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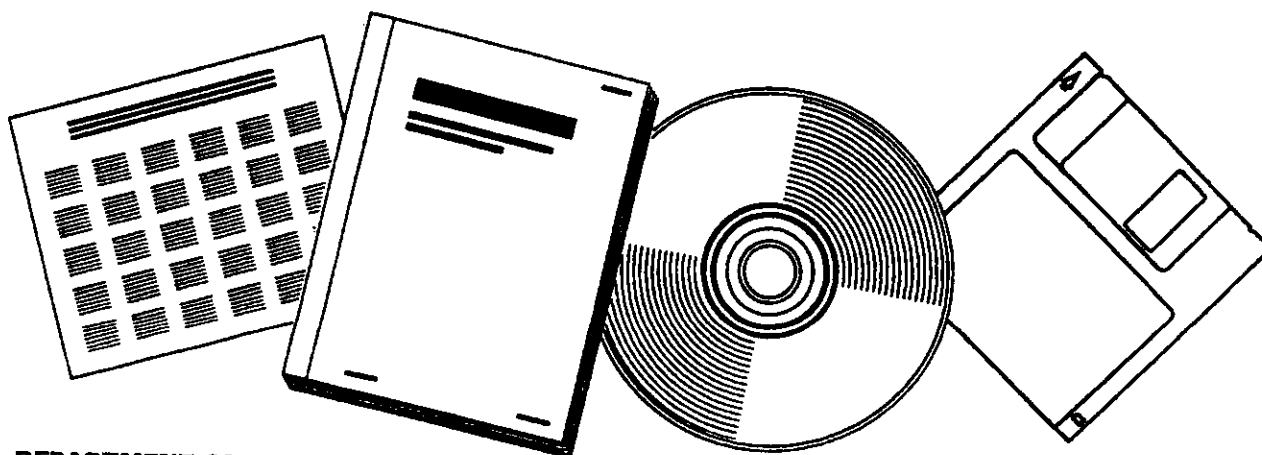
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**MICELLE-DERIVED CATALYSTS FOR EXTENDED  
SCHULZ-FLORY. TECHNICAL PROGRESS REPORT,  
OCTOBER 1, 1984-DECEMBER 31, 1984**

UOP, INC., DES PLAINES, IL. CORPORATE  
RESEARCH CENTER

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MICELLE-DERIVED CATALYSTS FOR EXTENDED SCHULZ-FLORY

Reporting Period: October 1, 1984 to December 31, 1984

Signal UOP Research Center, UOP Inc.  
50 UOP Plaza  
Des Plaines, Illinois 60016

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## ABSTRACT

C-73-1-101 iron ammonia synthesis catalyst from United Catalyst, Inc., was reduced in the laboratory with  $H_2$  at  $450^\circ C$ ,  $6000\text{ hr}^{-1}$  GHSV for 48 hours. The reduced catalyst has been examined with the Scanning Transmission Electron Microscope (STEM). Large iron crystallites,  $>100\text{\AA}$ , and a broad size distribution have been confirmed. The crystallite size distribution has been measured by the X-ray diffraction (XRD) technique. Only metallic iron was detected in the XRD analysis.

The reduced C-73-1-101 catalyst has been tested in the Fischer-Tropsch fixed-bed catalyst testing plant under four sets of reference conditions (Runs 3, 6, 7, 8). Preliminary analyses of these tests are described in this report. The presence of two independent parallel product recovery systems allowed separating the products collected initially during the line-out from those collected at the desired conversion level and also allowed multiple material balance periods in an extended run. The products recovered during the run and the wax retained on the catalyst were later analyzed by gas chromatography mostly to determine the carbon numbers. Argon was used as an internal standard to determine the conversion of the feed gas.

Relatively small amounts of catalyst diluted with  $\alpha\text{-Al}_2\text{O}_3$  powder were used to prevent excessive temperature increases. Total material recoveries, after correction by the amount of recovered argon, were 96-99% in all runs except in Run 8. The Anderson-Schulz-Flory plots, for the products recovered during the course of the runs, were mostly linear but indicate the possibility of further improvements in the product recovery and analysis techniques. A new GC technique will be used in the future to analyze the light hydrocarbons in gas phase with a significantly higher precision. The product distributions in Run 8 did

not seem to be satisfactory, and, therefore, the run is going to be repeated using a larger catalyst volume and higher feed rate. No significant catalyst temperature increase is expected at the higher feed rate that is going to be used. The chain growth probabilities,  $\alpha$ , calculated for the products recovered during the course of the runs, up to a carbon number of 35, were unique and all between 0.7 and 0.8. Here, it was assumed that the wax retained on the catalyst was mostly made during the line-out period. This is going to be clarified in the future.

Various ruthenium salts have been preliminarily evaluated for preparing catalysts by applying a micelle technique, and some promising salts were identified. TGA analysis performed on a micelle-derived catalyst supported on alumina indicates that 400°C may be a suitable calcination temperature. Another alumina-supported catalyst prepared using a micelle technique gave a broad size distribution of ruthenium particles in the STEM examination. The causes of this maldistribution are under investigation. Nine more supported catalysts have been made by variations of the micelle technique and are awaiting STEM analysis.

## OBJECTIVES

The objectives of this work were to reference the Fischer-Tropsch fixed-bed pilot plant with the C-73-1-101 iron reference catalyst from United Catalyst, Inc., to examine this catalyst via STEM and XRD, and to establish a preparation procedure for alumina-supported ruthenium catalysts by using micelle methods.

## EXPERIMENTAL

### Catalyst Testing Plant

All catalyst testing runs were conducted in Plant 700. The H<sub>2</sub>/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 4" above catalyst inlet. 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 these runs varied from 4 1/2" to 16 1/4" depending upon the amount of catalyst and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> diluent used. 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<sub>8</sub>-C<sub>35</sub> 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  $\sim -2^{\circ}\text{C}$ . The cold box contained two alternate Fischer Porter cylinders, kept at 50 psig, and where the  $\text{C}_5\sim\text{C}_{20}$  hydrocarbons and the rest of the aqueous phase were collected. The outlets from the cold box were followed by two alternate traps kept at atmospheric pressure in dry ice-acetone baths. Here, most of the  $\text{C}_3\sim\text{C}_{10}$  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  $\alpha\text{-Al}_2\text{O}_3$  diluent were loaded to the reactor at room temperature in a  $\text{N}_2$  glove bag. The reactor was then filled with  $\text{H}_2$  for pressure testing at 200 psig above testing pressure. After a successful pressure test, the pressure was reduced to 500 psig and the reactor heated to testing temperature under  $\text{H}_2$  flow. The  $\text{H}_2$  then was cut off, and the feed was introduced. Pressure was then raised to testing pressure if it was above 500 psig. The feed rate was adjusted during the first 1~2 days to achieve the desired conversion level, after which the effluent flow was switched to the alternate second product recovery system. The products collected during the line-out period were then recovered from the first product recovery system. The catalyst was then tested for an additional 1~4 days. The runs for which low feed rates were used were extended over relatively longer periods to collect enough products for accurate analysis. After the test, the reactor was cooled to room temperature under  $\text{N}_2$  flow and then unloaded.

### Run Analysis Procedure

The run analysis procedure is described in detail in Figure 1. The liquid and solid 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 and based on the analysis of the effluent gas. The wax extracted from the used catalyst by toluene was also analyzed by GC and reported, but this analysis was not incorporated initially into the calculation of the overall product distribution as will be later discussed.

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

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

### GC Reference Runs with ASTM D 2887 Method

A C<sub>10</sub>-C<sub>40</sub> n-paraffin mixture of known composition was prepared in toluene and analyzed with the ASTM D 2887 method in five runs to determine the extent of recoveries at individual carbon numbers. These results are summarized in Figure 2 and indicate average weight recoveries that range between 80 and 130%.

## RESULTS

### Pretreatment Procedure for the C-73-1-101 Reference Catalyst

C-73-1-101 iron catalyst (a typical composition as reported by G. A. Huff<sup>1</sup> is shown in Figure 3) from United Catalyst Inc. (sample number 3067-5) was

crushed from 6-10 mm size range to larger than 100 mesh. 228.9 g of this catalyst, which had a volume of 102 cc when loosely packed, was transferred to a 1 1/2" I.D. x 40" long quartz tube, which was then placed in an electric furnace. H<sub>2</sub> flow (Matheson zero gas, 99.99%) was initiated at 10 liters/min., resulting in a space velocity of 6000 hr<sup>-1</sup> GHSV. Catalyst temperature was then raised, at 5°C min., to 450°C under same H<sub>2</sub> flow, and maintained under these conditions for 48 hours. The progress of catalyst reduction was monitored by discoloration of a drierite bed. No further discoloration was occurring at the end of 48 hours, indicating virtual completion of reduction. The catalyst was then cooled to room temperature under H<sub>2</sub> and then flushed with N<sub>2</sub> before unloading. The catalyst was unloaded inside a N<sub>2</sub> glove bag and its apparent bulk density was measured to be 2.14 g/cc. The catalyst was then transferred in the glove bag to a series of glass vials and sealed for further use.

STEM Examination of the Reduced C-73-1-101 Reference Catalyst (Task 2.3)

The reduced C-73-1-101 catalyst was further ground to a fine powder with a mortar and pestle under a N<sub>2</sub> atmosphere. The powder was deposited on a holey carbon coated nylon grid which was treated with a drop of isopropanol. The excess powder was removed from the grid by gentle tapping. While under N<sub>2</sub>, the specimen was placed in the cartridge and placed into the HB-5 STEM. This was accomplished by transfer of the specimen in a N<sub>2</sub>-purged glove bag to the sample delivery chamber of the HB-5, which also is purged with N<sub>2</sub>. After the transfer was completed, the top of the HB-5 delivery chamber was put in place and the sample evacuated to 10<sup>-9</sup> torr.

<sup>1</sup>G. A. Huff, "Fischer-Tropsch Synthesis in a Slurry Reactor," Ph.D. thesis, Massachusetts Institute of Technology, April 1982.



Examination of the reduced C-73-1-101 catalyst showed several morphologically different species. This is clearly illustrated in Figure 4 through 7. In Figure 4, the porous nature of the Fe particle is apparent in the dark field image. (Dark field image is representative of elastically scattered electrons and is a function of Z number.) The image in Figure 5 shows some porous Fe with highly faceted iron crystallites. The size of those crystallites generally range from 15-40 nm. The particles shown in Figures 4 and 5 are typical of what was observed for this sample.

The crystallites shown in Figure 5 appear multidimensional as is indicated by Figures 6 and 7, which show multiple planes of diffraction for two small crystallites. Microdiffraction patterns have been taken for some of these particles and will be indexed in the future if necessary.

#### XRD Examination of the Reduced C-73-1-101 Reference Catalyst (Task 2.3)

The method of Fourier deconvolution of X-ray diffraction lineshapes has been applied to the reduced C-73-1-101 catalyst. A survey scan of the diffraction pattern (Figure 8) indicates the catalyst to be predominantly in the metallic iron form with no features due to oxides or other phases detectable (Be peaks in Figure 8 are due to the window material). The experiments were done in a special cell which could be loaded in a controlled atmosphere enclosure to prevent oxidation of the catalyst. Two different window materials (Be metal and Kapton) were used in order to compare the results obtained with each.

The procedure consisted of very long time scans of two Fe reflections (Figures 9 and 10), the (200) and (211), in order to accurately determine the full lineshape and adjoining background. Similar scans were done for an Fe powder where the lineshape is essentially the instrument function. The Fe standard and Fe catalyst lineshapes were then Fourier analyzed and the instru-

mental broadening removed from the catalyst lineshape to yield the true catalyst lineshape. The true lineshape is obtained as a Fourier series which is the preferred form, as the amplitudes of the Fourier coefficients contain the information about the distribution of crystallite sizes.

By plotting the amplitude of the Fourier coefficients versus the harmonic number, the extrapolated initial slope yields the mean crystallite size as the intercept of the abscissa (Figure 11). The distribution of sizes is obtained as the curvature of this plot versus harmonic number. The curvature is determined by numerical techniques which results in a loss of information at small crystallite size. At large size, the noise due to small Fourier coefficient leads to unrealistic curvatures, resulting in large, but unphysical, probabilities.

The results of two different scans with the different window materials are in excellent agreement. The mean crystallite size is found to be 115Å in one case and 105Å in the other. Further, the distribution of sizes forms an envelope from about 40Å to 140Å, with a broad maximum from 60Å to 100Å (Figure 12). At sizes larger than 140Å, the noise of the Fourier coefficients results in large, but physically meaningless, probabilities.

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

Eight runs were carried out with the reduced C-73-1-101 catalyst for referencing the fixed-bed pilot plant under four different sets of conditions. The operating conditions for these runs are summarized in Figure 13. Some of the key results, like total weight of hydrocarbons, the total weight of water made during the runs, the total weight recovery, the amount of wax extracted from the catalyst at the end of the run, percent coke on used catalyst, and  $\alpha$ , the growth probability, are also summarized in the same figure.

First Set of Reference Conditions [250°C Inlet Temperature, 500 psig, Inlet H<sub>2</sub>/CO = 1.5 (Molar), 80% Initial CO Conversion]

Very large catalyst temperature increases (up to 175°C) occurred in Run 1 with 10 cc catalyst loading. By reducing the catalyst loading by a factor of ~3 and diluting the catalyst with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (4:1 wt. ratio), the maximum catalyst temperature increase was lowered to ~10°C (Run 3). Good material balance (100.2%) was achieved in Run 1 which was conducted at high feed rates, whereas material balance was not as good as in Run 3 (103.1%) due to low feed rates.

Results obtained in Run 3 are described in Figures 14-17. The conversion was ~80% during the beginning of the material balance period (28 hours on stream), decreased to ~60% in ~12 hours and then remained steady (until the end of the run at 55 hours on stream). The Anderson-Schulz-Flory distribution (Figure 16) for the hydrocarbons plus oxygenates recovered during the course of the run (not including the wax retained on the catalyst) gave a chain growth probability,  $\alpha$ , equal to 0.71.

Second Set of Reference Conditions [250°C Inlet Temperature, 500 psig, Inlet H<sub>2</sub>/CO = 0.9 (Molar), 37% Initial CO Conversion]

In an attempt to achieve good material balance without causing excessive catalyst temperature increases, 2 to 3 times the amount of catalyst employed in Run 3 was used with the same ratio of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder diluent in Runs 4 and 5. However, large temperature increases took place. Run 6 (Figures 18-24) was carried out with the same amount of catalyst used in Run 3, but a 7:1 wt. ratio of diluent to catalyst was used. Catalyst temperature increases were 6~15°C, and material recoveries were better than that in Run 3, 100.7 and 102.6 in two successive material balance periods.

The CO conversion was 37% initially (14 hours on stream) and later stabilized at 26~30% (end of run at 60 hours on stream). The Anderson-Schulz-Flory distributions for hydrocarbons plus oxygenates recovered during the course of the run gave consistent  $\alpha$ 's, 0.79 and 0.80, respectively.

Third Set of Reference Conditions [208°C Inlet Temperature, 500 psig, Inlet H<sub>2</sub>/CO = 0.9 (Molar), 33% Initial CO Conversion]

Same amount of catalyst and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> diluent were used in Run 7 (Figures 25-29) as in Run 6. The catalyst temperature increases were only 4-5°C. The total material recovery was significantly over 100%, indicating that the low feed rates were not measured accurately. The material balance became 98.1% after correcting the feed rates by the ratio of recovered-to-fed argon.

The initial CO conversion was 33% and was steady around 30% during the rest of the run (end of run at 116 hours on stream). The Anderson-Schulz-Flory distribution for hydrocarbons and oxygenates recovered during the run gave  $\alpha = 0.74$ .

Fourth Set of Reference Conditions [207°C Inlet Temperature, 1500 psig, Inlet H<sub>2</sub>/CO = 0.9 (Molar), 28% Initial CO Conversion]

No significant temperature increases (1~2°C) were found in Run 8 (Figures 30-33). Feed rates were overestimated like in Run 8. After correcting the feed rates by the ratio of recovered-to-fed argon, the material balance became 103.9%.

The initial (32 hours on stream) CO conversion was 28% and decreased to 12~15% by the end of the run (108 hours on stream). The Anderson-Schulz-Flory distribution for hydrocarbons and oxygenates during the run indicated that C<sub>1</sub>-C<sub>4</sub> hydrocarbons were not analyzed accurately. An  $\alpha = 0.77$  was calculated from products with carbon numbers >4.

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

Five ruthenium salts were preliminarily evaluated. These salts had different solubilities in water, ranging from ~3 to ~85 mg ruthenium/cc water. Four of these salts formed, apparently, clear reversed micelle solutions. The presence of micelles is going to be confirmed by small angle X-ray scattering (SAXS) technique. The fifth salt came out of solution when its water solution was mixed with the organic phase and the surfactant to form the micelles.

A thermogravimetric analysis (TGA) performed on a 0.4% ruthenium on  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst (4956-16-1) prepared with a micelle technique indicated that burning of the surfactant in air was virtually complete at 400°C. Atomic absorption spectroscopy (AAS) analysis performed on an experimental catalyst (4956-17) treated at 400°C in air did not indicate any significant ruthenium loss from the catalyst. These results indicate that 400°C may be a suitable calcination temperature for this kind of a catalyst.

A ~0.8% Ru on  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst (4956-12) was prepared with one of these ruthenium salts using a micelle technique. This catalyst was examined with STEM and gave a broad size distribution of ruthenium particles. The causes of this maldistribution are under investigation. Since then, nine more catalysts have been prepared by variations of the technique used for catalyst 4956-12. Some of these catalysts are going to be examined with STEM.

DISCUSSION AND FUTURE PLAN

Fischer-Tropsch Run Analysis Procedure

The wax extracted from the used catalyst with toluene at the end of the runs were not included in calculating the overall product distributions and unique  $\alpha$ 's were obtained up to a carbon number of 35. Here, it was assumed that

this wax was mostly made during the early part of the run before switching to the material balance periods.

The analysis of products made during some of these runs was further extended by constructing Anderson-Schulz-Flory plots that included the wax retained on the catalyst (Figures 34-36). Calculations were 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  $\alpha$ 's, a small one at carbon numbers less than 20, and a larger one at carbon numbers greater than 20. It is not presently clear whether this wax is mostly made during the line-out period or whether the hydrocarbons with high enough boiling point to be retained on the catalyst during the run undergo further polymerization reactions to produce the heavier material that was observed. This is going to be clarified in the future by testing the reference catalyst from 0 hours on stream for different reaction times and by analyzing the amount and composition of wax retained on the catalyst each time.

#### Improved GC Analysis for the Effluent Gas

At low  $\text{CO}+\text{H}_2$  conversions, the amount of ethane, ethylene, propane, propylene, butane, and butylene in the effluent gas constitute, each,  $\sim 0.1\%$  or less of the total. Since this is very close to the detectability limit in the UOP GC Method 539, desired accuracy for the  $\text{C}_2\text{-C}_4$  hydrocarbons cannot be obtained. This is particularly apparent in the Anderson-Schulz-Flory plot for Run 8 (Figure 32), which seems to indicate poor recovery for the light hydrocarbons. For the future, an improved GC analysis technique will be used for detecting the hydrocarbons in the effluent gas with significantly higher precision.

The Low Temperature, High Pressure Run

As discussed previously, the product distribution that was obtained under the fourth set of reference conditions (Run 8) didn't seem to be satisfactory. This run will be repeated in the future by using a larger catalyst volume in an extended test period to accumulate more products. No significant catalyst temperature increase is expected at the higher feed rate that is going to be used.

Establishing a Preparation Procedure for Alumina-Supported Ruthenium Catalysts by Using Micelle Methods

Some of the catalysts that were prepared by variations of the technique used for catalyst 4956-12 are going to be examined with STEM. Based on these examinations, a suitable preparation technique will be identified, which also includes selection of the ruthenium salt, the micelle system, and the catalyst treatment temperatures. The next step would then be to upgrade the catalyst preparation procedure so that large enough quantities of catalysts could be prepared for testing in the fixed-bed catalyst testing plant.

Figure 1  
Fischer-Tropsch Run Analysis Procedure

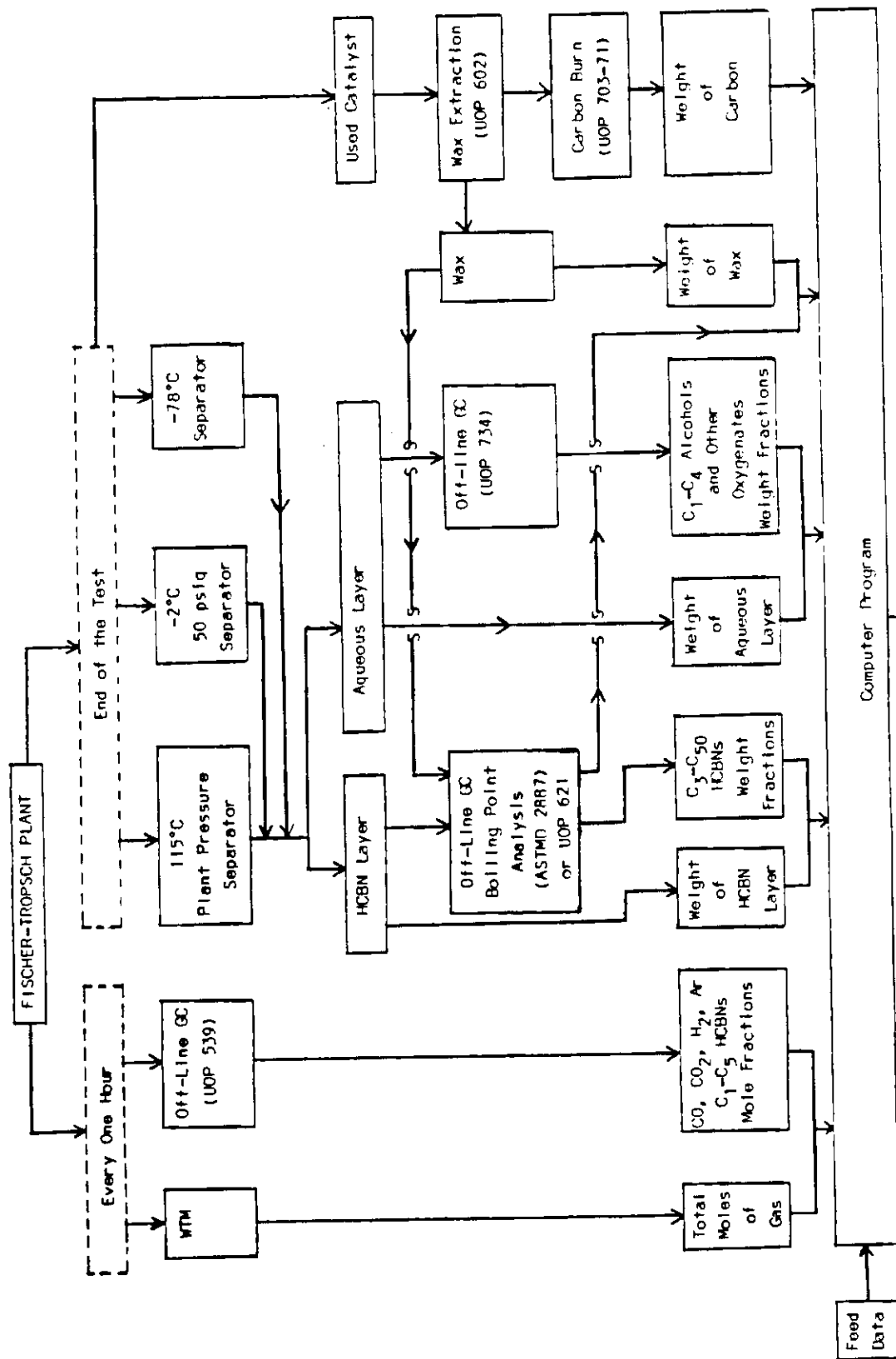




Figure 2

GC Reference Runs with ASTM D 2887 Method

Composition of Blend	Results of GC Analyses						Average	Recovery
	Run 1	Run 2	Run 3	Run 4	Run 5			
	<----- wt.% ----->							
n-C <sub>10</sub>	8.0	8.0	8.7	8.7	8.6	8.2	8.4	105
n-C <sub>15</sub>	7.6	7.2	8.3	8.1	7.5	8.0	7.8	102
n-C <sub>20</sub>	5.2	6.5	7.4	7.2	6.5	7.1	6.9	132
n-C <sub>26</sub>	6.1	6.8	7.8	7.5	6.8	7.4	7.3	119
n-C <sub>30</sub>	3.7	3.2	3.7	3.5	3.2	3.3	3.4	92
n-C <sub>36</sub>	4.2	4.8	5.5	5.3	4.7	5.0	5.1	119
n-C <sub>40</sub>	4.0	3.1	3.6	3.4	3.0	3.3	3.3	82
Toluene	61.2							

Figure 3Typical Properties of Ammonia Synthesis Catalyst

## Chemical Analyses (wt. % and dry basis):

FeO	30 - 37
Fe <sub>2</sub> O <sub>3</sub>	65 - 58
Free Fe	<0.5
Total Fe	67 - 69
Al <sub>2</sub> O <sub>3</sub>	2.0 - 3.0
K <sub>2</sub> O	0.5 - 0.8
CaO	0.7 - 1.2
SiO <sub>2</sub>	<0.4
P	<0.015
S	<0.001
Cl	<0.002
Fe <sup>2+</sup> /Fe <sup>3+</sup>	0.05 - 0.7

## Physical Characteristics:

bulk density, g/cc 2.9 ± 0.15



Figure 4 4966-2-VIII  
100KX



Figure 5 4966-2-VIII  
200KX

[100Å]



Figure 6 4966-2-VIII  
1MX

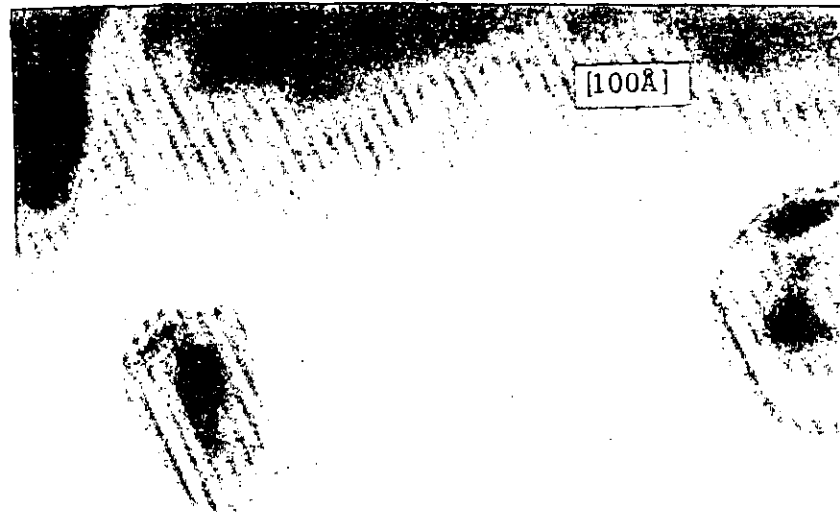
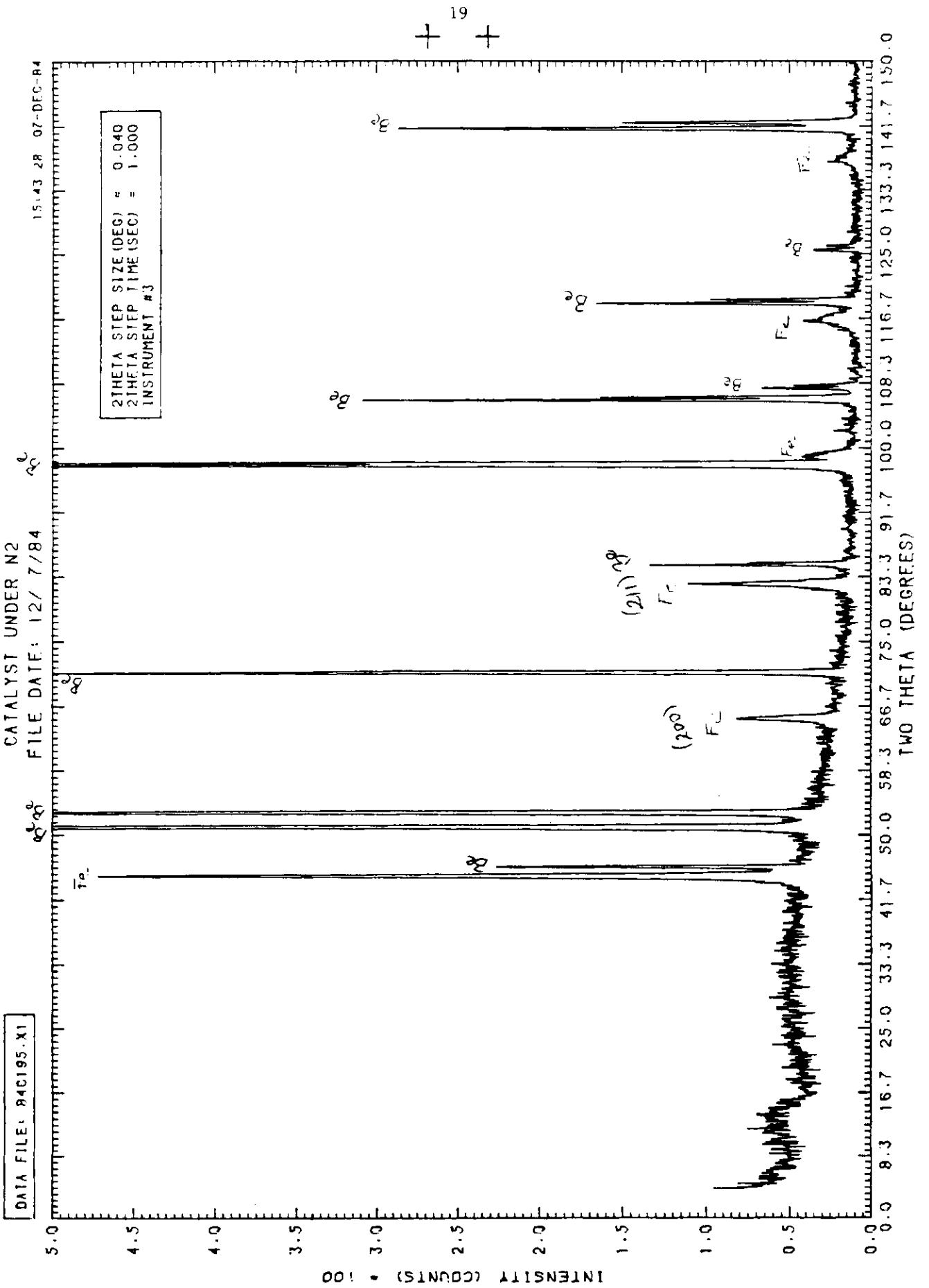


Figure 7 4966-2-VIII  
1MX

Figure 8 A Survey Scan of the diffraction patterns of reduced C-73-1-101 catalyst



Long Time Scans of the Fe (200) Reflection for the  
Reduced C-73-1-101 Catalyst and Ordinary Iron Powder

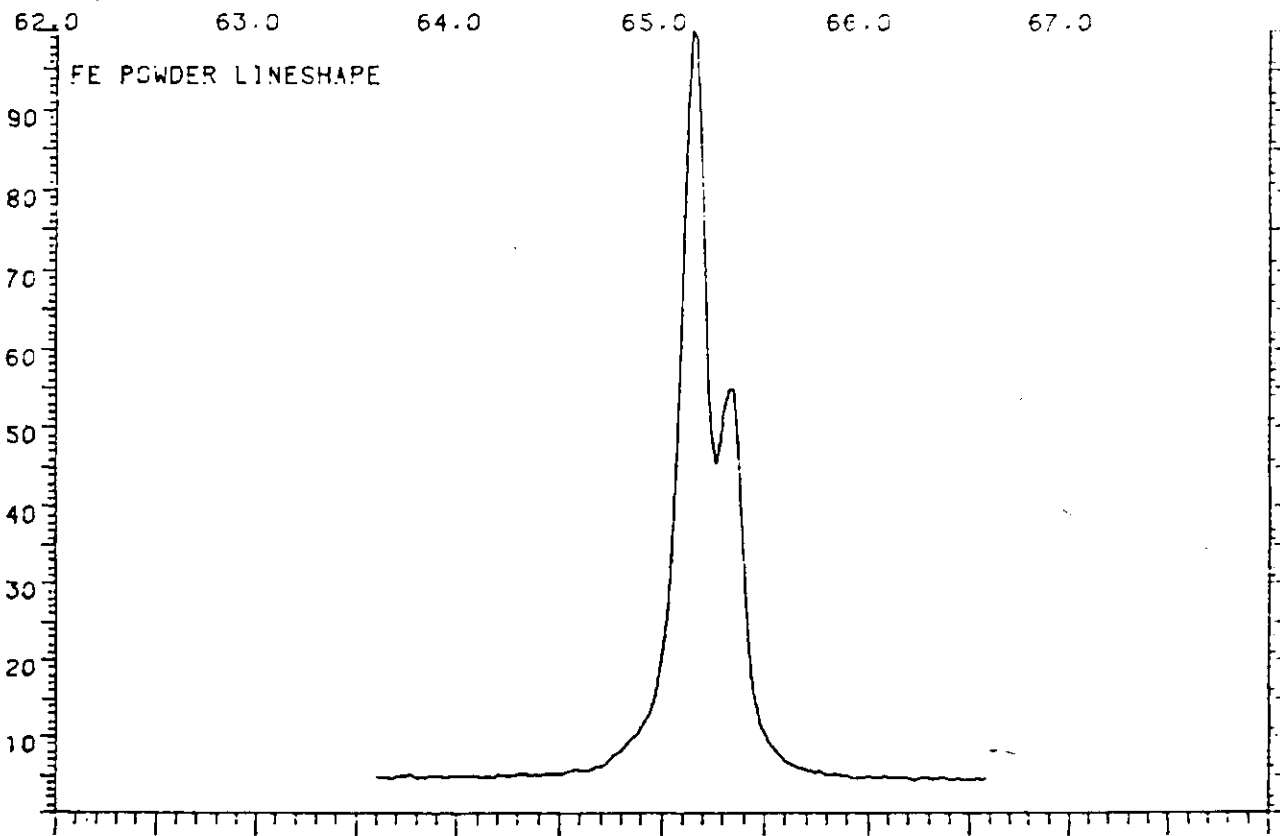
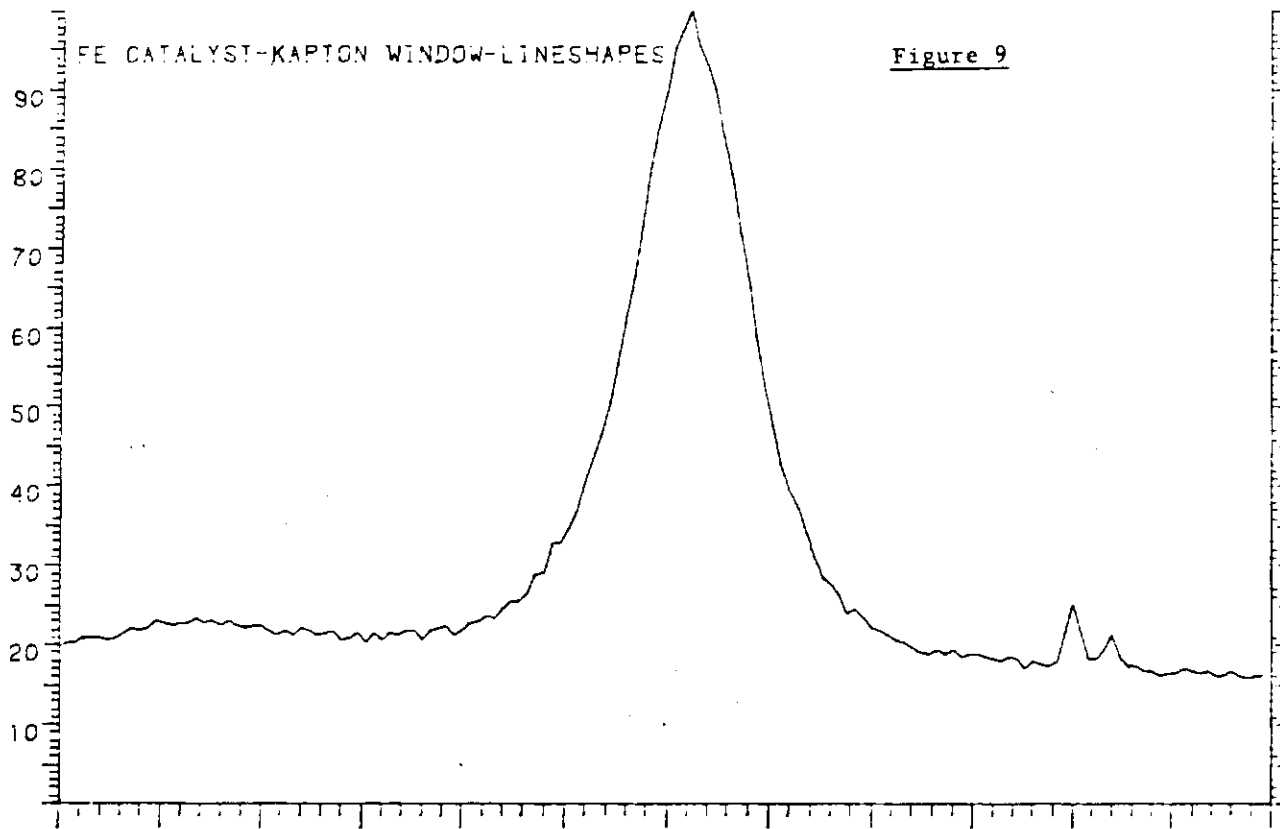


Figure 10 Long Time Scans of the Fe (211) Reflection for the Reduced C-73-1-101 Catalyst and Ordinary Iron Powder

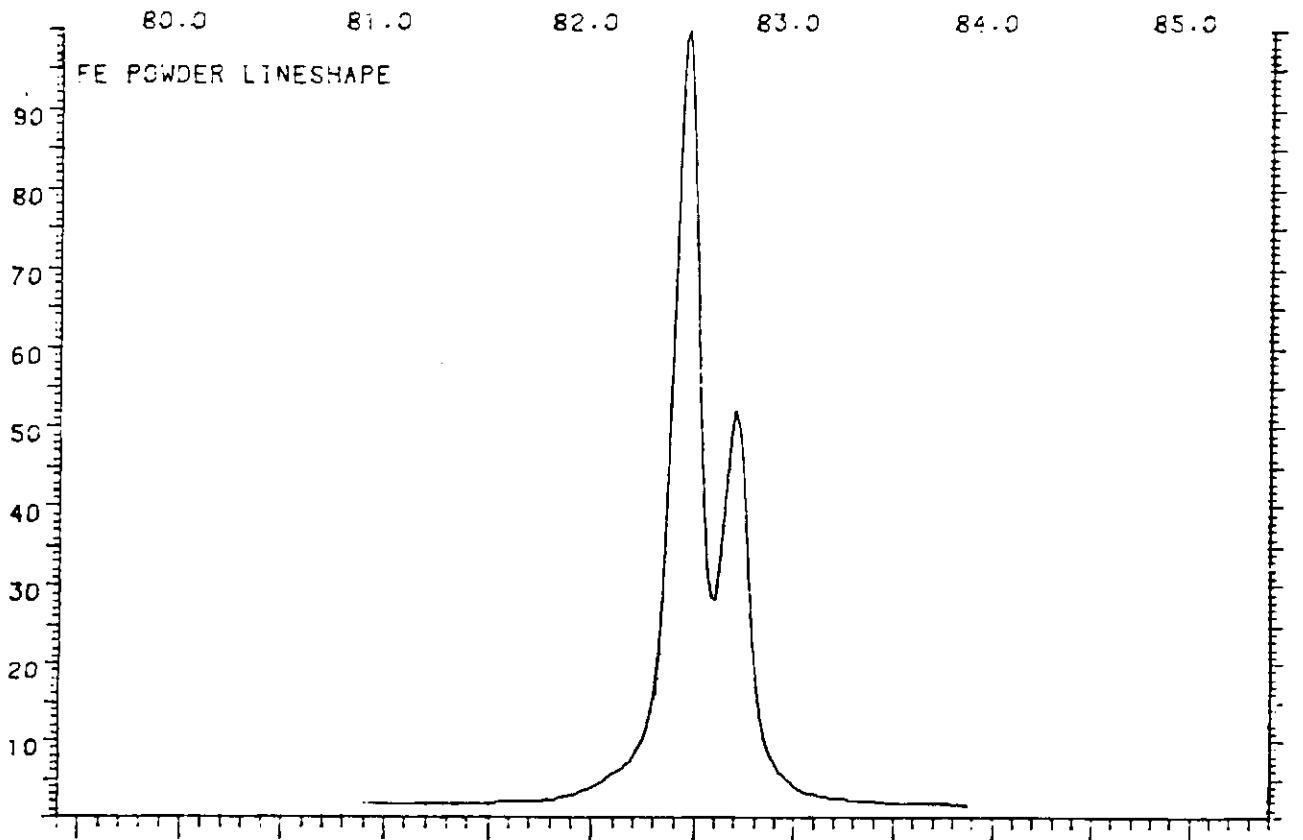
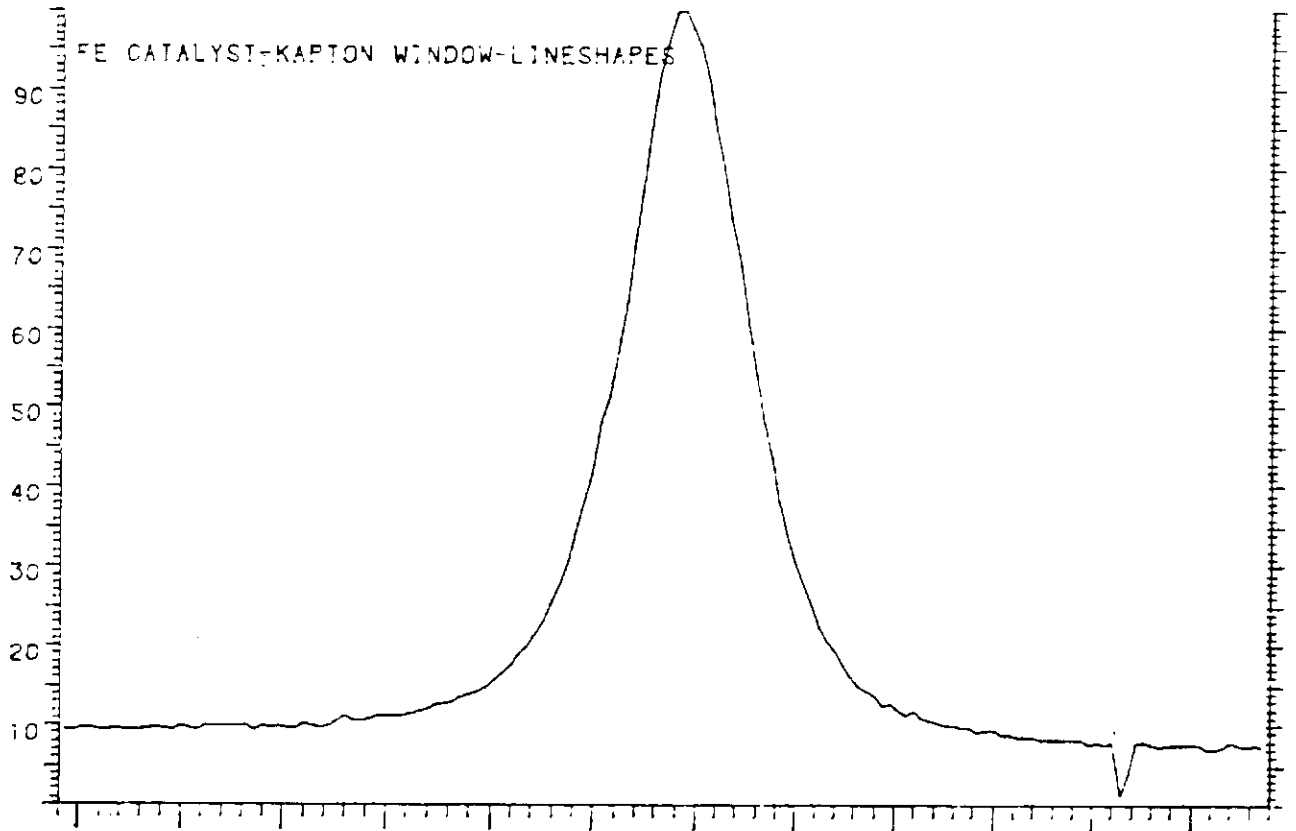


Figure 11  
Amplitude of the Fourier Coefficients vs. the Harmonic Number  
(Koptan Window)

○ 211 Reflection      - - - - Best EYEBALL f.t       $\langle D \rangle \approx 121 \text{ \AA}$   
 □ 200 Reflection      - - - -       $\langle D \rangle \approx 111 \text{ \AA}$

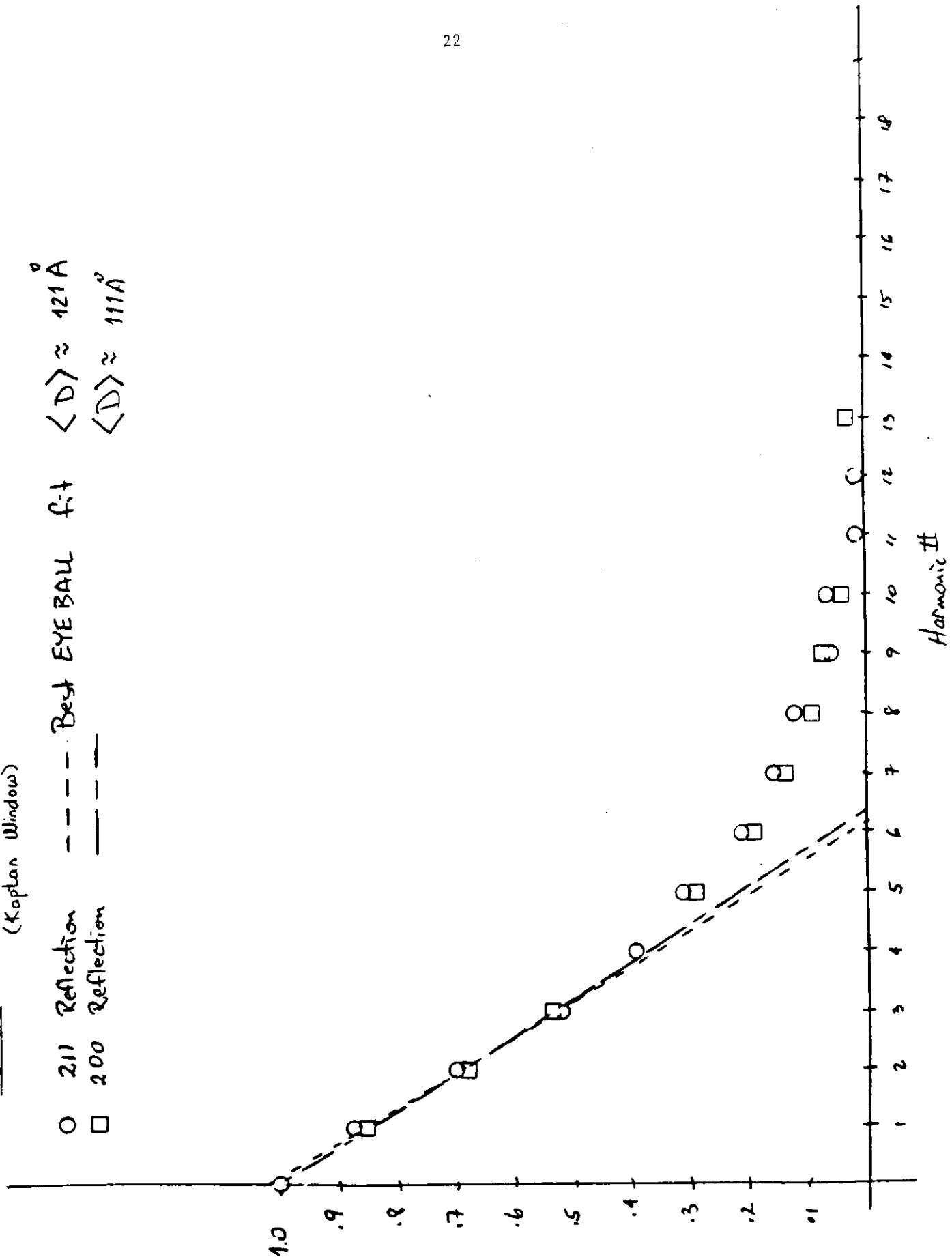




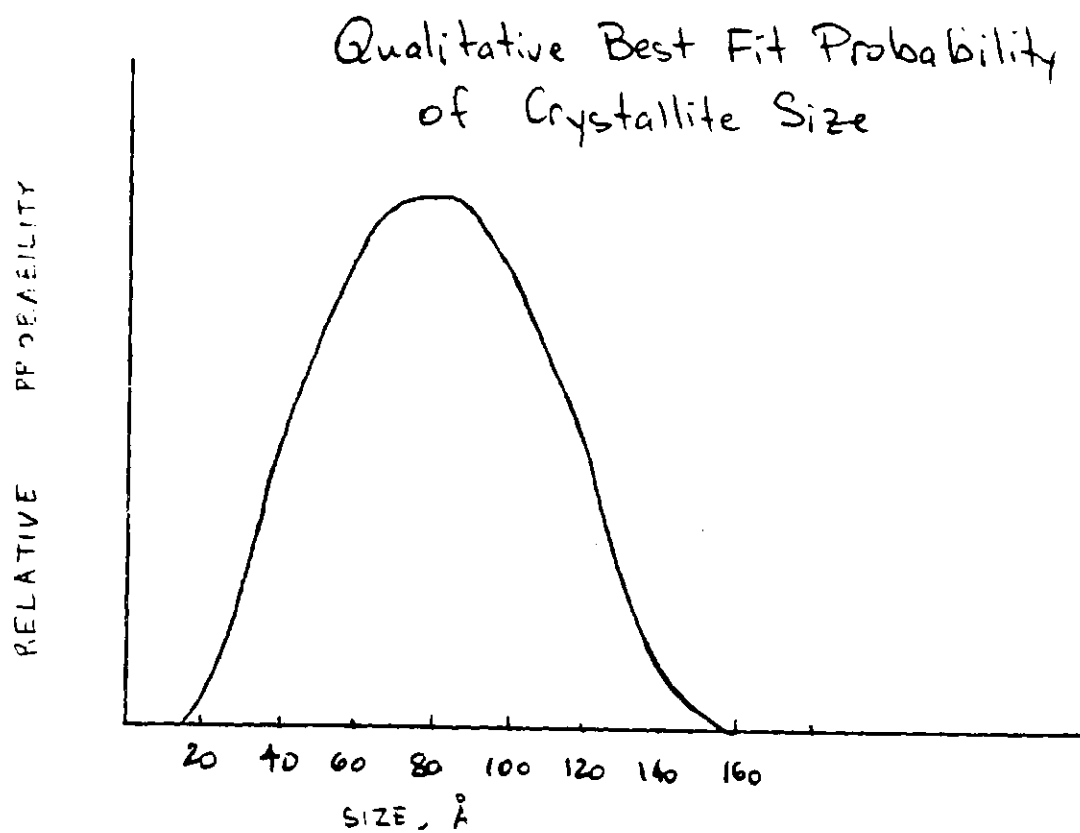
Figure 12

Figure 13  
Run Summary Data

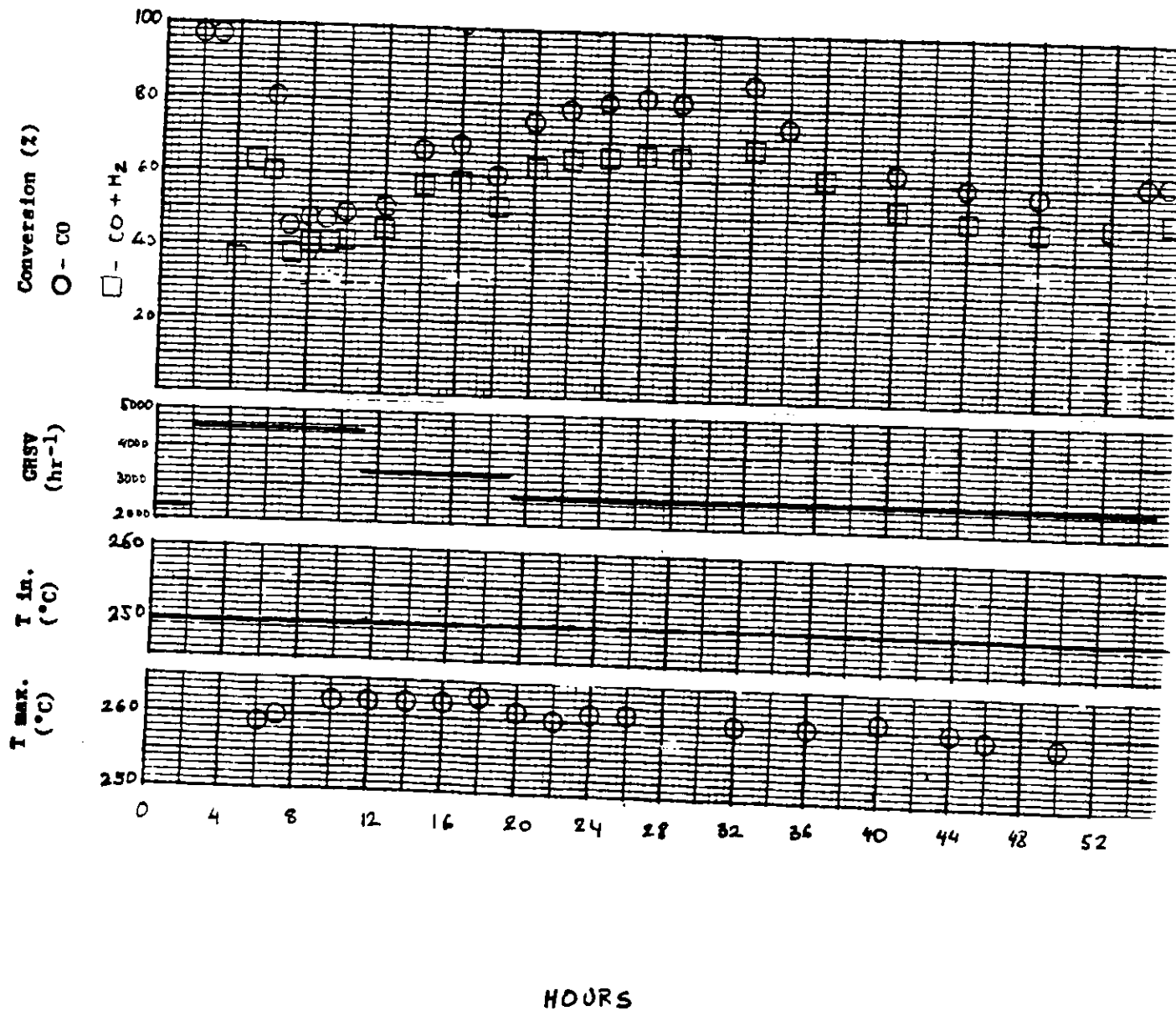
Run	Catalyst Wt. (g)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> Vol. (cc)	Bed Length (in.)	Inlet Temp. (°C)	Press. (psig)	H <sub>2</sub> /CO (Molar)	Feed Rate (SCFH)	CHSV	Hours	HCBR + Oxygenates Made (%) <sup>a</sup>	H <sub>2</sub> O Made (g)	Max Extracted from Catalyst at End of Run (g)	% C (wt.%) <sup>a</sup>	Argon Recov. (%) <sup>a</sup>	Total Wt. Recov. (%) <sup>a</sup>	Corrected Material Balance (%) <sup>a</sup>
1	21.4	10	0	4 1/2	250	500	1.5	0.850	2400	30-78				98.0	100.2	
2**	6.42	3	25.47		250	500	1.5	0.255	2400							
3	6.42	3	25.47	7	250	500	1.5	0.255	2400	28-55	10.7	4.6	1.4	107.1	103.1	96.3
4**	19.26	9	76.41	6	250	500	0.9	1.5	4710							
5**	14.27	6.7	56.60	16 1/4	250	500	0.9	1.24	5080 <sup>+</sup>							
							0.2	850								
6	6.42	3	45	12	250	500	0.9	0.6	5650	14-38	11.8	***	6.57	105.4	100.7	95.5
6	6.42	3	45	12	250	500	0.9	0.4	3800	38-60	9.4	***	6.57	104.1	102.6	98.6
7	6.42	3	42	13 1/8	208	500	0.9	0.1	950	38-116	11.6	4.3	1.85	117.4	115.2	98.1
8	6.42	3	42	9	208	1500	0.9	0.05	475	32-108	5.9	1.8	1.55	126.1	131.0	103.9

\*Doesn't include wax retained on catalyst.

\*\*Run shut down because of plant problems.

\*\*\*Max couldn't be recovered properly; exact weight not known.

Figure 14

FISCHER-TROPSCH SYNTHESIS ( PLANT 700)Run No. 3Catalyst No. 4966-56.42 g of reduced C-73 catalyst + 25.47 g d-Al<sub>2</sub>O<sub>3</sub>P = 500 psig (inlet) ; H<sub>2</sub>/CO = 1.5 (feed)

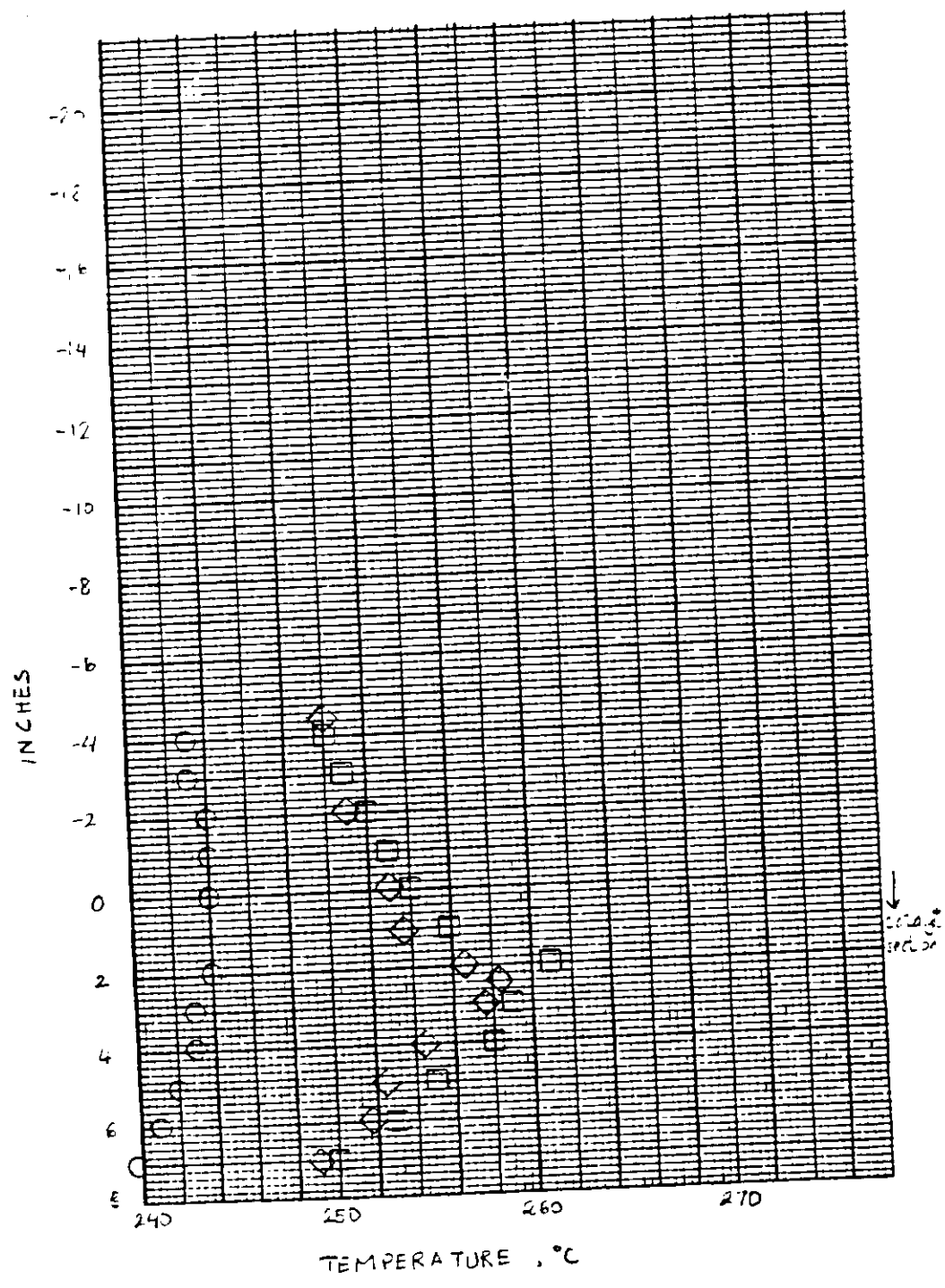
# TEMPERATURE PROFILE

## PLT 700 RUN 3

HOURS ON BLOCK TEMP, °C

STREAM	T	M	B
○ 11 A ONE	245	246	242
□ 28	242	240	240
◇ 50	242	240	240

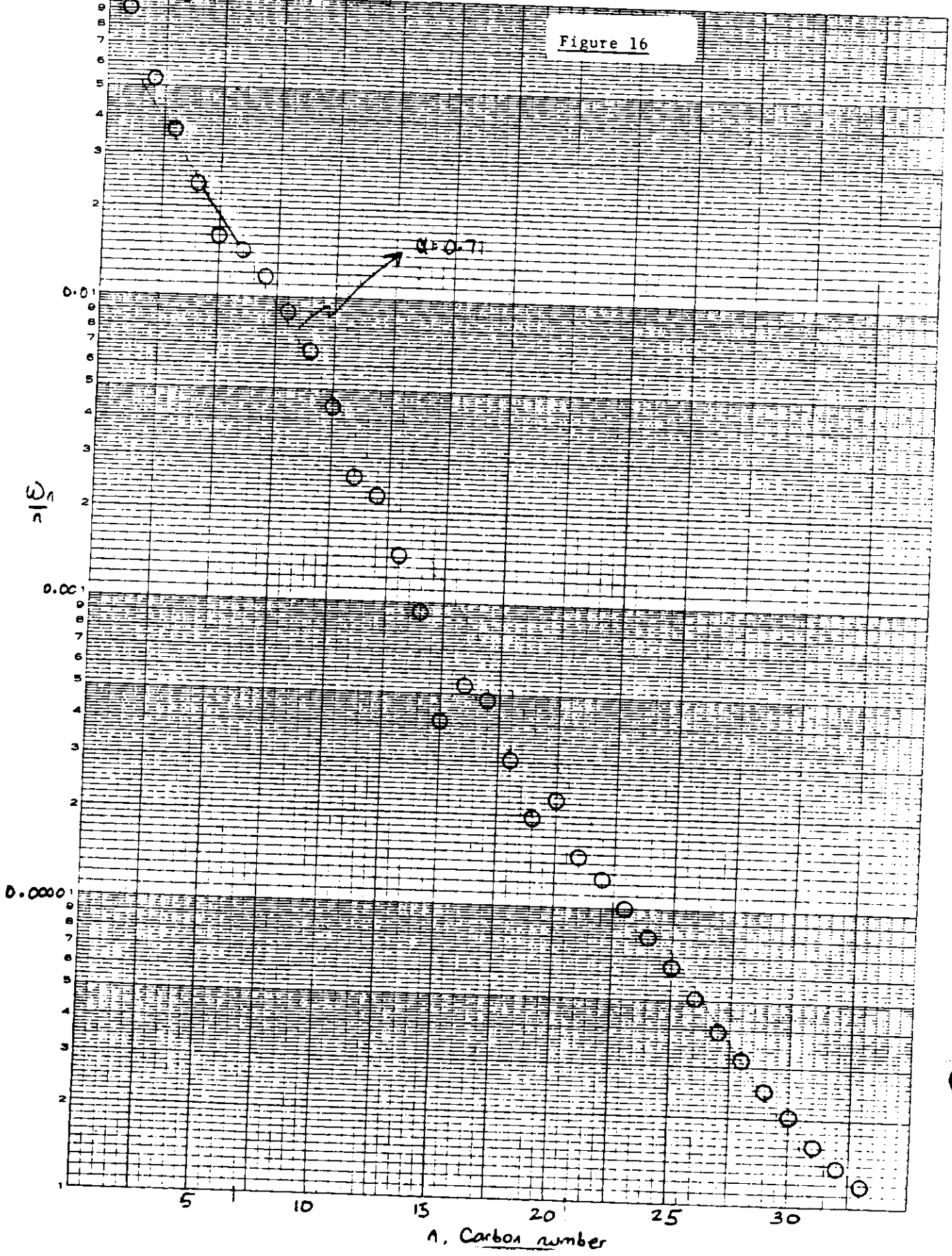
Figure 15



ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 3 (28-55 HOURS)

(Weight fraction of n-alk hydrocarbon)

Figure 16

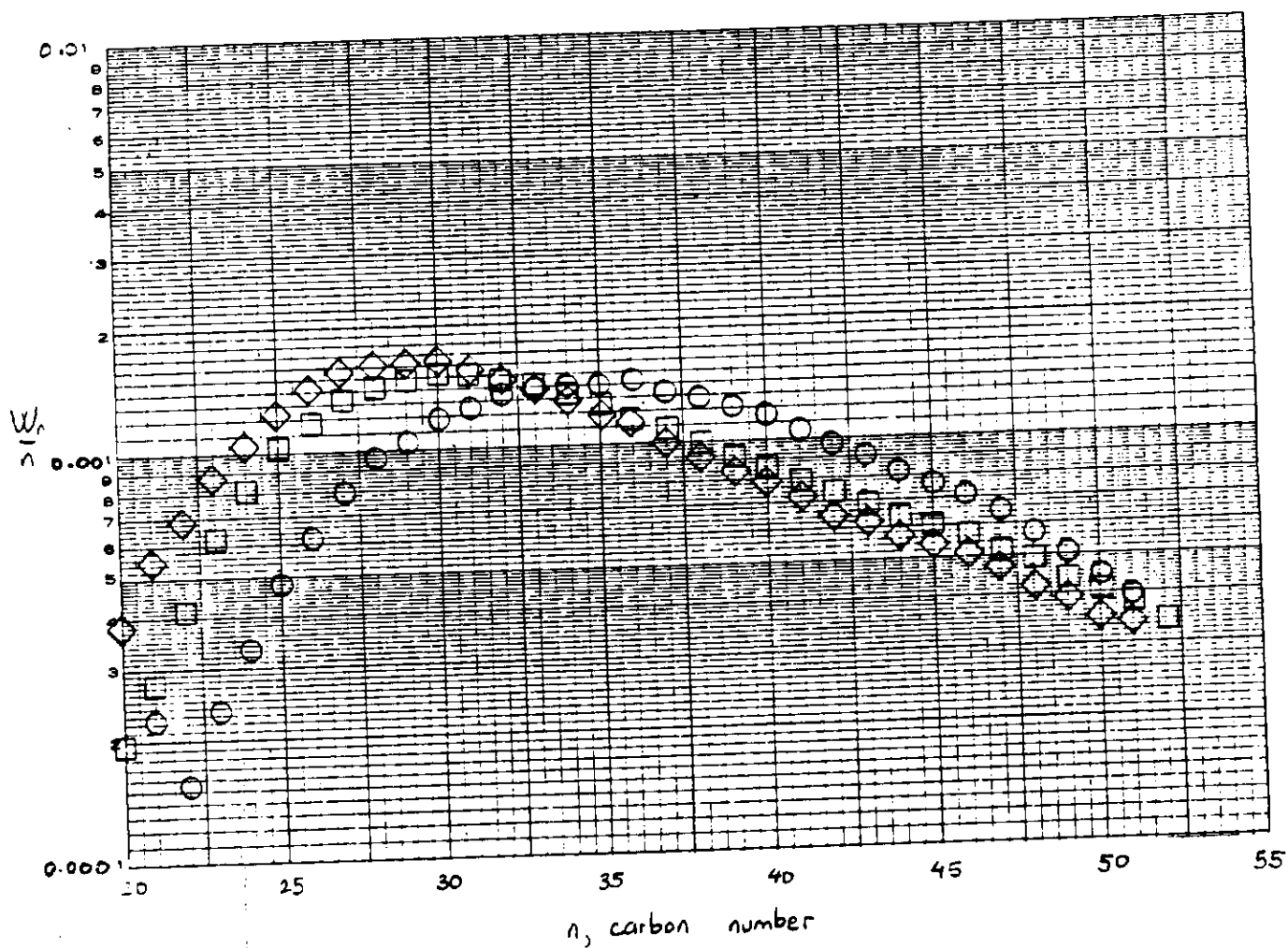


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best available copy.

Figure 17

ANDERSON-SCHULZ-FLORY DISTRIBUTION FOR THE WAX EXTRACTED  
FROM USED CATALYST IN RUN 3 (PLANT 700)

- FROM REACTOR TOP
- FROM REACTOR MIDDLE ZONE
- ◇ FROM REACTOR BOTTOM



$W_n$ : weight fraction of  $n$ th hydrocarbon in wax

Figure 18

FISCHER-TROPSCH SYNTHESIS ( PLANT 700)

Run No. 6

Catalyst No. 4966-8

6.42g of reduced C-73 catalyst + 45g d-Al<sub>2</sub>O<sub>3</sub>

P = 500 psig (inlet); H<sub>2</sub>/CO = 0.8 (feed)

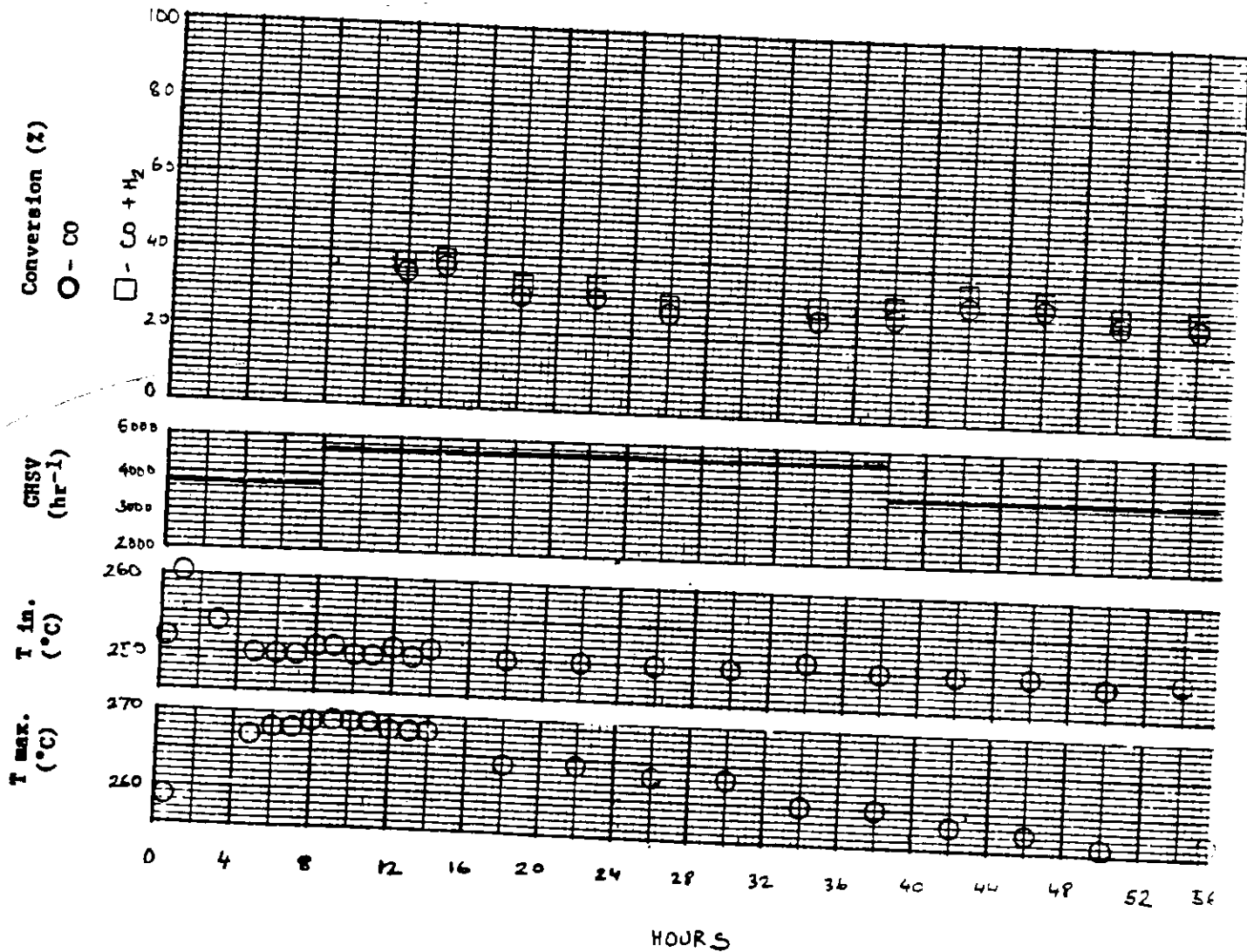


Figure 19

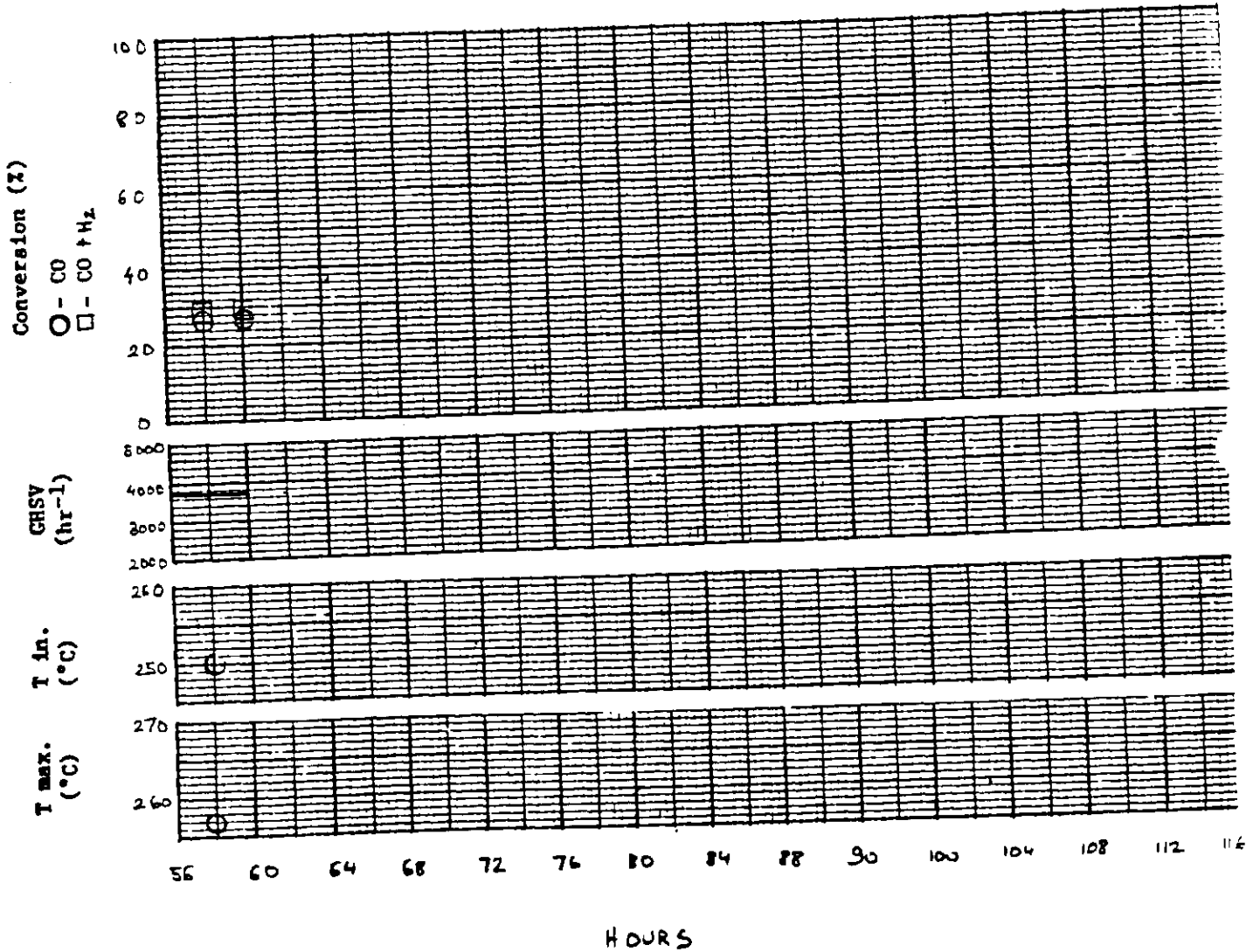
FISCHER-TROPSCH SYNTHESIS (PLANT 700)

Run No. 6

Catalyst No. 4966-8

6.42 g of reduced C-73 catalyst + 45 g  $\alpha$ - $Al_2O_3$

P = 500 psig (inlet) ;  $H_2/CO = 0.9$  (feed)



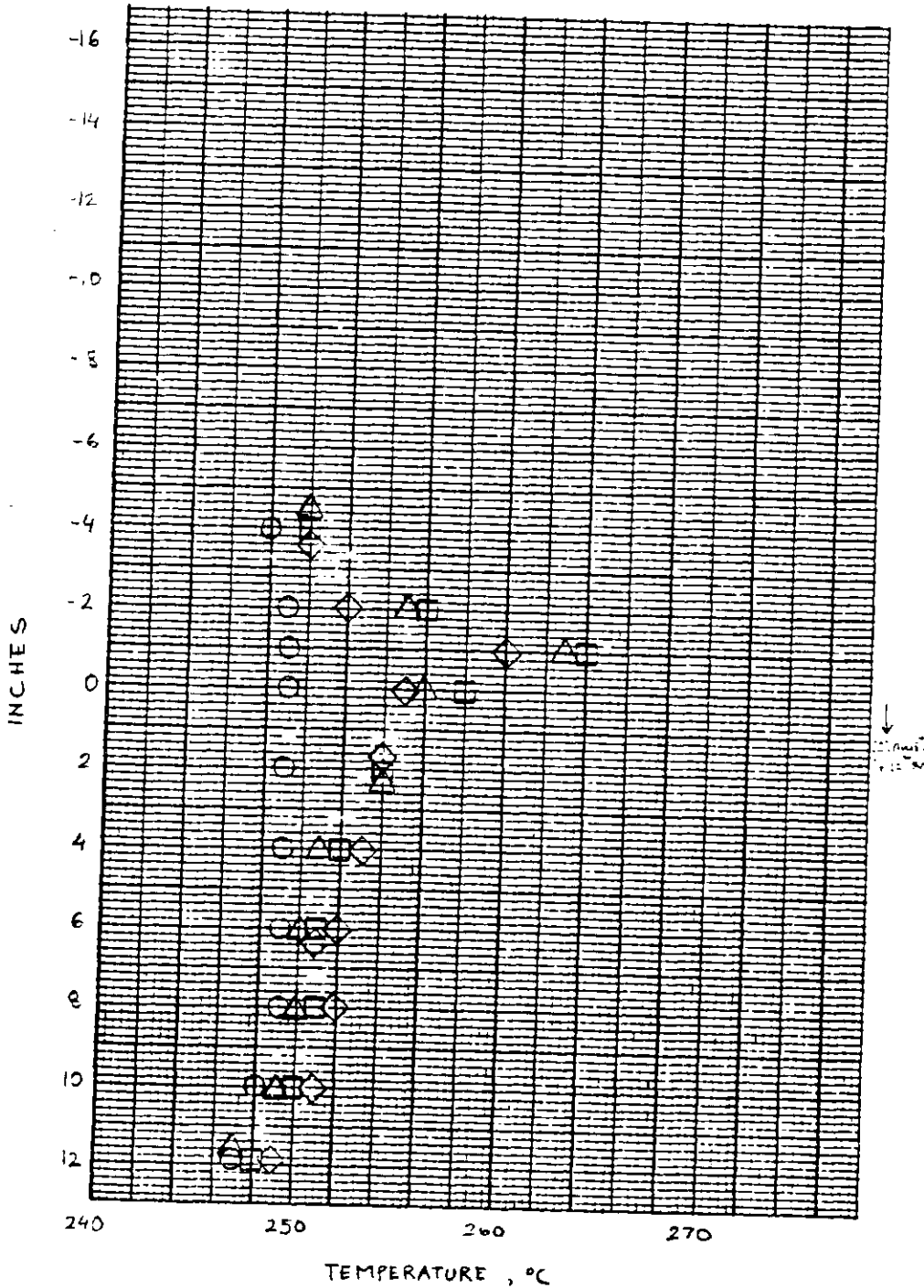


# TEMPERATURE PROFILE

31  
PLT 700 RUN 6

HOURS ON	BLOCK TEMP, °C		
STREAM	T	M	B
○ H <sub>2</sub> ALONE	250	250	250
□ 18	248	248	248
△ 30	248	248	248
◇ 38	250	248	248

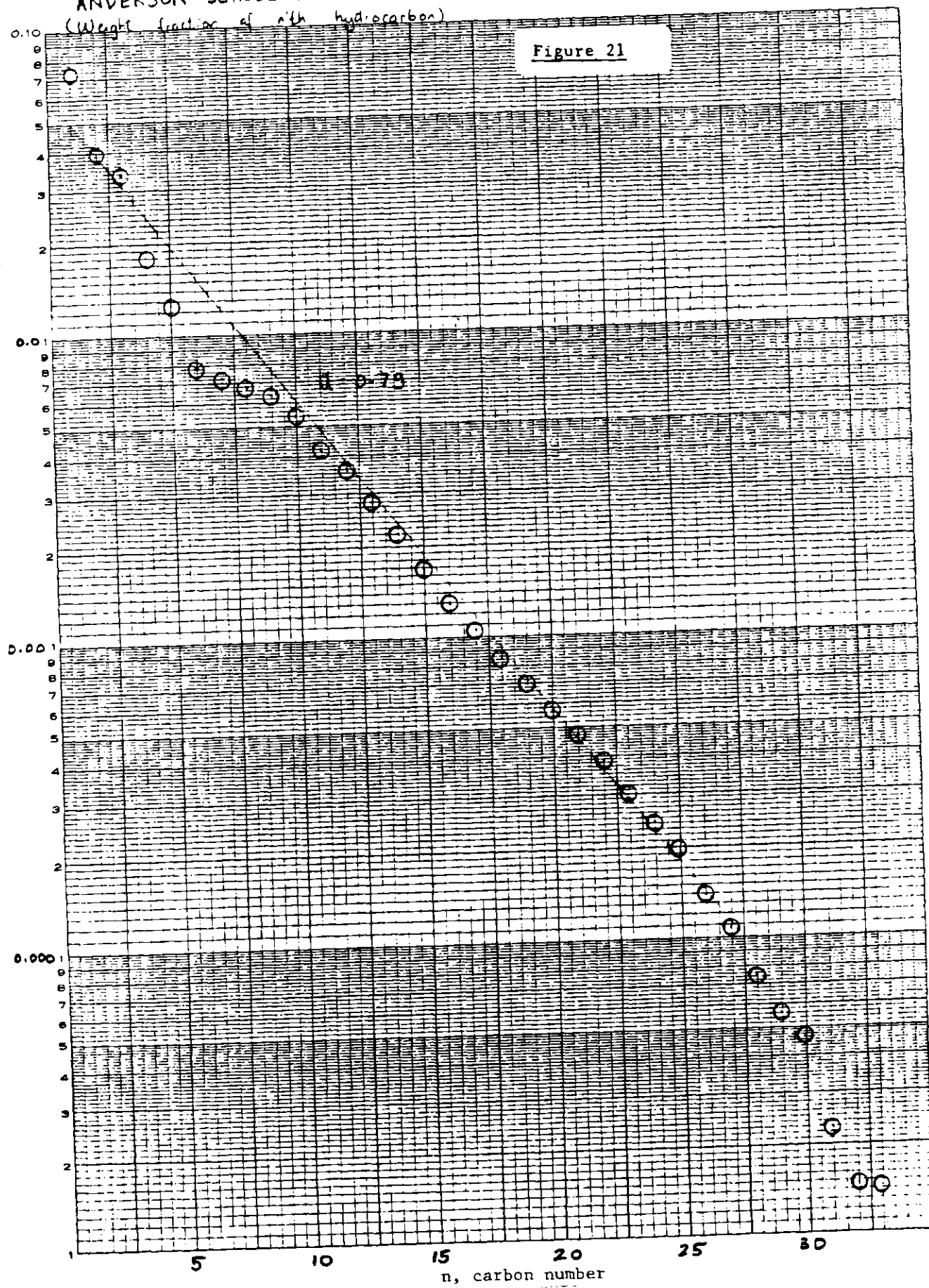
Figure 20



# ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 6 (14-38 HOURS)

(Weight fraction of  $n$ th hydrocarbon)

Figure 21



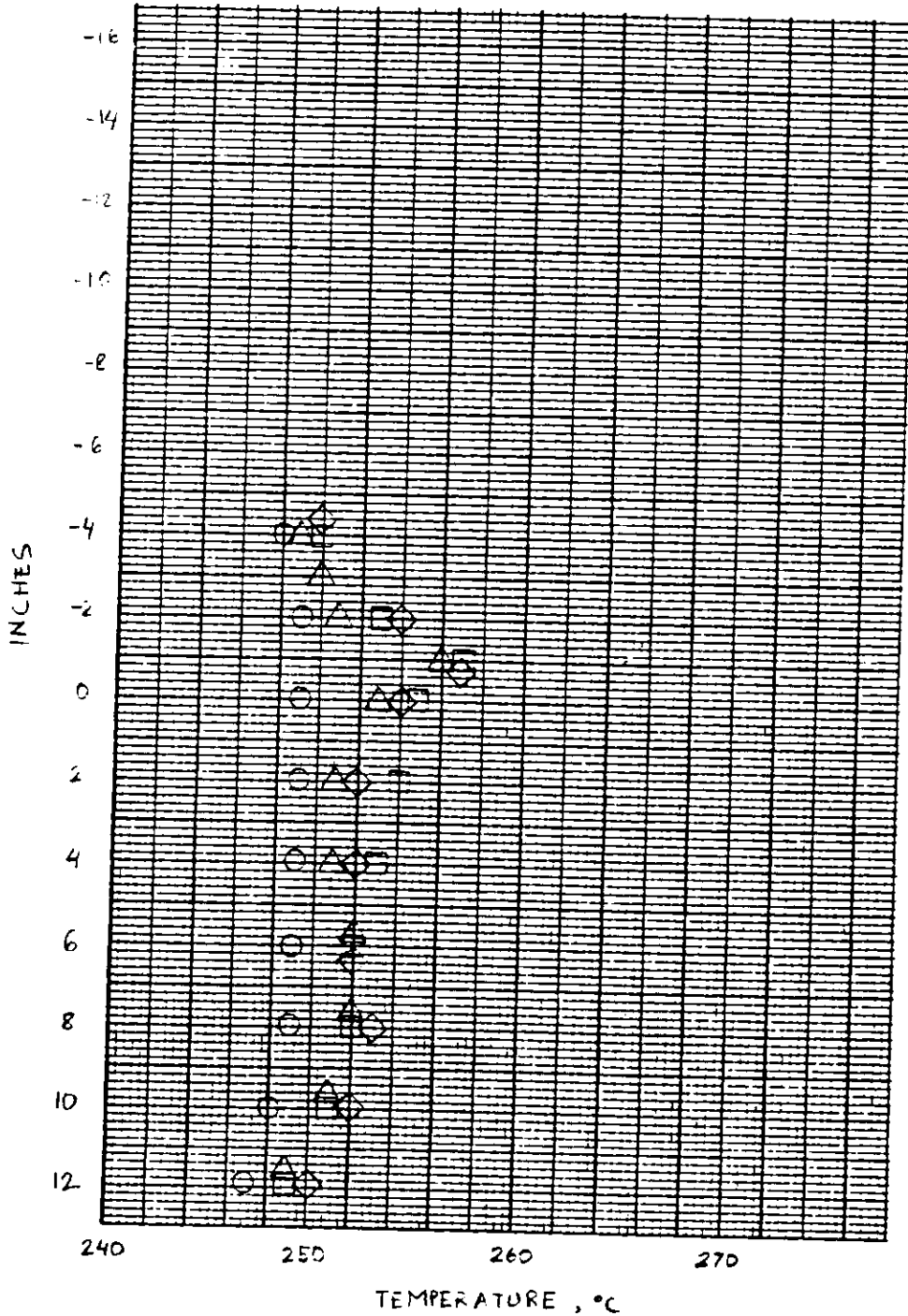
TEMPERATURE PROFILE

PLT 700 RUN 6

HOURS ON BLOCK TEMP, °C

STREAM	T	M	B
○ H <sub>2</sub> ALONE	250	250	250
□ 46	250	249	249
△ 57	249	249	249
◇ 58	250	250	250

Figure 22



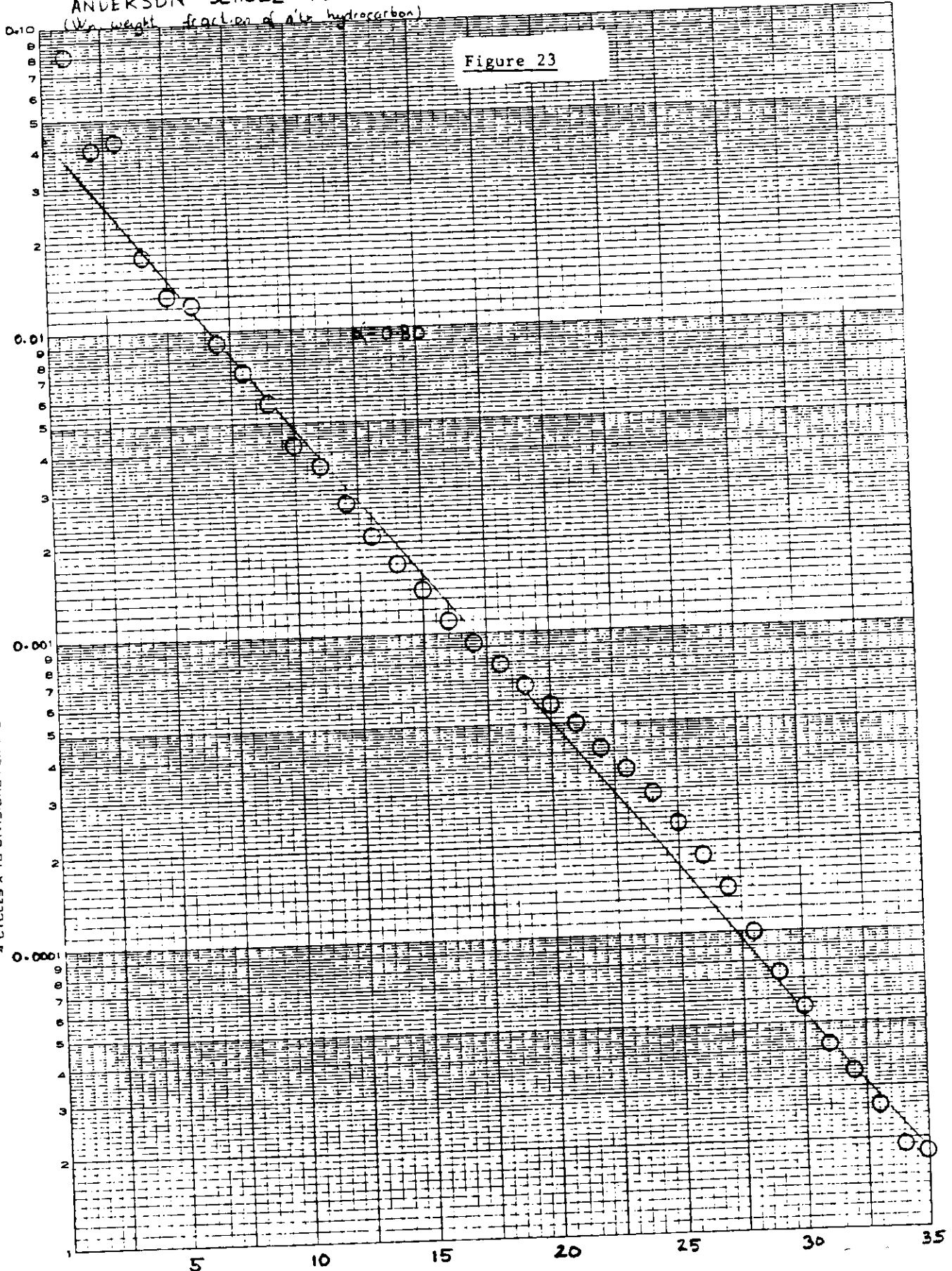
# ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 6 (38-60 HOURS)

( $W_p$  weight fraction of air hydrocarbon)

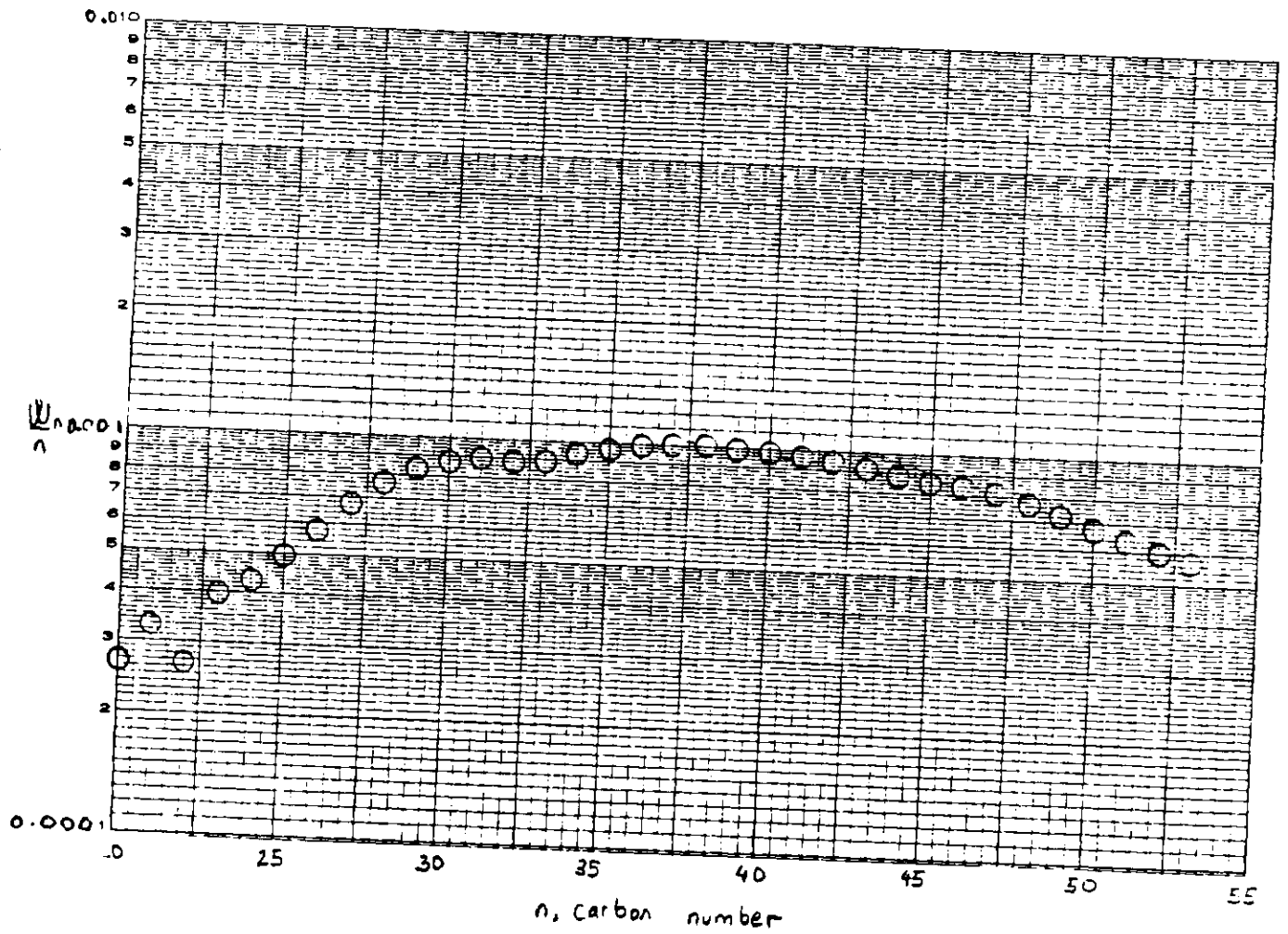
Figure 23

EUGENE DIETZGEN CO.  
MADE IN U.S.A.

NO. 340-L410 DIETZGEN GRAPH PAPER  
SEMI-LOGARITHMIC  
4 CYCLES X 10 DIVISIONS PER INCH

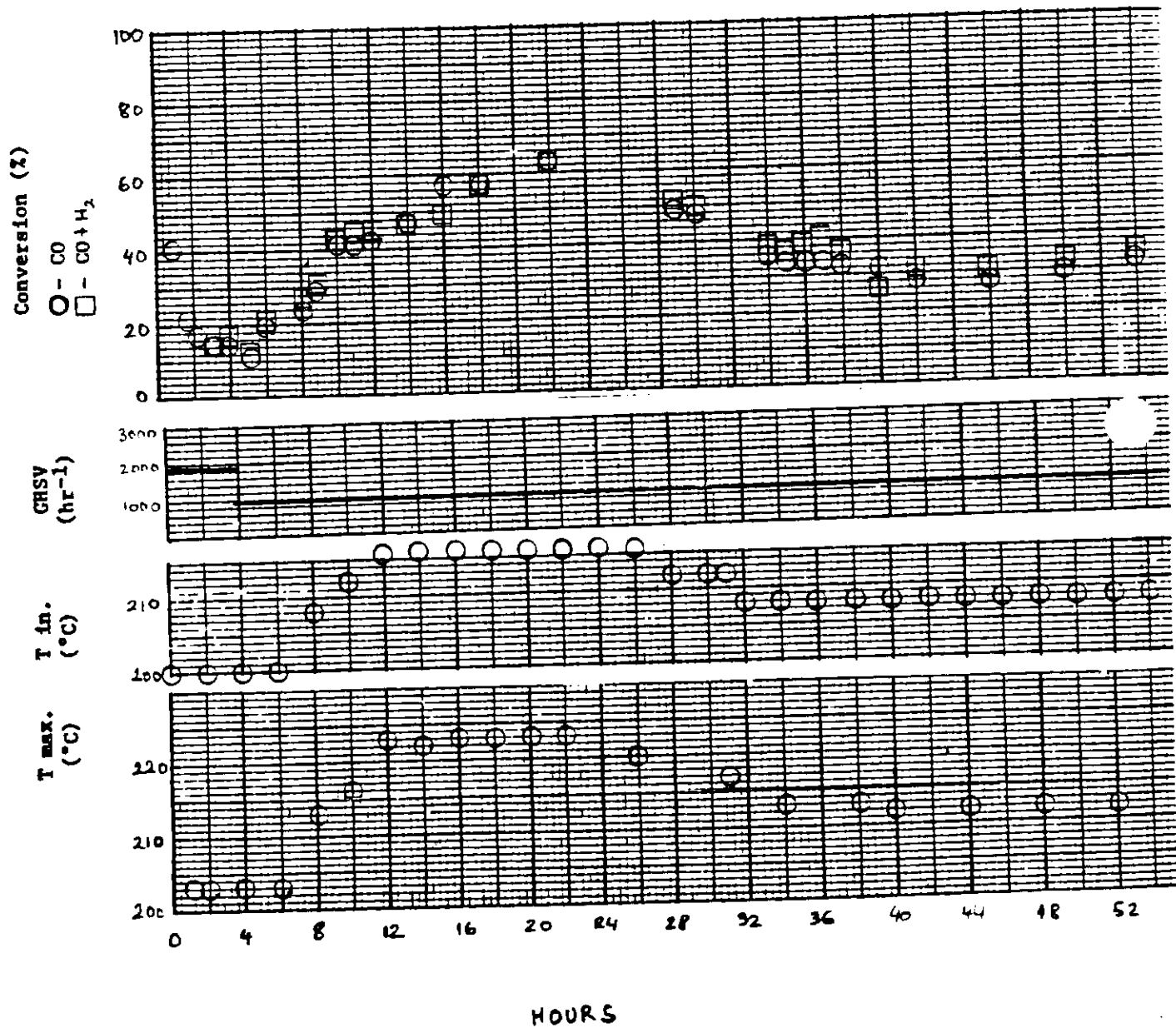


ANDERSON - SCHULZ-FLORY DISTRIBUTION FOR THE WAX EXTRACTED FROM USED CATALYST IN RUN 6 (PLANT 700)



$W_n$ : weight fraction of  $n$ th hydrocarbon in wax

Figure 25

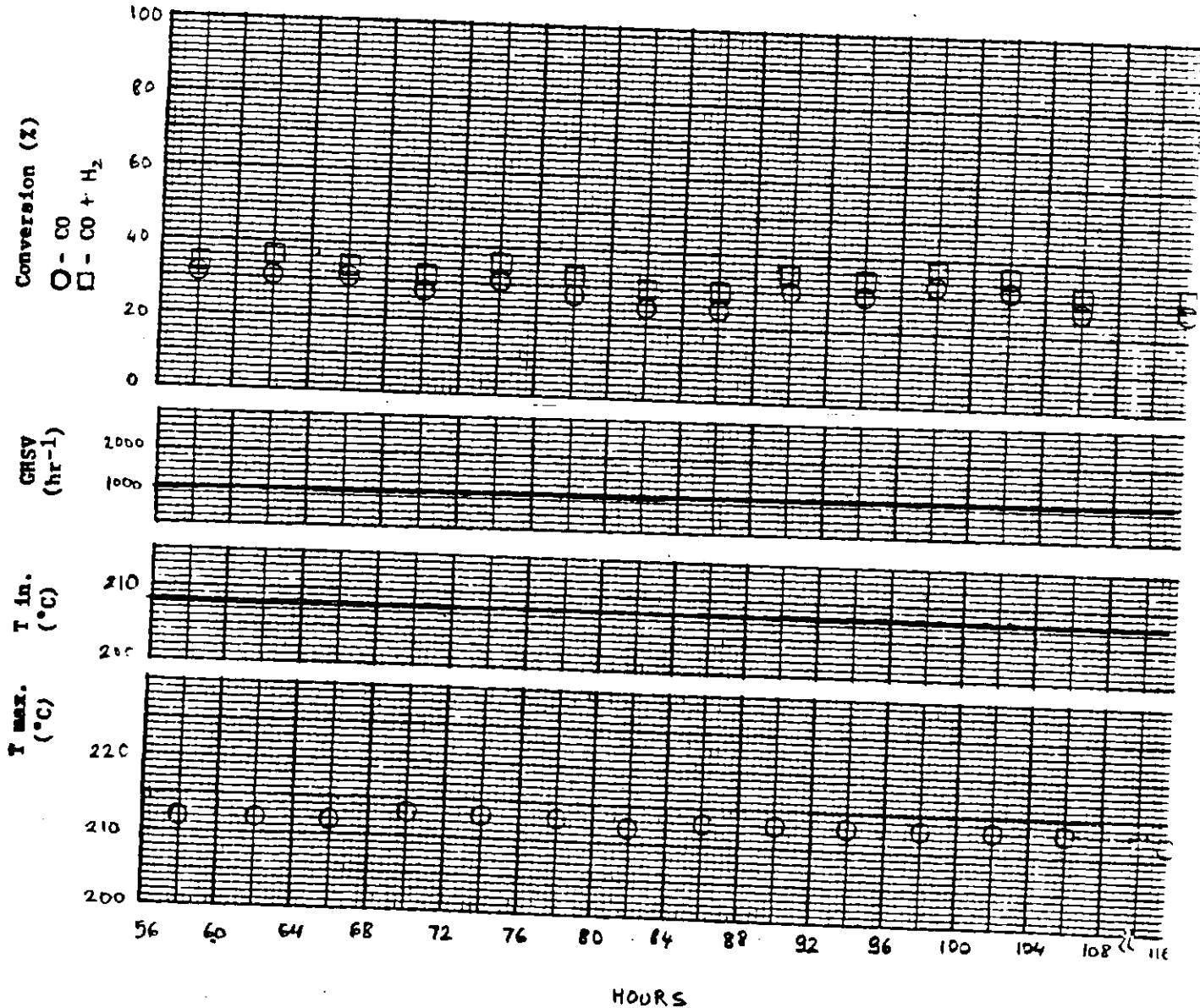
FISCHER-TROPSCH SYNTHESIS (PLANT 700)Run No. 7Catalyst No. 4966-126.42 g reduced C-73 catalyst + 42 g  $\alpha$ - $\text{Al}_2\text{O}_3$  $P = 500$  psig (inlet);  $\text{H}_2/\text{CO} = 0.9$  (feed)

FISCHER-TROPSCH SYNTHESIS (PLANT 700)

Run No. 7

Catalyst No. 4966-12

6.42g of reduced C-73 catalyst + 42g  $\alpha$ - $\text{Al}_2\text{O}_3$   
P = 500 psig (inlet);  $\text{H}_2/\text{CO} = 0.9$  (feed)

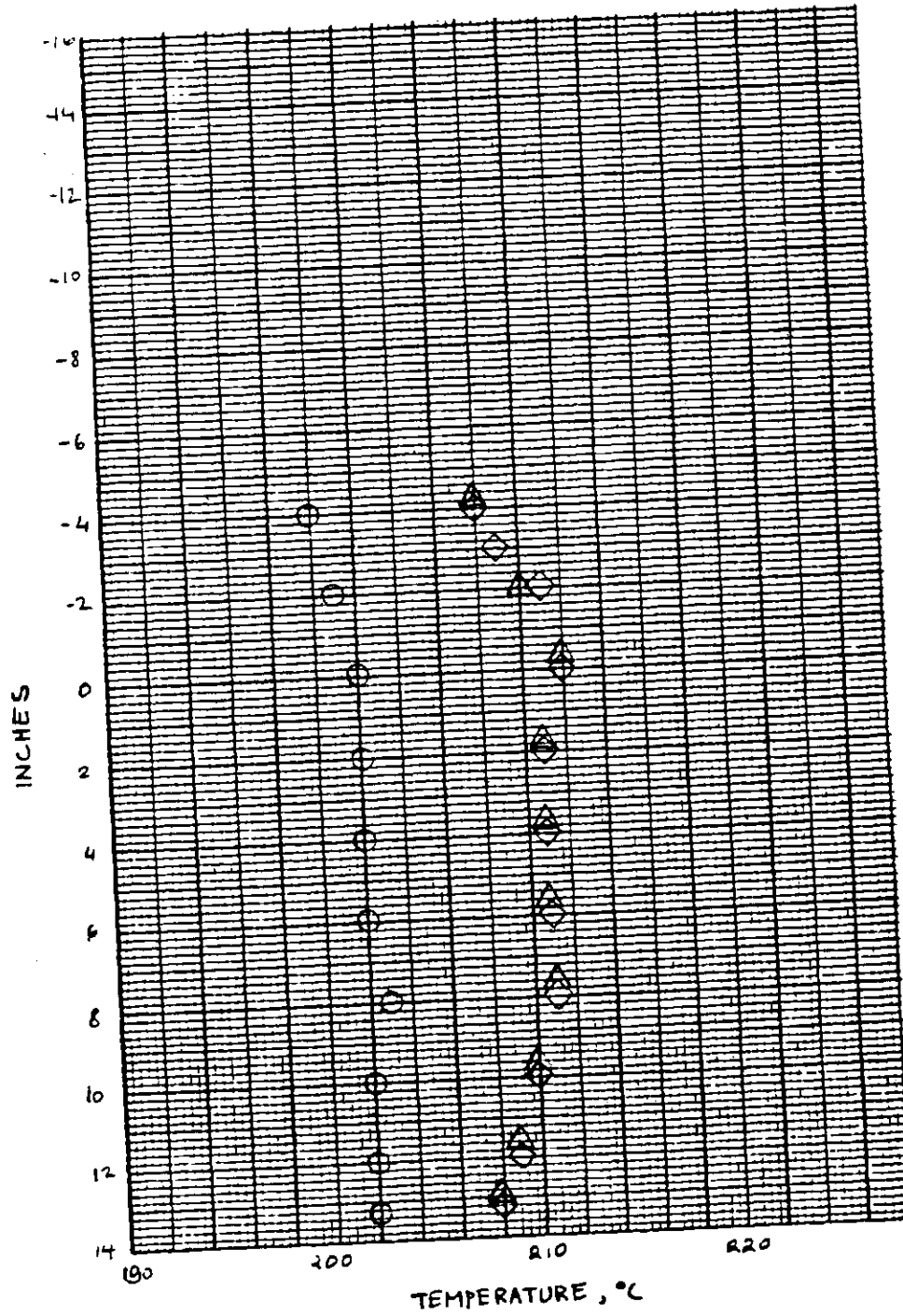


38

TEMPERATURE PROFILE      PLT 700 RUN 7

HOURS ON	BLOCK TEMP, °C		
STREAM	T	M	B
○ H <sub>2</sub> ALONE	201	201	202
△ 40	209	210	210
◇ 116	210	210	210

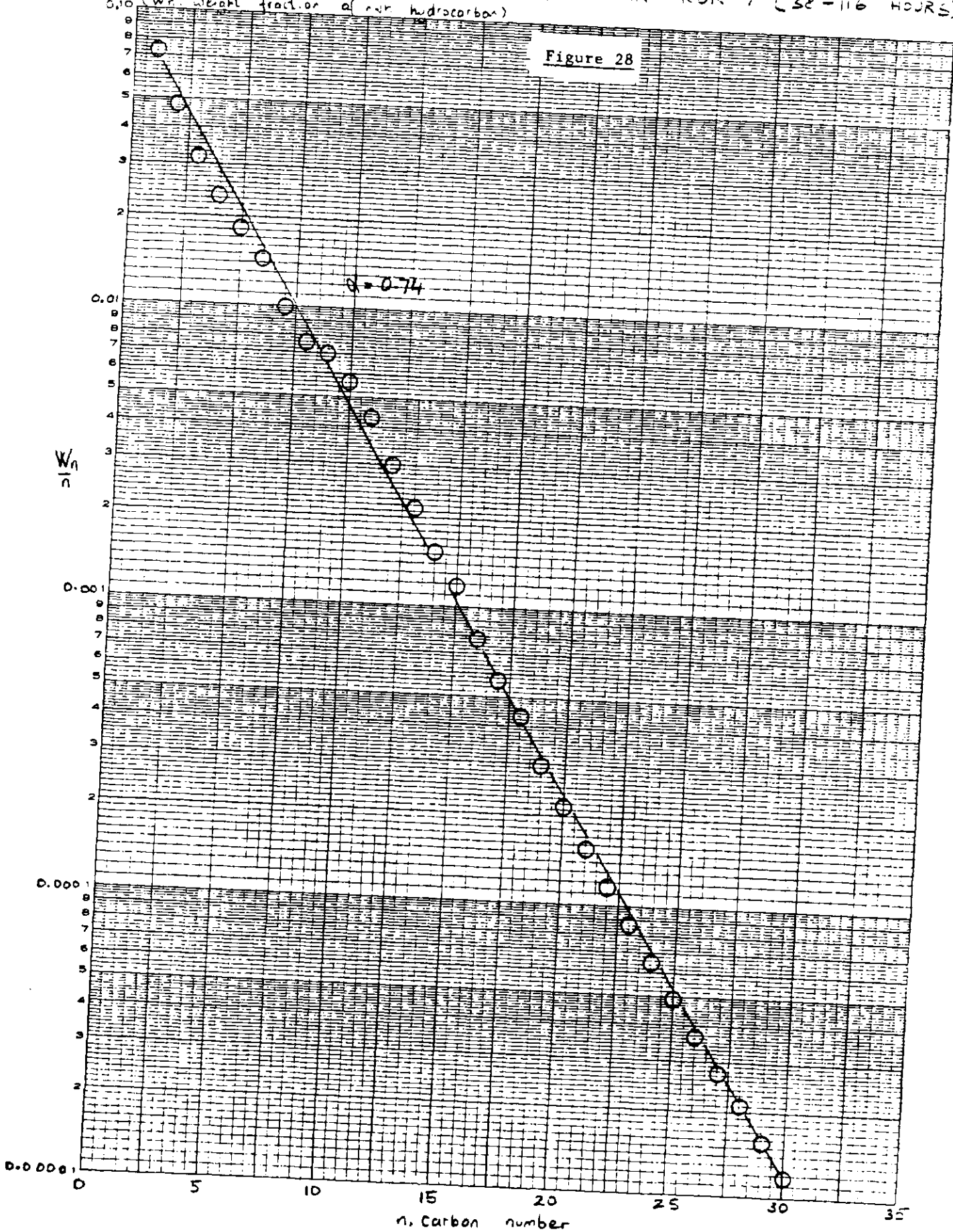
Figure 27



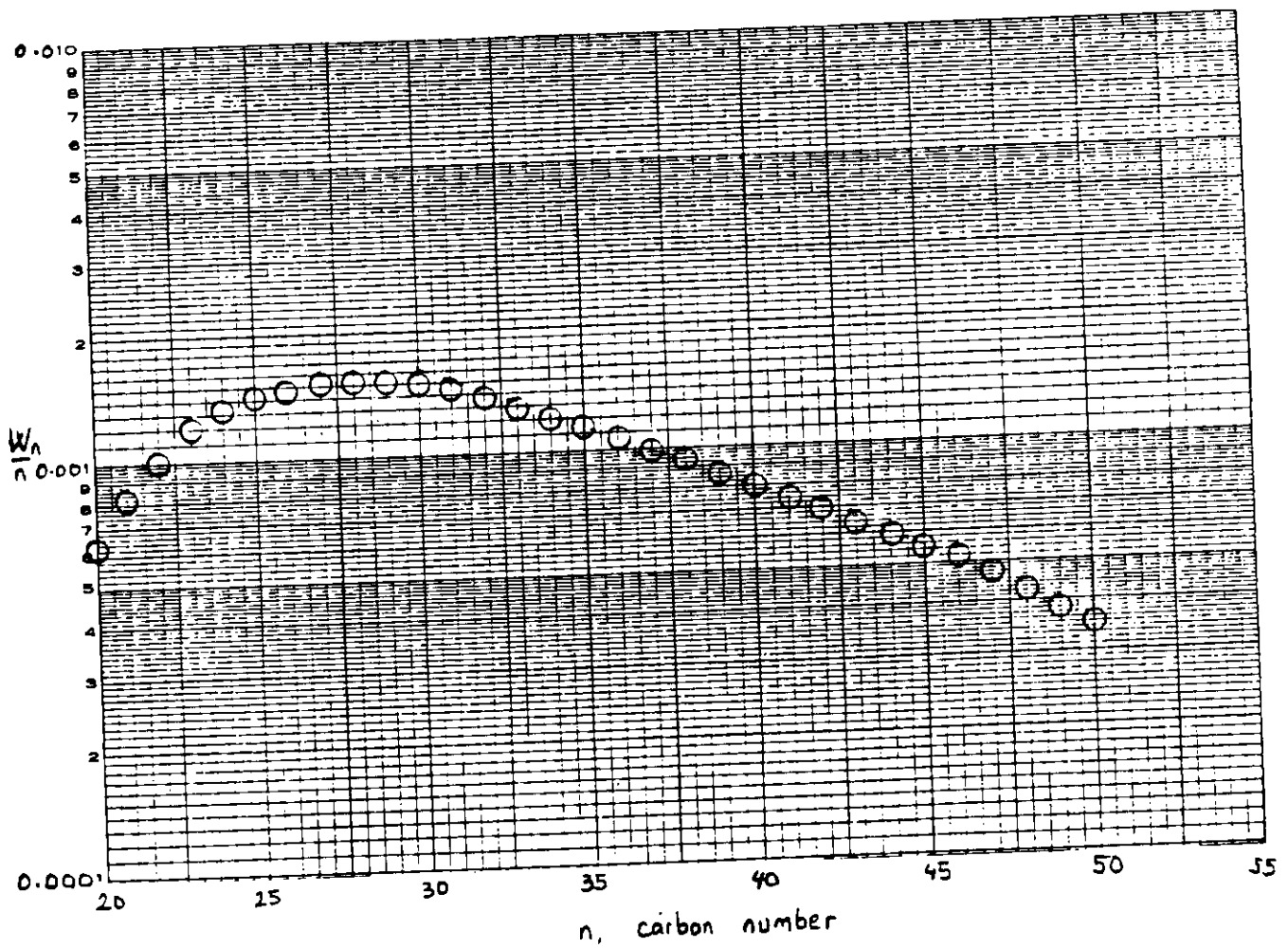


ANDERSON-SCHULZ-FLORY DISTRIBUTION <sup>39</sup>

(W<sub>n</sub> weight fraction of n-alkane hydrocarbon) IN RUN 7 (38-116 HOURS)



ANDERSON SCHULZ-FLORY DISTRIBUTION FOR THE WAX EXTRACTED  
FROM USED CATALYST IN RUN 7 (PLANT 700)



$W_n$ : weight fraction of nth hydrocarbon in wax

Figure 30

## FISCHER-TROPSCH SYNTHESIS (PLANT 700)

Run No. 8Catalyst No. 4966-13

6.42g of reduced C-73 catalyst + 42 g d- $^{11}$ O<sub>2</sub>  
 P = 1500 psig (inlet) ; H<sub>2</sub>/CO = 0.9 (feed)

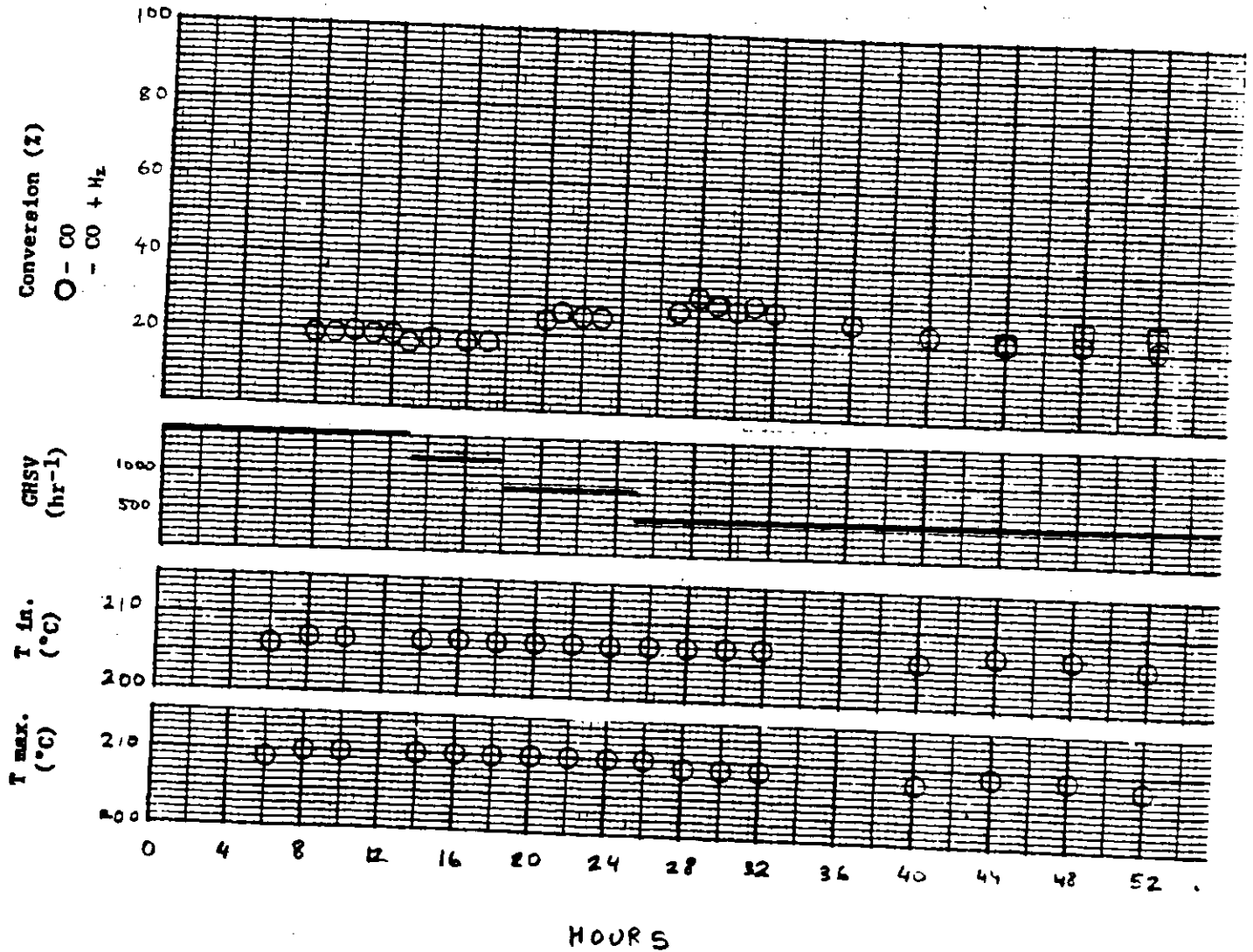
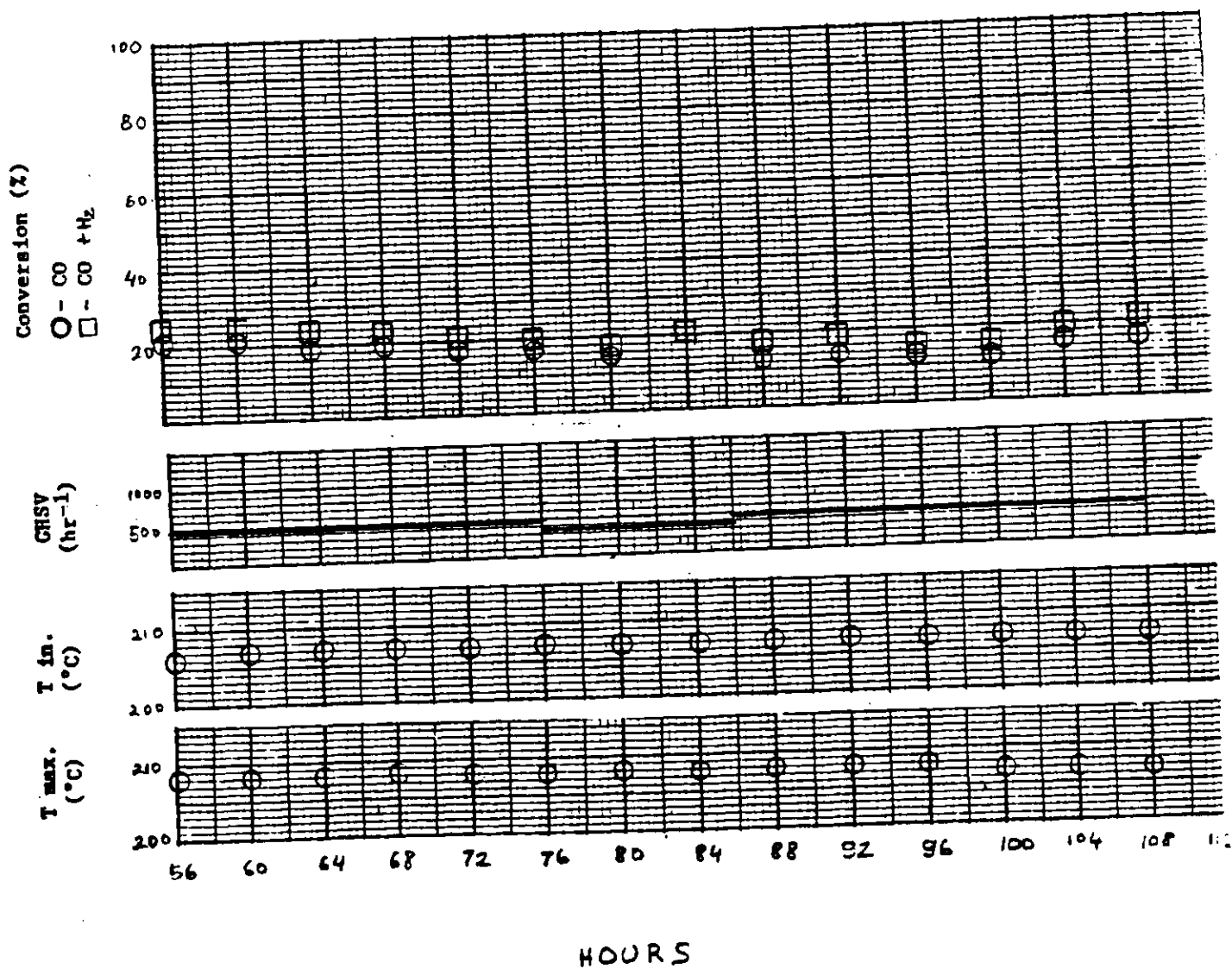


Figure 31

## FISCHER-TROPSCH SYNTHESIS ( PLANT 700 )

Run No. 8Catalyst No. 4966-13

6.42 g of reduced C-73 catalyst + 42 g  $\alpha$ - $Al_2O_3$   
 P = 1500 psig (inlet) ;  $H_2/CO = 0.9$  (feed)



43  
ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 8 (32-108 HOURS)  
( $W_n$ : weight fraction of  $n$ th hydrocarbon)

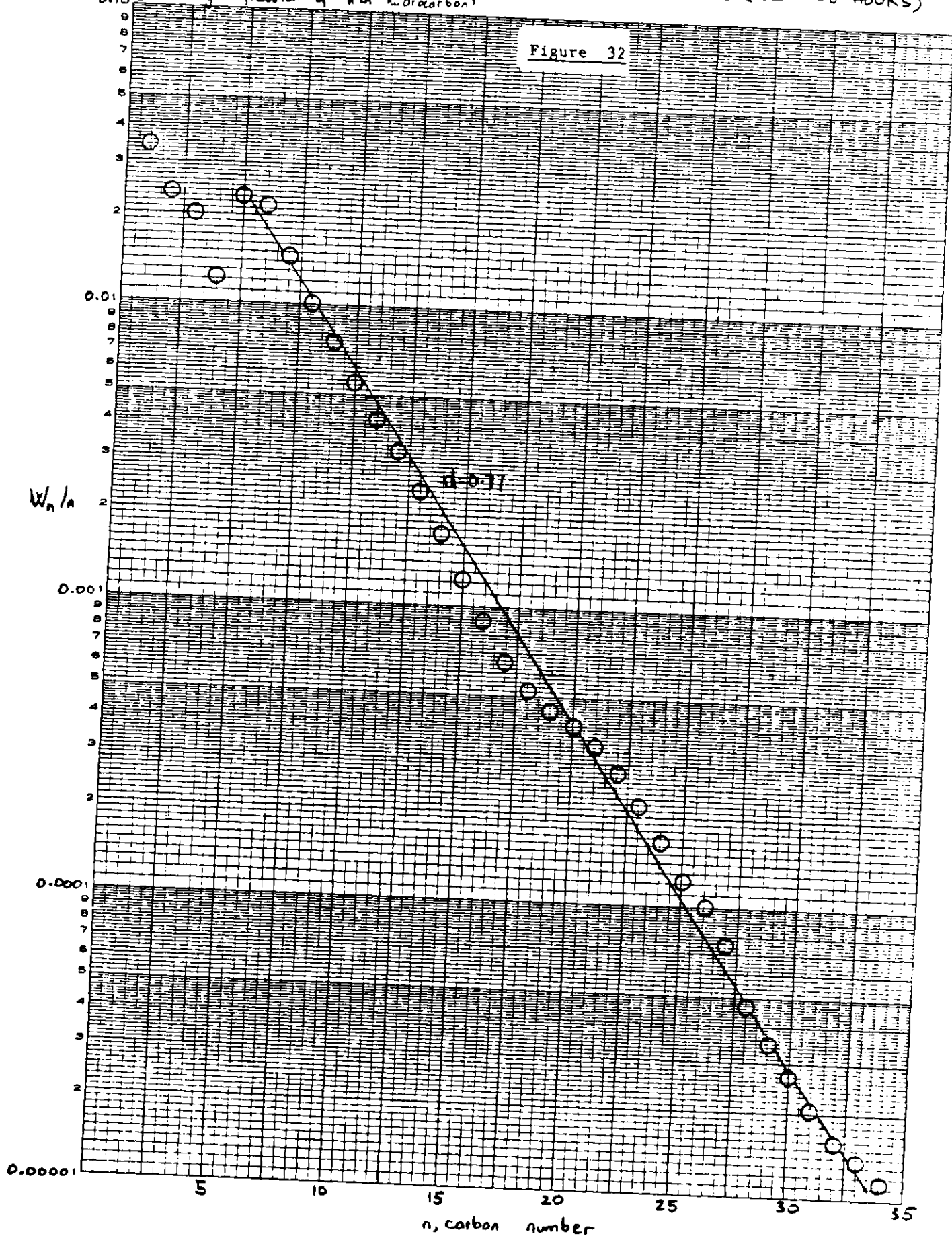
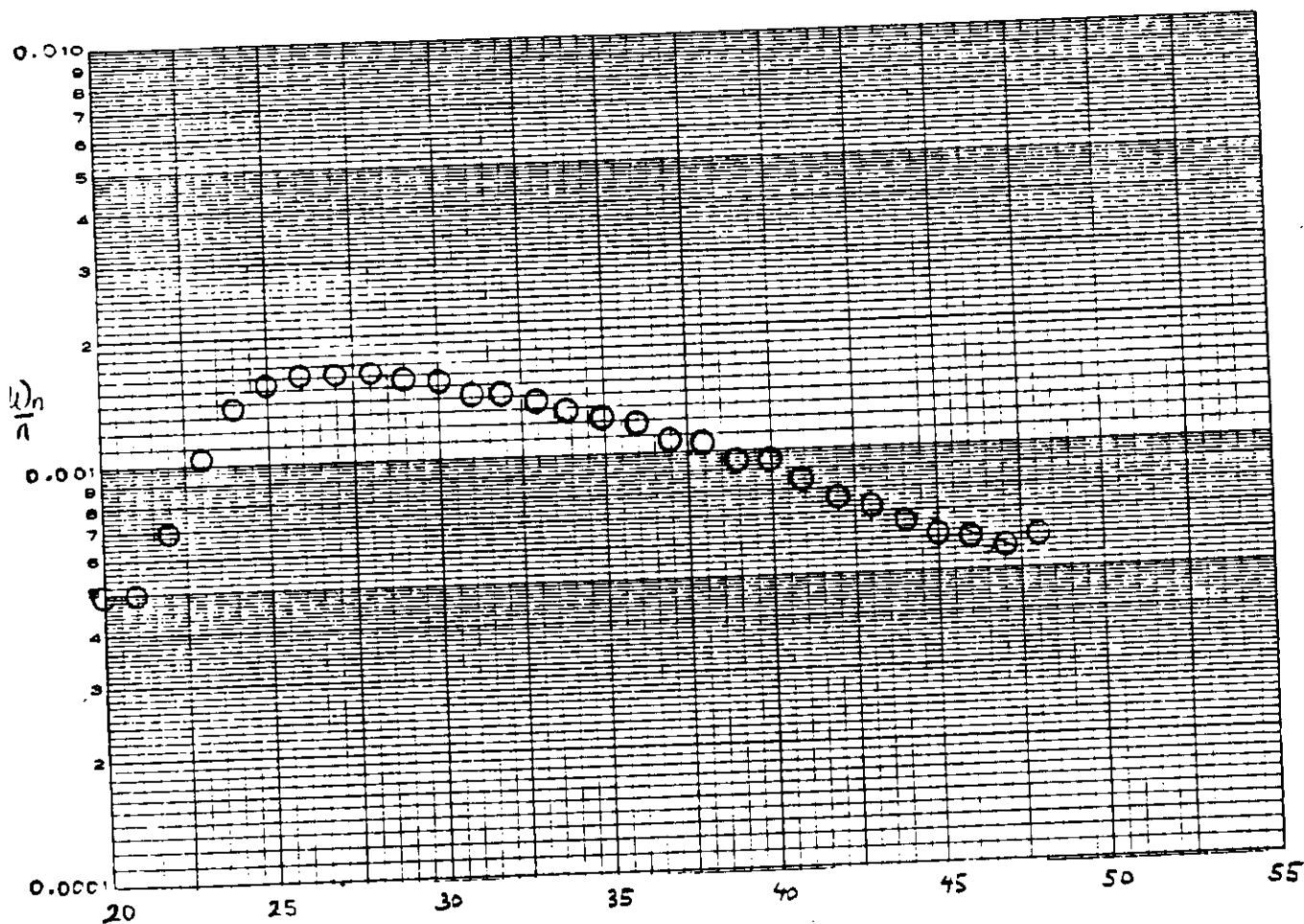


Figure 33

ANDERSON - SCHULZ-FLORY DISTRIBUTION FOR WAX EXTRACTED FROM USED CATALYST IN RUN 8 (PLANT 700)



n, carbon number

$W_n$ : weight fraction of n<sup>th</sup> hydrocarbon in wax

Figure 34

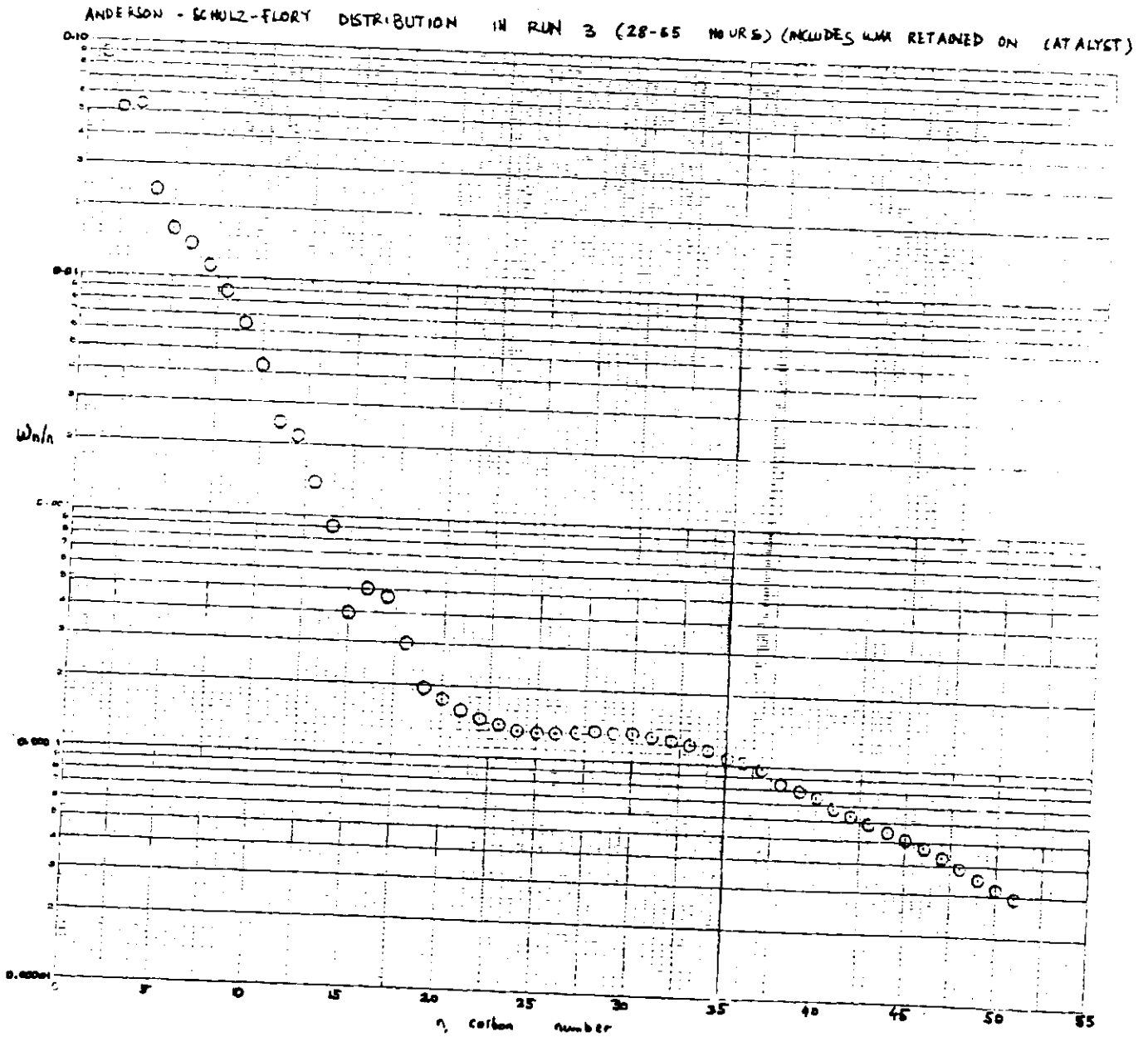
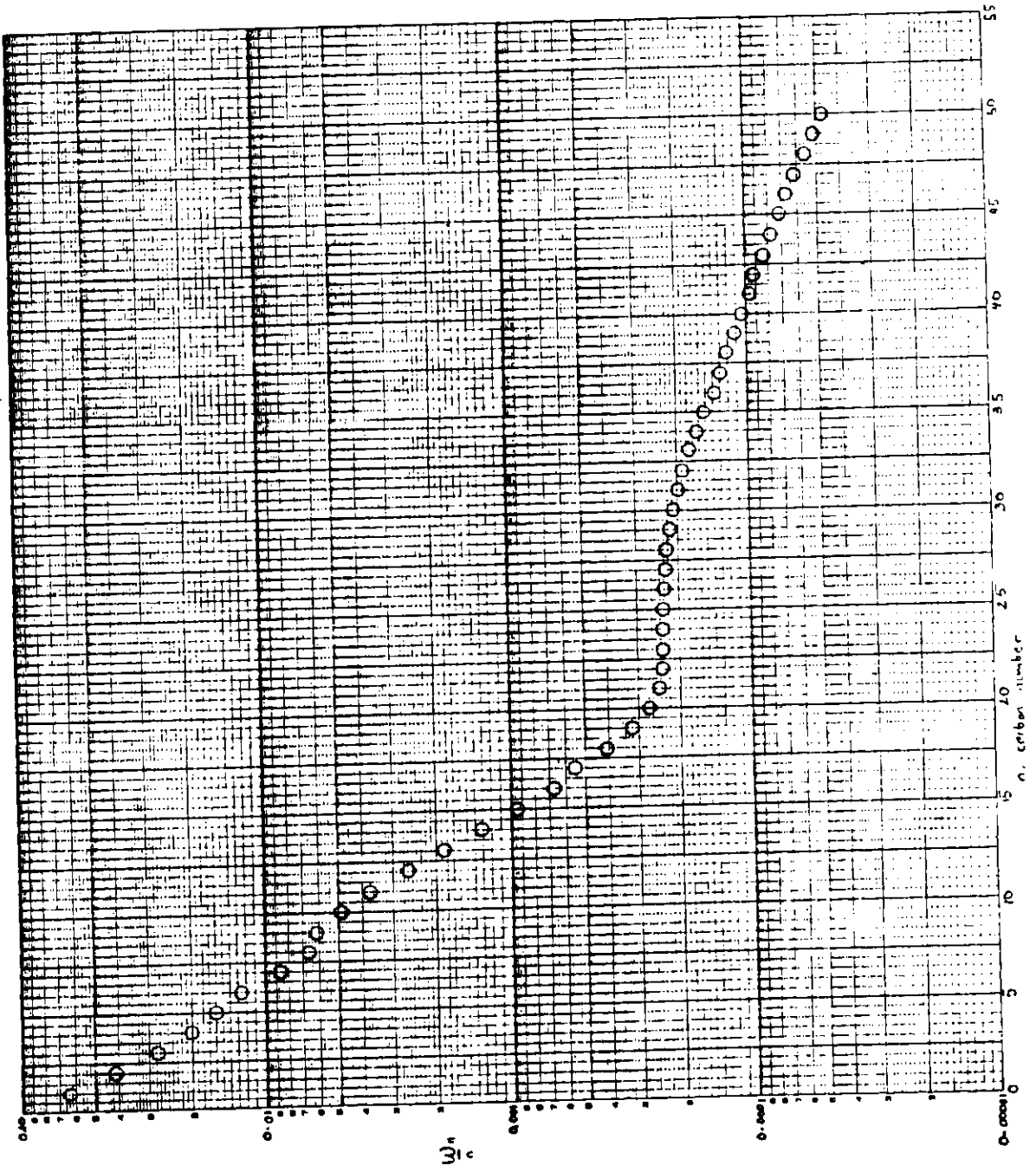


Figure 35

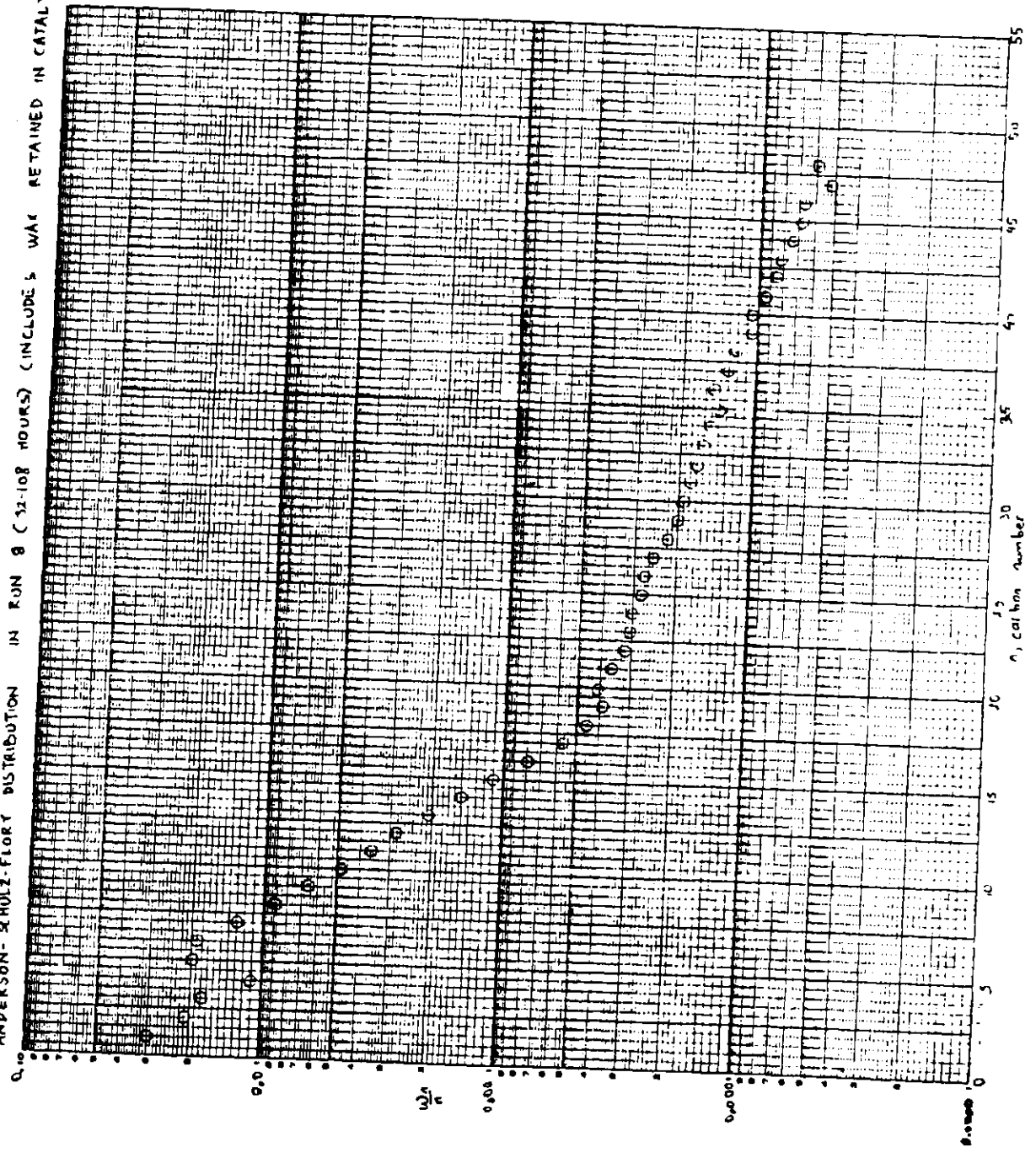
ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 7 (38-116 HOURS) (INCLUDES WAX RETAINED IN CATALYST)



$W_n$ : weight fraction of nth hydrocarbon



Figure 36  
ANDERSON-SCHULZ-FLORY DISTRIBUTION IN RUN 8 (32.108 HOURS) (INCLUDES WATER RETAINED IN CATALYST)



$W_n$ : weight fraction of nth hydrocarbon