5.2.1.4.1 Test at 0.9 H_2:CO Feed Ratio, 208°C at Inlet and 35 atm

Catalyst 4956-76 was the first successful micelle-derived catalyst with 4-6 nm ruthenium particles prepared in 30 gram quantity. This catalyst 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 5-152). The results obtained in Run 15 are described in detail in Tables 5-30 and 5-31 and Figures 5-153 through 5-161.

The CO conversion, during the first 25 hours, showed a rapid decrease from 68% to 30% and then leveled off around 28% until 60 hours on stream, followed by another decrease to 15% by 100 hours on stream, after which it remained between 10-15% until the end of the run at 248 hours on stream. Catalytic activity in Run 15 was much higher than that obtained in Runs 16 and 17 with catalysts having smaller ruthenium particles. Most of the initial drop in CO conversion was apparently due to the rapid loss of water gas shift activity of the catalyst, which was nil after about 6 hours (Figure 5-154). The H_2:CO usage ratio remained around 2, as would be expected in the absence of water gas shift activity.

During the run, the catalyst temperature increase over the inlet was initially 22°C and then decreased to -2°C (Figure 5-153).

The gel permeation chromatography results obtained in Run 15 are described in detail in Figure 5-158.

The wax first extracted from the used catalyst had a wide carbon number distribution with an average carbon number of about 50. A subsequent extraction was then conducted on the used catalyst and more wax was obtained but with a much narrower carbon number distribution, around 80. This result indicates that the higher molecular weight wax was harder to extract.

Table 5-30. Product Distributions in Run 15

GAS ANALYSIS, WT%	
HYDROGEN	3.0324
CARBON MONOXIDE	75.9822
CARBON DIOXIDE	0.8916
METHANE	0.0442
ETHANE	0.0036
ETHYLENE	0.0070
PROPANE	0.0155
PROPYLENE	0.0194
BUTANE	0.0235
BUTENE	0.0259
AQUEOUS ANALYSIS, WT%	
WATER	11.0649
ALCOHOLS	
C1	0.0014
C2	0.0057
C3	0.0000
C4	0.0113
C5	0.0299
C6	0.0000
C7	0.0000
C8	0.0000
C9	0.0000
C10	0.0000
ALDEHYDES	
C1	0.0000
C2	0.0000
C3	0.0000
C4	0.0000
C5	0.0000
C6	0.0000
C7	0.0000
C8	0.0000
C9	0.0000
C10	0.0000
OTHER OXYGENATES	
C1	0.0000
C2	0.0000
C3	0.0000
C4	0.0000
C5	0.0000
C6	0.0000
C7	0.0000
C8	0.0000
C9	0.0000
C10	0.0000

TOTAL PRODUCT DISTRIBUTION	
WEIGHT PCTS WITHOUT ARGON	
HYDROGEN	3.632
CARBON MONOXIDE	75.982
CARBON DIOXIDE	0.892
WATER	11.065
HYDROCARBONS	8.381
OXYGENATES	0.048
HYDROCARBON DISTRIBUTION	
C1	0.528
C2 - C4	1.133
C5 - C11	5.454
C12 - C18	5.670
C19 - C25	6.381
C26 PLUS	80.834
C1 - C44	36.289
C45 PLUS	63.711
OXYGENATES DISTRIBUTION	
ALCOHOLS	100.000
ALDEHYDES	0.000
OTHER OXYGENATES	0.000
MOLE PCTS WITHOUT ARGON	
HYDROGEN	34.852
CARBON MONOXIDE	52.471
CARBON DIOXIDE	0.392
WATER	11.881
HYDROCARBONS	0.391
OXYGENATES	0.013
RECOVERIES	
OVERALL	85.158
CARBON	84.511
HYDROGEN	85.445
OXYGEN	85.471
ARGON	85.706
CORRECTED RECOVERIES	
OVERALL	99.361
CARBON	98.606
HYDROGEN	99.695
OXYGEN	99.725

Table 5-31. Hydrocarbon Distributions in Run 15

C1	0.5278	C51	0.7551	C101	0.4752	C151	0.2237	C201	0.1004
C2	0.1263	C52	0.7452	C102	0.4706	C152	0.2196	C202	0.0988
C3	0.4169	C53	0.7357	C103	0.4660	C153	0.2155	C203	0.0973
C4	0.5898	C54	0.7264	C104	0.4614	C154	0.2115	C204	0.0957
C5	0.7968	C55	0.7175	C105	0.4569	C155	0.2075	C205	0.0942
C6	0.0786	C56	0.7209	C106	0.4524	C156	0.2035	C206	0.0927
C7	0.7102	C57	0.7125	C107	0.4311	C157	0.1996	C207	0.0913
C8	0.7991	C58	0.7044	C108	0.4266	C158	0.1957	C208	0.0898
C9	0.7860	C59	0.6963	C109	0.4222	C159	0.1918	C209	0.0884
C10	1.1418	C60	0.6882	C110	0.4179	C160	0.1880	C210	0.0870
C11	1.1412	C61	0.6801	C111	0.4135	C161	0.1843	C211	0.0857
C12	0.9811	C62	0.6719	C112	0.4092	C162	0.1806	C212	0.0843
C13	0.8379	C63	0.7076	C113	0.4049	C163	0.1770	C213	0.0830
C14	0.7579	C64	0.6989	C114	0.4006	C164	0.1734	C214	0.0817
C15	0.7358	C65	0.6900	C115	0.3963	C165	0.1700	C215	0.0804
C16	0.7285	C66	0.6811	C116	0.3921	C166	0.1665	C216	0.0792
C17	0.8239	C67	0.6721	C117	0.3878	C167	0.1632	C217	0.0780
C18	0.8048	C68	0.6632	C118	0.3836	C168	0.1599	C218	0.0767
C19	0.8379	C69	0.6545	C119	0.3794	C169	0.1641	C219	0.0756
C20	0.8520	C70	0.6460	C120	0.3751	C170	0.1609	C220	0.0744
C21	0.8856	C71	0.6321	C121	0.3709	C171	0.1579	C221	0.0732
C22	0.9160	C72	0.6242	C122	0.3667	C172	0.1549	C222	0.0721
C23	0.9457	C73	0.6167	C123	0.3625	C173	0.1520	C223	0.0710
C24	0.9669	C74	0.6095	C124	0.3436	C174	0.1491	C224	0.0699
C25	0.9769	C75	0.6026	C125	0.3394	C175	0.1464	C225	0.0689
C26	0.9850	C76	0.5959	C126	0.3351	C176	0.1437	C226	0.0678
C27	0.9795	C77	0.5894	C127	0.3309	C177	0.1410	C227	0.0668
C28	0.9766	C78	0.5831	C128	0.3267	C178	0.1384	C228	0.0658
C29	0.9691	C79	0.5769	C129	0.3224	C179	0.1359	C229	0.0648
C30	0.9797	C80	0.5709	C130	0.3182	C180	0.1335	C230	0.0639
C31	0.9497	C81	0.5852	C131	0.3140	C181	0.1311	C231	0.0629
C32	0.9340	C82	0.5793	C132	0.3097	C182	0.1287	C232	0.0620
C33	0.9530	C83	0.5736	C133	0.3055	C183	0.1264	C233	0.0611
C34	0.9127	C84	0.5679	C134	0.3012	C184	0.1242	C234	0.0602
C35	0.9169	C85	0.5623	C135	0.2970	C185	0.1220	C235	0.0593
C36	0.8934	C86	0.5568	C136	0.2928	C186	0.1199	C236	0.0585
C37	0.8660	C87	0.5514	C137	0.2885	C187	0.1178	C237	0.0576
C38	0.8617	C88	0.5460	C138	0.2843	C188	0.1157	C238	0.0567
C39	0.8416	C89	0.5407	C139	0.2800	C189	0.1137	C239	0.0559
C40	0.8376	C90	0.5354	C140	0.2758	C190	0.1118	C240	0.0551
C41	0.8241	C91	0.5302	C141	0.2716	C191	0.1098	C241	0.0543
C42	0.8248	C92	0.5251	C142	0.2673	C192	0.1080	C242	0.0536
C43	0.8125	C93	0.5140	C143	0.2631	C193	0.1061	C243	0.0529
C44	0.8060	C94	0.5090	C144	0.2530	C194	0.1043	C244	0.0521
C45	0.8420	C95	0.5040	C145	0.2488	C195	0.1025	C245	0.0514
C46	0.8312	C96	0.4991	C146	0.2446	C196	0.1008	C246	0.0508
C47	0.8204	C97	0.4942	C147	0.2404	C197	0.0991	C247	0.0501
C48	0.8096	C98	0.4894	C148	0.2362	C198	0.0974	C248	0.0494
C49	0.7990	C99	0.4846	C149	0.2320	C199	0.1036	C249	0.0488
C50	0.7652	C100	0.4799	C150	0.2278	C200	0.1020	C250	0.0481

Figure 5-153. Catalyst 4956-76 with 4-6 nm Ruthenium Particles: Conversions in Run 15 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 35 atm)

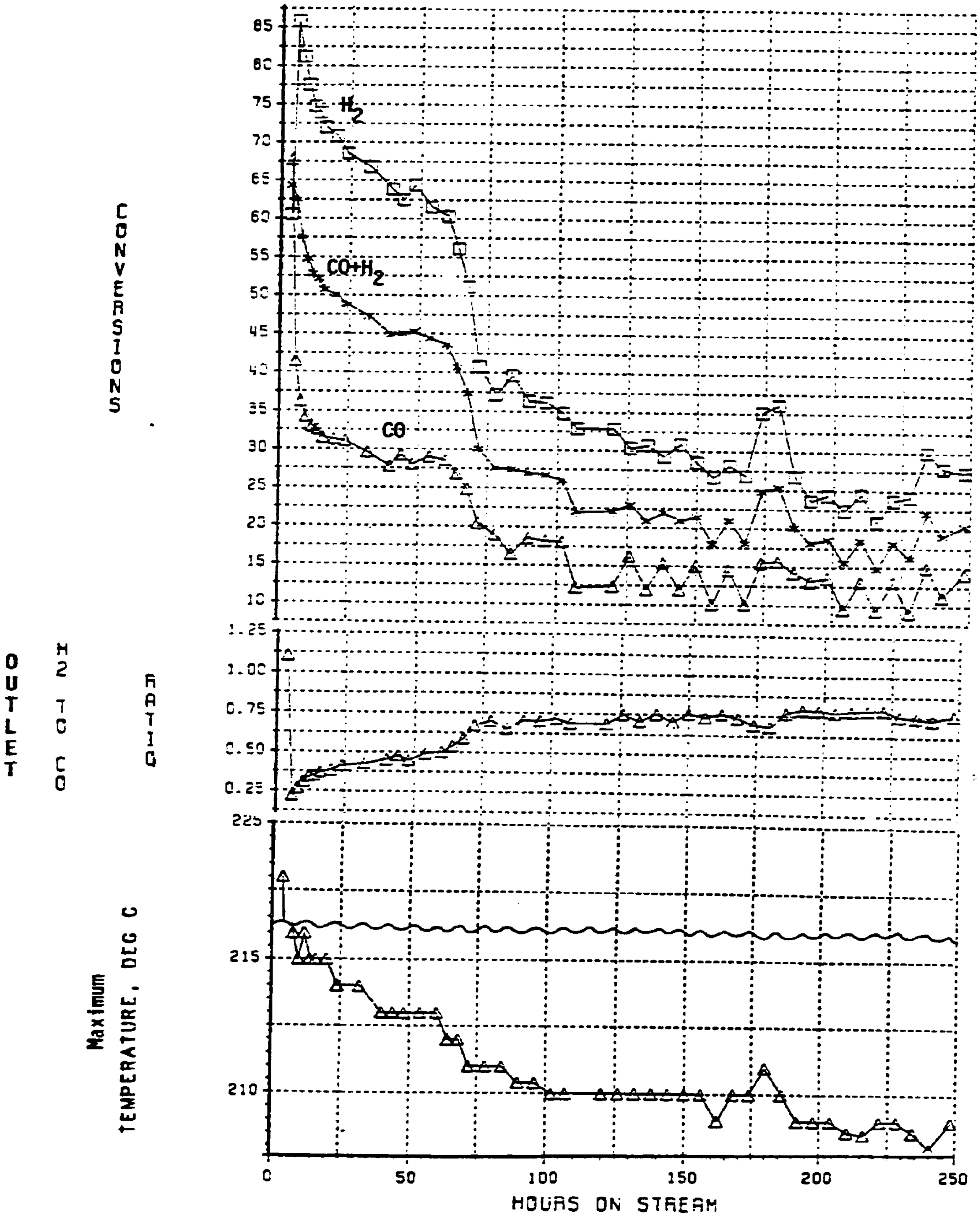


Figure 5-154. Catalyst 4956-76 with 4-6 nm Ruthenium Particles: Water Gas Shift Activity in Run 15 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 35 atm)

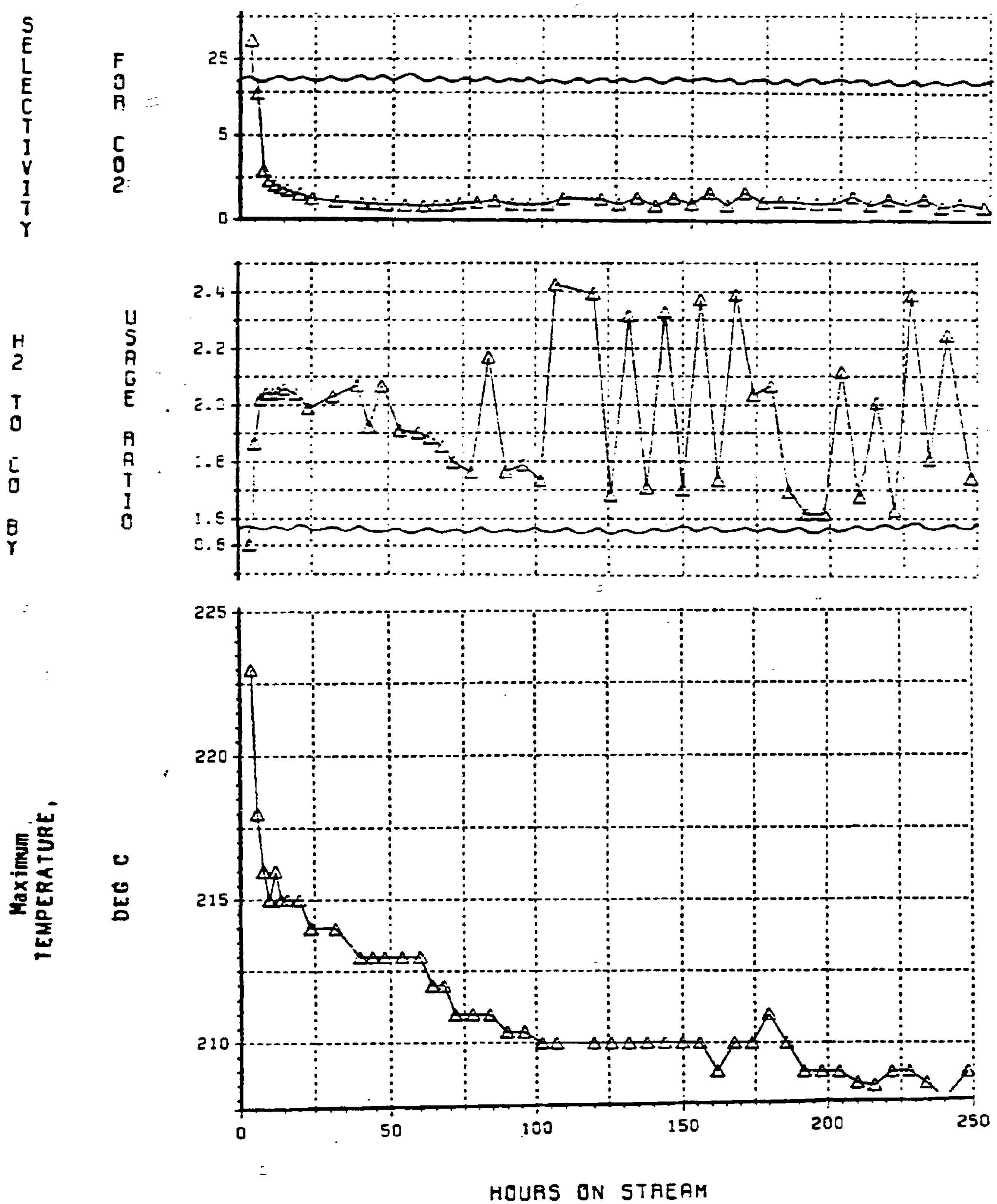


Figure 5-155. Catalyst 4956-76 with 4-6 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 15 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 35 atm)

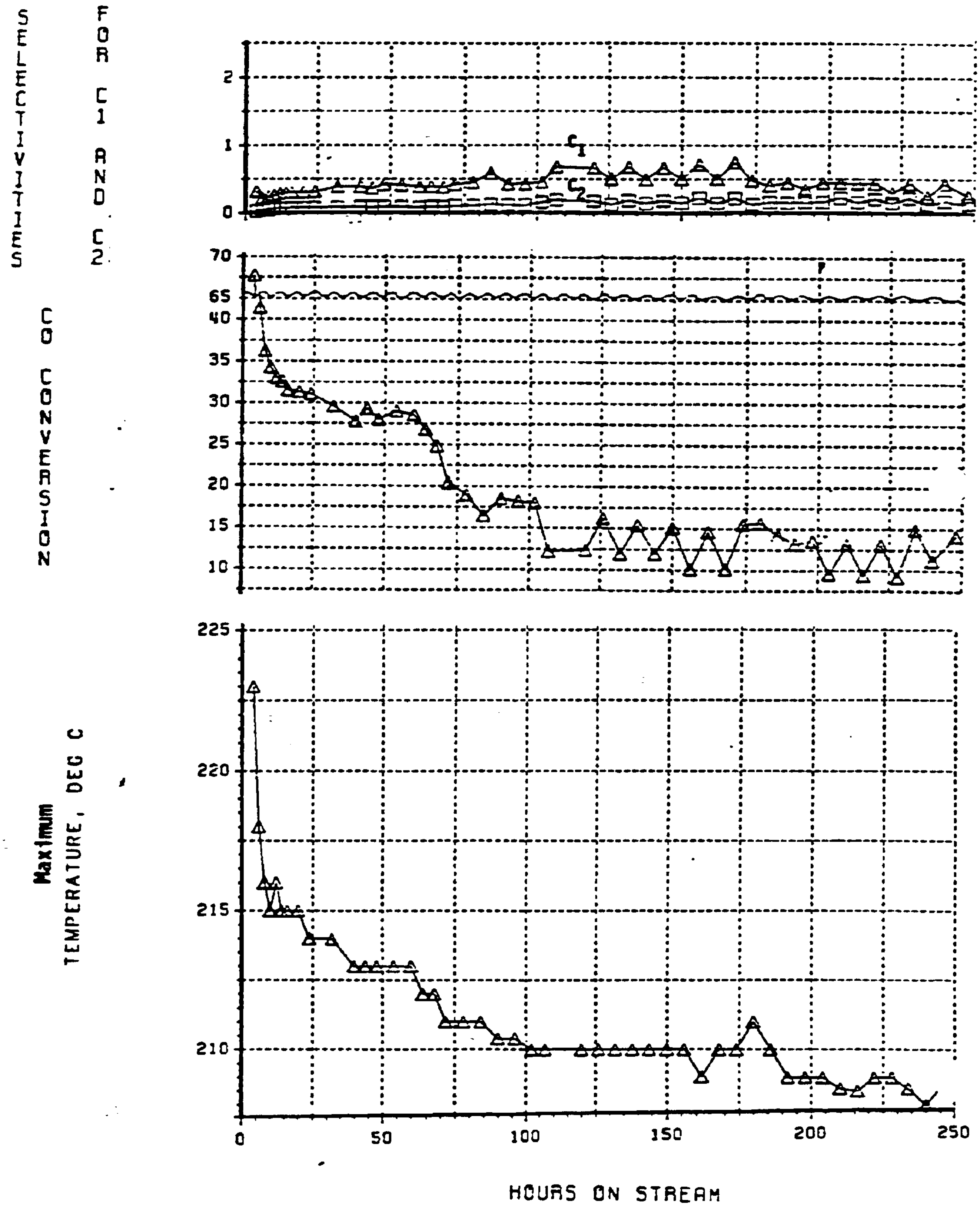


Figure 5-156. Catalyst 4956-76 with 4-6 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 15 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 35 atm)

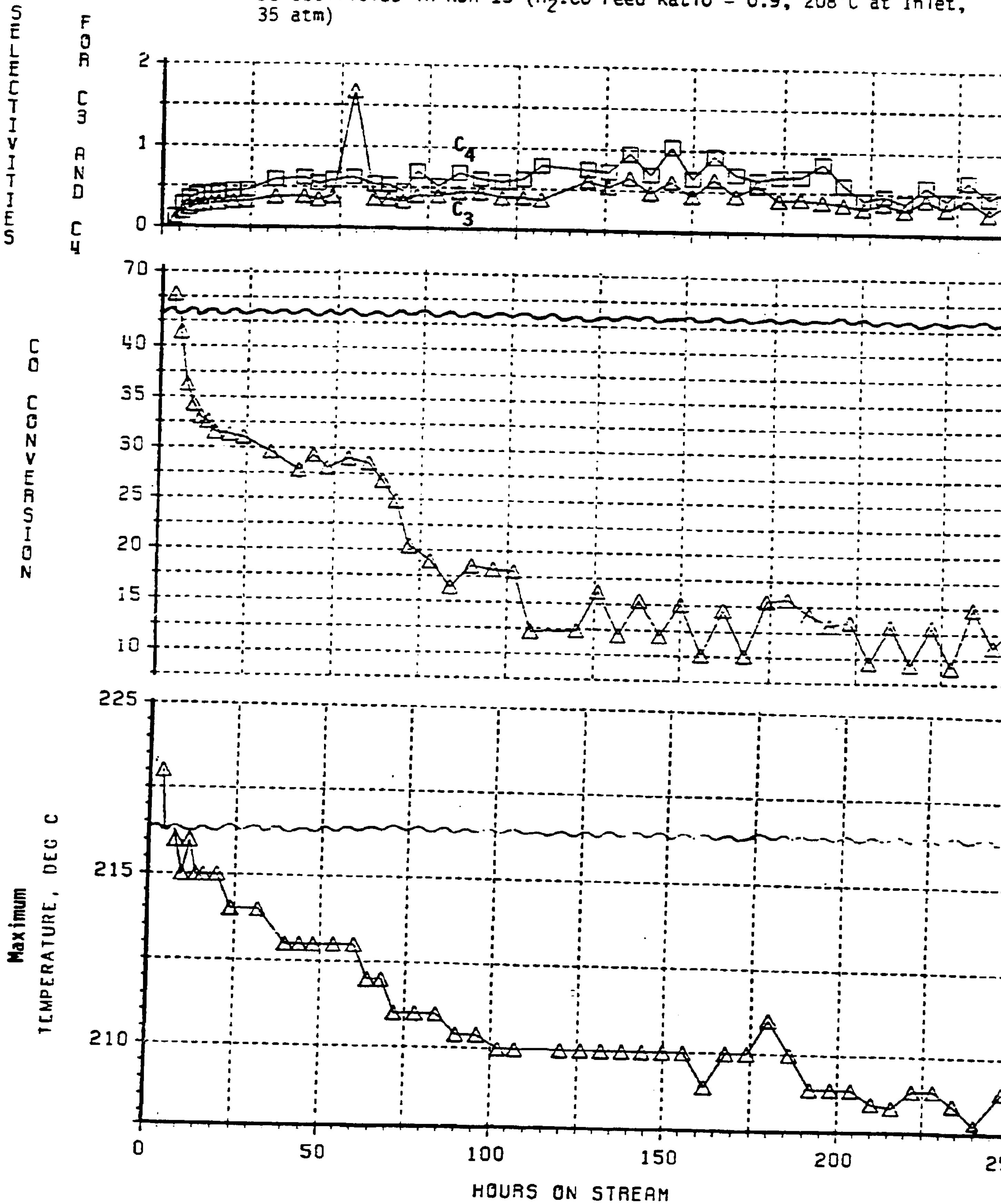


Figure 5-157. Catalyst 4956-76 with 4-6 nm Ruthenium Particles: Olefin: Paraffin Ratios in Run 15 (H_2:CO Feed Ratio = 0.9, 208°C at Inlet, 35 atm)

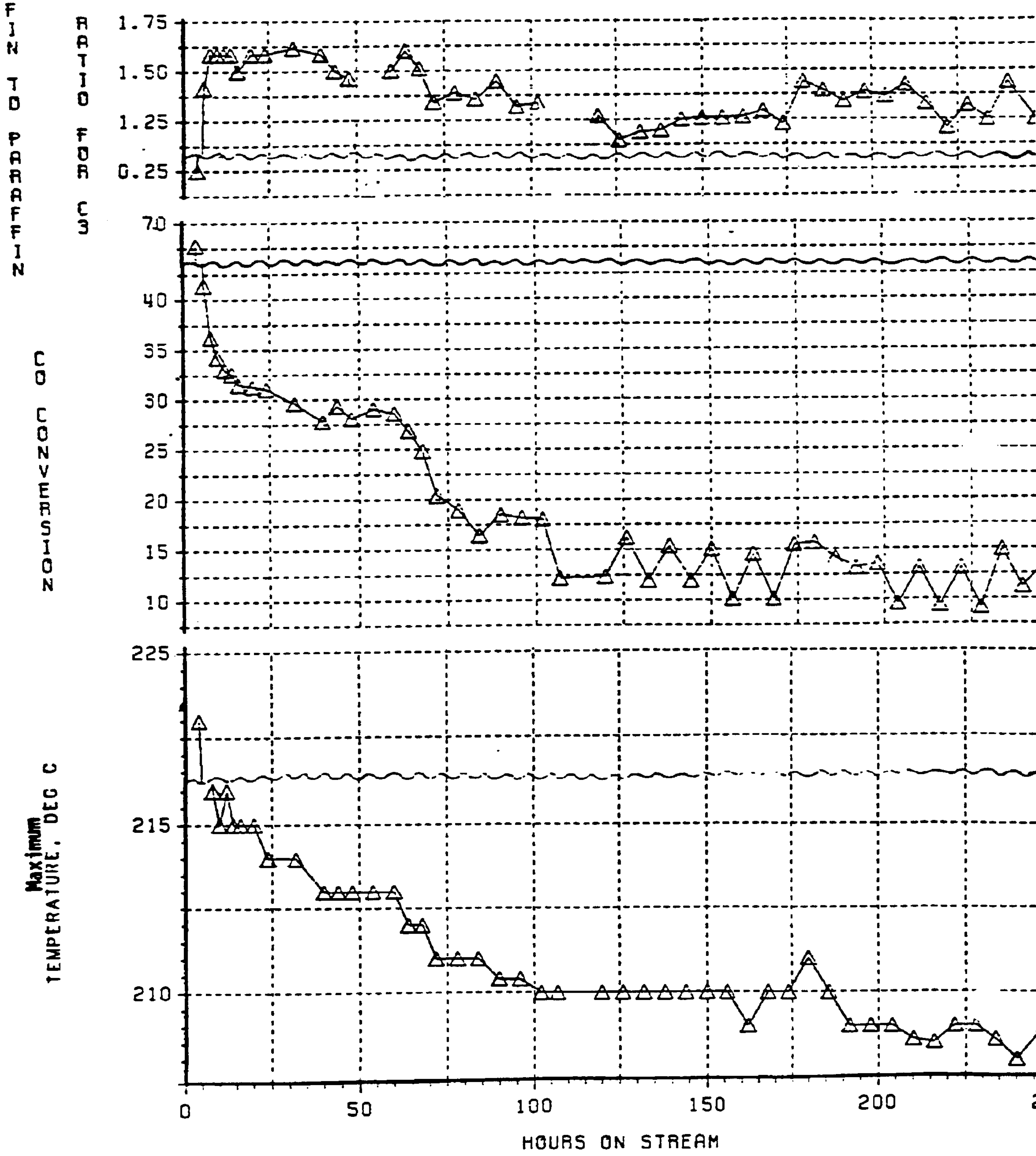


Figure 5-158. Carbon Number Distribution by Gel Permeation Chromatography of Run 15 Products

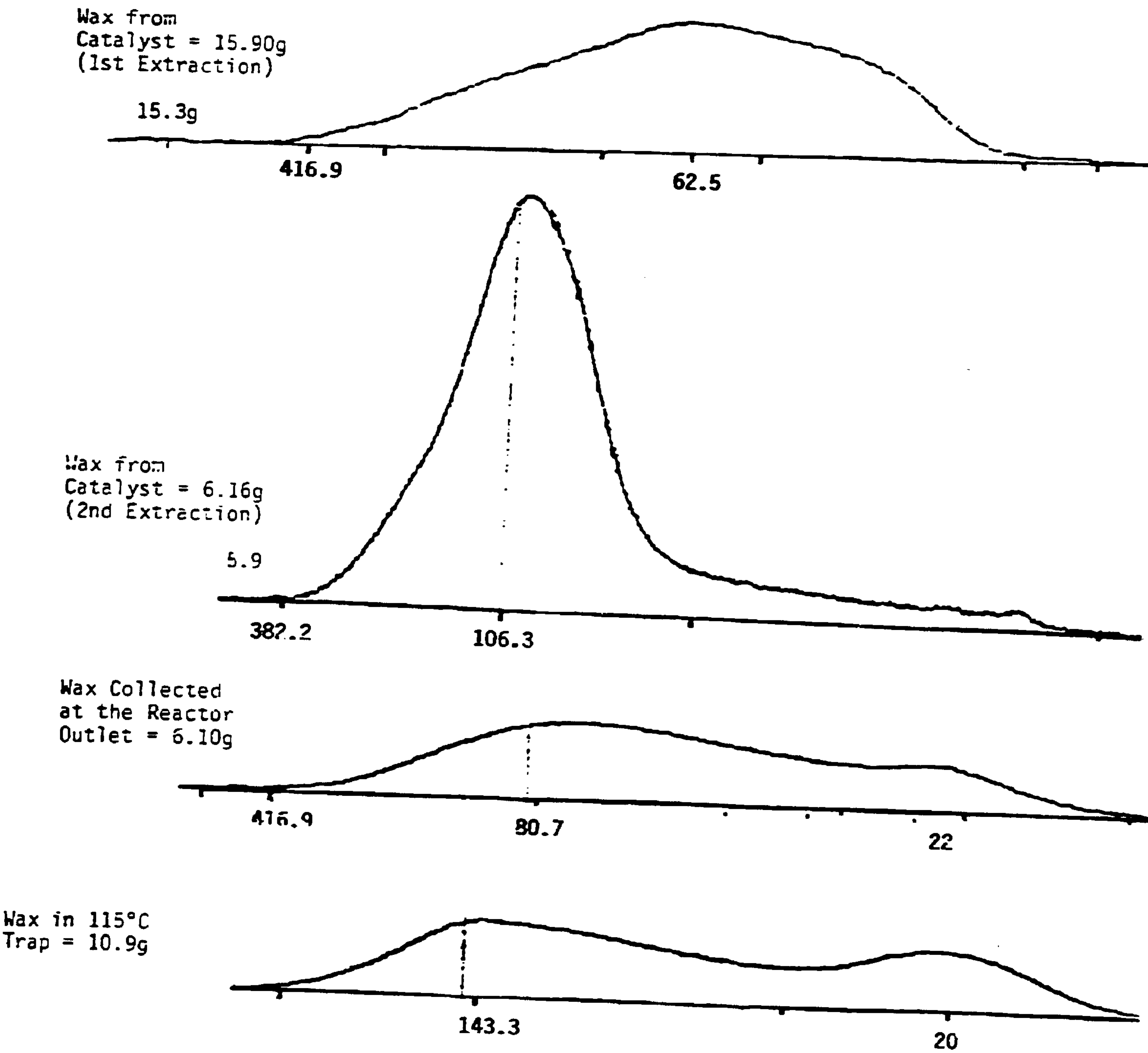


Figure 5-159. Anderson-Schulz-Flory Distribution with Catalyst 4956-76 Having 4-6 nm Ruthenium Particles in Run 15 (Hydrocarbons + Oxygenates)

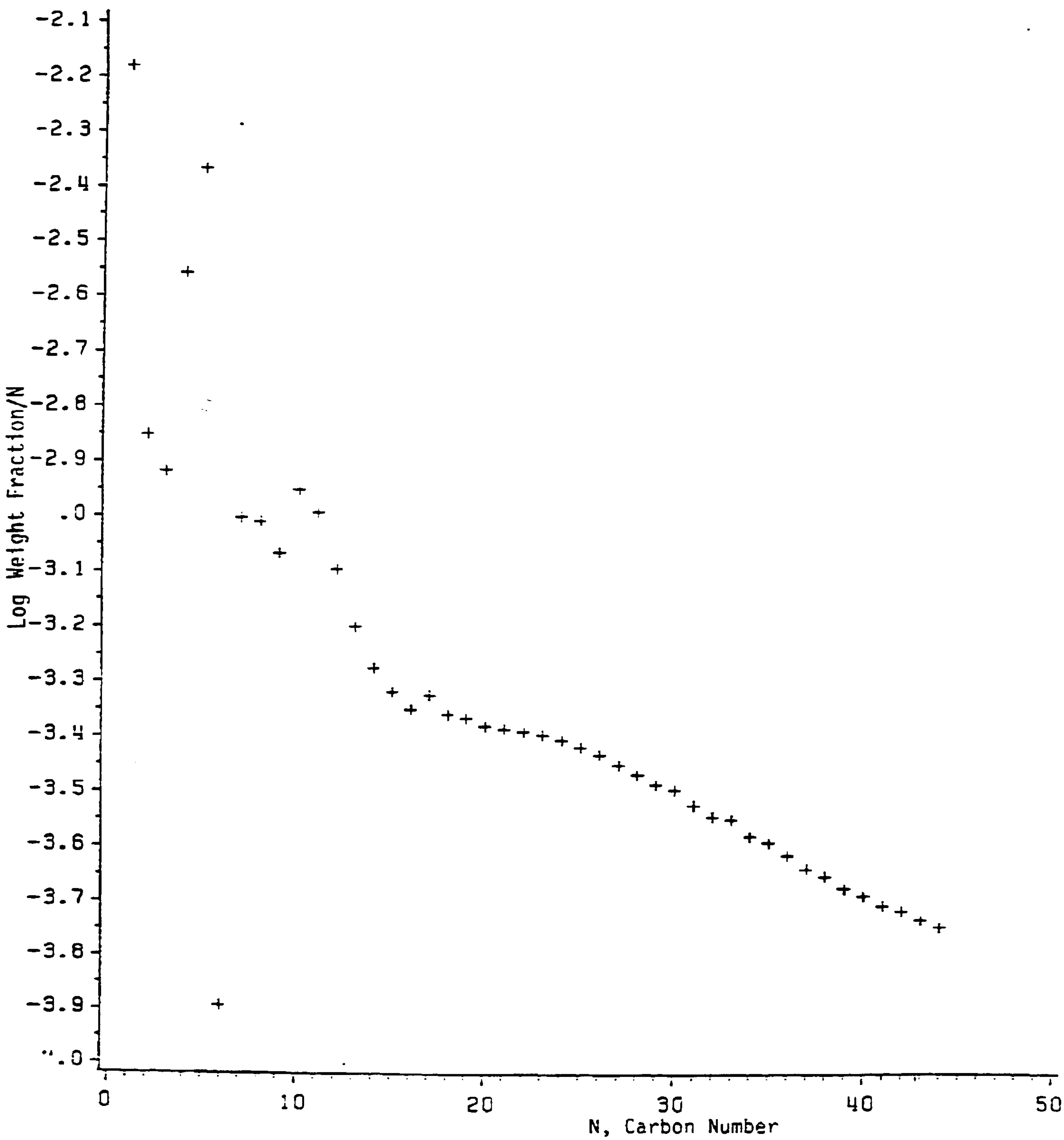


Figure 5-160. Anderson-Schulz-Flory Distribution with Catalyst 4956-76 Having 4-6 nm Ruthenium Particles in Run 15 (Hydrocarbons Only, C_1-C_{44})

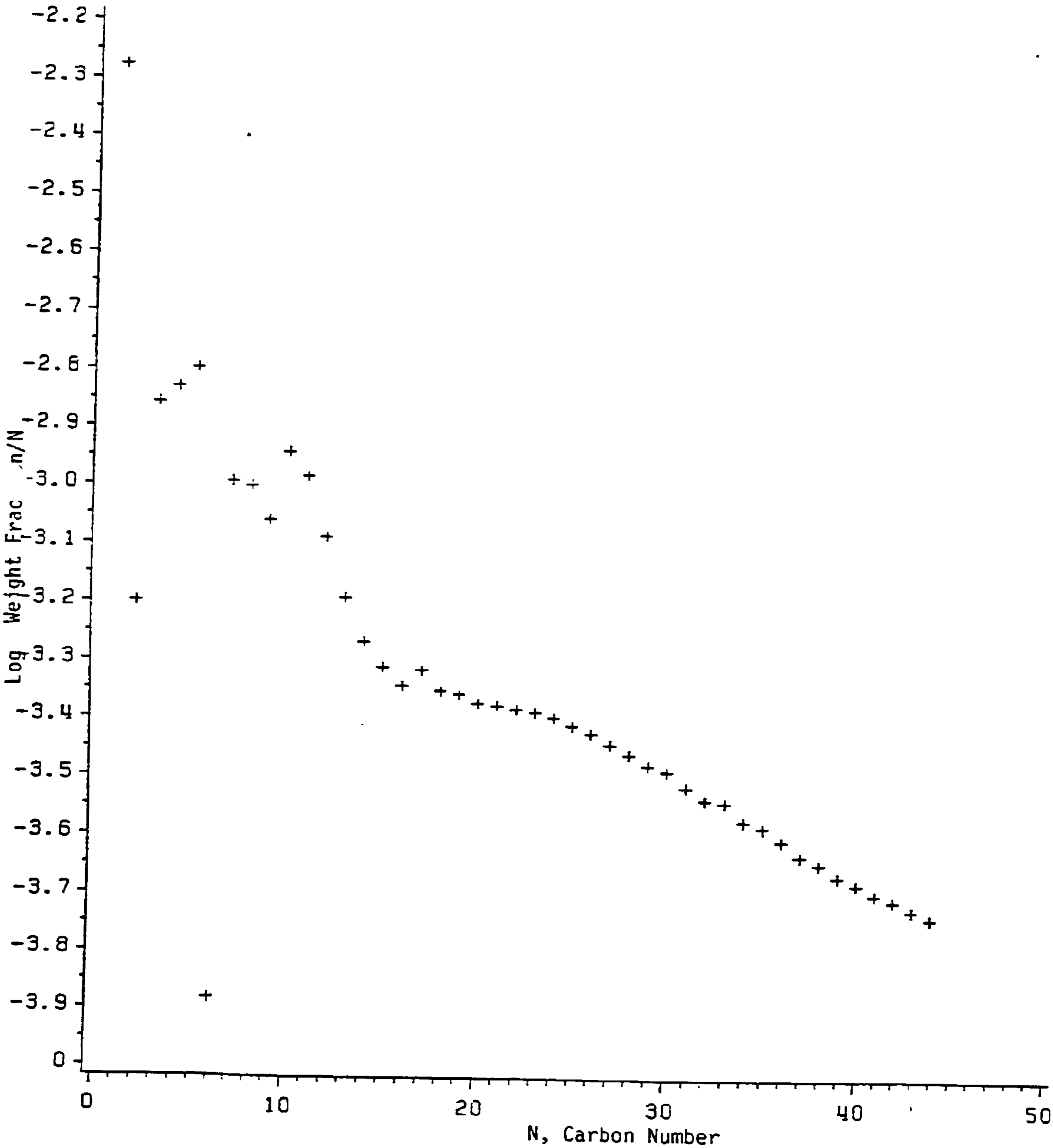
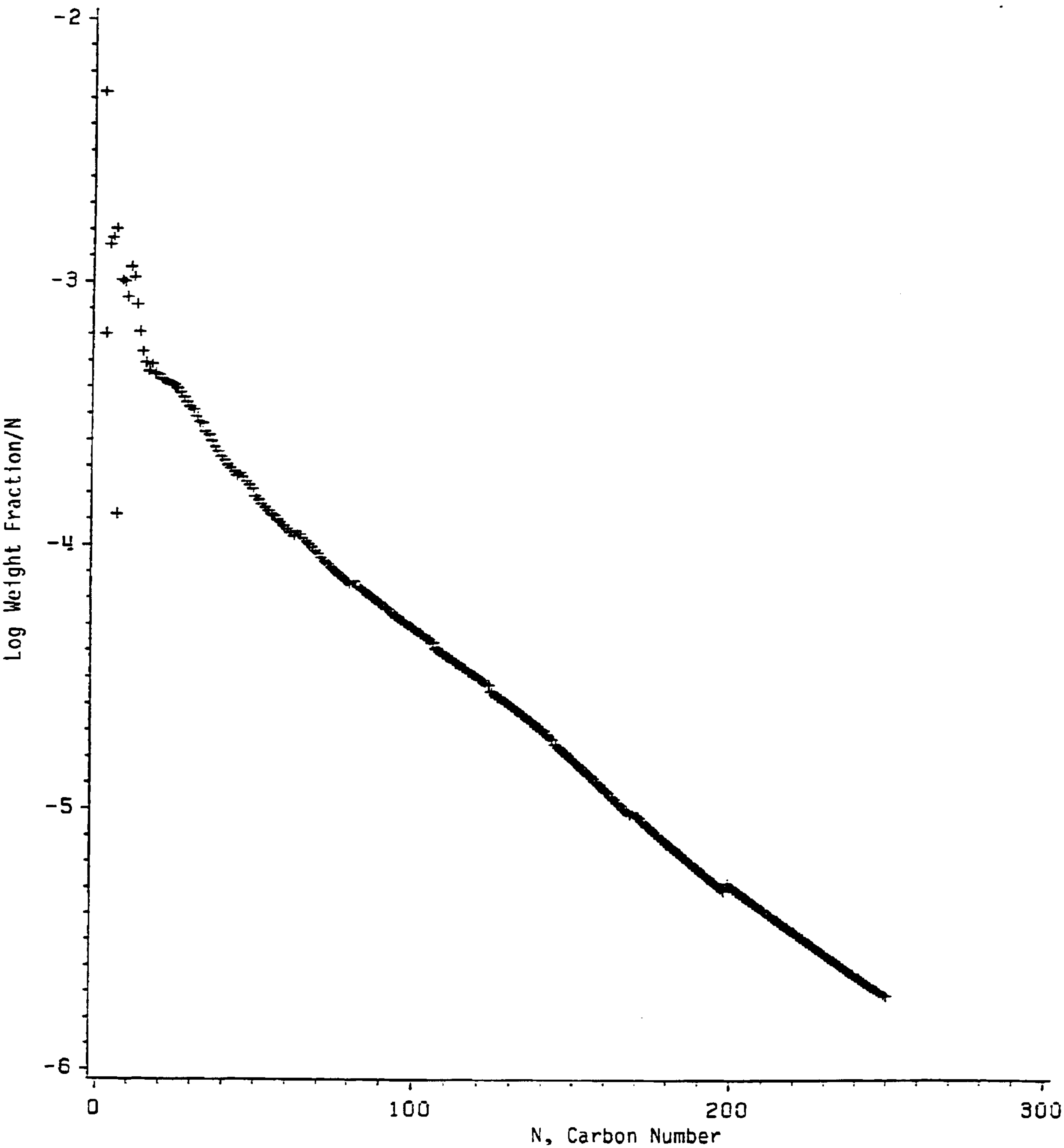


Figure 5-161. Anderson-Schulz-Flory Distribution with Catalyst 4956-76 Having 4-6 nm Ruthenium Particles in Run 15 (Hydrocarbons Only, C_1-C_{250})



In Run 15 a waxy product was also collected at the reactor outlet. This product apparently was collected after steady state wax production rate was reached and the catalyst pores were filled with the liquid product. The carbon number distribution for the products collected at the reactor outlet was consistent with the carbon number distribution of the wax extracted from the catalyst. This result may indicate that the hydrocarbon product distribution did not show a noticeable change during the run.

It is interesting to note that the product at the reactor outlet also contained lighter hydrocarbons with an average molecular weight similar to that obtained in the high temperature-high pressure separator.

The carbon number distributions for the products collected in the high temperature-high pressure separator were also bimodal. Apparently, the high molecular weight products were collected by liquid overflowing from the catalyst pores after steady state wax production rate was reached. The lighter hydrocarbons were probably representative of the typical carbon number range products collected in this separator during this entire run.

Assuming the high molecular weight products (with an average carbon number of about 80) at the reactor outlet and in the high temperature-high pressure separator were collected after the catalyst pores were filled with liquid product, it is roughly estimated that steady state wax production rate was achieved in about 170 hours in Run 15.

The selectivity to methane in Run 15 was higher than would be expected from the Anderson-Schulz-Flory analysis at higher carbon numbers. The carbon atom selectivity to C_2-C_4 products, in Run 15, as with other ruthenium catalysts, were significantly lower than expected from the Anderson-Schulz-Flory analysis at higher carbon numbers (Figure 5-160).

The Anderson-Schulz-Flory analysis for hydrocarbons resulted in the $\alpha = 0.830$ in C_1-C_{15} range, $\alpha = 0.966$ in the C_{15}-C_{60} carbon number range and $\alpha = 0.977$ in the C_{60}-C_{200} range (Figure 5-161). Chain growth probabilities obtained in Run 15 are higher relative to those obtained in Runs 16 and 17 with catalysts having smaller ruthenium metal particles.

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 particle size, which remained 4-6 nm (Figures 5-162 and 5-163). Also, there was no ruthenium loss from the catalyst.

Ruthenium Metal Particle Size Maintenance During Fischer-Tropsch Synthesis with 4-6 NM Ruthenium on γ-Al_2O_3

(STEM Micrographs)

Figure 5-162
FRESH

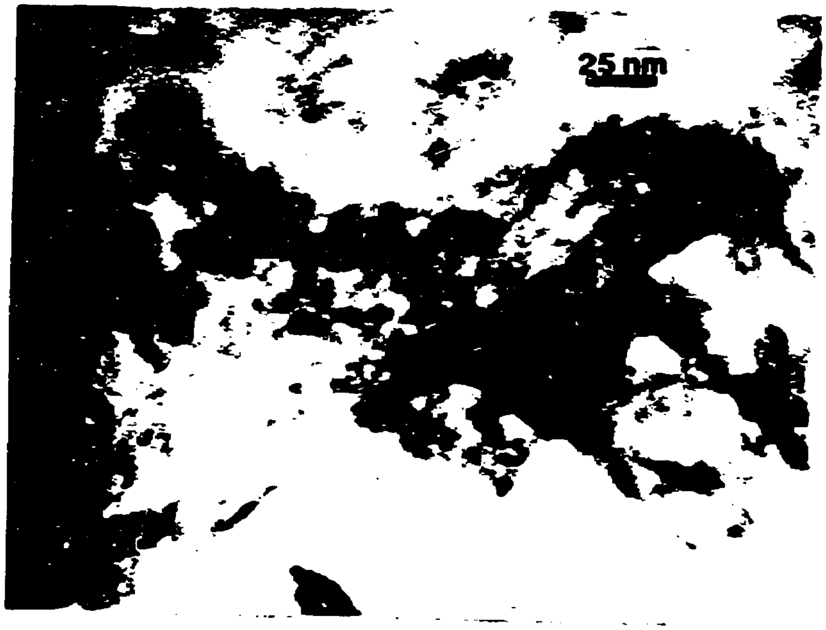
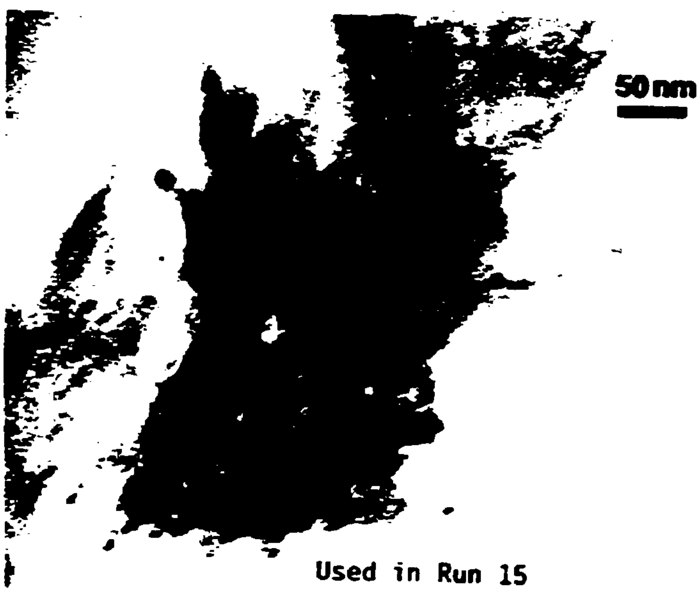


Figure 5-163
USED



Used in Run 15

5.2.1.4.2 Test with Inactive Catalyst

Test with Catalyst 4956-76 having 4-6 nm size ruthenium metal particles indicated that ruthenium metal agglomeration did not occur. Also, highest activity and lowest light hydrocarbon selectivities were obtained with 4-6 nm ruthenium particles relative to catalysts having smaller ruthenium metal particles. Further investigations with ~5 nm size ruthenium particles were conducted.

Catalyst 4966-108 had over 95% of the ruthenium particles in the 4-6 nm size range. This catalyst was tested in Run 26 at H_2:CO feed ratio = 2, 208°C, 35 atm and a gas hourly space velocity of 125 hr^{-1}. The catalyst was essentially inactive. The CO conversion decreased from 3% to <1 in 5 hours. In an attempt to reactivate the catalyst, the catalyst was treated with H_2 at 380°C for 4 hours, and then tested under the original conditions. However, the catalyst was still inactive. The CO conversion decreased from 6% to $\leq$1 in 3 hours. The attempts to increase the conversion by increasing the temperature to 225°C and by decreasing the space velocity failed, and therefore the run was terminated.

According to STEM examination of the used catalyst, there was no obvious change in the ruthenium metal particle size during the test. Leco sulfur analysis showed the sulfur level to be <0.01%.

Used Catalyst 4966-108 was also analyzed by emission for trace impurities. The following elements were found in relatively higher concentration than typically found in catalysts:

0.012% Cr

0.07% Ba

0.005% Sn

<0.0003% Ag

Used Catalyst 4966-108 was finally analyzed by XPS. The Cr 2p, Ba 3d and Ag 3d regions were carefully scanned (Figure 5-164). No Ba and Ag were found, however 0.21% of Cr was found. Also, some low level of Zn was detected. It is not presently clear how the catalyst was contaminated and whether any of these elements were responsible for the inactivity of Catalyst 4966-108.

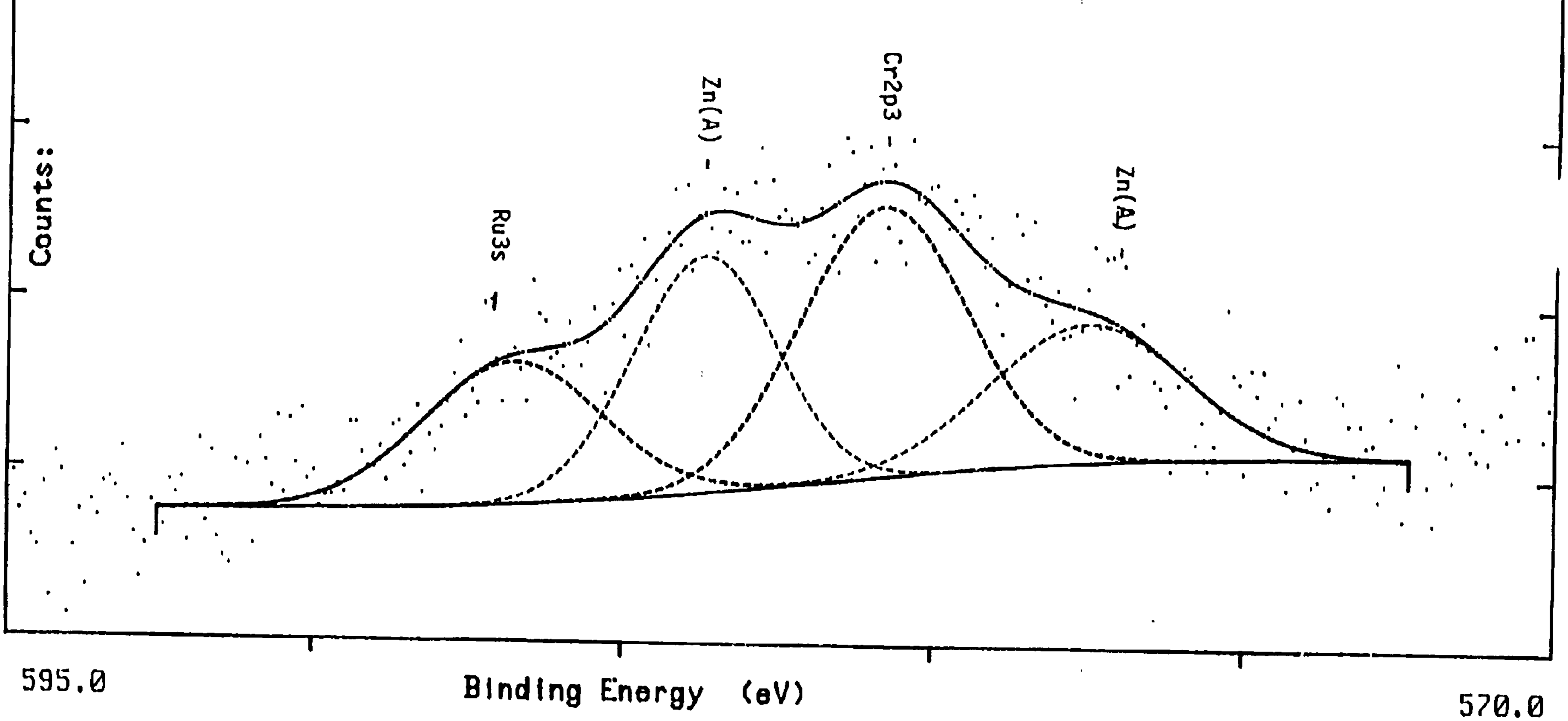
Figure 5-164. XPS Examination of Catalyst 4966-108 After Use in Run 26

File: 4966_108
MRS Region: 10
# of Scans: 90
Flood Gun: 0.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

Sample Description: 1% Ru on Gamma Alumina (40-60 A Ru crystallites) [Cr2p region]

2000

Energy	Width	Area	%
577.53	3.67	13844	20.6
580.79	3.12	22799	33.9
583.67	2.70	17304	25.8
586.73	3.42	13242	19.7



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