IV-1 Baseline Catalyst Testing

In order to evaluate advances achieved in catalyst synthesis, two baseline catalysts (Ruhrchemie and United Catalysts, Inc.) were tested in stirred tank reactors. In all tests a catalyst was crushed and sieved to either 270/325 mesh (44-53 μm in diameter) or less than 270 mesh size, prior to loading to a reactor. A pre-purified normal octacosane was used as the liquid (slurry) medium in tests of the Ruhrchemie catalyst, whereas Ethylflo 164 oil was used in tests of UCI catalysts. Two tests were conducted, during this contract, with the Ruhrchemie catalyst. In the test designated SB-0440, the catalyst was reduced with hydrogen externally, in a fixed bed reactor unit, and then transferred into the reactor in an inert gas atmosphere. A hot spot was detected during reduction with hydrogen in the fixed bed reactor (270°C instead of 220°C), which was quickly quenched by helium flow. During the test we have encountered several problems with product collection and handling, resulting in inaccurate mass and atomic balance closures. This test lasted 550 h, and the catalyst activity was stable throughout the test, however, product selectivities are not considered to be sufficiently accurate (Quarterly Technical Progress Report, January 1 - March 31, 1991). Results from this test will not be discussed here. In the second test, Run SB-1370, the catalyst was reduced in-situ with hydrogen. Results from this test, as well as from the test SA-0888 (CO pretreated catalyst) have been described and discussed in section III-4 of this report. The latter test (SA-0888) was completed during the course of our work on the previous DOE contract, and the complete results from this test were reported elsewhere (Bukur et al., 1989b; 1990c). Selected results from this test are also presented in this report for the sake of completeness.

IV-1.1 Testing of UCI Catalysts

Three tests were conducted with catalysts synthesized at United Catalysts, Inc. (UCI). These catalysts were potential candidates for use in a slurry bubble column reactor Fischer-Tropsch demonstration run at LaPorte, Texas in August 1992. Their compositions and BET surface areas and pore volumes , as supplied by manufacturer, are listed in Table IV-1.1. There are significant differences in promoter concentrations and physical properties among different catalysts.

In all three tests the catalysts were pretreated using a procedure similar to those used in slurry bubble column reactor tests at Mobil (Kuo, 1983; 1985). Briefly, after loading of a catalyst and the initial slurry medium, the reactor was sealed and pressurized to 153 psig with nitrogen, and stirring was initiated at 1100 rpm. Then the slurry temperature was raised linearly to 280°C in 3 hours under nitrogen flow. When 280°C was reached, the nitrogen flow was replaced with synthesis gas (H_2/CO molar ratio of about 0.67) at a flow rate of 2 Nl/g-Fe/h for 12 hours. Results from individual tests are described first, followed by comparison of performance of UCI catalysts, as well as between UCI catalysts and the Ruhrchemie catalyst.

IV-1.1.1 Run SA-3391 with UCI L-3950 Catalyst

After the pretreatment, the catalyst was initially tested at 265°C (actual temperature 270°C, see below), 290 psig (2.07 MPa), 3 Nl/g-Fe/h and $H_2/CO = 0.7$. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.1. (H_2+CO) conversion increased gradually from 76% at 3 h to 80% at 24 h, and then remained stable during the next 80 h of testing. During the same time period methane selectivity increased markedly from 4% to 7%. At about 103 h, gas flow rate was decreased to give the gas space velocity of 2.4 Nl/g-Fe/h in order to test the catalyst under the same process conditions as those employed at Universal Oil Products Inc. (UOP). Consequently (H_2+CO) conversion increased to 82-83% and remained stable during the next 60 h of testing. Since our values of syngas conversion (83%) and methane selectivity (~8%) were significantly higher than those obtained at UOP (70 and 4%, respectively) we suspected that there may be a problem with our

Table IV-1.1 Physico-Chemical Properties and Test Designations for UCI Catalysts.

RUN NUMBER	SA-3391	SA-1532	SA-2052
CATALYST DESIGNATION	L-3950	1207-175A	L-3950 (batch 3)
CATALYST COMPOSITION (wt.-%)			
K_2O	5.1	0.8	1.7
SiO_2	8.3	2.5	4.9
CuO	2.6	1.1	5.0
Fe_2O_3	69.6	86.9	76.6
LOI	14.8	9.5	11.8
CATALYST COMPOSITION			
Fe	100.0	100.0	100.0
Cu	4.3	1.4	7.5
K	8.7	1.1	2.6
SiO_2	17.0	4.1	9.2
SURFACE AREA (m^2/g)	251	167	136
PORE VOLUME (cc/g)	0.50	0.18	0.30

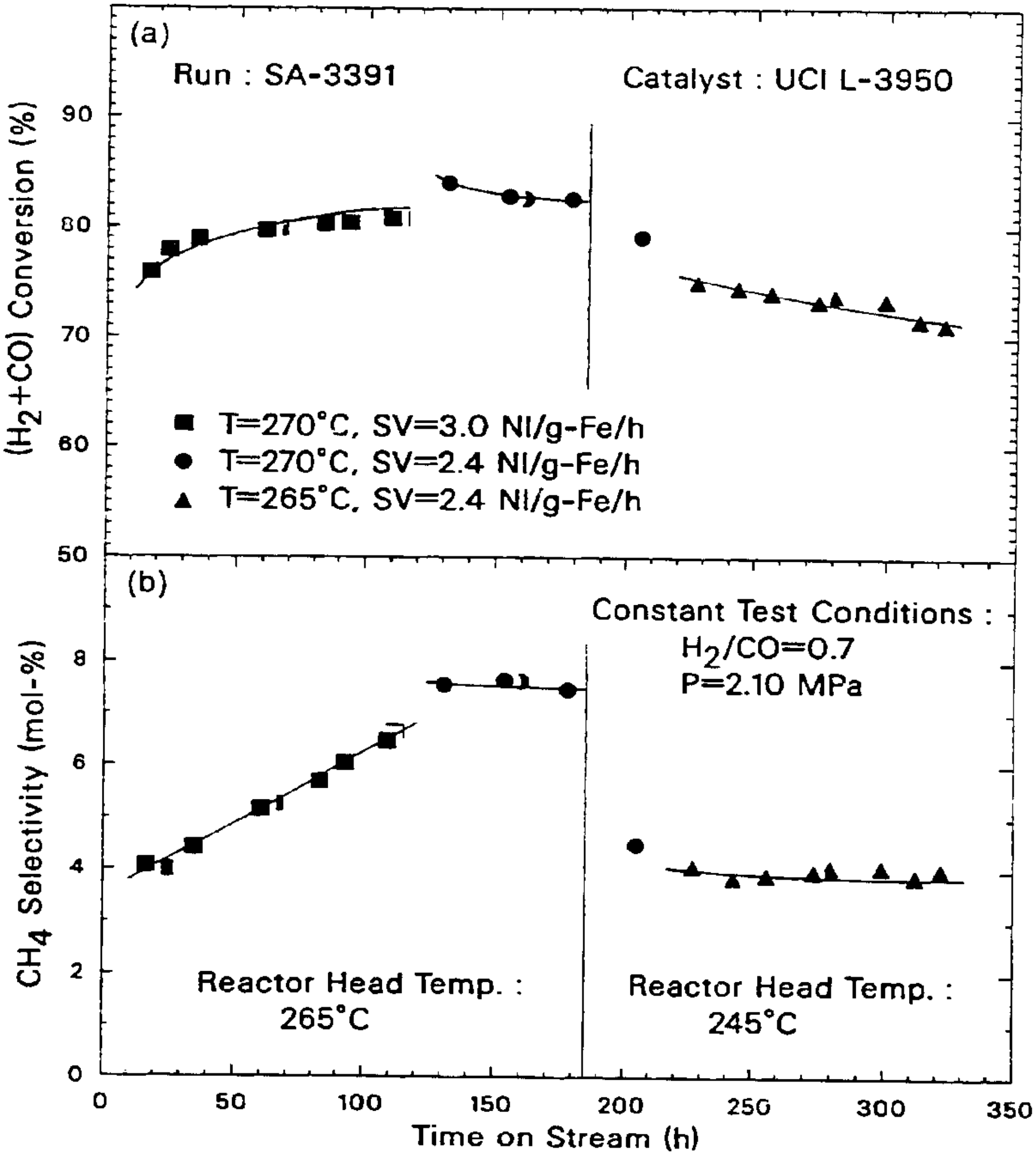

Figure IV-1.1 (H_2+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-3391.

instruments and/or apparatus. The (H_2+CO) conversion decreased to 79%, and methane selectivity to 4.5%, when the temperature of the reactor head was lowered from 265 to 245°C at 170 h on stream. After this run, a blank test was performed which showed significant FT activity. After the blank test the reactor shaft was disassembled and residual catalyst was found in the space between the stirrer shaft and its housing. This residual catalyst was responsible for higher than expected syngas conversion and methane selectivity in Run SA-3391. By lowering the reactor head temperature, the reaction in the stirrer shaft housing was quenched.

At about 170 h on stream, a malfunctioning of the temperature readout device was detected, and at 196 h the reactor temperature was brought to its desired value of 265°C, and at 212 h the (H_2+CO) conversion and methane selectivity decreased to 75% and 4%, respectively. During the remaining 100 h of testing, the conversion decreased slowly with time, reaching 71.5% at 310 h, whereas methane selectivity remained stable at about 4%. The latter values of syngas conversion and methane selectivity, are similar to those obtained at UOP.

Water-gas-shift activity was high and fairly stable throughout the test. The usage ratio varied between 0.56 and 0.61.

The information on hydrocarbon distribution obtained during six mass balances can be found in Table IV-1.2. The average hydrocarbon product distribution from the last two mass balances made at 265°C, 290 psig, 2.4 Nl/g-Fe/h, $H_2/CO = 0.67\text{-}0.70$ was: $CH_4 = 4.4$; (C_2 - C_4) = 16.5; (C_5-C_{11}) = 23.6 and $C_{12+} = 55.5$ wt%. Olefin content increased, whereas 2-olefin content decreased slightly with time (Table IV-1.2).

A typical carbon number product distribution, for products collected at 297 h on stream, is shown in Figure IV-1.2. The data are well represented by a three parameter model of Huff and Satterfield (1984). Numerical values of parameters are shown in Figure IV-1.2. Results of analysis of the reactor wax withdrawn from the reactor at 297 h are shown in Figure IV-1.3 in the form of ASF plot. Products with carbon number greater

Table IV-1.2 Summary of Slurry Reactor Test Results for Run SA-3391.

Period	1	2	3	4	5	6
Date	12/08/91	12/10/91	12/12/91	12/14/91	12/16/91	12/19/91
Time on Stream (*h*)	43.0	91.0	139.0	187.0	235.0	297.0
Balance Duration (*h*)	7.0	6.0	6.0	6.0	6.0	10.0
Average Temperature (°C)	270.	270.	270.	270.	265.	265.
Pressure (*MPa*)	2.10	2.10	2.10	2.10	2.10	2.10
H_2/CO Feed Ratio	.698	.698	.698	.698	.698	.669
Space Velocity (*Nl/g-cat·h*)[a]	1.71	1.71	1.37	1.37	1.37	1.37
Space Velocity (*Nl/g-Fe·h*)	2.99	2.99	2.39	2.39	2.39	2.40
GHSV (h^{-1})[b]	101.	101.	74.2	74.2	74.2	67.5
CO Conversion (%)	85.5	85.9	87.3	84.6	79.2	73.9
H_2+CO Conversion (%)	79.9	81.1	82.8	79.3	74.4	71.7
H_2/CO Usage	.587	.604	.612	.592	.595	.620
STY (*mols* H_2+CO/*g-cat·h*)[a]	.061	.062	.051	.048	.045	.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	21.4	22.5	21.6	22.3	18.8	13.8
Weight % of Outlet						
H_2	1.37	1.23	1.11	1.36	1.56	1.45
H_2O	1.60	1.45	1.53	1.46	1.37	1.28
CO	14.1	13.6	12.0	14.8	19.9	25.0
CO_2	61.9	62.9	62.7	62.1	57.9	53.2
Hydrocarbons	10.0	10.9	12.1	10.0	9.63	10.1
Oxygenates	.218	.204	.368	.368	.413	.409
Wax[c]	10.7	9.72	10.2	9.07	9.27	8.56
Yield (*g/Nm*^{3} H_2 + CO *Converted*)						
CH_4	12.2	14.9	17.2	10.3	8.91	8.45
C_2-C_4 Hydrocarbons	30.6	32.6	36.7	34.8	33.8	32.0
C_5-C_{11} Hydrocarbons	34.3	38.2	42.1	44.8	42.3	52.0
C_{12}+ Hydrocarbons	119.	109.	114.	104.	110.	111.
Wax[c]	101.	92.1	95.9	87.9	95.8	93.5
Oxygenates	2.06	2.78	3.47	3.56	4.27	4.47
Total	198.	198.	214.	197.	200.	208.
1+2 Olefins/*n*-Paraffin Ratio						
C_2	1.41	1.14	.871	1.59	2.38	2.50
C_3	6.13	5.61	5.19	6.19	6.11	6.22
C_4	5.41	5.01	4.78	5.57	5.61	5.48
C_8	2.91	2.85	2.57	3.44	3.70	3.29
C_{10}	2.28	2.08	2.25	2.69	2.96	2.68

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-1.2 (cont'd) Summary of Slurry Reactor Test Results for Run SA-3391.

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	6.20	7.64	8.19	5.30	4.56	4.15
Ethane	2.05	2.51	3.02	2.18	1.57	1.38
Ethylene	2.71	2.68	2.45	3.23	3.49	3.21
Propane	.915	1.04	1.15	1.04	1.01	.898
Propylene	5.35	5.57	5.70	6.14	5.89	5.33
n-Butane	.722	.832	.902	.829	.819	.762
1+2 Butenes	3.77	4.02	4.16	4.46	4.43	4.03
C_4 Isomers	.0614	.0689	.0716	.0825	.0897	.0857
n-Pentane	.621	.767	.846	.732	.728	.707
1+2 Pentenes	2.98	3.17	3.26	3.62	3.69	3.37
C_5 Isomers	.642	.693	.792	.837	.845	2.35
n-Hexane	.603	.703	.790	.729	.677	.820
1+2 Hexenes	2.10	2.18	2.34	2.76	2.50	2.82
C_6 Isomers	.793	.824	.880	1.06	.927	1.04
n-Heptane	.510	.625	.680	.666	.587	.636
1+2 Heptenes	1.72	1.93	1.95	2.38	2.26	2.34
C_7 Isomers	.680	.667	.686	.770	.559	.744
n-Octane	.452	.536	.577	.544	.470	.547
1+2 Octenes	1.29	1.50	1.45	1.84	1.71	1.77
C_8 Isomers	.527	.726	.442	.622	.386	.588
n-Nonane	.350	.436	.464	.443	.402	.475
1+2 Nonenes	.907	1.02	1.07	1.32	1.26	1.40
C_9 Isomers	.214	.294	.304	.418	.348	.503
n-Decane	.379	.476	.442	.490	.433	.527
1+2 Decenes	.852	.978	.981	1.30	1.26	1.39
C_{10} Isomers	.293	.375	.380	.492	.510	.789
n-Undecane	.383	.410	.422	.475	.419	.495
1+2 Undecenes	.859	.937	.918	1.20	1.22	1.43
C_{11} Isomers	.324	.331	.341	.437	.470	.784
C_2-C_4	15.6	16.7	17.5	18.0	17.3	15.7
C_5-C_{11}	17.5	19.6	20.0	23.1	21.7	25.5
C_{12}+	60.7	56.1	54.3	53.6	56.5	54.6
Wax[c]	61.6	47.3	45.6	45.4	49.0	45.9

[c] Unanalyzed wax withdrawn from reactor

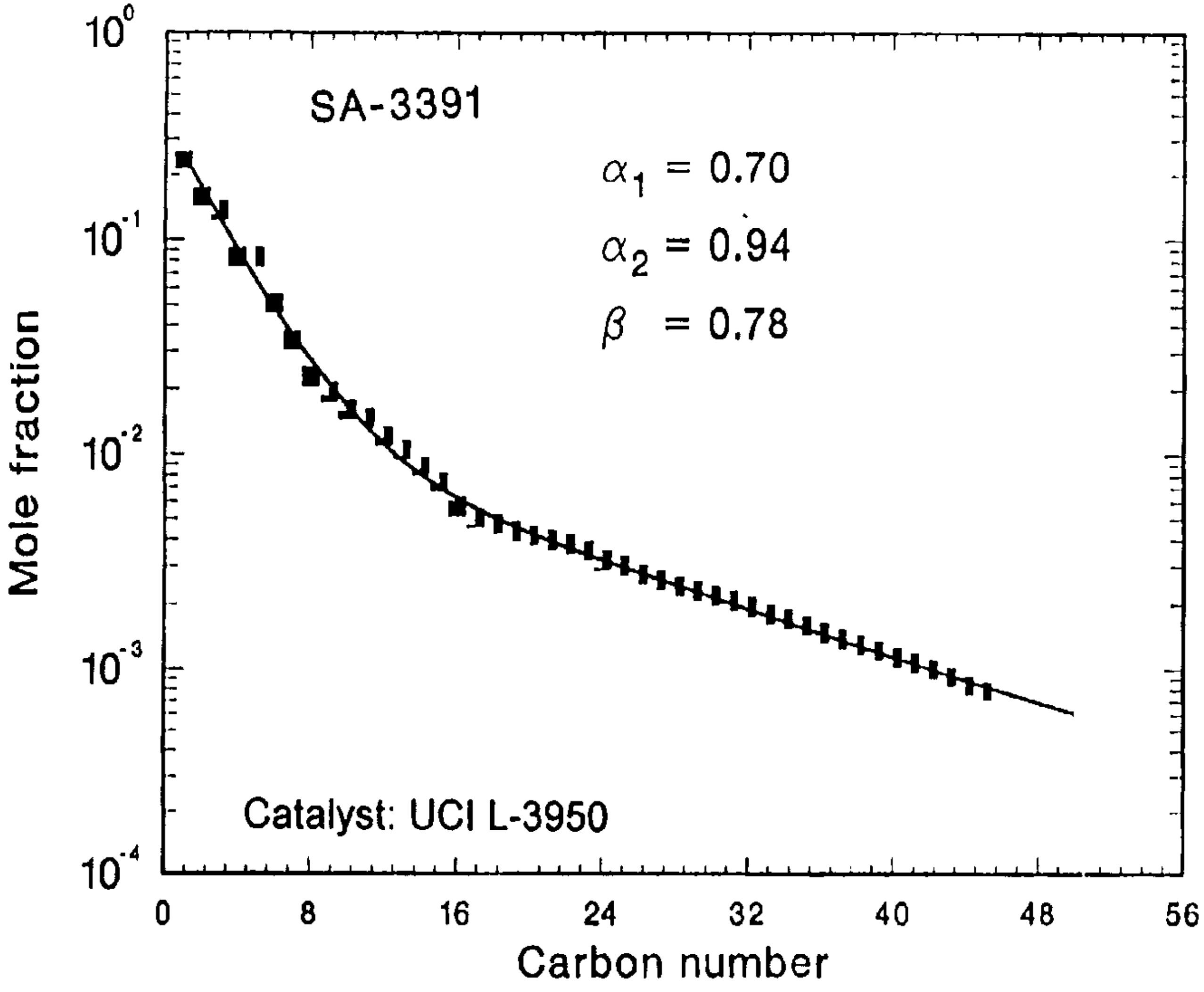

Figure IV-1.2. Carbon number product distribution for Run SA-3391 (TOS=297 h).

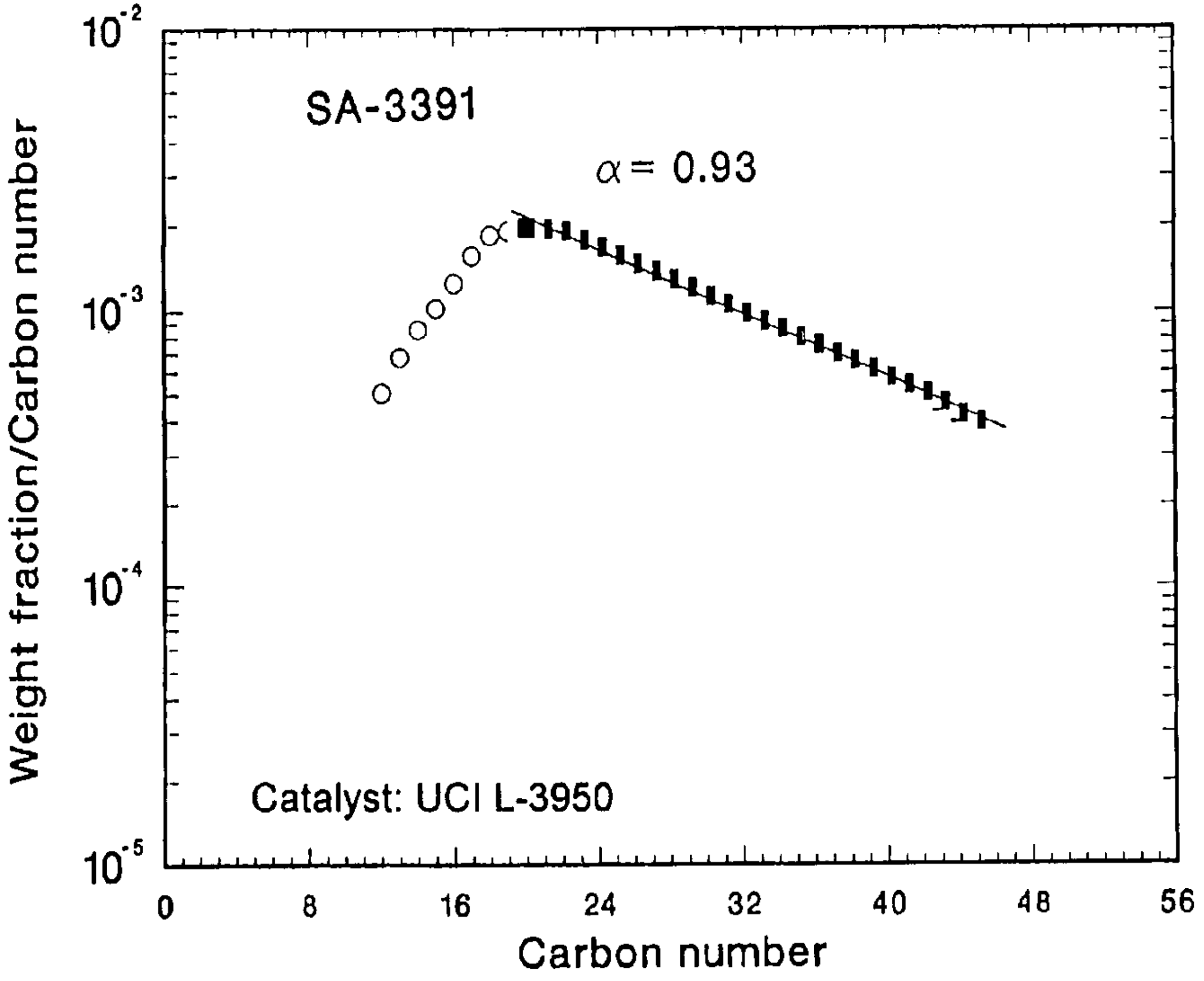

Figure IV-1.3 Carbon number distribution of wax product for Run SA-3391 (TOS=297 h).

than C_{20} can be fitted well with a straight line, giving the chain growth parameter of 0.93. This value is very close to the one obtained from the three parameter model (α_2 = 0.94).

IV-1.1.2 Run SA-1532 with UCI 1207-175A Catalyst

After the pretreatment, the catalyst was tested at 265°C, 290 psig (2.07 MPa), 2.4 Nl/g-Fe/h and H_2/CO = 0.7. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.4. The catalyst activity was not stable, and it decreased continuously with time. The maximum syngas conversion was 49%, at about 40 h , and then it decreased gradually to 32% at the end of the test. WGS activity of the catalyst was high throughout the test, and the usage ratio varied between 0.57 and 0.65.

Methane (Figure IV-1.4) and hydrocarbon selectivities (Table IV-1.3) were fairly stable during 300 h of testing. For example, methane selectivity increased slightly from 2.2 wt% at 45 h, to 2.4% at 260 h, (C_2-C_4) varied between 9.9 and 11.5%, (C_5-C_{11}) decreased slightly from 18% to 15%, while C_{12+} increased from 69% to 72%. Olefin selectivity (total olefin content, and 2-olefin content) did not vary with time (Table IV-1.3).

A typical ASF plot for products collected at 164 h on stream is shown in Figure IV-1.5. The experimental data were fitted well with a three parameter model, except for methane. Its concentration is significantly lower than expected from the ASF distribution. Estimated values of parameters are also shown in Figure IV-1.5.

During testing of the same catalyst at the UOP the following results were obtained: (H_2 + CO) conversion decreased from 70 to 45% during 280 h of testing, the usage ratio varied between 0.57 and 0.60, and methane selectivity was about 2.8 mol%. Except for higher syngas conversion, but nevertheless declining with time on stream as

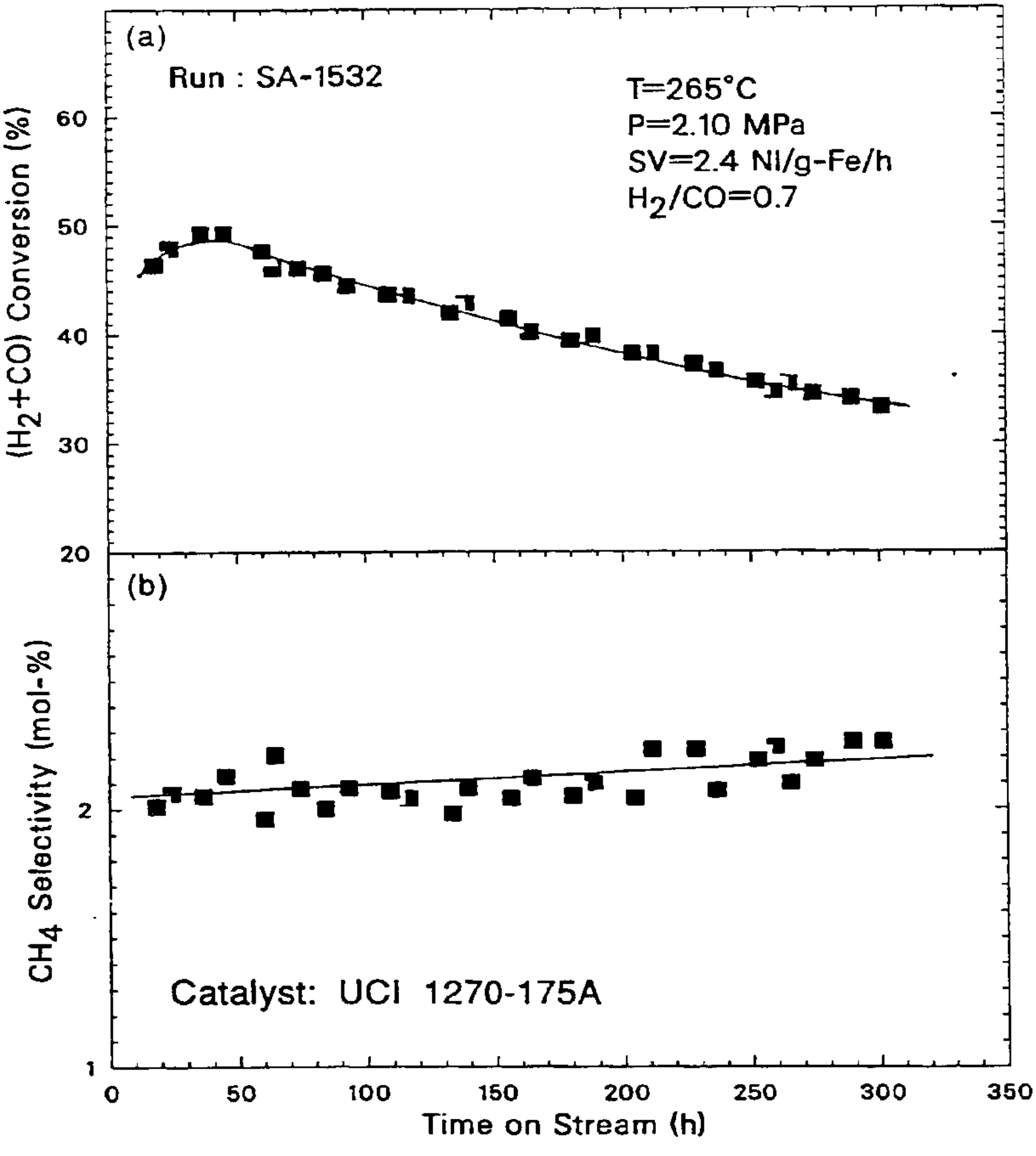

Figure IV-1.4 (H_2+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-1532.

Table IV-1.3 Summary of Slurry Reactor Test Results for Run SA-1532.

Period	1	2	3	4	5
Time on Stream (h)	45.0	117.0	164.0	212.0	260.0
Balance Duration (h)	17.0	16.2	16.0	16.0	15.0
Average Temperature (°C)	265.	265.	265.	265.	265.
Pressure (MPa)	2.10	2.10	2.10	2.10	2.10
H_2/CO Feed Ratio	.733	.709	.709	.715	.715
Space Velocity (Nl/g-cat·h)[a]	1.42	1.43	1.43	1.47	1.47
Space Velocity (Nl/g-Fe·h)	2.34	2.35	2.35	2.42	2.42
GHSV (h^{-1})[b]	98.4	94.8	94.8	91.4	91.4
CO Conversion (%)	52.1	46.7	43.3	40.1	37.8
H_2+CO Conversion (%)	48.6	42.9	40.0	38.5	36.3
H_2/CO Usage	.616	.569	.578	.644	.649
STY ($mols$ H_2+CO/g-cat·h)[a]	.031	.027	.026	.025	.024
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	13.8	10.7	10.7	9.94	8.97
Weight % of Outlet					
H_2	2.82	3.05	3.14	3.13	3.21
H_2O	.966	1.07	.978	.891	.937
CO	45.6	50.9	53.9	57.0	59.1
CO_2	37.9	33.4	31.5	28.4	27.2
Hydrocarbons	5.09	4.21	4.05	3.81	3.28
Oxygenates	.344	.379	.385	.381	.343
Wax[c]	7.36	7.00	6.01	6.45	5.95
Yield (g/Nm^3 $H_2 + CO$ *Converted*)					
CH_4	4.17	4.33	4.43	4.77	4.68
C_2–C_4 Hydrocarbons	21.3	21.1	22.3	20.2	20.5
C_5–C_{11} Hydrocarbons	35.2	32.3	32.6	31.1	28.7
C_{12}+ Hydrocarbons	133.	142.	134.	148.	141.
Wax[c]	115.	125.	115.	128.	126.
Oxygenates	5.37	6.77	7.41	7.59	7.25
Total	199.	207.	201.	212.	202.
1+2 Olefins/n-Paraffin Ratio					
C_2	5.10	5.30	6.11	6.42	6.15
C_3	5.83	5.10	5.92	7.80	5.30
C_4	4.03	3.93	4.00	4.10	4.16
C_8	2.92	2.82	3.30	3.41	3.12
C_{10}	3.04	3.07	3.12	3.32	3.14

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-1.3 (cont'd) Summary of Slurry Reactor Test Results for Run SA-1532.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH4	2.15	2.17	2.29	2.33	2.40
Ethane	.570	.531	.569	.477	.512
Ethylene	2.71	2.62	3.24	2.86	2.94
Propane	.637	.688	.633	.421	.654
Propylene	3.54	3.35	3.58	3.14	3.31
n–Butane	.651	.631	.660	.556	.570
1+2 Butenes	2.53	2.39	2.55	2.20	2.29
C_4 Isomers	.322	.309	.307	.248	.261
n–Pentane	.537	.409	.415	.235	.338
1+2 Pentenes	2.36	2.21	2.36	1.99	2.08
C_5 Isomers	.154	.148	.163	.154	.159
n–Hexane	.579	.556	.604	.504	.491
1+2 Hexenes	1.87	1.71	1.89	1.66	1.63
C_6 Isomers	.885	.694	.757	.601	.583
n–Heptane	.543	.488	.499	.437	.416
1+2 Heptenes	1.64	1.43	1.51	1.37	1.32
C_7 Isomers	.731	.516	.555	.572	.482
n–Octane	.555	.476	.419	.377	.411
1+2 Octenes	1.59	1.32	1.36	1.26	1.26
C_8 Isomers	.535	.380	.407	.442	.322
n–Nonane	.517	.415	.435	.388	.448
1+2 Nonenes	1.47	1.34	1.38	1.31	1.31
C_9 Isomers	.119	.185	.155	.165	.135
n–Decane	.453	.429	.441	.362	.364
1+2 Decenes	1.36	1.30	1.36	1.25	1.13
C_{10} Isomers	.240	.260	.246	.240	.242
n–Undecane	.407	.373	.377	.346	.292
1+2 Undecenes	1.26	1.22	1.25	1.21	.984
C_{11} Isomers	.339	.281	.313	.327	.321
C_2–C_4	11.0	10.5	11.5	9.89	10.5
C_5–C_{11}	18.2	16.1	16.9	15.2	14.7
C_{12}+	68.7	71.2	69.3	72.6	72.3
Wax[c]	59.1	62.4	59.8	62.9	64.5

[c] Unanalyzed wax withdrawn from reactor

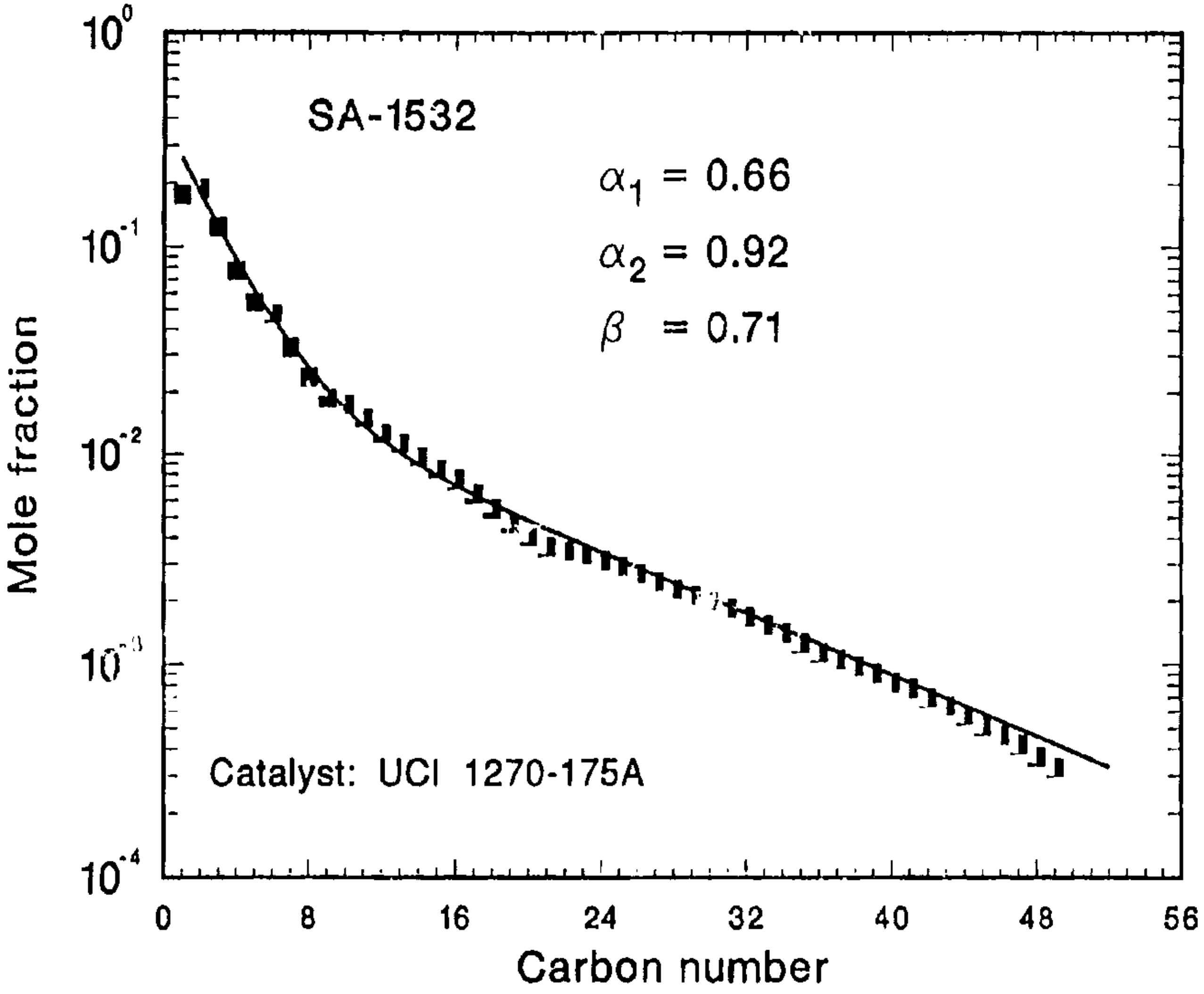

Figure IV-1.5. Carbon number product distribution for Run SA-1532 (TOS=164 h).

in the test at TAMU, the agreement between results obtained at tests conducted at TAMU and UOP is quite satisfactory.

IV-1.1.3 Run SA-2502 with UCI L-3905 (Batch 3) Catalyst

After the pretreatment, the catalyst was initially tested at 265°C, 290 psig (2.07 MPa), 2.4 Nl/g-Fe/h and $H_2/CO = 0.7$. Changes in syngas conversion and methane selectivity with time-on-stream are shown in Figure IV-1.6. Both the syngas conversion and methane selectivity increased with time during the first 140 h of testing. The (H_2 + CO) conversion increased from 51% to 65%, whereas methane selectivity increased from 3.5% to 4.5 mol%. At 140 h the reactor head temperature was lowered from 265°C to 235°C, in order to suppress FTS activity in the stirrer shaft housing above the reactor head. After this, the syngas conversion remained fairly stable 65-66%, but the methane selectivity decreased back to 3.5% and remained stable during the next 140 h of testing. At about 280 h on stream, the reaction pressure was lowered to 200 psig (1.48 MPa) while the remaining process conditions were kept constant. After an initial decrease the syngas conversion stabilized at 54%, and the methane selectivity increased to 3.9%. At 355 h the reaction pressure and the gas space velocity were increased simultaneously to 400 psig (2.86 MPa) and 4.6 Nl/g-Fe/h, respectively. This corresponds to the same contact (gas residence) time as that during testing at 200 psig and 2.4 Nl/g-Fe/h. Following the change in process conditions there was an initial decrease in conversion to 47.5%, followed by gradual increase to 55% (360-400 h). This resulted in nearly doubling of the reactor STY from 0.031 mol (H_2 + CO)/g-cat/h at 334 h to 0.061 mol (H_2 + CO)/g-cat/h at 384 h (Table IV-1.4). Methane selectivity decreased to 2.9% during testing at 400 psig. At 401 h on stream the baseline conditions (265°C, 290 psig , 2.4 Nl/g-Fe/h, $H_2/CO = 0.7$) were re-established and testing continued for another 40 h. The syngas conversion varied from 70 to 72% during this period, which is about 8% higher than during testing between 140 and 240 h on stream. Thus, the catalyst activity

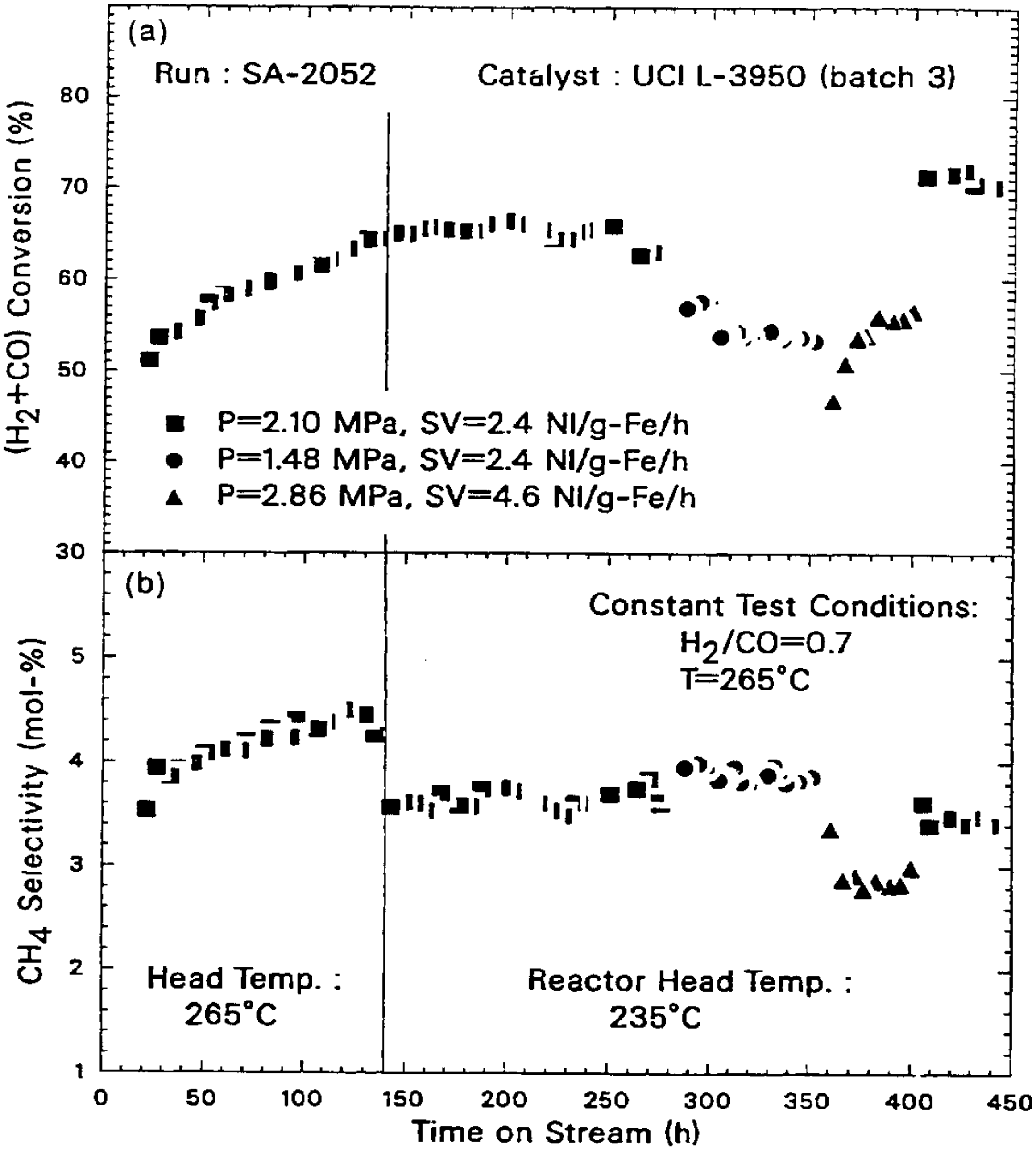

Figure IV-1.6 (H_2+CO) conversion (a) and methane selectivity (b) as a function of time on stream for Run SA-2502.

Table IV-1.4 Summary of Slurry Reactor Test Results for Run SA-2052.

Period	1	2	3	4	5	6	7
Time on Stream (*h*)	29.0	120.0	168.0	264.0	334.0	384.0	431.0
Balance Duration (*h*)	16.0	15.0	14.0	12.0	12.5	11.5	13.0
Average Temperature (°C)	266	265.	265.	265.	265.	265.	265
Pressure (*MPa*)	2.10	2.10	2.10	2.10	1.48	2.86	2.10
H_2/CO Feed Ratio	.73	.73	.73	.73	.72	.72	.70
Space Velocity (*Nl/g-cat·h*)[a]	1.25	1.25	1.25	1.32	1.27	2.45	1.2[illegible]
Space Velocity (*Nl/g-Fe·h*)	2.31	2.34	2.34	2.46	2.37	4.58	2.40
GHSV (h^{-1})[b]	90.	90.	90.	90.	87.	168.	88
CO Conversion (%)	61.0	67.1	68.3	66.1	56.3	56.6	73.5
H_2+CO Conversion (%)	59.6	64.2	65.2	63.4	53.0	56.0	69.9
H_2/CO Usage	.69	.66	.66	.66	.64	.69	.62
STY (*mols* H_2+CO/*g-cat·h*)[a]	.033	.036	.037	.037	.031	.061	.04[illegible]
$P_{CO_2}\cdot P_{H_2}/P_{CO}\cdot P_{H_2O}$	4.0	5.7	6.1	6.2	6.2	3.6	9.1
Weight % of Outlet							
H_2	2.13	1.99	1.95	2.02	2.45	2.22	1.7[illegible]
H_2O	3.47	2.94	2.82	2.66	2.17	3.26	2.20
CO	37.18	31.14	30.19	32.02	41.77	41.23	25.30
CO_2	42.10	46.55	47.07	46.34	40.10	38.43	54.73
Hydrocarbons	9.23	10.02	9.23	10.04	7.37	8.21	9.79
Oxygenates	.55	.36	.50	.57	.35	.66	.57
Wax[c]	5.31	7.01	8.24	6.35	5.80	6.00	7.65
Yield (*g/Nm*^{3} H_2 + CO *Converted*)							
CH_4	9.45	9.93	8.19	8.22	8.76	6.58	7.85
C_2-C_4 Hydrocarbons	43.11	40.58	37.60	36.76	35.14	33.21	35.17
C_5-C_{11} Hydrocarbons	46.63	42.40	42.57	48.96	37.16	45.26	40.97
C_{12}+ Hydrocarbons	85.31	108.89	114.68	103.40	105.00	108.91	107.5[illegible]
Wax[c]	67.43	83.06	95.78	76.47	81.95	81.66	51.03
Oxygenates	7.42	4.23	5.78	6.88	4.86	8.98	6.27
Total	191.93	206.03	208.82	201.22	190.94	202.94	197.80
1+2 Olefins/n-Paraffin Ratio							
C_2	2.00	1.53	1.57	1.59	1.57	3.22	1.51
C_3	5.57	5.92	5.94	5.53	6.47	5.69	5.99
C_4	4.90	6.12	5.08	4.98	5.29	4.49	5.00
C_8	3.27	3.00	3.43	3.52	3.63	3.75	3.20
C_{10}	2.67	2.38	2.75	2.80	2.93	3.35	2.62

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table IV-1.4 (cont'd) Summary of Slurry Reactor Test Results for Run SA-2052.

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH4	5.12	4.92	4.03	4.17	4.71	3.39	4.12
Ethane	2.33	2.21	2.02	2.04	2.07	1.11	2.12
Ethylene	4.36	3.15	2.96	3.02	3.02	3.33	2.98
Propane	1.48	1.24	1.13	1.22	1.09	1.09	1.11
Propylene	7.90	7.02	6.40	6.43	6.70	5.93	6.34
n-Butane	1.16	.99	.93	.94	.90	.97	.91
1+2 Butenes	5.49	4.91	4.57	4.49	4.61	4.19	4.42
C_4 Isomers	.65	.58	.50	.50	.48	.50	.48
n-Pentane	.99	.87	.80	.81	.75	.84	.80
1+2 Pentenes	4.70	4.14	3.84	3.83	3.96	3.72	3.80
C_5 Isomers	1.19	1.05	.95	.96	.85	.98	.99
n-Hexane	.72	.59	.54	.61	.52	.58	.56
1+2 Hexenes	3.05	2.44	2.23	2.33	2.29	2.40	2.31
C_6 Isomers	.94	.81	.64	.72	.83	.83	.77
n-Heptane	.60	.49	.44	.51	.43	.53	.44
1+2 Heptenes	2.21	1.70	1.71	1.89	1.81	1.98	1.68
C_7 Isomers	.90	.69	.63	.62	.69	.78	.65
n-Octane	.51	.42	.44	.52	.37	.47	.40
1+2 Octenes	1.64	1.23	1.48	1.81	1.33	1.72	1.25
C_8 Isomers	.75	.47	.50	.61	.41	.70	.47
n-Nonane	.51	.45	.45	.62	.37	.46	.45
1+2 Nonenes	1.48	1.15	1.43	1.89	1.20	1.64	1.31
C_9 Isomers	.40	.30	.43	.53	.34	.45	.39
n-Decane	.49	.50	.46	.69	.39	.46	.55
1+2 Decenes	1.29	1.17	1.23	1.89	1.13	1.52	1.43
C_{10} Isomers	.66	.41	.50	.69	.37	.66	.57
n-Undecane	.51	.50	.48	.74	.40	.46	.56
1+2 Undecenes	1.18	1.17	1.21	1.80	1.06	1.52	1.39
C_{11} Isomers	.54	.46	.58	.63	.48	.66	.60
C_2-C_4	23.38	20.11	18.52	18.63	18.88	17.12	18.36
C_5-C_{11}	25.26	21.01	20.97	24.81	19.97	23.34	21.39
C_{12}+	46.24	53.96	56.48	52.40	56.43	56.15	56.13
Wax[d]	36.54	41.16	47.17	38.75	44.05	42.20	43.87

[d] Unanalyzed wax withdrawn from reactor

increased slightly with time, and there was no deactivation after the testing at 400 psig. WGS activity increased with time as evidenced by decrease in the usage ratio from 0.69 at 29 h to 0.62 at 431 h on stream. Methane selectivity was about 3.5%, which is the same as that between 140 and 240 h on stream. Selected results from seven mass balances are summarized in Table IV-1.4. Hydrocarbon product distribution at the baseline conditions was stable after the reactor head temperature was decreased to 235°C (Mass balances 3,4 and 7). Olefin selectivity (total olefin content, and 2-olefin content) did not vary with time, during testing at the baseline conditions. The olefin content was slightly higher, whereas 2-olefin content was slightly lower at 400 psig relative to 200 psig (Table IV-1.4).

A typical ASF plot for products collected at 168 h on stream is shown in Figure IV-1.7. The experimental data were fitted well with a three parameter model. Estimated values of parameters are also shown in Figure IV-1.7.

This catalyst was also tested in a STSR at UOP Laboratories in Des Plaines, Illinois. During the first 120 h of testing at the baseline conditions the syngas conversion was very erratic and varied between 50 and 70%, whereas methane selectivity was about 3.5 mol%. These values are in good agreement with our results, confirming good reproducibility of data between these two Laboratories.

IV-1.2 Comparison of Baseline Catalysts

UCI catalysts were tested at a common set of process conditions (baseline conditions) which facilitates comparison of their activities and selectivities. Here, we are excluding results which were affected either by side reactions in the stirrer shaft housing (Runs SA-3391 and SA-2052) or by higher reaction temperature due to malfunctioning of the temperature readout (Run SA-3391, the first 200 h on stream).

Variation of syngas conversion with time for all three tests with UCI catalysts is shown in Figure IV-1.8a. During the first 300 h of testing the (H_2 + CO) conversion was

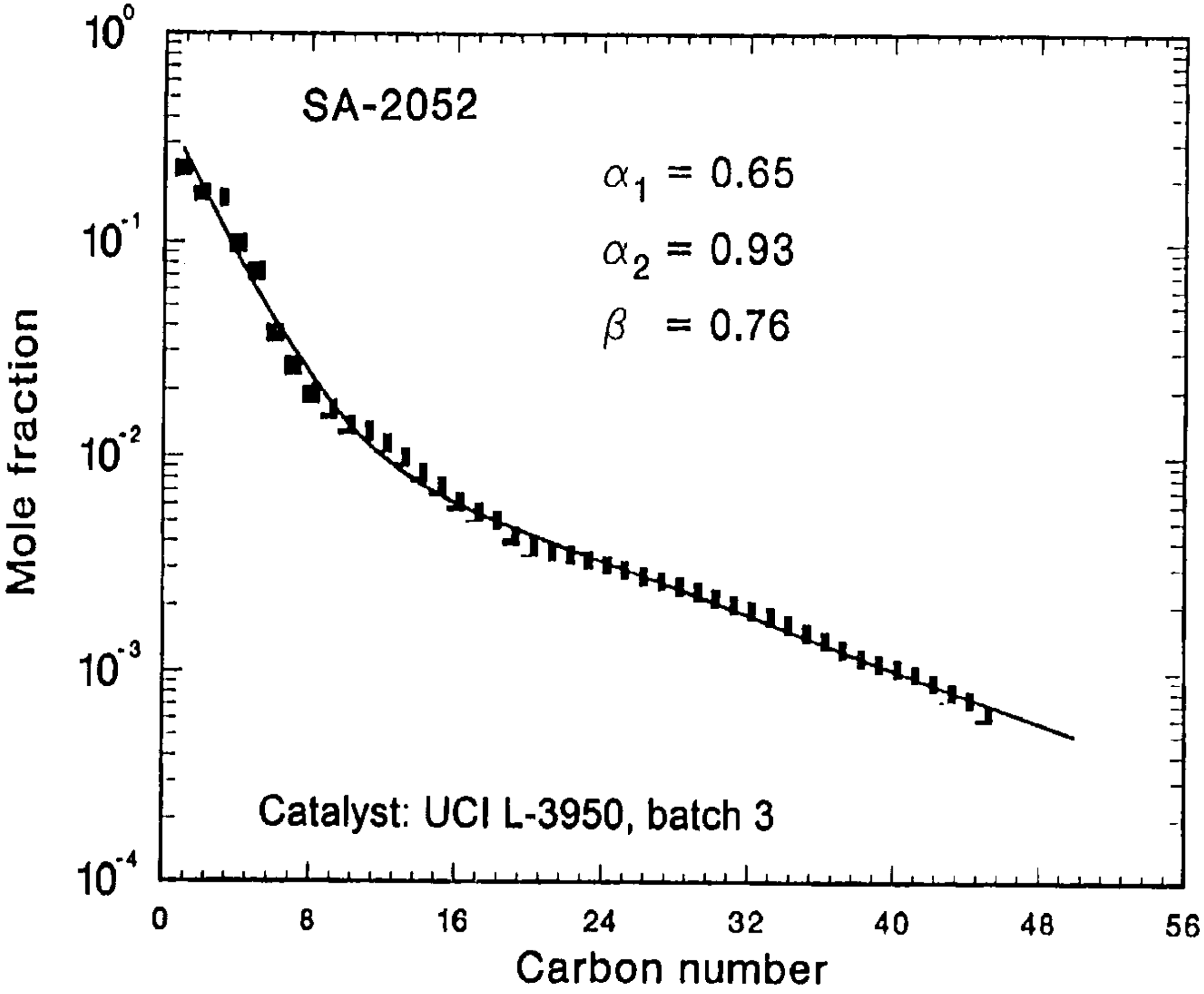

Figure IV-1.7 Carbon number product distribution for Run SA-2502 (TOS=168 h).

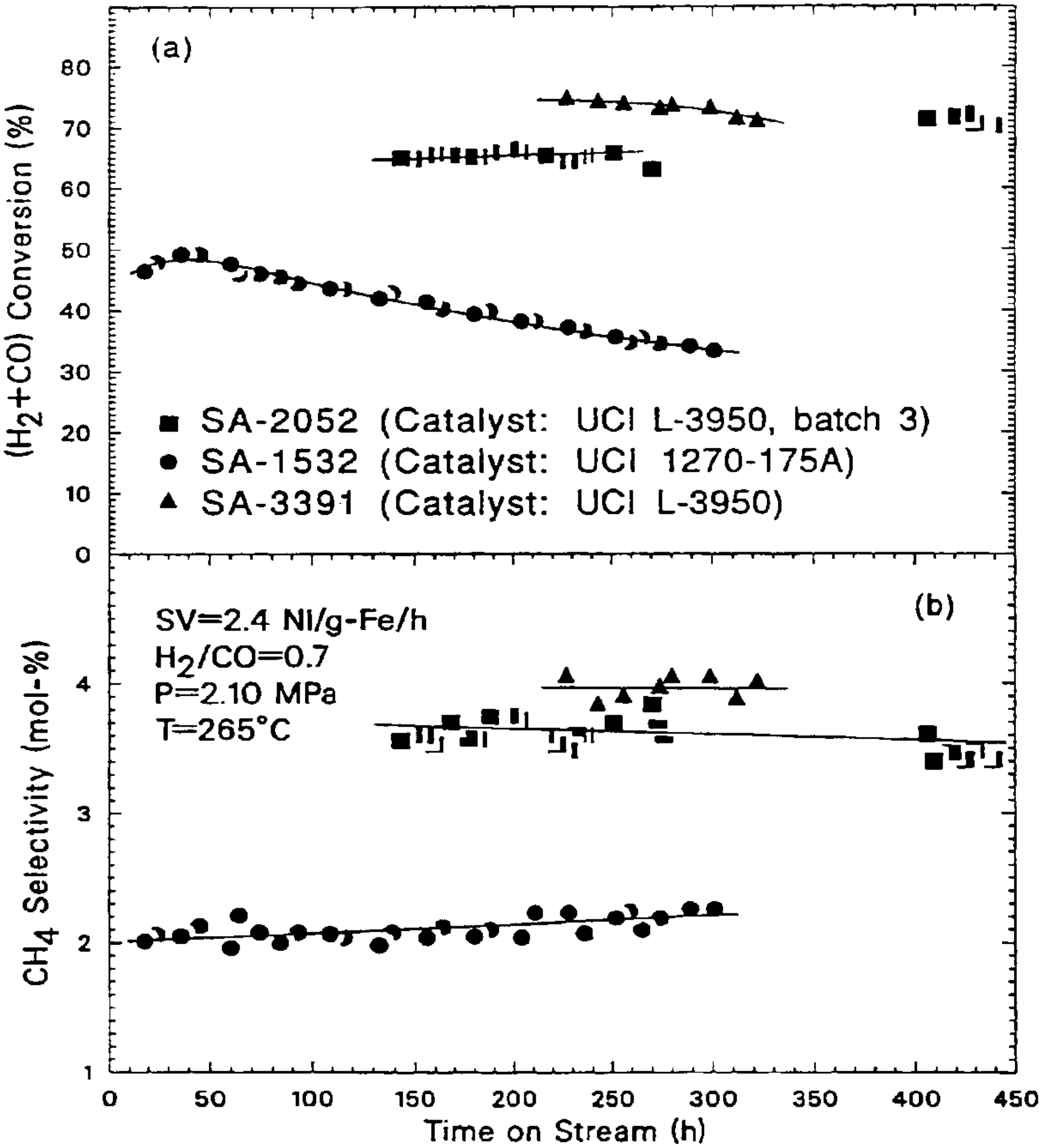

Figure IV-1.8 Effect of time on stream on (H_2+CO) conversion (a) and methane selectivity (b) for UCI catalysts.

the highest in test SA-3391, whereas the lowest syngas conversion was obtained in test SA-1532. Activities of these three catalysts are compared in Figure IV-1.9, in terms of values of apparent first order reaction rate constant evaluated at 260°C. The latter value was calculated from data at different temperatures by using the activation energy of 90 kJ/mol, which is a typical value for iron FT catalysts (Zimmerman and Bukur, 1990). These results show that the catalyst in Run SA-3391 was the most active, whereas the catalyst in Run SA-1532 was the least active. Also, both catalysts deactivated with time, whereas in Run SA-2052 the catalyst activity increased slightly with time. These data indicate that activity increases with the increasing silica and potassium contents of the catalyst (see Table IV-1.1). The most active catalyst (Run SA-3391) had the highest total surface area, but the activity in the other two tests does not correlate with the total surface area of the catalyst (Table IV-1.1). The apparent rate constants from two tests of the Ruhrchemie catalyst (Runs SA-0888 and SB-1370) are also shown in Figure IV-1.9 for comparison. Activity of the Ruhrchemie catalyst is markedly higher than that of the UCI catalysts, regardless of the pretreatment procedure employed (CO activation in test SA-0888, and H_2 reduction in SB-1370).

Values of the (H_2/CO) usage ratio and partial pressure quotient, K_p, provide information on relative rates of water-gas-shift reaction (lower usage ratios or higher values of K_p correspond to higher WGS activity). Catalyst used in Run SA-3391 had the highest WGS activity (UR = 0.56 - 0.62, K_p = 14 - 22), whereas the catalyst used in Run SA-2052 had the lowest WGS activity (UR = 0.61 - 0.70, K_p = 3.6 - 9). The WGS activity of the Ruhrchemie catalyst during testing at 1.48 MPa, 265°C, 3.8 Nl/g-Fe/h, H_2/CO = 0.67 was similar to that of the UCI catalysts (UR = 0.66, K_p = 4.4 - 11).

Variations of methane and hydrocarbon selectivities with time, for all three UCI catalysts, are shown in Figures IV-1.8b and IV-1.10, respectively. Catalyst with low silica and potassium contents, used in Run SA-1532, had the lowest methane and gaseous hydrocarbons selectivities. It favored the production of high molecular weight

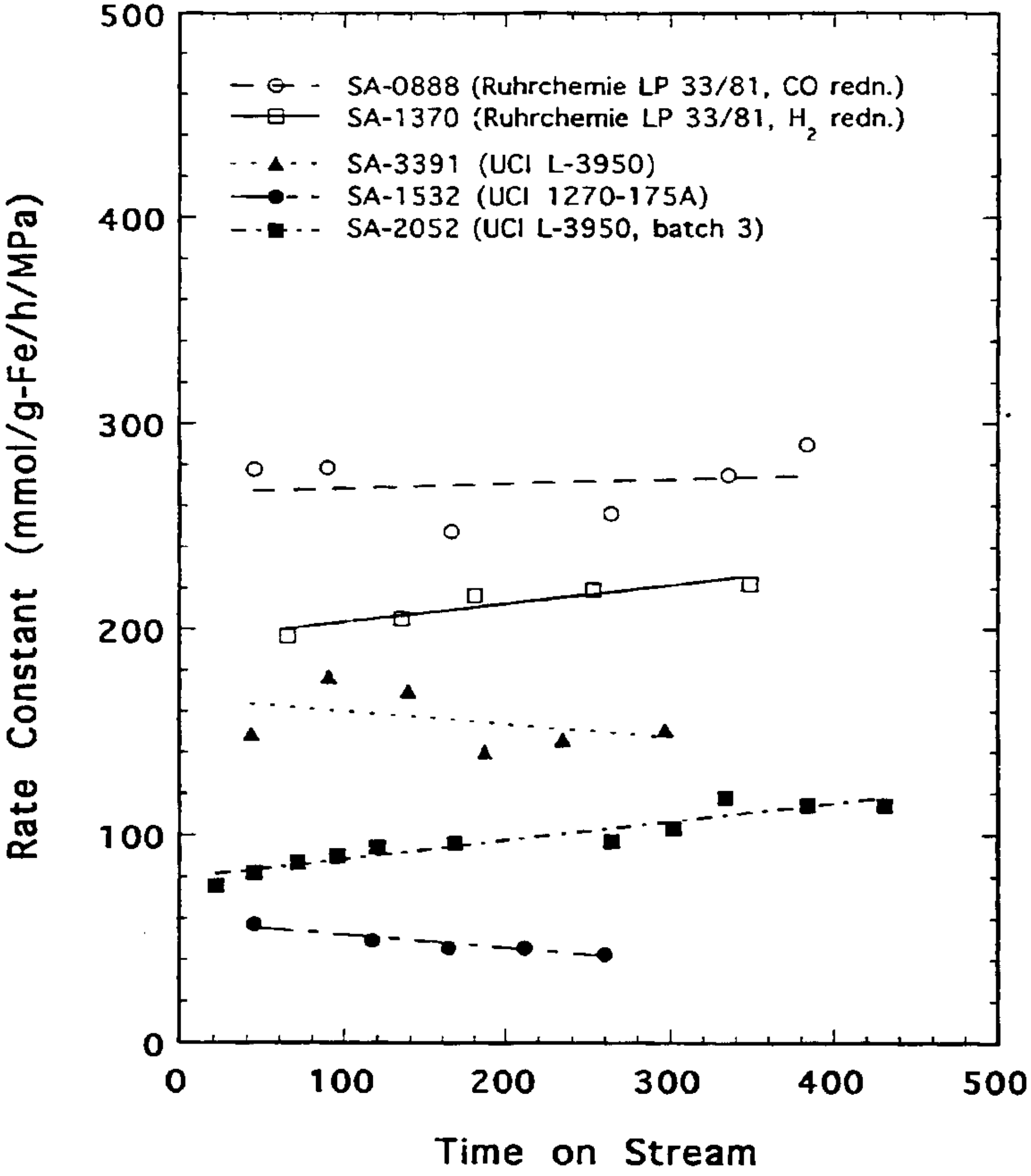

Figure IV-1.9 Apparent first order reaction rate constant of Ruhrchemie and UCI catalysts as a function of time on stream.

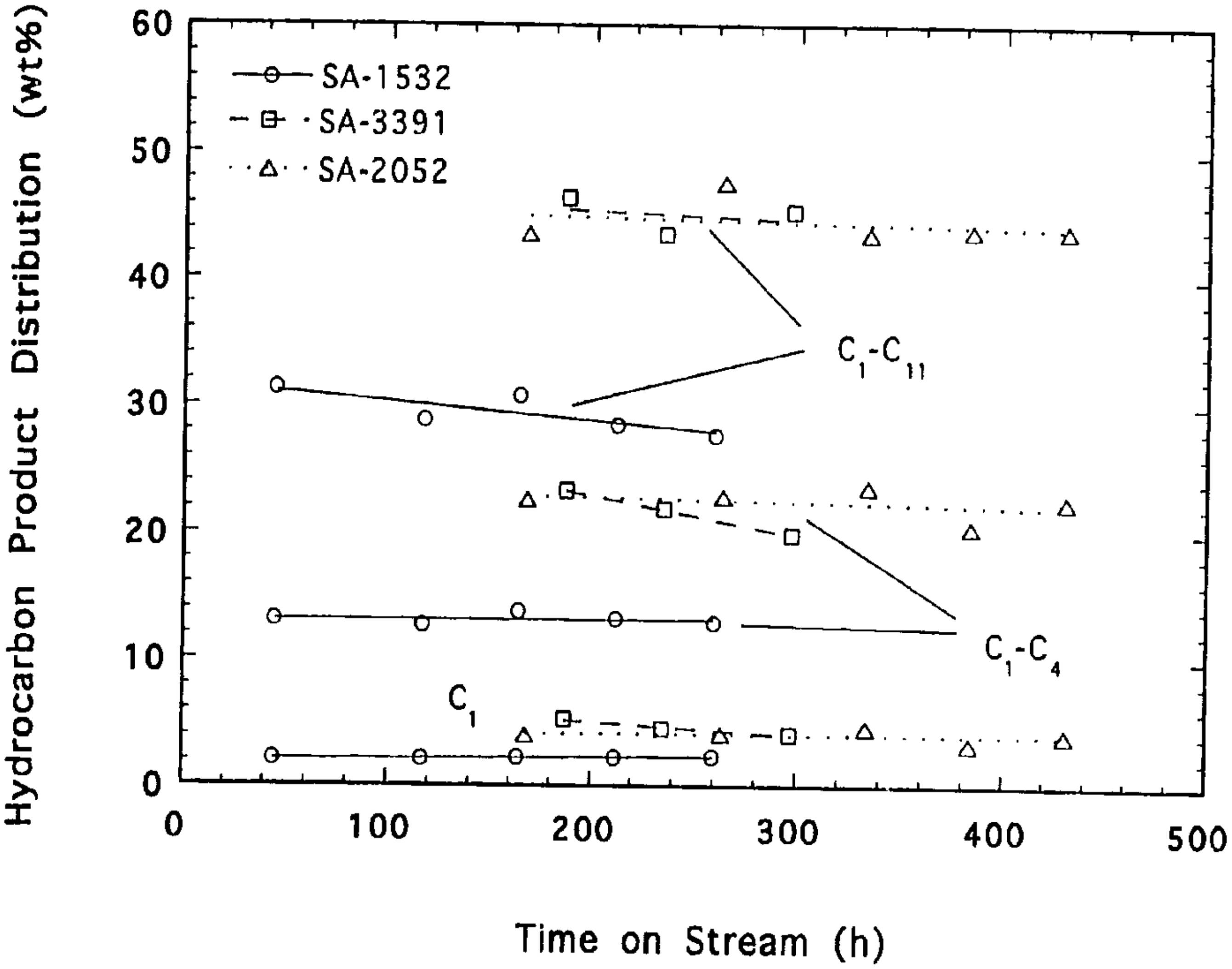

Figure IV-1.10 Comparison of hydrocarbon product distribution of UCI catalysts.

hydrocarbons (> 69 wt% of C_{12+} hydrocarbons), and its selectivity was fairly stable with time on stream. The other two catalysts, used in Runs SA-3391 and SA-2052, had similar selectivities. Methane selectivity was about 3.8 - 4 mol% (4.1 - 4.4 wt%), and C_{12+} selectivity varied between 52 and 56 wt%. The Ruhrchemie catalyst was tested under a different set of baseline process conditions (1.48 MPa, 250°C, 3.8 Nl/g-Fe/h, $H_2/CO = 0.67$) than the UCI catalysts. Average values of hydrocarbon selectivities obtained during the initial 360 h of testing at the baseline conditions are shown in Table IV-1.5. As can be seen the hydrocarbon selectivities in two tests of the Ruhrchemie catalyst were similar to those obtained in Runs SA-3391 and SA-2052. Results from testing of the Ruhrchemie catalyst at 265°C are also shown in this Table. In both tests there was a significant shift toward lower molecular weight hydrocarbons. Methane selectivity increased to : 6.0 wt% (SB-1370) and 7.0 wt% (SA-0888), whereas C_{12+} selectivity decreased to: 42.9 wt% (SB-1370) and 23.0 wt% (SA-0888). This shift toward low molecular weight products is not entirely due to higher reaction temperature, but also due to aging of the catalyst (See Section III-4 of this report) since data at 265°C were obtained at 570 - 590 h on stream.

Olefin hydrogenation activities of the UCI catalysts are compared in Figure IV-1.11. Olefin selectivities of the two catalysts used in Runs SA-3391 and SA-2052 were nearly the same, and followed the usual trend of declining selectivity with carbon number and relatively low ethylene selectivity (60 wt%). Low silica catalyst, used in Run SA-1532, had very high ethylene selectivity (85%) and higher olefin content in high molecular weight hydrocarbons (C_{11+} products) than the other two catalysts. Low hydrogenation activity of this catalyst is consistent with its low methane selectivity.

Comparison of olefin isomerization activity of the three catalysts at 164 - 187 h on stream is made in Figure IV-1.12. The 2-olefin selectivity of all three catalysts was rather low. Catalysts used in Runs SA-3391 and SA-2052 had similar 2-olefin selectivities, and the olefin isomerization activity increased with carbon number (C_{9+} products). The low

Table IV-1.5 Comparison of Slurry Reactor Test Results with UCI and Ruhrchemie Catalysts.

Run ID	SA-3391	SA-1532	SA-2052	SA-0888	SB-1370
Catalyst	UCI L-3950 (1309-37-1)	UCI 1207-175A	UCI L-3950 (batch 3)	Ruhrchemie	Ruhrchemie
Reduction Conditions	$H_2/CO=0.7$, 12 h 280°C	$H_2/CO=0.7$, 12 h 280°C	$H_2/CO=0.7$, 12 h 280°C	CO, 16 h 280°C	H_2, 1 h 220°C
TOS (h)	227-322	35-301	140-276, 401-444	0-343	0-360
%CO Conv.	73-80	35-52	68-75	40-43	34-39
%(H_2+CO) Conv.	71-75	33-49	65-72	43-46	38-41
Hydrocarbon Selectivities (wt-%):					
CH_4	4.4	2.3	4.1	4.7	4.5
C_2-C_4	16.5	10.7	18.5	20.6	15.5
C_5-C_{11}	23.6	16.2	22.4	23.2	27.7
C_{12+}	55.5	70.8	55.0	51.5	52.3

Test conditions for UCI Catalysts: 265°C, 2.10 MPa, 2.4 Nl/g-Fe/h, feed $H_2/CO=0.7$

Test conditions for Ruhrchemie Catalyst: 250°C, 1.48 MPa, 3.8 Nl/g-Fe/h, feed $H_2/CO=0.67$

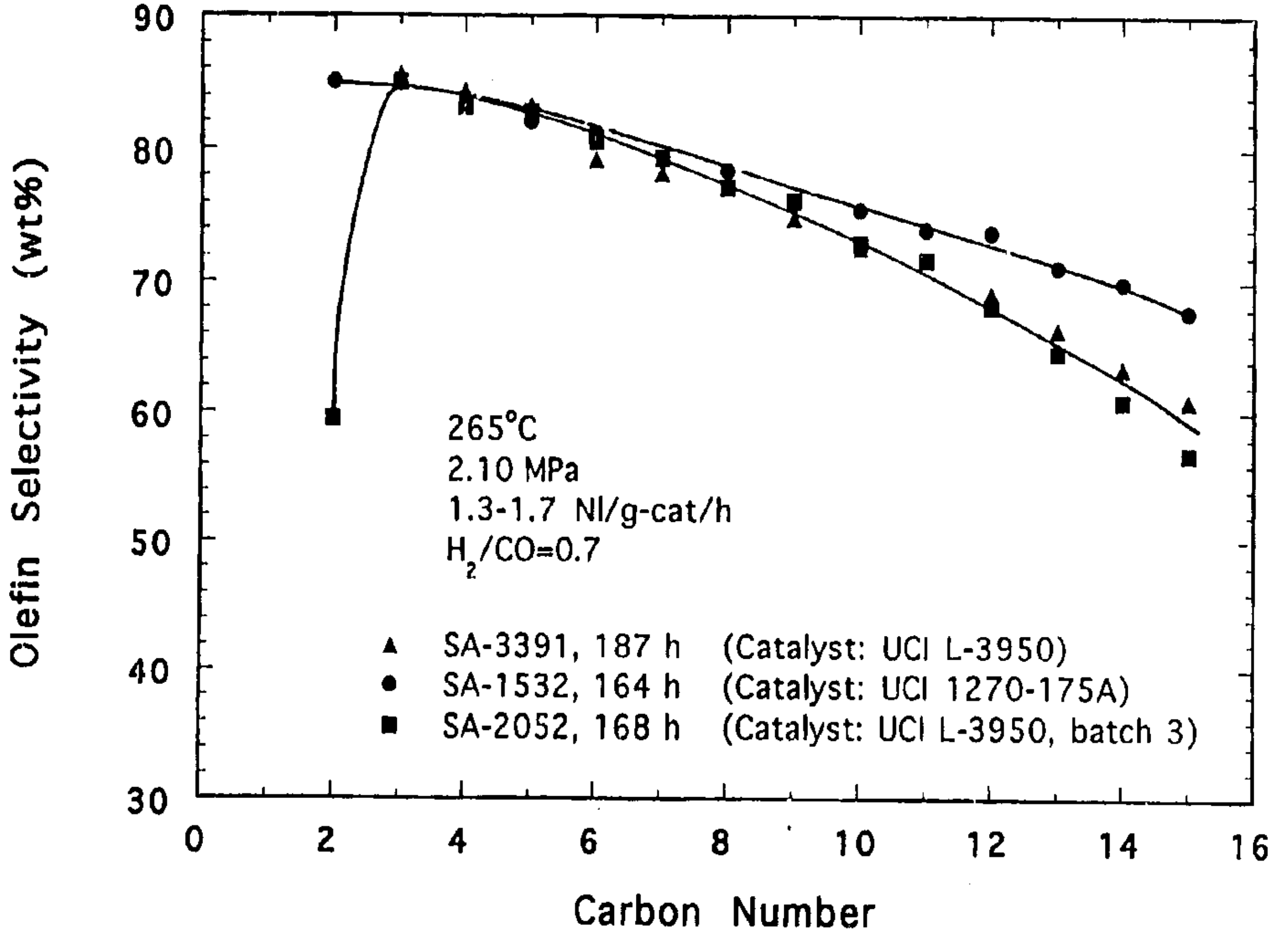

Figure IV-1.11 Comparison of olefin selectivities of UCI catalysts (time on stream 164 - 187 h).

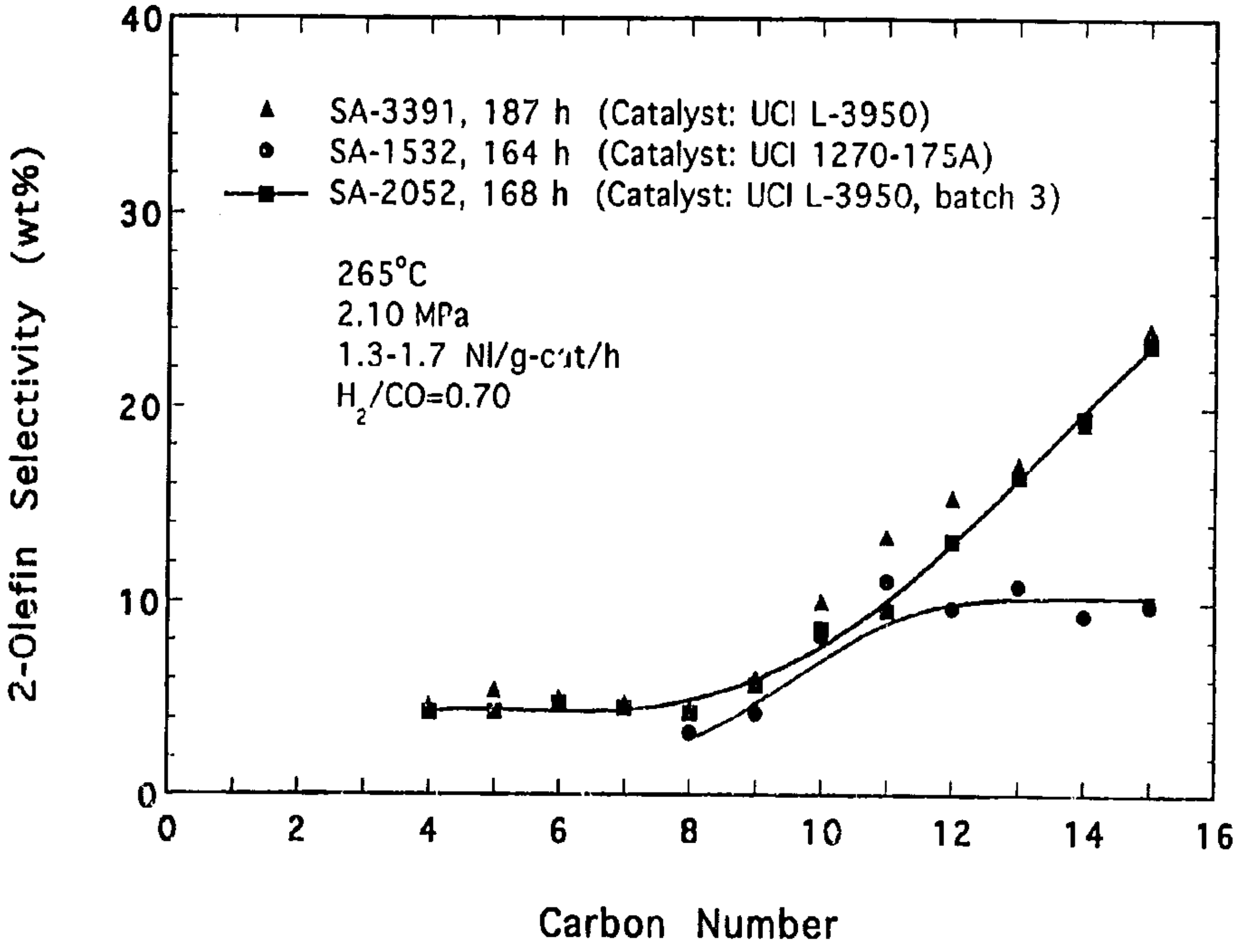

Figure IV-1.12 Comparison of 2-olefin selectivities of UCI catalysts (time on stream 164 - 187 h).

silica catalyst (SA-1532) had the lowest 2-olefin content , and the 2-olefin selectivity of C_{10+} olefins was fairly constant (~10%).

Olefin selectivities (total olefin content and 2-olefin content) of the Ruhrchemie catalyst during the first 150 h on stream were similar to those of the UCI catalysts used in Runs SA-3391 and SA-2052 (see Figures III-4.13 and 14, and Figures IV-1.11 and 12).

IV-1.3 Summary

Four catalysts prepared by two catalyst manufacturers (UCI and Ruhrchemie) were tested in stirred tank slurry reactors to determine their performance during Fischer-Tropsch synthesis. Precipitated iron was used as the active metal in all catalysts, and CuO, K_2O and SiO_2 were used as promoters. The amounts of promoters (in parts per weight per 100 parts of iron) in these four catalysts were as follows: SiO_2 = 4.1-25; K = 1.1-8.7 and Cu = 1.4 - 7.5. Total BET surface area varied between 136 and 290 m^2/g, and increased with the amount of silica, with the exception of two UCI catalysts having 4.1 and 9.2 g of SiO_2 per 100 g of Fe (see Table IV-1.1).

The Ruhrchemie and two of the UCI's catalysts (SA-3391 and SA-2052) had low deactivation rates, whereas the UCI catalyst with low silica content (SA-1532) deactivated more rapidly. The intrinsic activity of the low silica catalyst, measured by apparent first order reaction rate constant, was the lowest, whereas the Ruhrchemie catalyst had the highest activity (on per gram of iron basis). Activity of the Ruhrchemie catalyst was higher after CO pretreatment, than after hydrogen reduction. The intrinsic activity of catalysts correlates with total surface area, except for the UCI catalysts with 4.1 and 9.2 parts of SiO_2.

The low silica catalyst favored production of high molecular weight products. Methane selectivity in Run SA-1532 was only 2.2 - 2.4 wt%, and that of gaseous (C_2 - C_4) hydrocarbons 10 - 11 %. This catalyst also had low olefin hydrogenation and olefin isomerization activity. However, it was the least active and stable catalyst among the four catalysts tested. The Ruhrchemie and the other two UCI catalysts had similar hydrocarbon and olefin selectivities. Methane selectivity in tests with these three catalysts varied between 4.1 and 4.7 wt%, during the first 360 h of testing.

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