IV-2 Testing of Iron/Silica Catalysts Synthesized at TAMU

Eight catalysts containing potassium and copper as promoters and silicon oxide as a binder were evaluated in a stirred tank slurry reactor (STSR). In all tests a calcined catalyst was crushed and sieved to either 270/325 mesh size (44 - 53 μm) or less than 270 mesh size, prior to loading to a reactor. A pre-purified normal octacosane was used as the liquid (slurry) medium (about 400 cm^3 of static volume) in all tests. The initial amount of catalyst used in different tests was between 7 and 31 g, resulting in slurry concentrations of 2.5 to 11 wt% (typically, 3-5.5%). Test designations and physico-chemical properties of catalysts are summarized in Table IV-2.1.

In general, the elemental chemical composition of all catalysts, determined by atomic absorption, is in good agreement with the intended (nominal) catalyst composition. The potassium content of catalysts used in runs SB-0261, SB-0921, SB-1421 and SB-2141 was higher than the nominal one. The agreement between results of analysis performed at TAMU, and other laboratories (UOP, PETC and Sandia National Laboratory) is satisfactory. Our analysis tends to overestimate the potassium content of a catalyst.

The surface areas of all calcined catalysts were about the same (220 - 260 m^2/g), regardless of their silica contents. Also, the pore volumes of seven of the eight catalysts were between 0.6 and 0.7 cm^3/g. The catalyst with nominal composition 100 Fe/ 5 Cu/ 4.2 K/ 8 SiO_2 (Run SB-1910) had markedly lower pore volume (0.38 cm^3) than the other catalysts. One of the two catalysts with the same nominal composition, i.e. 100 Fe/ 5 Cu/ 4.2 K/ 16 SiO_2, was prepared in 1988 (Run SB-2270), and the other one in 1990 (Run SB-2832) by different researchers. Similarity in chemical composition and physical properties of these two catalysts is indicative of good reproducibility of the catalyst preparation procedure.

Table IV-2.1 Physico-Chemical Properties and Test Designation for Iron/Silica Catalysts.

Run ID	SA-1371	SB-0931	SB-1310	SB-0261	SB-2270	SB-2832	SB-1931	SB-3101
Nominal Catalyst Composition (Fe/Cu/K/SiO_2)	100/3/3/8	100/3/4/8	100/5/4.2/8	100/3/4/16	100/5/4.2/16	100/5/4.2/16	100/5/6/24	100/5/8/24
Actual Catalyst Composition (Fe/Cu/K/SiO_2)	100/3 3/4 5/12	100/3.1/4.7/9 6	100/4.6/4.6/9	100/3/6.7/15.5 100/3.1/5 9/15.5[c]	100/5.1/5/18.5 100/5/4.3/18[b]	100/5.6/6.3/18.5 100/5.6/3.9/14.2[a] 100/5.1/3.7/13.1[c]	100/5.1/8.1/26 100/5.5/6.6/24[a]	100/5 1/10 2/28
BET Surface Area (m^2/g)	225	225*	250	245	257	234	222	222**
Pore Volume (cm^3/g)	0.59	0.59	0.38	0.65	0.70	0.61	0.68	0 68

*: Catalysts 100 Fe/3 Cu/x K/8 SiO_2 (x = 3 or 4) have the same precursor

**: Catalysts 100 Fe/5 Cu/y K/24 SiO_2 (y = 6 or 8) have the same precursor

Measurements conducted at: (a) Pittsburgh Energy Technology Center
(b) Sandia National Laboratory
(c) Universol Oil Products, Inc.

Catalyst compositions are in mass basis.

On the basis of results obtained in the two most successful studies of FT synthesis in bubble column slurry reactors (Kölbel and Ralek, 1980; Kuo, 1985), the PETC had established guidelines for desired activity, selectivity and stability of the iron FT catalysts. These guidelines (target performance) were given in the DOE's Request for Proposal (No. DE-PR22-90PC90021) entitled "Technology Development for Iron Fischer-Tropsch Catalysts", and are reproduced in Table IV-2.2.

Results from individual tests (grouped according to their silicon oxide content) are described first followed by summary of results, including comparisons of the catalysts performance with the target performance and with other iron FT catalysts.

IV-2.1 Run SA-1371 with 100 Fe/3 Cu/3 K/8 SiO_2 Catalyst

The catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.7 Nl/g-cat/h and $H_2/CO = 0.67$ during the first 50 h. After withdrawal of a slurry sample the gas space velocity was increased to 1.87 Nl/g-cat/h. There were no major operational problem encountered during the test. The run was terminated after 360 h on stream. Results from five mass balances made during the test are summarized in Table IV-2.3, whereas major events are listed in Table IV-2.4.

Catalyst Activity and Stability

The catalyst deactivated continuously with time on stream. The (H_2+CO) conversion decreased from 82% initially to 52% at 360 h, while the VC decreased from 54% to 32% during the same time period (Figure IV-2.1). WGS activity of the catalyst was high, and the usage ratio varied between 0.54 – 0.58.

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn through a porous sintered metal filter with nominal pore size of 0.5 µm. The filter was placed horizontally at a height corresponding to the static slurry volume of 400 cc. Initial pressure drop across the filter was 15 psi but it

Table IV-2.2 Catalyst Target Performance

ACTIVITY	
(H_2+CO) conversion, %	88
CO conversion, %	90
$Nm^3(H_2+CO)$ reacted/(kg-Fe·h)	2.6
STY (kg C_3^+/m^3 reactor/day)	900
HYDROCARBON SELECTIVITY	
(g $HC/Nm^3(H_2+CO)$ reacted)	≥178
(g $C_3^+/Nm^3(H_2+CO)$ reacted)	≥166
(C_1+C_2), wt%	6.7-8.0

PROCESS CONDITIONS

(H_2/CO) feed ratio = 0.6-1.0

Pressure (bar) = 1-20

Temperature (°C) = 230-300

Space velocity = 2-4 (Nm^3/kg-Fe·h)

DEACTIVATION RATE: ≤ 1% per day during 30 days of continuous testing.

Table IV-2.3 Summary of Slurry Reactor Test Results for Run SA-1371.

Period	1	2	3	4	5
Time on Stream (h)	41.0	103.0	158.0	233.5	305.0
Balance Duration (h)	6.0	12.0	7.5	8.5	8.2
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.684	.684	.709	.704	.692
Space Velocity (Nl/g-cat·h)[a]	1.69	1.87	1.87	1.87	1.87
Space Velocity (Nl/g-Fe·h)	2.94	3.25	3.25	3.25	3.25
GHSV (h^{-1})[b]	44.0	45.3	45.3	45.3	45.3
CO Conversion (%)	87.2	83.4	80.5	71.6	62.0
H_2+CO Conversion (%)	82.2	77.0	74.5	66.4	57.9
H_2/CO Usage	.586	.554	.582	.580	.580
STY ($mols$ H_2+CO/g-cat·h)[a]	.062	.062	.062	.055	.048
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	31.2	53.2	53.8	34.7	62.5
Weight % of Outlet					
H_2	1.20	1.51	1.64	2.00	2.27
H_2O	1.12	.638	.558	.624	.263
CO	12.3	15.7	18.5	27.4	36.0
CO_2	63.1	62.1	59.4	52.1	46.0
Hydrocarbons	13.3	12.3	12.3	12.2	11.2
Oxygenates	.965	.923	1.17	1.10	1.00
Wax[c]	8.12	6.81	6.43	4.56	3.29
Yield (g/Nm^3 H_2 + CO *Converted*)					
CH_4	9.18	10.9	11.1	11.9	12.4
C_2-C_4 Hydrocarbons	36.3	39.1	37.9	37.8	40.8
C_5-C_{11} Hydrocarbons	64.0	58.7	60.2	66.1	70.0
C_{12}+ Hydrocarbons	90.8	86.1	85.5	76.1	71.2
Wax[c]	76.1	69.3	66.7	52.3	44.2
Oxygenates	9.05	9.39	12.1	12.6	13.5
Total	209.	204.	207.	205.	208.
1+2 Olefins/n-Paraffin Ratio					
C_2	1.16	1.62	2.04	2.54	3.16
C_3	5.35	4.70	5.15	4.23	4.19
C_4	4.46	4.10	3.74	3.40	3.22
C_6	2.63	2.69	2.52	2.51	2.28
C_{10}	2.19	2.41	2.01	2.40	2.46

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.3 (cont'd) Summary of Slurry Reactor Test Results for Run SA-1371.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH4	4.58	5.58	5.68	6.20	6.38
Ethane	2.16	2.17	1.80	1.56	1.48
Ethylene	2.33	3.27	3.43	3.70	4.38
Propane	1.20	1.45	1.32	1.53	1.63
Propylene	6.12	6.51	6.48	6.17	6.53
n-Butane	1.09	1.22	1.27	1.42	1.51
1+2 Butenes	4.70	4.84	4.58	4.66	4.70
C_4 Isomers	.542	.615	.595	.644	.732
n-Pentane	1.33	1.54	1.81	1.67	1.86
1+2 Pentenes	4.70	4.93	4.97	4.93	4.92
C_5 Isomers	.978	.973	1.00	1.03	.928
n-Hexane	1.03	1.05	1.18	1.30	1.45
1+2 Hexenes	3.34	3.18	3.26	3.68	3.34
C_6 Isomers	.878	1.02	1.07	1.47	1.64
n-Heptane	.939	.881	.957	1.14	1.37
1+2 Heptenes	2.52	2.22	2.37	2.70	2.84
C_7 Isomers	.718	1.32	.784	1.17	1.36
n-Octane	.946	.785	.921	1.01	1.17
1+2 Octenes	2.44	2.07	2.28	2.49	2.62
C_8 Isomers	.570	.616	.769	.848	1.22
n-Nonane	1.10	.769	.757	.975	.879
1+2 Nonenes	2.54	2.00	2.09	2.22	2.19
C_9 Isomers	.416	.425	.524	.306	.544
n-Decane	1.08	.828	.716	.946	.967
1+2 Decenes	2.33	1.97	1.84	2.24	2.35
C_{10} Isomers	.636	.518	.564	.649	.830
n-Undecane	.928	.733	.654	.885	.807
1+2 Undecenes	1.88	1.72	1.69	2.16	2.05
C_{11} Isomers	.645	.588	.704	.610	.710
C_2-C_4	18.1	20.1	19.5	19.7	21.0
C_5-C_{11}	31.9	30.1	30.9	34.5	36.0
C_{12}+	45.3	41.2	43.9	39.7	36.6
Wax[c]	38.0	35.6	34.2	27.3	22.8

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.4 Major Events in Run SA-1371.

TOS(h)	Event
	Slurry loading: 300 g n-octacosane, 11.0 g (particle size < 270 mesh) catalyst
	Catalyst pretreatment: H_2 at 240°C
	Slurry sample withdrawal: 19.3 g wax; 0.7 g catalyst
	Wax withdrawal through filter: 13.6 g
0	Initiate synthesis gas flow
2	Achieved process conditions: 260°C, 1.48 MPa, 1.7 Nl/g-cat/h, $H_2/CO = 0.67$
50	Slurry sample withdrawal: 18.4 g wax, 0.6 g catalyst
359	Two slurry sample withdrawals: 41.5 g wax, 1.5 g catalysts
360	End of run: 237 g wax, 7.3 g catalyst recovered from reactor
	Wax/catalyst removed during the run: 250 g wax, 2.1 g catalyst
	Catalyst recovery: 92%; Wax recovery: 90%

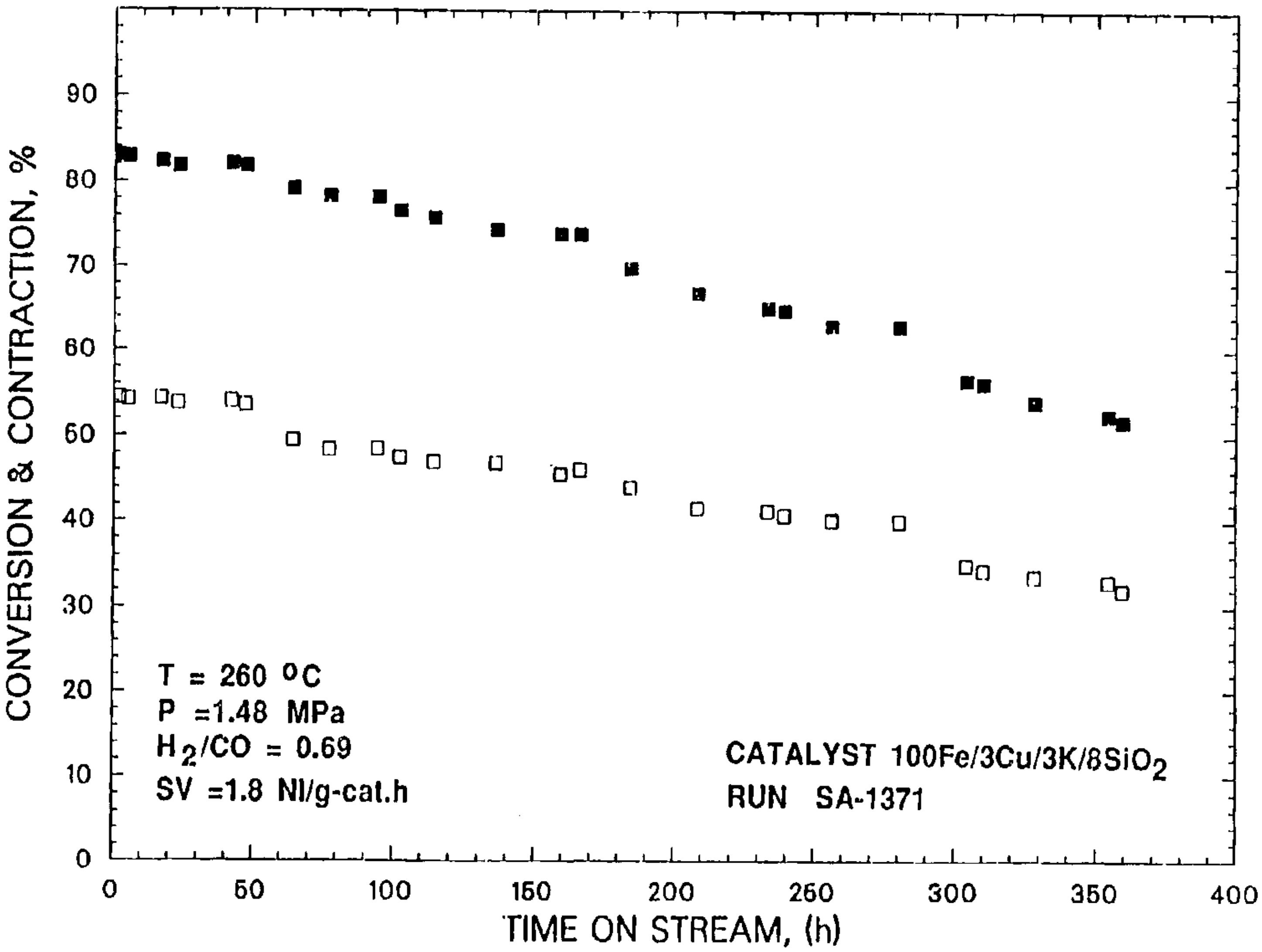

Figure IV-2.1 (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SA-1371.

reached equilibrium very quickly. Filtration had to be repeated many times in order to withdraw excess wax. No significant amount of catalyst was removed with the withdrawn wax (based on color of the wax). The wax production rate decreased from 1.1 to 0.5 g/h as catalyst deactivated with time on stream.

At the end of the test, 7.3 g of catalyst was recovered from the reactor (determined by burning slurry samples in a crucible). Another estimated 2.8 g was removed from the reactor during the test with three slurry samples for catalyst characterization (Table IV-2.4). The catalyst recovery was about 92% based on the amount of catalyst charged into the reactor, whereas the wax recovery was about 90%.

Catalyst Characterization by XRD and/or MES

After the reduction with hydrogen at 240°C for 2 h and prior to FT synthesis, magnetite was the only phase detected by XRD analysis. After 50 h of synthesis, there has been no change in the catalyst composition. A sample withdrawn at 359 h from the reactor in an inert atmosphere, and the one at the end of the run, after exposure to the air prior to catalyst/wax separation had similar XRD patterns, and in addition to magnetite the peaks characteristic to iron carbides were observed. Thus the catalyst was only partially carburized after 360 hours of FT synthesis.

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time on stream. For example, methane selectivity increased from 4.6% in balance 1 (TOS = 42 h) to 6.4% in balance 5 (TOS = 305 h), (C_2–C_4) varied between 18 - 21, (C_5–C_{11}) increased form 32 to 36, while C_{12}+ decreased from 45 to 37 wt %, respectively (Table IV-2.3).

A typical ASF plot for products collected in mass balance 3 (TOS = 158 h) is shown in Figure IV-2.2. The existence of double alpha phenomenon is evident from this plot, and experimental data are fitted well with the three parameter model.

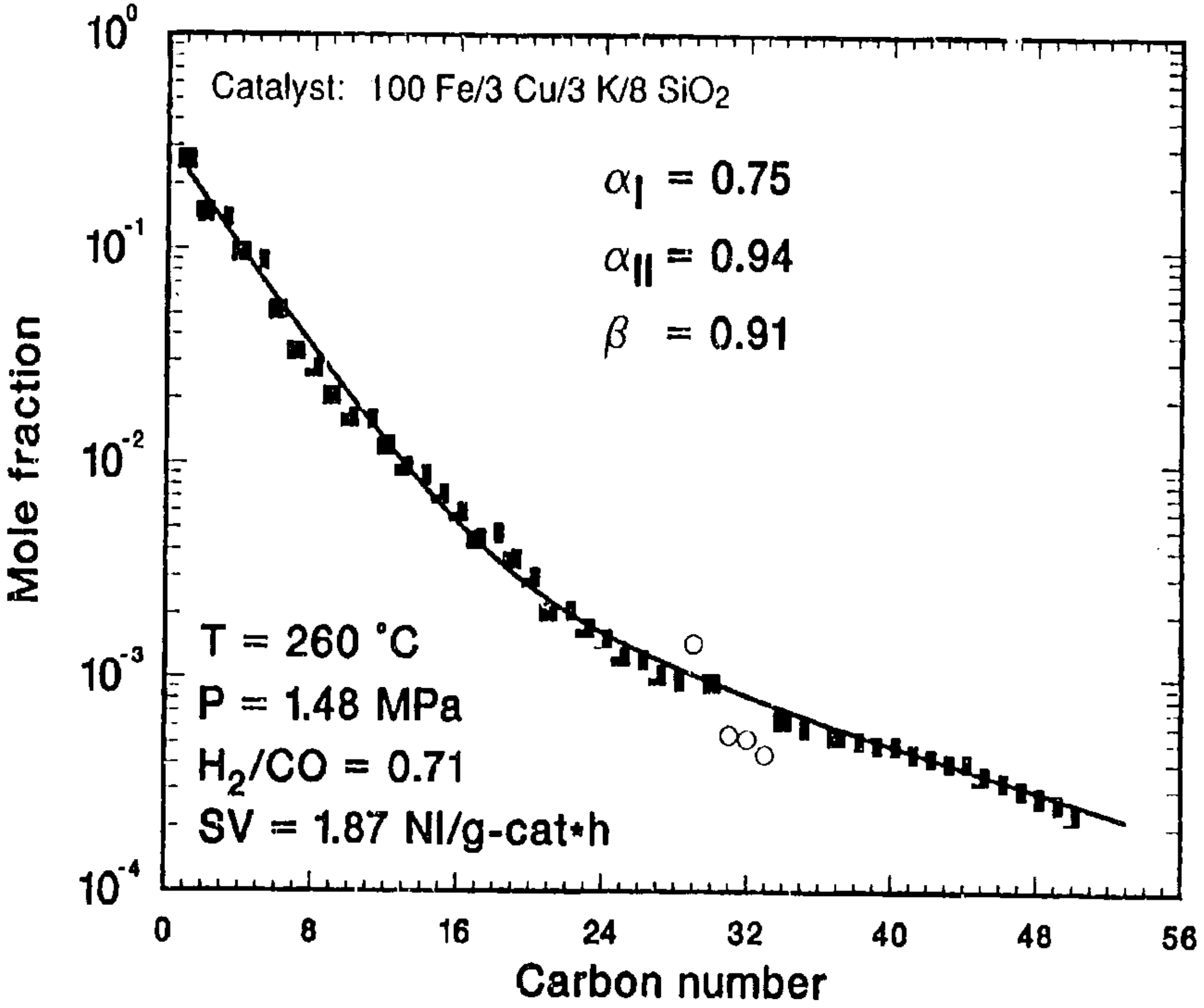

Figure IV-2.2 Carbon number product distribution for Run SA-1371 (TOS=158 h).

IV-2.2 Run SB-0931 with 100 Fe/3 Cu/4 K/8 SiO_2 Catalyst

Slurry reactor run SB-0931 was conducted to evaluate performance of a precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/8 SiO_2. Reaction pressure and syngas feed composition were held constant throughout the test at 1.48 MPa (200 psig) and H_2/CO = 0.66 – 0.69, respectively. On the basis of process conditions employed the run can be divided into three periods: 0 – 350 h (T = 260°C, SV = 1.25 – 1.5 Nl/g-cat/h); 350 – 460 h (T = 265°C, SV = 1.25 Nl/g-cat/h); and 460 – 560 h (T = 260°C, SV = 1.5 – 2.1 Nl/g-cat/h). The test was terminated voluntarily after 570 h on stream. Results from nine mass balances made during the test are summarized in Table IV-2.5, whereas major events are listed in Table IV-2.6.

Catalyst Activity and Stability

The catalyst deactivated slowly with time during the first 230 h of testing at 260°C, 200 psig, 1.5 Nl/g-cat/h and H_2/CO = 0.66. During this period the (H_2+CO) conversion varied between 80 and 88% (Figure IV-2.3), whereas the gas volumetric contraction (VC) was between 52 and 60% (Figure IV-2.4). The rate of catalyst deactivation was much higher during the next 30 h, and the (H_2+CO) conversion and VC decreased to 76% and 50%, respectively. At this point the gas flow rate was decreased (SV = 1.25 Nl/g-cat/h) in order to increase the (H_2+CO) conversion, and these conditions were maintained over the next 90 h (TOS = 260 – 350 h). During this period, the catalyst continued to deactivate with time (see Figures IV-2.3 and 2.4), and at 356 h the reaction temperature was increased to 265°C. Both the (H_2+CO) conversion and VC, increased initially and then started to decline with time. For example, the (H_2+CO) conversion decreased from 79.3% at 360 h to 71.8% at 458 h on stream, whereas the VC decreased from 53.2 to 45.8% during the same period of time.

At 460 h on stream the baseline conditions were reestablished (260°C, 250 cc/min), however, the gas space has velocity increased to about 1.6 Nl/g-cat/h due to

Table IV-2.5 Summary of Slurry Reactor Test Results for Run SB-0931.

Period	1	2	3	4	5
Time on Stream (h)	49.0	109.0	171.0	244.0	329.0
Balance Duration (h)	12.0	10.0	13.0	8.5	8.0
Average Temperature (°C)	260.	200.	260.	260.	200.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.661	.661	.661	.661	.661
Space Velocity (Nl/g-cat·h)[a]	1.49	1.49	1.51	1.53	1.25
Space Velocity (Nl/g-Fe·h)	2.44	2.44	2.48	2.52	2.06
GHSV (h^{-1})[b]	34.0	34.9	34.9	34.9	27.9
CO Conversion (%)	92.6	80.1	88.9	81.0	79.8
H_2+CO Conversion (%)	86.3	84.3	83.5	75.3	73.6
H_2/CO Usage	.547	.572	.559	543	.533
STY ($mols$ H_2+CO/g-cat·h)[a]	.057	.054	.054	.048	.041
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	49.8	42.6	41.8	39.1	73.6
Weight % of Outlet					
H_2	1.06	1.04	1.13	1.52	1.63
H_2O	1.17	.871	.955	.737	.387
CO	7.02	10.5	10.6	18.1	19.4
CO_2	68.3	65.4	66.9	60.5	59.5
Hydrocarbons	9.38	9.78	9.69	8.89	6.84
Oxygenates	.772	.510	.426	.422	.328
Wax[c]	12.3	11.9	11.3	9.87	11.9
Yield (g/Nm^3 H_2 + CO *Converted*)					
CH_4	4.86	5.34	5.53	5.07	6.78
C_2-C_4 Hydrocarbons	21.1	22.6	22.6	24.5	24.5
C_5-C_{11} Hydrocarbons	43.1	40.3	31.4	33.2	32.8
C_{12}+ Hydrocarbons	130.	134.	138.	132	136.
Wax[c]	113.	111.	106.	103.	127.
Oxygenates	7.08	4.76	4.02	4.41	3.50
Total	206.	207.	202.	209.	204.
1+2 Olefins/n-Paraffin Ratio					
C_2	2.15	2.26	2.26	3.05	3.17
C_3	6.85	7.07	7.05	6.54	6.42
C_4	5.68	6.27	6.28	5.62	5.47
C_8	4.27	3.66	3.72	4.17	3.98
C_{10}	8.80	2.51	3.20	3.66	3.07

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	6	7	8	9
Time on Stream (h)	397.0	446.0	545.0	554.0
Balance Duration (h)	9.0	12.0	6.0	10.0
Average Temperature (°C)	265.	265.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.695	.695	.695	.667
Space Velocity (Nl/g-$cat \cdot h$)[a]	1.26	1.30	2.05	1.44
Space Velocity (Nl/g-Fe$\cdot h$)	2.08	2.14	3.38	2.37
GHSV (h^{-1})[b]	27.9	27.9	34.9	24.4
CO Conversion (%)	81.6	79.0	66.6	76.5
H_2+CO Conversion (%)	75.2	71.7	60.3	71.1
H_2/CO Usage	.561	.538	.533	.549
STY ($mols\ H_2+CO/g$-$cat \cdot h$)[a]	.042	.037	.039	.046
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	136.	84.2	53.8	59.6
Weight % of Outlet				
H_2	1.64	1.86	2.33	1.71
H_2O	.233	.366	.384	.409
CO	17.7	20.1	31.8	22.6
CO_2	60.0	58.4	49.6	56.7
Hydrocarbons	10.0	10.9	9.91	10.4
Oxygenates	.198	.154	.160	.191
Wax[c]	10.2	8.19	5.75	7.94
Yield (g/Nm^3 H_2 + CO $Converted$)				
CH_4	7.22	7.73	7.51	7.80
C_2-C_4 Hydrocarbons	24.5	25.5	24.8	24.3
C_5-C_{11} Hydrocarbons	35.2	36.8	35.5	34.6
C_{12}+ Hydrocarbons	140.	136.	133.	135.
Wax[c]	105.	88.2	73.8	87.1
Oxygenates	2.02	1.66	2.05	2.09
Total	209.	208.	203.	203.
1+2 Olefins/n-Paraffin Ratio				
C_2	3.76	3.90	4.76	4.05
C_3	6.25	5.18	6.09	6.26
C_4	5.62	5.50	5.16	5.40
C_6	3.82	4.37	4.05	5.15
C_{10}	3.04	4.99	4.44	4.30

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH4	2.45	2.65	2.80	3.05	3.38
Ethane	.948	1.05	1.07	.942	.899
Ethylene	1.90	2.21	2.26	2.68	2.66
Propane	.533	.553	.564	.649	.645
Propylene	3.48	3.73	3.80	4.05	3.96
n-Butane	.533	.480	.489	.599	.598
1+2 Butenes	2.92	2.91	2.96	3.24	3.16
C_4 Isomers	.321	.276	.281	.324	.318
n-Pentane	.111	.436	.448	.587	.579
1+2 Pentenes	.605	2.54	2.61	3.06	2.92
C_5 Isomers	.215	.592	.627	.711	.557
n-Hexane	.389	.356	.549	.421	.409
1+2 Hexenes	1.72	1.39	1.74	1.65	1.70
C_6 Isomers	.739	.639	.939	.818	.644
n-Heptane	.338	.325	.305	.221	.299
1+2 Heptenes	1.38	1.29	1.20	.938	2.31
C_7 Isomers	.421	.717	.932	.324	.415
n-Octane	.330	.476	.251	.224	.327
1+2 Octenes	1.39	1.71	.917	.919	1.28
C_8 Isomers	.516	.725	.285	.213	.356
n-Nonane	.582	.558	.283	.382	.569
1+2 Nonenes	1.00	1.81	1.07	1.44	.923
C_9 Isomers	.216	.316	.191	.147	.0849
n-Decane	.177	.644	.340	.460	.298
1+2 Decenes	1.53	1.59	1.07	1.66	.902
C_{10} Isomers	2.69	.543	.253	.174	.164
n-Undecane	.272	.640	.422	.553	.305
1+2 Undecenes	1.77	1.63	1.15	1.78	.927
C_{11} Isomers	5.24	1.02	.318	.278	.311
C_2-C_4	10.6	11.2	11.4	12.5	12.2
C_5-C_{11}	21.7	19.9	15.9	17.0	16.4
C_{12}+	65.2	66.2	69.9	67.5	68.0
Wax^c	56.7	54.8	53.8	52.6	63.6

^{c} Unanalyzed wax withdrawn from reactor

Table IV-2.5 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0931.

Period	6	7	8	9
Weight % of Hydrocarbons				
CH4	3.49	3.76	3.74	3.87
Ethane	.733	.749	.634	.718
Ethylene	2.57	2.72	2.81	2.72
Propane	.664	.707	.722	.689
Propylene	3.96	4.17	4.19	4.12
n-Butane	.597	.630	.658	.608
1+2 Butenes	3.21	3.34	3.28	3.17
C_4 Isomers	.0911	.0793	.0738	.0674
n-Pentane	.620	.675	.713	.631
1+2 Pentenes	2.48	2.61	2.46	2.36
C_5 Isomers	1.39	.639	.553	.559
n-Hexane	.481	.595	.465	.440
1+2 Hexenes	1.64	1.98	1.56	1.48
C_6 Isomers	.616	.775	.408	.617
n-Heptane	.242	.401	.333	.253
1+2 Heptenes	.981	1.57	1.17	.962
C_7 Isomers	.400	.551	.467	.386
n-Octane	.229	.369	.337	.248
1+2 Octenes	.859	1.58	1.34	1.25
C_8 Isomers	.226	.414	.299	.170
n-Nonane	.364	.349	.377	.442
1+2 Nonenes	1.21	1.55	1.59	1.76
C_9 Isomers	.112	.0764	.0707	.0709
n-Decane	.560	.301	.482	.490
1+2 Decenes	1.68	1.48	2.11	2.08
C_{10} Isomers	.269	.0934	.156	.156
n-Undecane	.632	.330	.520	.521
1+2 Undecenes	1.53	1.44	2.16	2.16
C_{11} Isomers	.494	.0600	.113	.115
C_2-C_4	11.9	12.4	12.4	12.1
C_5-C_{11}	17.0	17.9	17.7	17.2
C_{12}+	67.6	66.0	66.2	66.9
Wax^c	60.6	42.8	36.7	43.3

^{c} Unanalyzed wax withdrawn from reactor

Table IV-2.6 Major Events in Run SB-0931.

TOS(h)	Event
	Slurry loading: 301 g n-octacosane, 10.4 g (270 – 325 mesh) catalyst Catalyst pretreatment: H_2 at 220°C Slurry sample removal: 8.9 g wax; 0.3 g catalyst Wax withdrawal through a filter: 42.4 g
1	Achieved initial process conditions: 260°C, 1.48 MPa, 250 cc/min, $H_2/CO=0.66$
49 – 252	Mass balances 1 – 4 at above conditions
262	Change gas flow rate to 200 cc/min
61 – 328	10 wax withdrawals (244 g of wax; 0.41 g catalyst)
329 – 337	Mass balance 5
352	Change reaction temperature to 265°C
374 – 495	9 wax withdrawals (128 g wax; 0.87 g catalyst)
397 – 458	Mass balances 6 and 7 at 265°C, 1.48 MPa, 200 cc/min , $H_2/CO = 0.69$
459	Change reaction temperature to 260°C and gas flow rate to 250 cc/min
497 – 500	Reactor overflow with accumulated wax; wax withdrawal through a dipleg to an external settler (106 g wax; 1.4 g catalyst)
519	Catalyst regeneration with H_2 at 220 – 245°C
545 – 551	Mass balance 8 at 260°C, 1.48 MPa 250 cc/min, $H_2/CO = 0.69$
551	Change gas flow rate to 175 cc/min
554 – 564	Mass balance 9 at 260°C, 1.48 MPa, 175 cc/min, $H_2/CO = 0.69$
565	Two slurry sample removals: 23.8 g wax; 0.32 g catalyst
570	End of run: 378.3 g wax; 6 g catalyst Catalyst recovery: 89.4%; Wax recovery: 89%

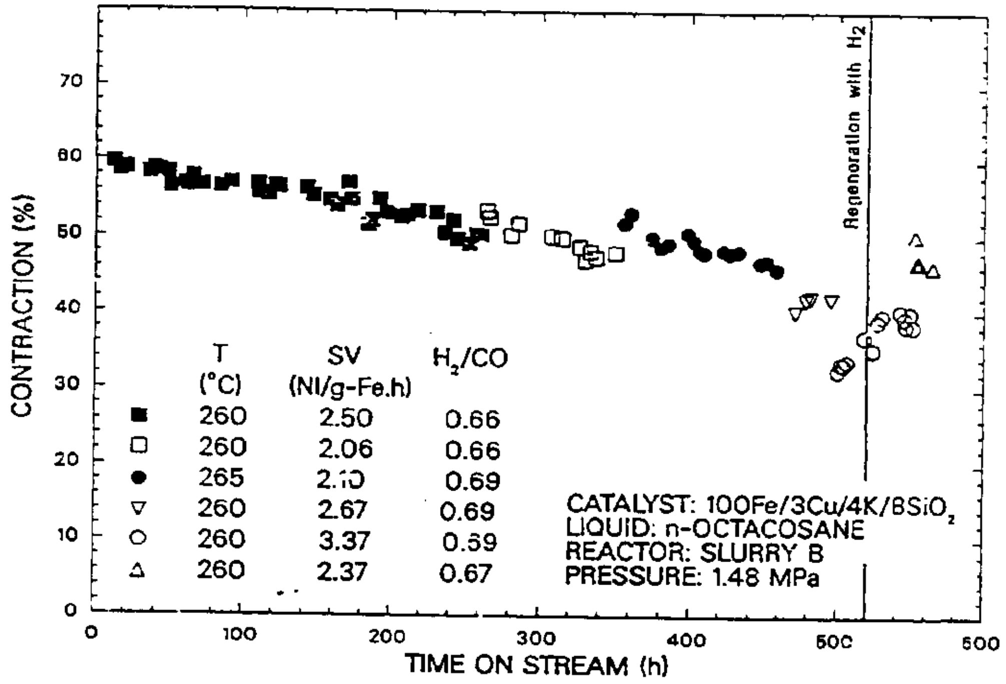

Figure IV-2.3 Volumetric contraction versus time on stream for Run SB-0931.

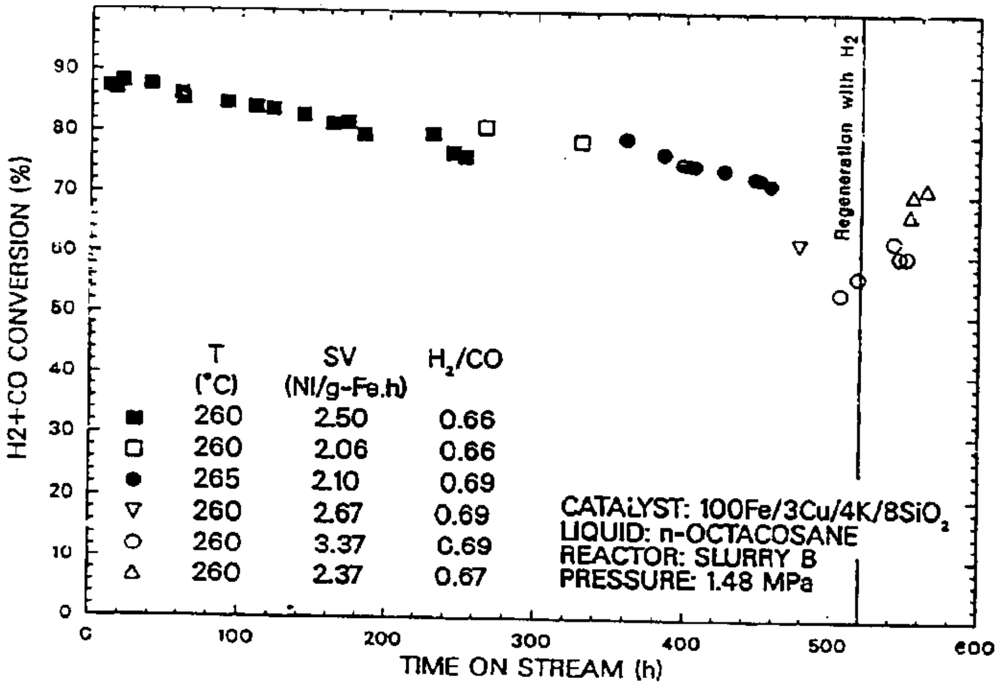

Figure IV-2.4 (H_2+CO) conversion versus time on stream for Run SB-0931.

losses of catalysts during wax withdrawals as discussed in the following section. As shown in Figures IV-2.3 and 2.4, a significant decrease in (H_2+CO) conversion and VC occurred at about 500 h, which may be attributed in part to the removal of the catalyst from the system following slurry withdrawal at 497 h through a dipleg. About 1.4 g of the catalyst was removed from the reactor, which resulted in increase of the gas space velocity to about 2.05 (Nl/g-cat/h). At 519 h, the catalyst was regenerated with H_2 at about 230°C for 2 h, and this resulted in marked increase in catalyst activity. At 550 h the gas flow rate was decreased in order to obtain the baseline gas space velocity of 1.5 Nl/g-cat/h. The (H_2+CO) conversion at 560 h was about 70%. The loss of conversion over 560 h of testing was about 39% (i.e. ~1.7% per day).

The water-gas-shift (WGS) activity was high throughout the test. The usage ratio varied between 0.54 and 0.60, with an average value of 0.56.

Wax and Catalyst Inventories/Withdrawals

During the first 500 h on stream the excess wax produced was withdrawn through a 2 µm porous metal filter placed horizontally at a height corresponding to a static slurry volume of 410 cm^3. The first two withdrawals (after the reduction – 42 g, and after the first mass balance at 65 h – 84 g) were successful. However, the subsequent wax withdrawals were not complete and as a result the wax continued to accumulate in the reactor. At about 490 h on stream, the amount of wax accumulated in the reactor was large enough to cause overflow, and shortly after that the excess wax (106 g) was withdrawn through a dipleg to an external settler. The wax withdrawn through the internal filter, as well as the wax from the external settler contained some catalyst. The amounts of catalyst in the wax withdrawn from the reactor, and in the slurry at the end of the run were determined by burning slurry (wax) samples in a crucible (see Table IV-2.6). The catalyst recovery was about 89%, based on the amount of catalyst charged into the reactor. Gas space velocities reported in Table IV-2.5 were adjusted to reflect partial removal of the catalyst throughout the test.

Due to incomplete wax withdrawals during the test, total mass, and atomic closures for carbon and hydrogen were low, however the oxygen atomic closures were within 100 ± 3% in all mass balances. Wax production rates in different mass balances were estimated to get good atomic closures. After adjustments in the wax production rates, total and atomic closures were all within 100 ± 3%. Hydrocarbon selectivities reported in Table IV-2.5 are based on estimated wax production rates. The estimated wax production rates were decreasing with time on stream and ranged from 0.75 to 1.3 g/h. Average (experimental) wax production rate for the entire test was 1.1 g/h.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 220°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. A sample withdrawn at 564 h from the reactor was analyzed by MES and found to contain: Superparamagnetic oxide/oxyhydrohide - 30%; magnetite - 20%; and ε'-carbide - 50%. The following phases were detected by XRD in a sample from the end of the run slurry (570 h) : magnetite, iron carbide(s) and iron carbonate. The catalyst was only partially carburized after 570 hours of FT synthesis.

Hydrocarbon and Carbon Number Product Distributions

During the first period of testing (0 – 350 h) at 260°C, methane and light gas selectivities increased with time on stream. Methane selectivity varied between 2.5 and 3.4%, whereas (C_2–C_4) selectivity varied between 10.6 and 12.5%. (C_1+C_2) selectivity was lower than 7% during this period. During testing at 265°C (350 – 460 h on stream) methane selectivity increased to 3.5% – 3.8%, whereas (C_1+C_2) selectivity was between 6.7 and 7.2%. After the catalyst regeneration, methane and (C_1+C_2) selectivities were about 3.8 and 7.3%, respectively.

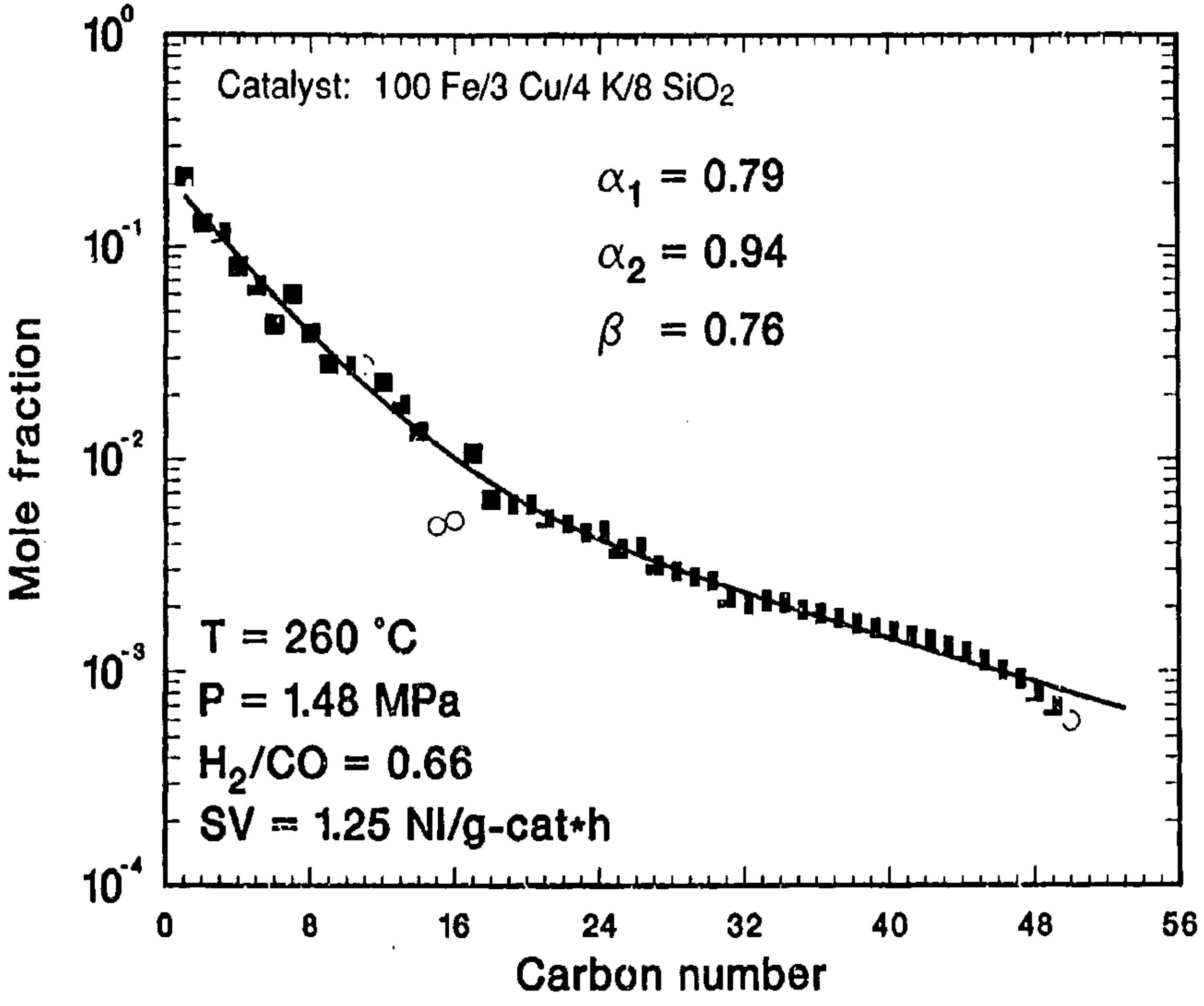

Figure IV-2.5 Carbon number product distribution for Run SB-0931 (TOS=329 h).

Carbon number product distribution is shown in Figure IV-2.5 (Mass balance 5, TOS = 329 h). The existence of "double alpha" phenomenon is evident from this plot. Chain growth probabilities are $\alpha_1 = 0.79$ and $\alpha_2 = 0.94$.

Concluding Remarks

Overall this run has been successful. Initial catalyst activity, selectivity, and deactivation rate were within the DOE targets. Catalyst deactivation rate increased with time on stream, however hydrocarbon selectivity remained within the target throughout the test. Regeneration procedure employed at the end of this test (H_2 at 220 – 240°C for 2 h) did not result in complete recovery of catalyst activity, and alternative procedures should be explored.

IV-2.3 Run SB-1910 with 100 Fe/5 Cu/4.2 K/8 SiO_2 Catalyst

This was the first slurry reactor test of one of the most active catalysts synthesized in our laboratory during the DOE Contract No. DE-AC22-85PC80011. This catalyst was evaluated in a fixed bed reactor (Runs FA-63-0418 and FA-63-1308), and results from these tests were reported previously (Bukur et al., 1989b). In both of these tests the catalyst was very active, and had excellent hydrocarbon selectivity (low methane yield and high yield of C_{12} + hydrocarbons) but its deactivation rate was higher than the target rate of 1% per day.

The catalyst was tested initially (first 160 h) at 250°C, 200 psig (1.48 MPa), 2Nl/g-cat/h using the synthesis gas with H_2 to CO molar ratio of about 0.7 (0.65-0.75). Two mass balances were made during this time period, but the (H_2+CO) conversion and volumetric gas contraction (VC) were monitored more frequently. After the second mass balance, the reaction temperature was increased to 258°C (160-270 h) in order to achieve higher (H_2+CO) conversion (mass balances 3 and 4). At 273 h on stream the gas flow rate was decreased to give the gas space velocity of 1.5 (Nl/g-cat/h) based on the initial amount of catalyst charged to the reactor. These operating conditions were maintained over next 94 h, and two additional mass balances were made (balances 5 and 6). At 365 h on stream the baseline conditions were established again to check the catalyst activity (365-397h). The run was terminated voluntarily after 400 h on stream. Results from all six mass balances are summarized in Table IV-2.7.

Catalyst Activity and Stability

The catalyst activity was very stable between 30 and 100 h on stream, as shown in Figures IV-2.6 (contraction vs. TOS) and IV-2.7 (conversion vs. TOS). During this time period the volumetric contraction (VC) was between 36 and 38%, whereas the (H_2+CO) conversion varied between 53.6 and 56.4%. After slurry withdrawal through a dipleg tube at about 110 h, the VC and (H_2+CO) values decreased by about 10%, but remained fairly stable during the next fifty hours (TOS = 110-160 h). This decrease may be attributed in part to loss of catalyst with wax removed from the system (1.7 catalyst, or about 6% of the total amount of the catalyst left in the reactor after the reduction and slurry sample withdrawal for catalyst characterization - Table IV-2.8).

At about 162 h on stream, the temperature was increased to 258°C, and during the next 44 hours (162-206 h on stream) the volumetric contraction and the (H_2+CO) conversion declined slightly with time (Figures IV-2.6 and IV-2.7). During the mass balance period 3 (201-207 h) the volumetric contraction varied between 41 and 43%, whereas after withdrawal of about 154 g of wax and 1.4 g of catalyst from the reactor the contraction decreased to 37.1% (Figure IV-2.6). Further drop in activity occurred at about 230 h on stream, VC = 32.6%, after a temporary stoppage (~2h) of syngas flow due to plugging of the reactor inlet line. The contraction continued to decrease slowly with time (TOS = 230-258 h), but another sharp decline occurred after the slurry withdrawal from the reactor (134 g of wax, and 1.5 g of catalyst) at about 270 h on stream (VC = 25.4%). At this time the feed flow rate was changed to 750 (cc/min), corresponding to the gas space velocity of 1.5 (Nl/g-cat/h) based on the initial amount

Table IV-2.7 Summary of Slurry Reactor Test Results for Run SB-1910.

Period	1	2	3	4	5	6
Date	07/12/90	07/14/90	07/18/90	07/20/90	07/23/90	07/24/90
Time on Stream (h)	55.0	102.5	201.0	247.0	316.5	340.5
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	258.	258.	258.	258.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.754	.639	.752	.754	.780	.821
Space Velocity ($Nl/g\text{-}cat\cdot h$)[a]	2.03	2.14	2.26	2.38	1.90	2.00
Space Velocity ($Nl/g\text{-}Fe\cdot h$)	3.30	3.47	3.67	3.87	3.08	3.25
GHSV (h^{-1})[b]	140.	140.	118.	118.	88.6	88.6
CO Conversion (%)	59.2	59.6	66.0	48.3	54.6	46.7
H_2+CO Conversion (%)	54.1	56.1	62.2	45.6	51.1	43.4
H_2/CO Usage	.602	.545	.650	.658	.671	.692
STY ($mols\ H_2+CO/g\text{-}cat\cdot h$)[a]	.049	.054	.063	.048	.043	.039
$P_{CO_2}\cdot P_{H_2}/P_{CO}\cdot P_{H_2O}$	21.2	30.6	34.1	31.0	36.6	33.9
Weight % of Outlet						
H_2	2.74	2.16	2.20	2.08	2.86	3.40
H_2O	.780	.467	.554	.383	.395	.367
CO	39.1	38.6	32.1	49.1	43.0	50.5
CO_2	41.4	44.8	48.6	34.4	38.1	32.5
Hydrocarbons	8.04	7.36	9.36	8.13	10.6	9.49
Oxygenates	.937	.823	1.19	.933	1.26	1.00
Wax[c]	7.06	5.74	6.07	4.07	3.71	2.81
Yield (g/Nm^3 H_2 + CO Converted)						
CH_4	6.43	6.16	6.30	7.68	6.85	7.67
C_2-C_4 Hydrocarbons	27.4	24.6	25.4	27.5	26.7	26.7
C_5-C_{11} Hydrocarbons	44.2	48.4	42.2	48.4	59.0	59.5
C_{12}+ Hydrocarbons	130.	107.	113.	117.	114.	112.
Wax[c]	97.1	81.7	73.7	67.0	53.7	47.0
Oxygenates	12.9	11.7	14.6	15.4	18.2	16.7
Total	221.	198.	202.	216.	225.	222.
1+2 Olefins/n-Paraffin Ratio						
C_2	4.28	3.92	3.79	4.89	4.30	4.44
C_3	4.34	4.23	4.49	4.39	4.28	4.19
C_4	3.42	3.39	3.31	3.50	3.48	3.26
C_8	1.57	1.37	1.57	1.65	1.83	1.46
C_{10}	1.74	1.39	1.01	2.11	1.99	1.92

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.7 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1910.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	3.10	3.30	3.36	3.83	3.32	3.73
Ethane	.707	.724	.771	.635	.680	.666
Ethylene	2.82	2.65	2.73	2.90	2.73	2.76
Propane	.952	.997	.968	1.00	.961	.984
Propylene	3.95	4.03	4.16	4.20	3.93	3.93
n-Butane	1.03	1.04	1.09	1.04	.980	1.03
1+2 Butenes	3.38	3.40	3.50	3.50	3.29	3.23
C_4 Isomers	.349	.354	.356	.417	.367	.374
n-Pentane	1.10	1.09	1.02	1.09	1.01	1.07
1+2 Pentenes	3.12	3.10	3.12	3.18	2.90	2.88
C_5 Isomers	.650	.555	.952	1.10	.763	1.07
n-Hexane	.699	.609	.673	.673	.731	1.02
1+2 Hexenes	2.98	1.82	1.98	1.95	1.85	1.88
C_6 Isomers	1.06	.661	.740	.762	.982	.742
n-Heptane	.687	.716	.703	.701	.900	.932
1+2 Heptenes	1.67	.967	1.02	1.24	1.85	1.19
C_7 Isomers	.693	.487	.593	.519	.558	.602
n-Octane	.751	.820	.620	.780	1.27	1.36
1+2 Octenes	1.16	1.10	.958	1.26	2.27	1.05
C_8 Isomers	.178	.132	.566	.0732	.886	.164
n-Nonane	.615	1.13	.946	.888	1.49	1.68
1+2 Nonenes	1.03	1.35	.969	1.65	2.75	2.82
C_9 Isomers	.107	.305	.248	.0781	.155	.140
n-Decane	.779	1.53	1.19	.923	1.38	1.87
1+2 Decenes	1.34	2.09	1.18	1.92	2.71	3.17
C_{10} Isomers	.423	2.34	1.85	2.67	.185	.261
n-Undecane	.890	.955	1.13	.744	.906	1.25
1+2 Undecenes	1.26	1.72	1.22	1.86	2.70	3.00
C_{11} Isomers	.307	2.49	.853	.162	.312	.218
C_2-C_4	13.2	13.2	13.6	13.7	12.9	13.0
C_5-C_{11}	21.3	26.0	22.6	24.1	28.6	29.0
C_{12}+	62.4	57.5	60.6	58.4	55.2	54.3
Wax[c]	46.7	43.8	39.3	33.4	26.0	22.9

[c] Unanalyzed wax withdrawn from reactor

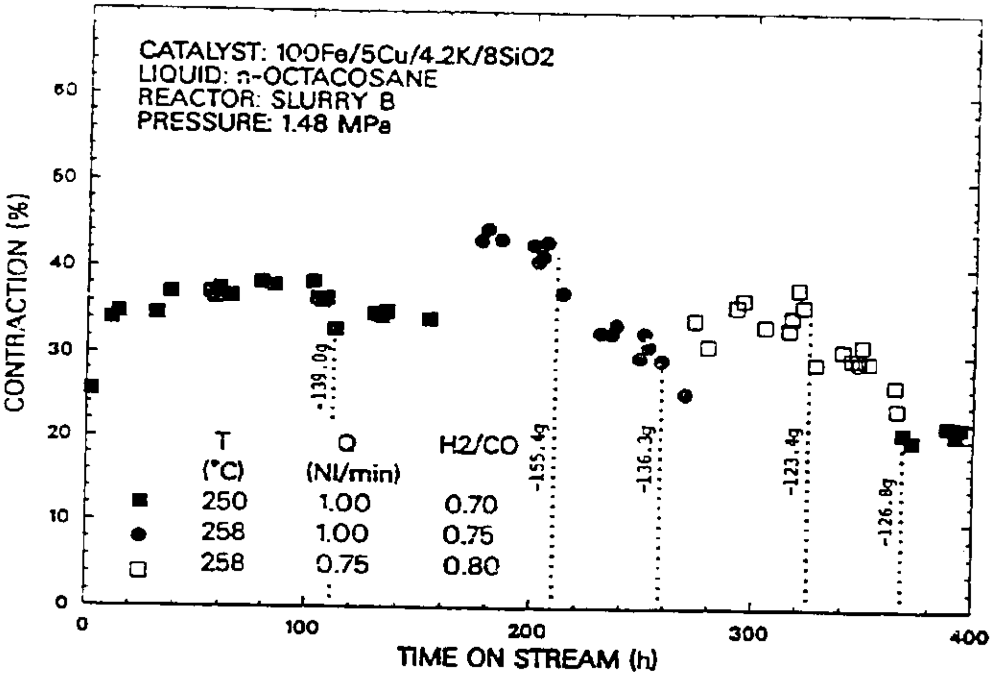

Figure IV-2.6 Volumetric contraction versus time on stream for Run SB-1910 (weight indicate amount of wax withdrawn).

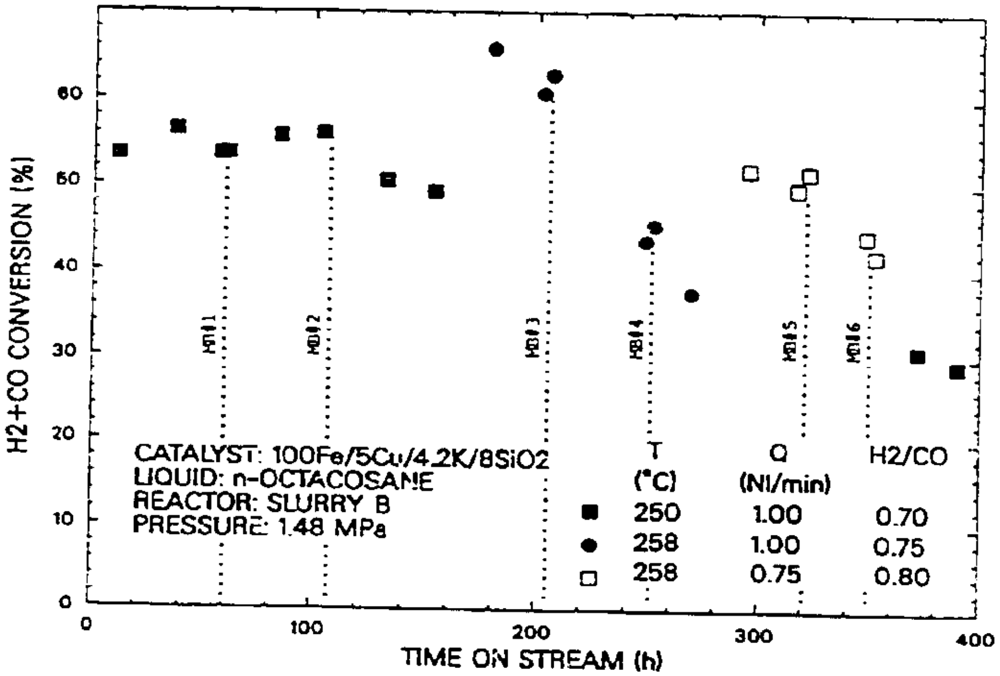

Figure IV-2.7 (H_2+CO) conversion versus time on stream for Run SB-1910.

of catalyst charged to the reactor. During the next fifty hours (TOS = 272-322 h) the volumetric contraction and the (H_2+CO) conversion were fairly stable, i.e. VC = 33.4-37% and (H_2+CO) = 49.7-51.9%. After the slurry withdrawal (122 g of wax, and 1.2 g of catalyst) at 324 h, a marked decrease in activity was observed again. The volumetric contraction was 29.1% at 328 h on stream, and is remained fairly stable during the next 24 hours. After another slurry withdrawal at 354-364 h, the contraction decreased to 26.5%. At this point the reaction temperature was decreased to 250°C, whereas the syngas flow rate was increased to 1000 cc/min (baseline conditions), and these conditions were maintained during the next 30 h. During this period the volumetric contraction varied between 20 and 21.7%, and the (H_2+CO) conversion between 29.2 and 31%.

Wax and Catalyst Inventories

Two methods of wax (slurry) withdrawal were employed during this run, i.e. wax withdrawal through a 10 µm vertical cylindrical element and slurry withdrawal to an external settler via a dipleg tube followed by wax removal and return of concentrated slurry to the reactor. Results from all wax (slurry) withdrawals are summarized in Table IV-2.8.

At the end of the reduction period 65 g of wax was removed from the reactor through the filter The withdrawn wax was clear in appearance, and contained trace amounts of solids only. At 62 h on stream about 17.5 g of wax was withdrawn through the filter. This wax had a black color, and it was suspected that the filter element had developed a crack. At this point it was decided to change the method of wax withdrawal, and slurry withdrawal through a dipleg tube was employed throughout the remainder of the test. At the end of the run the filter element was inspected and no cracks were found. This means that the catalyst particles had disintegrated to size smaller than 10 µm during the first 60 h of synthesis (The catalyst particles charged to the reactor were between 43 and 53 µm; 270/325 mesh particles).

Table IV-2.8 Wax and Solids Inventory for Run SB-1910.

TOS (h)	Description
	Slurry loading: 330 g wax, 30 g catalyst
	Wax filtration following reduction: 65 g wax
	Slurry withdrawal for catalyst characterization: 6.05 g (5.55 g of wax, 0.5 g of catalyst)
62	Wax filtration: 16.1 g wax, 1.46 g catalyst
110	Wax removal: 137.5 g wax, 1.48 g catalyst
210	Wax removal: 154.0 g wax, 1.34 g catalyst
254	Was removal: 134.8 g wax, 1.50 g catalyst
324	Wax removal: 122.2 g wax, 1.20 g catalyst
354	Wax removal: 125.3 g wax, 1.52 g catalyst
387	End of run: Slurry withdrawal for catalyst characterization: 10 g (9.35 g of wax, 0.65 g of catalyst)
	Slurry from the reactor: 299.5 g wax, 14.8 g catalyst
	Recoveries: 113% for wax; 77.3% for catalyst

Catalyst pretreatment: H_2 at 220°C

The wax transferred from the settling vessel was of black color. The amount of catalyst in the wax was determined by filtration, and subsequent burning of the solids material retained on the filter. As can be seen from results in Table IV-2.8, the catalyst content in the wax was about 1%. Therefore, the amount of catalyst remaining in the reactor was decreasing with each slurry withdrawal. The gas space velocities reported in Table IV-2.7 are based on the estimated amount of catalyst in the reactor.

At the end of the run, the catalyst content in the slurry was determined by the above procedure. The overall wax and catalyst recoveries were: 113 and 77.3%, respectively. (% Recovery = (Amount out)/(Amount in) x 100).

Catalyst Characterization by XRD and/or MES

The iron phases determined by MES analysis after hydrogen reduction at 220°C for 1 h were: 77% α - FeOOH (iron oxyhydrohide), and 23% magnetite. A sample withdrawn at 397 h on stream from the reactor was analyzed by MES and found to contain: Superparamagnetic oxides/oxyhydrohides - 17%; magnetite 55%; and ε'-carbide - 28%. The catalyst was only partially carburized after 390 hours of FT synthesis.

Hydrocarbon Product Distribution

Hydrocarbon selectivities were similar in all six mass balances, even though the process conditions were not constant throughout the test (T = 250-258°C, SV = 1.9-2.4 Nl/g-cat/h, (H_2/CO) = 0.64-0.82). Methane selectivity varied between 3.1 and 3.8%, and selectivity of light hydrocarbons (C_2-C_4) varied between 12.9 and 13.7%. Fraction of C_{12}^+ hydrocarbons decreased slightly with time on stream (TOS), whereas fraction of hydrocarbons in the gasoline range (C_5-C_{11}) increased with time (Table IV-2.7).

Overall the performance of this catalyst was very good. It is evident that loss of catalyst from the reactor had contributed to decrease in (H_2+CO) conversion with time on stream. The hydrocarbon selectivity of the catalyst was within the DOE target, i.e. $(C_1+C_2) \leq 8$ wt%.

IV-2.4 Run SB-0261 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

This test was conducted to evaluate performance of a silica containing precipitated iron catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO_2. During the first 168 h, and between 236 and 549 h on stream, the catalyst was tested at 260°C, 1.48 MPa (200 psig), 1.4 Nl/g-cat/h and $H_2/CO = 0.68 - 0.70$ (mass balances 1-3, 5-8). After the third mass balance, the reaction temperature was increased to 263°C (168 – 236 h) while keeping the remaining conditions constant (mass balance 4). Between 549 and 622 h, the catalyst was tested at a lower gas space velocity of 1 Nl/g-cat/h (260°C, 200 psig), whereas during the last 100 h (TOS = 622 – 722 h) the process conditions were: 260°C, 2.17 MPa (300 psig), 1.4 Nl/g-cat/h and $H_2/CO = 0.64$. The test was terminated voluntarily after 725 h on stream. Results from eleven mass balances made during the test are summarized in Table IV-2.9, whereas major events are listed in Table IV-2.10.

Catalyst Activity and Stability

The catalyst was very stable and active during the first 120 h on stream, as shown in Figure IV-2.8. The (H_2+CO) conversion and volumetric gas contraction (VC) varied between 80-83%, and 53-54%, respectively. The conversion and VC were decreasing between 120 and 165 h, and at 168 h the reaction temperature was increased to 263°C in attempt to increase the catalyst activity. After initial increase in activity, the catalyst continued to deactivate with time. At 170 h the (H_2+CO) conversion was 80%, whereas at 220 h the conversion was 75%. At about 240 h, the baseline conditions were reestablished (T=260°C), and the (H_2+CO) conversion was only 68.5%. This value is significantly lower in comparison to conversions obtained during the first 170 h of testing (76 – 83%). However, after this the catalyst activity

Table IV-2.9 Summary of Slurry Reactor Test Results for Run SB-0261.

Period	1	2	3	4	5	6
Date	01/29/91	01/31/91	02/02/91	02/05/91	02/08/91	02/11/91
Time on Stream (*h*)	44.0	92.0	140.0	214.0	286.0	356.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	263.	260.	260.
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.701	.701	.704	.704	.704	.676
Space Velocity (Nl/g-cat·h)[a]	1.39	1.39	1.39	1.39	1.40	1.40
Space Velocity (Nl/g-Fe·h)	2.39	2.39	2.39	2.39	2.41	2.41
GHSV (h^{-1})[b]	65.1	65.1	65.1	65.1	62.8	62.8
CO Conversion (%)	88.2	87.4	85.5	82.0	73.0	72.4
H_2+CO Conversion (%)	81.6	81.4	77.7	74.8	67.3	67.4
H_2/CO Usage	.574	.584	.547	.554	.572	.561
STY (*mols* H_2+CO/g-cat·h)[a]	.050	.050	.048	.046	.042	.042
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	39.8	24.1	31.8	37.8	16.7	20.7
Weight % of Outlet						
H_2	1.34	1.30	1.63	1.72	1.99	1.87
H_2O	1.10	1.64	1.32	.909	1.38	1.03
CO	11.3	12.0	13.9	17.3	26.0	26.5
CO_2	65.1	64.0	63.1	60.8	53.1	53.0
Hydrocarbons	9.20	9.87	10.8	11.0	9.38	8.44
Oxygenates	.229	.274	.218	.149	.245	.174
Wax[c]	11.7	10.9	8.96	8.16	7.89	8.98
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	4.47	5.40	6.37	5.66	4.63	4.35
C_2-C_4 Hydrocarbons	20.4	24.1	24.5	25.4	20.7	19.6
C_5-C_{11} Hydrocarbons	29.2	27.5	28.8	30.4	27.4	26.1
C_{12}+ Hydrocarbons	143.	139.	136.	135.	143.	151.
Wax[c]	110.	103.	88.1	83.6	89.3	103.
Oxygenates	2.16	2.59	2.14	1.53	2.78	2.00
Total	199.	109.	197.	198.	198.	203.
1+2 Olefins/n-Paraffin Ratio						
C_2	2.02	1.62	1.75	2.11	3.24	4.26
C_3	7.50	7.29	7.11	7.23	7.00	7.07
C_4	6.77	6.84	6.78	6.70	6.48	6.19
C_8	3.80	3.99	3.99	4.13	4.42	4.28
C_{10}	1.21	2.17	2.80	2.42	3.74	3.65

[a] Based on unreduced catalyst [b] Based on static slurry volume
[c] Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	7	8	9	10	11
Date	02/14/91	02/18/91	02/21/91	02/25/91	02/26/91
Time on Stream (*h*)	428.0	523.0	505.0	602.0	716.0
Balance Duration (*h*)	6.0	6.0	7.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (*MPa*)	1.48	1.48	1.48	2.17	2.17
H_2/CO Feed Ratio	.678	.678	.684	.684	.637
Space Velocity ($Nl/g\text{-cat}\cdot h$)[a]	1.40	1.29	.980	1.44	1.44
Space Velocity ($Nl/g\text{-Fe}\cdot h$)	2.41	2.22	1.69	2.48	2.48
GHSV (h^{-1})[b]	62.8	53.0	36.7	53.9	53.9
CO Conversion (%)	71.2	72.6	80.0	70.1	65.0
H_2+CO Conversion (%)	66.6	67.9	75.7	67.1	62.8
H_2/CO Usage	.608	.570	.574	.613	.580
STY (*mols* H_2+CO/$g\text{-cat}\cdot h$)[a]	.042	.039	.033	.043	.040
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	18.6	26.4	37.2	13.7	10.8
Weight % of Outlet					
H_2	1.90	1.81	1.50	1.74	1.79
H_2O	1.08	.798	.743	1.26	1.30
CO	27.7	20.0	18.2	28.5	33.6
CO_2	51.4	53.4	58.8	49.4	46.2
Hydrocarbons	8.27	7.25	9.22	7.56	7.51
Oxygenates	.160	.150	.165	.436	.360
Wax[c]	9.43	10.5	11.4	11.1	9.23
Yield (g/Nm^3 H_2 + CO *Converted*)					
CH_4	4.25	4.41	4.38	3.56	3.48
C_2-C_4 Hydrocarbons	19.1	19.2	18.8	17.2	18.1
C_5-C_{11} Hydrocarbons	25.2	32.1	26.7	28.2	29.8
C_{12}+ Hydrocarbons	157.	150.	162.	167.	160.
Wax[c]	109.	122.	117.	128.	117.
Oxygenates	1.85	1.74	1.70	5.06	4.56
Total	207.	207.	214.	221.	216.
1+2 Olefins/*n*-Paraffin Ratio					
C_2	4.45	3.44	2.64	3.54	4.49
C_3	7.22	7.11	7.26	6.35	6.39
C_4	6.23	6.22	6.45	5.16	5.40
C_8	4.16	4.30	4.19	4.34	4.00
C_{10}	3.00	3.33	4.24	3.91	4.32

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	2.27	2.75	2.76	2.83	2.37	2.17
Ethane	1.01	1.36	1.33	1.22	.746	.619
Ethylene	1.90	2.05	2.18	2.40	2.25	2.46
Propane	.497	.614	.644	.648	.544	.465
Propylene	3.56	4.28	4.37	4.47	3.63	3.14
n-Butane	.421	.517	.532	.550	.463	.404
1+2 Butenes	2.75	3.41	3.48	3.56	2.90	2.41
C_4 Isomers	.251	.0533	.0584	.0624	.0693	.246
n-Pentane	.397	.304	.316	.329	.280	.251
1+2 Pentenes	2.39	2.66	2.76	2.80	2.32	2.05
C_5 Isomers	.479	.664	.814	.788	.693	.998
n-Hexane	.352	.379	.403	.433	.339	.318
1+2 Hexenes	1.69	1.82	1.76	1.92	1.62	1.40
C_6 Isomers	.501	.573	.584	.696	.554	.470
n-Heptane	.279	.296	.308	.356	.298	.240
1+2 Heptenes	1.35	1.37	1.32	1.54	1.29	1.08
C_7 Isomers	.370	.404	.806	.508	.424	.352
n-Octane	.309	.282	.268	.328	.266	.256
1+2 Octenes	1.15	1.11	1.05	1.33	1.15	1.08
C_8 Isomers	.261	.224	.284	.338	.271	.267
n-Nonane	.472	.236	.251	.258	.240	.208
1+2 Nonenes	.927	.654	.933	.939	1.02	.917
C_9 Isomers	.0013	.0525	.0551	.0523	.0404	.0586
n-Decane	.759	.394	.314	.342	.204	.270
1+2 Decenes	.908	.844	.867	.816	1.08	.971
C_{10} Isomers	.0927	.0675	.0642	.0693	.0638	.0944
n-Undecane	.935	.503	.451	.627	.426	.438
1+2 Undecenes	.971	.880	1.05	.926	1.29	1.17
C_{11} Isomers	.134	.0928	.0948	.0956	.0717	.132
C_2-C_4	10.4	12.3	12.6	12.9	10.6	9.74
C_5-C_{11}	14.8	14.0	14.8	15.6	14.0	13.0
C_{12}+	72.5	71.0	69.9	68.8	73.0	75.1
Wax[c]	56.0	52.5	45.2	42.6	45.7	51.5

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.9 (cont'd) Summary of Slurry Reactor Test Results for Run SB-0261.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH4	2.07	2.15	2.00	1.05	1.04
Ethane	.601	.648	.761	.435	.418
Ethylene	2.33	2.08	1.88	1.44	1.75
Propane	.440	.460	.427	.470	.482
Propylene	3.03	3.12	2.96	2.85	2.94
n-Butane	.382	.395	.363	.421	.437
1+2 Butenes	2.30	2.37	2.26	2.10	2.28
C_4 Isomers	.237	.241	.222	.244	.258
n-Pentane	.242	.355	.336	.389	.429
1+2 Pentenes	1.95	1.94	1.97	1.95	2.08
C_5 Isomers	1.15	.405	.346	.359	.389
n-Hexane	.315	.372	.327	.319	.366
1+2 Hexenes	1.32	1.66	1.39	1.27	1.44
C_6 Isomers	.500	.461	.394	.438	.467
n-Heptane	.255	.301	.252	.270	.313
1+2 Heptenes	1.10	1.16	1.05	1.05	1.14
C_7 Isomers	.372	.377	.303	.362	.403
n-Octane	.211	.287	.217	.247	.274
1+2 Octenes	.864	1.21	.893	1.05	1.08
C_8 Isomers	.362	.410	.304	.316	.377
n-Nonane	.192	.342	.194	.205	.222
1+2 Nonenes	.768	1.22	.870	.974	1.10
C_9 Isomers	.0591	.391	.309	.241	.282
n-Decane	.272	.405	.241	.274	.277
1+2 Decenes	.802	1.33	1.01	1.06	1.18
C_{10} Isomers	.0891	.426	.367	.230	.266
n-Undecane	.430	.544	.354	.377	.359
1+2 Undecenes	.919	1.49	1.18	1.29	1.23
C_{11} Isomers	.114	.553	.291	.387	.394
C_2-C_4	9.28	9.32	8.87	7.95	8.56
C_5-C_{11}	12.3	15.6	12.6	13.1	14.0
C_{12}+	76.4	72.9	76.5	77.3	76.8
Wax[c]	53.3	59.2	55.3	59.4	55.1

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.10 Major Events in Run SB-0261.

TOS (h)	Event
	Slurry loading: 298 g n-octacosane, 20.2 g catalyst (325-270 mesh)
	Catalyst pretreatment: H_2 at 240°C
	Slurry sample withdrawal: 3 g wax, 0.2 g catalyst
	Wax withdrawal through filter: 43 g of wax
0	Initiate synthesis gas flow
2	Plug in inlet line – break in synthesis gas supply
6	Achieved initial process conditions: T=260°C, P=1.48 MPa, SV=1.4 N*l*/g-cat/h, $(H_2/CO)=0.70$
168	Temperature change from 260 to 263°C
220	Slurry sample withdrawal: 9 g wax, 0.7 g catalyst
236	Temperature change from 263 to 260°C
435	Slurry sample withdrawal: 22 g wax, 1.6 g catalyst
477	Wax removal through a dipleg: 183 g wax, 1.6 g catalyst
529	Space velocity change from 1.4 to 1.1 N*l*/g-cat/h
622	Pressure change from 1.48 to 2.17 MPa and space velocity from 1.1 to 1.4 N*l*/g-cat/h
721	Slurry sample withdrawal: 23 g wax, 0.7 g catalyst
722	End of run: 414 g wax, 13.1 g catalyst recovered from reactor
	Wax catalyst removed during the run: 1391 g of wax, 3.9 g of catalyst
	Catalyst recovery: 85%; wax recovery: 164%

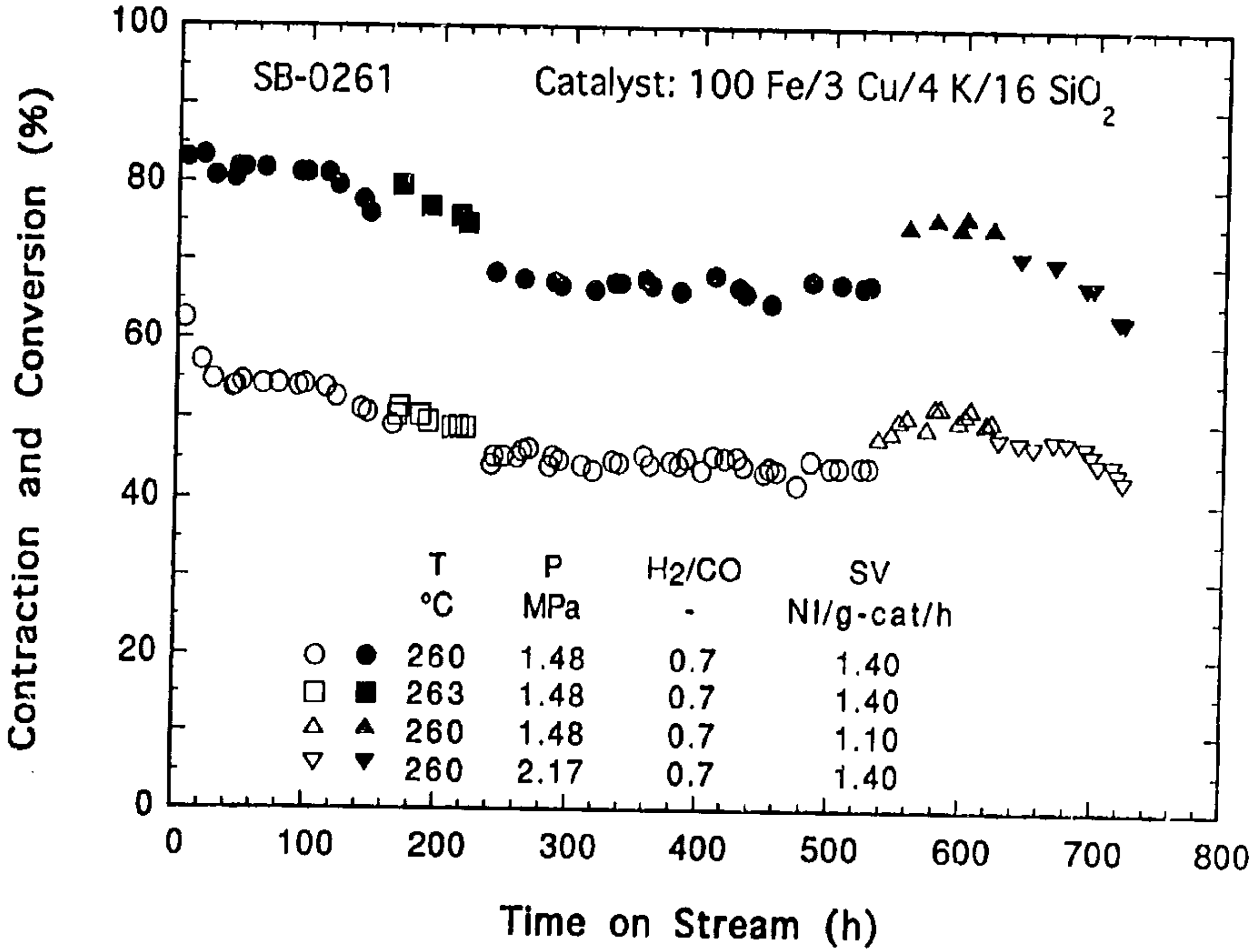

Figure IV-2.8 (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-0261.

remained stable during the next 300 h of testing. Between 240 and 530 h on stream, the (H_2+CO) conversion fluctuated between 65 and 68%. At about 550 h, the gas flow rate was decreased (SV = 1Nl/g-cat/h) in order to achieve higher conversion. During the next 70 h on stream (550 – 620 h) the catalyst was stable, and the (H_2+CO) conversion was between 75 and 76%. After that both the reaction pressure and the gas space velocity were increased to 2.17 MPa and 1.4 Nl/g-cat/h, respectively, and the testing continued at these conditions for additional 100 h. The catalyst deactivation was observed during this period. The (H_2+CO) conversion decreased from 70.7% at 643 h, to 62.7% at 722 h.

WGS activity of the catalyst was high and stable throughout the entire test. The usage ratio varied between 0.53 and 0.62, with an average value of 0.57.

Wax and Catalyst Inventories/Withdrawals

Wax was withdrawn through a cylindrical porous filter element with nominal pore size of 0.5 μm. The filter was placed horizontally at a height corresponding to a static slurry volume of 410 cc. Wax withdrawal rate decreased with time on stream. During the first 100 h, withdrawals were made at initial pressure drop (across the filter) of 15 psi, and the rate of wax withdrawal decreased from 60 g/h to 15 g/h. The latter rate of withdrawal was maintained during the next 100 h on stream by increasing gradually the pressure drop to 80 psi. During the period of 200 – 700 h, the initial pressure drop was maintained at 80 – 100 psi, but the rate of withdrawal decreased with time from 15 g/h to 5 g/h. One successful slurry withdrawal (183 g of slurry) to an external settling vessel was made at about 480 h, but this method had to be abandoned due to plugging of valves between the reactor and the settler.

The average wax production rate for the entire test was 1.90 g/h, whereas the range of wax production rates during the test was 0.7 – 3.1 g/h. At the end of the run 13.1 g of catalyst was recovered from the reactor (calculated from concentration of catalyst in the slurry, which was determined by burning slurry sample in a crucible), and another 4.8 g was removed from the reactor during the test (with slurry samples for catalyst characterization and with wax removed from the external settler). The catalyst recovery was about 89%, based on the amount of catalyst charged into the reactor. At the end of the run 413 g of the wax was found in the reactor, whereas the initial amount (after the slurry sample withdrawal following catalyst reduction) was 252 g (see Table IV-2.10). This indicates that wax withdrawals throughout the test were not complete, and that 161 g of wax had accumulated in the reactor.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 240°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. The following phases were detected by XRD in a sample withdrawn from the reactor at 220 h : magnetite, iron carbide(s) and iron carbonate. The same phases were identified in samples withdrawn from the reactor at 435 and 722 h on stream. It is presumed that carbon dioxide formed by water gas shift reaction may be responsible for the formation of $FeCO_3$ (siderite). The MES analysis of the above samples indicates the presence of superparamagnetic oxides/oxyhydrohides, magnetite and siderite in varying proportions. The amount of superparamagnetic phase was found to decrease with time, from 64% at 220 h to 19% at 722 h, whereas the amount of siderite was found to increase from 13 to 64% during the same period of time.

Hydrocarbon and Carbon Number Product Distributions

Selectivities of low molecular weight products (CH_4, C_2-C_4, C_5-C_{11}) passed through a local maximum at about 200 h on stream (mass balance 4), whereas selectivity C_{12}^+ products passed through a local minimum (Table IV-2.9). For example, methane selectivity increased from 2.3% in balance 1 (TOS = 44) to 2.8% in balances 2-4, and then decreased to 2.1 – 2.4% between 220 and 620 h on stream. During testing at 300 psig, methane selectivity was even lower ~1.6% (620-720 h). Selectivity of gaseous hydrocarbons was low throughout the entire test, (C_2-C_4) = 8-

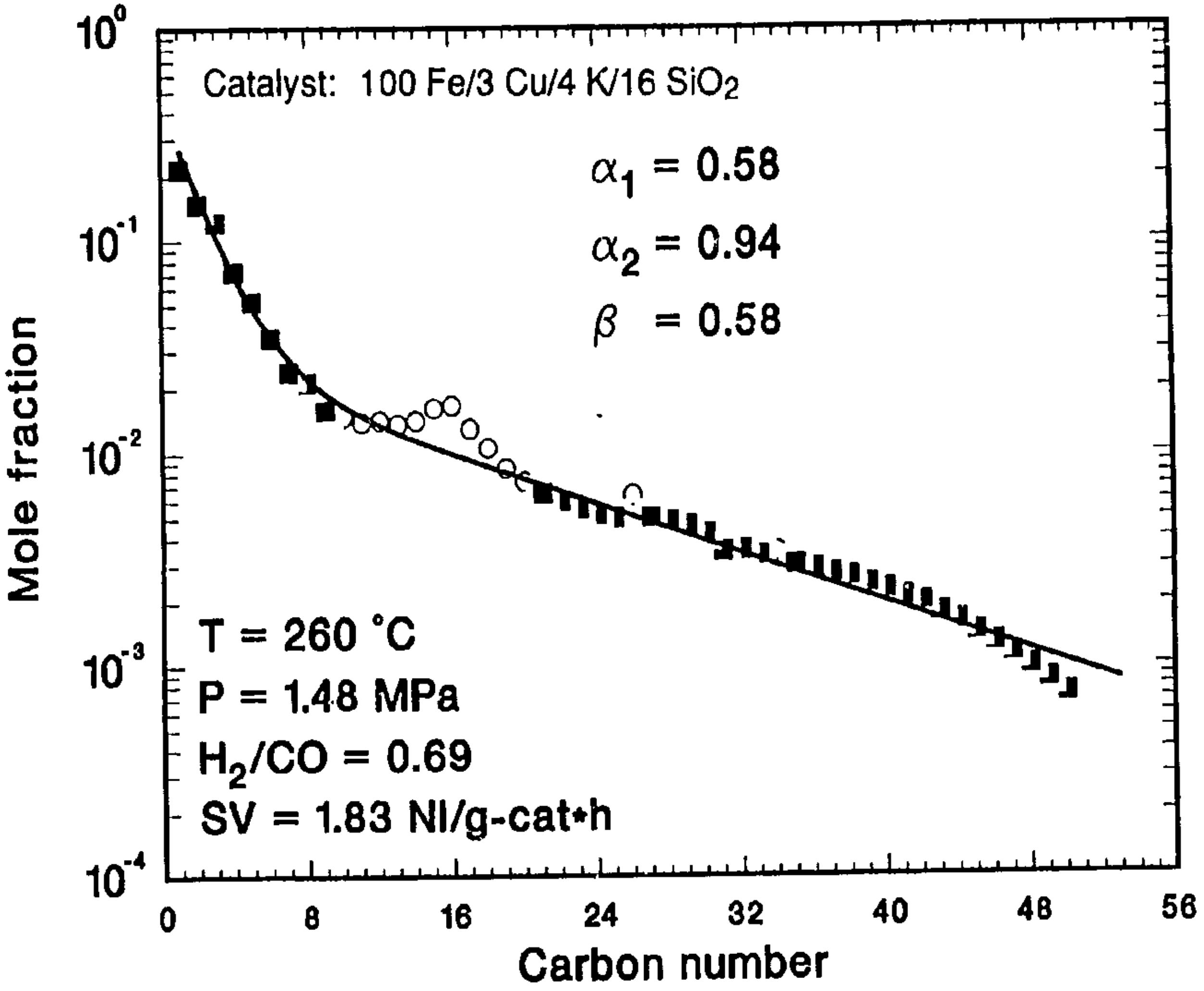

Figure IV-2.9 Carbon number product distribution for Run SB-0261 (TOS=92 h).

15%, whereas selectivity of C_{12}^{+} products was high (69-77%). Selectivity of (C_1+C_2) products was always within the DOE target (less than 8 %).

A typical carbon number distribution obtained at baseline conditions (TOS = 92 h), including the analyzed wax products collected in a high pressure trap is shown in Figure IV-2.9. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from the ASF distribution are noted in C_{11}-C_{17} carbon number range. We do not know whether this is due to the intrinsic catalyst selectivity or some experimental artifacts (e.g. loss of products and errors in the analysis).

Overall this run has been very successful. After initial drop in activity (first 220 h on stream), the activity remained very stable until the catalyst was exposed to higher reaction pressure (300 psig during the last 100 h on stream; 620–720 h). Hydrocarbon selectivity was within the DOE target throughout the entire test.

IV-2.5 Run SB-2270 with 100 Fe/5 Cu/4.2 K/16 SiO_2 Catalyst

The catalyst was tested initially (first 230 h) at 260°C, 200 psig (1.48 MPa), 1.4 Nl/g-cat/h using the synthesis gas with H_2 to CO molar feed ratio of 0.69, and three mass balances were made during this time period. Following this the reaction pressure and the gas space velocity were changed to 300 psig (2.17 MPa) and 2.3 (Nl/g-cat/h), respectively. At 300 h on stream the catalyst was regenerated in-situ with H_2 at 220°C, and 200 psig for 2 hours. Two mass balances were made at these process conditions, one before and the other one after the regeneration with H_2. The test was terminated voluntarily after 400 h on stream. Results from all five mass balances are summarized in Table IV-2.11.

Catalyst Activity and Stability

The catalyst activity, expressed in terms of volumetric contraction and (H_2+CO) conversion, declined slowly with time during the first 180 h on stream, as shown in

Table IV-2.11 Summary of Slurry Reactor Test Results for Run SB-2270.

Period	1	2	3	4	5
Date	08/16/90	08/18/90	08/21/90	08/26/90	08/28/90
Time on Stream (h)	45.0	93.5	162.0	284.5	332.0
Balance Duration (h)	14.0	20.0	20.0	11.5	14.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	2.17	2.17
H_2/CO Feed Ratio	.689	.689	.689	.689	.661
Space Velocity (Nl/g-cat·h)[a]	1.37	1.37	1.37	2.30	2.14
Space Velocity (Nl/g-Fe·h)	2.40	2.40	2.40	4.04	3.75
GHSV (h^{-1})[b]	33.7	33.7	33.7	56.6	52.6
CO Conversion (%)	68.7	67.2	64.9	35.2	40.5
H_2+CO Conversion (%)	65.7	64.2	61.7	34.5	44.2
H_2/CO Usage	.613	.612	.604	.656	.578
STY ($mols$ H_2+CO/g-cat·h)[a]	.040	.039	.038	.035	.042
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	19.0	20.9	22.5	6.80	0.22
Weight % of Outlet					
H_2	1.85	1.92	2.05	3.11	2.73
H_2O	.904	.786	.706	1.08	1.10
CO	30.0	31.5	33.6	61.2	51.6
CO_2	49.1	47.3	45.8	25.4	33.7
Hydrocarbons	6.97	6.22	10.0	6.64	6.76
Oxygenates	.587	.447	.521	.296	.356
Wax[c]	10.5	9.80	7.32	2.23	3.76
Yield (g/Nm^3 H_2 + CO *Converted*)					
CH_4	6.71	8.65	9.75	9.16	8.24
C_2-C_4 Hydrocarbons	25.9	32.5	39.9	39.1	37.2
C_5-C_{11} Hydrocarbons	25.7	35.5	40.6	38.1	34.5
C_{12}+ Hydrocarbons	146.	139.	127.	115.	105.
Wax[c]	123.	118.	91.7	50.6	66.2
Oxygenates	6.88	5.36	6.53	6.70	6.26
Total	212.	221.	224.	208.	192.
1+2 Olefins/n-Paraffin Ratio					
C_2	1.27	1.37	.846	1.38	1.55
C_3	4.99	4.74	4.85	4.49	4.32
C_4	4.34	4.25	4.29	4.03	3.83
C_6	2.28	2.19	2.40	2.42	2.87
C_{10}	1.48	2.01	1.99	2.60	2.95

[a] Based on unreduced catalyst
[b] Based on static slurry volume
[c] Unanalyzed wax withdrawn from reactor

Table IV-2.11 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2270.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH4	3.28	4.00	4.50	4.55	4.44
Ethane	1.57	2.04	2.65	2.03	2.29
Ethylene	1.85	2.60	2.10	2.62	3.33
Propane	.854	1.03	1.32	1.53	1.62
Propylene	4.07	4.65	6.13	6.55	6.67
n-Butane	.784	.870	1.12	1.25	1.20
1+2 Butenes	3.29	3.57	4.63	4.88	4.45
C_4 Isomers	.251	.290	.409	.582	.481
n-Pentane	.748	.791	1.00	1.07	.815
1+2 Pentenes	2.88	3.07	3.83	3.86	2.90
C_5 Isomers	.374	.424	.604	.831	.714
n-Hexane	.414	.456	.453	.655	.684
1+2 Hexenes	1.25	1.07	1.59	2.04	2.20
C_6 Isomers	.422	.520	.605	.976	1.08
n-Heptane	.270	.354	.496	.492	.537
1+2 Heptenes	.792	1.20	1.24	1.28	1.48
C_7 Isomers	.210	.303	.362	.927	.969
n-Octane	.211	.451	.547	.480	.487
1+2 Octenes	.473	.971	1.29	1.14	1.37
C_8 Isomers	.132	.393	.273	.157	.153
n-Nonane	.447	.689	.653	.620	.685
1+2 Nonenes	.749	1.14	1.42	1.24	1.41
C_9 Isomers	.0342	.0786	.151	.101	.125
n-Decane	.626	.605	.639	.355	.339
1+2 Decenes	.916	1.20	1.26	.912	.985
C_{10} Isomers	.156	.111	.169	.119	.154
n-Undecane	.477	.554	.686	.499	.363
1+2 Undecenes	.682	1.000	1.21	.989	.988
C_{11} Isomers	.278	.130	.192	.224	.199
C_2-C_4	12.7	15.0	18.4	19.5	20.1
C_5-C_{11}	12.5	16.4	18.7	19.0	18.6
C_{12}+	71.5	64.5	58.5	57.0	56.9
Wax[c]	60.1	54.4	42.2	25.2	35.7

[c] Unanalyzed wax withdrawn from reactor

Figures IV-2.10 and IV-2.11. After the wax withdrawal at 184 h, the volumetric contraction decreased markedly from 41% to 31%, whereas the (H_2+CO) conversion decreased from about 64% to 45%. During the next 40 hours, the volumetric contraction remained fairly stable (29-31%). Although, the reasons for this sharp drop in activity are not known, we suspect that it might have been caused by removal of the catalyst particles from the slurry. After withdrawal of approximately 280 cm^3 of wax, a significant portion of the catalyst remained above the slurry level (e.g. deposited on the reactor wall or on the internal filter element), and it appears that this catalyst is not as active as the one in the slurry.

At about 230 h on stream the reaction pressure and the gas space velocity were increased to 300 psig (2.17 MPa) and 2.3 (Nl/g-cat/h); respectively. During the next 60 hours, the activity remained fairly constant (VC=21-23%; (H_2+CO) = 33-34%). At 250 h on stream an attempt was made to increase the activity, by adding 65 g of wax to raise the liquid level in the slurry reactor. However, this did not result in increased catalyst activity.

At about 300 h on stream the catalyst was regenerated in-situ with H_2 at 220°C and 200 psig for two hours. After regeneration, the catalyst activity increased markedly. At 311 h on stream the values of volumetric contraction and (H_2+CO) conversion were: 33.8 and 47.6%, respectively. However, the activity declined with time and at 400 h the volumetric contraction was only 23.5%.

The WGS activity was rather high throughout the entire test, e.g. the H_2/CO usage ratio varied between 0.6 and 0.7, whereas the approach to equilibrium was between 0.1 and 0.3 (see Table IV-2.11).

Wax and Catalyst Inventories

The reactor was charged initially with 10 g of catalyst and 289 g of purified n-octacosane. We have deliberately chosen to add only a small amount of catalyst for this test, in order to minimize the need for wax withdrawals throughout the run. Wax

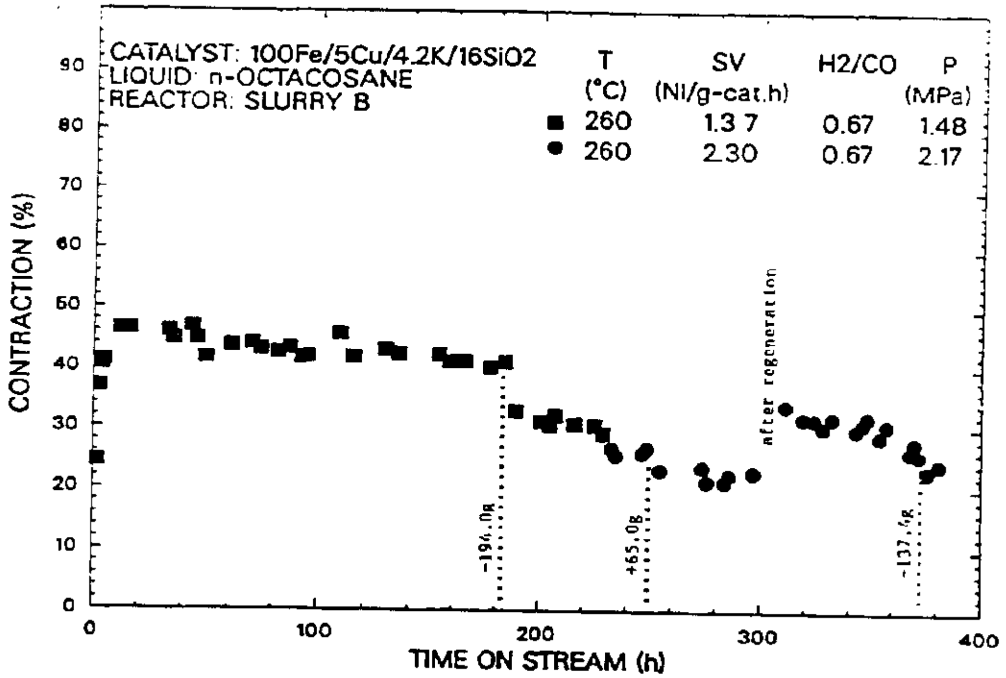

Figure IV-2.10 Volumetric contraction versus time on stream for Run SB-2270 (weights indicate amout of wax withdrawn (-) or added (+)).

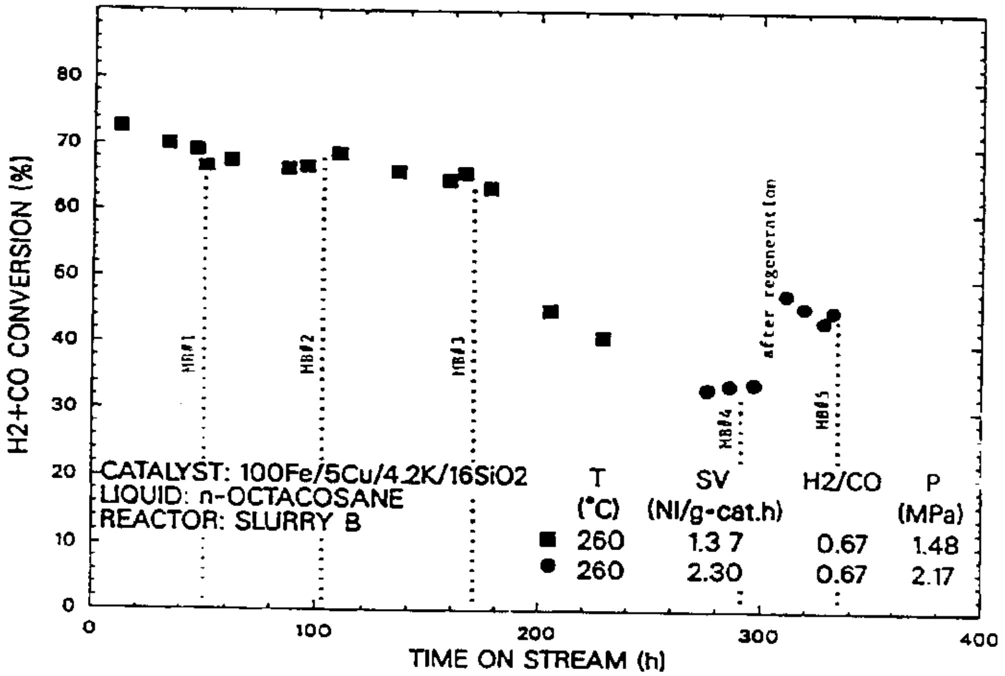

Figure IV-2.11 (H_2+CO) conversion versus time on stream for Run SB-2270.

withdrawals result in disturbance of the system and may have adverse effect on the rate of catalyst deactivation (Bukur et al., 1989b). Only three wax withdrawals were made through a 2 µm cylindrical filter element placed vertically in the reactor. Results from all withdrawals are summarized in Table IV-2.12.

There were no operational problems during wax withdrawals, and the collected wax was clear in appearance. At the end of the run 8.9 g of catalyst was recovered in the reactor, after separation from wax by filtration and burning in the air to convert the used catalyst into Fe_2O_3. It is estimated that about 0.3 g of catalyst was removed from the reactor with the slurry sample withdrawn at the end of reduction. The catalyst recovery was 92.6%, whereas the wax recovery was 78%.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 220°C for 2 h contained a small amount of catalyst which was insufficient for XRD analysis. MES analysis of the sample revealed the presence of superparamagnetic oxide/oxyhydrohide phases. No other samples were withdrawn from the reactor during or after the test.

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon selectivities were similar in balances 2-5, and the average values for methane and product group lumps by carbon numbers were: $(CH_4) = 4.2$; $(C_2\text{-}C_4) = 17.7$; $(C_5\text{-}C_{11}) = 17.7$, and $(C_{12}^{+}) = 60.4$ wt%.

During the first mass balance the fraction of high molecular weight products was markedly higher, and the methane yield was markedly lower in comparison to selectivities obtained in balances 2 to 5 (see Table IV-2.11).

A typical carbon number distribution of products collected at 162 h on stream is shown in Figure IV-2.12. Experimental data were fitted reasonably well with a three parameter model of Huff and Satterfield.

Table IV-2.12 Wax and Solids Inventory for Run SB-2270.

TOS	Description
	Slurry loading: 289 g wax, 10.0 g catalyst
	Wax filtration following reduction: 70.8 g
	Slurry withdrawal for catalyst characterization: 10 g (9.7 g of wax, 0.3 g of catalyst)
184	Wax filtration: 194 g
249	Wax addition: 65 g
372	Wax filtration: 137 g
400	End of run: 170 g of wax and 9 g of catalyst were recovered from the reactor. Wax recovery: 78%; Catalyst recovery: 92.6%

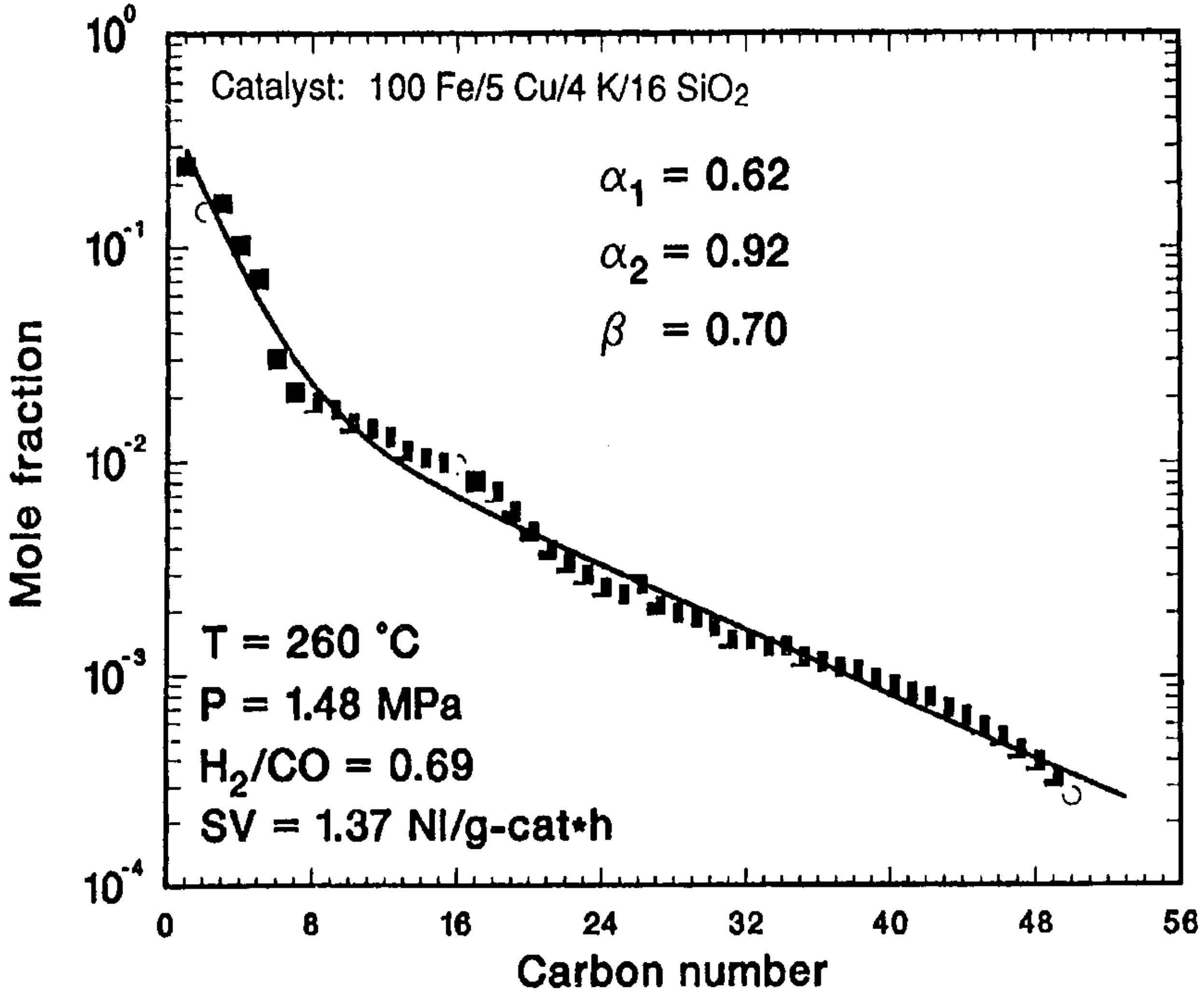

Figure IV-2.12 Carbon number product distribution for Run SB-2270 (TOS=162 h).

IV-2.6 Run SB-2832 with 100 Fe/5 Cu/4.2 K/16 SiO_2 Catalyst

The catalyst used in this test was synthesized in our laboratory during the current contract, whereas the catalyst used in Run SB-2270 was synthesized prior to the current contract in 1988. Physical properties of the two catalysts are similar as noted in section IV-2 of this report (Table IV-2.1). Catalyst from the same preparation batch as that used in Run SB-2832 was used in two other slurry reactor tests (Runs SA-3162 and SB-2932). Results from these tests were described in section III-5 of this report (Pretreatment Effect Research).

The catalyst was reduced with hydrogen at 0.8 MPa (100 psig), 240°C for 2 hours. After the reduction, the catalyst was tested at baseline conditions of 1.48 MPa (200 psig), 260°C, 1.5 Nl/g-cat/h (2.6 Nl/g-Fe/h) during the first 263 h on stream using syngas with $H_2/CO=0.7$. Between 263 and 526 h on stream the catalyst was tested at 2.17 MPa (300 psig) and gas space velocity (SV) of 2.2 Nl/g-cat/h (3.9 Nl/g-Fe/h), which corresponds to the same pressure to SV ratio as at the baseline conditions. At 527 h on stream the gas space velocity was reduced to 1.8 Nl/g-cat/h while other process conditions remained constant (2.17 MPa, 260°C, $H_2/CO=0.7$). The catalyst was regenerated at 664 h with hydrogen at 240°C, 1.48 MPa for 2h, and then the baseline conditions were reestablished. The test was terminated voluntarily after 720 h on stream. Results from eleven mass balances made during the tests are summarized in Table IV-2.13, while major events are listed in Table IV-2.14.

Catalyst Activity and Stability

The catalyst activity was high and it deactivated only moderately during this test. The initial (H_2+CO) conversion at baseline conditions was 84% at 17 h, then it gradually decreased to 77 % at 263 h. Volumetric gas contraction (VC) also decreased from 56 to 52 % during the same time period (Figure IV-2.13). The usage ratio during this period was about 0.58. When the pressure and SV were increased at 263 h, the syngas conversion decreased to 74 % at 284 h and further to 69 % at 480 h

Table IV-2.13 Summary of Slurry Reactor Test Results for Run SB-2832.

Period	1	2	3	4	5	6
Time on Stream (h)	41.0	92.0	139.0	210.0	308.0	355.0
Balance Duration (h)	7.5	6.0	6.5	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	2.17	2.17
H_2/CO Feed Ratio	.706	.704	.704	.681	.667	.667
Space Velocity ($Nl/g\text{-cat}\cdot h$)[a]	1.50	1.50	1.50	1.50	2.20	2.20
Space Velocity ($Nl/g\text{-Fe}\cdot h$)	2.63	2.63	2.63	2.63	3.86	3.86
GHSV (h^{-1})[b]	37.0	37.0	37.0	37.0	54.2	54.2
CO Conversion (%)	87.5	86.4	85.5	83.1	78.0	77.9
H_2+CO Conversion (%)	81.1	80.3	79.5	78.7	74.6	74.1
H_2/CO Usage	.581	.584	.585	.591	.594	.585
STY ($mols\ H_2+CO/g\text{-cat}\cdot h$)[a]	.054	.054	.053	.053	.073	.073
$P_{CO_2}\cdot P_{H_2}/P_{CO}\cdot P_{H_2O}$	37.4	36.9	28.4	20.4	22.2	18.5
Weight % of Outlet						
H_2	1.36	1.37	1.40	1.30	1.41	1.46
H_2O	1.09	.999	1.23	1.33	.959	1.17
CO	11.9	13.0	13.9	16.1	21.1	21.3
CO_2	62.8	61.7	60.7	59.2	56.1	55.4
Hydrocarbons	13.0	13.1	12.8	14.1	16.2	12.0
Oxygenates	.253	.226	.174	.230	.336	.604
Wax[c]	9.60	9.57	9.72	7.68	3.86	8.13
Yield ($g/Nm^3\ H_2$ + CO *Converted*)						
CH_4	9.60	10.1	10.3	9.73	10.0	9.36
C_2-C_4 Hydrocarbons	32.6	32.9	33.3	35.8	35.9	36.2
C_5-C_{11} Hydrocarbons	54.8	47.1	44.9	48.7	62.4	47.7
C_{12}+ Hydrocarbons	118.	126.	129.	121.	101.	118.
Wax[c]	91.0	91.3	93.7	75.9	40.3	85.5
Oxygenates	2.40	2.16	1.68	2.27	3.50	6.35
Total	217.	219.	219.	218.	213.	218.
1+2 Olefins/n-Paraffin Ratio						
C_2	.593	.794	.690	.885	1.05	1.27
C_3	4.70	4.84	4.74	4.93	4.81	4.70
C_4	4.05	4.25	4.28	4.60	3.90	3.99
C_8	1.77	2.09	2.20	2.28	2.37	2.50
C_{10}	1.50	1.47	1.64	1.80	1.95	2.18

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832

Period	7	8	9	10	11
Time on Stream (*h*)	427.0	498.0	570.0	641.0	713.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (*MPa*)	2.17	2.17	2.17	2.17	1.48
H_2/CO Feed Ratio	.681	.681	.695	.681	.681
Space Velocity (*Nl/g*-cat·*h*)[a]	2.20	2.20	1.80	1.80	1.46
Space Velocity (*Nl/g*-Fe·*h*)	3.86	3.86	3.16	3.16	2.56
GHSV (h^{-1})[b]	54.2	54.2	44.4	44.4	29.2
CO Conversion (%)	74.4	71.3	79.8	76.5	71.3
H_2+CO Conversion (%)	70.9	68.7	75.7	72.9	67.4
H_2/CO Usage	.602	.619	.609	.603	.589
STY (*mols* H_2+CO/*g*-cat·*h*)[a]	.069	.067	.061	.059	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	18.4	15.4	20.6	20.6	24.6
Weight % of Outlet					
H_2	1.61	1.65	1.45	1.52	1.80
H_2O	1.06	1.11	1.17	1.01	.781
CO	24.6	27.4	19.5	22.6	27.4
CO_2	52.5	50.3	56.8	54.7	51.5
Hydrocarbons	12.4	12.8	12.1	12.9	13.1
Oxygenates	.636	.748	.816	.701	.270
Wax[c]	7.07	5.96	8.28	6.48	5.12
Yield (*g/Nm*^{3} H_2 + CO *Converted*)					
CH_4	9.36	9.21	9.59	10.8	9.52
C_2-C_4 Hydrocarbons	34.6	34.0	32.4	35.8	33.4
C_5-C_{11} Hydrocarbons	49.2	47.9	43.9	51.0	49.5
C_{12}+ Hydrocarbons	120.	122.	120.	108.	117.
Wax[c]	77.1	67.5	83.8	68.8	59.1
Oxygenates	6.94	8.47	8.25	7.44	3.22
Total	220.	221.	214.	214.	213.
1+2 Olefins/n-Paraffin Ratio					
C_2	1.36	1.76	1.14	1.16	1.89
C_3	4.60	4.65	4.69	4.73	5.59
C_4	3.84	3.84	3.96	3.97	4.58
C_8	2.46	2.42	2.28	2.43	2.71
C_{10}	2.13	2.22	2.09	2.20	2.60

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	4.47	4.67	4.74	4.51	4.78	4.43
Ethane	2.33	2.26	2.38	2.32	2.33	2.10
Ethylene	1.29	1.68	1.53	1.92	2.27	2.49
Propane	1.14	1.08	1.13	1.18	1.24	1.25
Propylene	5.09	5.00	5.11	5.55	5.68	5.59
n-Butane	.990	.923	.918	.948	1.06	1.06
1+2 Butenes	3.87	3.79	3.79	4.21	4.01	4.09
C_4 Isomers	.476	.461	.463	.486	.550	.562
n-Pentane	1.10	.920	.897	.927	1.04	1.01
1+2 Pentenes	3.68	3.41	3.43	3.72	3.65	3.48
C_5 Isomers	.464	.445	.446	.465	.561	.518
n-Hexane	.950	.850	.844	.891	1.10	.926
1+2 Hexenes	2.75	2.59	2.65	3.04	3.32	2.71
C_6 Isomers	.829	.867	.895	.962	1.15	.950
n-Heptane	1.03	.787	.754	.799	1.10	.821
1+2 Heptenes	2.03	1.98	2.03	2.10	2.68	2.02
C_7 Isomers	.594	.563	.609	.705	.937	.686
n-Octane	1.04	.779	.669	.715	1.04	.701
1+2 Octenes	1.82	1.60	1.45	1.60	2.41	1.72
C_8 Isomers	.661	.439	.445	.653	.784	.456
n-Nonane	.853	.687	.529	.617	.813	.548
1+2 Nonenes	1.56	1.24	1.02	1.23	1.78	1.28
C_9 Isomers	.308	.124	.135	.187	.416	.229
n-Decane	1.02	.775	.622	.663	1.000	.605
1+2 Decenes	1.52	1.12	1.00	1.18	1.92	1.30
C_{10} Isomers	.368	.165	.154	.184	.532	.339
n-Undecane	1.12	.991	.765	.700	1.07	.634
1+2 Undecenes	1.45	1.25	1.11	1.07	1.92	1.26
C_{11} Isomers	.409	.178	.170	.157	.599	.375
C_2-C_4	15.2	15.2	15.3	16.6	17.1	17.1
C_5-C_{11}	25.5	21.8	20.6	22.6	29.8	22.6
C_{12}+	54.8	58.4	59.3	56.3	48.3	55.9
Wax[c]	42.4	42.2	43.1	35.2	19.2	40.4

[c] Unanalyzed wax withdrawn from reactor .

Table IV-2.13 (cont'd) Summary of Slurry Reactor Test Results for Run SB-2832.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH4	4.40	4.33	4.66	5.25	4.54
Ethane	1.92	1.78	1.99	2.16	1.64
Ethylene	2.44	2.93	2.11	2.33	2.90
Propane	1.21	1.11	1.16	1.28	.980
Propylene	5.32	4.94	5.20	5.77	5.22
n-Butane	1.03	.987	.982	1.08	.862
1+2 Butenes	3.81	3.66	3.75	4.15	3.81
C_4 Isomers	.539	.557	.568	.609	.532
n-Pentane	.967	.983	.923	1.02	.834
1+2 Pentenes	3.28	3.26	3.13	3.53	3.31
C_5 Isomers	.496	.484	.443	.504	.380
n-Hexane	.902	.817	.746	.909	.709
1+2 Hexenes	2.58	2.34	2.22	2.68	2.54
C_6 Isomers	1.15	.936	.732	.925	.843
n-Heptane	.841	.700	.719	.898	.697
1+2 Heptenes	1.98	1.66	1.68	2.04	1.87
C_7 Isomers	.673	.581	.437	.600	.693
n-Octane	.696	.615	.635	.768	.699
1+2 Octenes	1.68	1.47	1.42	1.84	1.86
C_8 Isomers	.450	.423	.387	.521	.462
n-Nonane	.593	.607	.627	.672	.650
1+2 Nonenes	1.35	1.41	1.35	1.57	1.73
C_9 Isomers	.325	.462	.301	.282	.319
n-Decane	.703	.722	.737	.759	.692
1+2 Decenes	1.48	1.58	1.52	1.65	1.70
C_{10} Isomers	.360	.491	.441	.440	.461
n-Undecane	.759	.796	.816	.823	.779
1+2 Undecenes	1.50	1.65	1.62	1.71	1.87
C_{11} Isomers	.352	.502	.429	.593	.532
C_2-C_4	16.3	16.0	15.8	17.4	15.9
C_5-C_{11}	23.1	22.5	21.3	24.7	23.6
C_{12}+	56.2	57.2	58.3	52.6	55.9
Wax[e]	36.2	31.7	40.7	33.4	28.2

[e] Unanalyzed wax withdrawn from reactor

Table IV-2.14 Major Events in Run SB-2832.

TOS (h)	Event
	Slurry loading: 300 g n-octacosane, 11.5 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: H_2, 240°C, 0.78 MPa, for 2 h
	Slurry sample withdrawal after the pretreatment: 24 g wax, 0.9 g catalyst
	Wax withdrawal through filter: 49 g of wax
0	Initiate synthesis gas flow
2	Achieve initial process conditions: T=260°C, P=1.48 MPa, SV=1.5 Nl/g-cat/h, (H_2/CO)=0.68
263	Pressure change from 1.48 to 2.17 MPa and space velocity from 1.5 to 2.2 Nl/g-cat/h
526	Space velocity change from 2.2 to 1.8 Nl/g-cat/h
665	Slurry sample withdrawal: 26 g wax, 1.1 g catalyst
666	Regeneration of catalyst: H2 at 240°C for 1 h
667	Slurry sample withdrawal: 20 g wax, 0.9 g catalyst
669	Change to initial baseline process conditions: T=260°C, P=1.48 MPa, SV=1.5 Nl/g-cat/h, (H_2+CO)=0.68
720	End of run: 207 g wax, 8.1 g catalyst recovered from reactor
	Wax and catalyst removal during the run: 754 g wax, 2 g catalyst
	Catalyst recovery: 95%; Wax recovery: 91%

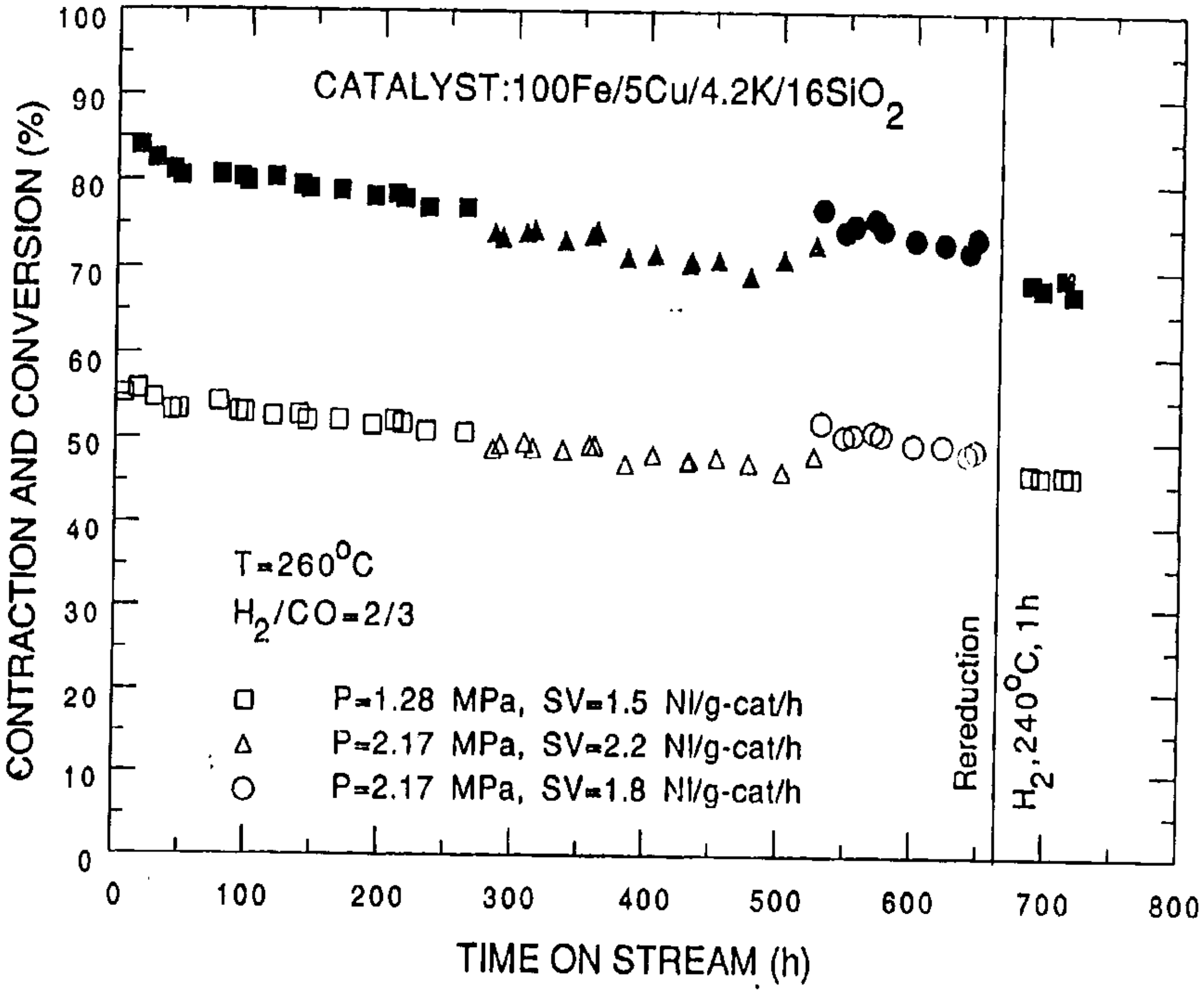

Figure IV-2.13 (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-2832.

on stream, while the usage ratio varied between 0.58 and 0.61. At 527 h, the space velocity was lowered to 1.8 Nl/g-cat/h in attempt to increase the catalyst activity. After initial increase in activity, the catalyst continued to deactivate slowly with time. The syngas conversion was about 77 % at 531 h, but became 74 % at 647 h. Regeneration with hydrogen at 664 h could not recover the catalyst activity. The syngas conversion was 68 % after the regeneration, in comparison with 77 % at 263 h under the same baseline conditions, indicating loss in catalyst activity.

Wax and Catalyst Withdrawal/Inventory

About 11.5 g of the catalyst (less than 270 mesh) was loaded initially and suspended in n-octacosane to give a 3.7 weight % catalyst slurry. During the test, wax was withdrawn periodically (approximately every 50 h) through a porous sintered metal filter with nominal pore size of 0.5 micron. The filter was placed horizontally at a height corresponding to a static slurry volume of 430 cc. A pressure drop of 15 psig across the filter was employed during the withdrawal. The rate of wax withdrawal decreased with time, varying from 85 g/h to 24 g/h.

One slurry sample was withdrawn after the reduction for catalyst characterization. Additional two slurry samples were taken, one just before and another one after the regeneration, at 665 and 667 h, respectively.

At the end of the run, about 206 g of wax was recovered from the autoclave reactor, while the initial amount (after the slurry sample and wax withdrawal following the pretreatment) was estimated to be 228 g (wax recovery of 90%). About 8.1 g of catalyst was recovered from the reactor at the end of the test, whereas approximately 2.9 g was removed with the slurry samples during the test (catalyst recovery of 88%).

Catalyst Characterization by XRD and/or MES

A catalyst sample withdrawn from the reactor after hydrogen reduction at 240°C for 2 h exhibited broad peaks (small crystallites), which were assigned to magnetite (Fe_3O_4) and/or maghemite (Fe_2O_3). A sample withdrawn at 665 h from the reactor contained mostly iron carbides, and some magnetite. After the regeneration with hydrogen at 240°C for 1 h, the peaks associated with magnetite had increased, whereas those associated with iron carbides have decreased. It is suggested that water formed during the reduction process may be responsible for partial reoxidation of the catalyst. On introduction of syngas after the catalyst regeneration, the amount of carbide(s) seemed to have increased (a sample withdrawn from the reactor at 720 h).

<u>Hydrocarbon and Carbon Number Product Distributions</u>

Hydrocarbon selectivity was fairly stable during the entire test at various process conditions although the catalyst deactivated slowly with time. For example, during the first 260 h under the baseline conditions, the average methane selectivity was 4.5 wt%, (C_2-C_4) =15.5 %, (C_5-C_{11}) =22 %, and C_{12+} = 58 %. At 300 psig and 2.2 Nl/g-cat/h, the average values of methane, C_2-C_4, C_5-C_{11} and C_{12+} selectivities were 4.4, 16.6, 23.1 and 57.0 wt%, respectively. Between 527 and 664h at 300 psig and 1.8 Nl/g-cat/h, methane selectivity increased from 4.5 to 5.2 wt%, while C_{12+} decreased from 58 to 52 wt%. After the catalyst regeneration and return to baseline conditions, the hydrocarbon selectivities were: 4.5 (methane), 16 (C_2-C_4), 23.5 (C_5-C_{11}) and 56 wt% of C_{12+}. These values are very similar to those obtained during the first 260 h of testing.

A typical carbon number distribution obtained at baseline conditions, including the analyzed wax products collected in a high pressure trap is shown in Figure IV-2.14. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from the ASF distribution are noted in C_{11}-C_{17} carbon number range. We do not know whether this is due to the intrinsic catalyst selectivity or some experimental artifacts (e.g. loss of products and errors in the analysis).

In summary, this test was quite successful. Syngas conversion was 78-84 %, and (C_1+C_2) selectivity 8.1 wt% during the first 200 h of testing. The catalyst

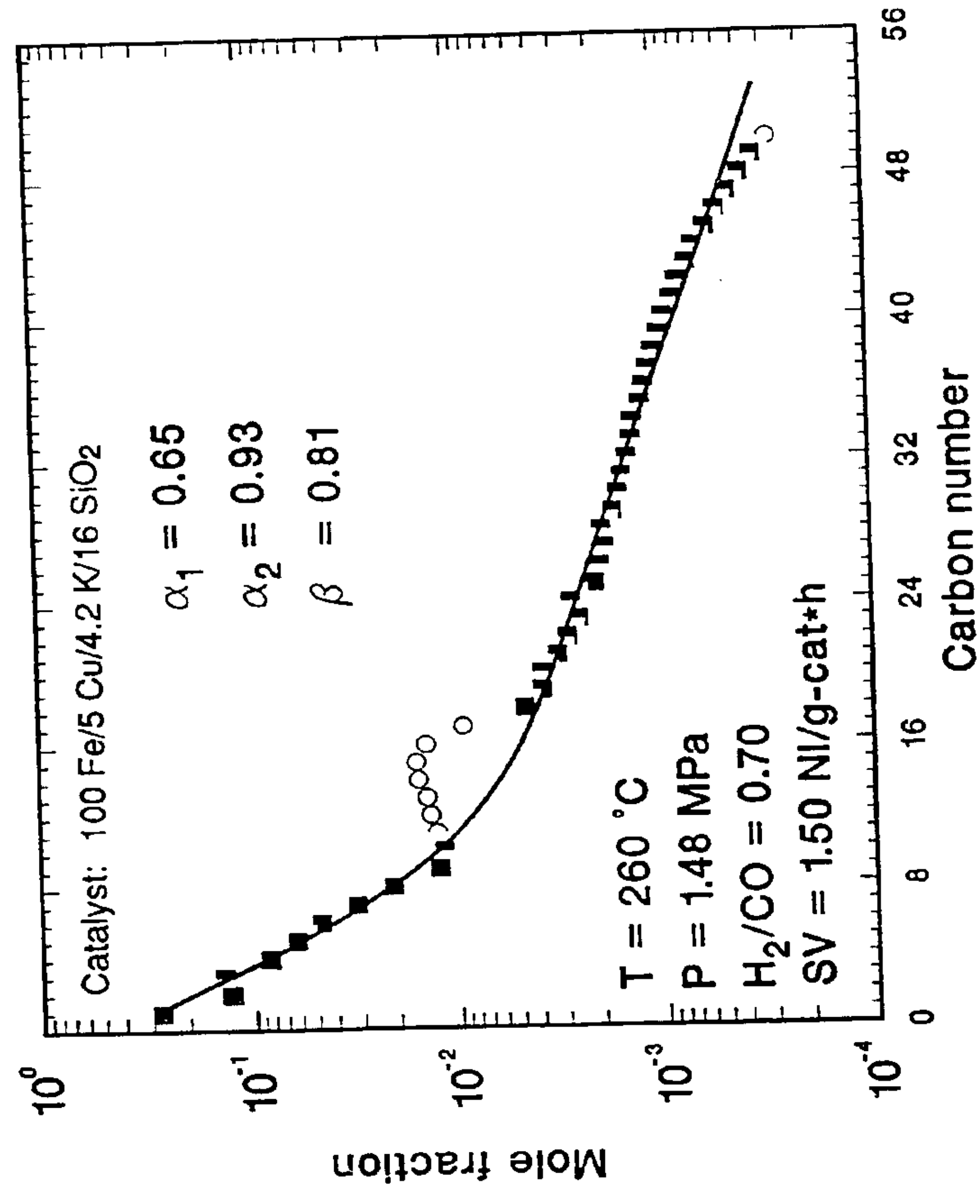

Figure IV-2.14 Carbon number product distribution for Run SB-2832 (TOS=139 h).

deactivated slowly at a rate of about 0.4 % (syngas conversion) per day during 27 days of continuous testing.

IV-2.7 Run SB-1931 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst

Slurry reactor run SB-1931 was conducted to evaluate performance of a precipitated iron catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2. Reaction pressure and syngas composition were maintained constant throughout the test at 1.48 MPa (200 psig) and (H_2/CO) = 0.66 – 0.69, respectively. Reaction temperature during the first 520 h of testing was maintained at 260°C, and then was increased to 265°C during the next 170 h. Gas space velocity varied between 2.2 Nl/g-cat/h and 1.2 (Nl/g-cat/h). The test was terminated voluntarily after 692 h on stream. Results from eleven mass balances made during the test are summarized in Table IV-2.15, whereas major events are listed in Table IV-2.16. There were three operational upsets at 15, 80 and 229 h on stream (see Table IV-2.16), which caused temporary disruptions in synthesis gas supply. However, we have not observed any adverse effects on the catalyst performance following these upsets.

Catalyst Activity and Stability

During the first 62 h of testing at 260°C, 1.48 MPa, H_2/CO = 0.66 and space velocity of 2.2 Nl/g-cat/h (H_2+CO) conversion increased gradually and stabilized at about 74% (Figure IV-2.15). Following this, the gas space velocity was decreased to 1.8 Nl/g-cat/h in attempt to increase conversion. At 76 h on stream the (H_2+CO) conversion was 77.6%, but then decreased to about 75% following the upset between 80 and 92 hours on stream (no syngas flow due to a plug in lines downstream of the reactor). At 138 h on stream gas space velocity was decreased to 1.6 Nl/g-cat/h and then maintained at this value during next 236 h (TOS = 138 – 374 h). During this period of time the (H_2+CO) conversion was very stable and its value fluctuated between 75 and 78% (balances 3 to 6). Between 375 and 520 h on stream, gas space

Table IV-2.15 Summary of Slurry Reactor Test Results for Run SB-1931.

Period	1	2	3	4	5	6
Date	04/04/91	04/07/91	04/09/91	04/11/91	04/14/91	04/17/91
Time on Stream (h)	42.0	98.0	162.0	208.0	280.0	351.0
Balance Duration (h)	7.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.689	.689	.689	.689	.689	.661
Space Velocity (Nl/g-cat·h)[a]	2.15	1.83	1.61	1.61	1.61	1.61
Space Velocity (Nl/g-Fe·h)	4.03	3.43	3.02	3.02	3.02	3.02
GHSV (h^{-1})[b]	33.5	28.5	25.1	25.1	25.1	25.1
CO Conversion (%)	78.2	78.4	81.2	81.4	81.6	80.8
H_2+CO Conversion (%)	74.0	75.1	77.2	77.3	77.3	77.3
H_2/CO Usage	.597	.618	.606	.605	.601	.588
STY ($mols$ H_2+CO/g-cat·h)[a]	.071	.061	.055	.056	.056	.056
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	23.5	9.85	11.6	10.6	16.1	15.1
Weight % of Outlet						
H_2	1.53	1.40	1.36	1.35	1.35	1.28
H_2O	.995	2.15	2.12	2.33	1.63	1.51
CO	20.8	20.6	18.1	17.7	17.4	18.3
CO_2	56.1	54.5	57.3	57.0	59.3	57.4
Hydrocarbons	9.97	8.56	11.0	11.6	12.5	11.7
Oxygenates	.243	.354	.377	.455	.358	.330
Wax[c]	10.3	12.5	9.79	9.52	7.44	9.41
Yield (g/Nm^3 H_2 + CO $Converted$)						
CH_4	5.22	6.01	5.89	5.95	6.57	6.28
C_2-C_4 Hydrocarbons	23.1	22.1	22.8	22.0	25.5	24.0
C_5-C_{11} Hydrocarbons	38.1	28.7	31.9	28.7	33.4	30.9
C_{12}+ Hydrocarbons	140.	160.	147.	155.	136.	154.
Wax[c]	108.	129.	98.0	95.8	75.5	95.9
Oxygenates	2.53	3.65	3.77	4.58	3.63	3.37
Total	215.	221.	212.	218.	206.	219.
1+2 Olefins/n-Paraffin Ratio						
C_2	1.77	2.08	1.60	1.81	1.40	1.49
C_3	5.72	5.94	6.99	7.95	6.82	6.96
C_4	6.09	5.30	6.84	5.82	5.91	6.24
C_6	2.80	3.28	3.34	3.76	3.70	3.58
C_{10}	1.22	2.73	2.68	3.00	3.02	3.02

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	7	8	9	10	11
Date	04/20/91	04/23/91	04/26/91	04/29/91	05/01/91
Time on Stream (h)	423.0	496.0	566.0	639.0	686.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	260.	260.	265.	265.	265.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.661	.684	.689	.689	.689
Space Velocity (Nl/g-cat·h)[a]	1.20	1.20	1.20	1.20	1.20
Space Velocity (Nl/g-Fe·h)	2.25	2.25	2.25	2.25	2.25
GHSV (h^{-1})[b]	18.7	18.7	18.7	18.7	18.7
CO Conversion (%)	84.8	83.3	84.7	81.6	79.7
H_2+CO Conversion (%)	81.2	79.5	80.7	78.7	75.7
H_2/CO Usage	.592	.608	.610	.630	.604
STY ($mols$ H_2+CO/g-cat·h)[a]	.043	.043	.043	.042	.041
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	14.6	20.1	31.2	29.7	20.8
Weight % of Outlet					
H_2	1.10	1.22	1.19	1.20	1.42
H_2O	1.77	1.30	.394	.768	.890
CO	14.7	16.0	14.7	17.5	19.3
CO_2	60.5	60.0	60.6	58.7	56.9
Hydrocarbons	15.0	15.2	15.9	16.6	17.3
Oxygenates	.338	.321	.279	.322	.354
Wax[c]	6.54	5.89	6.43	4.95	3.83
Yield (g/Nm^3 H_2 + CO $Converted$)					
CH_4	6.72	7.56	8.99	9.89	10.6
C_2-C_4 Hydrocarbons	28.5	30.1	33.7	37.3	38.6
C_5-C_{11} Hydrocarbons	36.2	40.3	42.4	47.5	51.5
C_{12}+ Hydrocarbons	138.	128.	129.	118.	117.
Wax[c]	62.8	57.3	61.6	49.0	39.4
Oxygenates	3.25	3.13	2.67	3.19	3.65
Total	210.	209.	217.	216.	221.
1+2 Olefins/n-Paraffin Ratio					
C_2	1.33	1.33	.774	.792	.815
C_3	6.63	6.41	6.04	5.91	5.77
C_4	5.85	5.68	5.51	5.77	5.27
C_8	3.08	3.07	2.64	2.56	2.54
C_{10}	2.67	2.51	2.17	1.96	2.02

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	2.46	2.77	2.83	2.79	3.26	2.02
Ethane	1.10	.997	1.26	1.23	1.53	1.30
Ethylene	1.82	1.93	1.88	2.07	1.90	1.81
Propane	.677	.608	.569	.483	.675	.583
Propylene	3.70	3.45	3.79	3.66	4.39	3.87
n-Butane	.560	.481	.474	.451	.546	.472
1+2 Butenes	2.75	2.46	2.68	2.54	3.11	2.84
C_4 Isomers	.286	.283	.309	.303	.365	.253
n-Pentane	.539	.433	.421	.394	.473	.423
1+2 Pentenes	2.51	2.14	2.42	2.27	2.73	2.47
C_5 Isomers	.282	.390	.394	.379	.509	.397
n-Hexane	.480	.361	.387	.352	.407	.366
1+2 Hexenes	1.81	1.48	1.73	1.63	1.90	1.74
C_6 Isomers	.550	.504	.543	.504	.680	.533
n-Heptane	.412	.316	.367	.317	.309	.360
1+2 Heptenes	1.33	1.16	1.33	1.22	1.53	1.41
C_7 Isomers	.392	.384	.415	.348	.400	.396
n-Octane	.391	.312	.385	.288	.415	.336
1+2 Octenes	1.08	1.10	1.26	1.06	1.51	1.18
C_8 Isomers	.405	.346	.393	.283	.362	.283
n-Nonane	.619	.323	.369	.273	.355	.277
1+2 Nonenes	.909	.974	1.11	.907	1.29	.930
C_9 Isomers	.405	.121	.196	.107	.160	.118
n-Decane	.759	.344	.415	.325	.382	.329
1+2 Decenes	.910	.925	1.09	.961	1.14	.979
C_{10} Isomers	1.49	.145	.235	.130	.161	.125
n-Undecane	.492	.347	.462	.439	.449	.427
1+2 Undecenes	.830	.909	1.17	1.12	1.19	1.09
C_{11} Isomers	1.36	.170	.250	.166	.211	.154
C_2-C_4	10.9	10.2	11.0	10.7	12.6	11.1
C_5-C_{11}	18.0	13.2	15.3	13.5	16.5	14.3
C_{12}+	68.7	73.8	70.9	73.0	67.6	71.6
Wax[c]	50.9	59.3	47.1	45.0	37.4	44.5

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.15 (cont'd) Summary of Slurry Reactor Test Results for Run SB-1931.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH4	3.25	3.67	4.19	4.64	4.86
Ethane	1.71	1.99	2.50	2.76	2.80
Ethylene	2.12	2.47	1.81	2.04	2.13
Propane	.680	.794	.936	1.05	1.08
Propylene	4.30	4.86	5.39	5.94	5.94
n-Butane	.544	.630	.729	.825	.863
1+2 Butenes	3.08	3.46	3.87	4.60	4.39
C_4 Isomers	.383	.433	.492	.288	.550
n-Pentane	.502	.553	.659	.712	.766
1+2 Pentenes	2.64	2.92	3.39	3.60	3.69
C_5 Isomers	.523	.660	.752	1.54	.785
n-Hexane	.495	.553	.537	.620	.678
1+2 Hexenes	1.77	2.31	2.26	2.50	2.65
C_6 Isomers	.548	.633	.666	.767	.830
n-Heptane	.418	.516	.544	.574	.680
1+2 Heptenes	1.33	1.71	1.65	1.78	2.06
C_7 Isomers	.452	.493	.551	.605	.713
n-Octane	.407	.545	.604	.570	.690
1+2 Octenes	1.23	1.64	1.46	1.43	1.72
C_8 Isomers	.421	.460	.413	.449	.621
n-Nonane	.408	.477	.478	.553	.624
1+2 Nonenes	1.20	1.37	1.20	1.30	1.46
C_9 Isomers	.316	.194	.235	.252	.276
n-Decane	.482	.525	.552	.684	.719
1+2 Decenes	1.27	1.30	1.18	1.32	1.43
C_{10} Isomers	.407	.205	.266	.328	.358
n-Undecane	.634	.727	.712	.837	.913
1+2 Undecenes	1.51	1.50	1.34	1.47	1.60
C_{11} Isomers	.528	.255	.369	.382	.417
C_2-C_4	12.8	14.6	15.7	17.5	17.8
C_5-C_{11}	17.5	19.6	19.8	22.3	23.7
C_{12}+	66.4	62.1	60.3	55.6	53.7
Wax[c]	30.3	27.9	28.7	23.0	18.1

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.16 Major Events in Run SB-1931.

TOS (h)	Event
	Slurry loading: 283 g n-octacosane, 7.2 g catalyst (<270 mesh)
	Slurry sample withdrawal after the pretreatment: 18 g wax, 0.5 g catalyst
	Wax withdrawal through filter: 9 g of wax
0	Initiate synthesis gas flow
1	Achieved initial process conditions: T=260°C, P=1.48 MPa, SV=2.2 Nl/g-cat/h, $(H_2/CO)=0.69$
15	Reactor was supplied with He during 2 hours due to the fume hood maintenance
63	Spave velocity change from 2.2 to 1.8 Nl/g-cat/h
80	Plug in outlet line – no flow through reactor for 12 hours
138	Spave velocity change from 1.8 to 1.6 Nl/g-cat/h
229	Break in power supply – no syngas flow, no mixing during 4 hours; reactor filled with helium, temperature decreased to 256°C
374	Spave velocity change from 1.6 to 1.2 Nl/g-cat/h
519	Temperature change from 260 to 265°C
691	Slurry sample withdrawal: 43 g wax, 1.0 g catalyst
692	End of run: 267 g wax, 6.2 g catalyst recovered from reactor
	Wax and catalyst removed during the run: 495 g of wax, 0 g of catalyst
	Catalyst recovery: 93%; Wax recovery: 104%

Catalyst pretreatment: H_2 at 250°C

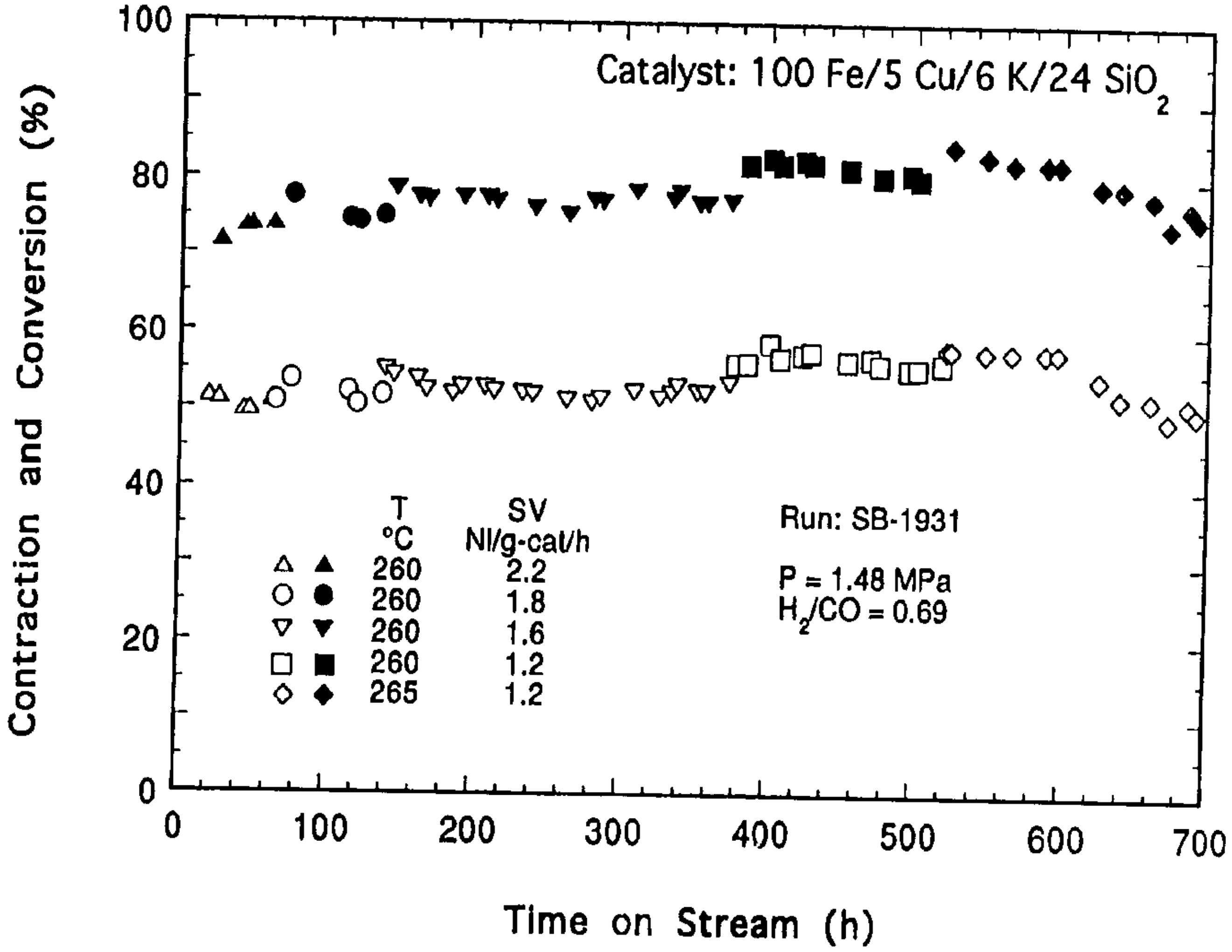

Figure IV-2.15 (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-1931.

velocity was maintained at 1.2 Nl/g-cat/h, and values of the (H_2+CO) conversion were between 80 and 82% (balances 7 and 8). During the last portion of the run (TOS = 520 – 692 h) the reaction temperature was 265°C. Following the initial increase in conversion (84.3% at 525 h) the catalyst deactivated with time. At the end of the run the (H_2+CO) conversion was 75% only.

Water-gas-shift (WGS) activity of the catalyst was high throughout the test. The usage ratio was about 0.6.

Wax and Catalyst inventories/Withdrawals

High molecular weight products which accumulate in the reactor were withdrawn periodically (approximately every 50 h) through a porous metal filter (0.5 µm pore size), which was placed horizontally to give a static slurry volume of 430 ml. Wax production rate during the test varied between 0.4 and 1.2 g/h, whereas the average production rate was 0.7 g/h.

At the end of the run, 6.2 g of catalyst was recovered from the reactor, and another 0.5 g was removed after reduction for catalyst characterization studies (Table IV-2.16). Catalyst and wax recoveries were: 93 and 104%, respectively.

Catalyst Characterization by XRD and/or MES

MES analysis of the catalyst sample withdrawn from the reactor after hydrogen reduction at 250°C for 4 h, indicates the presence of small superparamagnetic oxide/oxyhydrohide particles. Samples withdrawn from the reactor at 691 h (handled in an inert atmosphere) and at 692 h (exposed to air) were analyzed by XRD, and magnetite and iron carbide(s) were the only phases identified. The following phases were found by MES analysis in the latter sample : superparamagnetic oxides (69%), and χ-carbide (31%).

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time. For example, methane selectivity increased from 2.5% in

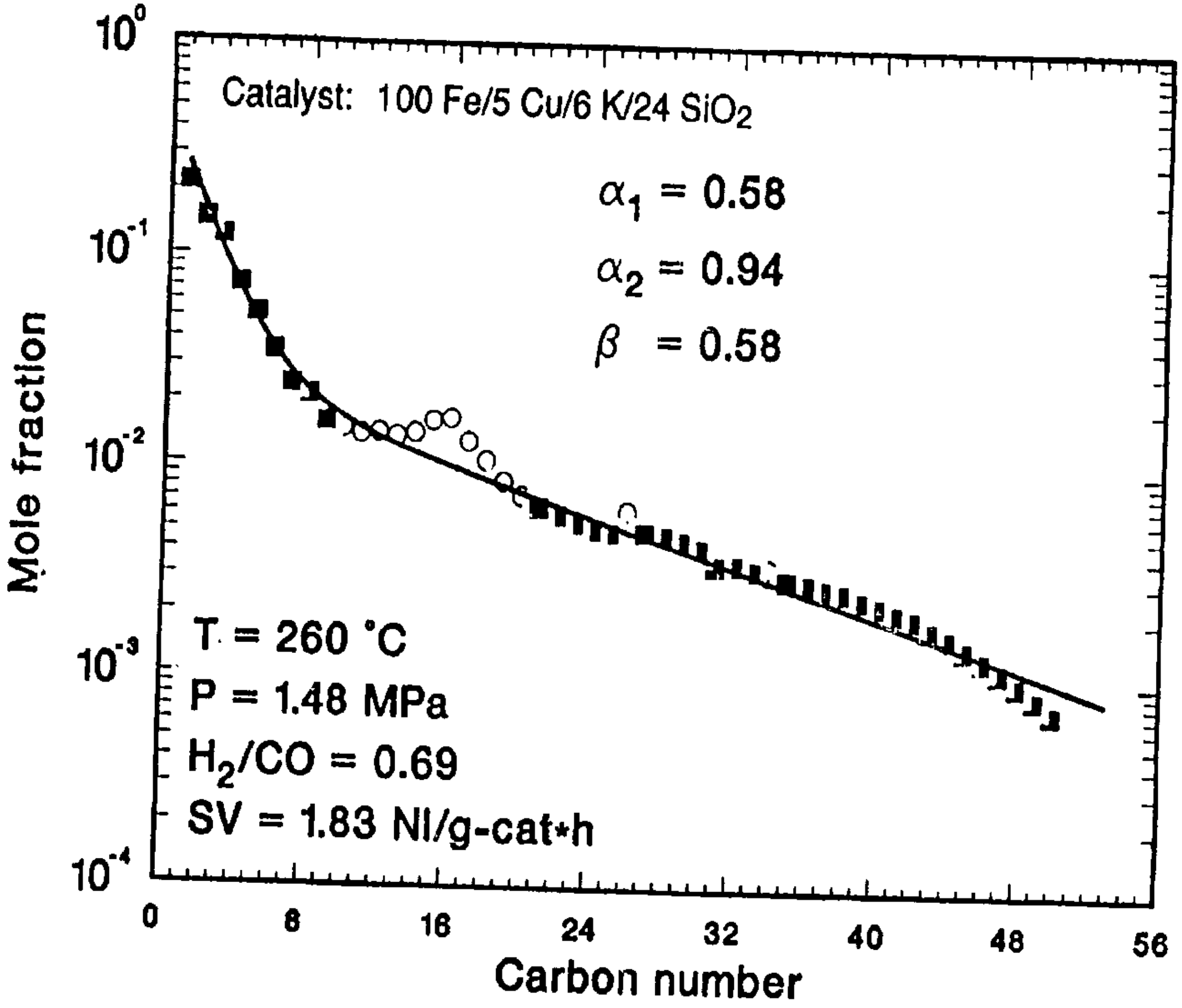

Figure IV-2.16 Carbon number product distribution for Run SB-1931 (TOS=98 h).

balance 1 (42 h) to 3.7% in balance 8 (496 h), while (C_2-C_4) increased from 11 to 14.6% and (C_5-C_{11}) from 18 to 19.6%, whereas C_{12}^+ selectivity decreased from 68.7 to 62.1% during the same period of time. (C_1+C_2) selectivity was below target value of 7% during first 450 h of testing at 260°C, but this target value was exceeded in balance 8 (500 h on stream) where (C_1+C_2) selectivity was 8.2%.

A typical carbon number product distribution (C_1-C_{50} carbon number range) is shown in Figure IV-2.16. Experimental data were fitted with a three parameter model of Huff and Satterfield. Some positive deviations from this model are noted in C_{14}-C_{19} carbon number range (diesel fuel). This type of behavior has been observed in other mass balances during this test, and in tests of some other iron/silica catalysts synthesized in our laboratory.

Concluding Remarks

This has been another successful test of a precipitated iron catalyst containing silicon oxide as a binder. We were able to achieve high values of (H_2+CO) conversion (74-84%), and the catalyst deactivation rate was low in spite of three operational upsets during the test. Also, hydrocarbon selectivity was within the target up to 450 h on stream.

IV-2.8 Run SB-3101 with 100 Fe/5 Cu/8 K/24 SiO_2 Catalyst

The catalyst was tested at : 260°C, 1.48 MPa (200 psig), 1.6 Nl/g-cat/h and H_2/CO = 0.64 throughout the entire test. A feed flowrate upset occurred at about 158 h, but it was corrected immediately by increasing slightly the cylinder delivery pressure. The run was terminated after 354 h on stream. Results from six mass balances made during the test are summarized in Table IV-2.17, whereas major events are listed in Table IV-2.18.

Table IV-2.17 Summary of Slurry Reactor Test Results for Run SB-3101.

Period	1	2	3	4	5	6
Date	11/08/91	11/10/91	11/13/91	11/16/91	11/19/91	11/21/91
Time on Stream (h)	39.0	86.0	171.0	243.0	302.0	339.5
Balance Duration (h)	8.0	6.5	11.0	12.0	6.5	11.0
Average Temperature (°C)	260.	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.645	.645	.650	.650	.650	.639
Space Velocity ($Nl/g\text{-cat}\cdot h$)[a]	1.62	1.62	1.62	1.60	1.63	1.63
Space Velocity ($Nl/g\text{-Fe}\cdot h$)	3.11	3.11	3.11	3.08	3.14	3.14
GHSV (h^{-1})[b]	44.0	44.0	44.0	40.2	40.9	40.0
CO Conversion (%)	78.6	75.2	70.5	67.1	65.0	62.8
H_2+CO Conversion (%)	74.4	72.3	67.7	64.1	61.3	60.1
H_2/CO Usage	.557	.581	.586	.577	.556	.570
STY ($mols$ H_2+CO/$g\text{-cat}\cdot h$)[a]	.054	.052	.049	.046	.044	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	50.5	42.6	26.3	26.1	28.2	32.1
Weight % of Outlet						
H_2	1.42	1.43	1.62	1.80	2.00	1.91
H_2O	.463	.456	.668	.633	.565	.447
CO	20.4	23.6	28.0	31.3	33.7	35.1
CO_2	59.0	56.6	53.3	50.4	47.2	46.3
Hydrocarbons	9.52	9.69	9.61	9.53	9.10	8.75
Oxygenates	.177	.201	.155	.129	.568	.465
Wax[c]	8.96	7.06	6.63	6.18	6.93	7.04
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	8.37	8.95	9.49	10.7	10.8	11.7
C_2-C_4 Hydrocarbons	29.0	29.0	30.4	33.7	33.1	35.1
C_5-C_{11} Hydrocarbons	49.6	50.1	51.9	51.5	47.9	48.0
C_{12}+ Hydrocarbons	111.	107.	99.7	99.1	114.	117.
Wax[c]	96.1	87.8	78.2	76.7	89.2	94.6
Oxygenates	1.90	2.22	1.82	1.60	7.31	6.24
Total	200.	197.	193.	197.	214.	218.
1+2 Olefins/n-Paraffin Ratio						
C_2	3.34	2.99	2.86	2.74	2.63	2.49
C_3	6.21	6.22	5.86	5.80	5.76	5.63
C_4	4.91	5.41	4.86	4.54	4.59	4.44
C_8	3.18	3.23	2.74	2.58	2.30	2.44
C_{10}	1.46	2.99	2.92	2.00	3.00	2.40

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.17 (cont'd) Summary of Slurry Reactor Test Results for Run SB-3101.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	4.22	4.60	4.96	5.49	5.22	5.52
Ethane	1.09	1.10	1.17	1.31	1.24	1.33
Ethylene	3.40	3.08	3.13	3.34	3.06	3.10
Propane	.805	.838	.945	1.04	.975	1.02
Propylene	4.77	4.97	5.28	5.74	5.35	5.48
n-Butane	.709	.773	.887	1.00	.924	.959
1+2 Butenes	3.36	4.04	4.16	4.40	4.09	4.11
C_4 Isomers	.514	.114	.300	.455	.423	.547
n-Pentane	.722	.771	.926	.973	.960	.937
1+2 Pentenes	3.15	3.37	3.63	3.76	3.52	3.54
C_5 Isomers	.720	2.43	2.27	2.35	2.13	2.26
n-Hexane	.855	.935	.989	.882	.911	.910
1+2 Hexenes	2.41	2.62	2.62	2.56	2.47	2.60
C_6 Isomers	.869	1.10	1.05	1.17	1.12	1.16
n-Heptane	.587	.667	.800	.809	.845	.814
1+2 Heptenes	1.80	2.03	2.07	2.08	1.93	1.94
C_7 Isomers	.612	.885	.819	.794	.663	.724
n-Octane	.550	.578	.749	.756	.746	.656
1+2 Octenes	1.72	1.84	2.02	1.91	1.69	1.57
C_8 Isomers	.513	.841	.503	.403	.471	.427
n-Nonane	.619	.453	.568	.538	.544	.469
1+2 Nonenes	1.54	1.50	1.77	1.63	1.26	1.09
C_9 Isomers	.471	.289	.334	.333	.278	.236
n-Decane	1.18	.568	.626	.570	.361	.393
1+2 Decenes	1.70	1.67	1.80	1.63	1.12	.929
C_{10} Isomers	1.27	.501	.450	.444	.363	.305
n-Undecane	.674	.549	.638	.600	.349	.335
1+2 Undecenes	1.71	1.81	2.00	1.83	1.09	1.06
C_{11} Isomers	1.37	.323	.459	.390	.387	.309
C_2-C_4	14.6	14.9	15.9	17.3	16.1	16.5
C_5-C_{11}	25.0	25.7	27.1	26.4	23.2	22.7
C_{12}+	56.1	54.7	52.1	50.8	55.5	55.3
Wax[c]	48.5	45.1	40.8	39.3	43.2	44.6

[c] Unanalyzed wax withdrawn from reactor

Table IV-2.18 Major Events in Run SB-3101.

TOS (h)	Event
	Slurry loading: 310 g n-octacosane, 12.5 g catalyst (particle size <270 mesh)
	Catalyst pretreatment: H_2 at 250°C
	Slurry sample withdrawal: 20.4 g wax, 0.8 g catalyst
	Wax withdrawal through filter: 6.31 g of wax
0	Initiate synthesis gas flow
1	Achieved process conditions: T=260°C, P=1.48 MPa, SV= 1.6 Nl/g-cat/h, (H_2/CO=0.64)
158	Discovered decrease in feed flow rate and restored to desired flow rate
182	Slurry sample withdrawal: 24.5 g wax, 0.9 g catalyst
352	Slurry sample withdrawal: 49.3 g wax, 1.4 g catalyst
354	End of run: 287 g wax, 8.5 g catalyst recovered from reactor
	Wax/catalyst removed during the run: 400 g of wax, 2.3 g of catalyst
	Catalyst recovery: 92.3%; Wax recovery: 101%

Catalyst Activity and Stability

The catalyst deactivated continuously with time on stream. The (H_2+CO) conversion decreased from initial value of 77% to 60% at 350 h on stream, while volumetric contraction (VC) decreased from 50% to 38% during the same time period. Changes of (H_2+CO) conversion and VC with time on stream are shown in Figure IV-2.17. WGS activity of the catalyst was high, and the (H_2/CO) usage ratio varied between 0.56-0.58.

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn periodically through a porous sintered metal filter with nominal pore size of 0.5 µm. No catalyst was found in the withdrawn wax. The wax production rate decreased from 1.4 to 1.0 g/h as the catalyst deactivated with time.

At the end of the run, 8.5 g of catalyst was recovered from the reactor slurry. Another estimated 2.4 g of catalyst was removed from the reactor during the test with slurry samples for catalyst characterization. Catalyst recovery was about 92%, whereas wax recovery was 101% based on the amounts of catalyst and wax charged into the reactor.

Catalyst Characterization by XRD and/or MES

A slurry sample withdrawn from the reactor after hydrogen reduction at 250°C for 4 h contained a small amount of catalyst which was insufficient for XRD analysis. The iron phases in this sample were determined by MES analysis. Superparamagnetic oxide/oxyhydrohide was the most dominant phase (96%) in the sample, the remainder being the metallic iron. Samples withdrawn from the reactor at 182 and 352 h on stream contained magnetite and iron carbide(s) phases, whereas iron carbide(s) was the only phase found in a sample withdrawn at 354 h on stream (XRD analysis). The MES analysis of the last two samples (352 and 354 h) reveals the presence of superparamagnetic oxide phase (probably magnetite based on XRD analysis) and ε' - carbide, in approximately equal amounts.

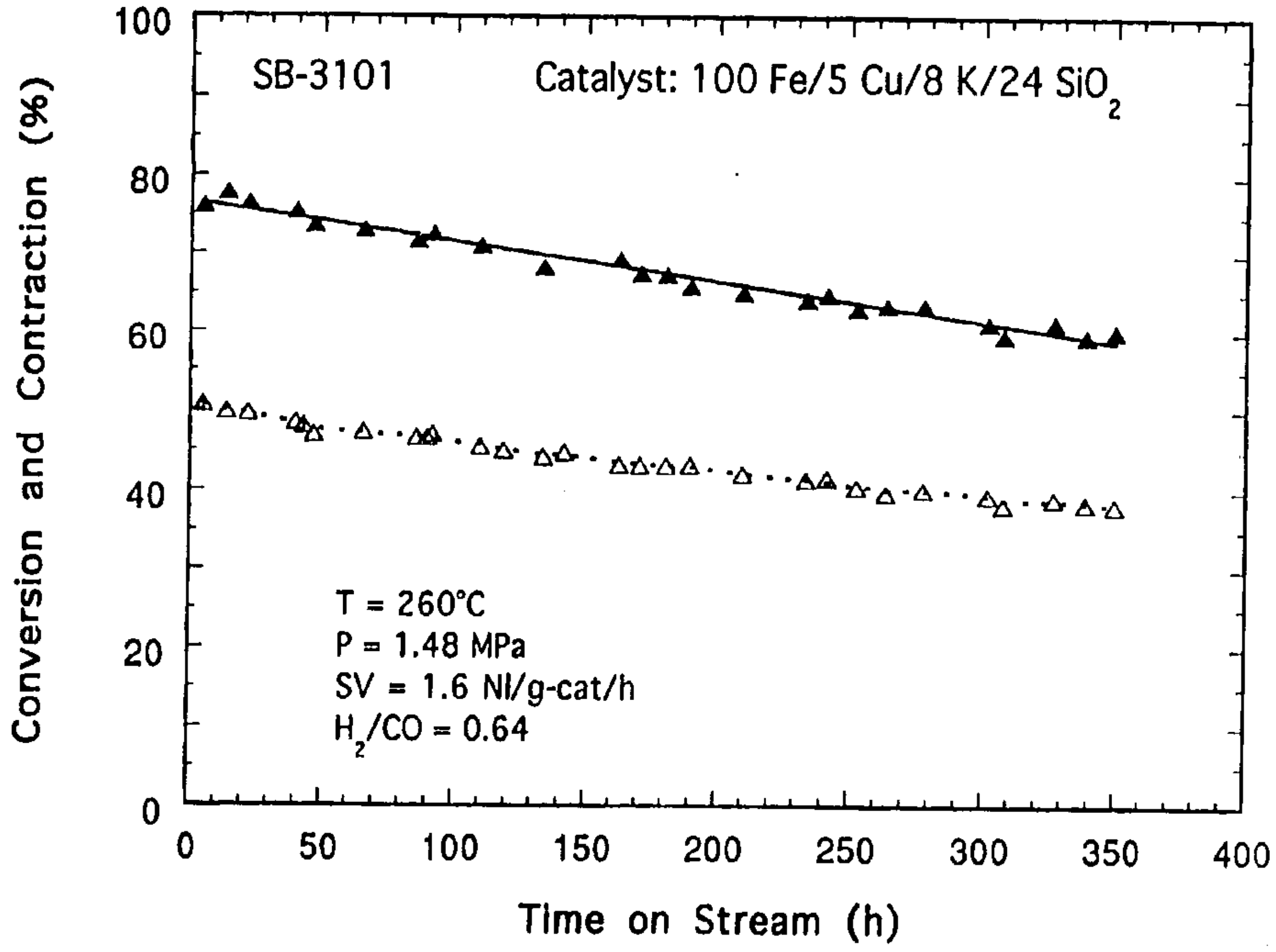

Figure IV-2.17 (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) as a function of time on stream for Run SB-3101.

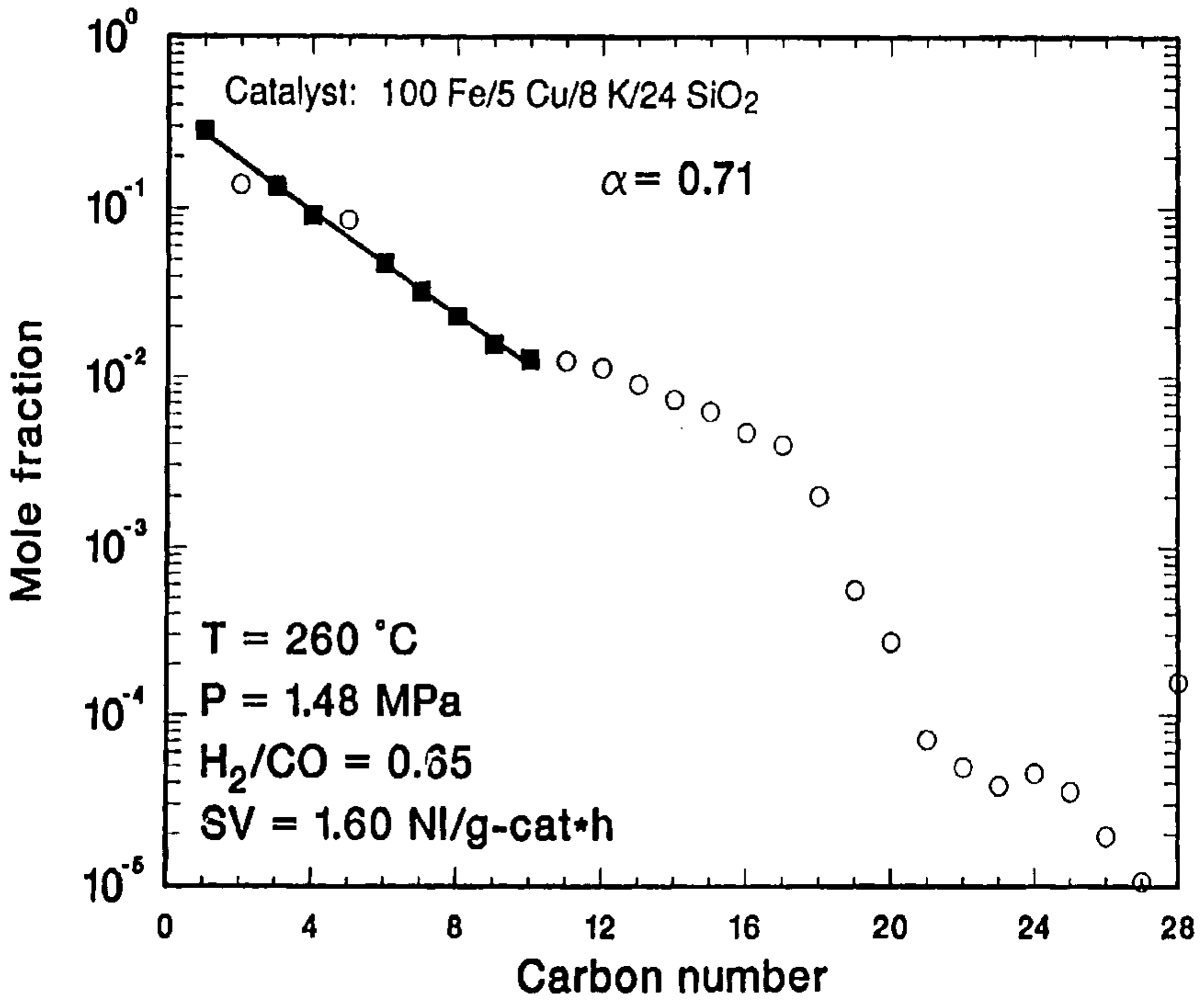

Figure IV-2.18 Carbon number product distribution for Run SB-3101 (TOS=243 h).

Hydrocarbon and Carbon Number Product Distributions

Hydrocarbon product distribution shifted gradually toward lower molecular weight products with time on stream. For example, at 40 h on stream, hydrocarbon selectivity was: (CH_4) = 4.2, (C_2–C_4) = 14.6, (C_5–C_{11}) = 25 and C_{12}+ = 56.2 wt%, while at 340 h, it became (CH_4) = 5.5%, (C_2–C_4) = 16.5, (C_5–C_{11}) = 23, and C_{12}+ = 55 wt%.

A typical carbon number product distribution is shown in Figure IV-2.18 in the form of ASF plot. This plot is based on products collected overhead (i.e. the wax from the reactor was not analyzed).

IV-2.9 Comparison of Catalyst Performance

Results illustrating performance of iron-silica catalysts synthesized in our laboratory are summarized in Table IV-2.19. None of the catalysts have met all of the activity targets listed in Table IV-2.2. The initial syngas conversions in five of the eight tests were above 80% (81-88%), but were nevertheless somewhat less than the target value of 88%. Also, these conversions could not be maintained over a long period of time due to catalyst deactivation. Catalyst productivity target of 2.6 $Nm^3(H_2+CO)$ reacted /kg-Fe/h was met in two of the tests (Runs SB-2832 and SB-1931). The water gas shift activity of all catalysts was high, and the usage ratio was less than 0.65.

Initial values of the apparent first order reaction rate constant were above 250 mmol/g-Fe/h/MPa in all tests except in Run SB-2270. In the latter test the initial value of the apparent rate constant was only 180 mmol/g-Fe/h/MPa. Low activity of the catalyst in this test may be attributed to low reduction temperature (220°C for 2h), i.e. low degree of reduction of the catalyst. Also, the activity of the catalyst used in Run SB-1910 (100 Fe/5 Cu/4.2 K/8 SiO_2) was lower than that of the other two catalysts containing 8 parts of silicon oxide per 100 parts of iron (Runs SA-1371 and SB-0931), due to lower degree of reduction (shorter duration of reduction and/or lower reduction

Table IV-2.19 Summary of Slurry Reactor Test Results of Iron-Silica Catalysts Synthesized at TAMU.

Run ID	SA-1371	SB-0931	SB-1910	SB-0261	SB-2270	SB-2832	SB-1931	SB-3101
Catalyst Composition ($Fe/Cu/K/SiO_2$)	100/3/3/8	100/3/4/8	100/5/4.2/8	100/3/4/16	100/5/4.2/16	100/5/4.2/16	100/5/6/24	100/5/8/24
ACTIVITY PARAMETERS								
(H_2+CO) (%)	52-84	55-88	42-63	63-83	34-73	67-81	74-81	60-74
CO (%)	56-90	58-93	46-70	65-90	35-75	71-88	78-85	63-79
UR (-)	.55-.59	.54-.61	.54-.69	.53-.60	.59-.69	.58-.62	.59-.60	55-.58
k (mmol/g-Fe/h/MPa) at 260°C	180-330	170-320	90-270	120-255	80-180	200-270	260-350	200-290
Nm^3 (H_2+CO)/kg-Fe/h	1.8-2.4	1.1-2.1	1.4-1.8	1.3-2.0	1.4-1.6	1.7-2.9	1.7-3.0	1.9-2.3
DR (%/day)	3.3	2.1	4.1	1.4	3.1	0.9	1.3	2.1
SELECTIVITY								
g HC/Nm^3 (H_2+CO) reacted	190-210	~200	185-208	195-215	205-217	205-217	203-218	194-212
g C_3+/Nm^3 (H_2+CO) reacted	~180	~188	~186	~194	~191	~191	~199	~183
(C_1+C_2), wt.%	9.1-11.5	5.3-7.1	6.6-7.2	3.5-6.4	6.7-9.2	8.1-9.8	5.4-8.2	8.5-9.9
CH_4	4.6-6.4	2.5-3.4	3.1-3.8	1.6-2.8	3.3-4.5	4.4-5.3	2.5-3.7	4.2-5.5
C_2-C_4	18-21	10.6-12.5	13-13.6	8-13	13-19	15.2-17.4	10-14.6	14.6-17.3
C_5-C_{11}	30-36	16-21.7	21-29	12-16	12-19	20.6-29.8	13-18	22.7-27.1
C_{12}	37-45	65-70	54-62	69-77	57-71	48.3-59.3	62-74	51-57

temperature). Silicon oxide is known to inhibit reduction of iron (Bukur et al., 1990b) and in order to compensate for this we have used higher reduction temperatures for catalysts with higher silica contents. As a result the initial activities of the catalysts containing 8 and 24 parts of SiO_2 were similar (300-350 mmol/g-Fe/h/MPa).

Catalyst deactivation rates listed in Table IV-2.19 were estimated using the following expression:

$$DR = [1 - k(t)/k(t_0)] \times 100/t$$

where: DR – deactivation rate in (%/day); k(t) and $k(t_0)$ – reaction rate constants at time t and t_0, respectively; t – time in days; t_0 – time at which the first mass balance was conducted (usually, after about 40 h on stream).

Deactivation rates calculated in this way varied between 0.9 and 4.1% per day. In general, catalysts with the lowest silica content (8 parts of SiO_2 per 100 parts of Fe) had higher deactivation rates. The estimated deactivation rates in all tests, except Run SB-2832, were higher than the target value of 1% per day. However, the above procedure provides a conservative estimate, since the deactivation rate is based on the initial catalyst activity. In some cases the catalyst activity goes through a maximum (induction period) before it starts decreasing or leveling off.

All of our catalysts have either met most or all of the selectivity targets listed in Table IV-2.2. Hydrocarbon productivity targets have been exceeded in all eight tests (both for total hydrocarbon products produced and C_3^+ hydrocarbons). The requirement that (C_1+C_2) selectivity be less than 8 wt%, was satisfied in four tests (see Table IV-2.19).

Results from STSR tests of the best three precipitated iron catalysts synthesized in our laboratory are shown in Figures IV-2.19 and IV-2.20. Variations in (H_2+CO) conversion with TOS for these three catalysts are shown in Figure IV-2.19. Process conditions in all tests were: 260°C,1.48 MPa, H_2/CO=0.66-0.70, whereas gas space velocity varied between 2.2 and 3.4 Nl/g-Fe/h (see Figure IV-2.19 for details). In two of

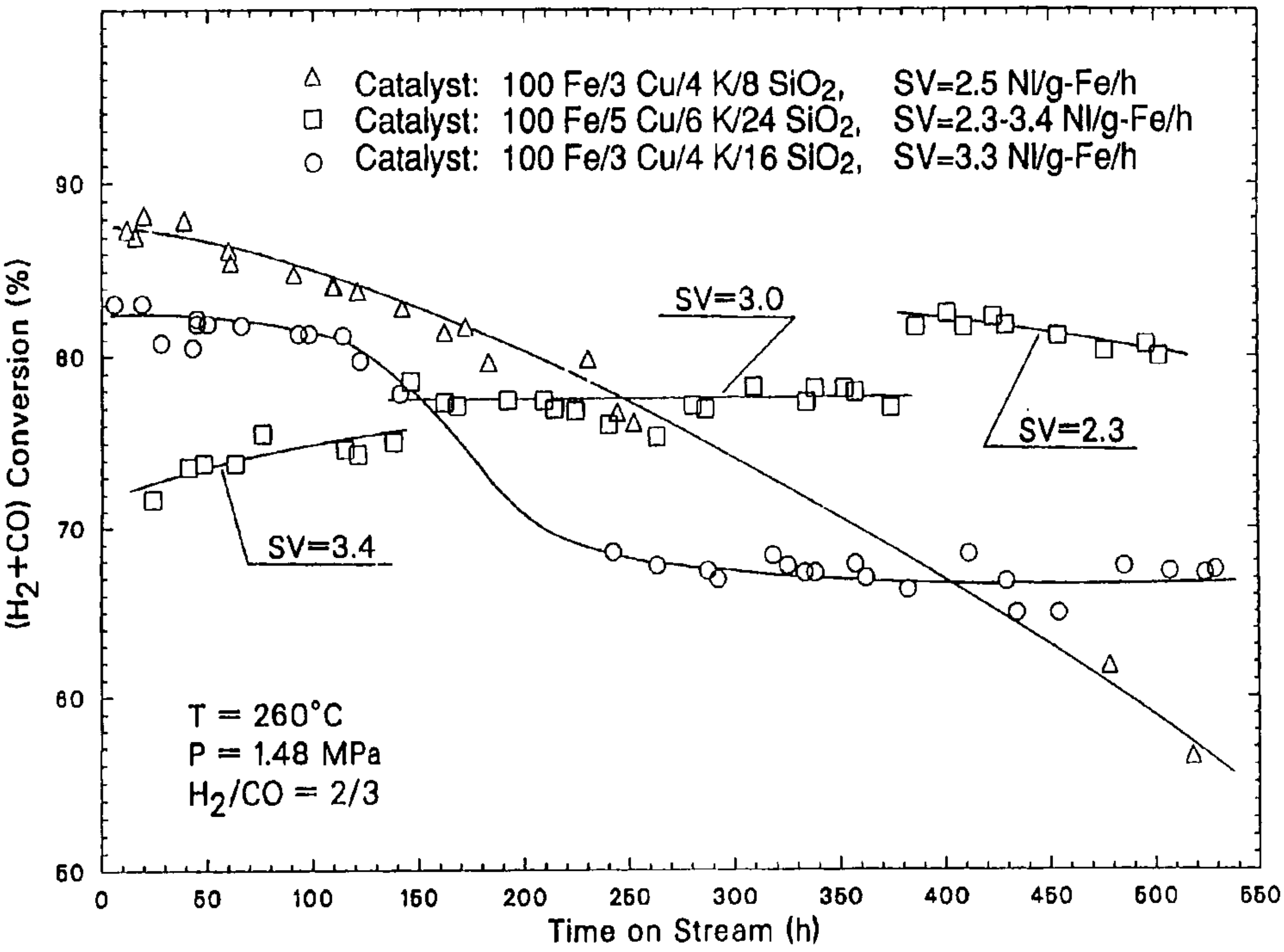

Figure IV-2.19 Variations in (H_2+CO) conversion with time on stream in STSR tests of precipitated iron catalysts synthesized at TAMU.

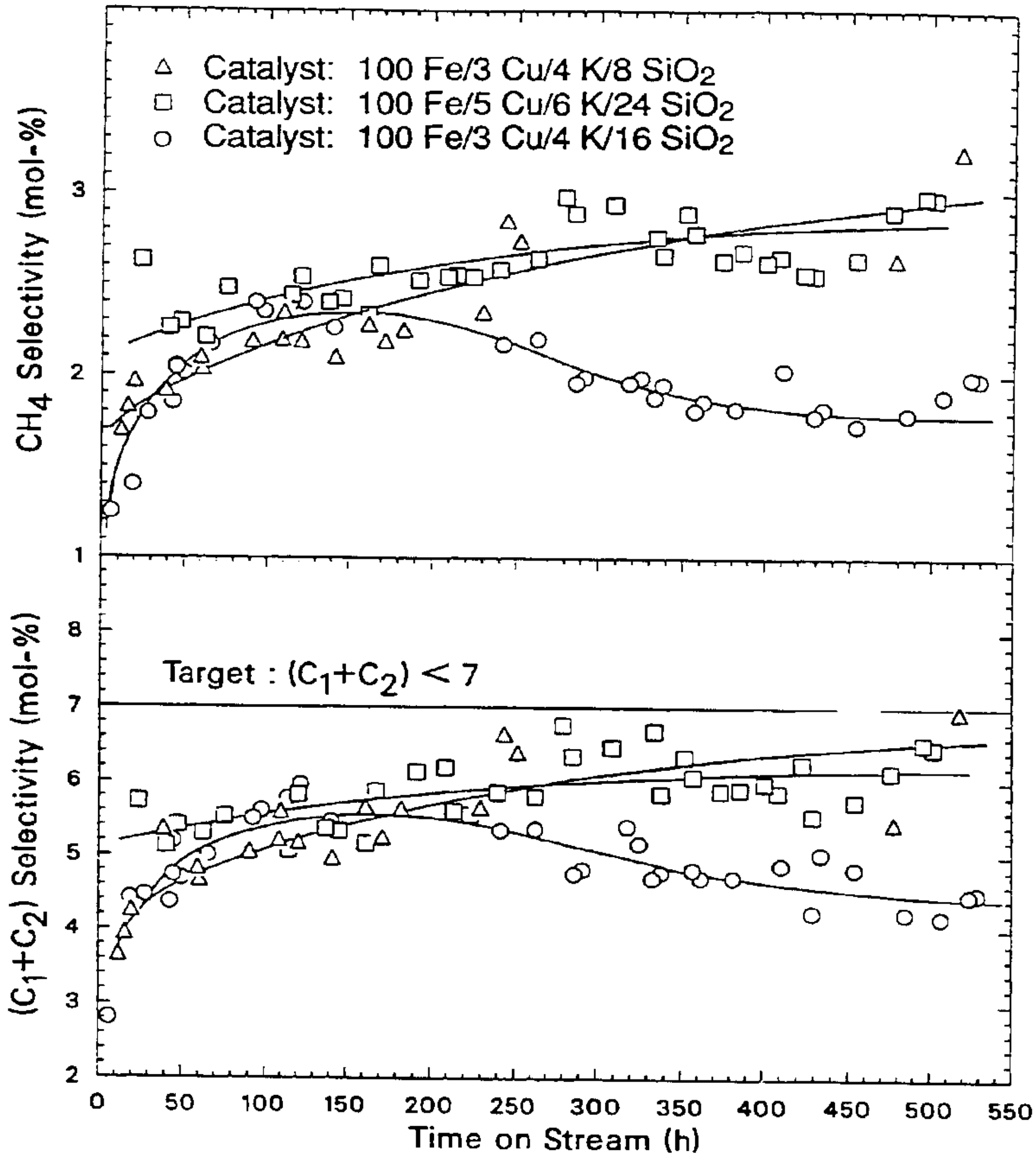

Figure IV-2.20 Selectivities of methane and (C_1+C_2) hydrocarbons in STSR tests of precipitated iron catalysts synthesized at TAMU.

the tests (Runs SB-0931 and SB-0261) process conditions were varied during the test, however results from these periods are not shown. Three types of catalyst behavior were observed in these tests. Catalyst with nominal composition 100 Fe/3 Cu/4 K/8 SiO_2 (SB-0931) had initially high conversion (~ 88%), but its activity decreased gradually with TOS. During the test of catalyst 100 Fe/3 Cu/4 K/16 SiO_2 (SB-0261) the (H_2+CO) conversion was initially about 81% decreasing to 76% at 150 h on stream. Between 160 and 240 h the catalyst was tested at 265°C (results not shown in Figure IV-2.19), and it continued to deactivate. Upon returning to the baseline conditions, the activity became stable as evidenced by nearly constant value of (H_2+CO) conversion (66-68%) between 240 and 530 h on stream. In the test of catalyst 100 Fe/5 Cu/6 K/24 SiO_2 (SB-1931) gas space velocity was decreased twice to obtain higher conversions. At a constant gas space velocity (3.4 and 3.0 Nl/g-Fe/h) the activity increased slightly with time up to about 390 h. During the last portion of the test (400-500 h) at gas space velocity of 2.3 Nl/g-Fe/h the catalyst exhibited some deactivation.

Performance of all three catalysts was somewhat below specified target values for activity (Table IV-2.2). For example, the (H_2+CO) conversions were between 68 and 88% and catalyst productivity varied between 1.5 and 2.5 Nm^3 (H_2+CO) converted/kg-Fe/h, whereas the corresponding target values are 88% and 2.6, respectively. It should be noted that these measures do not necessarily reflect the intrinsic catalyst activity. For a given catalyst these two measures (conversion and catalyst productivity) depend on the reactor type (e.g. fixed bed, STSR or bubble column slurry reactor-BCSR) and process conditions employed.

Selectivities of methane and (C_1+C_2) hydrocarbons obtained in tests of these three catalysts are shown in Figure IV-2.20. In tests SB-0931 and SB-1931 selectivities of methane and (C_1+C_2) hydrocarbons increased gradually with TOS, whereas in the test SB-0261 these two selectivities passed through a maximum at about 150 h. Methane selectivity of all three catalysts was less than 3% (mole %

carbon basis), whereas (C_1+C_2) selectivity was less than 7% throughout the entire test. The latter value is within the specified target performance.

Comparison of performance of the catalyst with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2 with other catalysts tested in our laboratory and elsewhere, is presented in Table IV-2.20. As can be seen the performance of this catalyst is very similar to that of the best Mobil's catalyst in the wax mode of operation (Kuo, 1985). The latter catalyst was tested in a bubble column slurry reactor, the behavior of which approaches that of a plug flow reactor. Our catalyst is significantly more active than the Mobil's catalyst used in run CT-256. We have chosen an apparent first order reaction rate constant evaluated at a common temperature of 260°C, as a measure of catalyst activity. Data obtained at other reaction temperatures were converted to 260°C assuming the activation energy of 90 kJ/mol. STSR was modeled as a perfectly mixed flow reactor, whereas the rate constant from a BCSR was estimated using a model which assumes that the gas phase is in plug flow and the liquid is unmixed (Bukur, 1983). This catalyst is also more active than the Ruhrchemie, UCI and UOP (Abrevaya et al., 1991) catalysts, and it produces less methane and gaseous hydrocarbons than these catalysts.

IV.2-10 Summary

Eight of iron FT catalysts synthesized in our laboratory have met specified performance targets for hydrocarbon selectivity, i.e. total hydrocarbon production greater than 178 g/$Nm^3(H_2+CO)$ reacted and more than 166 g $C_3^+/Nm^3(H_2+CO)$ reacted. Four of the catalysts have met the requirement that methane + ethane + ethylene selectivity be less than 8% of total hydrocarbons. Initial synthesis gas conversions in five tests were higher than 81%, and the catalyst deactivation rate in three tests was moderate, between 0.9 and 1.4% per day. Catalyst productivity target of greater than 2.6 $Nm^3(H_2+CO)$ reacted/(kg-Fe·h) has been met in two tests, whereas

Table IV-2.20 Catalyst Performance in Slurry Bed Reactors

Catalyst Designation	TAMU	Ruhrchemie	UCI	UOP	Mobil's Run**
Run ID	SB-1931	SA-0888	SA-3391	(1991)	CT-256-13
Process Conditions:					
Temp. (°C)	260	250	265	265	257
Pressure (MPa)	1.48	1.48	2.10	2.10	1.48
SV (Nl/g-Fe/h)	2.2-3.4	3.8	2.4	2.4	2.3
Feed (H_2/CO)	0.66-0.69	0.67	0.7	0.7	0.73
TOS (h)	40-520	0-343	227-322	15-370	475
% (H_2+CO) Conv.	74-84	40-43	73-80	69	82
Usage Ratio	0.56-0.62	0.74-0.84	0.58-0.62	0.57	0.59
Rate Const at 260°C (rel)	100	88	40	33	49-70
Hydrocarbon Selectivities (wt-%):					
CH_4	3.0	4.7	4.4		2.7
C_2-C_4	10.5	20.6	16.5		11.1
C_5-C_{11}	16.0	23.2	23.6		18.1
C_{12}+	70.5	51.5	55.5		68.1
C_1+C_2	6.1	10.8	9.2		5.6
Hydrocarbon Selectivities (mol-%):					
CH_4	2.7		3.9	4.5	
C_1+C_2	5.8		8.7	5.8*	

*CH_4+C_2H_6 only

**Slurry Bubble Column Reactor Test

in several other tests this target was not met by a small margin only. The activity targets for syngas conversion (≥ 88%) and catalyst productivity are very difficult to achieve in a stirred tank slurry reactor (nearly perfectly mixed reactor), but it is expected that some of our catalysts would exceed these targets in a bubble column slurry reactor. Several of our catalysts are more active than any other known iron FT catalysts developed for maximization of production of high molecular weight hydrocarbons (hydrocarbon wax).

IV.2-11 References

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