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TECHNICAL PROGRESS REPORT

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ABSTRACT

A micelle procedure was established for preparing, in 30 g quantity, catalysts with ruthenium crystallites of specific size.

A catalyst (4956-76) prepared by the micelle procedure and having 40-60 Å ruthenium crystallites, according to the scanning transmission electron microscope (STEM) analysis, was tested in the Fischer-Tropsch fixed-bed pilot plant and showed significantly improved stability over catalysts for which the micelle technique has not been successfully applied. A hydrocarbon cut-off number was not observed, in the C₁-C₁₈₀ carbon number range, with Catalyst 4956-76 containing 40-60 Å ruthenium crystallites. Catalyst 4956-76 was reexamined with STEM after 248 hours of testing and did not display any noticeable change in the ruthenium crystallite size.

Two new catalysts (4956-95 and 4956-97) were prepared with ruthenium crystallites of smaller size by the micelle procedure. Reverse micelle solutions with reverse micelles of smaller size were used for preparing these catalysts. Catalyst 4956-97, with mostly 20-30 Å ruthenium crystallites, is going to be evaluated to determine the effect of ruthenium crystallite size on selectivity.

X-ray diffraction (XRD) measurements were conducted on two ruthenium catalysts (1.1 and 1.7% Ru, by weight) prepared by a micelle technique, in order to confirm the narrow size distribution of ruthenium crystallites detected in the STEM examination. It was concluded that the XRD technique cannot be utilized to measure crystallite size distribution of (1-2 wt.% Ru) ruthenium on γ-alumina because of the interference of the strong signal from the alumina support.

In an attempt to compare ruthenium catalysts prepared by the micelle procedure to conventional ruthenium catalysts, a ruthenium catalyst (4956-86) was prepared by an aqueous impregnation technique. STEM examination indicated ruthenium to be very well dispersed with no observed crystallites. Catalyst 4956-86 was tested in the pilot plant and showed low activity compared to catalyst 4956-76. Also, the selectivity to methane was significantly higher with the "conventional" catalyst. Analysis of liquid and wax products obtained with the "conventional" catalyst are in progress and will be presented in the future. The "conventional" catalyst was later reexamined with STEM after 140 hours of testing and showed that significant agglomeration of ruthenium to 200-1000 Å particles occurred. Causes for the poor performance of the "conventional" catalyst are under investigation.

INTRODUCTION

Ruthenium crystallites, mostly in the 40 to 60 Å size range, were previously prepared on γ -alumina by a micelle technique. The narrow size distribution of ruthenium crystallites 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. Catalyst 4956-23, for which the micelle technique was not successfully applied, was tested in Run 9 (Plant 700) and showed rapid deactivation. Analysis of liquid products indicated the presence of iron and ruthenium. Also, iron was found on the used catalyst (Technical Progress Report 1/1/85-3/31/85).

The present work had three objectives. The first objective was to establish a procedure by which the micelle technique could be successfully applied to the preparation of ruthenium catalysts in large quantities. The second objective was to determine the causes of deactivation of the micelle-derived catalyst 4956-23. The third objective was to evaluate a micelle-derived catalyst with a narrow size distribution of ruthenium crystallites.

EXPERIMENTAL

Catalyst Testing Plant

All catalyst testing runs were conducted in Plant 700, which was previously described (Technical Progress Reports 10/1/84-12/31/84 and 1/1/85-3/31/85). An iron carbonyl scrubber was installed at the reactor inlet with Run 11. The stainless steel reactor was replaced with a glass-lined 7/8" I.D. reactor after Run 12; also, the walls of the iron carbonyl scrubber were glass lined.

Catalyst Testing Procedure

The catalyst testing procedure was the same as the one used for Run 10 (Technical Progress Report 1/1/85-3/31/85). The conditions were 208°C, 500 psig, and 0.9 H₂/CO feed ratio. The gas hourly space velocity was 64 hr⁻¹ to 84 hr⁻¹ for these tests.

Run Analysis Procedure

The run analysis procedure was previously described (Technical Progress Report 1/1/85-3/31/85). The wax made in Run 15 was analyzed by gel permeation chromatography in addition to being analyzed by gas chromatography. Size separation of the hydrocarbons was achieved using a chromatograph equipped with a differential refractometer as the detector. The separation columns were calibrated by analyzing C₆ through C₄₄ hydrocarbon standards and relating retention time to carbon number. A linear calibration curve was established. The results reported here, for hydrocarbons C₄₄ through C₁₈₀, were calculated by assuming that the linearity of retention time with carbon number was maintained beyond the calibration range. Also, constant refractive index was assumed for the entire carbon number range.

Characterization of Ruthenium Catalysts by Scanning Transmission Electron Microscopy

Catalysts were examined by scanning transmission electron microscopy (STEM) to determine the size distribution of ruthenium particles. The procedure used for STEM examination of catalysts was previously described (Technical Progress Report 10/1/84-12/31/84).

Characterization of Ruthenium Catalysts
and Ruthenium Powder by X-ray Diffraction

X-ray diffraction (XRD) measurements were done on two ruthenium catalysts with ruthenium crystallites mostly in the 40 to 60 Å size range. The objective was to confirm the results obtained in the STEM examination and to obtain a statistically more reliable determination of the distribution of crystallite sizes. Measurements were also done on a ruthenium metal powder in order to identify the ruthenium peaks best suited for lineshape analysis. The procedure used for the XRD measurements and for data analyses were previously described (Technical Progress Report 10/1/84-12/31/84).

Characterization of Reverse Micelle
Solutions by Small Angle X-ray Scattering

Small angle X-ray scattering (SAXS) was used to characterize new reverse micelle solutions with smaller size reverse micelles. The procedures used for conducting the SAXS experiments and for analyzing data were also previously described (Technical Progress Report 1/1/85-3/31/85).

RESULTS

The results in this work are presented in four sections.

The first section includes a description of STEM examination of ruthenium catalysts prepared by a micelle technique. Both successfully and unsuccessfully prepared catalysts, with 40-60 Å target ruthenium crystallite size, are described. Results are also presented for micelle-derived catalysts with ruthenium crystallites of smaller size. This section also includes the description of a ruthenium catalyst prepared by a conventional technique.

The second section consists of a description of XRD measurements on two ruthenium catalysts prepared by a micelle technique and XRD measurements done on ruthenium powder.

The results in the third section pertain to the characterization of two new reverse micelle solutions with smaller size reverse micelles, using SAXS. One of these new solutions was used for preparing a catalyst with very small ruthenium crystallite size.

The fourth section describes the testing of six ruthenium catalysts in Pilot Plant 700. For four of these catalysts, the micelle technique was not successfully applied. The fifth catalyst, prepared by a micelle technique, had mostly 40-60 Å ruthenium crystallites. Some results, i.e., conversion, are also presented for a ruthenium catalyst prepared by a conventional technique. Analysis of liquid and wax products obtained with the conventional catalyst were in progress during writing of this report, and further results will be presented in the future.

List of Figures

- 1 - Summary of STEM Examination of Ruthenium Catalysts
- 2 - STEM Micrographs of Catalyst 4956-76
- 3 - XRD Measurements on Ruthenium Metal Powder (4956-34)
- 4 - XRD Measurements on a Physical Mixture of Ruthenium Metal Powder with $\gamma\text{-Al}_2\text{O}_3$ (1:10, by wt.) (4956-46)
- 5 - XRD Measurements on Catalyst 4956-21
- 6 - XRD Measurements on Catalyst 4956-19
- 7 - XRD Measurements on $\gamma\text{-Al}_2\text{O}_3$ Support
- 8 - XRD Measurements on RuO_2 Powder

- 9 - SAXS Plot for the Reverse Micelle Solution 4966-50
- 10 - Guinier Plot for the Reverse Micelle Solution 4966-50
- 11 - Summary of SAXS Results
- 12 - SAXS Plot for the Reverse Micelle Solution 4966-52
- 13 - Guinier Plot for the Reverse Micelle Solution 4966-52
- 14 - Run Summary Data for Plant 700
- 15 - Comparison of CO Conversions for Different Runs with Micelle-Derived Catalysts (Plant 700)
- 16 - Temperature Profiles in Run 15 (Plant 700)
- 17 - CO Conversion vs. Hours on Stream in Run 15 (Plant 700)
- 18 - CO Conversion to CO₂ vs. Hours on Stream in Run 15 (Plant 700)
- 19 - H₂ Conversion vs. Hours on Stream in Run (Plant 700)
- 20 - CO + H₂ Conversion vs. Hours on Stream in Run 15 (Plant 700)
- 21 - Composition of the Effluent Gas vs. Hours on Stream in Run 15 (Plant 700)
- 22 - Anderson-Schulz-Flory Distribution in Run 15 (Plant 700) (Hydrocarbons Only)
- 23 - Anderson-Schulz-Flory Distribution in Run 15 (Plant 700) (Hydrocarbons + Oxygenates)
- 24 - Anderson-Schulz-Flory Distribution in Run 15 (Plant 700) (>C₁₀ Hydrocarbons Analyzed by Gel Permeation Chromatography)
- 25 - Product Distributions in Run 15 (Plant 700)
- 26 - CO Conversion vs. Hours on Stream in Runs 15 and 16 (Plant 700)
- 27 - CO Conversion to CO₂ vs. Hours on Stream in Runs 15 and 16 (Plant 700)
- 28 - H₂ Conversion vs. Hours on Stream in Runs 15 and 16 (Plant 700)
- 29 - CO + H₂ Conversion vs. Hours on Stream in Runs 15 and 16 (Plant 700)
- 30 - Composition of the Effluent Gas vs. Hours on Stream in Runs 15 and 16 (Plant 700)

1. STEM Examination of Ruthenium Catalysts

A summary of the STEM examination of ruthenium catalysts is in Figure 1.

Catalysts 4956-22, 4956-23, 4956-27, and 4956-56 were all unsuccessful attempts to prepare 30 g quantities of catalysts (~1 wt.% Ru) with 40-60 Å ruthenium crystallite size, by a micelle technique. These four catalysts all showed broad size distribution of ruthenium particles, with some very large particles of 1000-2000 Å. Catalyst 4956-76 (0.93 wt.% Ru) was the first successful micelle-derived catalyst prepared in 30 g quantity. A STEM micrograph of catalyst 4956-76 is in Figure 2. About 90% of ruthenium crystallites were 40-60 Å in size. The remaining crystallites were 100-150 Å (5-7%) and 200-250 Å (3-5%). Also, 70-80% of the alumina particles that were examined contained ruthenium.

Two other catalysts, 4956-95 (~0.23 wt.% Ru) and 4956-97 (~0.47 wt.% Ru), were later prepared using smaller reverse micelles. The reverse micelle solution (4966-50) used for the preparation of catalyst 4956-95 is discussed in the third section. The reverse micelles used for preparing catalyst 4956-97 were not characterized but were intermediate in size between the reverse micelles used for preparing catalyst 4956-95 (4966-50) and catalyst 4956-76 (4956-24-1). Catalyst 4956-95 did not show any ruthenium crystallites in the STEM examination, indicating that the crystallites were probably below 20 Å. Catalyst 4956-97 had over 70% of the crystallites in the 20-30 Å size range. The rest of the crystallites were slightly larger, 40-50 Å.

In an attempt to compare ruthenium catalysts prepared by a micelle technique to conventional ruthenium catalysts, a catalyst (4956-86) (1.1 wt.% Ru) was prepared by an aqueous impregnation technique on the same support that was used for the preparation of the micelle-derived catalysts. STEM examination of catalyst 4956-86 indicated that ruthenium was very well dispersed with no observed crystallites.

2. XRD Measurements on Ruthenium Catalysts and on Ruthenium Powder

The samples were transferred to an "o" ring sealed diffraction cell with Kapton window in a glove box to maintain an inert atmosphere. Measurements were made on the Rigaku diffractometer with a Mo X-ray source. Test scans of Ru metal powder (4956-34) spread onto the back of a piece of Kapton tape and a physical mixture of 10% Ru powder (-325 mesh) in alumina support (4956-46) were made in order to identify the Ru peaks best suited for the lineshape analysis. These scans are shown in Figures 3 and 4, respectively.

As can be seen in Figure 4, there is strong overlap of the sharp features of the relatively large Ru crystallites in the powder and the gamma alumina support material. It was thus not clear whether it would be possible to separate the broad bands expected for the small Ru crystallites from the background. A long time scan of catalyst 4956-21 is shown in Figure 5. No evidence for any Ru features can be found. Even if relatively large crystallites are present, it is doubtful that an easy separation of the background from the Ru peaks could be effected. In this case, where small crystallites with broad peaks are expected, the use of X-ray lineshape analysis can be completely ruled out.

Since the X-ray lineshape method is potentially the only method to give information about the distribution of sizes over a broad range without microscopic examination of many individual crystallites, a second catalyst on a gamma alumina support was tried. Only small quantities of this catalyst (4956-19) were available so that the normal cell loading procedure could not be used. A small portion of the catalyst was spread evenly on the back of a piece of Kapton tape on a normal sample slide. This required a measurement in air. Also, since only a very small amount of material was present, a long scan time was used in order to obtain even qualitative information. The results are shown in Figure 6. For comparison, the support material (4956-41-2) as measured via the normal

procedure is shown in Figure 7. The steep sloping background in the catalyst sample is due to scattering from the Kapton tape itself. There is excellent correspondence for each catalyst feature with features in the support only. (Two additional features can be seen in a number of the scans at 17.2° and 20° . These are due to the beam catching part of the sample holder.) Thus, Ru is again not detectable. Even though there is only a small amount of sample, the signal to noise ratio of the catalyst is clearly high enough to allow identification of the Ru features if they were visible.

Since the scan for catalyst 4956-19 was done in air and air sensitivity may be a problem with reduced Ru catalysts, the question of possible oxidation of the metal to RuO_2 must be considered. A scan of RuO_2 spread on Kapton tape is shown in Figure 8. The pattern has two strong peaks at low angle which should not be obscured in any of the other scans. Since no features are found in this range in the catalysts, it is concluded that crystalline RuO_2 is not present in a significant amount.

3. SAXS Examination of New Reverse Micelle Solutions

Two new reverse micelle solutions (4966-50 and 4966-52) were prepared with the objective of synthesizing reverse micelles smaller than the ones in solution 4956-24-1 (Technical Progress Report 1/1/85-3/31/85) that was used for the preparation of 4956-76 catalyst.

The SAXS curve for sample 4966-50 is shown in Figure 9. A diameter distribution cannot be calculated from this data since, as the strongly curving region at lower angles extending from 0.03 to 0.1 \AA^{-1} shows, a large amount of particle-particle interference is present. This is not surprising since this solution is concentrated.

Figure 10 is the Guinier plot for sample 4966-50. There is a region of appreciable curvature at lower h^2 , again due to particle-particle interference. A linear region, however, extends from about $h^2 = 0.014$ to 0.040 \AA^{-2} . From the slope of this region, the radius of gyration was calculated to be 12 \AA . From this value, the volume averaged diameter of the micelle core was calculated to be 31 \AA . Since in this average the larger cores are weighted more, the number averaged diameter may be smaller if the size distribution is not monodisperse. These results are summarized in Figure 11. Also listed in Figure 11 are the SAXS results for sample 4956-24-1 reported earlier (Technical Progress Report 1/1/85-3/31/85). The results indicate that the new reverse micelles are significantly smaller in size relative to the sample 4956-24-1 for which the diameter was 75-90 \AA .

Figure 12 is the SAXS curve for sample 4966-52. A slight inflection near 0.06 \AA^{-1} is seen which indicates some particle-particle interference; thus, a valid diameter distribution could not be calculated for this sample. Figure 13 is the Guinier plot for this sample. The plot is linear, and the slope yields a radius of gyration of 15 \AA . This leads to a volume averaged core diameter of 39 \AA . These results are also summarized in Figure 11.

4. Tests in the Fixed-Bed Pilot Plant

Six runs were conducted in Pilot Plant 700 with ruthenium catalysts. The operating conditions and key results for these runs are summarized in Figure 14.

Experimental Catalysts

Runs 11-14 were conducted with catalysts 4956-27, 4956-30, 4956-22 and 4956-56, respectively. The micelle technique was not successfully applied to these four catalysts, which showed very broad size distributions of ruthenium particles, some of which were 1000-2000 \AA .

The CO conversions obtained in these runs are summarized in Figure 15. Rapid catalyst deactivation had been previously observed in Run 9 with another unsuccessful micelle-derived catalyst (4956-12). Examination of that used catalyst showed 0.35 wt.% iron, and analysis of liquid products indicated the presence of ruthenium. Run 11 was conducted with an iron carbonyl scrubber held at 210°C on the CO/Ar feed line at the inlet of the reactor. Also, the operational pressure was lowered from 1500 psig to 500 psig to minimize migration and loss of ruthenium from the catalyst. The amount of iron on the catalyst in Run 11 was not lower than observed in Run 9; however, the amount of iron and ruthenium in liquid products was significantly lower. The same rapid deactivation was observed in Run 11 as in Run 9.

In Run 12, the temperature of the iron carbonyl scrubber was increased to 260°C. Less iron was analyzed both on the used catalyst and in liquid products. However, catalytic stability was not apparently affected.

A glass-lined reactor was used in Run 13 in addition to the iron carbonyl scrubber at the reactor inlet to minimize iron contamination. Very little iron was analyzed on the catalyst and in liquid products. However, catalytic stability was still poor.

Since relatively high coke levels, 5-7 wt.%, were analyzed on used catalysts in Runs 9 and 11-13, a higher H₂/CO feed ratio was used in Run 14 in order to minimize coking. The coke level in Run 14 was significantly lowered; however, the catalyst showed the same deactivation.

Catalyst 4956-76, the first successful micelle-derived catalyst prepared in a large quantity, was tested in Run 15 and showed significantly improved stability over previously tested catalysts, for which the micelle technique had not been successfully applied (Runs 9, 11-14) (Figure 15). The results obtained in Run 15 are described in detail in Figures 16-25.

During the run, the catalyst temperature increase over the inlet was initially 22°C and then decreased to ~2°C (Figure 16). The total weight recovery was 84.9%. The argon recovery was 87.3%. The total weight recovery became 97.3% after correcting the feed rates by the ratio of recovered-to-fed argon.

The CO conversion initially showed a rapid decrease from 65% to 35% and then leveled off around 16-18% after 100 hours on stream. Most of the initial drop in CO conversion was due to the rapid loss of water gas shift activity of the catalyst, which was nil after about 6 hours. The H₂ conversion was about twice the CO conversion, as would be expected in the absence of water gas shift activity (Figures 17-20). Analysis of all hydrocarbons made during the run indicated that Anderson-Schulz-Flory distribution, with a chain growth probability of about 0.96, was obeyed (Figure 22).

In order to gain further insight into the product selectivities obtained Run 15, the concentration of hydrocarbons in the effluent gas was plotted, in Figure 21, as a function of time on stream. The results indicate a gradual decline in the concentration of C₁-C₅ hydrocarbons, consistent with the gradual decline in the conversion level. It was surprising, however, to find out that no methane was detected in the effluent gas after 70 hours on stream.

Figure 23 is the Anderson-Schulz-Flory distribution for hydrocarbons + oxygenates made during Run 15. Since oxygenates comprise ~0.5 wt.% of the products (excluding H₂O and CO₂), they do not influence the product distribution significantly.

Gel permeation chromatography was also used in this run to characterize the Fischer-Tropsch wax which contained C₁₀-C₁₈₀ hydrocarbons. Results summarized in Figure 24 indicate that over the range C₁₀-C₆₀ gel permeation chromatography results are in close agreement to results obtained with GC.

Catalyst 4956-76 was reexamined with STEM after 248 hours of testing in Run 15. STEM examination did not show any noticeable change in the ruthenium crystallite size, which remained 40-60 Å.

Conventional Catalyst

A "conventional" ruthenium catalyst (4956-86) prepared by using an aqueous impregnation technique had very well dispersed ruthenium according to the STEM examination. Catalyst 4956-86 was tested in Run 16 and showed very low activity (Figures 26-29). The space velocity in Run 16 was therefore reduced after 30 hours. The effluent gas composition in Run 16 is shown as a function of time on stream in Figure 30. The results indicate that methane was made with significantly higher yields relative to C₂-C₅ hydrocarbons. The amount of methane in the effluent gas analyzed in Run 16 with the "conventional" catalyst was also significantly higher (2-3 times) than methane obtained in Run 15 with the micelle-derived catalyst although the conversion in Run 16 was lower. At the time of the writing of this report, the analyses of liquid and wax products were in progress, and, therefore, the total product distributions will be reported in the future.

Catalyst 4956-86 was later examined with STEM after 140 hours of testing and showed that significant agglomeration of ruthenium to 200-1000 Å particles occurred.

Causes of the poor performance of the "conventional" catalyst are under investigation.

DISCUSSION AND FUTURE PLAN

Analysis of Run 15, Plant 700

Catalyst Selectivity

A hydrocarbon cut-off number was not observed in the C_1 - C_{180} carbon number range with 40-60 Å ruthenium particles. Catalysts with smaller size ruthenium crystallites will be evaluated in the future to determine if a cut-off number will occur.

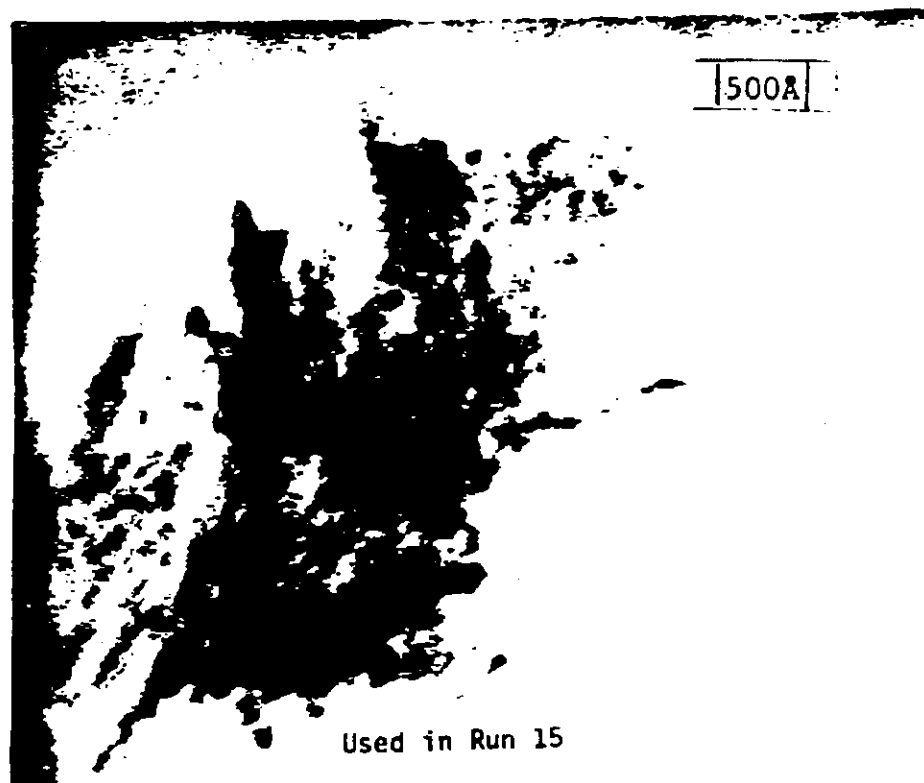
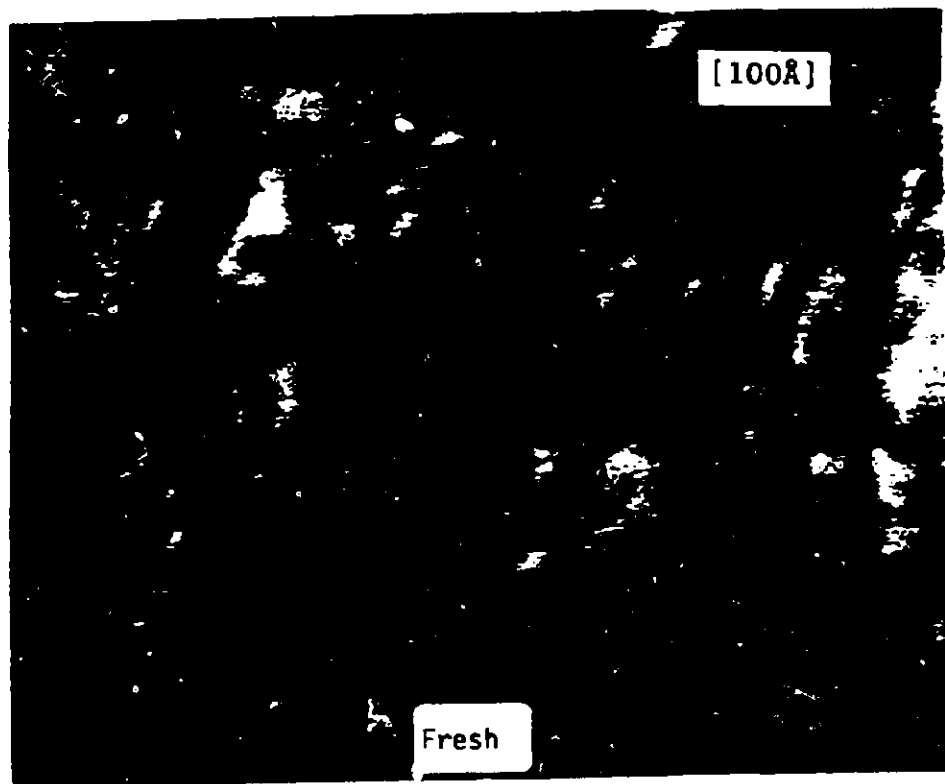
Catalyst Stability

Although micelle-derived 4956-76 catalyst, with 40-60 Å ruthenium crystallites, showed loss of conversion during the run, it should be remembered that the test conditions under which it was tested were very severe. Namely, a low H_2/CO feed ratio of 0.9 was artificially chosen despite the absence of significant water gas shift activity in order to obtain a high chain growth probability. Consequently, the H_2/CO ratio in the catalyst outlet varied from 0.3 at the beginning of the run to 0.8 at the end. The initially very low H_2/CO ratio may explain the initial rapid loss of conversion that was observed.

Figure 1

List of Alumina-Supported Ruthenium Catalysts

<u>Catalyst Number</u>	<u>% Ru (by Wt.)</u>	<u>Preparation Technique</u>	<u>Size of Preparation(g)</u>	<u>STEM Examination</u>
4956-12	0.7	Micelle	1	Broad size distribution
4956-19	1.7	Micelle	2	40-60Å ruthenium crystallites
4956-21	1.1	Micelle	2	40-60Å ruthenium crystallites
4956-22	1.1	Micelle	30	Broad size distribution
4956-23	1.1	Micelle	30	Broad size distribution (most 40-250Å, many >1000Å particles)
4956-27	1.1	Micelle	30	Broad size distribution (most 30-70Å, many 1000Å particles)
4956-56	1.1	Micelle	30	Broad size distribution
4956-76	0.93	Micelle	30	40-60Å ruthenium crystallites
4956-86	1.1	Conventional	30	No observed ruthenium crystallites
4956-95	0.23	Micelle	30	No observed ruthenium crystallites
4956-97	0.47	Micelle	30	70% 20-30Å ruthenium crystallites 30% 40-50Å " "



STEM Micrographs of Catalysts 4956-76

Figure 2

Figure 3
XRD Measurements on Ruthenium Metal Powder (4956-34)

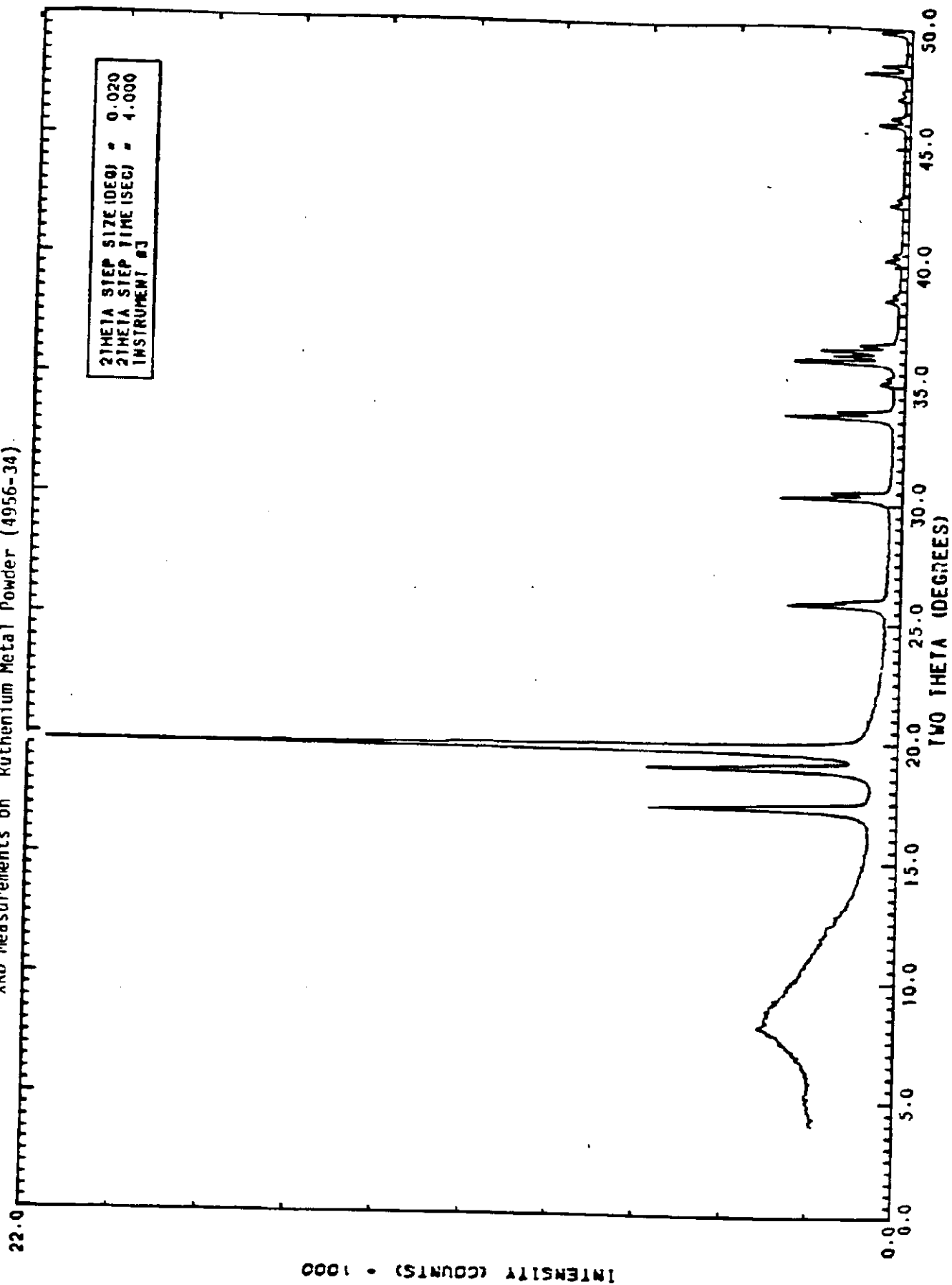


Figure 4

XRD Measurements on a Physical Mixture of Ruthenium Metal Powder with γ -Al₂O₃

(1:10, by wt.) (4956-46)

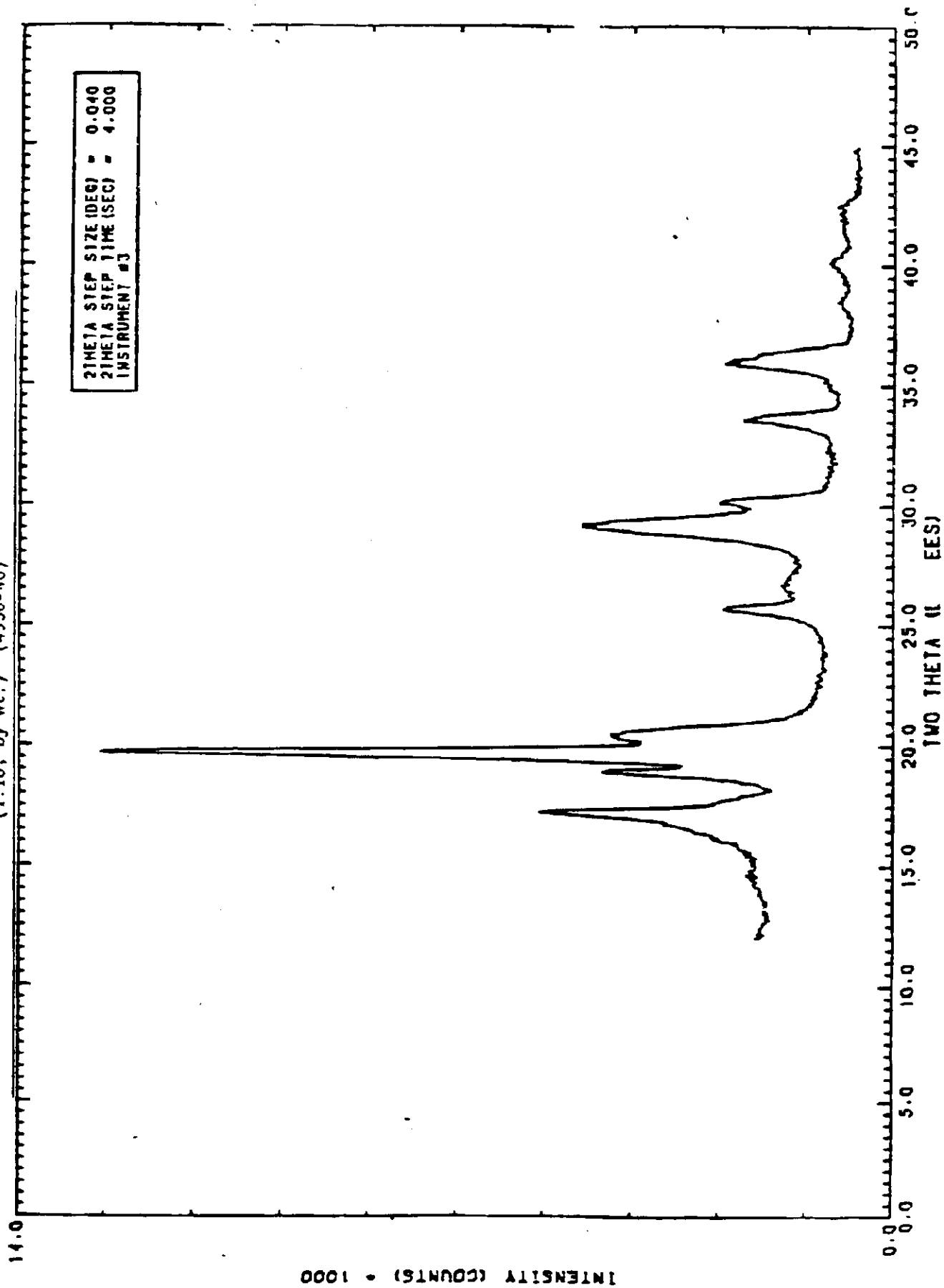


Figure 5

XRD Measurements on Catalyst 4956-21

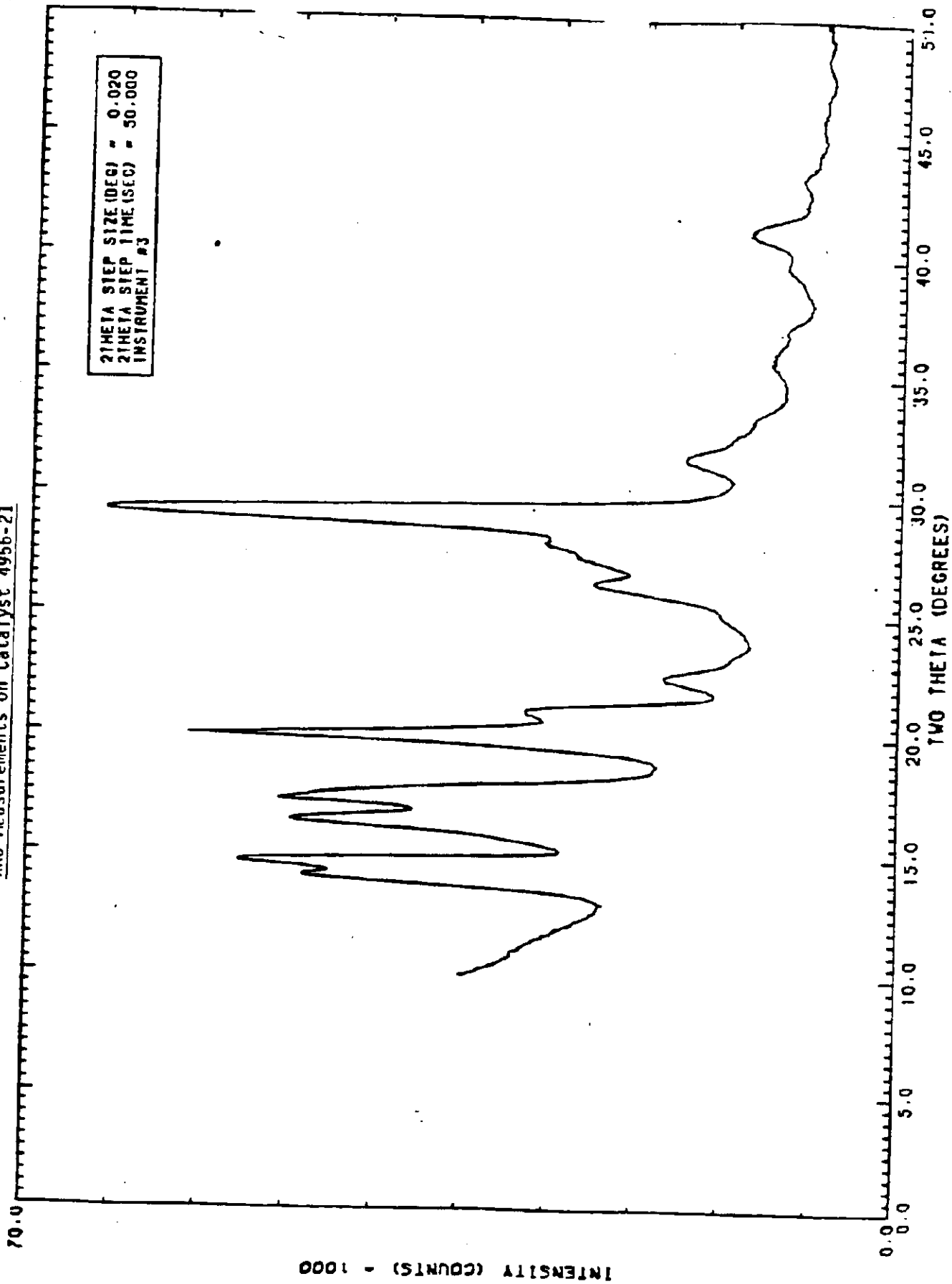


Figure 6

XRD Measurements on Catalyst 4956-19

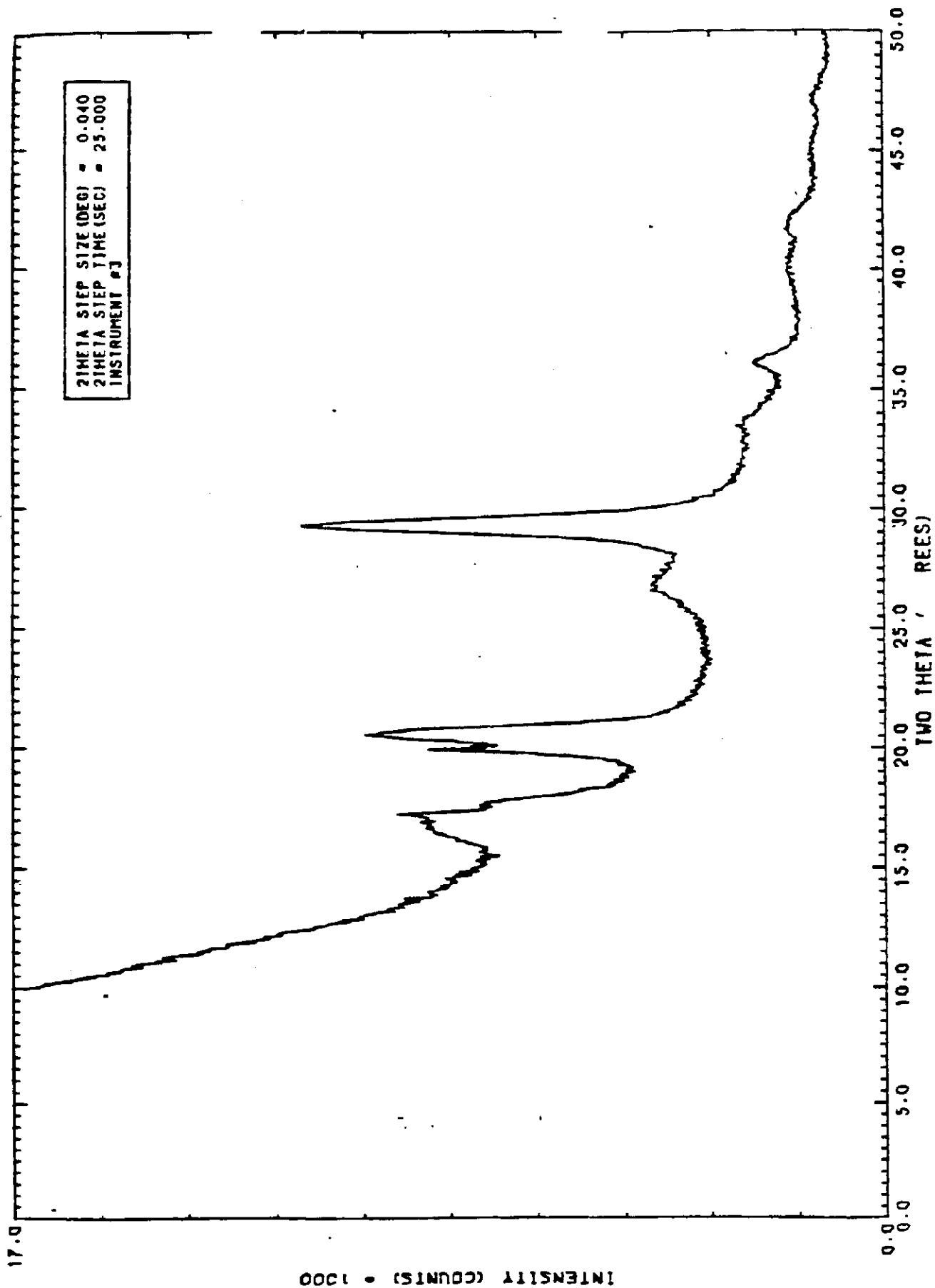


Figure 7

XRD Measurements on γ -Alumina Support

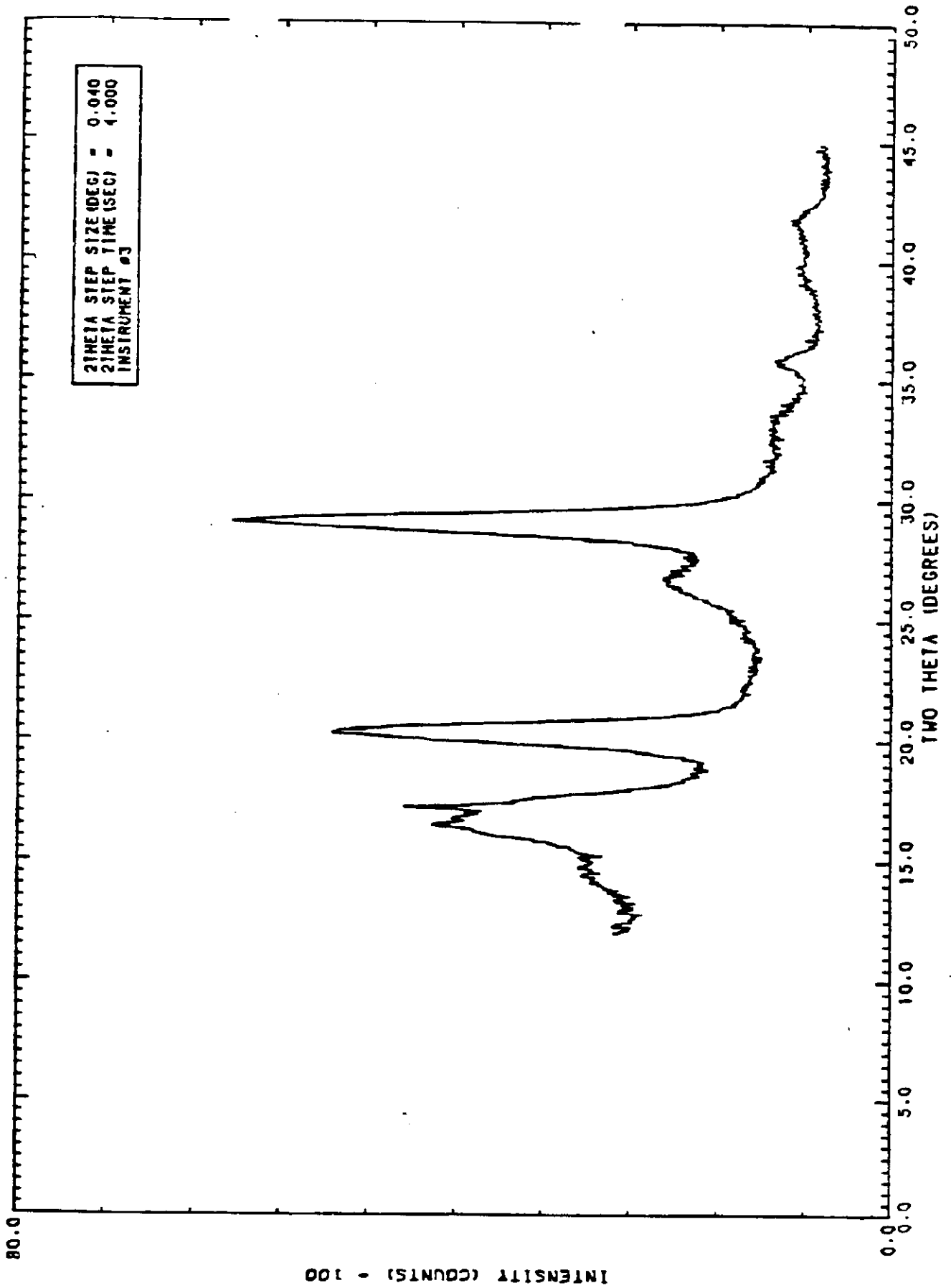


Figure 8

XRD Measurements on RuO₂ Powder

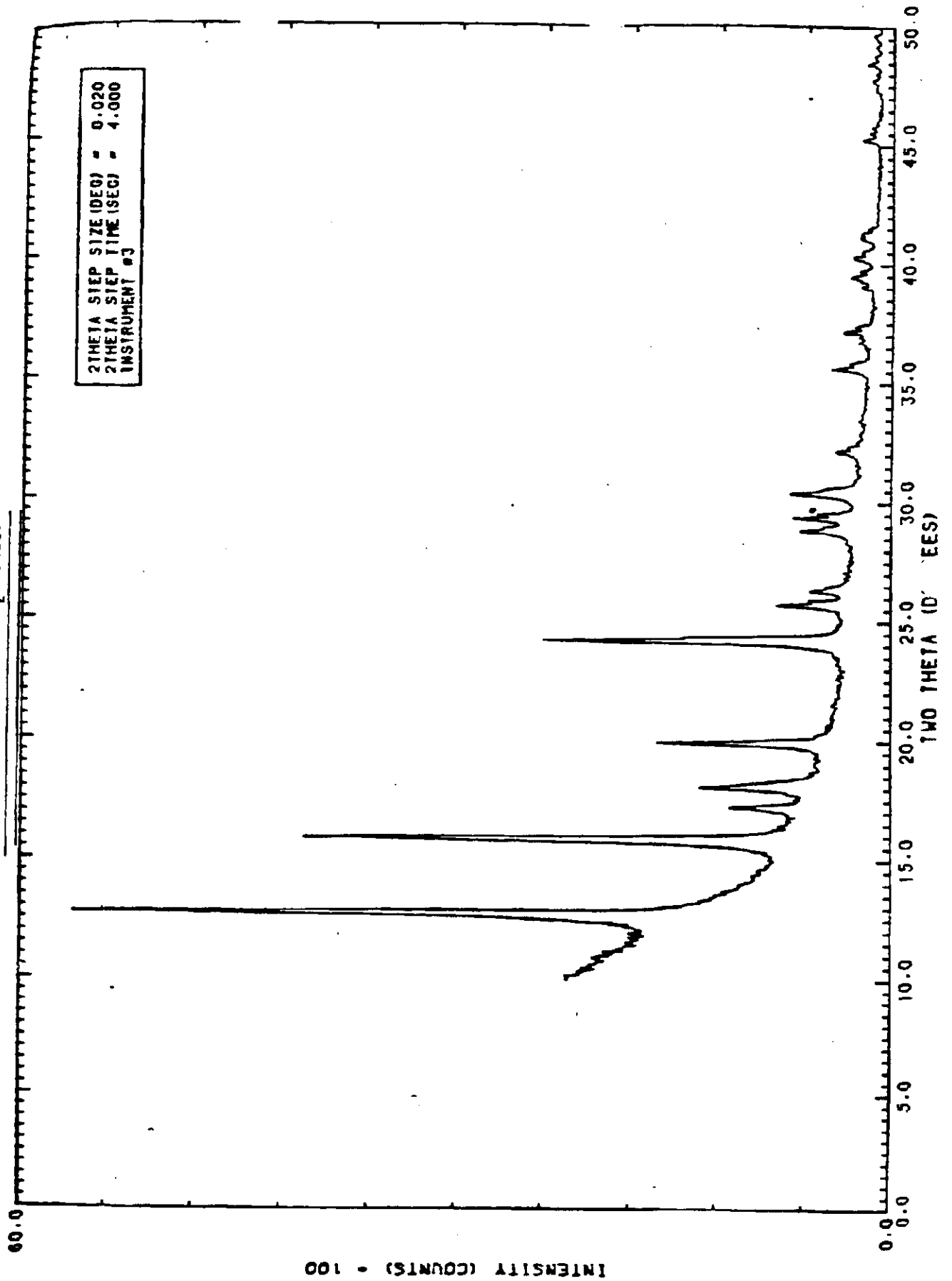


Figure 9

SAXS Plot for the Reverse Micelle Solution 4966-50

PLOT OF INTENSITY VERSUS h

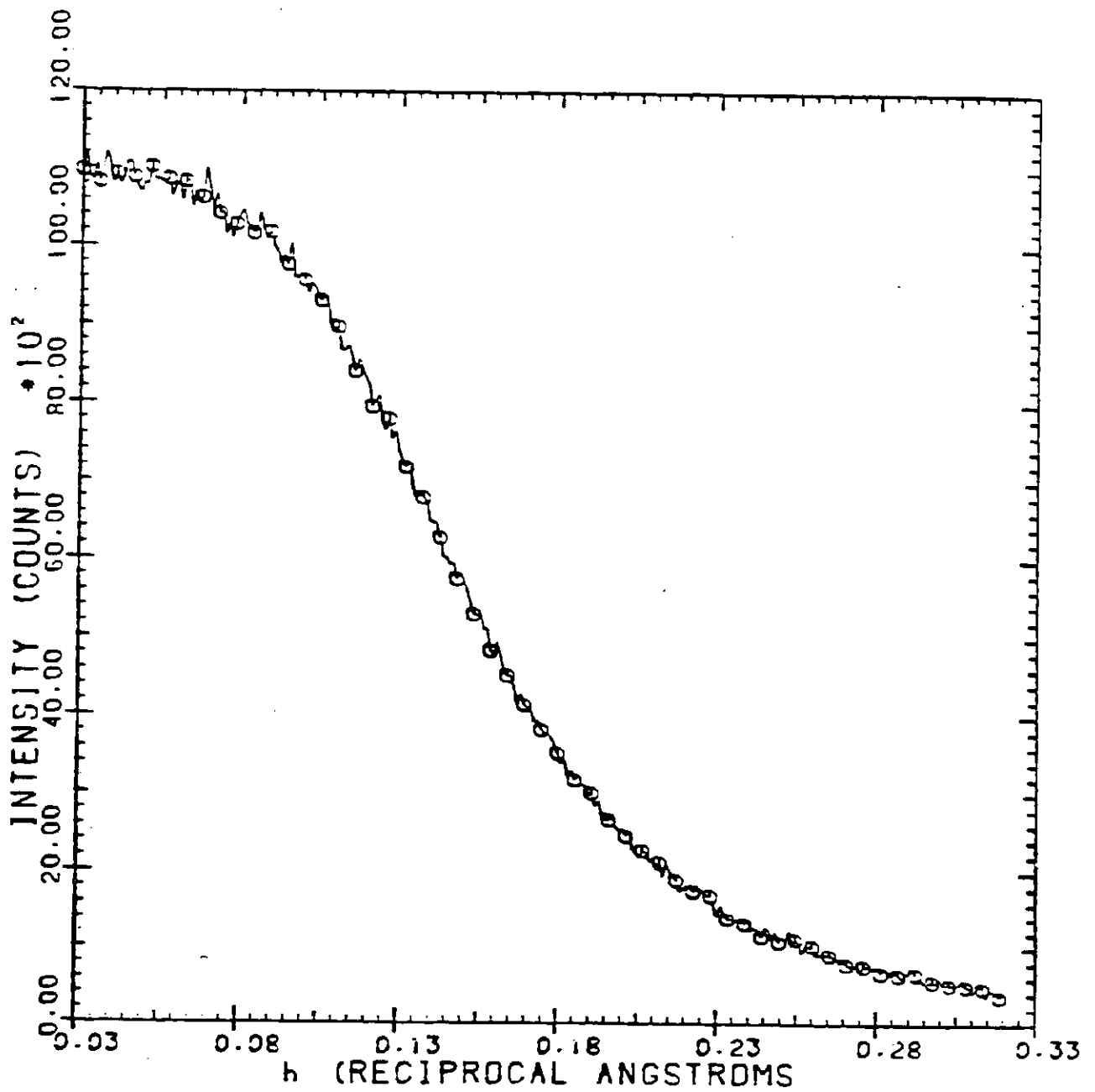


Figure 10

Guinier Plot for the Reverse Micelle Solution 4966-50

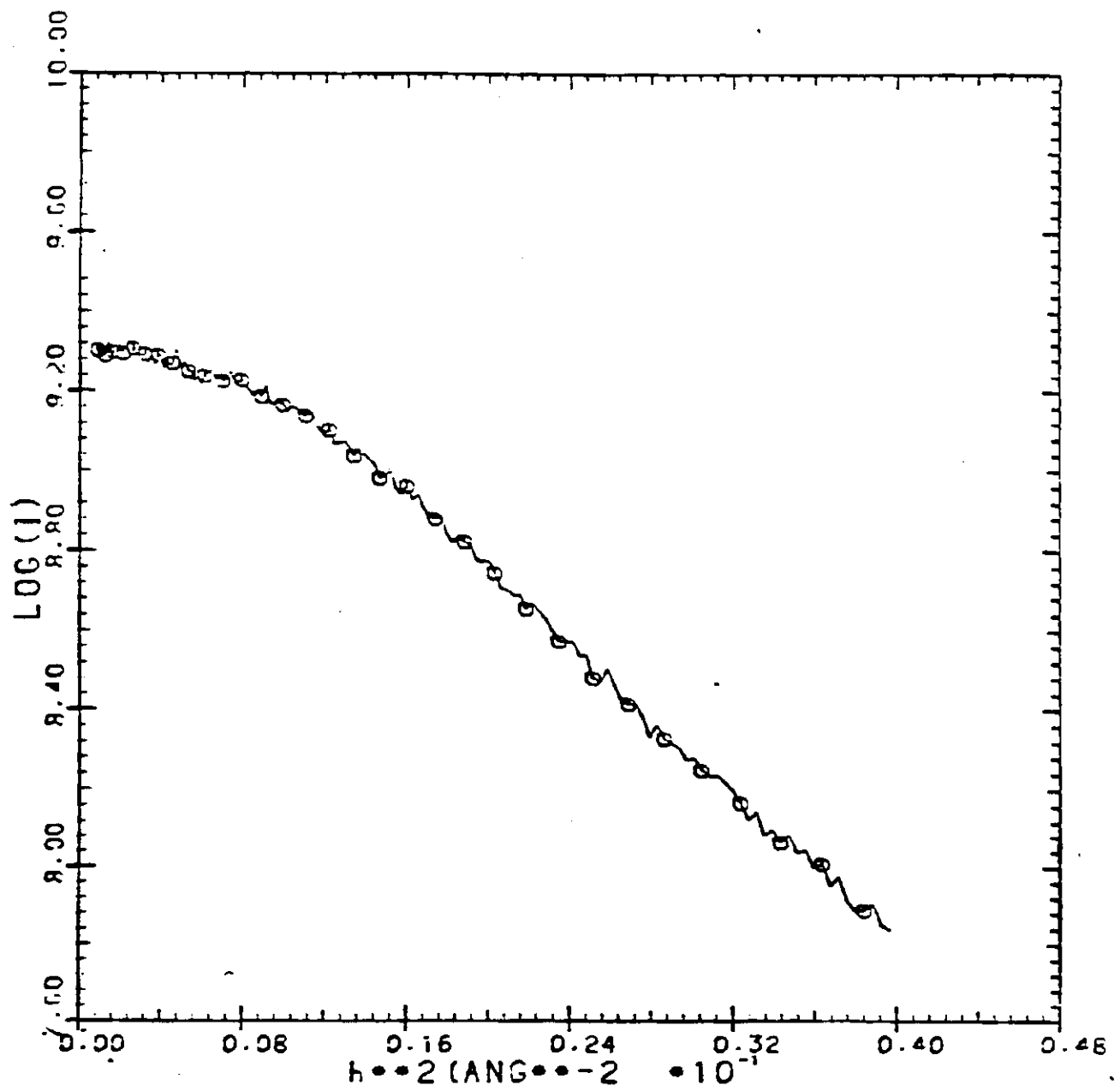


Figure 11

Summary of SAXS Results

<u>Sample</u>	<u>$R_G, \text{\AA}$</u> ^a	<u>Vol. Averaged</u> ^b <u>Diameter, \AA</u>
4956-24-1	29	75-90
4966-50	12	31
4966-52	15	39

a) Radius of gyration

b) Volume weighted diameter, equal to $2R_G \sqrt{5/3}$

Figure 12

SAXS Plot for the Reverse Micelle Solution 4966-52

PLOT OF INTENSITY VERSUS h

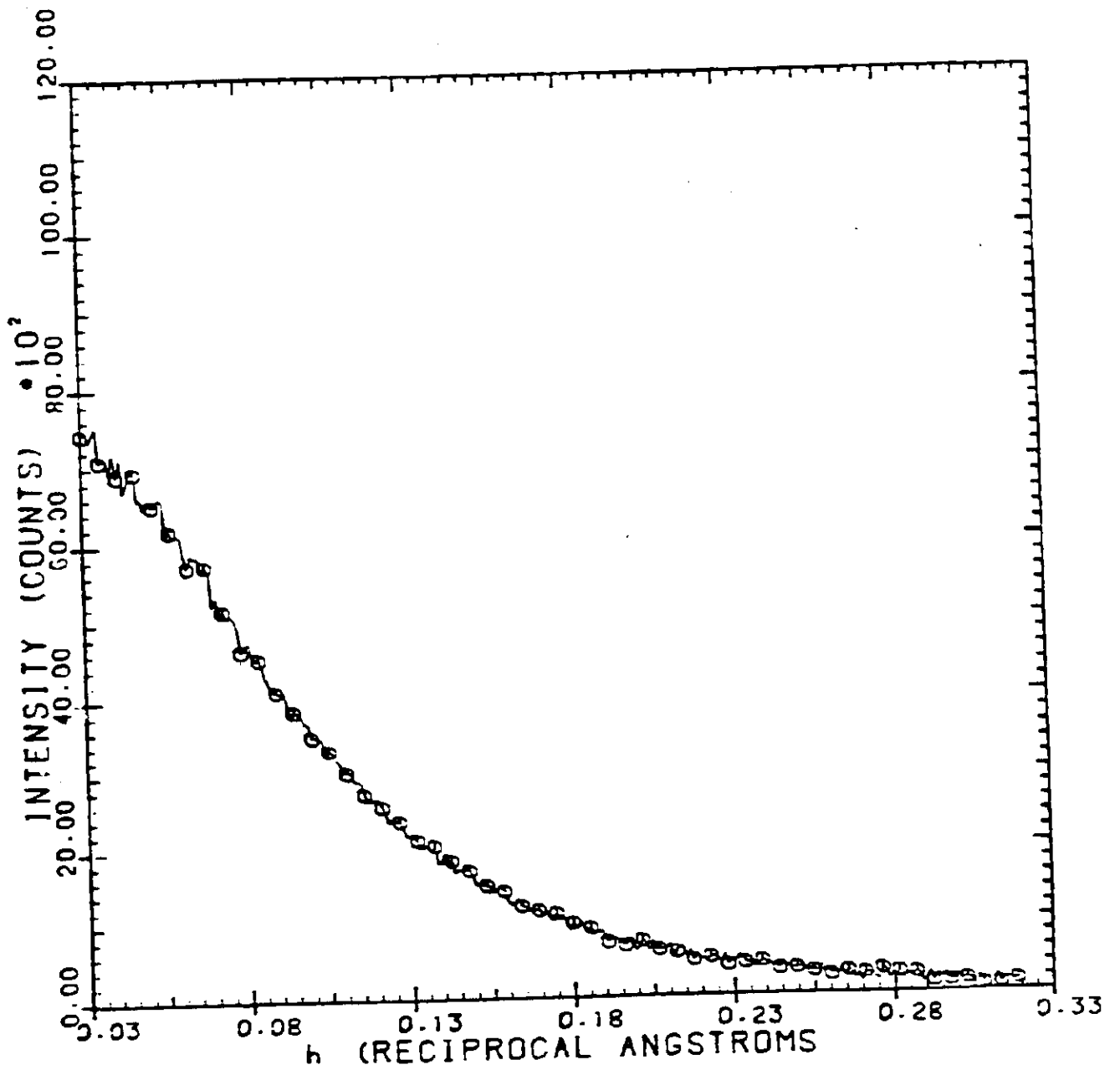


Figure 13

Guinier Plot for the Reverse Micelle Solution 4966-52

GUINIER PLOT

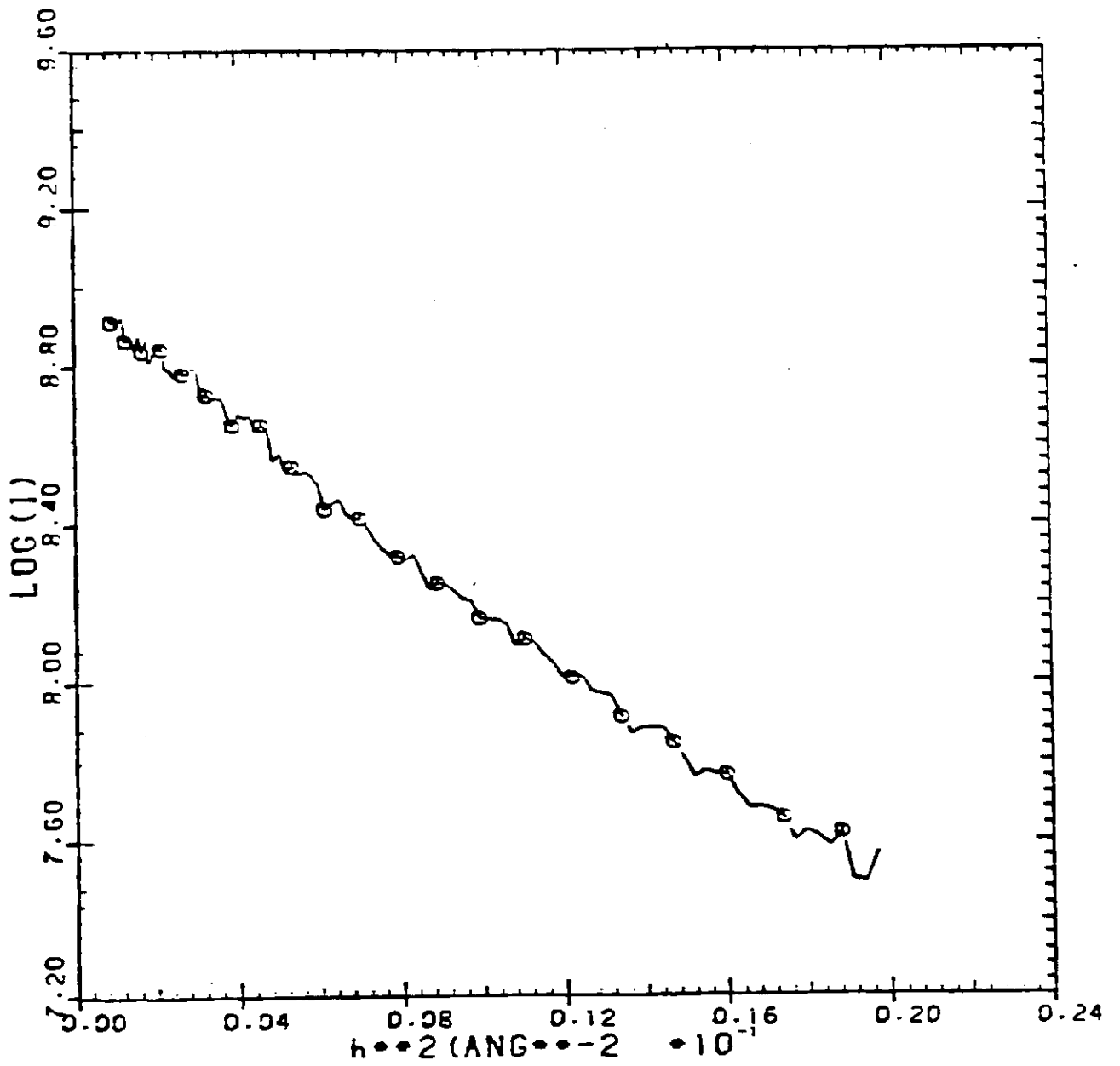


Figure 14

Run Summary Data for Plant 700

Run	Catalyst		Reactor	Bed Length (in.)	Inlet Temp. (°C)	Max. Catalyst Temp. (°C) (During hours)	Outlet Press. (psig)	H ₂ /CO (molar)	Feed Rate (SDH)	GHSV (hr ⁻¹)	Hours	Outlet H ₂ /CO Ratio (Molar)		Olefin/Paraffin Ratio (Molar)		Hydrocarbons Mole (g)	Oxygenates Mole (g)		
	Wt. (g)	Vol. (cc)										%	Wt.	C ₂	C ₃			C ₄	
9	20.00	75.0	1.19	4956-21	stainless steel	17 1/2	207	218 (2)	1500	0.88	0.20	75	0-81	0.8	0.5	0.4	0.4	13.4	1.0
10	6.42	3.0	C-73-101	4956-34	stainless steel	11 3/4	208	210 (201-212)	500	0.88	0.12	1140	0-252	0.8	2.4	2.2	1.7	47.4	3.5
11	22.0	80.3	1.1	4956-27	stainless steel	16	208	218 (4)	500	0.5	0.21	73	0-56	0.5	0.9	0.7			
12	21.5	79.4	1.3	4956-30	stainless steel	18 1/4	208	217 (1)	500	0.9	0.20	71	0-142	0.9	1.8	1.2	0.43		
13	10.93	40.4	1.1	4956-22	glass-lined	4	208	214 (2)	500	1.3	0.12	84	0-56	1.2	0.9	0.7			
14	13.8	51.0	1.1	4956-56	glass-lined	5	204+ 230+ 266	212 (8)	500	4.0	0.14	78	0-94	4.0	0.6	0.4			
15	15.71	58.0	0.926	4956-76	glass-lined	5 1/2	208	229 (1 1/2)	500	0.91	0.134	66	0-248	0.340, 0.8	2.6	1.3	1.1	41.5	0.25
16	15.80	58.4	1.09	4956-86	glass-lined	5 1/2	208	210	500	0.91	0.134	64	0-152	0.9					

Figure 14 (Cont.)

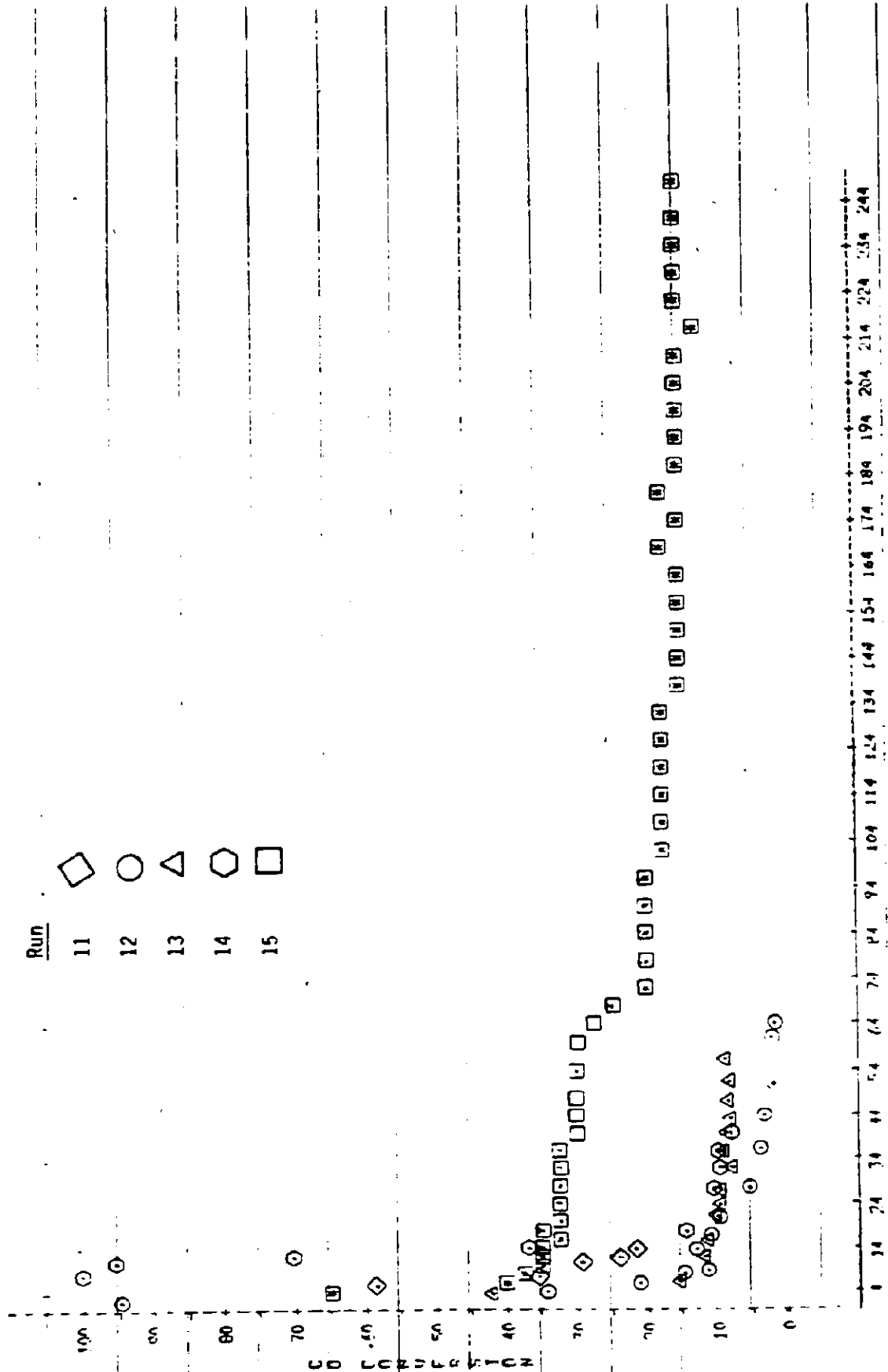
Run Summary Data for Plant 700

Run	H ₂ O Made (g)	Max from Used Catalyst (g)	Carbon on Used Catalyst (g)	% Max (by wt.)	% C (by wt.)	Iron Carbonyl Scrubber	Fe on Used Cat. + in Liq. Prod. (g)	% Fe on Used Cat. (by wt.)	Ru in Liquid Product (g)	Argon Recovered (%)	Total Weight Recovered (%)	Corrected Material Balance (%)
9	13.9	2.6	4.9	20.3	4.9	No	0.41	0.35	0.0068	95.0	94.2	99.2
10	25.7	4.6	2.1	9.2	2.1	No				93.2	92.7	99.5
11	6.6-7.6	1.62	1.62	25.1	6.84	Yes (208°C)	0.16	0.55	0.0018			
12	3.4	3.4	1.34	15.9	5.85	Yes (260°C)	0.04	0.18	0.0083			
13	8.0	8.0	0.72	8.98	6.22	Yes (260°C)	0.005	0.026	0.0004			
14	0.54	0.54	0.23	3.96	1.62	Yes (260°C)	0.00056 (+ cat.)		0.00015			
15	58.7	21.4	2.84	55.9	15.3	Yes (208°C)	0.0092 (+ cat.)		0.0022	87.3	84.9	97.3
16						Yes (208°C)						

Figure 15

Comparison of CO Conversions for Different Runs with Micelle-Derived Catalysts

(Plant 700)



HOURS ON STREAM AT END OF PERIOD

FISCHER - TROPSCH SYNTHESIS

(Plant 700)

Figure 16

Run 15

Catalyst 4956-76

Pressure 500

H₂/CO (feed) 0.92

TEMPERATURE PROFILE

HOURS ON BLOCK TEMP, °C

STREAM

○	0	208
□	1.5	208
△	4	207
◇	20	207
▽	66	207

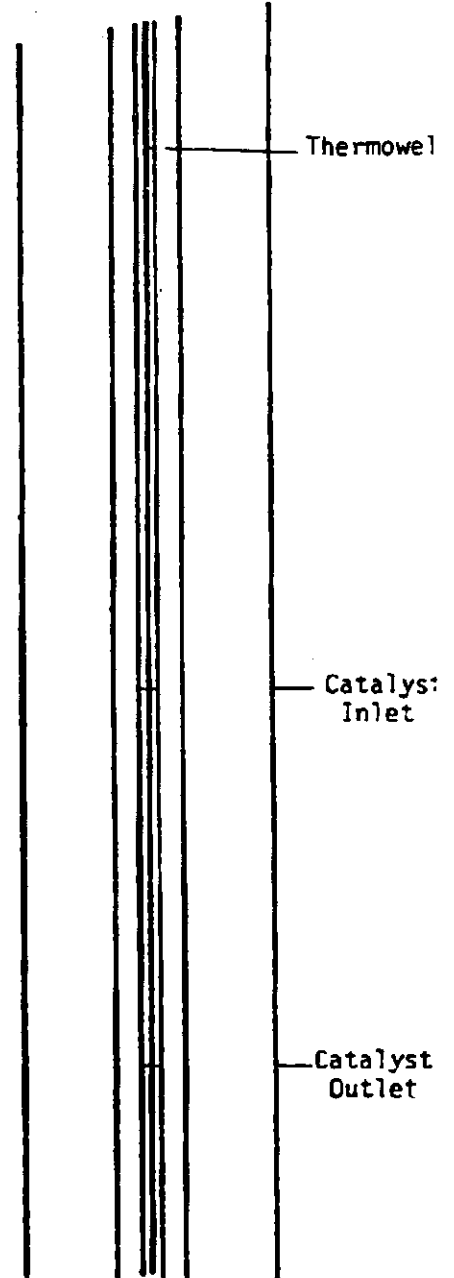
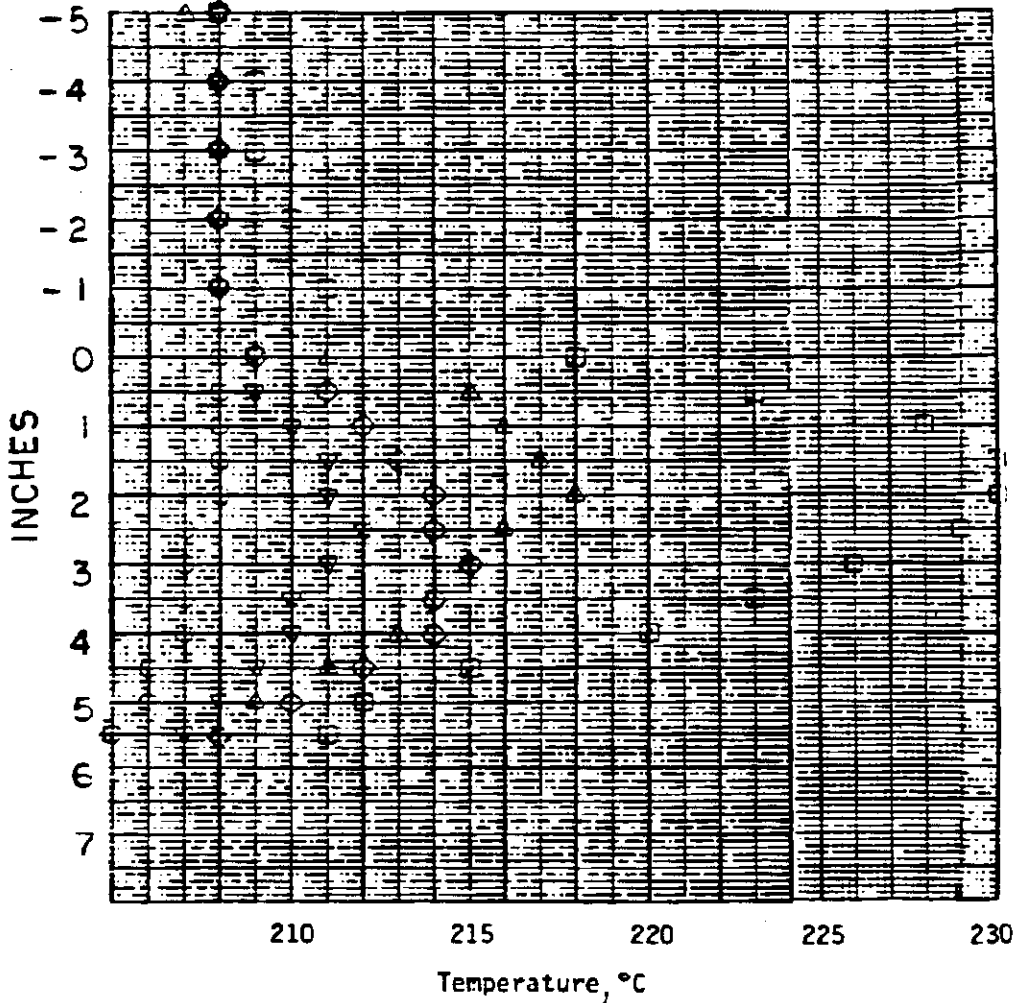
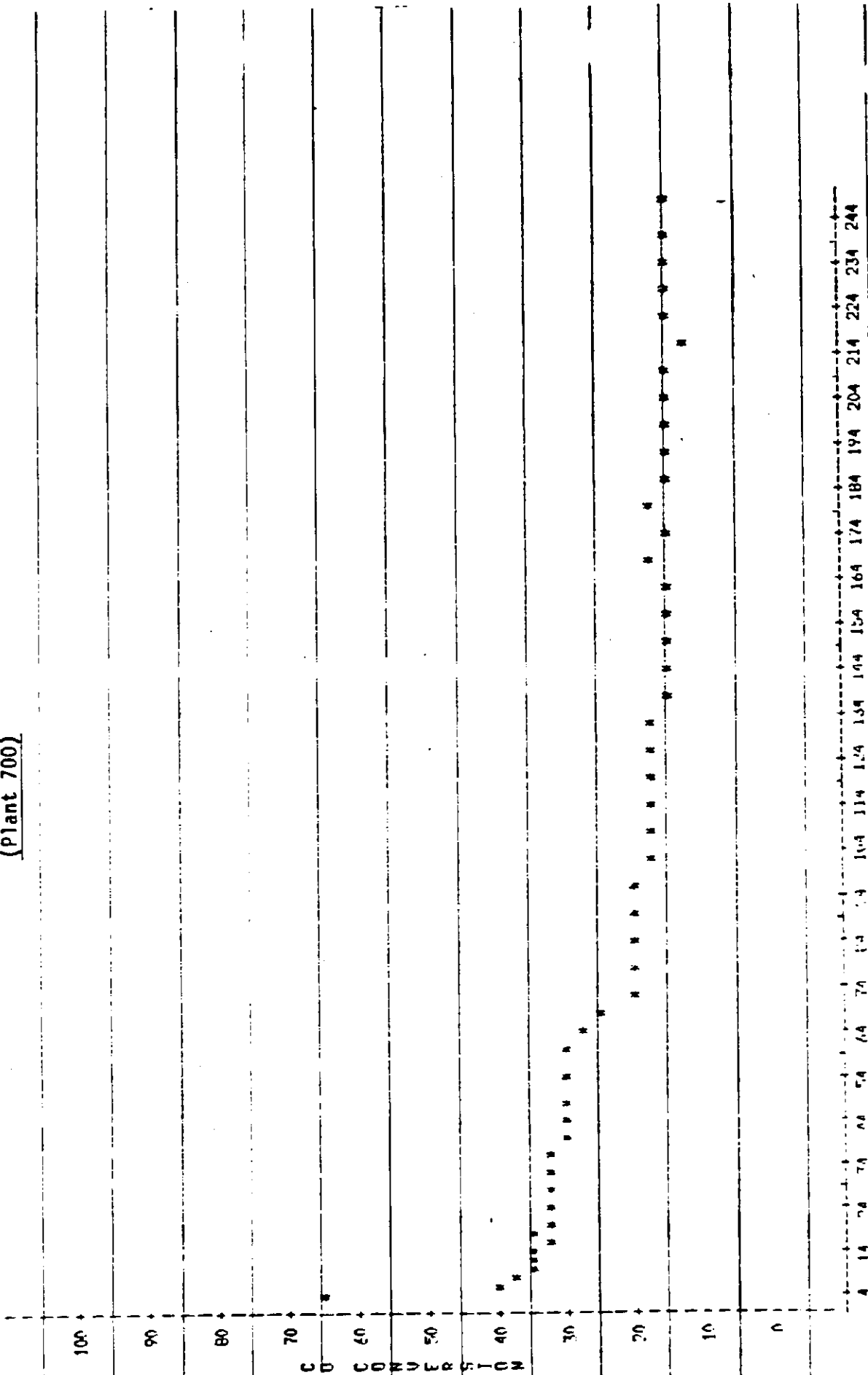


Figure 17

CO Conversion vs. Hours on Stream in Run 15

(Plant 700)

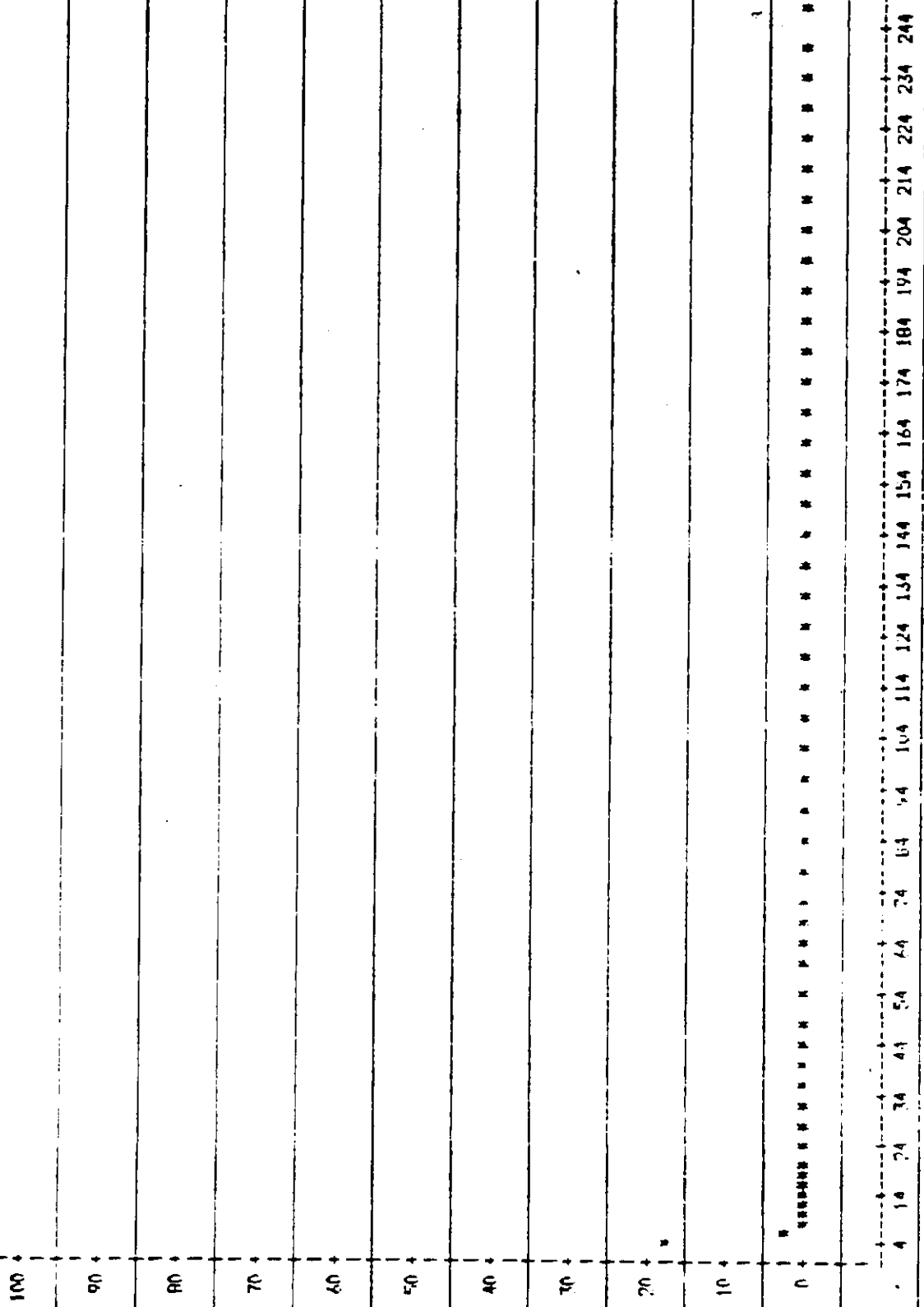


HOURS ON STREAM AT END ERIDU

Figure 18

CO-Conversion to CO₂ vs. Hours on Stream 1n-Run 15

(Plant 700)

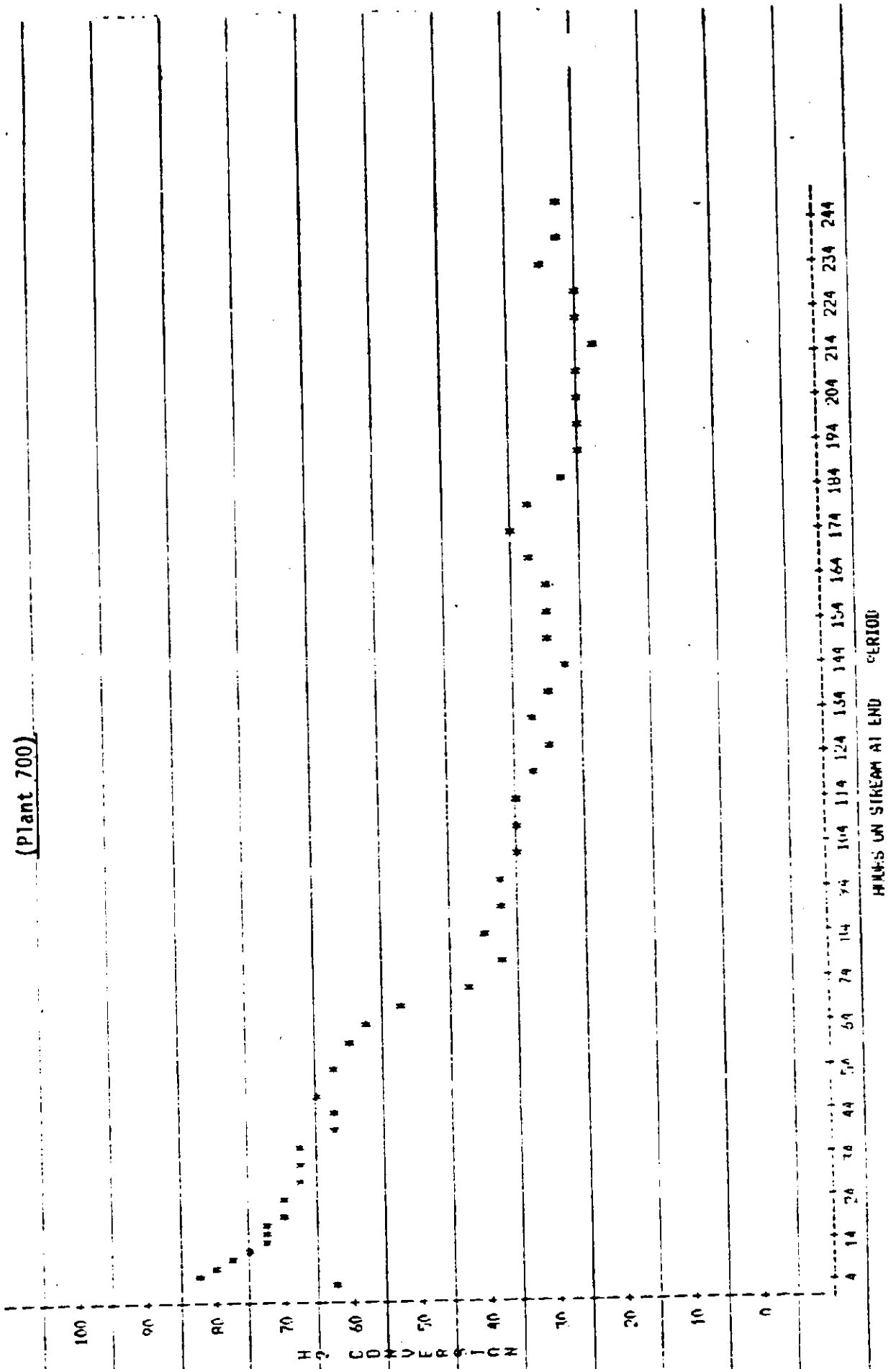


HOURS LW STREAM AT END OF PERIOD

Figure 19

H₂ Conversion vs. Hours on Stream in Run 15

(Plant 700)



HOURS ON STREAM AT END PERIOD

Figure 20

CO + H₂ Conversion vs. Hours on Stream in Run 15

(Plant 700)

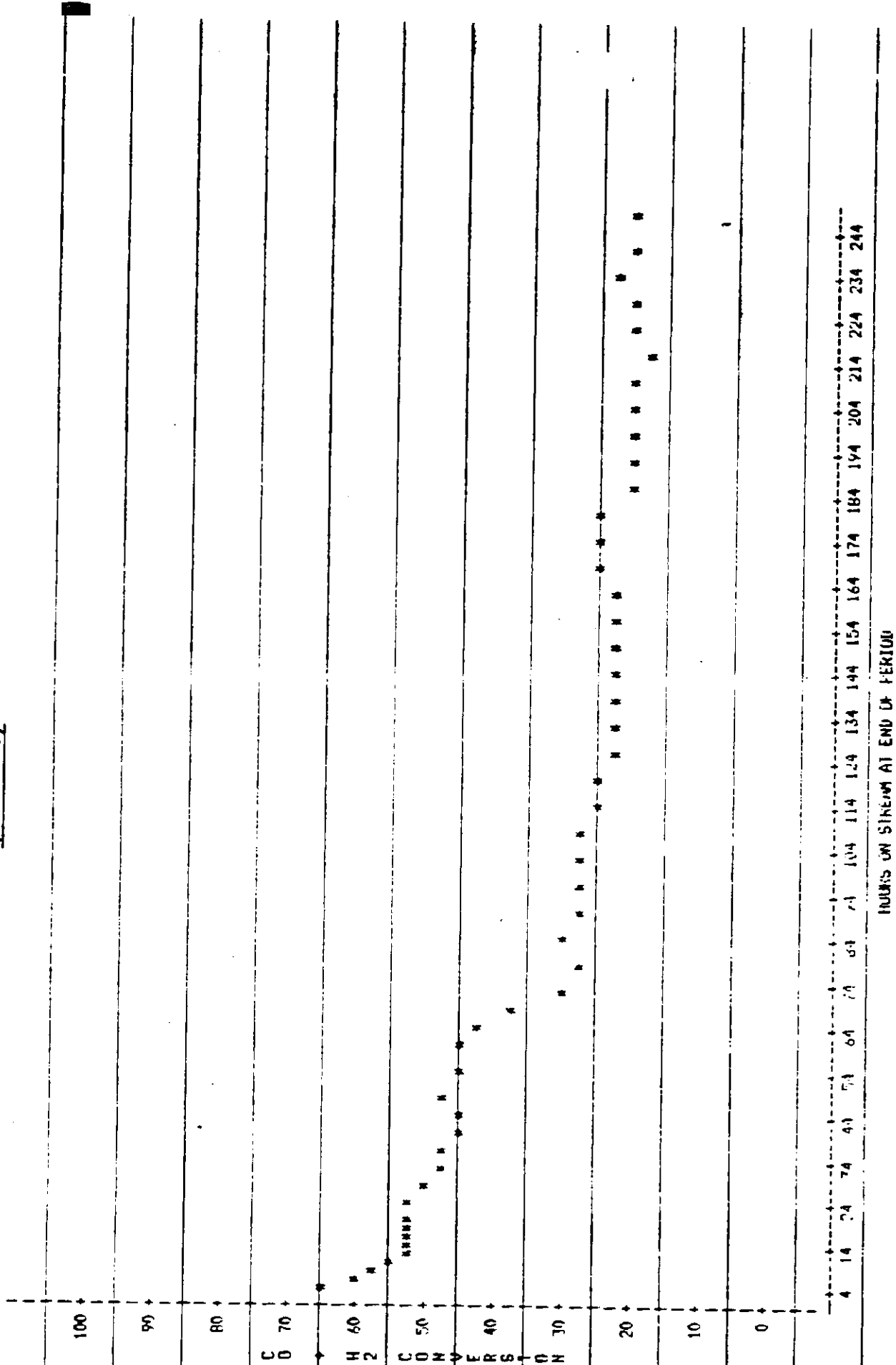


Figure 22
Anderson-Schulz-Flory Distribution in Run 15 (Plant 700)
(Hydrocarbons Only)

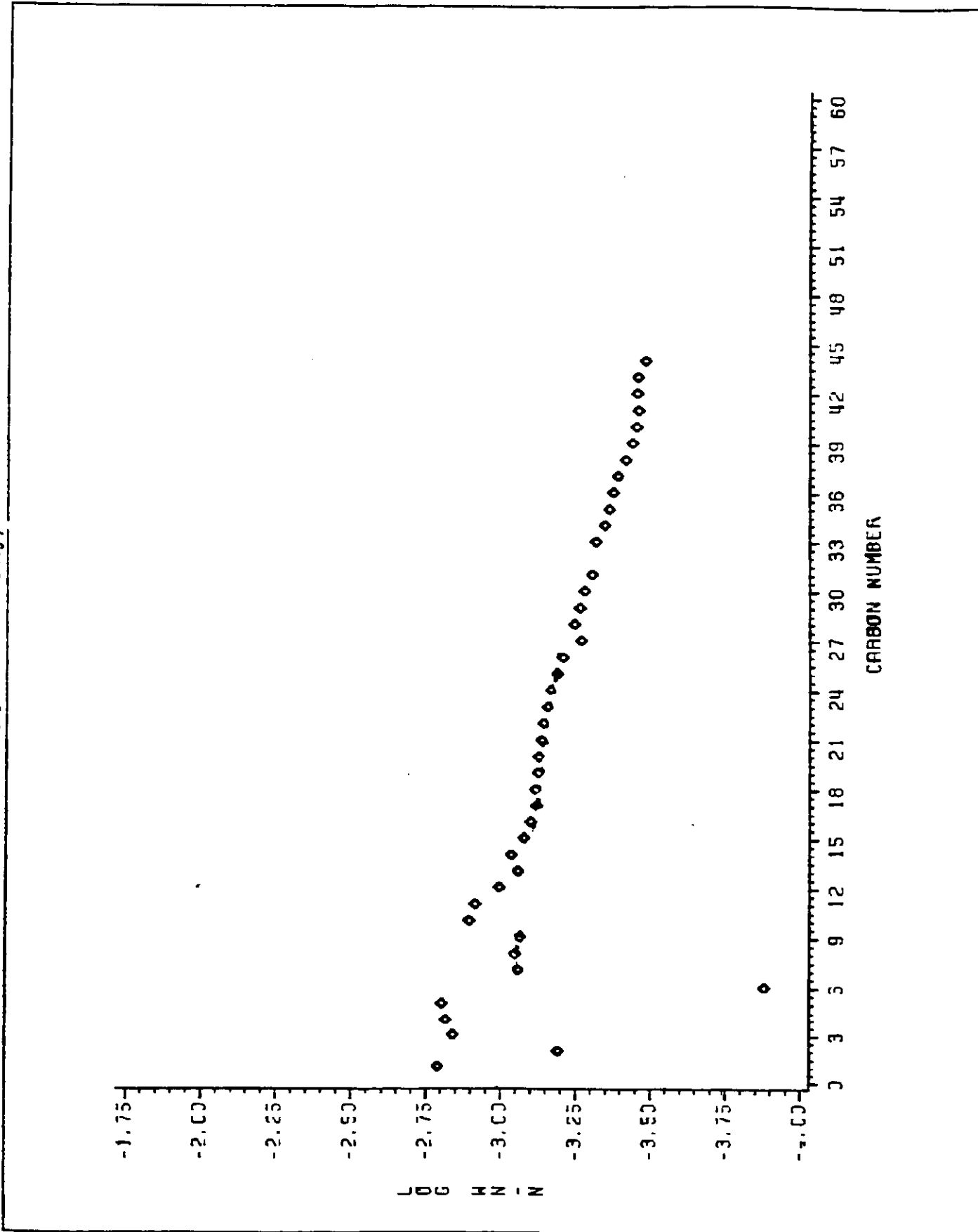


Figure 23

ANDERSON - SCHULZ - FLORY DISTRIBUTION
(Hydrocarbons + Oxygenates)

Catalyst	4956-76	Run	15	Hours	0-248	Plant	700
T(°C)	208	P(psig)	500	H ₂ /CO (Feed)	0.9		

W_n: Weight fraction of n'th hydrocarbon: n: carbon number

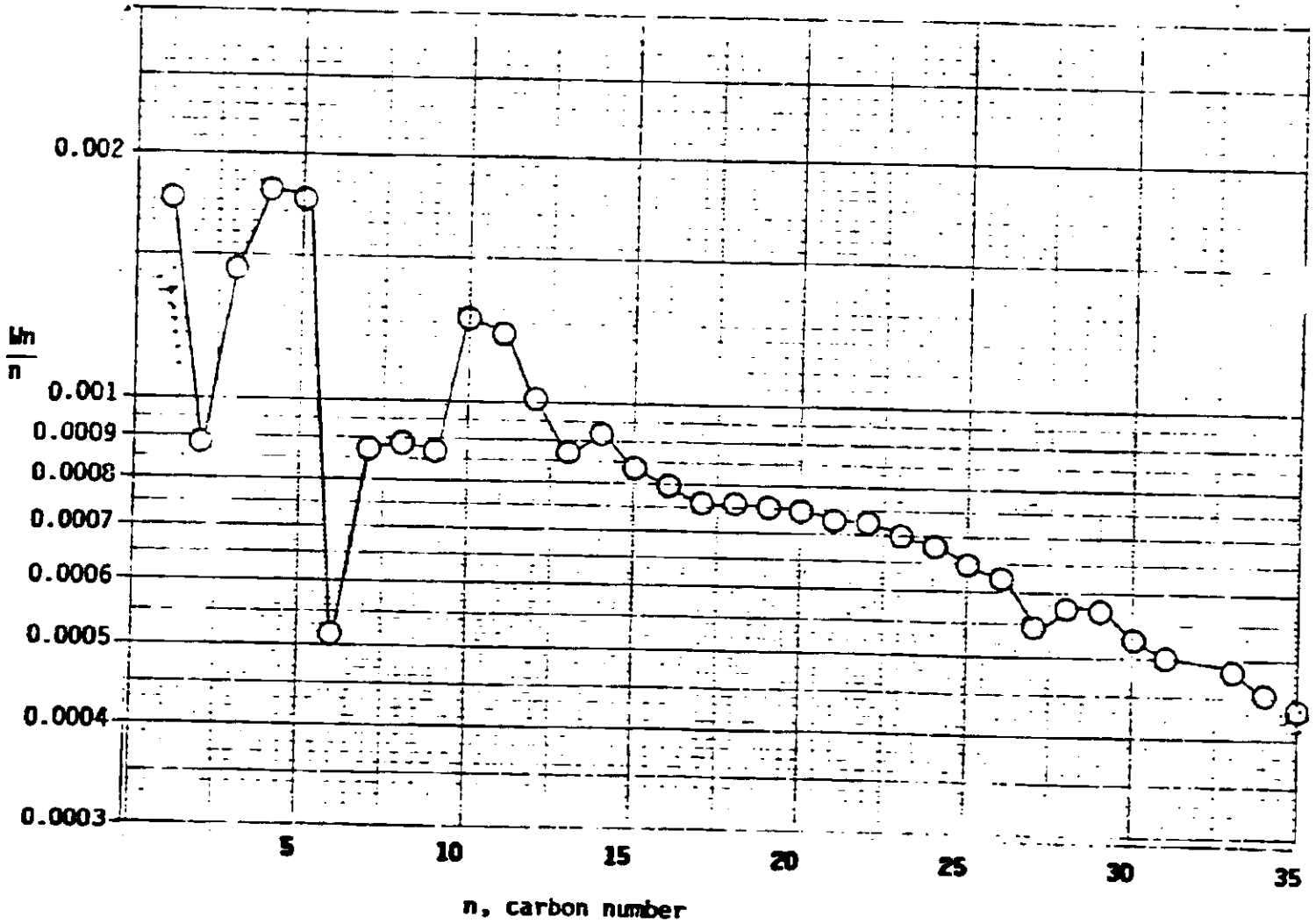


Figure 24

ANDERSON - SCHULZ - FLORY DISTRIBUTION

Catalyst 4956-76, Run 15, Plant 700, 0-248 Hours
208°C, 500 psig, 0.9 H₂/CO Feed Ratio (Molar)

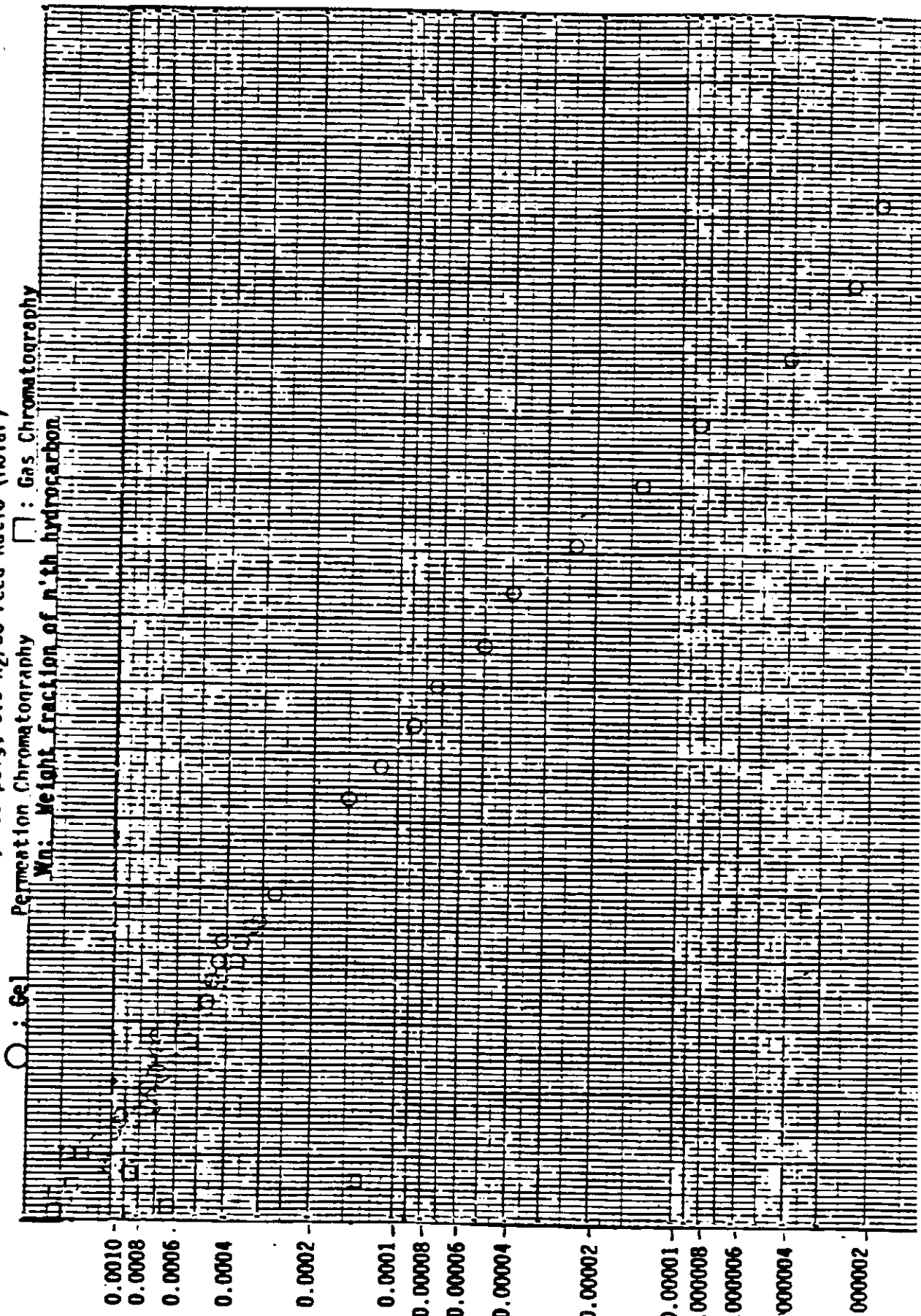


Figure 25

Product Distributions in Run 15 (Plant 700)

P1101 PLANT NO. 700 RUN NO. 15 TEST NO. 1 RUN SUMMARY REPORT
 ROCK NO. CATALYST NO. 4200-76 BEGINNING DATE 14JUN1985 END OF TEST DATE 24JUN1985

TOTAL PRODUCT DISTRIBUTION (W/O AROUGH)

OXYGENATES DISTRIBUTION

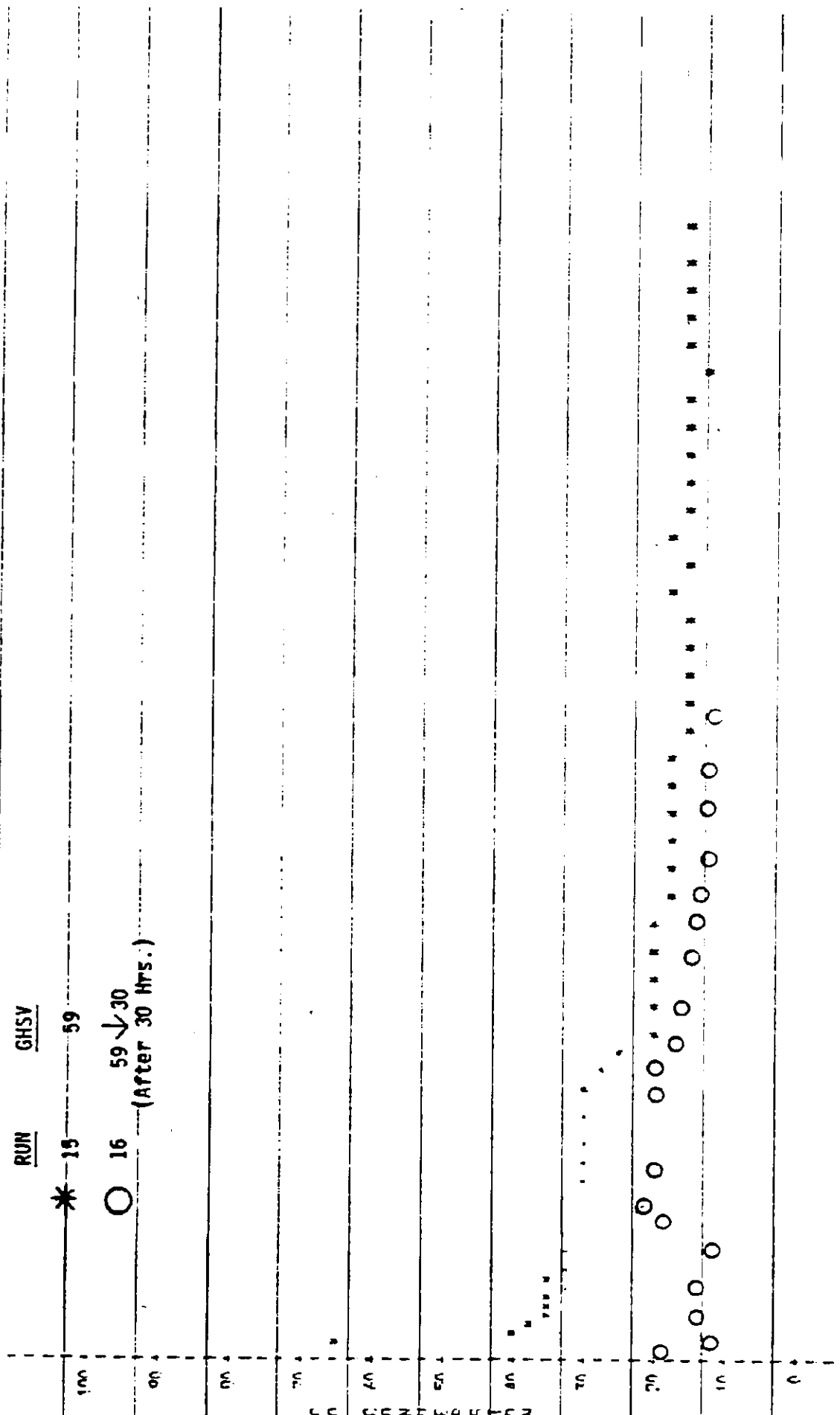
COMPONENT	WEIGHT %	COMPONENT	WEIGHT %
HC	3.64	C1	3.00
CO	74.82	C2	8.30
CO2	0.90	C3	0.00
HCN	10.96	C4	18.72
HYDROCARBON	7.05	C5	31.52
OXYGENATES	0.47	C6	38.44

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	COMPONENT	WEIGHT %
C24	0.16	C25	1.62
C2-C4	1.17	C26	1.62
C5-C11	5.57	C27	1.46
C12-C18	8.82	C28	1.60
C19-C25	10.90	C29	1.59
C26+	75.37	C30	1.58
		C31	1.55

COMPONENT	WEIGHT %	COMPONENT	WEIGHT %
C24	0.16	C33	1.60
C2P	0.04	C34	1.54
C2o	0.09	C35	1.53
C3	0.00	C36	1.53
C3P	0.19	C37	1.51
C3o	0.24	C38	1.46
C4	0.00	C39	1.42
C4P	0.29	C40	1.42
C4o	0.32	C41	1.43
C5	0.78	C42	1.48
C6	0.08	C43	1.51
C7	0.61	C44	1.45
C8	0.71	C45+	46.08
C9	0.70	C46	.
C10	1.27	C47	.
C11	1.34	C48	.
C12	1.21	C49	.
C13	1.14	C50	.
C14	1.29	C51	.
C15	1.25	C52	.
C16	1.27	C53	.
C17	1.29	C54	.
C18	1.37	C55	.
C19	1.43	C56	.
C20	1.49	C57	.
C21	1.53	C58	.
	1.59	C59	.
	1.61	C60	.
L24	1.63		

CO Conversion vs. Hours on Stream in Runs 15 and 16 (Plant 700)



0 10 20 30 40 50 60 70 80 90 100

HOURS ON STREAM AT 100% PERIOD

Figure 27

CO Conversion to CO₂ vs. Hours on Stream in Runs 15 and 16

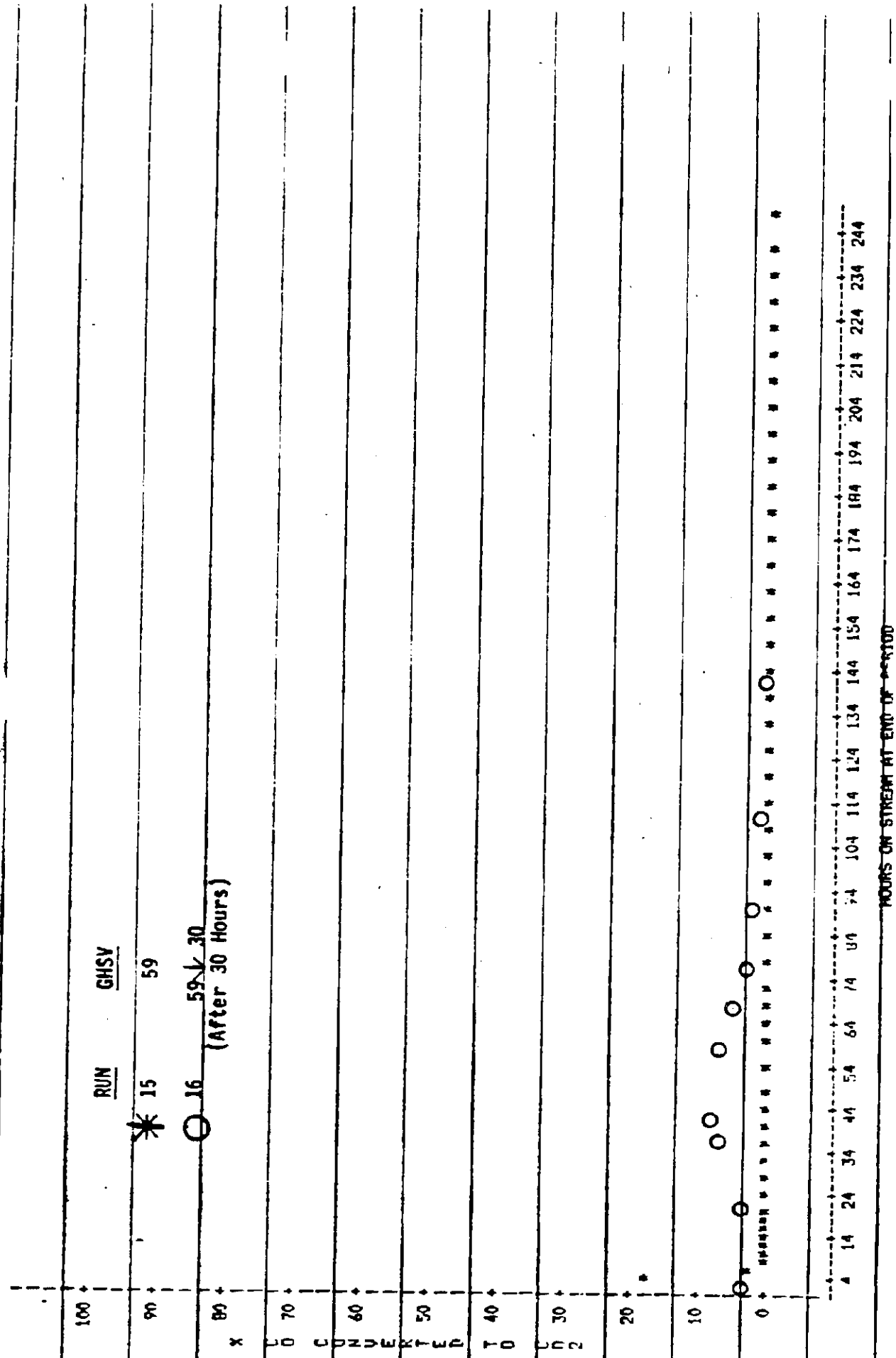
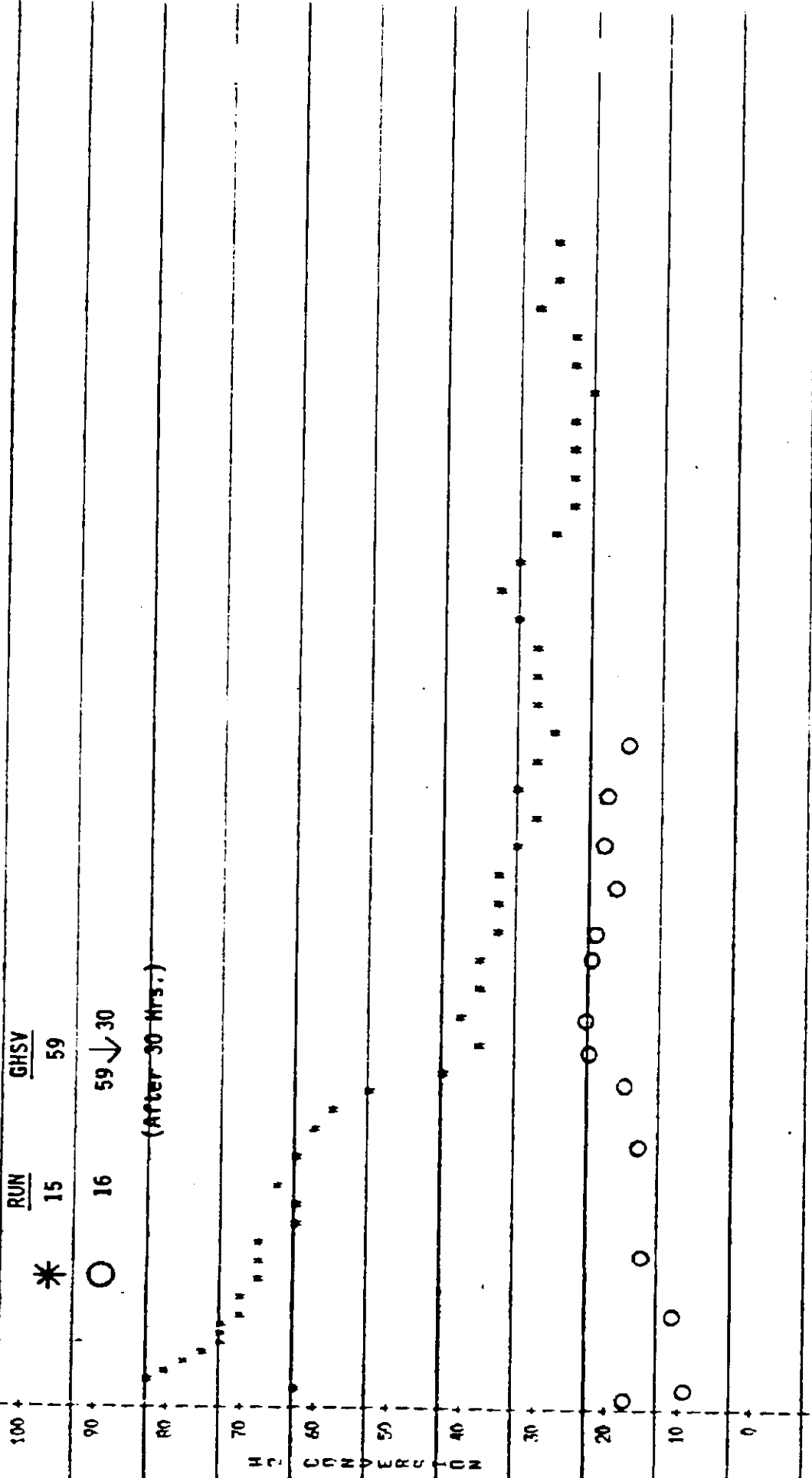


Figure 28

H₂ Conversion vs. Hours on Stream in Runs 15 and 16

(Plant 700)



(After 30 Hrs.)

14 24 34 44 54 64 74 84 94 104 114 124 134 144 154 164 174 184 194 204 214 224 234 244

HOURS ON STREAM AT END OF PERIOD

Figure 29

CO → H₂ Conversion vs. Hours on Stream in Runs 15 and 16

(Plant-700)

<u>RUN</u>	<u>GHSV</u>
15	59
16	59 ↓ 30
	(After 30 hrs.)

* ○

100 +
90 +
80 +
70 +
60 +
50 +
40 +
30 +
20 +
10 +
0 +

C
N
V
R
S
T
H

14	24	34	44	54	64	74	84	94	104	114	124	134	144	154	164	174	184	194	204	214	224	234	244
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HOURS ON STREAM AT END OF PERIOD

