5.3.3 Iridium-Modified Ruthenium Catalyst with 2.8% Ru

In an attempt to improve ruthenium's catalytic stability, the reverse micelle technique was applied for the preparation of an iridium-modified ruthenium catalyst. According to STEM examination of this Catalyst 4966-174, the metal particles were 3-5 nm in size and had atomic compositions varying mostly between 1 Ir:15 Ru to 1 Ir:23 Ru. The elongated crystal shapes of these particles have not been observed with unmodified ruthenium catalysts, and therefore, illustrates the effect of Ir on Ru morphology (Figure 5-278).

Catalyst 4966-174 was tested in Run 45 with $2H_2$:1CO feed gas at 210°C and 62 atm (Figures 5-279 through 5-283). The catalyst showed very low activity. Highest CO conversion was achieved at 75 gas hourly space velocity at 15 hours on stream. The iridium-modified ruthenium catalyst showed much higher selectivity to light hydrocarbons and very low olefin to paraffin ratios relative to unmodified alumina-supported ruthenium catalysts tested earlier. One remarkable feature of the iridium-modified catalyst, however, was that it apparently exhibited water gas shift activity, while similar particle size ruthenium only catalysts did not catalyze the water gas shift reaction.

Figure 5-278

STEM MICROGRAPHS OF Ru-Ir/Al_2O_3

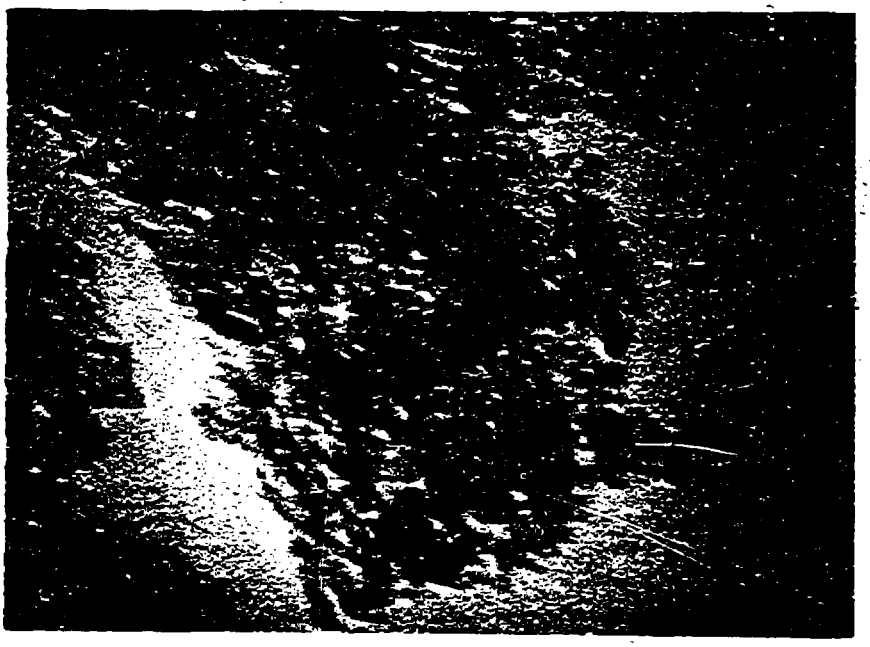


Figure 5-279. Ir-Modified Ruthenium Catalyst 4966-174:Conversions in Run 45 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

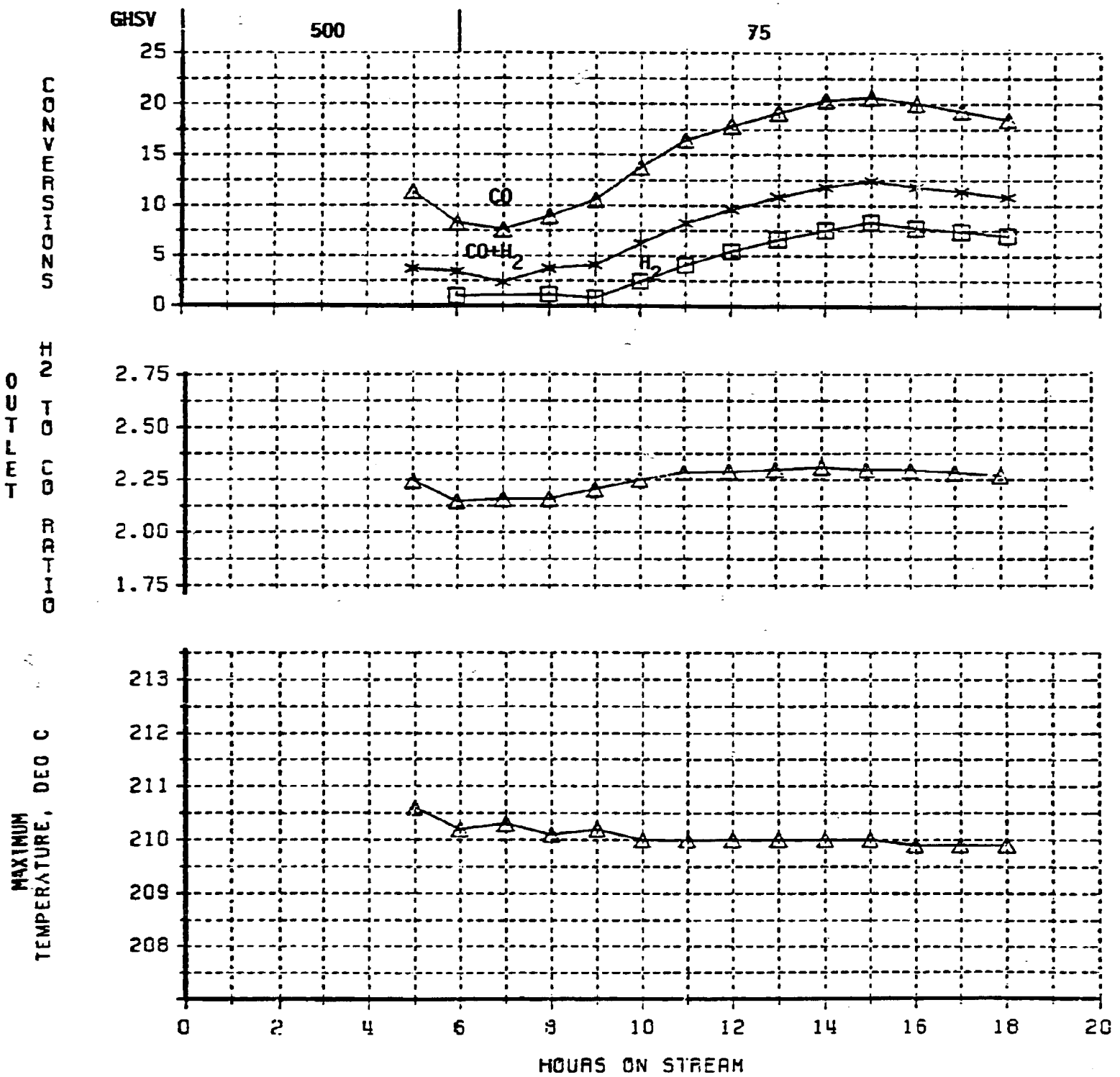


Figure 5-280. Ir-Modified Ruthenium Catalyst 4966-174:Water Gas Shift Activity in Run 45 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

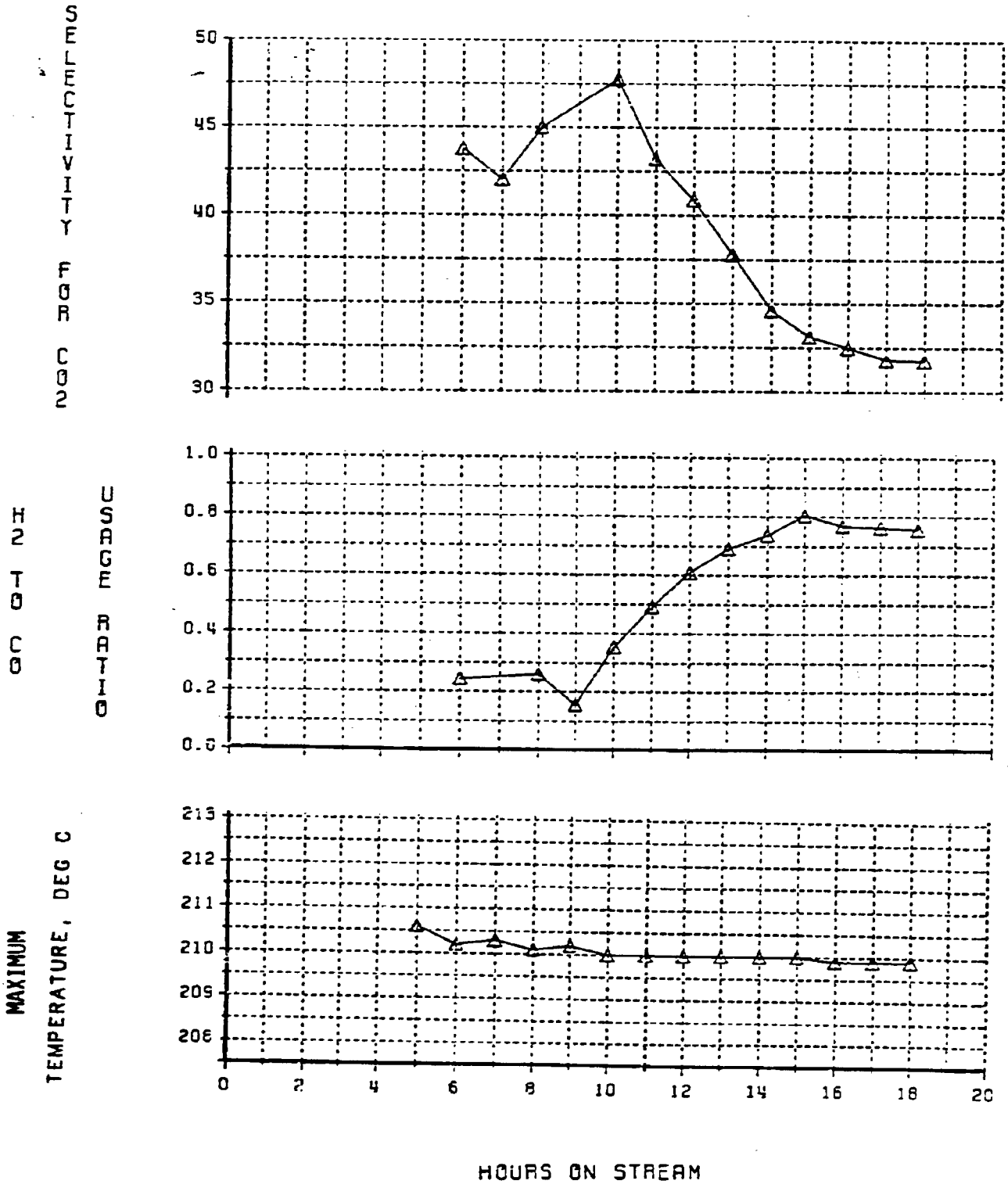


Figure 5-28i. Ir-Modified Ruthenium Catalyst 4966-174: C_1 Selectivity in Run 45 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

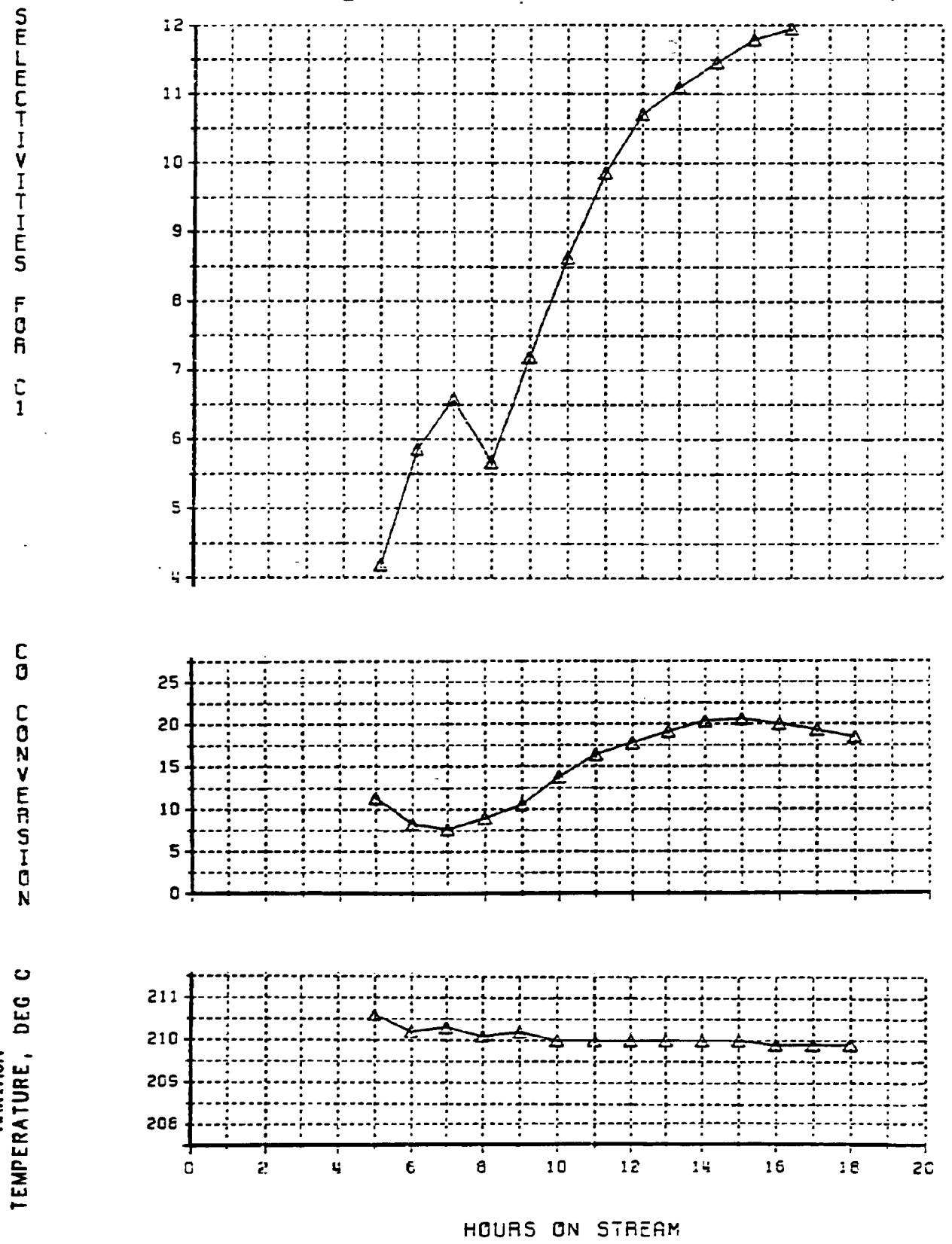


Figure 5-282. Ir-Modified Ruthenium Catalyst 4966-174: C_3 and C_4 Selectivities in Run 45 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)

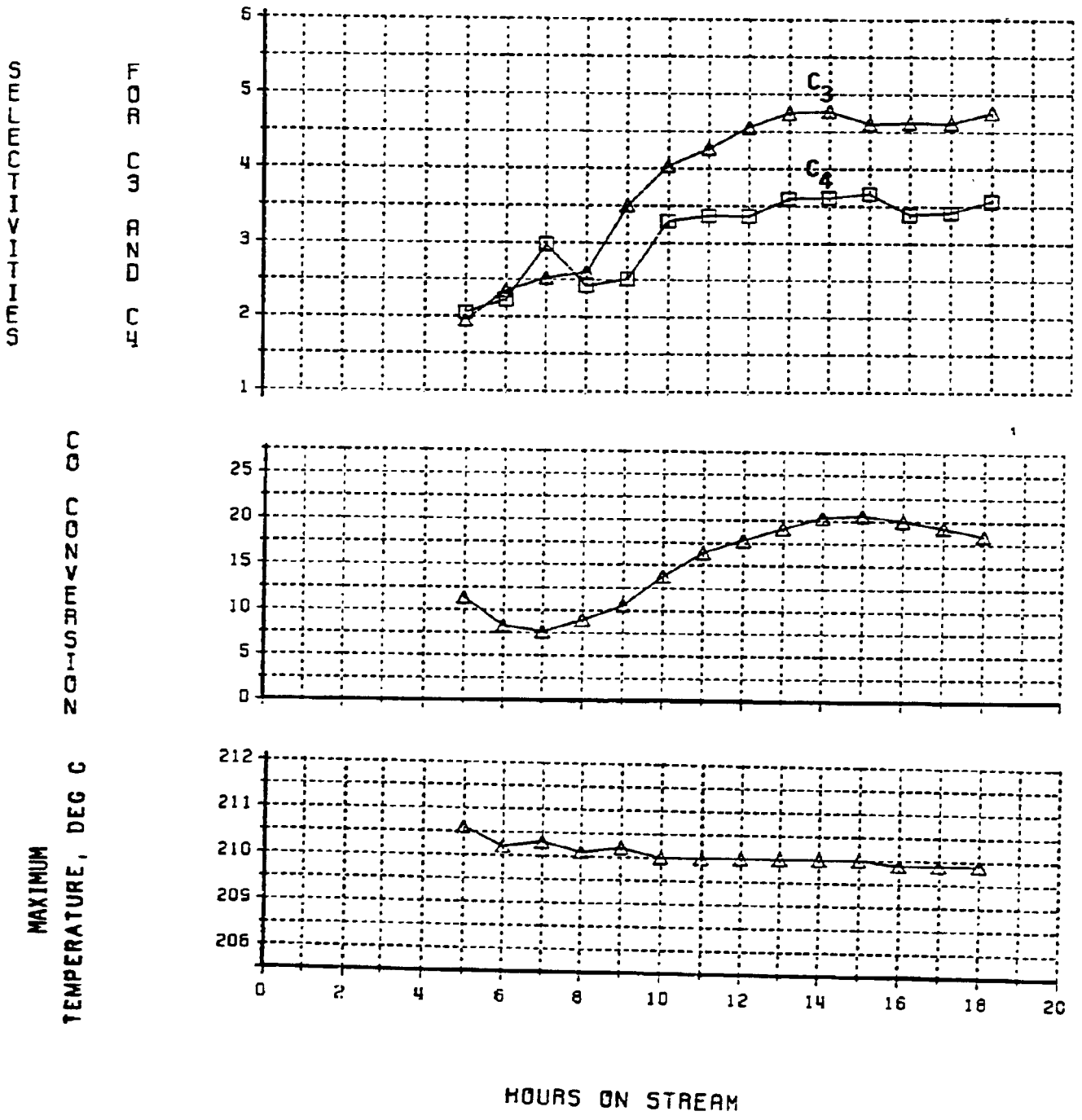
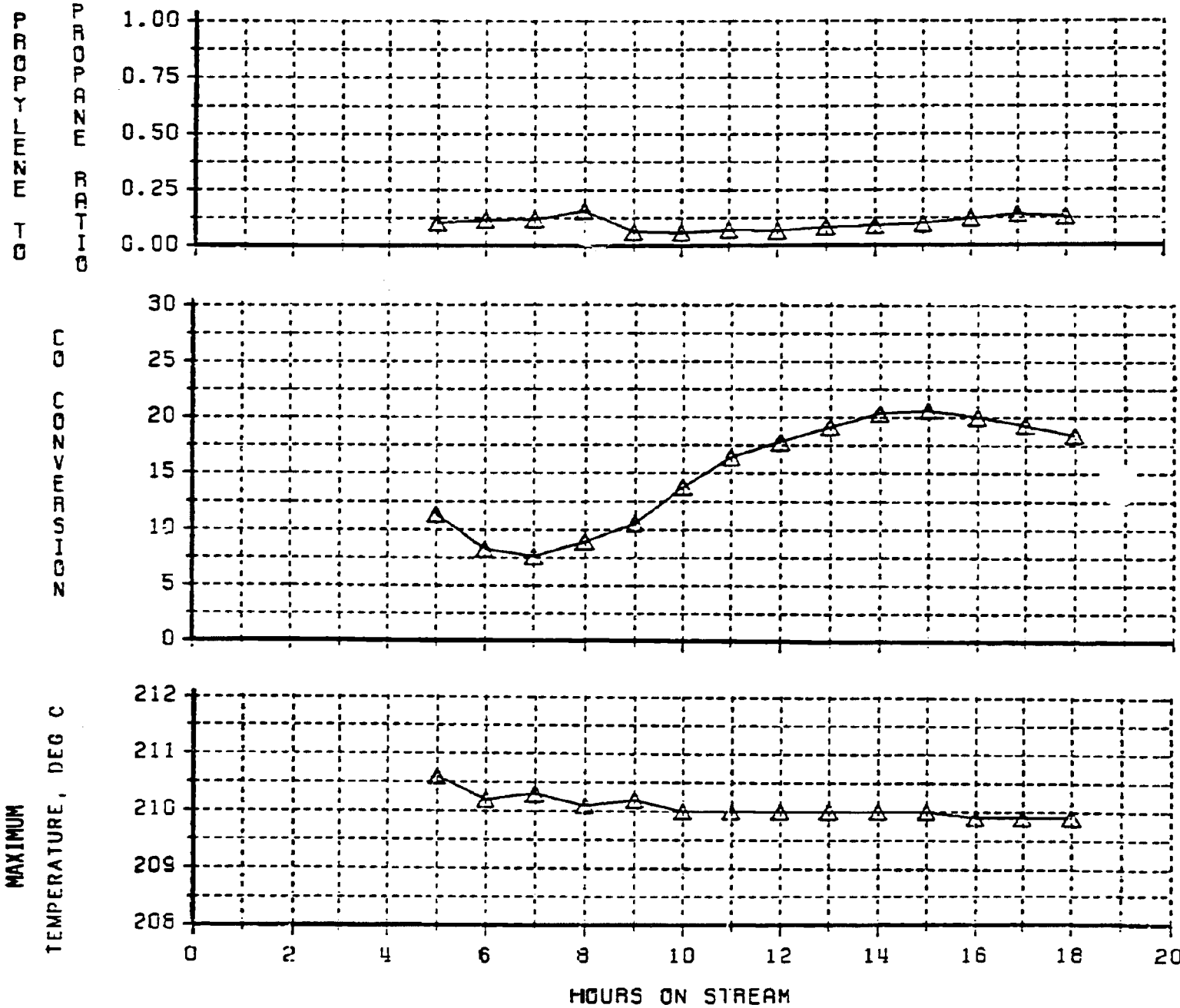


Figure 5-283. Ir-Modified Ruthenium Catalyst 4966-174: Propylene:Propane Ratio in Run 45 (H_2:CO Feed Ratio = 2.0, 210°C at Inlet, 62 atm)



5.3.4 New Modified-Ruthenium Catalyst Demonstration

In an attempt to improve stability, the reverse micelle technique was used to prepare a new modified-ruthenium catalyst with 2.8% Ru. This new catalyst, while it consisted mostly of 4-6 nm ruthenium particles, had also some 10-20% of the ruthenium in the 3-4 nm and 6-40 nm size range (Figure 5-284). This catalyst was tested in Run 46 under the same conditions as the unmodified ruthenium Catalyst 4966-198 with 2.8% Ru tested in Run 47. The initial activity of this catalyst was lower (Figure 5-285). The catalyst showed deactivation during the first 20 hours from about 60% to about 30% CO conversion. The gas hourly space velocity was lowered from 500 hr^{-1} to 125 hr^{-1} during the first 20 hours in order to achieve high conversion. The CO conversion increased close to 90%, followed by a decrease. The catalyst activity then gradually increased to achieve a CO conversion level of about 85% at 375 hours on stream, after which the gas hourly space velocity was gradually increased to 150 hr^{-1} by 595 hours to prevent the conversion from exceeding 85%. The catalyst temperature was increased by 2°C after 700 hours on stream in order to compensate for some of the space velocity increase which was apparently done too rapidly (Figure 5-285).

The modified-catalyst did not have water gas shift activity in Run 46. The H_2:CO feed ratio (1.92) was slightly lower than the H_2:CO usage ratio during the first 550 hours resulting in H_2:CO ratios which typically varied between 1.6 and 1.8 at the catalyst outlet. After 550 hours a new feed cylinder with slightly higher H_2:CO ratio (1.98) was installed. Since the new feed ratio was approximately equal to the usage ratio, the H_2:CO ratio did not decrease across the catalyst bed with increase in conversion level (Figure 5-286).

At 80% CO+H_2 conversion selectivities were compared at 32 and 604 hours in Anderson-Schulz-Flory type diagrams, as detected by the first on-line GC (Figures 5-287 through 5-289). The results indicate that the chain growth probability for paraffins, olefins, alcohols and aldehydes increased during this time period.

Figure 5-284

STEM Micrographs of Modified Ruthenium Catalyst 4966-180

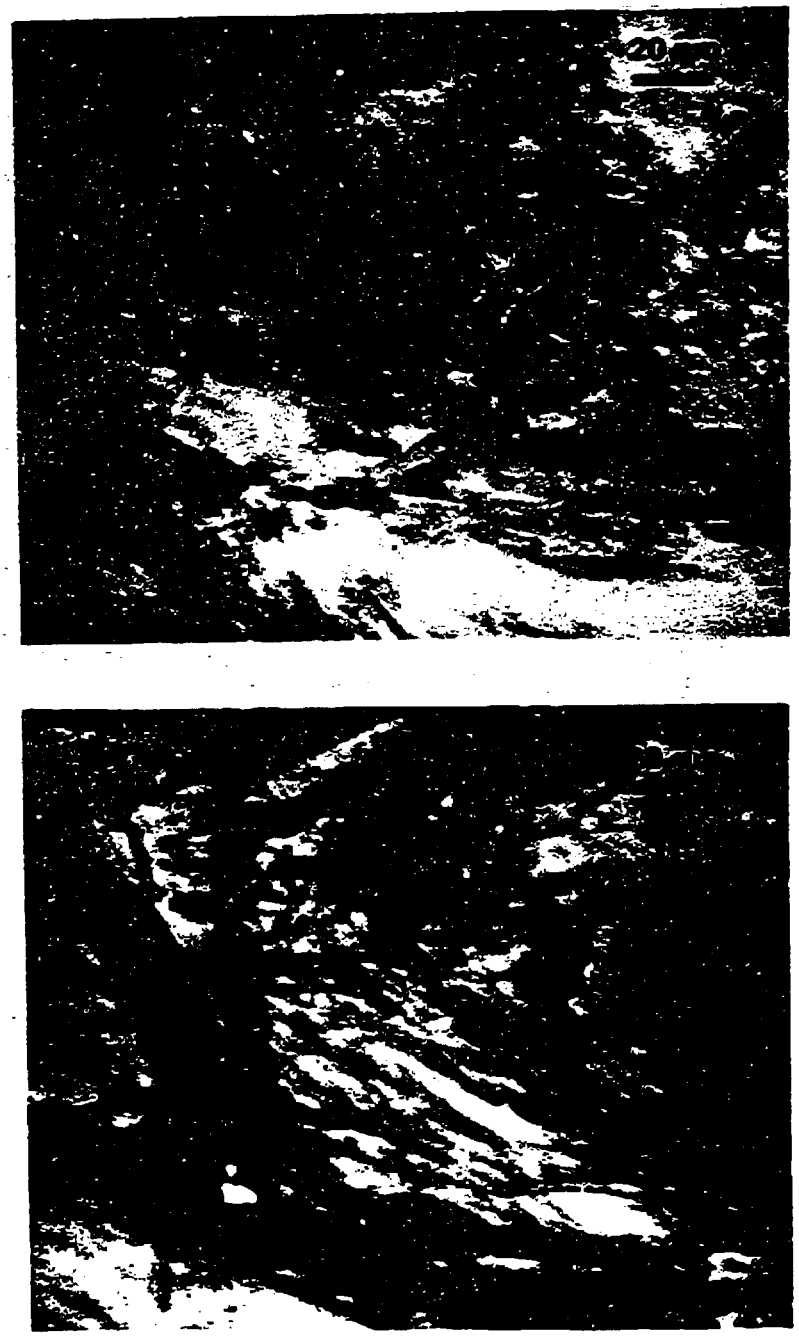


Figure 5-285. Modified Ruthenium Catalyst 4966-180:CO Conversion in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 0-825 Hours)

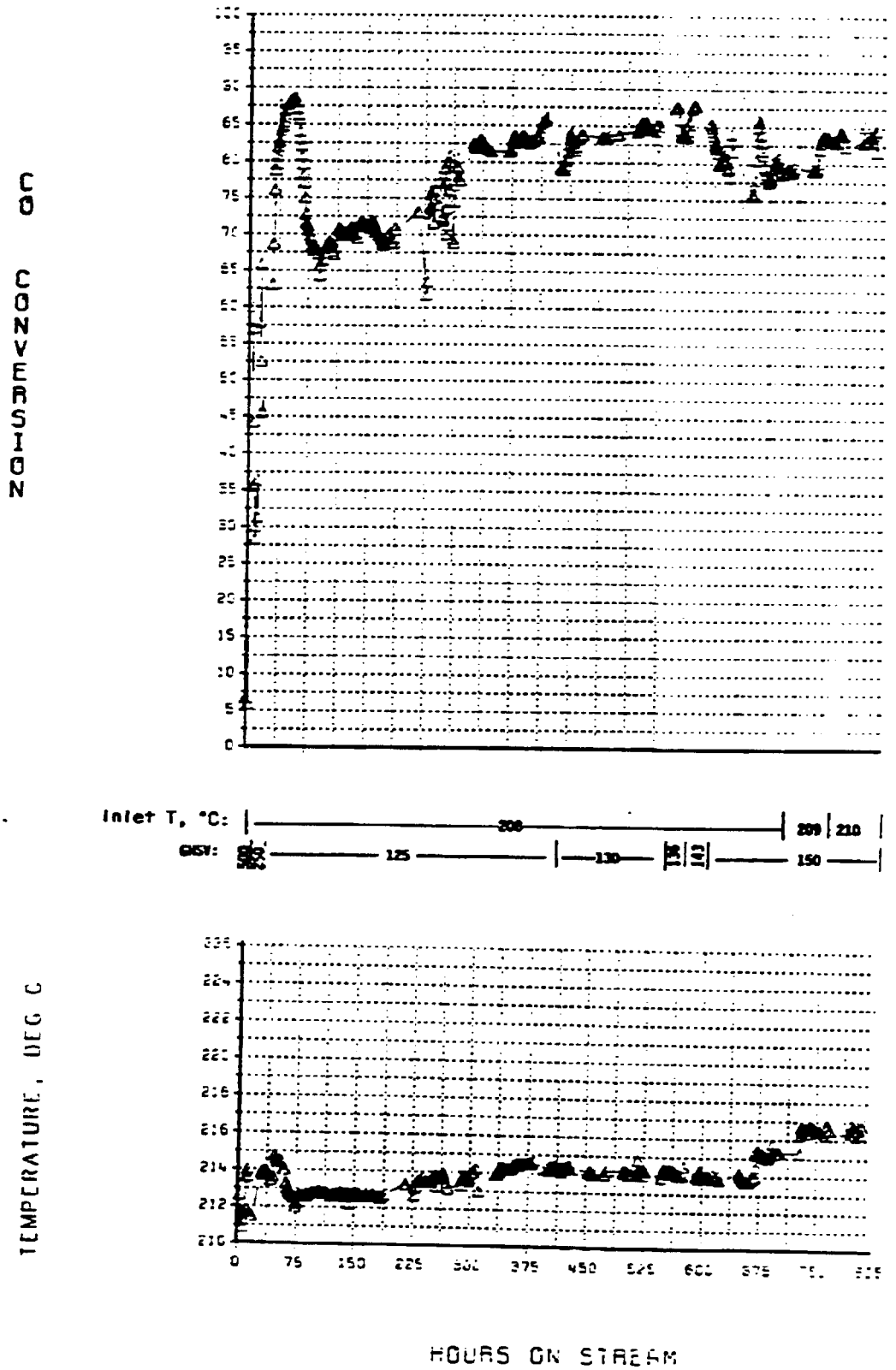


Figure 5-286. Modified Ruthenium Catalyst 4966-180: Water Gas Shift Activity in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 0-825 Hours)

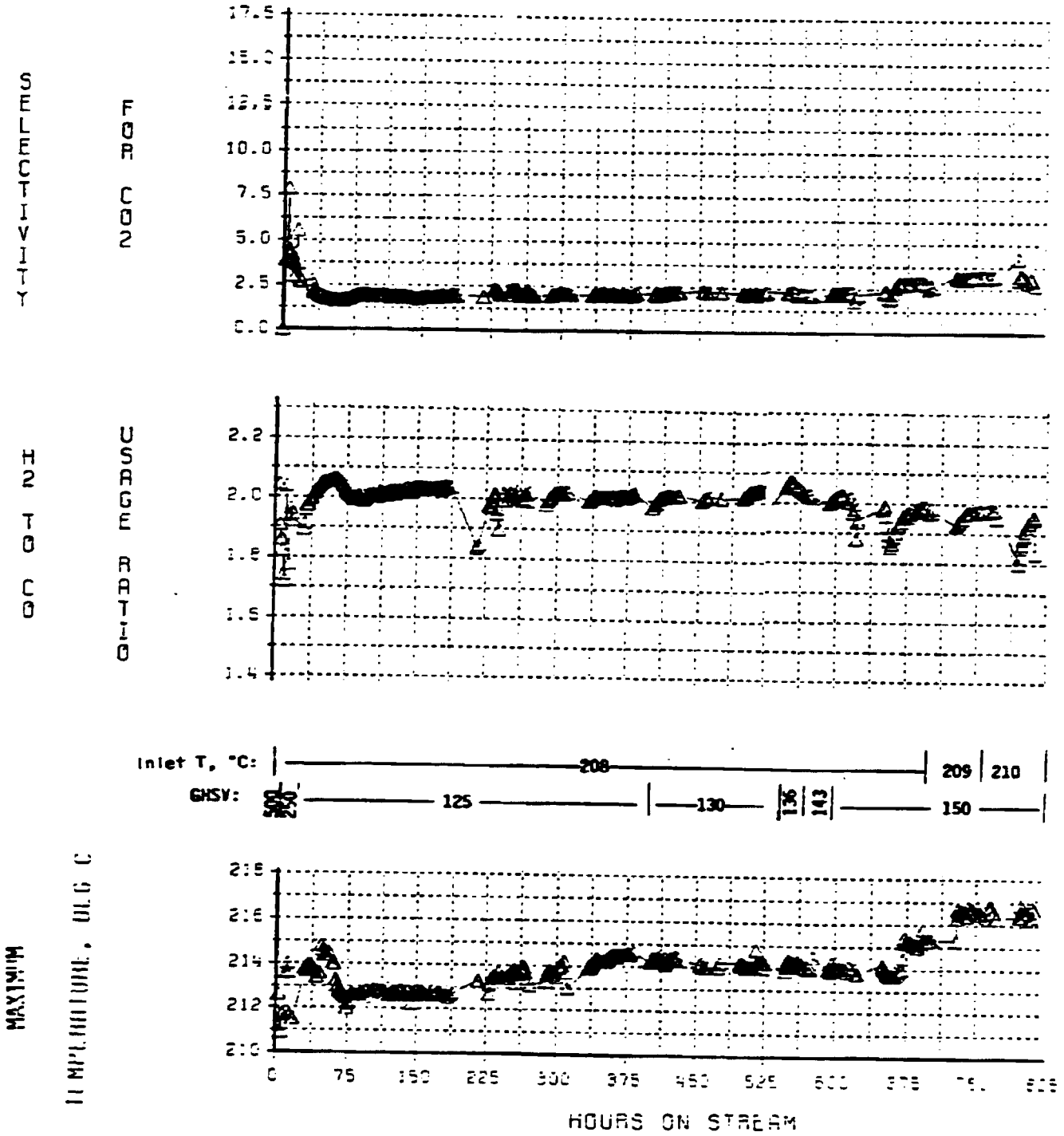


Figure 5-287. Anderson-Schulz-Flory-Type Distribution with Modified Ruthenium Catalyst 4966-180 at 32 Hours in Run 46 (Based on Effluent Gas Analysis with 1st On-Line GC)

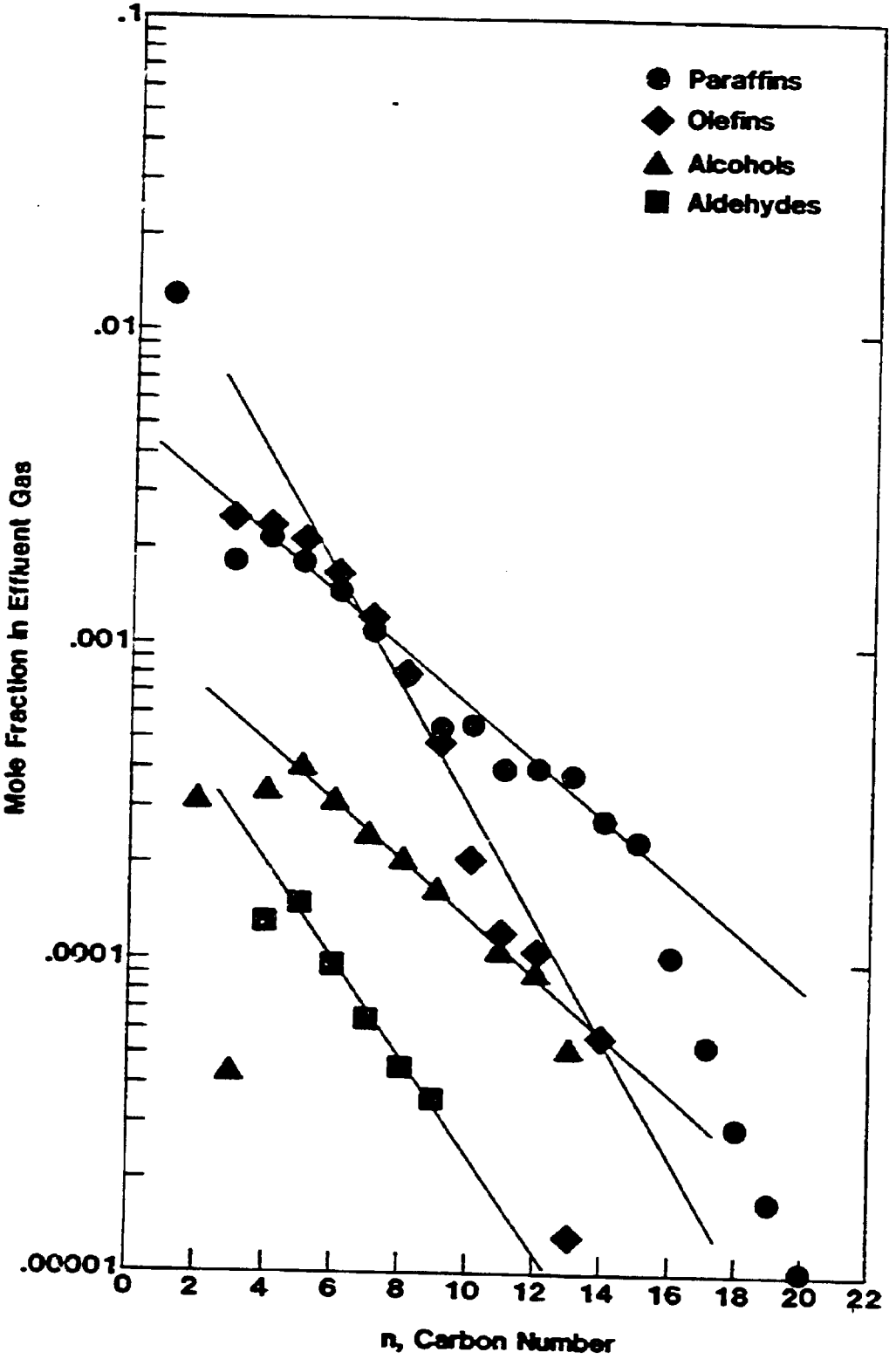


Figure 5-288. Anderson-Schulz-Flory-Type Distribution with Modified Ruthenium Catalyst 4966-180 at 604 Hours in Run 46 (Based on Effluent Gas Analysis with 1st On-Line GC)

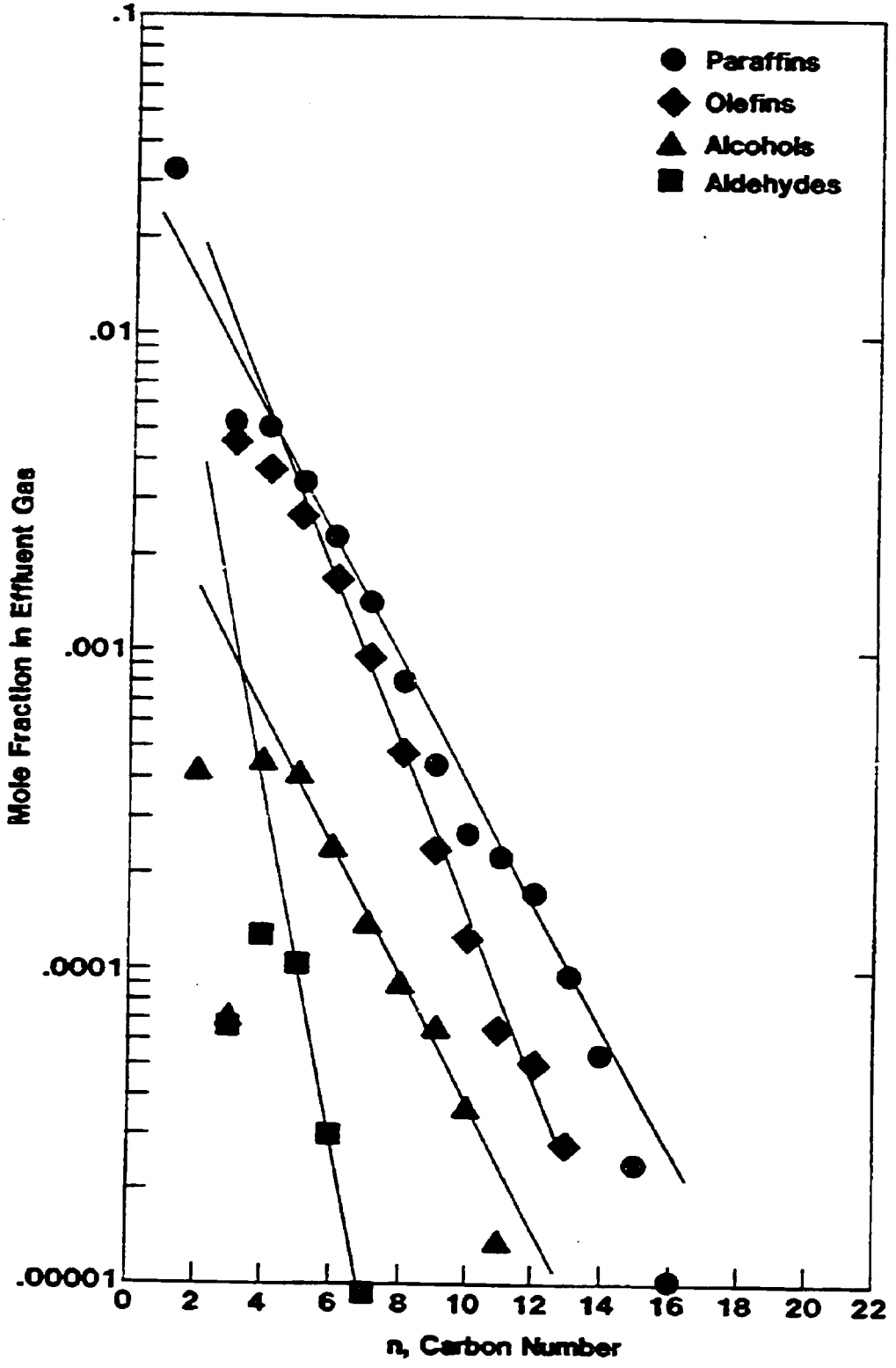
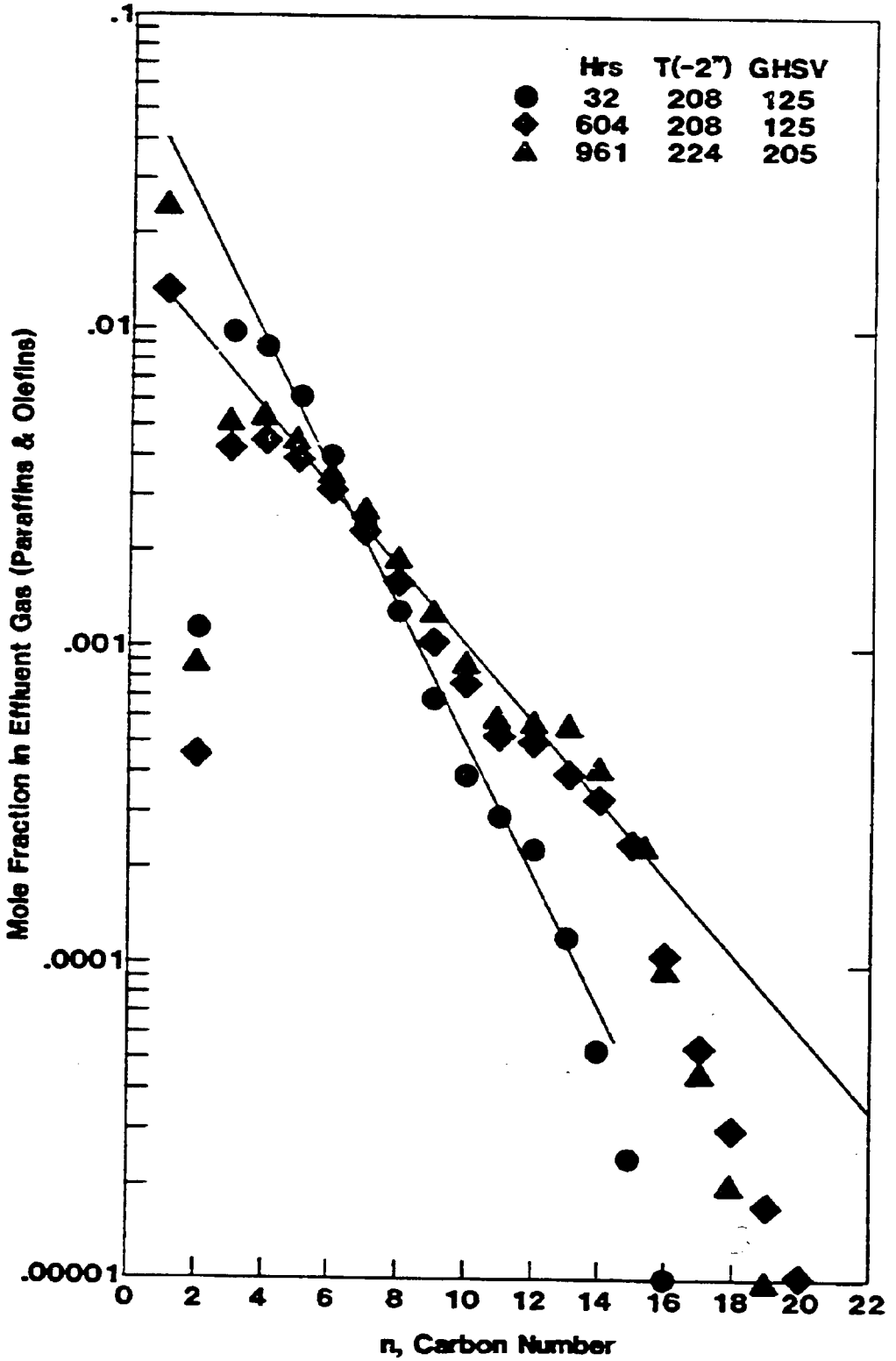


Figure 5-289. Anderson-Schulz-Flory-Type Distribution with Modified Ruthenium Catalyst 4966-180 at 80% Conversion in Run 46 (Based on Effluent Gas Analysis with 1st On-Line GC)



The change in catalytic selectivity during Run 46 is also illustrated in Figure 5-290 which summarizes the methane selectivities which decreased with time. After 500 hours, the methane selectivity was ~1.5%. The methane selectivity increase after 700 hours on stream is caused by 2°C temperature increase in the catalyst bed.

After 500 hours at 208°C inlet temperature and 80% conversion, there was essentially no C_2 formation ($\leq$0.2%), while the C_3 and C_4 selectivities were ~1.4 and ~2.0%, respectively, giving an overall C_1-C_4 selectivity no more than 5% (Figure 5-291). The H_2:CO usage and feed ratios were equal since there was essentially no water gas shift activity.

The olefin:paraffin ratio at carbon number of 3 increased during the first 400 hours, after which it remained constant (Figure 5-293).

Since the modified catalyst did not show a sign of deactivation at 208°C and 80% conversion after the initial activity loss during the first 20 hours, the severity of operation was increased during the second part of the test in order to determine the catalytic stability (Figure 5-295). Between 825 and 933 hours, the temperature and space velocity were increased in parallel from 210°C to 224°C and from 150 hr^{-1} to 205 hr^{-1}, respectively, in order to maintain about 80% conversion. During the temperature increase period some deactivation occurred. Therefore, the space velocity increase was less than expected, based on an apparent activation energy of about 25 kcal/mole. Deactivation possibly occurred because a conversion level of 80% was too severe a condition at the high temperature. The catalyst deactivated to 70% conversion during the following 200 hours, after which it maintained constant conversion for the next 400 hours.

Figure 5-290. Modified Ruthenium Catalyst 4966-180: C_1 and C_2 Selectivities in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 0-825 Hours)

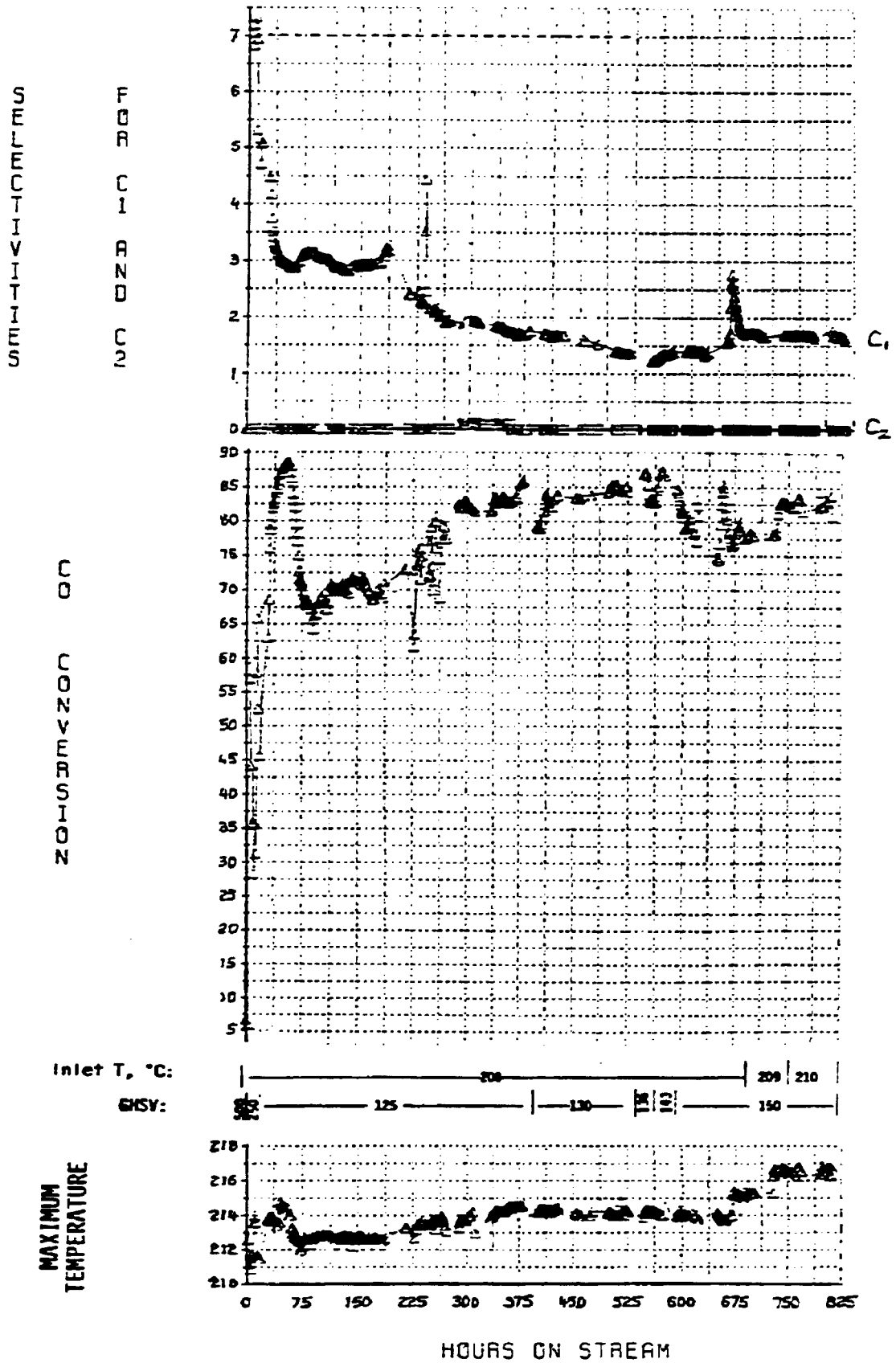


Figure 5-291. Modified Ruthenium Catalyst 4966-180 : C_3 and C_4 Selectivities in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 0-825 Hours)

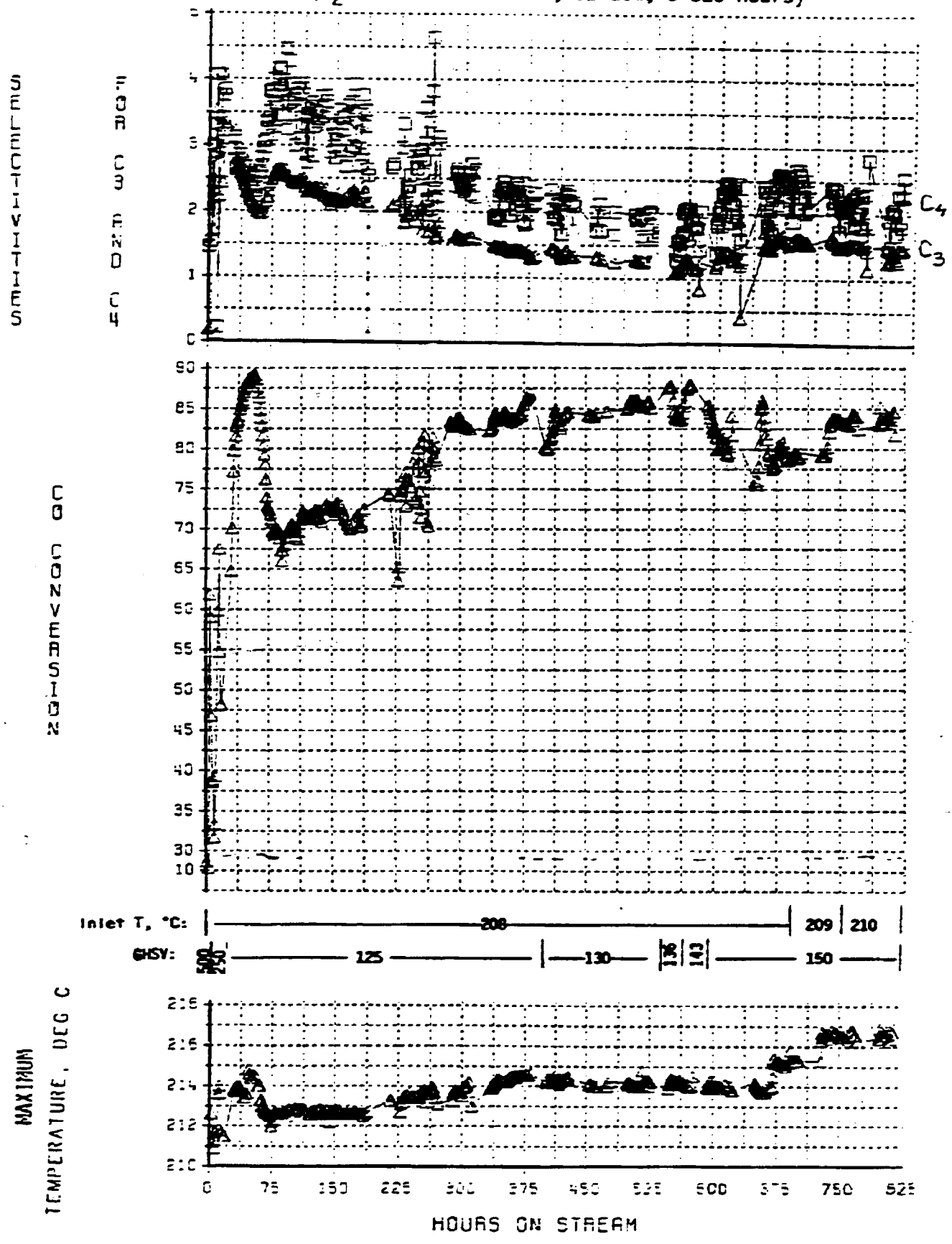


Figure 5-292. Modified Ruthenium Catalyst 4966-180: Propylene:Propane Ratios in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 0-825 Hours)

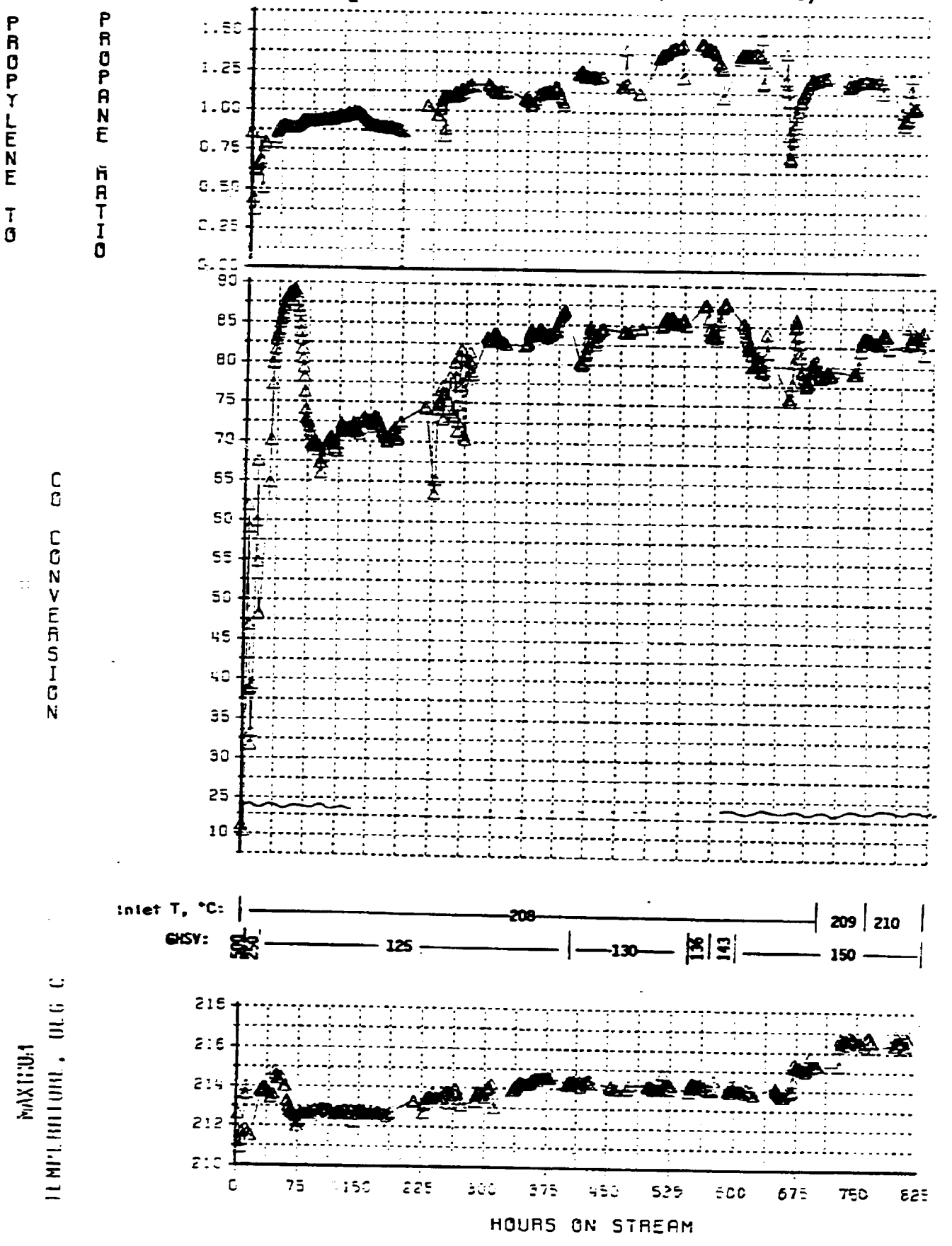


Table 5-49: Product Distributions in Run 46 (0-814 Hours)

HYDROCARBON DISTRIBUTION	
C1	2.969
C2 - C4	6.618
C5 - C11	20.044
C12 - C18	24.445
C19 - C25	15.446
C26 PLUS	30.478
C1 - C44	90.183
C45 PLUS	9.817

RECOVERIES	
OVERALL	83.274
CARBON	86.425
HYDROGEN	81.023
ARGON	97.454
CORRECTED RECOVERIES	
OVERALL	85.449
CARBON	88.683
HYDROGEN	83.140

GAS ANALYSIS, WT%	
HYDROGEN	3.0393
CARBON MONOXIDE	22.4535
CARBON DIOXIDE	3.2020
METHANE	1.0350
ETHANE	0.0038
ETHYLENE	0.0000
PROPANE	0.3457
PROPYLENE	0.3495
BUTANE	0.4837
BUTENE	0.5141
AQUEOUS ANALYSIS, WT%	
WATER	55.9101
ALCOHOLS	
C1	0.0317
C2	0.0759
C3	0.0106
C4	0.0768
C5	0.0954
C6	0.0640
C7	0.0421
C8	0.0269
C9	0.0152
C10	0.0084
ALDEHYDES	
C1	0.0000
C2	0.0000
C3	0.0052
C4	0.0145
C5	0.0251
C6	0.0194
C7	0.0118
C8	0.0084
C9	0.0051
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 5-50: Hydrocarbon Distributions in Run 46 (0-814 Hours)

C1	2.9691	C51	0.3787	C101	0.0263	C151	0.0020	C201	0.0005
C2	0.0109	C52	0.3589	C102	0.0256	C152	0.0020	C202	0.0005
C3	2.0340	C53	0.3404	C103	0.0256	C153	0.0020	C203	0.0005
C4	4.6733	C54	0.3228	C104	0.0248	C154	0.0020	C204	0.0005
C5	4.0965	C55	0.3055	C105	0.0241	C155	0.0020	C205	0.0005
C6	1.8163	C56	0.2898	C106	0.0233	C156	0.0019	C206	0.0005
C7	2.0162	C57	0.2737	C107	0.0225	C157	0.0019	C207	0.0005
C8	2.4059	C58	0.2576	C108	0.0216	C158	0.0019	C208	0.0005
C9	2.8244	C59	0.2412	C109	0.0208	C159	0.0018	C209	0.0005
C10	3.2907	C60	0.2271	C110	0.0200	C160	0.0018	C210	0.0005
C11	3.5935	C61	0.2102	C111	0.0177	C161	0.0017	C211	0.0005
C12	3.7819	C62	0.1936	C112	0.0170	C162	0.0017	C212	0.0005
C13	3.8042	C63	0.1777	C113	0.0162	C163	0.0014	C213	0.0005
C14	3.7404	C64	0.1624	C114	0.0154	C164	0.0014	C214	0.0005
C15	3.5988	C65	0.1488	C115	0.0146	C165	0.0014	C215	0.0005
C16	3.3965	C66	0.1369	C116	0.0139	C166	0.0013	C216	0.0005
C17	3.1799	C67	0.1272	C117	0.0131	C167	0.0013	C217	0.0005
C18	2.9437	C68	0.1151	C118	0.0124	C168	0.0012	C218	0.0005
C19	2.7078	C69	0.1097	C119	0.0117	C169	0.0011	C219	0.0005
C20	2.4994	C70	0.1060	C120	0.0109	C170	0.0011	C220	0.0005
C21	2.3162	C71	0.1034	C121	0.0103	C171	0.0010	C221	0.0005
C22	2.1692	C72	0.1017	C122	0.0097	C172	0.0010	C222	0.0005
C23	2.0314	C73	0.1008	C123	0.0092	C173	0.0009	C223	0.0005
C24	1.9083	C74	0.0999	C124	0.0087	C174	0.0009	C224	0.0005
C25	1.8138	C75	0.0989	C125	0.0082	C175	0.0008	C225	0.0005
C26	1.7251	C76	0.0976	C126	0.0078	C176	0.0008	C226	0.0005
C27	1.6229	C77	0.0999	C127	0.0073	C177	0.0007	C227	0.0005
C28	1.5591	C78	0.0972	C128	0.0070	C178	0.0007	C228	0.0005
C29	1.4661	C79	0.0939	C129	0.0066	C179	0.0007	C229	0.0005
C30	1.3830	C80	0.0900	C130	0.0063	C180	0.0006	C230	0.0000
C31	1.3226	C81	0.0856	C131	0.0060	C181	0.0006	C231	0.0000
C32	1.2509	C82	0.0811	C132	0.0057	C182	0.0006	C232	0.0000
C33	1.1558	C83	0.0762	C133	0.0054	C183	0.0005	C233	0.0000
C34	1.0931	C84	0.0713	C134	0.0052	C184	0.0005	C234	0.0000
C35	1.0544	C85	0.0663	C135	0.0050	C185	0.0005	C235	0.0000
C36	0.9879	C86	0.0606	C136	0.0048	C186	0.0005	C236	0.0000
C37	0.9248	C87	0.0563	C137	0.0046	C187	0.0005	C237	0.0000
C38	0.8653	C88	0.0523	C138	0.0045	C188	0.0005	C238	0.0000
C39	0.8369	C89	0.0464	C139	0.0044	C189	0.0005	C239	0.0000
C40	0.7701	C90	0.0433	C140	0.0029	C190	0.0005	C240	0.0000
C41	0.7097	C91	0.0405	C141	0.0028	C191	0.0005	C241	0.0000
C42	0.6858	C92	0.0381	C142	0.0027	C192	0.0005	C242	0.0000
C43	0.6323	C93	0.0360	C143	0.0027	C193	0.0005	C243	0.0000
C44	0.6146	C94	0.0342	C144	0.0027	C194	0.0005	C244	0.0000
C45	0.5373	C95	0.0326	C145	0.0026	C195	0.0005	C245	0.0000
C46	0.5052	C96	0.0312	C146	0.0026	C196	0.0005	C246	0.0000
C47	0.4743	C97	0.0300	C147	0.0021	C197	0.0005	C247	0.0000
C48	0.4472	C98	0.0289	C148	0.0021	C198	0.0005	C248	0.0000
C49	0.4224	C99	0.0280	C149	0.0021	C199	0.0005	C249	0.0000
C50	0.4000	C100	0.0271	C150	0.0021	C200	0.0005	C250	0.0000

Figure 5-293. Anderson-Schulz-Flory Distribution with Modified Ruthenium Catalyst 4966-180 in Run 46 (C_1-C_{44}; 0-814 Hours)

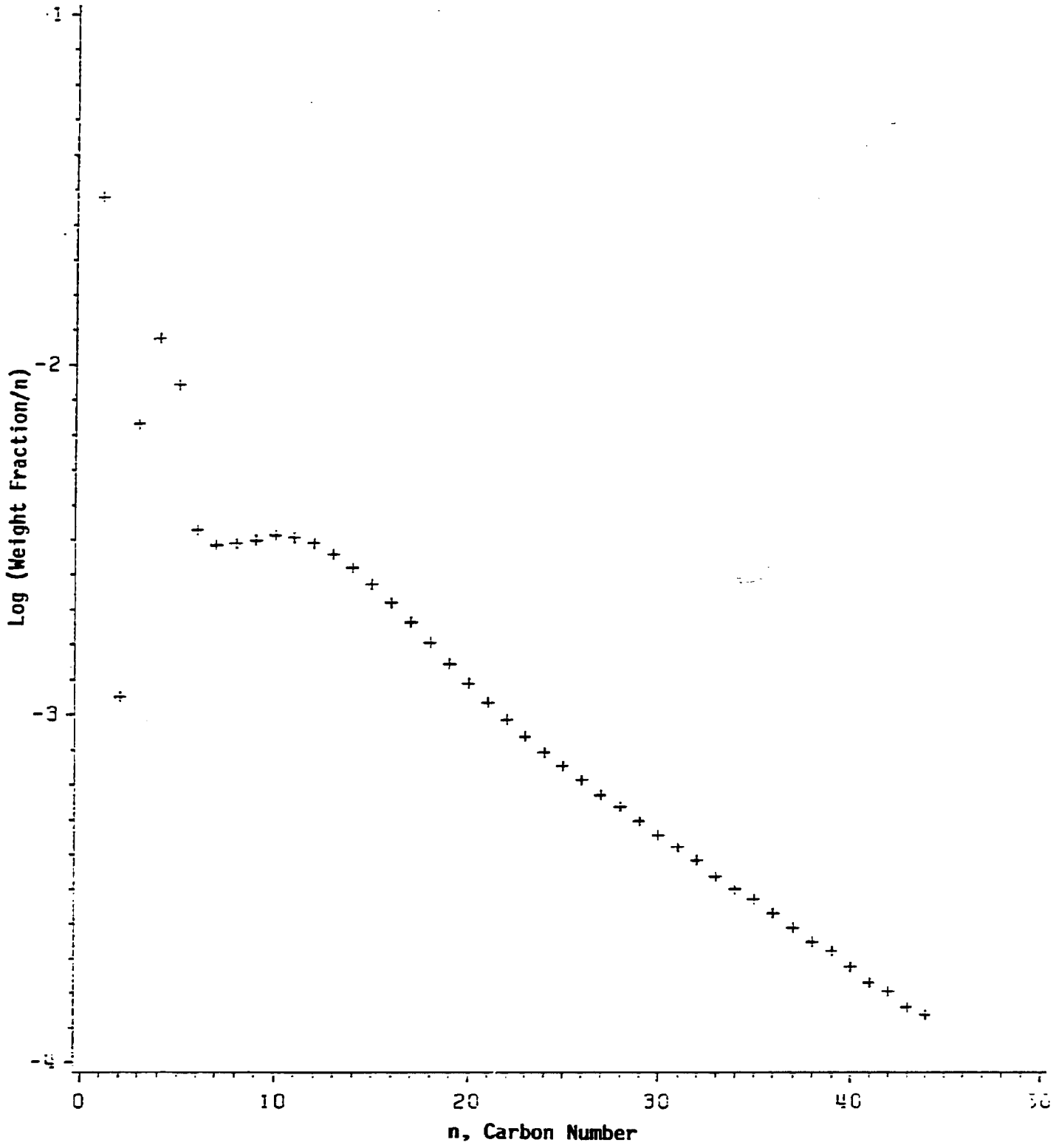


Figure 5-294. Anderson-Schulz-Flory Distribution with Modified Ruthenium Catalyst 4966-180 in Run 46 (C_1-C_{250}; 0-814 Hours)

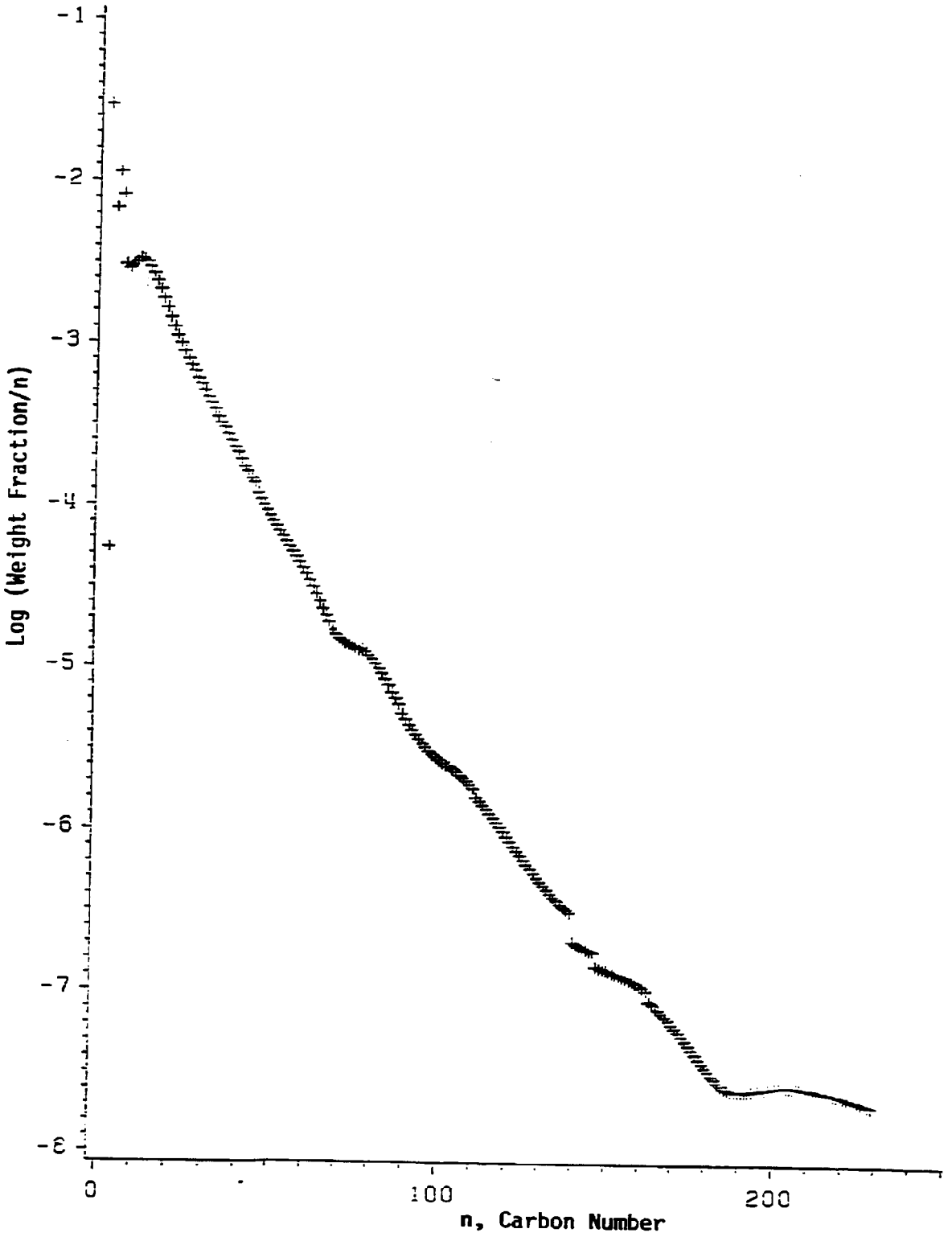
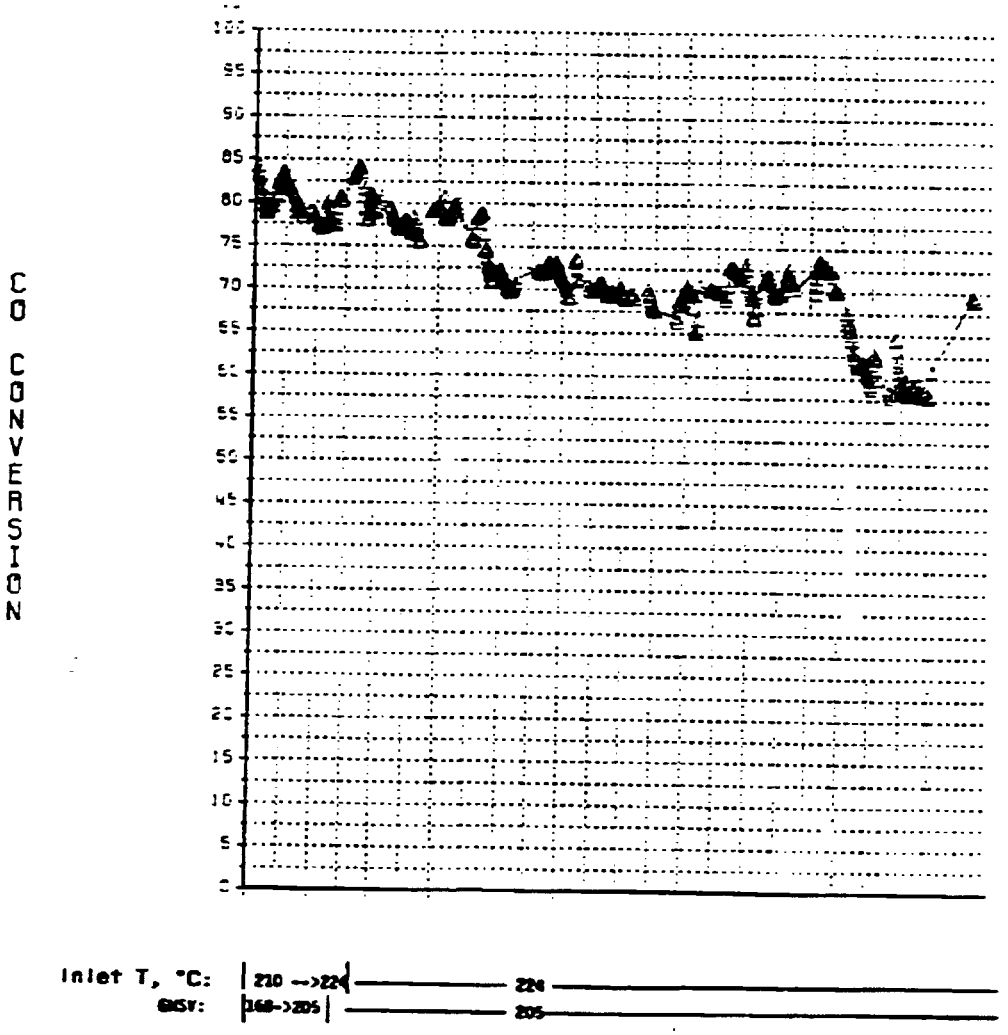


Figure 5-295. Modified Ruthenium Catalyst 4966-180:CO Conversion in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 825-1700 Hours)



The conversion decreased to 58-60% between 1542 and 1574 hours and showed no futher activity loss until 1618 hours. Between 1650 and 1700 hours the space velocity was lowered from 205 hr^{-1} to 182 hr^{-1}, and the CO conversion increased to 69%, after which the run was shut down. From the activity loss between 933 hours on stream to 1542 hours, a deactivation rate of about 0.016%/hour can be calculated at 224°C.

There are not presently enough data for calculating the life of the modified-ruthenium catalyst. Since there was no apparent deactivation at 208°C, half of the deactivation rate at 224°C was roughly estimated to be an upper bound to the average deactivation rate between 208°C and 224°C. A commercial run with beginning and end of run temperatures of 208°C and 224°C, respectively, may then result in about 1 year catalyst life at 70-80% CO conversion, given an apparent activation energy of about 25 kcal/mole if the pilot performance of the granular ruthenium catalyst is achieved commercially.

The average light ends selectivity between 208°C and 224°C would then be an upper bound to the yearly average light ends selectivity. The selectivities at 80% CO conversion and 208°C were described above. The selectivities at 224°C are illustrated in Figures 5-296 through 5-299. The increases in light ends selectivities between 825 hours and about 1050 hours are mostly due to the temperature increase from 210°C and 224°C between 835 and 933 hours on stream. Further increases in light ends selectivities later in the run are mostly due to decreases in the conversion level to below 80%. The selectivities at about 1050 hours are then taken to represent the 224°C performance. They are: 3.2% C_1, $\leq$0.2% C_2, 2.1% C_3 and 2.9% C_4. The upper bound to the yearly average selectivities are then estimated to be: 2.3% C_1, $\leq$0.2% C_2, 1.7% C_3 and 2.4% C_4.

Figure 5-296. Modified Ruthenium Catalyst 4966-180: Water Gas Shift Activity in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 825-1650 Hours)

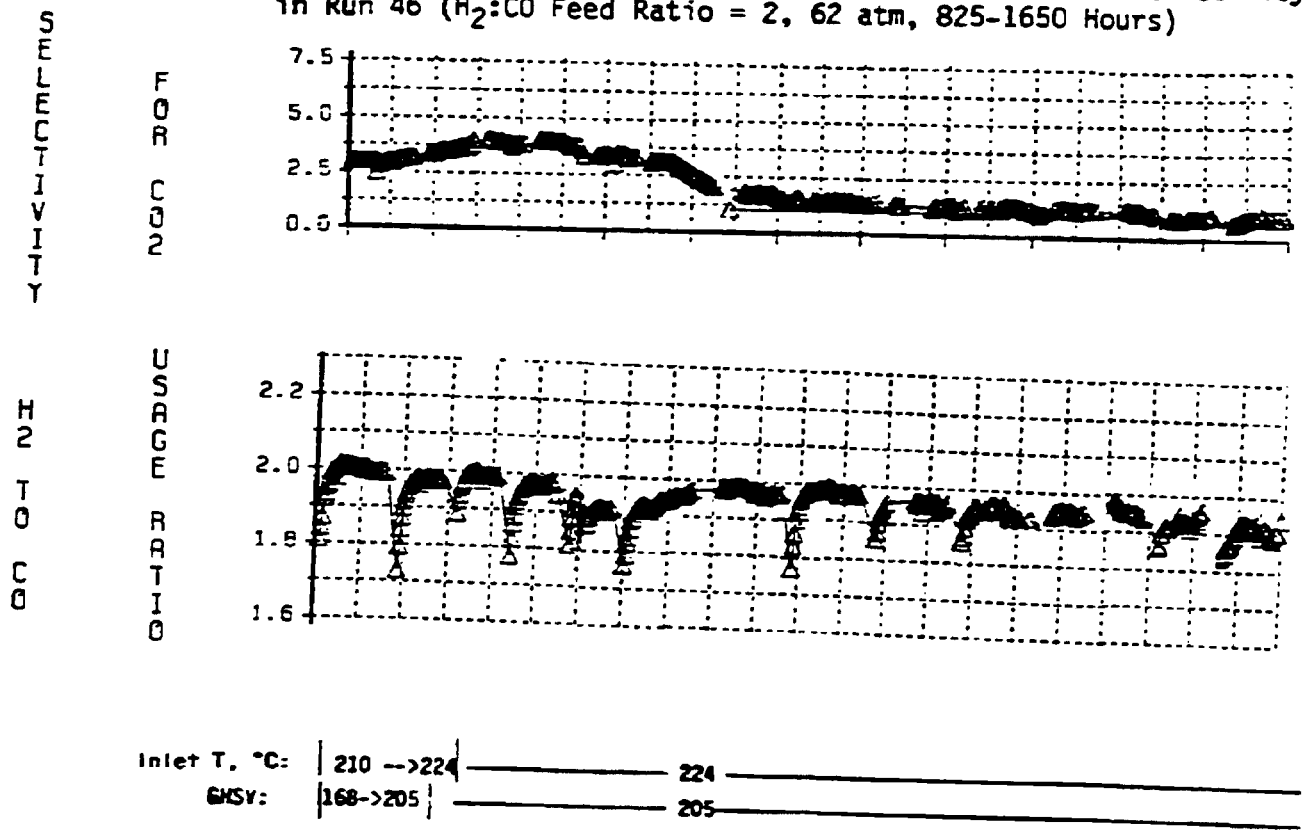


Figure 5-297. Modified Ruthenium Catalyst 4966-180 : C_1 and C_2 Selectivities in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 825-1650 Hours)

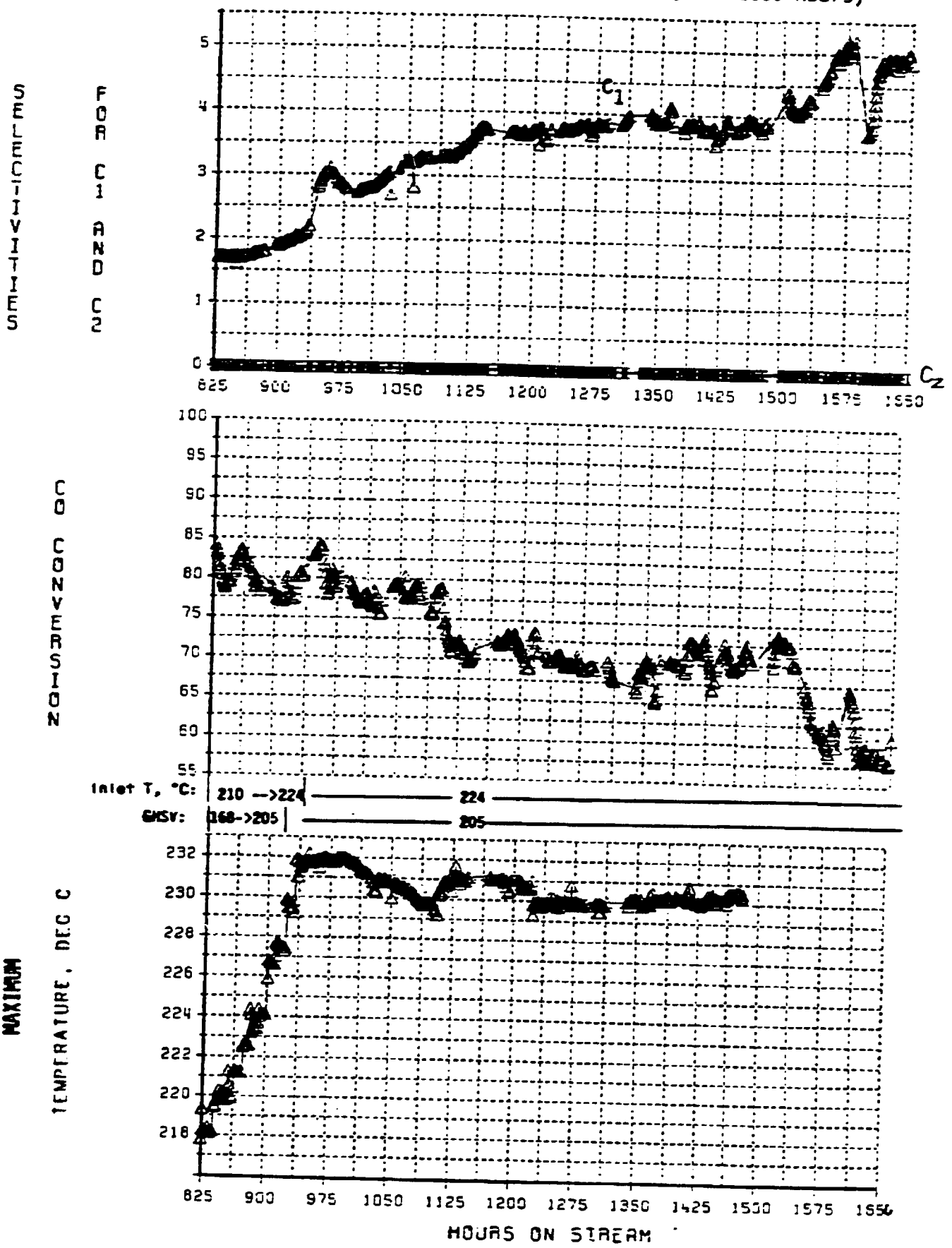


Figure 5-298. Modified Ruthenium Catalyst 4966-180 : C_3 and C_4 Selectivities in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 825-1650 Hours)

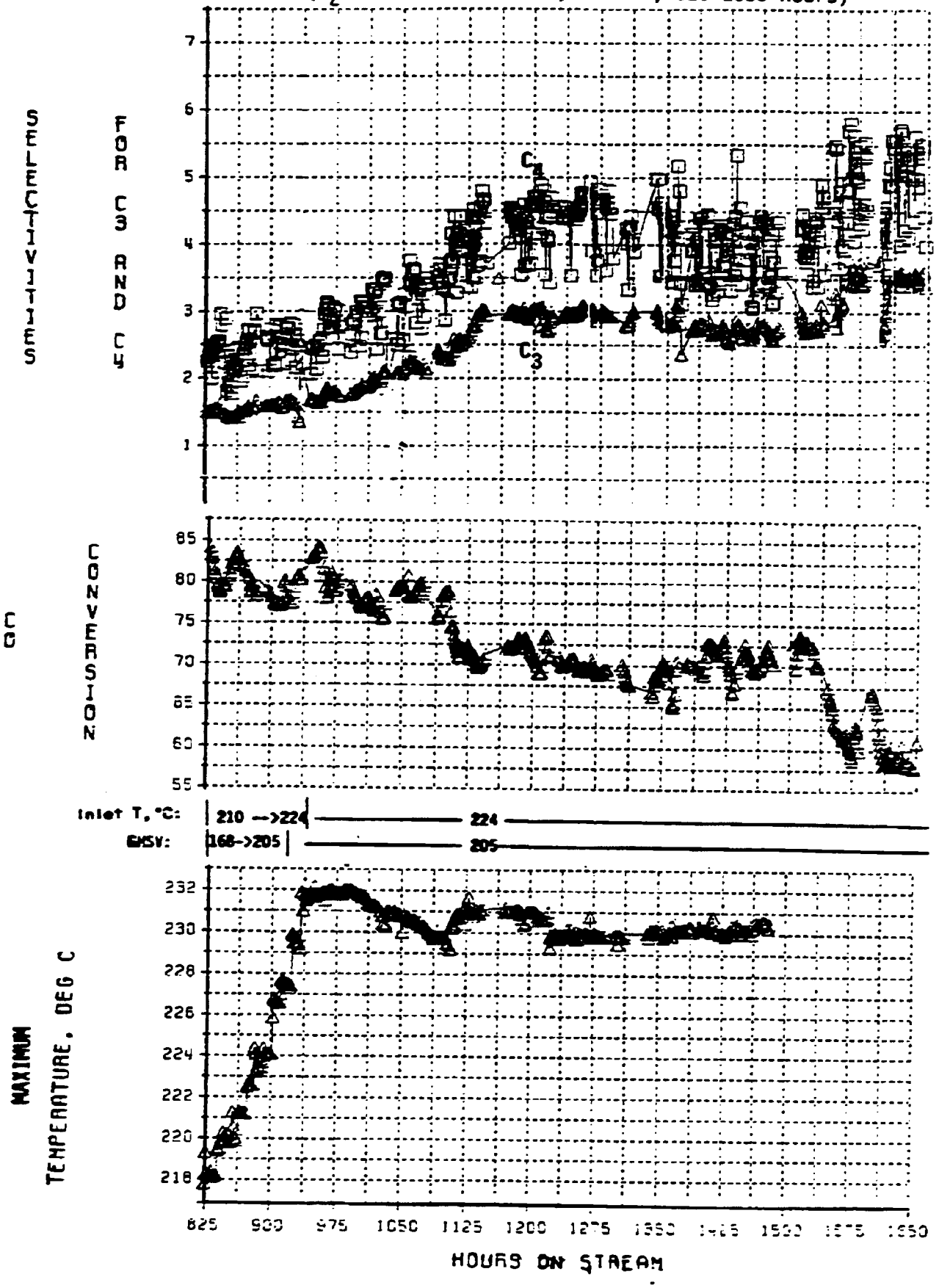


Figure 5-299. Modified Ruthenium Catalyst 4966-180: Propylene:Propane Ratios in Run 46 (H_2:CO Feed Ratio = 2, 62 atm, 825-1650 Hours)

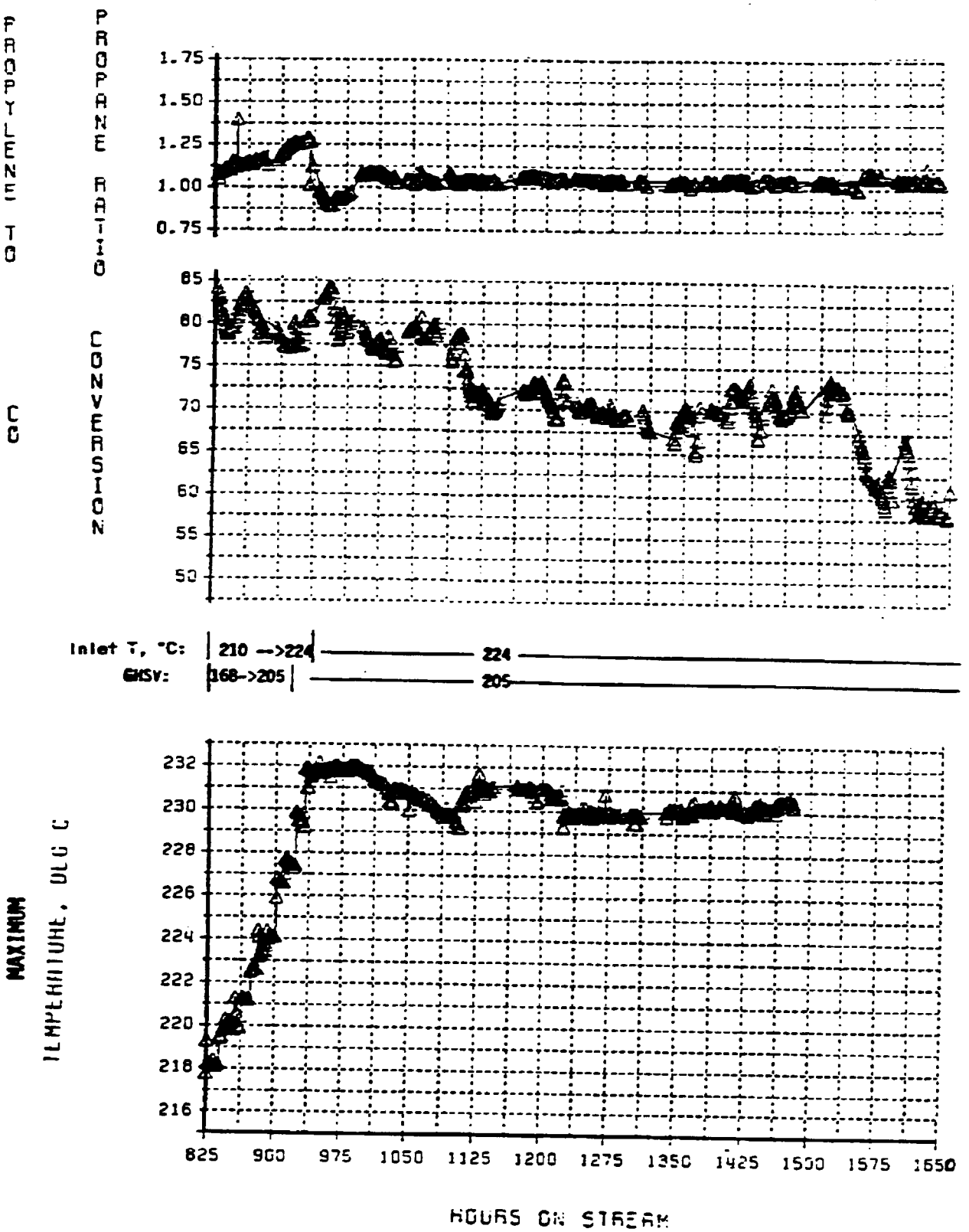


Table 5-51: Product Distributions in Run 46 (815-1700 Hours)

HYDROCARBON DISTRIBUTION	
C1	4.416
C2 - C4	8.445
C5 - C11	22.344
C12 - C18	21.746
C19 - C25	15.057
C26 PLUS	25.992
C1 - C44	90.983
C45 PLUS	9.017

RECOVERIES	
OVERALL	87.627
CARBON	84.936
HYDROGEN	90.729
ARGON	89.951
CORRECTED RECOVERIES	
OVERALL	97.417
CARBON	94.425
HYDROGEN	100.866

GAS ANALYSIS, WT%	
HYDROGEN	3.8515
CARBON MONOXIDE	25.1939
CARBON DIOXIDE	2.2306
METHANE	1.2994
ETHANE	0.0000
ETHYLENE	0.0000
PROPANE	0.4197
PROPYLENE	0.4186
BUTANE	0.5786
BUTENE	0.6336
AQUEOUS ANALYSIS, WT%	
WATER	38.6600
ALCOHOLS	
C1	0.0578
C2	0.1186
C3	0.0172
C4	0.0685
C5	0.1055
C6	0.0755
C7	0.0491
C8	0.0310
C9	0.0181
C10	0.0103
ALDEHYDES	
C1	0.0000
C2	0.0000
C3	0.0122
C4	0.0149
C5	0.0190
C6	0.0103
C7	0.0051
C8	0.0026
C9	0.0026
C10	0.0026
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 5-52: Hydrocarbon Distributions in Run 46 (815-1700 Hours)

C1	4.4164	C51	0.3321	C101	0.0266	C151	0.0017
C2	0.0000	C52	0.3149	C102	0.0253	C152	0.0016
C3	2.9265	C53	0.2983	C103	0.0241	C153	0.0016
C4	5.5187	C54	0.2825	C104	0.0229	C154	0.0015
C5	4.8103	C55	0.2676	C105	0.0219	C155	0.0015
C6	3.2219	C56	0.2536	C106	0.0209	C156	0.0014
C7	2.8627	C57	0.2405	C107	0.0200	C157	0.0013
C8	2.6869	C58	0.2280	C108	0.0192	C158	0.0013
C9	2.6285	C59	0.2165	C109	0.0184	C159	0.0012
C10	2.8911	C60	0.2058	C110	0.0177	C160	0.0012
C11	3.2423	C61	0.1955	C111	0.0170	C161	0.0012
C12	3.5114	C62	0.1858	C112	0.0164	C162	0.0011
C13	3.6897	C63	0.1769	C113	0.0158	C163	0.0011
C14	3.6316	C64	0.1678	C114	0.0153	C164	0.0010
C15	3.5013	C65	0.1591	C115	0.0147	C165	0.0010
C16	3.3353	C66	0.1507	C116	0.0112	C166	0.0010
C17	3.1291	C67	0.1428	C117	0.0110	C167	0.0009
C18	2.9480	C68	0.1354	C118	0.0079	C168	0.0009
C19	2.7387	C69	0.1284	C119	0.0076	C169	0.0009
C20	2.4872	C70	0.1218	C120	0.0074	C170	0.0008
C21	2.3071	C71	0.1156	C121	0.0071	C171	0.0008
C22	2.1283	C72	0.1100	C122	0.0069	C172	0.0008
C23	1.9652	C73	0.1048	C123	0.0066	C173	0.0008
C24	1.7839	C74	0.1000	C124	0.0064	C174	0.0007
C25	1.6464	C75	0.0956	C125	0.0061	C175	0.0007
C26	1.5376	C76	0.0914	C126	0.0059	C176	0.0007
C27	1.4136	C77	0.0875	C127	0.0057	C177	0.0007
C28	1.3187	C78	0.0837	C128	0.0055	C178	0.0007
C29	1.2207	C79	0.0800	C129	0.0053	C179	0.0006
C30	1.1524	C80	0.0765	C130	0.0051	C180	0.0006
C31	1.0655	C81	0.0731	C131	0.0049	C181	0.0006
C32	0.9953	C82	0.0698	C132	0.0047	C182	0.0006
C33	0.9255	C83	0.0665	C133	0.0045	C183	0.0006
C34	0.8825	C84	0.0634	C134	0.0044	C184	0.0005
C35	0.8277	C85	0.0604	C135	0.0042	C185	0.0005
C36	0.7874	C86	0.0574	C136	0.0041	C186	0.0005
C37	0.7286	C87	0.0546	C137	0.0039	C187	0.0000
C38	0.7021	C88	0.0519	C138	0.0038	C188	0.0000
C39	0.6588	C89	0.0494	C139	0.0037	C189	0.0000
C40	0.6188	C90	0.0469	C140	0.0028	C190	0.0000
C41	0.5840	C91	0.0446	C141	0.0028	C191	0.0000
C42	0.5490	C92	0.0424	C142	0.0026	C192	0.0000
C43	0.5319	C93	0.0402	C143	0.0024	C193	0.0000
C44	0.4942	C94	0.0382	C144	0.0023	C194	0.0000
C45	0.4603	C95	0.0363	C145	0.0022	C195	0.0000
C46	0.4351	C96	0.0344	C146	0.0021	C196	0.0000
C47	0.4123	C97	0.0327	C147	0.0020	C197	0.0000
C48	0.3904	C98	0.0310	C148	0.0019	C198	0.0000
C49	0.3699	C99	0.0295	C149	0.0019	C199	0.0000
C50	0.3501	C100	0.0280	C150	0.0018	C200	0.0000

Figure 5-300. Anderson-Schulz-Flory Distribution with Modified Ruthenium Catalyst 4966-180 in Run 46 (C_1-C_{44}; 814-1700 Hours)

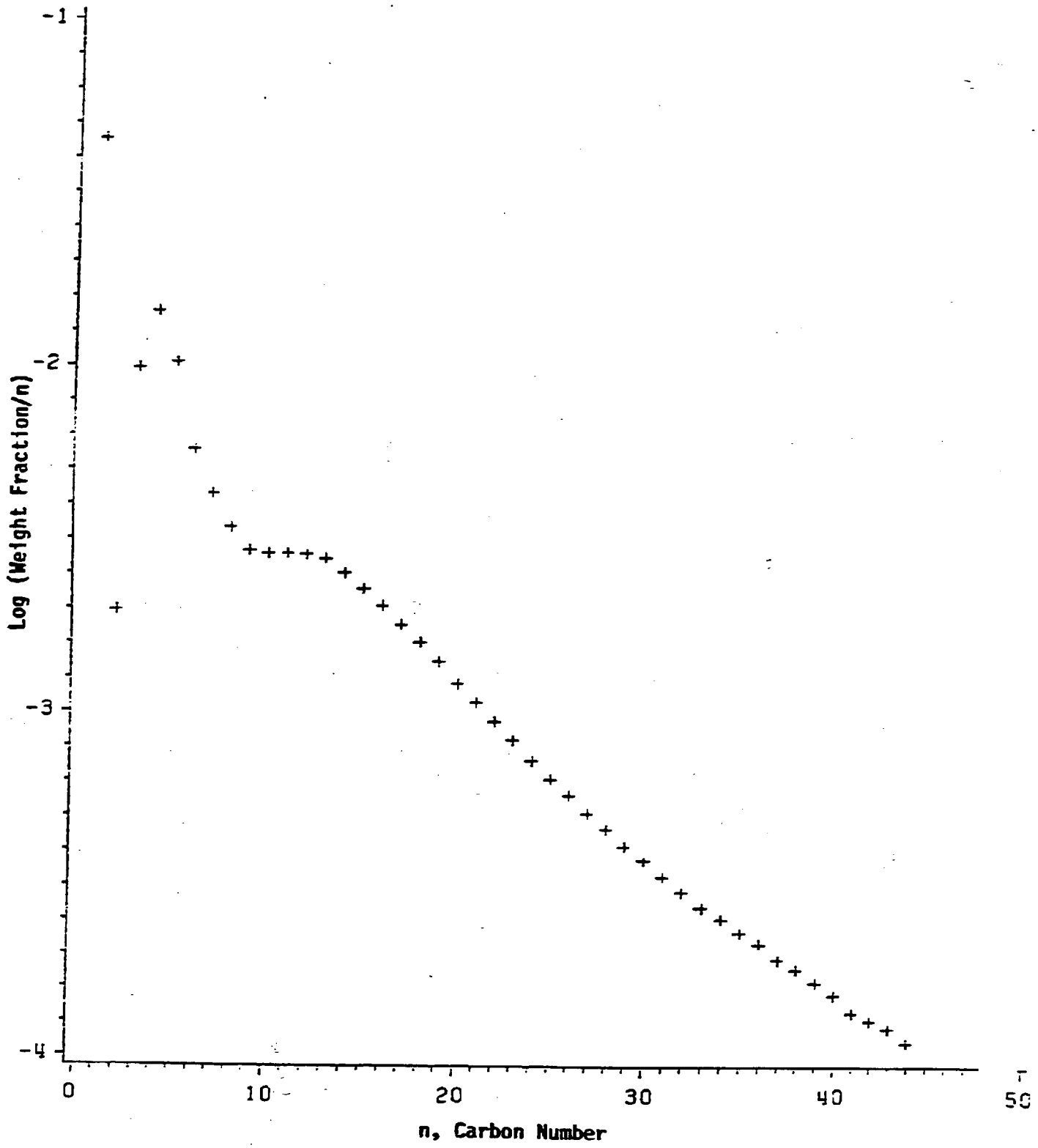
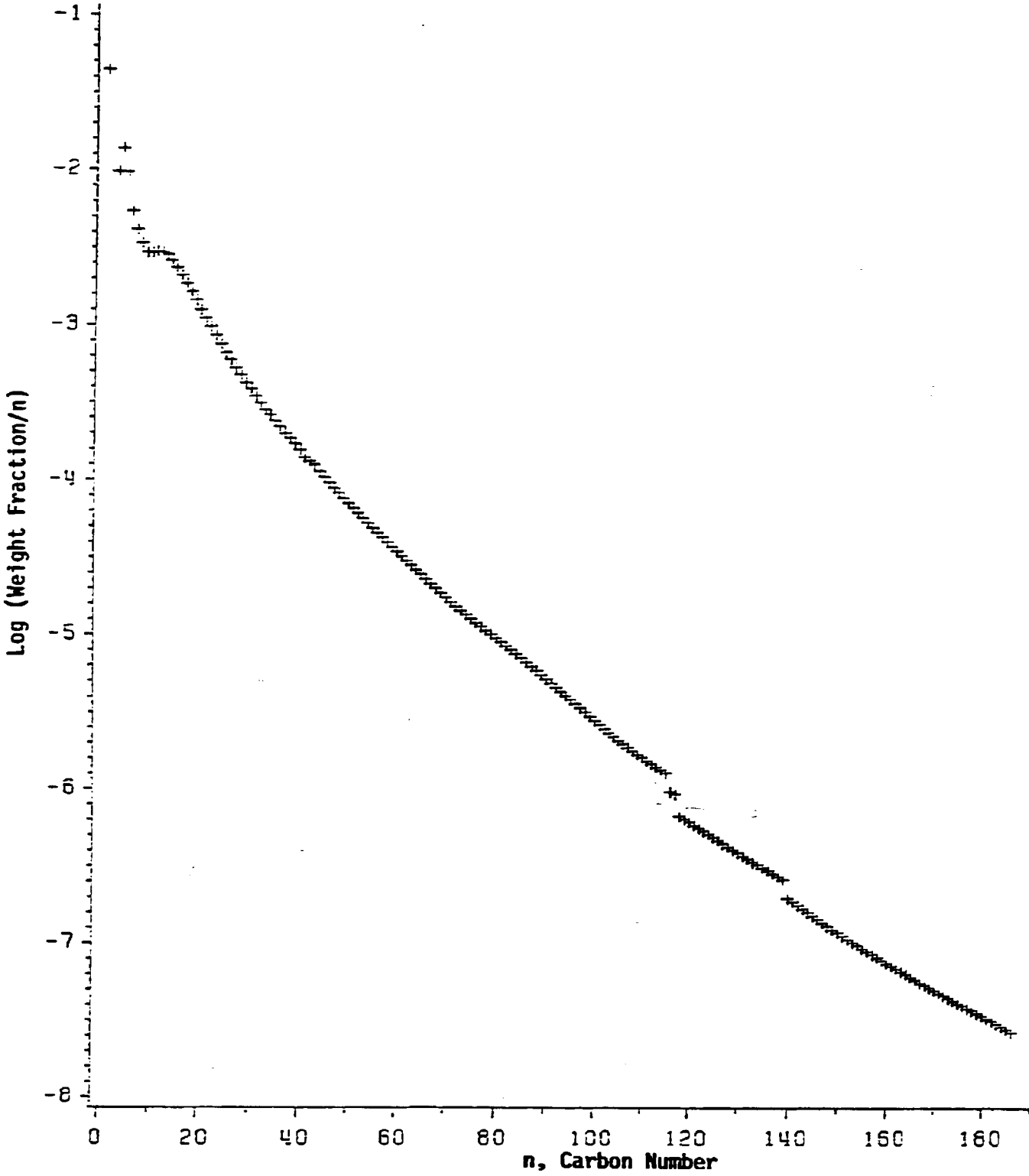


Figure 5-301 Anderson-Schulz-Flory Distribution with Modified Ruthenium Catalyst 4966-180 in Run 46 (C_1-C_{250}; 814-1700 Hours)



During Run 46, the products were collected by a procedure similar to t... used in Run 47. The wax extracted from the used catalyst at the end of 1700 hours was included in the analysis of products from the first 814 hours. A total of 20 samples were analyzed from the 71-day-run.

Typically, 80% of the products in the cooled receivers were hydrocarbons (mostly C_5–C_{15}), while the rest were alcohols and aldehydes. The products from the heated receiver had a wider carbon number range with much higher molecular weight. These products were analyzed by a chromatographic boiling point method. Carbon numbers were assigned based on the boiling point of n-paraffins. Accordingly, the oxygenates were lumped together with the n-paraffins with typically two lower carbon numbers.

The products obtained during the first 814 hours and between 814 and 1701 hours have been summarized in Tables 5-49, 5-50, 5-51 and 5-52. The Anderson-Schulz-Flory distributions are in Figures 5-293, 5-294, 5-300 and 5-301.

The Anderson-Schulz-Flory product distribution exhibited a maximum at a carbon number of about 15. This maximum was reproducible in three other tests conducted with ruthenium catalysts at 62 atm, but was not observed at 35 atm tests. This maximum occurs partly because, in contrast to C_5-C_{10} data, for most of the C_{10}+ products the carbon numbers were calculated based on the boiling point of the n-paraffins from the chromatographic distillation measurements. However, the distillate range contained about 20% linear pirmary alcohols + linear aldehydes which were lumped together during chromatography with the n-paraffin having -2 higher carbon numbers. This maximum in the Anderson-Schulz-Flory distribution becomes less significant when the oxygenates are plotted at their correct carbon numbers and the maximum may be totally eliminated if the oxygenates were not included in the Anderson-Schulz-Flory distribution.

Feed rates to the reactor were typically low and accordingly could not be measured very accurately. After correcting the feed rates by the ratio of

recovered to apparently fed Argon the overall material recoveries became 85% and 97% for the two test periods in Run 46.

For the first 814 hours the chain growth probabilities were 0.887 at C_{13}-C_{24}, 0.921 at C_{25}-C_{70} and 0.945 at C_{70}-C_{180}. For the rest of the run the chain growth probabilities were 0.883 at C_{14}-C_{27}, 0.929 at C_{27}-C_{70} and 0.944 at C_{70}-C_{120}.

Approximately 54% of the hydrocarbon products were in the distillate range (C_5-C_{22}) for the first 814 hours (20% in the C_5-C_{11} range), 9.5% of the products were light ends (C_1-C_4), and the balance was wax. It is important to mention again that the light ends selectivity decreased during the first 500 hours. Accordingly, the lined-out selectivities to light ends are much lower than the average values reported here.

The distillate fuel selectivity was 56% between 814 hours and 1700 hours, while the light ends was 13% (C_5-C_{11}:22%). The light ends were higher for the second test period because of the higher temperatures used and because of the lower conversion.

These results compare favorably with selectivities reported for the two commercial Sasol processes.

According to M. E. Dry [80] Arge process results in approximately 38% distillates, while the Synthol process gives about 48% distillates. The light ends selectivities are 14-18 and 43% for the two processes [34,80].

In order to verify the high distillate fuel selectivity results reported here, a sample recovered from the heated receiver between 625 hours and 700 hours on stream was vacuum distilled. This sample was representative of about 75% of the liquid and solid hydrocarbon and oxygenate products made during this 75 hours and showed that 46% of the products were in the C_5-C_{18} range, which is consistent with the GPC measurements done on the same sample. This product contained 19% linear primary alcohols + linear aldehydes, which was also consistent with products collected in colder receivers.