I. EXECUTIVE SUMMARY

Three slurry reactor tests were completed in continuation of our studies on the effect of pretreatment conditions on catalyst activity and selectivity. In two tests (SA-0946 and SB-1486) the catalyst was activated with CO at 280°C for 8 h, and in test SA-1626 the activation was done with the syngas ($H_2/CO = 0.67$) instead of CO. Exceptionally good performance was obtained in run SA-0946. During testing at 260°C, 2.17 MPa, 4.4 Nl/g-Fe/h and $H_2/CO = 0.67$ (250 - 440 h on stream) the CO and syngas conversions were 85-87 % and 80-83%, respectively, whereas methane and C_1+C_2 hydrocarbon (HC) selectivities were low (2.3 -2.5 mol% and 6 mol%). The catalyst space-time-yield (productivity) was estimated to be 0.72 g HC/g-Fe ·h. This is significantly higher than obtained previously (under similar conversions and selectivities). For example, the catalyst productivity in Rheinpreussen demonstration unit was 0.49 g HC/g-Fe ·h.

Syngas activated catalyst (SA-1626) had higher gaseous hydrocarbon selectivity than either CO or hydrogen activated catalyst. Also, it deactivated with time on stream.

One slurry reactor test with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) was completed under Task 7. Calcination Effect Research. Catalyst calcined at 700°C (SB-1276) had significantly lower activity than the catalyst calcined at 300°C (run SB-1295). Similar findings were obtained in previous tests with catalyst C, and it is concluded that flash calcination does not result in any improvements in the performance of these two catalysts.

The work on catalyst characterization by temperature programmed and isothermal reduction on a variety of iron catalysts, with different amounts of promoters, has been continued. These studies are complementing our work on Task 6, and provide additional insights into the effect of pretreatment procedures on the reduction behavior of iron catalysts.

II. OBJECTIVES AND SCOPE OF WORK

The overall contract objectives are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at Texas A&M University (TAMU) during the DOE Contract DE-AC22-89PC89868; (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst synthesis; (3) investigate performance of catalysts in a small scale bubble column slurry reactor, and (4) investigate feasibility of producing catalysts on a large scale in collaboration with a catalyst manufacturer. In order to achieve these objectives the work is divided into a number of tasks, which are described below together with the time schedule for their execution.

Task 1. Project Work Plan (April 1-April 30, 1994)

The objectives of this task are: (1) Prepare in detail all activities which shall be performed for the successful completion of the work for the entire duration of the contract; and (2) Provide a project work chart showing the key personnel/groups planned for each task, and the percentage of their time to be devoted to individual tasks.

Task 2. Engineering, Modification and Training of New Personnel (April 1-September 30, 1994)

The objective of this task is to perform the engineering design, procurement of new equipment, installation of the instruments and auxiliary gas supply lines and to provide training for new personnel prior to catalyst testing in laboratory reactors.

Task 3. Testing of Previously Synthesized Catalysts (October 1, 1994 - March 31, 1995)

The purpose of this task is to verify reproducibility of results obtained previously at TAMU with catalysts designated B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2). The catalysts from the same preparation batch shall be used, and the same pretreatment and process conditions shall be employed as in the previous slurry reactor tests of these two catalysts.

Task 4. Reproducibility of Catalyst Preparation (October 1, 1994 - September 30, 1995)

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. Catalysts B and C will be synthesized following procedures developed at TAMU. Catalysts with satisfactory physico-chemical properties will be initially tested in a fixed bed reactor for screening purposes (5 day tests). Following this the two catalysts will be tested in a stirred tank slurry reactor (STSR) using standard pretreatment and process conditions. The activity, selectivity, deactivation behavior of these new catalyst batches will be compared to that of the catalysts from the original (existing) batches.

Task 5. The Effect of Source of Potassium and Basic Oxide Promoter (October 1, 1994 - December 31, 1995)

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on the catalyst performance. Catalysts B and C will be synthesized using potassium silicate solution as the source of potassium promoter, and performance of these catalysts will be compared with that of catalysts synthesized using our standard procedure (i.e. using potassium bicarbonate as the source of potassium promoter).

The effect of CaO promotion on performance of catalysts B and C (two levels of promotion per catalyst) shall be investigated. Synthesized catalysts will be tested first in a fixed bed reactor, and if the satisfactory results are obtained the most promising catalyst formulations will be tested in the STSR.

Task 6. Pretreatment Effect Research (October 1, 1995 - November 30, 1996)

The effect of four different pretreatment procedures, in addition to the baseline procedure, on the performance of catalyst B (or C) will be studied in a STSR. In addition to STSR tests, the pretreatment effects will be studied by thermogravimetric analysis (TGA) , differential thermal analysis (DTA) and temperature programmed reduction (TPR). Iron phases in the catalyst will be determined by X-ray powder diffraction (XRPD).

Task 7. Calcination Effect Research (October 1, 1995 - July 31, 1996)

The effect of calcination temperature (300-500°C) on the catalyst physical properties and performance during FT synthesis shall be studied in a fixed bed reactor and a STSR. In addition to the baseline calcination temperature of 300°C, the calcination temperatures of 400 and 500°C will be employed in a fixed bed reactor with flowing air. Also, the effect of rapid heating (flash calcination) on performance of catalysts B and C shall be investigated.

Task 8. Catalyst Characterization (December 1, 1994 - March 28, 1997)

The objectives of this task are: (1) Provide basic characterization (by AA, BET, XRPD) of synthesized catalysts, and used catalysts (by XRPD, Mössbauer spectroscopy) in support of other tasks of the project; (2) Attempt to identify and quantify "surface" species on the catalyst after exposure to CO and/or synthesis gas by temperature programmed techniques (TPR/ TPD/ TPO/ TPRX) coupled with on-line gas analysis by mass spectrometry and gas chromatography.

Task 9. Catalyst Testing in a Bubble Column Slurry Reactor (October 1, 1996 - March 28, 1997)

A laboratory bubble column slurry reactor (BCSR) shall be designed, constructed and used for testing of catalysts B and C to quantify differences in the reactor space-time-yield and hydrocarbon selectivities between the STSR and the BCSR. This unit will be approximately 2.5 cm (~1 in) in diameter and 1.5 m (~5 ft) tall, with the effective (unexpanded or static) slurry volume of about 500 cm^3.

Task 10. Scale-Up of a Catalyst Synthesis Procedure (April 1, 1996 - March 28, 1997)

By the end of the first eighteen months of this project, the repeatability of the catalyst performance and catalyst preparation procedure shall be demonstrated. Subsequently, if the performance of the catalysts is found satisfactory by DOE the Contractor shall work with a catalyst manufacturer on synthesis of a large batches (~100 lb) of catalysts B and C. The cost estimate for the catalyst preparation will be provided upon reviewing details of the preparation procedure, and submitted to DOE for approval. Upon the DOE approval the Contractor will test catalysts synthesized by a catalyst manufacturer in a STSR.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III. 1 Task 1. Project Work Plan

The work on this task was completed. No additional activity to report.

III. 2 Task 2. Engineering Modifications and Training of New Personnel

The work on this task was completed. No additional activity to report.

III. 3 Task 3. Testing of Previously Synthesized Catalysts

The work on this task was completed. No additional activity to report.

III. 4 Task 4. Reproducibility of Catalyst Preparation

The work on this task was completed. No additional activity to report.

III. 5 Task 5. The Effect Of Source of Potassium and Basic Oxide Promoter

The work on this task was completed. No additional activity to report.

III. 6 Task 6. Pretreatment Effect Research

Work on the pretreatment effect research has continued in this quarter. Three slurry reactor tests were completed with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4. In two tests, SA-0946 and SB-1486, the catalyst was activated with CO at 280°C for 8 h, and in the third test, SA-1626, the catalyst was pretreated with synthesis gas ($H_2/CO = 0.67$) at 280°C for 8 h. Detailed description of the test results is given below, followed by comparison of results using different pretreatment procedures.

III. 6. 1 <u>Run SA-0946 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst</u>

Fifteen grams of the catalyst (< 270 mesh in size) was loaded for the test, together with 306 g Durasyn 164 oil as the initial slurry medium. The pretreatment conditions used were: CO at 280°C, 0.78 MPa (100 psig), 750 cm^3/min (3 Nl/g-cat/h) for 8 h. Major events are summarized in Table 1.

Following the reduction, the catalyst was tested at 260°C, 1.48 MPa, syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$) and gas space velocity of 2.34 Nl/g-cat/h. Catalyst activity, measured by CO conversion and (H_2+CO) conversion is shown in Figures 1a and 1b, respectively. Both conversions increased gradually with time on stream during the first 100 h and then stabilized at about 81%, CO conversion, and between 76 and 77% for (H_2+CO) conversion. The usage ratio (Figure 1c) decreased from the first recorded value of 0.71 to 0.58 at 100 h and did not changed significantly at these conditions. Methane selectivity (Figure 2a) after the reduction (3 h at process conditions) was 4 mol% and decreased to about 3.2 mol% after 100 h (Figure 2a). Similarly, C_1+C_2 hydrocarbon selectivity decreased from 8.3 to 7 mol% (Figure 2b), and C_2-C_4 hydrocarbon selectivity from 15 mol% to 14.5 mol% during the same time period (Figure 2c).

At 133 h on stream, the space velocity was decreased to 1.8 Nl/g-cat/h, while the other conditions remained constant. This resulted in the increase of CO and syngas conversions to 85 and 80%, respectively, but the usage ratio remained at 0.57-0.58. Gaseous hydrocarbon selectivities increased slightly during the operation at higher conversions (which corresponds to higher H_2/CO ratio in the reactor).

At 254 h, the reaction pressure was increased to 2.17 MPa and gas space velocity to 2.64 Nl/g-cat/h (4.4 Nl/g-Fe/h). After few hours at these conditions, the CO and syngas conversions were about 85 and 80%, respectively, and varied between 85-87% (CO) and 80-83% (H_2 + CO) from 250 to 440 h on stream. The catalyst space time yield at these process conditions is estimated to be about 0.72 (g hydrocarbons produced/g-Fe·h), assuming hydrocarbon yield of 200 gHC produced/Nm^3 of (H_2 + CO) converted. The latter value has been typically obtained in our laboratory with precipitated iron catalysts (the stoichiometric amount is 208 gHC produced/Nm^3 of (H_2 + CO) converted). This is the highest catalyst productivity obtained in our laboratory, and is significantly higher than that obtained in the two most successful bubble column slurry reactor operations at comparable conversions and low methane selectivities (Mobil's work, and Kölbel's Rheinpreussen demonstration plant unit). In Mobil's study (Kuo,

1985) the catalyst productivity of 0.39 (g hydrocarbons produced/g-Fe·h) was achieved at 257°C, 1.48 MPa, 2.3 Nl/g-Fe/h and $H_2/CO = 0.73$ (syngas conversion of 82%, methane selectivity of 2.7 wt%), whereas Kölbel et al. (1955) obtained 0.49 (g hydrocarbons produced/g-Fe·h) at 268°C, 1.2 MPa, 3.1 Nl/g-Fe/h and $H_2/CO = 0.67$ (syngas conversion of 89%, methane + ethane selectivity of 3.2 wt%). For comparison, we achieved the catalyst productivity of 0.72 (g hydrocarbons produced/g-Fe·h) at 260°C, 2.17 MPa, 4.4 Nl/g-Fe/h and $H_2/CO = 0.67$ (syngas conversion of 82%, methane selectivity of 2.3 mol%. The latter corresponds to approximately 2.6 wt%). Two main reasons for higher catalyst space-time-yield (productivity) obtained in the present study are: (1) the use of higher reaction pressure, and (2) higher intrinsic activity of our catalyst.

Gaseous hydrocarbon selectivities were decreasing during testing at 2.17 MPa with H2/CO = 0.67 (235-442 h), as shown in Figure 2. For example at 240 h on stream, methane and C_2-C_4 hydrocarbon selectivities were 2.8 and 14.6 mol%, respectively, whereas at 440 h on stream, the corresponding values were 2.4 and 13.3 mol%, respectively.

At 443 h on stream, the gas space velocity was decreased to 2 Nl/g-cat/h and the syngas with H_2/CO molar feed ratio of 0.6 was employed. This was done with the objective to increase the total syngas conversion, by operating with the feed gas composition which is close to the H_2/CO usage (consumption) ratio during the synthesis (0.57-0.58). The CO conversion increased initially to 89%, and the (H_2+CO) conversion to 87%, resulting in more balanced consumption of both reactants. However, during the next 120 h of testing the catalyst deactivated with time. At 540 h, the CO conversion was 84%, and the (H_2+CO) conversion was 82%. This demonstrates that the use of CO rich feed gas (high partial pressure of CO) has a detrimental effect on catalyst activity. The usage ratio was about 0.56, during testing with $H_2/CO = 0.6$ syngas feed.

Gaseous hydrocarbon selectivities were lower during testing with the CO rich feed gas. For example, the methane selectivity at 560 h on stream was only 2.1%, and C_1+C_2 selectivity was 5.2%.

III. 6. 2 Run SA-1486 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

The purpose of this test was to check reproducibility of results following the CO pretreatment, i.e. to repeat pretreatment conditions used in test SA-0946, and obtain results on catalyst activity and selectivity under the same process conditions. The activity/selectivity results during the initial periods of run SA-0946 were unexpected. Initial conversions were relatively low (~40%), and methane selectivity was relatively high (4 mol%). Also, there was a relatively long induction period of over 100 h, during which the catalyst activity increased (Figure 1) while methane selectivity decreased (Figure 2).

About 10 grams (< 270 mesh in size) of catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4, and 310 g of Durasyn 164 oil were loaded for the test. As in run SA-0946, the catalyst in this test was activated with CO at 280°C, 0.78 MPa (100 psig), 3.0 Nl/g-cat/h (520 cm^3/min) for 8 h.

Following activation, the catalyst was tested at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of $H_2/CO = 0.67$ and space velocity of 2.34 Nl/g-cat/h for 110 h. Changes in the (H_2+CO) conversion and H_2/CO usage ratio with time on stream during these two runs, SA-0946 and SB-1486, are shown in Figure 3a and 3b, respectively. Methane selectivity and lumped (C_2-C_4) selectivity for both tests, are shown in Figure 4.

Apparently, very reproducible results were obtained in these two tests in terms of both catalyst activity and gaseous hydrocarbon selectivity. This confirms the observations from run SA-0946, that following CO pretreatment (at the conditions used here), the initial conversion is low and methane selectivity is relatively high. The activity increased gradually during the synthesis (over a 100 h period), which was accompanied with decrease in methane and gaseous hydrocarbon selectivities.

As shown in Figure 12, after the CO pretreatment χ–carbide was formed. The results obtained in runs SA-0946 and SB-1486 suggest that carbided catalyst was not very active, and that excess methane is formed by reaction between hydrogen and iron carbide and/or carbon deposited on surface during the CO pretreatment. The carbided catalyst changes its composition (bulk and surface) when contacted with syngas, and this process continues over a long period of time (the syngas conversion was still increasing after 108 h on stream in run SB-1486). During this unsteady state period, the catalyst became more active and produced more high molecular weight hydrocarbons.

III. 6. 3 Run SA-1626 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

In this test we used syngas ($H_2/CO = 0.67$) as reductant, instead of CO. The pretreatment conditions were the same as in run SA-0946, i.e. 280°C, 0.78 MPa (100 psig) and 3 Nl/g-cat/h for 8 hours. The reactor was loaded with 15 g of catalyst and 307 g of Durasyn 164 oil. Major events are summarized in Table 2.

After the pretreatment, the catalyst was tested at 260°C, $H_2/CO = 0.67$, 1.48 MPa and 2.3 Nl/g-cat/h during the first 140 h on stream. The CO and syngas conversions increased (Figures 5a and 5b) during the first 40 h on stream, whereas the usage ratio decreased (Figure 5c). Steady state values (40 - 140 h) for the CO conversion, the syngas conversion, and H_2/CO usage ratio were approximately: 75%, 70% and 0.57, respectively. During the same period of time methane and gaseous hydrocarbon selectivities decreased with time (Figure 6). At 100 h on stream methane, C_1+C_2 and C_2-C_4 selectivities were: 4.5, 8.7 and 15.5 mol%, respectively.

As shown in Figure 12, after the pretreatment the crystalline phases detected by XRD were: ε'-carbide (and possibly some χ-carbide) and magnetite. Initial behavior of the catalyst in this test was similar to that observed following the CO pretreatment (runs SA-0946 and SB-1486), i.e. increase in activity and decrease in gaseous hydrocarbon selectivity with time. The induction period in this run was shorter, 40-50 h vs. 100 h in runs SA-0946 and SB-1486.

Between 140 and 260 h on stream, the catalyst was tested at a lower gas space velocity of 1.8 Nl/g-cat/h. Initially, the CO and the syngas conversions increased to 80 and 75%, respectively, but at 255 h on stream the corresponding values were: 74 and 70%, respectively. At 255 h methane, C_1+C_2 and C_2-C_4 selectivities were: 4.1%, 8.5% and 15%, respectively.

At 261 h, the reaction pressure and gas space velocity were simultaneously increased to 2.17 MPa and 2.6 Nl/g-cat/h, respectively. This resulted in continuous decrease of conversion values up to 360 h, followed by a period of stable activity during the last 40 h of testing. Gaseous hydrocarbon selectivities were fairly stable during testing at these conditions (Figure 6).

III. 6. 4 Comparison of Pretreatment Procedures

So far, we have employed five pretreatment procedures with the catalyst C from batch 4 in slurry reactor tests. They are: (1) baseline procedure with hydrogen at 240°C for 2 h (runs SB-2145 and SA-1665); (2) reduction with hydrogen at 250°C for 4 h (run SB-3425); (3) reduction with hydrogen at 280°C for 8 h (run SA-0376); (4) CO activation at 280°C for 8 h (runs SA-0946 and SB-1486), and (5) syngas activation at 280°C for 8 h (run SA-1626). Comparison of hydrogen reduction procedures was provided in the last quarterly report (January - March, 1996), but the key results will be repeated here for the sake of completeness. Also, comparisons illustrating the effect of different reductants will be presented in this section of the report.

Hydrogen Reductions

Changes in syngas conversion during the first 50 h on stream after hydrogen reductions at different conditions are shown in Figure 7. The important observation is that the catalyst quickly reaches its steady state activity (within 10 h or less). The iron phases in reduced catalysts, determined by XRD (Figure 8), were α-Fe, runs SA-0376 (280°C for 8 h) and SB-3425 (250°C for 4 h), and magnetite (Fe_3O_4), run SA-1665 (240°C for 2 h). Catalyst activity, measured in terms of apparent rate constant, is shown in Figure 9. The use of apparent rate constant enables one to compare the activity of catalysts tested at different reaction pressures, gas space velocities and/or feed compositions, but at a constant reaction temperature. Catalyst reduced at 250°C for 4 h had the highest initial activity (360 mmol/g-Fe/MPa), whereas initial activities in runs SA-0376 and SA-1665 were similar (230-260 mmol/g-Fe/MPa). It is important to note that the catalyst reduced to magnetite only (SA-1665) had higher activity than the catalyst which was partially reduced to metallic iron (run SA-0376). Catalyst in run SA-1665 maintained nearly constant activity up to 400 h on stream, whereas catalysts in runs SB-3425 and SA-0376 started to deactivated after about 100 h and 260 h on stream, respectively.

Methane selectivity increased with time during the first 100 h, and then became nearly constant (Figure 10). Catalyst reduced to magnetite only (SA-1665) had lower methane (and other gaseous hydrocarbon) selectivity, than catalysts which were partially reduced to α-Fe (runs SB-3425 and SA-0376).

Effect of Reductant Type

Effect of four pretreatment procedures on syngas conversion during the first 100 h of synthesis are shown in Figure 11. Hydrogen reduced catalysts quickly reach their steady state activity, whereas the syngas and CO activated catalysts require much longer time. After pretreatment, α–Fe was found in the hydrogen reduced catalysts, the CO activated catalyst was in the form of χ–carbide, and ε'-carbide, magnetite and possibly χ–carbide were found in the syngas activated catalyst (Figure 12). Activity comparison, in terms of the apparent reaction rate constant for first order reaction in hydrogen, is given in Figure 13. Initially, the catalyst reduced with hydrogen at 250°C for 4 h had the highest activity (k = 360 mmol/g-Fe/MPa), followed by the CO and syngas activated catalysts (k = 280 mmol/g-Fe/MPa) , whereas the catalyst reduced with hydrogen at 280°C for 8 h was the least active (k = 240 mmol/g-Fe/MPa). Activity of the CO and syngas catalysts increased with time during the first 100 h on stream, whereas the activity of hydrogen reduced catalysts remained fairly stable (this follows the same trends as syngas conversion in Figure 11). Thus, at 100 h on stream, the CO activated catalyst was the most active (k = 380 mmol/g-Fe/MPa), the activities of H_2 reduced catalyst at 250°C for 4 h and syngas activated catalyst were nearly the same (k = 330 mmol/g-Fe/MPa), and the H_2 reduced catalyst at 280°C remained the least active (k = 230 mmol/g-Fe/MPa). The CO activated catalyst retained its high activity up to 400 h (at different gas space velocity and/or reaction pressure), whereas the catalysts in the other three tests deactivated with time on stream (Figure 13).

Methane selectivities of hydrogen reduced catalysts increased during the first 100 h of synthesis and then became stable (~3.8 - 4 mol%), whereas methane selectivities of the syngas and CO activated catalysts exhibited the opposite trend, i.e. they decreased with time. Initially (first 20 h on stream) methane selectivities increased in the following order: hydrogen reduced catalysts (~3 mol%) < CO activated catalyst (3.6 - 4%) < syngas activated catalyst (5.8 - 6%). After 100 h on stream methane selectivity increased in the following order: CO activated catalyst < hydrogen reduced catalysts < syngas activated catalyst. During testing at 2.17 MPa (>240 h), methane selectivity of the CO activated catalyst (SA-0946) was low (2.2 - 2.8 mol%). This is similar to values obtained in run SA-1665 with catalyst reduced with hydrogen at 240°C for 2 h (Initially in the form of magnetite). However, the activity of the catalyst in run SA-1665 at 400 h on stream was significantly lower (k = 220 mmol/g-Fe/MPa).

Based on the above results the CO activation procedure (run SA-0946) resulted in the best long term performance: high and stable activity over a long period of time, low methane and gaseous hydrocarbon selectivities. As stated earlier (section III. 6. 1 of this report), the highest catalyst productivity (0.72 g hydrocarbons produced/g-Fe·h) was achieved using this activation procedure, while maintaining the desired selectivity (well within the DOE's performance targets). This is the best performance to date relative to catalysts developed for high wax production ("high alpha" catalysts) in our laboratory or anywhere else.

III. 7 Task 7. Calcination Effect Research

One slurry reactor test was completed during the reporting period. Run SB-1276 with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) was conducted to study effect of calcination temperature on the catalyst performance in a stirred tank slurry reactor. The catalyst was calcined at 700°C for 1 h in a furnace (flash calcination, for details please refer to Quarterly Technical Progress Report for October-December, 1995). With this test, all scheduled activities for this task have been completed.

III. 7. 1 Run SB-1276 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst (batch 3)

The catalyst used in this test was from batch 3, with nominal composition 100 Fe/5 Cu/6 K/24 SiO_2 (part per weight). Prior to testing the catalyst was calcined at 700°C for 1 h (flash calcination) in a high temperature oven. During calcination, the catalyst (total of 20 g) was distributed evenly into 4 small crucibles, placed side by side in the oven, in order to achieve uniform heating.

About 14 g of the catalyst (< 270 mesh in size) was used for slurry reactor test, and 309 g Durasyn 164 oil as the initial slurry medium. After hydrogen reduction at the standard conditions for Catalyst B: 250°C, 0.78 MPa (100 psig) for 4 h, the catalyst was tested at 260°C, 1.48 MPa (200 psig), syngas molar feed ratio of 0.67 ($H_2/CO = 0.67$) and gas space velocity of 2.15 Nl/g-cat/h for 48 h. The CO and syngas conversions were about 54 and 52%, respectively; and the H_2/CO usage ratio was about 0.60 (Figure 15). The catalyst had relatively high gaseous hydrocarbon selectivities. For example, methane selectivity was 5.5 mol%, C_1+C_2 selectivity was 11 mol%, and lumped C_2-C_4 selectivity was over 20 mol% (Figure 16).

From 48 - 186 h on stream, the gas feed space velocity was reduced to 1.8 Nl/g-cat/h. The CO conversion increased to 59 - 61%, and syngas conversion increased to 57 - 59%; whereas the usage ratio remained at 0.60. During this period methane selectivity gradually decreased to 4.9 mol%, and C_2-C_4 decreased from 22 to 18 mol%.

At 188 h on stream, the reaction pressure was increased to 2.17 MPa (300 psig) whereas other conditions remained the same. Higher conversions were achieved following the increase of reaction pressure, but later they slowly decreased with time. Over the next 120 h on stream, the CO conversion was 68 - 62%, and syngas conversion was 65 - 60%. Gaseous hydrocarbon selectivity continually decreased with time, e.g. selectivity to methane decreased to 3.7 mol%, and C_2-C_4 decreased to 15 mol%.

In order to get higher conversions, the space velocity of the feed syngas was reduced to 1.2 Nl/g-cat/h at 312 h on stream. This resulted in increase of the CO and syngas conversions to 77 and 73%, respectively, but after 72 h at these conditions they decreased to 73 and 69%, respectively. Methane selectivity was relatively stable around 4 mol% during this period, whereas C_1+C_2 selectivity was about 8 mol%. The run was terminated voluntarily after 384 h on stream. Major events during the run are summarized in Table 3.

Wax withdrawal was fast with a new filter of 2 µm nominal pore size. The wax from the first few withdrawals was dark, probably containing some catalyst fines which passed through the filter. During later withdrawals, the wax color was brownish and essentially free of catalyst.

III. 7. 2 Comparison of Results from Runs SB-1295 and SB-1276

Results from run SB-1295 (Quarterly Technical Progress Report for April - June, 1995) in which the catalyst was calcined at 300°C for 5 h, are compared with those obtained in run SB-1276 in Figures 17 and 18.

As shown in Figure 17, the CO and syngas conversions in run SB-1276 (catalyst calcined at 700°C) were significantly lower than those obtained in run SB-1295 (catalyst calcined at 300°C), under the same process conditions. On the other hand, methane and gaseous hydrocarbon selectivities were higher on the catalyst calcined at 700°C (Figure 18). Thus, the baseline calcination procedure (300°C) results in better catalyst performance relative to flash calcination procedure at 700°C.

III. 7. 3 Concluding Remarks on the Calcination Effect Research

We have conducted six fixed bed reactor tests, and two slurry reactor tests under this task. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a slurry reactor after flash calcination at 700°C for 1 h. Results from six fixed bed reactor tests were described in Quarterly Technical Reports for October - December, 1995 and January - March, 1996, whereas results from slurry reactor test SB-0676 of catalyst C (catalyst calcined at 700°C) and its comparison with runs SB-2145 and SA-1665 (catalyst C calcined at 300°C) were reported in Quarterly Technical Report for period January - March, 1996. For the sake of completeness, the main findings from these tests are summarized below.

Activities, as well as gaseous hydrocarbon selectivities, of catalysts B and C calcined at 400°C and 500°C, were similar to those of catalysts calcined at 300°C. Catalysts calcined at

700°C for 1 h had lower activity, than catalysts calcined at temperatures 0f 300 - 500°C. Gaseous hydrocarbon selectivities of catalyst C, were not strongly affected by the use of different calcination temperatures, whereas the catalyst B calcined at 700°C had higher gaseous hydrocarbon selectivities in comparison to catalysts calcined at lower temperatures (fixed bed reactor tests).

The main findings from slurry reactor tests are: (1) The activity of catalysts B and C calcined at 700°C is lower than that of catalysts calcined at 300°C, and (2) Gaseous hydrocarbon selectivities are higher on catalysts calcined at 700°C.

The main conclusion from all tests is that the use of flash calcination did not result in any improvements in the performance of these two catalysts.

III. 8 Task 8 Catalyst Characterization

III. 8. 1 BET Measurement Results

Surface areas of selected catalysts (with or without silica) before and after reduction in $5\%H_2/95\%N_2$ mixture at 280°C for 8 h are summarized in Table 4. Surface areas of calcined catalysts before the reduction were between 200 and 300 m^2/g, and are generally higher for catalysts containing silica as binder (~300 m^2/g). After the reduction surface areas of the three catalysts without silica were between 14 and 25 m^2/g, and the corresponding degrees of reduction were between 10 and 19%. These catalysts had a substantial loss in surface area even at relatively low degrees of reduction. The loss of surface area for the two silica containing catalysts (catalysts B and C used in reaction studies) was much smaller (111 - 156 m^2/g), even at higher degrees of reduction (21-23%) relative to catalysts without silica. The presence of silica helps to preserve the surface area of the catalyst.

III. 8. 2 XRD Measurement Results

III. 8. 2. 1 XRD Measurements of Catalyst Samples from Slurry Reactor Tests Conducted Under Task 6

Figure 19 illustrates changes in bulk iron phases with time on steam during run SA-0946 with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2 from batch 4). Iron carbide (χ-Fe_5C_2) and small amounts of magnetite (Fe_3O_4) were found (Figure 19-A) in the sample withdrawn immediately after the CO reduction (TOS = 0 h). During FT synthesis additional iron carbides were formed (Figures 13-B to 13-E), and magnetite was present in small amounts (TOS = 113 - 427 h). At the end of the run (TOS = 563 h) magnetite and carbides were present in significant quantities. Catalyst activity was fairly stable throughout the test, with some deactivation during the last 120 h on stream (section III. 6. 1 of this report), upon exposure of the catalyst to CO rich syngas ($H_2/CO = 0.6$).

After the syngas activation at 280°C for 8 h (run SA-1276) the catalyst contained both magnetite and ε'-$Fe_{2.2}C$ (Figure 20-A). The same phases were observed in samples withdrawn from the reactor during FTS (Figures 20 B-D), but the catalyst experienced deactivation after 100 h on stream (section III. 6. 3 of this report).

III. 8.2. 2 XRD Measurements of Catalyst Samples from Fixed Bed and Slurry Reactor Studies Conducted Under Task 7

Figure 21 illustrates changes in bulk iron phases with time on stream during run SB-1276 with catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) from batch 3. This catalyst was calcined at 700°C for 1 h prior to testing. Magnetite and α-Fe were found in the sample withdrawn immediately after the hydrogen reduction (TOS = 0 h) as shown in Figure 21-A. Both magnetite and the pseudo-hexagonal iron carbide (ε'-$Fe_{2.2}C$) were found in the samples withdrawn during FT synthesis (Figures 21-B to 21-E). The activity changes with time on stream are described in section III. 7. 1 of this report.

III. 8. 3. Temperature Programmed Reduction (TPR) Measurements

Temperature-programmed reduction (TPR) studies were performed using 5%H_2/95%N_2 as reductant. In a typical TPR experiment about 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5%H_2/95%N_2 (flow rate of 40 ml/min) from room temperature to 800°C at a heating rate of 20°C/min.

III. 8. 3. 1 Reproducibility of Results

In TPR experiments with 100 Fe/0.3 Cu catalyst conducted during the last quarter two peaks between 400 and 700°C, indicating the presence of different types of iron phases in the sample, were detected in addition to low temperature peak around 360 °C corresponding to reduction of Fe_2O_3 to Fe_3O_4. Two new experiments under the same conditions were conducted to verify these data, and results from all three tests are shown in Figure 22. Results from multiple tests of the same catalyst sample are very reproducible.

Two new tests were also conducted with the 100 Fe/5 Cu catalyst, which originally exhibited two peaks in low temperature region (240 - 280°C). Results from three tests with this catalyst are shown in Figure 23. Again, the peak positions and normalized areas under the peaks are in good agreement, indicative of excellent reproducibility of the instrument and operating procedures.

III. 8. 3. 2 Reduction Behavior of Catalysts B and C from Different Batches

Results from TPR experiments with catalysts C and B from different batches are shown in Figures 24 and 25, respectively. Peak positions (temperature values corresponding to maxima in hydrogen consumption) and degrees of reduction for both catalysts are summarized in Table 5.

Catalyst C has two peaks, corresponding to two stages of iron reduction, the first peak is located between 300°C and 330°C, and the second one between 530°C and 585°C. The degree of reduction for the first stage is 23 - 26% (Table 5), and total degree of reduction in the temperature programmed mode of operation is between 79 and 96%.

Catalyst B also has two peaks at 300 - 315°C and 570 - 580°C (Figure 25). The degree of reduction for the first stage of reduction is 23 - 27%, and the total degree of reduction varies between 88% (S5624-3) and 98% (S5624-2).

Similarity of peak positions and degrees of reduction of catalysts from different batches is indicative of good reproducibility of catalyst preparation, which was also confirmed in stirred tank reactor tests of these catalysts.

III. 8. 3. 3 Effect of Silica on the Reduction Behavior of Promoted Iron Catalysts

The effect of increasing amount of silica on the reduction behavior of catalysts with nominal composition 100 Fe/5 Cu/4.2 K/x SiO_2 (x =8, 16, 25, 40 and 100) is shown in Figure 26. The addition of silica retards the onset of iron reduction for both stages, and the peak positions shift to the right (higher values of temperature) with the increasing amount of silica binder.

III. 8. 4 Isothermal Reductions

In isothermal reductions, the temperature was ramped at a constant rate of 5°C/min to a final temperature of 280°C in a flow of 5%H_2/95%N_2 mixture (TPR unit). Then the catalyst sample was maintained at this temperature for 8 h in a flow of 5%H_2/95%N_2 (40 ml/min). The degree of reduction as a function of time was calculated from measured hydrogen consumption, and calibration data with standard CuO sample. In the TGA/DTA unit the catalyst sample was purged with helium (40 ml/min) and temperature was ramped at a rate of 5°C/min from a room temperature to 280°C. Then the helium flow was switched to hydrogen (99.995% purity) or 5%H_2/95%N_2 mixture at 40 ml/min, and the temperature was maintained at 280°C for a total period of 8 h. The degree of reduction was calculated from the weight loss vs. time data.

III. 8. 4. 1 Effect of Hydrogen Partial Pressure

The effect of hydrogen partial pressure on the reduction of 100 Fe/3 Cu and 100 Fe/5 Cu catalysts was investigated in a TGA/DTA unit (TA Instruments), and results are shown in Figure 27. In pure hydrogen (ambient pressure of approximately 760 Torr) the reduction is complete (within experimental errors) with both catalysts after 240 min (100 Fe/5 Cu) and 360 min (100 Fe/3 Cu). At low partial pressure of hydrogen (~ 38 Torr) the maximum degree of reduction is only 17% for both catalysts. These results clearly indicate the importance of hydrogen partial pressure on the reduction behavior of iron catalysts (the rate of reduction as well as the final degree of reduction).

III. 8. 4. 2 Effect of Sample Size

The effect of sample size on the degree of reduction of 100 Fe/3 Cu and 100 Fe/5 Cu catalysts was studied in the TPR unit (Micromeritics Inc.) using 5%H_2/95%N_2 mixture at 40 ml/min. With 20 mg samples the final degree of reduction was about 27% for both catalysts, and was achieved after 5 h of reduction (Figure 28). With 400 mg samples the degree of reduction after 540 minutes was only 20%, and the reduction process was incomplete (non zero slope in Figure 28). The lower degrees of reduction obtained in the experiments with larger samples, are due to a higher partial pressure of water produced during the reduction which inhibits the reduction of iron.

III. 8. 4. 3 Effect of Silica on the Reduction Behavior of Promoted Iron Catalysts

The effect of increasing amount of silica on the reduction behavior of catalysts with nominal composition 100 Fe/5 Cu/4.2 K/x SiO_2 (x =8, 16, 25, 40 and 100) was also investigated in the TGA/DTA unit under isothermal conditions in pure hydrogen. After 8 h of exposure to hydrogen at 280°C the reduction was not complete for all catalysts (Figure 29). Catalysts containing 8-25 parts of SiO_2 per 100 parts of Fe had similar final degrees of reduction 70 - 80%, whereas the degree of reduction of catalysts with $x = 40$ and $x = 100$ was significantly lower, 48% and 36%, respectively. These data show that the addition of silica ($x > 25$) inhibits reduction of iron.

III. 8. 4. 4 Isothermal Reductions of Catalysts B and C from Different Batches

Catalysts B and C from different batches were also reduced under isothermal conditions at 280°C for 8 h, and results are shown in Figures 30 - 33. For catalyst C the final degree of reduction in pure hydrogen was between 70% (S3416-2+K(2) batch) and 82-85% for all other batches (Figure 30). In dilute stream of hydrogen (5%H_2/95%N_2) the final degree of reduction for all four samples was much lower, between 17 and 19% (Figure 31).

For catalyst B the final degree of reduction in pure hydrogen was 89% (S5624-2 batch), and about 80% for the other three batches (Figure 32). In dilute stream of hydrogen ($5\%H_2/95\%N_2$) the final degree of reduction for all four samples was much lower, between 21 and 25% (Figure 33).

The above results are consistent with the ones obtained during the temperature programmed reduction (Table 5), and they indicate that there are no significant differences in the reduction behavior among catalysts from different batches.

III. 9 Catalyst Testing in a Bubble Column Slurry Reactor

The work on this task is not scheduled to begin yet. No activity to report.

III. 10 Scale-up of Catalyst Synthesis Procedure

The work on this task is not scheduled to begin yet. No activity to report.

Plans for the Next Quarter

During the next quarter we plan to continue : (a) with testing of catalysts under Task 6 , and (b) with characterization of catalysts at various stages of usage (Task 8).