5.1.2 Establishment of Catalyst Testing and Analytical Procedures with Reference C-73-1-101 Iron Catalyst

5.1.2.1 Characterization of Reference Iron Catalyst

Examination of the reduced C-73-1-101 catalyst showed several morphologically different species. This is illustrated in Figures 5-6 through 5-9. In Figure 5-6, the porous nature of the Fe particle is apparent in the dark field image which is representative of elastically scattered electrons and is a function of the atomic number. The image in Figure 5-7 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 5-8 and 5-9 are typical of what was observed for this sample.

The method of Fourier deconvolution of x-ray diffraction lineshapes has been applied to the reduced reference iron catalyst. A survey scan of the diffraction pattern (Figure 5-10) indicates the catalysts to be predominantly in the metallic iron form with no features due to oxides or other phases detectable (Be peaks in Figure 5-10 are due to the window material).

The results of two separate very long time scales (Figures 5-11 and 5-12) with the different window materials are in good agreement. The mean crystallite size is found to be 11.5 nm in one case and 10.5 nm in the other (Figure 5-13). The distribution of sizes range from about 2 nm to 15 nm, with a broad maximum from 6 nm to 10 nm (Figure 5-14). At sizes larger than 14 nm, the noise of the Fourier coefficients results in large, but physically meaningless, probabilities.

STEM Micrographs of Reduced C-73-1-101 Iron Catalyst

Figure 5-6

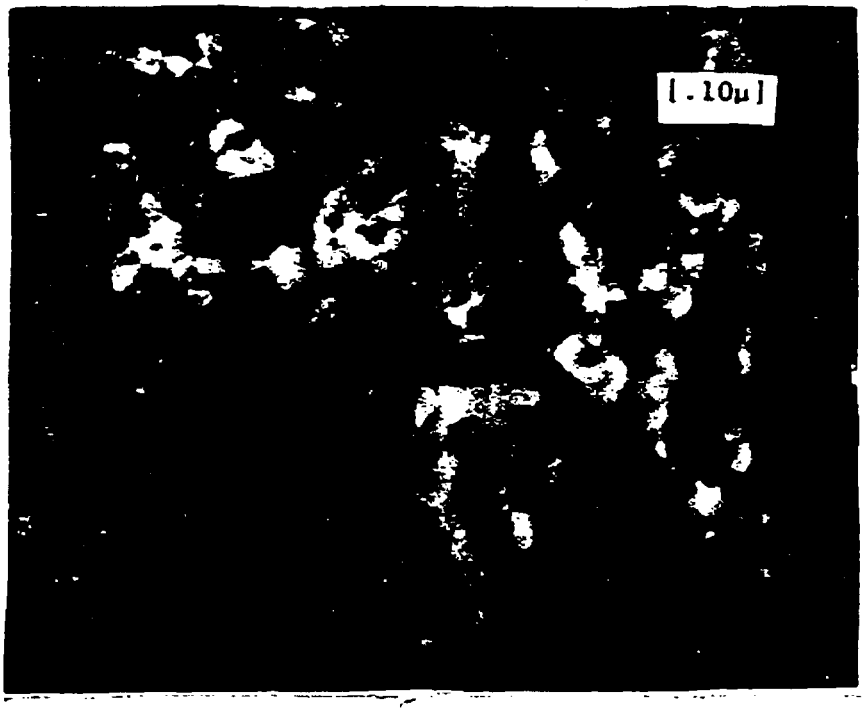
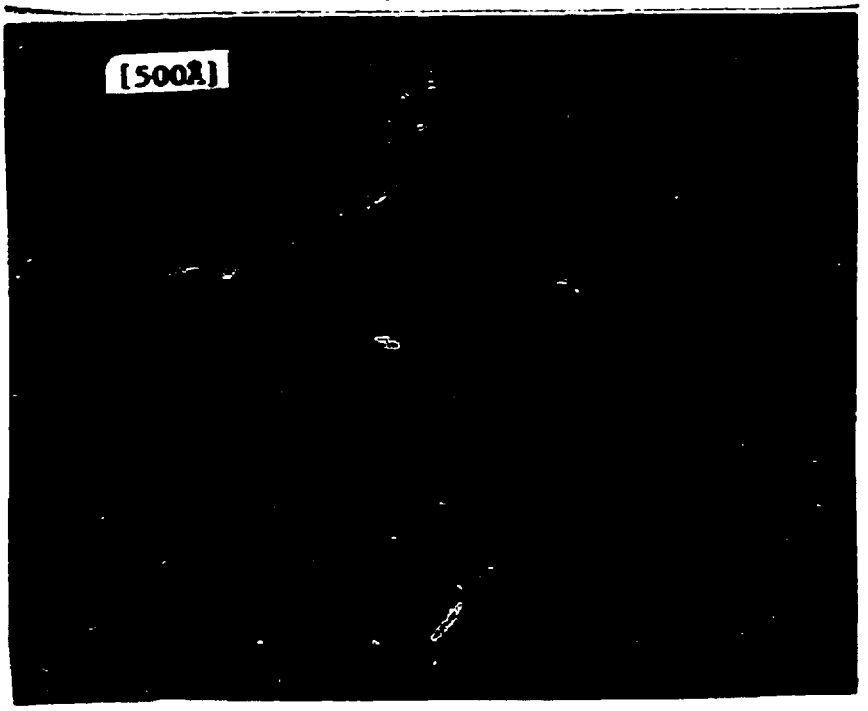


Figure 5-7



STEM Micrographs of Reduced C-73-1-101 Iron Catalyst

Figure 5-8

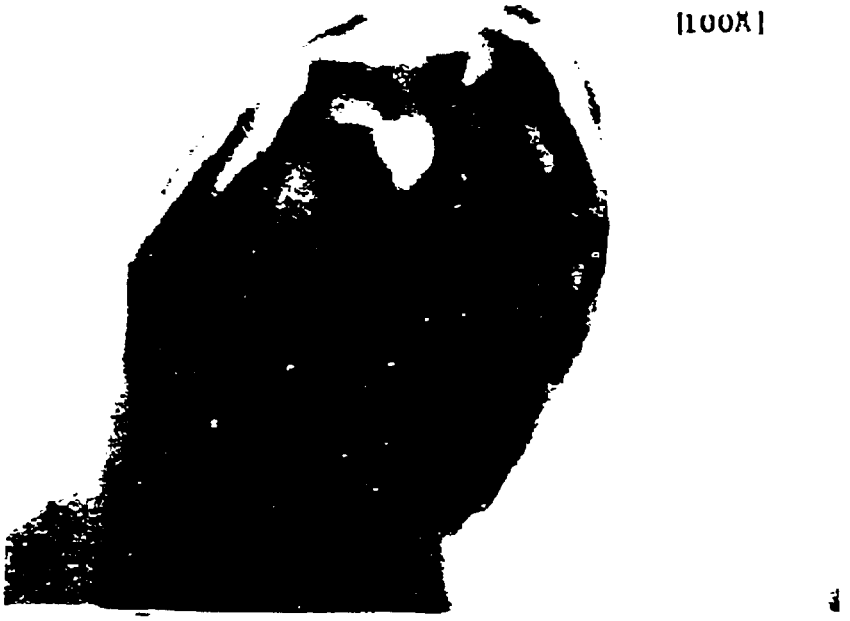
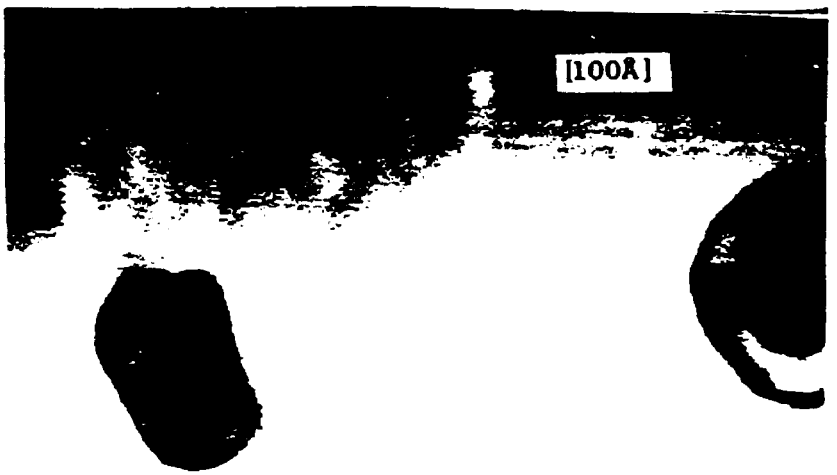


Figure 5-9



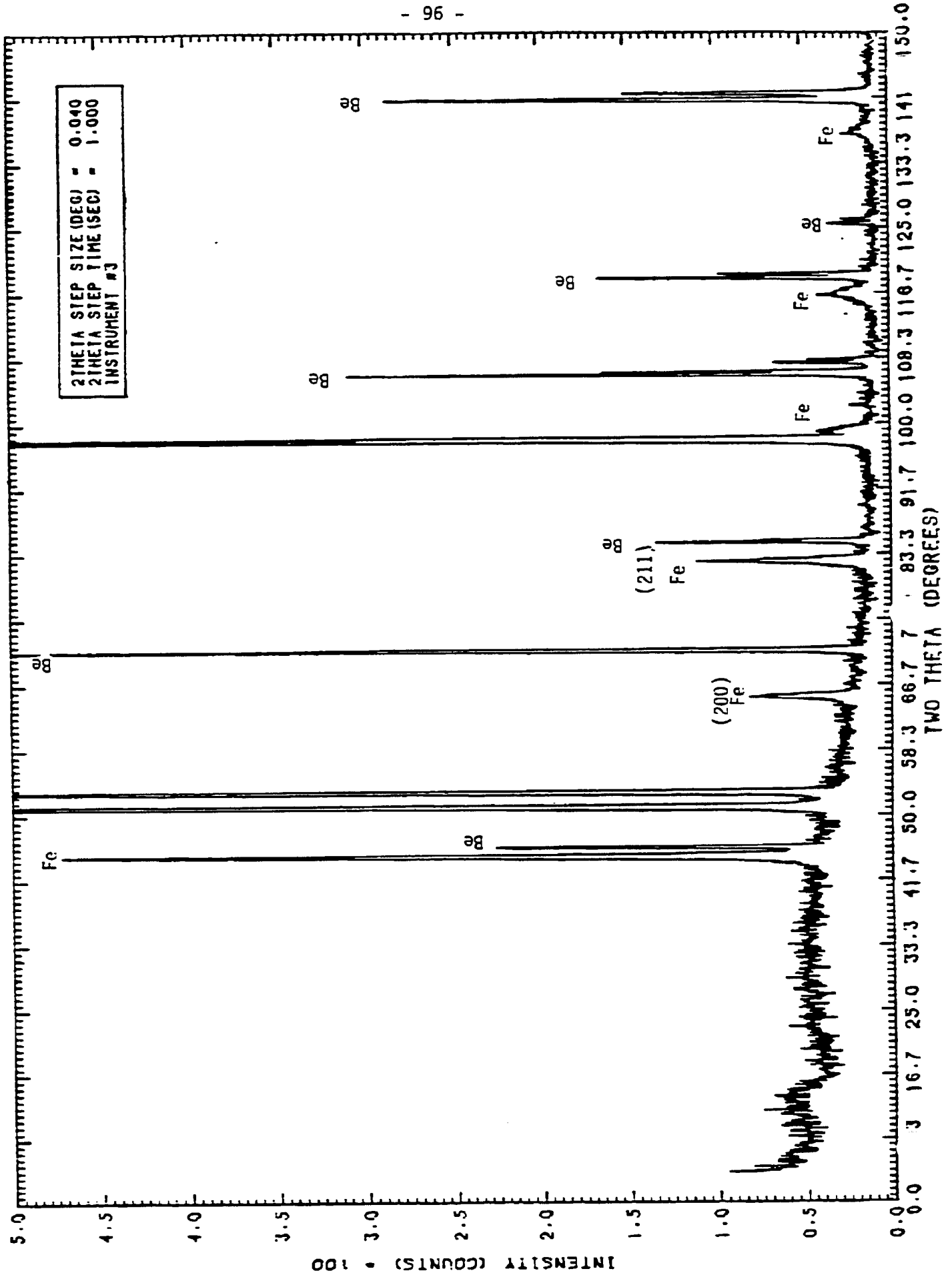


Figure 5-10 A Survey Scan of the Diffraction Pattern of Reduced C-73-1-101 Catalyst

Figure 5-11 Long Time Scans of the Fe (200) Reflection for the Reduced C-73-1-101 Catalyst and Ordinary Iron Powder

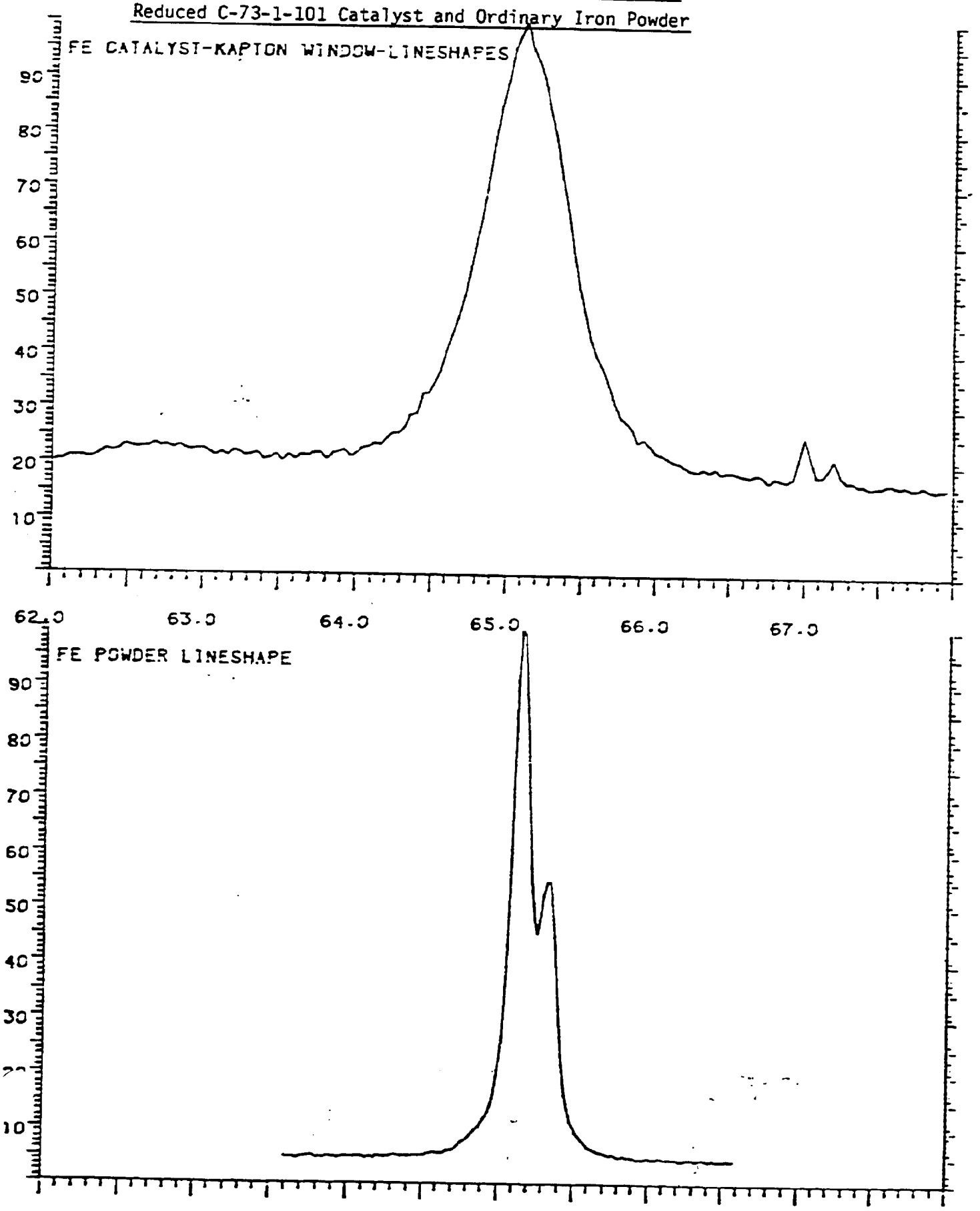


Figure 5-12 Long Time Scans of the Fe (211) Reflection for the Reduced C-73-1-101 Catalyst and Ordinary Iron Powder

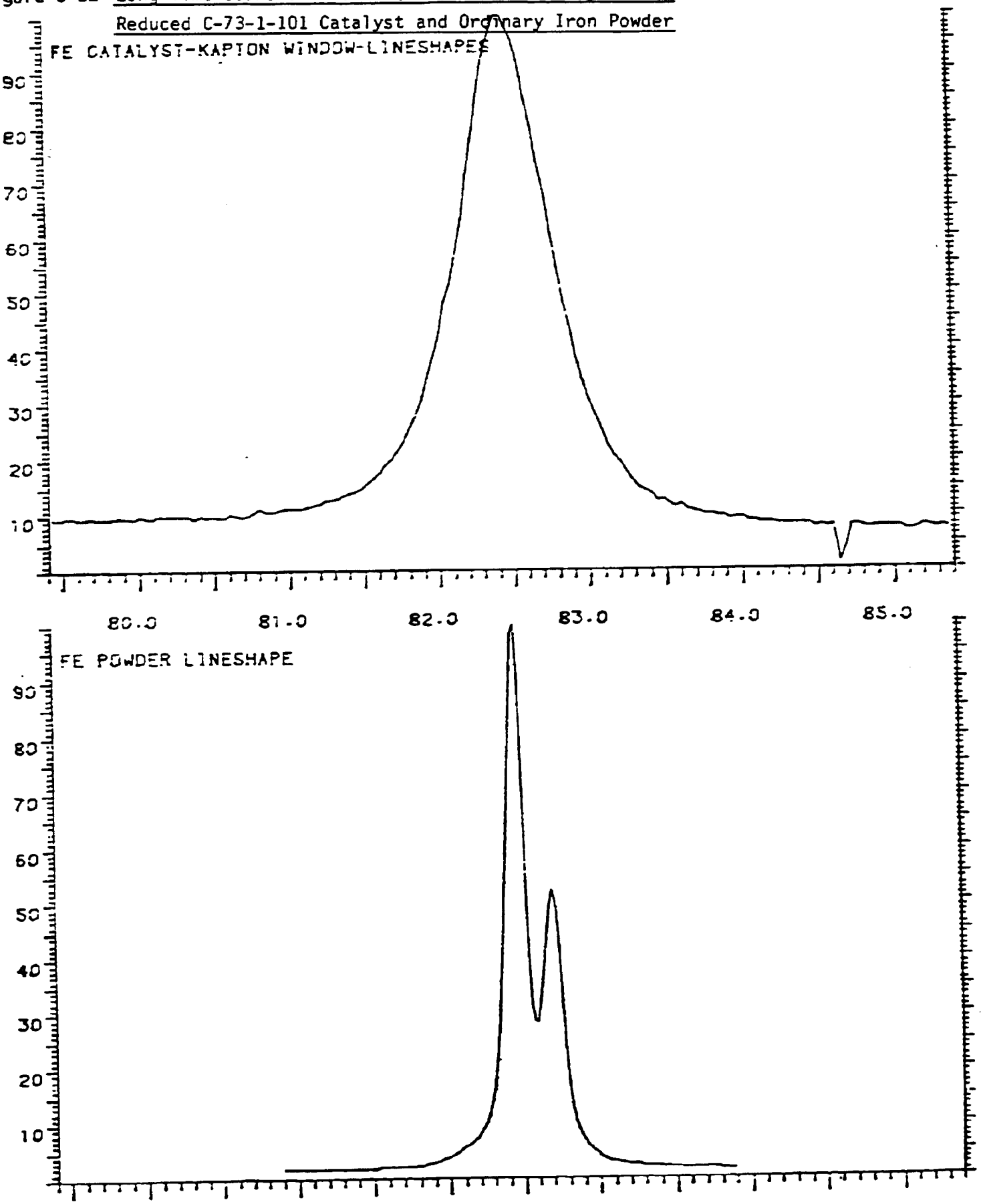


Figure 5-13. Amplitude of the Fourier Coeffi[illegible]its vs. the Harmonic Number (Kapton Window)

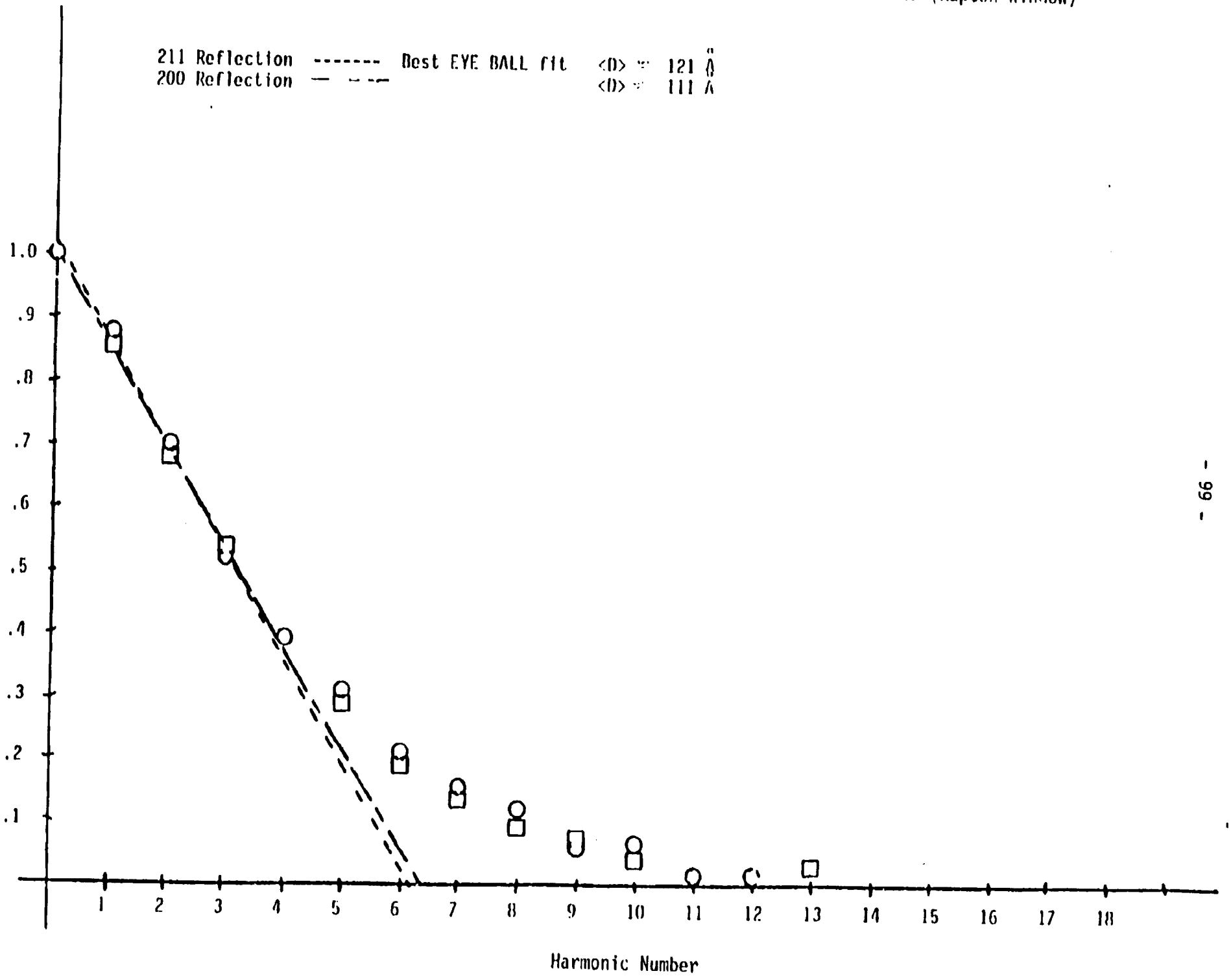
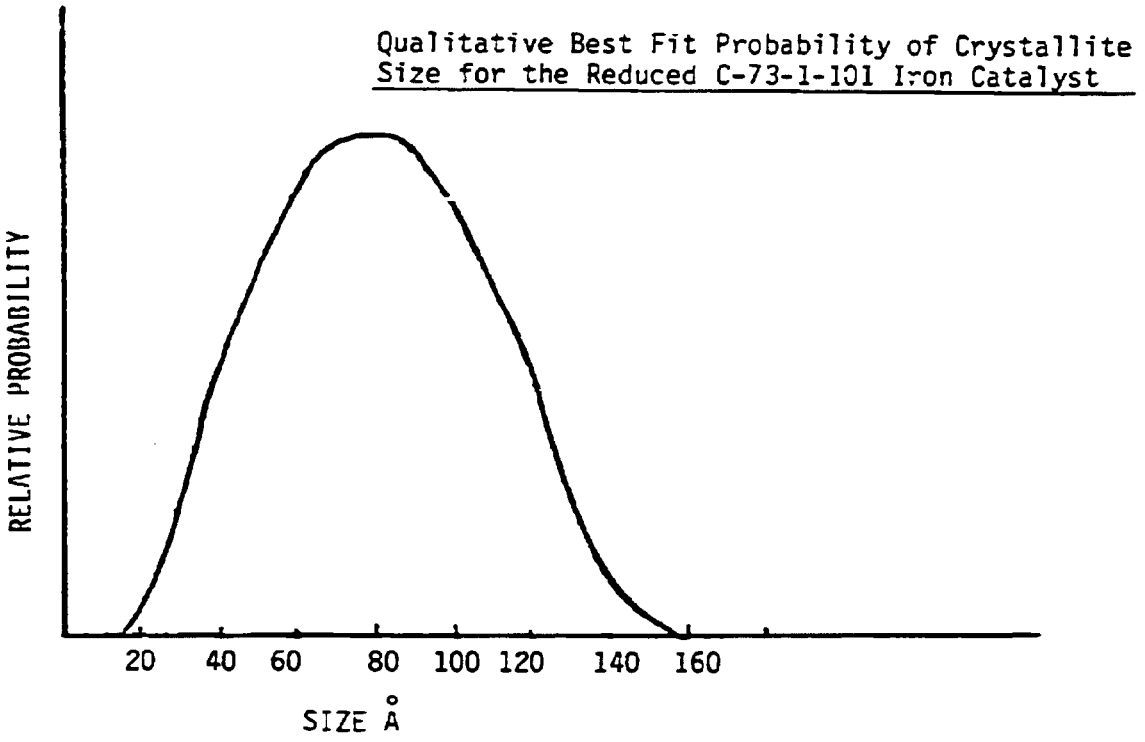


Figure 5-14


Qualitative Best Fit Probability of Crystallite Size for the Reduced C-73-1-101 Iron Catalyst
RELATIVE PROBABILITY
20
40
60
80
100
120
140
160
SIZE Å

5.1.2.2 Testing of the Reduced C-73-1-101 Iron Catalyst in Fixed-Bed Pilot Plant

Nine runs were conducted with the reduced C-73-1-101 catalyst for referencing the fixed-bed pilot plant under four different sets of conditions. The operating conditions and the type of reactor for these runs are summarized in Table 5-1. Some of the key results, such as total weights of hydrocarbons, oxygenates, and water made during the runs, H_2:CO ratios, olefin/paraffin ratios, the total weight recoveries, the amounts of wax extracted from the catalysts at the end of the runs, the amounts of coke on used catalyst, and α' (the growth probability), are also summarized in the same table.

5.1.2.2.1 Tests Under the First Set of Reference Conditions: 250°C Inlet Temperature, 35 atm, H_2:CO Feed Ratio = 1.5 (Molar), 80% Initial CO Conversion

Very large catalyst temperature increases (up to 175°C) occurred in Run 1 with a 10 cc catalyst loading. By reducing the catalyst loading by a factor of about 3 and diluting the catalyst with α-Al_2O_3 powder (4 α-Al_2O_3:1 catalyst wt. ratio), the maximum catalyst temperature increase was lowered to 12°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 in Run 3 (103.1%) due to low feed rates.

Results obtained in Run 3 are summarized in Table 5-7 and Figures 5-15 to 5-17. The gas hourly space velocity was raised from 2400 hr^{-1} to 4500 hr^{-1} and then lowered back to 2700 hr^{-1} during the first 28 hours in order to achieve a CO conversion of about 80% (Figure 5-15). The CO conversion then decreased to about 60% by 40 hours on stream, after which it remained steady until the end of

Table 5-7. Product Distributions in Run 3, 28-55 Hours

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	5.17	48.32
CO	29.31	19.70
CO2	34.46	14.74
H2O	9.29	9.70
HYDROCARBON	20.20	6.95
ALCOHOL	1.57	0.58

ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	12.84	20.23
ETHANOL	40.65	53.32
PROPANOL	4.05	3.41
BUTANOL	30.41	20.71
OTHER OXYGENATES	4.05	2.32

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	9.10	31.06
C2-C4	20.64	38.72
C5-C11	49.25	26.92
C12-C18	9.71	2.75
C19-C25	2.29	0.42
C26+	0.99	0.12
CH4	9.10	31.06
C2P	3.63	6.61
C2=	4.54	8.06
C3P	2.61	3.24
C3=	8.28	10.78
	3.84	3.68
C4P	1.47	1.39
C4=	4.27	4.16
C5	8.35	6.43
C6	8.43	5.42
C7	9.32	5.14
C8	8.16	3.95
C9	6.80	2.93
C10	4.97	1.93
C11	3.22	1.13
C12	3.06	0.99
C13	2.11	0.63
C14	1.45	0.40
C15	0.67	0.17
C16	0.92	0.22
C17	0.90	0.21
C18	0.60	0.13
C19	0.44	0.09
[illegible]	0.40	0.09
	0.36	0.07
[illegible]	0.32	0.06
C23	0.27	0.05
[illegible]	[illegible]	0.04

COMPONENT	WEIGHT %	MOLE %
C25	0.19	0.03
C26	0.16	0.02
C27	0.12	0.02
C28	0.10	0.01
C29	0.08	0.01
C30	0.07	0.01
C31	0.06	0.01
C33	0.05	0.01
C34	0.04	0.00
C35	0.03	0.00
C36	0.03	0.00
C37	0.03	0.00
C38	0.03	0.00
C39	0.03	0.00
C40	0.03	0.00
C41	0.03	0.00
C42	0.03	0.00
C43	0.03	0.00
C44	0.03	0.00
C45	0.03	0.00
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
[illegible]	.	.
[illegible]	.	.
C59	.	.
C60	.	.

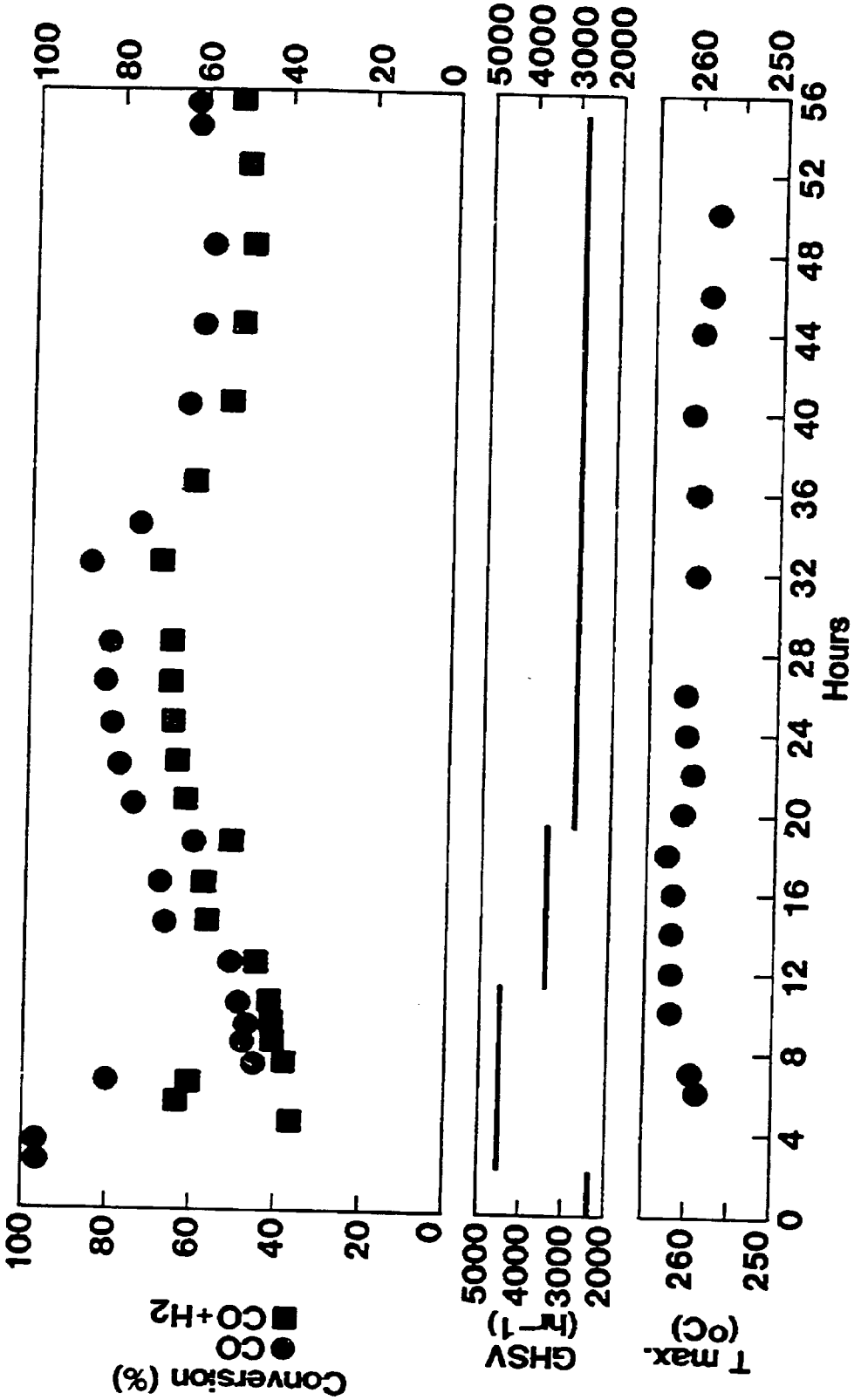


Figure 5-15. C-73-1-101 Iron Catalyst Test Under the First Set of Reference Conditions in Run 3 (H_2:CO Feed Ratio = 1.5, 250°C at Inlet, 35 atm)

Figure 5-16. Anderson-Schulz-Flory Distribution with C-73-1-101 Iron Catalyst Under the First Set of Reference Conditions in Run 3 (Hydrocarbons + Oxygenates; 28-55 Hours)

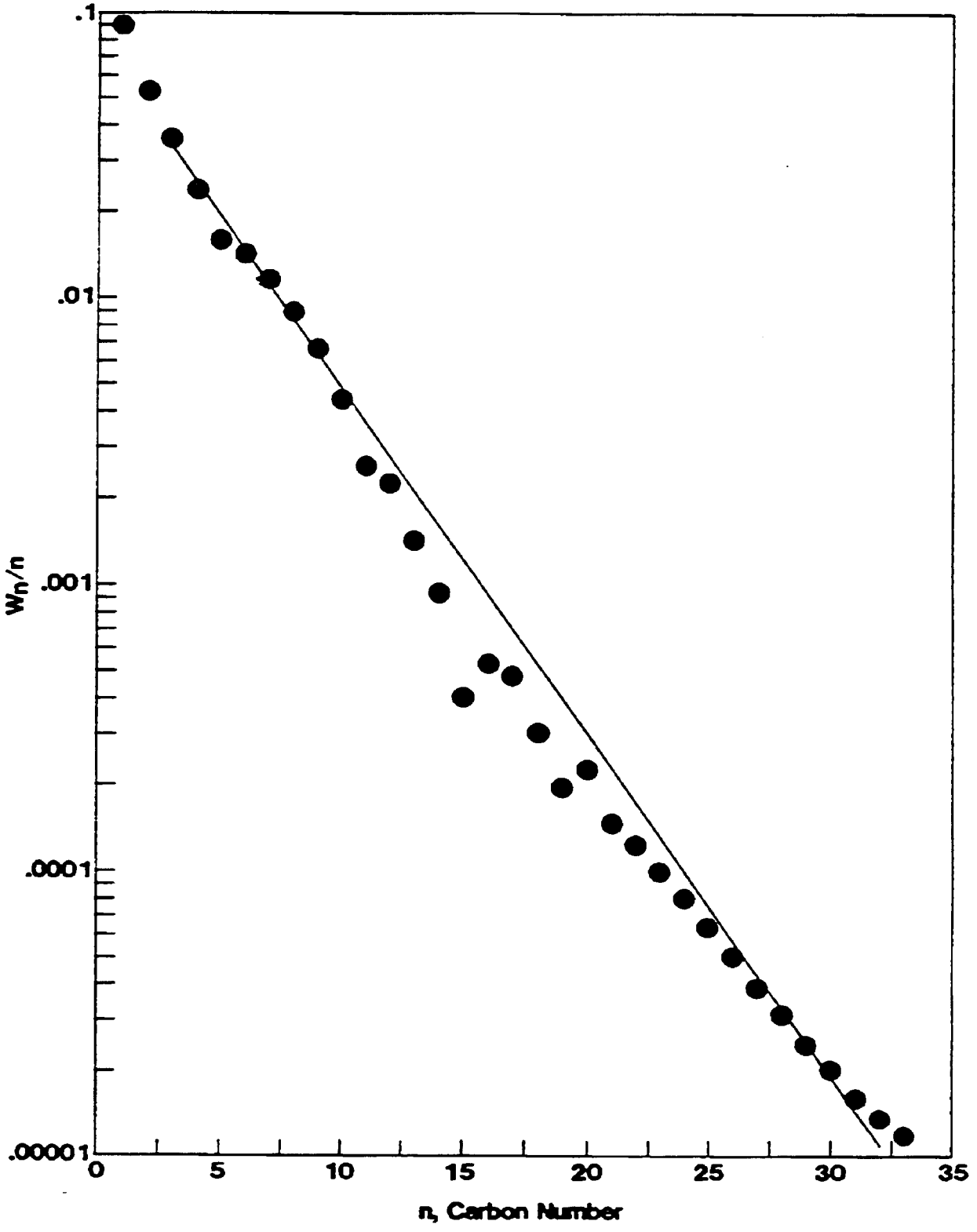
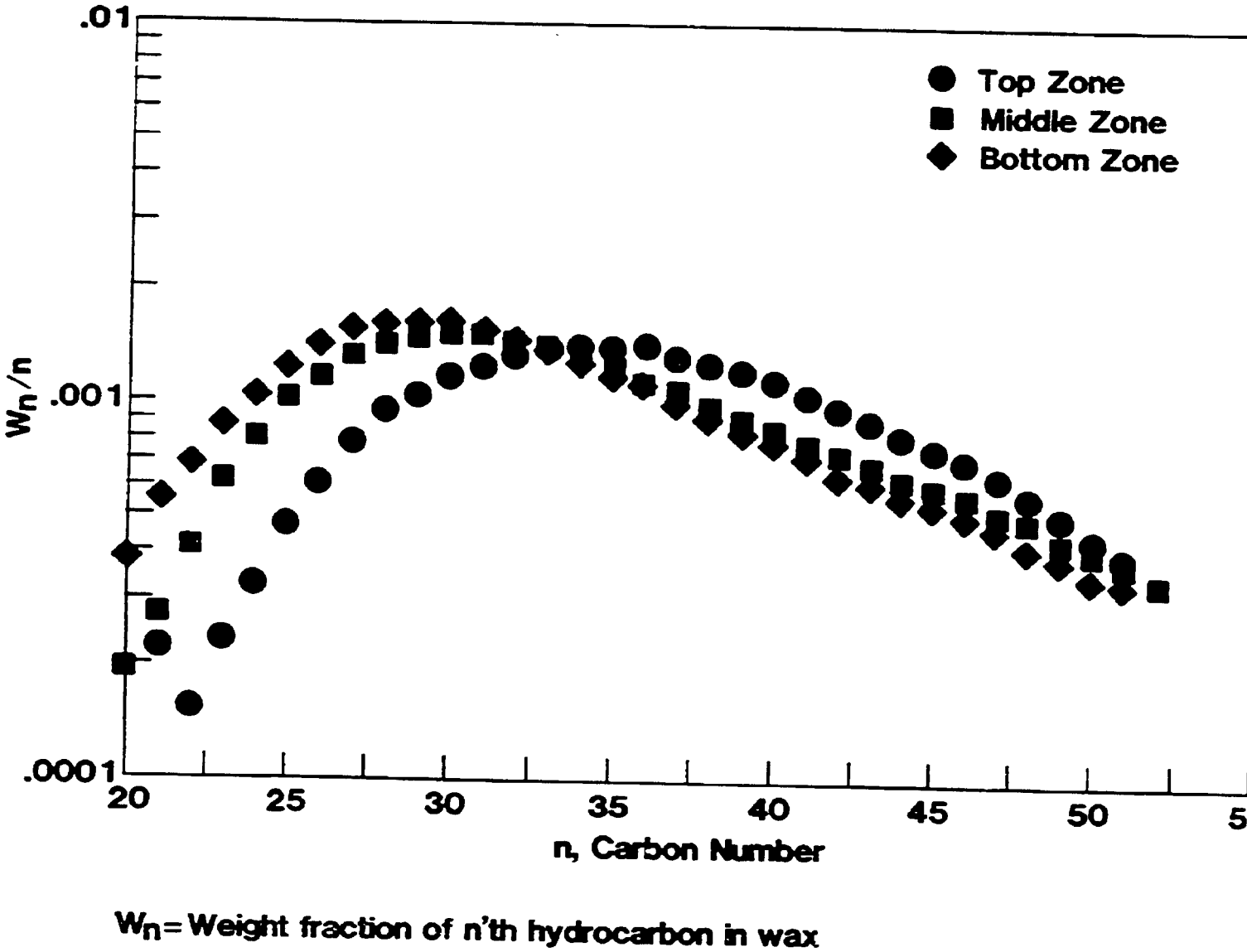


Figure 5-17. Anderson-Schulz-Flory Distribution for the Wax Extracted from C-73-1-101 Iron Catalyst Used in Run 3 Under the First Set of Reference Conditions



W_n = Weight fraction of n'th hydrocarbon in wax

the run at 55 hours on stream. The average H_2:CO usage ratio was 1.0. The Anderson-Schulz-Flory distribution for the hydrocarbons plus oxygenates recovered during the course of the run gave a chain growth probability, α, equal to 0.71 (Figure 5-16). The chain growth probability was much higher for the wax extracted from the used catalyst (Figure 5-17).

5.1.2.2.2 Tests Under the Second Set of Reference Conditions: 250°C Inlet Temperature, 35 atm, H_2:CO Feed Ratio = 0.9 (Molar), 30% Initial CO Conversion

In an attempt to achieve good material balance without causing excessive catalyst temperature increases in Runs 4 and 5, two to three times the amount of catalyst employed in Run 3 were used with the same ratio of α-Al_2O_3 powder diluent to catalyst. Nevertheless, large temperature increases took place.

Run 6 (Tables 5-8 and 5-9 and Figures 5-18 through 5-20) 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 above the inlet temperature were 6-15°C (Figure 5-18). Material recoveries were better than that in Run 3, 100.7 and 102.6 in two successive material balance periods.

Higher space velocities, 4650 and 3800 hr^{-1} GHSV, were used in Run 6 in two successive periods (18-38 hours and 38-60 hours), relative to 2400 hr^{-1} in Run 3, in order to achieve lower CO conversion. The CO conversion was initially 30% (at 18 hours on stream) and later stabilized at 26-30% (Figure 5-18). The average H_2:CO usage ratios for both periods were 1.1. The Anderson-Schulz-Flory distributions for hydrocarbons plus oxygenates recovered during the first and second material balance periods (excluding the wax extracted from the used catalyst) gave consistent α's, 0.79 and 0.80, respectively (Figure 5-19). Higher α was obtained in Run 6 relative to Run 3, probably because of the lower H_2:CO ratio in Run 6: 0.9 at inlet and 0.8 at outlet in Run 6 and 1.5 at inlet and 2.2 at outlet in Run 3.

Table 5-8. Product Distributions in Run 6, 18-38 Hours

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.99	38.20
CO	69.36	47.84
CO2	14.61	6.41
H2O	4.77	5.12
HYDROCARBON	7.02	2.33
ALCOHOL	0.25	0.10

ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	16.97	26.01
ETHANOL	46.27	49.33
PROPANOL	6.17	5.04
BUTANOL	24.42	16.18
OTHER OXYGENATES	6.17	3.44

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	8.66	31.40
C2-C4	29.27	42.49
C5-C11	35.63	19.16
C12-C18	18.91	5.55
C19-C25	6.07	1.19
C26+	1.45	0.21

CH4	8.66	31.40
C2P	2.24	4.34
C2=	5.71	11.84
C3	0.25	0.34
C3P	3.29	4.34
C3=	9.41	13.02
C4	0.75	0.77
C4P	1.04	1.04
C4=	6.58	6.82
C5	3.46	2.83
C6	5.78	3.95
C7	5.05	2.96
C8	5.45	2.80
C9	5.71	2.61
C10	5.38	2.22
C11	4.81	1.80
C12	4.26	1.46
C13	3.63	1.15
C14	3.09	0.91
C15	2.53	0.70
C16	2.11	0.55
C17	1.77	0.43
C18	1.53	0.35
C19	1.33	0.29
C20	1.14	0.24
C21	0.99	0.20
C22	0.85	0.16
C23	0.70	0.13
C24	0.58	0.10
C25	0.48	0.08
C26	0.36	0.06
C27	0.29	0.04
C28	0.22	0.03
C29	0.17	0.02
C30	0.15	0.02
C31	0.10	0.01
C33	0.05	0.01
C34	0.05	0.01
C35	0.02	0.00
C36	0.02	0.00
C37	0.02	0.00
C38	0.00	0.00
C39	0.00	0.00
C40	0.00	0.00
C41	0.00	0.00
C42	0.00	0.00
C43	0.00	0.00
C44	0.00	0.00
C45	0.00	0.00
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.

Table 5-9. Product Distributions in Run 6, 38-60 Hours

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.98	38.21
CO	67.71	46.84
CO2	14.52	6.39
H2O	5.42	5.03
HYDROCARBON	8.08	2.61
ALCOHOL	0.30	0.12

ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	14.92	22.92
ETHANOL	49.36	52.71
PROPANOL	6.50	5.32
BUTANOL	25.96	17.23
OTHER OXYGENATES	3.25	1.82

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	7.87	29.44
C2-C4	26.97	41.06
C5-C11	40.60	23.12
C12-C18	15.76	4.72
C19-C25	6.71	1.34
C26+	2.09	0.31

COMPONENT	WEIGHT %	MOLE %
CH4	7.87	29.44
C2P	3.84	7.67
C2=	4.38	9.38
C3	0.90	1.26
C3P	2.82	3.83
C3=	8.06	11.50
C4	1.78	1.87
C4P	0.00	0.00
C4=	5.19	5.55
C5	2.37	2.00
C6	9.46	6.67
C7	7.89	4.78
C8	6.64	3.52
C9	5.59	2.64
C10	4.49	1.91
C11	4.15	1.61
C12	3.31	1.17
C13	2.82	0.92
C14	2.51	0.76
C15	2.12	0.60
C16	1.87	0.50
C17	1.65	0.41
C18	1.47	0.35
C19	1.31	0.30
C20	1.20	0.26
C21	1.09	0.22
C22	0.96	0.19
C23	0.82	0.15
C24	0.71	0.13
C25	0.60	0.10
C26	0.49	0.08
C27	0.38	0.06
C28	0.29	0.04
C29	0.22	0.03
C30	0.18	0.03
C31	0.13	0.02
C33	0.09	0.01
C34	0.07	0.01
C35	0.07	0.01
C36	0.04	0.01
C37	0.04	0.01
C38	0.04	0.01
C39	0.02	0.00
C40	0.02	0.00
C41	0.00	0.00
C42	0.00	0.00
C43	0.00	0.00
C44	0.00	0.00
C45	0.00	0.00
C46	.	.
C47	.	.
C48	.	.
C49	.	.
C50	.	.
C51	.	.
C52	.	.
C53	.	.
C54	.	.
C55	.	.
C56	.	.
C57	.	.
C58	.	.
C59	.	.
C60	.	.

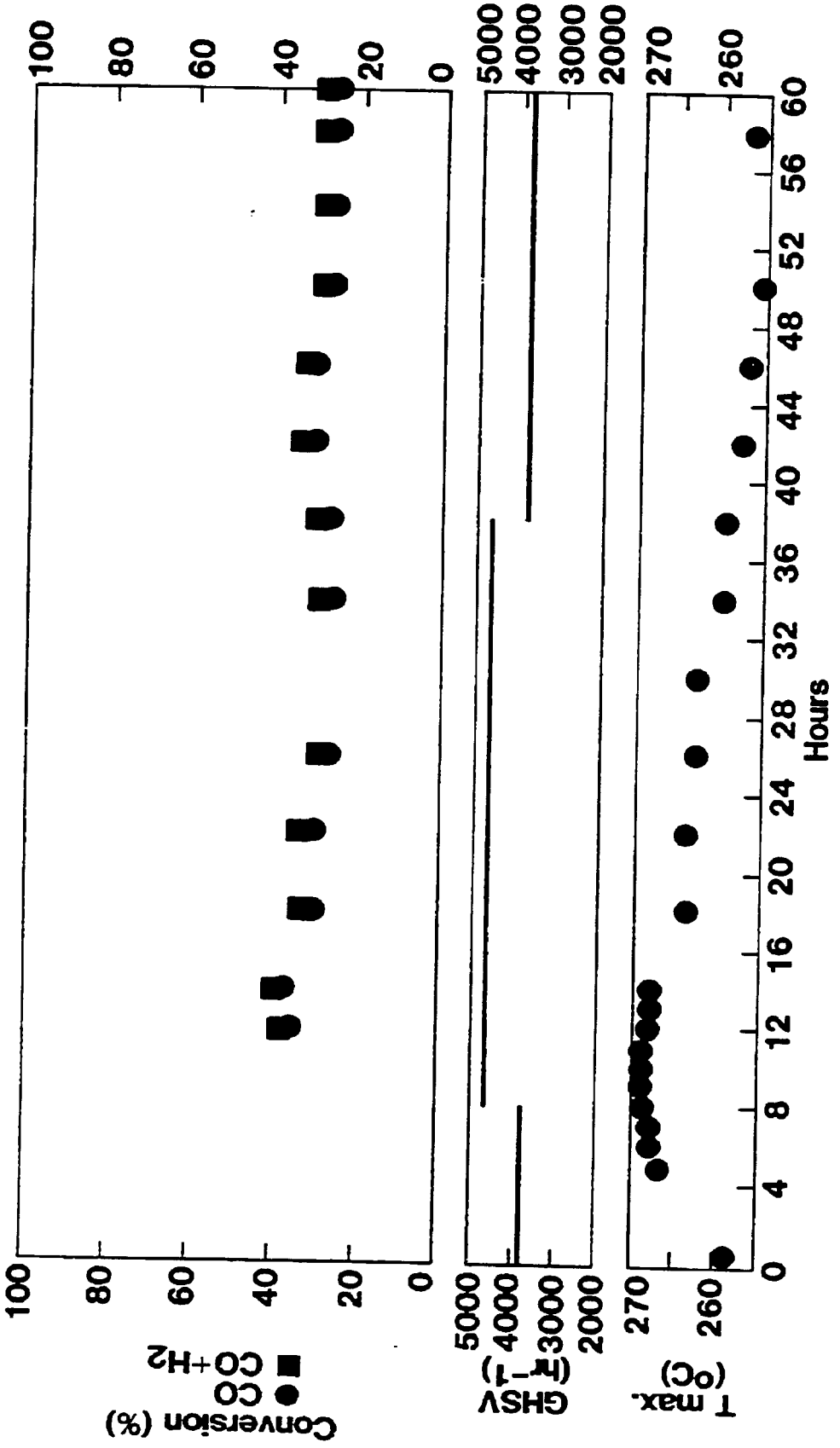


Figure 5-18. C-73-1-101 Iron Catalyst Test Under the Second Set of Reference Conditions in Run 6 (H_2:CO Feed Ratio = 0.9, 250°C at Inlet, 35 atm)

Figure 5-19. Anderson-Schulz-Flory Distribtuion with C-73-1-101 Iron Catalyst Under the Second Set of Reference Conditions in Run 6 (Hydrocarbon + Oxygenates; 18-38 Hours)

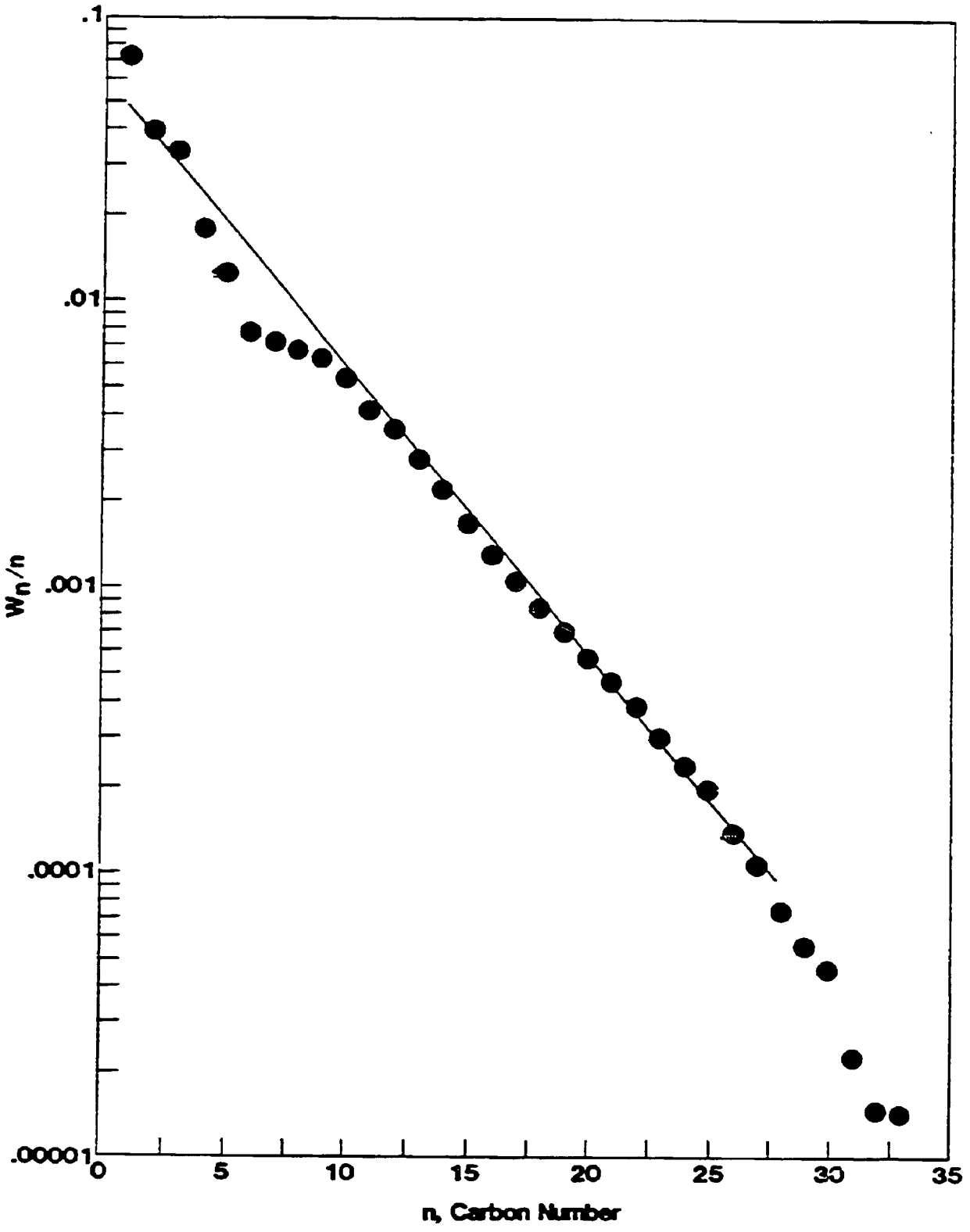
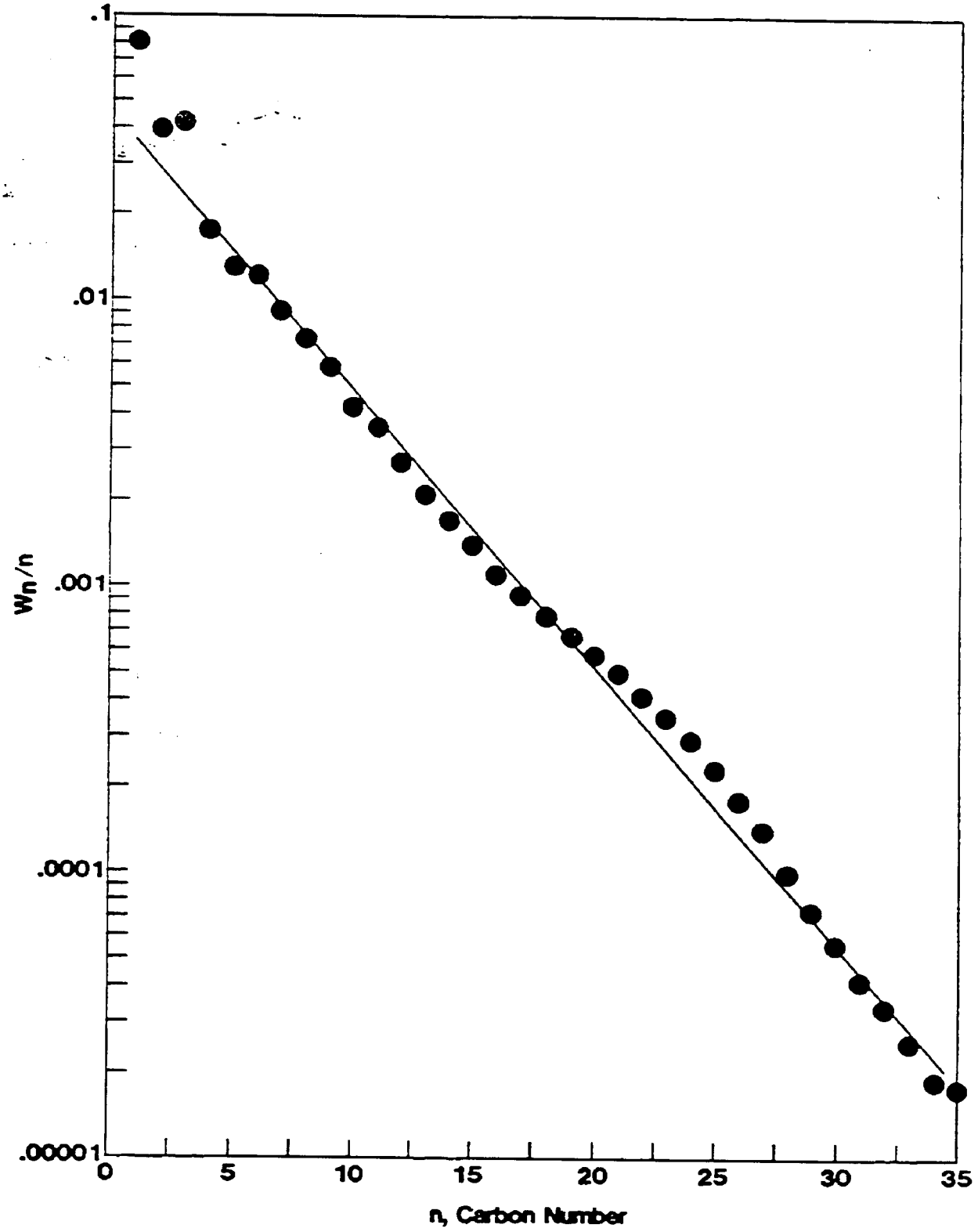


Figure 5-20. Anderson-Schulz-Flory Distribution with C-73-1-101 Iron Catalyst Under the Second Set of Reference Conditions in Run 6 (Hydrocarbons + Oxygenates; 38-60 Hours)



5.1.2.2.3 Test Under the Third Set of Reference Conditions: 208°C Inlet Temperature, 35 atm, H_2:CO Feed Ratio = 0.9 (Molar), ~30% Initial CO Conversion

The same amounts of catalyst and α-Al_2O_3 diluent were used in Run 7 (Table 5-10 and Figures 5-21 through 5-23) as in Run 6. The space velocity, however, was lowered to 950 hr^{-1} GHSV, in order to obtain, at lower temperature, conversions comparable to those in Run 6 (Figure 5-21). The catalyst temperature increases were only 4-5°C (Figure 5-21). The total material recovery was significantly higher than 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 CO conversion was steady around 30% between 38 hours on stream (beginning of the material balance period) and the end of the run (116 hours on stream) (Figures 5-21 and 5-22). The average H_2:CO usage ratio was 1.1. The Anderson-Schulz-Flory distribution for hydrocarbons and oxygenates recovered during the run gave α = 0.74 (Figure 5-23).

An apparently lower α in Run 7 at 208°C compared to Run 6 at 250°C seems surprising. These kinds of results, however, may occur, for instance, if steady state wax production rate was achieved during the line-out period for Run 6, but not for Run 7. Excluding from the overall product distribution the wax made during the material balance period and retained on the catalyst will cause an artificially low α. This will be discussed in a later section.

Table 5-10. Product Distributions in Run 7

TOTAL PRODUCT DISTRIBUTION (W/O ARGON)

COMPONENT	WEIGHT %	MOLE %
H2	3.83	37.01
CO	67.68	47.06
CO2	13.58	6.01
H2O	6.55	7.08
HYDROCARBON	7.64	2.57
ALCOHOL	0.71	0.26

ALCOHOL DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
METHANOL	13.24	21.75
ETHANOL	37.21	42.51
PROPANOL	8.83	7.73
BUTANOL	32.84	23.31
OTHER OXYGENATES	7.87	4.70

HYDROCARBON DISTRIBUTION

COMPONENT	WEIGHT %	MOLE %
CH4	7.86	28.33
C2-C4	28.12	40.70
C5-C11	47.70	26.39
C12-C18	13.71	4.10
C19-C25	2.17	0.43
C26+	0.35	0.05

COMPONENT	WEIGHT %	MOLE %
CH4	7.86	28.33
C2P	2.40	4.62
C2=	5.88	12.13
C3	0.32	0.43
C3P	2.94	3.85
C3=	8.01	11.01
C4	1.02	1.04
C4P	3.83	3.81
C4=	3.70	3.81
C5	8.14	6.62
C6	5.75	3.91
C7	6.20	3.61
C8	7.67	3.92
C9	7.78	3.54
C10	6.78	2.78
C11	5.45	2.03
C12	3.99	1.36
C13	2.94	0.93
C14	2.17	0.64
C15	1.66	0.45
C16	1.24	0.32
C17	0.96	0.23
C18	0.76	0.17
C19	0.58	0.13
C20	0.45	0.09
C21	0.34	0.07
C22	0.27	0.05
C23	0.21	0.04
C24	0.17	0.03
C25	0.14	0.02
C26	0.09	0.01
C27	0.07	0.01
C28	0.06	0.01
C29	0.04	0.01
C30	0.03	0.00
C31	0.03	0.00
C33	0.02	0.00
C34	0.00	0.00
C35	0.00	0.00
C36	0.00	0.00
C37	0.00	0.00
C38	0.00	0.00
C39	0.00	0.00
C40	0.00	0.00
C41	0.00	0.00
C42	0.00	0.00
C43	0.00	0.00
C44	0.00	0.00
C45	0.00	0.00
C46		
C47		
C48		
C49		
C50		
C51		
C52		
C53		
C54		
C55		
C56		
C57		
C58		
C59		
C60		

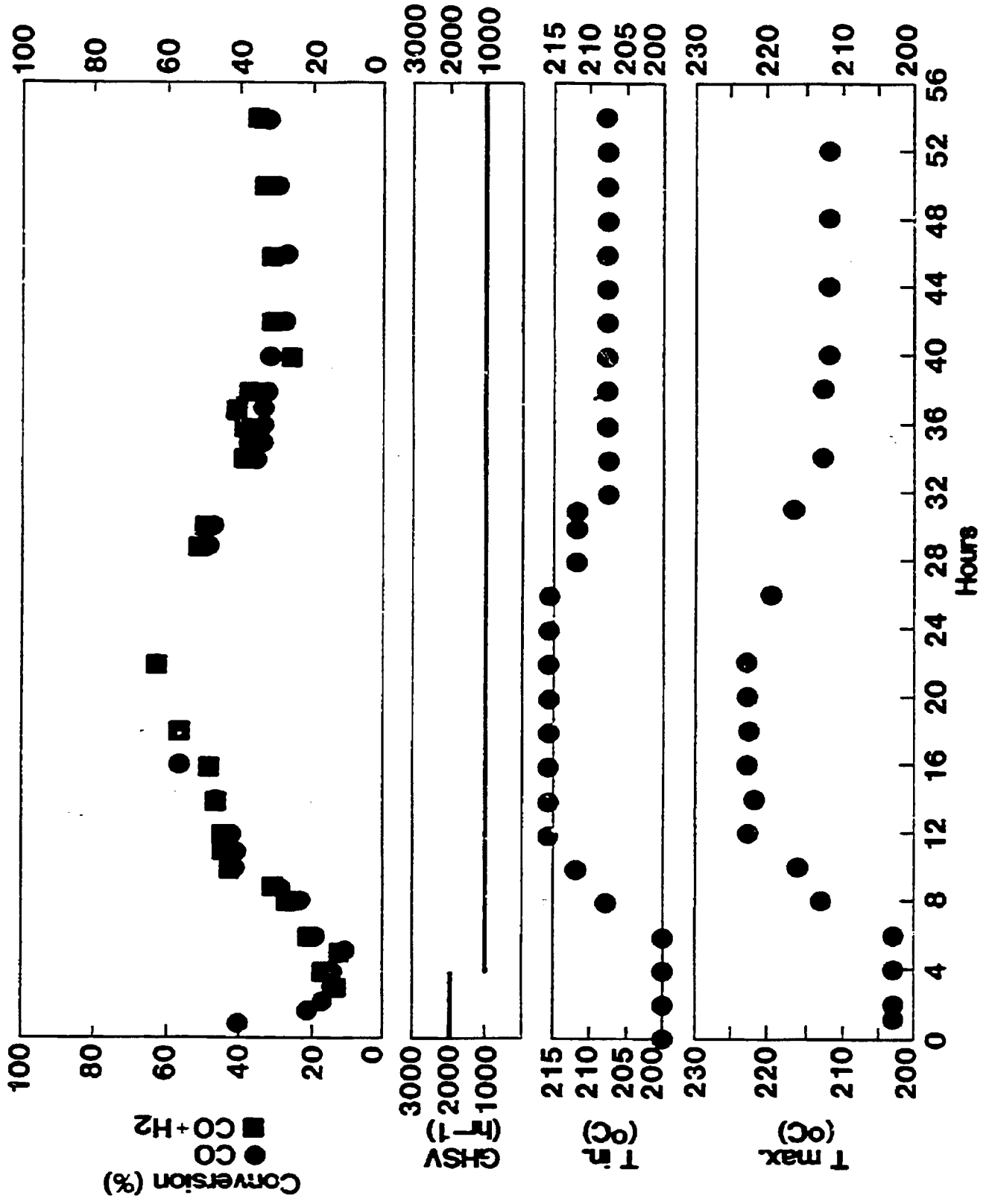


Figure 5-21. C-73-1-101 Iron Catalyst Test Under the Third Set of Reference Conditions in Run 7 (H_2:CO Feed Ratio = 0.9, 35 atm, 0-56 Hours)

Figure 5-22. C-73-1-101 Iron Catalyst Test Under the Third Set of Reference Conditions in Run 7 (H_2:CO Feed Ratio = 0.9, 35 atm, 56-112 Hours)

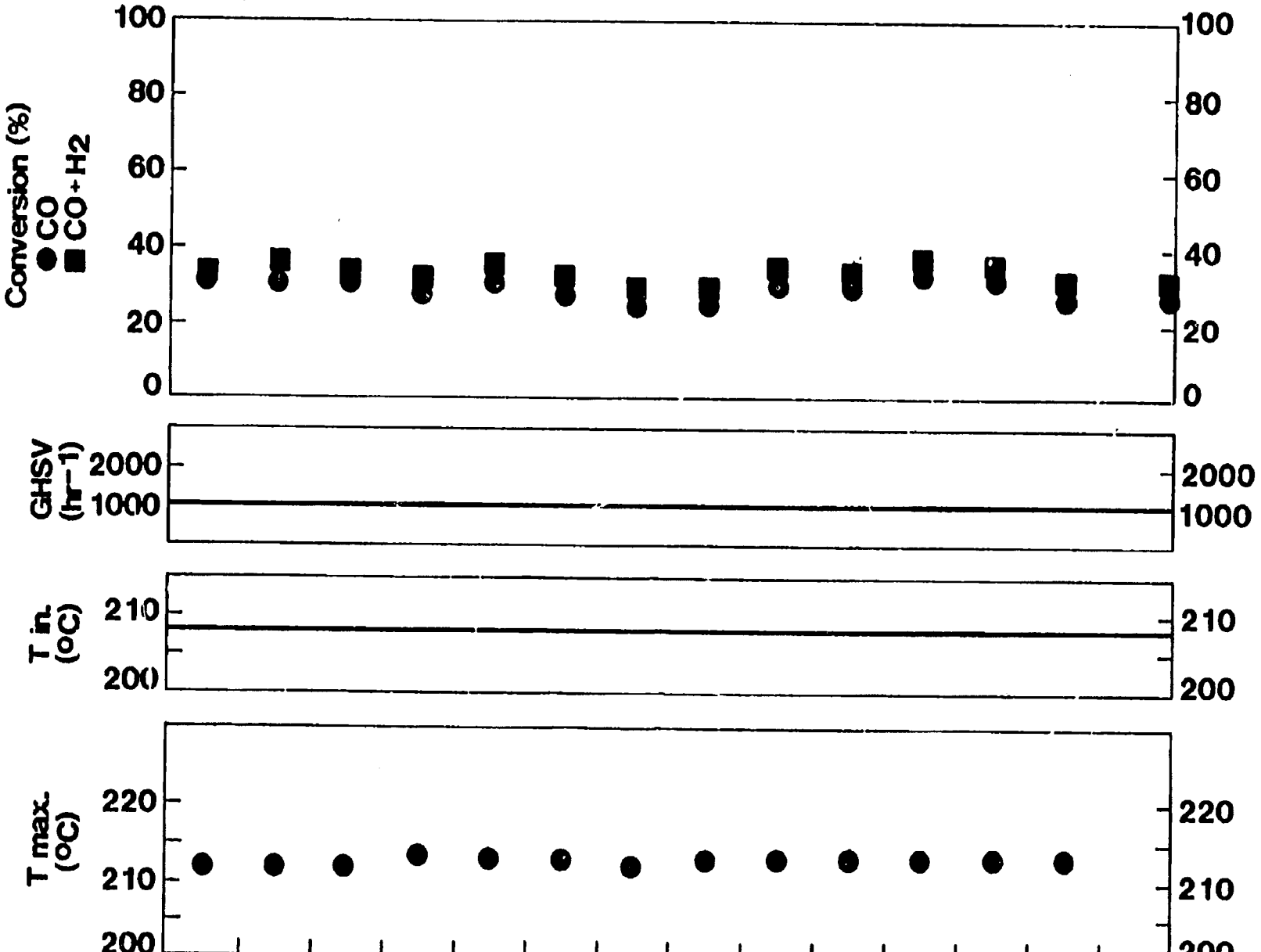


Figure 5-23. Anderson-Schulz-Flory Distribution with C-73-101 Iron Catalyst Under the Third Set of Reference Conditions in Run 7 (Hydrocarbons + Oxygenates; 38-116 Hours)