5.2.1.4.5 Establishment of Catalytic Stability with a Test at H_2:CO Feed Ratio = 2, 208°C at Inlet and 62 atm

Results obtained in Runs 33-36 indicated that alumina-supported ruthenium catalysts with mostly ~5 nm ruthenium particles were not stable at H_2:CO feed ratio = 2.0, 225°C at inlet and 35 atm. A lower temperature of 208°C at inlet and a higher pressure of 62 atm was used in Run 37 to establish stability of Catalyst 4966-119 with mostly ~5 nm ruthenium particles (Tables 32 and 33 and Figures 5-203 through 5-210).

In Run 37, initially, the pressure was 60 atm and the gas hourly space velocity was 500 hr^{-1}. The CO conversion decreased from 92% to 23% during the first 16 hours, after which the space velocity was lowered to 227 hr^{-1}. The CO conversion increased to 62% at 30 hours on stream. In order to achieve higher conversion, the feed flow was then stopped, and H_2 was introduced to raise the reactor pressure to 103 atm. The H_2/CO feed was then reintroduced at 295 hr^{-1} to achieve a CO conversion of 85%. The catalyst continued to deactivate to 54% CO conversion during the following 17 hours. Since the catalyst did not appear to be stable at 103 atm, the pressure was lowered to 62 atm at 56 hours on stream. Also, the space velocity was lowered, first to 150 hr^{-1}, and then to 114 hr^{-1}. The CO conversion then gradually increased to about 80% at 135 hours on stream, and then declined to a CO conversion of about 30% over the following 225 hours (Figure 5-203).

The light hydrocarbon selectivities between 56 and 136 hours on stream at 210°C and 62 atm were similar to those obtained in Run 24 with a catalyst having similar size ruthenium particles at 208°C and 35 atm (Figures 5-207). This result may indicate that selectivities were not noticeably affected by a pressure change from 35 atm to 62 atm.

Table 5-32. Product Distributions in Run 37

TOTAL PRODUCT DISTRIBUTION	
WEIGHT PCTS WITHOUT ARGON	
HYDROGEN	8.241
CARBON MONOXIDE	52.159
CARBON DIOXIDE	1.492
WATER	15.740
HYDROCARBONS	22.264
OXYGENATES	0.103
HYDROCARBON DISTRIBUTION	
C1	2.385
C2 - C4	3.959
C5 - C11	15.093
C12 - C18	22.151
C19 - C25	16.758
C26 PLUS	39.654
C1 - C44	90.218
C45 PLUS	9.782
OXYGENATES DISTRIBUTION	
ALCOHOLS	100.000
ALDEHYDES	0.000
OTHER OXYGENATES	0.000
MOLE PCTS WITHOUT ARGON	
HYDROGEN	58.453
CARBON MONOXIDE	26.627
CARBON DIOXIDE	0.485
WATER	12.493
HYDROCARBONS	1.914
OXYGENATES	0.027
RECOVERIES	
OVERALL	96.746
CARBON	105.017
HYDROGEN	100.899
OXYGEN	84.906
ARGON	108.091
CORRECTED RECOVERIES	
OVERALL	89.504
CARBON	97.156
HYDROGEN	93.347
OXYGEN	78.551

GAS ANALYSIS, WT%	
HYDROGEN	8.2411
CARBON MONOXIDE	52.1588
CARBON DIOXIDE	1.4925
METHANE	0.5310
ETHANE	0.0000
ETHYLENE	0.0000
PROPANE	0.1680
PROPYLENE	0.1646
BUTANE	0.2794
BUTENE	0.2030
AQUEOUS ANALYSIS, WT%	
WATER	15.7399
ALCOHOLS	
C1	0.0164
C2	0.0354
C3	0.0025
C4	0.0118
C5	0.0212
C6	0.0161
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 5-33. Hydrocarbon Distributions in Run 37

C1	2.3850	C51	0.2981	C101	0.0430	C151	0.0075	C201	0.0018
C2	0.0000	C52	0.2841	C102	0.0414	C152	0.0073	C202	0.0017
C3	1.4935	C53	0.2555	C103	0.0398	C153	0.0070	C203	0.0017
C4	2.4651	C54	0.2439	C104	0.0383	C154	0.0062	C204	0.0016
C5	2.6169	C55	0.2355	C105	0.0368	C155	0.0060	C205	0.0016
C6	1.8690	C56	0.2259	C106	0.0353	C156	0.0059	C206	0.0015
C7	1.9414	C57	0.2234	C107	0.0338	C157	0.0057	C207	0.0014
C8	1.5750	C58	0.2160	C108	0.0324	C158	0.0056	C208	0.0014
C9	2.0552	C59	0.2105	C109	0.0310	C159	0.0054	C209	0.0013
C10	2.3302	C60	0.2028	C110	0.0298	C160	0.0053	C210	0.0012
C11	2.7055	C61	0.1953	C111	0.0285	C161	0.0051	C211	0.0012
C12	3.0614	C62	0.1882	C112	0.0274	C162	0.0050	C212	0.0011
C13	3.4155	C63	0.1817	C113	0.0261	C163	0.0048	C213	0.0011
C14	3.3347	C64	0.1729	C114	0.0251	C164	0.0047	C214	0.0010
C15	3.2717	C65	0.1680	C115	0.0241	C165	0.0046	C215	0.0009
C16	3.0063	C66	0.1608	C116	0.0232	C166	0.0044	C216	0.0009
C17	3.1016	C67	0.1574	C117	0.0224	C167	0.0043	C217	0.0008
C18	2.9599	C68	0.1542	C118	0.0215	C168	0.0042	C218	0.0008
C19	2.6980	C69	0.1521	C119	0.0208	C169	0.0040	C219	0.0007
C20	2.6822	C70	0.1482	C120	0.0201	C170	0.0039	C220	0.0007
C21	2.5294	C71	0.1495	C121	0.0194	C171	0.0038	C221	0.0006
C22	2.3778	C72	0.1438	C122	0.0187	C172	0.0037	C222	0.0006
C23	2.2558	C73	0.1376	C123	0.0181	C173	0.0036	C223	0.0005
C24	2.1609	C74	0.1310	C124	0.0176	C174	0.0034	C224	0.0005
C25	2.0541	C75	0.1246	C125	0.0170	C175	0.0033	C225	0.0005
C26	1.9219	C76	0.1183	C126	0.0165	C176	0.0032	C226	0.0004
C27	1.8394	C77	0.1069	C127	0.0160	C177	0.0031	C227	0.0004
C28	1.7712	C78	0.1018	C128	0.0155	C178	0.0030	C228	0.0004
C29	1.6787	C79	0.0973	C129	0.0150	C179	0.0030	C229	0.0004
C30	1.5995	C80	0.0932	C130	0.0145	C180	0.0029	C230	0.0004
C31	1.5253	C81	0.0890	C131	0.0141	C181	0.0028	C231	0.0003
C32	1.4626	C82	0.0856	C132	0.0136	C182	0.0027	C232	0.0003
C33	1.3915	C83	0.0850	C133	0.0132	C183	0.0026	C233	0.0003
C34	1.3375	C84	0.0818	C134	0.0128	C184	0.0026	C234	0.0003
C35	1.2805	C85	0.0787	C135	0.0124	C185	0.0025	C235	0.0003
C36	1.2179	C86	0.0757	C136	0.0120	C186	0.0025	C236	0.0003
C37	1.1760	C87	0.0728	C137	0.0116	C187	0.0024	C237	0.0003
C38	1.1196	C88	0.0702	C138	0.0112	C188	0.0024	C238	0.0003
C39	1.0782	C89	0.0676	C139	0.0108	C189	0.0023	C239	0.0004
C40	1.0358	C90	0.0645	C140	0.0105	C190	0.0023	C240	0.0004
C41	1.0031	C91	0.0621	C141	0.0101	C191	0.0022	C241	0.0004
C42	0.9571	C92	0.0598	C142	0.0098	C192	0.0022	C242	0.0004
C43	0.9250	C93	0.0577	C143	0.0095	C193	0.0021	C243	0.0004
C44	5.5514	C94	0.0556	C144	0.0092	C194	0.0021	C244	0.0004
C45	0.3498	C95	0.0536	C145	0.0090	C195	0.0021	C245	0.0004
C46	0.3339	C96	0.0517	C146	0.0087	C196	0.0020	C246	0.0004
C47	0.3269	C97	0.0499	C147	0.00[illegible]	C197	0.0020	C247	0.0005
	0.3314	C98	0.0482	C148	0.0[illegible]	C198	0.0019	C248	0.0000
	0.3372	C99	0.0464	C149	0.00[illegible]	C199	0.0019	C249	0.0000
C50	0.3241	C100	0.0447	C150	0.0077	C200	0.0018	C250	0.0000

Figure 5-203. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: $CO+H_2$ Conversion in Run 37 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet)

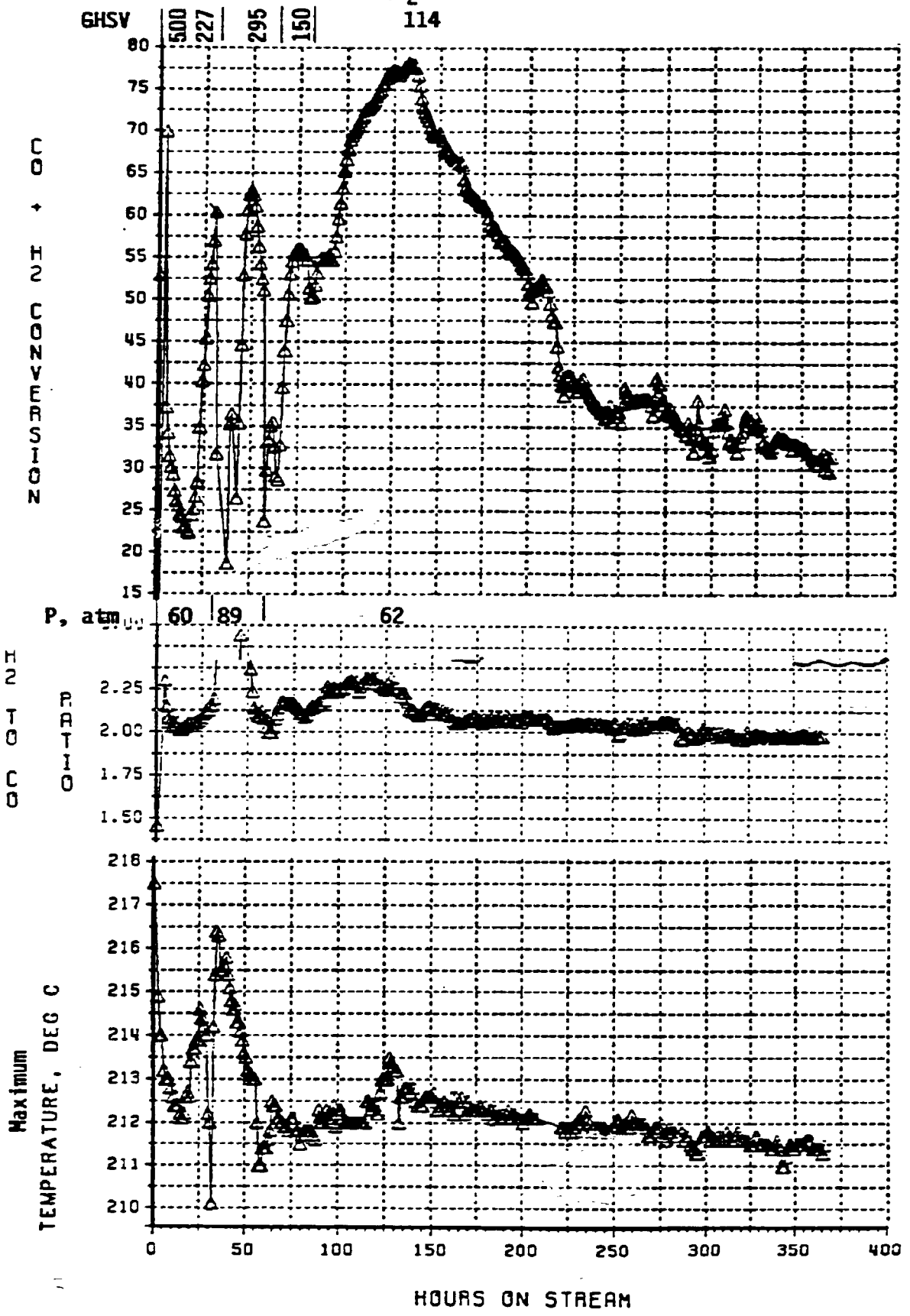


Figure 5-204. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles:Water Gas Shift Activity in Run 37 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet)

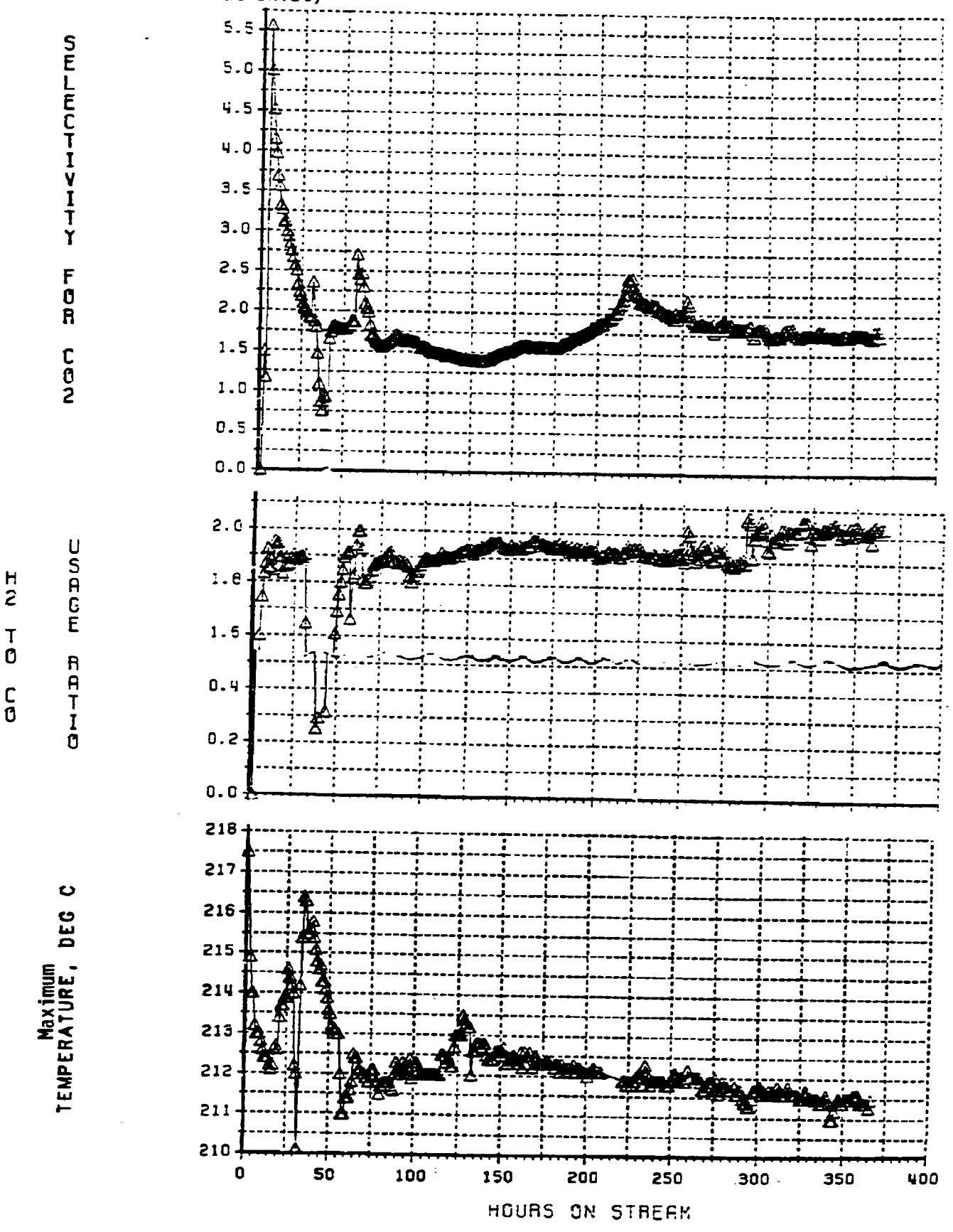


Figure 5-205. Catalyst 4966-119 with Mostly 4–6 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 37 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet)

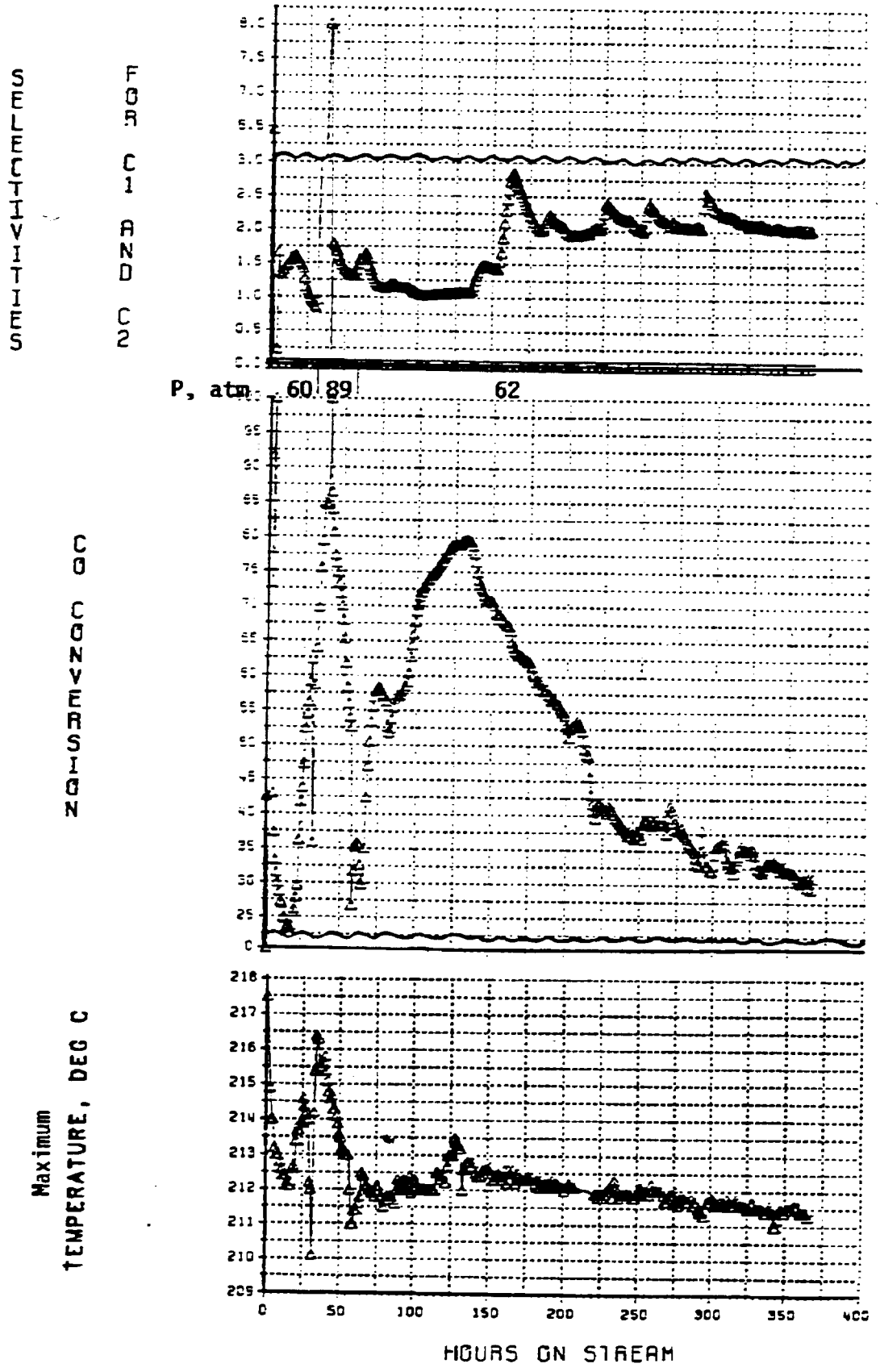


Figure 5-206. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 37 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet)

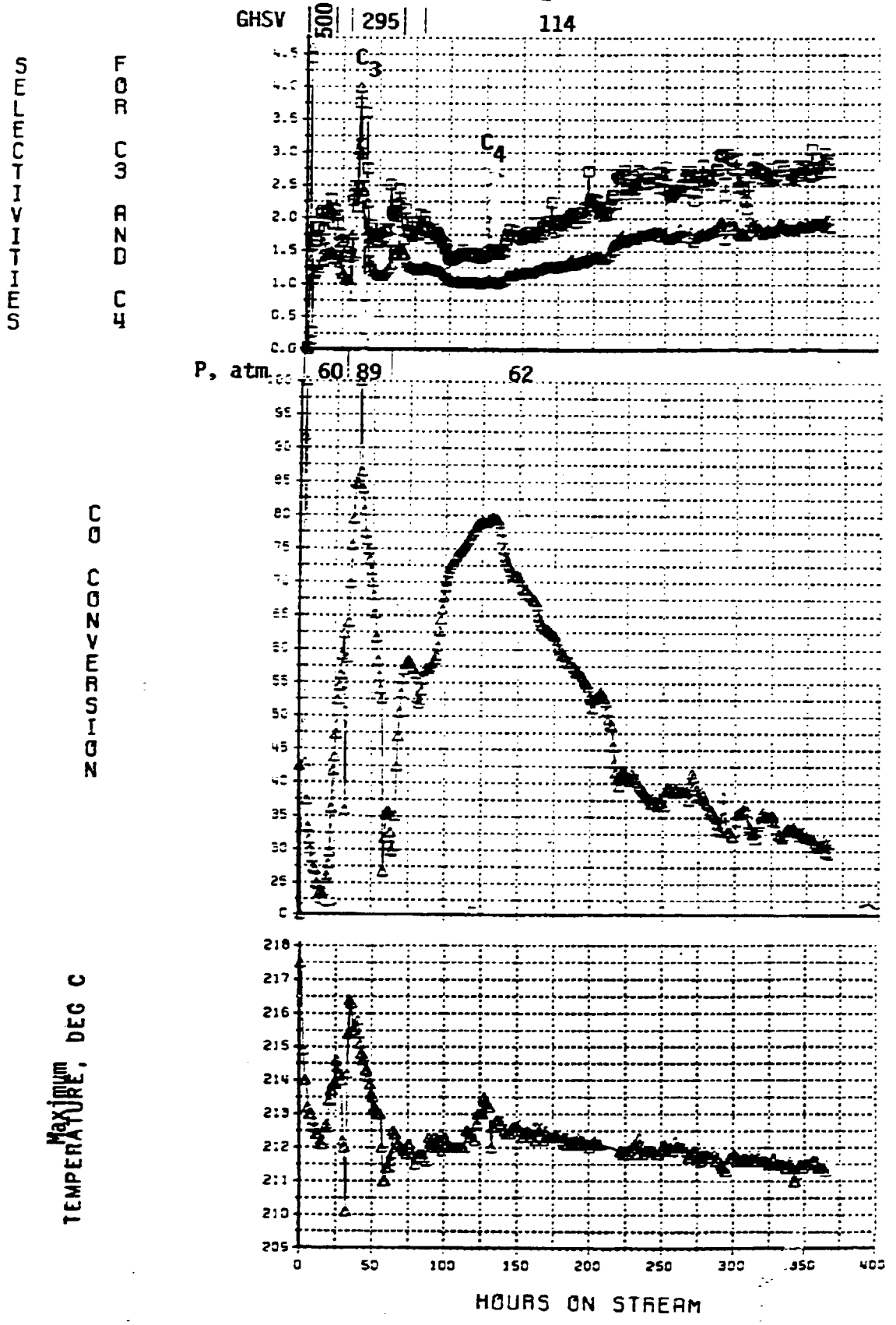


Figure 5-207. Light Hydrocarbon Selectivities in Run 37 with Catalyst 4966-119 Having Mostly 4-6 nm Ruthenium Particles (H_2:CO Feed Ratio = 2.0, 208°C at Inlet, 62 atm)

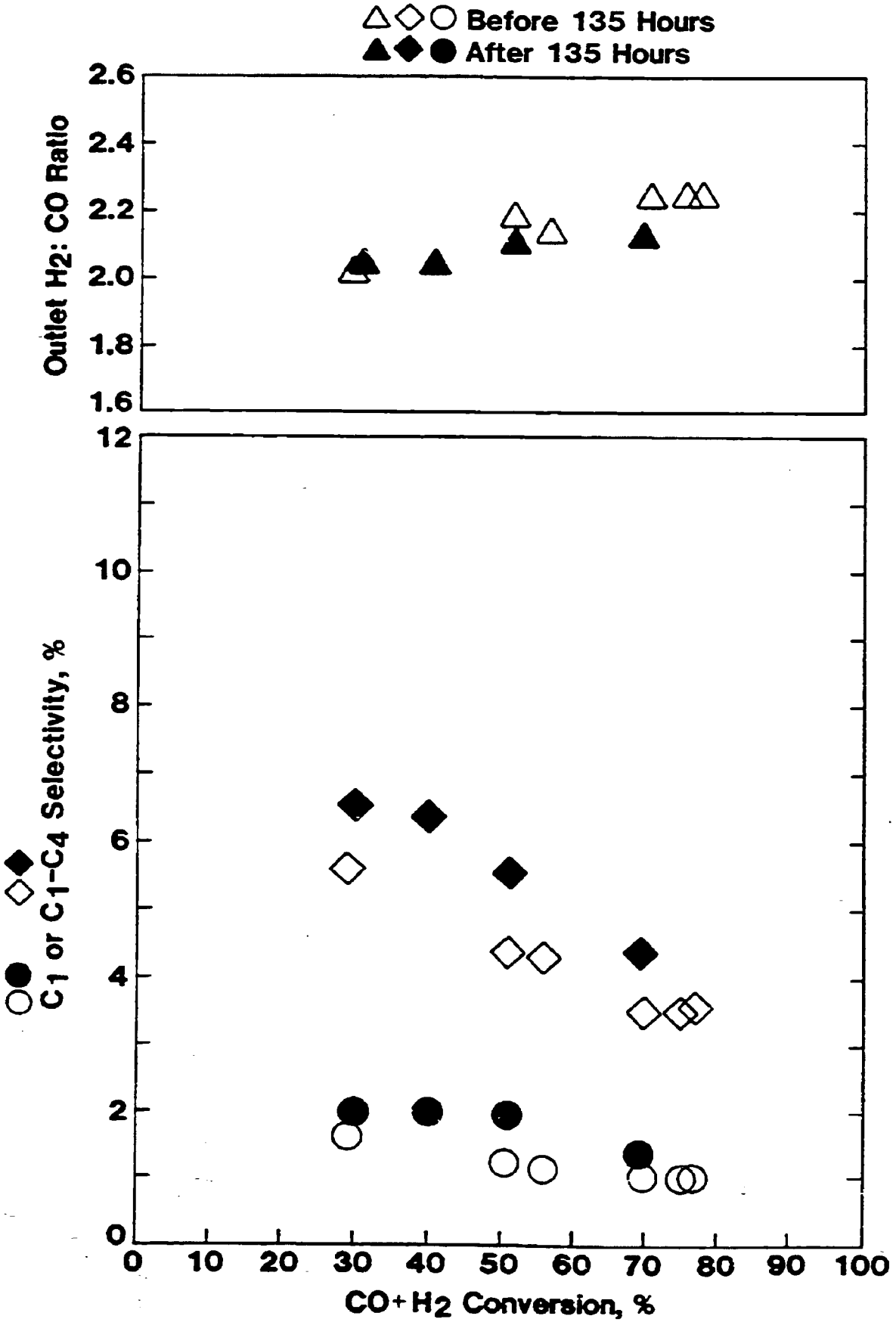


Figure 5-208. Catalyst 4966-119 with Mostly 4-6 nm Ruthenium Particles: Propylene:Propane Ratios in Run 37 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet)

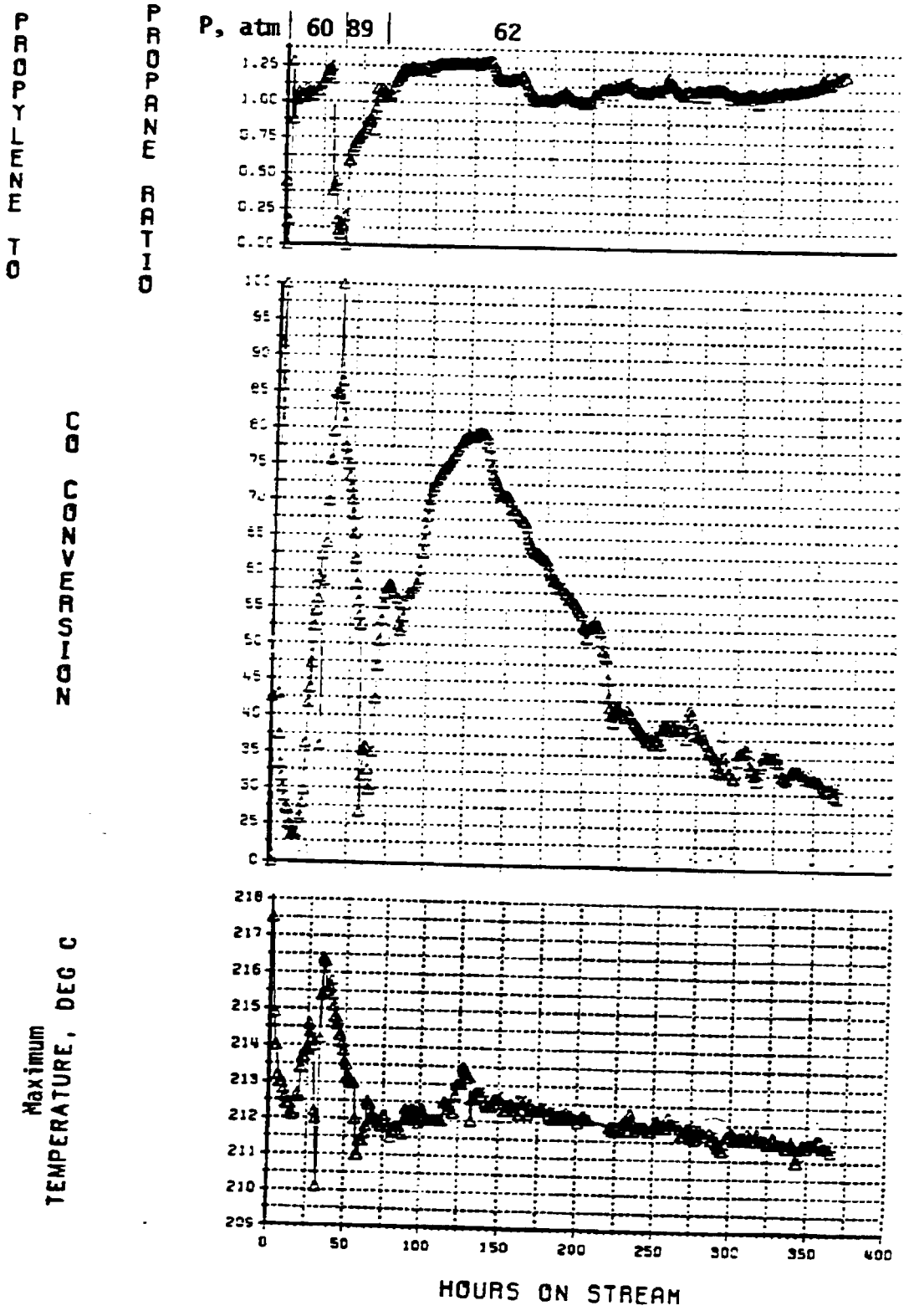


Figure 5-209. Anderson-Schulz-Flory Distribution in Run 37 with Catalyst 4966-119 Having Mostly 4-6 nm Ruthenium Particles (Hydrocarbons Only; C_1-C_{44})

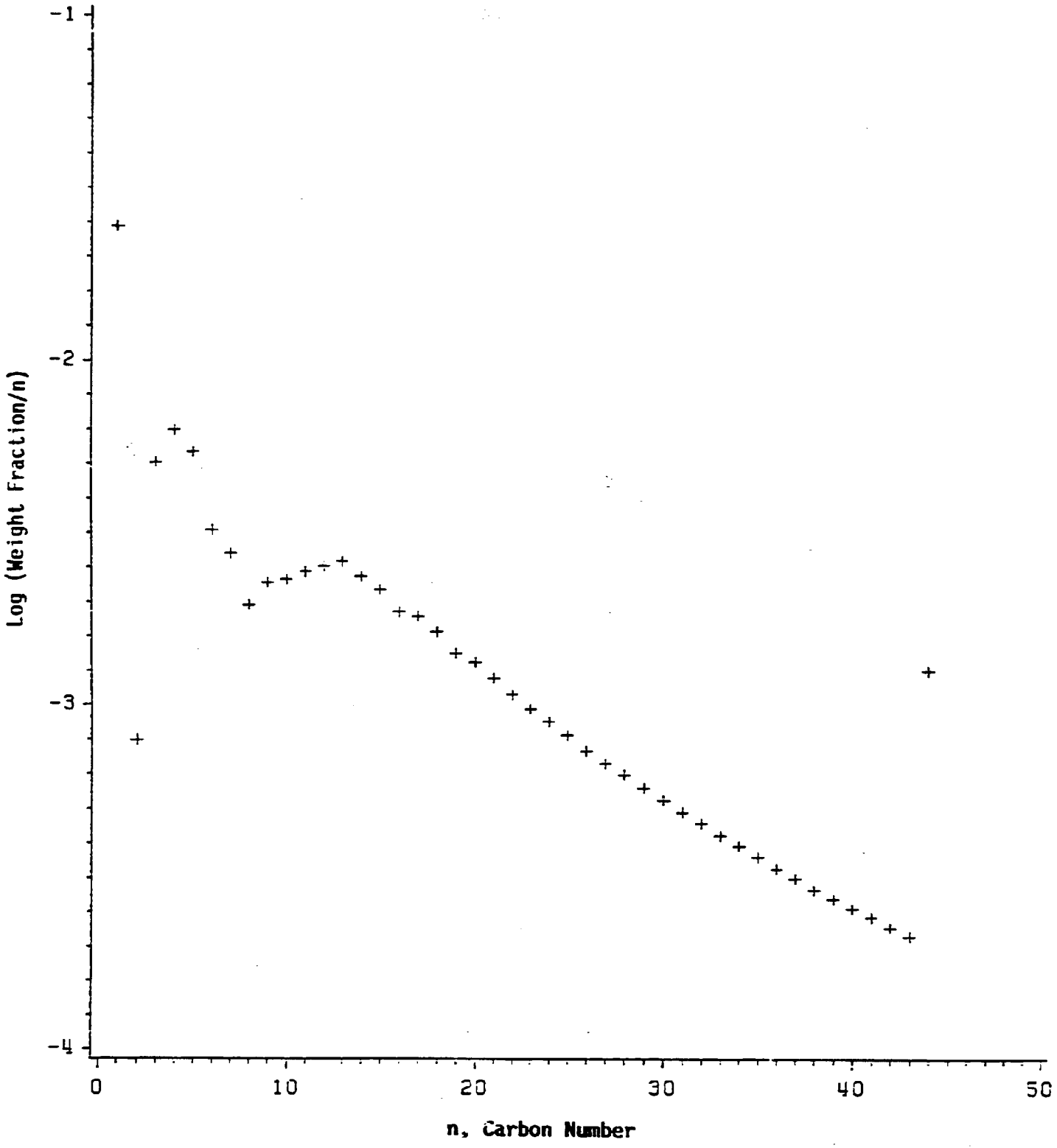
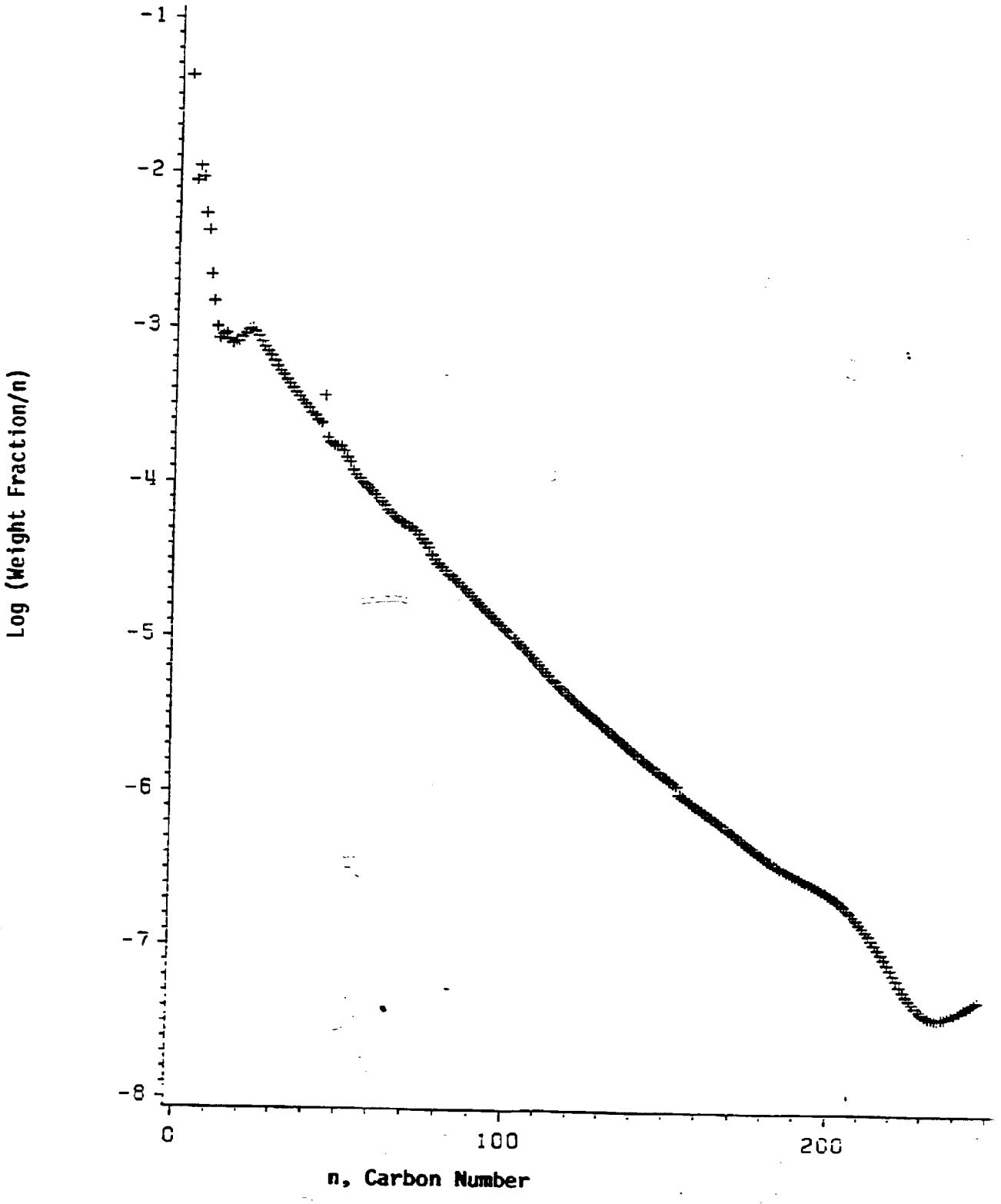


Figure 5-210. Anderson-Schulz-Flory Distribution in Run 37 with Catalyst 4966-119 Having Mostly 4-6 nm Ruthenium Particles (Hydrocarbons Only; C_1-C_{250})



The light hydrocarbon selectivities before and after 80% conversion level was reached were compared in Figure 5-207. Light hydrocarbon selectivities were higher after the peak conversion was achieved. This result may indicate that catalytic selectivity was adversely affected during the catalyst deactivation period.

Run 37 was terminated at 436 hours on stream after a brief period during which the H_2:CO feed ratio was lowered to 0.9 and lower light ends selectivities were obtained.

5.2.2 Performance of Ruthenium Catalysts Prepared on Other Supports

5.2.2.1 Ruthenium on Y-Zeolite

Ruthenium Catalyst 4966-114 with 6.3% Ru (by wt.) was prepared on Y-zeolite according to the recipe given in the literature (Table 5-34) [74]. According to STEM examination, ruthenium was in the form of 2-3 nm or smaller particles. EXAFS examination indicated the average ruthenium particle size to be narrow, around 1.5 nm. A temperature programmed oxidation experiment showed that with a 1% oxygen in helium mixture all of the ruthenium in the reduced catalyst could be oxidized at room temperature. This result, according to the discussion in the literature, is an indication that the ruthenium may be inside the zeolite [53].

The ruthenium catalyst prepared on Y-zeolite was tested under conditions (200°C, 14 atm, 1.5 H_2:CO feed ratio and ~30 CO conversion) at which cutoff at C_{11} was reported in the literature with such a catalyst (H. H. Nijs, P. A. Jacobs *et al*, Proceedings of Fifth Int. Conf. on zeolites, 1980). Test duration was kept short to minimize ruthenium agglomeration.

Catalyst 4966-114 was first tested in Run 27 without using an inert diluent at a gas hourly space velocity of 500 hr^{-1}. The maximum temperature in the catalyst bed increased from 200°C at the inlet to 260°C during the first hour of testing. Run 27 was, therefore, terminated. In Run 28 Catalyst 4966-114 was

Table 5-34

Preparation Procedure for Y-Zeolite Supported-Ruthenium Catalyst 4966-114

50g Y-Zeolite (LZY-52, 4714)

+

Treat with 0.1 M NaCl in 500 cc H_2O
(for three days)

+

Decant the Solution and Wash the
Zeolite with H_2O three times

+

Prepare 0.01 M $Ru(NH_3)_6 Cl_3$ Solution
in 627 cc H_2O

+

Adjust pH of Ru Solution to 6.2
by NH_4OH and HNO_3

+

Add the Ru Solution to the Zeolite
and Stir for 50 Hours

+

Decant the Solution

+

Oven Dry the Catalyst at 110°C for two hours

+

H_2 Reduce at 600°C for two hours

mixed with 8 g quartz sand:1g catalyst. Also, 8 x higher space velocity was initially used relative to Run 27.

The results obtained in Run 28 are summarized in Tables 5-35 and 5-36 and Figures 5-211 through 5-217.

The gas hourly space velocity was lowered from an initial value of 4240 hr^{-1} to 1248 hr^{-1} at 3 hours on stream, and finally to 936 hr^{-1} at 9 hours on stream to achieve at CO conversion of 30%. The CO conversion gradually declined during the run (Figure 5-211). The zeolite-supported ruthenium catalyst did not exhibit any water gas shift activity throughout the run (Figure 5-212). The light hydrocarbon selectivities increased with decrease in the conversion, like with alumina-supported ruthenium catalysts (Figures 5-213 and 5-214). However, the light hydrocarbon selectivities were higher with the zeolite-supported catalyst relative to the alumina-supported Catalyst 4966-76 tested under similar conditions in Run 20. The olefin to paraffin ratios in Run 28 were higher relative to those obtained with the alumina-supported catalyst (Figure 5-215). The olefin to paraffin ratio with the zeolite catalyst decreased with decrease in the conversion level after 12 hours on stream.

After 28 hours of testing, Catalyst 4966-114 was examined with STEM which indicated that there was no noticeable change in the ruthenium particle size (Figures 5-218 and 5-219). This result, in view of the results obtained in Run 20 with the alumina-supported catalyst having similar particle size, indicates that ruthenium metal agglomeration was substantially suppressed on Y-zeolite relative to alumina.

Products in the C_{10}-C_{23} range apparently were not fully recovered in the product receivers because of the short duration of the test. Nevertheless, 30% of the hydrocarbon products accumulated as wax on the catalyst, showed Anderson-Schulz-Flory distribution up to a carbon number of 160, and therefore it was possible to conclude that cutoff did not occur with 1.5 nm ruthenium particles on Y-zeolite (Figures 5-216 and 5-217).

Table 5-35. Product Distributions in Run 28

WEIGHT PCTS WITHOUT ARGON	
HYDROGEN	7.016
CARBON MONOXIDE	71.854
CARBON DIOXIDE	0.000
WATER	14.021
HYDROCARBONS	6.910
OXYGENATES	0.200
HYDROCARBON DISTRIBUTION	
C1	14.804
C2 - C4	13.966
C5 - C11	31.712
C12 - C18	11.180
C19 - C25	3.647
C26 PLUS	24.690
C1 - C44	88.724
C45 PLUS	11.276
OXYGENATES DISTRIBUTION	
ALCOHOLS	88.235
ALDEHYDES	11.765
OTHER OXYGENATES	0.000
MOLE PCTS WITHOUT ARGON	
HYDROGEN	50.143
CARBON MONOXIDE	36.962
CARBON DIOXIDE	0.000
WATER	11.214
HYDROCARBONS	1.626
OXYGENATES	0.055

Table 5-36. Hydrocarbon Distributions in Run 28

C1	14.8044	C51	0.3785	C101	0.0345	C151	0.0015	C201	0.0000
C2	1.2072	C52	0.3660	C102	0.0325	C152	0.0014	C202	0.0000
C3	5.3461	C53	0.3526	C103	0.0306	C153	0.0013	C203	0.0000
C4	7.4131	C54	0.3396	C104	0.0288	C154	0.0012	C204	0.0000
C5	5.5448	C55	0.3298	C105	0.0271	C155	0.0011	C205	0.0000
C6	5.4930	C56	0.3176	C106	0.0257	C156	0.0010	C206	0.0000
C7	3.4195	C57	0.3059	C107	0.0241	C157	0.0009	C207	0.0000
C8	4.0406	C58	0.2945	C108	0.0226	C158	0.0009	C208	0.0000
C9	4.6406	C59	0.2782	C109	0.0212	C159	0.0009	C209	0.0000
C10	4.5480	C60	0.2677	C110	0.0199	C160	0.0008	C210	0.0000
C11	4.0253	C61	0.2575	C111	0.0187	C161	0.0007	C211	0.0000
C12	3.2751	C62	0.2476	C112	0.0176	C162	0.0007	C212	0.0000
C13	2.4095	C63	0.2420	C113	0.0165	C163	0.0006	C213	0.0000
C14	1.7460	C64	0.2326	C114	0.0159	C164	0.0005	C214	0.0000
C15	1.2466	C65	0.2234	C115	0.0142	C165	0.0005	C215	0.0000
C16	0.9988	C66	0.2143	C116	0.0133	C166	0.0004	C216	0.0000
C17	0.8338	C67	0.2055	C117	0.0126	C167	0.0003	C217	0.0000
C18	0.6701	C68	0.1954	C118	0.0119	C168	0.0003	C218	0.0000
C19	0.4662	C69	0.1869	C119	0.0113	C169	0.0002	C219	0.0000
C20	0.3649	C70	0.1786	C120	0.0108	C170	0.0002	C220	0.0000
C21	0.3636	C71	0.1705	C121	0.0103	C171	0.0001	C221	0.0000
C22	0.4232	C72	0.1626	C122	0.0098	C172	0.0001	C222	0.0000
C23	0.5438	C73	0.1552	C123	0.0094	C173	-0.0000	C223	0.0000
C24	0.7506	C74	0.1477	C124	0.0081	C174	-0.0000	C224	0.0000
C25	0.7352	C75	0.1405	C125	0.0078	C175	-0.0001	C225	0.0000
C26	0.8073	C76	0.1335	C126	0.0074	C176	-0.0001	C226	0.0000
C27	0.8682	C77	0.1268	C127	0.0070	C177	-0.0001	C227	0.0000
C28	0.8876	C78	0.1185	C128	0.0067	C178	-0.0001	C228	0.0000
C29	0.8793	C79	0.1124	C129	0.0064	C179	-0.0001	C229	0.0000
C30	0.8627	C80	0.1067	C130	0.0060	C180	-0.0001	C230	0.0000
C31	0.8363	C81	0.1013	C131	0.0057	C181	-0.0001	C231	0.0000
C32	0.8044	C82	0.0961	C132	0.0055	C182	-0.0001	C232	0.0000
C33	0.7739	C83	0.0912	C133	0.0052	C183	-0.0001	C233	0.0000
C34	0.7420	C84	0.0862	C134	0.0049	C184	-0.0001	C234	0.0000
C35	0.7156	C85	0.0837	C135	0.0047	C185	-0.0001	C235	0.0000
C36	0.6865	C86	0.0794	C136	0.0044	C186	-0.0001	C236	0.0000
C37	0.6560	C87	0.0764	C137	0.0041	C187	-0.0001	C237	0.0000
C38	0.6296	C88	0.0715	C138	0.0039	C188	-0.0000	C238	0.0000
C39	0.6019	C89	0.0678	C139	0.0036	C189	0.0000	C239	0.0000
C40	0.5783	C90	0.0643	C140	0.0034	C190	0.0000	C240	0.0000
C41	0.5561	C91	0.0607	C141	0.0032	C191	0.0000	C241	0.0000
C42	0.5325	C92	0.0575	C142	0.0030	C192	0.0000	C242	0.0000
C43	0.5090	C93	0.0544	C143	0.0028	C193	0.0000	C243	0.0000
C44	0.4868	C94	0.0515	C144	0.0026	C194	0.0000	C244	0.0000
C45	0.4827	C95	0.0487	C145	0.0024	C195	0.0000	C245	0.0000
C46	0.4636	C96	0.0461	C146	0.0021	C196	0.0000	C246	0.0000
C47	0.4465	C97	0.0436	C147	0.0020	C197	0.0000	C247	0.0000
C48	0.4248	C98	0.0411	C148	0.0018	C198	0.0000	C248	0.0000
C49	0.4086	C99	0.0388	C149	0.0017	C199	0.0000	C249	0.0000
C50	0.3932	C100	0.0366	C150	0.0016	C200	0.0000	C250	0.0000

Figure 5-211. Y-Zeolite-Supported Ruthenium Catalyst 4966-114: Conversions in Run 28 (H_2:CO Feed Ratio = 1.5, 200°C at Inlet, 14 atm)

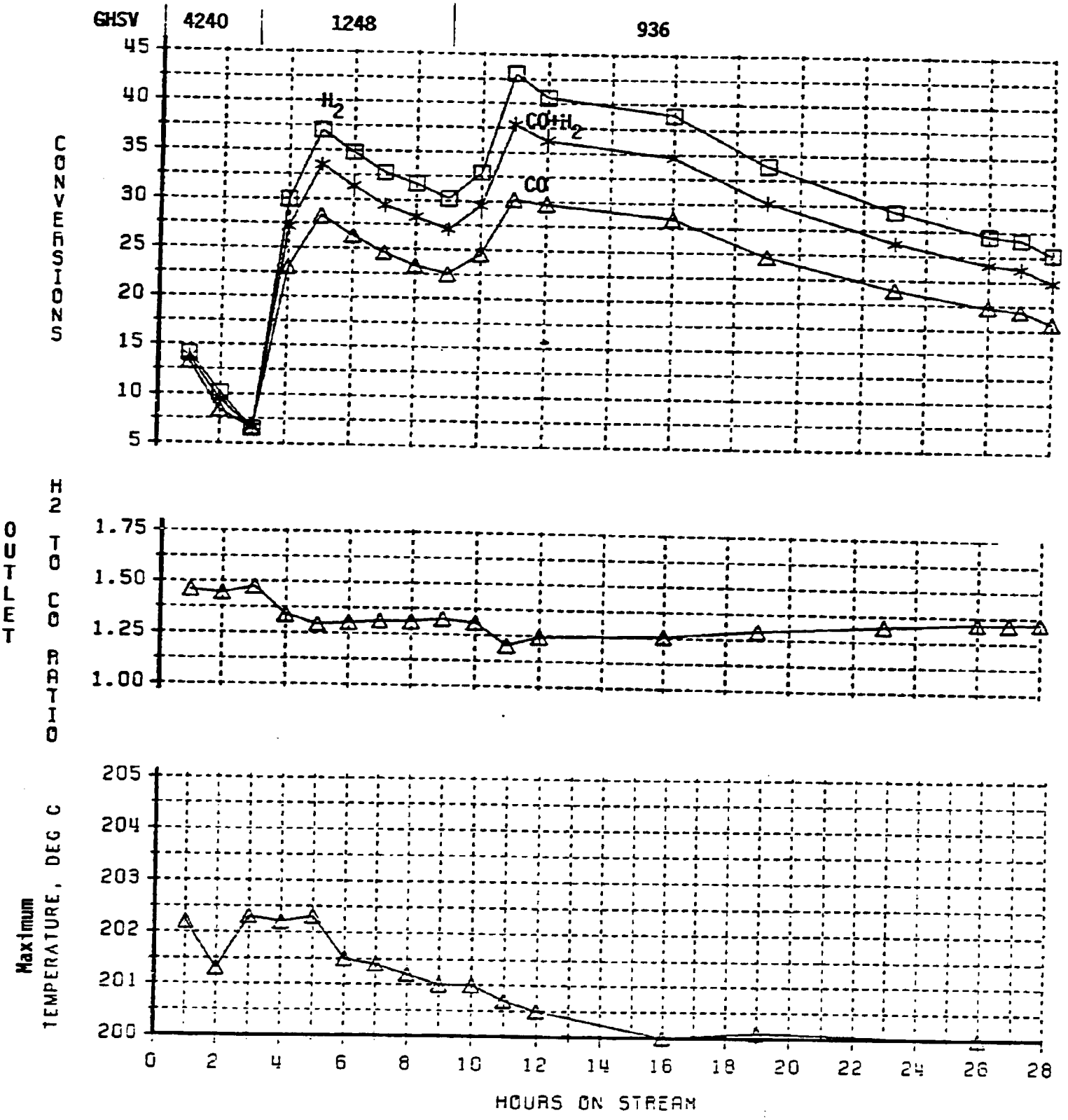


Figure 5-212. Y-Zeolite-Supported Ruthenium Catalyst 4966-114: Water Gas Shift Activity in Run 28 (H_2:CO Feed Ratio = 1.5, 200°C at Inlet, 14 atm)

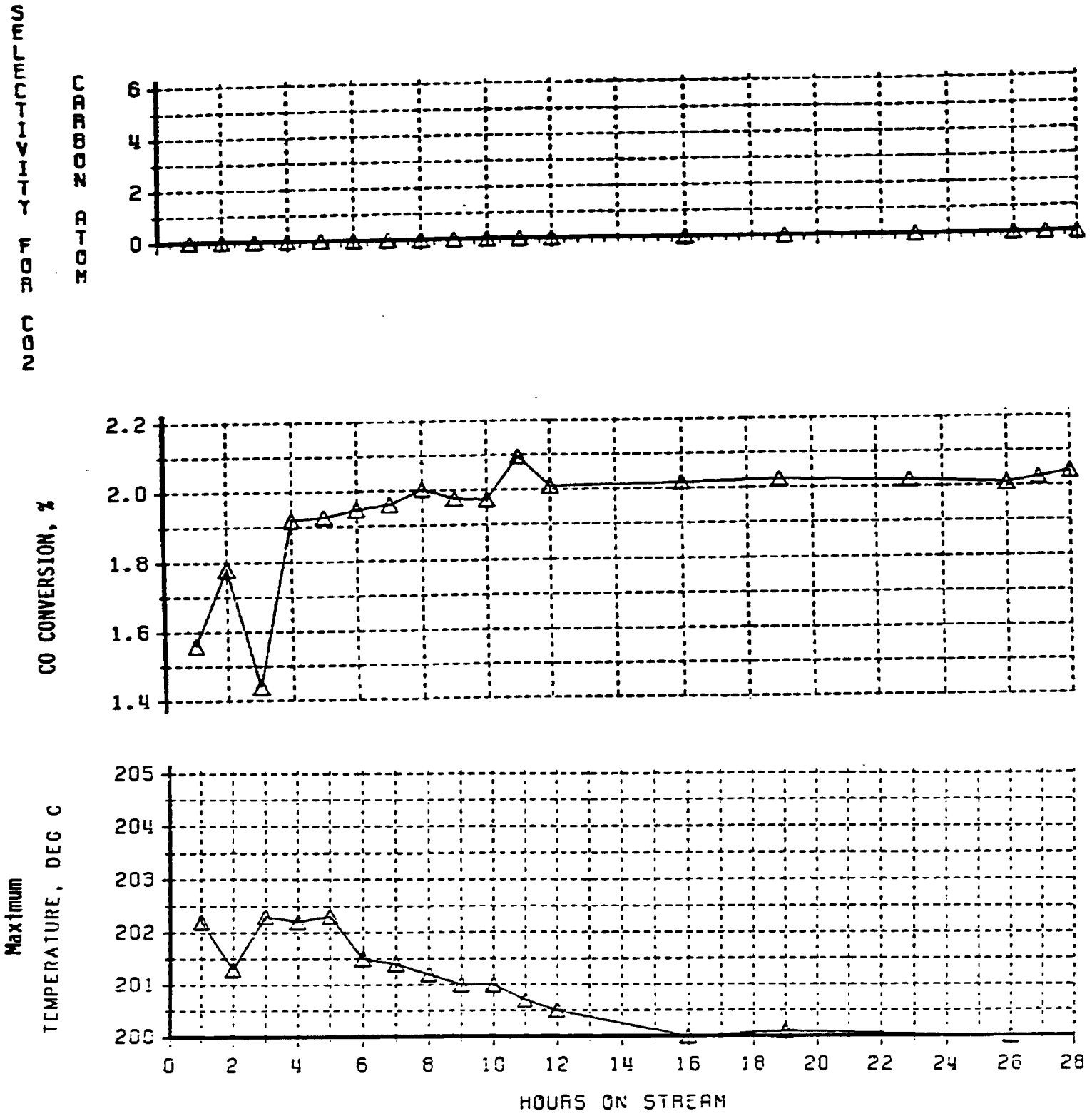


Figure 5-213. Y-Zeolite-Supported Ruthenium Catalyst 4966-114: C_1 and C_2 Selectivities in Run 28 (H_2:CO Feed Ratio = 1.5, 200°C at Inlet, 14 atm)

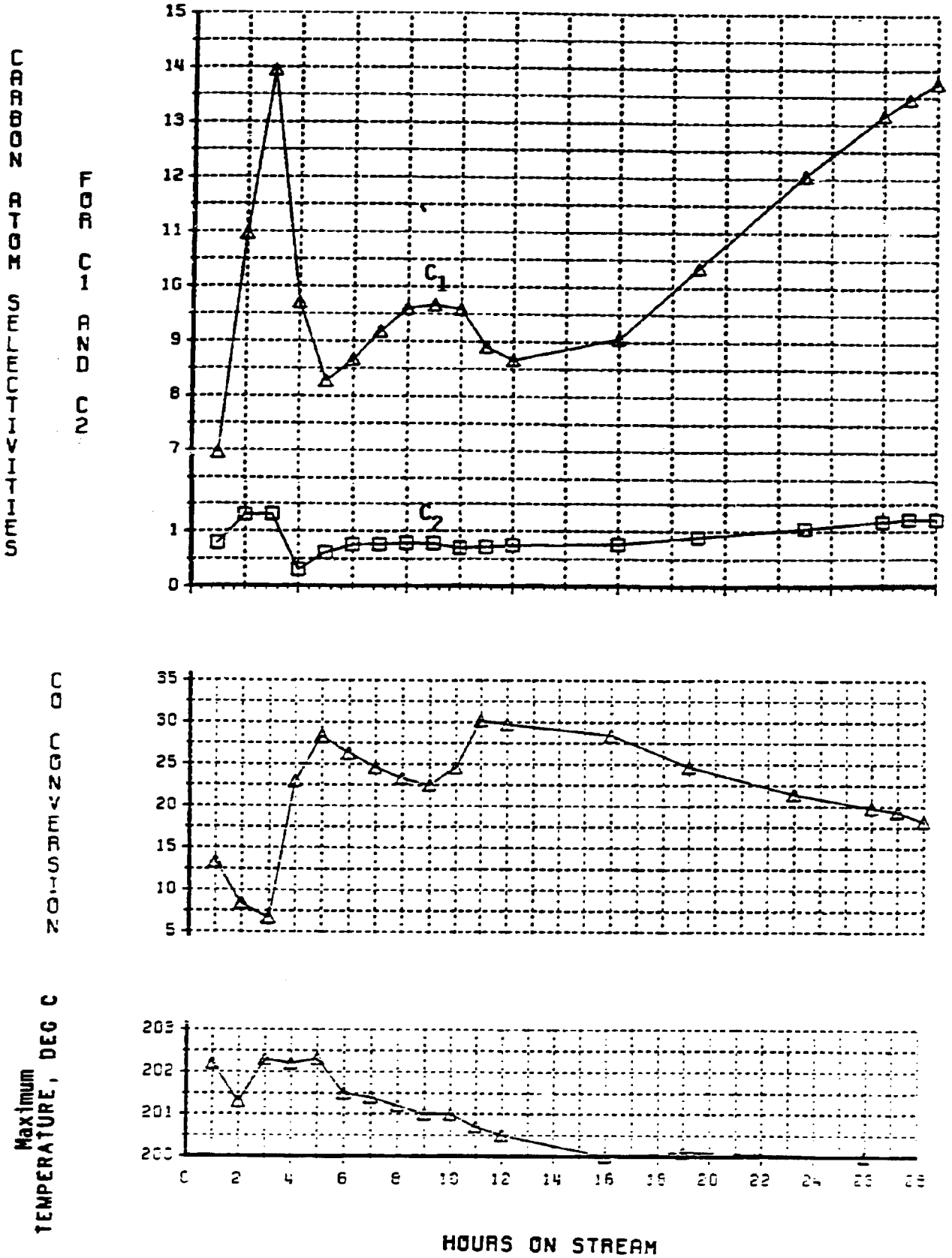


Figure 5-214. Y-Zeolite-Supported Ruthenium Catalyst 4966-114:C_3 and C_4 Selectivities in Run 28 (H_2:CO Feed Ratio = 1.5, 200°C at Inlet, 14 atm)

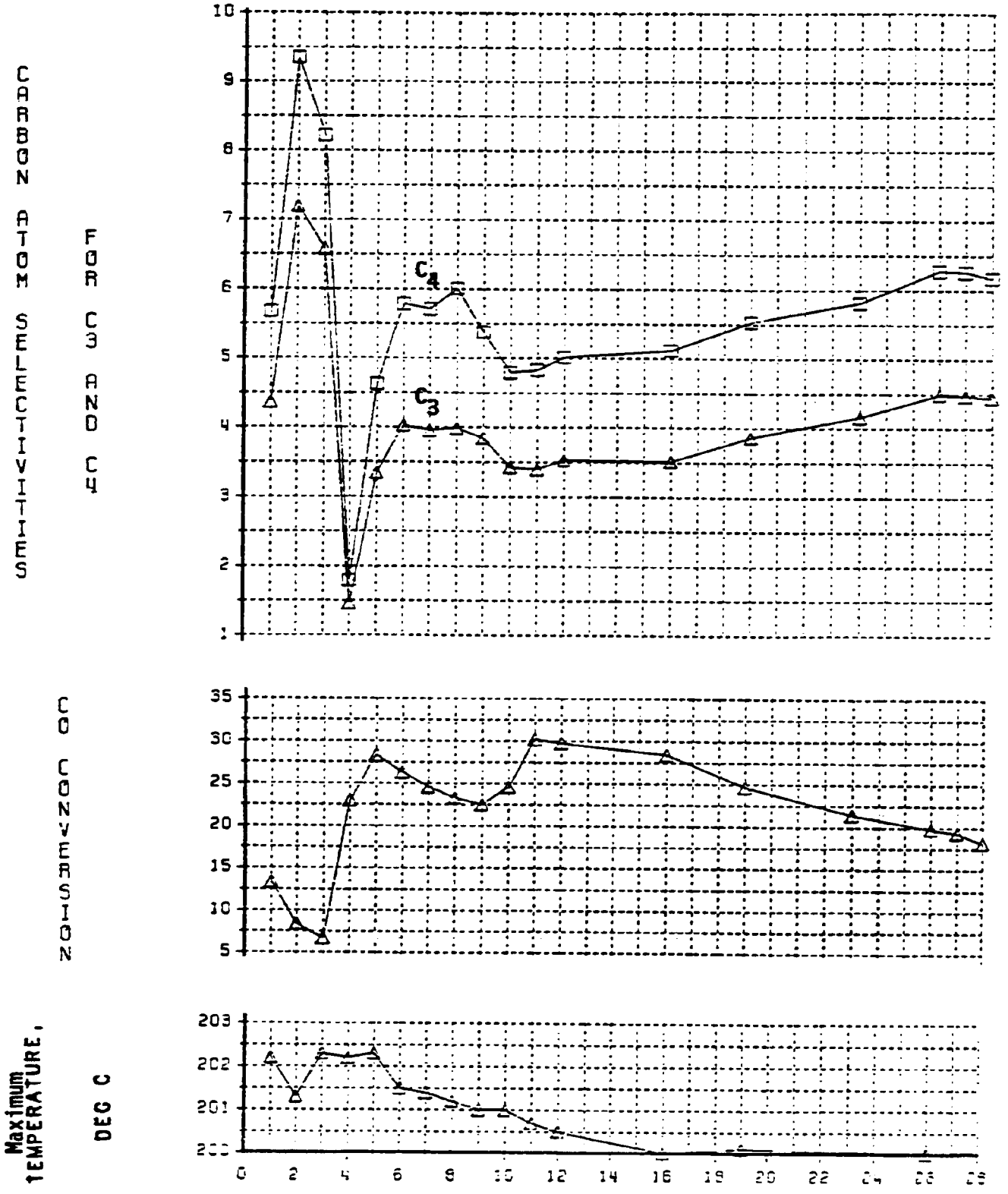


Figure 5-215. Y-Zeolite-Supported Ruthenium Catalyst 4966-114:Olefin:Paraffin Ratios in Run 28 (H_2:CO Feed Ratio = 1.5, 200°C at Inlet, 14 atm)

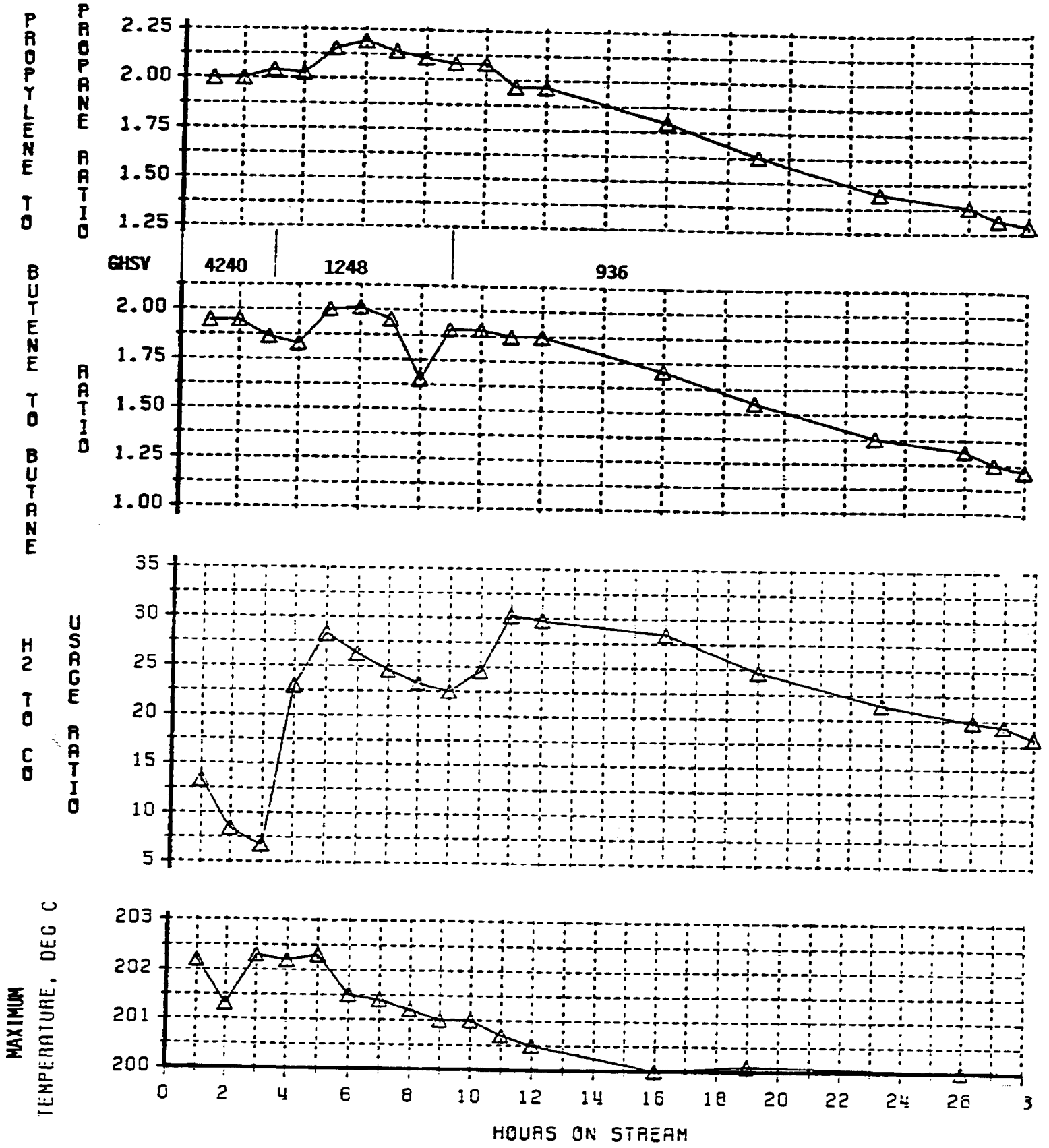


Figure 5-216. Anderson-Schulz-Flory Distributions with Y-Zeolite-Supported Ruthenium Catalyst in Run 28 (Hydrocarbons Only; C_1-C_{44})

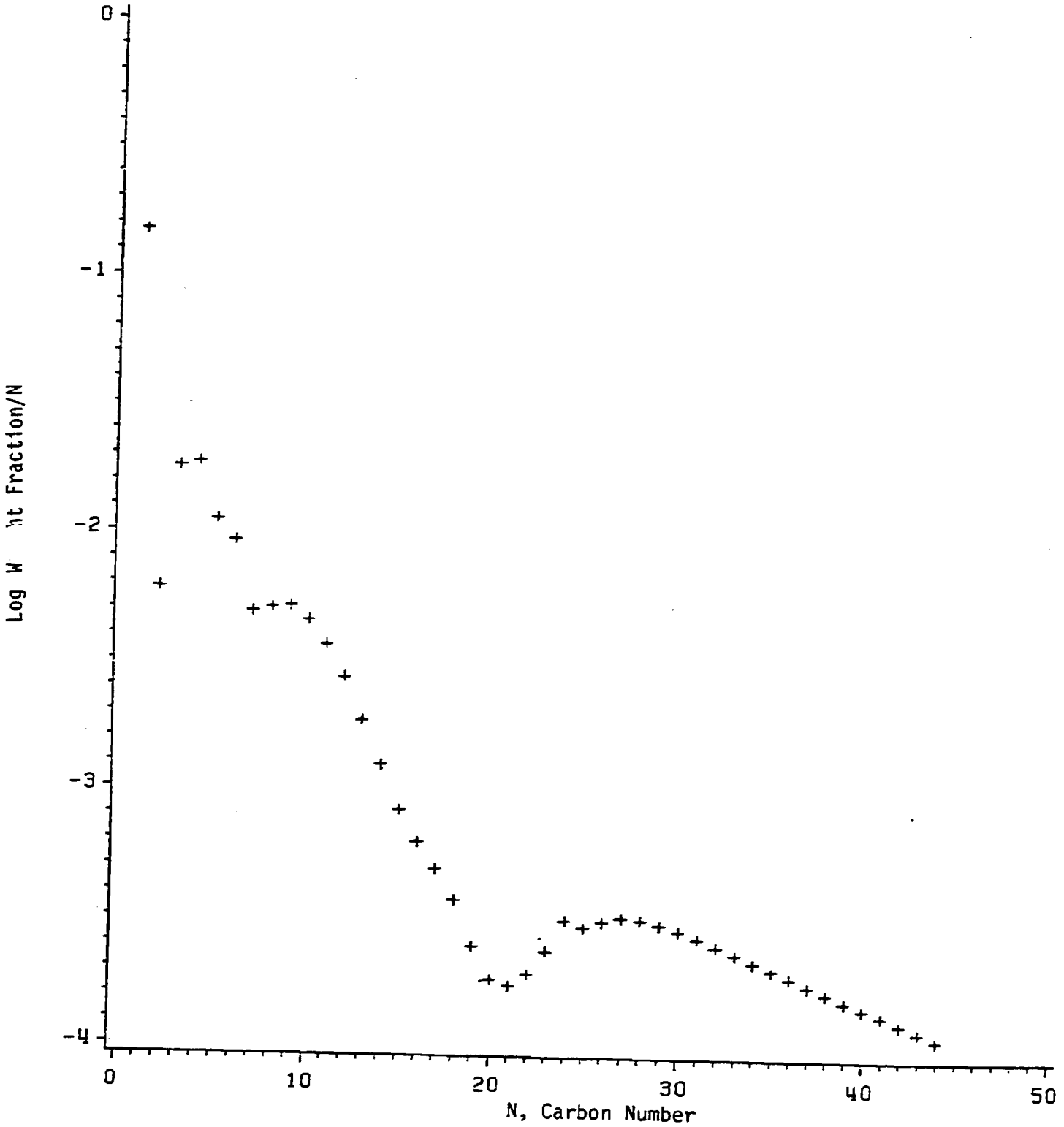
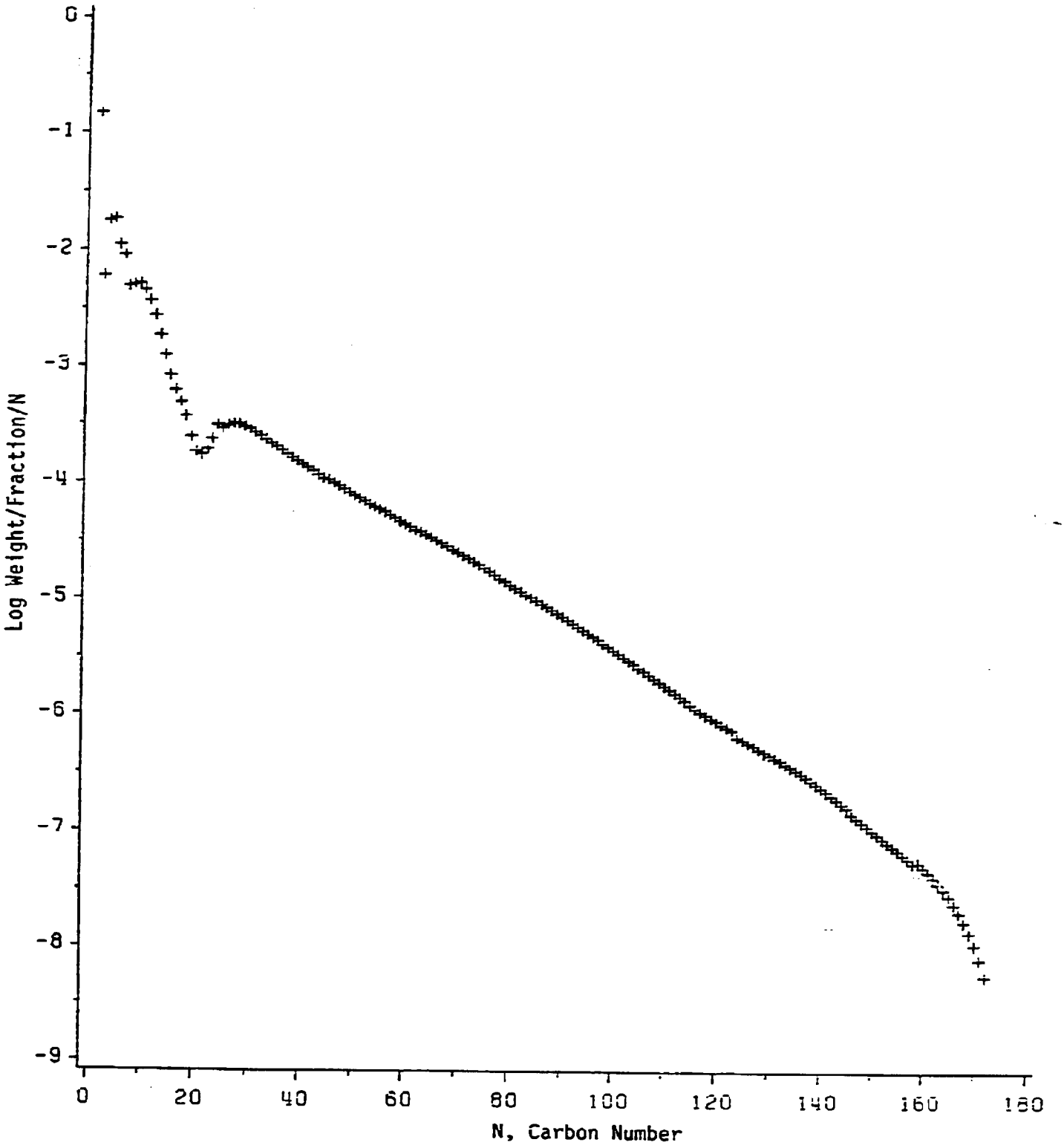


Figure 5-217. Anderson-Schulz-Flory Distributions with Y-Zeolite-Supported Ruthenium Catalyst in Run 28 (Hydrocarbons Only; C_1-C_{250})



RUTHENIUM METAL PARTICLE SIZE MAINTENANCE DURING
FISCHER-TROPSCH SYNTHESIS WITH Ru/Y-ZEOLITE CATALYST
(STEM MICROGRAPHS)

Figure 5-218 FRESH (1.5 NM Ru BY EXAFS)

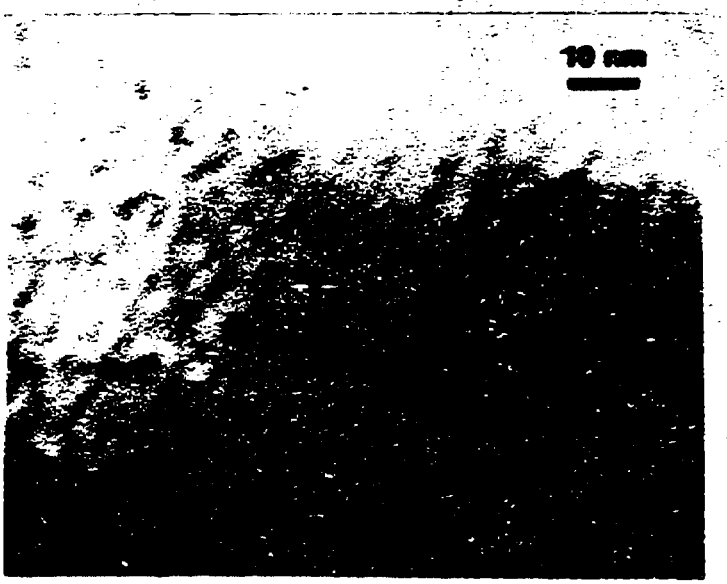


Figure 5-219 USED