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Development of Improved Iron Fischer-Tropsch Catalysts

**Quarterly Technical Progress Report
for the Period 1 January 1991 – 31 March 1991**

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* removed per Chicago Field Office

I. Executive Summary

Five tests (3 fixed bed reactor, and 2 slurry reactor tests) were completed during this period. In a fixed bed reactor run FB-0021, a precipitated iron catalyst with nominal composition 100 Fe/0.3 Cu/0.8 K was pretreated with CO at 280°C for 8 h, and then tested at 250°C, 2 NI/g-cat/h, 200 psig and $(H_2/CO)=0.67$. The (H_2+CO) conversion decreased with time on stream (80 to 65%), whereas the methane selectivity was about 3.4 wt.%. The same catalysts was also tested in a slurry reactor (Run SA-0791) after reduction with H_2 at 250°C for 2 h. The catalyst was very active and stable during the first 275h on stream; (H_2+CO) conversion of 80%. However, after this the reactor stirrer began to vibrate and the run was terminated at 325 h on stream. During the test, hydrocarbon selectivity shifted gradually towards low molecular weight products. For example, methane and (C_2-C_4) selectivities varied between 5.5 and 7.2 wt.%, and 19 to 26%, respectively.

Two silica containing catalysts with nominal composition 100 Fe/3 Cu/4 K/x SiO_2 (x=8 and 16) were evaluated in a fixed bed reactor at 250°C, 200 psig, 2 NI/g-cat/h and $H_2/CO = 0.67$. Both catalysts had high Fischer-Tropsch synthesis (FTS) and water-gas-shift (WGS) activities, and deactivated slowly with TOS. In both tests the (H_2+CO) conversion was about 80%, whereas methane selectivity was 3.7%.

A silica containing catalyst was tested in a slurry reactor (Run SB-0261) over a period of 720 h. Process conditions were varied throughout the test, and the (H_2+CO) conversion was between 62.5 and 82%. Hydrocarbon product distribution was within the DOE target, (C_1+C_2) selectivity less than 7 wt.%, throughout the entire test. Methane selectivity was low, between 1.6 and 2.8 wt.%, whereas the selectivity of C_{12}^+ products was high, 69-76.5%. After initial induction period of about 250 h on stream, the catalyst activity was stable until the catalyst was exposed to reaction pressure of 300 psig (620 - 720 h on stream). The catalyst deactivated during this time period.

Finally, a progress has been made on characterization of silica containing catalysts by X-ray diffraction. The following crystalline phases were identified in used catalyst samples from fixed bed reactor tests: magnetite (Fe_3O_4) and/or iron carbide(s) (Fe_xC).

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 it 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-hour 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 catalysts, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity

during Fischer-Tropsch synthesis (FTS). 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 FTS.

Task 3 – Improved Iron Silica Catalyst

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst with composition $100 Fe/x Cu/y K_2O/z SiO_2$ (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

Two tests (one fixed bed and one slurry reactor test) were conducted with precipitated iron catalyst with nominal composition 100 Fe/0.3 Cu/0.8 K to investigate effects of pretreatment conditions on catalyst activity, stability and selectivity.

III-1.1 Run FB-0021 with 100Fe/0.3Cu/0.8K Catalyst

Prior to synthesis the catalyst was pretreated with CO at 280°C, 3 NI/g-cat/h and ambient pressure for 8 h. Throughout the test average reaction temperature, pressure, gas space velocity and H₂/CO feed ratio were maintained at 250°C, 200 psig, 2 NI/g-cat/h, and 0.69, respectively. The run was terminated after 130 h on stream. Results from two mass balances are summarized in Table 1. During an initial portion of the test, 30-36 h on stream (i.e. 4-10 h at the process conditions) helium was inadvertently introduced into the reactor and the syngas flow was temporarily discontinued. No other operational problems were encountered during the test.

Catalyst Activity and Stability

Fischer-Tropsch synthesis (FTS) activity, measured by (H₂+CO) conversion and gas volumetric contraction (VC), decreased with time-on-stream (TOS) as shown in Figures 1a and 1b, respectively. The usage ratio, which is a measure of the water-gas-shift (WGS) activity, varied between 0.56 and 0.64 (Figure 1c). The latter values are indicative of high WGS activity, and are typical for catalysts promoted with potassium.

Hydrocarbon Selectivity

Hydrocarbon product distributions in balances 1 and 2 were similar (see Table 1), and average values for methane and other hydrocarbons were: 3.4 (CH₄); 18.1 (C₂-C₄); 23.0 (C₅-C₁₁) and 55.5 wt% (C₁₂⁺).

Methane and gaseous hydrocarbon selectivities obtained in this test were significantly lower, than those obtained in tests FA-2780 and FB-3480 (Technical Progress Report for October-December, 1990) where H_2 reduction was employed. However, the CO reduced catalyst deactivated more rapidly with time-on-stream than the H_2 reduced one.

III-1.2 Run SA-0791 with 100Fe/0.3Cu/0.8K Catalyst

This was the first slurry reactor test of this catalyst. The catalyst was reduced with H_2 at 250°C, 100 psig for 2 h. Process conditions throughout the entire test were: 260°C, 200 psig, 2 Nl/g-cat/h and $H_2/CO=0.67$. Several upsets were encountered during the test which lasted 325 h (Table 3). A temporary loss of electric power to the reactor furnace occurred at about 210 h on stream. The power was restored after 2 hours, and the reactor temperature decreased to 190°C during this time period. Between 214 and 234 h on stream a mass flow meter was not working properly, and the inlet gas flow rate was lower than the desired value. Finally, from 275 h until the end of the run the reactor stirrer became loose and made a lot of noise due to excessive vibrations. The run was terminated due to problems with the stirrer. Results from five mass balances are summarized in Table 2.

Catalyst Activity and Stability

The catalyst was very active and stable during the first 200 h of testing. The (H_2+CO) conversion varied between 80 and 82%, and the VC was between 52 and 54% (Figure 2). After the two upsets which occurred between 210 and 234 h, the (H_2+CO) conversion decreased slightly to about 79% (240-270 h). During the last 50 h of testing (275-325 h), the (H_2+CO) conversion and VC, decreased fairly rapidly. This loss in activity may be attributed to poor mixing in the reactor caused by malfunctioning of the stirrer. WGS activity of the catalyst was high, and the usage ratio was constant throughout the test (0.60-0.61).

Wax and Catalyst Withdrawals/Inventories

Wax was withdrawn periodically (approximately every 50 h) through a porous sintered metal filter with nominal pore size of 2 μm . The filter was placed horizontally at a height corresponding to the static slurry volume of 400 cc. There were no problems with filtration, and the excess wax withdrawn did not contain any catalyst.

At the end of the run it was found that the filter element was broken, probably by vibrating shaft of the stirrer during the last 50 h of testing. The wax recovery was 70% only, based on the amount of wax charged into the reactor. However, prior to the test an unknown amount of n-octacosane was lost from the reactor. The catalyst recovery, was greater than 100% (see Table 3), and we suspect that the initial amount of catalyst charged into the reactor was probably higher than the recorded value. The amount of catalyst in a slurry was determined by burning slurry samples in a crucible.

Hydrocarbon Selectivity

Hydrocarbon product distribution shifted gradually towards lower molecular weight products with time-on-stream. Selectivities of methane, gaseous hydrocarbons ($\text{C}_2\text{-C}_4$) and gasoline range products increased with time, whereas the selectivity of C_{12}^+ products decreased with time (Table 2). Selectivities of methane and other hydrocarbons (lumped by carbon number) varied as follows: $\text{CH}_4 = 5.5 - 7.2$; $(\text{C}_2\text{-C}_4) = 19 - 26$; $(\text{C}_5\text{-C}_{11}) = 30 - 41$; and $\text{C}_{12}^+ = 26 - 45.5$ wt. %.

Hydrocarbon product distribution obtained in this test between 110 and 270 h on stream, was similar to that obtained in Mobil's Run CT 256-3 (Kuo, J. C. W., Final DOE Report, Contract DE-AC22-83PC60019, 1985).

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

Three tests (2 screening tests in a fixed bed reactor and one catalyst aging slurry reactor test) were completed during the reporting period. Results from these tests are described in detail in subsections III-2.1, III-2.2 and Appendix I.

III-2.1 Run FA-0011 with 100Fe/3Cu/4K/8SiO₂

This was the second test of this catalyst in a fixed bed reactor. The previous test (Run FA-2500) was not successful due to development of a hot spot and subsequent plugging of the reactor (Technical Progress Report for the period July 1 – September 30, 1990). Following reduction with H₂ at 220°C, the catalyst was tested at 250°C, 2 N//g-cat/h, 200 psig using synthesis gas with H₂ to CO molar feed ratio of 2:3. Two mass balances were made during 130 h of testing, and results are summarized in Table 4. The exit lines were plugged with liquid (wax) products, three times during the test, at about 38, 64 and 83 h on stream, but these plugs were removed by using either helium flowing through the reactor (plug at 38 h) or through purge lines (plugs at 64 and 83 h). These temporary flow stoppages did not have marked effect on the catalyst activity (see Figures 3a and 3b).

Catalyst Activity and Stability

The FTS activity, measured by (H₂+CO) conversion and volumetric gas contraction, was high, but it decreased with time (Figures 3a and 3b). For example, the (H₂+CO) conversion was about 80% at 59 h, whereas at 113 h the conversion decreased to 73%. The WGS activity, measured by usage ratio, and the approach to equilibrium, was high as shown in Figure 3c and Table 4.

Hydrocarbon Selectivity

Methane and gaseous hydrocarbon selectivities were low, whereas the yield of liquid and solid products (C₅⁺ hydrocarbons) was high in both mass balances (Table 4). Average values of

methane and other hydrocarbon (lumped according to carbon numbers) selectivities were: 3.7 (CH₄); 16.6 (C₂-C₄), 24.5 (C₅-C₁₁) and 55.2 wt% (C₁₂⁺).

Carbon number product distribution for the second mass balance, in the form of Anderson-Shulz-Flory (ASF) plot, is shown in Figure 4. Solid product (wax) collected in a high pressure trap was not analyzed.

III-2.2 Run FB-0601 with 100Fe/3Cu/4K/16SiO₂ Catalyst

This was a screening test of catalyst with nominal composition 100 Fe/3 Cu/4 K/16 SiO₂ in a fixed bed reactor. The catalyst was tested at 250°C, 200 psig, 2 Nl/g-cat/h and H₂/CO = 0.64, after initial conditioning period of 24 h during which the temperature was raised gradually from 200 to 250°C. There were no major operational problems during the test, and the run was terminated after 170 h on stream (i.e. 145 h at the above set of process conditions). Results from three mass balances are summarized in Table 5.

Catalyst Activity and Stability

The (H₂+CO) conversion and the VC decreased slowly with time on stream, whereas the usage ratio was fairly constant throughout the test as shown in Figures 5a-5c. The FTS activity was high (high conversion and gas contraction), as well as the WGS activity (low usage ratio). Catalyst deactivation rate was moderate; the (H₂+CO) conversion decreased from 84% at 30 h on stream to 77% at 170 h on stream.

Hydrocarbon Product Distribution

Hydrocarbon selectivities in all three mass balances were similar (Table 5) and methane and gaseous hydrocarbon yields were low. Average values of methane and other hydrocarbon selectivities were: 3.7 (CH₄); 14.6 (C₂-C₄); 23.2 (C₅-C₁₁) and 58.5 wt% of C₁₂⁺.

A typical carbon number distribution (excluding unanalyzed products collected in a high pressure trap consisting primarily of C₁₂⁺ hydrocarbons) is shown in Figure 6. Chain growth

parameter for products in C_1 – C_{11} range is 0.73, and the product distribution in this range is described well by a straight line on the ASF plot.

The overall performance of the two silica containing catalysts (sections III-2.1 and III-2.2) was promising, and we plan to evaluate these two catalysts in slurry reactor tests.

III-2.3 Catalyst Characterization

Some preliminary results from XRPD (X-ray powder diffraction) analysis of calcined and used samples of the catalyst with nominal composition 100 Fe/5 Cu/4.2 K/8 SiO₂ were reported in the previous Quarterly Technical Progress Report (October – December, 1990). During the present reporting period the analysis of these data was completed (phase identification), and new data were obtained with catalysts having nominal composition 100 Fe/5 Cu/4.2 K/x SiO₂; (x = 0, 8, 16, 24 and 40). The used catalyst samples were from tests conducted in our Laboratory prior to the current DOE contract. Phases were identified by comparing peak positions (2 θ), relative d-spacing values and relative intensities (I), with data tabulated in literature. Results are summarized in Tables 6-9, and Figures 7-10.

X-ray patterns of the 100 Fe/5 Cu/4.2 K/8 SiO₂ catalyst, after calcination in air at 300°C for 5 h, and of the two used samples from fixed bed reactor tests FA-63-3448 (H₂ reduction) and FA-63-0418 (CO reduction) are shown in Figure 7. Major peaks are identified in Table 6, as well as in Figure 7. The calcined sample (Fig. 7a) showed two broad peaks, which may be ascribed to hematite (α -Fe₂O₃), indicating either a small crystallite size (less than ~30Å) or that the material has an amorphous structure. Both used catalyst samples have two sharp peaks in the region 2 θ = 21 – 24° which are attributed to paraffin wax. The noise in XRD patterns and shifts in baseline are caused by presence of glass beads in the sample. The glass beads were mixed with the catalyst to prevent development of hot spots, and to maintain nearly isothermal conditions in the reactor. The major crystalline phase in the used catalyst pretreated with CO (Fig. 7c) is magnetite, whereas iron carbides are present in a small amount. On the other hand, the XRD pattern of H₂ reduced catalyst

(Fig. 7b) shows relatively larger amounts of Fe_xC , and decrease in peak intensity of magnetite in comparison with the CO pretreated catalyst.

Figure 8 shows that removal of glass beads from a sample by magnetic separation (Fig. 8b), and the use of slow scan (Fig. 8c) provide additional information and aid in interpretation of results (better resolution of peaks, removal of baseline shifts and noise in the original data). From data in Figures 8b and 8c, it was concluded that the iron carbide phase in Fig. 8a is Fe_2C , and that particle size of magnetite (Fe_3O_4) crystallites is about $300\text{\AA}$.

Figure 9 shows XRD patterns of the catalyst with nominal composition 100 Fe/5 Cu/4.2 K/40 SiO_2 after (a) calcination; (b) H_2 reduction followed by FTS; and (c) CO pretreatment followed by FTS. The calcined sample shows broad peaks (probably of $\alpha\text{-Fe}_2\text{O}_3$) indicating either that the crystallite size is small or that material is amorphous. The used catalyst reduced with H_2 (9 b) shows peaks of wax, peak of iron carbide(s) and possibly some Fe_3O_4 , and a broad halo peak ($2\theta = 15 - 40^\circ$) of glass beads. On the contrary, the used catalyst pretreated with CO (Fig. 9c) consists primarily of Fe_3O_4 and a small amount of Fe_xC , in addition to paraffin wax.

Figure 10 shows XRD patterns of used catalysts containing different amounts of silica. The major crystalline phase of iron in all catalysts is Fe_3O_4 except for the catalyst containing 24 SiO_2 /100 Fe (Fig. 10d). In the latter case, the only peaks identified were those of wax. In addition to Fe_3O_4 , the catalyst without silica and the catalyst with 8 parts of SiO_2 contain some iron carbide(s). It appears that FeCO_3 is also present in the catalyst without silica. No simple relations could be obtained between the peak intensity and the silica content of the catalyst, since reaction conditions and times on stream were not the same in all tests.

Table 1. Summary of results for fixed bed run FB-0021 .

Catalyst: 3.50 g^a, 100Fe/0.3Cu/0.8K
Catalyst volume: 3.20 cc

Diluent: 36.22 g, Glass beads
Diluent Volume: 25.20 cc

Period	1	2
Date	01/05/90	01/06/90
Time on Stream (h)	68.0	88.5
Balance Duration (h)	8.5	6.5
Average Temperature (°C)	250.	250.
Maximum Δ Temperature (°C) ^b	6.00	5.00
Pressure (MPa)	1.48	1.48
H ₂ /CO Feed Ratio	.686	.686
Space Velocity (NI/g-cat-h) ^a	1.99	1.99
Space Velocity (NI/g-Fe-h)	2.89	2.89
GHSV (h ⁻¹) ^c	254.	254.
CO Conversion (%)	73.0	70.1
H ₂ +CO Conversion (%)	70.9	67.6
H ₂ /CO Usage	.637	.628
STY (mols H ₂ +CO/g-cat-h) ^a	.063	.060
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	19.6	19.0
Weight % of Outlet		
H ₂	1.50	1.69
H ₂ O	.916	.914
CO	25.4	28.4
CO ₂	53.5	51.3
Hydrocarbons	8.96	9.03
Oxygenates	.738	.724
Wax ^d	8.96	7.93
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	6.11	7.32
C ₂ -C ₄ Hydrocarbons	36.0	35.7
C ₅ -C ₁₁ Hydrocarbons	46.7	44.1
C ₁₂ + Hydrocarbons	110.	109.
Wax ^d	99.4	91.6
Oxygenates	8.19	8.36
Total	207.	204.
1+2 Olefins/n-Paraffin Ratio		
C ₂	2.42	2.55
C ₃	7.78	7.62
C ₄	7.01	6.87
C ₈	3.27	3.56
C ₁₀	3.32	3.39

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FB-0021 .

Period		1	2
Weight % of Hydrocarbons			
C114		3.07	3.74
Ethane		1.52	1.51
Ethylene		3.43	3.60
Propane		.851	.867
Propylene		6.32	6.31
n-Butane		.704	.713
1+2 Butenes		4.76	4.73
C ₄ Isomers		.501	.500
n-Pentane		.631	.631
1+2 Pentenes		3.96	3.88
C ₅ Isomers		.947	.928
n-Hexane		.601	.459
1+2 Hexenes		2.05	2.39
C ₆ Isomers		.661	.768
n-Heptane		.409	.406
1+2 Heptenes		1.50	1.73
C ₇ Isomers		.414	.563
n-Octane		.538	.424
1+2 Octenes		1.73	1.48
C ₈ Isomers		.971	.676
n-Nonane		.619	.582
1+2 Nonenes		2.04	1.75
C ₉ Isomers		.487	.560
n-Decane		.589	.487
1+2 Decenes		1.93	1.63
C ₁₀ Isomers		.624	.708
n-Undecane		.528	.425
1+2 Undecenes		1.78	1.46
C ₁₁ Isomers		.481	.568
C ₃ -C ₄		18.1	18.2
C ₅ -C ₁₁		23.5	22.5
C ₁₂ +		55.4	55.5
Wax ^d		50.0	46.8

^d Unanalyzed products collected from hot trap

Table 2. Summary of results for slurry run SA-0791.

Catalyst: 5.79 g^a, 100Fe/0.3Cu/0.8K

Slurry liquid: 321.0 g, n-C28

Reactor volume: 430. cc^b

Period	1	2	3	4	5
Date	03/22/91	03/25/91	03/27/91	04/01/91	04/02/91
Time on Stream (h)	39.0	111.0	159.0	266.0	278.0
Balance Duration (h)	10.0	8.8	10.0	11.0	26.5
Average Temperature (°C)	260.	260.	260.	260.	260.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.686	.686	.686	.686	.686
Space Velocity (Nl/g-cat.h) ^a	2.00	2.00	2.00	2.00	2.00
Space Velocity (Nl/g-Fe.h)	2.91	2.91	2.91	2.91	2.91
GHSV (h ⁻¹) ^a	26.9	26.9	26.9	26.9	26.9
CO Conversion (%)	86.1	86.8	86.6	82.4	79.0
H ₂ +CO Conversion (%)	81.8	82.3	82.4	78.7	75.3
H ₂ /CO Usage	.604	.605	.603	.611	.607
STY (mole H ₂ +CO/g-cat.h) ^a	.073	.074	.073	.070	.067
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}	33.2	42.2	38.5	39.6	80.6
Weight % of Outlet					
H ₂	1.15	1.10	1.13	1.25	1.42
H ₂ O	.916	.742	.827	.647	.292
CO	13.3	12.5	12.8	16.7	20.0
CO ₂	62.0	62.7	63.5	60.1	58.4
Hydrocarbons	12.8	15.5	14.9	16.6	15.9
Oxygenates	.876	.857	1.08	1.68	1.36
Wax ^c	8.92	6.62	5.74	3.02	2.56
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	11.3	12.5	12.7	13.2	13.7
C ₂ -C ₄ Hydrocarbons	39.0	44.7	44.9	46.5	49.4
C ₆ -C ₁₁ Hydrocarbons	61.4	80.8	74.7	79.4	77.4
C ₁₂ + Hydrocarbons	93.4	71.7	62.0	54.7	50.0
Wax ^c	84.4	62.7	54.0	29.9	26.4
Oxygenates	8.29	8.12	10.1	16.7	14.0
Total	213.	218.	204.	210.	205.
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.90	1.58	1.51	1.11	1.03
C ₃	4.76	4.72	4.76	4.46	4.48
C ₄	3.77	4.18	3.81	3.67	3.64
C ₈	2.48	2.38	2.28	2.19	2.25
C ₁₀	1.94	1.96	2.11	2.14	2.28

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

Table 2 (cont'd). Summary of results for slurry run SA-0791.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	5.49	5.96	6.51	6.79	7.20
Ethane	1.85	2.24	2.56	2.90	3.32
Ethylene	3.28	3.30	3.61	2.99	3.20
Propane	1.35	1.50	1.64	1.84	1.97
Propylene	6.13	6.77	7.46	7.84	8.43
n-Butane	1.28	1.39	1.55	1.72	1.84
1+2 Butenes	4.67	5.61	5.70	6.10	6.47
C ₄ Isomers	.446	.511	.578	.632	.717
n-Pentane	1.23	1.34	1.50	1.65	1.76
1+2 Pentenes	4.25	4.82	5.29	5.57	5.96
C ₅ Isomers	2.22	2.56	1.10	2.87	1.27
n-Hexane	.948	1.20	1.28	1.38	1.36
1+2 Hexenes	3.05	3.65	3.94	4.12	4.15
C ₆ Isomers	.899	1.04	1.12	1.12	1.06
n-Heptane	.990	1.21	1.29	1.46	1.52
1+2 Heptenes	2.23	2.73	3.02	3.27	3.31
C ₇ Isomers	.971	.914	1.12	.891	1.47
n-Octane	.877	1.30	1.43	1.53	1.47
1+2 Octenes	2.14	3.03	3.21	3.30	3.25
C ₈ Isomers	.635	1.27	.943	1.18	.990
n-Nonane	.844	1.20	1.24	1.22	1.34
1+2 Nonenes	1.90	2.74	2.99	2.76	2.94
C ₉ Isomers	.552	.897	.799	.819	.957
n-Decane	.786	1.16	1.17	1.08	.977
1+2 Decenes	1.51	2.25	2.43	2.28	2.20
C ₁₀ Isomers	.603	.942	.818	.833	.744
n-Undecane	.780	.973	.933	.974	.947
1+2 Undecenes	1.46	1.94	1.91	1.94	1.92
C ₁₁ Isomers	1.11	1.34	.949	.721	1.02
C ₇ -C ₄	19.0	21.3	23.1	24.0	25.9
C ₅ -C ₁₁	30.0	38.5	38.5	41.0	40.6
C ₁₂ +	45.5	34.2	31.9	28.2	26.2
Wax ^c	41.2	29.9	27.8	15.4	13.9

^c Unanalyzed wax withdrawn from reactor

Table 3. Major events in Run SA-0791

TOS (h)	Event
	Slurry loading: 322 g n-octacosane, 5.8 g catalyst (particle size < 270 mesh)
	Plug in lines, unknown amount of n-octacosane removed from the reactor
	Catalyst pretreatment: H ₂ at T=250°C, P=0.79 MPa, SV=78 Nl/g-cat/h, for 2 h
0	Initiate run by introducing syngas into the reactor
2	Achieved process conditions: T=260°C, P=1.48 MPa, SV=2.0 Nl/g-cat/h. Feed (H ₂ /CO)=0.69
193	Reactor outlet line temperature increased to 210°C
209-211	Loss of reactor power (furnace fuse blown)
213	Achieved desired process conditions
214-234	Malfunctioning of mass flowmeter
234	Achieved desired gas flow rate
275	Reactor stirrer rotating improperly (making noise)
325	End of Run SA-0791
	139.5 g wax removal during the run, 214 g wax and 9.8 g solid recovered from the reactor at end of the run; 70% wax recovery, 168% solid recovery.

Table 4. Summary of results for fixed bed run FA-0011 .

Catalyst: 3.50 g^a, 100Fe/3Cu/4K/8SiO₂
 Catalyst volume: 5.20 cc

Diluent: 36.10 g, Glass beads
 Diluent Volume: 24.00 cc

Period	1	2
Date	01/05/90	01/07/90
Time on Stream (h)	65.0	107.0
Balance Duration (h)	6.0	6.0
Average Temperature (°C)	250.	250.
Maximum Δ Temperature (°C) ^b	9.00	9.00
Pressure (MPa)	1.48	1.48
H ₂ /CO Feed Ratio	.686	.686
Space Velocity (NI/g-cat-h) ^a	1.99	1.99
Space Velocity (NI/g-Fe-h)	2.89	2.89
GHSV (h ⁻¹) ^c	254.	254.
CO Conversion (%)	83.2	77.3
H ₂ +CO Conversion (%)	78.6	73.5
H ₂ /CO Usage	.594	.604
STY (mole H ₂ +CO/g-cat-h) ^a	.070	.065
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	83.3	27.4
Weight % of Outlet		
H ₂	1.31	1.48
H ₂ O	.351	.833
CO	15.9	21.4
CO ₂	62.3	57.7
Hydrocarbons	8.42	10.1
Oxygenates	.424	.374
Wax ^d	11.3	8.20
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	7.13	7.37
C ₂ -C ₄ Hydrocarbons	31.5	33.9
C ₅ -C ₁₁ Hydrocarbons	39.6	56.6
C ₁₂ + Hydrocarbons	118.	98.3
Wax ^d	113.	88.0
Oxygenates	4.22	4.01
Total	201.	200.
1+2 Olefins/n-Paraffin Ratio		
C ₂	3.42	3.61
C ₃	7.83	8.15
C ₄	6.85	7.19
C ₅	4.24	5.12
C ₁₀	4.57	4.85

^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-0011.

Weight % of Hydrocarbons	Period	
	1	2
C114	3.63	3.76
Ethane	1.09	1.14
Ethylene	3.46	3.82
Propane	.739	.775
Propylene	5.52	6.03
n-Butane	.628	.635
1+2 Butenes	4.16	4.41
C4 Isomers	.446	.476
n-Pentane	.578	.547
1+2 Pentenes	3.52	3.54
C5 Isomers	1.57	2.09
n-Hexane	.435	.615
1+2 Hexenes	2.37	3.43
C6 Isomers	.732	1.17
n-Heptane	.462	.632
1+2 Heptenes	1.93	3.14
C7 Isomers	.598	.988
n-Octane	.389	.553
1+2 Octenes	1.62	2.78
C8 Isomers	.396	1.000
n-Nonane	.326	.515
1+2 Nonenes	1.31	2.39
C9 Isomers	.363	.306
n-Decane	.279	.437
1+2 Decenes	1.26	2.09
C10 Isomers	.406	.330
n-Undecane	.239	.322
1+2 Undecenes	1.04	1.68
C11 Isomers	.329	.307
C12-C4	16.0	17.3
C8-C11	20.2	28.8
C12+	60.2	50.1
Wax ^d	57.3	44.8

^d Unanalyzed products collected from hot trap

Table 5. Summary of results for fixed bed run FB-0601.

Catalyst: 3.50 g^a, 100Fe/3Cu/4K/16SiO₂
 Catalyst volume: 5.60 cc
 Diluent: 33.50 g, Glass beads
 Diluent Volume: 22.00 cc

Period	1	2	3
Date	03/04/91	03/06/91	03/08/91
Time on Stream (h)	67.0	113.5	161.5
Balance Duration (h)	6.0	6.0	7.5
Average Temperature (°C)	250.	250.	250.
Maximum Δ Temperature (°C) ^b	6.00	6.00	5.00
Pressure (MPa)	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.637	.637	.637
Space Velocity (NI/g-cat-h) ^a	2.00	2.00	2.00
Space Velocity (NI/g-Fe-h)	3.44	3.44	3.44
GHSV (h ⁻¹) ^c	253.	253.	253.
CO Conversion (%)	87.3	84.0	81.3
H ₂ +CO Conversion (%)	83.3	79.9	77.4
H ₂ /CO Usage	.562	.557	.559
STY (mols H ₂ +CO/g-cat-h) ^a	.074	.071	.069
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	37.2	57.3	67.3
Weight % of Outlet			
H ₂	1.00	1.17	1.26
H ₂ O	.807	.466	.356
CO	12.2	15.4	18.0
CO ₂	63.9	61.8	60.1
Hydrocarbons	9.70	9.67	9.72
Oxygenates	.922	.966	.979
Wax ^d	11.5	10.5	9.60
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄	7.89	7.38	7.21
C ₂ -C ₄ Hydrocarbons	30.1	29.2	28.7
C ₅ -C ₁₁ Hydrocarbons	45.4	48.4	45.7
C ₁₂ + Hydrocarbons	119.	116.	117.
Wax ^d	110.	105.	98.6
Oxygenates	8.82	9.60	10.1
Total	212.	210.	209.
1+2 Olefins/n-Paraffin Ratio			
C ₂	2.43	3.05	3.68
C ₃	4.87	4.86	4.72
C ₄	3.88	3.91	3.81
C ₅	1.51	3.06	2.59
C ₁₀	3.42	3.19	2.97

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

Table 5 (cont'd). Summary of results for fixed bed run FB-0601.

Weight % of Hydrocarbons	Period		
	1	2	3
C114	3.89	3.08	3.03
Ethane	1.19	.993	.872
Ethylene	2.70	2.83	2.99
Propane	1.06	1.03	1.02
Propylene	4.91	4.76	4.61
n-Butane	.962	.945	.963
1+2 Butenes	3.60	3.56	3.54
C ₄ Isomers	.434	.438	.449
n-Pentane	.961	.451	.473
1+2 Pentenes	3.54	3.46	3.18
C ₅ Isomers	.722	2.44	2.21
n-Hexane	1.31	.882	.718
1+2 Hexenes	2.50	2.46	2.14
C ₆ Isomers	.837	.994	.728
n-Heptane	1.24	.829	.694
1+2 Heptenes	1.81	2.02	1.63
C ₇ Isomers	.828	.917	.678
n-Octane	1.18	.731	.706
1+2 Octenes	1.74	2.19	1.80
C ₈ Isomers	.558	.785	.574
n-Nonane	.555	.508	.639
1+2 Nonenes	1.41	1.49	1.80
C ₉ Isomers	.345	.429	.454
n-Decane	.309	.393	.555
1+2 Decenes	1.04	1.24	1.62
C ₁₀ Isomers	.190	.450	.413
n-Undecane	.294	.322	.430
1+2 Undecenes	.818	.944	1.34
C ₁₁ Isomers	.184	.208	.259
C ₂ -C ₄	14.9	14.6	14.4
C ₅ -C ₁₁	22.4	24.1	23.0
C ₁₂ +	58.9	57.6	58.9
Wax ^d	54.2	52.1	49.7

^d Unanalyzed products collected from hot trap

Table 6. XRD peak identification of 100Fe/5Cu/4.2K/8SiO₂ catalyst after calcination and reaction.

100Fe/5Cu/4.2K/8SiO ₂ calcined			Run FA-63-3448 H ₂ treat. 220°C, 8 h TOS=264 h			Run FA-63-0418 CO treat. 280°C, 12 h TOS=169 h			Peak Identification
2θ	d(Å)	(I)	2θ	d(Å)	(I)	2θ	d(Å)	(I)	
34.9	2.566	(28)	21.6	4.111	(100)	21.7	4.096	(100)	wax
			24.1	3.684	(42)	24.2	3.672	(55)	wax
						30.2	2.953	(48)	Fe ₃ O ₄
									Fe ₂ O ₃ (?)
			35.6	2.517	(35)	35.6	2.521	(87)	Fe ₃ O ₄
63.0	1.474	(20)	43.0	2.102	(41)	43.1	2.096	(38)	Fe ₃ O ₄ +Fe _x C
						57.0	1.613	(36)	Fe ₃ O ₄
						62.7	1.481	(38)	Fe ₃ O ₄
									Fe ₂ O ₃ (?)

Table 7. XRD peak identification of used 100Fe/5Cu/4.2K/8SiO₂ catalyst (FA-63-3448) with and without glass beads.

With glass beads			Without glass beads			Peak Identification
2θ	d(Å)	(I)	2θ	d(Å)	(I)	
21.6	4.111	(100)	21.7	4.092	(100)	wax
24.1	3.684	(42)	24.1	3.690	(40)	wax
			30.4	2.940	(28)	Fe ₃ O ₄
35.6	2.517	(35)	35.7	2.512	(23)	Fe ₃ O ₄
			41.6	2.168	(23)	Fe _x C
43.0	2.102	(41)	42.8	2.111	(44)	Fe _x C + Fe ₃ O ₄
			57.2	1.609	(25)	Fe _x C + Fe ₃ O ₄
			62.8	1.479	(14)	Fe ₃ O ₄
			67.4	1.388	(20)	Fe _x C
			77.1	1.237	(15)	Fe _x C
			82.5	1.169	(13)	Fe _x C

Fe_xC = Fe₂C (?)

Table 8. XRD peak identification of 100Fe/5Cu/4.2K/40SiO₂ catalyst after calcination and reaction.

100Fe/5Cu/4.2K/40SiO ₂ calcined			Run FA-0099 H ₂ treat. 220°C, 1 h TOS=604.5 h			Run FB-0129 CO treat. 280°C, 24 h TOS=258 h			Peak Identification
2θ	d(Å)	(I)	2θ	d(Å)	(I)	2θ	d(Å)	(I)	
34.9	2.572	(28)	21.5	4.120	(100)	21.6	4.103	(127)	wax
			23.9	3.714	(37)	24.0	3.708	(70)	wax
						30.3	2.946	(47)	Fe ₃ O ₄
									Fe ₂ O ₃ (?)
						35.7	2.516	(66)	Fe ₃ O ₄
63.1	1.471	(27)	42.9	2.108	(30)				Fe _x C+Fe ₃ O ₄ (?)
						43.1	2.098	(49)	Fe ₃ O ₄ +Fe _x C
									Fe ₂ O ₃ (?)

Table 9. XRD peak identification of used 100Fe/5Cu/4.2K/xSiO₂ catalysts (x=0, 24, 16)

FA-31-1118 100Fe/5Cu/4.2K CO treat. 280°C, 12 h TOS=168 h			FA-66-0548 100Fe/5Cu/4.2K/24SiO ₂ CO treat. 280°C, 12 h TOS=144.5 h			FA-64-1049 100Fe/5Cu/4.2K/16SiO ₂ CO treat. 280°C, 12 h TOS=452 h			Peak Identification
2θ	d(Å)	(I)	2θ	d(Å)	(I)	2θ	d(Å)	(I)	
21.6	4.115	(92)	21.6	4.111	(100)	21.6	4.103	(79)	wax
			23.9	3.726	(44)	23.9	3.714	(46)	wax
30.2	2.959	(71)				30.1	2.965	(44)	Fe ₃ O ₄
32.1	2.783	(70)							FeCO ₃ (?)
35.6	2.523	(70)				35.5	2.525	(100)	Fe ₃ O ₄
43.2	2.093	(42)				43.2	2.094	(44)	Fe ₃ O ₄
53.0	1.725	(43)				53.5	1.711	(33)	Fe ₃ O ₄
57.1	1.612	(39)				57.0	1.614	(42)	Fe ₃ O ₄
62.7	1.481	(43)				62.6	1.482	(48)	Fe ₃ O ₄

Figure 1. (H₂+CO) conversion (a), volumetric contraction (b) and H₂/CO usage ratio (c) versus time on stream for run FB-0021.

Figure 2. (H_2+CO) conversion (solid symbols) and volumetric contraction (open symbols) versus time on stream for run SA-0791.

Figure 3. (H₂+CO) conversion (a), volumetric contraction (b) and H₂/CO usage ratio (c) versus time on stream for run FA-0011.

Figure 4. Anderson-Schulz-Flory plot for run FA-0011, balance 2.

Figure 5. (H₂+CO) conversion (a), volumetric contraction (b) and H₂/CO usage ratio (c) versus time on stream for run FB-0601.

Figure 6. Anderson-Schulz-Flory plot for run FB-0601, balance 2.

Fig.7 XRD patterns of 100Fe/5Cu/4.2K/8SiO₂ catalysts
 (a) after calcination, (b) after reduction with H₂
 followed by reaction, and (c) after reduction with
 CO followed by reaction.

Fig.8 XRD patterns of used 100Fe/5Cu/4.2K/8SiO₂ catalysts after reduction with H₂ (FA-63-3448)
 (a) with glass beads, (b) without glass beads, and
 (c) slow scan without glass beads.

Fig.9 XRD patterns of 100Fe/5Cu/4.2K/40SiO₂ catalysts (a) after calcination, (b) after reduction with H₂ followed by reaction, and (c) after reduction with CO followed by reaction.

Fig.10 XRD patterns of used
 $100\text{Fe}/5\text{Cu}/4.2\text{K}/x\text{SiO}_2$ catalysts
 after reduction with CO.
 (a) $x = 0$ (TOS = 169 h),
 (b) $x = 8$ (TOS = 169 h),
 (c) $x = 16$ (TOS = 453 h),
 (d) $x = 24$ (TOS = 145 h),
 (e) $x = 40$ (TOS = 307 h).

**DATE
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8 / 17 / 92**