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The Development of Precipitated Iron Catalysts with Improved Stability

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The Development of Precipitated Iron Catalysts with Improved Stability

Contract DE-AC22-87PC79812

Performance Period: Sept. 1987 to Sept. 1992

Final Report

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Executive Summary

Objective

The objective of this program was to identify the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of catalysts suitable for slurry reactors. The performance targets are 88% CO+H₂ conversion with less than 1% deactivation per day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 normal liters per hour per gram iron (NL/hr/gFe) using a synthesis gas with a 0.5 to 1.0 H₂:CO ratio in a slurry reactor.

Tasks in the Program

The program was divided into five major tasks to be conducted over a three-year period:

- **Task 1:** Upgrade the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities.
- **Task 2:** Evaluate the performance of reference precipitated iron catalysts. Under secrecy agreements not to characterize the catalyst, Mobil Research and Development Corporation provided an iron catalyst (MCSG-4) to be used for reference performance. This catalyst was evaluated in the fixed-bed reactor. Also a fused-iron ammonia synthesis catalyst C-73-1-101 was tested.
- **Task 3:** Construct an iron (Fe) catalyst preparation plant and develop a baseline iron catalyst.
- **Task 4:** Elucidate the deactivation chemistry for iron catalysts.
- **Task 5:** Modify the chemistry of the catalyst to improve its stability.

Key Results

Draining of Liquid Products from Slurry Autoclave

Several procedures were used to drain liquid products made in the slurry autoclave reactor. Typically, a filter was attached at the end of a stainless steel tube. The tube passed through the

autoclave head and formed the liquid (and sometimes gas) exit line for the reactor. A ceramic filter with a nominal pore diameter of 0.40 micron (μm) rapidly plugged with catalyst particles. This type of filter eventually disintegrated because of the pressure drop that developed between the inside and the outside of the filter. When filters with a larger pore size were used (5 or 17 μm nominal pore diameter) plugging did not occur, but a substantial amount of catalyst was lost.

Reference Iron Catalysts

A fused-iron ammonia synthesis catalyst C-73-1-101 cannot be fully activated with synthesis gas in situ at the relatively low temperatures that are typical of the Fischer-Tropsch process. The full reduction of Fe requires high temperatures. The observed difficulty in reduction is probably caused by the presence of a large amount of aluminum oxide (Al_2O_3) promoter in the fused-iron catalyst.

Assuming the Fe content in the Mobil MCSG-4 catalyst to be 60 to 65%, a space velocity that was five times lower was needed to achieve 80% conversion in the fixed-bed reactor relative to the space velocity reported by Mobil for the same catalyst in the slurry bubble-column reactor tests at similar temperature and pressure. The causes of this unexpectedly low activity are not currently understood but may be tentatively attributed to the specific catalyst-handling procedure used in this lab and to the differences in the activation treatments between the two tests.

Iron Catalyst Preparation Parameters

Several iron-copper (Fe-Cu) catalysts were prepared in the laboratory at different pH levels by coprecipitating the nitrates of Fe and Cu with sodium carbonate (Na_2CO_3) solution. The precipitates were washed with water, dried, and then calcined. The catalysts were examined by scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), temperature-programmed reduction (TPR), and nitrogen adsorption.

The findings of this work are:

- A pH of at least 2 is required to precipitate an iron nitrate solution by using sodium carbonate or ammonia solutions. A pH of at least 5 is required to precipitate a copper nitrate solution. However, in the presence of iron nitrate, copper precipitation occurs at lower pH's.
- An increase in calcination temperature decreases the surface area and pore volume of precipitated Fe-Cu catalysts. Therefore, the calcination temperature should be no higher than that required for forming ferric oxide (Fe_2O_3) from goethite ($\text{FeO}(\text{OH})$).
- The amount of crystalline Fe_2O_3 in a precipitated Fe-Cu catalyst is maximized when calcination is conducted at the high-temperature maximum in the DSC

curve. This result suggests that DSC experiments may be useful for determining the calcination temperature requirement for Fe-Cu catalysts.

- According to DSC measurements, the calcination temperature requirement for precipitated 100:1 Fe:Cu catalysts prepared from Na_2CO_3 increased from about 380°C to about 450°C as the pH of precipitation increased from 3.5 to 9.5.
- The Na_2CO_3 -derived Fe-Cu catalysts prepared at $\text{pH} \leq 6.5$ had small amorphous particles. Catalysts prepared at $\text{pH} \geq 7.9$ were increasingly crystalline and had with large hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles after drying at 110°C . These morphological differences remained through the calcination step. This result indicates that the pH of precipitation is the key variable for controlling the Fe-Cu particle size.
- The Na_2CO_3 -derived 100:0.5 Fe:Cu catalyst prepared at a 6.5 pH had large goethite ($\alpha\text{-FeO(OH)}$) particles. A 100:1 Fe:Cu catalyst and a 100:5 Fe:Cu catalyst prepared at the same pH had small amorphous particles. Because large goethite particles would develop into large hematite particle during calcination, the copper level may also be a key variable for controlling the Fe-Cu particle size.
- The formation of Fe_3O_4 from Fe_2O_3 occurred at lower temperatures with Na_2CO_3 -derived 100:5 Fe:Cu and 100:1 Fe:Cu catalysts relative to 100:0.5 Fe:Cu catalyst prepared at a 6.1 to 6.5 pH. This result indicates that Cu enhances the reduction of Fe_2O_3 to Fe_3O_4 .

- The formation of Fe_3O_4 from Fe_2O_3 occurred at a higher temperature, while formation of metallic iron from Fe_3O_4 occurred at a lower temperature after K_2CO_3 impregnation of Na_2CO_3 - derived catalysts prepared at $\text{pH}=6.1-6.5$. This result indicates that although potassium may inhibit the reduction of Fe_2O_3 to Fe_3O_4 , it may enhance the reduction of Fe_3O_4 to metallic iron.
- The NH_4OH -derived 100:1 Fe:Cu catalyst precipitated at a pH of 9.5 had small amorphous particles. The Na_2CO_3 -derived catalyst prepared at the same pH had large hematite particles after 110°C drying. However, after 450°C calcination, the average particle sizes were similar for both catalysts. This result indicates that the use of NH_4OH relative to Na_2CO_3 does not provide obvious advantage.
- The complete reduction of precipitated Fe-Cu catalysts requires temperatures in excess of 800°C . Because reduction temperatures no higher than 300°C can lead to very active catalysts, the reduction of Fe-Cu catalyst surface must be occurring at much lower temperatures than those required for bulk reduction.

Iron Catalyst Performance in Fixed-Bed Reactor

A precipitated iron catalyst prepared in the laboratory was evaluated in an extended 800-hour test in a fixed-bed reactor. The objective was to determine the catalyst stability at high conversion.

The results indicate that the activity of the experimental iron catalyst 5709-91 was not very stable in the fixed-bed reactor under the selected operating conditions: the deactivation rate was about 0.8% conversion/day. These operating conditions are more severe than those typically used in a slurry reactor for which this iron catalyst is intended. Specifically, the fixed-bed catalyst temperature reached as high as 295°C (compared with 255 to 280°C for slurry reactors), which may have enhanced the deactivation rate. Also, at the inlet of the catalyst bed where little water exists, the H₂:CO ratio may have reached a value much lower than the feed ratio (0.7) because of the essential absence of the water gas shift reaction.

Iron Catalyst Preparation Plant

A new pilot plant was constructed for the large-scale synthesis of iron catalysts. In this plant, approximately 250 grams per hour (g/hr) of iron and copper is precipitated on a continuous basis. This plant is not currently set up for unattended operation. Accordingly, the precipitation time has typically been limited to an 8-hour operation. Filtering and washing steps, which follow precipitation, are also performed in the plant. However, these two steps were not performed on a continuous basis because of equipment limitations. The subsequent steps of drying, grinding, calcination, impregnation, and calcination were performed in the laboratory.

The findings from lab-prepared Fe-Cu-K catalysts were applied to the preparation of larger scale catalyst synthesis in the newly constructed preparation Plant 752. A total of 16 runs were conducted in Plant 752. The catalyst prepared in Run 16 (6616-18) was evaluated in a

long-term stability test in a slurry autoclave reactor (Run 19, Plant 700B). Specific preparation conditions used for this catalyst, as well as its properties and batch size, are described in Table 1.

Iron Catalyst Performance in a Slurry Reactor

The activation procedure for the new iron catalyst 6616-18 involved 12 hours of CO+H₂ treatment at 2 NL/hr/gFe, 280°C and 15 atmosphere (atm). The new iron catalyst (from Run 16, Plant 752) is predicted to perform slightly below the performance targets for slurry bubble-column operation. Stability targets appear to be achievable. This catalyst did not noticeably deactivate during 1,740 hours on-stream. Compared to the selectivity target, an excess of 2% C₁+C₂ was formed at 265°C. A continuous stirred tank reactor (CSTR) model was used to predict activity in a slurry bubble-column reactor. Based on the initial catalyst inventory in the autoclave, the catalyst seems to be short of the activity target by a factor of 1.8 at 265°C and 1.3 at 275°C. However, actual specific activities are likely to be closer to target because of catalyst inventory loss across the filter during the run and because catalytic activities were underestimated at low conversions. At the end of the 2,250-hour run, (Run 19, Plant 700B), 30% of catalyst was lost through wax withdrawals.

Arge-type conditions but not under more severe slurry conditions. Possibly, an improvement in catalytic stability will be needed to make iron catalysts suitable for slurry operation.

This program is aimed at identifying the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of more stable catalysts. Originally, the program was divided into five major tasks to be conducted over a three-year period. Following is a description of these tasks:

- Task 1: Upgrade the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities. The major technical challenge in this task was expected to be the separation of catalyst fines (smaller than 5 to 10 μm) from the wax product in the slurry reactor.
- Task 2: Evaluate the performance of reference precipitated iron catalysts. Under this task, Mobil Research and Development Corporation provided an iron catalyst to be used for reference performance under secrecy agreements not to characterize the catalyst. This catalyst was evaluated in the fixed-bed reactor. Also a fused-iron ammonia synthesis catalyst was tested under this task.
- Task 3: Construct an iron catalyst preparation plant and develop a baseline iron catalyst. The major technical challenge in this task was expected to be the preparation of a superior precipitated iron catalyst. Major emphasis was given in this program to the design and construction of catalyst preparation equipment

Deactivation Chemistry for Iron Catalysts and Modification of Catalysts

No work was done under these tasks because the new iron catalyst developed in this program was very stable.

Contract Objective

The objective of this program was to identify the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of catalysts suitable for slurry reactors. The performance targets are 88% CO+H₂ conversion with less than 1% deactivation/day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 NL/hr/gFe using a synthesis gas with 0.5:1.0 H₂:CO ratio in a slurry reactor.

Introduction

Precipitated iron catalysts are expected to be used in next generation slurry reactors for large-scale production of transportation fuels from synthesis gas. These reactors are expected to operate at higher temperatures and lower H₂:CO ratios relative to the Sasol Arge reactor (Table 1A). The feasibility of using iron catalysts has been demonstrated under relatively mild

and to the development of a catalyst-preparation procedure that would result in superior catalysts.

- Task 4: Elucidate the deactivation chemistry for iron catalysts. The major technical challenge in this task was expected to be the identification of the form of carbon that leads to deactivation.
- Task 5: Modify the catalysts chemistry to improve its stability. The plan was to evaluate several approaches to suppress coking reactions on iron catalysts.

Conversion and Selectivity Calculations

Argon present in the synthesis gas feed at about a 6% (by mole) level was used as an internal standard to determine conversions and light hydrocarbon selectivities according to the following expressions:

$$CO \text{ Conversion, } \% = \frac{\left(\frac{CO}{Ar_{feed}} - \frac{CO}{Ar_{product}} \right) \times 100}{\left(\frac{CO}{Ar} \right)_{feed}}$$

The CO+H₂ conversion was calculated in a similar manner. The calculation for the carbon atom selectivities is:

$$CO_2 \text{ Selectivity, \%} = \frac{\left(\frac{CO_2}{Ar} \right)_{product}}{\left(\frac{CO}{Ar} \right)_{feed} - \left(\frac{CO}{Ar} \right)_{product}}$$

$$C_n \text{ Selectivity, \%} = \frac{\left(\frac{C_n}{Ar} \right)_{product}}{\left(\frac{CO}{Ar} \right)_{feed} - \left(\frac{CO}{Ar} \right)_{product}} \times 100 \times \left(\frac{100}{100 - CO_2 \text{ selectivity}} \right)$$

In the latter formula, the n is the number of carbon atoms in one molecule of hydrocarbon (C_n).

The selectivities of the light hydrocarbon and oxygenates carbon atom have been normalized to

100% by backing out carbon monoxide (CO) converted to carbon dioxide (CO_2).

Results and Discussion

Task 1. Upgrade of the Existing Pilot Plants

The existing fixed-bed pilot plant was upgraded with slurry-reactor testing capability. For the fixed-bed pilot plant (Figure 1) a premixed blend of CO, hydrogen (H₂), and argon (Ar) contained in an aluminum cylinder is compressed to about 3,000 pounds per square inch (psig) and then flows through a capillary restriction, where flow is controlled by regulating the pressure drop across the restriction. The feed gas then passes through a fixed bed of γ -Al₂O₃ particles at about 208°C, where iron carbonyl contaminant decomposes. The feed then flows downflow through a 7/8-inch ID glass-lined fixed-bed reactor situated in an electric furnace. The existing plant also has H₂-addition capability at the inlet of the reactor. The flow out of the reactor passes through a series of product collectors and is then metered by a wet test meter. The first collector, which is 100 cc in volume, is at 130°C. The reactor pressure is controlled by a back-pressure regulator past the first separator. The second product collector, which is also 100 cc, operates at 0°C and 50 psig. The third product collector operates at -78°C and 0 psig.

The first on-line gas chromatograph samples the flow out of the reactor, just past the back-pressure regulator, and analyzes paraffins, olefins, aldehydes, and alcohols in the C₁-C₃₀ carbon number range. The second on-line gas chromatograph samples the flow just past the second product collector and analyzes CO, H₂, CO₂, Ar, paraffins, and olefins in the C₁-C₄ carbon number range.

The slurry-reactor system (Figure 2) is essentially independent of the fixed-bed reactor system, except for sharing the same on-line gas chromatographs. Therefore, the integrated pilot plant provides the capability of running a fixed-bed experiment parallel with a slurry-bed experiment. The on-line gas chromatographs then need to be shifted between the two experiments every other hour.

The slurry reactor has an independent feed system that is similar to that of the existing fixed-bed reactor system. The product-collecting system for the slurry reactor is similar to that for the fixed-bed reactor except for the size of the collectors, which are larger: 1,000 cubic centimeter (cc) for the first collector and 300 cc for the second collector. Also, these collectors have drainage capability during the experiment.

The slurry reactor is a 1-liter stirred autoclave placed in a two-zone electric furnace. The reaction products are removed from the slurry autoclave through a filter located inside the reactor vessel. This internal filtration allows product removal but keeps all the catalyst at reaction conditions. The filter is connected to a hollow shaft brought into the top of the autoclave. Later in the program, researchers determined that Berty reactor testing was not necessary to meet the objectives of the program.

Task 2. Performance of Reference Catalysts

Under Task 2, the fused iron ammonia synthesis catalyst C-73-1-101 (from United Catalysts Inc.) was tested. A sample of this catalyst was externally reduced with H_2 at $450^\circ C$ and previously tested as a reference catalyst under Contract DE-AC22-84PC70023, "The Development of a Selective Ruthenium Fischer-Tropsch Catalyst."¹ The objective was to determine whether the fused iron catalyst, which is originally in the oxide form, can be activated with synthesis gas in situ at the relatively low temperatures that are used for Fischer-Tropsch processing.

Two runs, fixed-bed Runs 48 and 49, were conducted. Catalyst identification, nature of diluents, catalyst and diluent weights, catalyst and diluent mesh size ranges, and catalyst and diluent bed lengths are summarized in Tables 2 and 3. For all of these tests, the catalyst was first heated under nitrogen (N_2) flow at 1 atm to $100^\circ C$, and then synthesis gas was introduced. The reactor was pressured from 9 to 11 atm with synthesis gas, and the catalyst was heated to $280^\circ C$ under a synthesis gas flow. The test conditions were changed several times during these runs. Catalyst inlet temperatures (2 inches before the catalyst bed) and maximum temperatures, inlet and outlet pressures, feed compositions, feed rates, and space velocities at different hours on-stream are also summarized in Tables 2 and 3.

Catalyst C-73-1-101 showed only 9% CO conversion at $280^\circ C$, 11 atm, and 3.0 NL/hr/gFe with 0.7:1 H_2 :CO synthesis gas in fixed-bed Run 48. The test was repeated in

fixed-bed Run 49, and the performance obtained at various hours on-stream is summarized in Table 3. The low activity of the catalyst under conditions of fixed-bed Run 48 was confirmed. High conversion required the use of high pressure (35 atm) and low space velocity (0.54 NL/hr/gFe). Under these conditions, the CO+H₂ conversion was 69%, and the methane and CO₂ selectivities were 3.2 and 40%, respectively. A comparison of the fused iron catalyst activated in situ to the earlier results with the externally reduced fused iron catalyst show 6 to 7 times lower activity with the current results.¹

These results suggest that fused iron catalyst C-73-1-101 cannot be fully activated with synthesis gas in situ at the relatively low temperatures that are typical of Fischer-Tropsch process. Full reduction of iron requires high temperatures. The observed difficulty in reduction is probably caused by the presence of a large amount of Al₂O₃ promoter in the fused iron catalyst.

Iron Catalyst from Mobil

The iron catalyst by Mobil, MCSG-4, was tested in the fixed-bed pilot plant to establish reference performance. This catalyst was previously tested by Mobil in a slurry bubble-column reactor. In the Mobil test, after a 12-hour activation at 280°C, 11 atm, and 2.0 NL/hr/gFe feed rate with 0.7:1 H₂:CO feed, the catalyst showed 80% CO+H₂ conversion at 2.4 NL/hr/gFe, 257°C, and 14 atm with a synthesis gas having a H₂:CO ratio of 0.7.² The methane and ethane

selectivity typically increased during the tests. In Run 13, the increase in methane and ethane selectivity was from 2.5 to 4.5%.

The MCSG-4 catalyst was shipped to UOP after being slurried in an organic medium. The approximate weight was 500 grams. Two attempts were made to make the catalyst suitable for fixed-bed pilot plant testing. First, the catalyst was washed with *n*-hexane and then dried at 110°C before being tested in the pilot plant in fixed-bed Run 52. In the second attempt, the washed and dried catalyst was calcined with air at 380°C in an attempt to burn residual organics and then tested in fixed-bed Run 53.

Fixed-Bed Run 52

During the first 5 hours of Run 52, the MCSG-4 catalyst was heated from 110 to 250°C, under 0.7:1 H₂:CO synthesis gas and a space velocity of 1.7 NL/hr/g catalyst. During the following 35 hours, the catalyst inlet temperature was gradually increased to 280°C and was maintained there for another 11 hours. At 280°C inlet temperature, the maximum observable temperature in the catalyst bed was 294°C. The catalyst bed outlet pressure was 9 atm throughout the 51-hour activation treatment. The CO+H₂ conversion reached a level of about 81% by the end of the activation treatment. This level is equivalent to the conversion level reported for the same catalyst in the slurry bubble-column reactor at the end of a 12-hour activation treatment.²

After 51 hours, the catalyst inlet temperature was lowered to 257°C, and the catalyst outlet pressure was increased to 13 atm, which caused the conversion to decrease to about 40%. Under these conditions, the maximum temperature in the catalyst bed was no more than 260°C. Between 59 and 90 hours on-stream, the space velocity was lowered from 1.7 to 0.37 NL/hr/gFe catalyst, which increased the conversion to 79%. No further condition change was made after 90 hours. The conversion gradually decreased to 70% by 156 hours on-stream.

The catalytic activity observed with MCSG-4 catalyst at 257°C inlet temperature and 13 atm in the fixed-bed reactor was much lower than that reported for the same catalyst in the slurry bubble-column reactor, as is apparent from the space velocity differences between the two tests. The MCSG-4 catalyst was retested in Run 53 to verify the low activity observed in Run 52.

Fixed-Bed Run 53

The activation treatment in fixed-bed Run 53 was similar but not identical to that used in Run 52 (Tables 4 and 5). However, larger amounts of catalyst and diluent were used in fixed-bed Run 53, and so the pressure drop was slightly higher. At a 9 atm catalyst bed outlet pressure, the inlet pressure was about 13 atm. The CO+H₂ conversion gradually increased to 40% during the first 41 hours, and the catalyst inlet temperature was increased to 270°C (Figure 3). During the same period, the CO₂ selectivity gradually increased to about 25%, and the methane selectivity increased to 3.3% (Figures 4 and 5). Between 41 and 51 hours on-stream, when the

catalyst bed inlet temperature was increased to 280°C, the maximum observable temperature in the catalyst bed increased to 314°C. Under these conditions, the conversion increased to 82%, and the CO₂ and methane selectivities increased to 46% and 6.6%, respectively.

Following 51 hours of activation, the catalyst inlet temperature was lowered to 257°C, and the catalyst outlet pressure was increased to 13 atm, which lowered the conversion to about 40%. The space velocity was then gradually lowered to 0.28 NL/hr/gFe catalyst to achieve about 80% conversion. The maximum observable catalyst temperature was 263°C. Under these conditions, the CO₂ and methane selectivities lined out at about 45 and 3.2%, respectively, and the H₂:CO usage ratio was 0.63 (Figures 4-6). The CO+H₂ conversion gradually decreased to about 73% by the end of 265 hours on-stream.

The propylene to propane ratio reached a maximum level of about 10 during the early part of the run at about 14% CO+H₂ conversion and then gradually decreased with an increase in conversion level. The propylene to propane ratio remained mostly between 1.3 and 1.5 during the later part of the run at 70 to 75% conversion and a H₂:CO outlet ratio of about 0.85 (Figures 7 and 8).

Assuming the iron content in the MCSG-4 catalyst to be 60 to 65%, a space velocity that was five times lower was needed to achieve 80% conversion in the fixed-bed reactor relative to the space velocity reported by Mobil for the same catalyst in the slurry bubble-column reactor tests at similar temperature and pressure. The causes of this unexpectedly low activity are not

currently understood but may be tentatively attributed to the specific catalyst-handling procedure used in this lab and to the differences in the activation treatments between the two tests.

Task 3. Construction of a Catalyst Preparation Plant and Development of a Baseline Catalyst

Under Task 3, preliminary catalyst-preparation equipment was built in the laboratory for determining the significance of various catalyst preparation parameters. These data were then used for final design of the catalyst preparation equipment.

Several Fe-Cu catalysts were prepared at different pH levels by the coprecipitation of the nitrates of Fe and Cu with Na_2CO_3 solution. The preparation parameters and the properties for 12 of these catalysts are listed in Table 1. The precipitates were washed with water, dried, and then calcined. The catalysts were examined by STEM, XRD, DSC, TGA, TPR, and nitrogen adsorption. Only one of these catalysts were tested for its Fischer-Tropsch performance.

Determination of pH's for Precipitating Fe and Cu

A ferric nitrate ($\text{Fe}(\text{NO}_3)_3$) solution with 5.0 wt.% Fe was titrated against 1N solutions of Na_2CO_3 and NH_4OH at room temperature (Figures 9 and 10). In both cases, the Fe precipitation started to occur at a pH of about 2. Similarly, a solution of copper nitrate ($\text{Cu}(\text{NO}_3)_2$) with 0.5 wt.% Cu started to precipitate at a pH of about 5 (Figures 11 and 12). However, in the presence of $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$ precipitated at lower pH's.

Description of DSC and TGA Experiments

Catalyst 5685-61 was prepared by the coprecipitation of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ solutions with a Na_2CO_3 solution (100:1 Fe:Cu, by weight) at a pH of 3.5. According to STEM examination of the catalyst after drying at 110°C , the catalyst was made up of 2 to 4 nanometer (nm) amorphous Fe-Cu particles. Another catalyst, 5685-53, (100:1 Fe:Cu) precipitated with Na_2CO_3 at a pH of 4.3 showed similar morphology to catalyst 5685-61. These two catalysts were used for establishing the reproducibility of DSC experiments, which are useful for determining the calcination temperature requirement of Fe-Cu catalysts.

In DSC experiments, the uncalcined catalyst is heated from room temperature to 600°C at $5^\circ\text{C}/\text{min}$ under air flow, and the heat flow to or from the catalyst is measured. The results obtained with catalyst 5685-53 in two separate runs are described in Figure 13. A minimum in the DSC curve indicates the occurrence of an endothermic reaction. The minimum at 40 to 50°C is probably related to water evolution from the catalyst. A maximum in the DSC curve indicates the occurrence of an exothermic reaction. The maximum observed at about 390°C is probably related to the formation of Fe_2O_3 from goethite, $\alpha\text{-FeO}(\text{OH})$; this formation apparently illustrates the calcination temperature requirement for the catalyst. Secondary maxima appear at about 200°C . Not presently clear is whether the presence of multiple maxima indicates the presence of catalyst particles with different calcination temperature requirements or whether it indicates that calcination is a multistep process.

The results summarized in Figure 13 also indicate that the DSC experiments were quite reproducible. No more than 5°C difference is observed between the calcination temperature requirements measured in two separate runs with the same catalyst.

Catalyst 5685-53 was also evaluated in a TGA experiment, which involves measuring the percent of weight loss as the catalyst is heated up to 600°C at 5°C/min under air flow (Figure 14). The TGA experiment also provides the derivative of the catalyst weight loss with respect to time. A maximum in the derivative curve illustrates the temperature at which the rate of weight loss becomes maximum. Three maximas, at 56°C, 217°C, and 360°C, were observed. These maxima may correspond to the minimum and maxima observed in the DSC experiments at 40 to 50°C, 200°C, and 390°C. Not presently clear is why the high-temperature maxima (or minimum) differ by 20 to 50°C between the DSC and TGA experiments.

During the TGA experiment, catalyst 5685-53 lost about 12% weight between 100°C (the temperature at which significant fraction of the free water should have evolved) and 600°C. A 12.4% weight loss would occur for the reaction of $2\text{FeO}(\text{OH})$ to Fe_2O_3 and H_2O . This reaction presumably is the major calcination reaction.

The DSC results obtained with catalyst 5685-61 in two separate runs and the TGA results are described in Figures 15 and 16. For this catalyst, the secondary maximum at about 250°C is less apparent. Also the high-temperature maximum occurs at a lower temperature. These

DSC results again indicate that these experiments are quite reproducible, but this time, the high-temperature maxima for duplicate measurements on the same catalyst were 12°C apart.

Description of TPR Experiments

Catalyst 5685-145 with 100:1 Fe:Cu (by weight) was prepared by the coprecipitation of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ with Na_2CO_3 solution at a pH of 6.5, followed by drying at 110°C and calcining at 410°C. Based on XRD measurements on a similar catalyst, the Fe-Cu crystallite size in this catalyst is expected to be between 6 and 11 nm. Catalyst 5685-145 was used for establishing the reproducibility of TPR experiments, which are useful for determining the reduction temperature requirement of Fe-Cu catalysts.

In TPR experiments, the calcined catalyst is heated from room temperature to 800°C at 2°C/min under 5% H_2 in argon flow and the uptake of H_2 is measured. The results obtained with catalyst 5685-145 in two separate runs are described in Figure 17.

The first major TPR peak occurs between 140 and 160°C. In an attempt to identify the crystalline phases present at 150°C, another portion of catalyst 5685-145 was heated from room temperature to 150°C in 2 hours under 5% H_2 in argon flow, maintained at 150°C for 1 more hour, and then analyzed by XRD (Figure 18). A magnetite (Fe_3O_4) phase was observed to be present along with a maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phase.

The peak between 140 and 160°C was equivalent to about 0.15 millimole (mmole) H₂/g catalyst. Because this catalyst contains 0.11 mmole Cu/g catalyst, the TPR peak at 140 to 160°C may be partly attributed to the reduction of Cu.

The second major TPR peak occurs between 160 and 200°C. A portion of catalyst 5685-145 that was heated at 250°C under 5% H₂ in argon flow in 4 hours and maintained there for 1 more hour showed only magnetite phase, but no Fe₂O₃ (Figure 19).

The third major TPR peak occurs between 200 and 680°C. At higher temperatures, further H₂ uptake occurs. A portion of catalyst 5685-145 was heated to 800°C under 5% H₂ in argon flow in 6.5 hours and held there for 1 more hour. This catalyst showed metallic iron (α -Fe) along with wustite (α -FeO) (Figure 20).

These results suggest that the reduction of Fe-Cu catalyst may be occurring in at least three steps at specified temperature ranges:

- Step 1a. $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ at 140 to 160°C
 $\text{CuO} \rightarrow \text{Cu}$ (possibly)
- Step 1b. $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ at 160 to 200°C
- Step 2. $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ at 200 to 680°C
- Step 3. $\text{FeO} \rightarrow \text{Fe}$ at more than 680°C

Why two peaks may be associated with Fe_3O_4 formation from Fe_2O_3 is not presently clear.

The results summarized in Figure 17 indicate that duplicate TPR results obtained with the same catalyst are quite reproducible. No more than a 10°C difference occurs between the position of each corresponding TPR maxima.

The TPR results show that the complete reduction of Fe-Cu catalysts requires temperatures in excess of 800°C . However, temperatures higher than 300°C are not typically required to generate active catalysts. Thus, the reduction of the catalyst surface relative to the bulk occurs at much lower temperatures, as also discussed by M. P. Rosynek et al.³ Nevertheless, the TPR experiments are useful for monitoring differences between different Fe-Cu catalysts because the reduction behavior of these catalysts, as examined by TPR, is expected to vary sensitively with their chemical and morphological properties.

Use of DSC for Determining Calcination Temperature Requirement for Fe-Cu Catalysts

Previously described DSC measurements on 100:1 Fe:Cu catalyst 5685-53 precipitated at 4.3 pH showed a high-temperature maximum peak at about 390°C . Another catalyst precipitated at the same 4.3 pH was calcined at 275°C for 2 hours. The XRD measurements showed this catalyst to have 37.8% crystalline $\alpha\text{-Fe}_2\text{O}_3$ only. A portion of catalyst 5685-53 calcined at 380°C and another portion calcined at 450°C showed 79 and 80% $\alpha\text{-Fe}_2\text{O}_3$, which was the only detected crystalline phase. These results indicate that essentially maximum crystalline $\alpha\text{-Fe}_2\text{O}_3$

is obtained when calcination is done at the temperature that corresponds to the high-temperature maximum in the DSC measurement and that the amount of $\alpha\text{-Fe}_2\text{O}_3$ does not significantly increase at higher calcination temperatures. Because neither DSC nor XRD measurements show that any phase of transformation seems to take place in the Fe-Cu catalyst at temperatures higher than those corresponding to the high-temperature maximum in the DSC experiment ($-T_c$), a calcination temperature higher than T_c may be necessary.

Catalyst 5685-75 (100:1 Fe:Cu, by weight) was prepared by the coprecipitation of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ with a solution of Na_2CO_3 at a pH of 9.7. The DSC measurement on this catalyst showed a high-temperature maximum at 443°C (Figure 21). A portion of this catalyst was calcined at 380°C and another portion at 450°C , each for 2 hours. The XRD measurements showed the catalyst calcined at 380°C to be 77% $\alpha\text{-Fe}_2\text{O}_3$ and the catalyst calcined at 450°C to be 87% $\alpha\text{-Fe}_2\text{O}_3$. These results again indicate that the amount of $\alpha\text{-Fe}_2\text{O}_3$ is maximized when calcination is done at the high temperature DSC maximum.

Experiments were later conducted with catalysts 5685-111 and 5685-61 to determine whether an extended low temperature calcination would lower the final calcination temperature requirement. Catalyst 5685-111 was prepared by coprecipitating $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ (10:1 Fe:Cu) at a pH = 9.5 with ammonia solution. For this catalyst, the high temperature DSC maximum occurred at 458°C (Figure 22). During another DSC experiment, this catalyst was brought to 374°C at $5^\circ\text{C}/\text{min}$ and then maintained isothermally for 1.5 more hours (Figure 23).

The catalyst was then subjected to a standard DSC experiment, which indicated that the high temperature DSC peak position and shape had not essentially changed (Figure 24).

However, catalyst 5685-61, which had a maximum DSC peak at about 380°C was brought to 350°C during the DSC experiment and then maintained isothermally for 2 more hours (Figure 25). A subsequent standard DSC experiment did not show the 380°C peak anymore (Figure 26).

These two sets of results show that a low temperature calcination may lower the final calcination temperature requirement when the first calcination temperature is 30°C lower, but not when it is 100°C lower than the temperature at which the maximum in the DSC curve appears.

Effect of Calcination Temperature

Two separate portions each of 100:1 Fe:Cu catalysts 5685-53 and 5685-75 prepared at 4.3 and 9.7 pH, respectively, were calcined at 380 and 450°C and later examined by STEM, TPR, and N₂ adsorption to determine the effect of calcination temperature on Fe-Cu catalysts.

Catalyst prepared at 4.3 pH and calcined at 380°C showed 4 to 6 nm Fe-Cu particles in the STEM examination. The particle size was much larger (5 to 20 nm) for the catalyst

calcined at 450°C. The particle size remained large (10 to 40 nm) at calcination temperatures of 380 and 450°C for the catalyst prepared at a 9.7 pH.

Nitrogen adsorption measurements on a 4.3 pH catalyst calcined at 380 and 450°C are summarized in Figures 27-29. The results indicate that higher temperature calcination decreases the total pore volume from 0.22 to 0.17 cc/g, increases the average pore radius from 5.2 to 6.2 nm and decreases the total surface area from 83 to 53 m²/g. Similarly for 9.7 pH catalysts, higher temperature calcination increases the average pore radius from 5.2 to 8.9 nm and decreases the total surface area from 74 to 41 m²/g (Figures 30-32).

The results of TPR experiments with two different portions of catalyst 5685-53 precipitated at a 4.3 pH are summarized in Figure 33. The following differences were found with the portion calcined at 450°C relative to the portion calcined at 380°C:

- The low temperature TPR peak, which seems to be related to the Fe₂O₃ to Fe₃O₄ reaction, increased in magnitude and also shifted to 20°C lower temperature.
- The TPR peak between 350 and 700°C expanded by 20°C to higher temperature and increased in magnitude.

These results indicate that selection of suitable calcination temperatures for Fe-Cu catalysts is important because the morphological properties of iron catalysts, as determined by STEM and N₂ adsorption, are influenced significantly by the calcination temperature.

Furthermore, variations in TPR spectra also were observed with changes in calcination temperature. This observation suggest that the chemical properties of catalysts may also have been influenced by calcination temperature.

Effect of pH

Six catalysts were prepared by the precipitation of solutions containing $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ (100:1 Fe:Cu) with Na_2CO_3 solution at pH's of 3.5, 4.3, 5.5, 6.5, 7.9, and 9.7, respectively. These catalysts were characterized by DSC, TGA, STEM, TPR, and XRD to evaluate the effect of the pH of precipitation on Fe-Cu catalysts.

Catalysts 5685-61, 5685-53, 5709-73, and 5709-49 precipitated at a pH of 3.5, 4.3, 5.5, and 6.1 respectively, and dried at 110°C showed amorphous-looking Fe-Cu particles of 2 to 4 nm in the STEM examination (Figures 34 and 35). Catalyst 5685-69 precipitated at a pH of 7.9 and had 20 to 35% crystalline material with 10 to 20 nm of Fe-Cu particles (Figure 36). The rest of the catalyst was amorphous with 2 to 4 nm particles. Catalyst 5685-75 precipitated at a higher pH of 9.7 was 35 to 45% crystalline with 10 to 40 nm Fe-Cu particles (Figure 36). To identify the nature of the crystalline material, catalyst 5685-75 was also analyzed by XRD, which indicated 30.1% of the catalyst to be crystalline $\alpha\text{-Fe}_2\text{O}_3$. A minor amount of goethite phase was also detected in XRD (Figure 37).

Because high-pH catalysts showed increased amounts of crystalline Fe_2O_3 with large iron particles, a low pH and a high pH catalyst were calcined and then analyzed by STEM to determine whether differences in catalyst morphology observed after the 110°C drying step still existed after calcination. The STEM micrographs for catalysts with pH's of 4.3 and 9.7 after calcination at 380 and 450°C are in Figures 38 and 39. The low-pH catalyst was composed of 4 to 6 nm Fe-Cu particles after calcination at 380°C, and the high-pH catalyst was composed of 10 to 40 nm particles. Similarly, after 450°C calcination, the low-pH catalyst had 5 to 20 nm particles, and the high-pH catalyst had 10 to 40 nm particles. These results indicate that the Fe-Cu particle size increases with the increase in pH of precipitation, and these differences persist through the calcination step.

Catalysts precipitated at 3.5, 4.3, 7.9, and 9.7 pH were also examined by DSC after the drying step at 110°C (Figure 40). The minima observed at 40 to 50°C are probably related to water evolution. The DSC maximum high temperature peak decreases in magnitude and shifts to higher temperature from 367 to 444°C with an increase in pH from 3.5 to 9.7. All catalysts, regardless of pH, have a secondary maximum at about 250°C. Catalyst with a 7.9 and 9.7 pH also have a low temperature maximum at about 100°C, but catalysts with a 3.5 and 4.3 pH do not. The DSC maximum at about 100°C is apparently related to the formation of large iron oxide particles that are observed during STEM examination of the high-pH catalysts that were dried at 110°C.

The high-pH catalysts that were dried at 110°C lost less weight during the TGA experiment between 100 and 600°C relative to the low-pH catalysts: 5.3% for 7.9 pH catalyst and 4.0% for 9.7 pH catalyst relative to 12% for 3.5 and 4.3 pH catalysts (Figures 14, 16, 41, and 42). Less weight loss during the TGA experiments with high-pH catalysts that were dried at 110°C relative to low pH catalysts that were dried at 110°C is expected because the significant fraction of the reaction of $2\text{FeO}(\text{OH})$ to Fe_2O_3 and H_2O with high-pH catalysts seems to occur during the 110°C drying step before the TGA experiments.

The DSC and TGA experiments show distinct features for catalysts precipitated at different pH's, indicating that the properties of iron catalysts are significantly influenced by the pH of precipitation. These results suggest that DSC and TGA techniques may play a key role for the characterization of Fe-Cu catalysts in the future.

The effect of the pH of precipitation on the properties of Fe-Cu catalysts was further demonstrated by the TPR experiments (Figures 43 and 44). The TPR experiments show that catalysts with a pH of 9.7 can be reduced at lower temperatures relative to 4.5 pH catalysts, regardless of the calcination temperature. Not presently clear is whether these differences in reproducibility of Fe-Cu catalysts precipitated at different pH's are mainly caused by differences in the catalyst particle sizes that were previously discussed.

Effect of Cu Level

Three catalysts were prepared by the coprecipitation of solutions containing different ratios of $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ (100:0.5 Fe:Cu, 100:1 Fe:Cu, 100:5 Fe:Cu, by weight) with Na_2CO_3 solution at 6.1 to 6.5 pH. A fourth catalyst with 100:5 Fe:Cu was precipitated at 9.5 pH. These catalysts were characterized by DSC, TGA, STEM, XRD, and TPR to evaluate the effect of Cu level.

In the STEM examination, catalyst 5685-139 with 100:0.5 Fe:Cu showed partly crystalline morphology with 2 to 6nm particles after the 110°C drying step (Figure 45). The XRD analysis of the same catalyst indicated these crystallites to be goethite (Figure 46). As explained previously, crystallites observed with high-pH catalysts (7.9 and 9.5 pH) after 110°C drying were hematite ($\alpha\text{-Fe}_2\text{O}_3$) and not goethite ($\alpha\text{-FeO}(\text{OH})$).

Catalysts 5709-49 and 5685-135 with 100:1 Fe:Cu and 100:5 Fe:Cu, respectively, did not show crystallites and had amorphous-looking 2 to 4 nm particles (Figure 45 and 47). These results indicate that Cu may suppress the formation of goethite at 110°C. Because large hematite particles would result from large goethite particles during calcination, the Cu level may be a key variable to control Fe-Cu particle size in the finished catalyst.

Because large hematite particles were formed at 110°C with high pH catalysts and Cu suppressed the formation of large goethite particles at the same temperature, a high-pH catalyst

was prepared to determine whether formation of large hematite particles could be prevented by the use of a high Cu level. Catalyst 5709-37 with 100:5 Fe:Cu was prepared at a pH of 9.5. The amorphous nature of this catalyst indicates that a high Cu level indeed suppressed the formation of large hematite particles at 110°C (Figure 47).

The high and low Cu catalysts 5685-139 (100:0.5 Fe:Cu) and 5685-135 (100:5 Fe:Cu) precipitated at a pH of 6.1 to 6.5 also showed different features in the DSC and TGA experiments (Figures 48 and 49). The weight loss between 100 and 600°C with the low-Cu catalyst, which did not have hematite (α -Fe₂O₃), but only goethite (α -FeO(OH)) crystallites, was about 12%. This weight loss is similar to the weight loss observed with low-pH samples that had no hematite crystallites. These two sets of results are consistent because the weight loss during the TGA experiments between 100 and 600°C is probably attributed to the formation of hematite from FeO(OH). Not presently clear is why the weight loss is less with the high-Cu catalyst because that catalyst did not show hematite formation at 110°C.

Catalysts 5685-139, 5685-61, and 5685-135 with 100:0.5 Fe:Cu, 100:1 Fe:Cu and 100:5 Fe:Cu, respectively, were all calcined at 410°C and then examined by TPR (Figure 50). The low temperature peaks between 100 and 180°C are probably related to the onset of Fe₃O₄ formation or to the reduction of Cu, as discussed previously. The position of the low temperature peak decreased in temperature as the Cu level increased.

The higher temperature peaks between 180 and 210°C are apparently related to the Fe_3O_4 formation reaction. These peak positions were similar for catalysts with 100:5 Fe:Cu and 100:1 Fe:Cu but occurred at a higher temperature with catalyst having 100:0.5 Fe:Cu. These results are consistent with those obtained by other investigators and suggest that Cu may enhance the reduction of Fe_2O_3 to Fe_3O_4 .

The portions of the TPR experiments at temperatures higher than 250°C, which involve reduction of Fe_3O_4 to metallic Fe by FeO formation were different with the three catalysts containing different levels of Cu. However, no obvious trend in the ease of reduction to metallic Fe with Cu level was observed.

Effect of Potassium

Catalysts 5685-139 with 100:0.5 Fe:Cu and catalysts 5685-135 with 100:5 Fe:Cu were impregnated with potassium (K), in the form of potassium carbonate (K_2CO_3). The TPR behavior of these catalysts were compared before and after K impregnation. Results summarized in Figures 51 and 52 indicate that although K may inhibit the reduction of Fe_2O_3 to Fe_3O_4 , it certainly enhances the reduction of Fe_3O_4 to metallic Fe.

Catalysts Precipitated with NH_4OH

Different DSC features of 100:1 Fe:Cu catalysts 5685-75 and 5685-111 prepared by precipitation at 9.5 to 9.7 pH using Na_2CO_3 and NH_4OH solutions, respectively, were previously described (Figures 21 and 22). The STEM examination of these catalysts after 110°C drying indicated that although Na_2CO_3 -derived catalyst was partly crystalline, with 10 to 40 nm Fe-Cu particles, NH_4OH -derived catalyst had only amorphous-looking particles no larger than 2 to 4 nm. These two catalysts were later calcined at 450°C and further characterized to determine whether differences between them would continue to exist through the catalyst finishing steps. The STEM examination indicated that although the average Fe-Cu particle size was approximately the same with both catalysts, the particle size distribution was wider with Na_2CO_3 -derived catalyst (10 to 40 nm) relative to NH_4OH -derived catalyst (25 to 30 nm) (Figure 53). According to TPR experiments, although Fe_3O_4 formation seems to have shifted to about 20°C higher temperature, reduction to metallic Fe seems to have been enhanced with the NH_4OH -derived catalyst (Figure 54).

Summary of the Effect of Catalyst-Preparation Parameters

The observed effects of various catalyst preparation parameters is summarized in the following paragraphs:

- A pH of at least 2 is required to precipitate an iron nitrate solution by using sodium carbonate or ammonia solutions. A pH of at least 5 is required to precipitate Cu nitrate solution. However, in the presence of iron nitrate, the precipitation of Cu occurs at lower pH's.
- An increase in calcination temperature decreases the surface area and pore volume of precipitated Fe-Cu catalysts. Therefore, the calcination temperature should be no higher than that required for forming Fe_2O_3 from $\text{FeO}(\text{OH})$.
- The amount of crystalline Fe_2O_3 in a precipitated Fe-Cu catalyst is maximized when calcination is conducted at the high temperature maximum in the DSC curve. This result suggests that DSC experiments may be useful for determining the calcination temperature requirement for Fe-Cu catalysts.
- According to DSC measurements, the calcination temperature requirement for precipitated 100:1 Fe:Cu catalysts prepared from Na_2CO_3 increased from about 380°C to about 450°C as the pH of precipitation increased from 3.5 to 9.5.
- The Na_2CO_3 -derived Fe-Cu catalysts prepared at a pH of ≤ 6.5 had small amorphous particles. The catalysts prepared at a pH of ≥ 7.9 were increasingly crystalline, with large hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles, after 110°C drying. These morphological differences remained through the calcination step. This result indicates that the pH of precipitation is the key variable for controlling the Fe-Cu particle size.
- The Na_2CO_3 -derived 100:0.5 Fe:Cu catalyst prepared at a pH of 6.5 had large goethite ($\alpha\text{-FeO}(\text{OH})$) particles. The 100:1 Fe:Cu and 100:5 Fe:Cu catalysts

prepared at same pH had small amorphous particles. Because large goethite particles lead to large hematite particles during calcination, the Cu level may also be a key variable for controlling the Fe-Cu particle size.

- The formation of Fe_3O_4 from Fe_2O_3 occurred at lower temperatures with Na_2CO_3 -derived 100:5 Fe:Cu and 100:1 Fe:Cu catalysts relative to 100:0.5 Fe:Cu catalyst prepared at a 6.1 to 6.5 pH. This result indicates that Cu enhances the reduction of Fe_2O_3 to Fe_3O_4 .
- The formation of Fe_3O_4 from Fe_2O_3 occurred at a higher temperature. The formation of metallic Fe from Fe_3O_4 occurred at a lower temperature after K_2CO_3 impregnation of Na_2CO_3 -derived catalysts prepared at a 6.1 to 6.5 pH. This result indicates that although K may inhibit the reduction of Fe_2O_3 to Fe_3O_4 , it may enhance the reduction of Fe_3O_4 to metallic Fe.
- The NH_4OH -derived 100:1 Fe:Cu catalyst precipitated at a 9.5 pH had small amorphous particles, but Na_2CO_3 -derived catalyst prepared at the same pH had large hematite particles after 110°C drying. However, after 450°C calcination, the average particle sizes were similar for both catalysts. This result indicates that the use of NH_4OH relative to Na_2CO_3 does not provide an obvious advantage.
- The complete reduction of precipitated Fe-Cu catalysts require temperatures in excess of 800°C. Because reduction temperatures no higher than 300°C can lead to very active catalysts, the reduction of Fe-Cu catalyst surface must be occurring at much lower temperatures than those required for bulk reduction.

Catalysts Prepared in the Catalyst Preparation Plant

Catalyst Preparation Plant

In the catalyst preparation plant (Figure 55a), metal was not used as a material of construction for any wetted section to avoid catalyst contamination that may occur through the dissolution of metallic components in contact with acidic solutions. The materials of construction for the process lines, fittings, and reactor were either Teflon or polypropylene. The Fe-Cu nitrate and the sodium carbonate (Na_2CO_3) feed solutions are in two separate 15-gallon feed tanks. During the experiment, the weight of these solutions is continuously measured by two scales. The feed solutions are pumped separately to a precipitation reactor.

The detailed drawings of the precipitation reactor are in Figures 55b, 55c, 55d, 55e, and 55f. The reactor was designed specifically to prevent plugging during the precipitation of Fe and Cu. The two feed solutions get in contact with each other in a vertical rotating mixer zone. One of the pH probes is located at the outlet of the vertical mixing zone. Small strips attached to the end of the mixer help minimize, to some extent, the buildup of precipitate on the surface of the pH probe. Nevertheless, this pH probe did not provide reliable pH measurements (because of solids buildup). More reliable pH measurements were possible with another probe located 1 inch lower in the reactor. The surface of this second probe was kept relatively clean by means of a small horizontal water (deionized) stream.

The product, slurry, is pumped from the reactor directly to a centrifugal filter. The filter bags had 1 to 3 nm pore dimension and were supplied by Ketema, Inc. The specifications for the bags were Ketema STK 02-010S0-12 inch TOLHURSH olefin composition. The centrifuge effectively filters the precipitate and rejects the rest of the solution. Typically, the filter bag is replaced every 2 hours. However, during these 2 hours, the filtration rate is slower than the feed rate to the centrifuge. The excess slurry is collected in a 55-gallon drum. Following the termination of the run, the supernatant solution is decanted from the top of the drum. The concentrated slurry is pumped to the centrifuge for further collection of solids. After recovery, the solid precipitate is washed with water in separate batches. Typically, 100 grams of water was required for every gram of catalyst to achieve a sodium level less than 5 weight parts per million (wppm). Typically, 80 to 90% of the Fe and Cu pumped to the precipitation reactor was recovered from the washing step.

Drying, Calcination, Impregnation, and Calcination

Following the washing step, the catalyst was dried in an oven at 110°C for 24 hours. The oven-dried material was ground to more than 40 mesh and then calcined under 3 L/min air flow in a quartz tube furnace for 2 hours. Typical batch sizes for calcination have been 500 to 600 grams of catalyst. The calcined material was then ground to 140 to 400 mesh. Typically, 30% of the calcined material became more than 400 mesh and rejected from the rest of the catalyst preparation.

The calcined catalyst was then impregnated with a potassium carbonate (K_2CO_3) solution in a rotary impregnator. The impregnating solution to catalyst weight ratio was 1.26. Following 20 minutes of contact of the catalyst with the solution, steam was injected to the impregnator jacket to boil off the water. The evolution of water took another 2 hours. The catalyst recovery during the impregnation step is typically more than 98%.

Following impregnation, the catalyst was recalcined under air at $380^{\circ}C$ for 2 hours. The calcined catalyst was then sieved again to recover 140 to 400 mesh portion. The additional fines (more than 400 mesh) produced in this step is typically more than 5% of the calcined material.

Catalysts Prepared in the Plant

A total of 16 runs were performed in Plant 752. Some of these catalysts from these different runs were combined to make larger batches of catalysts. The preparation parameters and the properties of these catalysts that were actually evaluated in Fischer-Tropsch synthesis are summarized in Table 1. The same table also lists the batch size for the final finished catalysts as well as the pilot plant run numbers at which they were tested.

Example of Catalyst Characterization

As outlined previously, several different portions were obtained from any given precipitation run in Plant 752. These portions were separately filtered, washed, dried, calcined, and characterized

by STEM to check the uniformity of the preparations. Only portions that had similar size Fe-Cu oxide particles and with comparable Fe:Cu ratios were combined to make larger batches.

For example, six different portions were obtained during Run 15 (Plant 752). Portion 1B was collected in the filter bag during the precipitation run. Portions 1, 2, 3, 4, and 5 were collected from the 55-gallon drum. The aging times of Fe-Cu precipitate in the product slurry (for portions 1 to 5) were for several days compared to no more than 2 hours for portion 1B.

The STEM results for Run 15 (Plant 752) catalyst is summarized in Table 5a. According to the STEM examination, the Fe-Cu oxide particle size of the various portions, was either 10 to 20 nm or 10 nm and less. Portion 1B had ≤ 10 nm particles, which is identical to the particle size obtained from portions 4 and 5.

On the other hand, the Fe content was highest for portion 1B. This suggests that some dissolution of Cu occurred during the extended aging period.

Details of Preparation for Catalyst 6616-18

Catalyst 6618-18 was tested in the long-term stability test in Run 19, Plant 700B. The precipitation of Run 16 in Plant 752 produced four portions of catalyst. Drying and calcination occurred in the laboratory.

- 1) 0 to 3 hours of precipitation collected in filter bag during the run
- 2) 3 to 6 hours of precipitation collected in filter bag during the run
- 3&4) collected and recovered from the 55-gallon drum after the run

The following table summarizes the characterization results for the calcined portions:

Portion	Na, ppm	STEM Fe-Cu oxide particle size, nm	Average composition* of Fe:Cu (by weight)	Surface area (N ₂ adsorption), m ² /g
1	15	< 20	100:2.52	59
2	15	5-20	100:2.30	
3	4.5	5-20	100:2.11	90
4	2.4	5-20	100:5.52	
* Semiquantitative analysis				

Calcined portions 2 to 4 were combined and ground to 140 to 400 mesh: 940 grams ended up in the 140 to 400 mesh, and 530 grams ended up in the fines (> 400 mesh). The combined batch was analyzed and found to have 67.3% Fe and 100:1.23 Fe:Cu (by weight). A 300-gram portion of the combined portions 2 to 4 was impregnated with potassium carbonate solution. The impregnated catalyst was calcined. The final composition 100:1.15:1.57 Fe:Cu:K (by weight).

The final catalyst, 6616-18, was examined with STEM. The Fe-Cu-K oxide particles were 10 to 20 nm in size.(Figure 55g) The composition for 14 of these particles are reported

in Table 5b. The results in Table 5b reveal that Cu is more uniformly distributed among individual particles than K. The apparent high level of Cu observed during STEM examination of the individual particles (relative to bulk analysis) may result from the fact that the Cu analysis with STEM was not standardized against atomic absorption spectroscopy technique used for bulk Cu analysis. Furthermore, the Cu content of the Fe-Cu-K oxide particles observed during STEM may be higher than the Cu content of amorphous regions of the catalyst, resulting in an overall lower Cu content.

Experimental Fe Catalyst Evaluation in Fixed-Bed

An experimental Fe catalyst, 5709-91, prepared in the lab, was evaluated under Task 3. Two tests were done in the fixed-bed pilot plant in an attempt to provide future direction for the catalyst development work that is to be conducted in a slurry reactor. These studies were later pursued on completion of the slurry pilot plant.

Two runs were conducted: fixed-bed Runs 50 and 51. Catalyst identification, nature of diluents, catalyst and diluent weights, catalyst and diluent mesh-size ranges, and catalyst and diluent bed lengths are summarized in Table 6. For all of these tests, the catalyst was first heated under N₂ flow at 1 atm to 100°C, and then synthesis gas was introduced. The reactor was pressured to 9 to 11 atm with synthesis gas, and the catalyst was heated to 280°C under a synthesis gas flow. The test conditions were changed several times during these runs. Catalyst inlet temperatures (2 inches before the catalyst bed) and maximum temperatures, inlet and outlet

pressures, feed compositions, feed rates, and space velocities at different hours on-stream are also summarized in Table 6.

The results with the experimental Fe catalyst 5709-91 are summarized in Figures 56-63. The catalyst showed a high exotherm of 320°C when the catalyst inlet temperature was 279°C, at about 6 hours on-stream. After 6 hours, the catalyst inlet temperature was lowered to 250°C, the space velocity was lowered from 3.0 to 2.4 NL/hr/gFe, and the feed H₂:CO ratio was lowered from 0.7 to 0.5. Under these conditions, the catalyst maximum temperature was about 259°C. The CO+H₂ conversion gradually declined from 88% to somewhere between 62 and 68% by 200 hours on-stream. During the same period, the CO₂ selectivity, the H₂:CO usage ratio, and the H₂:CO outlet ratio were constant, but the methane selectivity gradually increased to a value of 2.4 to 2.6%. These results indicate that both catalytic activity and hydrocarbon selectivities were changing with time during the first 200 hours. Also, the propylene to propane ratio, which may show the hydrogenation activity of the catalyst, gradually decreased. This observation is consistent with the increase in methane selectivity. Later in the run, the pressure was increased from 13 to 33 atm. At this high pressure, the CO+H₂ conversion was stable at 82 to 83% between 202 and 322 hours on-stream. On the other hand, the propylene to propane ratio continued to decrease, and the methane selectivity gradually increased after an initial decrease.

The experimental Fe catalyst 5709-91 was evaluated in an extended 800-hour test in fixed-bed Run 51 (Table 7 and Figures 64-74). The objective was to determine the catalyst

stability at high conversion. Relatively low pressures, typical of what is used in other laboratories, were selected. After an initial 270°C treatment with synthesis gas during the first 26 hours, the catalyst inlet temperature was first lowered to 259°C, then to 240°C by 70 hours on-stream, and finally increased to 247°C by 260 hours on-stream. At this inlet temperature, the maximum catalyst temperature fluctuated between 270°C and 295°C (Figure 64). After 260 hours, other conditions were implemented: 13 atm, 0.7:1 H₂:CO feed ratio, and feed rate of 1.9 NL/hr/gFe. Between 260 and 800 hours, the CO+H₂ conversion gradually decreased from about 90% to about 75%. During the same period, the H₂:CO outlet ratio also decreased because the usage ratio was lower than the feed ratio. The methane selectivity fluctuated between 3.5 and 4.2% and the ethane plus ethylene selectivity increased from 2.0 to 3.0%. The methane and ethane selectivity was about 5.5% at lineout. Because approximately 50% of CO converts to CO₂, based on hydrocarbons and oxygenates only, the overall selectivity to methane and ethane was about 11%. The Anderson-Schulz-Flory distribution plots for hydrocarbons made during the run show the chain-growth probability to be 0.875 between carbon numbers 3 to 15. The chain-growth probability increased for higher carbon numbers and was 0.986 for carbon numbers between 60 and 140 (Figures 72 and 73).

The results indicate that the activity of the experimental Fe catalyst 5709-91 was not stable in the fixed-bed reactor under the current operating conditions: the deactivation rate was about 0.8% conversion/day. These operating conditions are more severe than those typically used in a slurry reactor for which this Fe catalyst is intended. Specifically, the fixed-bed catalyst temperature reached as high as 295°C (compared with 255-280°C for slurry reactors),

which may have enhanced the deactivation rate. Also, at the inlet of the catalyst bed where little water exists, the $H_2:CO$ ratio may have reached a value much lower than the feed ratio (0.7) because of the essential absence of the water gas shift reaction.

Shakedown of Slurry Pilot Plant

The slurry-bed pilot plant was described above (Task 1). Slurry-bed Run 1 was for pilot plant shakedown. The catalyst identification, the nature of the initial wax medium, the catalyst, and initial wax weights are summarized in Table 8. The C_{32} wax medium was from Humphrey Chemical Corp. According to the manufacturer, the major impurity, which is bromine, is introduced during the synthesis, which involves the Wurtz reaction. A detailed analyses of the wax was not made at UOP. The catalyst and the C_{32} paraffin wax medium were loaded into the 1-liter autoclave reactor at 65°C. The 1-liter autoclave was pressure-tested with N_2 at 65°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 120°C under N_2 flow. Synthesis gas was introduced at 120°C. The temperature was then gradually increased to 280°C under synthesis gas flow. The test conditions were changed several times during this run. Autoclave internal temperatures, pressures, feed compositions, feed rates, and space velocities at different hours on-stream are summarized in Table 8. The mechanical stirring of the slurry medium was achieved by a stirrer connected to the bottom of the autoclave.

The conversions and C_1 and CO_2 selectivities during slurry-bed Run 1 are summarized in Figures 75-79. The catalyst temperature was gradually raised during the first 21 hours from 120°C to 280°C under 2.1 NL/hr/gFe synthesis gas (0.7:1 H_2 :CO). At 280°C, three space velocity changes brought the $CO+H_2$ conversion up to 70% by the end of the activation treatment at 39 hours on-stream. The CO_2 and C_1 selectivities were 41 and 4.1%, respectively. At the end of the activation treatment, the temperature was lowered to 257°C, and the pressure was raised from 13 to 15 atm. With subsequent space velocity changes, 90% $CO+H_2$ conversion was achieved after 60 hours on-stream at 0.80 NL/hr/gFe. Under these conditions, the CO_2 and C_1 selectivities were 40 and 3.3%, respectively. At 63 hours on-stream, a new feedstock with 0.5:1 H_2 :CO ratio was introduced. Following the feedstock change, two additional space velocity changes were made these changes lowered the space velocity to 0.72 NL/hr/gFe. With the low H_2 :CO ratio feed gas, the $CO+H_2$ conversion decreased to somewhere between 70 and 75% at 172 hours on-stream. Run 1 was continued for another 35 hours under identical conditions. The $CO+H_2$ conversion continued to decrease and was about 57% at the end of the test at 207 hours on-stream. These results indicate that the catalyst was not stable with the low H_2 :CO feed gas. Catalyst deactivation was also apparent in the methane selectivity, which gradually increased following the feedstock change.

During this first test in the slurry pilot plant, operational parameters were frequently varied without any noticeable plant upsets. The response of the catalytic performance to operational changes were within expected ranges. Therefore, the shakedown of the slurry pilot plant was considered successful.

Evaluation of a Ceramic Filter in the Autoclave

A new filter assembly was used in this work. The new assembly consisted of a ceramic filter at the end of a stainless steel tube. The tube passed through the autoclave head and formed the gas and liquid exit line for the reactor. The distance between the bottom of the filter and the bottom of the autoclave was 4.6 inches. The filter nominal pore diameter was $0.15\ \mu\text{m}$, and the absolute diameter was $0.40\ \mu\text{m}$. The mechanical stirring of the slurry medium was achieved by an impeller at the end of a shaft that was connected to the bottom of the autoclave. The feed gas was introduced through a dip leg that extended to the bottom of the impeller.

Four runs were conducted (slurry-bed Runs 2 to 5), of which only one, slurry-bed Run 5, was successful. The Fe catalyst identification, the nature of the initial wax medium, the catalyst and initial wax weights, and the location and the pore size of the filter are summarized in Table 9. The catalyst and the C_{32} paraffin wax medium were loaded into the 1-liter autoclave reactor at 120°C . The 1-liter autoclave was pressure tested with N_2 at 120°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 280°C under N_2 flow. Synthesis gas was introduced at 280°C . The test conditions were changed several times during this run. Autoclave internal temperatures, pressures, feed compositions, feed rates, space velocities, and stirrer speeds in revolutions per minute (rpm) at different hours on-stream are also summarized in Table 9.

The autoclave leaked during the beginning of slurry-bed Run 2. The leak problem could not be solved, and therefore, the test was terminated. Slurry-bed Runs 3 and 4 were dedicated to measuring the temperature inside the thermowell, which extended vertically through the slurry medium. These measurements verified that the height at which the temperature showed a rapid drop corresponded, in fact, to the transition between the liquid phase and the gaseous phase. The height at which the temperature drop occurred can then be used to estimate the slurry level in the autoclave.

The results in slurry-bed Run 5 are summarized in Figures 80-85. A new catalyst activation procedure was used in slurry-bed Run 5, which involved 12 hours of 2 NL/hr/gFe synthesis gas (0.7:1 H₂:CO) at 280°C and 11 atm. Temperature surveys taken in the thermowell at 14, 34, and 36 hours on-stream are illustrated in Figure 80, which also shows the autoclave configuration. These results indicate that the slurry height varied between 3.5 and 5 inches during these hours. After 17 hours, the test conditions were established at 1.5 NL/hr/gFe, 257°C, and 14 atm. Under these conditions, a CO+H₂ conversion of about 70% was obtained with 2.8% methane selectivity and 3.1% methane plus ethane selectivity.

In slurry-bed Run 5, a pressure drop developed across the ceramic filter as a result of the buildup of solid particles. Therefore, the pressure in the exit line and in the high temperature and high pressure separator had to be gradually lowered to maintain the autoclave internal pressure at the specified level. The pressure drop gradually increased from 0.2 to 2 atm during the first 30 hours, after which the increase in the pressure drop was much more rapid. At 39

hours on-stream, the pressure drop reached a level of 17 atm, and the filter disintegrated. Significant catalyst loss occurred through the unfiltered exit line during the following hours.

In slurry-bed Run 5, the stirrer revolution per minute was originally set at 3500. The stirrer speed was lowered to 1,500 rpm after 33 hours on-stream. Subsequently, conversion dropped from 70% to about 40%. Several other revolution per minute changes were made later in the run. However, the effect of these changes on the conversion level cannot be interpreted because of the loss of catalyst from the autoclave reactor following the disintegration of the filter.

These results indicate that the ceramic filter used to drain the excess liquid from the autoclave reactor did not successfully operate. The filter rapidly plugged and disintegrated during the test.

Evaluation of Filter with Large Pore Sizes

In an attempt to prevent plugging, filters with larger pore sizes were used in the slurry autoclave reactor. An experimental Fe catalyst was tested four times with these type of filters (slurry-bed Runs 6 to 9).

The Fe catalyst identification, the nature of initial wax medium, the catalyst and initial wax weights, the height of the static slurry, and the location and pore size of the filter are

summarized in Tables 10, 10a, and 11. The catalyst and the C₃₂ paraffin wax medium were loaded into the 1-liter autoclave reactor at 120°C. The 1-liter autoclave was pressure tested with N₂ at 120°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 280°C under N₂ flow.

Synthesis gas with 0.7:1 H₂:CO feed ratio was introduced at 280°C. During the first 12 hours, the catalyst was activated at 280°C and 11 atm using a space velocity of 1.7 to 2.0 NL/hr/gFe. Conditions were changed between 12 and 15 hours on-stream. After 15 hours, the temperature was set at 258°C, the pressure at 15 atm, and the space velocity at 1.2 to 1.4 NL/hr/gFe. Autoclave internal temperatures, pressures, feed compositions, feed rates, space velocities, and stirrer speeds in revolutions per minute at different hours on-stream are also summarized in Table 10. The catalytic performances in Runs 6 to 9 are summarized in Figures 86 to 104.

In slurry-bed Run 6, a ceramic filter, which had a nominal pore size of 0.7 μm, was used. The bottom of the filter was 1.2 inches above the static liquid level in the autoclave. In slurry-bed Run 6 as in all other runs, the objective was to maintain the liquid level in the autoclave by continuously withdrawing the liquid products made. Liquid products were withdrawn by maintaining a pressure differential across the filter. The product gas also exited the autoclave through the filter. The outlet of the filter was connected to the high-temperature and high-pressure product collector. Following activation, a stable CO+H₂ conversion of about 78% was obtained at a space velocity between 1.2 and 1.4 NL/hr/gFe. The methane and ethane

selectivity gradually increased with time on-stream and was about 4% at 72 hours. The ceramic filter plugged during the run, as was apparent from the pressure drop across the filter that gradually increased to 16 atm by 72 hours on-stream. The run was shut down at the end of 72 hours.

In slurry-bed Run 7, a metallic filter with a nominal pore diameter of 17 μm and an absolute pore diameter of 45 μm was used to prevent the filter from plugging with catalyst particles. The bottom of the filter was initially immersed 1/8 inch in the static slurry. The filter did not plug during the run, but the products collected through the filter contained a lot of catalyst. Following activation, the $\text{CO} + \text{H}_2$ conversion gradually decreased to about 15% by 75 hours on-stream. The decline of the conversion probably resulted from the loss of catalyst across the filter. The selectivity to methane decreased during the run, and this result suggests that the methane selectivity is lower at low conversions.

In slurry-bed Run 8, the filter had a nominal pore size of 5 μm and an absolute pore size of 18 μm . The bottom of the filter was 1/4 inch above the static slurry level. The filter did not plug during the run, but the products that were collected through the filter still contained a lot of catalyst. Because the initial catalyst particle size was 37 to 105 μm , significant catalyst attrition must have occurred during the run. A gradual decline in conversion was again observed, probably because of the catalyst loss.

Slurry-bed Run 9 used the same type of filter that was used in slurry-bed Run 8, and similar results were obtained.

In summary, the 0.7- μm ceramic filter that was used for withdrawing the liquid products from the autoclave reactor rapidly plugged with catalyst particles.

When larger pore size metallic filters (5 or 17 μm nominal pore diameter) were used, plugging did not occur, but substantial amount of catalyst was lost. These data indicate that iron catalysts undergo significant attrition during tests in the slurry autoclave reactor.

Evaluation of Different Filtration Procedures

In an attempt to improve the operation of the slurry reactor, several different filtration procedures were evaluated. Nine runs were conducted (slurry-bed Runs 10 to 18). The Fe catalyst identifications, the nature of initial wax medium, the catalyst and initial wax weights, the heights of the static slurry, and the locations and pore sizes of the filters are summarized in Tables 11, 11a, 11b, and 11c. The catalyst and the C_{32} paraffin initial wax medium were loaded to the 1-liter autoclave reactor at 120°C. The 1-liter autoclave was pressure tested with N_2 at 120°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 280°C under N_2 flow. Synthesis gas with H_2 :CO feed ratio of 0.7:1 was introduced at 280°C. During the first 12 hours (except for slurry-bed Run 10, which was 6 hours), the catalyst was activated at 280°C and 11 atm using a space velocity of

1.9 to 2.0 NL/hr/gFe. Conditions were changed between 12 and 18 hours on-stream. The temperature was set at 258°C, the pressure at 15 atm, and the space velocity at 1.3 to 1.4 NL/hr/gFe. Autoclave internal temperatures, pressures, feed compositions, feed rates, space velocities, and stirrer speeds in revolutions per minute at different hours on-stream are also summarized in Table 11.

In previous tests, both the liquid product and the effluent gas exited the autoclave reactor through the filter. With slurry-bed Run 10, the autoclave was modified so that the effluent gas passed through an independent outlet port situated at the top of the autoclave. The autoclave pressure was controlled by a back-pressure regulator in the effluent gas line. The pressure drop across the filter used for draining the liquid products was controlled by independently regulating the pressure at the exit of the filter. This new filtration configuration was maintained for the rest of the work as well.

In slurry-bed Run 10, the metallic filter had a nominal pore diameter of 1 μm and an absolute pore diameter of 5 μm and was totally immersed in the liquid. A block valve past the filter was opened once a day, and about 0.7 atm pressure drop was exerted in an attempt to drain some of the liquid out of the autoclave. Substantial amounts of catalyst loss occurred during this procedure. Also, the filter plugged.

To prevent the catalyst loss problem, a 0.7- μm ceramic filter was used in Run 11. The filter was back-flushed with the synthesis gas that passed through the filter. No draining was

done during the first 28 hours, and the liquid level in the autoclave increased by about 3 inches. At 28 hours on-stream, the feed was diverted from the filter to the dip leg, and about 0.2 atm pressure drop was exerted. This drop in pressure caused about 2 inches of liquid to drain out (Figure 105). No further draining was done in slurry-bed Run 11, and therefore, the liquid level continued to rise during the later part of the test. A similar draining procedure was also successfully used in slurry-bed Run 12. However, in both slurry-bed Runs 11 and 12, significant problems were encountered in sealing the ceramic filter against the stainless steel tube extending from the autoclave head.

Operational problems occurred in slurry-bed Runs 13 and 14, and therefore, these runs were terminated early. Slurry-bed Runs 15 to 18 used a metallic filter to overcome the sealing problems observed with ceramic filters. The filter nominal pore size was $0.5\ \mu\text{m}$. The filter was immersed in liquid as was the case in slurry-bed Runs 10 to 12. However, when the draining procedure that was used in slurry-bed Runs 10 to 12 with the ceramic filter was applied to the metallic filter in slurry-bed Runs 15 to 17, draining was extremely fast, causing most of the liquid inventory of the autoclave to be lost (Figure 106).

To prevent the loss of the liquid inventory, the filter level was raised to $5\frac{5}{8}$ inches from the bottom of the autoclave in slurry-bed Run 18 so that the bottom of the filter ($0.5\ \mu\text{m}$) was $1\frac{1}{16}$ inch above the initial static slurry level. The slurry level gradually increased during the first 40 hours, after which the filter acted as a liquid level controller (Figure 107). Two filters were used. One of the filters was being continuously back-flushed with nitrogen gas, and

the other one was used for draining the liquid. At the end of a 4-hour cycle, the filters were switched. Draining of the liquid products typically required about 1 atm pressure drop. The liquid level was successfully maintained between 6 and 6.5 inches until 100 hours on-stream. Both filters plugged after 100 hours, and the run was terminated at the end of 126 hours.

In slurry-bed Run 18, a downflow propeller was placed on the stirring shaft 1-1/4 inch above the impeller to achieve good mixing. During the run, the CO conversion decreased from 80 to 60%, and the methane selectivity increased from 1.5 to 4.2% (Figures 108 and 109).

In summary, the slurry autoclave was modified so that the pressure drop across the filter can be controlled independently from the autoclave pressure. Draining of the liquid product out of the autoclave was achieved typically with a pressure drop of no more than 1 atm. Difficulties were encountered in sealing the ceramic filters against stainless steel tubes in the autoclave reactor. At comparable pore size, draining appeared to be much faster with a metallic filter. A 0.5- μ m metallic filter maintained the liquid level successfully for about 100 hours in the autoclave reactor. The liquid was maintained at a level that corresponds approximately to the bottom of the filter.

An experimental Fe catalyst showed a gradual decline in CO conversion from 80% to about 60% during the 126-hour test in Run 18. Longer testing periods are necessary to evaluate catalytic stability. During the same run, the selectivity to methane first showed a gradual

increase and then lined out at about 4.2%. Because the selectivity to ethane is about 1%, the overall methane and ethane selectivity seems to be within target.

Evaluation of Baseline Fe Catalyst in Run 19

A new precipitated Fe catalyst (6616-18) was prepared to evaluate its long-term performance in the slurry autoclave.

For the slurry test, 95 grams of calcined Fe catalyst were loaded into a 1-liter autoclave along with 380 grams of C₃₂ *n*-paraffin wax at 130°C. After the wax melted, the autoclave was sealed and pressure tested with N₂ at 25 atm. After a successful pressure test, the pressure was lowered to 14 atm, the stirring was initiated at 1,100 rpm, and the catalyst temperature was raised to 280°C in 3 hours under N₂ flow. A thermocouple inserted in a thermowell inside the slurry was used for temperature control. The temperature control point was 3 cm above the bottom of the autoclave. After 280°C was achieved, the N₂ feed was cut out, and synthesis gas with an H₂:CO molar ratio of 0.7:1 was introduced at 0.16 nm³/hr. After a 12-hour pretreatment, in situ, new test conditions were established, and the test continued. The conditions used in this run are summarized in Tables 11c and 11d.

Two 0.5- μ m filters (Mott Corporation, Farmington, CT) were placed at 6-5/8 inches from the bottom of the autoclave so that the liquid products could be drained periodically.

During the first 420 hours, one of the filters was continuously back-flushed with 0.2 NL/hr/gFe of N₂, and the other filter was being used for draining the liquid products.

Performance during the First 1,250 Hours

The performance of the new precipitated Fe catalyst during the first 1,250 hours of the test is summarized in Figures 110 through 145. The figures contain the following data: CO, H₂, and CO+H₂ conversions; outlet H₂:CO ratio; selectivities to methane, ethane, ethane and ethylene, ethanol, and carbon dioxide; and propylene to propane and butylene to butane ratios as well as the autoclave temperature.

After 12 hours of pretreatment with 2 NL/hr/gFe of synthesis gas at 280°C and 14 atm, the temperature was lowered to 258°C, the pressure was increased to 18 atm, and the feed rate was lowered to 1.4 NL/hr/gFe. The CO+H₂ conversion decreased from 78 to 72% during 12 to 27 hours on-stream. This decrease was followed by a pressure increase to 20 atm. The CO+H₂ conversion decreased to about 66% and remained there during 27 through 62 hours on-stream. This result appears to show an inverse relationship between activity and total pressure between 18 and 20 atm (Figure 111).

The feed rate was lowered to 1.2 NL/hr/gFe at 62 hours, and the temperature was increased to 265°C. Under these conditions, a stable CO+H₂ conversion of 70% was obtained between 115 and 280 hours on-stream (Figures 111 and 117). During the first 250 hours of the

run, methane selectivity gradually increased from 2 to 7% and remained constant between 250 and 280 hours on-stream (Figures 112 and 118).

The pressure increased to 21 atm at 280 hours, and the same test conditions were maintained until 420 hours on-stream. Under these conditions, a stable CO+H₂ conversion of 68% was obtained; selectivity to methane was about 6.1% and selectivity to ethane was 1.4% (Figure 117-119). During this period, the selectivity to ethane and ethylene, which was about 5 to 6%, could not be accurately determined because of problems associated with the gas chromatograph (GC) (Figure 120). Similarly, the selectivity to ethanol was about 2% but could not be determined more accurately because of GC problems. The propylene to propane ratio was 4 (Figure 121). The selectivity of CO to CO₂ was about 53%, indicating substantial water gas shift activity (Figure 116). Accordingly, the H₂:CO ratio increased from 0.7 at inlet to about 1.0 at the reactor outlet.

In an attempt to increase the conversion level, the temperature was increased to 275°C, between 420 and 452 hours on-stream, and the feed rate was lowered to 0.9 NL/hr/gFe at 465 hours. Also, the N₂ black-flush was ended because one of the filters was plugged, leaving essentially one filter in service for the rest of the run. Under these new conditions, the catalyst maintained a stable CO+H₂ conversion of about 83%; selectivity to methane was about 6.9% between 452 and 1,250 hours on-stream (Figures 117-118, 123-124, 131-132, 139-140). The selectivity to ethane was 2.5 to 3.0%, the selectivity to ethane and ethylene was 5 to 6%, and the selectivity to ethanol was 2.5 to 3.0% (Figures 119-120, 125-127, 133-135, 141-143). The

olefin to paraffin ratio was 5.5 to 6.0 at a carbon number of 3 and 4.0 to 4.5 at a carbon number of 4 (Figures 121, 128-129, 136-137, 144-145). Because the selectivity to CO_2 varied between 48 and 55%, the H_2 :CO ratio of at the reactor outlet varied in the range of 1.2 to 1.6.

These results indicate that a new stable Fe Fischer-Tropsch catalyst was developed for slurry reactors. This catalyst did not noticeably deactivate during 1,250 hours of testing at various conditions. As a followup, the performance of this catalyst was later investigated at different conversion levels after 1,250 hours on-stream in order to predict qualitatively its performance in a slurry bubble-column reactor.

Effect of Conversion Level on Reaction Rate

Starting from 1,260 hours on-stream, the space velocity was gradually increased, typically every 48 hours, from 0.9 to 4.0 NL/hr/gFe, by increasing the feed rate (Figures 146-152). At 1,510 hours on-stream, the temperature was lowered to 265°C, and the catalytic performance at different conversion levels was evaluated (Figures 153-160). At 1,640 hours on-stream, the space velocity was brought back to 1.2 NL/hr/gFe and maintained there until 1,740 hours on-stream. These latter test conditions were identical to those between 280 and 420 hours on-stream. Further space velocity and temperature changes were made between 1,740 and 1,950 hours on-stream (Figures 161-168). The run was shutdown at 1,996 hours because of a power outage. Catalyst performance after the shutdown is discussed in a later section (Figures 169-176).

The effect of reciprocal space velocity $(\text{NL/hr/gFe})^{-1}$ on the $\text{CO} + \text{H}_2$ at 265°C and 275°C is illustrated in Figure 177. These data were later used to determine the effect of conversion level on reaction rate in Figure 178. Here, the reaction rate is expressed as the product of space velocity and $\text{CO} + \text{H}_2$ conversion. The results, which are summarized in Figure 178, indicate that the reaction rate is adversely affected by the conversion level at conversion levels greater than 50%. The decrease in reaction rate with an increase in conversion level is caused by the decrease in the partial pressure of the reactants and possibly by the increase in the partial pressure of some of the reaction products. This effect is also likely to occur at lower conversions but to a lesser degree. However, insufficient data were available at low conversions to determine the relation of reaction rate with change in conversion at low conversions.

Catalytic Performance after Return to early Test Conditions

The $\text{CO} + \text{H}_2$ conversion between 1,640 and 1,740 hours on-stream was about 70%, which is 2% higher than that observed between 280 and 420 hours on-stream under the same test conditions (Figure 153). This result indicates that the catalyst did not deactivate during the first 1,740 hours on-stream. Between 1,640 and 1,740 hours, the selectivity to methane was about 4.5%, the selectivity to ethane was 1.5 to 2.0%, and the selectivity to ethane and ethylene was 4.5% (Figures 154-156). These selectivities were 6.1, 1.4, and 5.6% during 280 to 420 hours on-stream. These results indicate that catalytic selectivity was improving with time on-stream. Furthermore, the olefin to paraffin ratio and the water gas shift activity of the catalyst did not noticeably decrease (Figures 158-159).

Effect of Conversion Level on Catalytic Selectivity

The selectivities to methane and to ethane and ethylene at 265°C as a function of conversion are summarized in Figure 179. Because selectivity improved with time on-stream, only relatively more recent data are illustrated in this figure. These data indicate a noticeable increase in selectivity to light ends at conversions greater than about 65%.

Predicting Catalytic Performance in a Slurry Bubble-Column Reactor

Because the most likely candidate for a commercial-size slurry-phase reactor is a slurry bubble-column reactor, an attempt was made to predict the performance of the new precipitated Fe catalyst in a slurry bubble-column reactor based on the slurry autoclave data obtained here. The following assumptions were made:

- The slurry bubble-column reactor could be modeled as 11 slurry autoclave reactors in series operating at 8 to 80% CO+H₂ conversions.
- The reaction rate and selectivity did not change below 35% conversion because data at 265°C were not available at less than 35% CO+H₂ conversion.
- At 275°C, reaction rate and selectivity at less than 50% conversion were equal to the rate and selectivity at 50% conversion.

The calculations made using these assumptions are summarized in Table 12.

These calculations indicate that the selectivity to methane, ethane, and ethylene is estimated to be about 8.9% at 265°C and 11.8% at 275°C in a slurry bubble-column reactor. At 265°C, the selectivity to methane, ethane, and ethylene is about 2% higher than the selectivity target. At 275°C, the C₁+C₂ hydrocarbon selectivity was about 5% higher than the selectivity target.

The space velocity required to reach 88% CO+H₂ conversion was 1.1 NL/hr/gFe at 265°C and 1.6 NL/hr/gFe at 275°C. These results appear to indicate that the new precipitated Fe catalyst may be short of the activity target by a factor of 1.8 at 265°C and by about 1.3 at 275°C. However, actual specific activities are likely to be closer to target because of unknown catalyst inventory loss across the filter during the run and also because the catalytic activities were probably underestimated at low conversions, as discussed previously.

Catalytic Performance after Restart-Up following Cold Shutdown

The run was shut down at 1,996 hours on-stream because of a 24-hour power outage. The shutdown involved lowering the temperature to 125°C and maintaining a feed space velocity of 1.2 NL/hr/gFe. At 125°C, the synthesis gas feed was cut out, the reactor was blocked at a pressure of 21 atm, and the stirring was stopped. The feed was cooled to room temperature. Twenty-four hours later, the reactor was first heated to 90°C, stirring was initiated at 1,100 rpm, and the feed was cut in at 1.2 NL/hr/gFe to maintain a pressure of 21 atm. Then, the temperature was raised to 265°C, and the catalyst was maintained at these conditions for

another 250 hours. These test conditions were the same ones that prevailed at 280 to 420 hours and 1,640 to 1,740 hours.

The product wax drained from the reactor daily through the 0.5 μm filter during the test period of 2,000 to 2,250 hours was initially black in color and gradually attained its typical brown color. The same phenomenon was also observed during the initial part of this run. These results indicate that the new precipitated Fe catalyst is undergoing substantial attrition following a cold startup and that some of the catalyst was lost from the reactor during these periods. Quantitation of catalyst loss in the wax products was attempted, but reliable analytical data could not be obtained. Instead, at the end of the run (after 2,250 hours), the used slurry was unloaded and analyzed for its catalyst content. The weight of catalyst recovered was 67.2 grams, which indicates that 27.8 grams of catalyst were lost during the run.

The catalytic performance after the restartup is summarized in Figures 169 to 176. A slight deactivation of about 0.5% per day was observed during this period. This conversion loss was partly caused by catalyst loss across the filter. After the restartup, methane selectivity did not increase noticeably. The H_2 :CO ratio at the outlet was slightly less than earlier in the run. This result may be partly caused by the lower conversion level during this period rather than a loss of water gas shift activity of the catalyst. Because of problems associated with the analysis of CO_2 by GC, making a definite conclusion about the status of water gas shift activity after the restartup was not possible. Similarly, fluctuations in the propylene to propane ratios were too

large to reach conclusions concerning the state of the olefin to paraffin ratios after the restartup relative to their values before shutdown.

Product Distribution

The approximate product distribution based on the total amount of hydrocarbons and oxygenates recovered during 300 to 324 hours and 660 to 684 hours on-stream at 265°C and 68% CO+H₂ conversion and at 275°C and 83% CO+H₂ conversion, respectively, are summarized in Tables 13 and 14.

The results indicate that with increases in temperature and conversion, the selectivity to light ends and to gasoline range increases, and the selectivity to middle distillates and to wax decreases. The hydrocarbon products are 45 to 47% liquid fuels. The liquefied petroleum gas (LPG) and gasoline fractionations are olefinic. Linear α -olefins make up 83% of the LPG hydrocarbons. The linear α -olefin content is 43% in the gasoline-range hydrocarbons. Forty-one percent of the gasoline range has not been identified but is most likely to be internal olefins.

Conclusions

A new precipitated Fe catalyst was developed in this program for slurry reactor operation. The new Fe catalyst is predicted to perform slightly below the performance targets for slurry bubble-column operation. Stability targets appear to be achievable. This catalyst did not noticeably

deactivate during 1,740 hours on-stream. Compared to the selectivity target, an excess of 2% $C_1 + C_2$ was formed at 265°C. Based on the initial catalyst inventory in the autoclave, the catalyst seems to be short of the activity target by a factor of 1.8 at 265°C and 1.3 at 275°C. However, actual specific activities are likely to be closer to target because of catalyst inventory loss across the filter during the run and because catalytic activities were underestimated at low conversions.

No work was done under Tasks 4 and 5 because the new Fe catalyst developed in this program was very stable.

References

1. Hayim Abrevaya, "The Development of a Stable Ruthenium Catalyst," Final Report, Contract DE-AC22-84PC70023, 1991.
2. J. C. W. Kuo, Two Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels, Final Report, DOE/PC/60019-9, Mobil Research and Development Corp., Paulsboro, NJ, 1985.
3. M. P. Rosynek, Quarterly Technical Progress Report for January 1, 1988, to March 31, 1988, Texas A&M University, Contract DE-AC22-85PC8001.

TABLE 1
LIST OF CATALYSTS AND PROPERTIES

LIST OF CATALYSTS AND PROPERTIES

	PREP EQUIPMENT	RUN NO (PLANT)	PRECIPITATION		1ST CALCINATION		2ND CALCINATION		CATALYST	COMPOSITION WEIGHT-RATIOS	CATALYST PROPERTIES			PORE RADIUS Å	XRD	BATCH SIZE, g
			BASE	pH	MESH	T, °C	MESH	←T, °C→			% Fe	STEM SIZE	SURFACE AREA, m ² /g			
685-61	IN LAB		Na ₂ CO ₃	3.5	NO CALCINATION, 110°C DRIED					100Fe:1Cu 100Fe:1Cu:1K	Amorphous, ≤2-4 nm					42
					60-200	410										
685-53	IN LAB		Na ₂ CO ₃	4.3	NO CALCINATION, 110°C DRIED					100Fe:1Cu	Amorphous, ≤2-4 nm					47
					60-200	275					4-6 nm	83	0.22	52	79% Fe ₂ O ₃	
					60-200	380					5-20 nm	53	0.17	62	80% Fe ₂ O ₃	
					60-200	450										
709-73	IN LAB		Na ₂ CO ₃	5.5	60-200	380				100Fe:1Cu	Amorphous, ≤2-4nm					18
709-49	IN LAB		Na ₂ CO ₃	6.1	NO CALCINATION, 110°C DRIED					100Fe:1Cu	Amorphous, ≤2-4nm					42
685-135	IN LAB		Na ₂ CO ₃	6.5	NO CALCINATION, 110°C DRIED					100Fe:5.0Cu 100Fe:1Cu:0.7K	Amorphous, ≤2-4nm					25
					60-200	410										
685-145	IN LAB		Na ₂ CO ₃	6.5	60-200	410				100Fe:1Cu						13
685-139	IN LAB		Na ₂ CO ₃	6.5	NO CALCINATION, 110°C DRIED					100Fe:0.5Cu	2-6 nm				Goethite	60
					60-200	410										
685-69	IN LAB		Na ₂ CO ₃	7.9	NO CALCINATION, 110°C DRIED						some amorphous					35
709-37	IN LAB		Na ₂ CO ₃	9.5	NO CALCINATION, 110°C DRIED					100Fe:5Cu	Amorphous, ≤2-4nm					40
685-75	IN LAB		Na ₂ CO ₃	9.7	NO CALCINATION, 110°C DRIED					100Fe:1Cu	10-40 nm				30% Fe ₂ O ₃	33
					60-200	380					10-40 nm	74	0.20	52	77% Fe ₂ O ₃	
					60-200	450					10-40 nm	41	0.19	89	87% Fe ₂ O ₃	
685-111	IN LAB		NH ₄ OH	9.6	NO CALCINATION, 110°C DRIED					100Fe:1Cu	Amorphous ≤2-4nm 25-30 nm					25
					60-200	450										
709-91	IN LAB	50,51 (700A)	Na ₂ CO ₃	5.5	>170	380	170-200	380	67.0	100Fe:1.4Cu:0.38K						28
709-108	PLANT 752, RUN 5,6	1(700B)	Na ₂ CO ₃	4-5	>170	380	170-200	380	67.3	100Fe:1.03Cu:0.77K		72	0.35	98		101
709-119	PLANT 752, RUN 5 (PORTIONS 2 AND 3)	4, 5 (700B)	Na ₂ CO ₃	4.3-5.3	>40	380	140-200	380	63.2	100Fe:0.82Cu:1.31K	6-20 nm most 10-14 nm	84	0.21	49		272
709-139	PLANT 752, RUN 12 (PORTIONS 1,2A,3A,3B)	6-9, 16, 17 (700B)	Na ₂ CO ₃	3.1-5.3	>40	380	140-400	380	64.0	100Fe:1.03Cu:1.67K	4-25 nm most 10-15	78	0.27	70		528
709-184	PLANT 752, RUN 14 (PORTIONS 1,3,4)	10-15, 18 (700B)	Na ₂ CO ₃	4-4.5	>40	380	140-400	380	67.4	100Fe:0.62Cu:1.91K	5-25 nm most 8-12	67	0.17	50		774
6616-18	PLANT 752, RUN 16 (PORTION 2,3,4)	19 (700 B)	Na ₂ CO ₃	4-5	>40	380	140-400	380	64.4	100Fe:1.15Cu:1.52K	10-20 nm	61	0.19	61		285

Table 1A

**COMPARISON OF SLURRY VERSUS FIXED-BED
FISCHER-TROPSCH SYNTHESIS REACTORS**

	Fixed-Bed Reactor Current Technology (Sasol) South Africa	Slurry-Reactor Desired Technology
Temperature, °C	225	260
Syngas Feed H₂:CO	2.0	0.5
Advantages	Commercial	1. No water gas shift reactor 2. Simpler heat removal
Iron Catalyst Stability	Acceptable	Expected to be poor due to severe operating conditions

TABLE 2
Conditions for Fixed-Bed Runs 48 and 49 (Plant 700A)

Run	Plant	Catalyst							Diluent			Bed Inches	Temperature		Pressure		Feed						Hours
		Number	% Fe			Wt, g	Vol cc	Mesh	Nat.	Mesh	Wt, g		In °C	Max °C	In atm	Out atm	% H ₂	% CO	% Ar	H ₂ -CO	Rate sec/min	NL/h/g Fe	
48	700A	C-73-1-101	67-69			10	4	170-200	α -Al ₂ O ₃	60-200	100	8	100 [†] 280	100 [†] 280	11.2	11.0	37.95	56.52	5.53	0.67	335	2.96	0-8
													280	280	13.2	11.2-11.9							9-12
49	700A	C-73-1-101	67-69			10	4	> 100	α -Al ₂ O ₃	> 100	100	8	100 [†] 280	100 [†] 280	11.2	11.2							0-7
												—	280	281							↓	↓	7-12
												—	280	281							165	1.46	12-19
												—	280	281	↓	↓					61	0.54	19-31
													280	286	35.7	35							31-43
													249-250	250-251			↓	↓	↓	↓	↓	↓	43-58
													250	250	15.3	15.0	31.81	62.2	5.99	0.51	273	2.40	60-82

TABLE 3
Summary of Fixed-Bed Run 49 (Plant 700A)

Hours	T, °C	P, atm	H ₂ :CO feed	Ni/hr/gFe	Conversions, %		Selectivities	
					CO	CO + H ₂	C ₁	CO ₂
12	280	11	0.7	3	10	9	?	11
25	280	11	0.7	0.54	23	21	3.3	42
40	280	35	0.7	0.54	70	69	3.2	40
56	250	35	0.7	0.54	30	32	2.5	32
63	250	15	0.5	2.4	10	11	2.2	24

TABLE 4
Conditions for Fixed-Bed
Run 52 (Plant 700A)

Run	Plant	Catalyst						Diluent			Bed Inches	Temperature		Pressure		Feed						Hours
		Number	% Fe			Wt. g		Nature		Wt. g		In °C	Max °C	In atm	Out atm	% H ₂	% CO	% Ar	H ₂ :CO	Rate scc/min	ML/h/g cat	
52	700A	MCSG-4				6.29		α -Al ₂ O ₃		100	8 1/4	110↑ 250	110↑ 250		9	38.61	85.12	6.27	0.70	174	1.06	0-5
												250↑ 270	250↑ 276	9	↓							5-27
												270	276		↓							27-40
												280	294	↓	↓							40-51
												259	282		12.8					↓	↓	51-59
												257	280							90	.94	59-64
												257	280							90	.86	64-70
												↓	259	13.2						66	.63	70-80
												↓	↓	↓	↓					47	.45	80-90
												↓	↓	↓	↓	↓	↓	↓	↓	39	.37	90-103

TABLE 5
Conditions for Fixed-Bed Run 53 (Plant 700A)

Run	Plant	Catalyst					Diluent			Bed Inches	Temperature		Pressure		Feed						Hours
		Number	% Fe		Wt, g		Nature		Wt, g		In °C	Max °C	In atm	Out atm	% H ₂	% CO	% Ar	H ₂ CO	Rate sec/min	NL/h/g cat	
53	700A	MCSG-4			10		α-Al ₂ O ₃		159.09	14 1/4	110 246		11.9	9.2	38.61	65.21	6.27	0.70	257	1.5	0-5
											246	250	12.9								5-15
											258	264	13.3								15-23
											260	265									23-29
											270	262									29-41
											280	314									41-51
											260	270	12.6	9.8							51-64
											260	269	17.4	12.6							64-67
											257	265	16.0						127	.76	67-64
													15.3						104	.62	64-69
													14.3						66	.40	69-79
												264	13.3						57	.34	79-84
											257	263	12.9						47	.28	84-264

Table 5a

STEM CHARACTERIZATION OF CATALYST

PLANT 752, Run 15, portion 2
(particle size: 10-20nm)

Particle #	Weight %	
	Fe	Cu
1	98.07	1.93
2	98.49	1.51
3	97.88	2.12
4	98.23	1.77
5	98.20	1.80
6	98.46	1.54
7	97.88	2.12
8	98.06	1.94
9	98.31	1.69
10	97.94	2.06
Average	98.15 ± 0.22	1.85 ± 0.22

PLANT 752, Run 15, portion 1
(particle size: 10-20nm)

Particle #	Weight %	
	Fe	Cu
1	98.25	1.75
2	98.30	1.70
3	98.62	1.38
4	98.63	1.37
5	97.60	2.40
6	97.77	2.23
7	97.91	2.09
8	98.45	1.55
9	97.88	2.12
10	98.08	1.92
Average	98.15 ± 0.36	1.85 ± 0.36

Table 5a Cont'd

STEM CHARACTERIZATION OF CATALYST

PLANT 752, Run 15, portion 4
(particle size: $\leq 10\text{nm}$)

Particle #	Weight %	
	Fe	Cu
1	98.42	1.58
2	97.82	2.18
3	98.28	1.70
4	97.99	2.01
5	98.05	1.95
6	98.40	1.60
7	98.31	1.69
8	97.91	2.09
9	98.07	1.93
10	98.53	1.47
Average	98.18 ± 0.24	1.82 ± 0.24

PLANT 752, Run 15, portion 5
(particle size: $\leq 10\text{nm}$)

Particle #	Weight %	
	Fe	Cu
1	97.81	2.19
2	97.57	2.43
3	97.93	2.07
4	97.51	2.49
5	97.75	2.25
6	97.89	2.11
7	97.23	2.77
8	97.82	2.18
9	98.13	1.87
10	98.23	1.77
Average	97.79 ± 0.29	2.21 ± 0.29

Table 5a Cont'd

STEM CHARACTERIZATION OF CATALYST

PLANT 752, Run 15, portion 1B
(particle size: $\leq 10\text{nm}$)

Particle #	Weight %	
	Fe	Cu
1	96.01	3.99
2	94.83	5.17
3	97.00	3.00
4	96.89	3.11
5	97.29	2.71
6	96.78	3.22
7	96.94	3.06
8	97.33	2.67
9	96.90	3.10
10	96.78	3.22
Average	96.67 $\pm$ 0.74	3.33 $\pm$ 0.74

PLANT 752, Run 15, portion 3
(particle size: 10-20nm)

Particle #	Weight %	
	Fe	Cu
1	98.59	1.41
2	98.71	1.29
3	98.88	1.12
4	98.81	1.19
5	98.62	1.38
6	98.30	1.70
7	98.91	1.09
8	98.88	1.12
9	98.72	1.28
10	98.82	1.18
Average	98.75 $\pm$ 0.18	1.25 $\pm$ 0.18

TABLE 5b
STEM Examination of Catalyst 6616-18

<u>Particle #</u>	<u>Weight %</u>		
	<u>Fe</u>	<u>Cu</u>	<u>K</u>
1	95.53	3.58	0.89
2	95.77	3.63	0.60
3	89.63	3.00	7.37
4	95.91	3.22	0.87
5	95.63	3.63	0.74
6	95.84	3.17	0.99
7	95.68	3.23	1.09
8	95.52	3.43	1.04
9	95.88	3.20	0.92
10	95.29	2.86	1.85
11	96.05	2.51	1.44
12	95.98	3.17	0.85
13	94.92	4.05	1.03
14	95.94	2.57	1.49
Avg.	95.26 ± 1.65	3.23 ± 0.42	1.51 ± 1.72

TABLE 6
Conditions for Fixed-Bed
Runs 50 and 51 (Plant 700A)

Run	Plant	Catalyst						Diluent		Bed Inches	Temperature		Pressure		Feed						Hours
		Number	% Fe	Wt, g	Vol cc	Mesh	Nat.	Mesh	Wt, g		In °C	Max °C	In atm	Out atm	% H ₂	% CO	% Ar	H ₂ O	Rate sec/min	ML/h/lb Fe	
50	700A	5703-01	67	10			α -Al ₂ O ₃			8 1/4	100† 279	100† 320	9.9	9.9	38.92	95.98	8.92	0.89	335	3.00	8-6
											274† 250	310† 275		9.9† 13.0	↓	↓	↓	↓	↓	↓	7-15
											250	259	14-14.7	13.0	31.98	92.18	8.98	0.91	273	2.40	19-201
											250	261	33.7	33.0					273	↓	202-322
51	700A	5703-01	67	8.28			γ -Al ₂ O ₃		21	10 1/4	110† 270	110† 320	9.2	9.0	38.92	95.28	8.92	0.89	179	2.35	9-14
											270- 272	320† 301	9.5	9.0	↓	↓	↓	↓	228	3.23	14-28
											259	298	13.3	12.8	↓	↓	↓	↓	↓	↓	28-38
											259	300- 320			↓	↓	↓	↓	250	3.98	38-60
											240	251			↓	↓	↓	↓	185	2.35	60-65
											240	252			↓	↓	↓	↓	132	1.88	66-70
											247	270- 295	↓	↓	↓	↓	↓	↓	↓	↓	70-200
											↓	↓	↓	↓	38.91	95.12	8.27	0.79	↓	↓	200-800

Product Distributions in Run 51

06APR89

SIGNAL RESEARCH CENTER

PROGRAM 1016 - FISCHER/TROPSCH DATA BASE - OVERALL PRODUCT DATA ANALYSIS REPORT - PART 1 OF 6

PLANT NUMBER	700	700
RUN NUMBER	51	51
TEST NUMBER	1	1

Table 7

TOTAL PRODUCT DISTRIBUTION

WEIGHT PCTS WITHOUT ARGON

HYDROGEN	1.033	1.033
CARBON MONOXIDE	10.593	10.593
CARBON DIOXIDE	63.820	63.820
WATER	2.154	2.154
HYDROCARBONS	22.028	22.028
OXYGENATES	0.372	0.372

HYDROCARBON DISTRIBUTION

C1	7.649	7.649
C2 - C4	27.642	27.521
C5 - C11	45.850	38.560
C12 - C18	10.317	12.282
C19 - C25	3.436	6.490
C26 PLUS	5.106	7.497
C1 - C44	97.843	97.990
C45 PLUS	2.157	2.010

OXYGENATES DISTRIBUTION

ALCOHOLS	80.642	80.642
ALDEHYDES	19.358	19.358
OTHER OXYGENATES	0.000	0.000

MOLE PCTS WITHOUT ARGON

HYDROGEN	18.185	18.244
CARBON MONOXIDE	13.416	13.460
CARBON DIOXIDE	51.443	51.611
WATER	4.242	4.256
HYDROCARBONS	12.489	12.203
OXYGENATES	0.225	0.226

RECOVERIES

OVERALL	109.045	109.045
CARBON	108.940	108.983
HYDROGEN	113.982	113.620
OXYGEN	109.824	109.824
ARGON	104.958	104.958

CORRECTED RECOVERIES *

OVERALL	103.894	103.894
CARBON	103.794	103.835
HYDROGEN	108.598	108.253
OXYGEN	104.636	104.636

*

CORRECTED RECOVERY - (RECOVERY/Ar RECOVERY) * 100

Run	Plant	Catalyst					Diluent	Temp In °C	Press		Feed					Hours		
		Number	% Fe	Wt., g	Mesh	Nature			% Solids	Wt g (wet)	Out, atm	% H ₂	% CO	% Ar	H ₂ -CO		Rate cc/min	
1	700B	5708-108	67.3	35		C ₂₈	15	200	120 ↑ 260	12.9	33.61	85.12	0.27	0.70	802	2.1	0-21	
								260	260	↓	↓	↓	↓	↓	↓	614	1.6	21-30
								260	260	↓	↓	↓	↓	↓	↓	302	1.0	30-35
								260	260	↓	↓	↓	↓	↓	↓	330	0.84	35-39
								257	257	14.8	↓	↓	↓	↓	↓	330	0.84	39-47
								↓	↓	↓	↓	↓	↓	↓	↓	288	0.74	47-59
								↓	↓	↓	31.53	62.28	0.19	0.51	311	0.60	59-63	
								↓	↓	↓	↓	↓	↓	↓	↓	335	0.66	63-103
								↓	↓	↓	↓	↓	↓	↓	↓	263	0.72	103-217

Run	Plant	Catalyst						Diluent	Temp In °C	Press		Feed						Hours
		Number	% Fe	Wt., g	Mesh	Nature	% Solids			Wt g (wet)			% H ₂	% CO	% Ar	H ₂ -CO	Rate cc/min	
1	700B	5708-108	67.3	35		C ₂₈	15	200	120 ↑ 260	12.9	33.61	85.12	0.27	0.70	802	2.1	0-21	
								260	260						614	1.6	21-30	
								260	260						302	1.0	30-35	
								260	260						330	0.84	35-39	
								257	257	14.8					330	0.84	39-47	
															288	0.74	47-59	
											31.53	62.28	0.19	0.51	311	0.60	59-63	
															335	0.66	63-103	
															263	0.72	103-217	

TABLE 9
Conditions for Slurry-Bed
Run 5 (Plant 700B)

Run	Plant	Catalyst						Diluent			Rpm	Temp In °C	Filter		Press Out, atm	Feed						Hours																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
		Number	% Fe	Vol, g	Vol, cc	Mesh	Nature	% Solids	Wt, g (wet)	Pore Size, μ			Height, Inches	% H ₂		% CO	% Ar	H ₂ -CO	Rate sec/min	M/ h/g Fe																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					

TABLE 10
Conditions for Slurry-Bed
Run 6 (Plant 700B)

Run	Plant	Catalyst							Wax Medium			Rpm	Temp. in °C	Filter		Pres Out, atm	Feed						Hours
		Number	% Fe			Wt., g	Mesh Size	Static Hgt, in.	Nature	% Solids	Wt, g (wax)			Pore Size, μ	Height Inches		% H ₂	% CO	% Ar	H ₂ :CO	Rate sec/min	NL/hr /gFe	
6	700B	5708- 139	64.0			107.5	140- 400	4 11/16	C ₂₂	22	380	1000	280	0.7	5 1/4	11	39.17	55.19	5.64	0.71	2270	2.0	0-12
													258			15	↓	↓	↓	↓	↓	↓	12-15
													↓			↓	↓	↓	↓	↓	↓	↓	15-33
													↓			↓	36.90	55.03	6.07	0.71	1600	↓	33-56
													↓			↓	39.57	54.60	5.63	0.73	↓	↓	56-72

TABLE 10a
Conditions for Slurry-Bed
Runs 7 and 8

Run	Plant	Catalyst						Diluent			Temp, In, °C	Filter		Press Out, atm	Feed					Hours
		Number	% Fe	Wt, g	Mesh Size	Static Ht, in	Nature	% Solids	Wt, g (max)	Rpm		Pore Size, μ	Height Inches		% H ₂	% CO	% Ar	H ₂ CO	Rate sec/min	
7	7008	5709-139	64	107.5	140-400	4 1/4	C ₂₇	22	380	1000	17-45	4 1/4	11	39.49	54.56	5.95	0.72	1980	1.7	0-12
										↓			↓	↓	↓	↓	↓	↓	↓	12-15
										↓			15	↓	↓	↓	↓	↓	↓	15-27
										1250			↓	↓	↓	↓	↓	↓	↓	27-34
										↓			↓	39.49	54.68	5.83	0.72	↓	↓	34-51
										1000			↓	↓	↓	↓	↓	↓	↓	51-75
										↓			↓	↓	↓	↓	↓	↓	↓	
8	7008	5709-139	64	95	140-400	4 1/4	C ₂₇	20	360	1000	5-18	4 1/4	11	39.64	54.41	5.95	0.73	1980	2.0	0-12
										↓			↓	↓	↓	↓	↓	↓	↓	12-14
										1200			15	↓	↓	↓	↓	↓	↓	14-34
										↓			↓	39.49	54.77	5.74	0.72	↓	↓	34-56
										1300			↓	↓	↓	↓	↓	↓	↓	56-59
										1500			↓	39.57	54.47	5.98	0.73	↓	↓	59-62
										1300			↓	39.57	54.54	5.89	0.73	↓	↓	62-120
										↓			↓	39.27	54.63	6.10	0.72	↓	↓	120-144
										↓			↓	39.49	54.76	5.75	0.72	↓	↓	144-200
										↓			↓	39.49	54.76	5.75	0.72	830	.82	200-206
										↓			↓	39.57	54.55	5.86	0.73	↓	↓	206-216

Conditions for Slurry-Bed Runs 9, 10 and 11 (Plant 700B)

Run	Plant	Catalyst					Wax Medium				Rpm	Temp In, °C	Filter		Press Out, atm	Feed						Hr	
		Number	Fe, %			Wt., g	Mesh Size	Static Ht, in.	Nature	Solids, %			Wt., g (wax)	Pore Size, μm		Height in.	H ₂ , %	CO, %	Ar, %	H ₂ :CO	Rate sec/min		NL/h /gFe
9	700B	5709-139	64			95	140-400	4-5/8	C ₃₂	20	380	1000	280	5-18	4-14/16	11	39.49	54.77	5.74	0.72	1980	1.9	0-12
												↓	245			↓	39.49	54.62	5.89	0.72	1420	1.4	12-14
												1100	258			↓	↓	↓	↓	↓	↓	↓	14-28
												1200	↓			↓	↓	↓	↓	↓	↓	↓	28-30
												1300	↓			↓	39.35	54.95	5.88	↓	↓	↓	30-78
10	700B	5709-184	67.4			95	140-400	4-5/8	C ₃₂	20	380	1300	280	1-5	2-3/4	11	39.31	54.13	6.63	0.72	1980	1.9	0-6
												↓	258			↓	↓	↓	↓	↓	↓	↓	6-24
												↓	265			↓	↓	↓	↓	↓	↓	↓	24-36
11	700B	5709-184	67.4			95	140-400	4-9/16	C ₃₂	20	380	1300	280	0.7	2-7/8	11	38.76	58.44	6.32	0.65	1980	1.9	0-12
												↓	258			↓	↓	↓	↓	↓	↓	↓	12-14
												↓	↓			↓	39.48	53.98	6.00	0.73	↓	↓	14-18
												↓	↓			↓	↓	↓	↓	↓	1080	1.0	18-36
												↓	↓			↓	38.29	54.16	6.53	0.73	710	0.67	36-84

TABLE 11a
Conditions for Slurry-Bed
Runs 12-14 (Plant 700B)

Run	Plant	Catalyst				Wax Medium				Rpm	Temp in, °C	Filter		Press Out, atm	Feed						Hr		
		Number	Fe, %			Wt., g	Mesh Size	Static Ht. in.	Nature			Solids, %	Wt., g (wax)		Pore Size, μm	Height in.	H ₂ , %	CO, %	Ar, %	H ₂ :CO		Rate scc/min	NL/h /gFe
12	700B	5709-184	67.4			95	140-400	4-9/16	C ₃₂	20	380	1300	280	0.7	2-7/8	11	39.29	54.16	6.55	0.73	1982	1.9	0-12
												↓	280 ↓ 258			11 ↑ 15	40.18	53.29	6.53	0.75	1415	1.3	12-18
												↓	258			15	↓	↓	↓	↓	1415 486	1.3 0.46	18-28
																	↓	↓	↓	↓	486	0.46	28-76
																	40.5	52.99	6.51	0.76	↓	↓	76-131
																	40.41	53.51	6.06	0.76	↓	↓	131-154
13	700B	5709-184	67.4			95	140-400	4-9/16	C ₃₂	20	380	1300	280	0.15	2-7/8	11				0.7	1980	1.9	0-12
												↓	258			11 ↑ 15				↓	1420	1.3	12-18
												↓	↓			15				↓	↓	↓	18
14	700B	5709-184	67.4			95	140-400	4-9/16	C ₃₂	20	380	1300	280	0.15	2-7/8	11				0.7	1980	1.9	0-12
												↓	↓			11 ↑ 15				↓	1420	1.3	12-18
												↓	↓			15				↓	↓	↓	18

TABLE 11b

Run	Plant	Catalyst					Wax Medium					Temp In., °C	Filter		F ₂₅₅ Out, atm	Feed					H ₂	NL/hr /g-Fe	H ₂
		Number	Fe, %	Wt., g	Mesh Size	Static Ht, in.	Nature	Solids, %	Wt., g (wax)	Rpm	Pore Size, μm		Height in.	H ₂ , %		CO, %	Ar, %	H ₂ :CO	Rate sec/min				
15	7008	5709- 184	67.4	95	140-400	4-9/16	C ₁₇	20	380	1300	280	0.5	2-7/8	11				0.7	1980	1.9	0-12		
										↓	256			11 ↑				↓	1420	1.3	12-18		
										↓	↓			15				↓	↓	↓	18-67		
														15									
16	7008	5709- 139	64.0	95	140-400	4-9/16	C ₁₇	20	380	1500	280	0.5	2-7/8	11	53.49	40.35	6.16	0.75	1980	2.0	0-12		
										↓	280			11 ↑				↓	↓	↓	12-18		
										↓	258			15				↓	↓	↓	18-26		
										2000								↓	↓	↓	26-29		
										2500								↓	↓	↓	29-34		
										↓				↑	54.86	38.87	6.28	0.71	↓	↓	34-53		
17	7008	5709- 139	64.0	95	140-400	4-9/16	C ₁₇	20	380	1300	280	0.5	3-7/8	11	55.64	38.26	6.10	0.69	1080	2.0	0-12		
										↓	280			11	55.66	37.99	6.11	0.68	↓	↓	12-16		
										↓	258			15				↓	1420	1.4	16-30		
										1000								↓	↓	↓	30-36		
										1300								↓	↓	↓	16-43		

(Run 19, Plant 7008)

[illegible][illegible]

Table 12

Performance of Precipitated Iron Catalyst
in 11 Autoclave Reactors in Series at 21 ATM. 0.7 H₂: CO Feed
 (wt-%)

	<u>265°C</u>	<u>275°C</u>	<u>Target</u>
C ₁	4.3	5.8	--
C ₂ (Ethane + Ethylene)	4.6	6.0	--
C ₁ + C ₂	8.9	11.8	7
Sv, nL/h-gFe	1.1	1.6	≥2

Table 13

Approximate Product Distribution (Wt-%) at 68%
Conversion, 265°C, 300-324 Hours

	<u>N-Paraffin</u>	<u>α-Olefin</u>	<u>Alcohol</u>	<u>Aldehyde</u>	<u>Unidentified</u>	<u>Total</u>
C ₁	5.5	--	--	--	--	5.5%
C ₂	0.9	5.0	2.9	0.2	--	9.0%
C ₃ -C ₄	3.0	11.7	2.0	1.5	--	18.2%
C ₅ -C ₁₁	3.8	8.9	2.9	1.1	7.3	24.0%
C ₁₂ -C ₁₈	-3.0	-6.0	0	0	-4.0	13%
C ₁₉ -C ₂₅	--	--	--	--	9.9	9.9%
C ₂₆ ⁺	<u>--</u>	<u>--</u>	<u>--</u>	<u>--</u>	<u>20.4</u>	<u>20.4%</u>
	<u>16.2</u>	<u>31.6</u>	<u>7.8</u>	<u>2.8</u>	<u>41.6</u>	<u>100.0</u>

Table 14

Approximate Product Distribution (Wt-%) at 83%
Conversion, 275°C, 660-684 Hours

	<u>N-Parafin</u>	<u>α-Olefin</u>	<u>Alcohol</u>	<u>Aldehyde</u>	<u>Unidentified</u>	<u>Total</u>
C ₁	6.2	--	--	--	--	6.2%
C ₂	2.4	4.1	4.6	0.3	--	11.4%
C ₃ -C ₄	3.3	16.5	2.6	1.0	--	23.4%
C ₅ -C ₁₁	4.0	11.1	2.1	0.8	10.6	28.6%
C ₁₂ -C ₁₈	-3.0	-6.3	0	0	-1.9	11.2%
C ₁₉ -C ₂₅	--	--	--	--	4.7	4.7%
C ₂₆ ⁺	<u>--</u>	<u>--</u>	<u>--</u>	<u>--</u>	<u>14.5</u>	<u>14.5%</u>
	<u>18.9</u>	<u>38.0</u>	<u>9.3</u>	<u>2.1</u>	<u>31.7</u>	<u>100.0</u>

Figure 1

FISCHER TROPSCH CATALYST TEST PLANT
PROCESS FLOW DIAGRAM
PART I

88-34221

Figure 2-1. Integrated Fischer-Tropsch Pilot Plant

Figure 2

FISCHER TROPSCH CATALYST TEST PLANT
PROCESS FLOW DIAGRAM
PART 2

88-34221

PRR - Pressure Reducing Regulator
BPR - Back Pressure Regulator
T - Temperature Indicator
C - Temperature Indicator and Control
P - Pressure Indicator

Both capillaries in constant temperature both.
Hot and cold separator systems in constant temperature boxes.

Figure 3

MOBIL MCSG-4 IRON CATALYST

CO + H₂ CONVERSION

Figure 4

MOBIL MCSG-4 IRON CATALYST

CO₂ SELECTIVITY

Figure 5

MOBIL MCSG-4 IRON CATALYST

C₁ SELECTIVITY

Figure 6

MOBIL MCSG-4 IRON CATALYST

H₂ TO CO USAGE RATIO

MOBIL MCG-4 IRON CATALYST

Figure 7

Figure 8

MOBIL MCSG-4 IRON CATALYST

H₂ TO CO RATIO

Figure 9

TITRATION OF $\text{Fe}(\text{NO}_3)_3$ SOLUTION (5 WT. % Fe) WITH 1N Na_2CO_3 SOLUTION

Figure 10 TITRATION OF $\text{Fe}(\text{NO}_3)_3$ SOLUTION (5 WT. % Fe) WITH 1N NH_4OH SOLUTION

Figure 11

TITRATION OF $\text{Cu}(\text{NO}_3)_2$ SOLUTION (0.5 WT. % Cu) WITH 1N Na_2CO_3 SOLUTION

Figure 12

TITRATION OF $\text{Cu}(\text{NO}_3)_2$ SOLUTION (0.5 WT. % Cu) WITH 1N NH_4OH SOLUTION

Figure 13

REPRODUCIBILITY OF DSC EXPERIMENTS WITH pH=4.3 CATALYST 5685-53

Figure 14

TGA OF pH=4.3 CATALYST 5685-53

Figure 15 REPRODUCIBILITY OF DSC EXPERIMENTS WITH pH=3.5 CATALYST 5685-61

Figure 16

TGA OF pH=3.5 CATALYST 5685-61

Figure 17 REPRODUCIBILITY OF TPR FOR Fe/Cu CATALYSTS (5685-145)

1

Figure 19 XRD OF pH-6.5 CATALYST 5685-145 AFTER H_2 TREATMENT AT $250^\circ C$

Figure 20 XRD OF PH-6.5 CATALYST 5685-145 AFTER H₂ TREATMENT AT 800°C

Figure 21

DSC OF pH-9.7 CATALYST 5685-75 PRECIPITATED BY Na_2CO_3

Figure 22 DSC OF pH=9.5 CATALYST 5685-111 PRECIPITATED BY NH_4OH

Figure 23 ISOTHERMAL DSC AT 350°C OF pH=9.5 CATALYST 5685-111 PRECIPITATED BY NH_4OH

Figure 24 STANDARD DSC AFTER ISOTHERMAL DSC OF pH=9.5 CATALYST 5685-111 PRECIPITATED
BY NH_4OH

Figure 25 ISOTHERMAL DSC AT 350°C OF pH=3.5 CATALYST 5685-61

Figure 26

STANDARD DSC AFTER ISOTHERMAL DSC OF pH=3.5 CATALYST 5685-61

QUANTA CHRO1

Figure 27

CUMULATIVE PORE VOLUME WITH pH=4.3 CATALYSTS CALCINED AT 380°C AND 450°C

Figure 28 PORE SIZE DISTRIBUTION WITH pH=4.3 CATALYSTS CALCINED AT 380°C AND 450°C

Figure 29

CUMULATIVE SURFACE AREA WITH PH-4.3 ACATALYSTS CALCINED AT 380°C AND 450°C

AUTOSORB

Sp-A

- #5685-137A, 450°C
- ◇ #5885-129A, 380°C

Figure 30 CUMULATIVE PORE VOLUME WITH PH-9.7 CATALYSTS CALCINED AT 380°C AND 450°C

AUTOSORB

Figure 31 PORE SIZE DISTRIBUTION WITH pH=9.7 CATALYSTS CALCINED AT 380°C AND 450°C

ASTOSORB

Figure 32 CUMULATIVE SURFACE AREA WITH pH-9.7 CATALYSTS CALCINED AT 380°C AD 450°C

Figure 33
EFFECT OF CALCINATION TEMPERATURE ON TPR OF Fe/Cu CATALYSTS
PRECIPITATED AT PH 4.3

Figure 34 STEM MICROGRAPHS OF pH-3.5 AND pH-4.3 CATALYSTS AFTER 110°C DRYING

Figure 35 STEM MICROGRAPHS OF pH-5.5 AND pH-6.5 CATALYSTS AFTER 110°C DRYING

pH-5.5

pH-6.5

Figure 36

STEM MICROGRAPHS OF pH-7.9 AND pH-9.7 CATALYSTS AFTER 110°C DRYING

pH-7.9

pH-9.7

Figure 37 XRD OF pH-9.7 CATALYST AFTER 110°C DRYING

Figure 38

STEM MICROGRAPHS OF pH-4.3 AND pH-9.7 CATALYSTS AFTER 380°C CALCINATION

pH-4.3

pH-9.7

Figure 39

STEM MICROGRAPHS OF pH-4.3 AND pH-9.7 CATALYSTS AFTER 450°C CALCINATION

pH-4.3

pH-9.7

Figure 40 **DIFFERENTIAL SCANNING CALORIMETRY**

Fe/Cu CATALYSTS PRECIPITATED AT DIFFERENT pH'S

Figure 41

TGA OF pH-7.9 CATALYST 5685--69

Figure 42

TGA OF pH=9.7 CATALYST 5685-75

Figure 43

EFFECT OF pH OF PRECIPITATION ON TPR OF Fe/Cu CATALYSTS
CALCINED AT 380C

Figure 44

EFFECT OF pH OF PRECIPITATION ON TPR OF Fe/Cu CATALYSTS
CALCINED AT 450C

Figure 45

STEM MICROGRAPHS OF 100 Fe:0.5 Cu AND 100 Fe:5Cu CATALYSTS AFTER 110°C DRYING

Cu LEVEL EFFECT ON PRECIPITATED Fe/Cu CATALYST MORPHOLOGY (110°C DRIED)

5% Cu

100 Fe:5.0 Cu

0.5% Cu

100 Fe:0.5 Cu

Figure 46 XRD OF 100 Fe:0.5 Cu CATALYST 5685-139 AFTER 110°C DRYING

Figure 47

STEM MICROGRAPH OF 100 Fe:5 Cu CATALYST

Figure 48

DSC OF 100 Fe:0.5 Cu AND 100 Fe:5 Cu CATALYSTS

Figure 49

TGA OF 100 Fe:0.5 AND 100 Fe:5 Cu CATALYSTS

Figure 50

COPPER LEVEL EFFECT ON TPR OF Fe/Cu CATALYSTS
PRECIPITATED AT pH 6.1-6.5

Figure 51
EFFECT OF K₂CO₃ IMPREGNATION ON TPR OF Fe/Cu CATALYSTS
Fe TO Cu RATIO 100:1

Figure 52
EFFECT OF K₂CO₃ IMPREGNATION ON TPR OF Fe/Cu CATALYSTS
FE TO CU RATIO 100:5

Figure 53

STEM MICROGRAPHS OF NH_4OH AND Na_2CO_3 -DERIVED pH-9.5-9.7 CATALYSTS AFTER 110°C DRYING

NH_4OH -DERIVED

Na_2CO_3 -DERIVED

Figure 54

EFFECT OF PRECIPITATION BASE ON TPR OF Fe/Cu CATALYSTS

Figure 55a

Plant 752
Fischer-Tropsch Catalyst Prep.
Rev. 5 9/20/87 PSG

556

Assembled Reactor
Cutaway View

Reactor Side View
Valve Detail

Plant 752
Reactor

1/3/89 PS6

SSd

Detail B
Reactor
Bottom

Plant 752 Reactor
Detail B
1/3/89 PSG

55e

Detail C
Mixer

Mixer, Unassembled

↑ Tygon tubing
1/4" OD, 1/8" ID
cut in as many
small strips as
feasible.

Mixer, Assembled

Plant 752 Reacto
Detail C
12/29/88 PSG

55f

Detail D Valve Inset

O-ring grooves
groove depth 0.05 ± 0.001 "
max. groove width 0.090 ± 0.003 "
size O14 O-ring

~ 1/4" hole drilled & tapped to accept screw which will serve as valve handle

Plant 752 Reactor
Detail D

1/3/89 PSG

FIGURE 55g
STEM Micrographs for Catalyst 6616-18

Figure 56

EXPERIMENTAL IRON CATALYST IN RUN 50

CO PLUS H₂ CONVERSION

Figure 57

EXPERIMENTAL IRON CATALYST IN RUN 50

CO CONVERSION

Figure 58

EXPERIMENTAL IRON CATALYST IN RUN 50

H₂ CONVERSION

Figure 59

EXPERIMENTAL IRON CATALYST IN RUN 50

CO₂ SELECTIVITY

Figure 60

EXPERIMENTAL IRON CATALYST IN RUN 50

Figure 61
EXPERIMENTAL IRON CATALYST IN RUN 50
H₂ TO CO USAGE RATIO

Figure 62

EXPERIMENTAL IRON CATALYST IN RUN 50

PROPYLENE TO PROPANE RATIO

Figure 63

EXPERIMENTAL IRON CATALYST IN RUN 50

C, SELECTIVITY

Figure 64

MAXIMUM TEMPERATURES IN THE CATALYST BED IN RUN 51

Figure 65

EXPERIMENTAL IRON CATALYST IN RUN 51

CO + H₂ CONVERSION

Figure 66

EXPERIMENTAL IRON CATALYST IN RUN 51

CO CONVERSION

Figure 67

EXPERIMENTAL IRON CATALYST IN RUN 51

H₂ CONVERSION

Figure 68

EXPERIMENTAL IRON CATALYST IN RUN 51

H₂ TO CO RATIO

Figure 69

EXPERIMENTAL IRON CATALYST IN RUN 51

H₂ TO CO USAGE RATIO

Figure 70

EXPERIMENTAL IRON CATALYST IN RUN 51

CO₂ SELECTIVITY

Figure 71

EXPERIMENTAL IRON CATALYST IN RUN 51

C₁ AND C₂ SELECTIVITIES

Figure 72
EXPERIMENTAL IRON CATALYST IN RUN 51
ETHYLENE TO ETHANE RATIOS

Figure 73

EXPERIMENTAL IRON CATALYST
ANDERSON-SCHULZ-FLORY DISTRIBUTION

RUN 51

$T_{IN} = 244^{\circ}C$, 13 ATM , 0.7 H₂: CO FEED

HYDROCARBONS ONLY - OIL ANALYZED BY GPC ONLY

Figure 74

EXPERIMENTAL IRON CATALYST
ANDERSON-SCHULZ-FLORY DISTRIBUTION

RUN 51

$T_{IN} = 244^{\circ}C$, 13 ATM , 0.7 H₂: CO FEED

HYDROCARBONS ONLY - OIL ANALYZED BY GPC ONLY

Figure 75

SLURRY PILOT PLANT SHAKE-DOWN

CO PLUS H₂ CONVERSION

Figure 76

SLURRY PILOT PLANT SHAKE-DOWN

CO CONVERSION

Figure 77

SLURRY PILOT PLANT SHAKE-DOWN

H₂ CONVERSION

Figure 78

SLURRY PILOT PLANT SHAKE-DOWN

CO₂ SELECTIVITY

Figure 79

SLURRY PILOT PLANT SHAKE-DOWN

METHANE SELECTIVITY

Figure 80
TEMPERATURE SURVEYS IN THE AUTOCLAVE IN RUN 5

Figure 81

EVALUATION OF PRECIPITATED IRON CATALYST 5709-119 IN SLURRY REACTOR - RUN 5

Figure 82

EVALUATION OF PRECIPITATED IRON CATALYST 5709-119 IN SLURRY REACTOR - RUN 5

Figure 83

EVALUATION OF PRECIPITATED IRON CATALYST 5709-119 IN SLURRY REACTOR - RUN 5

Figure 84

EVALUATION OF PRECIPITATED IRON CATALYST 5709-119 IN SLURRY REACTOR - RUN 5

Figure 85

EVALUATION OF PRECIPITATED IRON CATALYST 5709-119 IN SLURRY REACTOR - RUN 5

Figure 86

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 87

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 88

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 89

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 7008 RUN 6

Figure 90

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 91

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 92

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 7008 RUN 6

Figure 93

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

Figure 94

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

Figure 95

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

Figure 96

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

Figure 97

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

Figure 98

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8

H₂/CO USAGE RATIO
CO₂ SELECTIVITY, %
H₂/CO OUTLET RATIO
CO CONVERSION, %

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8

Figure 99

Figure 100

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8

Figure 101

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8

Figure 102

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 9

Figure 103

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 9

Figure 104

EVALUATION OF PRECIPITATED IRON CATALYST 5719 139 IN SLURRY REACTOR - RUN 9

Figure 105

LIQUID LEVEL Vs. HOURS ON-STREAM

FOR RUN 11 IN PLANT 700B

Figure 106

LIQUID LEVEL Vs. HOURS ON-STREAM

FOR RUN 16 IN PLANT 700B

Figure 107

LIQUID LEVEL Vs. HOURS ON-STREAM

FOR RUN 18 IN PLANT 700B

Figure 108

EVALUATION OF PRECIPITATED IRON CATALYST 5709-184 IN SLURRY REACTOR 700B DURING RUN 18

Figure 109

EVALUATION OF PRECIPITATED IRON CATALYST 5709-184 IN SLURRY REACTOR 700B DURING RUN 18

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 110

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 111

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 112

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 113

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 114

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 115

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 116

Figure 117

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 118

Figure 119

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 120

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 121

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 122

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 124

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 125

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 129

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 130

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 138

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 139

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 140

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 141

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 142

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 143

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 144

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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Figure 146

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 147

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18
IN SLURRY REACTOR 700B RUN 19

Figure 148

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 149

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 150

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 151

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 155

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 156

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 163

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 164

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 165

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 166

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 168

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 169

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 170

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18
IN SLURRY REACTOR 700B RUN 19

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18
IN SLURRY REACTOR 700B RUN 19

Figure 171

Figure 172

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

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EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 176

EVALUATION OF PRECIPITATED IRON CATALYST 6616-18 IN SLURRY REACTOR 700B RUN 19

Figure 177

CONVERSION vs. CONTACT TIME
PRECIPITATED IRON CATALYST
21 atm, 0.7 H₂:CO IN FEED

Figure 178

EFFECT OF CONVERSION LEVEL ON REACTION RATE
WITH PRECIPITATED IRON CATALYST

Figure 179

EFFECT OF CONVERSION LEVEL ON SELECTIVITY

265 C, 21 atm, 0.7 H₂:CO IN FEED

DATE

FILMED

4/20/94

END