Also, some 20-100 nm ruthenium particles were observed, while the fresh catalyst analysis had not shown any visible ruthenium particles.

5.2.1.1.2 Tests at H_2:CO Feed Ratio = 2.9, 208°C at Inlet and 35 atm

In an attempt to suppress formation of the volatile ruthenium carbonyl species and thereby prevent ruthenium metal agglomeration, another highly dispersed ruthenium Catalyst 4966-72 was tested in Run 18 at a lower CO partial pressure (Tables 5-20 and 5-21 and Figures 5-107 through 5-113). The CO pressure was lowered relative to that in Run 16 by increasing the H_2:CO feed ratio from 0.9 to 2.9. Other conditions were 208°C at the inlet, 35 atm and 70 GHSV. In this run the pressure test at 208°C lasted unusually long (4 days) due to leaks in the reactor system.

The initial CO conversion was 35%, which is higher than that observed in Run 16, probably because of the higher H_2 partial pressure (Figure 5-107). The CO conversion decreased during the run, apparently because of the rapid decrease of catalyst's water gas shift activity (Figure 5-108). The CO+H_2 conversion, on the other hand, remained steady at about 15% level. At 60 hours on stream there was a plant upset, and the flow in and out of the reactor was stopped for about 10 hours. Interruption of the flow caused high conversion of the feed gas inside the reactor. After the flow was reinstated the catalytic performance gradually reached the level it had before the upset. It is important to note that during the 10-hour-period in which the flow was interrupted the selectivities to C_2-C_4 hydrocarbons increased and the olefin to paraffin ratios decreased (Figures 5-109 and 5-110). With ruthenium catalysts, C_2-C_4 hydrocarbons, particularly the olefins, are typically made with selectivities below the Anderson-Schulz-Flory prediction. These results, then, suggest that under long contact time, no-flow conditions reaction pathways which result in selective disappearance of C_2-C_4 hydrocarbons are not favored, possibly because of the saturation of the olefins.

Table 5-20. Product Distributions in Run 18

TOTAL PRODUCT DISTRIBUTION	
WEIGHT PCTS WITHOUT ARGON	
HYDROGEN	14.962
CARBON MONOXIDE	63.148
CARBON DIOXIDE	4.995
WATER	8.151
HYDROCARBONS	8.429
OXYGENATES	0.316
HYDROCARBON DISTRIBUTION	
C1	12.569
C2 - C4	11.487
C5 - C11	23.396
C12 - C18	11.817
C19 - C25	7.104
C26 PLUS	33.627
C1 - C44	78.308
C45 PLUS	21.692
OXYGENATES DISTRIBUTION	
ALCOHOLS	100.000
ALDEHYDES	0.000
OTHER OXYGENATES	0.000
MOLE PCTS WITHOUT ARGON	
HYDROGEN	71.611
CARBON MONOXIDE	21.754
CARBON DIOXIDE	1.095
WATER	4.366
HYDROCARBONS	1.118
OXYGENATES	0.056
RECOVERIES	
OVERALL	89.675
CARBON	89.962
HYDROGEN	90.264
OXYGEN	89.090
ARGON	89.957
CORRECTED RECOVERIES	
OVERALL	99.686
CARBON	100.006
HYDROGEN	100.341
OXYGEN	99.036

GAS ANALYSIS, WT%	
HYDROGEN	14.9615
CARBON MONOXIDE	63.1483
CARBON DIOXIDE	4.9946
METHANE	1.0594
ETHANE	0.0466
ETHYLENE	0.0728
PROPANE	0.2707
PROPYLENE	0.1668
BUTANE	0.2684
BUTENE	0.1446
AQUEOUS ANALYSIS, WT%	
WATER	8.1506
ALCOHOLS	
C1	0.0376
C2	0.1127
C3	0.0335
C4	0.0788
C5	0.0537
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

Table 5-21. Hydrocarbon Distributions in Run 18

C1	12.5690	C51	0.4886	C101	0.1404	C151	0.0313	C201	0.0063
C2	1.4168	C52	0.4690	C102	0.1361	C152	0.0305	C202	0.0063
C3	5.0750	C53	0.4500	C103	0.1319	C153	0.0297	C203	0.0062
C4	4.9954	C54	0.4324	C104	0.1278	C154	0.0290	C204	0.0061
C5	2.9912	C55	0.4170	C105	0.1238	C155	0.0283	C205	0.0060
C6	1.5732	C56	0.3654	C106	0.1199	C156	0.0276	C206	0.0059
C7	2.6214	C57	0.3561	C107	0.1150	C157	0.0270	C207	0.0058
C8	4.2662	C58	0.3493	C108	0.1115	C158	0.0264	C208	0.0057
C9	4.7566	C59	0.3444	C109	0.1081	C159	0.0258	C209	0.0056
C10	3.9928	C60	0.3406	C110	0.1048	C160	0.0252	C210	0.0055
C11	3.1943	C61	0.3375	C111	0.1017	C161	0.0247	C211	0.0054
C12	2.2832	C62	0.3342	C112	0.0987	C162	0.0242	C212	0.0053
C13	1.7238	C63	0.3627	C113	0.0959	C163	0.0237	C213	0.0052
C14	1.4164	C64	0.3578	C114	0.0931	C164	0.0232	C214	0.0051
C15	2.6905	C65	0.3521	C115	0.0905	C165	0.0227	C215	0.0050
C16	1.2017	C66	0.3457	C116	0.0879	C166	0.0223	C216	0.0049
C17	1.3620	C67	0.3386	C117	0.0855	C167	0.0218	C217	0.0048
C18	1.1397	C68	0.3311	C118	0.0831	C168	0.0214	C218	0.0047
C19	1.1258	C69	0.3233	C119	0.0808	C169	0.0211	C219	0.0047
C20	1.0862	C70	0.3153	C120	0.0786	C170	0.0207	C220	0.0046
C21	1.0384	C71	0.2948	C121	0.0764	C171	0.0203	C221	0.0045
C22	1.0429	C72	0.2867	C122	0.0743	C172	0.0199	C222	0.0044
C23	0.9724	C73	0.2787	C123	0.0722	C173	0.0195	C223	0.0043
C24	0.9558	C74	0.2708	C124	0.0705	C174	0.0191	C224	0.0042
C25	0.8823	C75	0.2631	C125	0.0685	C175	0.0188	C225	0.0041
C26	0.8428	C76	0.2556	C126	0.0666	C176	0.0184	C226	0.0041
C27	0.8125	C77	0.2483	C127	0.0646	C177	0.0181	C227	0.0040
C28	0.7749	C78	0.2413	C128	0.0627	C178	0.0177	C228	0.0039
C29	0.7539	C79	0.2347	C129	0.0609	C179	0.0174	C229	0.0038
C30	0.7522	C80	0.2285	C130	0.0591	C180	0.0170	C230	0.0037
C31	0.7092	C81	0.2227	C131	0.0573	C181	0.0167	C231	0.0037
C32	0.6729	C82	0.2173	C132	0.0555	C182	0.0164	C232	0.0036
C33	0.6482	C83	0.2123	C133	0.0539	C183	0.0161	C233	0.0035
C34	0.6284	C84	0.2077	C134	0.0522	C184	0.0158	C234	0.0035
C35	0.6143	C85	0.2033	C135	0.0506	C185	0.0155	C235	0.0034
C36	0.5990	C86	0.1992	C136	0.0490	C186	0.0152	C236	0.0033
C37	0.5776	C87	0.1953	C137	0.0475	C187	0.0149	C237	0.0033
C38	0.5559	C88	0.1914	C138	0.0461	C188	0.0146	C238	0.0032
C39	0.5356	C89	0.1877	C139	0.0446	C189	0.0143	C239	0.0031
C40	0.5188	C90	0.1840	C140	0.0433	C190	0.0140	C240	0.0031
C41	0.5060	C91	0.1803	C141	0.0420	C191	0.0137	C241	0.0030
C42	0.4914	C92	0.1765	C142	0.0407	C192	0.0134	C242	0.0030
C43	0.4772	C93	0.1746	C143	0.0395	C193	0.0131	C243	0.0029
C44	0.4641	C94	0.1705	C144	0.0382	C194	0.0128	C244	0.0029
C45	0.5694	C95	0.1664	C145	0.0370	C195	0.0126	C245	0.0028
C46	0.5530	C96	0.1621	C146	0.0360	C196	0.0123	C246	0.0028
C47	0.5370	C97	0.1578	C147	0.0350	C197	0.0120	C247	0.0027
C48	0.5207	C98	0.1535	C148	0.0340	C198	0.0117	C248	0.0027
C49	0.5037	C99	0.1491	C149	0.0330	C199	0.0065	C249	0.0027
C50	0.5080	C100	0.1447	C150	0.0322	C200	0.0064	C250	0.0026

Figure 5-107. Highly Dispersed Ruthenium Catalyst 4966-72 Conversions in Run 18 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

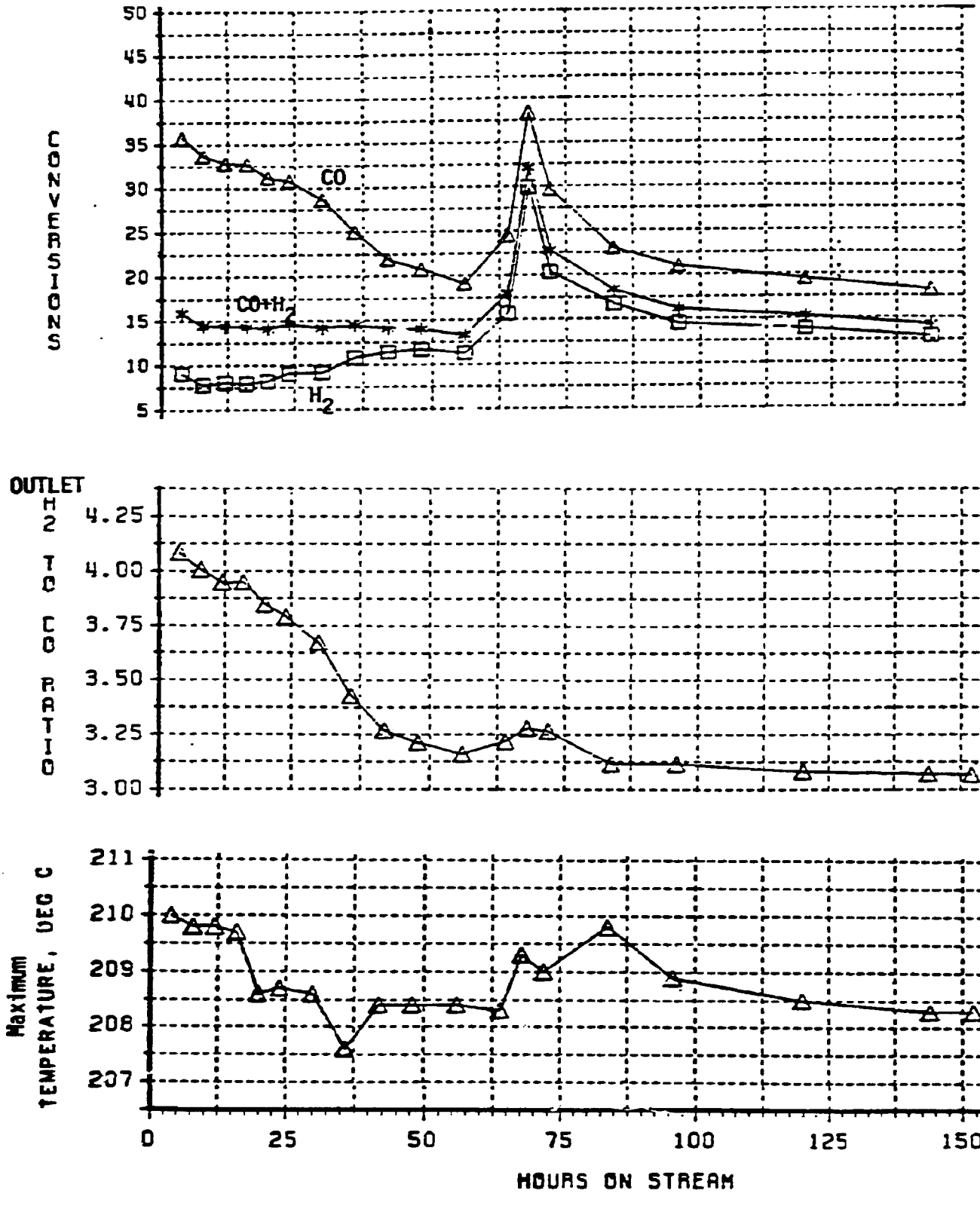


Figure 5-108. Highly Dispersed Ruthenium Catalyst 4966-72 Water Gas Shift Activity in Run 18 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

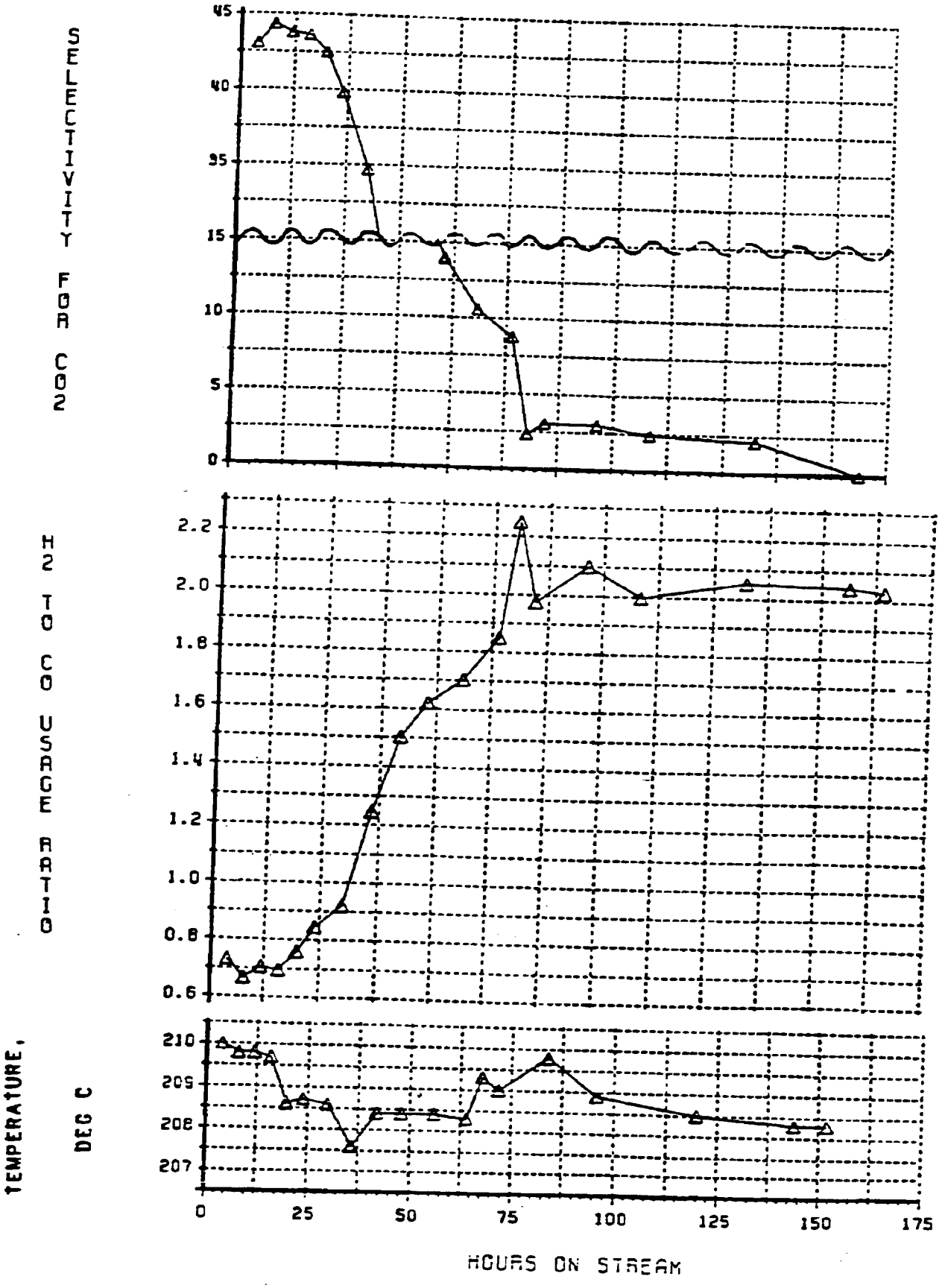


Figure 5-109. Highly Dispersed Ruthenium Catalyst 4966-72 C_1 and C_2 Selectivities in Run 18 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

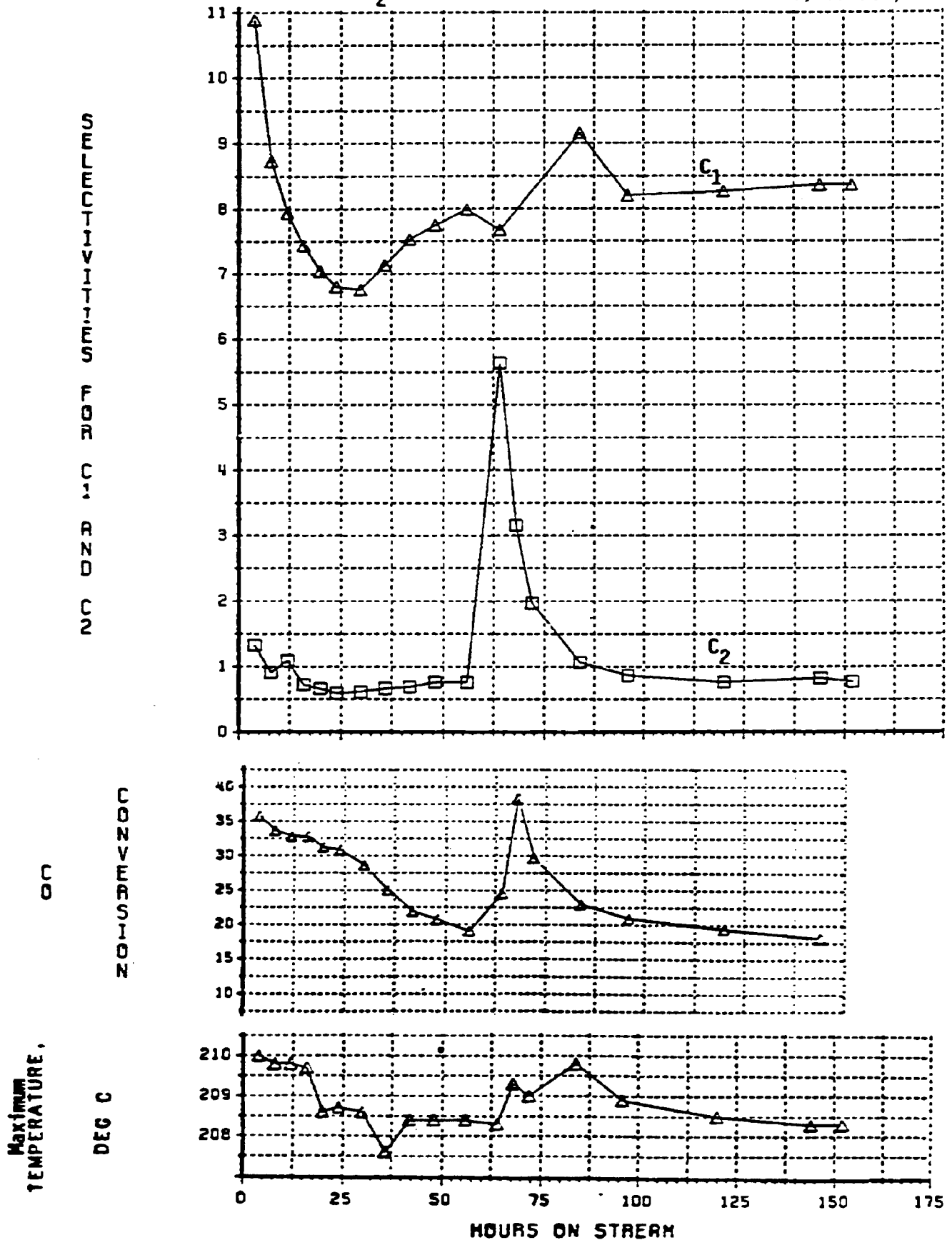


Figure 5-110. Highly Dispersed Ruthenium Catalyst 4966-72 C_3 and C_4 Selectiviti in Run 18 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

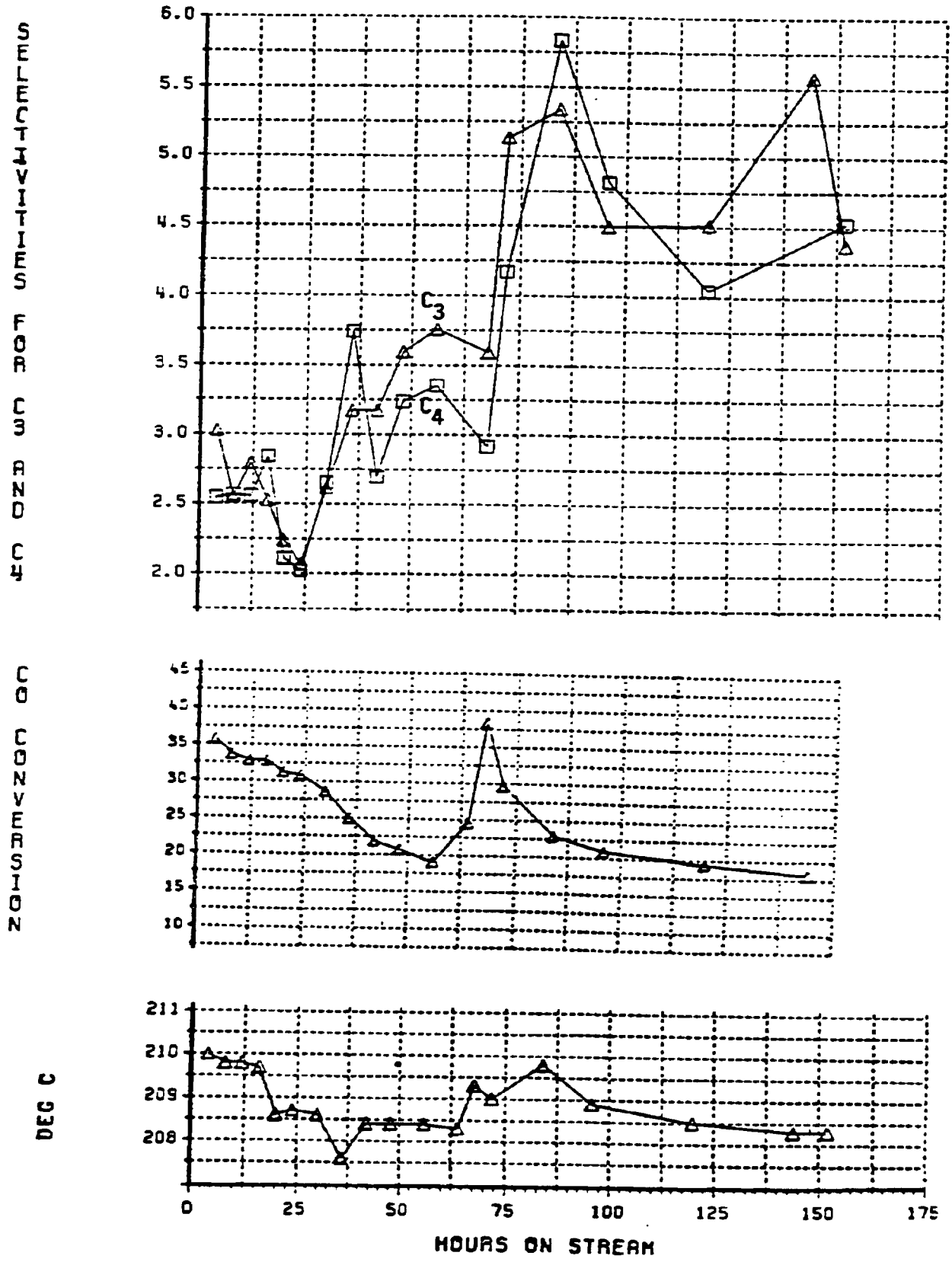


Figure 5-111. Highly Dispersed Ruthenium Catalyst 4966-72 Olefin to Paraffin Ratios in Run 18 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

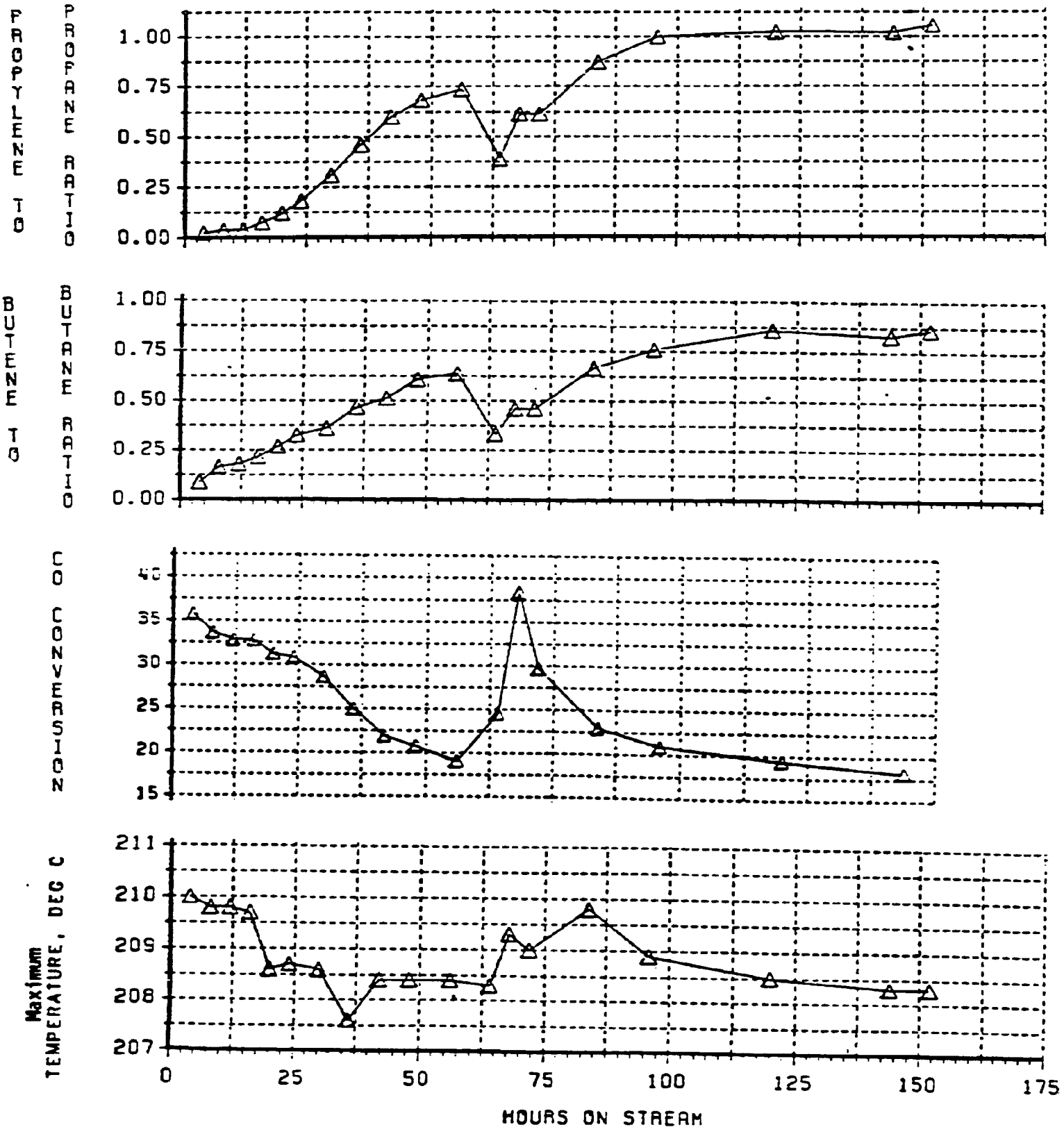


Figure 5-112. Anderson-Schulz-Flory Distribution with Highly Dispersed Ruthenium Catalyst 4966-72 in Run 18 (Hydrocarbons + Oxygenates)

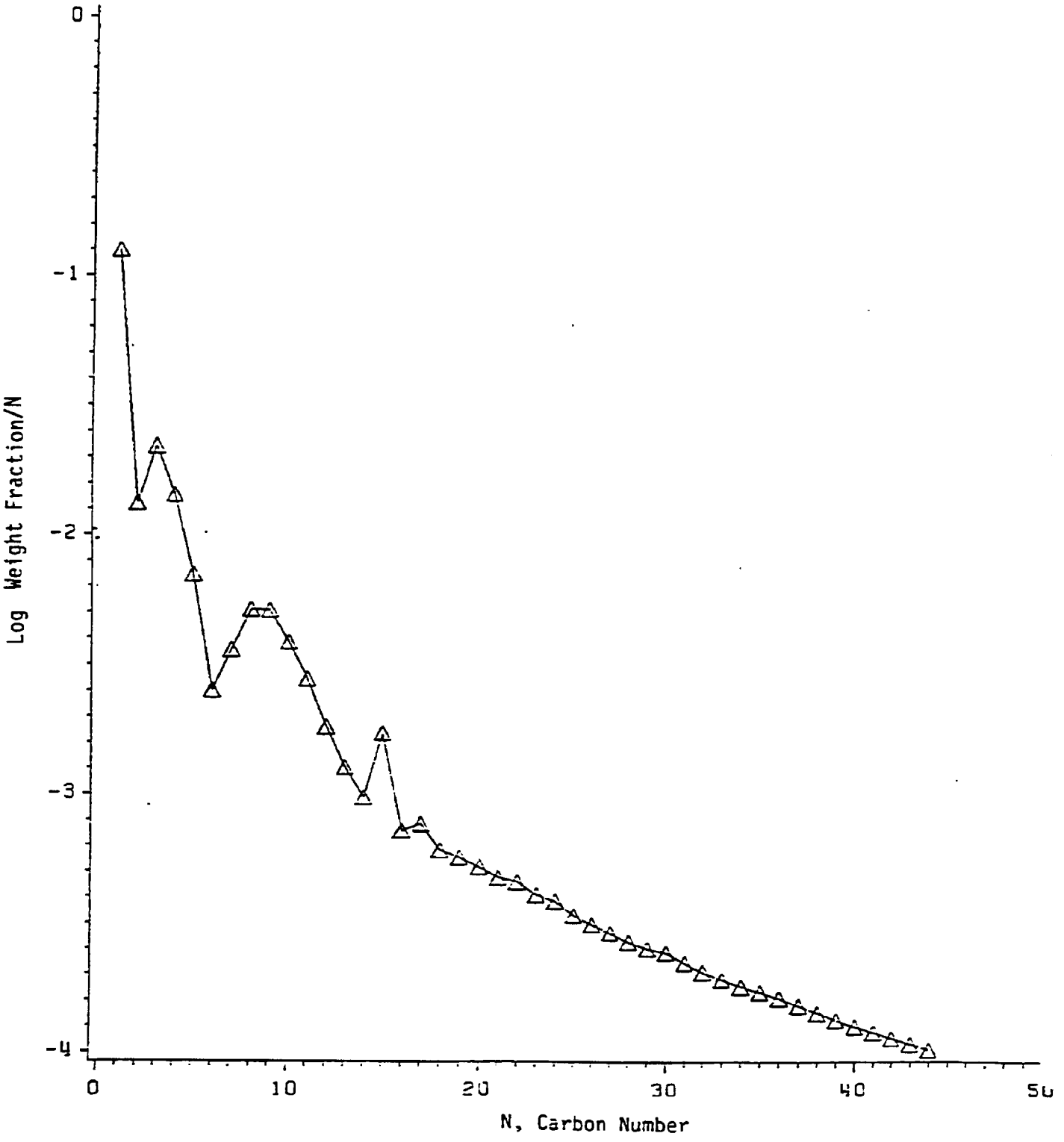
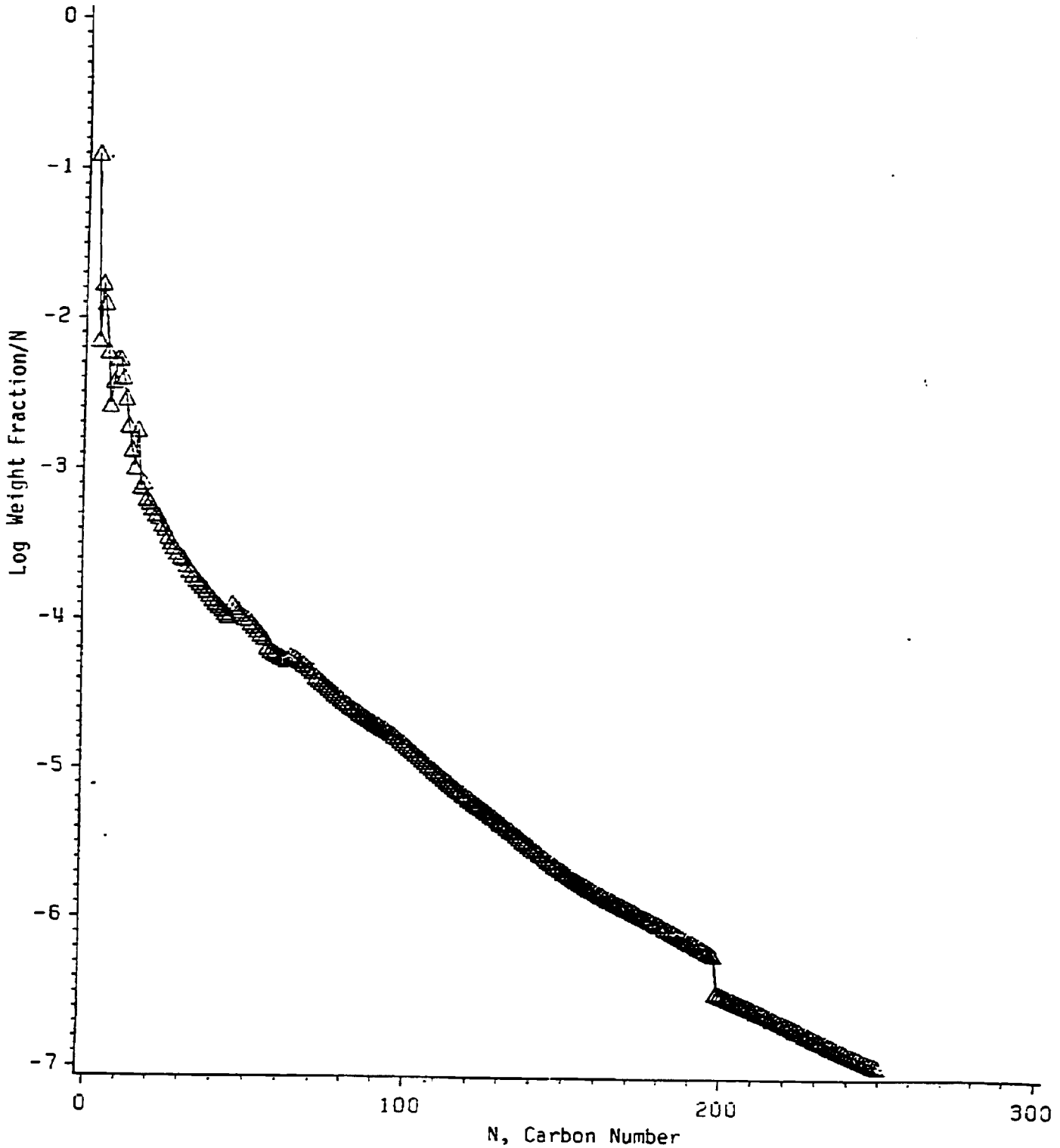


Figure 5-113. Anderson-Schulz-Flory Distribution with Highly Dispersed Ruthenium Catalyst 4966-72 in Run 18 (Hydrocarbons Only)



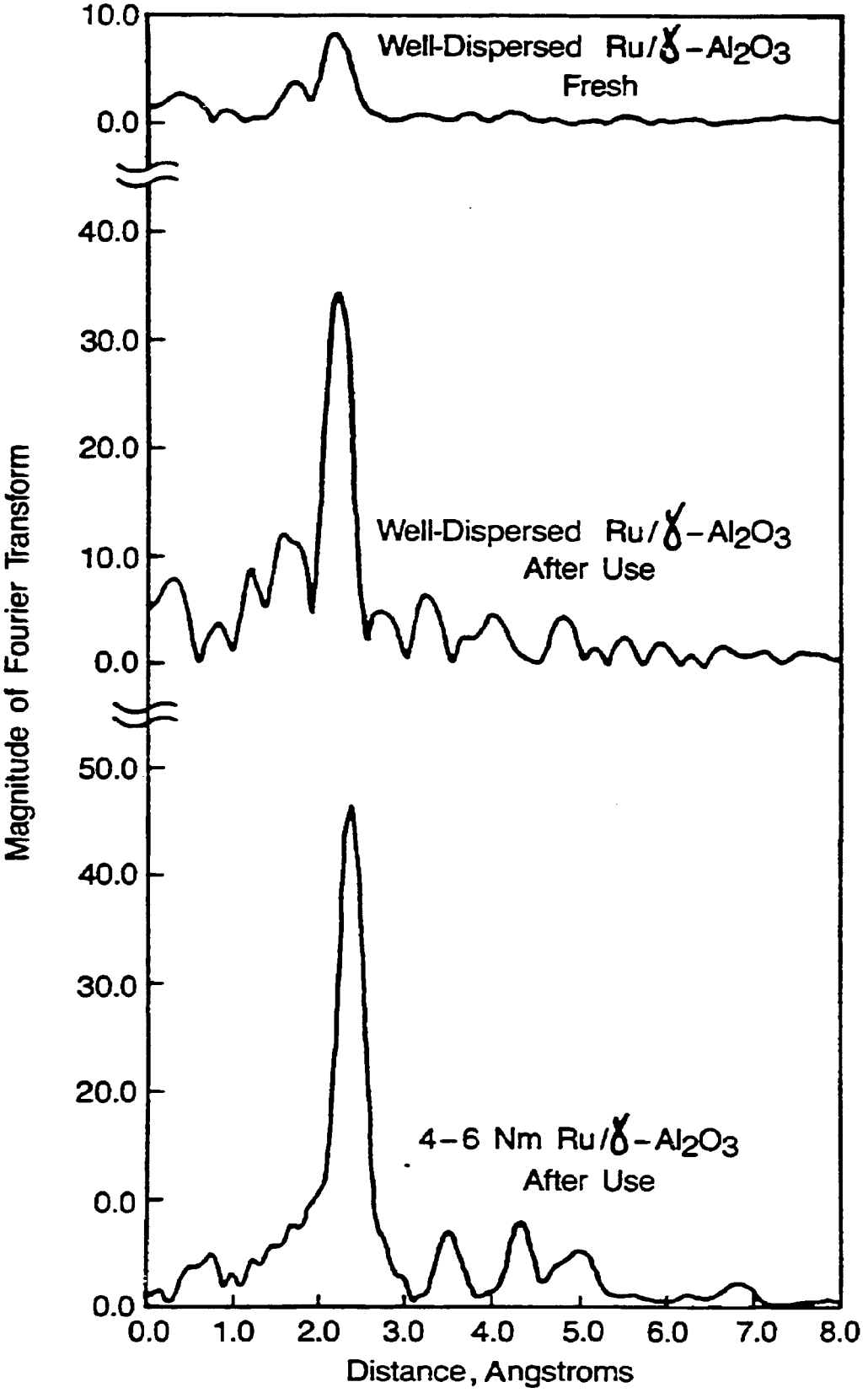
The chain growth probability was 0.783 at C_3-C_{16}, 0.918 at C_{17}-C_{30} and 0.964 at C_{40}-C_{150} carbon number ranges. Comparison of these results with those obtained in Run 16 with another highly dispersed ruthenium catalyst at a lower H_2:CO feed ratio = 0.9 may indicate that H_2:CO ratio mainly influences the chain growth probabilities at low carbon numbers, but not at high carbon numbers.

Analysis of the inlet and outlet portions of the catalyst after a 152-hour-test showed 0.925% and 1.13% (by wt.) ruthenium, respectively. Although there was no overall ruthenium loss from the catalyst, some ruthenium migration still occurred across the catalyst bed. The mobility of ruthenium was also apparent in the STEM examination. While approximately 60% of the alumina particles examined from the inlet portion of the catalyst bed did not have observable ruthenium particles, 40% of the alumina particles still had 3-15 nm ruthenium particles. The number of alumina particles with observable ruthenium metal particles was half for the outlet portion of the catalyst bed relative to the inlet.

A sample from the reactor inlet portion of used Catalyst 4966-72 was analyzed by EXAFS.

The Fourier transform oscillations of ruthenium in fresh Catalyst 4966-72 is shown in Figure 5-114. The major peak at about 2.2Å results from back-scattering of electrons from nearest neighbors. From a curve-fitting analyses of the Fourier filtered χ, a coordination number of about 3.4 was determined which should give a ruthenium metal particle size of about 0.8 nm. The Fourier transform of the used Catayst 4966-72 is very similar to that of Catalyst 4956-76 with 4-6 nm ruthenium particles after use in Run 15. This result confirms the STEM observation that a significant fraction of the ruthenium metal agglomerated to sizes 4 nm or larger during Fischer-Tropsch synthesis.

Figure 5-114 **FOURIER TRANSFORMS OF RUTHENIUM EXAFS IN ALUMINA SUPPORTED CATALYSTS**



The results in Run 18 indicated that mobility of ruthenium was suppressed but not totally eliminated, apparently, by increasing the H_2:CO feed ratio from 0.9 to 2.9. At the higher H_2:CO ratio, the mobility of ruthenium may have been suppressed by suppressing the formation of the volatile ruthenium carbonyl.

Highly dispersed ruthenium Catalyst 4966-72 was retested in Run 21 under the same conditions that were used in Run 18, but only for 12 hours (Tables 5-22 and 5-23 and Figures 5-115 through 5-121). The CO+H_2 conversion was much higher in Run 21 relative to Run 18 (Figure 5-115). The unexpectedly lower catalytic activity in Run 18 may be possibly attributed to the unusually long start-up for that run.

The CO conversion was 100% during the second half of Run 21 (Figure 5-115). Since the H_2 conversion was less than 100% the outlet H_2:CO ratio became infinitely large. This caused very high selectivity to methane and apparently caused the extent of the water gas shift reaction to become minimal (Figure 5-116).

Because of the short duration of the test, products in the C_5-C_{23} range were not fully recovered in the product receivers. The chain growth probability was 0.936 in the C_{24}-C_{150} range.

The inlet and outlet portions of Catalyst 4966-72 used in Run 21 showed less ruthenium than fresh catalyst: 0.81% and 0.84% Ru (by wt.), respectively, relative to 1.04% Ru on the fresh catalyst. STEM examination indicated that almost all of the alumina particles had 2-5 nm agglomerated ruthenium particles, while the fresh catalyst had none. The possibility that the high steam partial pressure, caused by suppression of the water gas shift reaction in Run 21, may have enhanced ruthenium agglomeration was further investigated in Run 25.

Table 5-22. Product D. ;ibutions in Run 21

GAS ANALYSIS, WT%	
HYDROGEN	5.5624
CARBON MONOXIDE	4.8440
CARBON DIOXIDE	9.9460
METHANE	8.4129
ETHANE	0.4604
ETHYLENE	0.0000
PROPANE	1.2307
PROPYLENE	0.0000
BUTANE	1.4738
BUTENE	0.0000
AQUEOUS ANALYSIS, WT%	
WATER	48.6152
ALCOHOLS	
C1	0.0000
C2	0.0463
C3	0.0000
C4	0.0472
C5	0.0702
C6	0.0463
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

WEIGHT PCTS WITHOUT ARGON	
HYDROGEN	5.562
CARBON MONOXIDE	4.844
CARBON DIOXIDE	9.946
WATER	48.615
HYDROCARBONS	30.022
OXYGENATES	0.210
HYDROCARBON DISTRIBUTION	
C1	27.295
C2 - C4	10.268
C5 - C11	16.220
C12 - C18	4.516
C19 - C25	5.165
C26 PLUS	36.536
C1 - C44	79.392
C45 PLUS	20.608
OXYGENATES DISTRIBUTION	
ALCOHOLS	100.000
ALDEHYDES	0.000
OTHER OXYGENATES	0.000
MOLE PCTS WITHOUT ARGON	
HYDROGEN	42.254
CARBON MONOXIDE	2.648
CARBON DIOXIDE	3.461
WATER	41.327
HYDROCARBONS	10.265
OXYGENATES	0.044
RECOVERIES	
OVERALL	75.143
CARBON	65.510
HYDROGEN	73.986
OXYGEN	86.776
ARGON	67.957
CORRECTED RECOVERIES	
OVERALL	110.575
CARBON	96.400
HYDROGEN	108.873
OXYGEN	127.693

Table 5-23. Hydrocarbon Distributions in Run 21

C1	27.2948	C51	0.6101	C101	0.0777	C151	0.0000	C201	0.0000
C2	1.4937	C52	0.5919	C102	0.0742	C152	0.0000	C202	0.0000
C3	3.9928	C53	0.5742	C103	0.0708	C153	0.0000	C203	0.0000
C4	4.7815	C54	0.5571	C104	0.0677	C154	0.0000	C204	0.0000
C5	3.1974	C55	0.5405	C105	0.0647	C155	0.0000	C205	0.0000
C6	2.0162	C56	0.5245	C106	0.0624	C156	0.0000	C206	0.0000
C7	1.5906	C57	0.5072	C107	0.0598	C157	0.0000	C207	0.0000
C8	1.9019	C58	0.4923	C108	0.0573	C158	0.0000	C208	0.0000
C9	2.6048	C59	0.4777	C109	0.0549	C159	0.0000	C209	0.0000
C10	2.6960	C60	0.4636	C110	0.0527	C160	0.0000	C210	0.0000
C11	2.2133	C61	0.4498	C111	0.0506	C161	0.0000	C211	0.0000
C12	1.6523	C62	0.4376	C112	0.0486	C162	0.0000	C212	0.0000
C13	1.0674	C63	0.4243	C113	0.0467	C163	0.0000	C213	0.0000
C14	0.5881	C64	0.4112	C114	0.0449	C164	0.0000	C214	0.0000
C15	0.3301	C65	0.3984	C115	0.0432	C165	0.0000	C215	0.0000
C16	0.1918	C66	0.3858	C116	0.0416	C166	0.0000	C216	0.0000
C17	0.4002	C67	0.3734	C117	0.0400	C167	0.0000	C217	0.0000
C18	0.2858	C68	0.3613	C118	0.0384	C168	0.0000	C218	0.0000
C19	0.3082	C69	0.3484	C119	0.0370	C169	0.0000	C219	0.0000
C20	0.3402	C70	0.3368	C120	0.0356	C170	0.0000	C220	0.0000
C21	0.5335	C71	0.3254	C121	0.0343	C171	0.0000	C221	0.0000
C22	0.8130	C72	0.3141	C122	0.0330	C172	0.0000	C222	0.0000
C23	0.9549	C73	0.3031	C123	0.0318	C173	0.0000	C223	0.0000
C24	1.1143	C74	0.2921	C124	0.0306	C174	0.0000	C224	0.0000
C25	1.1013	C75	0.2812	C125	0.0295	C175	0.0000	C225	0.0000
C26	1.0967	C76	0.2713	C126	0.0284	C176	0.0000	C226	0.0000
C27	1.0745	C77	0.2606	C127	0.0274	C177	0.0000	C227	0.0000
C28	1.0500	C78	0.2499	C128	0.0264	C178	0.0000	C228	0.0000
C29	1.0277	C79	0.2393	C129	0.0255	C179	0.0000	C229	0.0000
C30	0.9986	C80	0.2289	C130	0.0246	C180	0.0000	C230	0.0000
C31	0.9522	C81	0.2186	C131	0.0237	C181	0.0000	C231	0.0000
C32	0.9079	C82	0.2085	C132	0.0229	C182	0.0000	C232	0.0000
C33	0.8747	C83	0.1987	C133	0.0220	C183	0.0000	C233	0.0000
C34	0.8434	C84	0.1892	C134	0.0212	C184	0.0000	C234	0.0000
C35	0.8189	C85	0.1791	C135	0.0205	C185	0.0000	C235	0.0000
C36	0.7923	C86	0.1701	C136	0.0198	C186	0.0000	C236	0.0000
C37	0.7613	C87	0.1615	C137	0.0191	C187	0.0000	C237	0.0000
C38	0.7325	C88	0.1532	C138	0.0185	C188	0.0000	C238	0.0000
C39	0.7101	C89	0.1452	C139	0.0178	C189	0.0000	C239	0.0000
C40	0.6878	C90	0.1376	C140	0.0172	C190	0.0000	C240	0.0000
C41	0.6722	C91	0.1304	C141	0.0166	C191	0.0000	C241	0.0000
C42	0.6585	C92	0.1235	C142	0.0161	C192	0.0000	C242	0.0000
C43	0.6408	C93	0.1170	C143	0.0155	C193	0.0000	C243	0.0000
C44	0.6275	C94	0.1108	C144	0.0150	C194	0.0000	C244	0.0000
C45	0.7308	C95	0.1050	C145	0.0144	C195	0.0000	C245	0.0000
C46	0.7079	C96	0.0997	C146	0.0139	C196	0.0000	C246	0.0000
C47	0.6888	C97	0.0947	C147	0.0134	C197	0.0000	C247	0.0000
C48	0.6678	C98	0.0900	C148	0.0129	C198	0.0000	C248	0.0000
C49	0.6477	C99	0.0856	C149	0.0124	C199	0.0000	C249	0.0000
C50	0.6282	C100	0.0815	C150	0.0119	C200	0.0000	C250	0.0000

Figure 5-115. Highly Dispersed Ruthenium Catalyst 4966-72 Conversions in Run 21 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

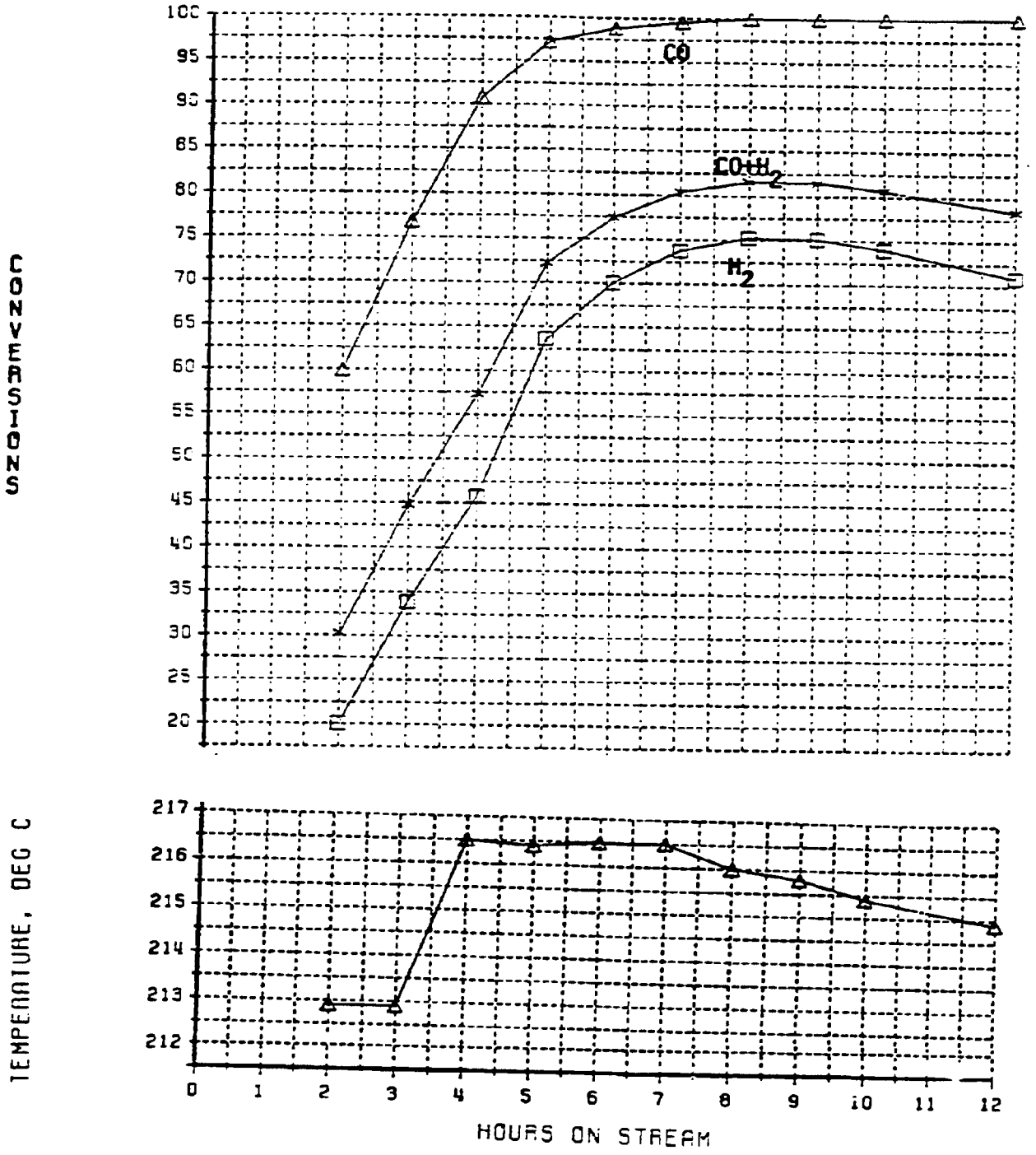


Figure 5-116. Highly Dispersed Ruthenium Catalyst 4966-72 Water Gas Shift Activity in Run 21 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

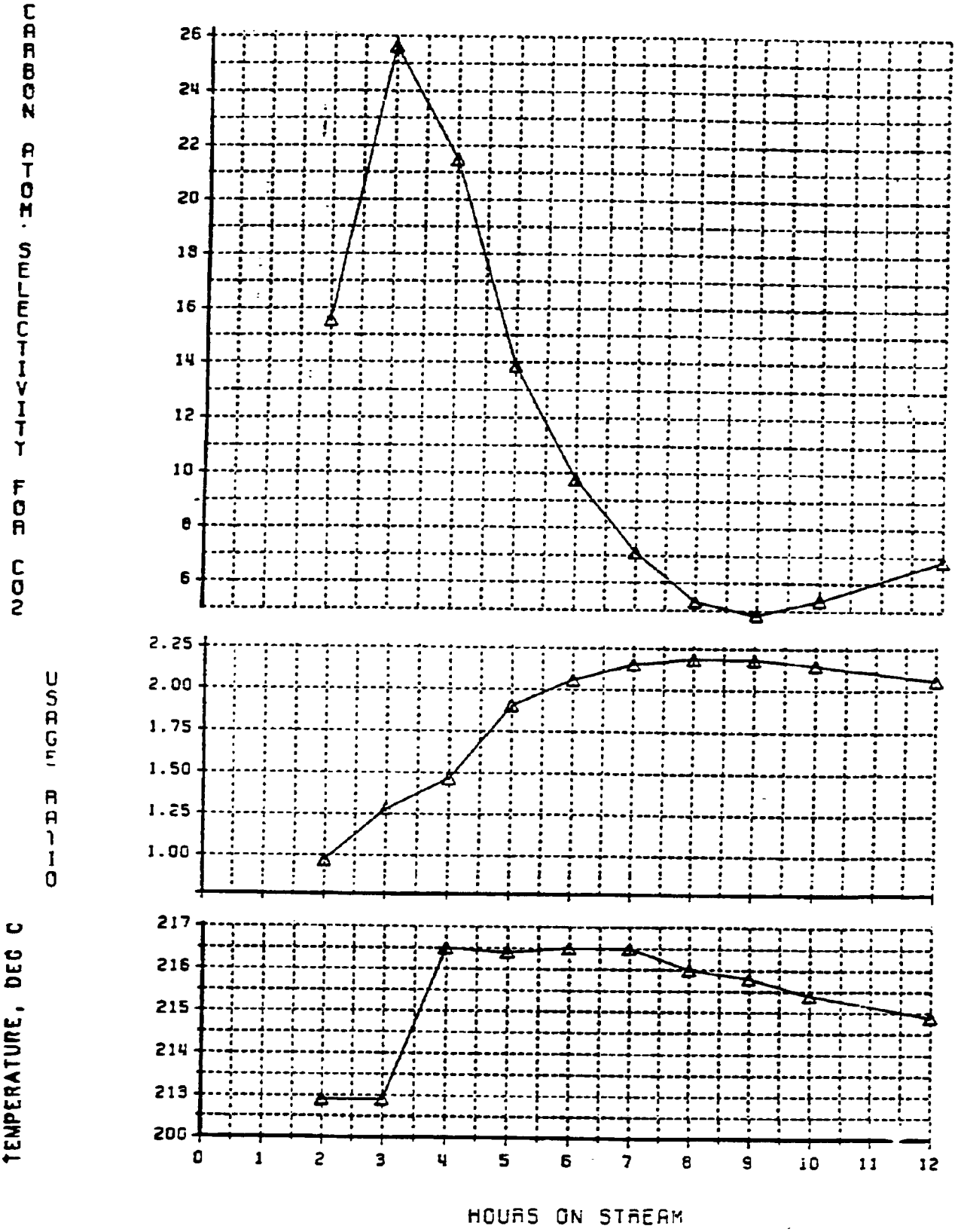


Figure 5-117. Highly Dispersed Ruthenium Catalyst 4966-72 C_1 and C_2 Selectivities in Run 21 (H_2:CO Feed Ratio = 2.9, 208°C, 35 atm)

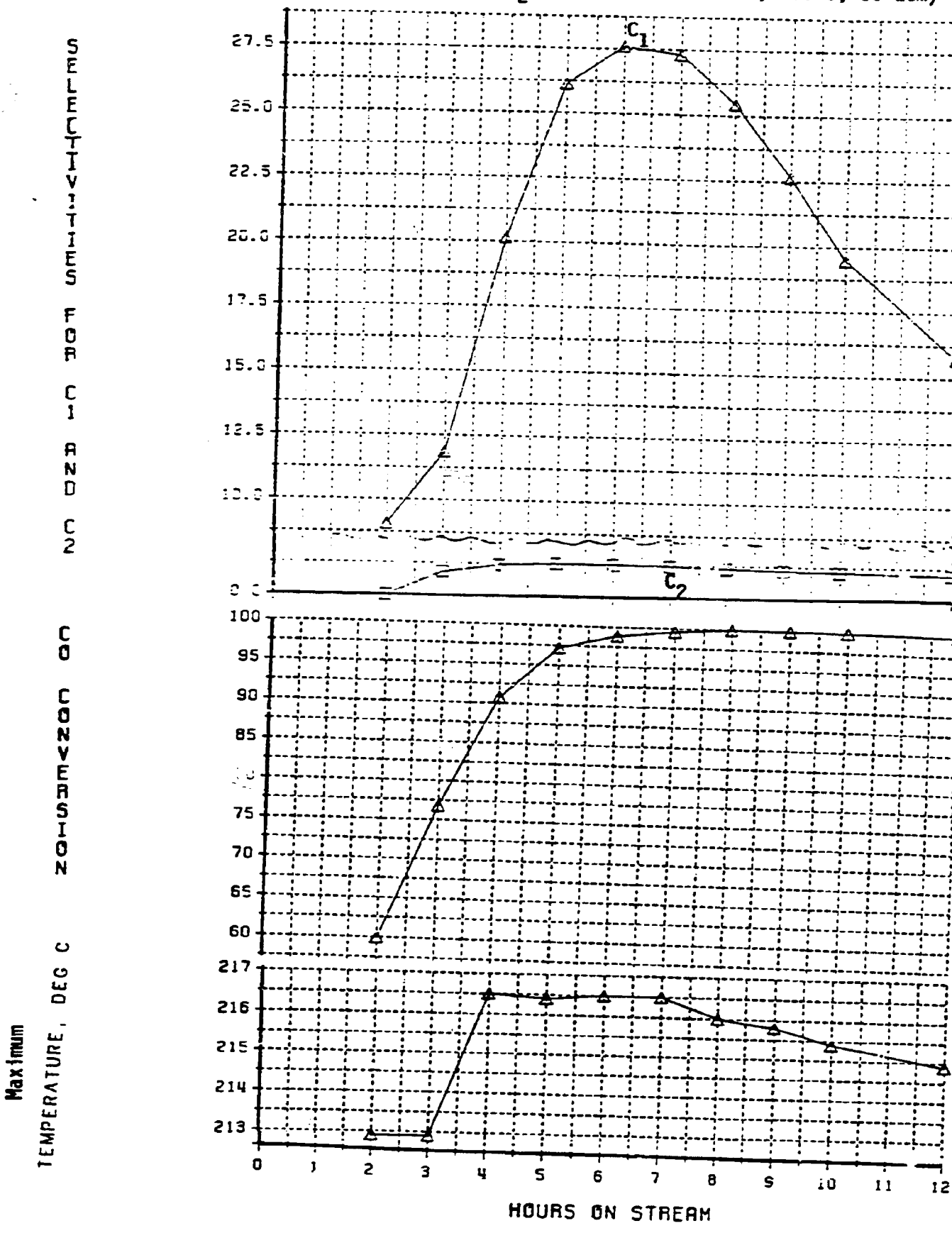


Figure 5-118. Highly Dispersed Ruthenium Catalyst 4966-72 C_3 and C_4 Selectivities in Run 21 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)

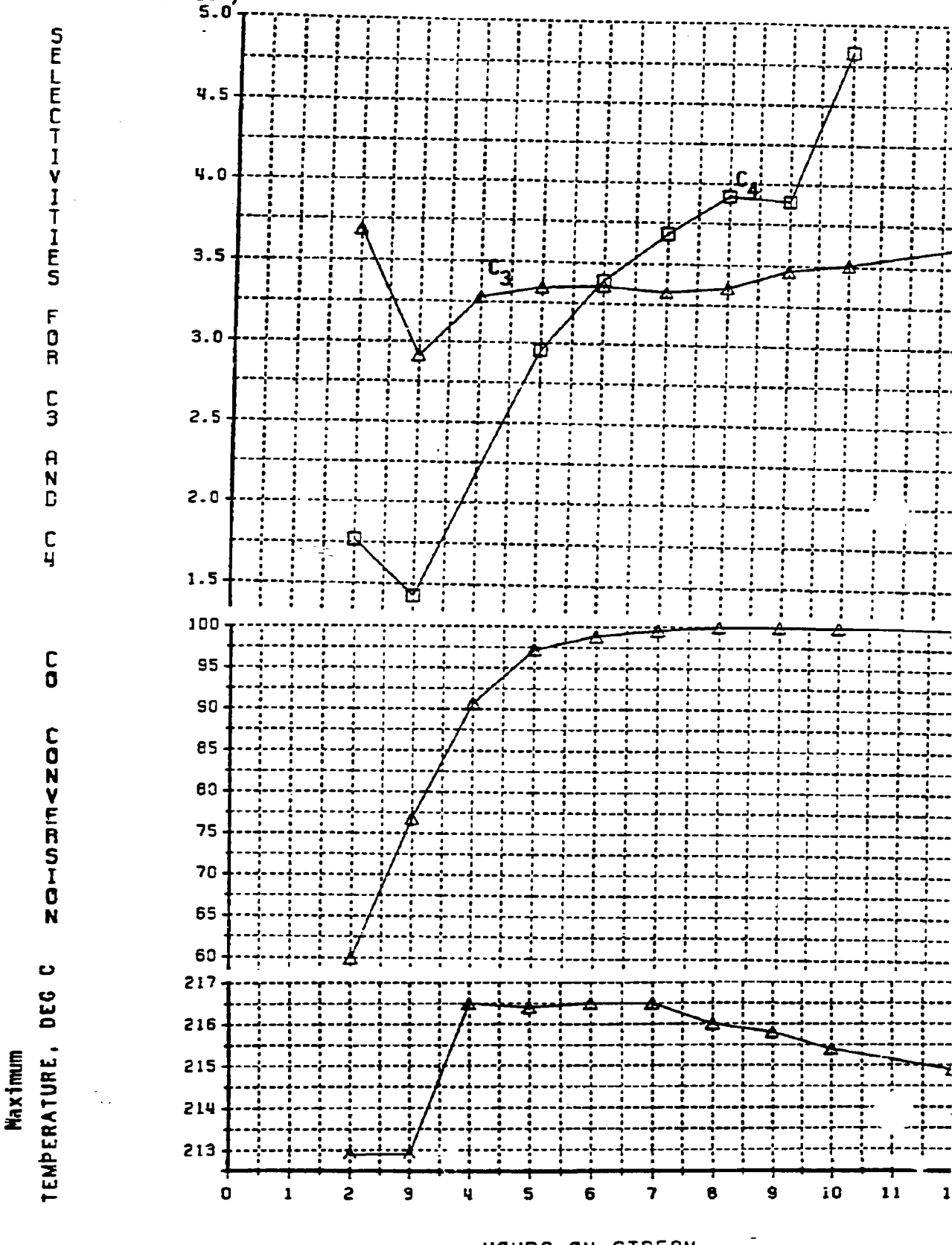
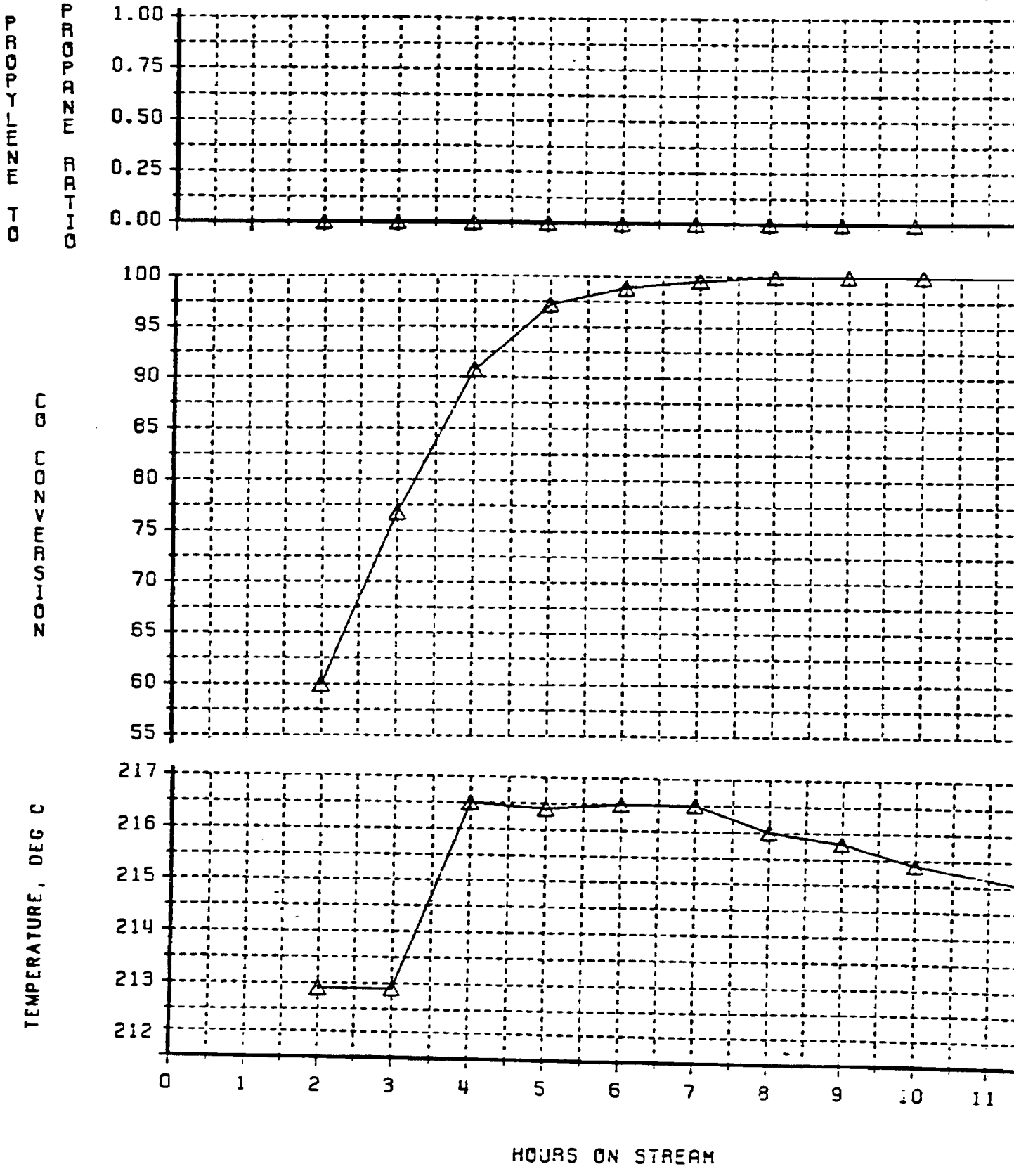


Figure 5-119. Highly Dispersed Ruthenium Catalyst 4966-72 Olefin to Paraffin Ratios in Run 21 (H_2:CO Feed Ratio = 2.9, 208°C at Inlet, 35 atm)



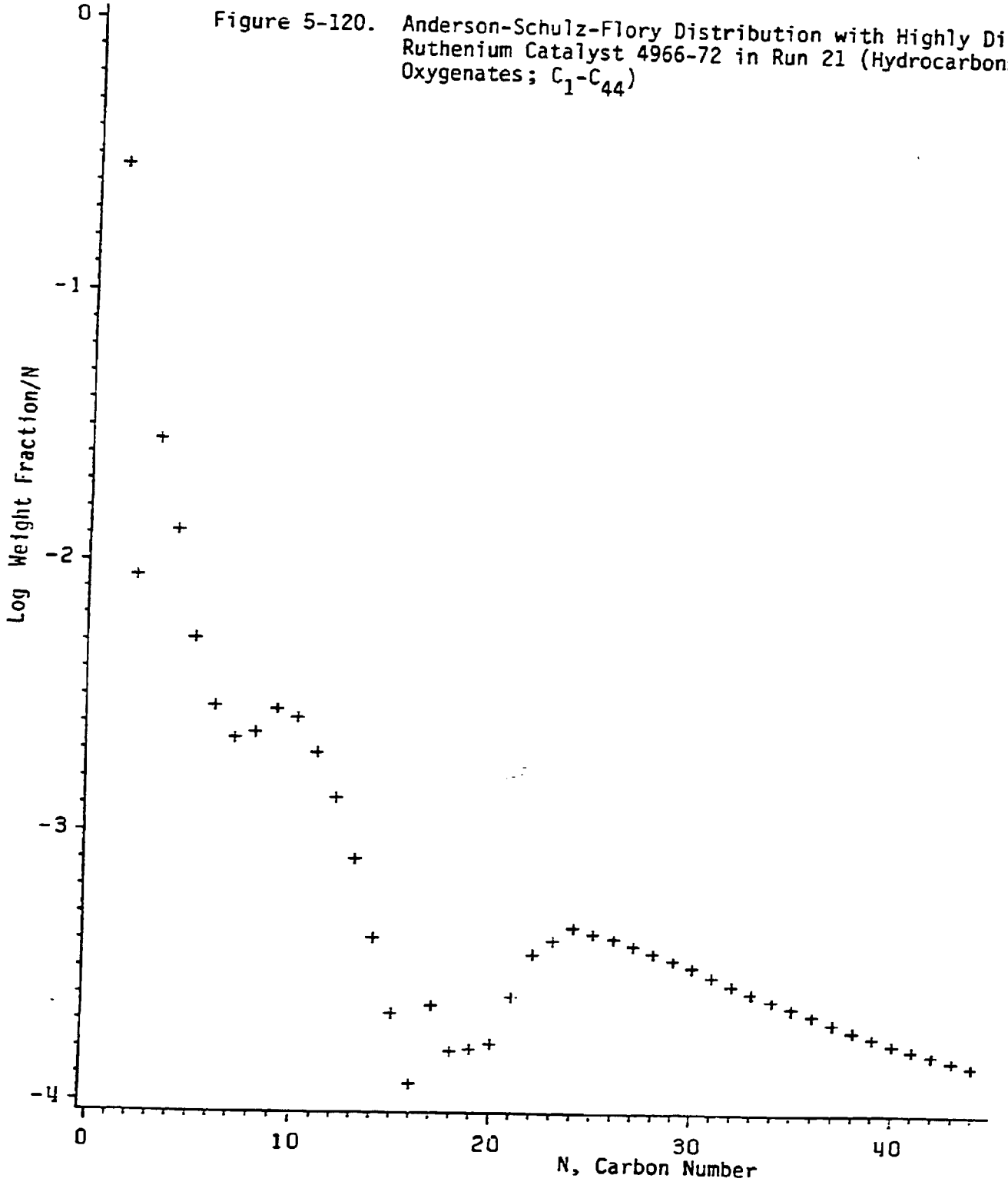


Figure 5-120. Anderson-Schulz-Flory Distribution with Highly Dispers
Ruthenium Catalyst 4966-72 in Run 21 (Hydrocarbons +
Oxygenates; C_1-C_{44})

Figure 5-121. Anderson-Schulz-Flory Distribution with Highly Dispersed Ruthenium Catalyst 4966-72 in Run 21 (Hydrocarbons Only; C_1-C_{250})