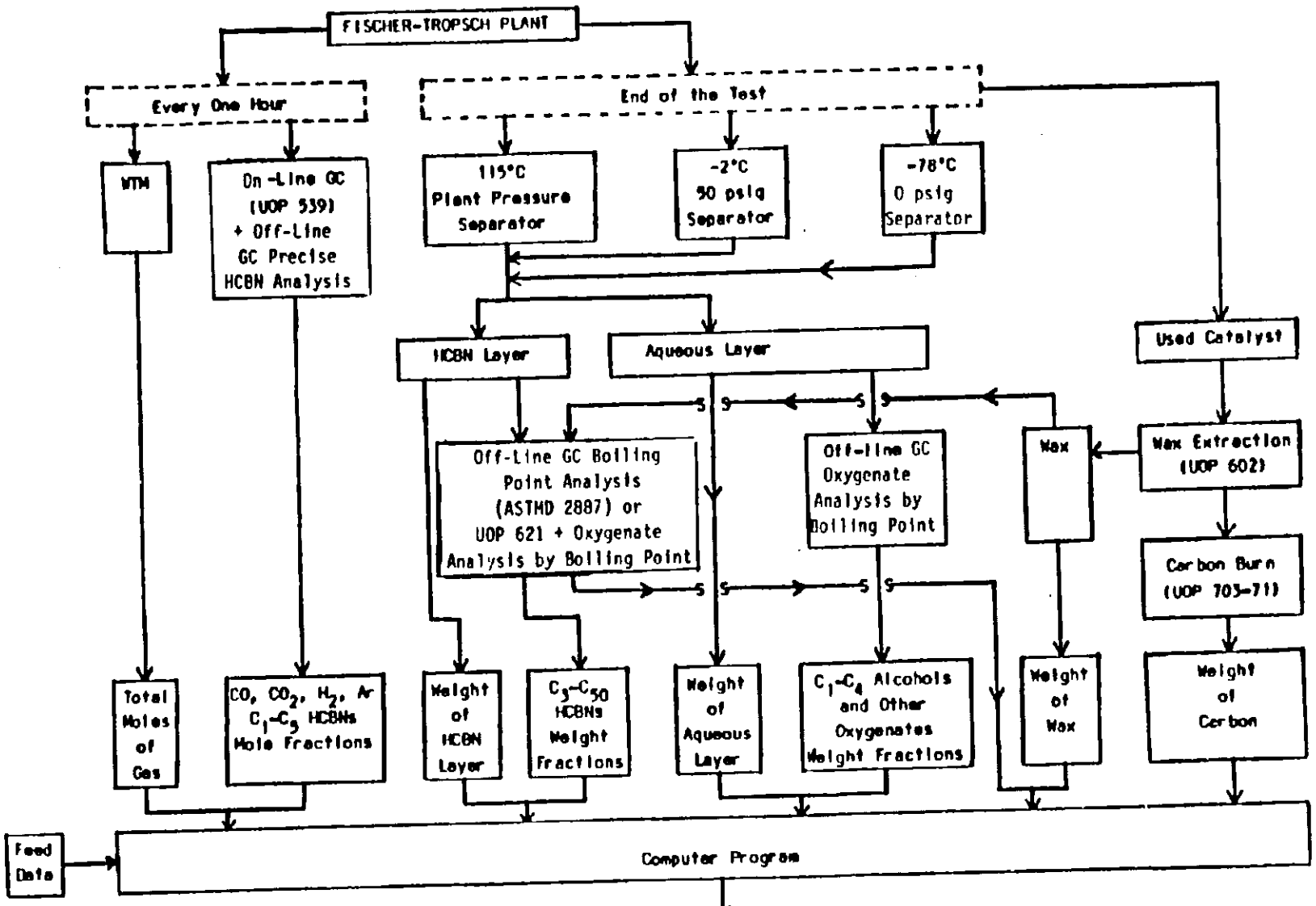
The average size and the size distribution for the reversed micelles used in the preparation of the ruthenium catalysts could not be accurately determined, apparently because of the large concentration of the reversed micelles in solution. A better estimate of the size and the size distribution, however, may possibly be made by collecting SAXS data on solutions with intermediate concentration between the solution used in catalyst preparations and the 1:1 diluted solution. SAXS technique will continue to be used in this program in the future to help in the design of the ruthenium particle size.

Establishment of a Procedure for the Preparation of Supported Ruthenium Catalysts by a Micelle Technique

Major effort in the future will be focused on the establishment of a micelle procedure by which narrow particle size distribution supported ruthenium catalysts can be prepared in large enough quantities (20~30 g) to be tested in the plant. Also, various methods of improving catalytic stability will be evaluated. Catalysts of various ruthenium particle size will then be evaluated in the pilot plant to determine the effect of particle size on selectivity, as discussed in the Work Plan.

Figure 1

Fischer-Tropsch Run Analysis Procedure



Schultz-Flory Distribution

Product Distributions (by Mole Fraction and Weight Fraction);

$CO+H_2$, H_2 and CO Conversions vs. Time (Plots, Tables);

Olefin to Paraffin Ratios;

Hydrocarbon Product Yields (Gas, Gasoline, Diesel, Gas Oil, Wax Ranges)

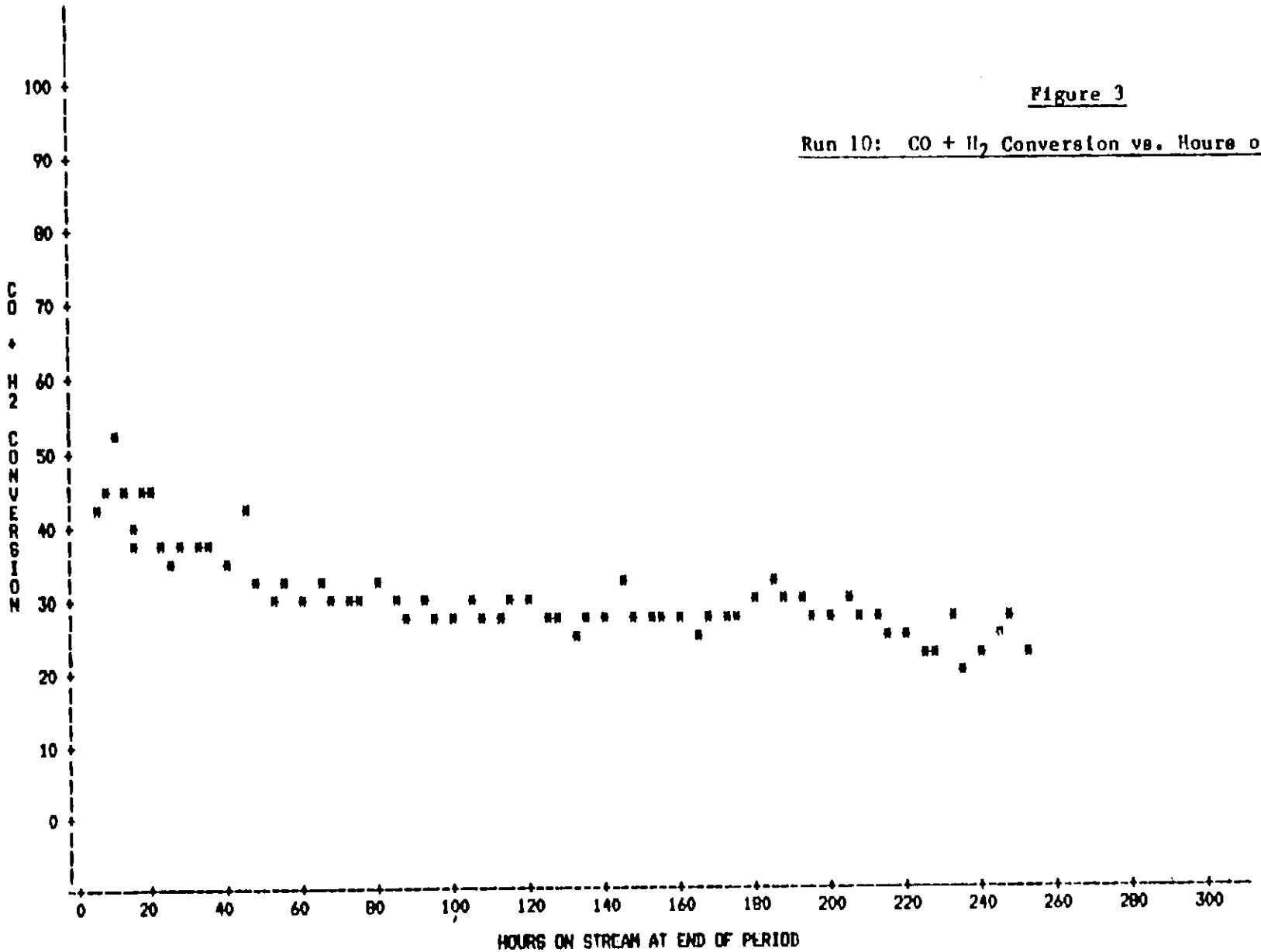
Figure 2

Run Summary Data

	Catalyst			α-Al_2O_3	Bed	Inlet		Feed				Outlet	Olefin/Paraffin Ratio (Molar)			Hydro-carbons	Oxygenates	H_2O	Wax from Used	Carbon on Used				
	Wt.	Vol.	Comp.	Wt.	Length	Temp.	Press.	H_2/CO	Rate	GHSV		H_2/CO				Made	Made	Made	Catalyst	Catalyst		Argon	Total Weight	Corrected Material
n	(g)	(cc)	(%,wt)	(g)	(in.)	(°C)	(psig)	(molar)	(SCFH)	(hr^{-1})	Hours	Ratio (Molar)	C_2	C_3	C_4	(g)	(g)	(g)	(g)	(g)	α	Recov. (%)	Recov. (%)	Balance (%)
9	20	75	Ru 1.19	0	17 1/2	207	1500	0.68	0.20	75	0-81	0.77	0.5	0.4	0.4	13.4	1.0	13.9	2.6	4.9	0.78 (C_8-C_{21}) 0.93 (C_{22}-C_{40})	95.0	94.2	99.2
0	8.42	5		42	11 3/4	208	500	0.68	0.12	1140	0-252	0.75	2.4	2.2	1.7	47.4	3.5	25.7	4.6	2.1	0.78 (C_1-C_{19}) 0.88 (C_{16}-C_{45})	93.2	92.7	99.5

FISCHER-TROPSCH PILOT PLANT AT RESEARCH
CONVERSIONS VS. HOURS ON STREAM
PILOT PLANT NUMBER=700 RUN NUMBER=10 TEST NUMBER=1

PLOT OF CONVC*ENDPER SYMBOL USED IS *



NOTE: 1 OBS HIDDEN

Figure 3

Run 10: CO + H_2 Conversion vs. Hours on Stream

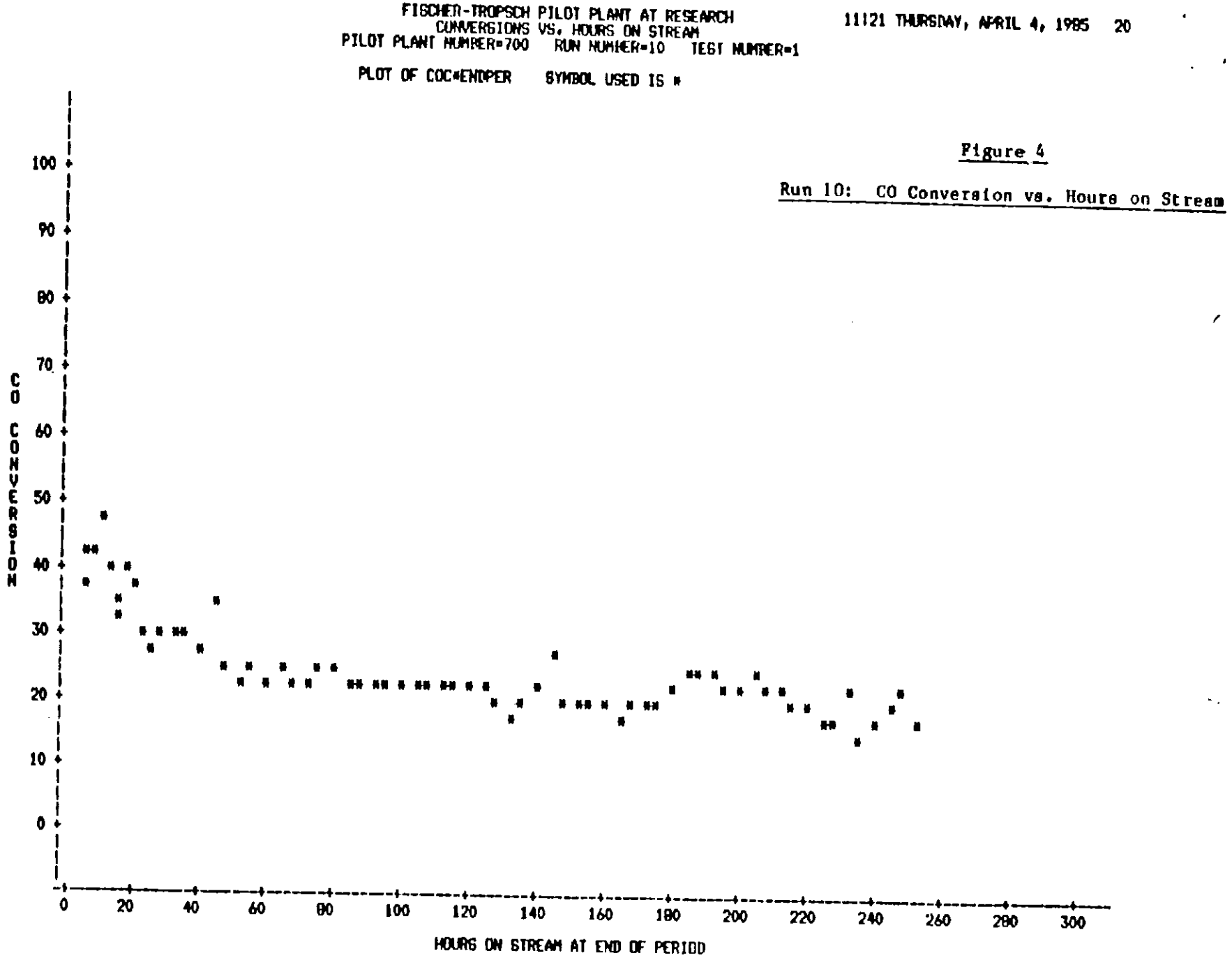


Figure 4

Run 10: CO Conversion vs. Hours on Stream

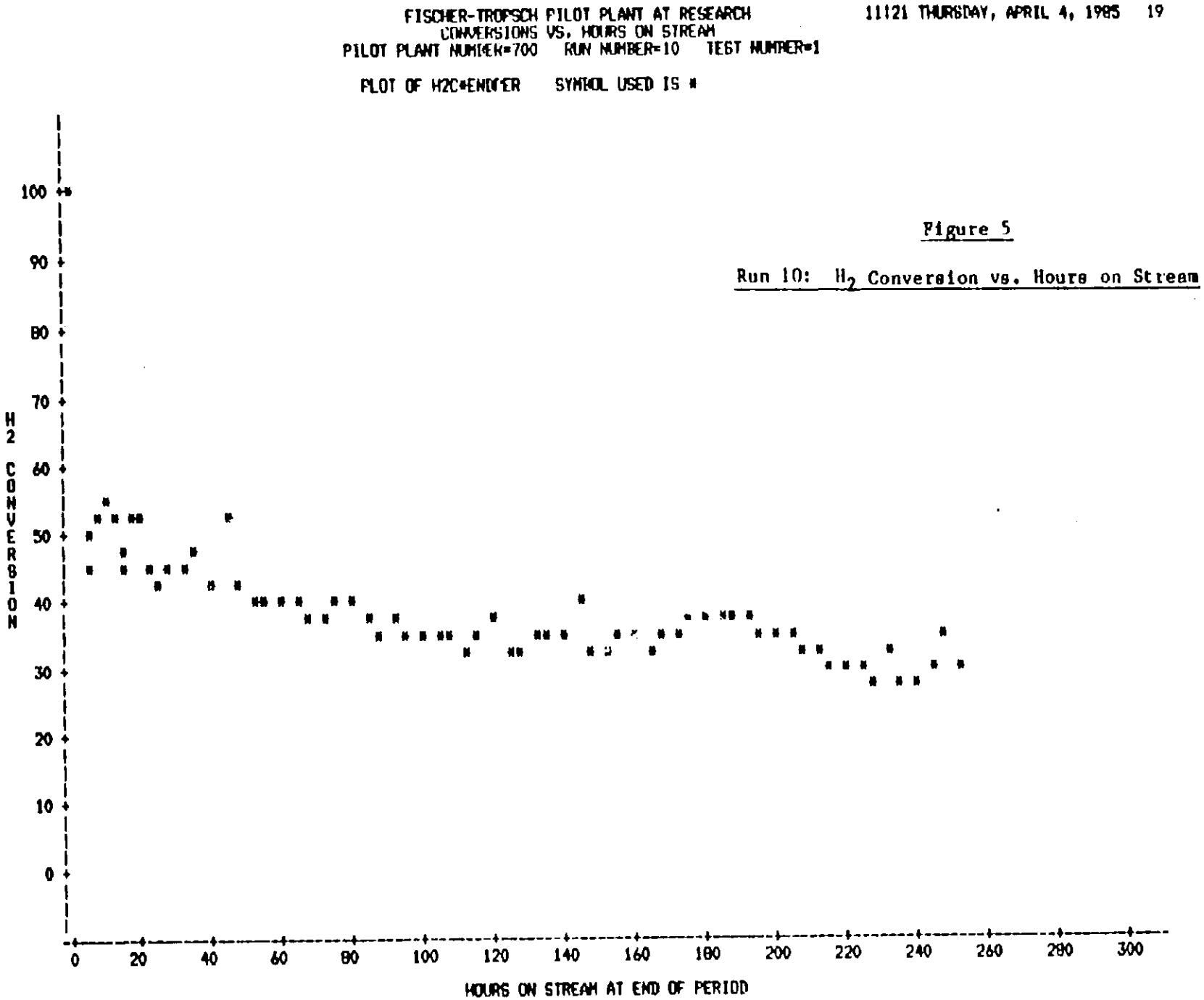
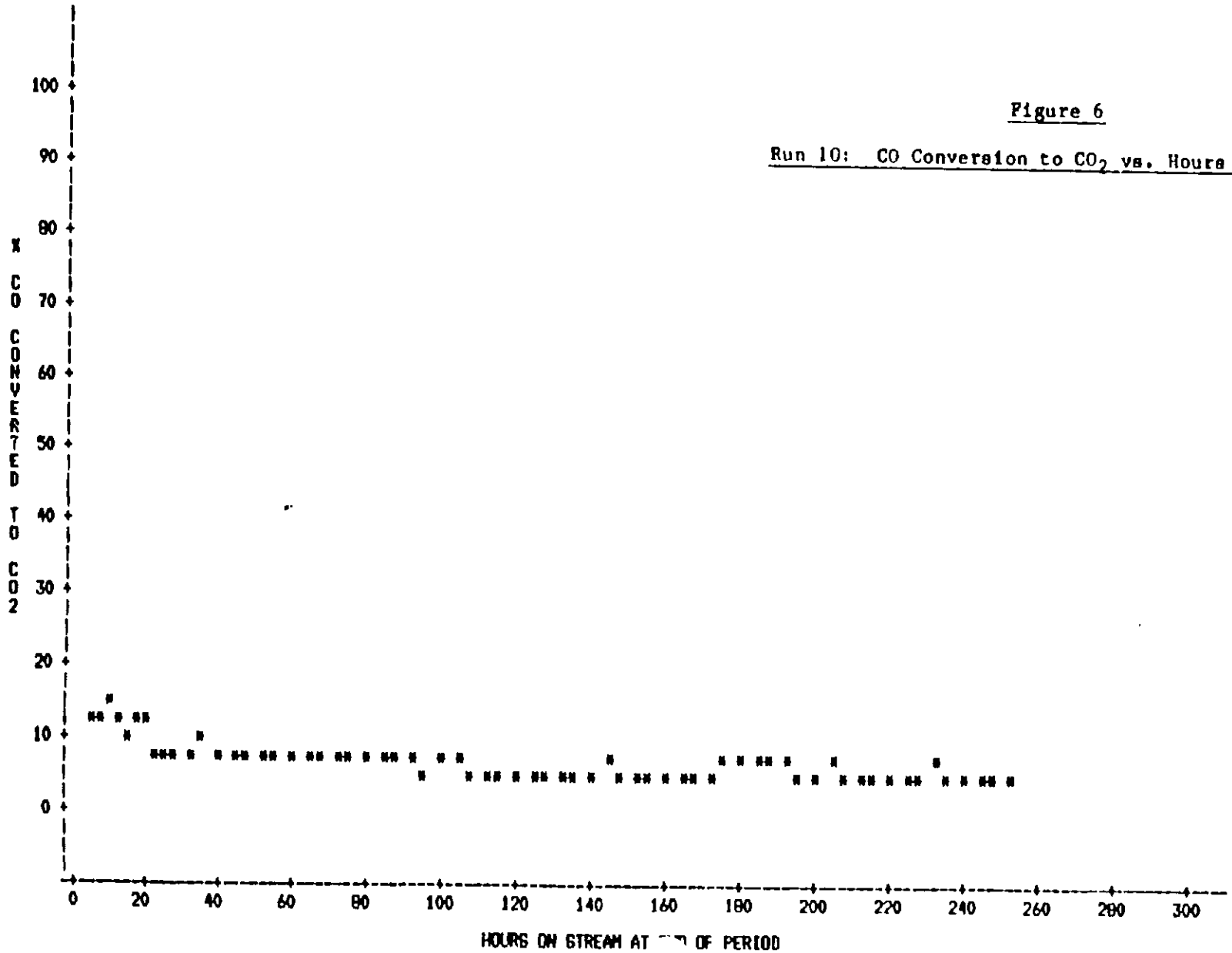


Figure 5

Run 10: H_2 Conversion vs. Hours on Stream

FISCHER-TROPSCH PILOT PLANT AT RESEARCH 11121 THURSDAY, APRIL 4, 1985 21
CONVERSIONS VS. HOURS ON STREAM
PILOT PLANT NUMBER=700 RUN NUMBER=10 TEST NUMBER=1

PLOT OF COTOCO2*ENDPER SYMBOL USED IS *



NOTE: 2 OBS HIDDEN

Figure 6

Run 10: CO Conversion to CO_2 vs. Hours on Stream

Figure 7: Run 10: Product Distributions

RE1016SAS FISCHER-TROPSCH DATA REDUCTION PROGRAM— EXECUTED ON 15APR85:08:04

PILOT PLANT NO. 700 RUN NO. 10 TEST NO. 1 RUN SUMMARY REPORT
BOOK NO. CATALYST NO. 4966-34 BEGINNING DATE 18FEB1985 END OF TEST DATE 28FEB1985

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.78	36.90
CO	71.92	50.60
CO2	9.85	4.41
H2O	4.85	5.31
HYDROCARBON	9.02	2.56
ALCOHOL	0.58	0.21

ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	12.18	20.29
ETHANOL	35.60	41.23
PROPANOL	16.52	14.67
BUTANOL	19.16	13.79
OTHER OXYGENATES	16.55	10.02

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	5.74	24.80
C2-C4	22.76	39.34
C5-C11	39.33	27.36
C12-C18	15.97	5.48
C19-C25	7.60	1.75
C26+	8.60	1.27

COMPONENT	WEIGHT %	MOLE %
CH4	5.74	24.80
C2P	2.08	4.80
C2=	4.73	11.70
C3	0.13	0.21
C3P	2.68	4.21
C3=	5.59	9.22
C4	1.41	1.71
C4P	2.35	2.80
C4=	3.79	4.68
C5	8.26	8.05
C6	6.52	5.31
C7	5.45	3.81
C8	5.64	3.45
C9	5.28	2.88
C10	4.47	2.19
C11	3.72	1.66
C12	3.11	1.27
C13	2.71	1.03
C14	2.43	0.85
C15	2.24	0.73
C16	2.06	0.63
C17	1.80	0.52
C18	1.62	0.44
C19	1.44	0.37
C20	1.27	0.31
C21	1.19	0.28
C22	1.05	0.24
C23	0.97	0.21
C24	0.88	0.18
C25	0.80	0.16
C26	0.74	0.14
C27	0.67	0.12
C28	0.64	0.11
C29	0.60	0.10
C30	0.55	0.09
C31	0.52	0.08
C33	0.47	0.07
C34	0.44	0.06
C35	0.39	0.06
C36	0.39	0.05
C37	0.33	0.04
C38	0.31	0.04
C39	0.27	0.03
C40	0.25	0.03
C41	0.22	0.03
C42	0.20	0.02
C43	0.18	0.02
C44	0.16	0.02
C45+	1.26	0.14
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
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C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.

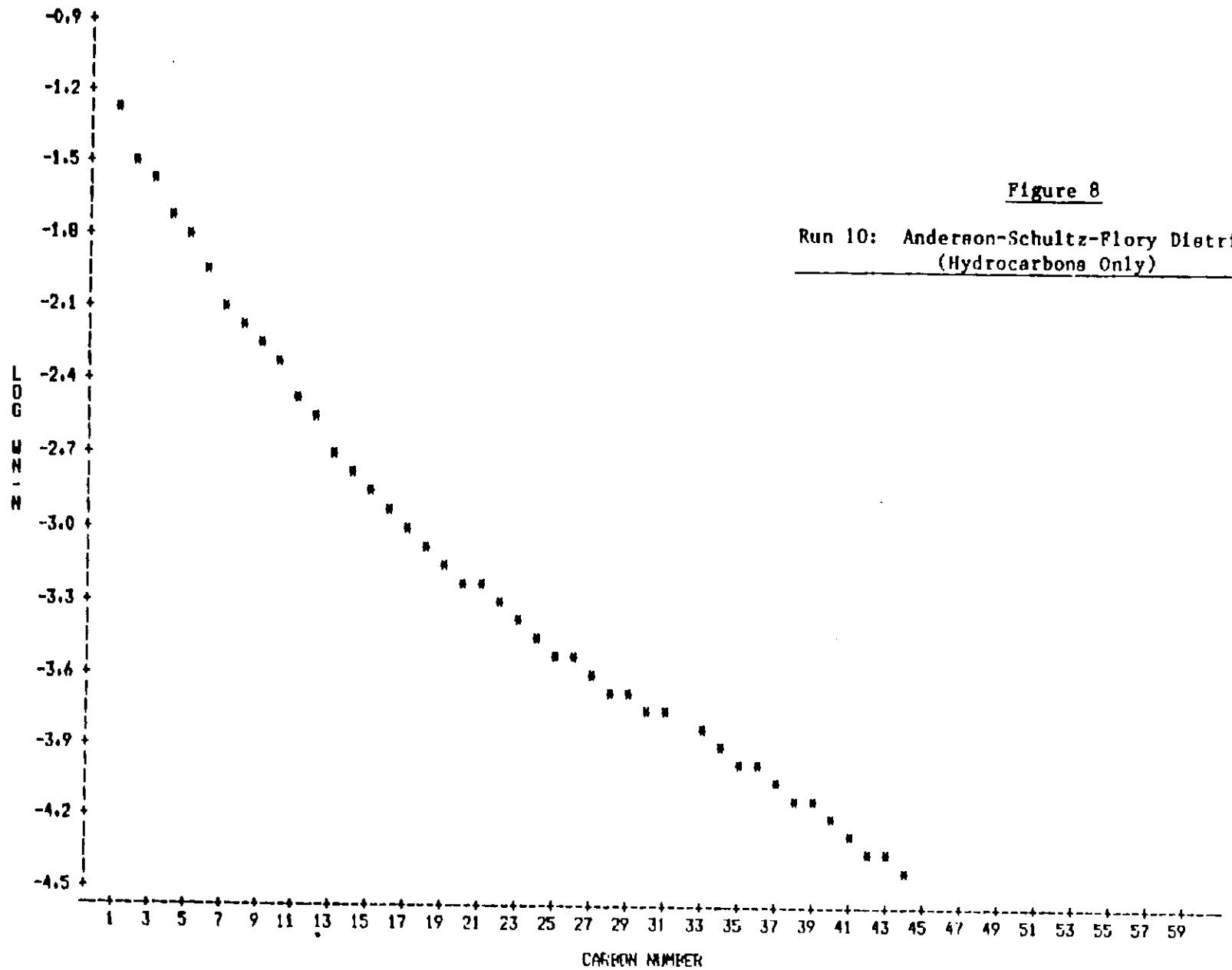
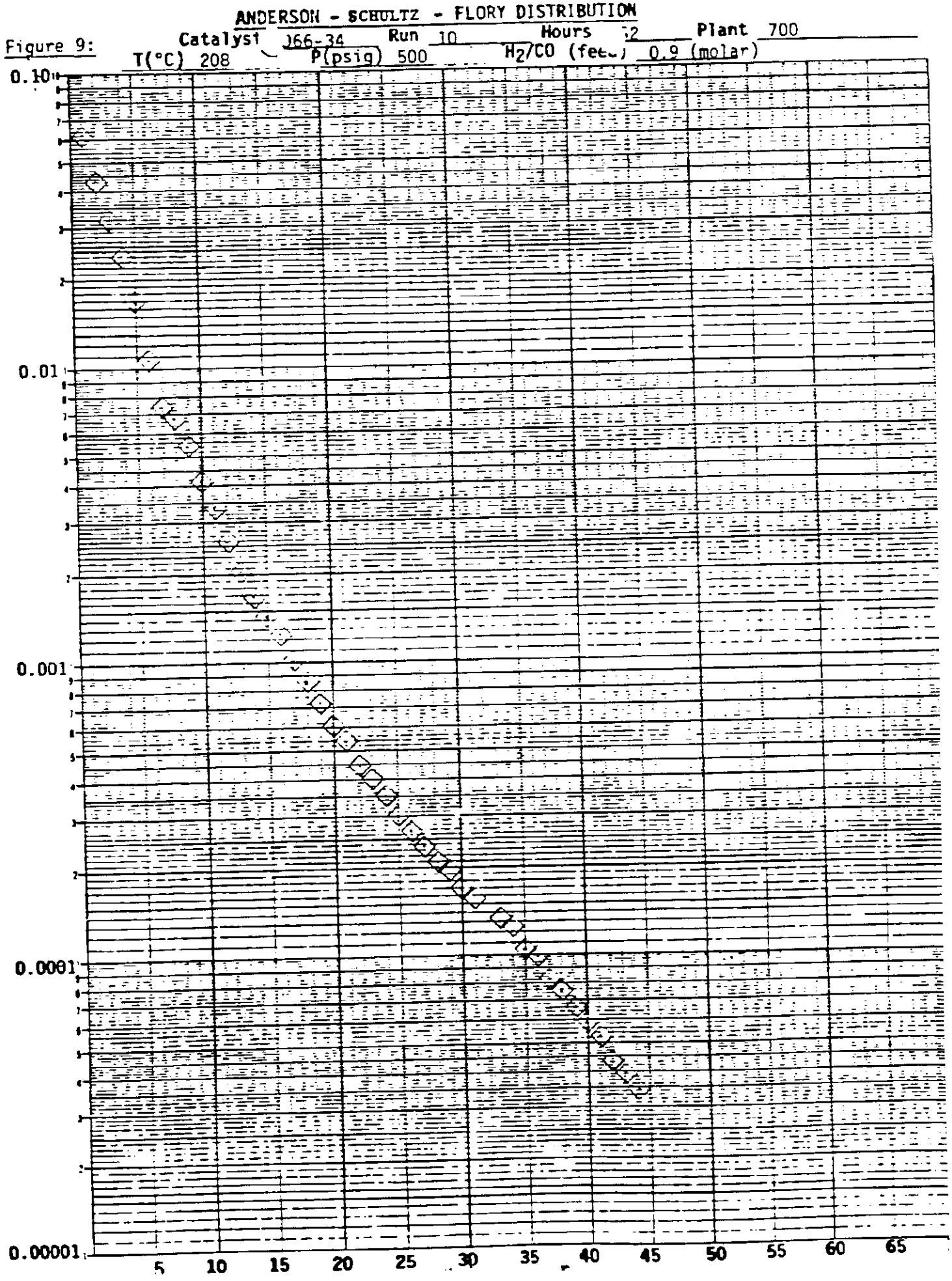


Figure 8

Run 10: Anderson-Schultz-Flory Distribution
(Hydrocarbons Only)

Figure 9:


ANDERSON - SCHULTZ - FLORY DISTRIBUTION
Catalyst J66-34 Run 10 Hours 12 Plant 700
T(°C) 208 P(psig) 500 H2/CO (feed) 0.9 (molar)
Wn/n (Weight fraction of n'th HCBN/n)
0.10
0.01
0.001
0.0001
0.00001
5
10
15
20
25
30
35
40
45
50
55
60
65

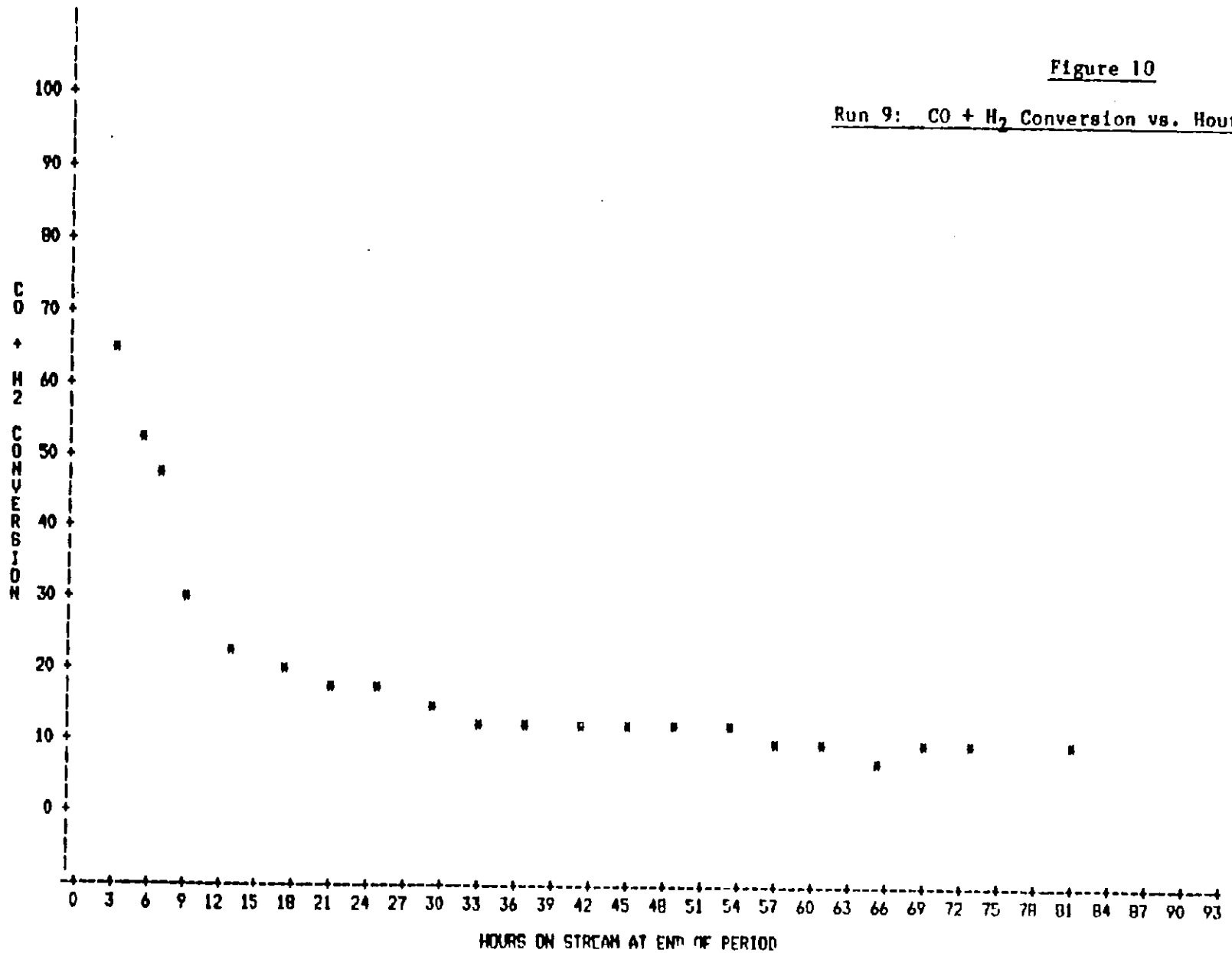


Figure 10

Run 9: CO + H_2 Conversion vs. Hours on Stream

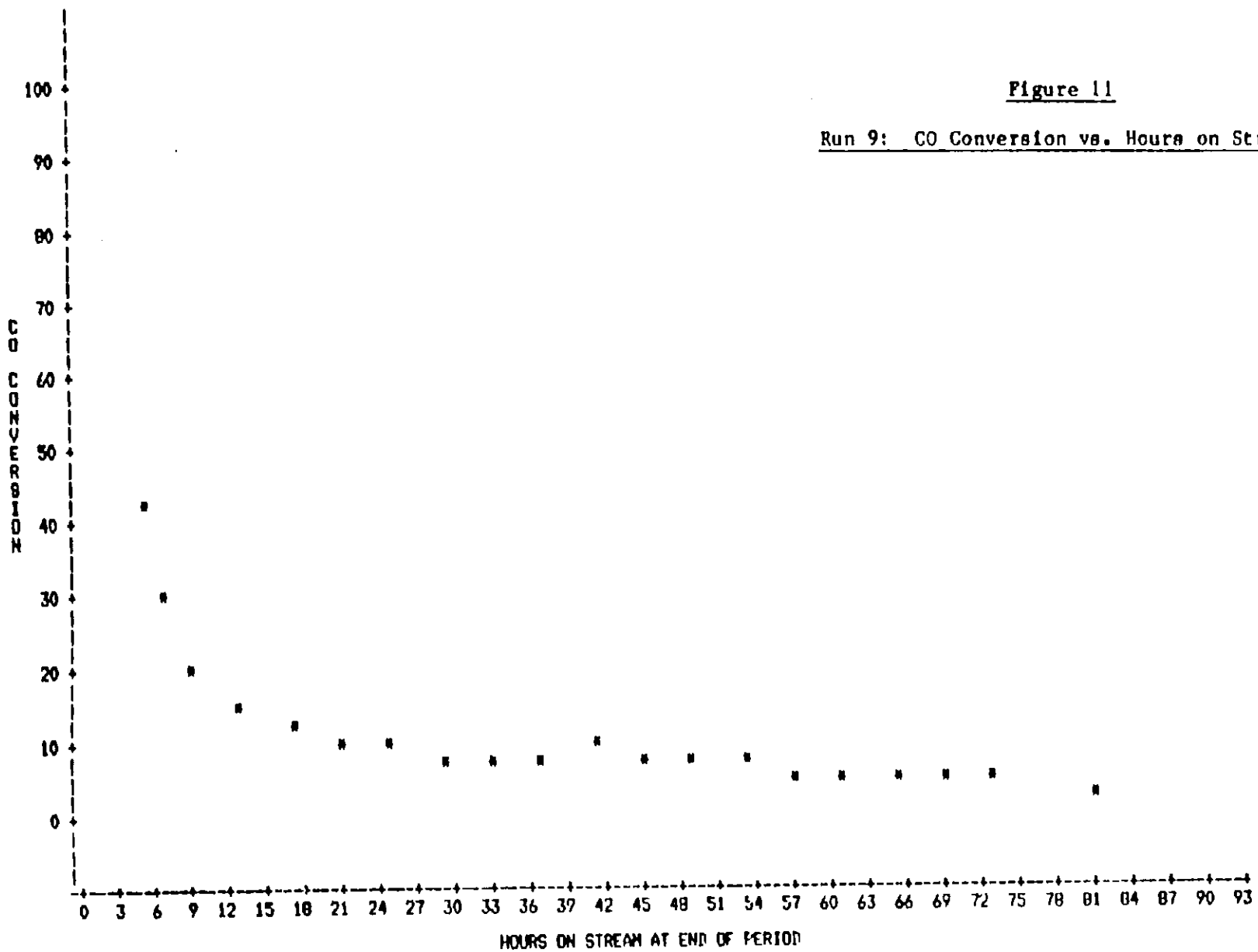


Figure 11

Run 9: CO Conversion vs. Hours on Stream

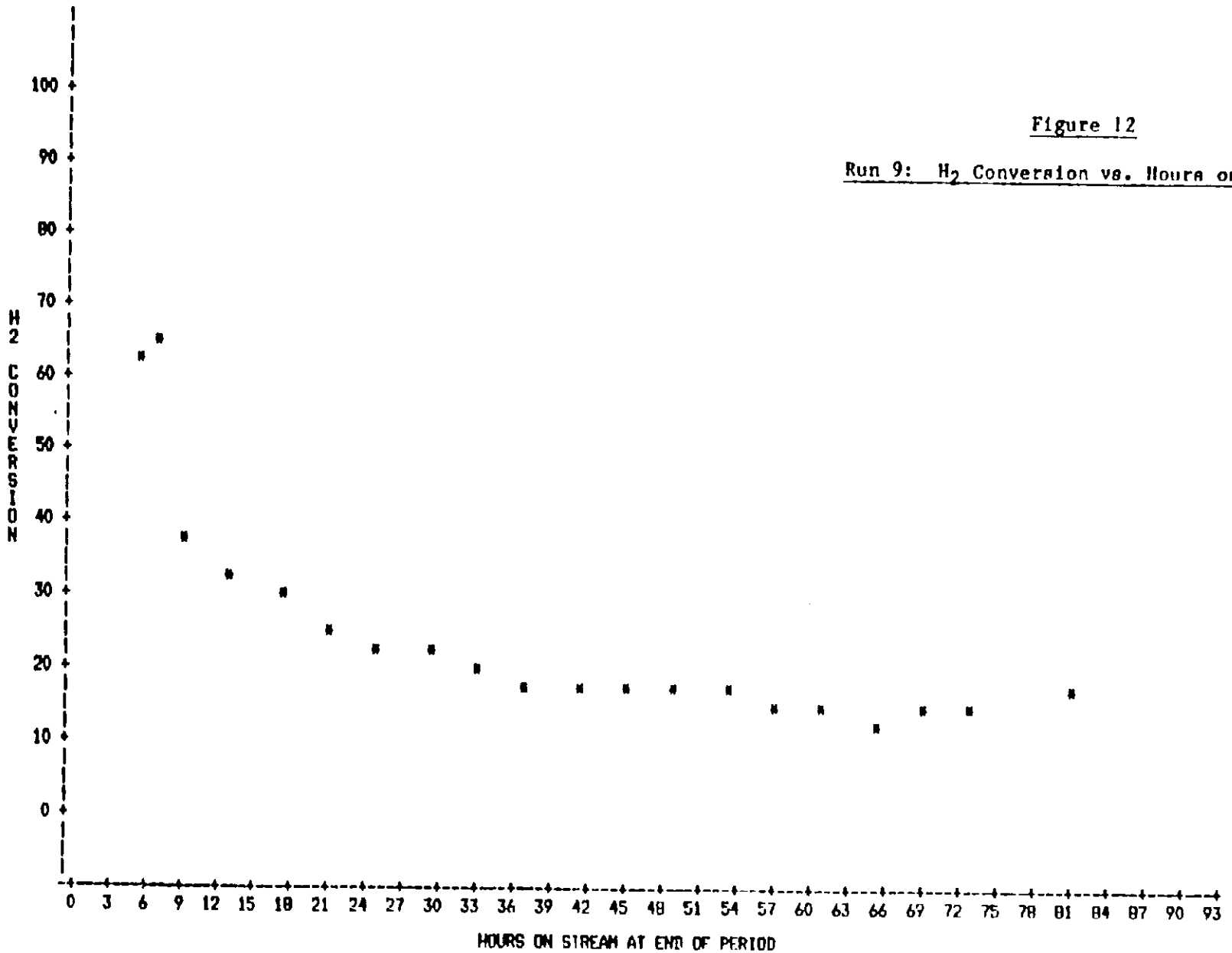


Figure 12

Run 9: H_2 Conversion vs. Hours on Stream

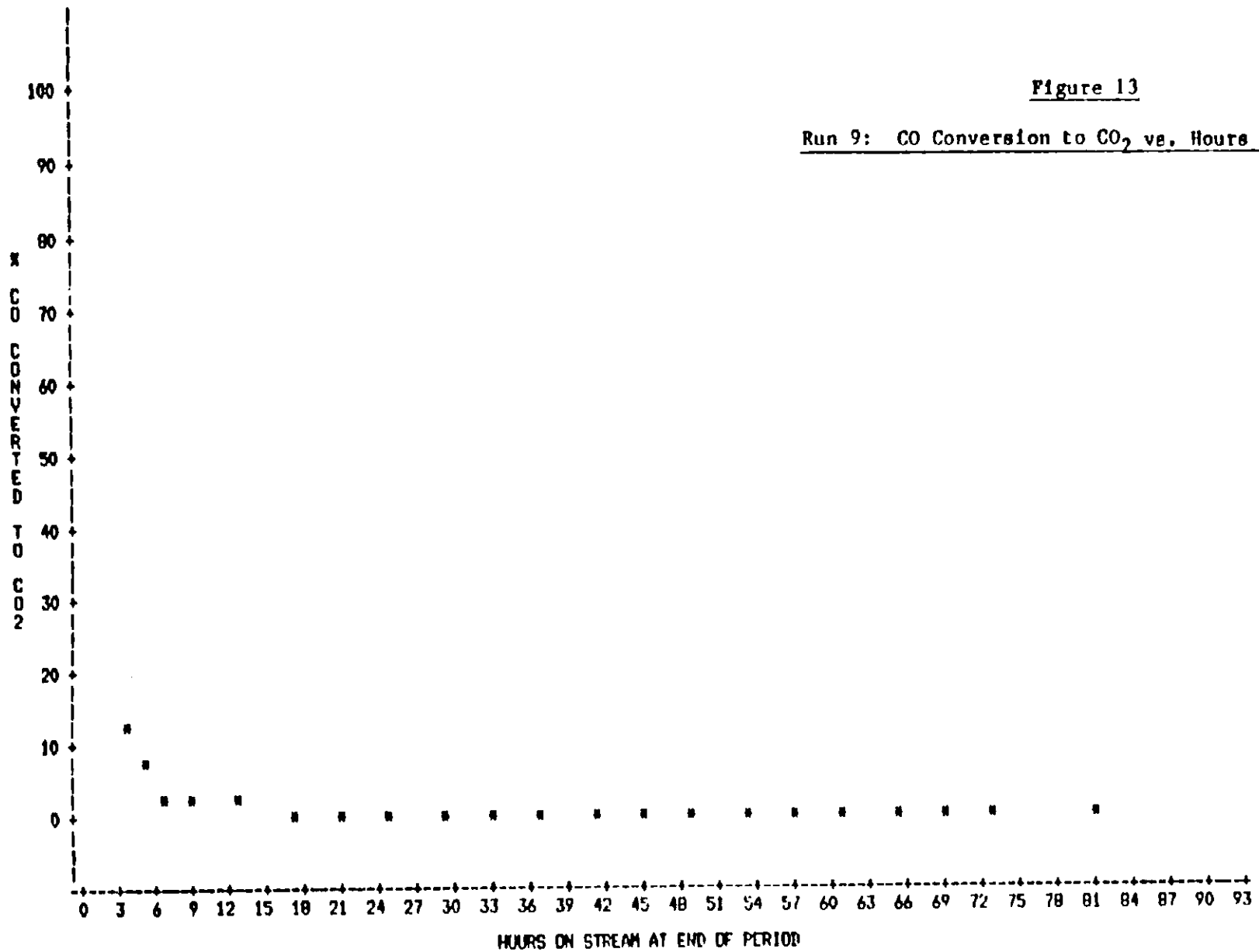


Figure 13

Run 9: CO Conversion to CO_2 vs. Hours on Stream

Figure 14: Run 9: Product Distributions

RE1016SAS FISCHER-TROPSCH DATA REDUCTION PROGRAM-- EXECUTED ON 15APR85108100

PILOT PLANT NO. 700 RUN NO. 9 TEST NO. 1 RUN SUMMARY REPORT
BOOK NO. CATALYST NO. 4956-23 BEGINNING DATE 08FEB1985 END OF TEST DATE 11FEB1985

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	4.63	40.64
CO	83.68	52.92
CO2	1.50	0.61
H2O	4.82	4.74
HYDROCARBON	4.91	0.89
ALCOHOL	0.46	0.20

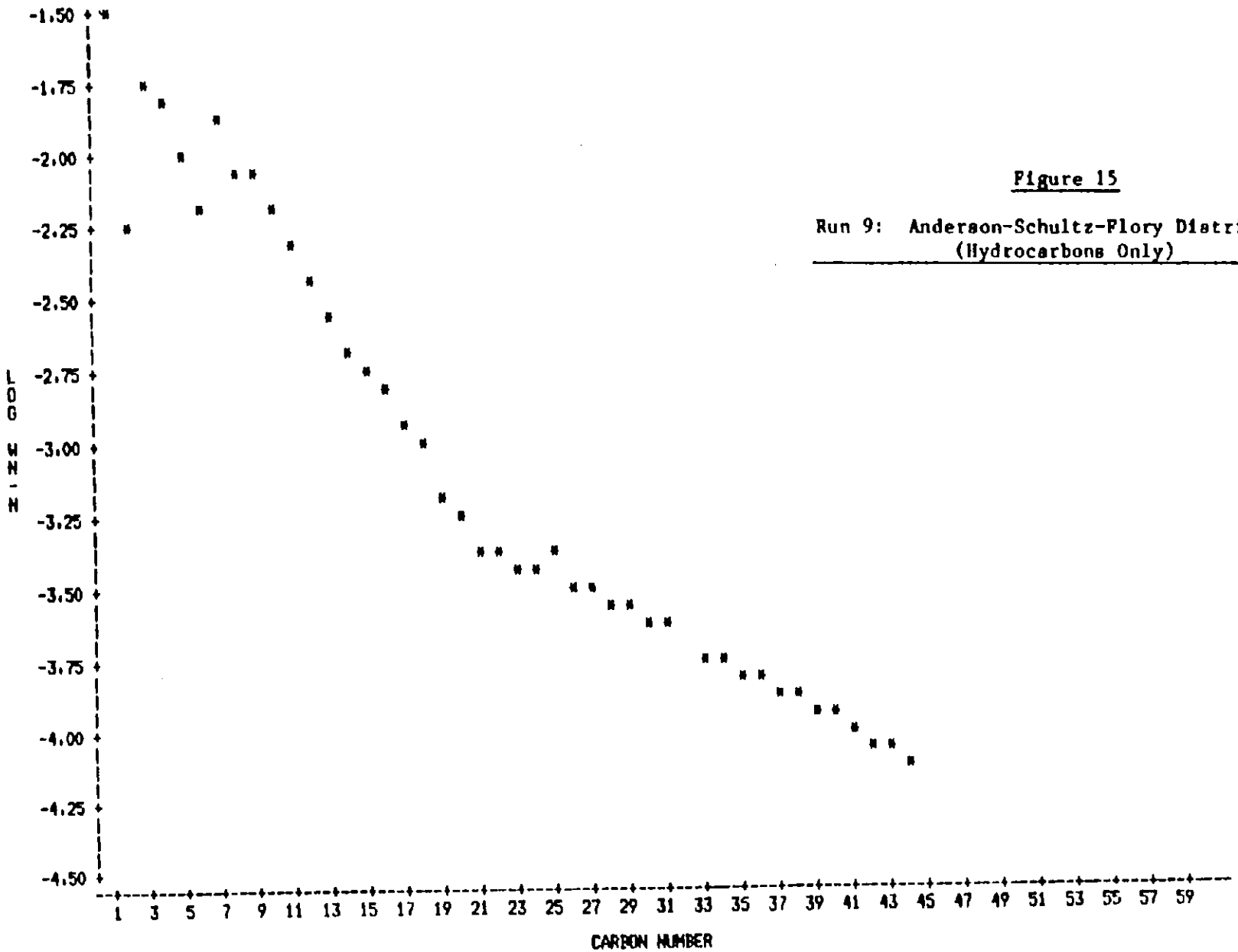
ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	44.65	57.04
ETHANOL	33.48	29.75
PROPANOL	10.64	7.25
BUTANOL	8.54	4.72
OTHER OXYGENATES	2.69	1.25

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	3.23	19.61
C2-C4	12.52	25.78
C5-C11	44.62	40.25
C12-C18	19.36	9.45
C19-C25	7.10	2.27
C26+	13.17	2.63

COMPONENT	WEIGHT %	MOLE %
CH4	3.23	19.61
C2P	0.73	2.35
C2=	0.34	1.18
C3	0.03	0.06
C3P	3.31	7.31
C3=	1.84	4.25
C4	0.31	0.53
C4P	4.43	7.42
C4=	1.54	2.67
C5	5.31	7.27
C6	3.64	4.16
C7	9.55	9.38
C8	6.74	5.80
C9	7.91	6.06
C10	6.33	4.37
C11	5.13	3.22
C12	4.26	2.45
C13	3.59	1.91
C14	3.00	1.48
C15	2.50	1.15
C16	2.32	1.00
C17	1.94	0.79
C18	1.75	0.67
C19	1.32	0.48
C20	1.13	0.39
C21	0.90	0.30
C22	0.95	0.30
C23	0.89	0.27
C24	0.91	0.26
C25	1.00	0.28
C26	0.83	0.22
C27	0.81	0.21
C28	0.79	0.20
C29	0.78	0.19
C30	0.73	0.17
C31	0.71	0.16
C33	0.63	0.13
C34	0.60	0.12
C35	0.58	0.11
C36	0.58	0.11
C37	0.52	0.10
C38	0.50	0.09
C39	0.46	0.08
C40	0.45	0.08
C41	0.41	0.07
C42	0.38	0.06
C43	0.36	0.06
C44	0.34	0.05
C45+	2.69	0.42
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.



NOTE: 15 OBS HAD MISSING VALUES

Figure 15

Run 9: Anderson-Schultz-Flory Distribution
(Hydrocarbons Only)

ANDERSON - SCHULTZ - FLORY DISTRIBUTION

Catalyst 4956-23 Run 9 Hours 81 Plant 700

T(°C) 207 P(psig) 1500 H_2/CO (Feed) 0.9 (molar)

Figure 16 Run 9: Anderson-Schultz-Flory Distribution (Hydrocarbons + Oxygenates)

Wn: Weight fraction of n'th hydrocarbon; n: carbon number

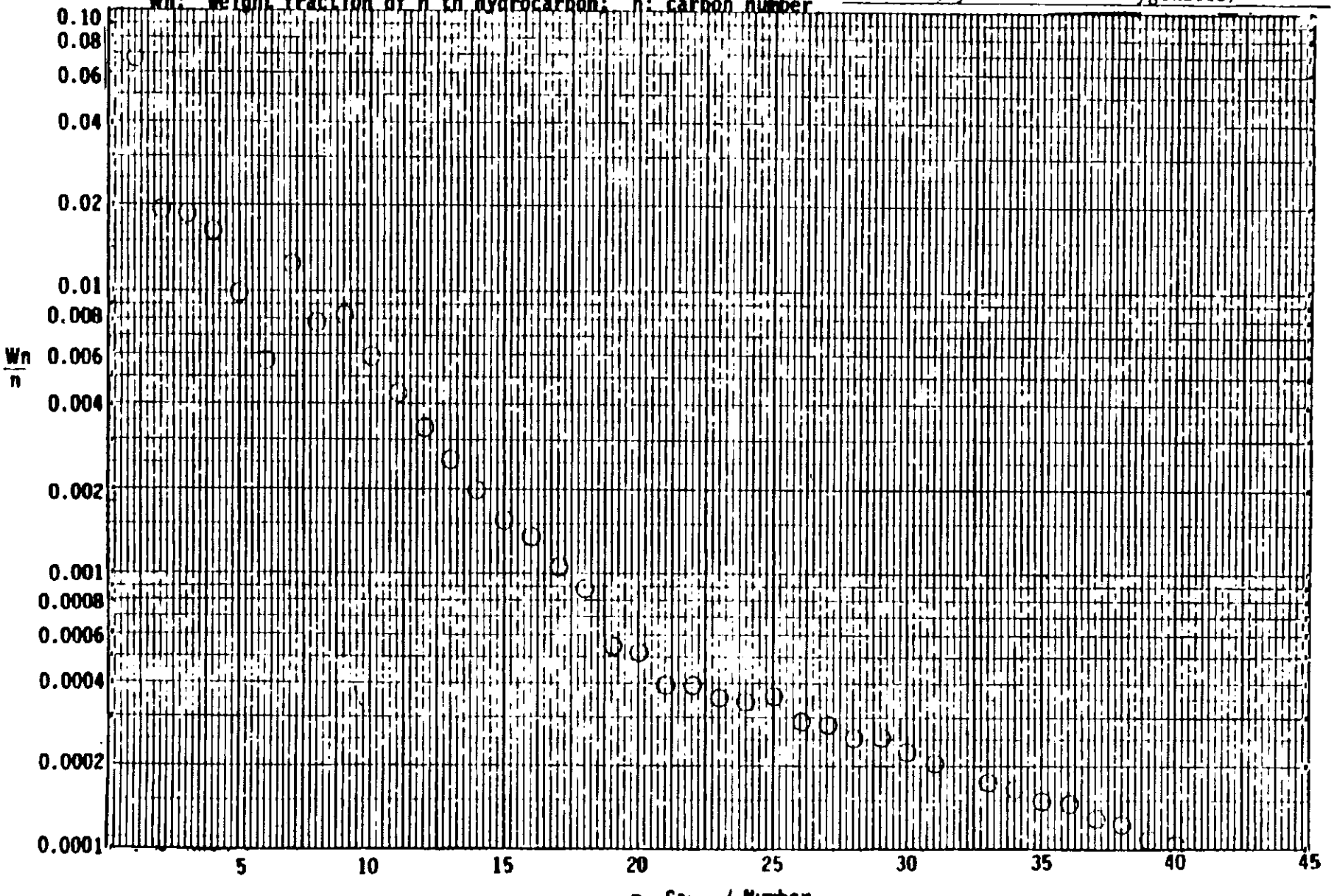


Figure 17

List of Alumina-Supported Ruthenium Catalysts Prepared by Micelle Methods

Catalyst Number	% Ru (by wt.)	Size of Preparation (g)	STEM Examination
4956-12	0.7	1	Broad Size Distribution
4956-19	1.7	2	40-60 Å Ruthenium Particles
4956-21	1.1	2	40-60 Å Ruthenium Particles
4956-23	1.1	30	Broad Size Distribution
4956-27	1.1	30	Broad Size Distribution

Figure 18

STEM Micrograph for Catalyst 4956-19

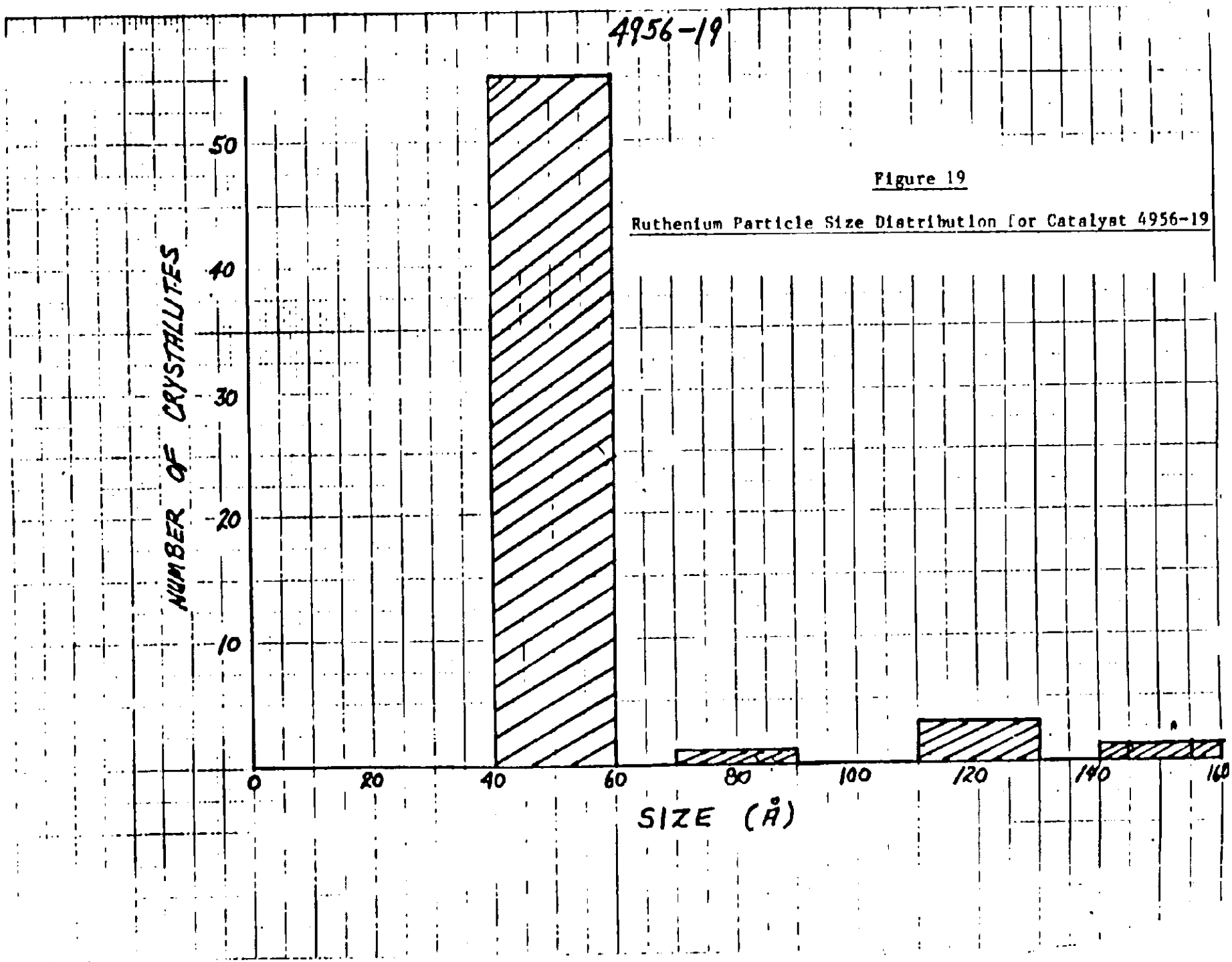


Figure 19

Ruthenium Particle Size Distribution for Catalyst 4956-19

Figure 20

Percent Ruthenium Analysis on
Several Alumina Particles for Catalyst 4956-19

(Alumina Particles Containing Ruthenium)

Particle #	WEIGHT %			
	Al	$Ru_{L\alpha}$	Al	$Ru_{K\alpha}$
1	97.7	2.3		Y
2	99.1	0.9		Y
3	92.9	7.1		Y
4	98.4	1.6		Y
5	98.8	1.2		Y
6	82.7	17.3	85.5	14.5
7	80.0	20.0	75.1	24.9
8	80.6	19.4	76.9	23.1
9	90.4	9.6	92.8	7.2
10	98.0	2.0	97.8	2.2
11	98.4	1.6		Y
12	98.1	1.9		Y
13	98.9	1.1		Y
14	96.9	3.3	97.1	2.9
15	97.5	2.5	98.2	1.8
16	96.8	3.2		Y
17	97.3	2.7		Y
18	98.4	1.6		Y
19	98.1	1.9		Y
20	98.8	1.2		Y
21	99.0	1.0		N
22	100			N
23	99.4	0.6		N
24	99.2	0.8		N
25	98.7	1.3		N
26	99.0	1.0		N
27	99.2	0.8		N
28	99.3	0.7		N
29	98.9	1.1		N
30	98.9	1.1		N
31	99.0	1.0		N

Y - Designates small $Ru_{K\alpha}$ peak observed but not distinguished from background by the computer.

N - No $Ru_{K\alpha}$ line observed.

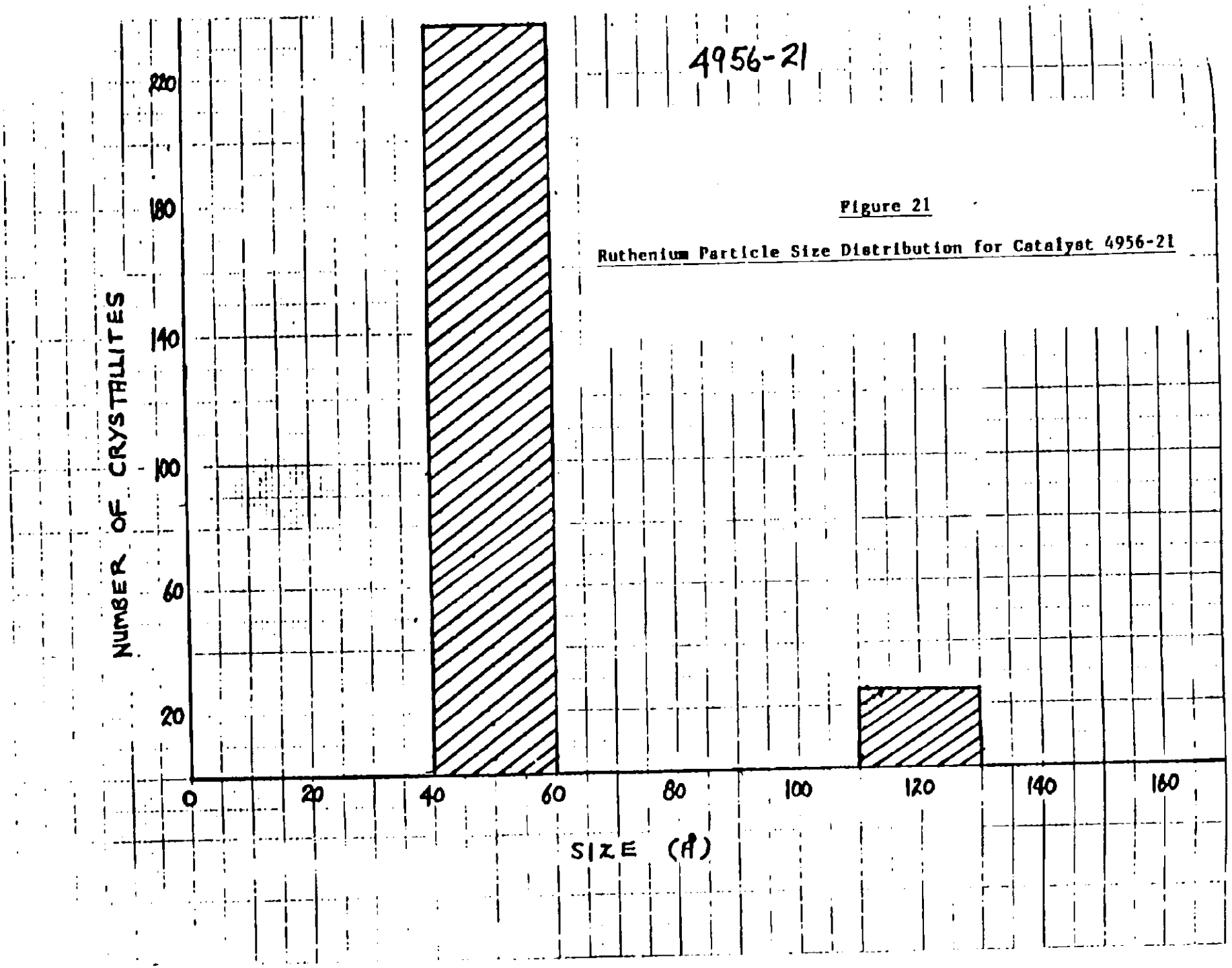


Figure 21

Ruthenium Particle Size Distribution for Catalyst 4956-21

Figure 22

Percent Ruthenium Analysis on
Several Alumina Particles for Catalyst 4956-21

(Alumina Particles Containing Ruthenium)

Particle #	WEIGHT %			
	Al	$Ru_{L\alpha}$	Al	$Ru_{K\alpha}$
1	98.9	1.1		
2	98.9	1.1		
3	99.1	0.9		
4	87.6	12.4		
5	88.3	11.7		
6	97.3	2.7		
7	96.7	3.3	96.3	3.5
8	97.6	2.4		
9	96.1	3.9	93.5	6.5
10	84.8	15.2		
11	96.9	3.1	91.9	8.1
12	98.7	1.3	98.8	1.2
13	99.0	1.0		
14	99.6	0.4		
15	98.3	1.7	98.2	1.8
16	98.8	1.2		

Ru crystallites were present on all the particles analyzed above.

Figure 23

SAXS Plot for the Reversed Micelle Solution (4956-24-1)
Used in the Preparation of Ruthenium Catalysts

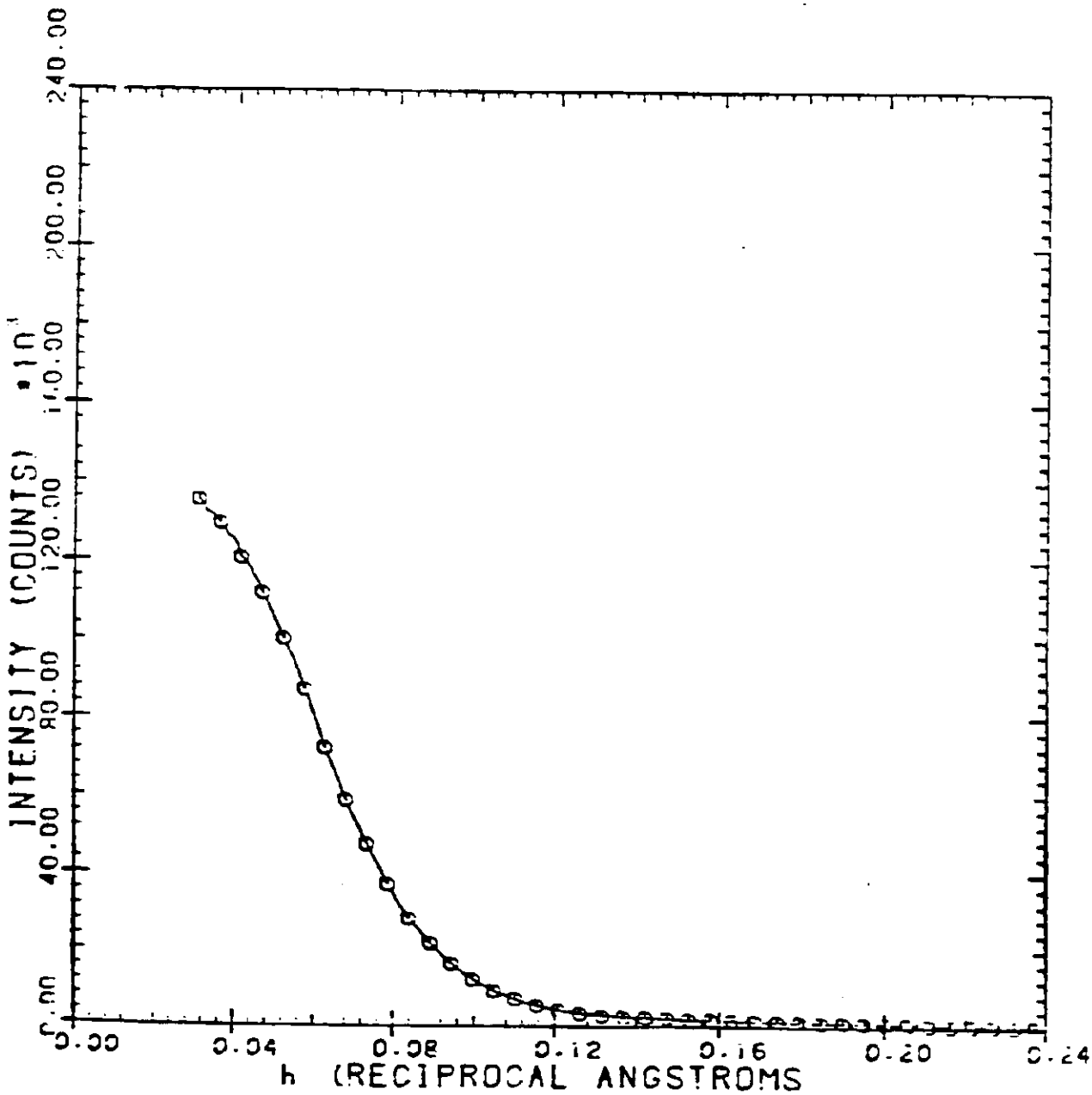


Figure 24

Guinier Plot for the Reversed Micelle Solution (4956-24-1)
Used in the Preparation of Ruthenium Catalysts

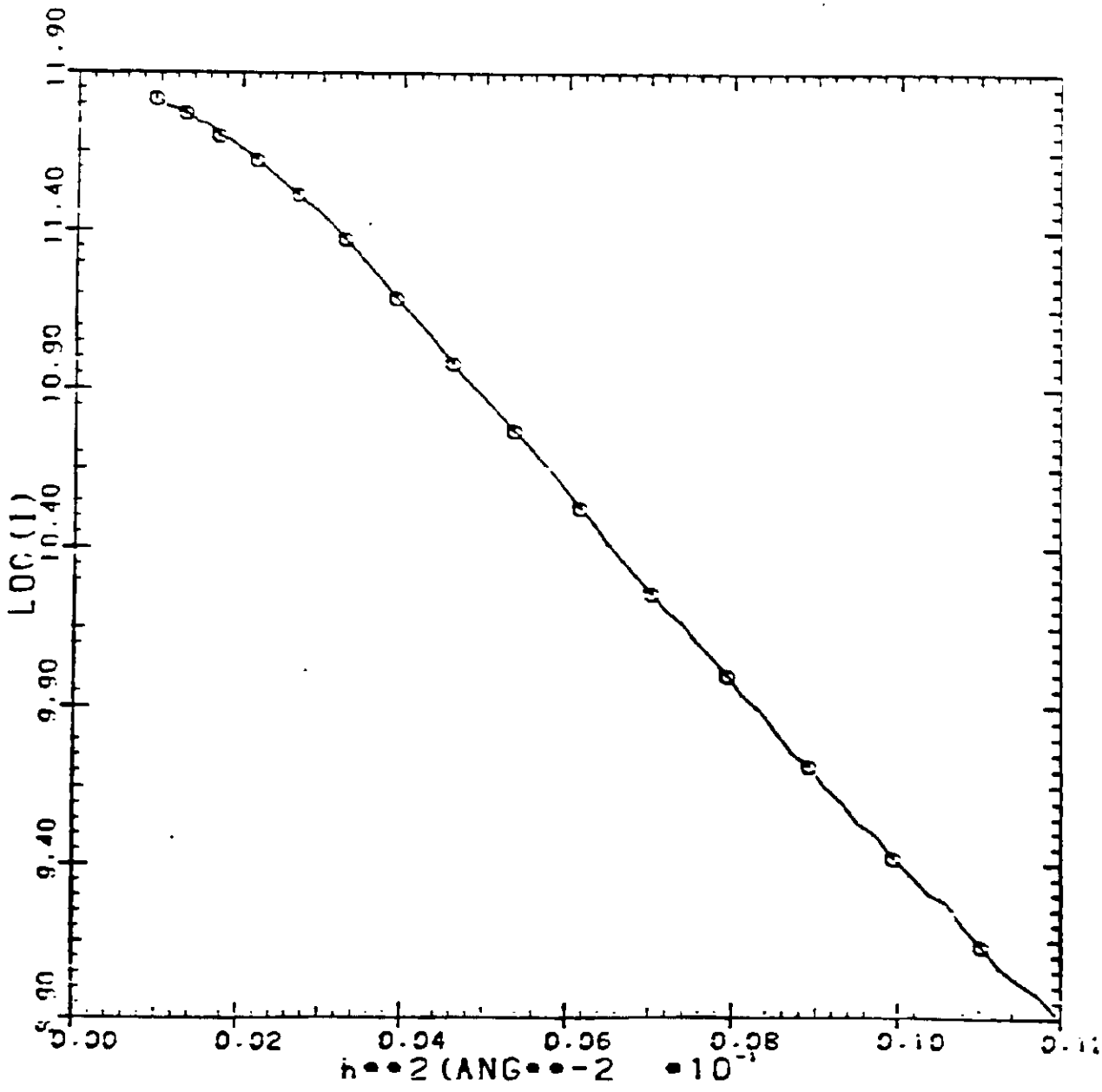


Figure 25

SAXS Plot for the Reversed Micelle Solution (4956-31)
Diluted 1:1 with the Organic Solvent

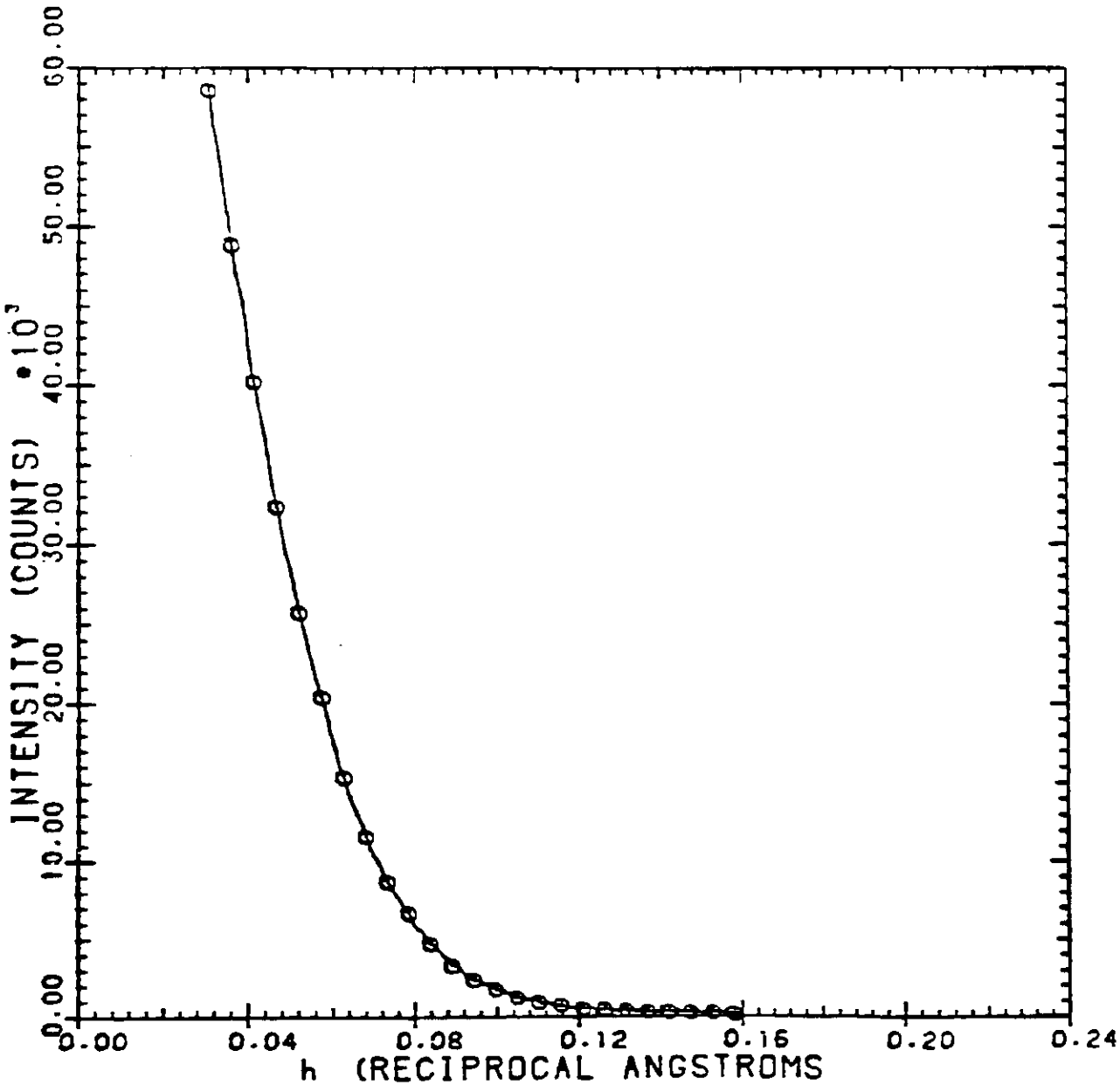


Figure 26

Guinier Plot for the Reversed Micelle Solution (4956-31)
Diluted 1:1 with the Organic Solvent

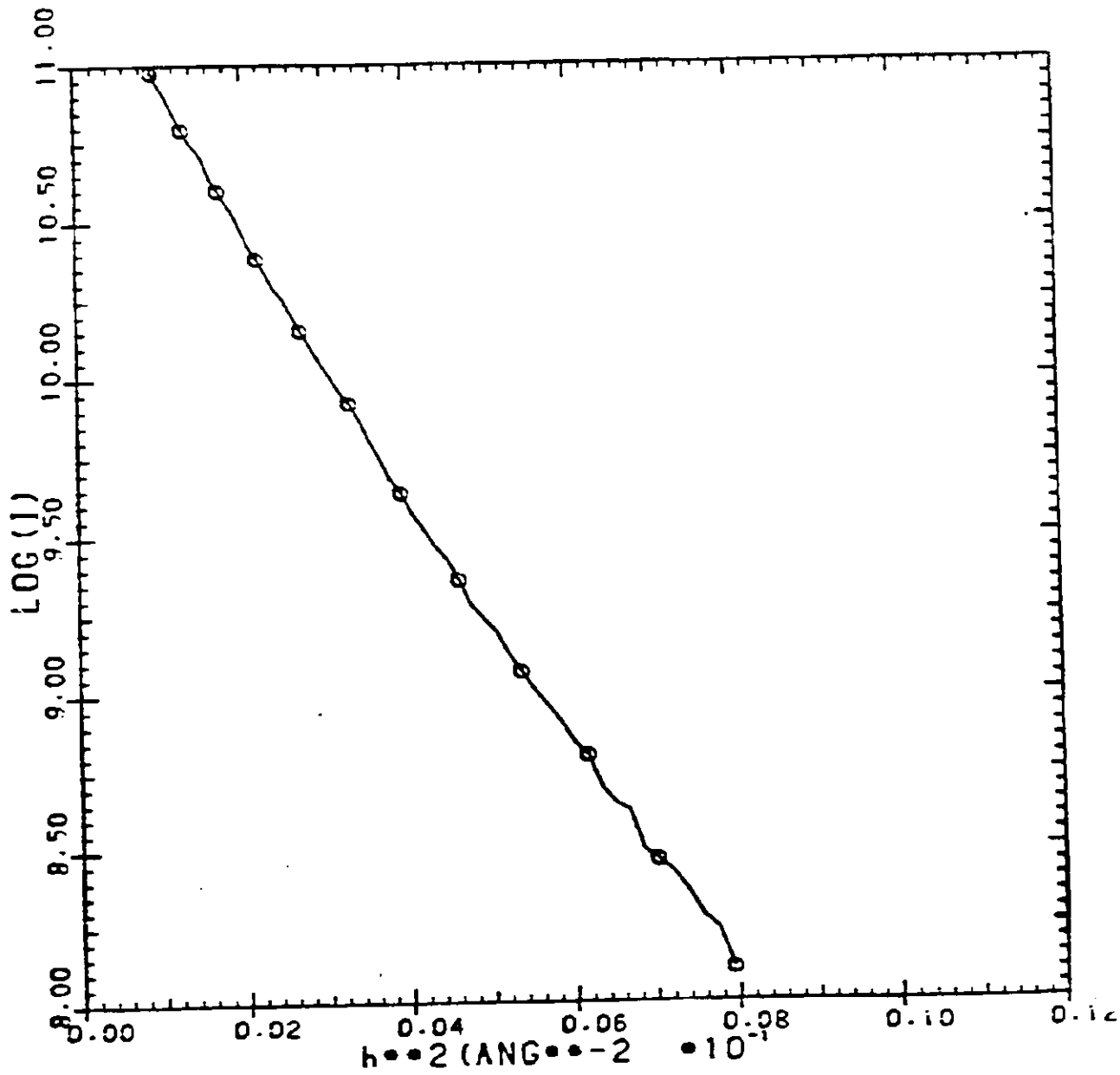
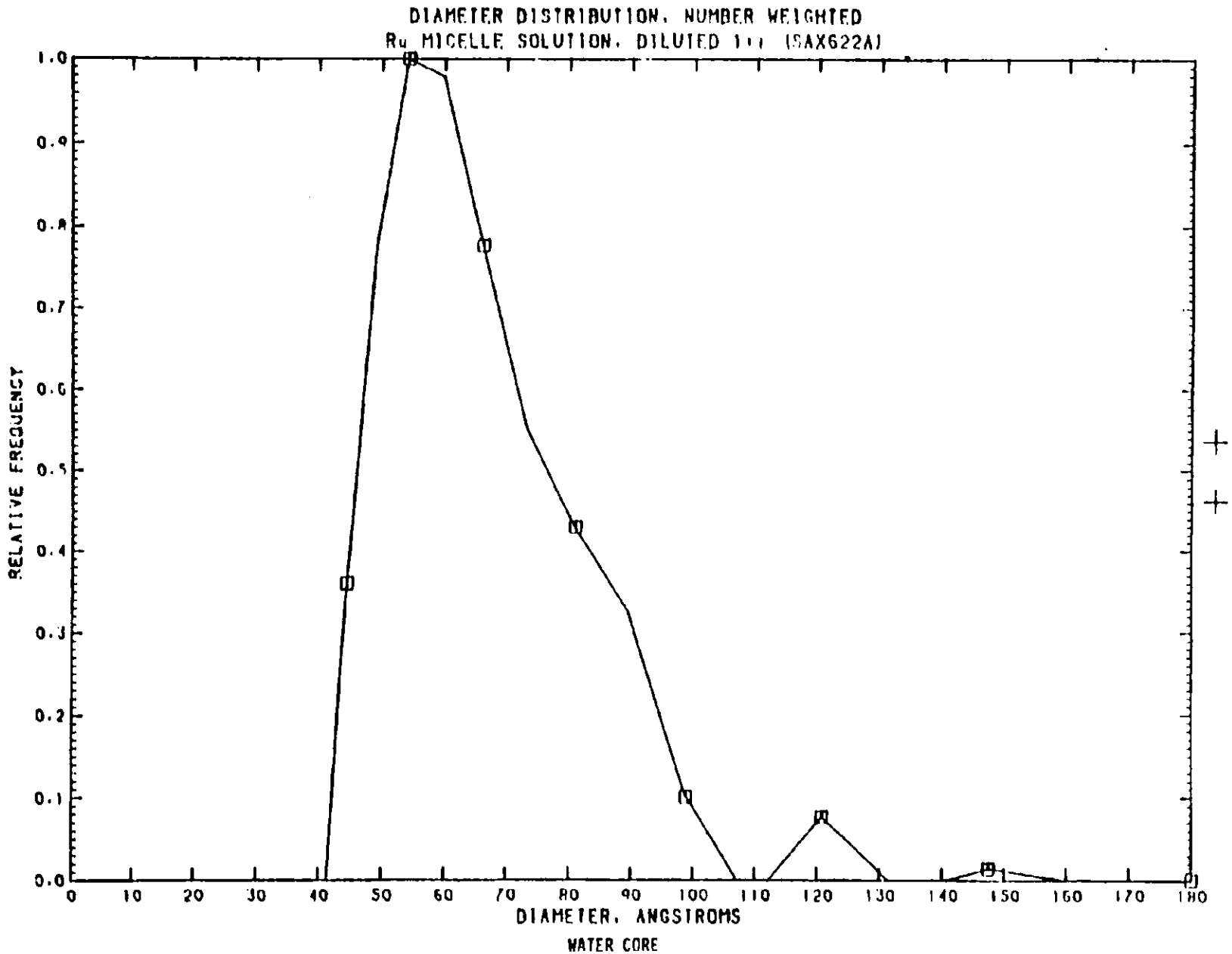


Figure 27

Diameter Distribution for the Reversed Micelle Solution (4956-31) Diluted 1:1 with the Organic Solvent



FISCHER-TROPSCH PILOT PLANT AT RESEARCH 13128 FRIDAY, JANUARY 18, 1985 14
CONVERSIONS VS. HOURS ON STREAM
PILOT PLANT NUMBER=700 RUN NUMBER=7 TEST NUMBER=2

PLOT OF CONV2C*ENDPER SYMBOL USED IS *

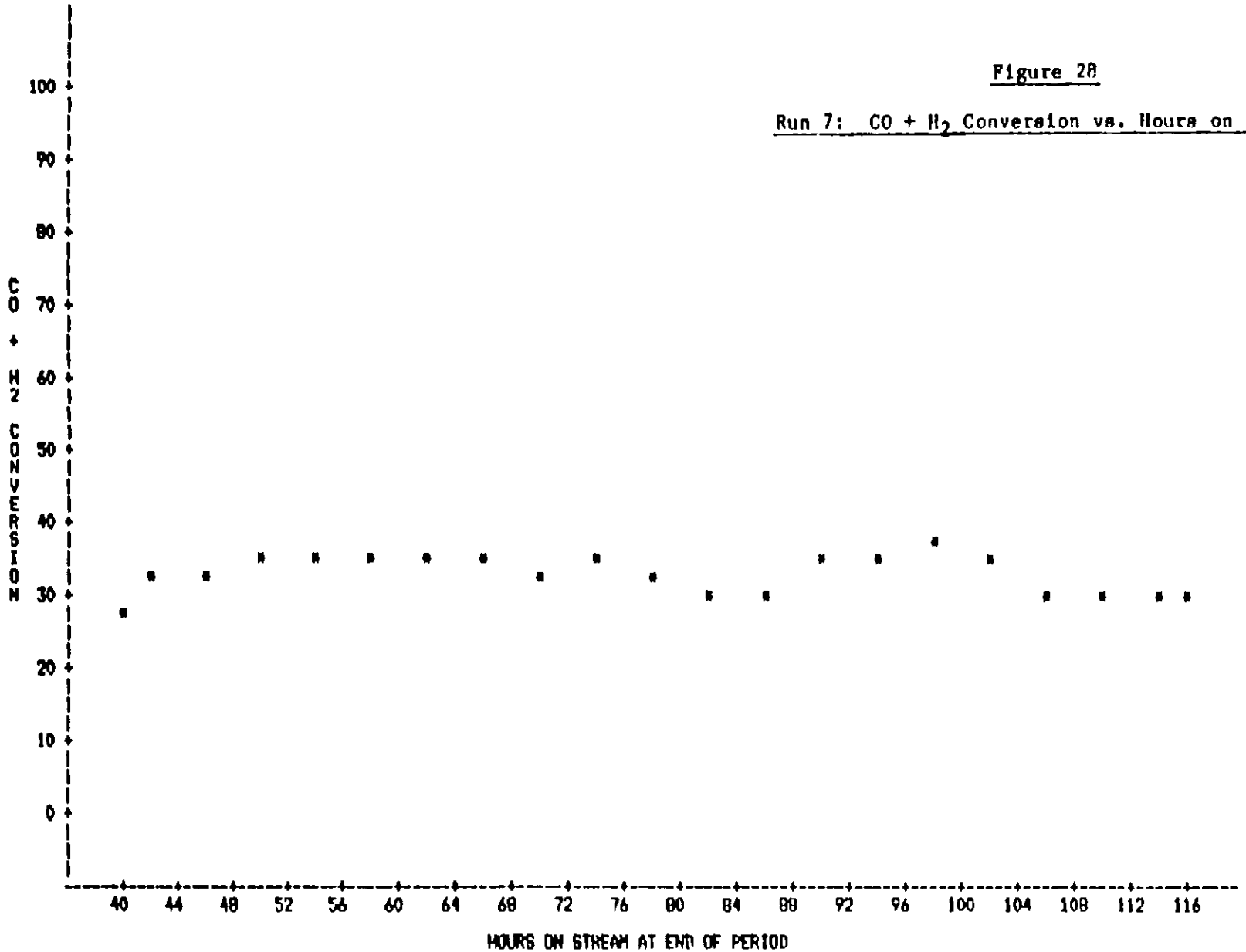


Figure 28

Run 7: CO + H_2 Conversion vs. Hours on Stream

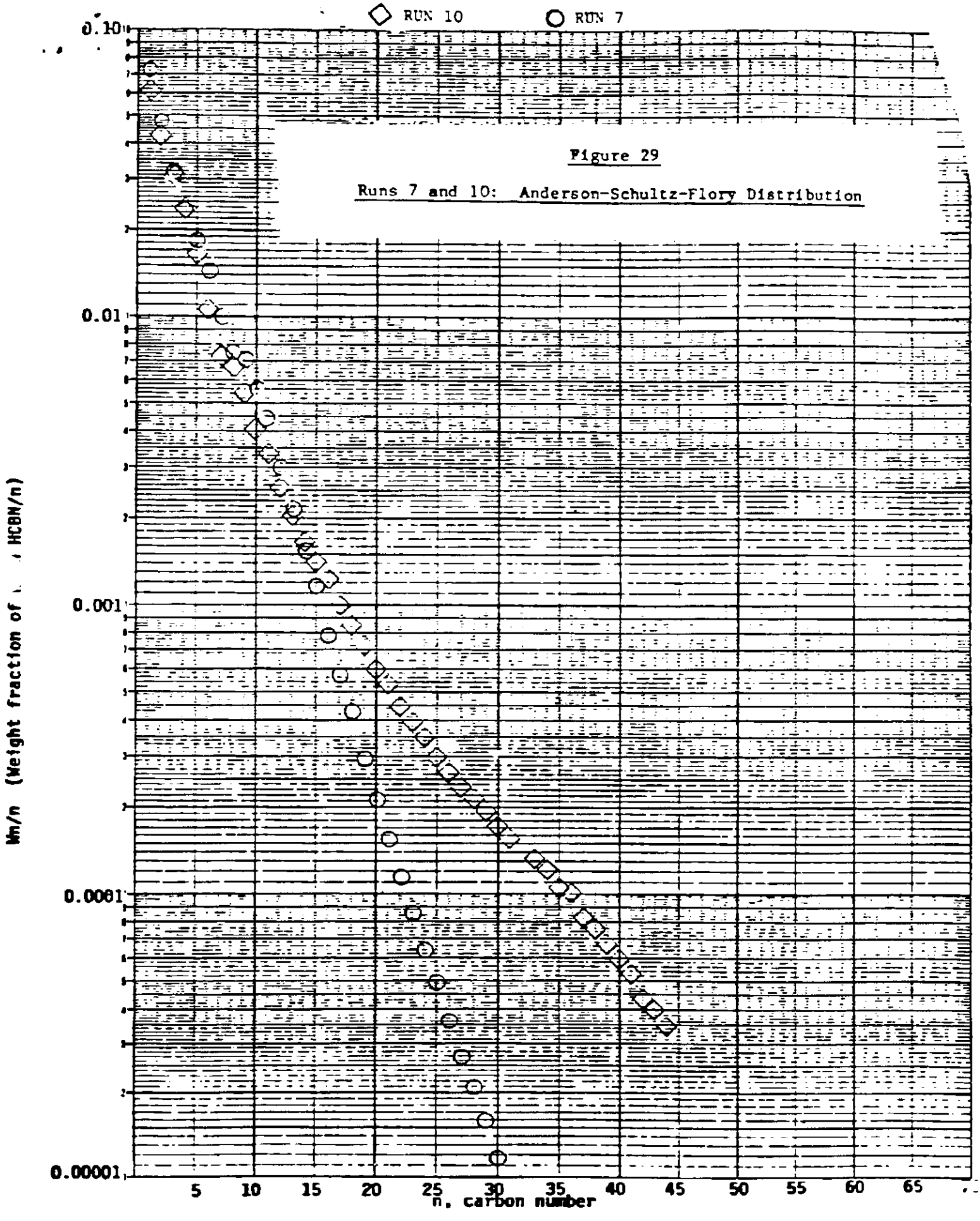


Figure 29

Runs 7 and 10: Anderson-Schultz-Flory Distribution

Figure 30

Runs 7 and 10: Amount of Wax Recovered from Used Catalyst

FISCHER TROPSCH SYNTHESIS

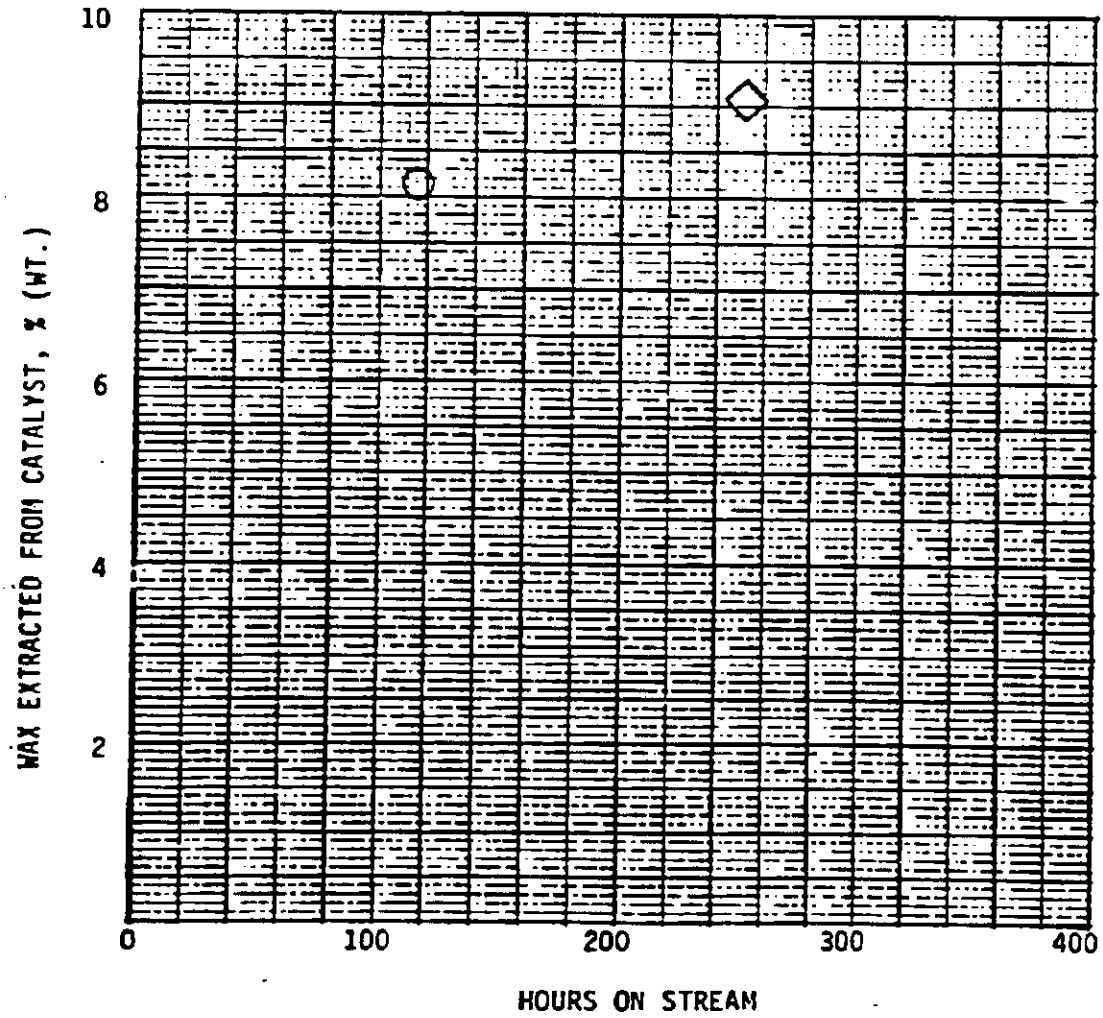
(PLANT 700)

AMOUNT OF WAX RECOVERED FROM CATALYST FOR DIFFERENT RUN TIMES

REDUCED C-73 IRON CATALYST

208°C, 500 psig, H_2/CO FEED = 0.9,

	RUN	GHSV	CO CONVERSION, %
○	7	950	∿ 30
◇	10	1140	∿ 25



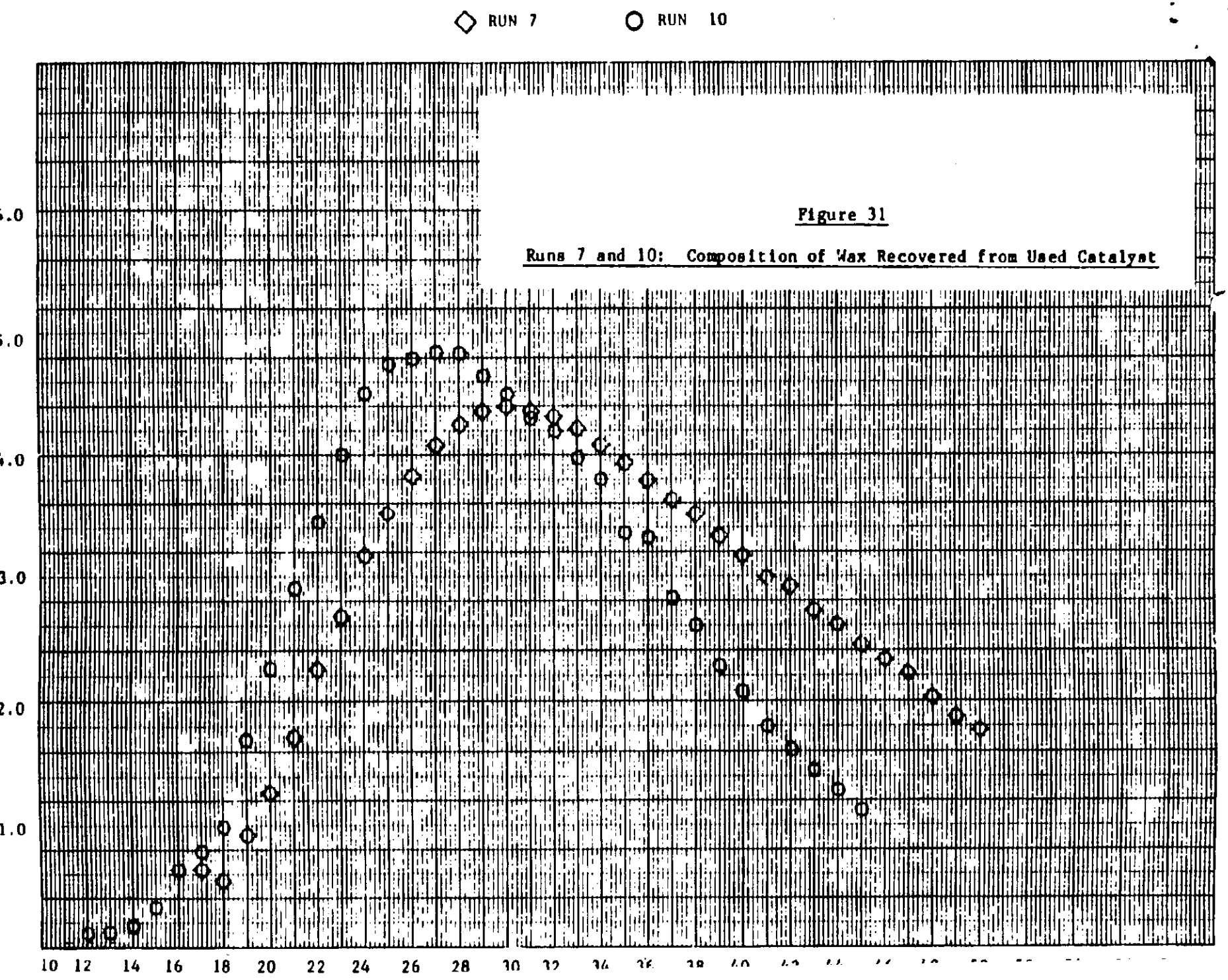


Figure 31

Runs 7 and 10: Composition of Wax Recovered from Used Catalyst