Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
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I. EXECUTIVE SUMMARY

Another slurry reactor run of the Ruhrchemie catalyst was conducted during this reporting period. The catalyst was reduced in situ with H_2 at $220^\circ C$ before exposure to the synthesis gas. The run was terminated voluntarily after 770 h on stream. During the first 350 h the catalyst was tested at baseline process conditions ($250^\circ C$, 200 psig, 2 Nl/g-cat/h, $H_2:CO = 2:3$) and it had excellent stability during this period of time. The (H_2+CO) conversion varied between 38 and 41%, and the hydrocarbon selectivity was also stable during this period: (CH_4) = 4.5; ($C_2 - C_4$) = 15.4; ($C_5 - C_{11}$) = 26.7, and $C_{12}^+ = 53.4$ wt.%. The process conditions were varied between 360 and 620 h on stream to investigate the effect of gas space velocity and reaction temperature on the catalyst activity and selectivity. When the baseline conditions were repeated (620 – 670 h) the (H_2+CO) conversion was 41%, i.e. no loss of activity occurred during the first 670 h on stream. There were no major operational problems during the run, and wax was removed periodically through an internal filter without any difficulties.

A screening test of a silica containing catalyst with a nominal composition (100 Fe/5 Cu/4.2 K/16 SiO_2) was made in a fixed bed reactor (Run FA-54-1580). The run was hampered by a variety of operational problems, and the catalyst deactivated with time on stream. The run was terminated voluntarily after 329 h of testing. In general, the methane selectivity was low (4-6 wt.%) and the initial activity was high (H_2+CO conversion of 70% at $235^\circ C$, 2 Nl/g-cat/h, 200 psig and $H_2/CO=1$). This catalyst will be evaluated in a slurry reactor.

Four catalysts have been synthesized (3 containing silica and one without) by continuous coprecipitation method. Two of the silica containing catalysts have been characterized by BET surface area measurement, and by atomic absorption to determine the actual bulk catalyst composition.

II. OBJECTIVE AND SCOPE OF WORK

The objective of proposed research is development of catalysts with enhanced slurry phase activity and better selectivity to fuel range products, through a more detailed understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (silica) on catalyst performance. In order to accomplish this objective, the work shall be divided into several tasks which are described in the following subsections.

Task 1 – Project Management

Within 60 days of project initiation, the contractor shall prepare and submit to the DOE Project Manager a detailed project work plan covering the entire period of performance of the project. The plan shall present, in detail, all activities that will be performed to successfully complete proposed research and its shall consist of the following: (1) detailed description of the methods and technical approach that shall be used to achieve the objectives of this project; (2) a detailed project schedule for each task or other logical segment of work to be performed; (3) graphs reflecting cumulative estimated costs and person-hours expended by month for each task or other logical segment of work, and for the total project effort; (4) a project work chart showing the key personnel/groups planned to work on each task and percentage of their time devoted to the tasks; and (5) a Work Breakdown Structure (WBS) dictionary to establish the framework for contract execution and to report cost schedule and technical performance.

All project status, milestone schedule, and cost management reports, as well as topical reports, if any, shall be submitted in accordance with the DOE reporting requirements.

Task 2 – Catalyst Pretreatment Research

This task is aimed at developing optimal pretreatment conditions for precipitated unsupported (1 catalyst) and supported (or silica containing; 1-2) iron catalyst, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity during Fischer-Tropsch (F-T) synthesis. This shall be accomplished by examining the effect of various activation conditions on physical and chemical properties of the catalyst as well as on catalytic behavior in fixed and slurry bed reactors. Parameters such as type of reductant (H_2 vs. CO vs. syngas), reductant flow rate, temperature and duration shall be studied. Selected catalysts shall be extensively characterized using a variety of physical, chemical and instrumental techniques with the objective to establish correlations between the physical/chemical properties of the catalysts and their observed catalytic behavior during F-T synthesis.

Task 3 – Improved Iron/Silica Catalysts

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst with composition $100 Fe/5 Cu/xK_2O/ySiO_2$ (in parts per weight). The effect of SiO_2 and K_2O on catalytic activity, selectivity and stability shall be determined to arrive at promoter/binder concentrations for an improved catalyst performance. The screening tests shall be conducted in fixed bed reactors to obtain preliminary indication of F-T activity and selectivity at different process conditions. Catalysts which show enhanced activity and/or selectivity towards transportation fuels shall be tested in slurry reactors up to 30 days on stream. Selected catalysts shall be extensively characterized, to determine relations between the physico-chemical properties of catalyst and their catalytic behavior during F-T synthesis.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III-1. Task 2. Catalyst Pretreatment Research

III-1.1 Run SB-99-1370 with the Ruhrchemie Catalyst

This was a repetition of the earlier test SB-99-0440 (Quarterly Technical Progress Report for Jan. – March, 1990), with the exception that the catalyst reduction was conducted in-situ with H_2 at 220°C.

The catalyst was tested initially (first 360 h) at 250°C, 200 psig, 2 NI/g-cat/h using the synthesis gas with (H_2/CO) molar feed ratio of about 0.65. Following the stability portion of the test the process conditions were varied between 360 and 620 h on stream (mass balances 6-9). The baseline conditions were repeated in balances 10 and 11 (620 – 670 h), and then the (H_2/CO) feed ratio was changed to 1 (balances 12 and 13, 670 – 770 h). The run was terminated voluntarily after 770 h on stream. Results from thirteen mass balances conducted during this period of time are summarized in Table 1.

Catalyst Activity and Stability

The catalyst activity reached the steady state after about 40 h on stream, as shown in Figures 1 and 2 (volumetric contraction or (H_2+CO) conversion versus time on stream). The catalyst was very stable, and it had not deactivated during the process variable studies. The catalyst activity at 620 – 670 h on stream was essentially the same as that observed during the first 360 h on stream (baseline process conditions). These results are in general agreement with those obtained in our earlier tests of the same catalyst (Runs SA-99-0888, and SB-99-0440), i.e. the Ruhrchemie catalyst has excellent stability but its activity is rather low relative to unsupported precipitated iron catalysts.

Wax and Catalyst Inventories

A total of ten wax withdrawals were made during the run through a 10 μ m cylindrical filter element. Results from all withdrawals are summarized in Table 2, whereas other major events during the run are listed in Table 3.

There were no operational problems during wax withdrawals, and in particular we have not experienced any loss in activity following wax withdrawals. The wax collected was clear in appearance, which is an indication that catalyst particles did not pass through the filter during wax withdrawals.

At the end of the run (after separation from wax, washing and burning in air) 26.2 g of the catalyst was recovered (~87% of the amount charged). It should be noted that the catalyst charged to the reactor (30 g was not dried, and it contained about 12% of moisture (This was determined after the run using fresh catalyst). After correction for the moisture adsorbed on the catalyst the recovery was 99%. The wax recovery was 80.3%.

Catalyst Selectivity

We have not encountered problems with liquid product collection, loss due to evaporation or other experimental artifacts. However, we have encountered some problems with product analysis by gas chromatography during the latter portion of the run (balances 9-13), and thus some of the results reported here need to be treated with caution.

Hydrocarbon product distribution was very stable during the first 360 h on stream (balances 1-5), and the average values for CH_4 and product groups lumped according to carbon numbers were: $(\text{CH}_4) = 4.5$; $(\text{C}_2 - \text{C}_4) = 15.4$; $(\text{C}_5 - \text{C}_{11}) = 26.7$; and $\text{C}_{12}^+ = 53.4$ wt.%. The baseline conditions were repeated in balances 10 and 11. Hydrocarbon selectivities in balance 10 were not accurate (see Table 1); too low CH_4 and C_{12}^+ products. Atomic closures and product yields obtained in mass balance 11 were good, and thus the hydrocarbon selectivity from this balance may be compared to that obtained in balances 1-5. Methane selectivity remained

unchanged (662 h vs. 65-349 h on stream), but the selectivity of ($C_2 - C_4$) and ($C_5 - C_{11}$) hydrocarbons increased, whereas the selectivity of C_{12}^+ products decreased with time on stream.

Carbon number distribution is shown in Figures 3 and 4 for data from mass balances 4 and 13, respectively. In both balances there were no significant deviations from classical Anderson-Schulz-Flory distribution for products in $C_1 - C_{10}$ carbon number range, confirming that there were no problems with product collection, handling and analysis. It is obvious that the double alpha phenomena would have been observed, if the wax produced were analyzed. The tailing off of products with increasing carbon number is due to accumulation of high molecular weight products in the reactor.

In general, the methane selectivity during this test was rather low (3-6%), which is consistent with results obtained in the previous two slurry reactor tests of the same catalyst (Runs SA-99-0888 and SB-99-0440).

III-2. Task 3. Improved Iron/Silica Catalysts

III-2.1 Run FA-64-1580 with the 100 Fe/5 Cu/4.2 K/16 SiO₂

This was a screening test of a silica containing catalyst in a fixed bed reactor. The catalyst was reduced in H_2 at 220°C for 1 h before exposure to the synthesis with $H_2:CO$ feed ratio of 1:1. Nine mass balances were performed during this run and results are summarized in Table 4. The test was terminated voluntarily after 325 h on stream. This test was hampered by a variety of operational problems (frequent flow stoppages, failure of electrical heaters, drift in mass flow meter calibration), some of which were caused by inexperienced operators. In some balances there were significant losses of the liquid products collected, and performance of the Carle GC was erratic throughout the entire test. As a result of these adverse factors the mass balance closures were not good in several balances. The worst mass balance closures were 78.6 and 111.5%, and they were obtained in balances 5 and 3, respectively. In view of the above we do not consider hydrocarbon selectivities reported in Table 4, to be reliable enough for assessment of the catalyst performance.

Initial catalyst activity was rather high, e.g. the (H_2 +CO) conversion was about 70% during the first 60 h on stream, whereas the volumetric contraction was about 49%. However, after several flow interruptions, which occurred between 70 and 90 h, the (H_2 +CO) conversion dropped to 60% in balance 1 (TOS = 93 h). After this, the process conditions were varied (balances 2-5; 104-210 h on stream) and the baseline conditions were repeated in balance 6 (240 h). The (H_2 +CO) conversion was only 32.4%, indicating that the catalyst had deactivated.

In balances 7-9 the synthesis gas with H_2 :CO feed ratio of 2:3 was used, and testing was performed under a fixed set of process conditions (250°C, 2 Nl/g-cat/h, and 200 psig). The catalyst activity was fairly stable during this period of time (275-330 h), and (H_2 +CO) conversion was about 47%.

Selectivities of methane and light gases ($\text{C}_2 - \text{C}_4$) were rather low in general and its initial activity was high. We plan to evaluate this catalyst in a slurry reactor during the next quarter.

III-2.2 Catalyst Characterization

Two silica containing catalysts have been analyzed by atomic absorption analysis using a Varian Spectra AA 30 absorption spectrophotometer. Samples were dissolved in a nitric acid before the analysis. Silica is not soluble in this acid, and its concentration was determined by weighing the amount of solid material not dissolved in the acid. The intended nominal and actual analyzed compositions of each sample are summarized below:

<u>Nominal Composition</u>	<u>Actual Composition</u>
(100 Fe/5 Cu/4.2 K/8 SiO_2)	(100 Fe/5.2 Cu/4.4 K/6.7 SiO_2)
(100 Fe/5 Cu/4.2 K/16 SiO_2)	(100 Fe/4.1 Cu/5.3 K/19.7 SiO_2)

As can be seen the analyzed contents of copper, potassium and silica are within acceptable limits relative to their expected (nominal) values.

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The two silica containing catalysts were also characterized by BET surface area measurement before and after calcination in air at 300°C for 5 h. Results are summarized in Table 5. The total surface areas are essentially independent of silica content of catalyst, and they decrease slightly after thermal treatment at 300°C.

III-2.3 Catalyst Synthesis

We have synthesized four catalysts using the controlled-pH, continuous precipitation that has been described in our previous reports. Three silica containing catalysts (30-40 g of each), and a (100 Fe/0.3 Cu/0.8 K) catalyst (~80 g) were synthesized during the current reporting period, and they will be tested first in fixed bed reactors.

III-3. Product Analysis by Gas Chromatography (Tasks 2 and 3)

A new capillary column RSL-160 (Alltech Associates) has been used successfully to analyze both the tail gas and the aqueous phase products of Fischer-Tropsch synthesis on Varian 3400 gas chromatography equipped with an FID detector.

Injections of aqueous phase products from slurry reactor run SB-99-1370, balance 13, showed good agreement between the Varian analysis and the Sigma 1B (packed column) for the major components (see Table 6), whereas selectively large differences were noted for minor components in the mixture.

Using tail gas samples from the slurry bed run SB-99-1370, balance 6, injections were made on the Varian and Sigma 1B. A comparison of results between the two analysis is given in Table 7. Again, the agreement is very good for the major components, whereas larger differences occur for minor components. A capillary column (Varian GC) gives better separation than the packed column (Sigma 1B) for higher hydrocarbons. However, we were not able to obtain separation of C₃ hydrocarbons (propane and propylene) on the capillary column.

Based on these and other results (not presented here), we plan to use the RSL-160 column for analysis of tail gas and aqueous phase products in the future.

Table 1. Summary of results for slurry run SB-99-1370.

Slurry liquid: 330.0 g, n-C28

Catalyst: 30.00 g^a, LP 33/81Reactor volume: 430. cc^b

Period	1	2	3	4	5	6	7
Date	05/20/90	05/23/90	05/25/90	05/29/90	06/01/90	06/03/90	06/06/90
Time on Stream (h)	65.0	134.5	181.0	253.0	349.0	402.0	470.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	250.	250.	250.	250.	250.	250.	235.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.620	.702	.612	.651	.651	.667	.608
Space Velocity (NI/g-cat·h) ^a	2.00	2.00	2.00	2.00	2.00	1.07	2.00
Space Velocity (NI/g-Fe·h)	3.81	3.81	3.81	3.81	3.81	2.03	3.81
GHSV (h ⁻¹) ^b	140.	140.	140.	140.	140.	74.5	140.
CO Conversion (%)	34.0	34.2	39.0	38.8	38.3	53.2	16.5
H ₂ +CO Conversion (%)	37.9	37.9	40.8	39.8	39.3	58.6	20.2
H ₂ /CO Usage	.805	.888	.689	.692	.695	.836	.970
STY (mols H ₂ +CO/g-cat·h) ^a	.034	.034	.036	.035	.035	.028	.018
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	4.25	2.83	3.13	3.00	2.42	2.58	.874
Weight % of Outlet							
H ₂	2.36	2.62	2.34	2.58	2.62	1.41	3.06
H ₂ O	1.22	2.08	1.97	2.30	2.65	2.93	2.38
CO	62.5	60.1	57.7	57.3	58.3	41.2	79.4
CO ₂	24.1	23.8	26.8	27.0	25.1	38.8	9.49
Hydrocarbons	6.93	8.39	8.24	8.69	9.20	12.9	4.76
Oxygenates	.221	.325	.300	.381	.420	.540	.312
Wax ^c	2.66	2.69	2.64	1.69	1.70	2.20	.612
Yield (g/Nm ³ H ₂ + CO Converted)							
CH ₄	8.16	10.8	9.56	10.6	9.95	8.37	6.14
C ₂ -C ₄ Hydrocarbons	31.6	33.1	34.5	32.4	37.5	33.4	39.5
C ₅ -C ₁₁ Hydrocarbons	53.2	59.7	67.3	58.1	64.6	69.7	96.6
C ₁₂ + Hydrocarbons	113.	131.	107.	110.	110.	108.	74.8
Wax ^c	57.2	57.1	53.1	34.4	34.8	31.9	24.7
Oxygenates	4.74	6.89	6.03	7.74	8.58	7.84	12.6
Total	211.	242.	225.	219.	231.	227.	230.
1+2 Olefins/n-Paraffin Ratio							
C ₂	1.14	1.88	1.66	1.60	1.56	1.06	2.56
C ₃	4.55	5.84	6.14	5.18	5.51	5.56	5.40
C ₄	4.72	5.46	5.43	5.24	5.36	5.24	4.98
C ₈	2.61	3.69	3.22	2.91	2.85	2.54	2.32
C ₁₀	2.32	2.58	2.50	2.37	2.41	2.11	1.61

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

Table 1 (cont'd). Summary of results for slurry run SB-99-1370 .

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH ₄	3.95	4.60	4.37	5.03	4.47	3.82	2.83
Ethane	.931	1.55	1.73	1.83	2.00	1.92	1.51
Ethylene	.987	2.71	2.69	2.73	2.91	1.90	3.50
Propane	.928	.716	.790	.882	.935	.886	1.06
Propylene	4.03	3.99	4.63	4.36	4.91	4.70	5.48
n-Butane	.795	.809	.912	.876	.948	.917	1.07
1+2 Butenes	3.62	4.26	4.77	4.43	4.91	4.64	5.16
C ₄ Isomers	4.04	.0373	.239	.230	.269	.256	.320
n-Pentane	.888	.941	1.04	.983	1.04	1.04	1.15
1+2 Pentenes	4.59	4.90	5.49	5.11	4.79	4.45	5.01
C ₆ Isomers	.400	.325	.347	.353	.409	.392	.471
n-Hexane	.794	.821	1.15	1.08	1.13	1.07	1.16
1+2 Hexenes	3.04	3.54	3.97	3.59	3.94	3.40	3.98
C ₆ Isomers	.0821	.530	.458	.402	.546	.435	.773
n-Heptane	.926	.626	.941	.814	.878	.944	.816
1+2 Heptenes	2.27	2.46	3.06	2.51	2.87	2.35	2.67
C ₇ Isomers	.270	.355	.476	.381	.282	.459	1.53
n-Octane	.876	.571	.838	.772	.836	1.11	1.27
1+2 Octenes	2.25	2.07	2.65	2.21	2.34	2.78	2.89
C ₈ Isomers	.0628	.190	.116	.103	.231	.281	.0557
n-Nonane	.673	.560	.805	.718	.739	1.06	2.46
1+2 Nonenes	1.90	1.56	2.18	1.83	1.92	2.47	4.45
C ₉ Isomers	.0462	.0451	.0702	.0847	.0874	.140	1.55
n-Decane	.973	.771	1.02	.923	.973	1.36	3.31
1+2 Decenes	2.23	1.96	2.53	2.16	2.31	2.82	5.27
C ₁₀ Isomers	.104	.0618	.0911	.111	.117	.149	.0879
n-Undecane	1.02	.923	1.08	1.07	1.10	1.67	2.60
1+2 Undecenes	1.98	2.09	2.38	2.21	2.35	3.18	2.93
C ₁₁ Isomers	.425	.0875	.0928	.123	.130	.178	.0803
C ₂ -C ₄	15.3	14.1	15.8	15.3	16.9	15.2	18.2
C ₅ -C ₁₁	25.8	25.4	30.8	27.5	29.0	31.8	44.5
C ₁₂ +	54.9	55.9	49.1	52.1	49.6	49.2	34.5
Wax ^c	27.7	24.3	24.3	16.3	15.6	14.6	11.4

^c Unanalyzed wax withdrawn from reactor

Table 1 (cont'd). Summary of results for slurry run SB-99-1370.

Catalyst: 30.00 g^a, LP 33/81

Slurry liquid: 330.0 g, n-C28

Reactor volume: 430. cc^b

Period	8	9	10	11	12	13
Date	06/08/90	06/11/90	06/13/90	06/14/90	06/16/90	06/18/90
Time on Stream (h)	519.0	589.0	638.0	662.0	710.0	758.0
Balance Duration (h)	6.0	6.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	258.	265.	250.	250.	250.	250.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.610	.636	.636	.600	1.00	1.12
Space Velocity (NI/g-cat.h) ^a	2.00	2.00	2.00	2.00	2.00	2.00
Space Velocity (NI/g-Fe.h)	3.81	3.81	3.81	3.81	3.81	3.81
GHSV (h ⁻¹) ^b	140.	140.	140.	140.	140.	140.
CO Conversion (%)	49.4	59.1	38.9	37.5	49.3	52.6
H ₂ +CO Conversion (%)	49.5	60.3	41.7	40.0	51.5	49.0
H ₂ /CO Usage	.614	.668	.751	.707	1.09	.976
STY (mols H ₂ +CO/g-cat.h) ^a	.044	.054	.037	.036	.046	.044
P _{CO₂} : P _{H₂} / P _{CO} : P _{H₂O}	4.57	11.2	4.18	3.18	3.71	4.01
Weight % of Outlet						
H ₂	2.13	1.61	2.23	2.27	2.86	3.96
H ₂ O	1.91	.968	1.45	1.91	3.49	4.14
CO	48.7	37.9	55.2	58.7	43.4	42.7
CO ₂	35.1	44.8	26.4	27.7	34.6	31.5
Hydrocarbons	11.0	12.5	13.8	8.37	12.8	14.1
Oxygenates	.401	.349	.374	.407	.853	1.45
Wax ^c	.782	1.90	.591	.601	1.94	2.17
Yield (g/Nm ³ H ₂ + CO Converted)						
CH ₄	9.44	11.9	7.46	8.33	12.5	9.41
C ₂ -C ₄ Hydrocarbons	40.4	39.6	92.1	47.3	48.6	40.6
C ₅ -C ₁₁ Hydrocarbons	66.9	61.1	127.	74.1	69.1	70.6
C ₁₂ + Hydrocarbons	74.7	84.7	66.4	57.0	79.0	95.7
Wax ^c	12.7	26.0	12.0	12.5	27.5	28.9
Oxygenates	6.53	4.79	7.60	8.48	12.1	19.3
Total	198.	202.	301.	195.	221.	236.
1+2 Olefins/n-Paraffin Ratio						
C ₂	1.05	.136	.0152	2.28	1.07	.740
C ₃	5.23	4.29	5.00	5.68	4.34	3.99
C ₄	4.99	4.39	4.88	4.98	3.73	3.63
C ₅	2.50	1.95	1.74	2.13	1.63	1.60
C ₁₀	2.00	1.61	1.92	2.02	1.45	1.38

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

Table 1 (cont'd). Summary of results for slurry run SB-99-1370 .

Period	8	9	10	11	12	13
Weight % of Hydrocarbons						
C114	4.93	6.04	2.55	4.46	5.98	4.35
Ethane	2.49	2.96	20.9	2.56	3.35	2.79
Ethylene	2.43	.377	.297	5.44	3.35	1.93
Propane	1.32	1.62	.889	1.36	1.64	1.52
Propylene	6.58	6.63	4.24	7.38	6.79	5.78
n-Butane	1.36	1.55	.841	1.40	1.66	1.41
1+2 Butenes	6.54	6.55	3.97	6.74	5.99	4.95
C ₄ Isomers	.368	.365	.272	.454	.444	.382
n-Pentane	1.70	1.78	.904	1.51	1.75	1.30
1+2 Pentenes	6.47	5.57	3.61	6.08	4.80	3.98
C ₆ Isomers	.620	.563	.377	.667	.600	.322
n-Hexane	1.34	.737	3.02	1.62	2.18	1.20
1+2 Hexenes	4.67	2.62	8.69	4.80	4.32	3.30
C ₆ Isomers	.895	1.01	1.37	1.22	.659	.496
n-Heptane	1.14	.843	1.99	1.18	1.41	1.28
1+2 Heptenes	3.43	1.43	6.19	2.82	2.72	2.20
C ₇ Isomers	.359	.178	1.23	.894	.409	.274
n-Octane	1.17	1.13	3.52	.960	1.36	1.51
1+2 Octenes	2.87	2.17	6.01	2.01	2.18	2.38
C ₈ Isomers	.280	.113	.136	.0787	.419	.138
n-Nonane	.978	1.52	.572	.604	1.05	1.63
1+2 Nonenes	2.12	2.67	1.22	1.31	1.68	2.49
C ₉ Isomers	.168	.228	.0587	.0908	1.52	.245
n-Decane	1.09	1.63	.744	.750	1.17	1.87
1+2 Decenes	2.15	2.58	1.41	1.50	1.67	2.54
C ₁₀ Isomers	.181	.212	.0782	.0930	.186	.275
n-Undecane	1.16	1.62	.821	.839	1.25	2.21
1+2 Undecenes	1.96	2.20	1.33	10.5	1.51	2.69
C ₁₁ Isomers	.177	.183	.0921	.102	.182	.312
C ₂ -C ₄	21.1	20.1	31.4	25.3	23.2	18.8
C ₅ -C ₁₁	34.9	31.0	43.4	39.7	33.0	32.6
C ₁₂ +	39.0	42.9	22.7	30.5	37.8	44.2
Wax ^c	6.65	13.2	4.10	6.70	13.1	13.4

^c Unanalyzed wax withdrawn from reactor

Table 2. Wax and Solids inventory for run SB-99-1370

TOS(h)	Event
	Reactor Charged with: 300 g n-octacosane 30.0 g catalyst
-1	Wax removed after reduction: 75.7 g
114	Wax removed using internal filter: 130.6 g
188	Wax removed: 99.1 g
356	Wax removed: 135.0 g
445	Wax removed: 50.0 g
476	Wax removed: 7.9 g
525	Wax removed: 17.4 g
596	Wax removed: 64.0 g
668	Wax removed: 20.0 g
765	Wax removed: 80.0 g
770	End of run: 203.8 g-wax, 26.2 g-catalyst removed wax recovery: 80%; catalyst recovery 87%

Table 3. Major events occurring in run SB-99-1370

TOS(h)	Event
-3	Catalyst pretreatment in situ, using H ₂ at 220°C
0	Initiated synthesis gas (H ₂ /CO=0.67)
3	Achieved desired operating conditions: 250°C, 1.48 MPa, (H ₂ /CO)=0.67, 2.0 nl/g-cat/h
65	Conditions stable, (H ₂ +CO)-conversion: 37.9%
402	Changed process conditions: 260°C, 1.48 MPa, (H ₂ /CO)=0.67, 1.0 NI/g-cat/h
420	4 h TOS break for feed flow checking
470	Changed process conditions: 235°C, 1.48 MPa, (H ₂ /CO)=0.67, 2.0 NI/g-cat/h
519	Changed process conditions: 258°C, 1.48 MPa, (H ₂ /CO)=0.67, 2.0 NI/g-cat/h
589	Changed process conditions: 265°C, 1.48 MPa, (H ₂ /CO)=0.67, 2.0 NI/g-cat/h
638	Replication of initial process conditions: (H ₂ +CO) conversion=41.7%
662	Conditions stable, (H ₂ +CO) conversion=40.0%
710	Changed process conditions: 250°C, 1.48 MPa, (H ₂ +CO)=1.0, 2.0 NI/g-cat/h
758	Conditions stable, (H ₂ +CO) conversion=49.0%
770	Voluntary termination of run SB-99-1370

Table 4. Summary of results for fixed bed run FA-64-1580 .

Catalyst: 3.50 g^a, 100Fe/5Cu/4.2K/16 SiO₂
 Catalyst volume: 5.40 cc
 Diluent: 36.70 g, Glass beads
 Diluent Volume: 24.00 cc

Period	1	2	3	4	5
Date	06/11/90	06/13/90	06/14/90	06/15/90	06/16/90
Time on Stream (h)	92.7	125.8	156.7	175.5	204.0
Balance Duration (h)	12.0	6.0	6.0	6.0	6.0
Average Temperature (°C)	235.	235.	248.	220.	235.
Maximum Δ Temperature (°C) ^b	-3.00	-3.00	8.30	2.00	7.00
Pressure (MPa)	1.48	1.48	1.48	1.48	2.17
H ₂ /CO Feed Ratio	1.00	1.00	1.00	1.00	1.00
Space Velocity (NI/g-cat-h) ^a	2.00	3.99	4.00	1.15	3.00
Space Velocity (NI/g-Fe-h)	3.40	6.80	6.81	1.96	5.10
GHSV (h ⁻¹) ^c	238.	475.	476.	137.	357.
CO Conversion (%)	60.2	18.2	40.8	29.1	41.4
H ₂ +CO Conversion (%)	59.7	23.5	36.0	26.9	32.4
H ₂ /CO Usage	.982	1.58	.764	.845	.564
STY (mols H ₂ +CO/g-cat-h) ^a	.053	.042	.064	.014	.043
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	4.33	4.56	5.98	5.09	1.05
Weight % of Outlet					
H ₂	2.54	4.29	4.69	4.92	6.55
H ₂ O	4.07	1.30	2.23	1.99	4.06
CO	34.3	68.4	56.0	64.3	69.5
CO ₂	42.0	16.6	28.0	23.2	7.99
Hydrocarbons	6.53	6.65	4.59	4.17	6.84
Oxygenates	.723	.397	.301	.261	.476
Wax ^d	9.84	2.35	4.12	1.14	4.55
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	12.1	21.7	9.63	14.1	3.07
C ₂ -C ₄ Hydrocarbons	33.3	76.3	43.9	47.7	49.1
C ₆ -C ₁₁ Hydrocarbons	32.1	102.	30.0	41.9	52.5
C ₁₂ + Hydrocarbons	121.	86.0	76.1	32.4	80.2
Wax ^d	119.	74.8	75.5	29.2	73.8
Oxygenates	8.76	12.6	5.52	6.68	7.73
Total	207.	299.	165.	143.	193.
1+2 Olefins/n-Paraffin Ratio					
C ₂	.656	.0463	4.88	5.29	4.63
C ₃	3.36	3.38	4.43	3.53	1.10
C ₄	3.05	3.02	3.62	2.85	2.77
C ₆	.981	5.27	3.75	3.75	2.93
C ₁₀	1.66	.900	.793	.793	1.25

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 4 (cont'd). Summary of results for fixed bed run FA-64-1580.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	6.10	7.59	6.03	10.4	1.66
Ethane	2.05	15.2	2.03	2.64	3.15
Ethylene	1.25	.655	9.25	13.1	13.6
Propane	1.75	1.36	1.67	2.36	2.62
Propylene	5.62	4.39	7.04	7.96	2.75
n-Butane	1.39	1.12	1.48	1.98	1.03
1+2 Butenes	4.10	3.26	5.16	5.44	2.75
C ₄ Isomers	.625	.679	.855	1.62	.704
n-Pentane	1.27	1.09	2.74	1.80	1.18
1+2 Pentenes	3.39	2.86	4.77	4.49	2.84
C ₅ Isomers	.548	.546	.842	1.01	.608
n-Hexane	.252	3.48	1.84	2.71	2.16
1+2 Hexenes	2.99	8.87	3.25	4.60	4.74
C ₆ Isomers	.404	1.29	.828	1.82	2.35
n-Heptane	.829	1.44	.0443	2.48	1.32
1+2 Heptenes	2.04	5.92	2.69	3.57	3.21
C ₇ Isomers	.379	1.92	.631	.755	1.86
n-Octane	1.03	.256	.0430	.276	.341
1+2 Octenes	.991	1.32	.158	1.01	.982
C ₈ Isomers	.0174	.00000	.00122	.00782	.0473
n-Nonane	.232	.768	.129	.830	.732
1+2 Nonenes	.421	1.10	.173	1.11	1.23
C ₉ Isomers	.0356	.00000	.00736	.0472	.204
n-Decane	.267	1.36	.196	1.26	.998
1+2 Decenes	.437	1.21	.153	.981	1.23
C ₁₀ Isomers	.0402	.00000	.0137	.0877	.246
n-Undecane	.226	1.19	.171	1.10	.925
1+2 Undecenes	.319	1.14	.110	.703	.957
C ₁₁ Isomers	.0426	.00000	.0187	.120	.217
C ₁₂ -C ₁₄	16.8	26.6	27.5	35.1	26.6
C ₁₅ -C ₁₁	16.2	35.8	18.8	30.8	28.4
C ₁₂ +	60.9	30.0	47.7	23.8	43.4
Wax ^d	60.1	26.1	47.3	21.5	39.9

^d Unanalyzed products collected from hot trap

Table 4 (cont'd). Summary of results for fixed bed run FA-64-1580 .

Catalyst: 3.50 g^a, 100Fe/5Cu/4.2K/
Catalyst volume: 5.40 cc
Diluent: 36.70 g, Glass beads
Diluent Volume: 24.00 cc

Period	6	7	8	9
Date	06/17/90	06/18/90	06/20/90	06/21/90
Time on Stream (h)	240.5	275.0	298.0	322.0
Balance Duration (h)	14.0	6.0	6.0	6.0
Average Temperature (°C)	235.	250.	250.	250.
Maximum Δ Temperature (°C) ^b	5.00	-6.00	4.00	4.00
Pressure (MPa)	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.00	.667	.667	.667
Space Velocity (Nl/g-cat·h) ^a	2.00	2.00	2.00	2.00
Space Velocity (Nl/g-Fe·h)	3.41	3.41	3.41	3.41
GHSV (h ⁻¹) ^c	238.	238.	238.	238.
CO Conversion (%)	31.8	56.6	57.0	51.7
H ₂ +CO Conversion (%)	32.4	46.8	47.2	48.4
H ₂ /CO Usage	1.04	.379	.381	.561
STY (mols H ₂ +CO/g-cat·h) ^a	.029	.042	.042	.043
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}	3.41	38.3	10.8	11.2
Weight % of Outlet				
H ₂	4.59	3.56	3.46	2.72
H ₂ O	2.39	.402	1.38	1.01
CO	64.9	47.5	46.0	48.4
CO ₂	20.2	36.1	34.9	35.7
Hydrocarbons	3.44	4.78	5.62	4.73
Oxygenates	.315	.0969	.416	.627
Wax ^d	4.09	7.62	8.29	6.83
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	13.1	7.29	7.78	7.72
C ₂ -C ₄ Hydrocarbons	26.0	28.7	27.9	28.7
C ₅ -C ₁₁ Hydrocarbons	26.8	31.9	41.7	31.8
C ₁₂ + Hydrocarbons	87.0	113.	130.	111.
Wax ^d	83.0	111.	123.	106.
Oxygenates	6.39	1.42	6.19	9.71
Total	159.	183.	213.	189.
1+2 Olefins/n-Paraffin Ratio				
C ₂	.711	.493	3.89	3.82
C ₃	16.4	5.38	5.11	5.13
C ₄	2.87	4.05	4.12	4.05
C ₈	3.24	1.33	1.36	1.18
C ₁₀	1.10	.793	.915	.829

^a Based on unreduced catalyst^c Based on reactor volume^b Maximum axial temperature difference^d Unanalyzed products collected from hot trap

Table 4 (cont'd). Summary of results for fixed bed run FA-64-1580 .

Period	6	7	8	9
Weight % of Hydrocarbons				
CH ₄	8.58	4.02	3.76	4.32
Ethane	2.05	2.47	.939	1.13
Ethylene	1.36	1.11	3.41	4.04
Propane	.393	1.07	.836	1.00
Propylene	6.15	5.48	4.07	4.90
n-Butane	1.53	1.01	.738	.882
1+2 Butenes	4.25	3.95	2.94	3.45
C ₄ Isomers	1.27	.739	.557	.647
n-Pentane	1.41	.791	.568	.653
1+2 Pentenes	3.51	3.29	2.54	2.74
C ₅ Isomers	.793	.493	.376	.426
n-Hexane	.742	1.00	1.01	1.12
1+2 Hexenes	1.60	1.77	1.68	1.77
C ₆ Isomers	.627	1.69	1.61	.786
n-Heptane	.419	1.18	1.05	.792
1+2 Heptenes	1.09	1.81	1.70	.980
C ₇ Isomers	.230	.110	.158	.459
n-Octane	.379	.838	.866	.884
1+2 Octenes	1.21	1.10	1.16	1.03
C ₈ Isomers	.0439	.0424	.0393	.0343
n-Nonane	.568	.676	1.36	.942
1+2 Nonenes	1.06	.623	2.16	1.03
C ₉ Isomers	.00760	.0485	.0426	.101
n-Decane	.935	.627	1.00	1.10
1+2 Decenes	1.02	.490	.904	.896
C ₁₀ Isomers	.0554	.109	.196	.200
n-Undecane	.969	.449	.873	.923
1+2 Undecenes	.755	.336	.680	.631
C ₁₁ Isomers	.109	.112	.173	.291
C ₂ -C ₄	17.0	15.8	13.5	16.1
C ₅ -C ₁₁	17.5	17.6	20.1	17.8
C ₁₂ +	56.9	62.6	62.6	61.8
Wax ^d	54.3	61.5	59.6	59.1

^d Unanalyzed products collected from hot trap

Table 5. Compositions and surface areas of iron/silica catalysts

Nominal composition	Surface area (m ² /g)	
	Uncalcined	Calcined
100 Fe/5 Cu/4.2 K/8 SiO ₂	287	238
100 Fe/5 Cu/4.2 K/16 SiO ₂	285	257

Table 6. Comparison of aqueous phase samples from run SB-99-1370, balance 13, on the Varian 3400 and Sigma 1 GC's.

Species	Sigma 1 ^(a)	Varian ^(b)	% Diff ^(c)
Methanol	31.3	128.6	-8.63
Ethanol	48.1	50.6	5.20
1-Propanol	13.2	13.8	4.55
1-Butanol	4.08	4.11	0.74
2-Butanol	0.20	0.18	-10.0
Butanol	0.24	0.43	79.17
1-Pentanol	1.35	1.47	8.89
1-Hexanol	1.53	0.71	-53.6

(a) C1500 on 80/100 Graphpac GC packed column

(b) RSL-300 capillary column

(c) $100 (\text{Varian} - \text{Sigma}) / \text{Sigma}$

Table 7. Comparison of tail gas samples from run SB-99-1370, balance 6, on the Varian 3400 and Sigma 1 GC's using Poropak Q column.

Species	Sigma 1	Varian FID	% Diff ^(a)
Methane	35.6	36.5	2.62
Ethylene	7.10	7.07	-0.47
Ethane	7.30	7.29	-0.19
Propylene	14.1	18.1	27.33
Propane	2.41	0.00	-100
C ₄ Isomes	0.42	0.44	4.38
1-Butene	9.32	9.66	1.47
<i>n</i> -Butane	3.99	1.82	-54.48
C ₅ Isomers	0.70	1.29	84.91
1-Pentene	6.75	6.34	-6.13
<i>n</i> -Pentane	2.29	1.30	-4.30
C ₆ Isomers	0.59	0.80	36.2
1- Hexene	4.05	4.00	-1.29
<i>n</i> -Hexane	1.35	0.93	-31.00
C ₇ Isomers	0.51	0.32	-36.6
1-Heptene	1.75	2.05	18.70
<i>n</i> -Heptane	0.62	0.52	-15.82
C ₈ Isomers	0.14	0.15	4.38
1-Octene	0.74	1.16	56.6
<i>n</i> -Octane	0.32	0.55	72.9

(a) $100 (\text{Varian} - \text{Sigma}) / \text{Sigma}$

Figure 1. Volumetric contraction versus time on stream for run SB-99-1370
 (weights indicate amount of wax withdrawn (-))

Figure 2. Stability plot, (H₂+CO) conversion versus time on stream, for run SB-99-1370

Figure 3. Anderson-Schulz-Flory plot for run SB-99-1370 (Balance #4), total products excluding wax.

Figure 4. Anderson-Schulz-Flory plot for run SB-99-1370 (Balance #13), total products excluding wax.

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