5.1.2.2.4 Test Under the Fourth Set of Reference Conditions: 208°C Inlet Temperature, 103 atm, H_2:CO Feed Ratio = 0.9 (Molar), ~25% Initial CO Conversion

No significant temperature increases (1-2°C) were found in Run 8 at 103 atm psig (Table 5-11 and Figures 5-24 through 5-26). Catalytic activity was lower at the higher pressure; therefore, the space velocity was lowered from 950 hr^{-1} GHSV in Run 7 to 475 hr^{-1} GHSV in order to maintain about the same conversion level as in Run 7 (Figure 5-24). Feed rates were overestimated, as in Run 7. After the feed rates were corrected by the ratio of recovered to fed argon, the material balance became 103.9%.

The initial CO conversion was 25% at 32 hours on stream (the beginning of line-out period), but it decreased to 12-15% by the end of the run at 108 hours on stream (Figures 5-24 and 5-25). The H_2:CO usage ratio was 1.4, less than that at 35 atmospheres. The Anderson-Schulz-Flory distribution for hydrocarbons and oxygenates recovered during the run indicated that the C_1-C_4 hydrocarbons may not have been analyzed accurately. An α value of 0.77 was calculated from products with carbon numbers greater than 4 (Figure 5-26).

5.1.2.2.5 Analyses of Wax Fractions Extracted from Used Catalysts

The wax fractions extracted from the used catalysts with toluene at the end of Runs 3, 6, 7, and 8 were not included in calculating the overall product distributions and unique α's were obtained up to a carbon number of 35. Here, it was assumed that these wax fractions were mostly made during the early part of the runs 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. Calculations were done by assuming that the wax on

Table 5-11. Product Distributions in Run 8

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	4.44	39.98
CO	78.63	51.00
CO2	5.02	2.07
H2O	5.00	5.04
HYDROCARBON	6.60	1.83
ALCOHOL	0.23	0.08

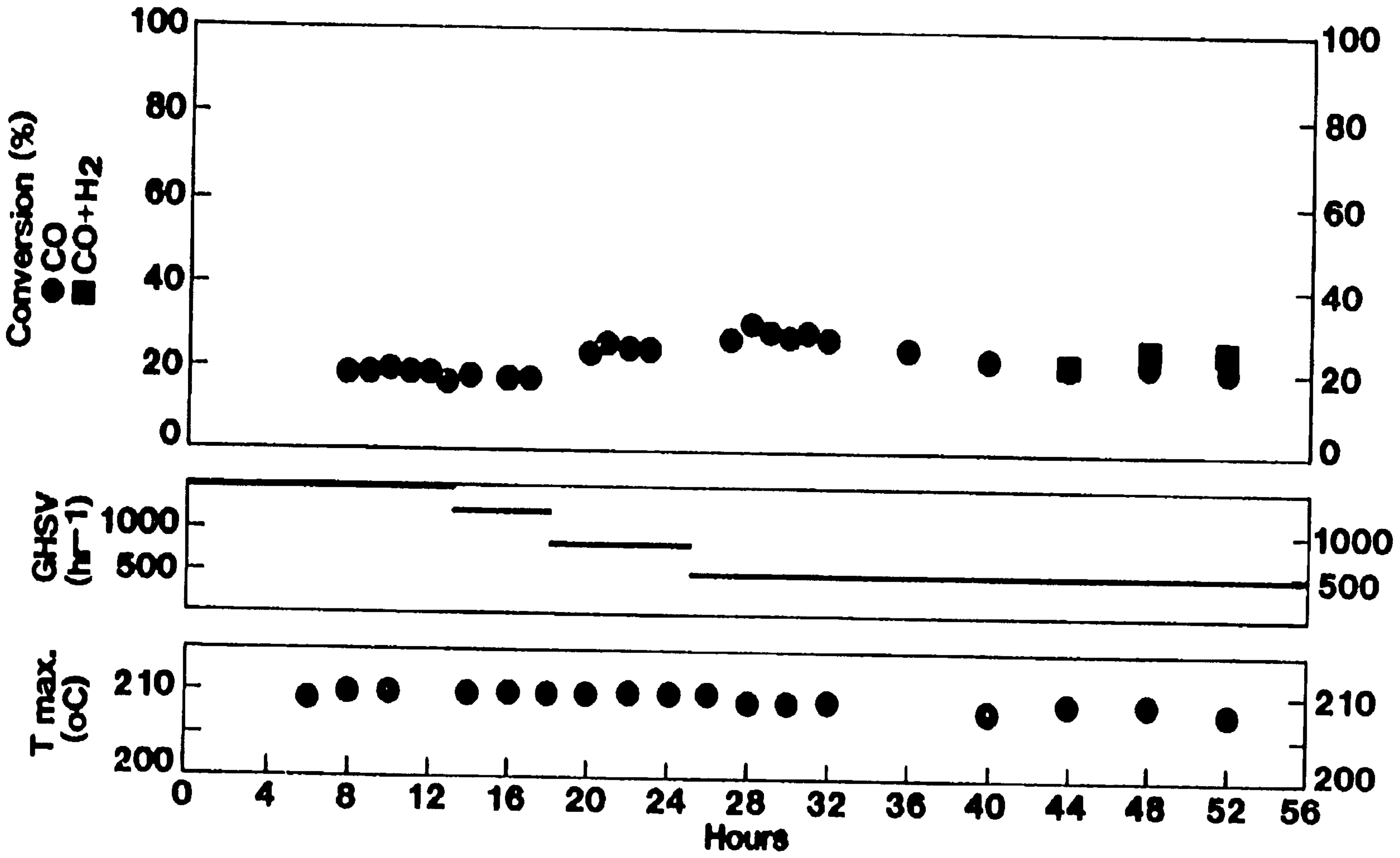
ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	11.45	20.15
ETHANOL	28.32	34.67
PROPANOL	4.77	4.48
BUTANOL	43.06	32.76
OTHER OXYGENATES	12.40	7.93

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %	COMPONENT	WEIGHT %	MOLE %
CH4	4.30	17.72	C25	0.01	0.00
C2-C4	19.09	31.12	C26	0.00	0.00
C5-C11	70.78	49.09	C27	0.00	0.00
C12-C18	5.54	2.01	C28	0.00	0.00
C19-C25	0.20	0.04	C29	0.00	0.00
C26+	0.09	0.01	C30	0.00	0.00
			C31	0.00	0.00
CH4	4.30	17.72	C33	0.00	0.00
C2P	2.59	5.70	C34	0.00	0.00
C2=	2.70	6.36	C35	0.00	0.00
C3	0.26	0.40	C36	0.05	0.01
C3P	3.83	5.74	C37	0.00	0.00
C3=	3.92	6.16	C38	0.00	0.00
C4	1.81	2.09	C39	0.00	0.00
C4P	0.94	1.07	C40	0.04	0.01
C4=	3.06	3.61	C41	0.00	0.00
C5	15.42	14.34	C42	0.00	0.00
C6	16.05	12.47	C43	0.00	0.00
C7	12.65	8.44	C44	0.00	0.00
C8	9.65	5.64	C45	0.00	0.00
C9	7.63	3.97	C46	.	.
C10	5.53	2.59	C47	.	.
C11	3.85	1.64	C48	.	.
C12	2.58	1.01	C49	.	.
C13	1.50	0.54	C50	.	.
C14	0.78	0.26	C51	.	.
C15	0.34	0.11	C52	.	.
C16	0.18	0.05	C53	.	.
C17	0.09	0.02	C54	.	.
C18	0.06	0.02	C55	.	.
C19	0.05	0.01	C56	.	.
C20	0.04	0.01	C57	.	.
C21	0.03	0.01	C58	.	.
	0.02	0.00		.	.
	0.02	0.00		.	.
C24	0.02	0.00			

Figure 5-24. C-73-1-101 Iron Catalyst Test Under the Fourth Set of Reference Conditions in Run 8 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 103 atm, 0-56 Hours)



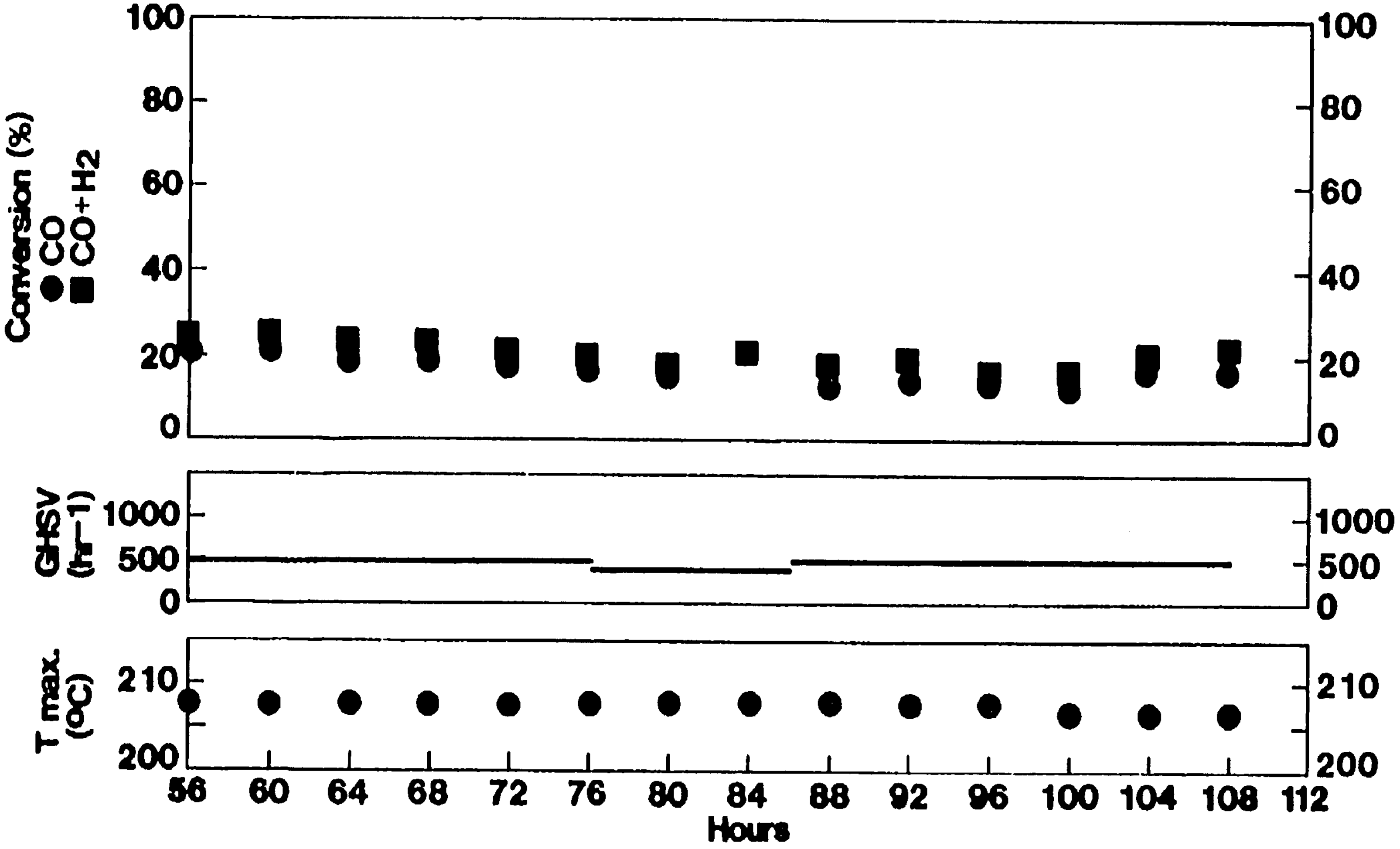
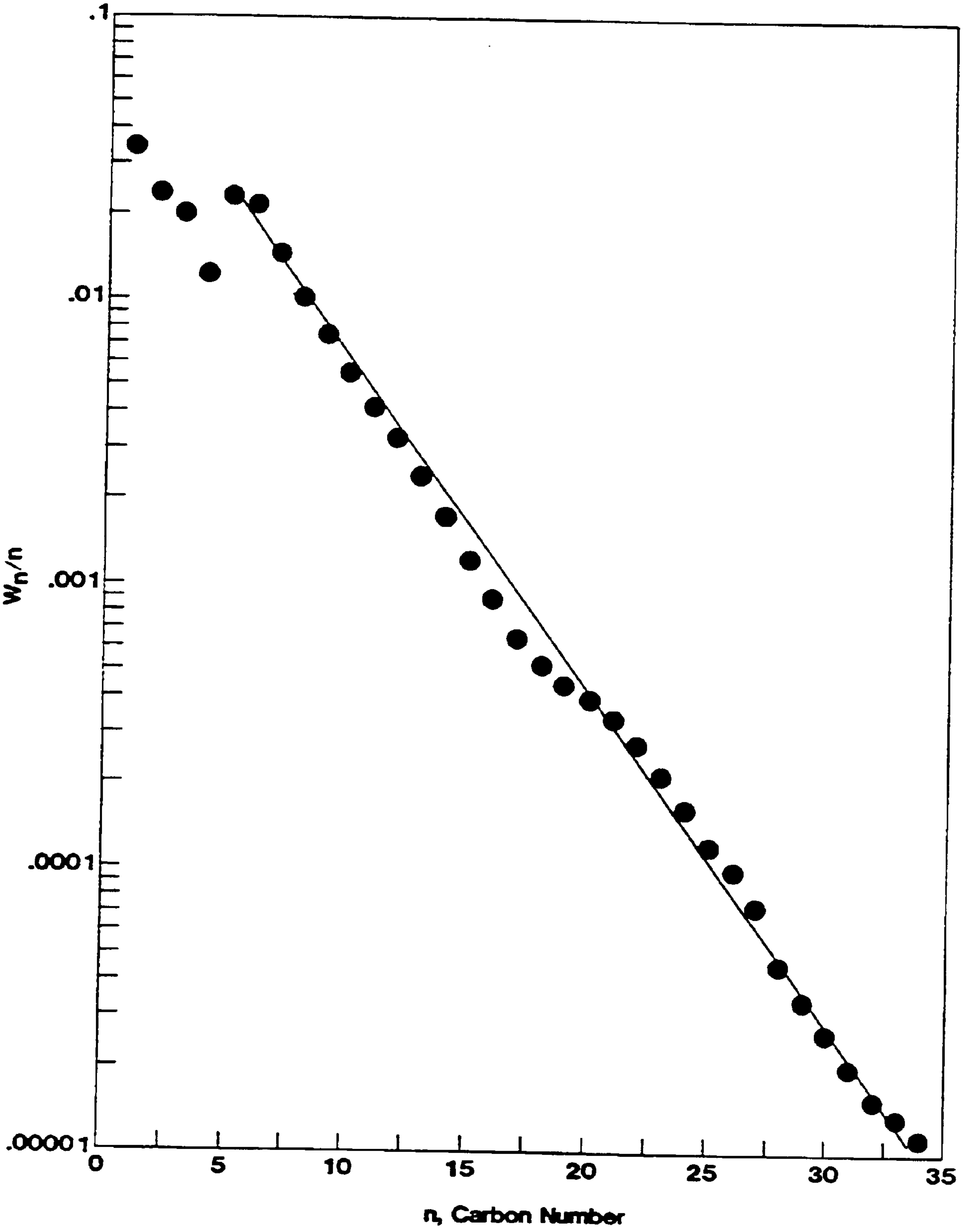


Figure 5-25. C-73-1-101 Iron Catalyst Test Under the Fourth Set of Reference Conditions in Run 8 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 103 atm, 56-112)

Figure 5-26. Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Fourth Set of Reference Conditions in Run 8 (Hydrocarbons + Oxygenates, 32-108 Hours)



the catalyst accumulated linearly with time during the whole course of the run. These new plots all showed two different α's, a small one at carbon numbers less than 20, and a large one at carbon numbers greater than 20. An example of such an Anderson-Schulz-Flory plot for Run 3 is in Figure 5-27.

5.1.2.2.6 Repeated Test Under the Third Set of Reference Conditions

The reduced C-73-1-101 catalyst was tested again in Run 10 after it was tested in Run 7 under the third set of operating conditions: 208°C, 35 atm, 0.9 H_2:CO feed ratio, ~30% initial CO conversion. The space velocity in Run 10 was 1140 hr^{-1} GHSV compared to 950 hr^{-1} GHSV in Run 7.

In Run 10 the feed rates were not changed throughout the entire 252 hours, and the product analyses included all products made during the run, including the wax retained on the catalyst. The results are described in Table 5-12 and Figures 5-28 through 5-34. During the run, the catalyst temperature increase above the inlet temperature was 1-2°C. The total recovery was 92.7%. The material balance became 99.5% after the feed rates were corrected by the ratio of recovered to fed argon.

The CO conversion was initially 50% and then remained between 20 and 25% after 50 hours on stream (Figure 5-29). This value is 5-10% lower than the value obtained in Run 7, probably because of the slightly higher space velocity used in Run 10.

The average H_2:CO usage ratio was 1.4. Analysis of carbon atom selectivities during the run indicated that the selectivity of CO to CO_2 was steady at 25-30% (Figure 5-30). Similarly, the selectivity of CO to each of the paraffinic or olefinic light hydrocarbons, C_1-C_4, remained steady (Figures 5-31 through 5-33). These indicate that the selectivity of CO to liquid + wax products also remained steady.

gure 5-27. Anderson-Schulz-Flory Distribution with C-73-1-101 Iron Catalyst Under the First Set of Reference Conditions in Run 3, (Includes Wax Retained on the Catalyst, 28-55 Hours)

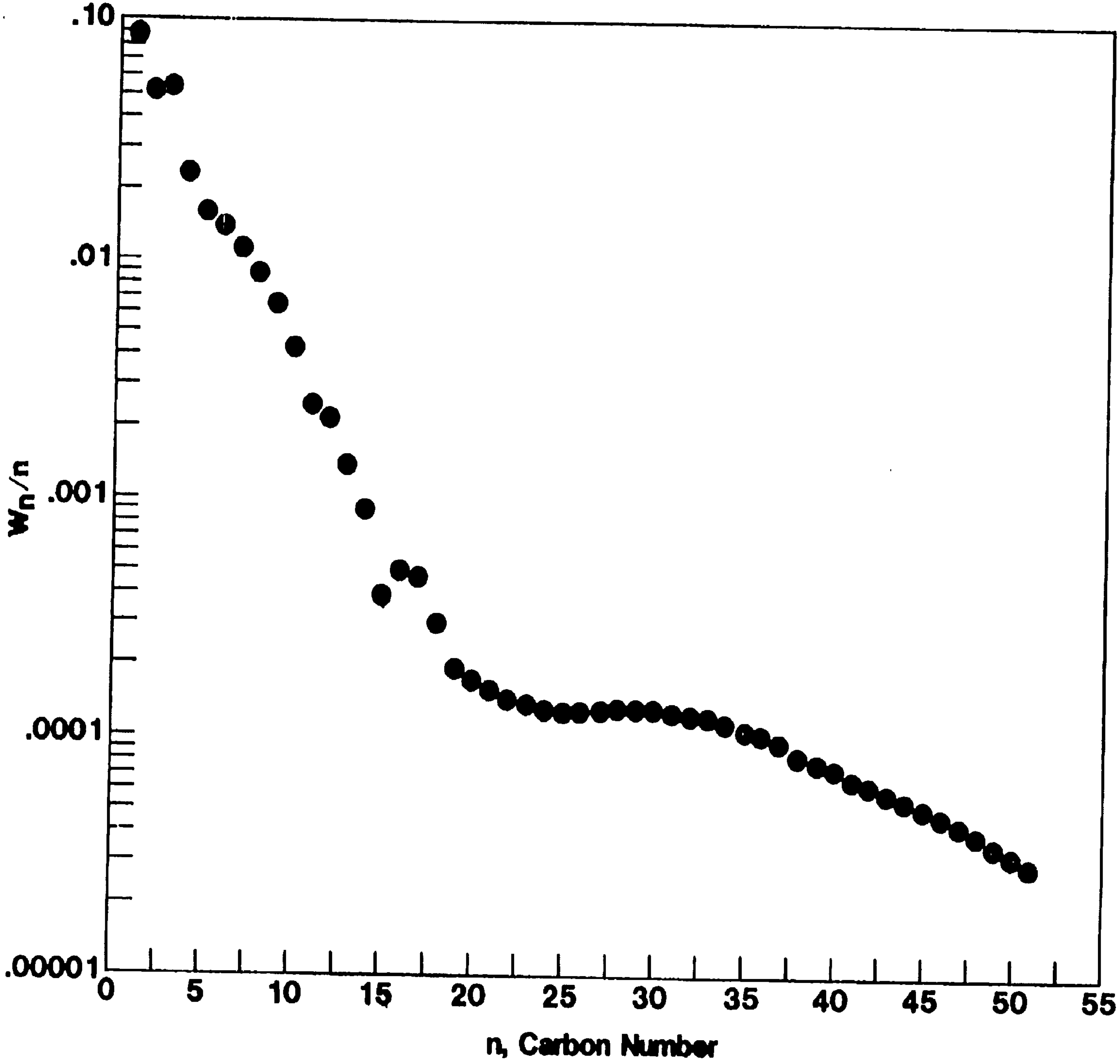


Table 5-12. Product Distributions in Run 10 <u>(doesn't take into account GPC analysis)</u>

PILOT PLANT NO. 700	RUN NO.	10	TEST NO. 1	R U N	S U M M A R Y	R E P O R T
BOOK NO.	CATALYST NO.	4966-34	BEGINNING DATE	18FEB1985	END OF TEST DATE	20FEB1985

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.77	36.90
CO	71.92	50.60
CO2	9.84	4.41
H2O	4.85	5.31
HYDROCARBON	9.03	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	5.73	24.83
C2-C4	22.73	39.38
C5-C11	39.28	27.39
C12-C18	15.90	5.48
C19-C25	7.21	1.67
C26+	9.15	1.26
CH4	5.73	24.83
C2P	2.08	4.81
C2=	4.73	11.71
C3	0.13	0.21
C3P	2.67	4.21
C3=	5.59	9.23
C4	1.41	1.71
C4P	2.34	2.80
C4=	3.78	4.69
C5	8.25	8.06
C6	6.51	5.31
C7	5.45	3.82
C8	5.61	3.45
C9	5.27	2.88
C10	4.48	2.20
C11	3.71	1.66
C12	3.11	1.28
C13	2.71	1.03
C14	2.43	0.86
C15	2.24	0.74
C16	2.04	0.63
C17	1.78	0.52
C18	1.59	0.44
C19	1.44	0.37
C20	1.28	0.32
C21	1.18	0.28
C22	1.01	0.23
C23	0.89	0.19
C24	0.76	0.16

COMPONENT	WEIGHT %	MOLE %
C25	0.65	0.13
C26	0.58	0.11
C27	0.50	0.09
C28	0.46	0.08
C29	0.43	0.07
C30	0.39	0.06
C31	0.37	0.06
C33	0.34	0.05
C34	0.32	0.05
C35	0.31	0.04
C36	0.30	0.04
C37	0.28	0.04
C38	0.28	0.04
C39	0.27	0.03
C40	0.26	0.03
C41	0.25	0.03
C42	0.24	0.03
C43	0.23	0.03
C44	0.22	0.02
C45+	3.14	0.34
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.

gure 5-28. C-73-1-101 Iron Catalyst CO+H_2 Conversion Under the Third Set of Reference Conditions in Run 10

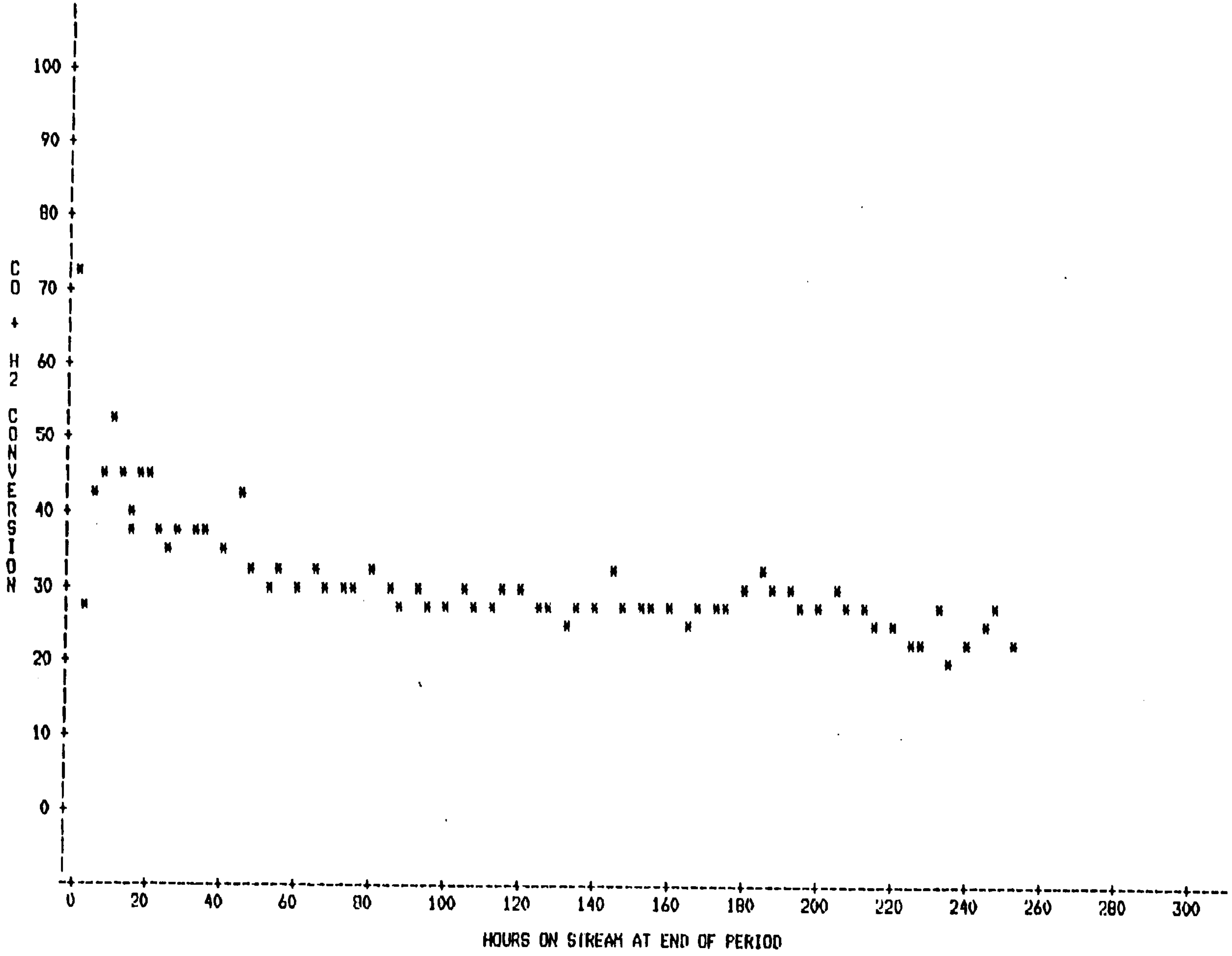


Figure 5-29. C-73-1-101 Iron Catalyst CO Conversion Under the Third Set of Reference Conditions in Run 10

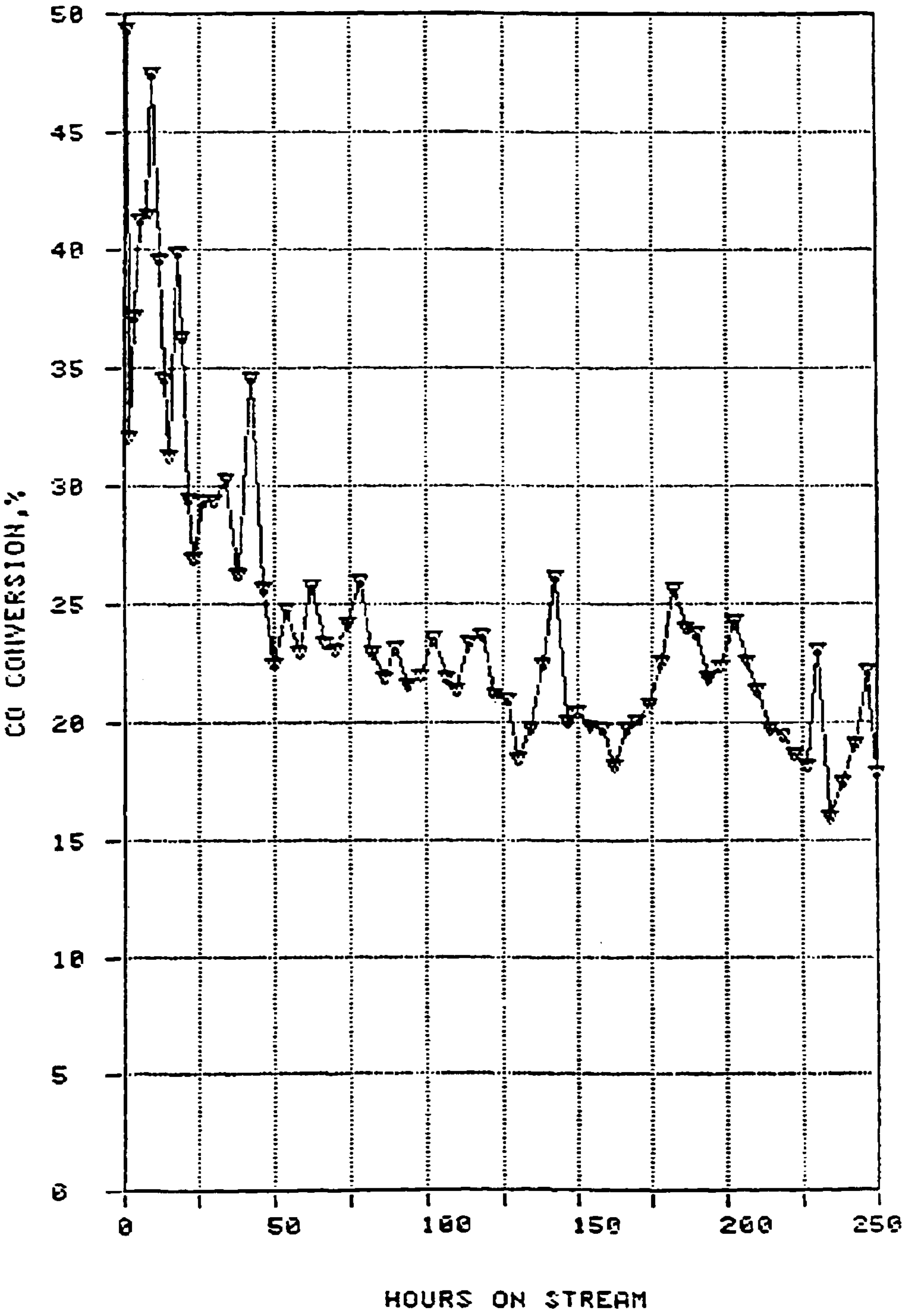


Figure 5-30. C-73-1-101 Iron Catalyst CO_2 Selectivity Under the Third Set of Reference Conditions in Run 10

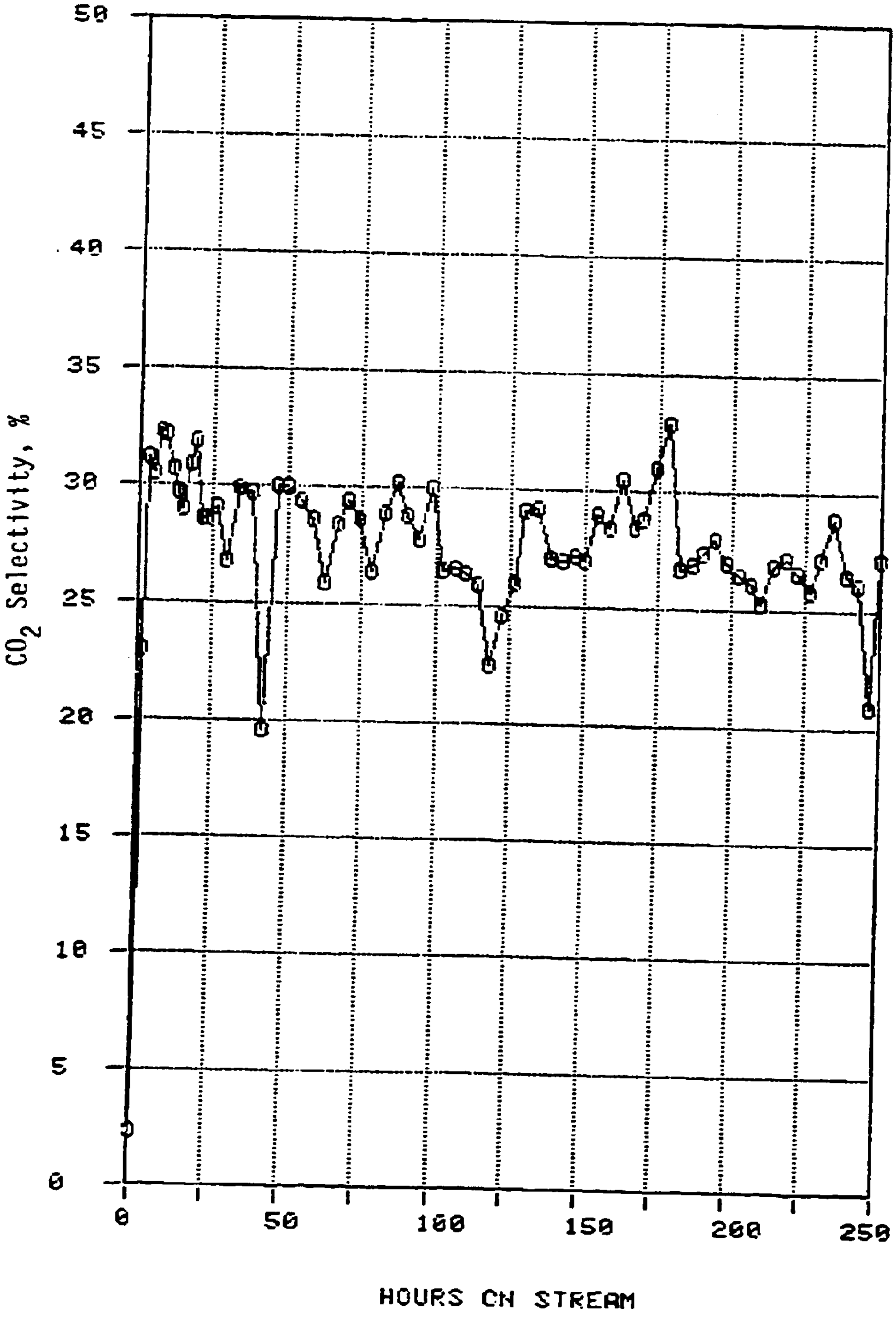


Figure 5-31. C-73-1-101 Iron Catalyst C_1 and C_2 Selectivities Under The Third Set of Reference Conditions in Run 10

△ C_1 □ C_2

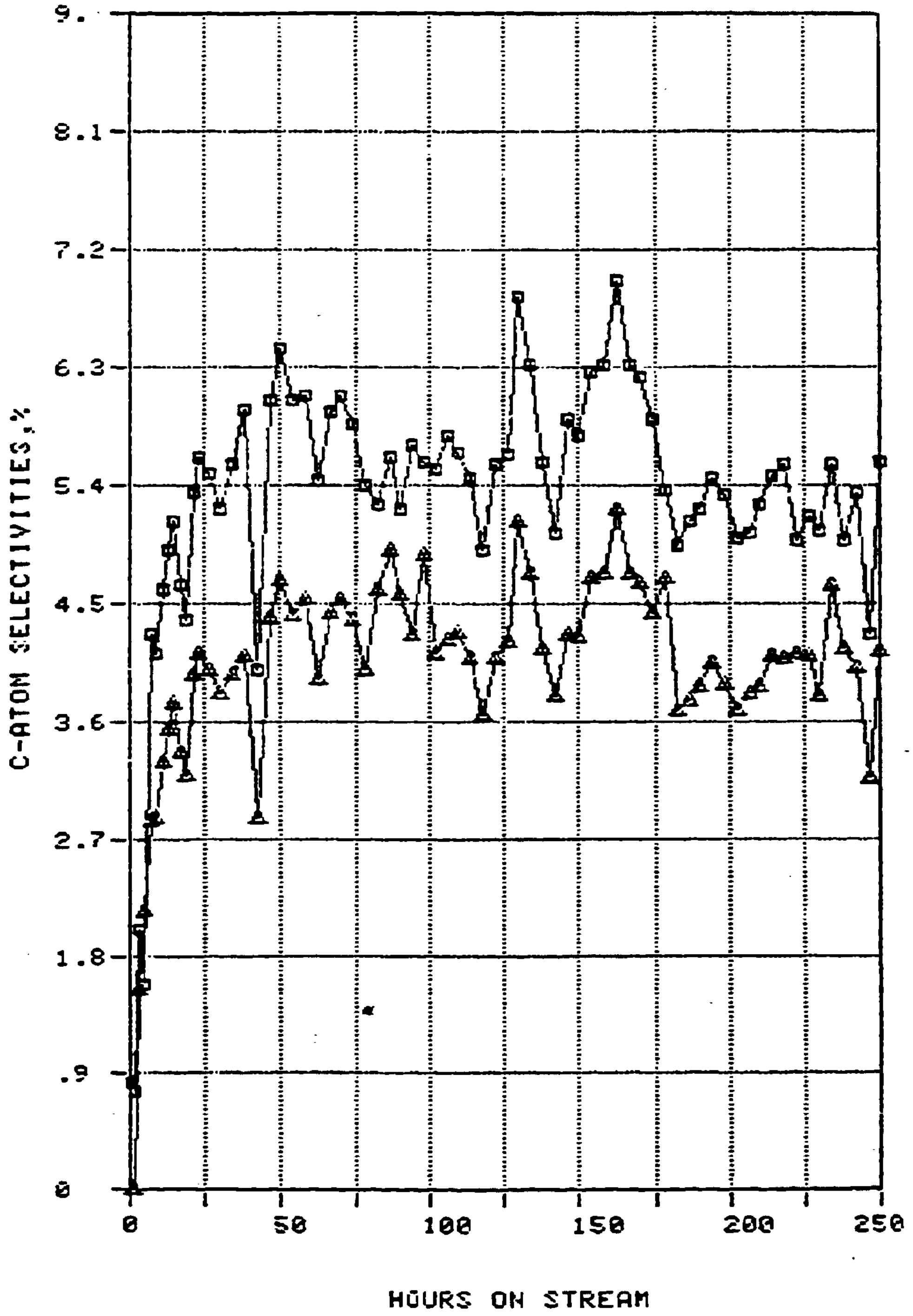


Figure 5-32. C-73-1-101 Iron Catalyst C_3 and C_4 Selectivities Under the Third Set of Reference Conditions in Run 10

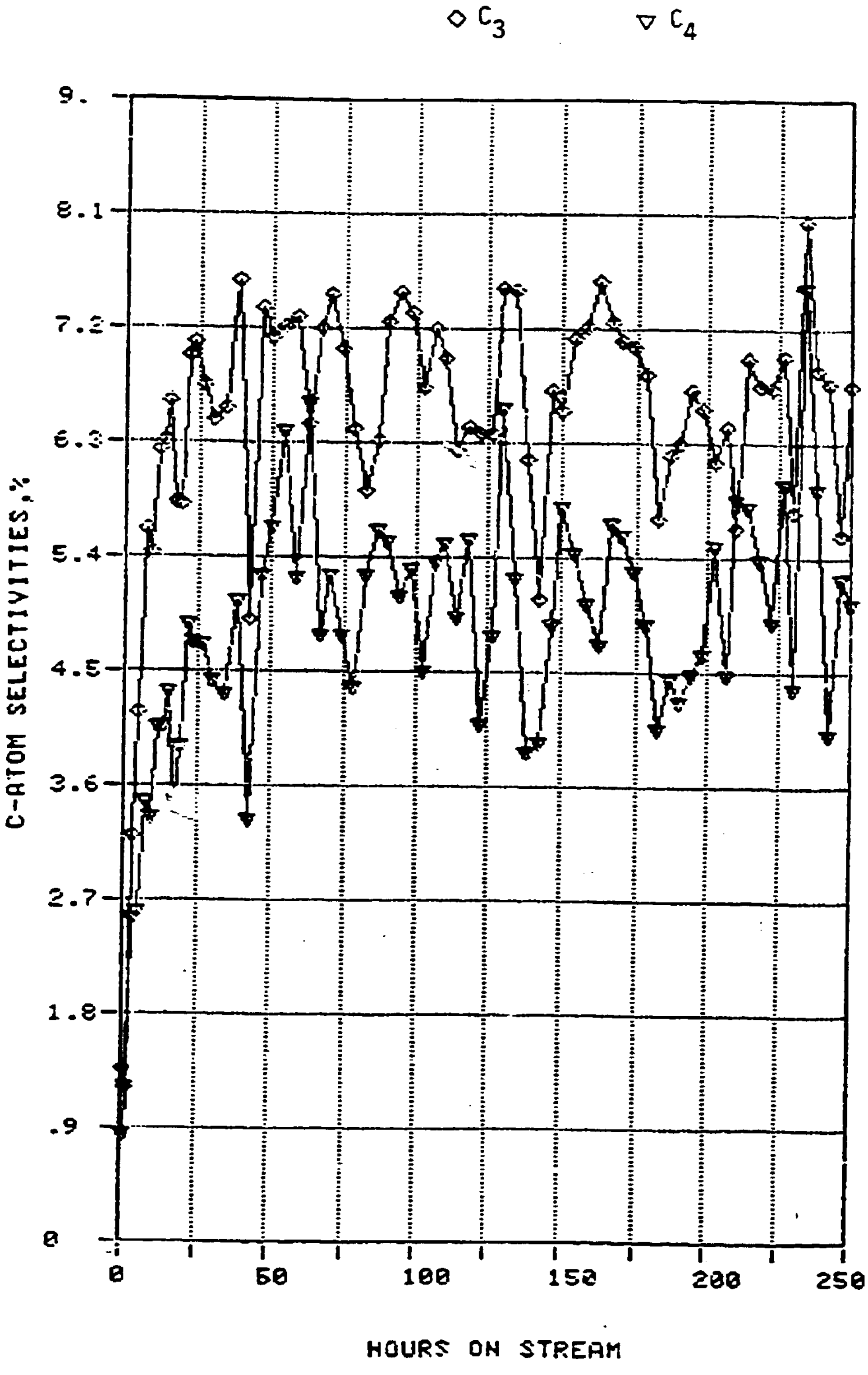
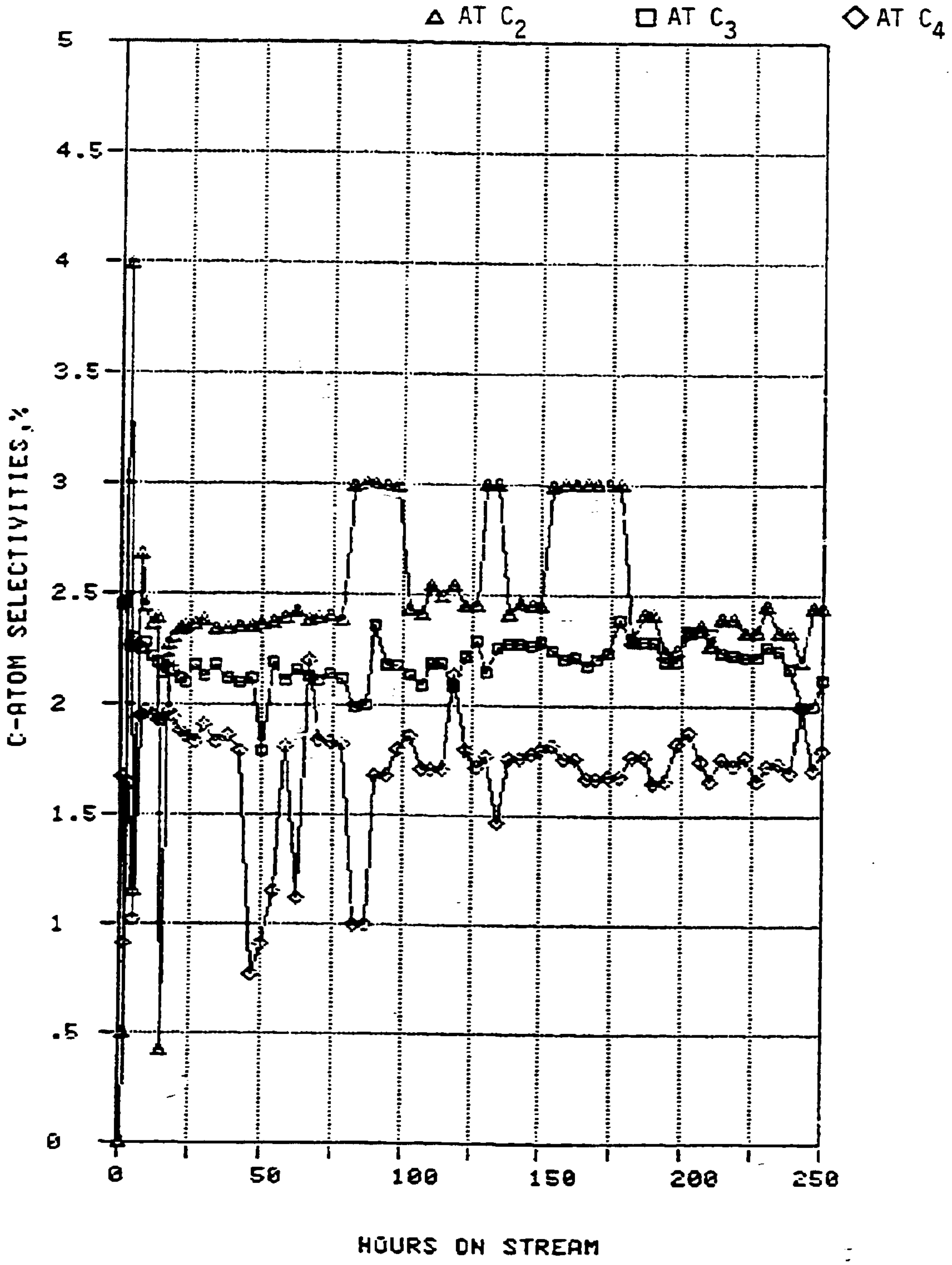


Figure 5-33. C-73-1-101 Iron Catalyst C_3 and C_4 Olefin to Paraffin Ratios Under the Third Set of Reference Conditions in Run 10



The product distributions in Run 10 were first analyzed by GC only (Table 5-12 and Figure 5-34). According to this analysis, the Anderson-Schulz-Flory diagram for hydrocarbons may be interpreted as showing four different α's between carbon numbers 1 to 44: $\alpha = 0.750$ at C_1-C_{12}, $\alpha = 0.832$ at C_{13}-C_{24}, $\alpha = 0.893$ at C_{25}-C_{32} and $\alpha = 0.934$ at C_{33}-C_{44}.

The Anderson-Schulz-Flory distribution for the products made between 38 to 116 hours in Run 7, excluding the wax recovered from the catalyst, is shown in Figure 5-35. 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 were similar. The higher α's at carbon numbers greater than 15 in Run 10 may indicate the assumption that the wax recovered from the catalyst in Run 7 was made during the first 38 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 5-36), the steady state wax production rate should have been reached somewhere between 38 and 116 hours.

Gel permeation chromatography analysis (Figure 5-37) of the wax extracted from the used catalyst in Run 10 indicates that hydrocarbons with carbon numbers greater than about 20 accumulate preferentially in the catalyst pores. Hydrocarbons with carbon number greater than 20 comprise about 14 wt.% of all the hydrocarbons. Since 47.4 g of hydrocarbons were made in 252 hours, the average C_{21}^+ (C_{21} and higher) production rate was about 0.026 gram/hour. According to this analysis, it would take about 70 hours to fill the catalyst pores.

Figure 5-34 Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Third Set of Reference Conditions in Run 10 (Hydrocarbons only; doesn't take into account GPC analysis)

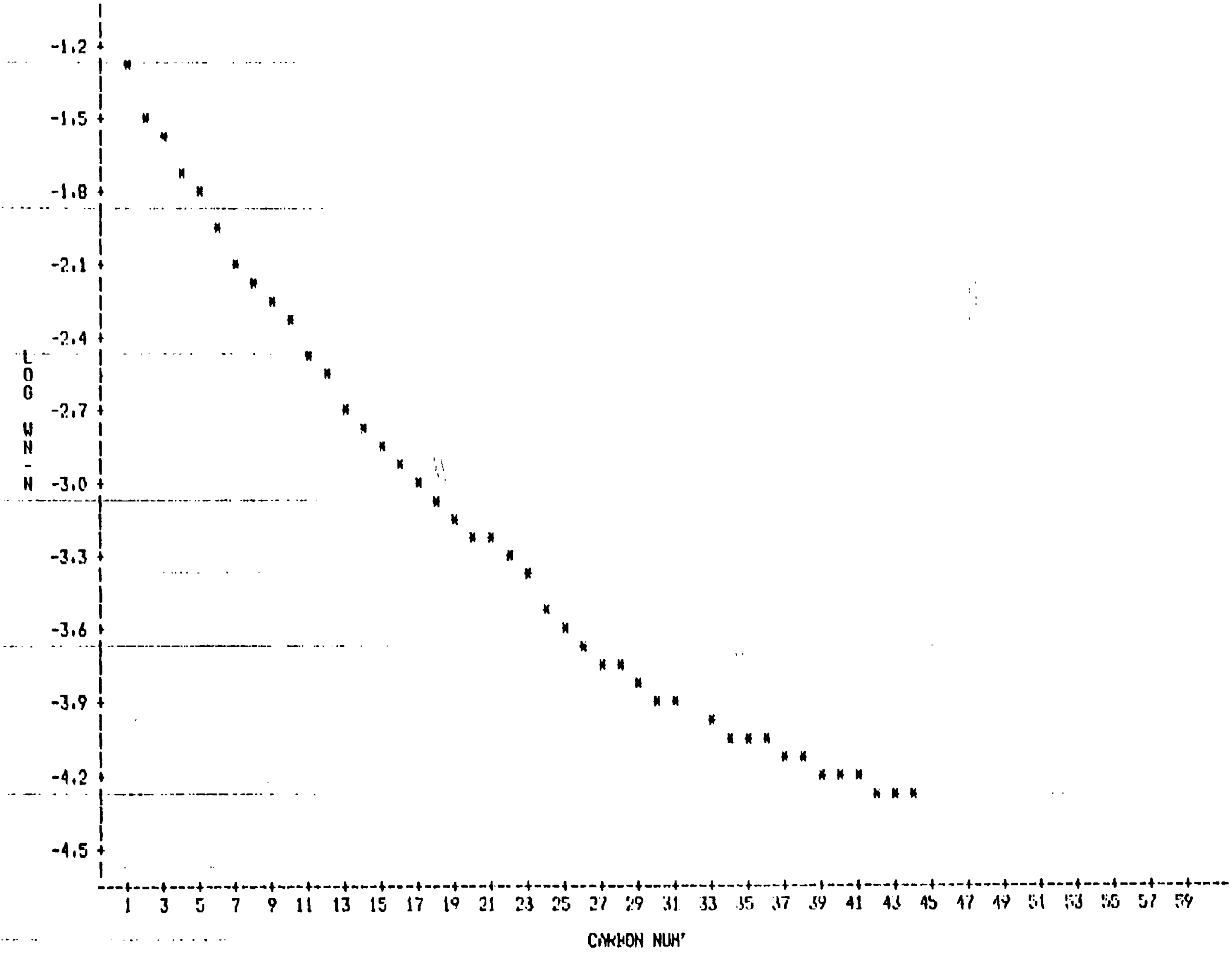


Figure 5-35. Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Third Set of Reference Conditions in Runs 7 and 10

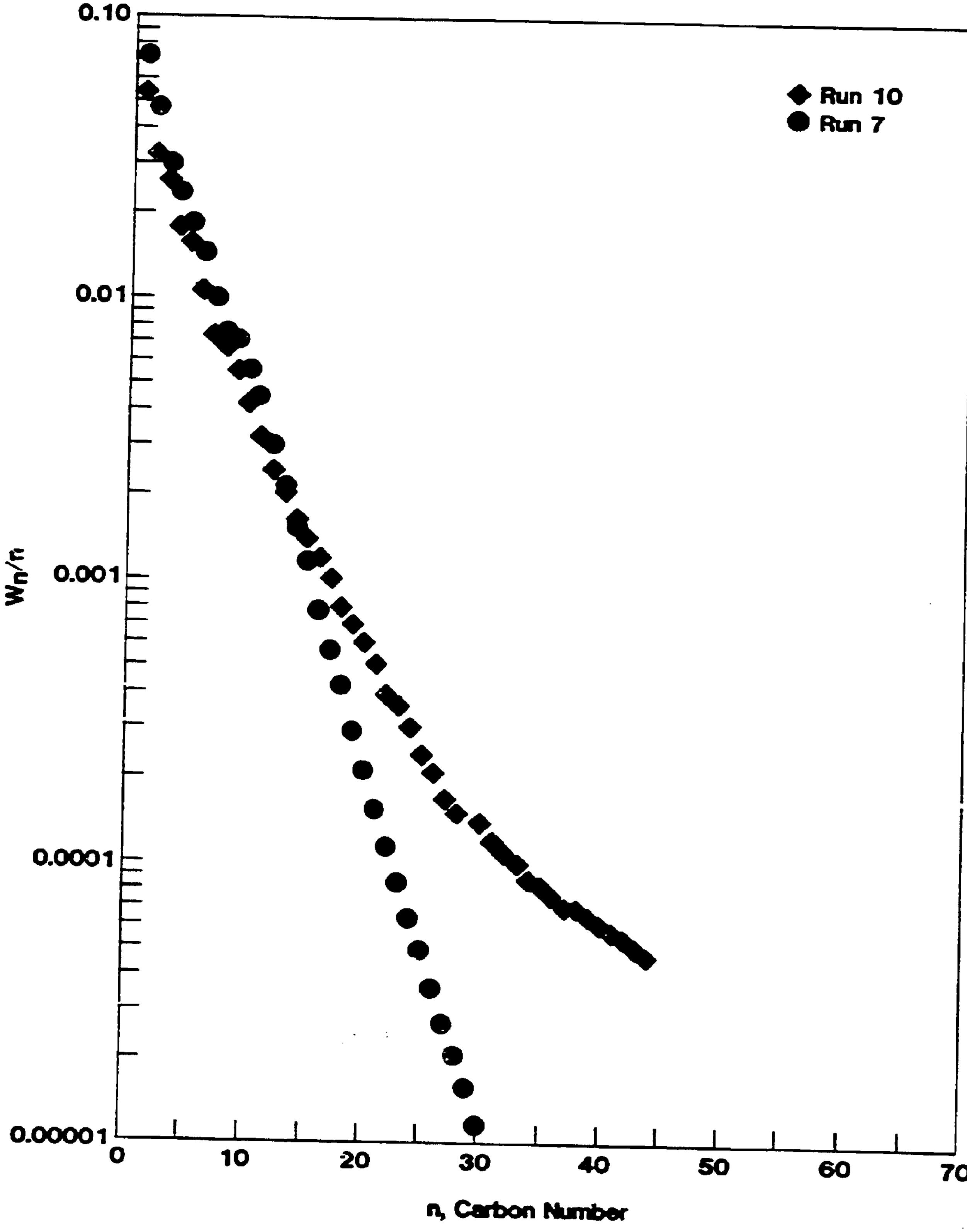


Figure 5-36. Amount of Wax Recovered from Used Catalysts in Runs 7 and 10 Under the Third Set of Reference Conditions

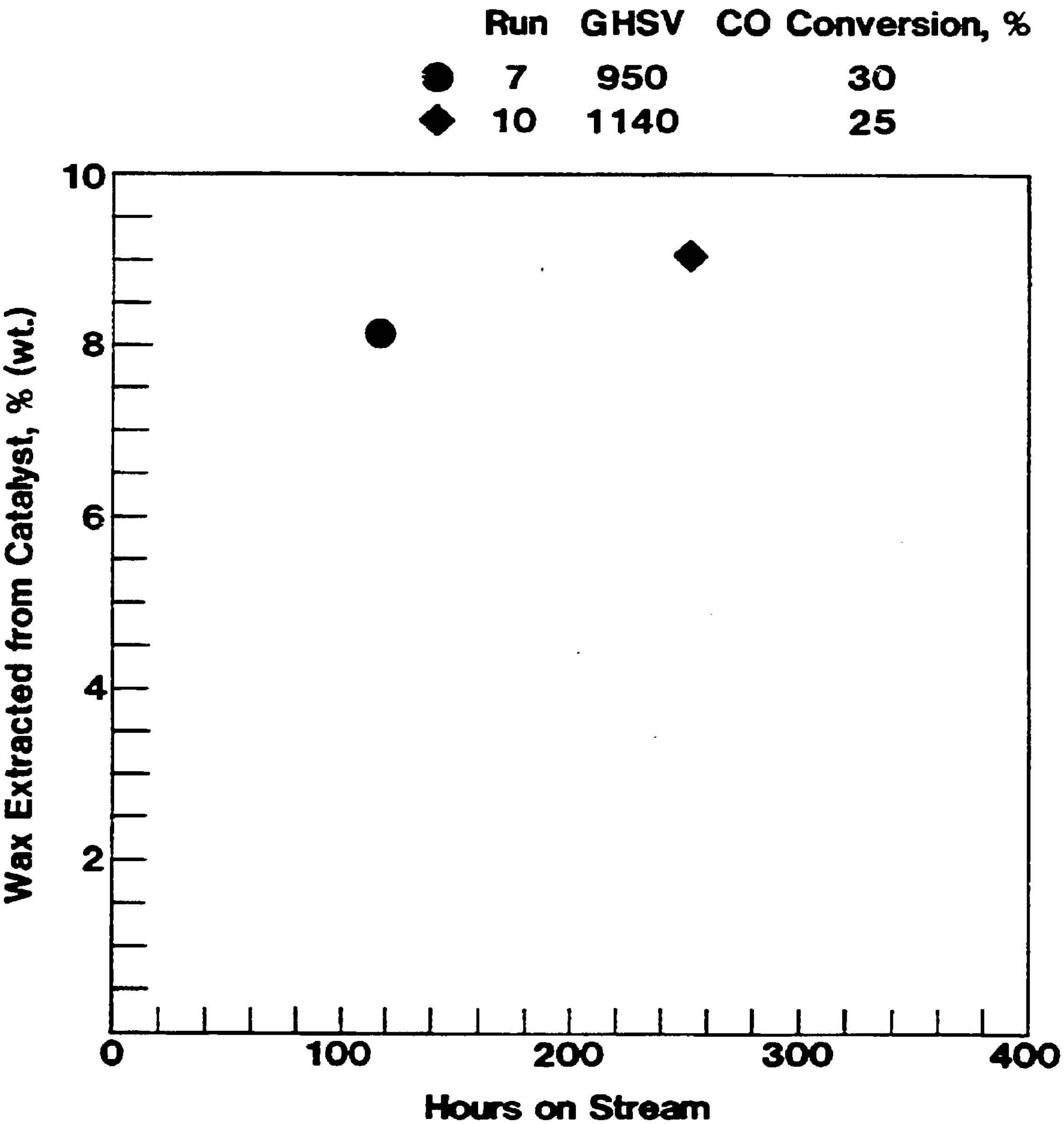
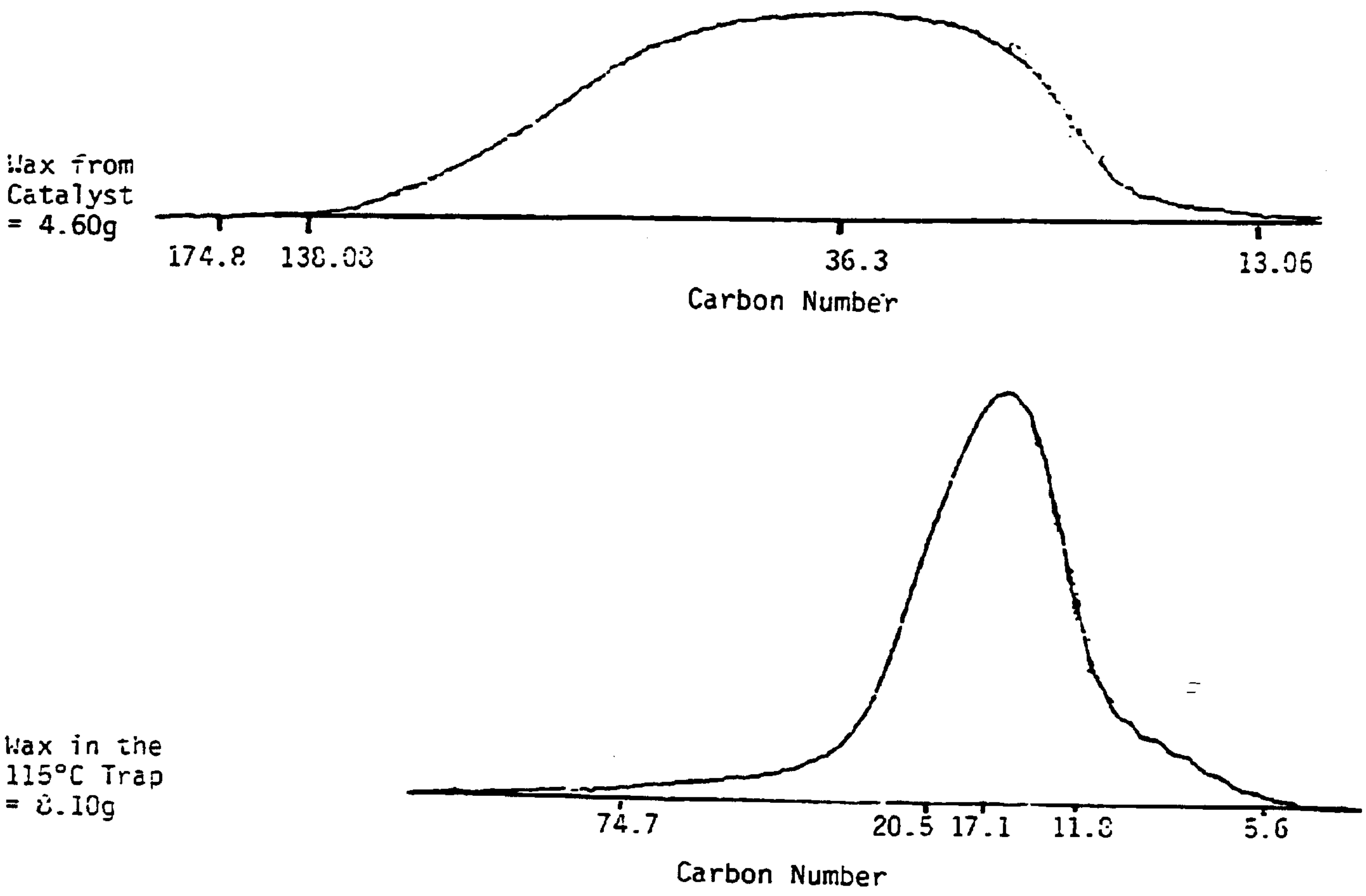


Figure 5-37. Carbon Number Distribution by Gel Permeation Chromatography Under the Fourth Set of Reference Conditions in Run 10



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 than 15, the composition of the wax recovered from catalyst in Runs 7 and 10 were compared in Figure 5-38. 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.

The results reported here indicate that Run 7 cannot be used as a reliable reference run since steady state wax production was reached after 38 hours and the wax extracted from the used catalyst was not taken into account in calculating the product distribution between 38 and 116 hours.

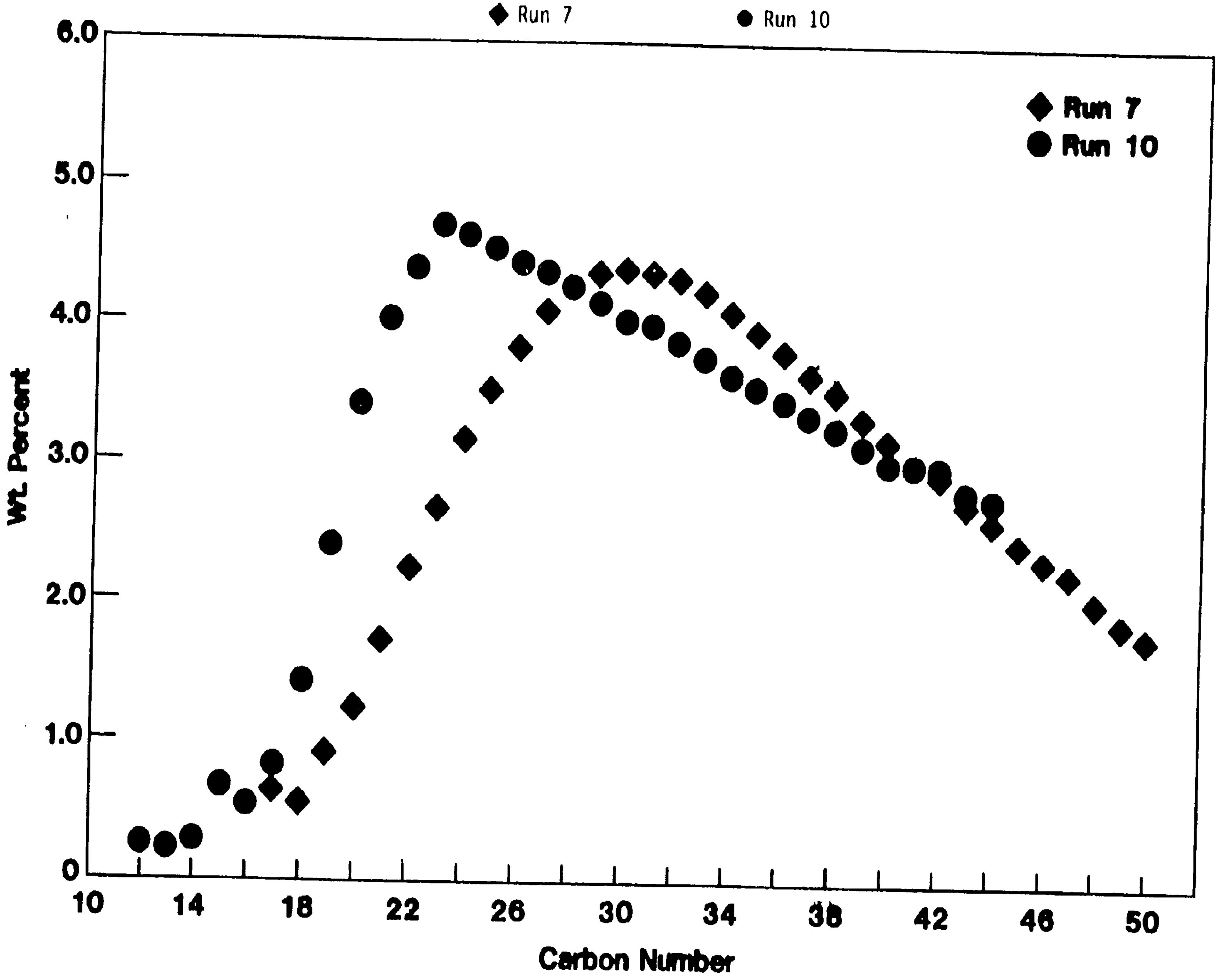
The time required to reach steady state wax production rate in Run 8 possibly was longer than in Run 7 because of the lower feed rates that were used. The material balance period in Run 8 was initiated from 40 hours on stream, and therefore Run 8 may not be a reliable reference by similar arguments.

Since the time required to reach steady state wax production rates in Runs 3 and 6 are not known, it is not clear whether these runs could be used as reference runs.

All products made during Run 10 were considered for calculating the product distribution, and therefore Run 10 will be used as a reliable reference run.

The products collected in the high temperature-high pressure separator and the wax extracted from the catalyst by gel permeation chromatography (GPC) were also analyzed, at a later date. GPC analysis indicated that these two samples actually contained a significant amount of hydrocarbons with too high a carbon

Figure 5-38. Composition of Wax Recovered from Used Catalysts in Runs 7 and 10 Under the Third Set of Reference Conditions



number (>55) to be detected by GC. Accordingly, the weights of these two samples were corrected by leaving out the fraction of the sample not detected by GC, based on the GPC analysis (Table 5-13). The Anderson-Schulz-Flory diagrams, revised according to the GPC analysis for products in the C_1-C_{44} range, are in Figures 5-39 and 5-40. The results indicate that hydrocarbons >C_{15} were overestimated in the original analysis which did not take into account GPC. Accordingly, the linear region for the intermediate α (= 0.83) now extends to higher carbon numbers from C_{13} to C_{29}, while α at C_{30}-C_{40} is about the same for both analyses.

These results indicate that significant errors could be made in calculating α's when the product samples contain hydrocarbons with too large a carbon number to elute from the GC column.

A complete analysis of the products obtained in Run 10 at C_1-C_{120} is in Figure 5-41. The Anderson-Schulz-Flory diagram in the C_1-C_{44} range was constructed according to the GC analysis; however, the weights of the product samples were corrected according to the GPC analysis, as explained above. The Anderson-Schulz-Flory analysis at carbon numbers greater than 44 in Figure 5-41 was based on GPC results. The smooth transition at carbon number 44 demonstrates the consistency of both types of measurements.

The results summarized in Figure 5-41 indicate that the C-73-1-101 reference catalyst with an average iron crystallite size of 11 nm showed a constant α (= 0.948) in the C_{35}-C_{120} range and did not result in hydrocarbon cutoff.

Table 5-13. Product Distributions in Run 10 (takes into account GPC analysis)

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.77	36.91
CO	71.91	50.61
CO2	9.84	4.41
H2O	4.85	5.31
HYDROCARBON	9.04	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	5.72	24.86
C2-C4	22.71	39.43
C5-C11	39.24	27.41
C12-C18	15.74	5.44
C19-C25	6.75	1.57
C26+	9.84	1.30
CH4	5.72	24.86
C2P	2.08	4.81
C2=	4.72	11.73
C3	0.13	0.21
C3P	2.67	4.22
C3=	5.58	9.24
C4	1.41	1.72
C4P	2.34	2.81
C4=	3.78	4.69
C5	8.24	8.07
C6	6.51	5.32
C7	5.44	3.82
C8	5.60	3.44
C9	5.27	2.88
C10	4.47	2.20
C11	3.71	1.66
C12	3.10	1.27
C13	2.69	1.02
C14	2.41	0.85
C15	2.22	0.73
C16	2.01	0.62
C17	1.75	0.51
C18	1.56	0.43
C19	1.39	0.36
C20	1.22	0.30
C21	1.11	0.26
C22	0.94	0.21
C23	0.82	0.18
C24	0.69	0.14

COMPONENT	WEIGHT %	MOLE %
C25	0.58	0.11
C26	0.51	0.10
C27	0.44	0.08
C28	0.40	0.07
C29	0.36	0.06
C30	0.33	0.05
C31	0.31	0.05
C33	0.28	0.04
C34	0.27	0.04
C35	0.25	0.04
C36	0.25	0.03
C37	0.23	0.03
C38	0.23	0.03
C39	0.22	0.03
C40	0.21	0.03
C41	0.20	0.02
C42	0.20	0.02
C43	0.19	0.02
C44	0.18	0.02
C45+	4.79	0.53
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.

Figure 5-39. Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Third Set of Reference Conditions in Run 10 (Hydrocarbons + Oxygenates)

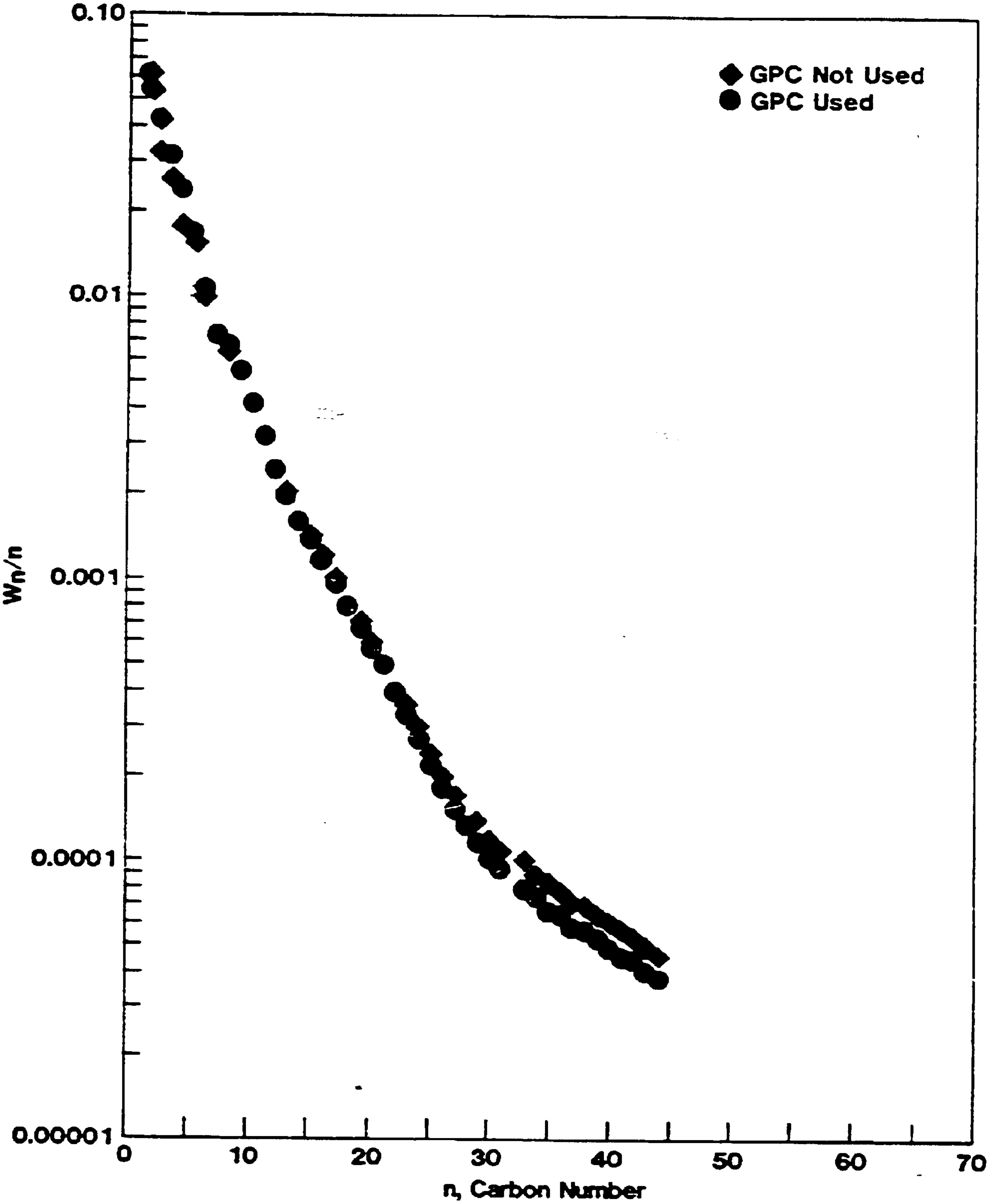


Figure 5-40. Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Third Set of Reference Conditions in Run 10 (Hydrocarbons Only)

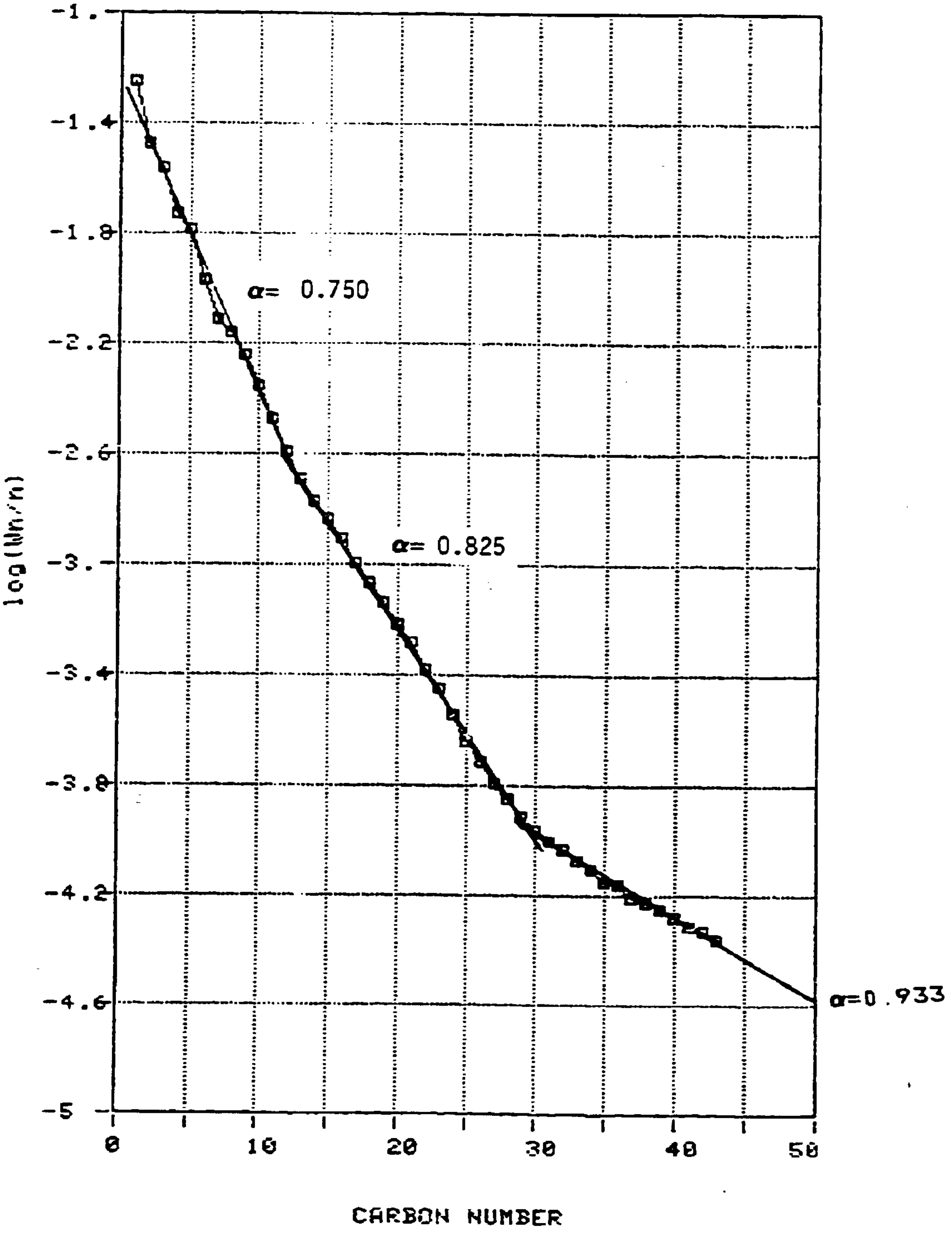
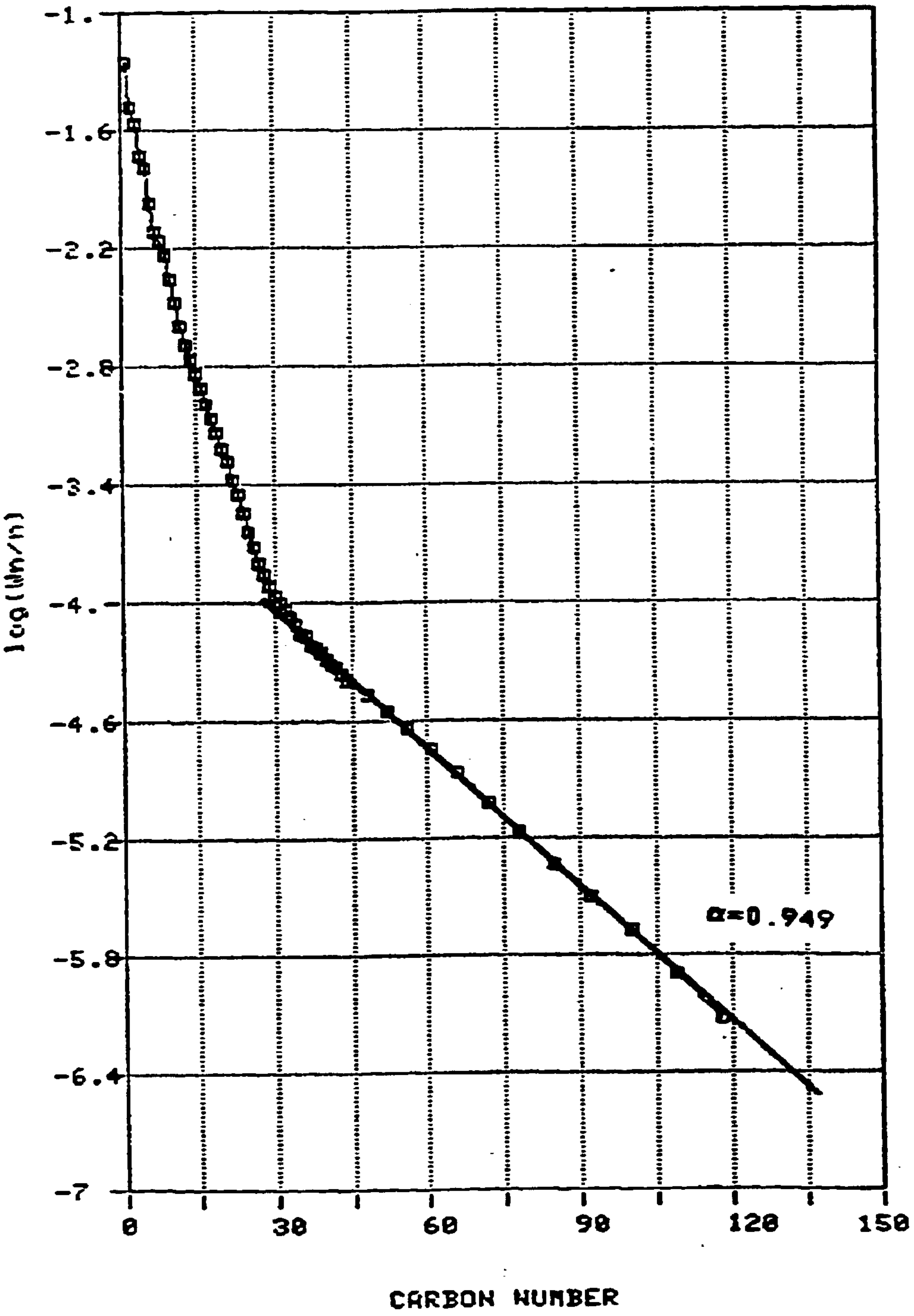


Figure 5-41. Anderson-Schulz-Flory Distributions with C-73-1-101 Iron Catalyst Under the Third Set of Reference Conditions in Run 10 (Hydrocarbons + Oxygenates)



5.1.3 Application of the Reverse Micelle Technique to Ruthenium Catal

5.1.3.1 Characterization of Reverse Micelle Solutions by SAXS

Three different reverse micelle solutions were considered for preparin ruthenium catalysts.

The SAXS curve (I vs. h) for the reverse micelle solution 4956-24-1 is shown in Figure 5-42. The inflection point near 0.04Å^{-1} indicates that the number of reverse micelles per unit volume is large enough to cause interac between individual reverse micelles, and therefore the size distribution of reverse micelles cannot be accurately calculated. An approximate radius of gyration of 29Å was calculated for the water core from the slope of the Gui plot (Figure 5-43). The reverse micelle solution was then diluted with an volume of the organic solvent. The SAXS curve for the diluted system (Figu 5-44) did not show an inflection point, indicating the absence of interacti between individual reverse micelles. The radius of gyration calculated from slope of the Guinier plot (Figure 5-45) was then 35Å, resulting in a volume averaged sphere diameter of 75 to 90Å. The radius of gyration of the water of the reverse micelles actually used in the catalyst preparations seems to between 29 and 35Å. Figure 5-46 shows the diameter distribution for the dil reverse micelle solution. The distribution was between 40 to 110Å, with a p near 55Å.

Two other reverse solutions (4966-50 and 4966-52) were prepared with th objective of synthesizing reverse micelles smaller than the ones in solution 4956-24-1.

Figure 5-42

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

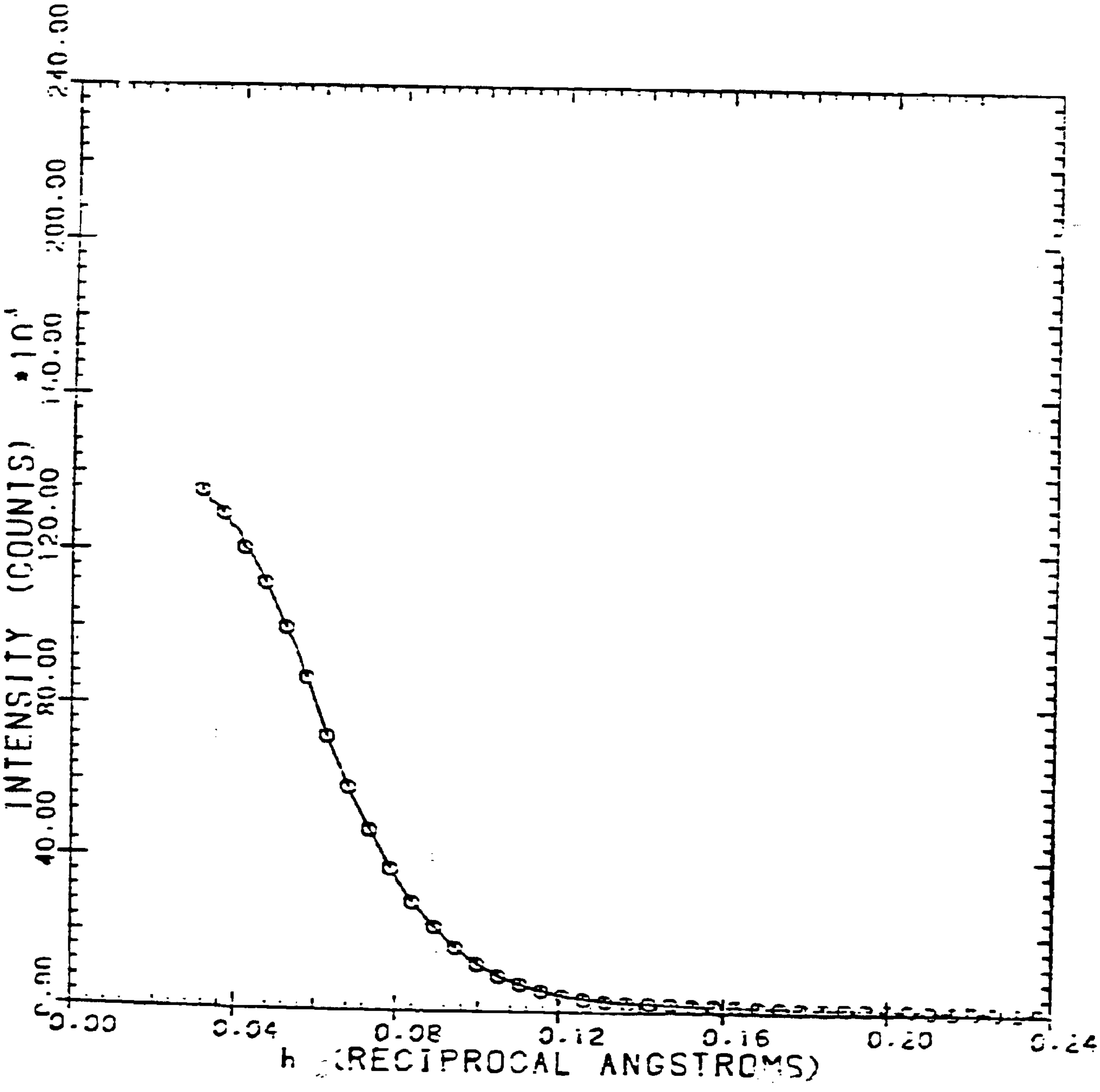


Figure 5-43

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

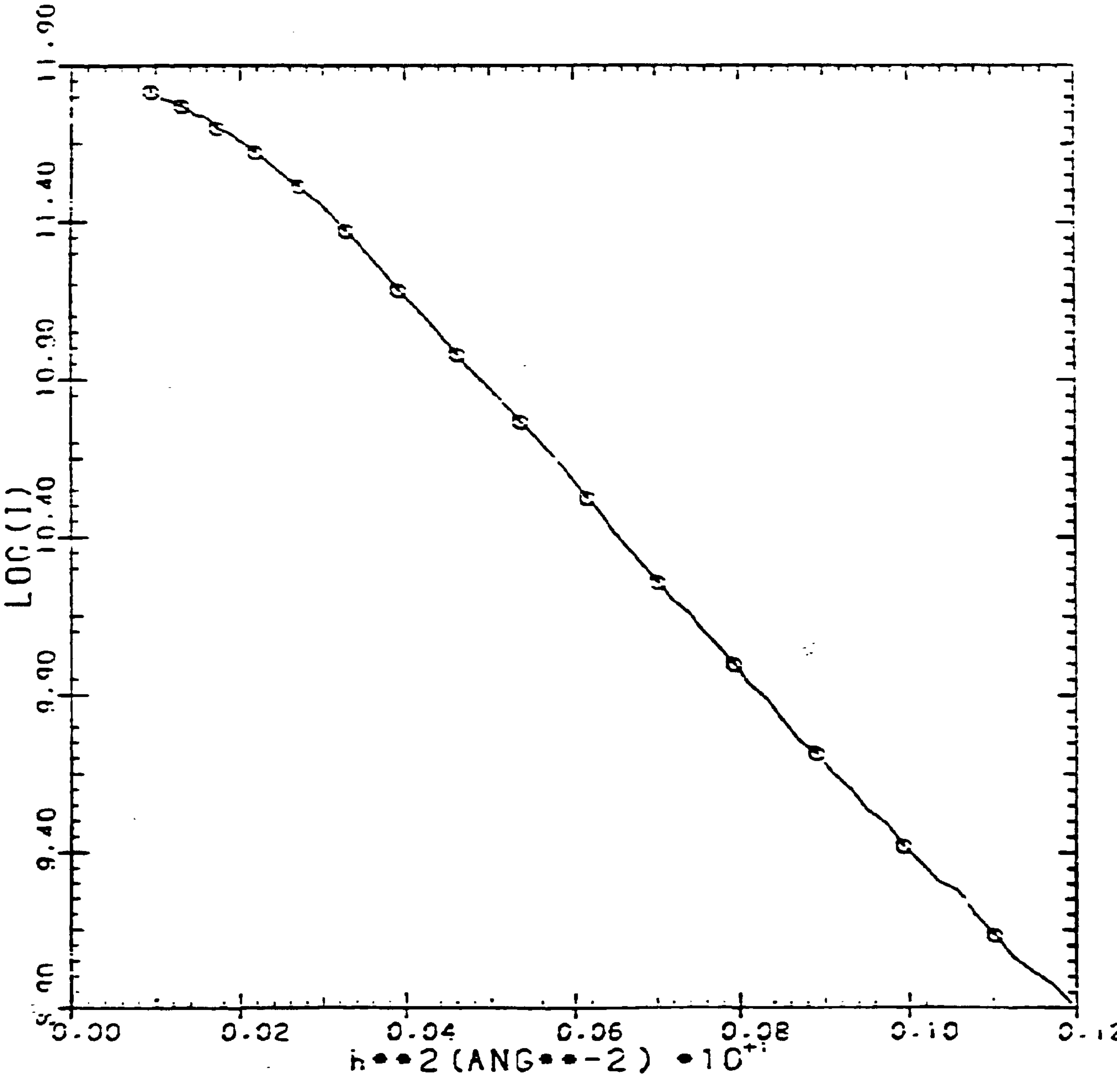


Figure 5-44

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

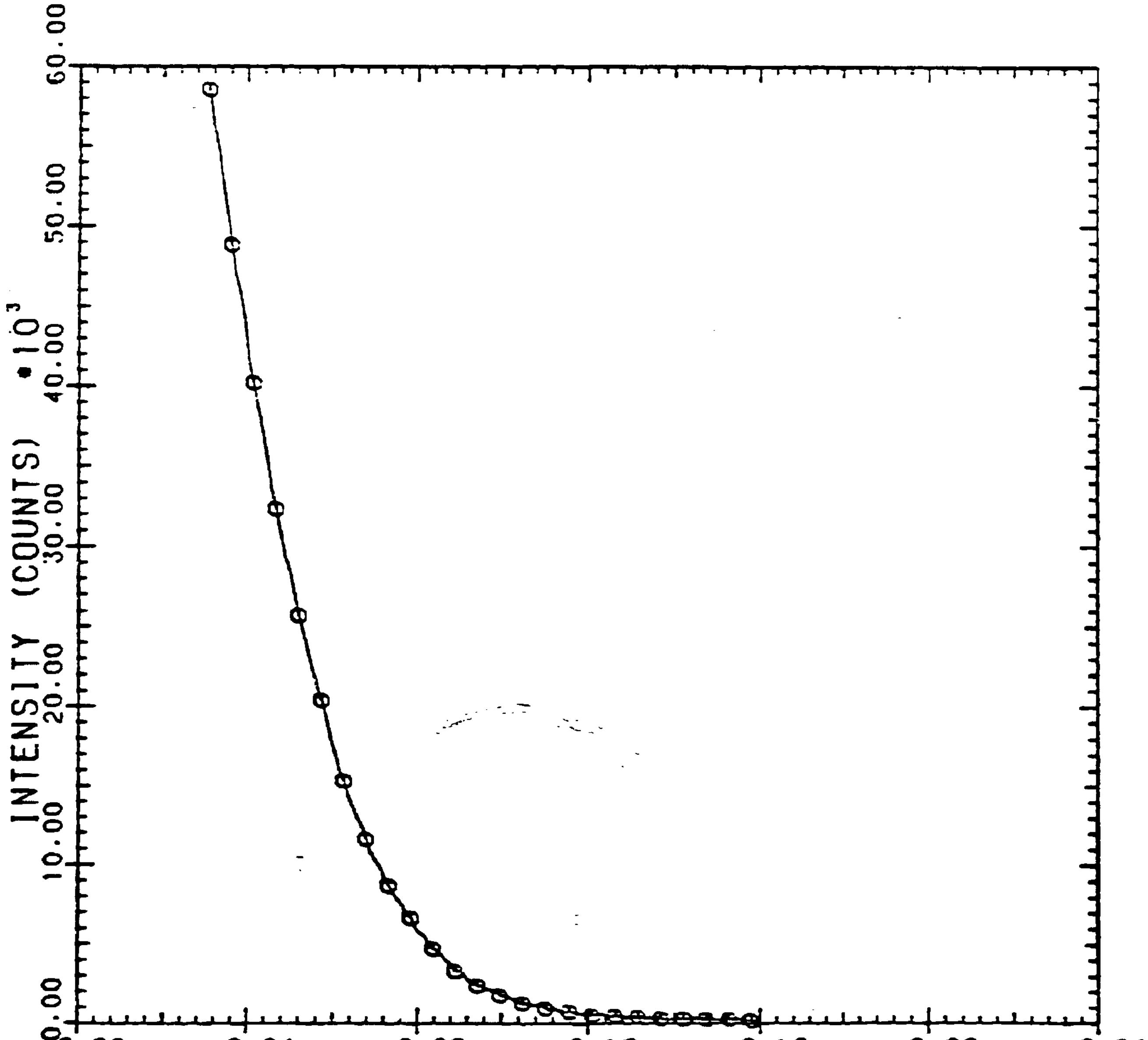


Figure 5-45

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

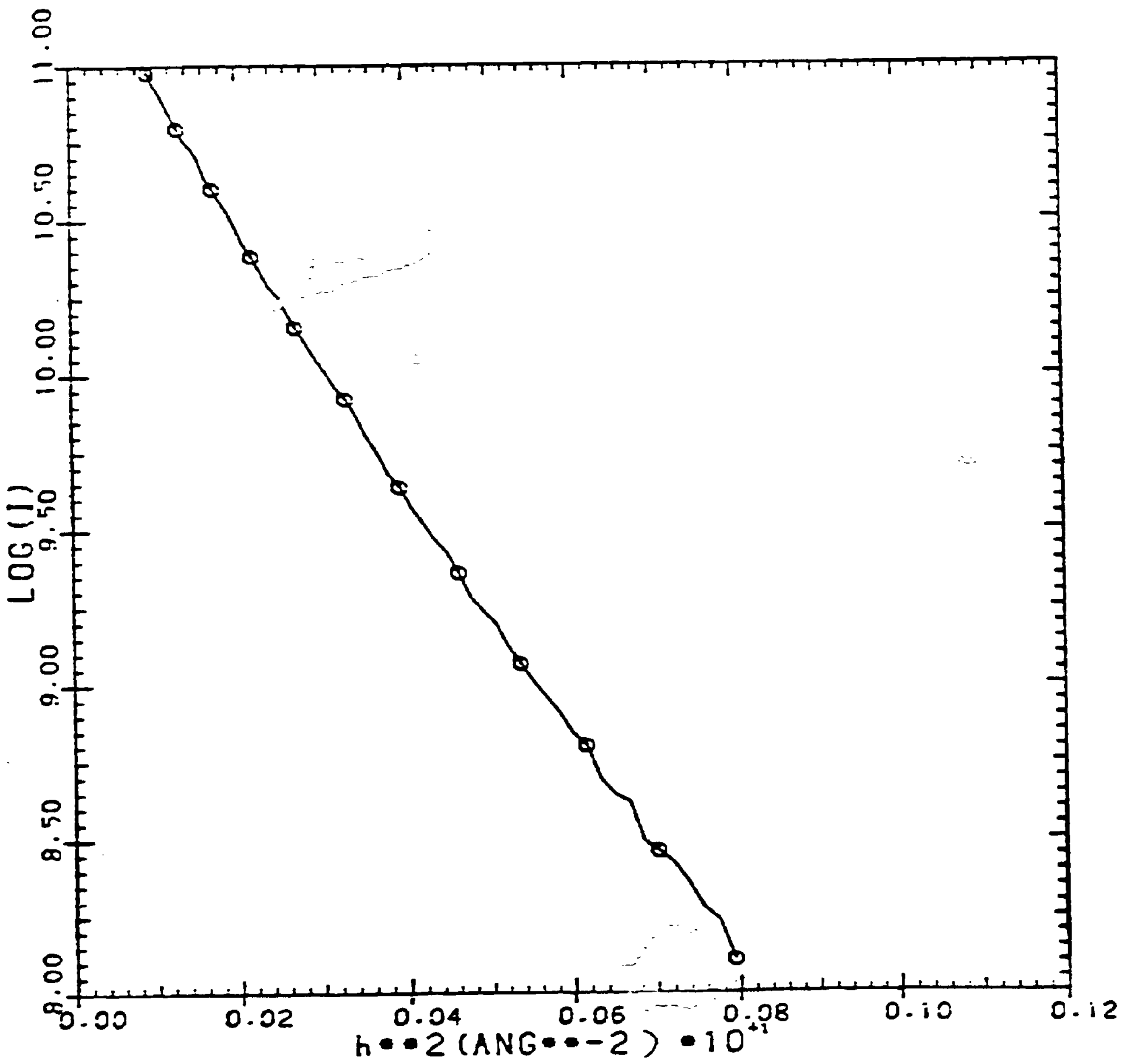
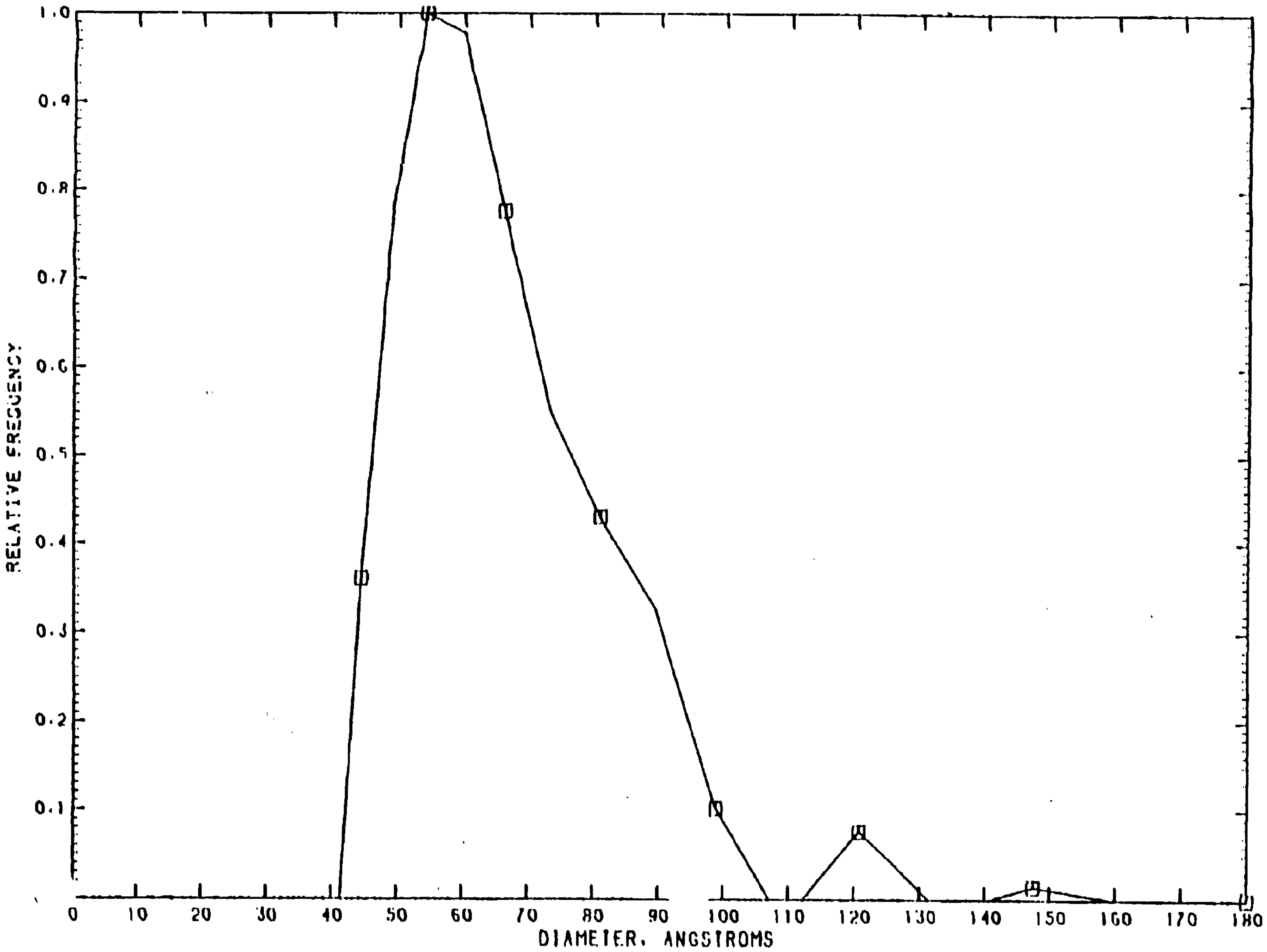


Figure 5-46

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



The SAXS curve for sample 4966-50 is shown in Figure 5-47. A diameter distribution cannot be calculated from this data since, as the strongly curving region at lower angles extending from 0.03 to 0.1Å^{-1} shows, a large amount of particle-particle interference is present.

Figure 5-48 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 0.040Å^{-2}. From the slope of this region, the radius of gyration was calculated to be 12Å. From this value, the volume averaged diameter of the micelle core was calculated to be 31Å. Since in this average the larger cores are weighted more, the number averaged diameter may be smaller if the size distribution is not monodispersed. These results are summarized in Table 5-14. Also listed in the same table are

Table 5-14

Summary of SAXS Results

Sample	R_G, Å^a	Vol. Averaged^b Diameter, Å
4956-24-1	29	75-90
4966-50	12	31
4966-52	15	39

a) Radius of gyration.

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

the SAXS results for sample 4956-24-1. The results indicate that the new reverse micelles are significantly smaller in size relative to sample 4956-24-1, for which the diameter was 75-90Å.

Figure 5-47

SAXS Plot for the Reverse Micelle Solution 4966-50

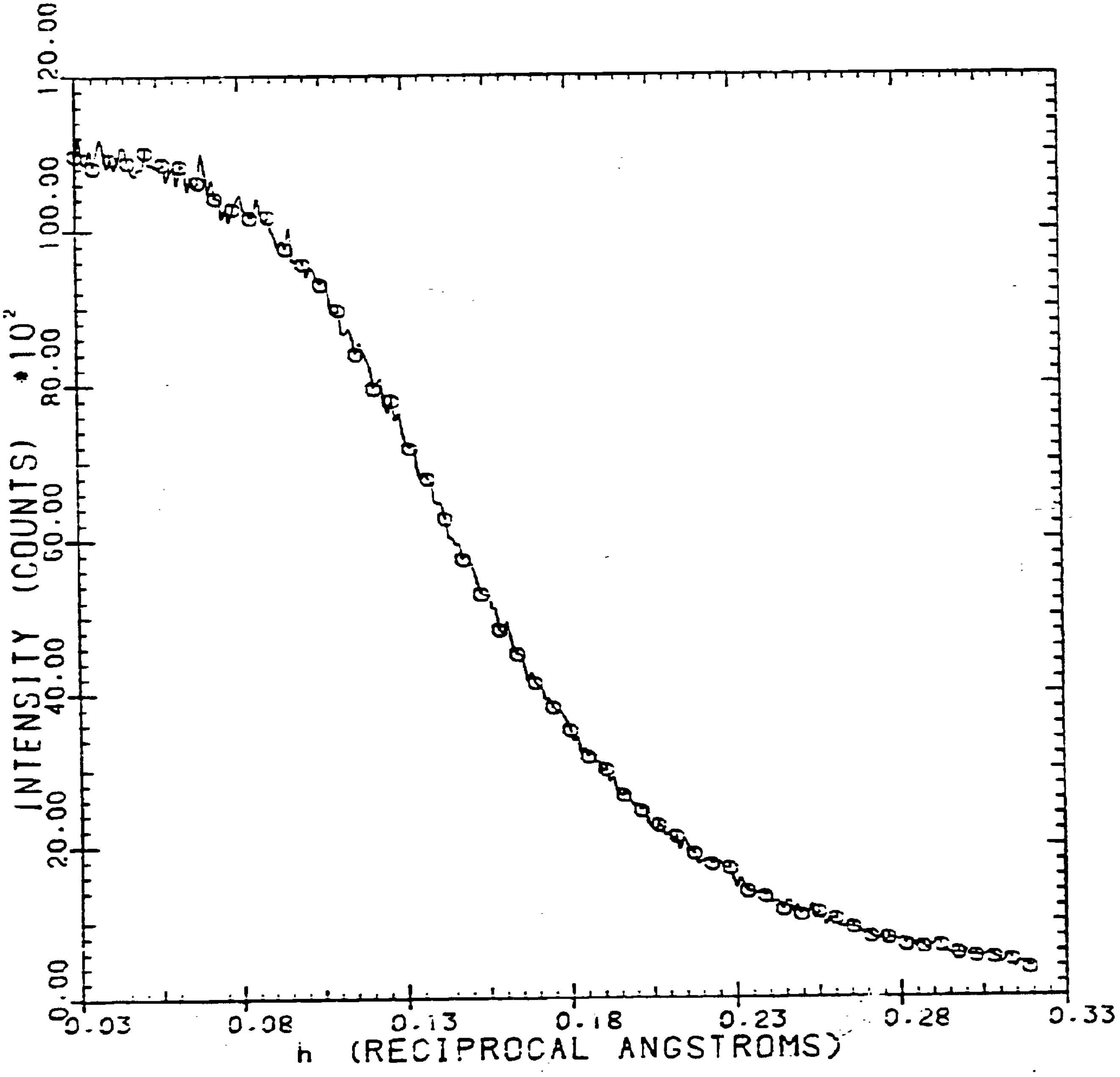


Figure 5-48

Guinier Plot for the Reverse Micelle Solution 4966-50

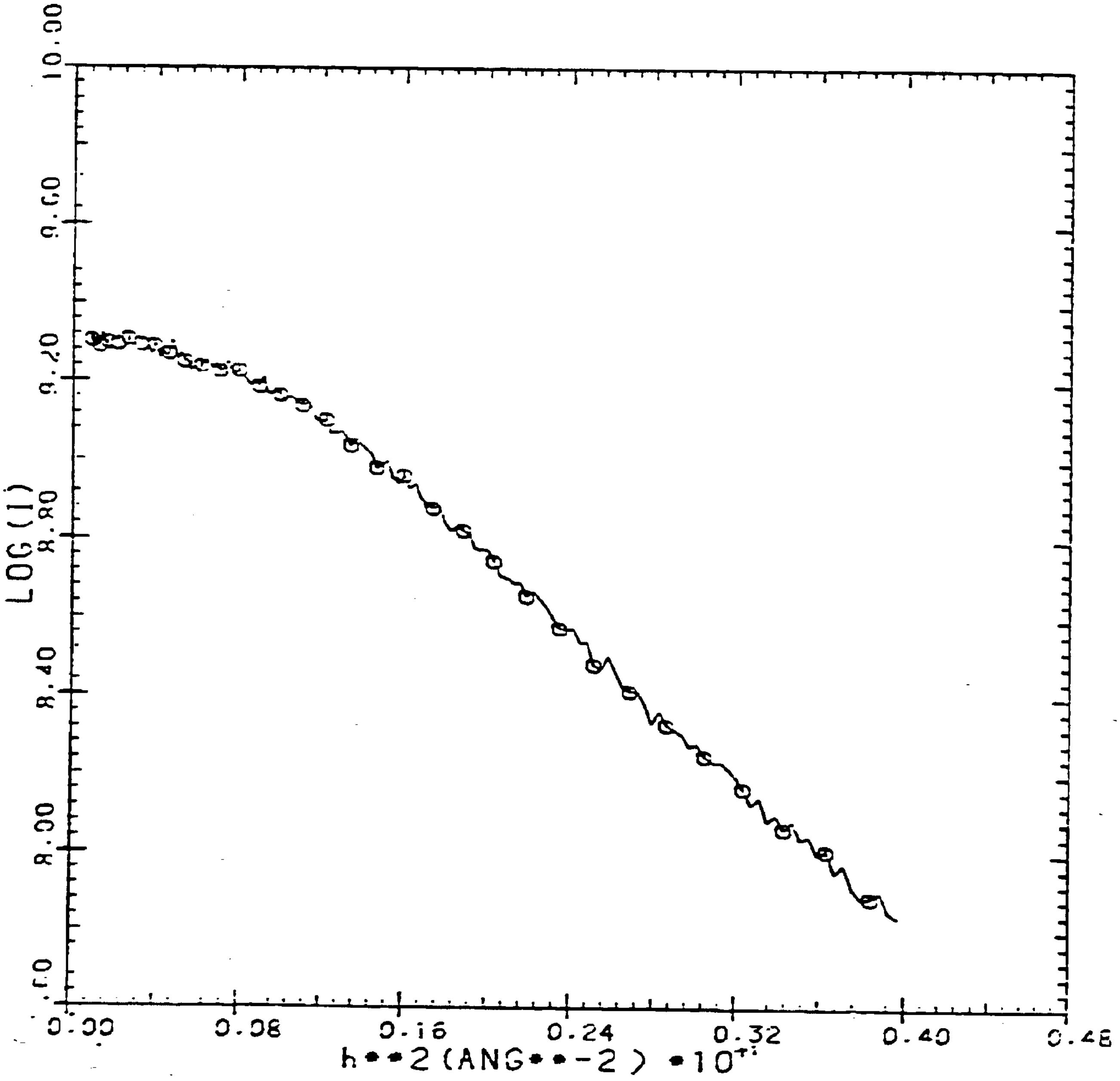


Figure 5-49 is the SAXS curve for sample 4966-52. A slight inflection near $0.06Å^{-1}$ is seen which indicates some particle-particle interference; thus, a valid diameter distribution could not be calculated for this sample. Figure 5-50 is the Guinier plot for this sample. The plot is linear, and the slope yields a radius of gyration of 15Å. This leads to a volume averaged core diameter of 39Å. These results are also summarized in Table 5-14.

Figure 5-49

SAXS Plot for the Reverse Micelle Solution 4966-52