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Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 January 1992 - 31 March 1992

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I. Executive Summary

Three tests (two fixed bed and one stirred tank slurry reactor) were completed during the reporting period. Also, the work on catalyst characterization by different techniques (AA, BET, XRD) has been continued.

The performance of a precipitated iron catalyst with nominal composition 100Fe/0.3Cu/0.8K has been evaluated in two fixed bed reactor tests designated FB-0142 and FB-0352 following pretreatment with syngas ($H_2/CO=0.67$) at 280°C, 3NL/g-cat/h and atmospheric pressure for 8 hours. Flow interruption occurred in the first test (FB-0142) at about 72h on stream, and the second test (FB-0352) was conducted to assess any potential adverse effects of this flow interruption on performance of the catalyst. The catalyst was tested at 250°C, 200 psig, 2NL/g-cat/h using syngas of the same composition as that employed during the pretreatment. Initial conversions in both tests were high (about 84%) but the catalyst deactivated fairly rapidly. The ($H_2 + CO$) conversion at the end of the first test (120h on stream) was about 52%, whereas the syngas conversion at the end of the second test (150h) was about 55%, indicating that the brief flow interruption during test FB-0142 had resulted in higher deactivation rate. Hydrocarbon selectivities in both tests were similar and their average values were: $(CH_4) = 4.7$, $(C_2-C_4) = 19.5$, $(C_5 - C_{11}) = 25.3$ and $C_{12}^+ = 50.5$ wt%.

A blank reactor test (without any catalyst) was conducted to determine whether our Autoclave reactor Unit A exhibits any Fischer-Tropsch synthesis activity under reaction conditions employed in run SA-3391 (270°C, 290 psig, 2.4 NL/g-Fe/h, $H_2/CO = 0.7$). During the latter test with UCI iron/silica catalyst (October 1 - December 31, 1991 Quarterly Report) we observed higher than expected values of syngas conversion and methane selectivity when the inlet line and reactor head temperatures were kept at 270°C. Results from the blank test (SA-0582) clearly show that our apparatus catalyzes the FT synthesis reaction, and that hydrocarbon cracking and hydrogenolysis are not causing additional methane production to a significant extent. The reasons for the observed CO hydrogenation activity of our apparatus are still not known, but we suspect that it is primarily due to presence of residual catalyst from the previous tests. This will be investigated and corrective measures will be implemented to eliminate these undesirable effects.

A procedure for separation of catalyst from slurry samples withdrawn from our slurry reactors and its preservation in an inert atmosphere has been developed. Several samples of the UCI catalyst withdrawn from the reactor during run SA-3391 have been characterized by XRD providing information on changes of bulk phases with time on stream.

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 fixed bed tests were carried out with the precipitated iron catalyst (100Fe/0.3Cu/0.8K) to continue the investigation of pretreatment condition effects on catalyst activity, selectivity and stability.

III-1.1 Run FB-0142 and FB-0352 with 100Fe/0.3Cu/0.8K Catalyst

In both tests, the pretreatment conditions were: syngas ($H_2/CO=0.67$) reduction at $280^\circ C$, 3NL/g-cat/h and ambient pressure for 8h. After reduction, the catalyst was tested at average temperature of $250^\circ C$, pressure of 1.48 MPa (200 psig), space velocity of 2NL/g-cat/h and H_2/CO feed ratio 0.67-0.69. During the first test (FB-0142), feed flow interruption occurred at 42h under process conditions (72h on stream) because of leakage of the gas through a valve in the gas feed manifold system. The process conditions were re-established after three hours, and two mass balances were made before the run was terminated around 127h on stream. In order to assess any adverse effects of the feed flow interruption on our results, this test was repeated in Run FB-0352 using the same pretreatment and test procedures. No operational problems were encountered in the latter test, and this test was terminated voluntarily after 150h on stream. The data from two mass balances made in run FB-0142 and three balances in run FB-0352 are summarized in Tables 1 and 2, respectively.

Catalyst Activity and Stability

Catalyst activity, measured by ($H_2 + CO$) conversion and gas volumetric contraction (VC), is plotted against time-on-stream (TOS) in Figure 1 for both tests. The initial activities in both tests were similar. The ($H_2 + CO$) conversions after 6h at process condition and 36h under synthesis gas were 84% in both cases, indicating good reproducibility of results after pretreatment. The catalyst activity decreased fairly rapidly with time-on-stream. For example, the ($H_2 + CO$) conversion decreased to 73.5% at 55h on stream and to 52.3% at 125h (with flow interruption) in

run FB-0142. During run FB-0352, it decreased to 77.5% at 55h on stream, which is similar to that in FB-0142, and to 58% at 150h, which is somewhat higher than that in run FB-0142. Therefore, it is concluded that the feed flow interruption in the first test had some adverse effect on the catalyst activity. The water gas shift (WGS) activity of the catalyst in both tests was high. The (H_2/CO) usage ratio varied between 0.58 - 0.64 in run FB-0142, and between 0.56 to 0.58 in run FB-0352.

Hydrocarbon and Carbon Number Products Distributions

Hydrocarbon product distributions in run FB-0142 were determined after the gas feed flow interruption, and were similar in both mass balances (see Table 1). The average value for methane and other hydrocarbons selectivities were: 4.7 (CH_4), 20.5 (C_2-C_4), 28.4 (C_5-C_{11}) and 46.3 wt% (C_{12}^+).

In run FB-0352, the hydrocarbon distribution shifted towards lower molecular weight hydrocarbons as the catalyst deactivated with time. For example, at 72h on stream with (H_2+CO) conversion of 71%, hydrocarbon selectivity was 4.3 (CH_4), 18.6 (C_2-C_4), 23.1 (C_5-C_{11}) and 54.0 wt% (C_{12}^+); while at 144h on stream, with (H_2+CO) conversion of 55%, it became 5.0 (CH_4), 20.6 (C_2-C_4), 24.4 (C_5-C_{11}) and 50.0 wt% (C_{12}^+) (see Table 2). Hydrocarbon product distributions in these two tests were similar.

Typical carbon number product distribution, in the form of Anderson-Shulz-Flory (ASF) plot, is shown in Figure 2 for run FB-0142 and in Figure 3 for run FB-0352. Chain growth parameter for products in C_1-C_{11} range were 0.74 and 0.72, respectively. Solid product (wax) collected in a high pressure trap was not analyzed in both cases.

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

The activities related to this task include: (1) Determination of reactor activity for FTS reaction (Section III-2.1) and (2) Characterization of iron/silica catalysts by atomic absorption and X-ray powder diffraction (Section III-3)

III-2.1 Run SA-0582 (Blank Test)

In a previous slurry reactor test (Run SA-3391) of UCI catalyst we have observed higher than expected values of syngas conversion and methane selectivity during initial 190 hours of testing. These values were tentatively ascribed to Fischer-Tropsch synthesis reaction in tubing downstream of the reactor and/or cracking of hydrocarbon products outside the reactor (Quarterly Report October 1 - December 31, 1991). Both the syngas conversion and methane selectivity decreased significantly when the reactor head and exit line temperature were decreased by 30-50°C. A blank test (without a catalyst) was conducted to clarify these observations.

About 300g of ETHYLFLO™ 164 oil, which was also used in run SA-3391, was loaded as the initial liquid medium. After sealing of the reactor, the same operation procedures and conditions for catalyst reduction as employed during run SA-3391 were followed (280°C, 153 psig, $H_2/CO=0.70$ at a feed flowrate of 475 cm³/min for 12h). After the pretreatment, the blank test was conducted at 270°C, 290 psig with a synthesis gas of $H_2/CO=0.70$ at a feed flow rate of 490 cm³/min (corresponding to 2.4 NL/g-Fe/h in run SA-3391). Reactor tail gas flow rates and compositions were frequently measured as during the catalyst test. Methane and other light hydrocarbons, as well as carbon dioxide were detected. At 57h on stream, the temperature of the reactor exit line was decreased by 50°C to 200°C; and subsequently at 77h on stream, the temperatures of the reactor head and inlet line (both heated by a single heating tape) were lowered from 270 to 240°C. The reactor inlet and exit lines, as well as the reactor head temperatures were restored to their original values at 101h on stream. Then, at 119h and 145h on stream, about 70g (100 ml) of n-hexadecane ($n-C_{16}$) was added to the reactor in order to investigate whether hydrocarbon cracking occurs under the reaction conditions and how it affects the methane formation. At 166h on stream, the third batch of 70g of n-hexadecane was added to the reactor, and the synthesis gas flow was replaced by pure hydrogen flow (same total flow rate as the syngas) to assess the possibility of hydrogenolysis reaction, and its effect on methane formation. Syngas feed ($H_2/CO=0.70$) was again introduced at 194h on-stream to replace hydrogen, and the

blank test was continued for additional 50h. The major events during the test are summarized in Table 3.

Blank Reactor Activity

Although no catalyst was loaded into the reactor, the system had exhibited FT synthesis activity during the blank reactor test. FTS activity, measured by (H_2+CO) conversion and gas volumetric contraction increased gradually during first 80h on stream, as shown in Figure 4. For example, (H_2+CO) conversion increased from 11% at 1h to 27% at 77h on stream while volumetric contraction increased from 8.4 to 16.8%. Decreasing of the exit line temperature at 57h on stream did not have any effect on conversion. However, after the inlet line and the Autoclave reactor head temperatures were decreased from 270 to 240°C, the FTS activity markedly decreased. Fifteen hours after decreasing these temperatures the (H_2+CO) conversion became 4% only and remained low until the temperatures were raised again to 270°C at 100h on stream (see Fig. 4). When n-hexadecane was added twice into the reactor with syngas flowing (at 119 and 145h), the tail gas flowrate and composition were analyzed frequently to monitor this transient behavior. The (H_2+CO) conversion and VC increased slightly following addition of hexadecane. However, this may not be necessarily caused by cracking reaction, but rather to increase of activity with time on stream. The amount of hexadecane added to the system in this run was significantly higher than the amount of all volatile hydrocarbons present in the slurry during run SA-3391 with the UCI catalyst, and thus the effect of cracking on (H_2+CO) conversion and methane production rate is considered to be minor in comparison to direct CO hydrogenation via FT synthesis reaction. At 166h, hexadecane was added again, and the gas feed was switched to pure hydrogen. The volumetric gas contraction decreased to practically zero, soon after CO was removed from the feed. These results show that neither cracking nor hydrogenolysis of high molecular weight paraffins is the major route causing blank activity. Methane and other light hydrocarbons produced in the blank test were formed mainly by hydrogenation of carbon monoxide. This reaction was probably catalyzed by residual FT catalyst remaining in the reactor apparatus. When syngas feed was

introduced after about 30h of pure hydrogen flow, the FT synthesis was observed again, and (H_2+CO) conversion and VC continued to increase with time-on-stream until the end of the test.

Carbon dioxide was found in the tail gas, and H_2/CO usage ratio decreased from 1.1 to 0.74 with time-on-stream. Therefore, the WGS reaction also took place and increased with time during the blank test.

Methane Formation and Hydrocarbon Selectivity

Figure 5 shows change in methane formation rate, in (g/h) calculated from tail gas flowrate and composition measurements, at various periods during the blank test. Generally, its trend follows that of the overall (H_2+CO) conversion and VC (Figure 4), i.e., methane formation rate increased with TOS, except when the temperature of inlet line/reactor head was decreased to 240°C , and when pure hydrogen was used as a feed. In the first case, methane formation rate decreased from 0.26 (g/h), before lowering of the reactor head temperature, to 0.03 (g/h) after lowering the reactor head temperature to 240°C . During run SA-3391, the decrease in methane production after a similar cooling in the inlet line/head temperature was about 0.16 (g/h), whereas in the present test a decrease of 0.23 (g/h) was observed. Therefore, the unusually high methane selectivity obtained during the first 190h on-stream in run SA-3391 was caused by the additional 'blank' activity induced by our reactor apparatus. In the second case (pure hydrogen feed) methane formation dropped rapidly as CO was removed from the feed. No significant increase in methane formation was found after addition of hexadecane into the reactor (120-165h). On the other hand, methane formation became much higher after 30h of pure hydrogen feed. It increased from 0.31 (g/h) to 0.44-0.50 (g/h), while the activity did not change much, as can be seen by comparing Figures 4 and 5. If we assume that the 'blank' activity observed here was a catalytic one (caused by some unknown-yet source), feeding of pure hydrogen acted as hydrogen reduction of the catalyst. It has been demonstrated in our work on pretreatment effect that catalysts reduced with hydrogen usually give high methane selectivity, as was found here.

Carbon number product distribution from C_1 to C_6 , based on a typical gas phase analysis, is shown in Figure 6 in the form of ASF plot; C_2 is found always below the ASF line, whereas methane is slightly above. The chain growth parameter for C_1 - C_5 (excluding C_2) hydrocarbons is 0.58 for this case. It gradually decreased to 0.50 as methane formation rate increased with time-on-stream.

Results from the blank test indicate that the slurry reactor A apparatus provided additional FT catalytic activity, which caused hydrogenation of CO to form methane and other light hydrocarbons. Cracking and hydrogenolysis reactions were probably not important factor for the observed activity. We plan to examine and change tubing or other parts on the reactor head and/or inlet line which contain residual catalyst from previous tests, in order to prevent this problem occurring in future tests. This has not been completed yet, by the end of this reporting period.

III-3 Catalyst Characterization

During the current reporting period, we have continued our catalyst characterization studies of as prepared, calcined and used catalysts by atomic absorption (AA), BET surface area and pore size distribution and X-ray powder diffraction (XRPD). Results from these studies are summarized below.

Elemental Analysis of Catalysts

The composition of several silica containing catalysts was determined by atomic absorption. The contents of iron, copper and potassium were determined directly, whereas the amount of SiO_2 was determined by calculation. Results obtained in our Laboratory as well as those from Galbraith Laboratories, Inc., using ICP method, are summarized in Table 4.

Results in Table 4 represent the part by weight of copper, potassium and silica (SiO_2) to 100 parts by weight of iron. The analyzed copper and SiO_2 contents in all samples are close to the nominal values. On the other hand, potassium contents are generally higher than expected. These results are in good agreement with values obtained earlier at TAMU. In comparison of our results

with that from Galbraith Laboratory, good agreements are observed in copper and silica contents in the 100Fe/5Cu/4.2K/100SiO₂ catalyst; however, level of potassium determined in our laboratory is significantly higher than that determined by Galbraith (8.0 vs. 5.8). Also, the potassium content of the UCI catalyst, was significantly higher than the nominal content supplied to us by DOE.

Surface Area and Pore Size Distribution

Surface areas and pore volumes were measured by physical adsorption of N₂ at 77 K. Results of measurement for three catalysts are shown in Table 5.

We suspected that the value of surface area determined previously at our laboratory for the catalyst with nominal composition 100Fe/5Cu/4.2K/100SiO₂ is in error (Quarterly report for period 1 October - 31 December 1991), in comparison to the surface areas of catalysts containing smaller amounts of silica. Therefore, this catalyst, and two other samples (with and without silica), were submitted for surface area determination to Sandia National Laboratory. For the 100 Fe/5Cu/4.2K/100SiO₂ catalyst, the values of surface area (SA) and pore volume (V_p) determined by Sandia National Laboratory are in excellent agreement with those measured at TAMU (150 vs 152 m²/g for SA, and 0.83 vs 0.82 cm³/g for V_p, respectively). Good agreement was also obtained for the catalyst containing 40 parts of silica, whereas the surface area of the 100Fe/0.3Cu/0.8K catalyst sample determined at SNL was 28% lower than that measured at TAMU. This difference is larger than expected, and may be caused by different sample handling procedures and/or by nonuniformity of catalyst samples.

The catalyst with nominal composition of 100 Fe/0.3Cu/0.8K (C-0308-3) was reduced under various conditions (Quarterly report for period 1 October - 31 December 1991). The surface area and pore volume data of this catalyst after three pretreatment (reduction) procedures are shown in Table 6.

In all cases surface area and pore volume decreased after reduction with either CO or H₂. For example, the surface area (SA) decreased from 130 to 42-44 m²/g after the catalyst was reduced with CO at 280°C for 8h, or with H₂ at 220°C for 1h. A larger decrease in surface area

was observed after the reduction with H_2 at $280^\circ C$ for 8h. The pore volume of reduced catalyst, when compared to the calcined one, decreased 24% after CO reduction at $280^\circ C$, as well as after H_2 reduction at $220^\circ C$. A smaller change of pore volume, 15%, was detected for reduction with H_2 at $280^\circ C$ (8h). The average pore diameter, calculated on the basis of measured total pore volume and surface area ($d_p = 4 \times V_p / SA$), of the catalyst reduced with H_2 at $280^\circ C$ is more than twice larger than that of the other two samples.

Figure 7 shows differential pore volume distribution of reduced and calcined catalyst. A shift in peak maximum from about 100 Å (calcined sample) to 150-200 Å (H_2 reduction at $220^\circ C$), and to 500 Å (H_2 reduction at $280^\circ C$) is in agreement with observed decrease in surface area. The pore volume distributions of catalysts after H_2 reduction (220 or $280^\circ C$) have only one maximum, while that for catalyst after CO reduction has tendency toward bimodal pore distribution with clear maximum at about 150-200 Å and increased fraction of pores with small diameter (about 20 Å).

X-Ray Diffraction of Used UCI Catalyst from Slurry Reactor

During the current reporting period several used UCI catalyst samples, which were taken during slurry test SA-3391, were separated from slurry in an inert atmosphere using the procedures outlined in the Appendix I of this report. The phases of UCI catalyst at different times on stream were identified by X-ray diffraction analysis.

Figure 8 shows XRD patterns of UCI catalyst at 98, 265 and 307 (end of run) hours on stream. Generally, the XRD peaks were identified as magnetite (Fe_3O_4), siderite ($FeCO_3$) and iron carbides (mostly as Fe_2C -monoclinic and hexagonal form, and $\chi Fe_{2.5}C$). Carburization of iron catalyst increased with time on stream as well as formation of siderite. The dominant phases of the catalyst samples withdrawn from the reactor at 98h on stream were Fe_3O_4 and Fe_xC , and their crystallite size was very small. Crystallinity increased with TOS and at 265 and 307h on stream, the crystallites were greater than 500 Å. The form of iron carbide also changed with time on stream. For example, after 98h on-stream, the Fe_2C -monoclinic carbide was the dominant form, while the intensity of XRD peaks corresponding to other forms of iron carbides (Fe_2C -hexagonal

and $\chi\text{-Fe}_{2.5}\text{C}$) increased with time on stream. No significant differences in iron phases and or crystallinity were observed between samples withdrawn at 265 and 307h on stream.

Substantial amount of slurry sample taken after the reduction in run SA-3391 was lost during handling and separation. Only 80mg of reduced UCI catalyst was recovered from the slurry sample, and this amount is too small for XRD analysis, but it is sufficient for Mössbauer analysis (MES). This sample of reduced UCI catalyst was sent to University of Kentucky (CFFLS) for characterization by MES.

X-Ray Diffraction of Used Catalyst from Fixed Bed

XRD patterns of used 100 Fe/0.3Cu/0.8K catalyst from Run FB-0352 are shown in Figure 9. Iron carbides are the dominant phase in the sample taken from the top part of the bed (reducing atmosphere), whereas both magnetite and carbides are present in significant quantities in the sample from the bottom part of the bed (oxidizing atmosphere). Peaks in the region $2\theta=21\text{-}24^\circ$ correspond to wax.

Mössbauer Effect Spectroscopy (MES)

A total of 19 catalyst samples from fixed bed and slurry reactor tests have been mailed to University of Kentucky for characterization by MES.

During the reporting period we have received results of MES characterization of 18 catalyst samples which were sent earlier. In general, the iron phases determined by MES are in agreement with our results reported previously using XRPD method. However, in addition to phase identification MES provides information on relative amounts of iron phases in the sample, and thus complements XRPD data. A detailed description of MES characterization results will be presented in our future reports.

Table 1. Summary of results for fixed bed run FB-0142 .

Catalyst: 3.00 g^a, 100Fe/0.3Cu/0.8K
 Catalyst volume: 3.20 cc
 Diluent: 35.70 g, Glass beads
 Diluent Volume: 23.50 cc

Period	1	2
Date	01/19/92	01/20/92
Time on Stream (h)	97.0	120.0
Balance Duration (h)	7.0	7.0
Average Temperature (°C)	250.	250.
Maximum Δ Temperature (°C) ^b	2.00	2.00
Pressure (MPa)	1.48	1.48
H ₂ /CO Feed Ratio	.695	.695
Space Velocity (NI/g-cat.h) ^a	2.00	2.00
Space Velocity (NI/g-Fe.h)	2.91	2.91
GHSV (h ⁻¹) ^c	229.	229.
CO Conversion (%)	60.4	55.2
H ₂ +CO Conversion (%)	57.4	52.0
H ₂ /CO Usage	.610	.598
STY (moles H ₂ +CO/g-cat.h) ^a	.051	.046
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	7.34	9.98
Weight % of Outlet		
H ₂	2.23	2.49
H ₂ O	1.99	1.34
CO	37.6	42.5
CO ₂	43.3	40.1
Hydrocarbons	8.95	7.50
Oxygenates	.632	.524
Wax ^d	5.38	5.51
Yield (g/Nm ³ H ₂ + CO Converted)		
CH ₄	8.86	9.29
C ₂ -C ₄ Hydrocarbons	39.3	40.4
C ₅ -C ₁₁ Hydrocarbons	55.3	54.5
C ₁₂ + Hydrocarbons	90.4	90.4
Wax ^d	72.8	82.4
Oxygenates	8.55	7.83
Total	202.	202.
1+2 Olefins/n-Paraffin Ratio		
C ₂	2.22	2.08
C ₃	7.68	7.63
C ₄	7.41	7.48
C ₆	5.14	4.92
C ₁₀	1.56	4.63

^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-0142.

Weight % of Hydrocarbons	Period	
	1	2
CH ₄	4.57	4.78
Ethane	1.86	2.01
Ethylene	3.85	3.90
Propane	.984	1.01
Propylene	7.21	7.34
n-Butane	.773	.779
1+2 Butenes	5.52	5.62
C ₄ Isomers	.0810	.0878
n-Pentane	.692	.678
1+2 Pentenes	4.57	4.57
C ₅ Isomers	2.25	2.05
n-Hexane	.557	.533
1+2 Hexenes	3.19	3.10
C ₆ Isomers	.930	.983
n-Heptane	.476	.463
1+2 Heptenes	2.50	2.42
C ₇ Isomers	.675	.891
n-Octane	.430	.419
1+2 Octenes	2.17	2.02
C ₈ Isomers	1.01	1.06
n-Nonane	.453	.468
1+2 Nonenes	2.15	2.13
C ₉ Isomers	.733	.616
n-Decane	.417	.426
1+2 Decenes	1.87	1.94
C ₁₀ Isomers	.695	.771
n-Undecane	.397	.344
1+2 Undecenes	1.67	1.43
C ₁₁ Isomers	.695	.688
C ₂ -C ₄	20.3	20.7
C ₅ -C ₁₁	28.5	28.0
C ₁₂ +	46.6	46.5
Wax ^d	37.5	42.4

^d Unanalyzed products collected from hot trap

Table 2. Summary of results for fixed bed run FB-0352.

Catalyst: 3.00 g^a, 100Fe/0.3Cu/0.8K
 Catalyst volume: 3.20 cc
 Diluent: 35.70 g, Glass beads
 Diluent Volume: 23.50 cc

Period	1	2	3
Date	02/08/92	02/10/92	02/11/92
Time on Stream (h)	72.0	120.0	144.0
Balance Duration (h)	8.5	8.0	7.5
Average Temperature (°C)	250.	250.	250.
Maximum Δ Temperature (°C) ^b	2.00	3.00	3.00
Pressure (MPa)	1.48	1.48	1.48
H ₂ /CO Feed Ratio	.695	.695	.695
Space Velocity (NI/g-cat.h) ^a	2.00	2.00	2.00
Space Velocity (NI/g-Fe.h)	2.91	2.91	2.91
GHSV (h ⁻¹) ^c	229.	229.	229.
CO Conversion (%)	76.8	63.5	59.7
H ₂ +CO Conversion (%)	70.7	58.8	55.7
H ₂ /CO Usage	.560	.569	.581
STY (mols H ₂ +CO/g-cat.h) ^a	.063	.052	.050
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	20.2	15.0	17.8
Weight % of Outlet			
H ₂	1.79	2.27	2.37
H ₂ O	1.30	1.17	.874
CO	21.8	34.5	38.1
CO ₂	56.4	46.8	44.1
Hydrocarbons	9.71	7.96	7.54
Oxygenates	.692	.547	.525
Wax ^d	8.33	6.75	6.45
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄	8.64	9.59	9.83
C ₂ -C ₄ Hydrocarbons	37.3	40.4	40.4
C ₅ -C ₁₁ Hydrocarbons	46.2	47.7	47.0
C ₁₂ + Hydrocarbons	108.	97.5	98.9
Wax ^d	92.5	89.6	90.4
Oxygenates	7.68	7.26	7.36
Total	208.	202.	203.
1+2 Olefins/n-Paraffin Ratio			
C ₂	2.05	1.71	1.73
C ₃	7.62	7.52	7.38
C ₄	7.17	7.26	7.14
C ₈	4.90	4.37	4.32
C ₁₀	4.59	4.59	4.43

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

Table 2 (cont'd). Summary of results for fixed bed run FB-0352.

Weight % of Hydrocarbons	Period		
	1	2	3
CH ₄	4.31	4.91	5.01
Ethane	1.83	2.33	2.28
Ethylene	3.50	3.73	3.68
Propane	.913	1.02	1.04
Propylene	6.64	7.30	7.31
n-Butane	.709	.772	.777
1+2 Butenes	4.91	5.41	5.35
C ₄ Isomers	.134	.149	.141
n-Pentane	.610	.727	.649
1+2 Pentenes	4.16	4.41	4.31
C ₅ Isomers	2.23	2.55	2.54
n-Hexane	.498	.515	.518
1+2 Hexenes	2.84	2.90	2.83
C ₆ Isomers	.815	.946	.940
n-Heptane	.391	.456	.438
1+2 Heptenes	2.10	2.26	2.17
C ₇ Isomers	.403	.632	.647
n-Octane	.358	.392	.374
1+2 Octenes	1.72	1.68	1.59
C ₈ Isomers	.429	.534	.510
n-Nonane	.323	.333	.327
1+2 Nonenes	1.58	1.54	1.49
C ₉ Isomers	.505	.453	.442
n-Decane	.298	.302	.314
1+2 Decenes	1.35	1.37	1.37
C ₁₀ Isomers	.439	.468	.455
n-Undecane	.303	.291	.316
1+2 Undecenes	1.25	1.18	1.25
C ₁₁ Isomers	.463	.492	.495
C ₂ -C ₄	18.6	20.7	20.6
C ₅ -C ₁₁	23.1	24.4	24.0
C ₁₂ +	54.0	49.9	50.4
Wax ^d	46.2	45.9	46.1

^d Unanalyzed products collected from hot trap

Table 3. Major events in Run SA-0582

TOS (h)	Event
	Liquid loading: 300g ETHYLFLO™ 164 (C ₃₀) liquid, Pretreatment: H ₂ /CO=0.70, T=280°C, P=1.14 MPa, Flowrate=475 cc/min, for 12h Temperature was lowered from 280 to 270°C over 3h
0	Achieved initial process conditions: T=270°C, P=2.10MPa, Flowrate=490 cc/min, feed (H ₂ /CO)=0.70
57	Decreased exit line temperature from 250 to 200°C
77	Decreased reactor head temperature from 270 to 240°C
101	Increased exit line temperature to 250, and reactor head temperature to 270°C (base line conditions)
119	Added 70g of n-hexadecane (n-C ₁₆) to the reactor
145	Added 70g of n-hexadecane (n-C ₁₆) to the reactor
166	Added 70g of n-hexadecane (n-C ₁₆) to the reactor. Stopped syngas flow and introduced hydrogen, flowrate=490 cc/min
194	Switched back to syngas, flowrate=490 cc/min, (H ₂ /CO=0.70)
245	End of run.

Table 4. Catalyst Composition Determined by Atomic Absorption

Nominal Composition 100Fe/xCu/yK/zSiO ₂	Sample Code	x	Actual Composition y	z	Remarks	Ref
100Fe/5Cu/4.2K	#31	5.1	4.1		(a)	
	#31	4.4±0.4	4.9±0.6			1
100Fe/5Cu/4.2K/8SiO ₂	#63.1	4.5±0.4	4.5±0.5	8.0±0.6	(a)	
	#63.1	4.3	5.3	11.4	(a)	
100Fe/5Cu/4.2K/16SiO ₂	#64	5.4	4.9	12.6	(a)	
	#64	5.6±0.5	6.3±0.8	18.5±7.7		2
100Fe/5Cu/4.2K/100SiO ₂	#69	4.1	5.8	91.3	(G)	
	#69	4.6±0.4	8.0±1.1	95±8		3
100Fe/4.3Cu/8K/17SiO ₂	UCI	4.6	9.6	21.8	(a)	

(a)-determined at TAMU; (G)-determined at Galbraith Lab - (ICP Method)

(1)-Quarterly report (1 April - 30 June 1991);

(2)-Quarterly report (1 October - 31 December, 1990);

(3) - Quarterly report (1 October - 31 December, 1991).

Table 5. Surface Area and Pore Size Distribution of Calcined Catalysts

Catalyst nominal composition	Catalyst Code	SA (m ² /g)	PV (cm ³ /g)	d _p (Å)	Remarks
100Fe/0.3Cu/0.8K	C-0308-1	151	0.26	69	TAMU*
	C-0308-1	108	0.25	92	SNL
100Fe/5Cu/4.2K/24SiO ₂	#66	336	0.51	61	TAMU
	#66	293	0.48	66	SNL
100Fe/5Cu/4.2K/100SiO ₂	#69	150	0.83	221	TAMU*
	#69	152	0.82	216	SNL

*reported in Quarterly report (1 October - 31 December, 1991)

SNL = Sandia National Laboratory

Table 6. Surface Area and Pore Volume of 100Fe/0.3Cu/0.8K Catalyst (batch C-0308-3)

Catalyst State	pretreatment conditions				SA (m ² /g)	V _p (cc/g)	d _p (Å)	Remarks
	gas	flow rate (cc/min)	temp (°C)	time (h)				
as prepared					190	0.36	76	a
calcined	Air	750	300	6	130	0.33	102	a
reduced	CO	175	280	8	44	0.25	230	
reduced	H ₂	3350	220	1	48	0.25	210	
reduced	H ₂	175	280	8	21	0.28	529	

(a) reported earlier in Quarterly Report (1 April - 30 June, 1991)

Figure 1. (H₂+CO) conversion (open symbols) and volumetric contraction (solid symbols) versus time on stream for runs FB-0421 and FB-0352.

Figure 2. Anderson-Schulz-Flory plot for run FB-0142, balance 2, total products excluding wax.

Figure 3. Anderson-Schulz-Flory plot for run FB-0352, balance 1, total products excluding wax.

Figure 4. $(H_2 + CO)$ conversion (open symbols) and volumetric contraction (solid symbols) versus time on stream for run SA-0582.

Figure 5. Methane formation rate versus time on stream for run SA-0582.

Figure 6. Anderson-Schulz-Flory plot for run SA-0582, at time on stream of 54 h.

Figure 7. Pore size distribution for 100Fe/0.3Cu/0.8K catalyst (batch: C-0308-3)

- a) as prepared catalyst
- b) calcined catalyst
- c) reduced catalyst with CO (280°C, 8 h)
- d) reduced catalyst with H₂ (220°C, 1 h)
- e) reduced catalyst with H₂ (280°C, 8 h)

Figure 8. XRD patterns of used UCI catalyst in slurry reactor (run SA-3391)
 a) TOS=98 h; b) TOS=265 h; c) TOS=307 h (end of run)

Figure 9. XRD patterns of used 100Fe/0.3Cu/0.8K catalyst reduced with syngas ($\text{H}_2/\text{CO}=0.69$) at 280°C for 8 h (run FB-0352)
 a) top part of reactor (after 150 h)
 b) bottom part of reactor (after 150 h)

Appendix I. Separation of Used Catalyst from Wax and Sample Handling

Results of XRPD (X-ray powder diffraction) analysis of catalyst from slurry reactor tests depend mostly on effective separation of catalyst particles from wax and ability to avoid any contact of catalyst with oxidizing atmosphere (air). With the goal to identify the actual iron phases present during slurry tests, a procedure for catalyst handling and separation from wax in an inert atmosphere was developed. This procedure can be divided into two parts: (1) separation by paper filtration using varsol and toluene; and (2) separation by soxhlet extraction using xylene and methyl ethyl ketone.

Catalyst separation from wax is performed in an inert atmosphere, and the first part of our procedure is carried in a glove box filled with helium (He). Brief description of catalyst separation is as follows: A sample of slurry (about 20g), from the slurry sampling cylinder, is dissolved in a warm and degassed varsol (100 cm³) and then filtered through a filter paper (#2, medium filtration speed) at about 80°C. The filter cake, mostly catalyst and small amount of wax, is then rinsed with warm degassed toluene (75cm³). The wet cake is later dried in vacuum at ambient temperature in a pre-chamber of the glove box. After drying, the cake/filter paper is put into an extraction thimble which is placed inside a small sealable plastic bag.

The transfer of thimble (with catalyst) into a soxhlet extraction tube, and the assembly of the entire soxhlet extraction apparatus is done inside a large glove-bag filled with He. After that, the assembled apparatus is taken out of the glove-bag and extraction is performed first with xylene for 36h, followed by methyl ethyl ketone for additional 18h. The top of the condenser of the extraction unit is closed using a valve, so that no air could enter the apparatus during extraction. During replacement of solvent, helium is fed from the top of the condenser, through the extraction tube, to avoid contact of catalyst with air. At the end of extraction, the thimble with filter paper and catalyst is removed from the soxhlet tube in a glove bag filled with He, and placed into a small sealable plastic bag which is then transferred into the glove-box. Finally, inside the glove-box, the catalyst is removed from the thimble and filter paper and stored in a sealed vial. The catalyst sample is kept in the glove box until it is submitted for characterization using a special sample holder.

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