analytical techniques and/or by differences in the way the selectivities were reported (relative quantities vs. concentrations in the product stream).

V.2.1.4. Summary

Promotion of iron with potassium in the range 0.2 - 1 wt%, increases activity of the Fischer-Tropsch and water-gas-shift reactions, and the average molecular weight of hydrocarbon and other organic (primarily alcohols) products. It also causes suppression of olefin hydrogenation and isomerization reactions. Potassium promotion inhibits iron reduction and as a result the potassium promoted catalysts require longer time to achieve the steady state activity.

Promotion of iron with copper (100 Fe/3 Cu) also increases rates of FT and WGS reactions. Copper is a more effective promoter than potassium in increasing the rate of FT, whereas the opposite applies to the WGS activity. Also, promotion with copper facilitates reduction of iron and thus decreases time required to achieve the steady state activity. In the presence of copper, the hydrocarbon product distribution shifts toward higher molecular weight products, but the magnitude of changes is significantly smaller than that observed with potassium promotion. Copper promotion enhances slightly the secondary reactions (olefin hydrogenation and isomeriza[illegible]).

The FT activity of the two doubly promoted catalysts (100 Fe/3 Cu/0.2 K and 100 Fe/3 Cu/0.5 K) was independent of their potassium content and higher than that of any of the singly promoted catalysts. In tests over a long period of time (up to 460 hours on stream) the catalyst with higher potassium content lost about 9% of its maximum activity, whereas the 100 Fe/3 Cu/0.2 K catalyst lost only 2%. The WGS activity of the doubly promoted catalysts was similar to that of the Fe/K catalysts. Selectivity behavior of the doubly promoted catalyst was strongly influenced by their potassium content. The catalyst containing 0.2 wt% K had selectivities (hydrocarbon product distribution, olefin content) similar to that obtained with the 100 Fe/3 Cu catalyst, whereas the 100 Fe/3 Cu/0.5 K catalyst had selectivities similar to that obtained with the 100 Fe/0.5 K catalyst. This shows that, in the presence of copper, higher potassium loadings are needed to achieve promotional effects on product selectivity.

V.2.2. Fixed bed Reactor Tests of Catalysts Activated with Carbon Monoxide

These tests were conducted during the early period of this contract before the two zone temperature control was employed, and consequently significant axial temperature gradients were often observed. Also, the catalysts deactivated with time on stream. Only selected results, obtained in the absence of large temperature gradients and during early periods of tests, will be discussed.

Eight precipitated catalysts were tested to study the effect of copper and potassium promotion on catalyst activity and selectivity in fixed bed reactors. The catalysts were calcined before use, with air at 300°C and ambient pressure for 5 h. They were ground to 30/60 mesh, and diluted 1:7 with glass beads of the same mesh size range before loading the reactor. Reduction of the catalysts was performed using pure CO at 4-4.5 Nl/g-Fe.h, 280°C, and ambient pressure for 8h. The process conditions employed during these tests are listed in Table V.2-3.

The effect of potassium promotion at 235°C, 1.48 MPa (200 psig), 2 Nl/g-cat.h and $H_2/CO=1$ for catalysts containing either 1 or 3 parts of Cu per 100 parts of Fe are shown in Table V.2-4 and Figures V.2-12 and V.2-13. As shown in Table V.2-4, FT activity (i.e., (H_2+CO) conversion) increased initially with potassium addition, and then decreased for the 100Fe/1Cu/xK (x=0,0.2 and 0.8) catalyst, whereas an increase in activity was observed with the 100Fe/3Cu/xK (x=0.2 or 0.5) catalyst. However these trends might have been affected by non-uniformities in temperature and/or pressure in these tests. The WGS activity of all catalysts, measured by extent of the WGS, increased with potassium loading.

The effect of potassium on hydrocarbon and olefin selectivities for the catalysts containing 1 and 3 parts of Cu per 100 parts of Fe is shown in Figures V.2-12 and V.2-13, respectively. The trends with potassium loading are qualitatively the same irrespective of the copper content of the catalyst, i.e., the production of methane and gaseous hydrocarbons decreases, whereas the olefin selectivity increases with addition of potassium. Similar trends were observed at other process conditions.

In summary, promotional effects of potassium observed with the CO activated catalysts are similar to those found in tests with the H_2 reduced catalysts. Catalyst activity and selectivity displayed no discernible trends with copper promotion.

V.2.3. Promoter Effect / Kinetic Studies in Stirred Tank Slurry Reactors

Four of the most active doubly promoted precipitated Fe/Cu/K catalysts were tested in stirred tank slurry reactors. These tests had a dual purpose: (1) to determine promoter effects in slurry phase, and (2) to determine kinetic parameters from tests at different process conditions. These goals were not completely achieved due to a lack of catalyst stability with time on stream and problems with quantification of the high molecular weight products (wax) which accumulate in the reactor. In two of the four tests, catalyst activity increased with time on stream (Runs SA-05-2957 and SB-07-0458), whereas in the other two, catalysts deactivated

Table V.2-3. Summary of fixed bed tests and testing conditions for promoter effect reserch.[a]

Test ID	Catalyst	220°C 1.48 MPa 2 Nl/g-cat.h	235°C 1.48 MPa 2 Nl/g-cat.h	235°C 1.48 MPa 4 Nl/g-cat.h	250°C 1.48 MPa 2 Nl/g-cat.h	235°C 2.86 MPa 4Nl/g-cat.h
FB-05-2287	100/.3/.2	48(1)[d]	90(2)[d]	121(3)[b,d]		
FB-07-2057	100/.3/.5	46(1)[c]	94(2)[c]		118(3)[b,c,d]	
FB-33-2287	100/1/0	40(1)	73(2)			
FA-13-2217	100/1/.05	37(1)	61(2)			
FA-15-2097	100/1/.2	40(1)	64(2)	88(3)	134(5)[b]	184(6)
FA-17-2307	100/1/.8	30(1)	60(2)[d]	84(3)[d]	131(5)	147(6)[b]
FB-25-2447	100/3/.2	33(1)	58(2)	83(3)	107(4)[d]	131(5)
FA-27-2557	100/3/.5	38(1)	63(2)	87(3)	111(4)	135(5)

[a] Time on stream, h (balance period) are indicated; $H_2/CO=1$ for all tests
[b] Catalyst had partially deactivated
[c] SV = 3 Nl/g-cat.h for this test
[d] Large axial temperature gradient

Table V.2-4. Effect of promoters on catalyst performance[a]

Run Designation	A-2287	A-2097	A-2367	B-2447	A-2557
Catalyst	100/1/0	100/1/.2	100/1/.8	100/3/.2	100/3/.5
Time on Stream (*h*)	73	64	60	58	63
CO Conversion (%)	41.6	82.3	68.2	54.6	74.3
H_2+CO Conversion (%)	45.5	72.9	56.1	54.5	62.9
Extent of WGS($p_{CO_2}/p_{CO_2}+p_{H_2O}$)	.30	.77	.74	.60	.85
HC Selectivities (wt.%)					
CH_4	9.6	9.9	6.9	7.8	5.8
C_2-C_4	35.5	33.3	30.9	37.3	25.2
C_5-C_{11}	26.8	25.6	21.3	29.6	22.4
C_{12}+	28.1	31.2	40.9	25.3	46.6
CO Conversion to Products (%)					
Hydrocarbons	62.10	55.3	43.6	36.9	47.3
Oxygenates	3.2	1.2	1.6	1.7	0.01
CO_2	29.14	40.6	43.1	35.1	41.7
Unaccounted	5.6	2.9	11.7	19.6	9.6
Olefin Selectivity					
C_2-C_4(wt%)	67.5	68.4	75.7	75.3	75.6
C_5-C_{11}(wt%)	56.9	62.3	67.6	68.4	72.5
2 Butene/1-Butene	.37	.29	.08	.12	.06

[a]all tests were made at 200 psig, SV = 2 Nl/g-cat.h, 235°C

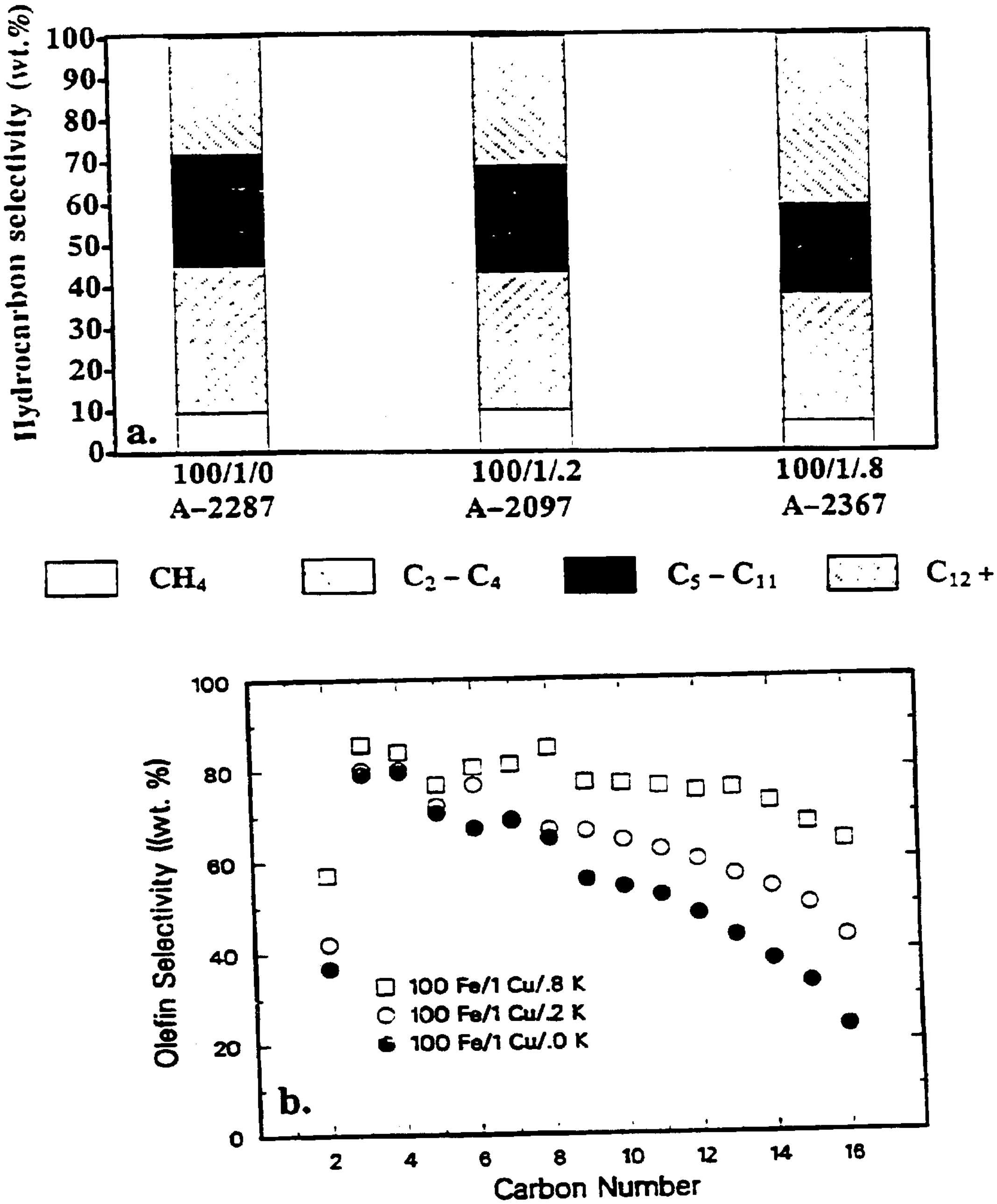

Figure V-2.12. Effect of potassium content on (a) hydrocarbon distribution, and (b) olefin selectivity (235°C,1.48 *MPa*, H_2/CO = 1, SV = 2 *Nl/g-cat.h*; catalyst composition given as parts by weight of Fe/Cu/K).

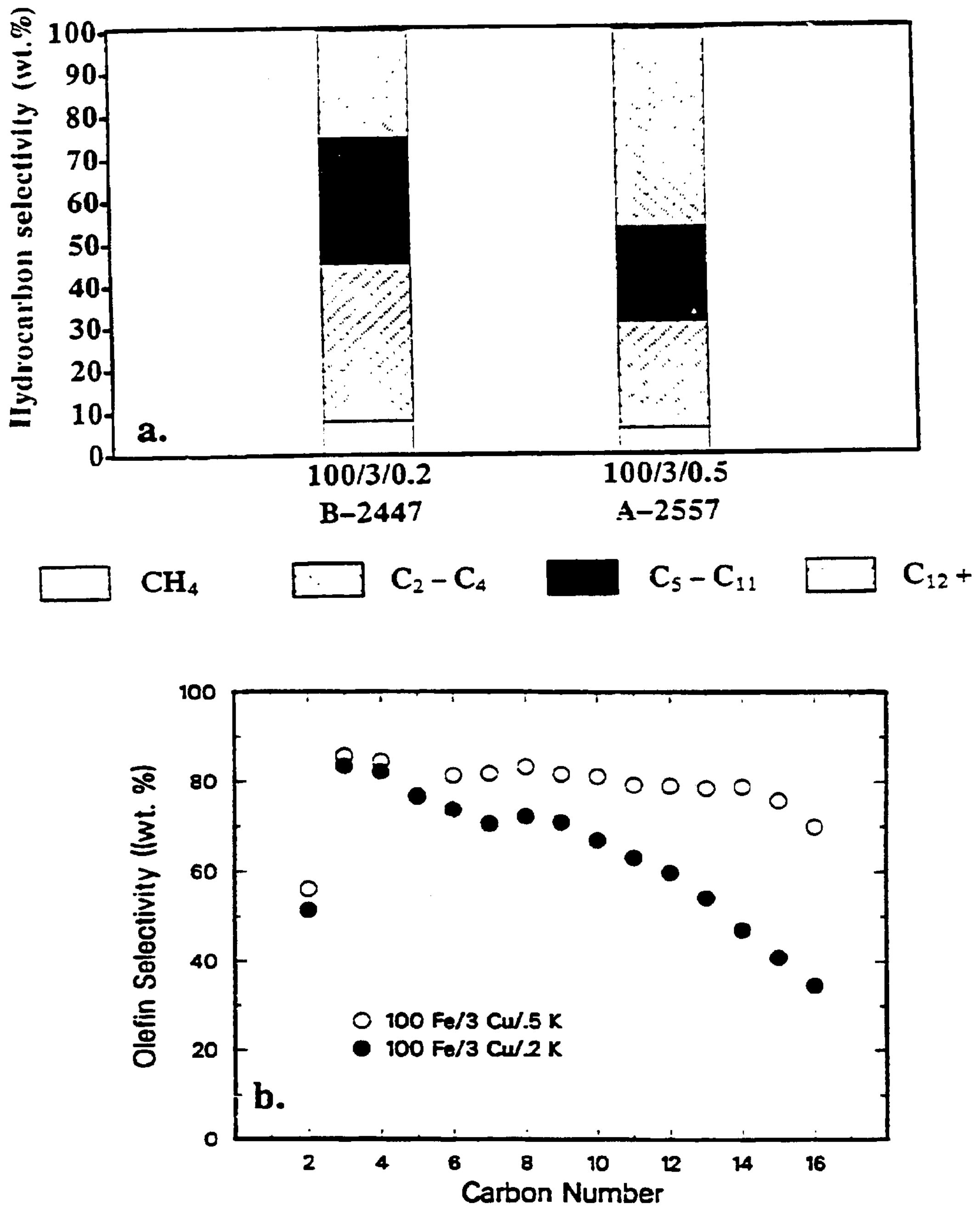

Figure V-2.13. Promoter effects on (a) hydrocarbon distribution, and (b) olefin selectivity (235°C,1.48 *MPa*. H_2/CO = 1, SV = 2 *Nl/g-cat.h*; catalyst composition given as parts by weight of Fe/Cu/K).

rather rapidly with time on stream (Runs SA-25-3657 and SA-07-0468). Also, during run SA-05-2957 (100 Fe/ 0.3Cu/0.2K catalyst), the wax was withdrawn only three times during the test which prevented us from obtaining accurate mass balance closures and hydrocarbon product selectivities. Results from the latter portions of runs SA-05-2957 and SB-070458 were used to estimate kinetic parameters of the FT and WGS reactions (see Section V.3 of this report). In this section, the results from these four slurry reactor tests will be described, followed by a brief summary of the major findings.

V.2.3.1. Run SA – 05 – 2957 with the 100 Fe / 0.3 Cu / 0.2 K Catalyst

This run was made as a retest of the unsuccessful run SA-05-2777, using the 100Fe/0.3 Cu/0.2K catalyst. A hard paraffin wax (FT-300, from Dura Commodities, New York) was used as the slurry liquid, and an excess of wax was loaded with catalyst (< 325 mesh) into the reactor prior to reduction. The catalyst was reduced in situ using CO at 250°C. Following reduction, the excess wax was withdrawn from the reactor to a preset static slurry volume of about 440 cm^3. A total of 18 mass balances were made during the run, and the run was voluntarily terminated after about 550 hours of operation. The results obtained during the run are summarized in Table V.2-5.

Wax which accumulated in the reactor during the synthesis was withdrawn only three times during the course of the run, with withdrawals of 163, 395, and 148 g of wax after balances 7, 12, and 18, respectively. Several methods were tested to allocate the wax collected over multiple periods to individual mass balances. The simplest was to assume that the wax was accumulated in the reactor at a constant rate between withdrawals, regardless of operating conditions. Under this assumption, the rate of wax accumulation in the reactor was 0.79 g/h in balances 1-7, 2.2 g/h in balances 8-12, and 0.55 g/h in balances 13-18. This method of wax allocation often gave poor mass closures and unrealistic estimates of total product yield.

Two methods of wax allocation based on mass closures were also tried. The first method assumed that the amount of wax produced at a given set of conditions was proportional to discrepancy of the total closure obtained during the mass balance period. The amount of wax needed to obtain 100% closure for all balances was then normalized to agree with the actual amount of wax withdrawn. The second allocation method distributed the wax in order to optimize the carbon and hydrogen atomic closures obtained during the mass balance periods. With the exception of balance 12, this method gave good total mass closures, and in most cases, reasonable values for the total yield. Balance 12 had inherently poor atomic C-H closures,

Table V.2-5 Summary of results for slurry run SA 05 2957.

Catalyst: 25.9 g[a], 100 Fe/0.3 Cu/0.2 K

Slurry liquid: 295 g, FT-300

Reactor volume: 442 cc[b]

Period	1	2	3	4	5	6
Date	10/20/87	10/27/87	10/29/87	10/30/87	10/31/87	11/01/87
Time on Stream (h)	33.0	56.5	106.0	129.0	153.0	177.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	220	235	250	250	250	264
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.02	1.02	1.02	1.02	1.02	1.02
Space Velocity (Nl/g-cat·h)[a]	2.00	2.00	2.00	4.00	1.01	2.00
Space Velocity (Nl/g-Fe·h)	2.87	2.87	2.87	5.75	1.45	2.87
GHSV (h^{-1})[b]	117	117	117	234	59	117
CO Conversion (%)	18.4	37.1	66.9	40.0	87.0	85.9
H_2+CO Conversion (%)	22.4	36.2	55.6	40.9	68.8	70.3
H_2/CO Usage	1.45	.97	.68	.79	.60	.65
STY ($mols$ H_2+CO/g cat·h)[a]	.020	.032	.050	.073	.031	.063
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	.9	2.0	5.0	6.0	45.9	37.9
Weight % of Outlet						
H_2	5.06	4.44	3.68	4.38	3.29	3.03
H_2O	3.51	4.58	6.00	2.63	2.17	2.19
CO	76.2	58.8	29.8	50.1	11.9	12.9
CO_2	8.80	21.2	42.6	31.5	63.5	62.2
Hydrocarbons	2.72	6.63	17.3	7.09	18.5	18.3
Oxygenates	.30	.31	.57	.21	.38	.32
Wax[c]	3.36	4.01	.00	4.08	.30	1.02
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	8.82	8.03	12.1	7.84	22.3	22.5
C_2-C_4 Hydrocarbons	34.8	27.4	39.4	28.8	57.8	58.0
C_5-C_{11} Hydrocarbons	33.4	50.5	79.3	45.2	69.0	60.9
C_{12}+ Hydrocarbons	103	109	83.0	100	35.1	45.1
Wax[c]	99.3	73.3	.0	66.5	2.97	9.85
Oxygenates	8.95	5.63	6.99	3.49	3.75	3.06
Total	189	200	221	185	189	190
1+2 Olefins/n Paraffin Ratio						
C_2	1.54	2.55	.87	2.78	.26	.24
C_3	4.80	5.40	4.04	4.93	2.20	2.39
C_4	4.10	4.33	3.28	3.83	2.17	2.44
C_8	2.38	3.18	2.03	2.14	1.00	.98
C_{10}	1.58	3.51	1.12	2.11	.95	.87

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Calculated wax produced during balance

Table V.2.5 (cont'd). Summary of results for slurry run SA-05-2957.

Period	7	8	9	10	11	12
Date	11/02/87	11/04/87	11/05/87	11/06/87	11/07/87	11/08/87
Time on Stream (h)	201.0	248.5	272.5	297.0	321.0	345.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250	220	235	250	250	250
Pressure (MPa)	.79	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.02	.67	.69	.71	.72	.65
Space Velocity ($Nl/g\cdot cat\cdot h$)[a]	1.05	2.00	2.11	2.03	4.07	1.02
GHSV (h^{-1})[b]	62	117	117	113	225	50
CO Conversion (%)	79.0	21.3	42.8	76.2	50.2	73.0
H_2+CO Conversion (%)	61.1	20.5	40.0	70.2	49.4	80.8
H_2/CO Usage	.50	.60	.61	.58	.69	.83
STY ($mols\ H_2+CO/g\cdot cat\cdot h$)[a]	.029	.018	.038	.064	.090	.037
$P_{CO_2}\cdot P_{H_2}/P_{CO}\cdot P_{H_2O}$	45.6	3.5	5.6	18.8	9.7	5.2
Weight % of Outlet						
H_2	3.84	3.79	2.97	1.86	2.49	.33
H_2O	1.38	1.03	1.69	1.37	1.15	.80
CO	19.4	77.08	54.4	22.7	46.5	25.8
CO_2	56.1	12.7	30.2	55.1	36.5	57.7
Hydrocarbons	16.4	2.24	3.59	11.5	4.20	9.19
Oxygenates	.18	.05	.22	.19	.14	.15
Wax[c]	2.68	3.18	6.85	7.26	9.06	6.03
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	23.1	2.93	3.25	4.90	3.31	2.38
C_2-C_4 Hydrocarbons	55.7	14.6	14.4	18.5	13.4	20.7
C_5-C_{11} Hydrocarbons	12.0	27.2	23.8	42.3	25.0	37.3
C_{12}+ Hydrocarbons	68.5	158	158	140	168	87.7
Wax[c]	20.2	119	131	79.4	143	59.1
Oxygenates	1.95	1.95	4.18	2.10	2.26	1.47
Total	211	205	203	207	211	151
1+2 Olefins/n-Paraffin Ratio						
C_2	.20	1.46	2.66	1.64	3.36	1.14
C_3	2.26	4.16	4.89	5.59	5.95	5.76
C_4	2.40	3.20	3.77	4.47	4.46	4.63
C_8	.63	2.08	2.29	2.78	2.39	2.51
C_{10}	.62	1.20	2.70	2.43	2.43	2.38

[a] Based on unreduced catalyst
[b] Based on static slurry volume
[c] Calculated wax produced during balance

Table V.2-5 (cont'd). Summary of results for slurry run SA 05 2957.

Period	13	14	15	16	17	18
Date	11/10/87	11/11/87	11/12/87	11/14/87	11/15/87	11/16/87
Time on Stream (*h*)	393.0	415.5	445.0	491.0	517.0	541.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	265	250	250	250	250	250
Pressure (*MPa*)	1.48	.79	1.48	1.48	2.24	2.96
H_2/CO Feed Ratio	.71	.67	.68	1.06	1.03	1.03
Space Velocity (*Nl/g cat·h*)[a]	2.24	1.12	1.00	2.00	3.00	4.00
GHSV (h^{-1})[b]	113	56	50	100	151	201
CO Conversion (%)	83.6	57.9	84.7	82.0	80.8	78.8
H_2+CO Conversion (%)	76.8	55.9	84.7	67.1	68.8	66.1
H_2/CO Usage	.57	.70	.68	.69	.72	.70
STY (*mols* H_2+CO/*g cat·h*)[a]	.077	.029	.038	.060	.092	.118
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	23.5	25.2	94.6	63.0	27.2	17.1
Weight % of Outlet						
H_2	1.64	1.77	.73	3.37	3.08	3.37
H_2O	1.59	.43	.18	1.07	1.06	2.94
CO	16.1	39.5	15.0	16.9	18.6	21.0
CO_2	64.5	42.8	59.7	59.6	56.7	55.0
Hydrocarbons	15.4	7.87	13.3	18.7	16.5	15.2
Oxygenates	.25	.07	.12	.36	.46	.76
Wax[c]	.45	7.58	10.9	0.0	2.67	1.77
1+2 Olefins/*n* Paraffin Ratio						
C_2	.35	.97	.57	.23	.30	.51
C_3	3.38	5.53	4.34	2.26	2.52	2.81
C_4	3.04	4.28	3.63	2.07	2.25	2.29
C_8	1.34	1.72	1.74	.70	.70	1.23
C_{10}	1.00	1.25	1.25	.55	.67	.88
Yield (*g/Nm*^{3} H_2 + CO *Converted*)						
CH_4	16.8	11.5	8.36	22.3	16.5	12.6
C_2-C_4 Hydrocarbons	44.9	33.7	23.9	54.6	45.0	37.3
C_5-C_{11} Hydrocarbons	62.4	43.9	53.8	69.4	59.2	61.3
C_{12}+ Hydrocarbons	30.3	121	132	33.4	57.0	49.3
Wax[c]	4.36	103	98.1	0.0	24.7	10.7
Oxygenates	2.39	.94	1.12	3.50	4.23	7.15
Total	157	211	219	183	182	168

[a] Based on unreduced catalyst [b] Based on static slurry volume
[c] Calculated wax produced during balance

Table V.2-5 (cont'd). Summary of results for slurry run SA-05-2957.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	4.91	4.12	5.66	4.31	12.0	12.1
Ethane	2.93	1.22	2.54	1.11	6.74	6.54
Ethylene	4.21	2.90	2.05	2.89	1.66	1.48
Propane	1.12	.84	1.44	1.03	3.85	3.63
Propylene	5.13	4.32	5.56	4.85	8.09	8.28
n Butane	1.10	.85	1.54	1.18	3.29	3.13
1+2 Butenes	4.34	3.53	4.87	4.37	6.90	7.36
C_4 Isomers	.52	.41	.44	.39	.71	.67
n Pentane	1.53	1.13	1.91	1.56	3.50	3.37
1+2 Pentenes	4.44	5.69	5.20	4.32	7.44	6.49
C_5 Isomers	.48	.31	.64	.29	2.30	2.03
n-Hexane	1.39	.98	1.25	1.11	2.85	2.11
1+2 Hexenes	3.51	2.01	3.15	3.17	3.06	2.76
C_6 Isomers	.00	1.43	.68	.59	.60	.44
n-Heptane	1.22	.00	.85	.79	1.92	1.61
1+2 Heptenes	2.36	1.80	1.85	2.33	1.87	1.67
C_7 Isomers	.04	.95	.38	.49	.54	.39
n-Octane	.55	.41	.63	.81	1.69	1.47
1+2 Octenes	1.29	1.20	1.26	1.70	1.65	1.42
C_8 Isomers	.05	.21	.24	.32	.46	.20
n Nonane	.19	.36	1.89	.51	1.51	1.36
1+2 Nonenes	.36	1.55	2.32	1.25	1.45	1.25
C_9 Isomers	.07	.09	.18	.12	.52	.23
n Decane	.19	.02	3.09	.77	1.49	1.45
1+2 Decenes	.30	2.13	3.41	1.60	1.40	1.24
C_{10} Isomers	.08	.12	.22	.22	.41	.27
n Undecane	.19	.82	3.75	.91	1.41	1.47
1+2 Undecenes	.24	2.38	3.77	1.70	1.28	1.14
C_{11} Isomers	.09	.16	.42	.28	.44	.29
C_2–C_4	19.4	14.1	18.4	15.8	31.2	31.1
C_5–C_{11}	18.6	26.0	37.1	24.9	37.8	32.7
C_{12}+	57.2	55.9	38.8	55.0	19.0	24.2
Wax[c]	55.2	37.7	.00	36.5	1.61	5.28

[c] Calculated wax produced during balance

Table V.2-5 (cont'd). Summary of results for slurry run SA-05-2957.

Period	7	8	9	10	11	12
Weight % of Hydrocarbons						
CH4	11.1	1.44	1.63	2.39	1.58	2.20
Ethane	5.81	1.22	.70	1.06	.41	2.55
Ethylene	1.42	1.67	1.75	1.61	1.30	2.71
Propane	3.15	.44	.43	.52	.36	.68
Propylene	0.79	1.74	2.02	2.79	2.04	3.74
n-Butane	2.68	.47	.40	.53	.40	.72
1+2 Butenes	0.37	1.46	1.68	2.27	1.72	3.21
C_4 Isomers	.48	.17	.17	.22	.16	.29
n-Pentane	3.02	.64	.63	.69	.57	.96
1+2 Pentenes	4.41	2.60	1.66	2.68	1.71	2.80
C_5 Isomers	1.03	.12	.12	.32	.10	.22
n-Hexane	3.05	.84	.93	.65	.54	1.24
1+2 Hexenes	2.65	1.98	1.81	1.56	1.51	3.11
C_6 Isomers	.52	.67	.77	.25	.20	.51
n-Heptane	2.03	.75	.60	.69	.54	1.57
1+2 Heptenes	1.30	1.74	1.22	1.50	1.25	3.78
C_7 Isomers	.34	.50	.34	.28	.27	.68
n Octane	1.53	.39	.33	.73	.42	.81
1+2 Octenes	.95	.79	.75	1.98	.99	1.99
C_8 Isomers	.12	.04	.16	.27	.13	.28
n-Nonane	1.41	.19	.17	.74	.30	.54
1+2 Nonenes	.88	.23	.49	1.01	.77	1.30
C_9 Isomers	.08	.05	.07	.22	.09	.20
n-Decane	1.61	.33	.22	.82	.33	.61
1+2 Decenes	.99	.42	.59	1.97	.79	1.44
C_{10} Isomers	.13	.08	.11	.23	.09	.25
n-Undecane	1.68	.40	.26	.91	.37	.68
1+2 Undecenes	.94	.52	.65	1.95	.79	1.64
C_{11} Isomers	.16	.12	.08	.25	.10	.36
C_2-C_4	26.7	7.17	7.22	9.00	6.38	13.9
C_5-C_{11}	29.4	13.4	12.0	20.6	11.9	25.0
C_{12}+	32.8	78.0	79.3	68.0	80.1	58.9
Wax[c]	14.0	58.7	65.6	38.7	68.3	39.6

[c] Calculated wax produced during balance

Table V.2-5 (cont'd). Summary of results for slurry run SA-05-2957.

Period	13	14	15	16	17	18
Weight % of Hydrocarbons						
CH4	10.9	5.46	3.84	12.4	9.28	7.88
Ethane	6.01	2.65	1.78	0.92	5.45	4.22
Ethylene	1.96	2.39	.94	1.50	1.54	2.02
Propane	2.56	.88	.81	3.65	2.89	2.41
Propylene	8.26	4.66	3.37	7.87	6.97	6.47
n-Butane	2.47	1.02	.80	3.26	2.50	2.35
1+2 Butenes	7.24	4.20	3.01	6.53	5.42	5.20
C_4 Isomers	.56	.26	.18	.67	.57	.55
n-Pentane	2.86	1.36	1.00	3.47	2.62	2.46
1+2 Pentenes	5.03	4.22	2.87	6.11	5.04	5.21
C_5 Isomers	.87	.30	.30	.63	.56	.59
n-Hexane	2.75	1.25	1.08	3.25	2.30	2.11
1+2 Hexenes	4.61	3.32	3.04	3.47	3.34	3.50
C_6 Isomers	.69	.59	.78	.57	.44	.40
n-Heptane	1.84	.88	1.11	2.87	1.09	2.09
1+2 Heptenes	2.50	1.95	1.78	2.17	2.09	2.47
C_7 Isomers	1.09	.42	.31	.47	.44	.60
n-Octane	1.73	.73	1.20	2.47	1.88	2.15
1+2 Octenes	2.28	1.23	2.04	1.71	1.20	2.60
C_8 Isomers	.25	.22	.17	.25	.23	.38
n-Nonane	2.11	.55	1.23	2.29	1.09	2.13
1+2 Nonenes	2.33	.75	1.74	1.30	1.50	2.13
C_9 Isomers	.16	.09	.19	.21	.14	.34
n-Decane	2.16	.65	1.30	2.41	2.18	2.30
1+2 Decenes	2.13	.80	1.61	1.32	1.43	1.99
C_{10} Isomers	.18	.11	.14	.18	.20	.35
n-Undecane	2.04	.68	1.28	2.24	2.16	2.34
1+2 Undecenes	1.73	.72	1.38	1.02	1.23	1.73
C_{11} Isomers	.16	.12	.15	.20	.25	.30
C_2-C_4	29.1	16.1	11.0	30.4	25.3	23.2
C_5-C_{11}	40.4	20.9	24.7	38.6	33.3	38.2
C_{12}+	19.6	57.6	60.5	18.6	32.1	30.7
Wax[c]	2.82	49.1	45.0	0.0	13.9	10.4

[c] Calculated wax produced during balance

thus the total closure allocation was used to estimate the amount of wax accumulated during this period. The optimized C-H closure allocation was used for all remaining periods.

The effect of space velocity was studied at 250 °C, 1.48 MPa with nominal (H_2/CO) feed ratios of 1.0 (balances 5, 3 and 16, and 4) and 0.67 (balances 12 and 15, 10, and 11) at 1, 2, and 4 Nl/g-cat.h. The (H_2—CO) conversion decreased approximately linearly with space velocity. The catalyst appeared to become more active with time on stream, as shown by the (H_2 — CO) conversions obtained in balances 3 and 16 at 250°C, 1.48 MPa, (H_2/CO)=1 with 2 Nl/g-cat.h space velocity. During balance 3 (approximately 106 h on stream) the (H_2—CO) conversion was 55.6%, while during balance 16 (approximately 494 h on stream) the conversion had increased to 67.1%. At the same process conditions using a 0.67 (H_2/CO) feed ratio, the (H_2—CO) conversion was roughly constant at 345 and 445 hours on stream, 80.8 (balance 12) and 84.7% (balance 15), respectively. The increasing catalyst activity may be due to continuing catalyst activation during synthesis testing. The in situ catalyst reduction conditions of 250°C for 8 h may not have completely reduced the catalyst, however, catalyst activation would have continued at the elevated synthesis temperature with the synthesis feed gas.

At the same process conditions, the (H_2/CO)=0.67 feed ratio favored higher conversions over the (H_2/CO)=1 feed ratio. Also, the lower feed ratio accelerated wax production. During balances 8-12, of 91 h duration, 395 g of wax were produced, whereas during balances 1-7, of 177 h duration, only 163 g of wax were produced. Balances 8-12 were all made using the lower (H_2/CO) feed ratio, and balances 1-7 were made using an (H_2/CO)=1 feed ratio. Also, balances 1-7 consisted of 5 balances (1-5) at the same temperature, pressure, and space velocity as balances 8-12, plus two additional balances at other process conditions. Thus wax production must have been much higher at the lower feed ratio.

A plot of the space time yield versus pressure is given in Figure V.2-14. The space time yield was found to vary roughly linearly with pressure over the range of pressures studied. The precipitated catalyst did not deactivate at high pressure in the slurry reactor, as was found in the fixed bed tests of these catalysts.

Comparison of hydrocarbon selectivities at different process conditions is difficult due to the approximate nature of wax allocation, which may have had a significant effect on the results. Methane yield varied from 1.4% (balance 8) to 12.1% (balance 6), whereas the yield of C_2-C_4 hydrocarbons was between 6.4 and 31.1% (balances 11 and 6, respectively). Inspite of some uncertainties in hydrocarbon selectivities it is clear that much less CH_4 and gaseous

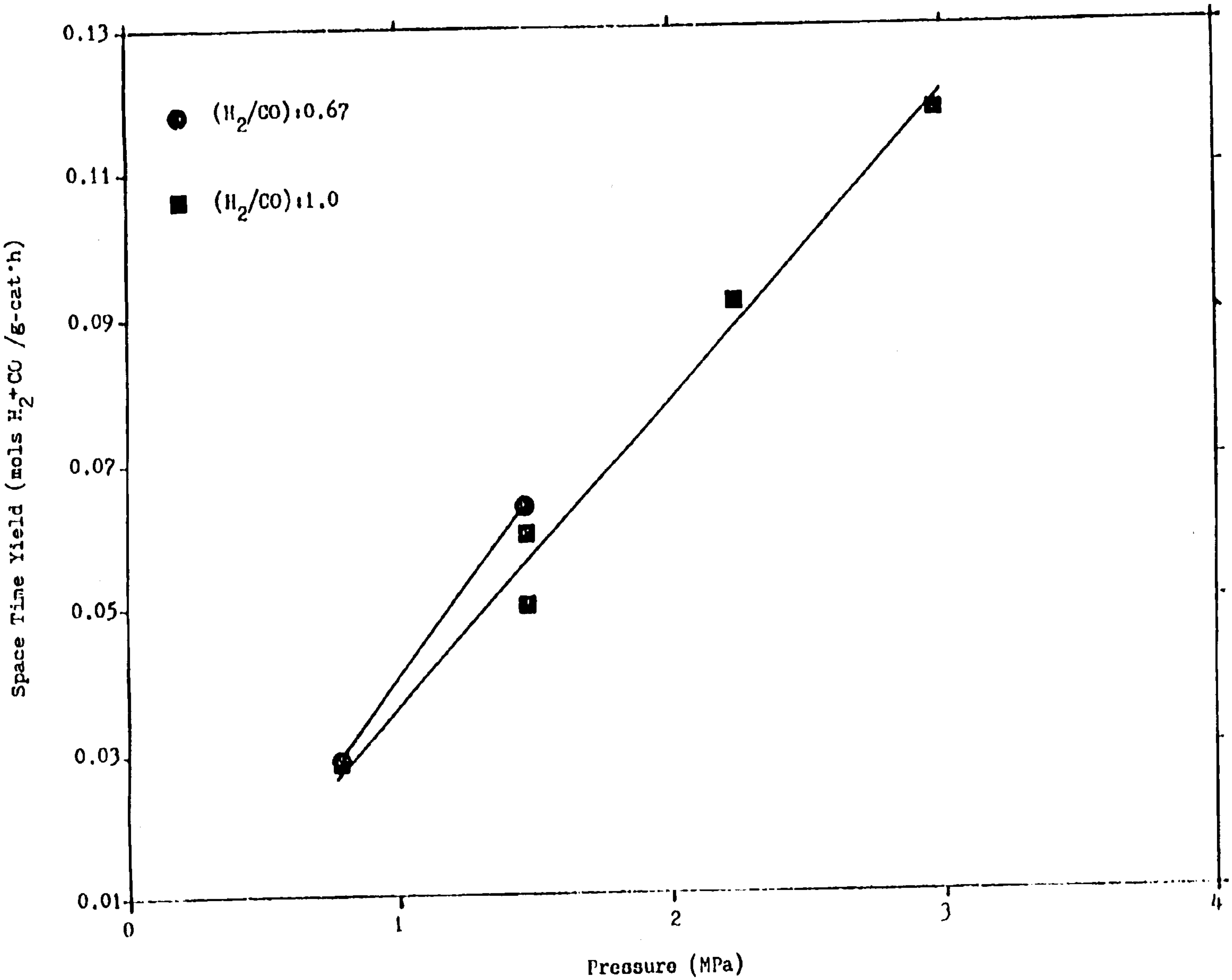

Figure V.2-14 Space time yield as a function of pressure at constant P/SV, 250 °C, (H_2/CO) = 0.67 and 1.0

hydrocarbons (C_2-C_4) were produced when the CO rich feed gas was used ($H_2/CO=0.67$). Reproducibility of results for balances at the same process conditions (250°C, 200 pisg, 2 Nl/g-cat.h) was not good with $H_2/CO=1$ feed gas (balances 3 and 16), but was quite satisfactory with $H_2/CO=0.67$ feed (balances 12 and 15).

V.2.3.2. Run SA – 25 – 3657 with the 100 Fe / 3 Cu / 0.2 K Catalyst

Run SA–25–3657 was performed to test the precipitated 100 Fe/3 Cu/0.2 K catalyst under a variety of process conditions. Excess purified n–octacosane (C_{28}, Humphry Chemical) was loaded with catalyst (< 325 mesh) into the reactor prior to reduction, and the catalyst was reduced in situ with CO at 280°C. Following reduction, the excess wax was withdrawn from the reactor to the preset static slurry volume of 478 cc. Eight material balances were made during this run, which was terminated voluntarily after 430 h of operation. The results obtained in each of the eight balances are summarized in Table V.2-6.

A power loss occurred at about 129 h on stream, causing a flow interruption to the reactor. The reactor also cooled from 235 to 80°C. Power was restored after 5 h, and the reactor was brought to its original temperature over a 4 h period. The catalyst was deactivating prior to the power failure, and continued to deactivate once the run continued. The deactivation made it difficult to determine what effect the interruption had on catalyst performance. Table V.2-7 lists the major events occurring during run SA–25–3657.

The initial catalyst activity was very good, with an (H_2+CO) conversion during balance 1 (250°C, 1.48 MPa, (H_2/CO) = 1, 2 Nl / g–cat·h) of 83.0 %. No signs of deactivation were observed before the end of period 1 (50 h on stream), but after the wax withdrawal and an increase in space velocity to 4 Nl / g–cat·h a sharp decline in activity occurred. Over the 46 h period these conditions were maintained, the gas contraction decreased steadily from 48 to 36 %. The process conditions of balance 1 were repeated during balance 4, by which time the (H_2+CO) conversion decreased from 83.0 to 28.5 %.

In all cases, feed gas with (H_2/CO) = 0.67 (nominal) gave product distributions with lower methane yield (3.2-4 %). In addition, the lower feed ratio produced larger amounts of high molecular weight products (C_{12}+). Catalyst deactivation may have skewed the selectivity trends of the run. For example, the methane and C_2–C_4 product fractions decreased as the catalyst deactivated between balances 1 and 4. The more active catalyst produced 9.31 % methane and 35.9 % C_2–C_4, as compared to 4.87 % and 21.7 %, respectively, during balance

Table V.2-6. Summary of results for slurry run SA-25-3657.

Catalyst: 38.4 g[a], 100 Fe/3 Cu/0.2 K — Slurry liquid: 307 g, n Octacosane

Reactor volume: 436. cc[b]

Period	1	2	3	4	5	6	7	8
Date	1/3/88	1/5/88	1/8/88	1/10/88	1/12/88	1/12/88	1/16/88	1/18/88
Time on Stream (h)	44.0	91.0	158.5	200.0	251.0	302.0	350.0	398.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	235.	250.	250.	250.	265.	235.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.094	.094	.980	1.01	.663	.682	.678	.669
Space Velocity (Nl/g-cat·h)[a]	2.02	4.03	2.01	2.00	1.01	2.01	2.02	1.01
Space Velocity (Nl/g-Fe·h)	2.93	5.93	2.95	2.94	1.48	2.96	2.93	1.49
GHSV (h^{-1})[b]	177.	350.	174.	173.	86.0	171.	171.	85.0
CO Conversion (%)	93.9	47.6	15.5	28.3	48.3	16.6	27.8	10.8
H_2+CO Conversion (%)	83.0	46.7	21.4	28.5	41.6	18.6	29.3	13.0
H_2/CO Usage	.762	.057	1.74	1.02	.513	.893	.770	1.14
STY ($mols$ H_2+CO/g-cat·h)[a]	.075	.084	.019	.025	.020	.017	.026	.000
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	22.6	1.53	.321	.647	.806	.442	1.01	.431
Weight % of Outlet								
H_2	1.93	3.68	4.82	5.08	3.33	3.79	3.24	3.72
H_2O	5.30	6.93	5.46	6.49	7.62	3.37	3.67	2.78
CO	5.86	49.7	79.6	70.3	59.6	82.3	70.2	81.7
CO_2	64.0	25.2	5.08	10.2	19.4	5.69	14.1	4.82
Hydrocarbons	19.7	10.4	3.55	4.57	6.17	3.05	5.51	2.41
Oxygenates	.647	.494	.170	.129	.220	.138	.202	.101
Wax[c]	2.50	3.59	1.30	3.24	3.68	1.65	3.09	1.48
Yield (g/Nm^3 H_2 + CO Converted)								
CH_4	16.2	9.06	6.93	8.46	4.52	6.11	7.66	8.89
C_2-C_4 Hydrocarbons	62.6	44.1	40.5	37.7	29.4	39.2	37.9	56.1
C_5-C_{11} Hydrocarbons	68.0	55.3	44.4	39.9	39.6	53.1	45.3	40.7
C_{12}+ Hydrocarbons	27.5	89.0	62.1	87.8	69.7	91.6	134.	115.
Wax[c]	19.6	50.8	42.0	72.1	53.5	66.7	80.7	83.8
Oxygenates	5.07	7.00	5.51	2.87	3.20	5.59	5.29	5.87
Total	179.	204.	159.	177.	146.	196.	230.	220.
1/2 Olefins/n-Paraffin Ratio								
C_2	.242	1.40	1.61	2.72	1.20	1.16	1.40	1.29
C_3	2.57	6.47	6.01	6.57	6.97	7.48	8.27	4.01
C_4	3.06	5.37	4.54	5.69	5.80	5.92	6.48	4.35
C_6	.697	2.60	2.61	2.75	3.08	2.52	3.46	1.25
C_{10}	.315	1.80	2.82	2.64	3.17	2.61	4.33	2.19

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table V.2-6 (cont'd). Summary of results for slurry run SA-25 3657.

Period	1	2	3	4	5	6	7	8
Weight % of Hydrocarbons								
CH4	9.31	4.59	4.50	4.87	3.10	3.21	3.41	4.04
Ethane	7.22	2.59	3.82	1.69	3.11	4.77	2.95	4.28
Ethylene	1.63	3.39	5.75	4.02	3.49	5.16	3.65	5.14
Propane	4.29	1.19	1.29	1.16	.934	.675	.586	1.56
Propylene	10.5	7.35	7.37	7.29	6.21	4.82	4.63	5.99
n-Butane	2.82	1.16	1.39	1.08	.958	.719	.610	1.43
1+2 Butenes	8.32	6.03	6.06	5.93	5.30	4.11	3.85	6.01
C_4 Isomers	1.11	.639	.604	.592	.468	.388	.369	1.05
n-Pentane	3.11	1.64	1.66	1.52	1.18	1.01	.903	1.30
1+2 Pentenes	6.75	6.30	6.93	5.18	4.18	3.72	3.51	4.82
C_5 Isomers	.841	.757	1.05	.384	.300	.277	.260	.430
n-Hexane	2.71	1.14	1.26	.952	1.05	1.62	.911	1.59
1+2 Hexenes	3.87	2.68	3.86	3.13	4.52	4.50	2.94	1.99
C_6 Isomers	.653	.620	.851	.661	.899	.988	.687	.640
n-Heptane	2.52	.731	.863	.898	1.09	1.46	.659	1.02
1+2 Heptenes	2.19	1.69	2.39	1.83	2.83	2.98	1.81	1.27
C_7 Isomers	.642	.432	.609	.490	.804	.801	.530	.419
n-Octane	2.44	.609	.550	.466	.631	.676	.339	.429
1+2 Octenes	1.67	1.56	1.41	1.26	1.91	1.07	1.15	.527
C_8 Isomers	.636	.250	.329	.0868	.651	.157	.291	.423
n-Nonane	2.31	.737	.304	.303	.292	.400	.179	.154
1+2 Nonenes	1.29	1.65	1.07	1.06	1.39	1.30	1.06	.465
C_9 Isomers	.468	.251	.144	.111	.0959	.242	.0732	.0219
n-Decane	2.61	1.00	.588	.542	.587	.068	.305	.375
1+2 Decenes	.887	1.84	1.64	1.41	1.84	1.72	1.56	.808
C_{10} Isomers	.514	.410	.280	.172	.178	.383	.143	.0655
n-Undecane	1.64	1.18	.810	.725	.877	.902	.597	.504
1+2 Undecenes	.746	1.80	1.85	1.54	2.04	1.95	1.87	1.05
C_{11} Isomers	.483	.526	.366	.234	.287	.488	.243	.107
C_2-C_4	35.9	22.3	26.3	21.7	20.5	20.6	16.9	25.5
C_5-C_{11}	39.0	28.0	28.6	23.0	27.6	27.9	20.2	18.5
C_{12}+	15.8	45.1	40.4	50.5	48.7	48.2	59.6	52.0
Wax[c]	11.2	25.7	27.7	41.5	37.3	35.1	35.9	38.1

[c] Unanalyzed wax withdrawn from reactor

Table V.2-7. Major events in run SA-25-3657.

TOS (h)	Event
-28	Catalyst pretreatment
0	Initiate run
4	Achieve initial process conditions: T = 250°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
51	Change process conditions: T = 250°C, P = 1.48 MPa SV = 4.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
94	Change process conditions: T = 235°C, P = 1.48 MPa SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
129	Loss of reactor power
134	Power to reactor restored
138	Achieve desired process conditions
166	Change process conditions: T = 250°C, P = 1.48 MPa SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
214	Change process conditions: T = 250°C, P = 1.48 MPa SV = 1.0 Nl/g–cat·h, Feed (H_2/CO) = 0.67
260	Leak in reactor feed valve discovered and repaired
262	Change process conditions: T = 250°C, P = 1.48 MPa SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.68
310	Change process conditions: T = 265°C, P = 1.48 MPa SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.68
357	Wax plug in reactor feed line repaired
358	Change process conditions: T = 235°C, P = 1.48 MPa SV = 1.0 Nl/g–cat·h, Feed (H_2/CO) = 0.67
406	Change process conditions: T = 265°C, P = 2.96 MPa SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.67
430	End of Run SA-25-3657

4 at the same nominal process conditions (250°C, 1.48 MPa, $(H_2/CO) = 1$, 2 Nl / g-cat·h) after catalyst deactivation.

Wax was removed from the reactor at the end of each material balance. The reactor stirring and feed to the reactor were discontinued after purging the reactor for about 5 min with helium. The catalyst was allowed to settle for approximately 30 min, after which wax was withdrawn through a dipleg in the reactor at a preset height. The wax and catalyst withdrawals made during this run are summarized in Table V.2-8.

V.2.3.3. Run SB – 07 – 0458 with the 100 Fe / 0.3 Cu / 0.5 K Catalyst

This was the first run made in the new slurry reactor unit B. The precipitated 100 Fe/0.3 Cu/0.5 K catalyst was reduced in situ using H_2 as the reductant at 280°C. The catalyst (< 325 mesh) was suspended in a FT–300 wax to obtain a 10 weight % catalyst slurry. The slurry withdrawal dipleg was preset to give a static slurry volume of 375 cc. Ten material balances were performed during the run, and the run was voluntarily terminated after 458 h on stream. The results obtained during these ten mass balances are summarized in Table V.2-9.

At 4 h on stream, the inlet feed line had to be repaired due to a block that appeared following the withdrawal of excess wax from the reactor after catalyst reduction. No other major operational problems were encountered during the run. The major events of Run SB–07–0458 are summarized in Table V.2-10.

The initial activity of the catalyst was low, which is consistent with previous observations made in fixed bed reactors with 100 Fe/3 Cu/0.2 K catalyst reduced using H_2. The (H_2-CO) conversion obtained during balance 1 was 24.8 %, which is comparable with the 26.0 % conversion obtained in the fixed bed test with 100 Fe/3 Cu/0.2 K catalyst reduced under similar conditions (280°C for 24 h, run FB–25–3227 ,Section V.1.3). The catalyst appeared to have become more active with time on stream, as is evident from the (H_2-CO) conversions obtained in balances 1 and 9 at 250 °C, 1.48 MPa, $(H_2/CO)=1$ and a nominal space velocity of 2 Nl / g–cat·h. During balance 1 (approximately 45 h on stream) the (H_2-CO) conversion was 24.8%, while during balance 9 (approximately 428 h on stream) the conversion had increased to 35.5 %. Catalyst activity improved following balance 4, during which a 0.67 (H_2/CO) feed ratio was used, while a 1.0 (H_2/CO) feed ratio was used in the previous three balances. During the period of low catalyst activity (balances 1 through 4), the (H_2-CO) conversion increased from 24.8 % (balance 1) to 30.8 % (balance 3) as temperature increased from 250°C to 265°C, whereas the increase was from 42.5 % (balance 5) to 70.8 % (balance 7) once the catalyst

Table V.2-8. Wax and solids inventory for run SA–25–3657.

TOS (h)	Event
-48	Slurry loading: 424 g wax, 38.60 g solids
-1	Wax removal following reduction: 120 g wax, 0.24 g solids
50	Wax removal: 57 g wax, 0.55 g solids
93	Wax removal: 161 g wax, 0.26 g solids
164	Wax removal: 90 g wax, 0.29 g solids
212	Wax removal: 71 g wax, 0.13 g solids
261	Wax removal: 36 g wax, 0.09 g solids
308	Wax removal: 43 g wax, 0.07 g solids
355	Wax removal: 81 g wax, 0.16 g solids
404	Wax removal: 20 g wax, 0.05 g solids
430	Wax removal: 60 g wax, 0.11 g solids
430	End of run: 289 g wax, 33.06 g solids recovered from reactor. 95 % wax recovery, 96 % solids recovery

Table V.2-9. Summary of results for slurry run SB-07-0158.

Catalyst: 29.8 g^a, 100 Fe/.3 Cu/0.5 K — Slurry liquid: 294 g, FT-300

Reactor volume: 375. cc^b

Period	1	2	3	4	5
Date	2/17/88	2/19/88	2/21/88	2/23/88	2/25/88
Time on Stream (h)	45.0	92.0	139.5	188.0	236.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	265.	250.	250.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.05	1.05	1.05	.711	.735
Space Velocity (Nl/g cat·h)[a]	2.16	1.07	2.13	2.13	1.06
Space Velocity (Nl/g·Fe·h)	3.11	1.54	3.07	3.06	1.53
GHSV (h^{-1})[b]	172.	83.4	166.	165.	82.4
CO Conversion (%)	29.2	44.1	36.7	23.0	45.4
H_2+CO Conversion (%)	24.8	36.0	30.8	21.3	42.5
H_2/CO Usage	.742	.676	.717	.583	.623
STY (mols H_2+CO/g-cat·h)[a]	.024	.017	.029	.020	.020
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	6.06	11.2	7.49	13.4	10.9
Weight % of Outlet					
H_2	5.94	5.15	5.55	4.12	3.10
H_2O	1.26	1.32	1.44	.305	.971
CO	70.2	53.3	62.1	76.5	52.0
CO_2	15.9	26.9	21.2	13.4	31.2
Hydrocarbons	4.22	8.57	7.24	3.76	7.04
Oxygenates	.252	.805	.610	.167	.555
Wax[c]	2.26	3.96	1.89	1.82	5.07
Yield (g/Nm^3 H_2 + CO *Converted*)					
CH_4	7.33	8.82	10.0	5.96	5.95
C_2–C_4 Hydrocarbons	40.0	37.5	38.4	29.3	25.6
C_5–C_{11} Hydrocarbons	36.3	50.1	48.2	46.0	43.0
C_{12}+ Hydrocarbons	76.4	126.	87.5	111.	141.
Wax[c]	55.7	70.4	38.1	62.8	90.1
Oxygenates	6.23	14.3	12.3	5.77	9.85
Total	166.	237.	196.	198.	225.
1+2 Olefins/n-Paraffin Ratio					
C_2	1.20	1.56	1.39	.899	1.90
C_3	4.06	4.52	5.27	4.92	5.13
C_4	3.61	3.61	4.11	3.66	3.84
C_8	3.03	2.60	2.67	3.29	2.80
C_{10}	2.29	2.69	2.71	2.55	2.61

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

Table V.2-9 (cont'd). Summary of results for slurry run SB-07-0458.

Period	6	7	8	9	10
Date	2/27/88	2/29/88	3/02/88	3/04/88	3/05/88
Time on Stream (h)	284.0	284.0	380.0	428.0	452.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	265.	265.	235.	250.	265.
Pressure (MPa)	1.48	1.48	1.48	1.48	2.96
H_2/CO Feed Ratio	.703	.721	.710	1.06	.727
Space Velocity (Nl/g-$cat{\cdot}h$)[a]	2.15	1.08	1.08	2.10	2.04
Space Velocity (Nl/g-$Fe{\cdot}h$)	3.10	1.56	1.56	3.15	2.94
GHSV (h^{-1})[b]	164.	80.8	79.1	157.	144.
CO Conversion (%)	55.6	75.9	31.0	44.4	79.2
H_2+CO Conversion (%)	51.2	70.8	29.2	35.5	73.0
H_2/CO Usage	.569	.600	.611	.648	.592
STY ($mols$ H_2+CO/g-$cat{\cdot}h$)[a]	.049	.034	.014	.035	.067
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	25.7	39.7	10.8	13.5	25.3
Weight % of Outlet					
H_2	2.78	1.72	3.52	5.38	1.79
H_2O	.543	.612	.616	1.23	1.12
CO	44.3	22.1	64.7	53.5	20.1
CO_2	39.2	54.9	21.6	28.9	55.8
Hydrocarbons	7.12	10.5	5.05	6.58	10.5
Oxygenates	.534	.597	.305	.648	.905
Wax[c]	5.54	9.62	4.24	3.78	9.79
Yield (g/Nm^3 H_2 + CO Converted)					
CH_4	6.11	7.29	5.23	6.76	6.69
C_2-C_4 Hydrocarbons	24.6	25.7	22.2	25.4	27.2
C_5-C_{11} Hydrocarbons	38.2	46.2	40.3	41.3	56.7
C_{12}+ Hydrocarbons	113.	145.	180.	110.	118.
Wax[c]	79.4	108.	113.	66.9	101.
Oxygenates	7.66	6.07	8.13	11.5	9.32
Total	189.	231.	256.	195.	218.
1+2 Olefins/n-Paraffin Ratio					
C_2	2.07	2.45	3.99	3.56	2.29
C_3	5.63	5.70	4.48	4.35	4.47
C_4	4.13	4.44	3.33	3.27	3.42
C_8	2.59	4.05	2.79	2.47	2.65
C_{10}	2.61	3.78	2.69	2.24	2.42

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

Table V.2-9 (cont'd). Summary of results for slurry run SB-07-0458.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH4	4.58	3.90	5.44	3.10	2.76
Ethane	4.78	2.56	3.73	4.03	1.57
Ethylene	5.34	3.73	4.85	3.38	2.79
Propane	1.30	.988	1.03	.694	.644
Propylene	5.05	4.27	5.19	3.26	3.15
n-Butane	1.74	1.09	1.12	.792	.737
1+2 Butenes	6.05	3.70	4.43	2.80	2.73
C_4 Isomers	.765	.421	.487	.289	.267
n-Pentane	1.57	1.30	1.44	1.08	.990
1+2 Pentenes	3.92	3.50	4.01	2.72	2.64
C_5 Isomers	.245	.211	.236	1.18	.741
n-Hexane	1.10	1.07	1.40	2.24	.817
1+2 Hexenes	3.90	2.75	3.74	3.92	2.41
C_6 Isomers	1.10	.514	.844	2.07	.588
n-Heptane	.720	.632	.816	.859	.685
1+2 Heptenes	2.20	1.64	2.07	1.87	1.07
C_7 Isomers	.715	.413	.561	.713	.513
n Octane	.481	.671	.659	.365	.520
1+2 Octenes	1.43	1.71	1.73	1.18	1.45
C_8 Isomers	.297	.278	.322	.0858	.222
n Nonane	.418	.644	.631	.423	.548
1+2 Nonenes	.890	1.65	1.62	.980	1.30
C_9 Isomers	.0764	.135	.204	.0756	.105
n-Decane	.503	.681	.718	.528	.608
1+2 Decenes	1.13	1.81	1.92	1.33	1.57
C_{10} Isomers	.105	.166	.299	.120	.158
n-Undecane	.405	.610	.630	.441	.516
1+2 Undecenes	1.25	1.85	2.04	1.59	1.65
C_{11} Isomers	.136	.205	.288	.160	.194
C_2-C_4	25.0	16.8	20.9	15.3	11.9
C_5-C_{11}	22.7	22.5	26.2	23.9	20.0
C_{12}+	47.7	57.2	47.9	58.1	65.8
Wax[c]	34.8	31.6	20.7	32.6	41.9

[c] Unanalyzed wax withdrawn from reactor

Table V.2-9 (cont'd). Summary of results for slurry run SB-07-0458.

Period	6	7	8	9	10
Weight % of Hydrocarbons					
CH4	3.36	3.25	2.11	3.68	3.21
Ethane	1.75	1.10	.546	.914	1.14
Ethylene	3.38	2.51	2.03	3.03	2.44
Propane	.007	.618	.601	.984	.924
Propylene	3.58	3.41	2.57	4.09	3.94
n-Butane	.773	.071	.097	1.06	.990
1+2 Butenes	3.08	2.88	2.24	3.36	3.27
C_4 Isomers	.292	.253	.203	.400	.335
n-Pentane	1.08	.928	.920	1.36	1.20
1+2 Pentenes	2.97	2.71	2.19	3.10	3.07
C_5 Isomers	.577	.140	.620	.813	.000
n-Hexane	.758	.679	.435	1.22	1.05
1+2 Hexenes	2.19	2.41	1.09	2.18	2.99
C_6 Isomers	.817	.648	.484	.519	.350
n-Heptane	.528	.486	.443	.597	.954
1+2 Heptenes	1.33	1.42	1.22	1.46	2.13
C_7 Isomers	.298	.252	.388	.345	.258
n-Octane	.601	.436	.393	.654	1.01
1+2 Octenes	1.53	1.74	1.08	1.50	2.62
C_8 Isomers	.255	.191	.0587	.109	.180
n-Nonane	.672	.500	.450	.816	1.03
1+2 Nonenes	1.65	1.86	1.14	1.65	2.49
C_9 Isomers	.175	.124	.0540	.0874	.125
n-Decane	.728	.580	.582	.895	1.04
1+2 Decenes	1.87	2.16	1.55	1.97	2.48
C_{10} Isomers	.242	.182	.0822	.122	.165
n-Undecane	.608	.597	.535	.754	.959
1+2 Undecenes	1.95	2.27	1.81	2.10	2.31
C_{11} Isomers	.221	.254	.138	.152	.176
C_2-C_4	13.5	11.5	8.94	13.8	13.0
C_5-C_{11}	21.1	20.6	16.2	22.5	27.2
C_{12}+	62.4	65.0	73.0	60.5	56.6
Wax[c]	43.7	47.9	45.7	36.5	48.3

[c] Unanalyzed wax withdrawn from reactor

Table V.2-10. Major events in run SB–07–0458.

TOS (h)	Event
-28	Catalyst pretreatment
0	Initiate run
4	Wax plug in reactor feed line repaired
5	Achieved initial process conditions: T = 250°C. P = 1.48 MPa, SV = 2.2 Nl/g–cat·h, (H_2/CO) = 1.05
53	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 1.1 Nl/g–cat·h, (H_2/CO) = 1.05
100	Changed process conditions: T = 265°C, P = 1.48 MPa, SV = 2.1 Nl/g–cat·h, (H_2/CO) = 1.05
148	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 2.1 Nl/g–cat·h, (H_2/CO) = 0.71
196	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 1.1 Nl/g–cat·h, (H_2/CO) = 0.74
244	Changed process conditions: T = 265°C, P = 1.48 MPa, SV = 2.2 Nl/g–cat·h, (H_2/CO) = 0.70
292	Changed process conditions: T = 265°C, P = 1.48 MPa, SV = 1.1 Nl/g–cat·h, (H_2/CO) = 0.72
340	Changed process conditions: T = 235°C. P = 1.48 MPa, SV = 1.1 Nl/g–cat·h, (H_2/CO) = 0.71
388	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 2.2 Nl/g–cat·h, (H_2/CO) = 1.06
436	Changed process conditions: T = 265°C, P = 2.96 MPa, SV = 2.0 Nl/g–cat·h, (H_2/CO) = 0.73
458	End of run SB–07–0458

became active, although the differences in space velocity and (H_2/CO) feed ratio may have influenced the results.

The catalyst selectivity shifted towards lower molecular weight products with an increase in temperature, once the catalyst became active (i.e., following balance 4). For example, the distribution at 235°C, 1.48 MPa, 1 Nl / g–cat·h, (H_2/CO) = 0.67 (nominal) during balance 8 was 2.1 (CH_4), 8.9 (C_2-C_4), 16.0 (C_5-C_{11}), and 73.0 % (C_{12}^+), as compared to 2.8 (CH_4), 11.9 (C_2-C_4), 20.0 (C_5-C_{11}), and 65.3 % (C_{12}^+) at 250 °C (balance 5), and 3.2 (CH_4), 11.4 (C_2-C_4), 20.6 (C_5-C_{11}), and 64.8 % (C_{12}^+) at 265 °C (balance 7). The effect of temperature on selectivity at other conditions were not consistent with the above example, probably because of differences in catalyst activity.

During the process variable studies in the test SB-0458, the catalyst was tested under conditions similar to that employed in Mobil's study in a bubble column slurry reactor (Kuo, 1985). Comparison of catalyst performance between our catalyst and Mobil's catalyst I-B in high wax mode of operation is shown in Table V.2-11. Hydrocarbon product selectivities of the two catalyst are very similar, but the activity of our catalyst was lower. However, the activity of our catalyst can be significantly improved by using a lower activation temperature and/or shorter duration (Sections V.1.3 and V.1.6).

V.2.3.4. Run SA – 07 – 0468 with the 100 Fe / 0.3 Cu / 0.5 K catalyst

Slurry run SA–07–0468 was made with precipitated 100 Fe/0.3 Cu/0.5 K catalyst reduced in situ using CO as the reductant at 280°C. The catalyst (<325 mesh) was suspended in FT–300 wax to obtain a 10 weight % catalyst slurry. The slurry withdrawal dipleg was preset to give a static slurry volume of 385 cc. Eleven material balances were performed during the run, before being voluntarily terminated after 466 h on stream. The results obtained are summarized in Table V.2-12.

Beginning at about 20 h on stream, the H_2 mass flow controller began behaving erratically, giving lower than expected flowrates. To achieve the desired flowrates and feed ratios, the feed was switched from pure gas to premixed gas at about 52 h on stream. At about 78 h on stream, an improperly mixed feed gas cylinder containing approximately 95 % H_2 was installed, exposing the catalyst to nearly pure H_2 for about 1 h before the problem was discovered and

Table V.2-11. Comparative catalyst performance data for tests conducted in slurry reactors

Catalyst Reduction Conditions	TAMU[a] 100 Fe/0.3 Cu/0.5 K H_2, 280°C, 24h		Mobil[b] Fe/Cu/K_2O H_2/CO = 0.7, 280°C, 12h
Run Designation	SB-0458	SB-0458	CT-250-13
Temperature, °C	265	265	258
Pressure, atm	15	15	15
SV, Nl/g-Fe.h	3.1	1.6	2.4
(H_2/CO)	0.70	0.72	0.67
(CO+H_2) Conversion (%)	51.2	70.8	82.2
HC Selectivities (wt.%)			
C_1	3.3	3.2	2.7
C_2-C_4	13.4	11.4	11.1
C_5-C_{11}	21.0	20.4	18.1
C_{12}+	62.3	65.0	68.1

[a] test made in a stirred tank slurry reactor
[b] test made in a bubble column slurry reactor

Table V.2-12. Summary of results for slurry run SA-07-0468.

Catalyst: 29.5 g^a, 100 Fe/.3 Cu/0.5 K

Slurry liquid: 270 g, FT-300

Reactor volume: 385. cc^b

Period	1	2	3	4	5	6
Date	2/18/88	2/20/88	2/22/88	2/24/88	2/24/88	2/24/88
Time on Stream (h)	40.5	86.0	135.0	183.0	215.0	254.0
Balance Duration (h)	6.0	0.0	6.0	6.0	17.0	6.0
Average Temperature (°C)	250.	250.	265.	235.	235.	235.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.10	.976	1.03	.957	.985	.653
Space Velocity (Nl/g-cat·h)[a]	2.04	4.05	4.00	2.08	4.18	1.02
Space Velocity (Nl/g-Fe·h)	2.94	5.84	5.76	3.00	6.03	1.47
GHSV (h^{-1})[b]	150.	301.	291.	144.	277.	66.4
CO Conversion (%)	91.7	70.9	71.4	33.5	15.3	38.5
H_2+CO Conversion (%)	74.8	58.4	55.5	28.4	12.7	35.6
H_2/CO Usage	.710	.628	.576	.661	.649	.530
STY ($mols$ H_2+CO/g-cat·h)[a]	.068	.106	.099	.026	.024	.016
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	30.7	20.3	27.8	6.86	2.42	10.1
Weight % of Outlet						
H_2	3.11	3.52	4.03	4.98	0.01	3.01
H_2O	3.34	1.86	1.56	1.47	1.53	.827
CO	8.07	26.8	26.1	62.6	70.8	57.3
CO_2	60.6	50.7	49.2	22.4	8.07	27.9
Hydrocarbons	12.0	8.54	8.09	3.01	2.44	3.00
Oxygenates	1.04	.638	.801	.341	.207	.183
Wax[c]	10.9	7.90	0.64	5.26	1.31	7.21
Yield (g/Nm^3 H_2 + CO Converted)						
CH_4	13.4	7.06	8.37	5.20	5.82	4.90
C_2-C_4 Hydrocarbons	43.6	35.9	38.0	24.0	31.0	27.1
C_5-C_{11} Hydrocarbons	39.9	40.1	44.6	30.4	58.7	30.7
C_{12}+ Hydrocarbons	98.7	110.	132.	137.	100.	184.
Wax[c]	89.6	92.7	118.	126.	98.0	164.
Oxygenates	8.55	7.48	9.76	8.16	10.9	4.17
Total	204.	200.	233.	206.	207.	251.
1+2 Olefins/n-Paraffin Ratio						
C_2	1.26	2.21	2.51	6.50	1.66	4.32
C_3	6.06	6.33	0.55	5.32	5.29	5.95
C_4	5.10	4.98	5.13	4.07	4.05	4.46
C_8	3.73	4.92	3.85	2.83	1.92	2.93
C_{10}	3.49	5.33	4.40	3.08	3.06	3.69

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table V.2-12 (cont'd). Summary of results for slurry run SA-07-0468.

Period	7	8	9	10	11
Date	2/29/88	3/02/88	3/04/88	3/06/88	3/07/88
Time on Stream (*h*)	302.5	351.0	390.5	437.0	460.0
Balance Duration (*h*)	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	265.	250.	265.
Pressure (*MPa*)	1.48	1.43	1.48	1.48	2.96
H_2/CO Feed Ratio	.653	.689	.641	1.03	.640
Space Velocity (*Nl/g-cat·h*)[a]	1.01	2.05	2.03	2.03	2.04
Space Velocity (*Nl/g-Fe·h*)	1.46	2.96	2.93	2.93	2.94
GHSV (h^{-1})[b]	65.5	129.	126.	124.	124.
CO Conversion (%)	57.4	26.2	29.8	24.6	42.4
H_2+CO Conversion (%)	54.2	24.0	28.2	17.4	38.9
H_2/CO Usage	.501	.548	.550	.432	.503
STY (*mols* H_2+CO/*g-cat·h*)[a]	.024	.022	.026	.016	.035
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	20.5	12.4	14.8	8.76	12.3
Weight % of Outlet					
H_2	2.34	3.86	3.30	6.33	3.02
H_2O	.478	.421	.309	.865	.715
CO	41.8	72.5	67.4	72.0	56.6
CO_2	39.9	17.3	21.2	15.2	20.1
Hydrocarbons	6.86	2.06	3.49	3.15	5.56
Oxygenates	.422	.199	.226	.261	.525
Wax[c]	8.15	3.05	3.95	2.18	4.47
Yield (*g/Nm*^{3} H_2 + CO *Converted*)					
CH_4	5.24	5.74	7.74	9.00	7.12
C_2-C_4 Hydrocarbons	27.4	26.7	29.8	34.2	30.8
C_5-C_{11} Hydrocarbons	41.5	30.7	42.0	52.7	53.5
C_{12}+ Hydrocarbons	130.	110.	130.	102.	108.
Wax[c]	116.	95.4	111.	81.2	89.0
Oxygenates	6.00	6.23	6.37	9.71	10.5
Total	210.	185.	216.	268.	210.
1+2 Olefins/*n*-Paraffin Ratio					
C_2	2.12	4.83	5.47	4.29	3.24
C_3	6.29	5.97	6.10	4.44	4.04
C_4	4.73	4.31	4.32	3.22	2.95
C_6	3.54	3.34	3.08	2.35	2.03
C_{10}	3.65	3.11	3.17	1.95	2.01

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

Table V.2-12 (cont'd). Summary of results for slurry run SA-07-0468.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	0.86	3.66	3.75	2.63	2.07	1.09
Ethane	3.32	2.09	1.83	.507	2.47	.704
Ethylene	3.90	4.29	4.27	3.07	3.82	3.20
Propane	1.20	.891	.798	.765	.822	.538
Propylene	0.94	5.39	4.99	3.88	4.15	3.00
n-Butane	1.07	.928	.782	.800	.898	.590
1+2 Butenes	5.27	4.46	3.88	3.17	3.51	2.54
C_4 Isomers	.595	.571	.466	.381	.433	.284
n-Pentane	1.31	1.12	1.08	1.10	1.34	.850
1+2 Pentenes	4.22	3.60	3.31	3.02	3.66	2.43
C_5 Isomers	.288	.238	.222	.229	.283	.157
n-Hexane	.846	.771	.742	1.66	2.50	.820
1+2 Hexenes	2.61	2.31	2.47	1.95	4.00	1.86
C_6 Isomers	.918	.559	.577	.611	1.20	.528
n-Heptane	.464	.376	.451	.438	1.50	.402
1+2 Heptenes	1.56	1.17	1.47	1.26	3.90	1.19
C_7 Isomers	.356	.392	.490	.412	1.02	.411
n-Octane	.396	.203	.391	.258	.998	.199
1+2 Octenes	1.45	1.41	1.48	.717	1.88	.571
C_8 Isomers	.360	.253	.299	.0773	.268	.0669
n-Nonane	.357	.331	.363	.196	.384	.145
1+2 Nonenes	1.31	1.84	1.59	.580	1.08	.505
C_9 Isomers	.180	.221	.285	.0779	.108	.0555
n-Decane	.402	.424	.388	.288	.570	.208
1+2 Decenes	1.38	2.23	1.70	.876	1.72	.757
C_{10} Isomers	.182	.267	.332	.122	.243	.0812
n-Undecane	.381	.433	.383	.314	.531	.201
1+2 Undecenes	1.29	2.24	1.60	1.02	2.22	.915
C_{11} Isomers	.153	.321	.347	.164	.361	.116
C_2-C_4	22.3	18.6	17.0	12.6	16.1	11.0
C_5-C_{11}	20.4	20.8	20.0	15.4	29.9	12.5
C_{12}+	50.4	57.0	59.3	69.5	51.3	74.6
Wax[c]	45.8	48.1	52.6	63.6	34.9	66.7

[c] Unanalyzed wax withdrawn from reactor

Table V.2-12 (cont'd). Summary of results for slurry run SA-07-0468.

Period	7	8	9	10	11
Weight % of Hydrocarbons					
CH4	2.46	3.21	3.69	4.54	3.56
Ethane	1.60	.853	.712	1.03	1.18
Ethylene	3.16	3.84	3.64	4.12	3.57
Propane	.586	.792	.752	1.17	1.11
Propylene	3.52	4.51	4.38	4.98	4.29
n-Butane	.652	.877	.843	1.32	1.26
1+2 Butenes	2.98	3.64	3.51	4.10	3.57
C_4 Isomers	.325	.420	.392	.547	.456
n-Pentane	.932	1.31	1.25	1.75	1.04
1+2 Pentenes	2.90	3.48	3.28	3.88	3.40
C_5 Isomers	.165	.266	.193	1.45	1.21
n-Hexane	.999	.900	1.20	1.14	.882
1+2 Hexenes	2.25	2.73	1.98	3.31	2.50
C_6 Isomers	.010	.900	.610	1.34	.686
n-Heptane	.490	.706	.544	1.42	.084
1+2 Heptenes	1.59	1.90	1.39	2.97	1.82
C_7 Isomers	.442	.651	.375	1.30	.469
n-Octane	.314	.397	.344	.521	.865
1+2 Octenes	1.09	1.30	1.04	1.20	1.73
C_8 Isomers	.138	.125	.0799	.0853	.211
n-Nonane	.353	.305	.443	.454	1.05
1+2 Nonenes	1.32	.889	1.33	.820	1.90
C_9 Isomers	.0930	.0558	.0806	.0609	.154
n-Decane	.530	.480	.033	.713	1.16
1+2 Decenes	1.94	1.47	1.98	1.37	2.28
C_{10} Isomers	.179	.123	.103	.157	.246
n-Undecane	.622	.475	.540	.001	.943
1+2 Undecenes	2.23	1.86	2.30	1.79	2.40
C_{11} Isomers	.245	.193	.201	.218	.248
C_2-C_4	12.8	14.9	14.2	17.3	15.4
C_5-C_{11}	19.5	20.5	20.0	26.6	20.8
C_{12}+	65.4	61.4	62.1	51.9	54.4
Wax[c]	54.3	53.4	53.1	40.9	44.5

[c] Unanalyzed wax withdrawn from reactor

corrected. The exposure to H_2 did not appear to harm the catalyst, as the catalyst activity (conversions and contraction) of the catalyst before and after the interruption was comparable. No other major operational problems were encountered during the run. The major events of run SA–07–0468 are summarized in Table V.2-13.

The activity of the catalyst during balance 1 was high, (250°C, 1.48 MPa, $(H_2/CO)=1.0$), and comparable to the fixed bed test of a similar catalyst composition (100 Fe/3 Cu/0.5 K, run FA–27–2557) at the same nominal conditions. During the test in the fixed bed, the (H_2-CO) conversion was 70.4 %, as compared to the 74.8 % obtained in the slurry test. Catalyst deactivation occurred when the temperature was increased to 265°C between balances 2 and 3 (at 1.48 MPa, (H_2/CO) = 1, 4 Nl / g–cat·h). The (H_2+CO) conversion dropped from 58.4 % in balance 2 (250°C) to 55.5 % in balance 3 (265°C), in spite of the 15 °C temperature increase. In later balances using 0.67 (H_2/CO) feed gas, the increase in temperature from 250 to 265°C also did not significantly increase conversion. In balances 8 (250°C) and 9 (265°C) the (H_2+CO) conversions increased only slightly from 24.0 to 28.2 %. The catalyst was severely deactivated by balance 10, which was a repeat of the conditions used during balance 1. The conversion dropped from 74.8 % to 17.4 % between the two balances.

Increases in temperature shifted catalyst selectivity to lower molecular weight products. For example, the distribution at 235°C, 1.48 MPa, 1 Nl / g–cat·h, $(H_2/CO)=0.67$ (nominal) during balance 6 was 2.0 (CH_4), 11.0 (C_2-C_4), 12.5 (C_5-C_{11}), and 74.5 % ($C_{12}+$), as compared to 2.5 (CH_4), 12.8 (C_2-C_4), 19.5 (C_5-C_{11}), and 65.2 % ($C_{12}+$) at 250°C (balance 7). Similar shifts in the distribution were observed at other conditions, although catalyst deactivation may have influenced the results. Comparisons of balances 1 and 10 shows the effect deactivation may have on selectivity at 250°C, where the deactivated catalyst produced fewer molecular weight products (4.5 % CH_4 and 17.3 % C_2-C_4) than the more active catalyst at the same nominal process conditions during balance 1 (6.9 % CH_4 and 22.3 % C_2-C_4). The shift in lower molecular weight products changed the percentage of the C_5-C_{11} fraction, while the $C_{12}+$ products remained constant between the two balances.

Wax withdrawals were made following catalyst reduction, and at the end of each mass balance period, by removing excess accumulated slurry from the reactor to the external settling vessel. After separation by settling, the wax and trace quantities of catalyst were quantified, and are shown in Table V.2-14 for each withdrawal. In all cases, the weight of catalyst removed with the wax (after settling) was small, less than 2 weight % of the wax.

Table V.2-13. Major events in run SA-07-0468.

TOS (h)	Event
-20	Catalyst pretreatment
0	Initiate run
4	Achieve initial process conditions: T = 250°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
19-39	Problems with hydrogen flow rate
39	Switched from pure gases to premixed gas
47	Replaced hydrogen flow controller; switched to pure gases
47-52	Problems with hydrogen flow rate
52	Switched from pure gases to premixed gas
68	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 4.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
78	Replaced feed gas cylinder. Gas not properly mixed; 95% hydrogen
79	Replaced problem cylinder, Feed (H_2/CO) = 1.0
93	Changed process conditions: T = 265°C, P = 1.48 MPa, SV = 4.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
139	15°C rise in temperature of reflux condenser
141	Repeated wax removal twice due to excessive wax production
143	Changed process conditions: T = 235°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
191	Changed process conditions: T = 235°C, P = 1.48 MPa, SV = 4.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
233	Changed process conditions: T = 235°C, P = 1.48 MPa, SV = 1.0 Nl/g–cat·h, Feed (H_2/CO) = 0.66
261	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 1.0 Nl/g–cat·h, Feed (H_2/CO) = 0.64
311	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.69
359	Changed process conditions: T = 265°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.64
398	Changed process conditions: T = 250°C, P = 1.48 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 1.0
444	Changed process conditions: T = 265°C, P = 2.96 MPa, SV = 2.0 Nl/g–cat·h, Feed (H_2/CO) = 0.64
466	End of Run SA-07-0468

Table V.2-14. Wax and solids inventory for run SA-07-0468.

TOS (*h*)	Event
-48	Slurry loading: 400 *g* wax, 30.25 *g* solids
-1	Wax removal following reduction: 156 *g* wax, 0.80 *g* solids
64	Wax removal: 241 *g* wax, 0.86 *g* solids
92	Wax removal: 162 *g* wax, 0.55 *g* solids
141	Wax removal: 342 *g* wax, 1.37 *g* solids
189	Wax removal: 94 *g* wax, 1.16 *g* solids
231	Wax removal: 38 *g* wax, 0.40 *g* solids
260	Wax removal: 40 *g* wax, 0.23 *g* solids
309	Wax removal: 75 *g* wax, 0.61 *g* solids
357	Wax removal: 54 *g* wax, 0.39 *g* solids
396	Wax removal: 72 *g* wax, 0.37 *g* solids
443	Wax removal: 31 *g* wax, 0.14 *g* solids
466	Wax removal: 38 *g* wax, 0.11 *g* solids
466	End of run: 241 *g* wax, 21.65 *g* solids recovered from reactor. 98 % wax recovery, 94 % solids recovery

V.2.3.5. Summary

No conclusions can be drawn with regard to promoter effects on catalyst activity and/or selectivity due to changes in activity with time on stream. However, some general observations concerning hydrocarbon selectivity can be made. Methane and gaseous hydrocarbon (C_2-C_4) selectivities were, in general, rather low and the fraction of liquid products (C_5+) was high in all four tests. Hydrocarbon selectivities were comparable to those reported by workers at SASOL and MOBIL (Section III). In two tests : CO activated 100Fe/0.3Cu/0.2K catalyst (Run SA-05-2957), and H_2 activated 100Fe/0.3Cu/0.5K catalyst (Run SB-07-0458) the activity increased with time on stream . Both tests were terminated voluntarily after 550 and 460 hours on stream , respectively. On the other hand, a rather rapid deactivation was observed in tests using 100Fe/3Cu/0.2K (Run SA-25-3657) and 100Fe/0.3Cu/0.5K (Run SA-07-0468) catalysts, both of which were activated with CO at 280°C. Initial activity was high in both tests, but catalysts started to deactivate after the first or second wax withdrawal. It is not clear whether deactivation was caused or accelerated by the wax withdrawal or by use of improper activation procedures. Catalyst deactivation was also observed in fixed bed tests when CO activation were employed (Sections V.1.3, V.1.8). Also, frequent changes in process conditions made during slurry reactor tests might have contributed to loss in activity. Tests at a fixed set of process conditions over a long period of time without wax withdrawals are needed to establish causes of catalyst deactivation in slurry reactors.