I. EXECUTIVE SUMMARY

Two stirred tank slurry reactor tests of catalysts with nominal compositions 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 (run SB-3115) and 100 Fe/5 Cu/6 K/24 SiO_2 (run SA-3155) were completed under Task 5. The Effect of Source of Potassium and Basic Oxide Promoter, during the reporting period. With these two tests all scheduled activities on this task have been completed. Our assessment of the effects of addition of CaO promoter to our baseline catalysts B and C, and the use of potassium silicate as the source of potassium promoter is as follows.

The activity of catalysts containing CaO was either lower or the same as that of the baseline catalysts. At the reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at the reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. In general, the addition of CaO promoter did not result in improved performance of the baseline catalysts. The use of CaO promoter may be best suited for operation at higher reaction pressures.

The baseline procedure utilizing impregnation of Fe-Cu-SiO_2 precursor with aqueous solution of $KHCO_3$ as the source of potassium promoter is the preferred method of preparation. The procedure which utilizes aqueous K_2SiO_3 solution as the source of potassium also provides satisfactory results, and may be used as an alternative.

A slurry reactor test (run SB-3425) was completed during the reporting period, following the catalyst pretreatment with H_2 at 250°C for 4 h (Task 6. Pretreatment Effect Research). This pretreatment resulted in higher catalyst activity (initially, about 40% higher) than our baseline procedure (H2 at 240°C for 2 h), but also higher methane and gaseous hydrocarbon selectivities (about 10-20% higher).

The work on Task 7. Calcination Effect Research, was initiated and five fixed bed reactor tests were completed during the reporting period. Two tests were done with catalyst B (runs FA-2925 and FB-2975), and three with catalyst C (runs FA-3095, FA-3305 and FA-3495), to study the effects of calcination temperature on the catalyst activity, selectivity and stability. Catalyst C calcined at 700°C for 1 h had lower activity, than catalysts calcined at 300°C - 500°C for 5 h. Gaseous hydrocarbon selectivity was not significantly affected by calcination temperature.

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

During the reporting period we completed two stirred tank slurry reactor tests of catalysts with nominal compositions 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 (run SB-3115) and 100 Fe/5 Cu/6 K/24 SiO_2 (run SA-3155). The latter catalyst was synthesized using potassium silicate solution as a source of potassium promoter. Here, we describe results from these two tests, and compare the catalyst performance in these two tests with that of the baseline catalysts B and C. Also, we provide the overall assessment of the effect of source of potassium promoter and the use of CaO promoter, on the basis of results from all fixed bed and slurry reactor tests conducted under this task. With these two tests the work on this task has been completed.

III.5.1 Run SB-3115 with 100 Fe/3 Cu/2 Ca/4 K/16 SiO_2 Catalyst

This catalyst is a modification of the catalyst C (100 Fe/3 Cu/4-6 K/16 SiO_2), and was prepared from batch 3 of the 100 Fe/3 Cu/16 SiO_2 precursor. It was tested previously in a fixed bed reactor (run FA-1525), and its performance was found to be similar to that of the baseline catalyst C in run FA-1605 (Quarterly Technical Progress Report for the period April-June, 1995).

About 7.6 g of catalyst (< 270 mesh in size) and 300 g of Durasyn 164 oil were charged into the reactor for this test. After the reduction with H_2 at 240°C, 100 psig for 2 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 space velocity of 1.4 Nl/g-cat/h for about 160 h. After that the catalyst was tested at higher reaction pressure and gas space velocity (2.17 MPa (300 psig) and SV = 2.05 Nl/g-cat/h) for another 190 h, and the test was terminated at 354 h on stream. Table 1 lists major events during the run.

A new sulfur removal guard bed packed with an UCI G-72D ZnO catalyst was installed in the feed line before this test. Initially the guard bed was heated to 300°C. However, methanol, formed from the syngas on the ZnO catalyst, was detected in the tail gas stream. At 23 h on stream, the temperature of the ZnO catalyst bed was lowered until no methanol trace was detected by the GC, and the guard bed temperature was maintained at 100°C during the remainder of the test. The ZnO catalyst will adsorb hydrogen sulfide at lower temperatures, but it has a longer lifetime when operating in high temperature range (285-400°C).

Changes in the CO conversion, the syngas conversion, and the usage ratio with time on stream are shown in Figure 1, whereas methane, C_1+C_2, and C_2-C_4 hydrocarbon selectivities are shown in Figure 2. During testing at P = 1.48 MPa and SV = 1.4 Nl/g-cat/h, the catalyst activity was stable, CO conversion was at 72-74 %, the syngas conversion at 69 - 70 %, and the H_2/CO usage ratio was about 0.57 - 0.59. However, the selectivity to methane and gaseous hydrocarbons increased with time. For example, methane selectivity increased from 3 mol% (at 35 h) to 4.8 mol% (at 163 h), and C_2-C_4 selectivity increased from 12 to 18 mol%.

At 164 h the reaction pressure and gas feed space velocity were increased proportionally to 2.17 MPa and 2.0 Nl/g-cat/h, respectively. During the next 50 h, the CO and syngas conversions were stable at 73 and 71%, respectively, whereas the H_2/CO usage ratio increased slightly to 0.6. However, methane selectivity decreased from 4.6 to 3.8 mol%, and C_2-C_4 selectivity decreased from 18 to 16 mol%. After that, the catalyst began to deactivate. From 230 h to 352 h on stream, the CO conversion decreased from 72 to 61%, and the syngas conversion

decreased from 70 to 59 %. The gaseous hydrocarbons selectivities remained stable, e. g. methane selectivity was between 3.4 - 3.6 mol%, and C_2-C_4 selectivity was about 16 mol%.

Comparison of Results from Runs SB-3115 and SA-1665

Results from run SB-1665 with the baseline catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4, are also shown in Figures 1 and 2 for comparison. The Fe-Cu-SiO_2 precursors for these two catalysts were from two different batches. However, since the test results from different batches of baseline catalyst C were reproducible (Quarterly Technical Progress Report for July-September, 1995), data from the run SA-1665 can be used to evaluate the effect of CaO promotion. Run SB-1665 lasted about 500 h, but only the data from first 400 h are shown in these two figures.

Figure 1 shows that the CaO containing catalyst tested in run SB-3115 had lower activity, about 10% lower CO and syngas conversions, than the catalyst C in run SA-1665. The CaO containing catalyst started to deactivate around 220 h on stream, whereas the catalyst C in run SA-1665 was fairly stable during 400 h of testing. Also, the CaO containing catalyst had higher methane (Figure 2a), C_1+C_2 (Figure 2b) and C_2-C_4 (Figure 2c) hydrocarbon selectivities during testing at 1.48 MPa. After the pressure was increased to 2.17 MPa (while proportionally increasing the gas space velocity to 2.0 Nl/g-cat/h) in run SB-3115, the methane and gaseous hydrocarbons selectivities started to decrease (170 - 220 h), and then remained stable (220 - 350 h). This decrease of gaseous hydrocarbon selectivity with increase in reaction pressure was also observed in run SA-2405, with the 100 Fe/5 Cu/5 K/2 Ca/24 SiO2 catalyst (Quarterly Technical Progress Report for July-September, 1995). The hydrocarbon selectivity of the CaO containing catalysts seems to depend on the reaction pressure (with constant P/SV ratio), whereas this was not observed in tests of catalysts B and C without CaO promoter.

III.5.2. Run SA-3155 with 100 Fe/5 Cu/6 K/24 SiO_2 Catalyst

The purpose of this slurry test was to study the effect of potassium source on the catalyst performance. The potassium promoter in this catalyst came from K_2SiO_3 solution, used as the source of SiO_2 binder. The precursor of this catalyst is from preparation batch #5. This catalyst was tested previously in a fixed bed reactor (run FA-1725), and its performance was found to be similar to that of the baseline catalyst B in run FB-1715 (Quarterly Technical Progress Report for the period April-June, 1995).

About 9.5 g of catalyst (< 270 mesh in size) and 300 g of Durasyn 164 oil were charged into the reactor for this test. After the reduction with H_2 at 250°C, 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 40 h, then at space velocity of 1.8 Nl/g-cat/h for the next 165 h. From 220 h until the end of the test at 400 h, the reaction pressure was increased to 2.17 MPa (300 psig), and space velocity was either 2.2 Nl/g-cat/h (211 - 235 h) or 1.8 Nl/g-cat/h (235 - 400 h). The major events during the test are summarized in Table 2.

Figure 3 shows variations of the CO and syngas conversions, and the H_2/CO usage ratio with time and reaction conditions. The catalyst deactivation was rapid initially, e.g. the CO conversion decreased from 73 to 63 % in 40 h (Figure 3a), and the syngas conversion decreased from 69 to 62% during the same time period (Figure 3b). At 42 h on stream, the space velocity was reduced to 1.8 Nl/g-cat/h, and during the next 160 h of testing the catalyst activity was more stable. The CO and syngas conversions varied between 60 - 62 %, and 59 - 61 %, respectively. The usage ratio varied between 0.63-0.65 (Figure 3c). Methane selectivity was relatively low in the begining, about 2 mol% during the first 40 h, then increased to 4.4 mol% at 200 h (Figure 4a). Selectivities of $C_1 + C_2$, and C_2-C_4 hydrocarbons followed the same trend (Figures 4b and 4c).

At 220 h on stream, the reaction pressure was increased to 2.17 MPa (300 Psig), and the gas space velocity to 2.2 Nl/g-cat/h (if increasing proportionally to maintain the same contact time, the SV would be 2.6 Nl/g-cat/h). The syngas conversion was only 62 % after 20 h at these

conditions. In order to achieve a higher conversion, the gas space velocity was reduced further to 1.8 Nl/g-cat/h at 235 h on stream. Following this the CO conversion reached 70 %, and the syngas conversion 68 %. The conversions remained stable for 40 h, and then gradually decreased with time on stream. At 400 h, the CO and the syngas conversions were 65 and 64 %, respectively. The usage ratio during this time was relatively high, about 0.63-0.65. Selectivities to methane and gaseous hydrocarbons were stable during testing at the reaction pressure of 2.17 MPa. For example, methane selectivity was 4.0 - 4.2 mol%, whereas C_2-C_4 selectivity was 16 - 18 mol%. Selectivity fluctuations seen in Figure 4 were caused by analyses differences, arising from the use of two different gas chromatographs.

Comparison of Results from Runs SA-3155 and SB-1295

Results from run SB-1295 with the baseline catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) from batch 3 (Quarterly Technical Progress Report for April-June, 1995), are also shown in Figures 3 and 4 for comparison. The Fe-Cu-SiO_2 precusors for these two catalysts were from two different preparation batches. However, since the test results from different batches of baseline catalyst B were reproducible (Quarterly Technical Progress Report for July-September, 1995), data from the run SB-1295 can be used to evaluate the effect of source of potassium. The baseline catalyst is prepared by impregnation of 100 Fe/5 Cu/24 SiO_2 precursor with potassium bicarbonate ($KHCO_3$), whereas potassium silicate solution (K_2SiO_3) was used as the source of potassium promoter in run SA-3155.

The catalyst using K_2SiO_3 as potassium source was less active (Figures 3a and 3b). The CO and syngas conversions were about 15 % lower than those obtained in run SB-1295, and the H_2/CO usage ratio was higher, indicating also a lower WGS reaction activity.

Methane and gaseous hydrocarbon selectivities in run SA-3155 (K from K_2SiO_3) were significantly lower during the first 100 h on stream, but these differences in selectivity diminished with time and the catalyst selectivities in the two tests were nearly the same after 140 h (Figure 4).

III. 5. 3 Concluding Remarks on the Effect of Source of Potassium and CaO Promoter

Effect of Source of Potassium

Two catalysts (B and C) were prepared using two different methods of potassium promotion. Baseline catalysts were prepared by incipient wetness impregnation of Fe-Cu-SiO_2 precursor with an aqueous solution of $KHCO_3$. In a modified procedure, aqueous solution of potassium silicate is added to the Fe-Cu precursor as a source of silicon oxide, and then the excess amount of potassium is removed by washing to get a desired level of potassium promotion.

Some differences in catalyst performance were observed in fixed bed tests of catalysts B (runs FA-1725 and FB-1715) and C (runs FA-1605 and FB-1985) prepared by different methods (Quarterly Technical Progress Report for July-September, 1995). In both cases, the activity of catalysts prepared using potassium silicate as the source of potassium promotion was somewhat higher, and their methane selectivities were higher than those of the corresponding catalysts prepared by incipient wetness impregnation using $KHCO_3$ as the source of potassium promoter. However, these differences were not that large, and may have been caused by experimental artifacts (e.g. existence of local hot spots in a reactor). On the other hand, in the two slurry reactor tests of catalyst B (SB-1295 - K from $KHCO_3$, and SA-3155 - K from K_2SiO_3) it was found that the activity of the catalyst prepared from K_2SiO_3 (SA-3155) is about 15 % lower than that of the catalyst prepared by $KHCO_3$ impregnation, whereas gaseous hydrocarbon selectivities were similar after about 140 h on stream.

On the basis of these results we conclude that the baseline procedure utilizing impregnation of Fe-Cu-SiO_2 precursor with aqueous solution of $KHCO_3$ is the preferred method of preparation. The second procedure, which avoids the impregnation step, also provides satisfactory results, and may be used as an alternative.

Effect of CaO Promoter

We have synthesized and tested a total of four catalysts with two levels of CaO promotion, which represent modifications of our baseline catalysts B and C. Nominal compositions of these catalysts are: 100 Fe/3 Cu/4 K/x Ca/16 SiO_2 and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2, where x = 2 or 6. Results from screening fixed bed reactor tests of these four catalysts were reported in the Quarterly Technical Progress Report for April-June, 1995, together with results from fixed bed reactor tests of the two baseline catalysts (B - 100 Fe/5 Cu/6 K/24 SiO_2 and C - 100 Fe/3 Cu/4 K/16 SiO_2). The major findings from these tests were that the addition of small amounts of CaO promoter (x = 2) results in the catalyst performance (activity and gaseous hydrocarbon selectivity) similar to that of the baseline catalysts, whereas the addition of a larger amount of CaO (x = 6) results in markedly lower catalyst activity in comparison to baseline catalysts. Selectivity of the two catalysts with x = 6, was similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate the two catalysts with x = 2 in a stirred tank slurry reactors.

The 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst was tested in run SA-2405, and its performance was compared to that of the baseline catalyst B in run SB-1295 (Quarterly Technical Progress Report for July-September, 1995), whereas results from run SB-3115 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst and its comparison with the catalyst C in run SA-1665 were described in Section III. 5. 1 of this report.

General trends in tests with CaO containing catalysts showed some similarities, as well as differences. For example the activity of the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst (run SA-2405) was nearly the same as that of the baseline catalyst B(run SB-1295) but its stability with time (deactivation rate) was better, whereas the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher. At the reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at the reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity

decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. It appears that the selectivity of the CaO promoted catalysts improves at higher reaction pressures, whereas the selectivity of the catalyst C is essentially independent of reaction pressure (at a constant P/SV ratio to maintain a constant value of the gas residence time at different pressiures). In general, the addition of CaO promoter did not result in improved performance of the baseline catalysts. The use of CaO promoter may be best suited for operation at higher reaction pressures. Finally, it is possible that the performance of CaO promoted catalysts may be improved with the use of different pretreatment procedures. However, this type of investigation is beyond the scope of the present study.

III. 6 Task 6. Pretreatment Effect Research

The work on this task was initiated during the current quarter. We have selected catalyst C (100 Fe/3 Cu/4 K/2 Ca/16 SiO_2) from batch 4, for this task, since its overall performance has been slightly better than that of catalyst B. We are planning to employ four different pretreatment procedures, in addition to our standard activation procedure (H_2 reduction at 240°C for 2 h) used in the previous four tests of this catalyst from the same preparation batch (Quarterly Technical Progress Report for July-September, 1995). A slurry reactor test (run SB-3425) was completed during the reporting period, following the catalyst pretreatment with H_2 at 250°C for 4 h.

III. 6. 1. Run SB-3425 with 100 Fe/3 Cu/4 K/16 SiO_2 Catalyst

About 20 g of the catalyst (< 270 mesh in size) was loaded for the test, together with 300 g Durasyn 164 oil as the initial slurry medium. The pretreatment (reduction) conditions employed were: H_2 at 250°C, 0.8 MPa (100 psig), 7,500 cm^3/min for 4 h. These are our standard pretreatment conditions for catalyst B. In comparison with the standard pretreatment conditions for catalyst C (H_2 at 240°C, 100 psig, 7,500 cc/min for 2 h), the conditions used in this test are more severe (higher reduction temperature, 250°C vs. 240°C, and longer duration , 4 h vs. 2 h). Major event for run SB-3425 are summarized in Table 3.

After the reduction, 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 2.34 Nl/g-cat/h (3.9 Nl/g-Fe/h). At 9 h on stream, the CO and syngas conversions reached 80% (Figure 5a) and 75% (Figure 5b), respectively, whereas methane selectivity was 3.1 mol% (Figure 6a). The catalyst activity gradually decreased with time, and the CO and syngas conversions at 157 h on stream were 75% and 70 %, respectively. During the same time period, methane selectivity increased to 3.8 mol%, and $C_1 + C_2$ selectivity to 8 mol% (Figure 6b). The usage ratio was stable at about 0.56-0.57 (Figure 5c).

At 159 h on stream, the gas space velocity was changed to 1.8 Nl/g-cat/h. As a result the CO and syngas conversions increased temporarily, to 83% and 78%, respectively, but then continued to decline with time. At 300 h on stream, they became 75% and 71 %, respectively. Selectivities to gaseous hydrocarbons were stable during this period, in spite of catalyst deactivation, e.g., methane selectivity was 3.6 - 3.9 mol%, $C_1 + C_2$ about 8 mol%, and $C_2 - C_4$ selectivity about 15 mol%. The usage ratio also did not change, it remained between 0.56 and 0.57.

At 310 h on stream, the feed composition was changed from $H_2/CO = 0.67$ gas to $H_2/CO = 0.6$ gas. The reason for this was to obtain higher conversions for both CO and hydrogen by choosing a feed with composition which is close to the H_2/CO consumption (usage) ratio. Between 311 to 330 h, the reaction temperature, pressure and gas SV were kept constant and only the feed composition was changed. The CO conversion decreased from 75% to 67%, and the syngas conversion from 70% to 66 %, due to lower reaction rate (lower partial pressure of hydrogen in the feed and the reactor). The usage ratio was about 0.56, and the exit H_2/CO ratio (tail gas ratio) was about 0.70. With $H_2/CO = 0.67$ syngas feed, the exit ratio was about 0.96. Therefore, the tail gas and feed gas composition became more balanced with $H_2/CO = 0.6$ syngas feed. The methane selectivity decreased somewhat from 3.8 to 3.5 mol%.

At 330 h, the space velocity was lowered to 1.0 Nl/g-cat/h, to increase the syngas conversion. The CO and syngas reached 84% and 81 %, respectively, followed by decrease with

time. At 355 h, the reaction temperature was increased to 266°C and the CO and syngas conversions reached 86% and 83 %, respectively, at 360 h. However, the catalyst continued to deactivate and at 380 h on stream, the CO and syngas conversion were only 83% and 80 %, respectively. The usage ratio remained at 0.55, but the exit ratio increased to 0.90. Methane selectivity was about 3.5 mol%, and it did not increase during operation at the higher temperature. The run was terminated at 382 h on stream.

Slurry samples, for catalyst characterization, were removed from the reactor after nearly every 100 h on stream (111 h, 230 h and 330 h). Also, the slurry samples were withdrawn after the H_2 reduction (TOS = 0 h), and before the run was terminated (TOS = 382 h).

Comparison of Results from Runs SB-3425, SB-2145 and SA-1665

The standard hydrogen pretreatment conditions were used in runs SB-2145 (Quarterly Technical Progress Report for July-September, 1995) and SA-1665 (Quarterly Technical Progress Report for April-June, 1995), and results from these two tests are compared with those obtained in run SB-3425 in Figures 7 and 8. In all three tests the catalyst was tested initially at 260°C, 1.48 MPa, H_2/CO = 0.67, and gas space velocity of either 1.4 Nl/g-cat/h (runs SB-2145 and SA-1665) or 2.3 Nl/g-cat/h (run SB-3425). Due to the use of different gas space velocities, one can not use values of the CO or syngas conversion for comparison of catalyst activities. Instead, the values of apparent rate constant (assuming the first order reaction in hydrogen partial pressure) were used to compare catalyst activities in these three tests (Figure 7). Clearly, the catalyst reduced under more severe conditions (run SB-3425) was the most active, which is to be expected, whereas the initial activities of the catalyst in runs SA-1665 and SB-2145 were essentially the same. The catalyst deactivated much more rapidly in runs SB-2145 and SB-3425, than in run SA-1665. The reasons for differences in deactivation rates are not clear at the present time. However, the observed results are consistent with assumption that deactivation is due to sulfur poisoning, since higher catalyst loadings and higher flow rates were used in runs SB-3425 (20 g of catalyst) and SB-2145 (30 g of catalyst) than in run SA-1665 (10 g). The amount of

sulfur is proportional to the syngas flow rate, and if the gas purification traps were not effective for complete sulfur removal, the breakthrough sulfur would poison the catalyst.

Methane, and gaseous hydrocarbon selectivities were higher on the catalyst which was reduced under more severe conditions (run SB-3425) as shown in Figure 8. This is consistent with results obtained previously in our laboratory, with other iron Fischer-Tropsch catalysts.

III. 7 Task 7. Calcination Effect Research

The work on this task was initiated during the current quarter, and five fixed bed reactor tests were completed during the reporting period. Two tests were done with catalyst B (runs FA-2925 and FB-2975), and three with catalyst C (runs FA-3095, FA-3305 and FA-3495), to study the effects of calcination temperature on the catalyst activity, selectivity and stability. Both catalysts were calcined in air at 400°C and 500°C for 5 h, to study the effect of calcination temperature relative to our standard procedure: 300°C for 5 h. These calcinations were done in a downflow fixed bed reactor unit. Catalyst C was also calcined at 700°C for 1 h (run FA-3495) in a high temperature furnace. The furnace was preheated to 700°C first, and the catalyst was spread over a preheated crucible to form a thin layer. During the calcination the air flow was fed into the surface, passing over a thin layer of catalyst. This procedure is referred to as flash calcination. The calcined catalysts (about 3 - 3.5 g) were loaded into a fixed bed reactor and diluted with inert glass beads of the same particle size (30 - 60 mesh), and then reduced with hydrogen. The hydrogen reduction was carried out at 250°C for 4 h for the catalyst B (runs FA-2925 and FB-2975), and at 240°C for 2 h for the catalyst C (runs FA-3095, FA-3305 and FA-3495). The process conditions in all five tests were: 250°C, 1.48 MPa (200 psig), 2 Nl/g-cat/h using syngas with H_2/CO molar feed ratio of about 0.67, and the test duration was 120 - 140 h, including the 30 h conditioning period to reach the reaction temperature of 250°C.

III. 7. 1 Fixed Bed Reactor Tests of Catalyst C, 100 Fe/3 Cu/4 K/16 SiO_2

Results from four fixed bed reactor tests, including the baseline calcination conditions of 300°C for 5 h (run FA-1605, Quarterly Technical Progress Report for April-June, 1995) are shown in Figures 9 and 10. As shown in Figures 9a and 9b, the initial CO and syngas conversions of catalysts calcined at 400°C (FA-3305) and 500°C (FA-3095), were the same as those of the calcined at 300°C (FA-1605). However, the catalysts calcined at 400°C and 500°C deactivated faster than the catalyst calcined at 300°C, and at 100 h on stream the conversions in these two tests were about 8% less than those obtained in run FA-1605. The catalyst calcined at 700°C had significantly lower activity (i.e. CO and syngas conversions). Its surface area, after the calcination, was only 108 m^2/g (Table 4). This value is much smaller in comparison to surface areas of the catalysts calcined at lower temperatures (190 - 280 m^2/g, which may be responsible for lower catalyst activity in run FA-3495. The usage ratios in all three tests were about the same, 0.57 - 0.60 (Figure 9c).

Gaseous hydrocarbon selectivities in all four tests were similar (Figure 10). For example methane selectivity was generally between 5% and 6% (Figure 10a), and C_2-C_4 selectivities were between 21% and 25% (Figure 10c). Gaseous hydrocarbon selectivity was not strongly affected by calcination temperature and differences in surface areas.

III. 7. 2 Fixed Bed Reactor Tests of Catalyst B, 100 Fe/5 Cu/6 K/24 SiO_2

Results from three tests using three different calcination temperatures are shown in Figures 11 and 12. Before the feed interruption at about 70 h on stream, the catalyst calcined at 400°C (run FB-2975) had higher conversions (Figures 11a and 11b), and higher methane and C_1+ C_2 selectivities (Figures 12a and 12b) than the catalyst calcined at 300°C (run FB-1715). Upon resumption of the test, the conversions and selectivities in run FB-2975 approached those in run FB-1715. The catalyst calcined at 500°C (run FA-2925) had the same activity and deactivation trends as the catalyst calcined at 300°C. It also had similar methane, and gaseous hydrocarbon selectivities (Figure 12). In general, increasing the calcination temperature from

300°C to 500°C did not have a significant effect on the catalyst activity and selectivity, in spite of decrease in total surface area (Table 4).

III. 8 Task 8. Catalyst Characterization

During the reporting period the catalysts were characterized by BET surface area and pore volume, and X-ray diffraction (XRD) measurements, in support of Tasks 4, 5 and 7.

III. 8. 1 BET Measurement Results

Results of BET measurements illustrating the effect of calcination temperature on the surface area of catalysts B and C are summarized in Table 4. In general, the surface area decreases with either increasing temperature or increasing time at a given temperature. The surface areas of the catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) from batch 4 varied between 108 m^2/g (flash calcination at 700 °C for 1 h) and 310 m^2/g (calcination at 300°C for 5 h). Flash calcined catalysts at 500°C for 30 - 60 minutes had the surface area of about 230 m^2/g, whereas the catalyst calcined in downflow fixed bed reactor at 500°C for 5 h had the surface area of 186 m^2/g. The surface area of catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) decreased with increasing calcination temperature from 284 m^2/g at 300°C to 193 m^2/g at 500°C (multi-point BET data). BET measurements after flash calcination at 500°C and 700°C have not been completed, yet.

III. 8. 2 XRD Measurement Results

Calcined samples of catalyst C were also characterized by XRD (Figure 13). Samples calcined at 300 - 500°C for 5 h (13a - 13c), have low degree of crystallinity , whereas the sample calcined at 700°C (Fig. 13d) has a distinct pattern corresponding to α-Fe_2O_3.

Used catalysts from fixed bed and slurry reactor tests were also characterized by XRD. We describe results according to the project tasks.

III. 8. 2 -1 XRD Measurements of Catalyst Samples from Slurry Reactor Studies Conducted under Tasks 3 and 4

XRD scans of samples withdrawn from the reactor immediately after the reduction (TOS = 0) with hydrogen at: 240°C for 2 h (Catalyst C from batches 2 - 4, Figures 14a - 14c), or at 250°C for 4 h (Catalyst B from batches 4 and 5, Figures 14d and 14e) are shown in Figure 14. Both magnetite (Fe_3O_4) and, to a smaller extent, α-Fe were found in all reduced samples. Even after the reduction, the catalysts had low degree of crystallinity (small particles), except in run SB-2145, in which large magnetite particles were formed during the reduction.

Figure 15 illustrates changes in bulk iron phases with time on stream during run SB-2145 with catalyst C from batch 4. Both magnetite and ε'-$Fe_{2.2}C$ (pseudo-hexagonal iron carbide) were found in samples withdrawn during FT synthesis (Figures 15b - 15e). It appears that the relative amount of magnetite decreased, whereas that of iron carbide increased with time on stream. However, the catalyst activity continued to decline with time (Quarterly Technical Progress Report for July-September, 1995).

Figures 16 and 17 illustrate XRD patterns of catalyst C from different tests, which were withdrawn from the reactor at similar times on stream (120 -150 h in Figure 16, and 400-530 h in Figure 17). In general, the XRD patterns of samples from different tests were similar, and magnetite and ε'-carbide were found in all samples. Also, the iron carbonate, $FeCO_3$, was found in four of the seven samples shown in Figures 16 and 17. In all these tests no significant differences in the catalyst performance were observed, and similarity of XRD patterns is consistent with this observation.

XRD patterns of catalyst B from three different tests (TOS = 120 -353 h) are shown in Figure 18. All three patterns are similar, and both magnetite and ε'-carbide were identified in all samples.

III. 8. 2 -2 XRD Measurements of Catalyst Samples from Fixed Bed and Slurry Reactor Studies Conducted under Task 5

Figure 19 shows XRD patterns of catalyst samples obtained from studies on the effect of source of potassium promoter (run SA-3155), or addition of CaO promoter (run SA-2405) relative to the baseline catalyst B (run SB-1295). Both magnetite and ε'-carbide were found in catalyst samples from runs SB-1295 and SA-2405 (Figures 19a and 19b), whereas only ε'-carbide was found in the sample from run SA-3155 (Figure 19c). The catalyst in run SA-3155 was less active than the catalyst in run SB-1295 (see text following Section III. 5. 2), even though the former had only ε'-carbide, and no magnetite, whereas the latter had both.

XRD patterns of catalysts from fixed bed reactor tests FA-1605 (100 Fe/3 Cu/4 K/16 SiO_2), FA-1525 (100 Fe/3 Cu/4 K/2 Ca/16 SiO_2) and FA-1515 (100 Fe/3 Cu/4 K/6 Ca/16 SiO_2) are shown in Figure 20. The baseline catalyst (FA-1605) and the catalyst containing the smaller amount of CaO promoter (FA-1525) had similar performance, and ε'-carbide was the only phase found in the samples at the end of these two runs. The used catalyst samples, from both top and bottom portions of the reactor, in run FB-1515 had magnetite and ε'-carbide. The activity of this catalyst was lower than that of catalysts in runs FA-1605 and FA-1525. The catalyst containing 6 parts of Ca per 100 parts of Fe, had much lower surface area, so its lower activity is not necessarily related to the presence of magnetite.

III. 8. 2 -3 XRD Measurements of Catalyst Samples from Fixed Bed Reactor Studies Conducted under Task 7

XRD patterns of used catalyst samples at the end of runs FA-3305, FA-3095 and FA-3495, conducted to evaluate the effect of calcination temperature on the catalyst performance, are shown in Figure 21. The pseudo-hexagonal iron carbide was found in all six samples, whereas magnetite was found only in the sample from the bottom of the reactor in run FA-3495 (Figure 21f). The catalyst in run FA-3495 was the least active, but it also had the lowest surface area.

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: (a) continue with testing of catalysts under Tasks 6 and 7 of the contract, and (b) continue with catalyst characterization of catalysts at various stages of usage (Task 8).