VI. Task 3. PROCESS EVALUATION RESEARCH

The original purpose of this task was to evaluate several of the most improved catalysts developed during this contract, in slurry bed reactors with following objectives: (1) to determine catalyst aging and deactivation with time on stream (long term stability tests), and (2) to perform process variable studies over a wider range of conditions than in Task 2 (Promoter Effect Research and Kinetic Studies), and to obtain improved kinetic parameters. On the basis of results obtained from slurry reactor tests in Task 2, which showed significant catalyst deactivation, it was decided to focus primarily on the first objective and to pursue the second one whenever feasible (i.e., in the absence of significant deactivation). Also, it was decided to evaluate catalysts in our fixed bed reactors with objective to obtain information on the intrinsic loss of catalyst activity, i.e., the loss which is not caused or accelerated by the wax withdrawal. Our fixed bed reactors operate under nearly isothermal conditions, and it is believed that they provide a good indication of catalyst stability and selectivity.

Five catalysts were evaluated in fixed bed reactors: three tests were made with silica containing catalysts (Ruhrchemie LP 33/81-the state-of-the-art catalyst and 100 Fe/5 Cu/4.2 K/x SiO_2 catalysts, x =8 or 24), and four tests with unsupported precipitated iron catalysts (100 Fe/1 Cu/0.2 K and 100 Fe/3 Cu/0.5 K). Four tests were conducted in slurry bed reactors with Ruhrchemie LP 33/81, 100 Fe/5 Cu/4.2 K/ 24 SiO_2, 100Fe/3Cu/0.2K and 100 Fe/3 Cu/0.5 K catalysts. As can be seen, several catalysts were tested both in fixed bed and slurry bed reactors, and this provides additional information on the effect of reactor type on catalyst activity and product selectivity.

VI.1. Fixed Bed Reactor Tests with Silica containing Catalysts

VI.1.1. Run FA – 63 – 1308 with the 100 Fe / 5 Cu / 4.2 K / 8 SiO_2 Catalyst

Run FA–63–1308 was made as a long term fixed bed stability test of the catalyst containing 8 parts SiO_2/100 parts Fe, which was among the most active of the catalysts tested during this contract and it also showed desirable selectivity behavior (Section V.4). The catalyst was reduced in situ at 280°C for 16 h with CO. Stability testing was conducted over a 552 h period, at 235°C, 1.48 MPa, 2.0 Nl / g–cat·h, using (H_2/CO)=1.0 synthesis gas (up to 271 h) and (H_2/CO)=0.67 synthesis gas (272-552 h). Three mass balances were completed with each feed ratio tested. A single mass balance was made at 250°C during balance 7, and a repeat of the original conditions was made in balance 8. The results obtained during these balances are summarized in Table VI-1.

Table VI-1 . Summary of results for fixed bed run FA-03-1308.

Catalyst: 3.40 g[a], 100 Fe/5 Cu/4.2 K/8 SiO2
Catalyst volume: 3.60 cc

Diluent: 35.1 g, Glass beads
Diluent Volume: 23.0 cc

Period	1	2	3	4	5	6	7	8
Date	5/11	5/15	5/19	5/23	5/27	5/31	6/3	6/6/88
Time on Stream (*h*)	48.0	144.0	240.0	336.5	432.0	528.0	600.0	662.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.5	7.5	6.5	7.2
Average Temperature (°C)	235.	235.	235.	235.	235.	235.	250.	235.
Maximum Δ Temperature (°C)[b]	2.30	1.50	1.40	2.00	1.40	1.50	1.50	2.40
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.03	1.03	1.03	.689	.689	.680	.689	1.03
Space Velocity (*Nl/g-cat·h*)[a]	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99
Space Velocity (*Nl/g-Fe·h*)	3.24	3.24	3.24	3.24	3.24	3.24	3.24	3.24
GHSV (h^{-1})[c]	251.	251.	251.	251.	251.	251.	251.	251.
CO Conversion (%)	94.6	87.5	68.1	48.6	43.7	41.2	48.7	37.1
H_2+CO Conversion (%)	77.9	71.8	56.9	46.0	42.1	40.1	46.4	31.7
H_2/CO Usage	.669	.664	.693	.598	.630	.647	.609	.740
STY (*mols* H_2+CO/*g-cat·h*)[a]	.069	.064	.051	.041	.037	.036	.041	.028
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	34.1	13.7	6.63	4.52	3.71	3.56	4.48	2.99
Weight % of Outlet								
H_2	2.70	3.04	3.76	2.75	2.88	2.92	2.71	5.11
H_2O	5.53	6.01	4.09	2.29	2.34	2.32	2.36	3.71
CO	5.11	11.8	29.9	49.3	54.4	56.5	49.1	59.0
CO_2	62.7	55.8	43.6	32.6	28.9	28.1	33.8	22.5
Hydrocarbons	15.0	15.6	11.2	8.10	7.20	6.86	8.00	6.95
Oxygenates	1.33	1.58	1.11	.519	.427	.340	.416	.602
Wax[d]	7.58	6.17	5.75	4.39	3.84	2.96	2.97	2.10
Yield (*g/Nm*^{3} H_2 + CO *Converted*)								
CH_4	8.01	6.91	7.88	6.67	7.46	8.10	12.0	13.1
C_2-C_4 Hydrocarbons	33.6	32.4	32.4	27.4	29.4	30.3	38.3	40.2
C_5-C_{11} Hydrocarbons	40.3	38.7	36.8	34.5	31.2	27.3	30.0	33.9
C_{12}+ Hydrocarbons	106.	120.	118.	141.	133.	123.	113.	94.1
Wax[d]	63.1	56.1	66.4	73.6	60.8	56.8	49.6	43.4
Oxygenates	11.1	14.3	12.9	8.70	7.76	6.04	6.93	12.5
Total	199.	212.	208.	218.	208.	195.	200.	200.
1+2 Olefins/n-Paraffin Ratio								
C_2	2.68	2.84	2.70	2.59	3.27	2.08	1.62	1.94
C_3	6.49	6.59	6.44	7.52	7.35	7.40	7.78	6.28
C_4	5.23	5.28	5.28	6.17	6.05	6.12	6.56	5.16
C_6	5.00	4.17	3.72	4.62	5.59	4.20	4.98	3.86
C_{10}	3.99	3.33	3.35	3.79	3.87	3.48	2.91	2.92

[a] Based on unreduced catalyst

[b] Maximum axial temperature difference

[c] Based on reactor volume

[d] Unrecovered products from wax analysis

Table VI-1 (cont'd). Summary of results for mixed bed run [illegible].

Period	1	2	3	4	5	6	7	8
Weight % of Hydrocarbons								
CH4	4.25	3.49	4.03	3.19	3.72	4.34	6.19	6.90
Ethane	1.48	1.33	1.49	1.24	1.55	1.78	2.74	2.94
Ethylene	3.71	3.53	3.73	2.00	3.27	3.45	4.14	5.32
Propane	.940	.847	.869	.591	.674	.739	.873	1.30
Propylene	5.82	5.32	5.35	4.24	4.73	5.21	6.48	7.80
n-Butane	.896	.709	.773	.633	.597	.655	.709	1.12
1+2 Butenes	4.52	4.07	3.94	3.18	3.49	3.87	4.49	5.60
C_4 Isomers	.471	.432	.414	.309	.342	.375	.436	.575
n-Pentane	1.23	1.10	1.06	.779	.810	.937	1.03	1.42
1+2 Pentenes	4.00	3.67	3.39	2.74	2.93	3.27	3.59	4.41
C_5 Isomers	.270	.249	.240	.167	.185	.210	.235	.366
n-Hexane	.552	.454	.633	.458	.362	.477	.415	.674
1+2 Hexenes	2.29	1.97	2.17	1.73	1.76	1.92	1.91	2.32
C_6 Isomers	.448	.381	.463	.390	.416	.464	.504	.555
n-Heptane	.373	.347	.480	.328	.231	.299	.247	.414
1+2 Heptenes	1.76	1.52	1.46	1.28	1.28	1.20	1.18	1.43
C_7 Isomers	.267	.235	.304	.276	.205	.252	.299	.272
n-Octane	.366	.397	.376	.255	.189	.194	.182	.223
1+2 Octenes	1.80	1.62	1.37	1.16	1.04	.800	.888	.847
C_8 Isomers	.250	.130	.164	.0542	.0987	.0371	.0651	.0989
n-Nonane	.462	.457	.415	.326	.282	.214	.212	.241
1+2 Nonenes	2.02	1.70	1.40	1.38	1.17	.839	.883	.822
C_9 Isomers	.164	.197	.147	.110	.0862	.0760	.106	.0837
n-Decane	.522	.561	.504	.475	.412	.321	.424	.437
1+2 Decenes	2.05	1.84	1.67	1.77	1.57	1.10	1.22	1.26
C_{10} Isomers	.290	.365	.257	.267	.215	.190	.243	.184
n-Undecane	.422	.517	.489	.479	.452	348	.390	.442
1+2 Undecenes	1.65	1.69	1.57	1.79	1.65	1.14	1.32	1.36
C_{11} Isomers	.232	.222	.223	.243	.205	.210	.222	.264
C_2-C_4	17.8	16.3	16.6	13.1	14.7	16.1	19.9	24.7
C_5-C_{11}	21.4	19.5	18.8	10.5	15.5	14.5	15.6	18.1
$C_{12}+$	56.5	60.7	60.6	67.3	66.1	65.1	58.4	50.2
Wax[d]	33.5	28.3	34.0	35.2	34.8	30.1	25.7	23.2

[d] Unrecovered products from wax analysis

A stability plot of the (H_2-CO) conversion versus time on stream is given in Fig. VI-1. The catalyst deactivated steadily with the (H_2/CO)=1.0 synthesis gas, with the (H_2-CO) conversion dropping from an initial value of 77.4 % (24.5 h) to a final value of 55.0 % (264 h). Deactivation continued after the switch to (H_2/CO)=0.67 feed gas, but the rate of deactivation decreased. Between 294.5 and 552 h, the (H_2+CO) conversion dropped from 47.5 to 39.0 %. The average deactivation rates (average change in conversion/unit time) were 0.094 and 0.033 %/h with (H_2/CO) = 1.0 and 0.67, respectively.

The difference in deactivation behavior with feed ratio is difficult to explain as we do not know with any certainty the cause of deactivation in the fixed bed reactors. Decreasing the (H_2/CO) feed ratio from 1.0 to 0.67 between balances 3 and 4 caused the CO partial pressure to increase from 0.36 to 0.64 MPa and the H_2 partial pressure to decrease from 0.63 to 0.49 MPa (exit values). The higher CO partial pressure drives the water-gas shift (WGS) reaction to the right, thus the CO_2 and H_2O partial pressures changed from 0.34 and 0.09 MPa to 0.27 and 0.05 MPa, respectively. If the primary cause of deactivation is carbon fouling, higher CO partial pressure should increase the rate of deactivation (Dry, 1981), which is not what is observed. If the primary cause of deactivation is catalyst reoxidation, the higher CO partial pressures can explain the decreased deactivation in several ways: (1) as we have found that CO is a more effective reductant than H_2 (Section V.1), a lower feed ratio will lend to a stronger reducing environment in the reactor to offset oxidation, (2) the excess CO consumes oxidizing H_2O via the WGS and decreases the rate of oxidation, or (3) higher CO partial pressures compete more effectively with water for surface sites on the catalyst, inhibiting oxidation.

The effect of time on stream on the selectivity of the silica-containing catalyst is shown in Fig. VI-2 for both feed ratios. The lower (H_2/CO) feed ratio decreases CH_4 and C_2-C_4 selectivity, increasing the amount of $C_{12}-$ products formed. The olefin/paraffin ratios using (H_2/CO)=0.67 synthesis gas are higher than or comparable to those using (H_2/CO)=1.0 feed. Little change is seen in the first three balances with (H_2/CO)=1.0 or the balances using (H_2/CO)=0.67 feed gas. However, after the catalyst was heavily deactivated (balance 8, 662 h), the product distribution shifted towards lighter products (CH_4 and C_2-C_4) at the expense of $C_{12}-$. There was no definite trend in the olefin/paraffin ratios with catalyst deactivation.

The ASF plots for active catalyst at 235°C, (H_2/CO)=1.0 (balance 1), (H_2/CO)=0.67 (balance 4), and deactivated catalyst at (H_2/CO)=1.0 (balance 8) are shown in Figs. VI-3 to VI-5. The feed ratio had little effect on α_2, which varied between 0.90 and 0.91 for the three

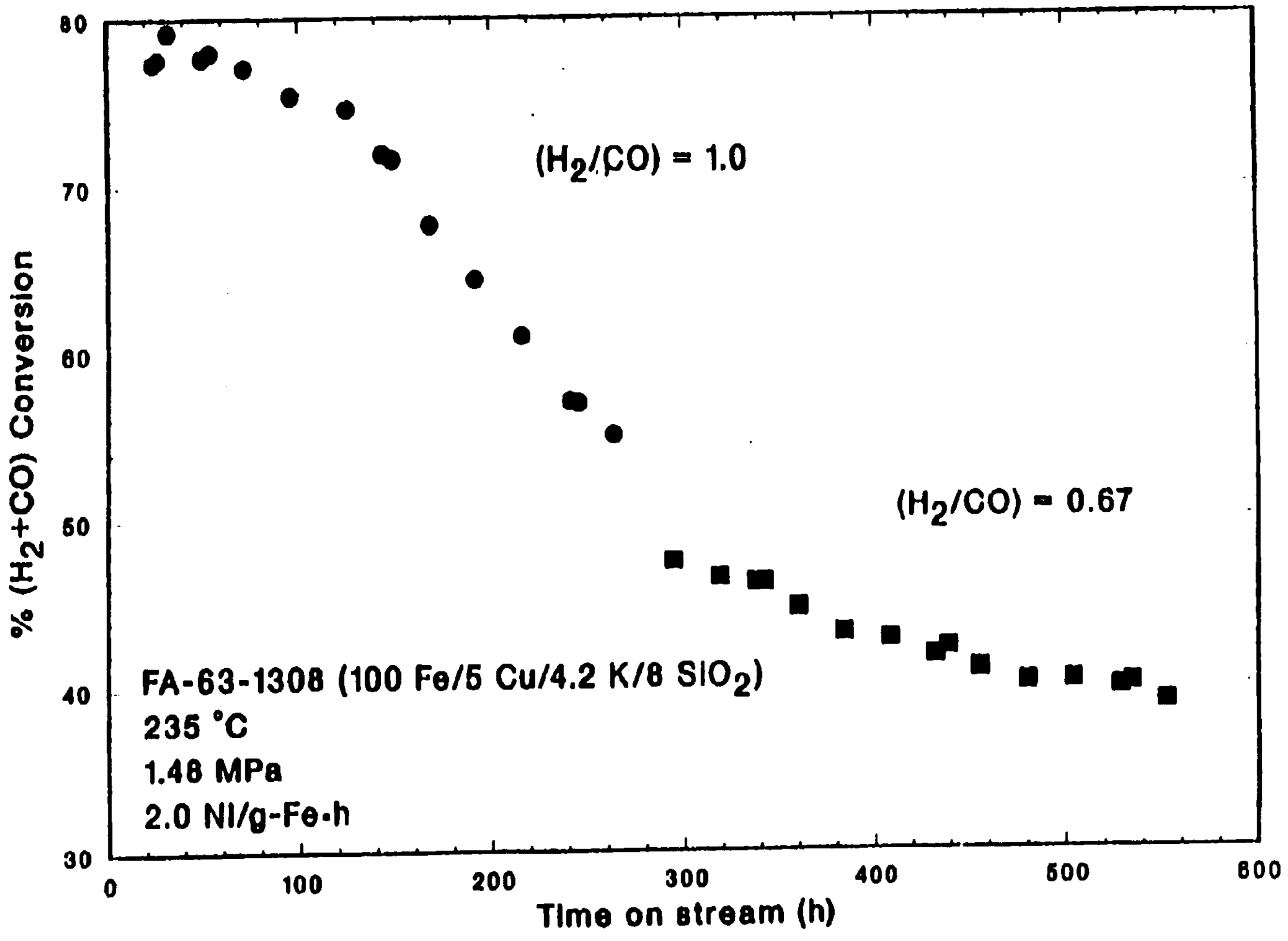

Figure VI-1 Stability plot, (H_2+CO) conversion versus time on stream, for run FA-63-1308.

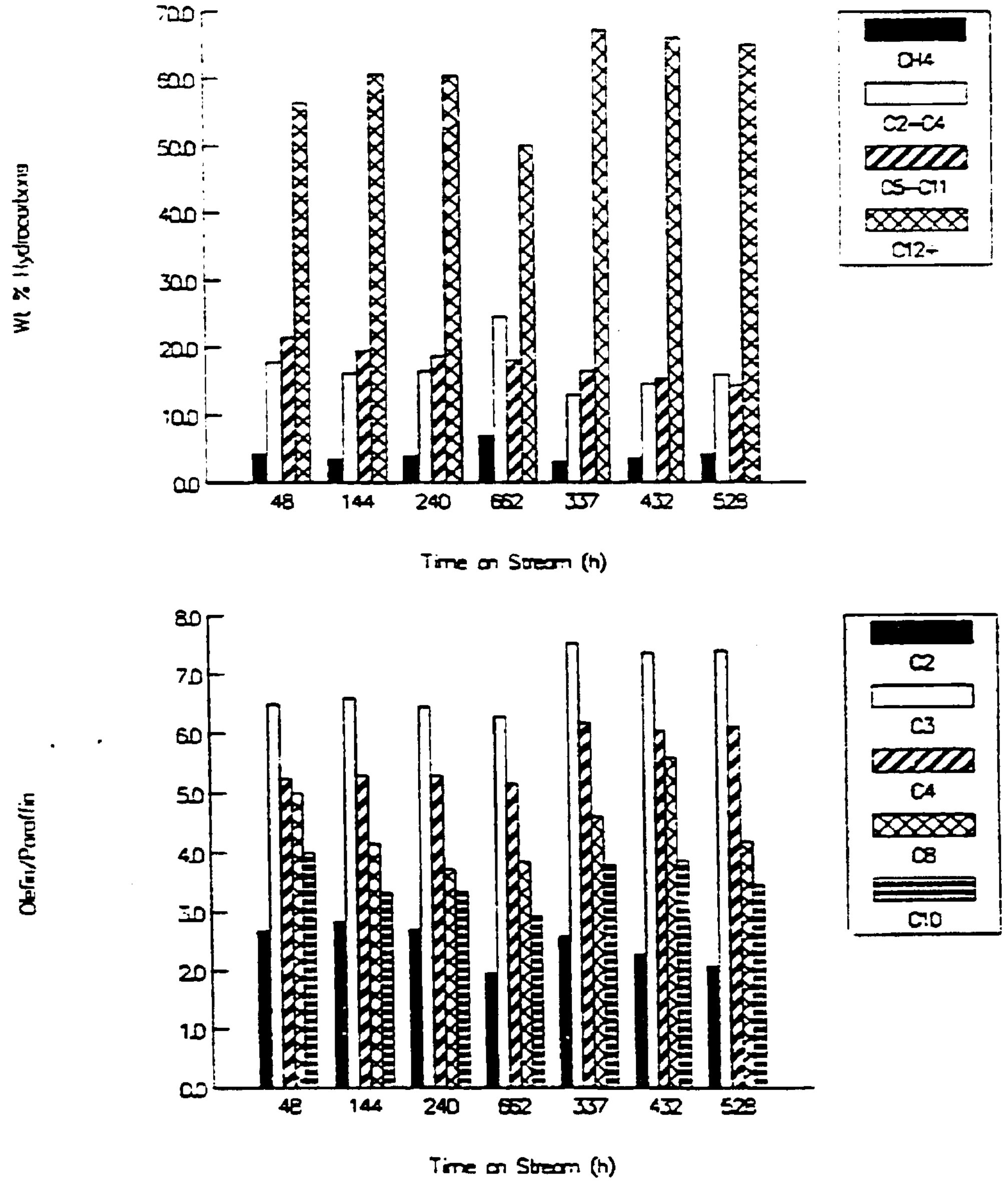

Figure VI-2. Effect of time on stream on 100 Fe/5 Cu/4.2 K/8 SiO_2 catalyst selectivity for run FA-63-1308: 235 °C, 1.48 *MPa*, 2 *Nl/g*-cat·*h*, (H_2/CO) = 1.0 (48–240, 662 *h*) and 0.67 (337–528 *h*).

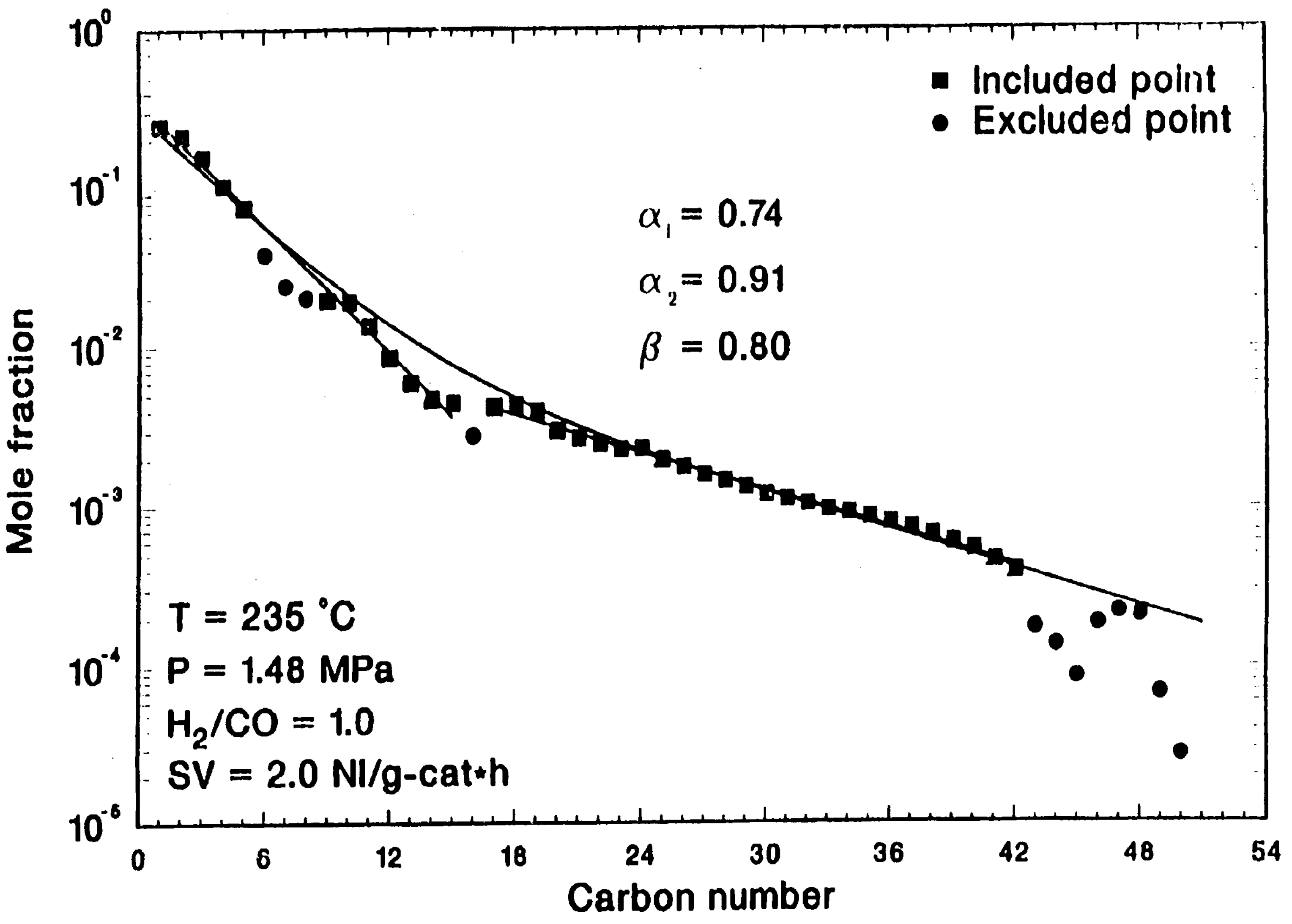

Figure VI-3. Anderson-Schulz-Flory plot for run FA-63-1308-1, total products excluding unrecovered wax.

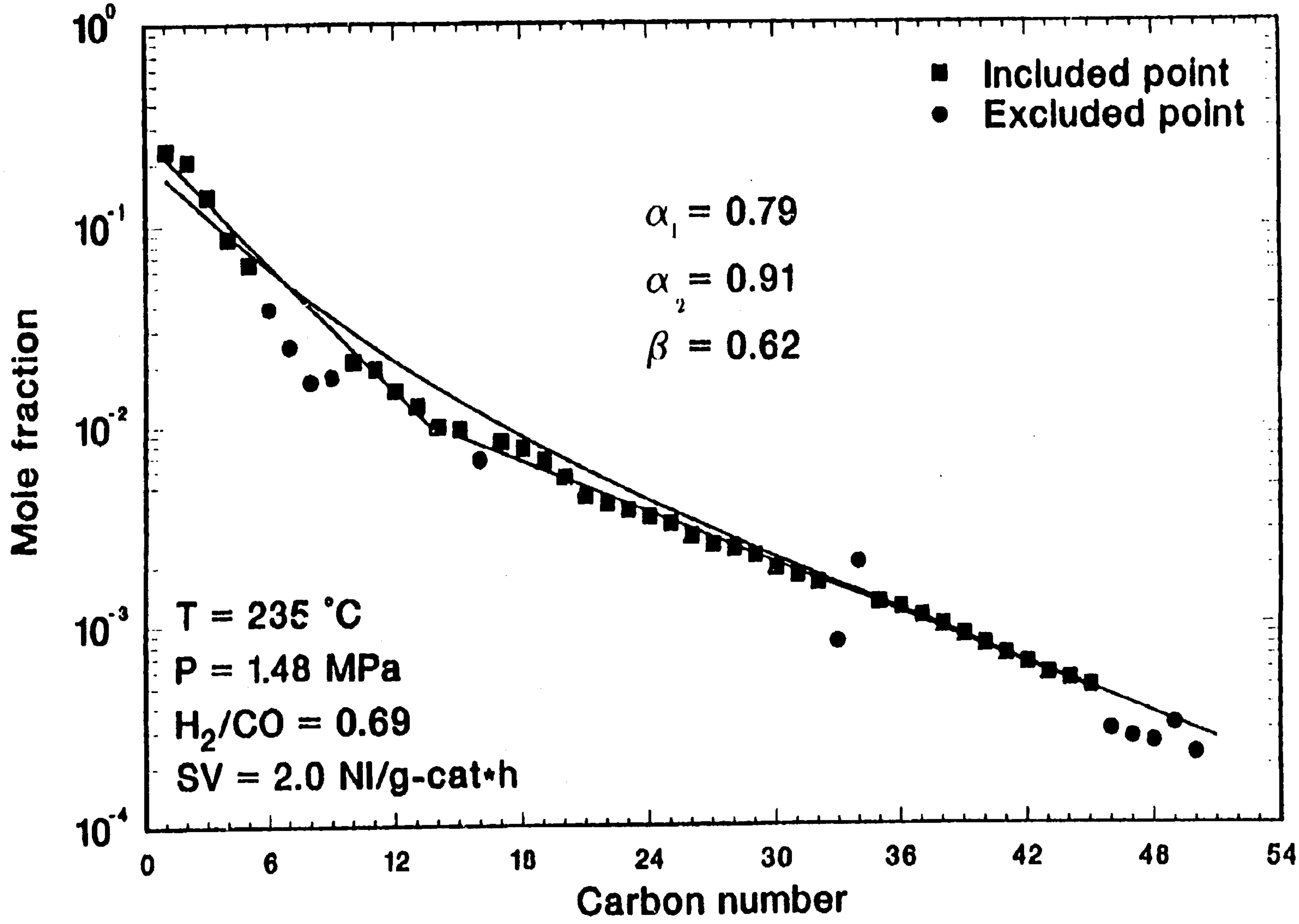

Figure VI-4. Anderson-Schulz Flory plot for run FA-63 1308-4, total products excluding unrecovered wax.

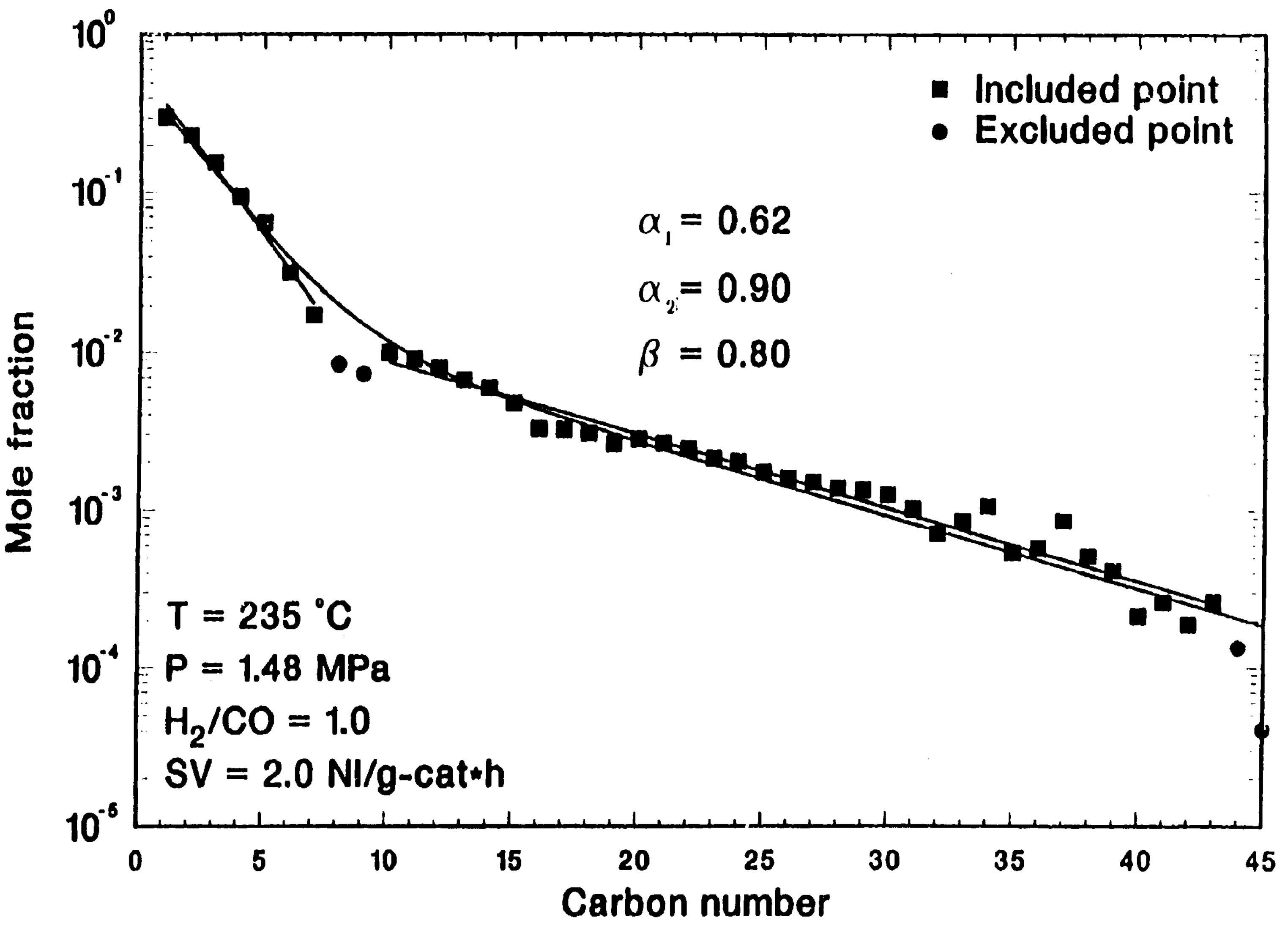

Figure VI-5. Anderson-Schulz-Flory plot for run FA-63-1308-8, total products excluding unrecovered wax balances. α_1 increased from 0.74 to 0.79 and β decreased from 0.80 to 0.62 as the feed ratio decreased from 1.0 to 0.69, which are representative of the higher hydrocarbon selectivity of the lower feed ratio. Deactivation caused a decrease in α_1, from 0.74 to 0.62, with minimal change in either β or α_2, thus the gaseous hydrocarbons are the most strongly influenced by deactivation.

In the first balance of the run before deactivation, the catalyst activity and selectivity was similar to the previous test of this catalyst (Run FA–63–0418, Section V.4) at the same conditions (235°C, 1.48 MPa, 2.0 Nl / g–cat·h). The (H_2–CO) conversion at these conditions was 77.9 % as compared to the 76.7 % obtained previously. The weight % hydrocarbon distribution during run FA–63–0418 was 3.5 (CH_4), 16.4 (C_2–C_4), 20.1 (C_5–C_{11}), and 60.0 % (C_{12}–), compared to 4.3, 17.8, 21.4, and 56.5 % obtained in this run. At 250 °C (balance 7) the catalyst was deactivated and the (H_2–CO) conversion was only 46.4 %, while in the previous run the (H_2–CO) conversion at the same temperature and double the space velocity (4 Nl / g–cat·h, balance 3) was 65.1 %. The hydrocarbon selectivity did not change significantly with deactivation at these conditions.

VI.1.2. Run FB – 99 – 1588 with the Ruhrchemie LP 33 / 81 Catalyst

Run FB–99–1588 was a long term stability test of the Ruhrchemie LP 33/81 commercial catalyst, and was intended to complement the slurry run SA–99–0888 (Section VI.3.1). The initial process conditions for the stability test were 250°C, 1.48 MPa, (H_2/CO)=0.67, 2.0 Nl / g–cat·h, which are the same as those during the first five balances of slurry run SA–99–0888. The results of the seven balances of run FB–99–1588 are summarized in Table VI-2. The calcined Ruhrchemie catalyst (30/60 mesh particles) was reduced in situ at 280°C, using CO reductant for 12 h. The stability plot of (H_2–CO) conversion versus time is shown in Fig. VI-6. After an initial rapid decline in catalyst activity, the activity was relatively stable, with the conversion dropping from 58.3 % to 53.6 % between about 100 and 340 h. At 382 h, a power failure occurred, interrupting the run for approximately 50 min, which caused an immediate decrease in the (H_2–CO) conversion to 50 % after the process conditions were reestablished. The catalyst was stable, at lower activity, after the interruption. After the fifth mass balance was completed the feed ratio was changed to 1.0 (nominal) at the same temperature, pressure, and space velocity. The (H_2–CO) conversion increased to 57.2 % at 49 h and declined slightly to 55.7 % at 630 h.

Table VI-2. Summary of results for fixed bed run FB-99-1588.

Catalyst: 3.40 g[a], Ruhrchemie LP 33/81
Catalyst volume: 5.40 cc

Diluent: 35.6 g, Glass beads
Diluent Volume: 23.0 cc

Period	1	2	3	4	5	6	7
Date	6/9/88	6/13/88	6/17/88	6/21/88	6/25/88	6/28/88	7/2/88
Time on Stream (h)	71.0	167.0	262.5	360.0	426.5	528.0	622.5
Balance Duration (h)	7.0	7.2	7.0	6.8	7.0	7.1	7.5
Average Temperature (°C)	250.	250.	250.	250.	250.	250.	250.
Maximum Δ Temperature (°C)[b]	4.00	4.00	5.00	6.00	6.00	6.00	6.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.689	.689	.686	.686	.686	.980	.980
Space Velocity ($Nl/g \cdot cat \cdot h$)[a]	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Space Velocity ($Nl/g\ Fe\ h$)	3.81	3.81	3.81	3.81	3.81	3.81	3.81
GHSV (h^{-1})[c]	239.	239.	239.	239.	239.	239.	239.
CO Conversion (%)	56.4	52.4	51.6	50.1	46.0	59.1	50.1
H_2+CO Conversion (%)	68.6	55.3	54.4	53.2	50.2	56.0	55.5
H_2/CO Usage	.757	.780	.778	.790	.803	.878	.859
STY ($mols\ H_2+CO/g \cdot cat \cdot h$)[a]	.052	.049	.040	.048	.045	.050	.050
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	2.22	2.03	2.05	2.14	1.97	2.97	2.83
Weight % of Outlet							
H_2	1.88	1.99	1.99	2.01	2.14	3.16	3.24
H_2O	3.97	3.86	3.81	3.48	3.62	5.50	5.76
CO	43.4	47.0	47.0	48.1	51.1	39.0	39.0
CO_2	36.8	32.5	32.4	31.2	29.9	35.5	34.5
Hydrocarbons	11.4	9.26	9.43	9.43	8.96	13.0	12.9
Oxygenates	.645	.545	.503	.398	.421	.988	.900
Wax[d]	2.88	4.82	4.91	5.36	3.87	2.92	3.63
Yield (g/Nm^3 H_2 + CO Converted)							
CH_4	10.1	10.2	11.2	11.5	12.6	16.1	15.5
C_2-C_4 Hydrocarbons	41.2	40.3	45.8	46.2	49.1	55.8	54.7
C_5-C_{11} Hydrocarbons	33.6	35.8	40.7	42.8	46.4	47.6	45.9
C_{12}+ Hydrocarbons	96.2	104.	103.	113.	88.7	69.0	81.2
Wax[d]	30.5	65.2	68.8	77.3	59.4	34.0	43.2
Oxygenates	8.18	7.37	7.05	5.72	6.46	11.7	10.8
Total	189.	198.	208.	210.	203	200.	208.
1+2 Olefins/n-Paraffin Ratio							
C_2	1.68	1.92	1.99	2.09	2.10	1.44	1.54
C_3	7.65	7.83	7.80	7.75	7.74	6.44	6.50
C_4	6.22	6.35	6.33	6.23	6.22	5.13	5.20
C_8	3.80	4.06	3.71	4.03	4.15	3.25	3.10
C_{10}	2.62	2.66	2.78	2.81	3.00	2.27	2.31

[a] Based on unreduced catalyst

[b] Maximum axial temperature difference

[c] Based on reactor volume

[d] Unrecovered products from wax analysis

Table VI-2 (cont'd). Summary of results for fixed bed run FB-99-1588.

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH4	5.55	5.34	5.58	5.41	6.38	8.54	7.87
Ethane	2.48	2.18	2.25	2.00	2.33	3.50	3.12
Ethylene	3.87	3.92	4.18	3.90	4.56	4.70	4.49
Propane	1.05	.975	1.04	.983	1.13	1.50	1.48
Propylene	7.70	7.29	7.76	7.27	8.35	0.79	9.20
n-Butane	1.01	.878	.984	.996	1.14	1.57	1.46
1+2 Butenes	6.05	5.39	6.01	5.99	6.85	7.78	7.35
C_4 Isomers	.586	.509	.543	.524	.598	.670	.624
n-Pentane	1.43	1.15	1.35	1.46	1.65	2.04	1.87
1+2 Pentenes	5.11	4.18	5.10	5.51	6.21	6.85	6.38
C_5 Isomers	.333	.263	.305	.325	.372	.499	.450
n-Hexane	.634	.709	.605	.065	.701	.826	.755
1+2 Hexenes	2.56	2.66	2.87	2.72	3.50	3.30	3.00
C_6 Isomers	.578	.536	.583	.594	.632	.595	.517
n-Heptane	.372	.392	.401	.469	.469	.550	.497
1+2 Heptenes	1.51	1.66	1.69	1.93	2.02	1.03	1.76
C_7 Isomers	.343	.323	.347	.377	.442	.389	.306
n Octane	.292	.311	.324	.295	.363	.465	.422
1+2 Octenes	1.09	1.24	1.18	1.17	1.48	1.48	1.32
C_8 Isomers	.165	.192	.174	.258	.146	.163	.152
n-Nonane	.280	.383	.370	.288	.377	.553	.475
1+2 Nonenes	.872	1.16	1.14	.013	1.20	1.38	1.22
C_9 Isomers	.0998	.107	.110	.0676	.0631	.102	.126
n-Decane	.359	.457	.450	.369	.472	.621	.564
1+2 Decenes	.027	1.20	1.23	1.02	1.40	1.39	1.28
C_{10} Isomers	.174	.181	.224	.121	.119	.100	.173
n-Undecane	.418	.475	.473	.408	.502	.602	.603
1+2 Undecenes	.892	1.01	1.09	.959	1.26	1.16	1.15
C_{11} Isomers	.150	.185	.195	.124	.158	.175	.202
C_2-C_4	22.7	21.1	22.8	21.7	25.0	29.6	27.7
C_5-C_{11}	18.6	18.8	20.2	20.0	23.6	25.3	23.2
C_{12}+	53.1	54.7	51.4	52.9	45.1	36.8	41.2
Wax[d]	20.2	34.2	34.2	36.2	30.2	18.4	21.9

[d] Unrecovered products from wax analysis

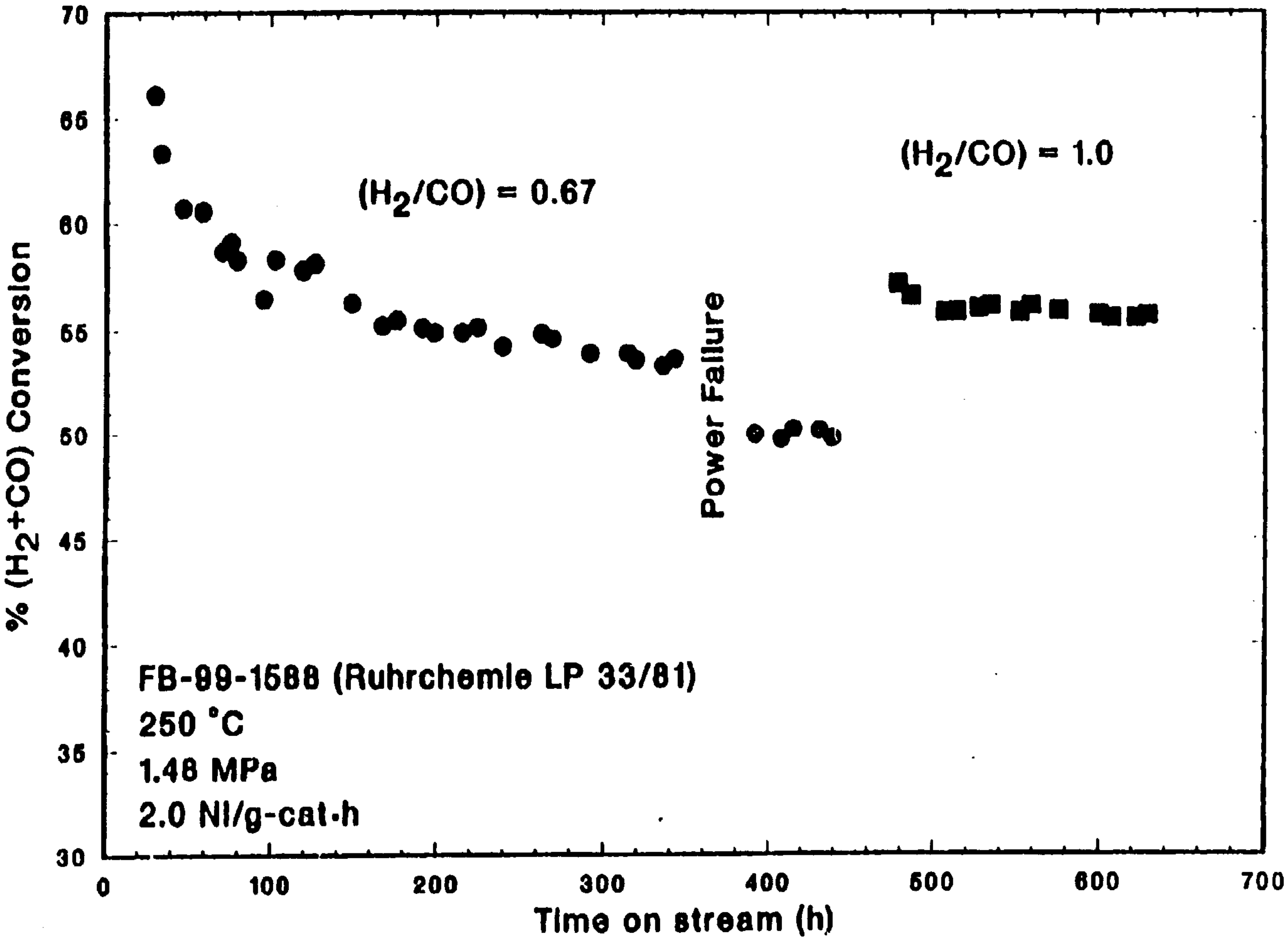

Figure VI-6. Stability plot, (H_2+CO) conversion versus time on stream, for run FB-99-1588.

Catalyst selectivity as a function of time on stream is shown in Fig. VI-7 for run FB-99-1588. The selectivity was not strongly affected by time on stream, and neither the weight % hydrocarbon distribution nor the olefin/paraffin ratios show any specific trends as the catalyst aged. At higher feed ratio, more gaseous hydrocarbons were formed, increasing from 6.4 (CH_4) and 25.0 % (C_2-C_4) in balance 5 ($H_2/CO=0.67$) to 8.5 and 29.6 %, respectively, in balance 6 ($H_2/CO=1.0$). The olefin/paraffin ratios decreased as well when the concentration of H_2 in the feed was increased.

Catalyst activity was higher in a fixed bed reactor than in a slurry reactor, with a conversion of 53.2 % in the fixed bed (balance 4) before the power failure compared to the 44.4 % conversion obtained in the slurry reactor (balance 5) at approximately the same time on stream. With the (H_2/CO)=1.0 feed gas, the fixed bed run gave a conversion of 56.0 % in balance 6 (250°C, 1.48 MPa, 2.0 Nl / g-cat·h) while during balance 12 of run SA-99-0888 at the same conditions, the conversion was 45.4 %, although catalyst deactivation occurred before this measurement was made.

The selectivities obtained in the fixed bed and slurry bed tests are compared in Fig. VI-8. The hydrocarbon selectivities in two runs with (H_2/CO)=0.67 were similar, with the weight % of hydrocarbons in fixed bed (balance 2) at 5.3 (CH_4), 21.1 (C_2-C_4), 18.8 (C_5-C_{11}), and 54.7 % (C_{12}-) while in slurry (balance 3) the distribution was 5.1, 20.8, 21.9, and 52.2 %, respectively. With (H_2/CO)=1.0, the slurry reactor produced more CH_4 and C_2-C_4 products than fixed bed. This is probably due to catalyst deactivation which recurred in the slurry reactor prior to tests with (H_2/CO)=1.0 feed gas. We observed that the deactivated catalyst produces more lower molecular weight products than the fresh catalyst. Also, the differences in the C_5-C_{11} and C_{12}+ fractions may be due to differences in the product collection procedures for the two systems, as the C_5- fractions are not as dissimilar. The olefin/paraffin ratios, which are also compared in Fig. VI-8, were lower in slurry than in the fixed bed, which may be due to differences in flow patterns (i.e., plug flow vs. completely backmixed) of the two reactors.

VI.1.3. Run FB - 66 - 1948 with the 100 Fe / 5.0 Cu / 4.2 K / 24 SiO_2 Catalyst

Run FB-66-1948 was made as a long term stability test of the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst. The first 5 mass balances (up to 457 h) were made at a fixed set of process conditions: 250°C, 1.48 MPa, 2.0 Nl / g-cat·h, and $H_2/CO=0.69$, to determine the catalyst stability. Balance 10 was a repeat of these conditions. The effect of space velocity was studied

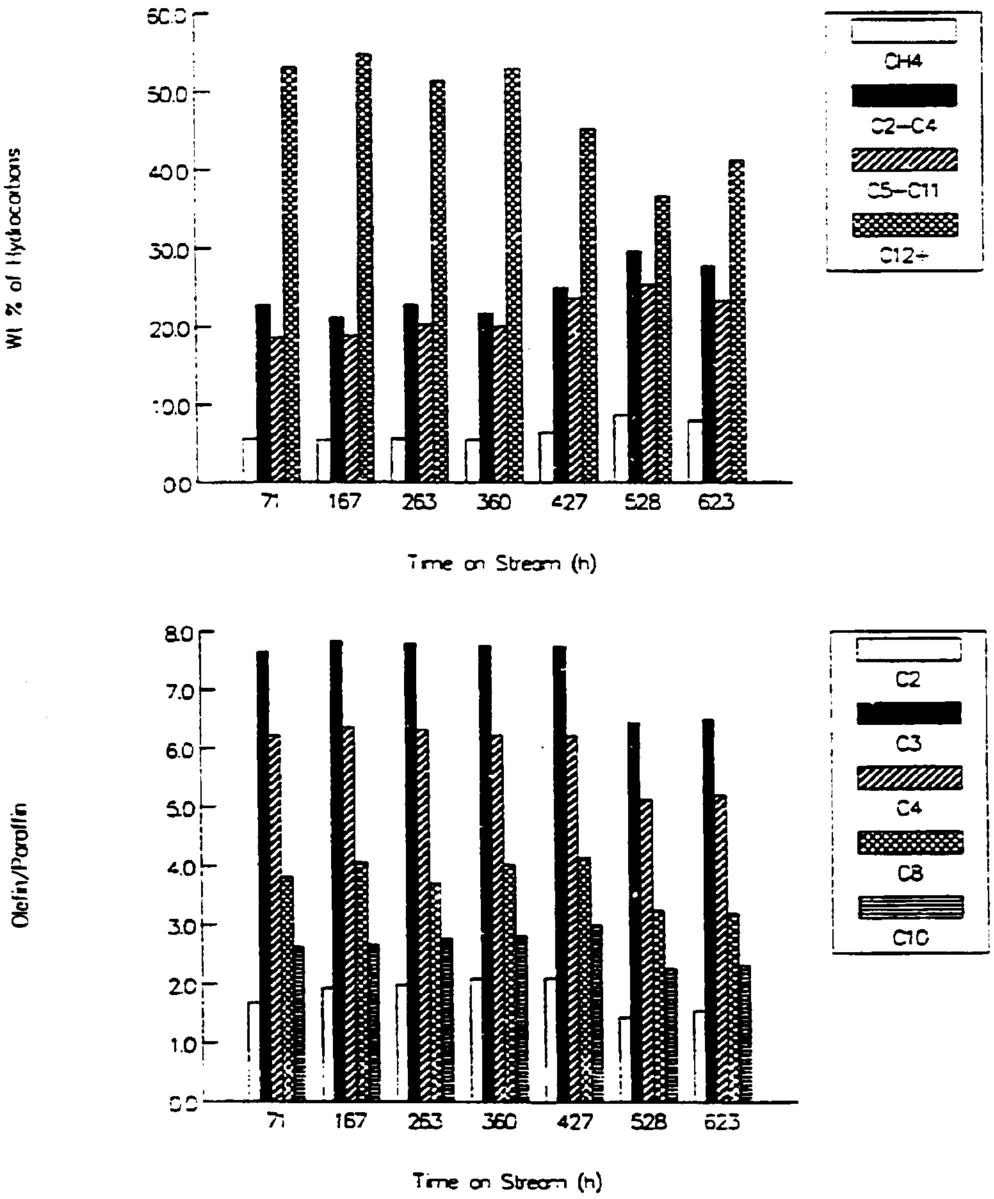

Figure VI-7. **Effect of time on stream on Ruhrchemie LP 33/81 selectivity for run FB-99-1588: 250 °C, 1.48 *MPa*, 2 *Nl/g*-cat·*h*, (H_2/CO) = 0.67 (71–427 *h*) and 1.0 (528, 623 *h*).**

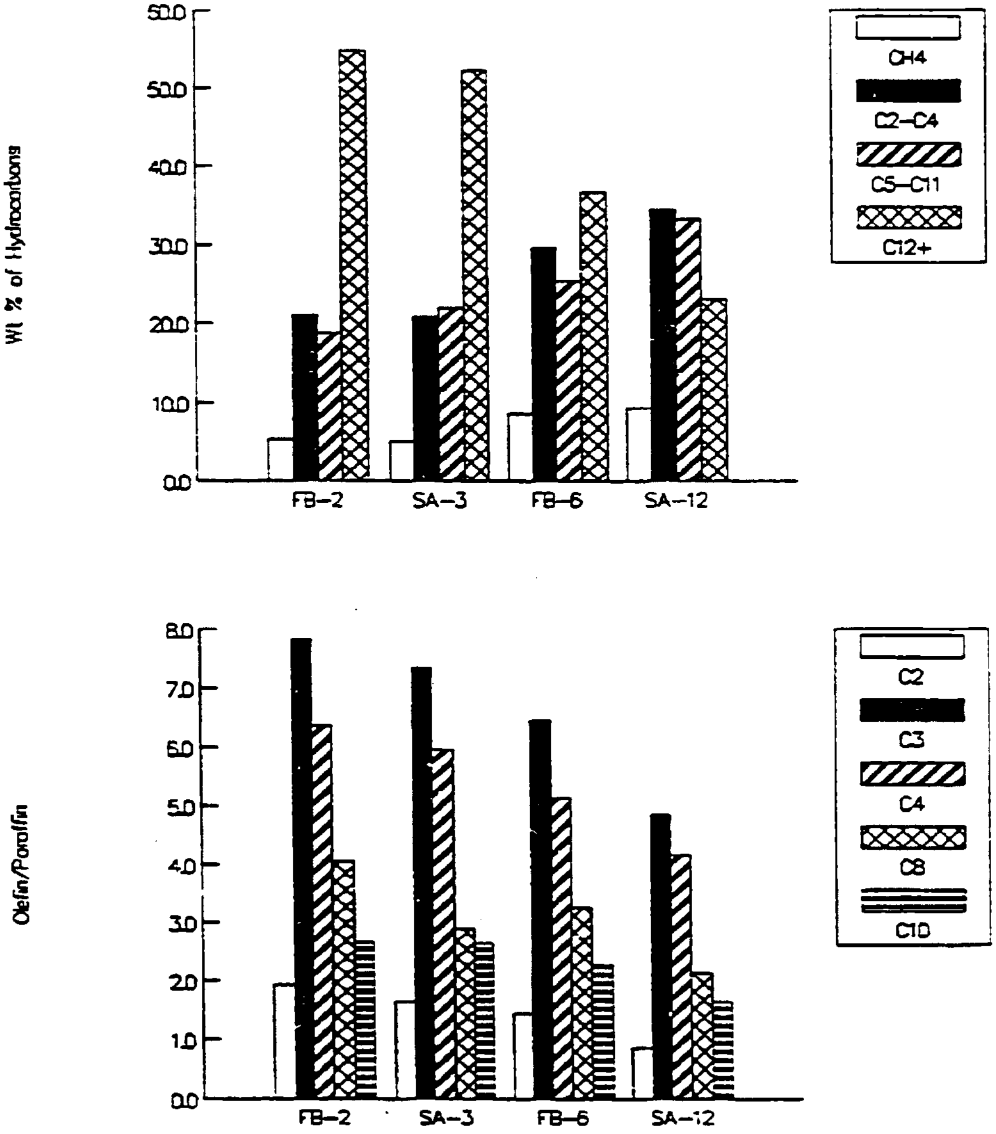

Figure VI-8. **Comparison of fixed bed and slurry reactor selectivity with Ruhrchemie LP 33/81 catalyst (FB = FB-99-1588. SA = SA-99-0888): 250 °C. 1.48 *MPa*. 2.0 *Nl/g*-cat·*h*. (H_2/CO) = 0.67 (FB-2 and SA-3) and 1.0 (FB-6 and SA-12).**

in balances 6 (4.0 Nl / g–cat·h) and 7 (1.0 Nl / g–cat·h), and the effect of feed ratio was studied in balances 8 and 9 (H_2/CO=1.03). With an H_2/CO=0.70 feed, temperature was varied in balances 11 (265°C) and 12 (235°C). The twelve mass balances completed during this run are summarized in Table VI-3.

The 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst was very stable, and the stability plot for the run (up to 457 h) is shown in Fig. VI-9. The (H_2–CO) conversion decreased from an initial value of 68.7 % to 64.3 % after 457 h. In the repeat of conditions (balance 10, 765 h) the conversion was still high, 57.7 %, although it is clear that varying the process conditions accelerated the rate of deactivation. The activity was superior to that of the Ruhrchemie LP 33/81 catalyst, whose stability plot for run FB–99–1588 is also shown in Fig. VI-9. The initial activities of both catalysts were approximately equal, but at about 340 h, the Ruhrchemie catalyst gave an (H_2–CO) conversion of 44.2 % while our 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst gave a conversion of 65.5 %. The 24 parts SiO_2 catalyst was also more stable, but less active, than the catalyst containing only 8 parts of SiO_2. The (H_2–CO) conversions at 235°C (H_2/CO=1.0) obtained with the 8 parts SiO_2 catalyst, shown in Fig. VI-9, are higher initially than those obtained with either the 24 parts SiO_2 catalyst or the Ruhrchemie LP 33/81 at 250°C (H_2/CO=0.69). However, the catalyst containing 8 parts SiO_2 deactivated rapidly, in spite of being tested at milder conditions (235°C).

The effect of time on stream on catalyst selectivity is shown in Fig. VI-10. There was a very mild shift towards lighter products as the catalyst aged, a trend which has also been seen with other catalysts. Between 71 (balance 1) and 477 h (balance 5), methane increased from 5.8 to 6.5 % while the C_{12}– products decreased from 50.9 to 41.0 %. There was no effect of time on the olefin/paraffin ratios measured during the stability portion of the run. In balances 6–9, 11 and 12, the conditions were varied to study catalyst activity and selectivity at different sets of process conditions. The (H_2+CO) conversions and weight percent hydrocarbon distribution at the different process conditions used in these balances are shown in Fig. VI-11. In this figure, the average results from balances 1–5 (250°C, 2.0 Nl / g–cat·h, H_2/CO=0.69) and balances 8 and 9 (250°C, 2.0 Nl / g–cat·h, H_2/CO=1.0) are shown. The hydrocarbon distribution is shown as a series of bars and the (H_2+CO) conversion is shown as symbols connected by a line. Conversion increases with temperature, which is expected, and the hydrocarbon distribution shifts towards lower molecular weight products. The selectivity trend is weak between 235°C (balance 12) and 250°C (balances 1–5), however the first five balances do not reflect the effect

Table VI-3. Summary of results for fixed bed run FB 66 1948.

Catalyst: 3.40 g^a, 100 Fe/5.0 Cu/4.2 K/24 SiO_2
Catalyst volume: 4.60 cc

Diluent: 36.4 g, Glass beads
Diluent Volume: 24.0 cc

Period	1	2	3	4	5	6
Date	07/15/88	07/19/88	07/23/88	07/27/88	08/01/88	08/03/88
Time on Stream (h)	71.0	167.5	263.5	356.0	476.5	524.0
Balance Duration (h)	6.5	6.5	6.5	7.0	6.8	6.5
Average Temperature (°C)	250.	250.	250.	250.	250.	250.
Maximum Δ Temperature (°C)[b]	2.10	2.00	3.00	3.00	3.00	4.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.686	.686	.686	.686	.712	.712
Space Velocity (Nl/g-cat·h)[a]	2.01	2.01	2.01	2.01	2.01	4.02
Space Velocity (Nl/g-Fe·h)	3.58	3.58	3.58	3.58	3.58	7.16
GHSV (h^{-1})[c]	239.	239.	239.	239.	239.	477.
CO Conversion (%)	69.4	68.8	67.7	67.9	66.1	40.3
H_2+CO Conversion (%)	67.9	67.1	65.6	65.5	64.0	41.5
H_2/CO Usage	.650	.643	.634	.628	.657	.704
STY ($mols$ H_2+CO/g-cat·h)[a]	.061	.060	.059	.059	.057	.074
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	3.41	3.09	3.17	3.98	3.96	1.93
Weight % of Outlet						
H_2	1.61	1.70	1.78	1.79	1.91	2.76
H_2O	4.45	4.82	4.08	3.94	3.91	3.85
CO	29.1	30.2	31.0	30.7	32.4	56.6
CO_2	48.2	46.6	45.6	47.3	46.1	26.8
Hydrocarbons	11.0	11.5	11.5	11.4	9.26	7.20
Oxygenates	.715	.769	.581	.649	.563	.308
Wax[d]	4.09	4.32	4.89	4.21	5.80[e]	2.36
Yield (g/Nm^3 H_2 + CO Converted)						
CH_4	10.5	10.6	10.8	11.4	11.6	12.3
C_2-C_4 Hydrocarbons	40.1	40.8	43.1	45.0	45.9	47.4
C_5-C_{11} Hydrocarbons	39.3	40.5	45.6	44.4	44.6	45.0
C_{12}+ Hydrocarbons	93.2	88.9	92.7	83.2	77.7	72.8
Wax[d]	57.2	49.3	57.5	49.7	69.2[e]	43.8
Oxygenates	8.20	8.77	6.83	7.07	6.71	7.39
Total	191.	190.	199.	192.	186.	185.
1+2 Olefins/n-Paraffin Ratio						
C_2	2.12	2.38	2.50	2.31	2.29	2.46
C_3	7.98	8.11	8.10	8.29	8.26	7.06
C_4	6.47	6.48	6.48	6.57	6.57	6.50
C_8	4.64	4.83	5.14	4.88	4.72	5.17
C_{10}	3.92	4.16	4.34	4.13	4.14	4.35

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[a] Based on unreduced catalyst

[b] Maximum axial temperature difference

[c] Based on catalyst volume

[d] [illegible]

[e] Unanalyzed products collected from hot trap

Table VI-3 (cont'd). Summary of results for fixed bed run FB 66 1948.

Period	7	8	9	10	11	12
Date	08/05/88	08/08/88	08/11/88	08/13/88	08/15/88	08/17/88
Time on Stream (h)	572.0	644.5	715.5	764.5	812.5	860.0
Balance Duration (h)	8.0	6.5	7.0	6.8	6.2	6.7
Average Temperature (°C)	250.	250.	250.	250.	265.	235.
Maximum Δ Temperature (°C)[b]	3.00	4.00	3.00	4.00	5.00	2.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.712	1.03	1.03	.704	.704	.704
Space Velocity (Nl/g-$cat \cdot h$)[a]	1.01	2.01	2.01	2.01	2.01	2.01
Space Velocity ($Nl/g \cdot Fe \cdot h$)	1.70	3.58	3.58	3.58	3.58	3.58
GHSV (h^{-1})[c]	120.	239.	239.	239.	239.	239.
CO Conversion (%)	86.4	68.5	68.3	57.7	77.7	32.4
H_2+CO Conversion (%)	82.3	60.6	60.6	57.7	74.1	35.5
H_2/CO Usage	.631	.800	.802	.702	.626	.862
STY ($mols\ H_2+CO/g\ cat \cdot h$)[a]	.037	.054	.054	.052	.060	.032
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	10.1	3.38	3.78	2.94	5.95	.958
Weight % of Outlet						
H_2	1.14	3.22	3.24	2.04	1.51	2.88
H_2O	3.03	7.85	7.12	3.92	3.71	5.23
CO	12.8	29.1	29.4	40.1	21.5	63.7
CO_2	60.9	42.2	43.0	40.0	55.4	19.5
Hydrocarbons	16.3	12.8	12.4	9.44	12.8	5.39
Oxygenates	672	1.02	.907	.513	.781	.625
Wax[d]	5.17	3.84	3.87	4.02	4.31	2.66
Yield (g/Nm^3 H_2+CO Converted)						
CH_4	12.1	14.7	14.3	11.7	15.1	10.7
C_2-C_4 Hydrocarbons	47.9	53.6	51.8	43.8	49.0	42.9
C_5-C_{11} Hydrocarbons	58.0	45.8	45.0	43.4	45.5	37.3
C_{12}+ Hydrocarbons	83.0	68.1	67.0	81.6	65.4	85.7
Wax[d]	48.6	42.2	42.3	53.9	44.2	58.4
Oxygenates	6.32	11.2	9.01	6.88	8.01	13.7
Total	208.	193.	188.	187.	184.	190.
1+2 Olefins/n-Paraffin Ratio						
C_2	1.70	2.11	2.28	2.57	1.56	3.17
C_3	8.38	6.91	6.99	8.15	8.54	7.18
C_4	6.67	5.55	5.61	6.62	7.04	5.94
C_8	4.80	4.04	4.08	4.67	4.80	4.60
C_{10}	3.87	3.12	3.54	4.14	3.72	3.56

[a] Based on unreduced catalyst

[c] Based on catalyst volume

[b] Maximum axial temperature difference

[d] Unrecovered products from wax analysis

Table VI-3 (cont'd). Summary of results for fixed bed run FB 66 1918.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	5.75	5.80	5.63	6.20	6.45	6.91
Ethane	2.19	2 07	1.98	2.25	2.34	2.39
Ethylene	4.33	4.61	4.61	4.86	5.00	5.49
Propane	.975	.985	.075	1.04	1.09	1.16
Propylene	7.43	7.62	7.54	8.20	8.56	8.79
n-Butane	.893	.933	.937	1.03	1.08	1.13
1+2 Butenes	5.58	5.84	5.86	6.51	6.85	7.10
C_4 Isomers	.523	.533	.536	.586	.611	.636
n-Pentane	1.28	1.30	1.31	1.48	1.53	1.64
1+2 Pentenes	4.79	5.19	5.03	5.74	5.89	6.31
C_5 Isomers	.279	.292	.296	.323	.336	.361
n-Hexane	.461	.462	.541	.569	.591	.721
1+2 Hexenes	2.63	2.61	2.90	3 06	3.18	3.95
C_6 Isomers	.645	.520	.577	.628	.660	1.01
n-Heptane	.366	.345	.409	.411	.479	.526
1+2 Heptenes	1.85	1.78	2.04	2.11	2.36	2.74
C_7 Isomers	.353	.310	.313	.372	.433	.702
n-Octane	.371	.390	.426	.415	.424	.341
1+2 Octenes	1.69	1.88	2.15	1.99	1.96	1.73
C_8 Isomers	.272	.369	.253	.338	.534	.203
n-Nonane	.474	.407	.426	.398	.386	.254
1+2 Nonenes	1.54	1.74	1.92	1.69	1.64	1.21
C_9 Isomers	.225	.237	.166	.208	.237	.127
n-Decane	.410	.411	.443	.398	.382	.200
1+2 Decenes	1.58	1.69	1.90	1.62	1.56	1.24
C_{10} Isomers	.244	.274	.201	.247	.285	.187
n-Undecane	.417	.395	.437	.398	.342	.260
1+2 Undecenes	1.44	1.48	1.76	1.45	1.31	1.17
C_{11} Isomers	.238	.254	.224	.258	.267	.211
C_2-C_4	21.9	22.6	22.4	24.5	25.5	26.7
C_5-C_{11}	21.4	22.4	23.7	24.1	24.8	25.3
C_{12}+	50.9	49.2	48.2	45.2	43.2	41.0
Wax[d]	31.2	27.3	29.9	27.0	38.5[e]	24.7

[d] Unrecovered products from wax analysis

[e] Unanalyzed wax collected from hot trap

Table VI-3 (cont'd). Summary of results for fixed bed run FB 66 1948.

Period	7	8	9	10	11	12
Weight % of Hydrocarbons						
CH4	5.98	8.07	8.03	6.50	8.62	6.07
Ethane	2.66	2.97	2.83	2.25	3.57	1.91
Ethylene	4.22	5.86	6.01	5.39	5.19	5.66
Propane	1.03	1.49	1.46	1.05	1.10	1.15
Propylene	8.23	9.85	9.76	8.17	9.68	7.91
n-Butane	.953	1.35	1.31	.928	1.02	1.05
1+2 Butenes	6.14	7.23	7.07	5.93	6.95	6.04
C_4 Isomers	.541	.059	.642	.548	.627	.584
n-Pentane	1.37	1.74	1.69	1.34	1.52	1.49
1+2 Pentenes	5.14	6.00	5.85	5.11	5.74	5.38
C_5 Isomers	.334	.422	.405	.304	.370	.317
n-Hexane	.587	.786	.700	.605	.606	.715
1+2 Hexenes	3.20	3.45	3.14	3.25	3.44	3.49
C_6 Isomers	.574	.715	.673	.640	.805	.833
n-Heptane	.531	.575	.497	.459	.474	.524
1+2 Heptenes	2.70	2.38	2.09	2.27	2.32	2.47
C_7 Isomers	.416	.557	.434	.431	.543	.584
n Octane	.604	.464	.489	.424	.455	.376
1+2 Octenes	2.85	1.84	1.96	1.95	2.14	1.70
C_8 Isomers	.348	.182	.500	.343	.489	.400
n Nonane	.646	.427	.466	.380	.410	.161
1+2 Nonenes	2.67	1.46	1.71	1.61	1.66	.593
C_9 Isomers	.305	.237	.198	.251	.373	.0564
n Decane	.657	.430	.469	.405	.422	.197
1+2 Decenes	2.51	1.32	1.63	1.65	1.54	.691
C_{10} Isomers	.351	.276	.239	.348	.420	.110
n-Undecane	.657	.415	.431	.377	.406	.188
1+2 Undecenes	2.27	1.23	1.41	1.48	1.33	.728
C_{11} Isomers	.331	.257	.273	.410	.419	.133
C_2-C_4	23.8	29.4	29.1	24.3	28.2	24.3
C_5-C_{11}	29.1	25.2	25.2	24.0	25.9	21.1
C_{12}+	41.2	37.4	37.7	45.2	37.3	48.5
Wax[d]	24.1	23.2	23.8	29.9	25.2	33.1

[d] Unrecovered products from wax analysis

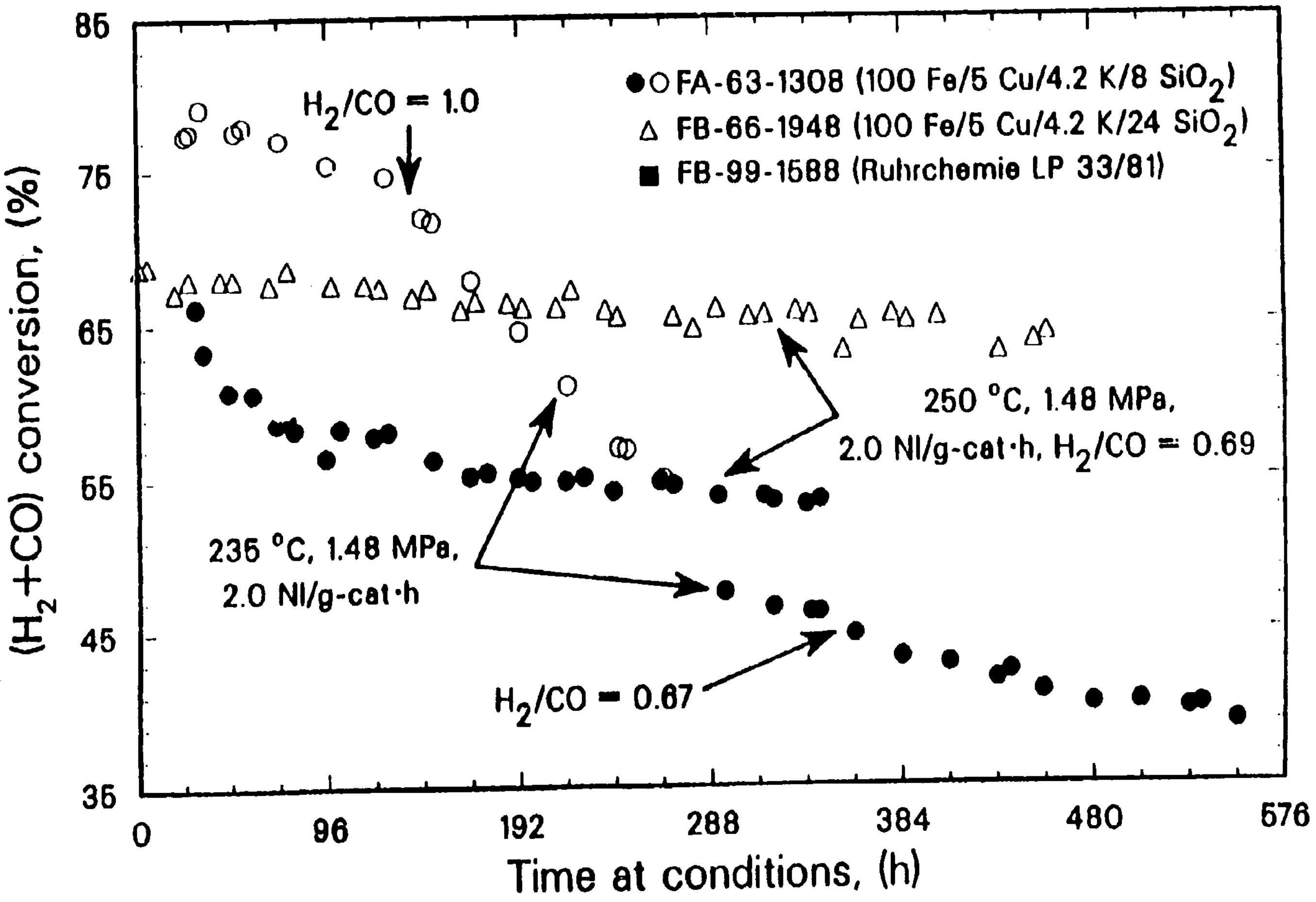

Figure VI-9. Stability plot, (H_2+CO) conversion versus time on stream, for run FB-66-1948 (100 Fe/5.0 Cu/4.2 K/24 SiO_2) and comparison to runs FB-99-1588 (Ruhrchemie LP 33/81) and FA-63-1308 (100 Fe/5.0 Cu/4.2 K/8 SiO_2).

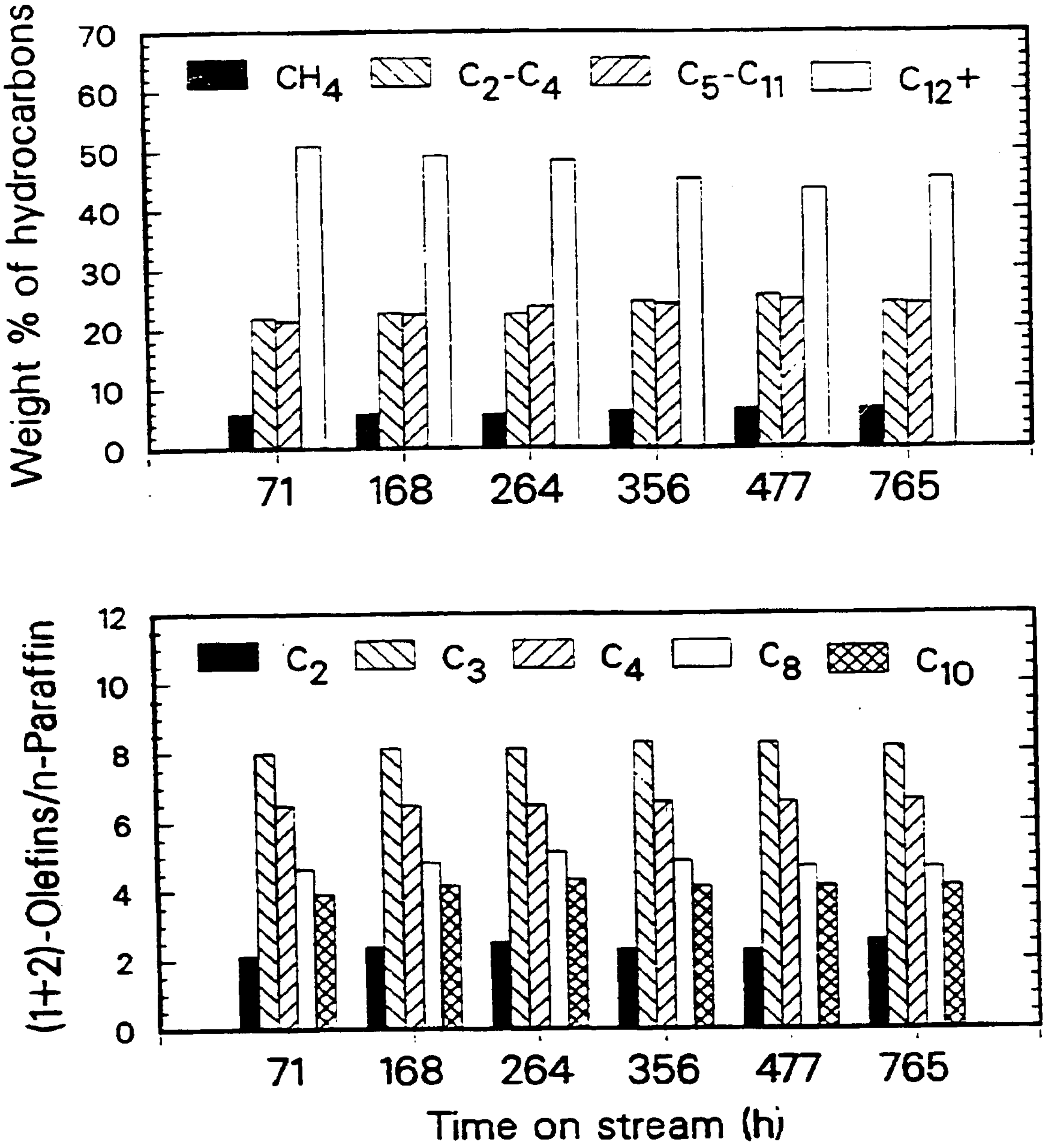

Figure VI-10. Effect of time on stream on catalyst selectivity for run FB-66-1948 (100 Fe/5.0 Cu/4.2 K/24 SiO_2). (250 °C. 1.48 *MPa*. 2.0 *Nl/g*-cat-*h*. $H_2/CO = 0.69$).

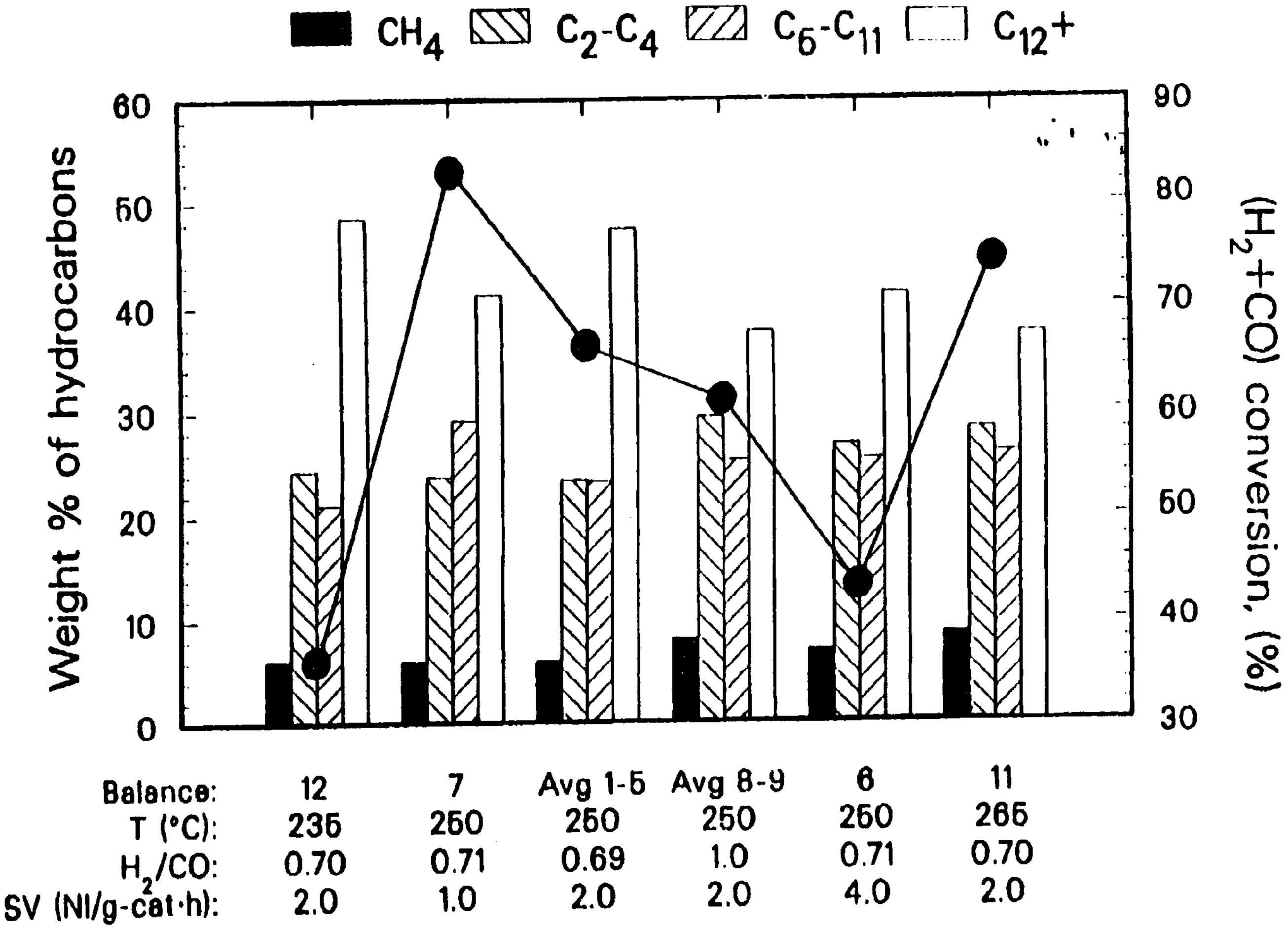

Figure VI-11. Effect of process conditions on catalyst activity and selectivity for run FB 66 1948 (100 Fe/5.0 Cu/4.2 K/24 SiO$_2$).

of deactivation on selectivity. Deactivation causes more methane to be formed. For example, in balances 12, 10, and 11 at 235, 250, and 265°C, respectively, CH_4 increases from 6.1 to 6.5 and 8.6 % while $C_{12}+$ decreases from 48.5 to 45.2 and 37.3 %. The space velocity was varied at 250°C in balances 7, 1–5, and 6 at 1.0, 2.0, and 4.0 Nl / g–cat·h. Conversion decreased with higher space velocity, and there was no clear effect on the hydrocarbon distribution. The CH_4 and C_2–C_4 fractions remained fairly constant, while shifting occurred between the C_5–C_{11} and C_{12}– products. The conversion using a higher H_2/CO feed ratio was lower than the initial conversion, decreasing from an average 66 % (balances 1–5, $H_2/CO=0.69$) to 60.6 % (balances 8–9, $H_2/CO=1.0$), but this may be due to catalyst deactivation. The (H_2+CO) conversion obtained in balance 10 at the same conditions with $H_2/CO=0.70$ was only 57.7 %. Less C_{12}– products and more gaseous hydrocarbons were produced using the $H_2/CO=1$ feed ratio than in any of the balances (1–5, 10) using the lower feed ratio, which we have also observed in tests with other catalysts.

The selectivities obtained during the stability test of the 24 parts SiO_2 catalyst are compared to those obtained in the stability tests of 8 parts SiO_2 catalyst and Ruhrchemie LP 33/81 catalyst (runs FA–63–1308 and FB–99–1588) in Fig.VI-12. Lower silica concentration improves production of C_{12}– products and decreases the fractions of CH_4 and C_2–C_4. Similar results were obtained during the initial tests of these catalysts. The 8 parts SiO_2 catalyst also had higher initial activity, but it deactivated more rapidly than the catalyst with 24 parts SiO_2. The selectivities of the 24 parts SiO_2 catalyst and the Ruhrchemie catalyst are very similar, while our catalyst is more stable.

VI.2. Fixed Bed Reactor Tests with Unsupported Precipitated Iron Catalysts

VI.2.1. Runs FA – 15 – 1698 / FA – 15 – 1768 with the 100 Fe / 1 Cu / 0.2 K Catalyst

Runs FA-15-1698 and FA-15-1768 were made to evaluate the performance of a precipitated catalyst (100 Fe/1 Cu/0.2 K) over the long period of time in a fixed bed reactor. For both runs, 30/60 mesh catalysts were employed and the catalyst was reduced with CO at 280°C for 16 h. Following the activation treatment, the catalyst was tested at a fixed set of operating conditions (235°C, 1.48 MPa, 2.0 Nl / g–cat·h, $H_2/CO=0.71$). Rapid deactivation occurred during both tests. Only a single mass balance was completed in run FA–15–1698 before it was terminated due to the deactivation. During the retest, run FA–15–1768, 6 mass balances were completed. The first two mass balances (up to 175 h) were made at the conditions above, and balances 3 and 4 (up to 367 h) were made using $H_2/CO=1.03$ feed gas. During balances 5

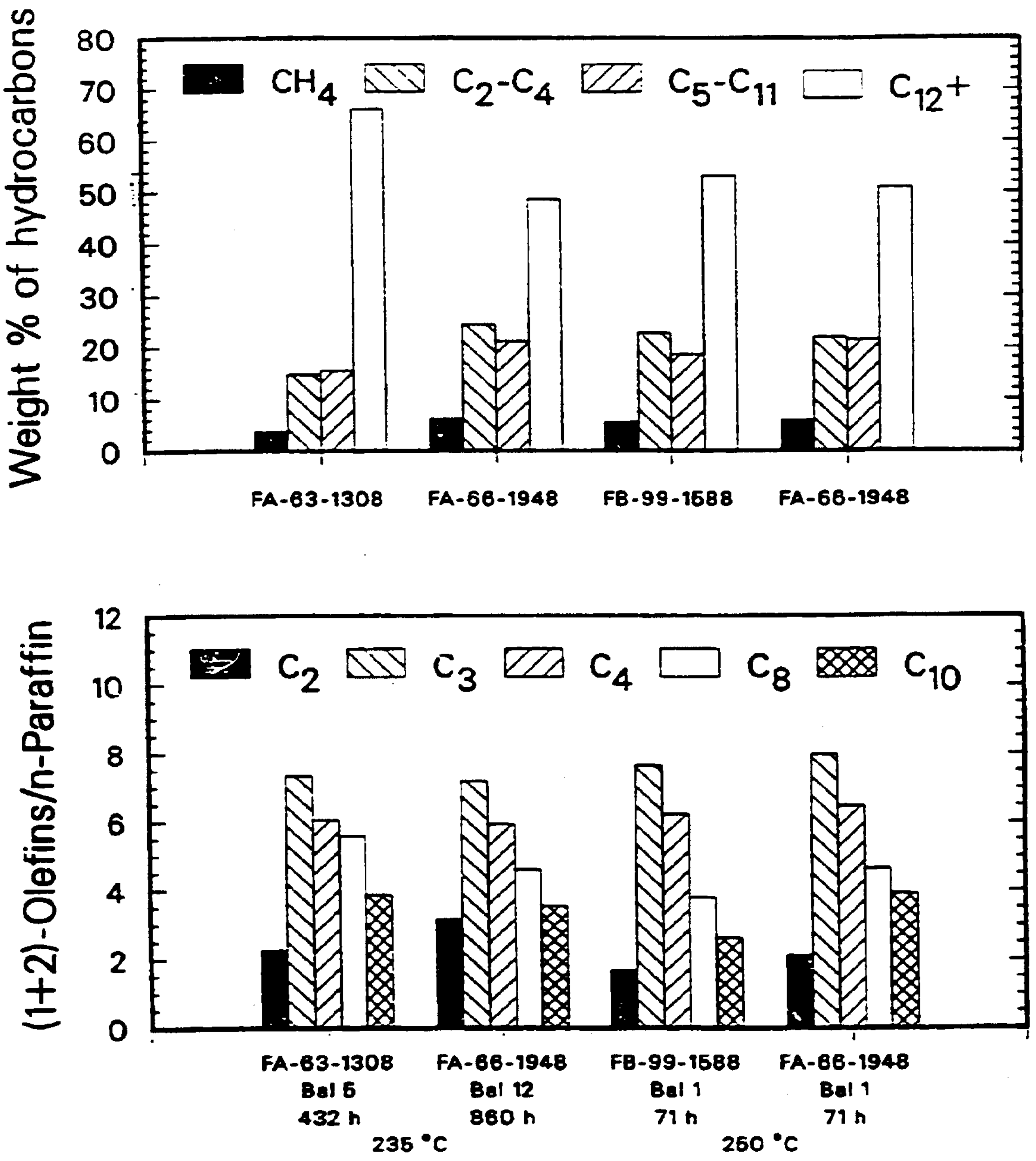

Figure VI-12. Comparison of catalyst selectivity for 100 Fe/5.0 Cu/4.2 K/8 and 24 SiO_2 catalysts and Ruhrchemie LP 33/81. (2.0 *Nl/g*–cat-*h*, 1.48 *MPa*. H_2/CO = 0.67 nominal).

Table VI 1. Summary of results for fixed bed runs FA 15 1698 and FA 15 1768

Catalyst: 100 Fe/1.0 Cu/0.2 K, 4.50 g^a (FA 15 1698), 3.40 g^a (FA-15-1768)
Diluent: Glass beads, 35.5 g (FA-15-1698), 30.0 g (FA-15-1768)
Catalyst volume. 3.60 cc (FA-15-1698), 3.00 cc (FA-15-1768) Diluent Volume: 23.0 cc (FA-15-1698), 24.0 cc (FA-15-1768)

Run	FA-15-1698	FA-15-1768					
Period	1	1	2	3	4	5	6
Date	6/19/88	6/27/88	7/1/88	7/5/88	7/9/88	7/13/88	7/15/88
Time on Stream (*h*)	39.5	72.0	168.0	263.5	359.0	456.0	505.0
Balance Duration (*h*)	7.5	6.8	7.5	7.1	7.8	7.0	7.2
Average Temperature (°C)	235.	234.	235.	235.	235.	250.	250.
Maximum Δ Temperature (°C)[b]	2.10	3.30	3.30	2.90	2.60	1.60	2.10
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.712	.712	.712	1.03	1.03	.712	.712
Space Velocity (Nl/g-cat·h)[a]	2.01	2.00	2.00	2.00	2.00	2.00	2.00
Space Velocity (Nl/g-Fe·h)	2.91	2.89	2.89	2.89	2.89	2.89	2.89
GHSV (h^{-1})[c]	330.	252.	252	252.	252.	252.	252.
CO Conversion (%)	52.3	38.2	29.5	31.8	29.0	34.0	32.3
H_2+CO Conversion (%)	52.6	41.1	31.3	29.8	26.5	32.7	31.6
H_2/CO Usage	.720	.840	.820	.900	.860	.650	.670
STY (mols H_2+CO/g-cat·h)[a]	.047	.037	.028	037	.024	.029	.028
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	2.50	1.30	1.20	1.70	1.90	3.40	3.60
Weight % of Outlet							
H_2	2.30	2.70	3.24	5.04	5.33	3.41	3.40
H_2O	4.08	4.64	4.03	4.49	3.71	2.10	1.87
CO	45.4	39.3	67.4	64.1	67.2	63.4	61.6
CO_2	35.1	23.2	17.0	17.5	15.9	23.1	22.4
Hydrocarbons	7.19	6.19	4.89	5.45	5.13	5.00	5.21
Oxygenates	0.48	0.58	0.40	0.51	0.38	0.25	0.25
Wax[d]	5.42[e]	3.43	2.97	2.88	2.34	2.68	2.31
Yield (g/Nm^3 H_2 + CO *Converted*)							
CH_4	8.67	7.18	6.54	8.29	8.56	10.5	10.5
C_2-C_4 Hydrocarbons	39.4	32.7	29.4	34.0	34.3	36.5	36.2
C_5-C_{11} Hydrocarbons	45.7	37.5	34.0	33.9	31.4	31.0	33.2
C_{12}+ Hydrocarbons	90.1	101.	121.	106.	108.	101.	102.
Wax[d]	79.0[e]	63.5	72.3	63.2	57.3	62.3	56.0
Oxygenates	7.07	10.7	9.84	11.2	9.21	5.90	6.17
Total	191.	189.	201.	194.	192.	185.	188.
1+2 Olefins/n-Paraffin Ratio							
C_2	2.37	3.15	3.09	2.30	2.24	1.79	1.80
C_3	8.02	8.00	7.40	6.22	6.18	7.32	7.62
C_4	6.74	6.33	6.18	5.24	5.20	6.56	6.89
C_8	5.02	4.90	5.15	4.14	4.31	5.17	5.35
C_{10}	4.75	4.00	4.05	3.60	3.08	4.80	4.52

[a] Based on unreduced catalyst
[b] Maximum axial temperature difference
[c] Based on catalyst volume
[d] Unrecovered products from wax analysis
[e] Unanalyzed products collected from hot trap

Table VI-4 (cont'd). Summary of results for fixed bed runs FA 15 1608 and FA 15 1768.

Run	FA-15-1608	FA-15-1768					
Period	1	1	2	3	4	5	6
Weight % of Hydrocarbons							
CH4	4.72	4.03	3.42	4.51	4.08	5.87	5.78
Ethane	1.80	1.37	1.21	1.83	1.91	2.40	2.31
Ethylene	4.17	4.01	3.49	3.03	3.08	4.01	3.88
Propane	.93	.78	.69	1.00	1.00	.93	.88
Propylene	7.12	5.98	4.90	5.91	5.90	6.47	6.39
n-Butane	.89	.80	.67	.90	.91	.80	.75
1+2 Butenes	5.80	4.89	3.98	4.54	4.56	5.09	4.97
C_4 Isomers	.61	.51	.41	.50	.51	.73	.70
n-Pentane	1.40	1.24	1.03	1.25	1.27	1.26	1.21
1+2 Pentenes	5.37	4.65	3.78	4.11	4.13	4.65	4.57
C_5 Isomers	.30	.25	.22	.20	.31	.31	.20
n-Hexane	.64	.58	.54	.65	.56	.48	.50
1+2 Hexenes	3.24	3.01	2.78	2.88	2.54	2.37	3.20
C_6 Isomers	.68	.61	.50	.69	.54	.07	.73
n-Heptane	.48	.38	.37	.41	.37	.29	.31
1+2 Heptenes	2.33	1.94	1.83	1.76	1.55	1.34	1.68
C_7 Isomers	.49	.41	.50	.35	.31	.54	.67
n-Octane	.41	.26	.24	.36	.22	.16	.17
1+2 Octenes	2.03	1.24	1.22	1.45	.93	.82	.91
C_8 Isomers	.36	.09	.05	.15	.06	.07	.10
n-Nonane	.36	.31	.18	.21	.16	.17	.16
1+2 Nonenes	1.78	1.31	.94	.81	.77	.89	.77
C_9 Isomers	.20	.11	.05	.05	.05	.07	.06
n-Decane	.40	.41	.31	.31	.30	.25	.23
1+2 Decenes	1.85	1.69	1.42	1.11	1.18	1.20	1.01
C_{10} Isomers	.29	.24	.12	.10	.11	.12	.11
n-Undecane	.35	.42	.35	.34	.35	.28	.25
1+2 Undecenes	1.58	1.57	1.55	1.17	1.29	1.23	1.07
C_{11} Isomers	.31	.29	.20	.14	.15	.19	.15
C_2-C_4	21.4	18.3	15.3	18.6	18.8	20.4	19.9
C_5-C_{11}	21.9	21.0	18.2	18.6	17.2	17.4	18.3
C_{12}+	40.0	56.6	63.0	58.3	59.4	50.3	50.1
Wax[d]	43.0[e]	35.6	37.8	31.6	31.3	34.9	30.7

[d] Unrecovered products from wax analysis

[e] Unanalyzed wax collected from hot trap

and 6 (up to 511 h), the temperature was increased to 250°C and a $H_2/CO=0.71$ feed gas was used. The results for both runs FA–15–1698 and FA–15–1768 are summarized in Table VI-4.

With the exception of run FA–15–2097 (Section V.2.2), the 100 Fe/1.0 Cu/0.2 K catalyst deactivated quickly during catalyst testing. In the last two tests, the initial activity of the catalyst was high, but decreased with time. The stability plot for the two runs is shown in Fig. VI-13. In run FA–15–1768, the (H_2-CO) conversion dropped from 59.1 % at 25.5 h to 31.2 % at 175 h. Switching to an $H_2/CO=1.03$ synthesis gas increased conversion slightly to 33.7 % at 191 h, but the catalyst continued to deactivate. At these same nominal conditions (235°C, 1.48 MPa, 2.0 Nl / g–cat·h, $H_2/CO=1.0$) during the successful run FA–15–2097, the H_2/CO conversion was 72.9 %. The increase in temperature to 250°C at about 392 h increased the conversion to only 34.5 %.

Product selectivities obtained from these two tests (FA–15–1698/FA–15–1768) of the 100 Fe/1.0 Cu/0.2 K catalyst are shown in Fig. VI-14 (235°C, $H_2/CO=0.71$). The hydrocarbon selectivity during the first test was more towards lower molecular weight hydrocarbons than that obtained during the retest, and the $C_{12}-$ weight percent decreased from 63 % to 49 % (balance 1) between the two runs. A comparison of the selectivity for run FA–15–1768 and the two previous tests (FA–15–2097, Technical Progress Report for 1 July–30 September 1987; FA–15–0278, Technical Progress Report for 1 January–31 March 1988) is shown in Fig. VI-15 (235°C, $H_2/CO=1.0$, nominal). The test results from FA-15-1768 show higher selectivity to high molecular weight products with a substantially greater $C_{12}-$ fraction of hydrocarbons. The olefin/paraffin ratios are also higher than in previous tests, although this may be due to the deactivation of the catalyst. The (H_2+CO) conversions for the four balances shown in Fig. VI-15 were 29.8 (balance 3) and 26.5 % (balance 4) in run FA–15–1768, 72.9 % in run FA–15–2097, and 44.7 % in run FA–15–0278, and the differences in conversion may have affected the olefin/paraffin ratios. There was no significant effect of time on stream on the weight percent hydrocarbon distribution during Run FA–15–1768 at any of the 3 sets of conditions used.

VI.2.2. Runs FB – 27 – 2438 / FA – 27 – 2518 with the 100 Fe / 3.0 Cu / 0.5 K Catalyst

Runs FB–27–2438 and FA–27–2518 were made as long term stability tests of the 100 Fe/3.0 Cu/0.5 K catalyst. This catalyst was tested previously during the Promoter Effect Research portion of this investigation in runs FA–27–2557 and FB–27–3368 (Technical Progress Reports for 1 July–30 September 1988 and 1 October - December 31, 1988, respectively. Also, see Sections V.2.1.3 and V.2.3). The two most recent runs differed in the procedure used to acti-

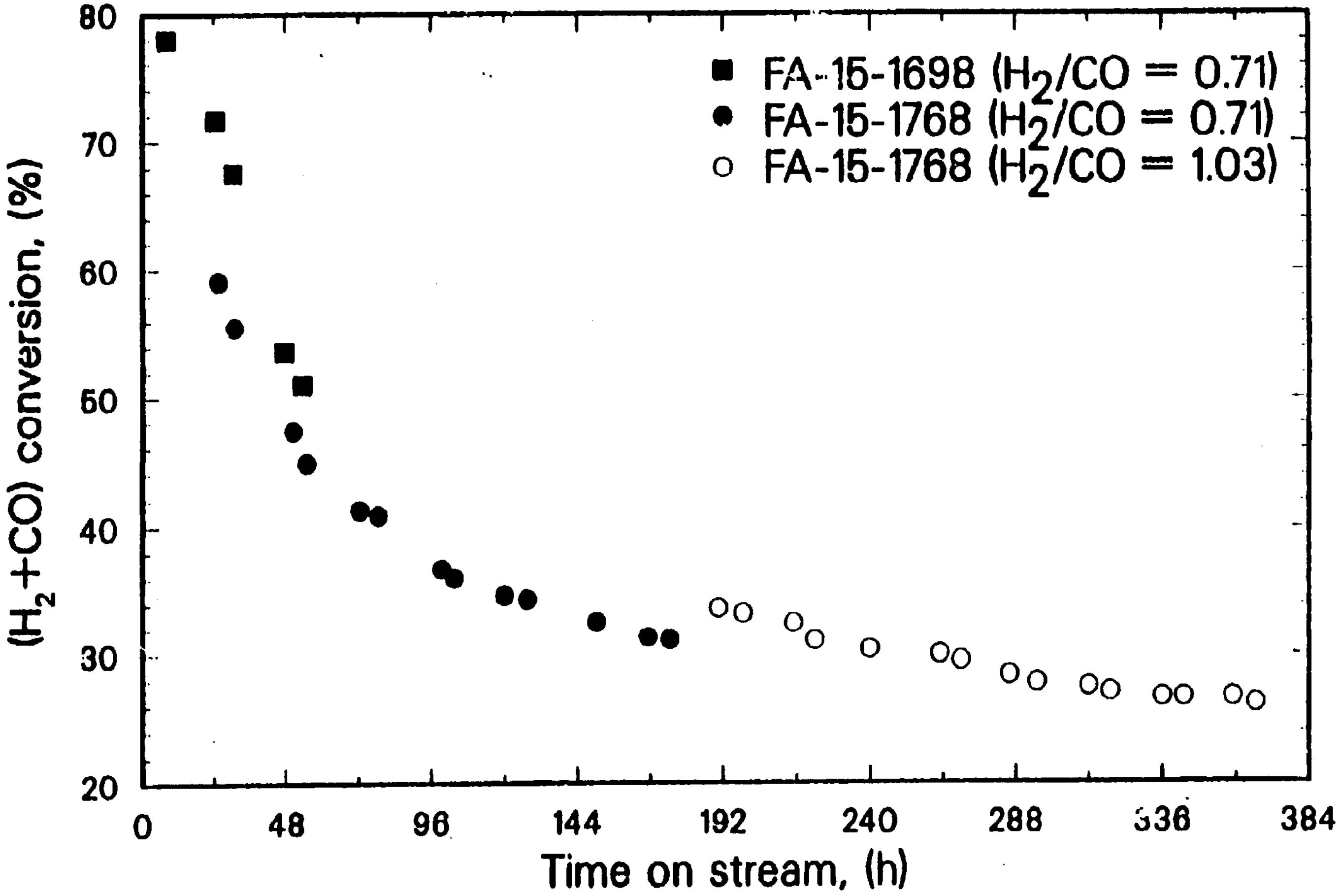

Figure VI-13. Stability plot, (H_2+CO) conversion versus time on stream, for runs FA-15-1698 and FA-15-1768 (100 Fe/1.0 Cu/0.2 K catalyst, 235 °C, 1.48 *MPa*, 2.0 *Nl/g cat·h*).

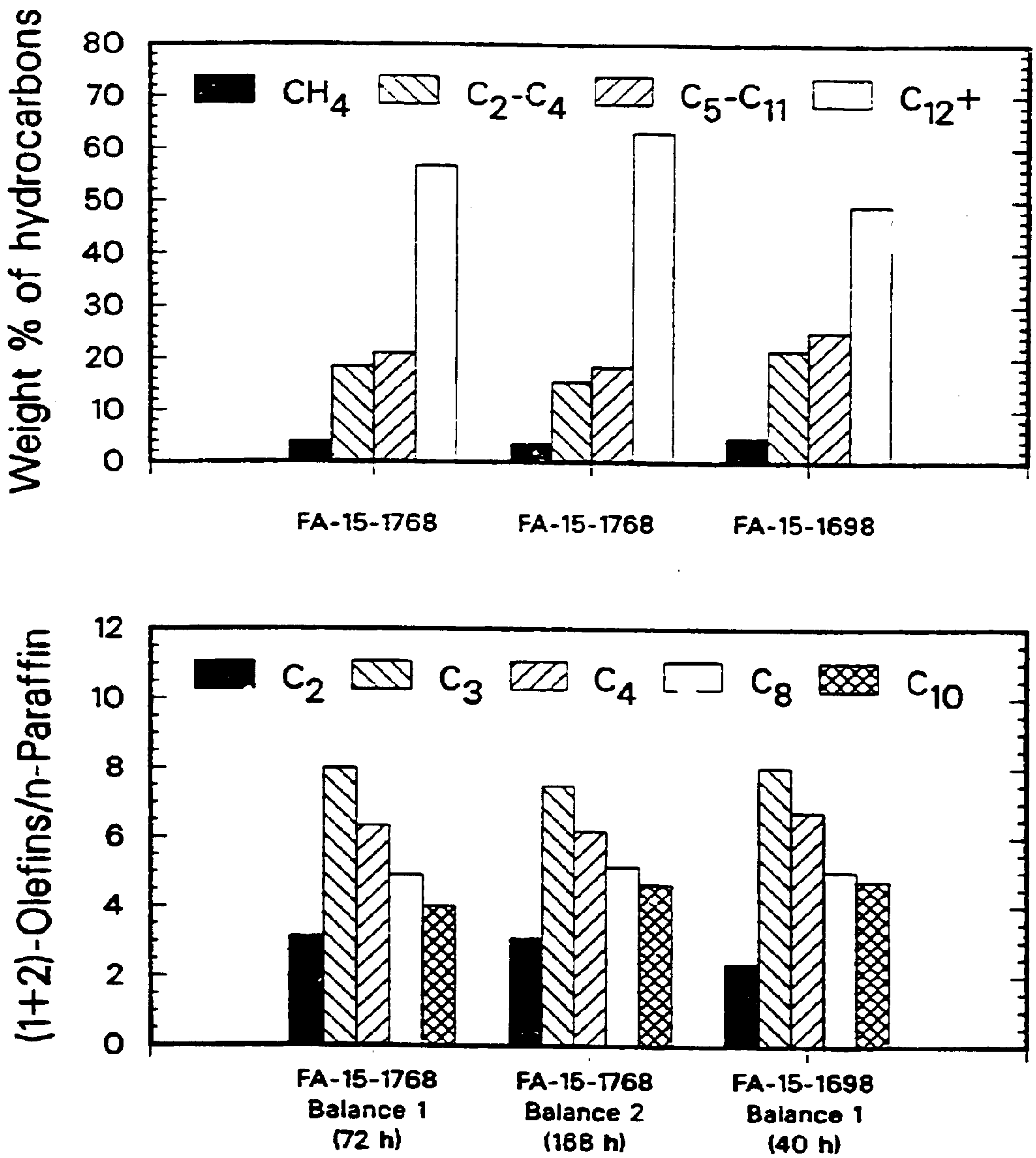

Figure VI-14. Comparison of catalyst selectivity in runs FA-15-1698 and FA-15-1768 (100 Fe/1.0 Cu/0.2 K catalyst, 235 °C, 1.48 *MPa*, 2.0 *Nl/g*-cat-*h*, $H_2/CO = 0.71$).

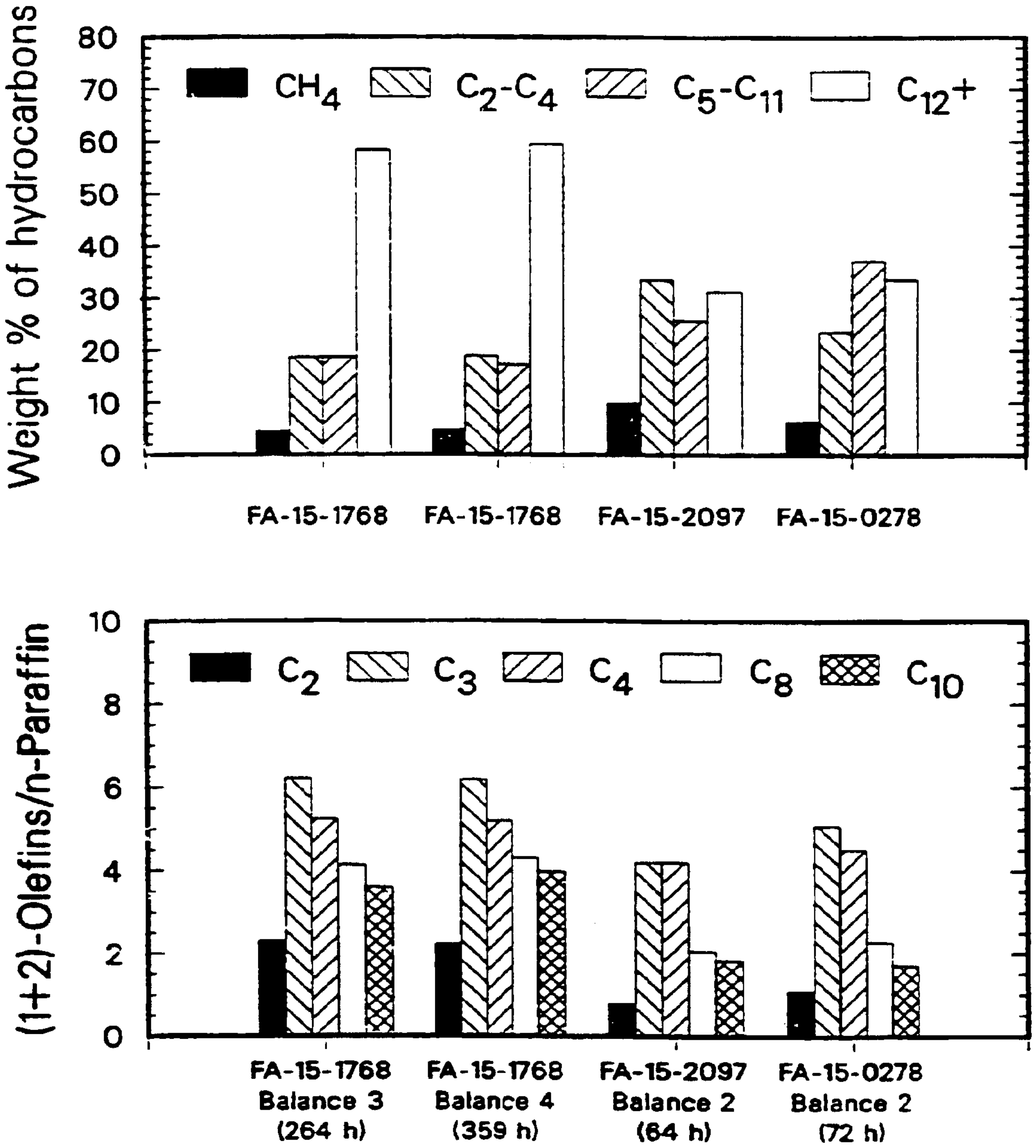

Figure VI-15. Selectivity comparison for fixed bed tests of 100 Fe/1.0 Cu/0.2 K catalyst (235 °C, 1.48 *MPa*, 2.0 *Ni/g*–cat·*h*. $H_2/CO = 1.0$).

vate the catalyst. In both runs, the reductant used was CO at ambient pressure, and the catalyst was ground to 30/60 mesh and diluted with glass beads before loading the reactor. In run FB-27-2438, the catalyst was reduced at 280°C for 12 h. After the 12 h pretreatment, the reactor was cooled to 260°C in helium (4.0 Nl / g-cat·h), and the reactor pressure was increased to 1.48 MPa. Synthesis gas (H_2/CO=0.69) was then introduced while continuing to feed He, and the syngas flow rate was gradually increased from 0.5 to 2.0 Nl / g-cat·h over a 4 h period. After the full syngas flow was established, the He flow was phased out over a 2.5 h period. A hot spot (280°C) developed about 15 cm below the top of the bed after the He flow was discontinued, and He was reintroduced at 0.7 Nl / g-cat·h to cool the reactor. After 17 h at these conditions, the He was again discontinued and the stability run was begun (260°C, 1.48 MPa, H_2/CO=0.69, 2.0 Nl / g-cat·h). In run FA-27-2518, the catalyst was reduced at 335°C for 24 h, which is similar to the optimum procedure studied by Pichler (Anderson, 1956, pp 176-180). This procedure was reported to give high activity and stability over a long period of time.

Three mass balances were performed during run FB-27-2438 and the results are summarized in Table VI-5. The results for the two mass balances performed during run FA-27-2518 are summarized in Table VI-6. All balances were performed at 260°C, 1.48 MPa, 2.0 Nl / g-cat·h, using an H_2/CO=0.67 (nominal) feed gas. The stability plot for both runs is shown in Fig. VI-16. The catalyst activated at 335°C for 24 h (FA-27-2518) deactivated rapidly, with the (H_2+CO) conversion dropping from an initial 74.2 % to 47.2 % at 143 h at conditions. The conversion for catalyst activated at 280°C for 12 h (FB-27-2438) initially increased to a maximum 88.2 % at 7.5 h at conditions, then began deactivating. The deactivation was less severe than during run FA-27-2518 and the conversion was still 72 % at 143 h. After 265 h, the (H_2+CO) conversion dropped to 66.7 %.

The hydrocarbon selectivity and olefin/paraffin ratios as a function of time are compared in Fig. VI-17 for both runs. During run FB-27-2438, the weight percent hydrocarbon distribution shifted towards lower molecular weight products as the catalyst deactivated with time. The shift to lighter products was not significant during run FA-27-2518, although the catalyst was already deactivated during both balances (the average conversions were 57.5 and 47.3 %, respectively, during the two balances). No strong trend in the olefin/paraffin ratios occurred for either catalyst test. While it is difficult to distinguish between the effects of deactivation and reduction procedure in these two runs, it appears that the higher reduction temperature

Table VI-5. Summary of results for fixed bed run FB–27–2438. Catalyst reduced using CO at 280 °C for 12 *h*. 3.0 *Nl*/*g*–cat·*h*.

Catalyst: 3.80 g^c. 100 Fe/3.0 Cu/0.5 K
Catalyst volume: 3.40 *cc*

Diluent: 38.1 *g*. Glass beads
Diluent Volume: 25.0 *cc*

Period	1	2	3
Date	09/02/88	09/06/88	09/10/88
Time on Stream (*h*)	72.0	167.0	264.0
Balance Duration (*h*)	6.8	7.0	6.8
Average Temperature (°C)	260.	260.	260.
Maximum Δ Temperature (°C)[b]	3.00	2.00	2.00
Pressure (*MPa*)	1.48	1.48	1.48
H_2/CO Feed Ratio	.704	.704	.704
Space Velocity (*Nl*/*g*–cat·*h*)[a]	2.01	2.01	2.01
Space Velocity (*Nl*/*g*–Fe·*h*)	2.95	2.95	2.95
GHSV (h^{-1})[c]	268.	268.	268.
CO Conversion (%)	83.3	76.5	72.3
H_2+CO Conversion (%)	78.4	72.1	67.8
H_2/CO Usage	.604	.606	.598
STY (*mols* H_2+CO/*g*–cat·*h*)[a]	.070	.065	.061
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	15.2	12.8	17.5
Weight % of Outlet			
H_2	1.36	1.63	1.84
H_2O	1.97	1.81	1.23
CO	15.7	22.2	26.2
CO_2	60.8	55.6	53.7
Hydrocarbons	14.4	15.0	14.4
Oxygenates	.408	.302	.236
Wax[d]	5.37	3.47	2.41
Yield (*g*/*Nm*^{3} H_2 + CO *Converted*)			
CH_4	12.6	14.4	15.4
C_2–C_4 Hydrocarbons	49.8	53.7	55.3
C_5–C_{11} Hydrocarbons	63.4	74.2	74.3
C_{12}+ Hydrocarbons	70.2	56.8	47.7
Wax[d]	53.3	37.4	27.7
Oxygenates	4.05	3.25	2.71
Total	200.	202.	195.
1+2 Olefins/*n*–Paraffin Ratio			
C_2	1.25	.974	1.00
C_3	8.31	7.04	7.28
C_4	7.27	6.01	6.11
C_8	4.58	3.18	3.09
C_{10}	3.74	2.40	2.25

[a] Based on unreduced catalyst

[b] Maximum axial temperature difference

[c] Based on catalyst volume

[d] Unanalyzed products collected from hot trap

Table VI-5 (cont'd). Summary of results for fixed bed run FB-27-2438. Catalyst reduced using CO at 280 °C for 12 *h*. 3.0 *Nl*/*g*–cat·*h*.

Period	1	2	3
Weight % of Hydrocarbons			
CH4	6.41	7.25	7.99
Ethane	3.34	3.83	4.06
Ethylene	3.90	3.48	3.79
Propane	1.10	1.35	1.38
Propylene	8.74	9.04	9.56
n–Butane	.951	1.25	1.32
1+2 Butenes	6.68	7.23	7.77
C_4 Isomers	.709	.780	.826
n–Pentane	1.55	1.90	2.04
1+2 Pentenes	5.82	6.22	6.74
C_5 Isomers	.440	.610	.680
n–Hexane	.622	.918	.807
1+2 Hexenes	3.41	4.03	3.48
C_6 Isomers	.726	.814	.693
n–Heptane	.591	1.000	.864
1+2 Heptenes	2.96	3.50	3.06
C_7 Isomers	.842	1.17	.629
n–Octane	.644	.997	1.15
1+2 Octenes	2.90	3.12	3.50
C_8 Isomers	.785	.696	.706
n–Nonane	.659	1.03	1.30
1+2 Nonenes	2.66	2.75	3.35
C_9 Isomers	.706	.587	.679
n–Decane	.639	1.05	1.30
1+2 Decenes	2.35	2.47	2.87
C_{10} Isomers	.795	.643	.701
n–Undecane	.608	1.04	1.20
1+2 Undecenes	1.97	2.09	2.22
C_{11} Isomers	.668	.620	.589
C_2–C_4	25.4	27.0	28.7
C_5–C_{11}	32.3	37.3	38.6
C_{12}+	35.8	28.5	24.8
Wax[d]	27.2	18.8	14.4

[d] Unanalyzed wax collected from hot trap

Table VI-6. Summary of results for fixed bed run FA-27-2518. Catalyst reduced using CO at 335 °C for 24 h. 3.0 Nl/g–cat·h.

Catalyst: 3.45 g^a, 100 Fe/3.0 Cu/0.5 K
Catalyst volume: 2.50 cc

Diluent: 37.2 g. Glass beads
Diluent Volume: 24.5 cc

Period	1	2
Date	09/10/88	09/14/88
Time on Stream (h)	77.0	166.0
Balance Duration (h)	6.5	6.8
Average Temperature (°C)	260.	260.
Maximum Δ Temperature (°C)[b]	1.80	1.70
Pressure (MPa)	1.48	1.48
H_2/CO Feed Ratio	.639	.639
Space Velocity (Nl/g–cat·h)[a]	2.00	2.00
Space Velocity (Nl/g–Fe·h)	2.95	2.95
GHSV (h^{-1})[c]	256.	256.
CO Conversion (%)	57.6	46.5
H_2+CO Conversion (%)	57.5	47.3
H_2/CO Usage	.637	.667
STY ($mols$ H_2+CO/g–cat·h)[a]	.051	.042
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	5.76	3.53
Weight % of Outlet		
H_2	1.87	2.26
H_2O	1.92	2.31
CO	40.5	51.0
CO_2	42.1	32.3
Hydrocarbons	10.1	8.91
Oxygenates	.274	.265
Wax[d]	3.25	2.95
Yield (g/Nm^3 H_2+CO *Converted*)		
CH_4	18.2	18.7
C_2–C_4 Hydrocarbons	48.7	53.9
C_5–C_{11} Hydrocarbons	51.4	58.4
$C_{12}+$ Hydrocarbons	66.3	70.0
Wax[d]	45.0	50.0
Oxygenates	3.79	4.48
Total	188.	205.
1+2 Olefins/n–Paraffin Ratio		
C_2	1.27	1.40
C_3	7.84	8.11
C_4	7.08	7.41
C_8	4.67	5.51
C_{10}	4.13	4.59

[a] Based on unreduced catalyst

[b] Maximum axial temperature difference

[c] Based on reactor volume

[d] Unanalyzed products collected from hot trap

Table VI-6 (cont'd). Summary of results for fixed bed run FA-27-2518. Catalyst reduced using CO at 335 °C for 24 *h*. 3.0 *Nl*/*g*–cat·*h*.

Period	1	2
Weight % of Hydrocarbons		
CH_4	9.86	9.29
Ethane	3.91	3.98
Ethylene	4.63	5.20
Propane	1.13	1.10
Propylene	8.47	8.51
n–Butane	.959	.900
1+2 Butenes	6.55	6.43
C_4 Isomers	.722	.707
n–Pentane	1.46	1.41
1+2 Pentenes	5.93	7.00
C_5 Isomers	.459	.807
n–Hexane	.586	.475
1+2 Hexenes	3.57	3.53
C_6 Isomers	.660	.805
n–Heptane	.479	.434
1+2 Heptenes	2.66	2.53
C_7 Isomers	.489	.514
n–Octane	.482	.402
1+2 Octenes	2.21	2.18
C_8 Isomers	.511	.497
n–Nonane	.469	.405
1+2 Nonenes	1.97	1.95
C_9 Isomers	.387	.349
n–Decane	.476	.448
1+2 Decenes	1.94	2.02
C_{10} Isomers	.502	.530
n–Undecane	.451	.439
1+2 Undecenes	1.73	1.84
C_{11} Isomers	.425	.491
C_2–C_4	26.4	26.8
C_5–C_{11}	27.8	29.1
C_{12}+	35.9	34.8
Wax[d]	24.4	24.9

[d] Unanalyzed products collected from hot trap

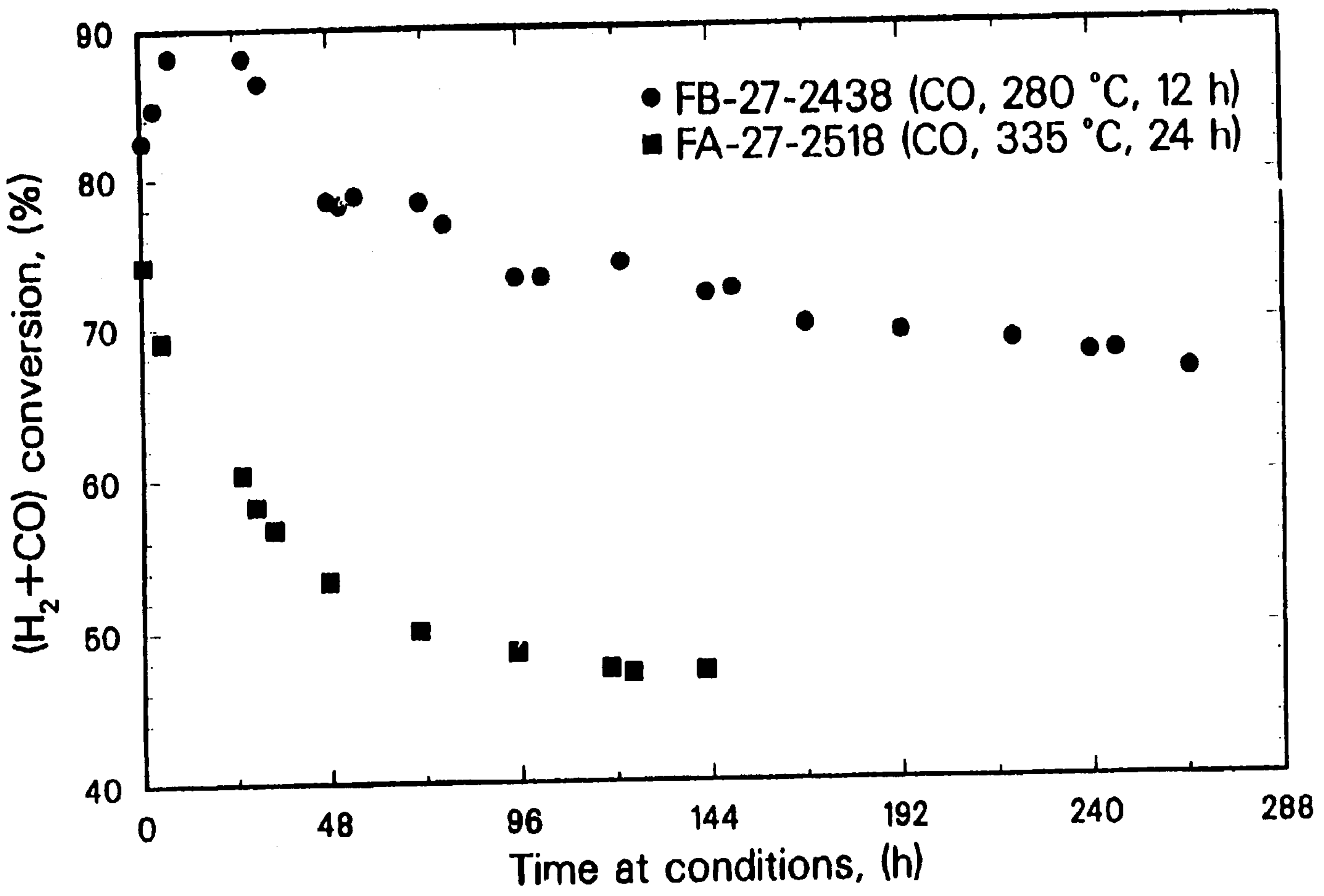

Figure VI-16. Stability plot, (H_2+CO) conversion versus time on stream, for runs FB-27-2438 and FB-27-2518 (100 Fe/3.0 Cu/0.5 K catalyst, 260 °C, 1.48 *MPa*, 2.0 *Nl/g* cat·*h*, H_2/CO = 0.67 nominal).

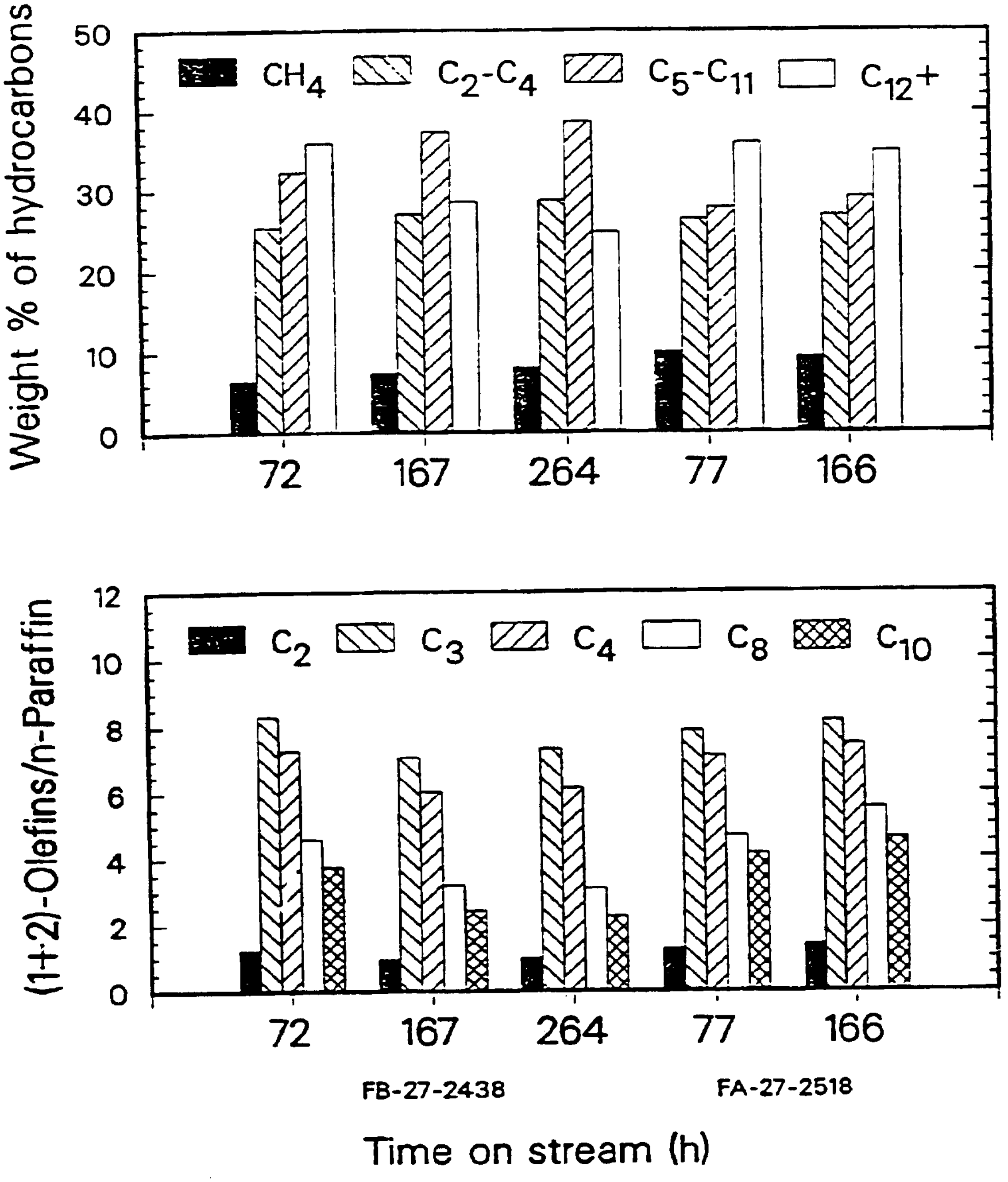

Figure VI-17. Effect of time on stream on catalyst selectivity for runs FB-27-2438 and FB-27-2518 (100 Fe/3.0 Cu/0.5 K catalyst, 260 °C, 1.48 *MPa*, 2.0 *Nl/g-cat-h*, $H_2/CO = 0.67$ nominal).