(335°C, FA–27–2518) causes the catalyst to produce more lower molecular weight products. For example, the lowest methane percentage, 9.3 % (FA–27–2518, balance 2, 166 h), for the high temperature reduction was greater than the highest methane percentage, 8.0 % (FB–27–2438, balance 3, 240 h), for the lower reduction temperature.

VI.3. Stirred Tank Slurry Reactor Test with Silica containing Catalysts

VI.3.1. Run SA – 99 – 0888 with the Ruhrchemie LP 33 / 81 Catalyst

Run SA–99–0888 was a long term test of the commercial, state–of–the–art, Ruhrchemie LP 33/81 catalyst. The calcined catalyst was reduced in situ with CO at 280°C. 34.6 g of the catalyst was charged to the reactor, and purified n–octacosane was used as the initial slurry liquid. The run was divided into two portions: during the first part of the run (up to 343 h on stream), catalyst stability was evaluated at a fixed set of conditions: 250°C, 1.48 MPa, (H_2/CO)=0.67, 2.0 Nl / g–cat·h; during the last part of the run, process conditions were varied to evaluate their effect on catalyst activity and selectivity: 235–265°C, 1.48–2.96 MPa, (H_2/CO) = 0.67–1.0, 1.0–4.0 Nl/g–cat·h. The major events occurring during run SA–99–0888 are summarized in Table VI-7 . Five mass balances were performed during the stability portion of the run and 8 mass balances were performed during the process variable studies. The results obtained during these balances are summarized in Table VI-8.

A stability plot, (H_2+CO) conversion versus time on stream, is shown in Fig. VI-18 for the first part of the run. The catalyst was very stable, and no significant deactivation occurred during 343 h on stream. At 46 h, the (H_2+CO) conversion was 46.0 %, and at 338 h, the conversion was 44.2 %. The conversions obtained during the stability test varied between 42.6 and 46.4 %. Wax was withdrawn after the catalyst activation and at the end of balances 2, 3, 4, and 5 using the external settling tank system. The selectivity of the catalyst changed with time on stream, with more gaseous products formed as the catalyst aged. The effect of time on catalyst selectivity is shown in Fig. VI-19. During balance 1 (49 h) the weight % hydrocarbon distribution was 4.3 CH_4, 17.8 C_2–C_4, 22.1 C_5–C_{11}, and 55.8 % C_{12}+ while during balance 5 (336 h) the distribution was 4.6 CH_4, 21.3 C_2–C_4, 29.5 C_5–C_{11}, and 44.6 % C_{12}+. The olefin/paraffin ratios decreased with time, for example, the C_2 ratio decreased from 1.8 in balance 1 to 1.5 in balance 5. A repeat of the baseline conditions was made in balance 11 (619 h), after 5 balances at different process conditions. The (H_2+CO) conversion dropped to 35.9 % in balance 11, showing that the process variable studies had accelerated deactivation of the catalyst. The trends in selectivity seen in balances 1–5 were also evident

Table VI-7. Major events occurring in run SA-99-0888.

TOS (*h*)	Event
– 17	Catalyst pretreatment: CO, 280 °C, 0.79 *MPa*, 16 *h*.
0	Initiated synthesis gas.
4.0	Achieved desired operating conditions: 250 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 2.0 *Nl/g*–cat·*h*
49.0	Conditions stable, (H_2+CO) conversion = 45.9 %.
94.5	Conditions stable, (H_2+CO) conversion = 46.1 %.
166.5	Conditions stable, (H_2+CO) conversion = 43.1 %.
264.0	Conditions stable, (H_2+CO) conversion = 43.8 %.
336.0	Conditions stable, (H_2+CO) conversion = 44.4 %.
343.0	Changed process conditions: 250 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 4.0 *Nl/g*–cat·*h*
391.0	Changed process conditions: 250 °C, 1.48 *MPa*, (H_2/CO) = 0.65, 1.0 *Nl/g*–cat·*h*
439.0	Changed process conditions: 235 °C, 1.48 *MPa*, (H_2/CO) = 0.65, 2.0 *Nl/g*–cat·*h*
488.0	Changed process conditions: 235 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 1.0 *Nl/g*–cat·*h*
531.0	Changed process conditions: 265 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 2.0 *Nl/g*–cat·*h*
584.0	Changed process conditions: 250 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 2.0 *Nl/g*–cat·*h*
619.0	Replication of initial process conditions: (H_2+CO) conversion = 36.0 %.
627.0	Changed process conditions: 250 °C, 1.48 *MPa*, (H_2/CO) = 1.0, 2.0 *Nl/g*–cat·*h*
699.0	Changed process conditions: 250 °C, 2.96 *MPa*, (H_2/CO) = 1.0, 4.0 *Nl/g*–cat·*h*
721.5	Voluntary termination of run SA-99-0888.

Table VI-8. Summary of results for slurry run SA-09-0888.

Catalyst: 34.0 g[a], LP 33/81

Slurry liquid: 270 g, Purified n-octacosane

Reactor volume: 385 cc[b]

Period	1	2	3	4	5	6	7
Date	3/30/88	4/1/88	4/4/88	4/7/88	4/10/88	4/13/88	4/15/88
Time on Stream (*h*)	49.0	94.5	166.5	264.0	336.0	385.0	385.0
Balance Duration (*h*)	7.0	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	250.	250.	250.	250.	250.
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.667	.667	.667	.667	.667	.667	.652
Space Velocity (*Nl/g-cat·h*)[a]	2.00	2.00	2.00	2.00	2.01	4.00	1.00
Space Velocity (*Nl/g Fe·h*)	3.81	3.81	3.81	3.81	3.82	7.62	1.91
GHSV (h^{-1})[b]	180.	180.	172.	171.	171.	336.	82.9
CO Conversion (%)	42.7	43.2	41.2	41.1	40.4	25.7	50.0
H_2+CO Conversion (%)	45.9	46.1	43.1	43.8	44.4	28.3	56.1
H_2/CO Usage	.790	.779	.740	.774	.835	.835	.655
STY (*mols* H_2+CO/*g·cat·h*)[a]	.041	.041	.038	.039	.040	.050	.025
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	1.21	1.26	1.19	1.35	1.20	.706	2.54
Weight % of Outlet							
H_2	2.33	2.34	2.52	2.45	2.28	3.21	2.01
H_2O	4.86	4.86	5.13	4.31	4.48	4.16	3.60
CO	56.3	55.8	56.0	57.7	57.2	73.2	43.1
CO_2	25.0	25.7	24.2	24.0	23.7	11.8	35.4
Hydrocarbons	5.85	5.63	5.81	6.18	7.34	5.23	10.9
Oxygenates	.505	.407	.552	.643	.366	.252	.676
Wax[c]	5.24	5.24	4.83	4.78	4.61	2.14	4.23
Yield (*g/Nm*^{3} H_2 + CO *Converted*)							
CH_4	7.86	8.33	9.73	9.86	9.67	10.5	12.0
C_2-C_4 Hydrocarbons	32.9	37.5	39.7	42.8	44.9	43.6	55.3
C_5-C_{11} Hydrocarbons	40.7	35.0	41.9	43.8	62.0	61.6	67.4
C_{12}+ Hydrocarbons	103.	98.8	99.8	95.3	93.8	82.8	72.9
Wax[c]	87.1	86.6	86.8	83.6	81.1	57.6	58.2
Oxygenates	8.40	6.72	9.92	11.2	6.44	6.79	9.30
Total	193.	186.	201.	203.	217.	205.	217.
1+2 Olefins/n-Paraffin Ratio							
C_2	1.82	1.68	1.64	1.52	1.45	2.21	.843
C_3	7.51	6.61	7.33	7.02	6.91	7.32	5.73
C_4	6.21	5.61	5.96	5.82	5.58	6.00	4.97
C_8	3.32	3.30	2.89	2.95	2.85	3.39	2.28
C_{10}	2.80	2.77	2.63	2.44	2.36	2.78	1.86

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalysed wax withdrawn from reactor

Table VI-8 (cont'd). Summary of results for slurry run SA-09-0888.

Period	8	9	10	11	12	13
Date	4/17/88	4/19/88	4/21/88	4/23/88	4/25/88	4/27/88
Time on Stream (*h*)	481.5	528.0	571.0	619.0	667.5	715.5
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	235.	235.	265.	250.	250.	250.
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	2.96
H_2/CO Feed Ratio	.652	.667	.667	.669	1.00	1.02
Space Velocity (*Nl/g*-cat·*h*)[a]	2.01	1.00	2.00	2.02	2.02	4.03
Space Velocity (*Nl/g*-Fe·*h*)	3.83	1.91	3.82	3.85	3.86	7.68
GHSV (h^{-1})[b]	165.	82.3	164.	163.	162.	321.
CO Conversion (%)	18.8	30.6	57.3	32.8	48.5	36.6
H_2+CO Conversion (%)	23.0	35.8	50.9	35.0	46.4	39.8
H_2/CO Usage	1.01	.946	.853	.829	.869	1.20
STY (*mole* H_2+CO/*g*-cat·*h*)[a]	.021	.016	.051	.032	.041	.071
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	.418	.706	4.38	1.13	1.05	.590
Weight % of Outlet						
H_2	3.23	2.60	2.06	2.80	4.04	4.11
H_2O	4.26	5.19	2.52	3.97	6.35	8.53
CO	78.9	66.6	41.9	65.7	50.0	62.2
CO_2	7.66	16.5	30.4	18.5	27.0	13.4
Hydrocarbons	4.54	6.65	11.0	6.53	10.0	9.01
Oxygenates	.318	.479	.426	.527	.670	.836
Wax[c]	1.10	2.02	2.63	2.05	1.90	1.91
Yield (*g/Nm*^{3} H_2 + CO *Converted*)						
CH_4	11.1	10.7	15.0	12.8	15.8	11.6
C_2-C_4 Hydrocarbons	57.4	51.1	54.0	52.6	58.3	50.8
C_5-C_{11} Hydrocarbons	70.8	67.9	64.9	59.8	56.1	60.4
C_{12}+ Hydrocarbons	51.8	59.6	49.0	57.6	39.0	50.3
Wax[c]	37.3	44.1	35.3	43.6	27.0	30.3
Oxygenates	10.8	10.5	5.73	11.2	9.49	13.2
Total	202.	200.	180.	194.	179.	186.
1+2 Olefins/*n*-Paraffin Ratio						
C_2	2.19	1.70	.700	1.47	.805	1.44
C_3	6.61	6.58	5.12	6.59	4.86	4.62
C_4	5.33	5.01	4.68	5.43	4.16	3.81
C_6	2.98	2.85	2.23	2.53	2.13	2.50
C_{10}	2.39	2.34	1.71	2.05	1.63	1.92

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalysed wax withdrawn from reactor

Table VI-8 (cont'd). Summary of results for slurry run SA-99-0888

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH4	4.26	4.64	5.09	5.14	4.60	5.30	5.78
Ethane	1.89	2.30	2.40	2.66	2.60	1.97	4.51
Ethylene	3.22	3.70	3.76	3.78	3.62	4.06	3.56
Propane	.709	1.00	.959	1.06	.996	1.02	1.56
Propylene	5.73	6.33	6.71	7.08	6.57	7.14	8.54
n-Butane	.818	1.06	.943	1.09	1.09	1.07	1.35
1+2 Butenes	4.90	5.76	5.42	6.10	5.86	6.17	6.47
C_4 Isomers	.480	.652	.533	.556	.511	.522	.652
n Pentane	1.18	1.22	1.28	1.40	1.39	1.41	1.79
1+2 Pentenes	4.46	4.61	4.62	5.45	5.12	5.41	5.50
C_5 Isomers	.297	.310	.351	.431	.410	.326	.801
n Hexane	.881	.680	1.12	.944	1.34	1.09	1.40
1+2 Hexenes	2.64	1.91	2.62	2.75	4.02	3.96	3.94
C_6 Isomers	.506	.446	.473	.415	.549	.580	.627
n-Heptane	.537	.446	.394	.592	1.00	1.01	1.26
1+2 Heptenes	1.74	1.35	1.62	1.69	2.71	2.97	2.75
C_7 Isomers	.333	.281	.367	.259	.383	.450	.442
n-Octane	.478	.357	.459	.477	.816	.773	1.09
1+2 Octenes	1.66	1.19	1.30	1.38	2.29	2.54	2.44
C_8 Isomers	.242	.111	.558	.159	.281	.230	.419
n Nonane	.462	.436	.438	.498	.745	.707	1.05
1+2 Nonenes	1.46	1.35	1.28	1.34	2.02	2.28	2.16
C_9 Isomers	.0922	.166	.252	.168	.268	.209	.376
n Decane	.639	.573	.565	.628	.870	.883	1.05
1+2 Decenes	1.77	1.57	1.46	1.51	2.02	2.42	1.90
C_{10} Isomers	.135	.149	.335	.232	.301	.257	.457
n-Undecane	.721	.654	.637	.687	.878	.946	1.02
1+2 Undecenes	1.78	1.56	1.43	1.42	1.73	2.22	1.58
C_{11} Isomers	.106	.204	.362	.308	.315	.348	.420
C_2-C_4	17.8	20.9	20.8	22.3	21.3	22.0	26.6
C_5-C_{11}	22.1	19.5	21.9	22.8	29.5	31.0	32.5
C_{12}+	56.8	56.0	52.2	49.7	44.6	41.7	35.1
Wax[c]	47.2	48.2	45.4	43.6	38.6	29.0	28.1

[c] Unanalysed wax withdrawn from reactor

Table VI-8 (cont'd). Summary of results for slurry run SA-99-0888.

Period	8	9	10	11	12	13
Weight % of Hydrocarbons						
CH4	5.83	5.63	8.15	7.00	9.35	6.08
Ethane	3.39	3.31	5.35	3.86	5.78	3.82
Ethylene	6.93	5.26	3.50	5.29	4.66	5.15
Propane	1.42	1.34	1.87	1.42	2.28	2.01
Propylene	8.93	8.38	9.14	8.94	10.5	8.86
n-Butane	1.42	1.38	1.01	1.38	2.07	1.87
1+2 Butenes	7.30	6.70	7.28	7.23	8.31	6.87
C_4 Isomers	.064	.037	.081	.663	.841	.752
n-Pentane	1.85	1.69	2.17	1.02	2.45	2.13
1+2 Pentenes	8.32	6.53	6.68	7.54	7.23	6.80
C_5 Isomers	.978	.670	1.14	.889	1.02	.823
n-Hexane	2.80	1.76	1.70	1.57	1.66	1.53
1+2 Hexenes	5.03	4.24	3.63	4.43	4.07	4.86
C_6 Isomers	.983	.694	.787	.893	.784	.852
n-Heptane	1.05	1.53	1.43	1.06	1.14	1.15
1+2 Heptenes	2.85	3.07	2.62	2.67	2.41	3.02
C_7 Isomers	1.03	.442	.079	.647	.515	.626
n-Octane	.724	1.04	1.05	.779	.894	.962
1+2 Octenes	2.12	2.92	2.29	1.93	1.87	2.36
C_8 Isomers	.283	.288	.507	.334	.393	.398
n-Nonane	.698	.911	1.00	.643	.848	.860
1+2 Nonenes	1.88	2.46	2.03	1.47	1.52	1.82
C_9 Isomers	.280	.310	.535	.256	.383	.308
n-Decane	.809	1.03	1.18	.806	1.000	.983
1+2 Decenes	1.91	2.38	1.98	1.63	1.60	1.86
C_{10} Isomers	.473	.409	.648	.386	.463	.385
n-Undecane	.823	1.05	1.16	.880	1.02	1.04
1+2 Undecenes	1.66	2.01	1.68	1.52	1.39	1.71
C_{11} Isomers	.488	.418	.624	.459	.509	.437
C_2-C_4	30.0	27.0	29.4	28.8	34.5	29.3
C_5-C_{11}	37.0	35.9	35.4	32.7	33.2	34.9
C_{12}+	27.1	31.5	27.0	31.5	23.0	29.1
Wax[c]	10.6	23.3	19.2	23.9	15.9	17.5

[c] Unanalyzed wax withdrawn from reactor

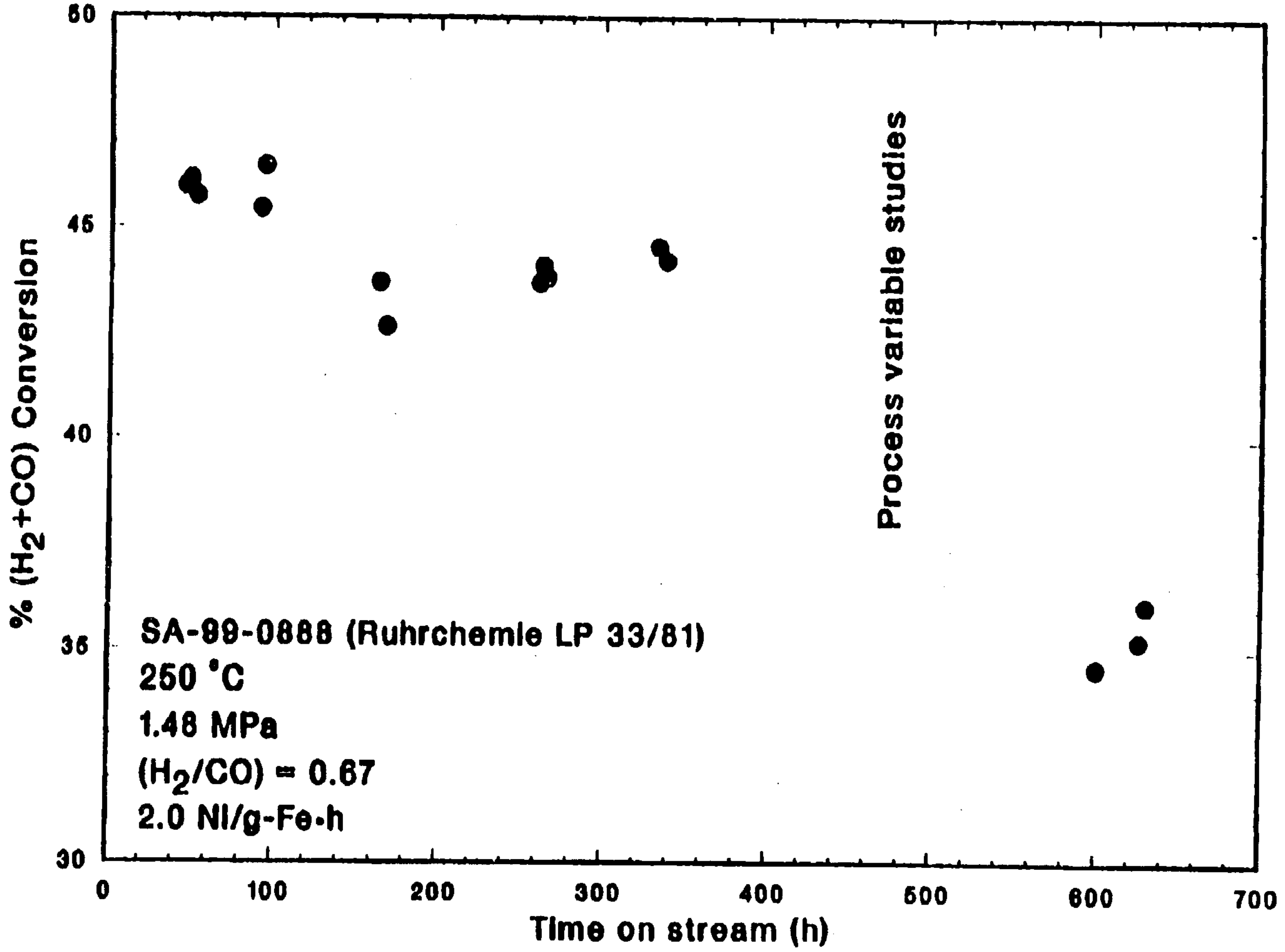

Figure VI-18 . Stability plot, (H_2+CO) conversion versus time on stream, for run SA-99-0888.

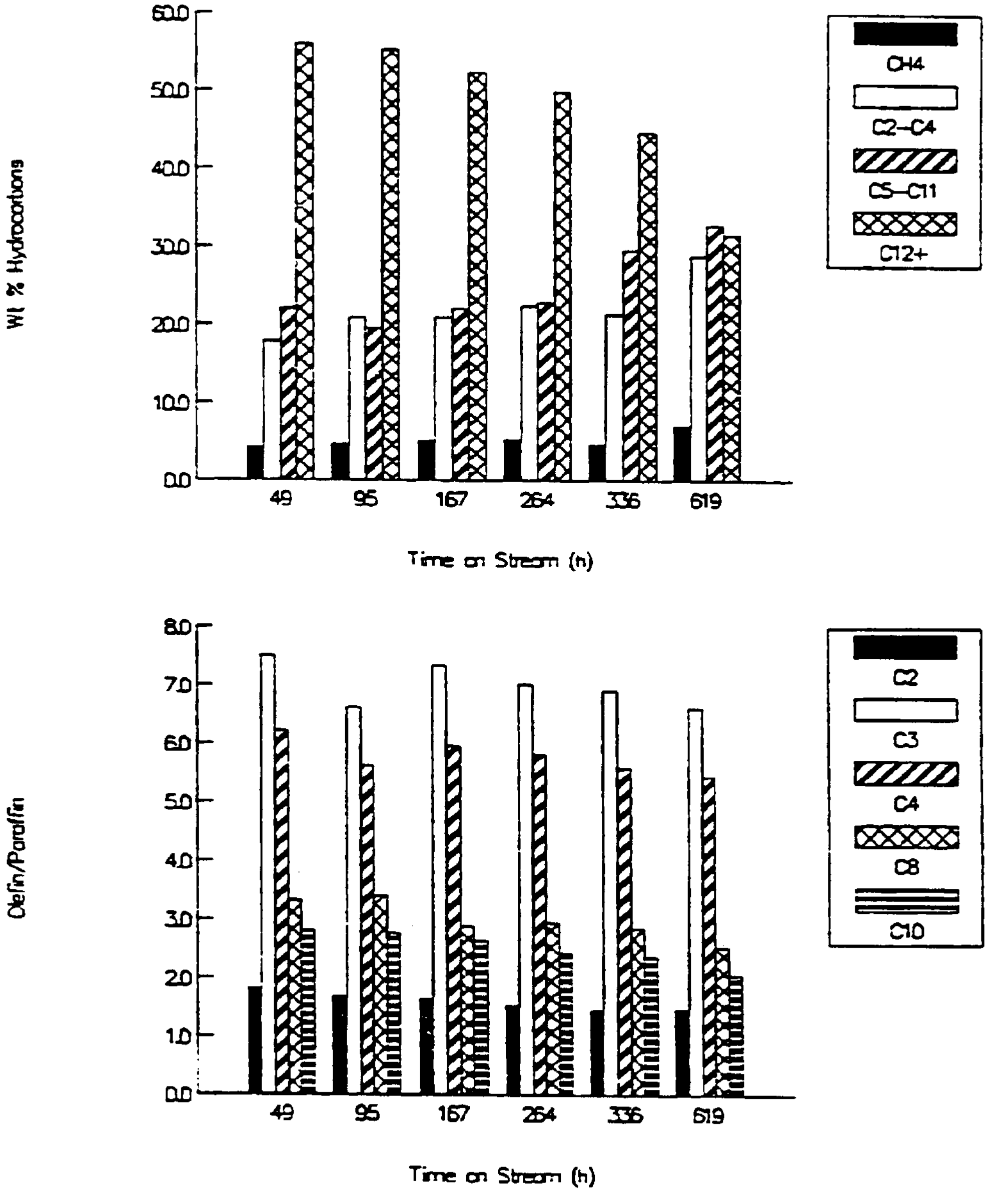

Figure VI-19. **Effect of time on stream on Ruhrchemie LP 33/81 selectivity for run SA-99-0888: 250 °C. 1.48 *MPa*. 2 *Nl/g*-cat-*h*, (H_2/CO) = 0.67.**

during balance 11. The weight % of methane increased to 7.0 % and $C_{12}-$ decreased to 31.5 %. The weak trend in decreasing olefin/paraffin ratios continued as well.

During the process variable studies, the effect of temperature was studied at 2.0 Nl/g–cat·h in balances 8 (235°C), 5 (250°C), and 10 (265°C), and at 1.0 Nl/g–cat·h in balances 9 (235°C) and 7 (250°C), with all balances at 1.48 MPa and $(H_2/CO)=0.67$. A comparison of catalyst selectivity at these conditions appears in Fig. VI-20. Conversion increases as expected with temperature: 23.0 (235°C), 44.4 (250 °C), and 56.9 % (265°C) at 2.0 Nl / g–cat·h, and 35.8 (235°C) and 56.1 % (250°C) at 1.0 Nl / g–cat·h. Temperature had little effect on the weight % hydrocarbon distribution between 235 and 265°C (2 Nl / g–cat·h) and 235 and 250°C (1.0 Nl / g–cat·h). Olefin/paraffin ratios decreased with increase in temperature, indicating that hydrogenation activity increases with temperature.

The feed gas space velocity was varied at 235°C in balances 9 (1.0 Nl / g–cat·h) and 8 (2.0 Nl / g–cat·h), and at 250°C in balances 7 (1.0 Nl / g–cat·h), 5 (2.0 Nl / g–cat·h) and 6 (4.0 Nl/g–cat·h). Space velocity has a minimal effect on the weight % hydrocarbon distribution, as shown in Fig. VI-21. Olefin/paraffin ratios increased with space velocity at both temperatures. A higher (H_2/CO) feed ratio, 1.0 (balance 12) increased the (H_2+CO) conversion from 35.9 % $(H_2/CO=0.67$, balance 11) to 45.4 %. The $(H_2/CO)=1.0$ feed also increased the amount of methane formed from 7.0 to 9.4 % and decreased the percentage of $C_{12}+$ products, as shown in Fig. VI-22. An increase in pressure to 2.96 MPa in balance 13 showed a decrease in (H_2-CO) conversion to 39.8 % which indicates that some catalyst deactivation occurred at the higher pressure. The higher pressure suppressed the formation of gaseous hydrocarbons, and the selectivities at the two pressures are also compared in Fig. VI-22.

VI.3.2. Run SB – 66 – 2468 with the 100 Fe / 5.0 Cu / 4.2 K / 24 SiO_2 Catalyst

Run SB-66-2468 was made as a long term stability test of the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst. Results from this run will also be used to compare the catalyst performance in slurry and fixed bed reactor tests (Run FB-66-1948, Section VI.1.3). The catalyst was reduced in situ using CO as the reductant at 280°C. The reactor was charged with 35.1 g catalyst (270–325 mesh) and 282 g of purified n-octacosane. The first five mass balances (up to 460 h on stream) were made at 250°C, 1.48 MPa, 2.0 Nl / g–cat·h, $H_2/CO=0.67$ to determine catalyst stability. These conditions were repeated following balance 7. The effect of space velocity was studied in balances 6 (4.0 Nl / g–cat·h) and 7 (1.0 Nl / g–cat·h). The run was voluntarily terminated after 582 hours on stream. The major events occurring during the

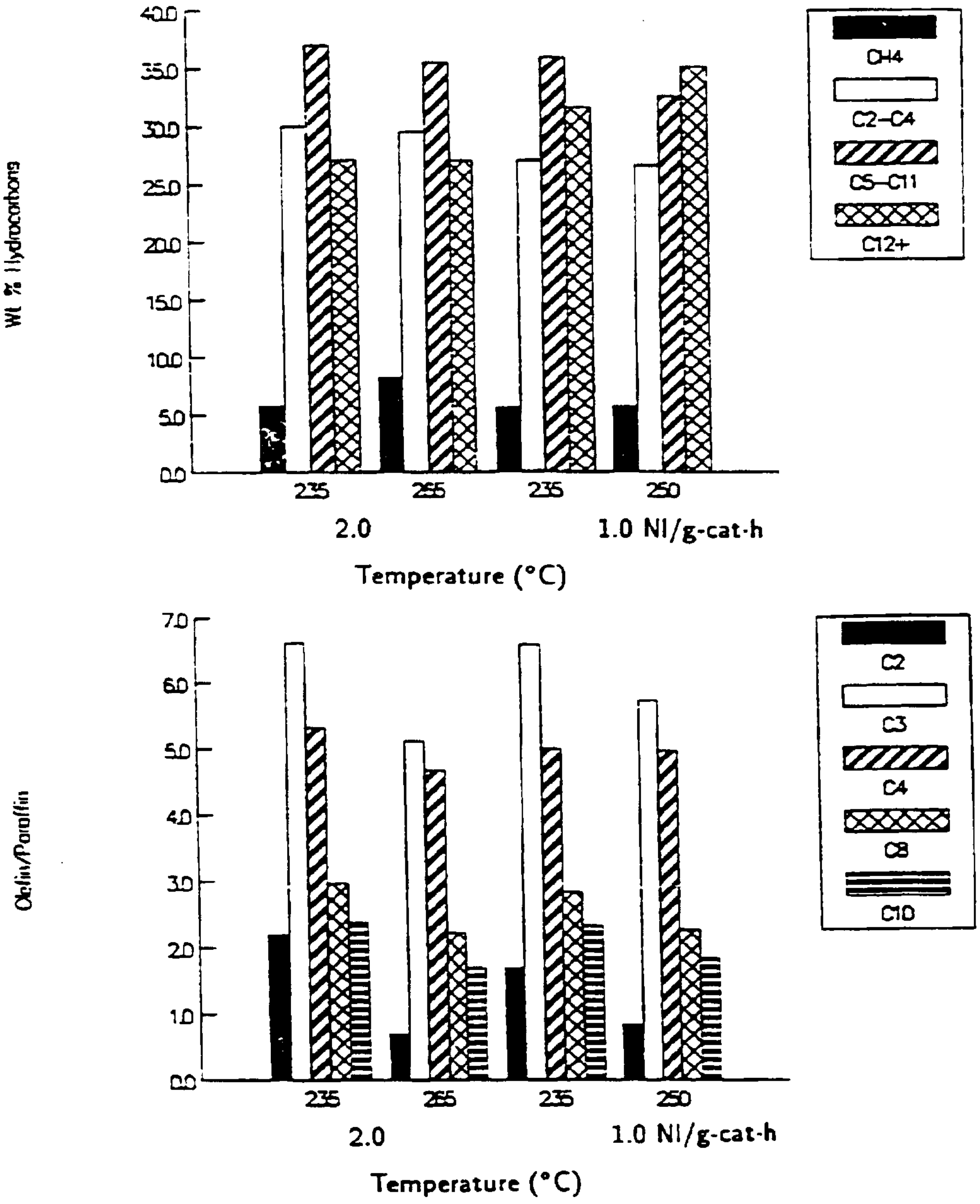

Figure VI-20. **Effect of temperature on Ruhrchemie LP 33/81 selectivity for run SA-99-0888: 1.48** *MPa*, **$(H_2/CO) = 0.67$.**

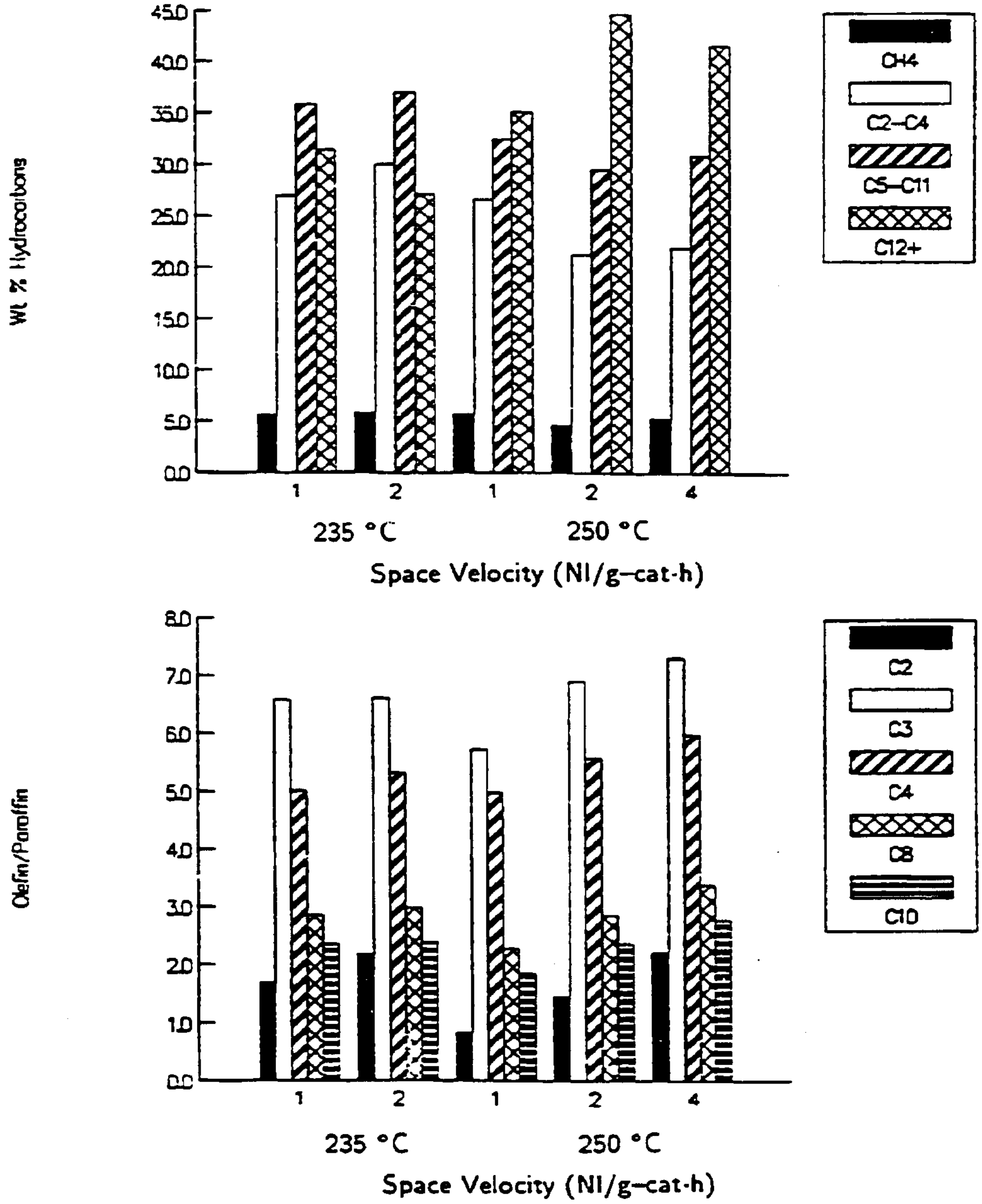

Figure VI-21. Effect of space velocity on Ruhrchemie LP 33/81 selectivity for run SA-99-0888: 1.48 *MPa*, $(H_2/CO) = 0.67$.

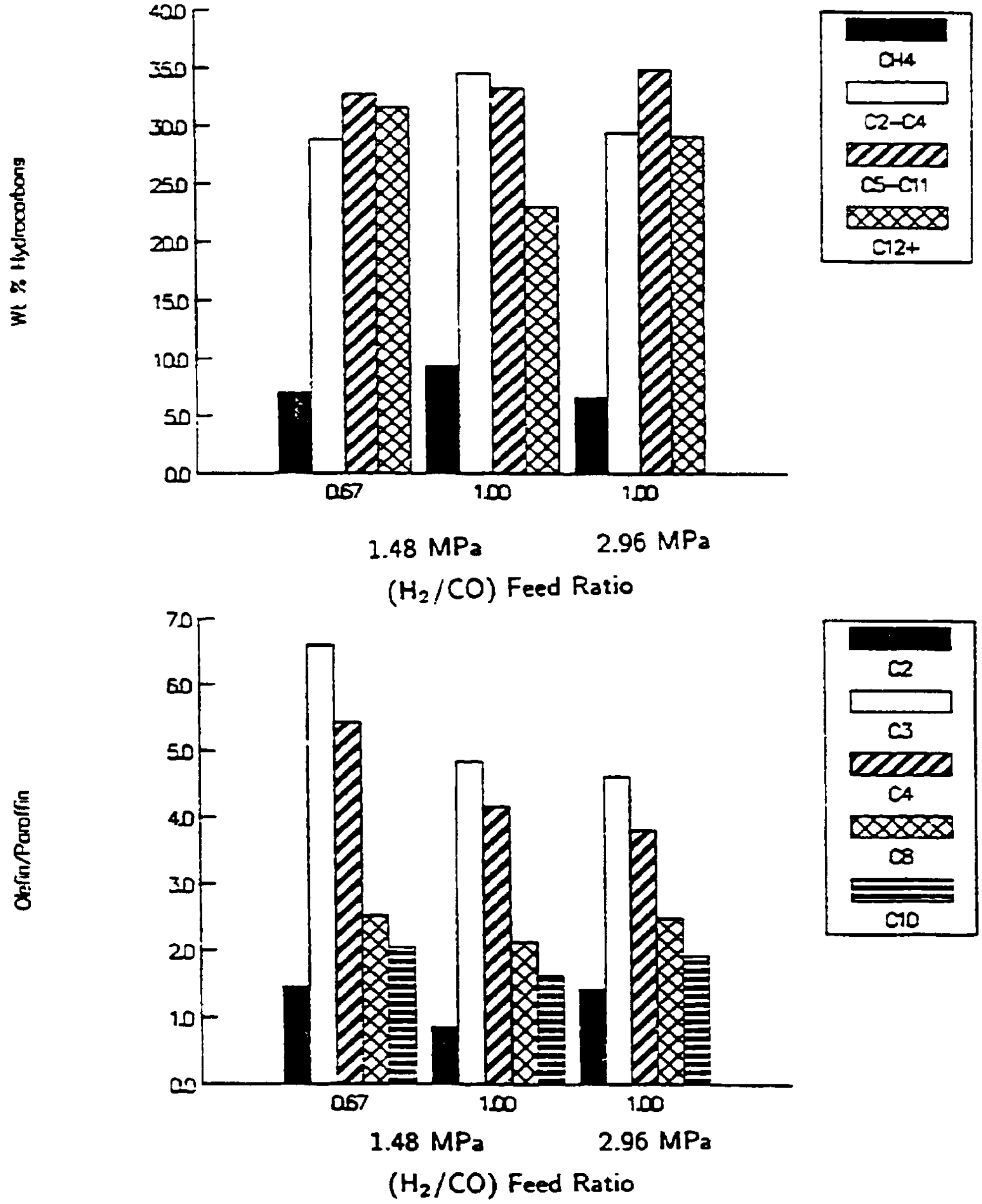

Figure VI-22. Effect of feed ratio and pressure on Ruhrchemie LP 33/81 selectivity for run SA–99–0888: 250 °C.

run are summarized in Table VI-9. The results obtained from the seven mass balances made during the run are summarized in Table VI-10.

Following reduction the reactor was cooled to 230°C with flowing helium and the excess wax was withdrawn through a cylindrical filter element (1.0–cm OD by 3.8–cm long). The withdrawal of 65 g of wax took only 5 minutes and the clarity of the wax confirmed successful operation of the filter. After increasing the pressure to 1.48 MPa, syngas with $H_2/CO=0.67$ was introduced at a gas space velocity of 2 Nl / g–cat·h and the reactor temperature was gradually raised to 250°C. These conditions were maintained for 19 days (455 hours). Over this period of time, five mass balances and twelve wax withdrawals (through the internal filter) were made. The durations for the wax withdrawals ranged between 5 and 40 minutes, depending on the quantity of wax withdrawn. It was possible to withdraw as much as 150 g of wax in 30-40 minutes without the need to backflush the filter.

The activity plot for this catalyst (gas contraction versus time on stream) is shown in Figs. VI-23 (0–240 h TOS) and VI-24 (241–460 h TOS). Also shown on these plots are the instances when wax was withdrawn from or added to the reactor together with the respective amounts. Catalyst activity initially increased and the contraction reached 40.4% at 33 hours on stream at which point in time 142 g of wax was withdrawn from the reactor through the internal filter. Immediately following the wax withdrawal, contraction dropped sharply from 40.4 to 14.7% (corresponding to a drop in (H_2-CO) conversion from 56.6 to 17.9%). There appeared to be no catalyst present in the wax withdrawn from the reactor, therefore the sudden loss in activity was probably due to the removal of a large portion of the catalyst from the synthesis zone. Accumulation of the catalyst in the vicinity of the filter element was suspected and corrective measures were taken. During the withdrawal of the wax through the filter, the catalyst must have been left on the reactor wall (as the slurry level dropped gradually) and some of it must have collected in the narrow space between the filter element and the reactor wall. Backflushing of the filter with a small quantity of hexane (20 cc) did not improve the contraction significantly (contraction increased from 14.7% to 21.3%). We then added 98 g of wax back to the reactor through the external settling tank. The activity was restored to pre-withdrawal level within 18 hours following the addition of the wax (contraction reached 40.5%). Apparently the addition of wax increased the slurry volume and the agitation was sufficient to flush the accumulated catalyst back into the slurry. Following the first mass balance (TOS = 76 h), wax was again withdrawn from the reactor, however, the withdrawal

Table VI-9. Major Events occuring in run SB-66-2468.

TOS (h)	Event
– 14	Catalyst Pretreatment: CO at 280°C
– 2	Cooled to 260°C and pressurized to 1.48 MPa using He
0	Run initiated
5	Achieved desired operating conditions: 260°C, 1.48 MPa, $H_2/CO = 0.69$, 2 Nl/g–cat·h
33	Sharp drop in catalyst activity following wax withdrawal
61	Activity recovered following addition of wax to reactor
69	Conditions stable. H_2+CO conversion = 56.1%
165	Conditions stable. H_2+CO conversion = 51.9%
171	Sharp drop in catalyst activity following wax withdrawal
201	Activity recovered following addition of wax to reactor
261	Conditions stable, H_2+CO conversion = 53.2%
269	Sharp drop in catalyst activity following wax withdrawal
271	Activity recovered following addition of wax to reactor
357	Conditions stable, H_2+CO conversion = 49.3%
364	Small drop in catalyst activity following wax withdrawal
384	Activity recovered following addition of wax to reactor
453	Conditions stable. H_2+CO conversion = 44.3%
460	Changed operating conditions: 260°C, 1.48 MPa, $H_2/CO = 0.69$, 4 Nl/g–cat·h
509	Changed operating conditions: 260°C, 1.48 MPa, $H_2/CO = 0.69$, 1 Nl/g–cat·h
555	Small drop in catalyst activity following wax withdrawal
557	Activity recovered following addition of wax to reactor
558	Changed operating conditions: 260°C, 1.48 MPa, $H_2/CO = 0.69$, 2 Nl/g–cat·h
582	Voluntary termination of run SB-66-2468

Table VI-10. Summary of results for slurry run SB 66 2468

Catalyst: 100 Fe/5.0 Cu/4.2 K /24 SiO_2 Slurry liquid: n octacosane

Reactor volume: 312 cc[b]

Period	1	2	3	4	5	6	7
Date	09/06/88	09/10/88	09/14/88	09/18/88	09/22/88	09/24/88	09/24/88
Time on Stream (*h*)	69.0	105.0	201.0	357.0	453.0	500.0	540.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0	7.0	6.0
Average Temperature (°C)	250.	250.	250.	250.	250.	250.	250.
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.69	.69	.69	.69	.69	.69	.75
Space Velocity (*Nl/g-cat·h*)[a]	2.00	2.00	2.00	2.00	2.00	4.00	1.01
Space Velocity (*Nl/g-Fe·h*)	3.57	3.57	3.57	3.57	3.57	7.13	1.80
GHSV (h^{-1})[b]	225.	225.	225.	225.	225.	450.	113.
CO Conversion (%)	54.6	49.4	51.7	47.2	42.3	22.3	61.0
H_2+CO Conversion (%)	56.1	51.9	53.2	49.3	44.3	26.2	61.1
H_2/CO Usage	.74	.78	.75	.77	.78	.99	.76
STY (*mols* H_2+CO/*g·cat·h*)[a]	.050	.046	.047	.044	.040	.047	.027
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	2.5	1.7	2.0	1.9	1.5	.9	2.7
Weight % of Outlet							
H_2	2.02	2.20	2.15	2.29	2.54	3.32	1.95
H_2O	3.60	4.35	4.23	4.04	4.38	3.26	4.51
CO	44.1	49.9	46.5	50.8	55.5	75.6	30.2
CO_2	35.0	29.8	32.8	29.2	25.4	11.7	40.0
Hydrocarbons	8.79	8.46	9.90	9.91	9.43	5.17	12.4
Oxygenates	.19	.51	.36	.50	.50	.24	.70
Wax[c]	6.25	4.88	3.99	3.25	2.24	.74	4.23
Yield (*g/Nm*^{3} H_2 + CO *Converted*)							
CH_4	7.89	7.57	8.87	11.3	12.8	13.4	15.5
C_2-C_4 Hydrocarbons	36.5	34.6	40.5	44.6	44.1	47.4	51.1
C_5-C_{11} Hydrocarbons	42.2	40.6	50.1	49.9	47.6	37.3	40.0
C_{12}+ Hydrocarbons	117.	109.	100.	98.9	97.7	73.0	93.5
Wax[c]	84.6	70.3	57.3	50.6	38.8	21.5	53.2
Oxygenates	2.56	7.33	5.17	7.79	8.68	7.00	8.87
Total	200.	200.	205.	213.	211.	178.	218.
1+2 Olefins/*n*-Paraffin Ratio							
C_2	1.83	2.10	1.58	1.18	1.08	1.81	.44
C_3	7.34	7.34	6.58	5.50	5.02	5.38	3.54
C_4	5.97	6.03	5.40	4.48	4.82	4.53	3.05
C_8	4.29	2.52	3.16	2.46	1.96	2.56	1.42
C_{10}	3.09	3.07	2.49	1.81	1.63	2.10	1.15

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH4	3.88	3.94	4.44	5.53	6.32	7.82	7.40
Ethane	1.85	1.81	2.60	3.38	3.73	3.53	5.47
Ethylene	3.16	3.54	3.83	3.72	3.74	5.95	2.23
Propane	.84	.83	1.02	1.26	1.42	1.62	2.08
Propylene	5.87	5.82	6.39	6.62	6.79	8.33	7.01
n-Butane	.84	.81	.95	1.17	1.04	1.42	1.77
1+2 Butenes	4.86	4.72	4.06	5.07	4.86	6.22	5.21
C_4 Isomers	.51	.48	.53	.57	.23	.66	.66
n Pentane	1.16	1.17	1.32	1.52	1.65	1.86	2.12
1+2 Pentenes	4.35	4.30	5.48	5.00	4.99	5.56	4.05
C_5 Isomers	.27	.31	.58	.63	.42	.73	.54
n-Hexane	.77	.08	.96	1.06	.84	1.13	1.00
1+2 Hexenes	2.15	2.11	3.01	2.69	2.13	3.11	1.59
C_6 Isomers	.02	.47	.68	.66	.52	.81	.44
n-Heptane	.39	.45	.53	.85	.65	.77	.75
1+2 Heptenes	1.04	1.48	1.92	1.86	1.50	1.62	1.28
C_7 Isomers	.44	.36	.54	.37	.40	.58	.28
n-Octane	.33	.00	.50	.58	.63	.34	.82
1+2 Octenes	1.41	1.48	1.56	1.41	1.21	.85	1.23
C_8 Isomers	.44	.28	.35	.27	.13	.17	.20
n-Nonane	.37	.42	.50	.61	.76	.26	1.12
1+2 Nonenes	1.33	1.42	1.34	1.23	1.36	.60	1.32
C_9 Isomers	.14	.23	.28	.18	.17	.07	.26
n-Decane	.52	.58	.67	.83	1.04	.44	1.31
1+2 Decenes	1.60	1.76	1.65	1.48	1.08	.90	1.48
C_{10} Isomers	.25	.30	.41	.37	.32	.15	.46
n-Undecane	.63	.65	.74	.93	1.16	.59	1.37
1+2 Undecenes	1.63	1.73	1.61	1.44	1.59	1.09	1.40
C_{11} Isomers	.31	.31	.46	.42	.39	.10	.39
C_2-C_4	17.9	18.0	20.3	21.8	21.8	27.7	24.4
C_5-C_{11}	20.7	21.1	25.1	24.4	23.5	21.8	23.5
C_{12}+	57.5	57.0	50.2	48.3	48.3	42.7	44.7
Wax[c]	41.6	36.6	28.7	24.7	19.2	12.6	25.4

[c] Unanalyzed wax withdrawn from reactor

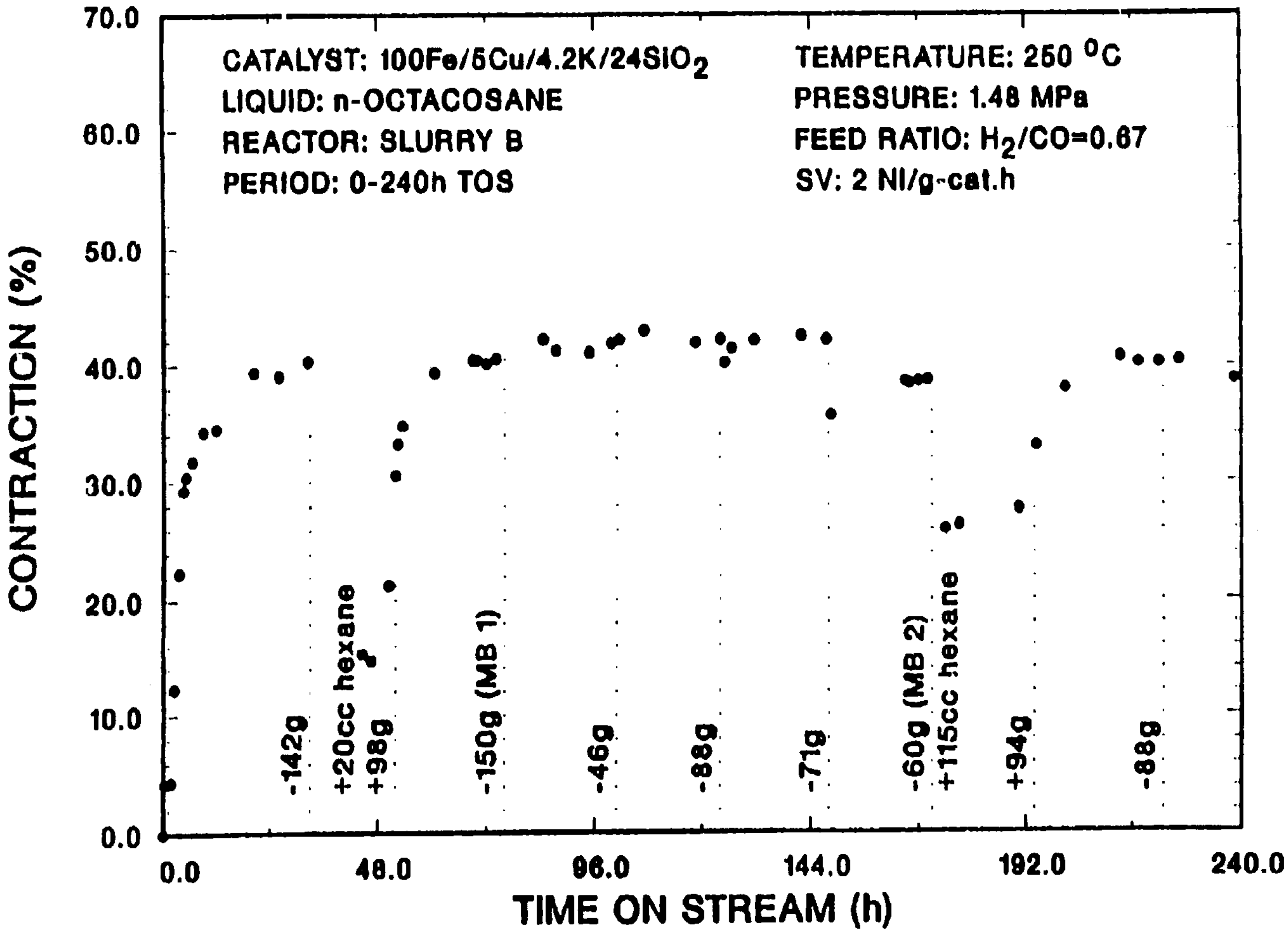

Figure VI-23. Catalyst activity for run SB-66-2468 (weights indicate amount of wax withdrawn (−) or added (+)). 0 to 240 *h* on stream. (250 °C, 1.48 *MPa*, 2.0 *Nl/g* cat·*h*, H_2/CO = 0.67 nominal).

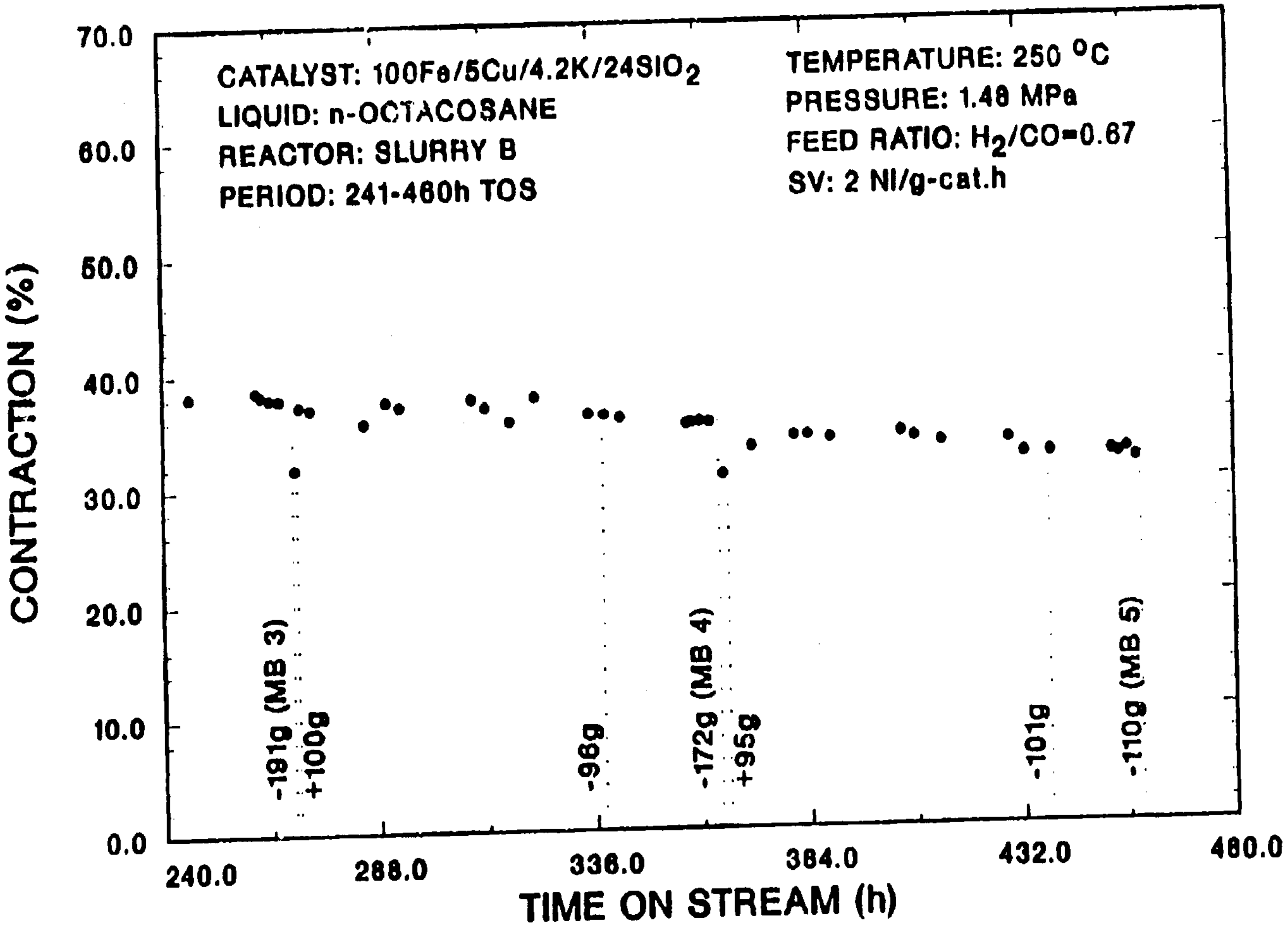

Figure VI-24. Catalyst activity for run SB-60-2468 (weights indicate amount of wax withdrawn (−) or added (+)). 240 to 480 *h* on stream. (250 °C, 1.48 *MPa*, 2.0 *Nl/g-cat·h*, H_2/CO = 0.67 nominal).

procedure was stopped short of complete withdrawal of all excess wax. The contraction did not change following this withdrawal, probably because the slurry level was sufficiently above the filter element to prevent any catalyst accumulation. However, following the majority of the subsequent wax withdrawals, a drop in contraction was observed and wax had to be returned to the reactor. Also, following each wax addition to the reactor, an equivalent amount of wax was withdrawn from the reactor 24 hours following the addition, i.e., after enough wax was produced to cover the filter element. Using this procedure, it was possible to prevent any significant wax withdrawal related losses in catalyst activity. No other operating problems were encountered during the entire run.

The 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst was fairly stable in comparison to slurry tests with other catalysts, with some loss in activity over the first 19 days (constant conditions). The stability plot for the run over this period is shown in Fig VI-25. Also included are the (H_2—CO) conversion values obtained following the seventh mass balance, when the initial conditions were repeated. Catalyst activity increased initially and reached a maximum at 107 hours on stream (H_2+CO conversion of 58.7%), thereafter it steadily declined and the (H_2+CO) conversion at 460 hours on stream was 44% (a 25% loss in activity). The reasons for catalyst deactivation are not known. One possibility is that small quantities of air were introduced into the reactor during the wax addition. The wax addition procedure involved the addition of molten wax to the external settling tank, following which the tank was purged with helium. The wax was then forced into the reactor using a slight over pressure in the settling tank. Any air dissolved in the wax, or present in the settling tank would be introduced into the reactor and would have a detrimental effect on catalyst activity. When the same conditions were repeated after mass balance 7, the (H_2+CO) conversion was 35.4% (at 558 hours on stream), which represents a 20% drop in activity in comparison to balance 5 conducted at 453 hours on stream. The accelerated catalyst deactivation is probably due to the combined effects of frequent changes in process conditions and the repeated introduction of small quantities of air into the reactor during the wax addition procedure. Another possibility is that deactivation was caused by the catalyst which had accumulated in the vicinity of the filter element and on the reactor wall following each wax withdrawal. The catalyst above the slurry level is in direct contact with the synthesis gas and this may lead to localized hot spots, leading to loss in activity with time on stream. Inspection of the reactor, following the completion of the run, showed that a layer of slurry was adhering to the reactor wall above the slurry level, and it is possible that the

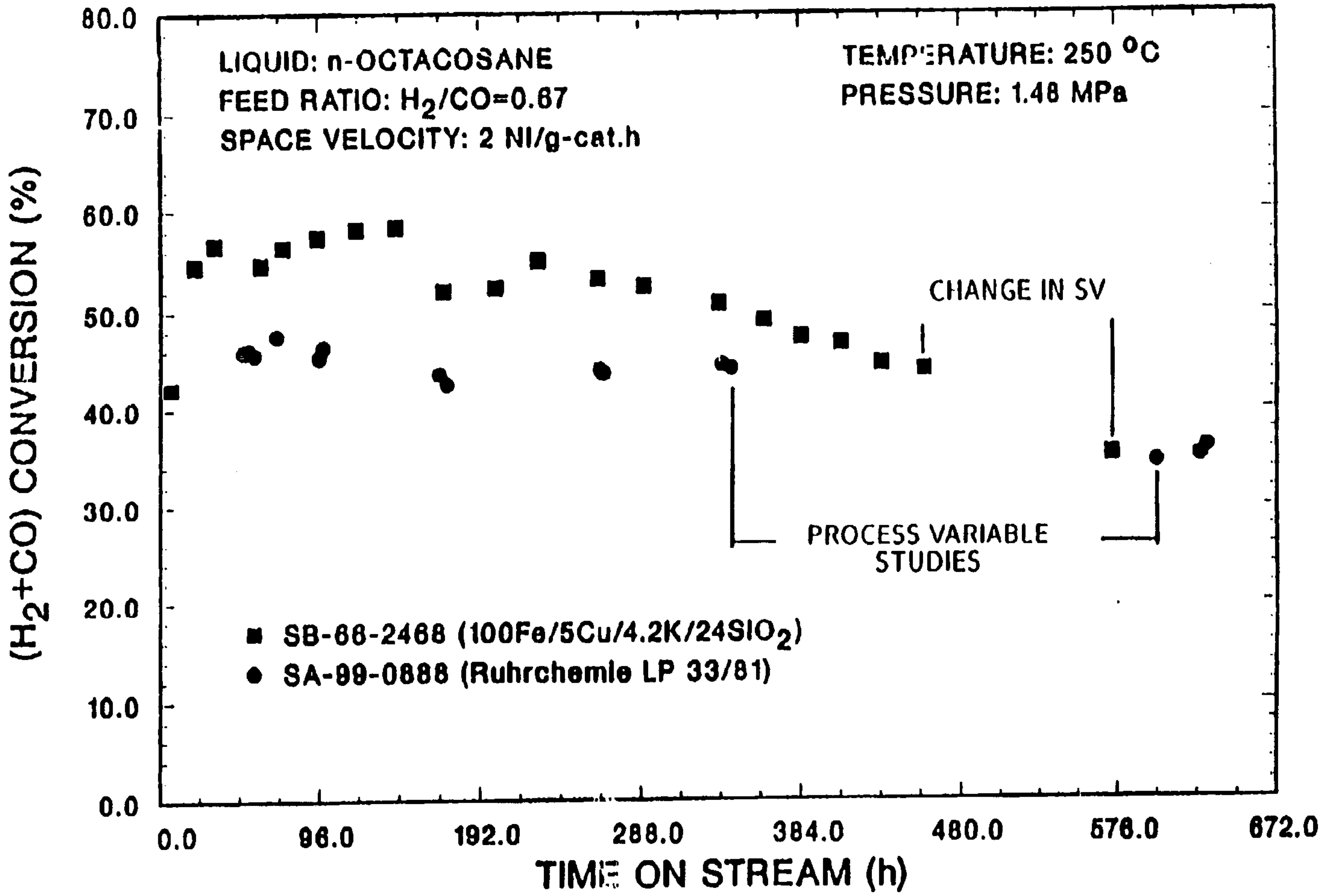

Figure VI-25. Stability plot, (H_2+CO) conversion versus time on stream, for run SB-66-2468. (250 °C, 1.48 *MPa*, 2.0 *Nl/g*-cat·*h*, H_2/CO = 0.67 nominal).

catalyst entrained in this layer would have deactivated more rapidly. When the same catalyst was tested in the fixed bed reactor (Run FB–66–1948, section VI.1.3), it was very stable and more active than in the slurry reactor. (H_2+CO) conversion in the fixed bed was 68.7% initially and declined to 64.3% after 457 hours on stream, a drop of only 6.4% in activity.

The activity of this catalyst was higher than that of the Ruhrchemie LP 33/81 catalyst as shown in Fig. VI-25. The initial activity of the Ruhrchemie catalyst was lower (with H_2–CO conversion of around 46%) in comparison to our catalyst (H_2–CO conversion of around 56%). However, at 336 hours on stream the differences in activities for the two catalysts were smaller. The (H_2+CO) conversion with the Ruhrchemie catalyst was about 45% vs. 51% with our catalyst. Activities for the two catalysts at the end of the respective runs were the same (H_2–CO conversions of about 35%), as a result of partial deactivation of both catalysts.

With a decline in catalyst activity over the first 19 days (constant conditions), the hydrocarbon selectivity shifted slightly towards lighter products (Fig. VI-26). At 69 hours on stream (balance 1) the hydrocarbon fractions were 3.9 (CH_4), 17.9 (C_2–C_4), 20.7 (C_5–C_{11}) and 57.5% (C_{12}+), whereas at 453 hours on stream (balance 5) they were 6.3 (CH_4), 21.8 (C_2–C_4), 23.5 (C_5–C_{11}) and 48.3% (C_{12}+). During the same period, the olefin/paraffin ratios decreased for all carbon numbers (Fig. VI-26). A similar, although weaker, trend for hydrocarbon selectivity was observed when this catalyst was tested in the fixed bed reactor as shown in Fig. VI-10. In general, more light products were produced in the fixed bed than in the slurry reactor test (Fig.VI-27). In balances 5,6 and 7 of this run, the effect of space velocity (1,2 and 4 Nl / g–cat·h) on the catalyst activity and product selectivity was studied. Conversion decreased with higher space velocity, as would be expected, with an (H_2+CO) conversion of 26.2% at 4 Nl / g–cat·h at 500 h (balance 6) compared to 61.1% at 1 Nl / g–cat·h at 549 h (balance 7). Hydrocarbon selectivity shifted toward lighter products with an increase in space velocity (Fig.VI-28). The olefin/paraffin ratios for most carbon numbers increased at the same time. When a lower space velocity was used (1 Nl / g–cat·h in balance 7), hydrocarbon selectivities were comparable to those obtained in balance 5 at 2 Nl / g–cat·h, but the olefin/paraffin ratios showed a significant decrease for all carbon numbers (Table VI-10 and Fig.VI-28).

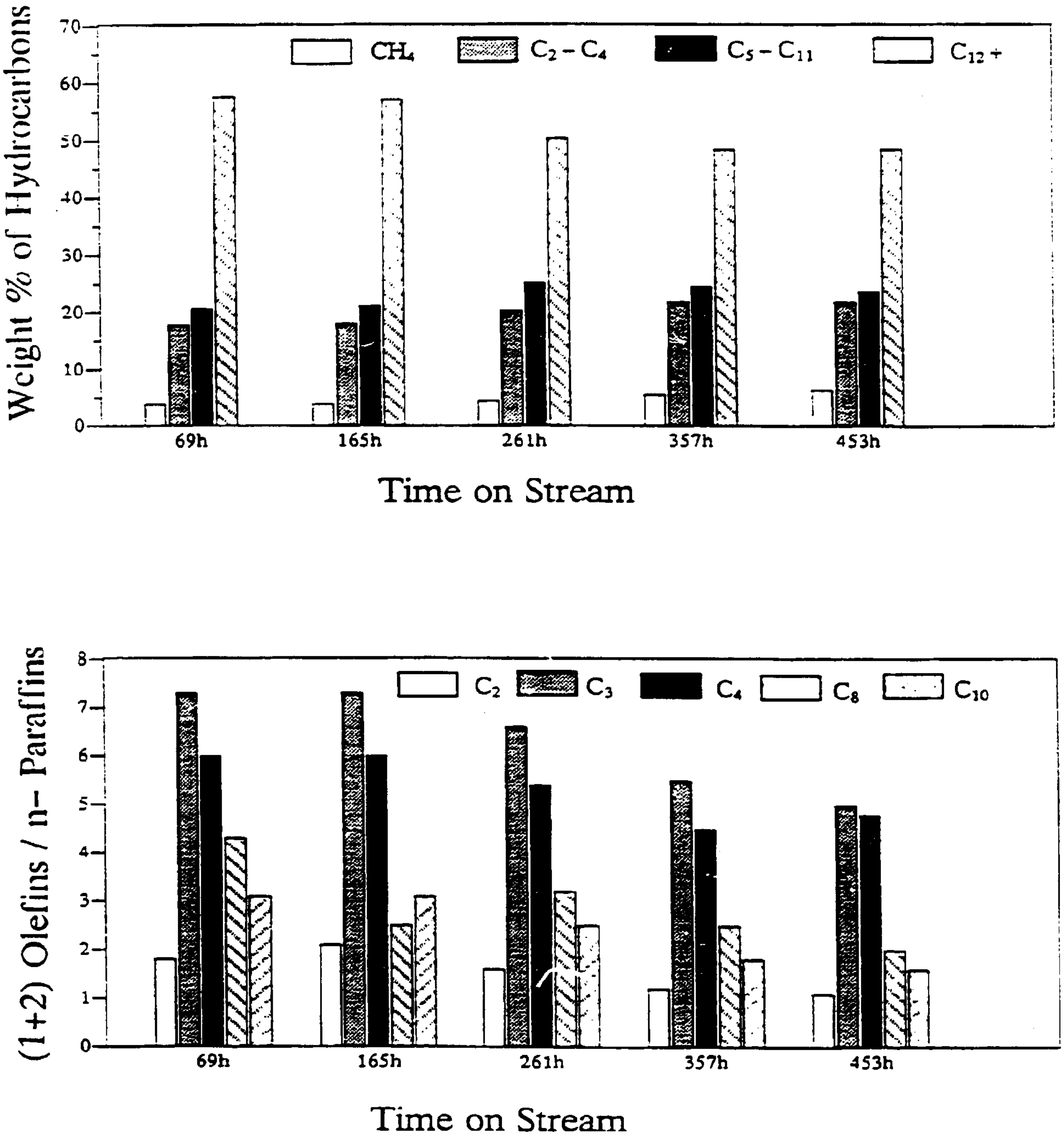

Figure VI-26 Effect of time on stream on 100 Fe/5 Cu/4.2 K/24 SiO_2 catalyst selectivity for Run SB-66-2468 (250°C. 1.48 MPa. SV=2 Nl/g-cat.h. $H_2/CO=0.69$)

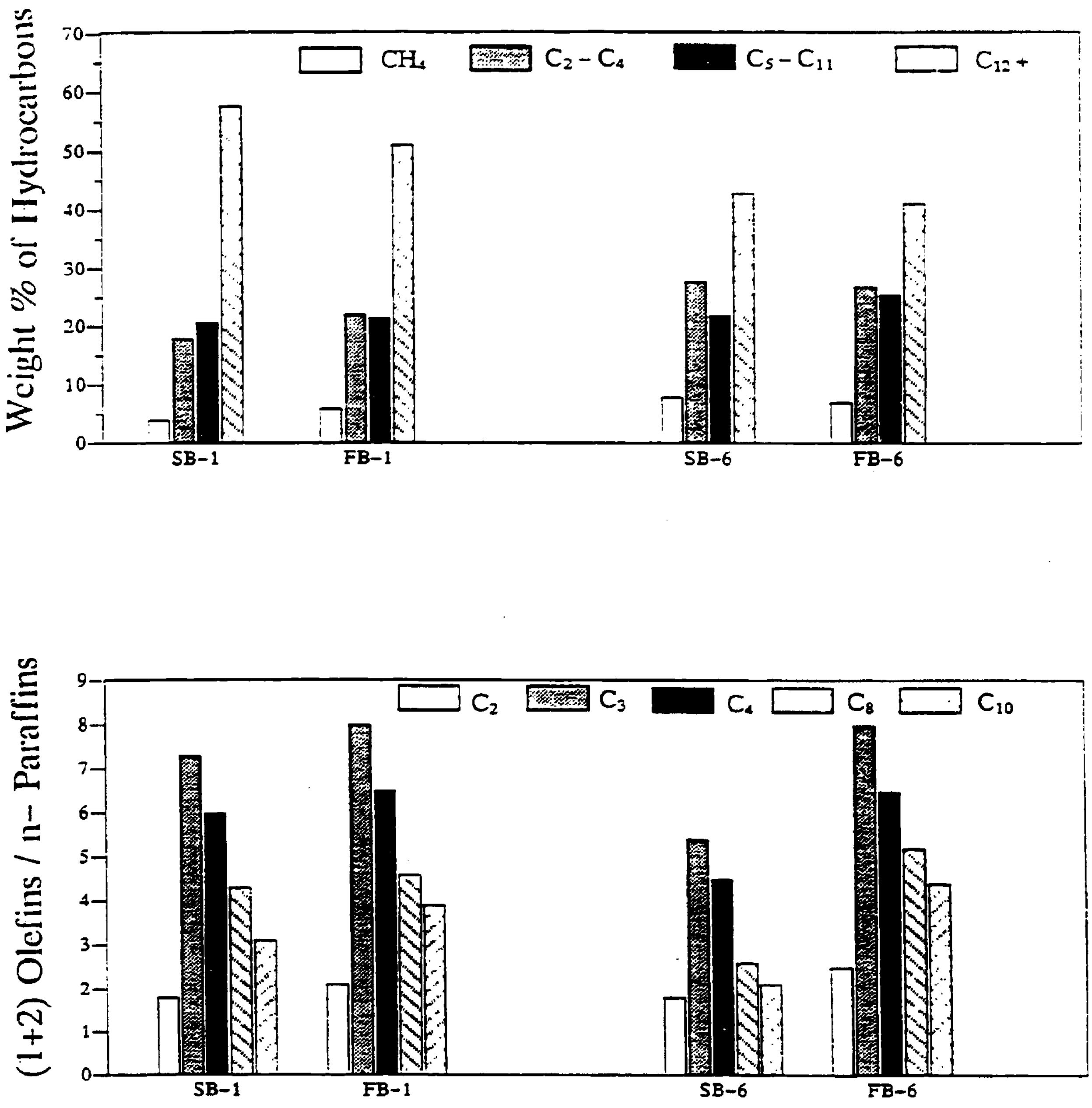

Figure VI-27 Comparison of fixed bed and slurry reactor selectivity with 100 Fe/5 Cu/4.2 K/24 SiO_2 catalyst (FB=FB-66-1948 . SB=SB-66-2468)(250°C. 1.48 MPa. $H_2/CO=0.69$. SV=2 Nl/g-cat.h (FB-1 and SB-1) and 4.0 (FB-6 and SB-6))

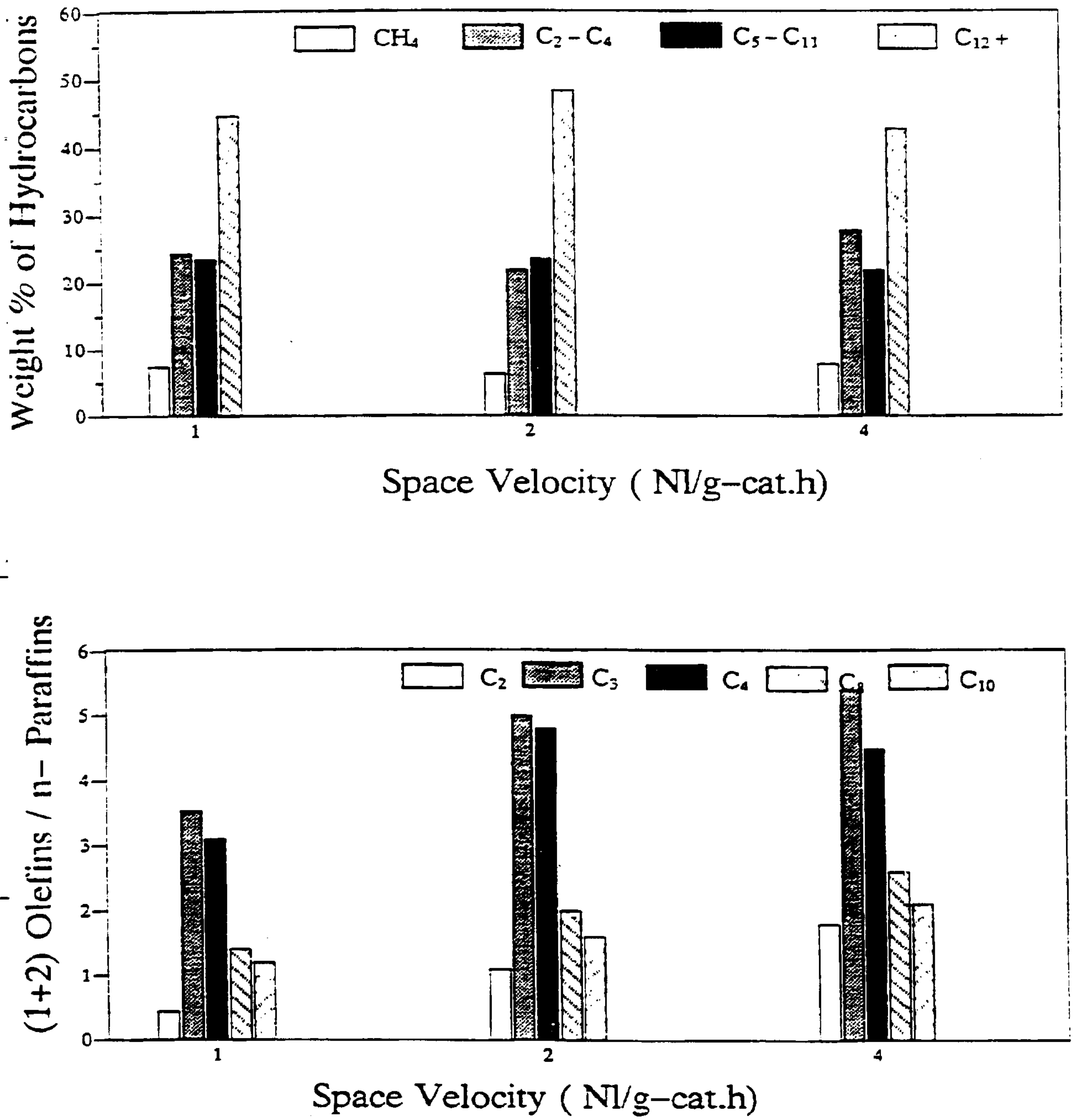

Figure VI-28 Effect of space velocity on 100 Fe/5 Cu/4.2 K/24 SiO$_2$ catalyst selectivity for Run SB-66-2468 (250°C. 1.48 MPa. H$_2$/CO=0.69)