VI.4. Stirred Tank Slurry Reactors Tests with Unsupported Precipitated Iron Catalysts

VI.4.1. Run SB – 27 – 2168 with the 100 Fe / 3.0 Cu / 0.5 K Catalyst

Slurry run SB–27–2168 was intended to be a long term test of a precipitated 100 Fe/3.0 Cu/0.5 K catalyst reduced in situ using CO as the reductant at 280°C. The reactor was charged with 45.2 g catalyst (270–325 mesh) and 295 g of purified n–octacosane to obtain a 13 weight % catalyst slurry. The slurry withdrawal dipleg, attached to a cylindrical 20 μm filter element (1.0–cm OD by 3.8–cm long), was preset to give a static slurry volume of 370 cc. Four mass balances were performed during the run, and the run was voluntarily terminated after 339 hours on stream. The process conditions used during the run were: 260°C, 1.48 MPa, (H_2/CO) = 0.67–1.0, 2.0–3.0 Nl / g–cat·h. The major events occurring during this run are summarized in Table VI-11 . The results obtained from the mass balances are summarized in Table VI-12.

Following catalyst reduction, the reactor was cooled down with flowing helium to 260°C and excess wax withdrawn through the filter. The slurry withdrawn was very dark in color and subsequently it has been determined that 6 g of catalyst was removed together with 42 g of wax. After increasing the pressure to 1.48 MPa, syngas with an H_2/CO feed ratio of 0.7 was introduced at a space velocity of 0.5 Nl / g-cat·h while maintaining the helium flow at 4 Nl / g-cat·h. During the next 27 hours the syngas flow rate was gradually increased to 2 Nl / g–cat·h and helium flow was phased out. However, the gas contraction was very low, and the feed and tail gas sample analyses showed only CO in the former and no hydrocarbon products in the latter. At this point it was discovered that the helium purge from the slurry A reactor system was accidentally diverted through the H_2 mass flow meter. This means that the catalyst was exposed to a mixture of CO and He at 260°C and 1.48 MPa for 27 hours, in addition to 12 h activation with pure CO at 280°C and 0.79 MPa. After the problem was corrected, gas contraction showed an increase with time on stream. Slurry was again withdrawn through the filter element after 22 hours at the process conditions. The 101 g of slurry withdrawn was found to contain 8.7 g of catalyst, providing further evidence of filter malfunction, possibly due to a leak in the filter element (at the end of the run, it was found that the filter had cracked due to its proximity to the stirring shaft in the reactor). All subsequent withdrawals were made through the external settling tank system. No further operational problems were encountered during the remainder of the run.

A stability plot, (H_2+CO) conversion versus time on stream, is shown in Fig. VI-29. The initial activity of the catalyst was relatively high, (H_2+CO) conversion of 68.3% at 46 hours on

Table VI-11. Major events occurring in run SB-27-2168.

TOS (*h*)	Event
− 44	Catalyst pretreatment: CO at 280 °C
− 27	Cooled to 260 °C, pressurized to 1.48 *MPa* with He
− 25	Began blending synthesis gas with He
− 24	Wax plug in high pressure unsteady state trap repaired
− 20	First attempt to initiate run
− 18	Reactor exit gas showed no H_2 peak
− 2	Feed gas difficulty corrected (He, instead of H_2, was flowing into inlet line)
0	Run initiated
2.0	Achieved desired operating conditions: 260 °C, 1.48 *MPa*, (H_2/CO) = 0.67, 2.3 *Nl*/*g*–cat·*h*
46.0	Conditions stable, (H_2+CO) conversion = 68.2 %
141.0	Conditions stable, (H_2+CO) conversion = 31.3 %
238.0	Conditions stable, (H_2+CO) conversion = 15.8 %
246.0	Changed process conditions: 260 °C, 1.48 *MPa*, (H_2/CO) = 1.00, 2.0 *Nl*/*g*–cat·*h*
339.0	Voluntary termination of run SB-27-2168

Table VI-12. Summary of results for slurry run SB-27 2168.

Catalyst: 100 Fe/3.0 Cu/0.5 K

Slurry liquid: n octacosane

Reactor volume: 370 cc[b]

Period	1	2	3	4
Date	08/06/88	08/10/88	08/14/88	08/18/88
Time on Stream (*h*)	45.5	141.0	236.8	333.0
Balance Duration (*h*)	6.0	6.0	6.2	6.2
Average Temperature (°C)	260.	260.	260.	260.
Pressure (*MPa*)	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.67	.67	.67	1.00
Space Velocity (*Nl/g*-cat·*h*)[a]	2.96	2.34	2.34	2.01
Space Velocity (*Nl/g*-Fe·*h*)	4.37	3.45	3.46	2.96
GHSV (h^{-1})[b]	244.	165.	165.	138.
CO Conversion (%)	72.7	33.5	16.7	13.6
H_2+CO Conversion (%)	68.3	31.2	15.9	10.8
H_2/CO Usage	.57	.56	.58	.59
STY (*mols* H_2+CO/*g*-cat·*h*)[a]	.090	.033	.017	.010
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	21.0	8.1	4.9	2.6
Weight % of Outlet				
H_2	1.77	3.32	3.96	6.24
H_2O	.97	.87	.59	1.25
CO	26.3	63.7	80.1	81.4
CO_2	53.6	23.9	10.3	7.33
Hydrocarbons	9.30	4.99	2.64	1.83
Oxygenates	.27	.19	.09	.11
Wax[c]	7.78	3.04	2.36	1.82
Yield (*g*/*Nm*^{3} H_2 + CO *Converted*)				
CH_4	7.46	6.16	7.10	11.6
C_2-C_4 Hydrocarbons	29.4	28.5	28.4	36.3
C_5-C_{11} Hydrocarbons	39.6	36.1	23.2	20.1
C_{12}+ Hydrocarbons	118.	130.	187.	156.
Wax[c]	88.6	76.1	116.	112.
Oxygenates	3.06	4.87	4.21	6.79
Total	198.	206.	250.	231.
1+2 Olefins/*n*-Paraffin Ratio				
C_2	2.57	4.40	4.50	2.12
C_3	7.12	6.16	4.77	3.41
C_4	6.70	4.97	4.12	2.02
C_8	5.16	4.33	4.19	1.92
C_{10}	4.33	3.85	3.18	2.39

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Period	1	2	3	4
Weight % of Hydrocarbons				
CH4	3.84	3.07	2.89	5.17
Ethane	1.30	.80	.63	1.59
Ethylene	3.11	3.26	2.63	3.14
Propane	.68	.72	.69	1.24
Propylene	4.03	4.21	3.16	4.04
n-Butane	.74	.81	.80	1.42
1+2 Butenes	4.16	3.87	3.18	4.01
C_4 Isomers	.48	.53	.48	.74
n-Pentane	.92	1.00	.81	1.23
1+2 Pentenes	3.27	3.05	2.18	2.59
C_5 Isomers	.19	.21	.18	.27
n-Hexane	.49	.53	.32	.56
1+2 Hexenes	2.50	2.37	.64	1.54
C_6 Isomers	.50	.73	.30	.00
n-Heptane	.43	.39	21	.53
1+2 Heptenes	2.10	1.76	.98	1.13
C_7 Isomers	.37	.49	.15	.00
n-Octane	.36	.31	.13	.25
1+2 Octenes	1.82	1.30	.54	.48
C_8 Isomers	.26	.09	.02	.00
n-Nonane	.37	.30	.17	.03
1+2 Nonenes	1.71	1.14	.52	.06
C_9 Isomers	.15	.10	.04	.00
n-Decane	.42	.37	.23	.04
1+2 Decenes	1.81	1.41	.72	.09
C_{10} Isomers	.19	.17	.08	.01
n-Undecane	.45	.39	.21	.04
1+2 Undecenes	1.81	1.57	.90	.11
C_{11} Isomers	.22	.26	.11	.01
C_2-C_4	15.1	14.2	11.6	16.2
C_5-C_{11}	20.3	17.9	9.46	8.97
C_{12}+	60.7	64.8	76.1	60.7
Wax[c]	45.5	37.9	47.2	49.8

[c] Unanalyzed wax withdrawn from reactor

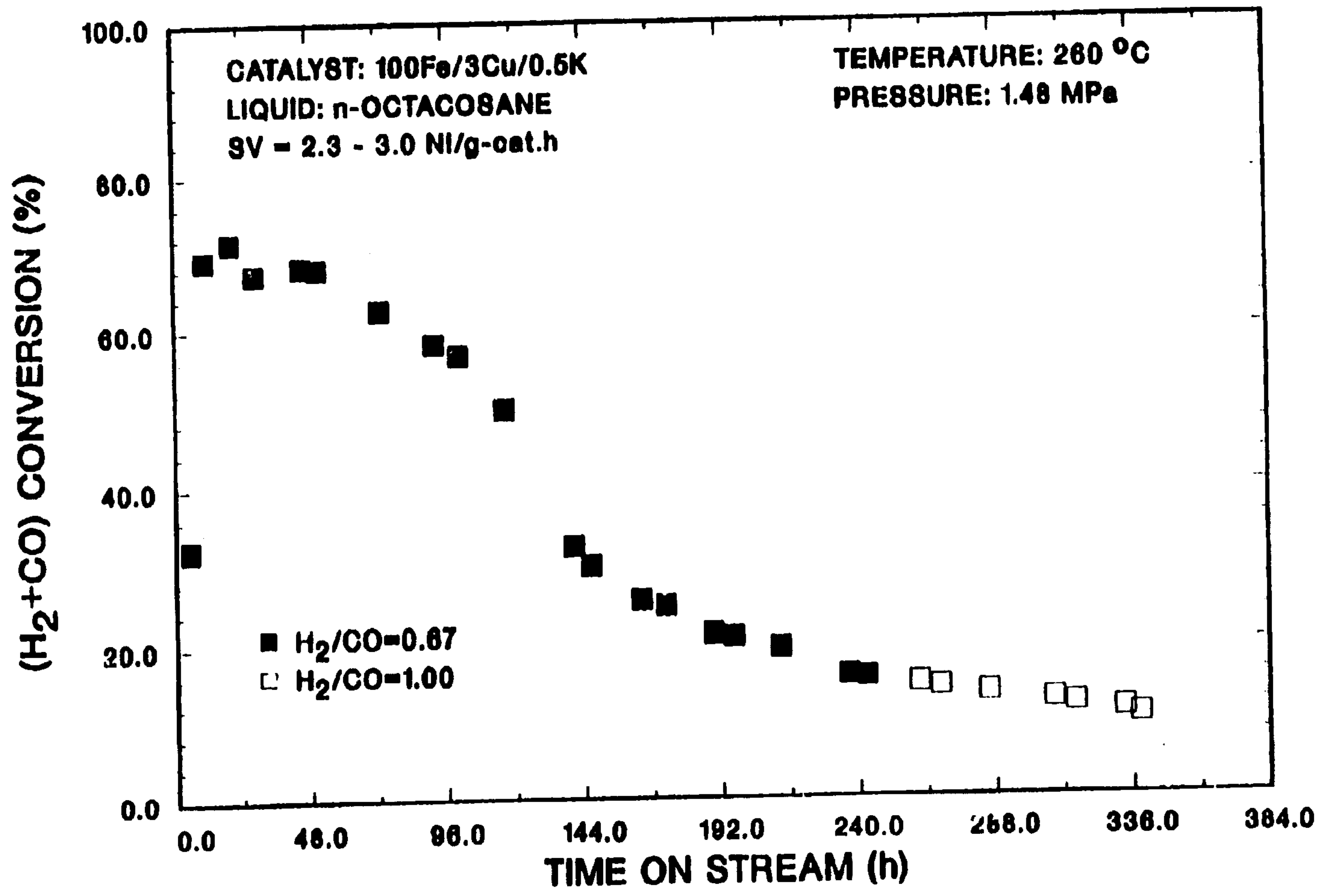

Figure VI-20. Stability plot, (H_2+CO) conversion versus time on stream, for run SB-27-2168. (260 °C, 1.48 *MPa*, 2.3-3.0 *Nl/g-cat·h*).

stream, however, the catalyst activity declined rapidly with time on stream, and the (H_2+CO) conversion dropped to 13.6% at 333 hours on stream. During this period, the hydrocarbon distribution shifted toward higher molecular weight products. At 46 hours on stream (balance 1) the hydrocarbon fractions were: 3.8 (CH_4), 15.1 (C_2–C_4), 20.3 (C_5–C_{11}) and 60.7% (C_{12}+), whereas at 237 hours on stream (balance 3) they were 2.9 (CH_4), 11.6 (C_2–C_4), 9.5 (C_5–C_{11}) and 76.0% (C_{12}+). When this catalyst was tested in a fixed bed reactor (run FB–27–2438, Section VI.2.2), the deactivation was slower and the hydrocarbon distribution shifted toward lower molecular weight products with time on stream. In general, more light hydrocarbons were produced in the fixed bed test than in the slurry reactor test under similar operating conditions. Hydrocarbon selectivities during the first mass balances for the two runs were 3.8 and 6.4 (CH_4), 15.1 and 25.4 (C_2–C_4), 20.3 and 32.3 (C_5–C_{11}), and 60.7 and 35.8% (C_{12}+) for the slurry and fixed bed tests, respectively. When syngas with H_2/CO=1.0 was used in the slurry run (balance 4), more light products were produced. The rapid deterioration of catalyst activity in the slurry reactor test was probably due to the prolonged exposure of the catalyst to CO. Following the completion of the run, solids were separated from the slurry remaining in the reactor by filtering the slurry. The carbon was then burnt to recover the catalyst (in the oxidized form). Image analysis was used to determine particle size distribution for this catalyst and it was found that almost all of the catalyst was less than 15μm compared to the 45-53μm size cut for the original catalyst that was charged to the reactor.

VI.4.2. Run SB – 25.2 – 2878 with the 100 Fe / 3.0 Cu / 0.2 K Catalyst

Slurry run SB–25.2–2878 was made with a new batch of the 100 Fe/3.0 Cu/0.2 K catalyst. Our studies on the effect of pretreatment conditions on subsequent catalytic performance showed that pretreatment in pure CO or syngas resulted in active catalysts which favored production of liquid products and wax (Section V.1.8). However, these catalysts deactivated fairly rapidly during synthesis. On the other hand, H_2 reduced catalysts exhibited good stability, but favored production of methane and other gaseous hydrocarbons. To minimize catalyst deactivation and achieve better stability, an H_2 reduction was employed in this run.

The reactor was initially charged with 35 g of catalyst and 283 g of purified n–octacosane. The catalyst was activated in the slurry reactor using H_2 at 230°C for 8 h. Following the activation, 40 g of wax was withdrawn from the reactor to an external settling tank, and the feed was switched to a H_2/CO=0.67 syngas at 2.0 Nl/g-cat.h. The reactor pressure was raised to 1.48 MPa, and the temperature was gradually increased to 260°C. These conditions were maintained throughout the run. The major events occurring during this run are listed in Table VI-13 . Three mass balances were completed before the run was terminated at about 245 h, and the results from these balances are summarized in Table VI-14.

During the first balance at 70 h, the (H_2+CO) conversion was 77.2 %. An activity plot, which shows gas contraction versus time on stream, is given in Fig. VI-30. This figure also shows the times at which wax withdrawals were made and the amount of wax removed during each withdrawal. A stability plot for this run, (H_2+CO) conversion versus time on stream, is shown in Fig. VI-31. Catalyst activity was high and stable up through the first mass balance. Hydrocarbon distribution in the first balance was 10.4 (CH_4), 24.1 $(C_2\text{-}C_4)$, 39.2 $(C_5\text{-}C_{11})$, and 26.3 % $(C_{12}+)$. Relatively high methane selectivity was expected for an H_2 reduced catalyst. Following balance 1, a withdrawal was made to the external settling tank (40 g removed) and a second withdrawal (127 g removed) was made through an internal filter (20 μm, 3/8" OD by 1.5"). This caused the (H_2+CO) conversion to drop to 67.3 %, and catalyst activity continued to decline steadily with time from that point on. Catalyst activity improved after about 150 h, but during the second balance (166 h), the (H_2+CO) conversion was only 37.6 %. Hydrocarbon selectivity improved somewhat during the second balance, as less methane and other gaseous hydrocarbons were produced. A withdrawal of 65 g wax after the second mass balance decreased catalyst activity again, and the (H_2+CO) conversion was only 13.7 %. We attempted to regain activity by adding 59 g wax in order to suspend any catalyst on the reactor wall and/or the withdrawal filter, but this effort was unsuccessful. During the third balance (240 h), the (H_2+CO) conversion was only 15.2 %, and hydrocarbon selectivity shifted toward lower molecular weight hydrocarbons. The run was terminated after this balance due to severe catalyst deactivation.

Inspection of the reactor after the run showed that as the wax level dropped during withdrawal, about 5 g of the catalyst settled on the filter and adhered to the sides of the reactor. This loss in suspended catalyst can account for some of the decline in activity observed following wax withdrawals. While we knew from the previous slurry run (SB–66–2468) that adding wax after withdrawals restored catalyst activity, we decided not to add wax during this run, but to make more frequent withdrawals to prevent an excessive drop in the slurry level. It was felt that the slow rise in the wax level during the course of reaction would wash the filter element and reactor walls, restoring catalyst activity. In Fig. VI-30 we see a large increase in contraction from 11 to 27 % at about 170 h, and an appreciable increase in contraction after

Table VI-13. Major events occuring in run SB-25.2-2878.

TOS (h)	Event
-3	Catalyst Pretreatment:H_2 at 230 °C
-1	Pressurized to 1.48 M Pa using H_2
0	Run initiated
5	Achieved desired operating conditions: 260°C,1.48 M Pa,H_2/CO=0.69,2 Nℓ/g-cat.h
71	Conditions stable. H_2+CO conversion = 77.2%
98	Drop in catalyst activity following wax withdrawals
121	Further drop in catalyst activity following wax withdrawal
167	H_2+CO conversion = 41.0%
194	Further drop in catalyst activity following wax withdrawal
198	Wax added but no improvement in activity observed
241	Conditions unstable. H_2+CO conversion = 17.5%
245	Voluntary termination of run SB-25-2878

Table VI-14. Summary of results for slurry run SB-25.2-2878.

Catalyst: 35.0 g^a, 100 Fe/3.0 Cu/0.2 K   Slurry liquid: 243 g. n-octacosane
Reactor volume: 375 cc^b

Period	1	2	3
Date	10/17/88	10/21/88	10/24/88
Time on Stream (h)	70.0	165	239
Balance Duration (h)	6.00	6.00	6.00
Average Temperature (°C)	260	260	260
Pressure (MPa)	1.48	1.48	1.48
H_2/CO Feed Ratio	0.79	0.72	0.72
Space Velocity (Nl/g–cat·h)[a]	2.01	2.01	2.11
Space Velocity (Nl/g–Fe·h)	2.95	2.95	3.10
GHSV (h^{-1})[b]	187	187	197
CO Conversion (%)	85.3	38.8	15.7
H_2+CO Conversion (%)	77.2	37.6	15.2
H_2/CO Usage	0.62	0.67	0.66
STY ($mols$ H_2+CO/g–cat·h)[a]	0.069	0.034	0.014
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	39.0	11.4	6.50
Weight % of Outlet			
H_2	1.78	3.12	4.30
H_2O	1.15	0.78	0.46
CO	14.1	57.0	81.2
CO_2	62.4	28.6	9.96
Hydrocarbons	18.6	9.41	4.00
Oxygenates	0.69	0.19	0.10
Wax[c]	1.32	0.92	0.00
Yield (g/Nm^3 H_2 + CO *Converted*)			
CH_4	19.6	21.0	32.0
C_2–C_4 Hydrocarbons	45.7	48.4	54.2
C_5–C_{11} Hydrocarbons	74.4	66.2	55.7
C_{12}+ Hydrocarbons	49.9	78.2	55.9
Wax[c]	12.5	19.0	0.00
Oxygenates	6.56	4.00	5.00
Total	196	218	203
1–2 Olefins/n–Paraffin Ratio			
C_2	0.30	1.40	1.40
C_3	2.88	4.20	3.90
C_4	2.42	3.30	2.98
C_8	1.21	2.53	2.45
C_{10}	0.87	1.65	1.88

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table VI-14 (cont'd).Summary of results for slurry run SB-25.2-2878

Period	1	2	3
Weight % of Hydrocarbons			
CH4	10.4	9.83	16.2
Ethane	5.05	3.17	4.43
Ethylene	1.41	4.15	5.77
Propane	2.46	1.59	1.95
Propylene	6.77	6.37	7.24
n–Butane	2.36	1.61	1.89
1+2 Butenes	5.51	5.12	5.43
C_4 Isomers	0.52	0.63	0.71
n–Pentane	2.64	2.04	2.13
1+2 Pentenes	4.38	6.00	6.34
C_5 Isomers	0.64	0.86	1.04
n–Hexane	1.59	1.24	2.21
1+2 Hexenes	2.11	3.30	4.27
C_6 Isomers	1.72	0.72	1.29
n–Heptane	2.42	0.81	1.18
1+2 Heptenes	3.01	2.44	2.64
C_7 Isomers	0.26	0.47	0.96
n–Octane	2.36	0.79	0.58
1+2 Octenes	2.80	1.96	1.39
C_8 Isomers	0.34	0.17	0.13
n–Nonane	2.43	0.93	0.33
1+2 Nonenes	2.38	1.72	0.62
C_9 Isomers	0.20	0.17	0.03
n–Decane	2.58	1.27	0.47
1+2 Decenes	2.22	2.07	0.87
C_{10} Isomers	0.32	0.22	0.05
n–Undecane	2.59	1.52	0.57
1+2 Undecenes	1.90	2.12	1.00
C_{11} Isomers	0.35	0.15	0.07
C_2–C_4	24.1	22.6	27.4
C_5–C_{11}	39.2	31.0	28.2
C_{12}+	26.3	36.6	28.2
Wax^c	6.60	8.89	0.00

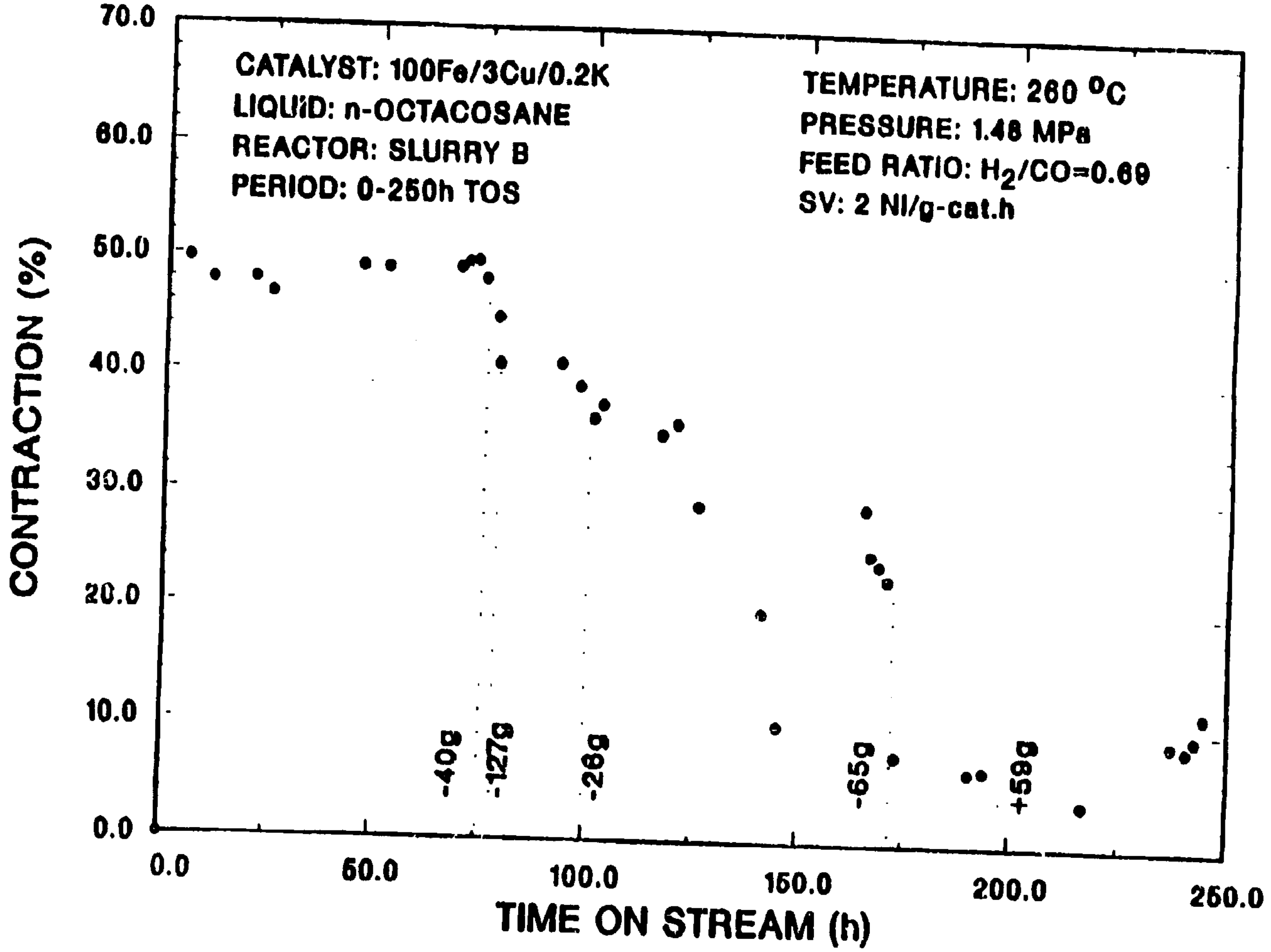

Figure VI-30 Activity plot, % contraction vs. time on stream, for Run SB-25.2-2878. weights indicate wax withdrawn (-) or added (+) to reactor

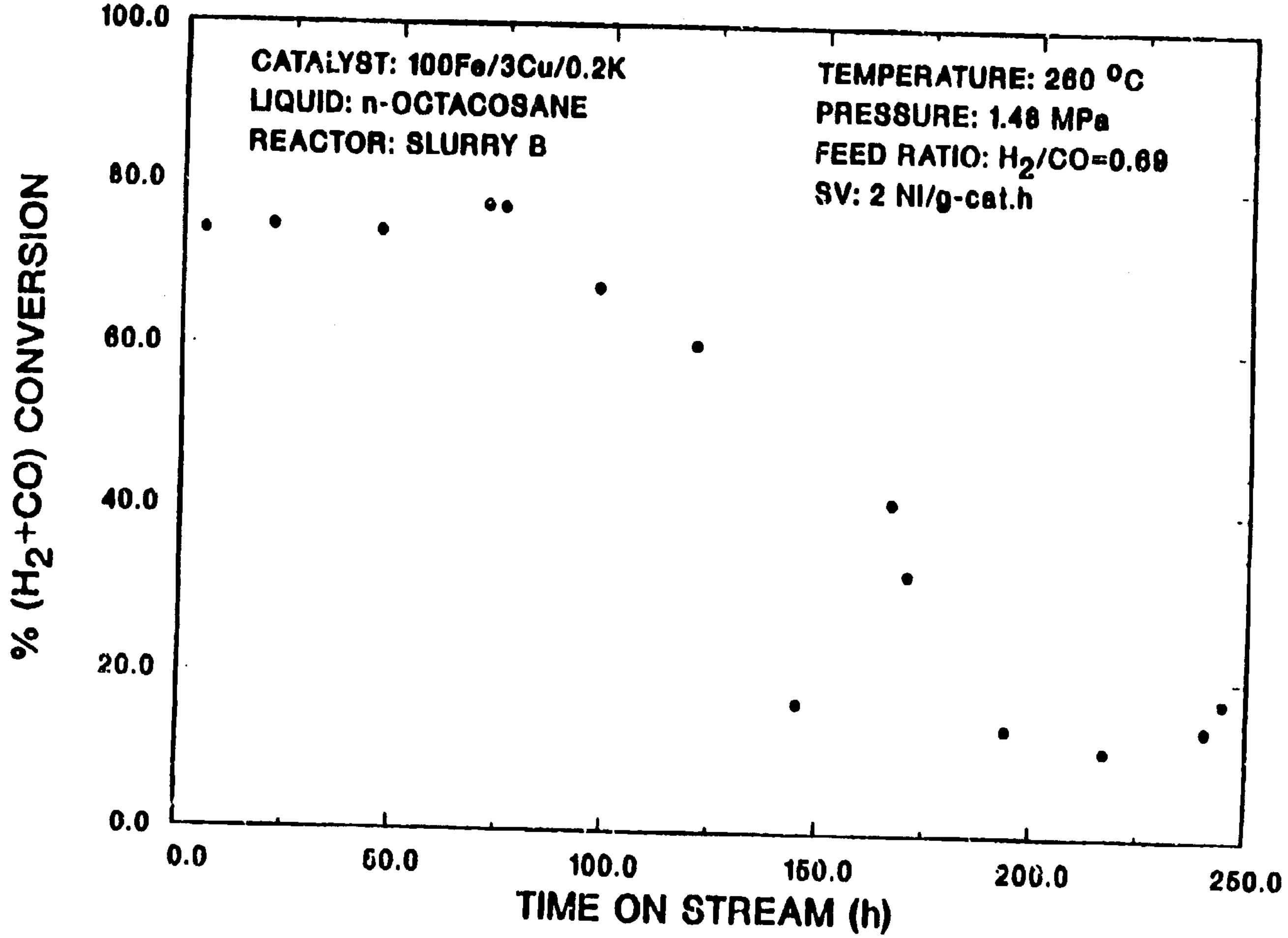

Figure VI-31 Stability plot, (H_2+CO) conversion vs. time on stream, for Run SB-25.2-2878

200 h on stream, which is due to slow buildup of wax in the reactor. It appears from this run that wax needs to be reintroduced immediately following wax withdrawal in order to raise the slurry level to the same position it had prior to the withdrawal. This would bring catalyst that adheres to the filter element and the reactor wall back to the slurry, and thus prevent rapid deactivation caused by development of hot spots.

VI.5. Summary

Major findings from the above process evaluation studies are summarized below.

(1) Catalysts containing about 24 parts of SiO_2 per 100 parts of Fe exhibited very good stability in both fixed and slurry reactor tests, but they were less active than unsupported catalysts. Also, their selectivity toward liquid hydrocarbon products (C_5+) was not as high as that achieved in Mobil's bubble column slurry reactor in high wax mode of operation (70-75% vs. 86%) and methane yields were higher (5-6% vs. 2.7%).

(2) The 100 Fe/5 Cu/4.2 K/24 SiO_2 catalyst, synthesized at Texas A&M University, had higher activity (~20%) than commercial Ruhrchemie LP 33/81 catalyst. Both catalysts had similar hydrocarbon selectivities during tests in fixed bed and slurry bed reactors (no effect of reactor type on hydrocarbon selectivity), but the catalyst activity was higher in the fixed bed reactor (Table VI-15).

(3) Catalysts with low silica content (100 Fe/5 Cu/4.2 K/8 SiO_2) or without any silica (100 Fe/3Cu/0.2K or 0.5K, and 100 Fe/1 Cu/0.2 K) had high initial activity but lacked stability. Catalyst deactivation was fairly rapid in both fixed bed and slurry bed reactor tests. Hydrocarbon selectivities in some of the tests were better (less CH_4 and gaseous hydrocarbons) than those obtained in tests with the catalysts having about 24 parts of SiO_2 per 100 parts of Fe. However, the stability of these catalysts needs to be improved by using different activation procedures and/or by modifications in their composition.

(4) As demonstrated earlier (Sections V.1.3,V.2.1 and V.2.3) hydrogen reduced, unsupported catalysts have both high activity and long term stability, but they produce more low molecular weight products than the CO activated catalysts. However, good stability was not achieved in the slurry reactor run SB-25.2-2878 with the 100Fe/3 Cu/0.2K catalyst reduced with H_2. On the other hand the same catalyst displayed remarkable stability and high activity in a fixed bed reactor test (FB-25.2-0029, Section V.2.1.3). It seems that withdrawal of accumulated wax accelerates catalyst deactivation, and further improvements in wax withdrawal procedure are needed.

Table VI-15. Activity and Selectivity Comparison of SiO_2 Containing Catalysts

	Process Conditions								Weight % of Hydrocarbons			
Catalyst/ Reactor Type	Pressure (atm)	Temp (°C)	SV (Nl/g-Fe.h)	H_2/CO feed	TOS (h)	% Conv. ($CO+H_2$)	STY[a]	Yield (g-HC/Nm^3)	CH_4	C_2-C_4	C_5-C_{11}	C_{12}+
Ruhrchemie LP 33/81	15	250	3.6	0.69	71	58.6	.052	181	5.5	22.7	18.6	53.1
fixed bed	"	"	"	"	360	53.2	.048	212	5.4	21.7	20.0	52.9
Ruhrchemie LP 33/81	"	"	"	0.67	94	46.1	.041	182	4.6	20.9	19.5	55.0
slurry	"	"	"	"	336	44.1	.040	212	5.1	22.3	22.8	49.7
100 Fe/5 Cu/4.2 K/24 SiO_2	"	"	"	0.69	71	67.9	.061	183	5.7	21.9	21.5	50.9
fixed bed	"	"	"	"	356	65.5	.059	184	6.2	24.5	24.1	45.2
100 Fe/5 Cu/4.2 K/24 SiO_2	"	"	"	0.69	69	56.1	.050	203	3.9	17.9	20.7	57.5
slurry	"	"	"	"	357	49.3	.044	205	5.5	21.8	24.4	48.3
Ruhrchemie LP 33/81	"	"	"	0.98	528	56.0	.050	189	8.5	29.6	25.3	36.6
fixed bed	"	"	"	"	623	55.5	.050	197	7.9	27.7	23.2	41.2
100 Fe/5 Cu/4.2 K/24 SiO_2	"	"	"	1.03	644	60.6	.054	182	8.0	29.3	24.9	37.8
fixed bed	"	"	"	"	716	60.6	.054	178	8.0	29.0	24.8	38.2
100 Fe/5 Cu/4.2 K/8 SiO_2	"	235	3.2	1.03	48	77.9	.069	188	4.2	17.8	21.4	56.5
fixed bed	"	"	"	"	240	50.9	.051	195	4.0	16.6	18.8	60.6

[a] STY in moles (H_2+CO) converted/g-cat.h