DE96007858

DOE/PC/90018--T12

LIQUID PHASE FISCHER-TROPSCH (II) DEMONSTRATION IN THE LAPORTE ALTERNATIVE FUELS DEVELOPMENT UNIT

RECEIVED
MAR 04 1996
OSTI

Topical Report

FINAL

(Volume I/II: Main Report)

Task 1: Engineering Modifications (Fischer-Tropsch II Demonstration)

and

Task 2: AFDU Shakedown, Operations, Deactivation and Disposal
(Fischer-Tropsch II Demonstration)

Contractor:

AIR PRODUCTS AND CHEMICALS
Allentown, PA 18195

Bharat L. Bhatt
September 1995

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-91PC90018
Contract Period October 1990 - December 1995

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

TABLE OF CONTENTS

ABSTRACT

This report presents results from a demonstration of Liquid Phase Fischer-Tropsch (LPFT) technology in DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas. The run was conducted in a bubble column at the AFDU in May-June 1994. The 10-day run demonstrated a very high level of reactor productivity for LPFT, more than five times the previously demonstrated productivity (1). The productivity was constrained by mass transfer limitations, perhaps due to slurry thickening as a result of carbon formation on the catalyst. With a cobalt catalyst or an improved iron catalyst, if the carbon formation can be avoided, there is significant room for further improvements.

The run was sponsored by the U. S. Department of Energy (DOE), Air Products & Chemicals, Inc., and Shell Oil. The reactor was operated with 0.7 H_2/CO synthesis gas in the range of 2400 - 11700 sl/hr-kg Fe, 175 - 750 psig and 270 - 300°C. The inlet gas velocity ranged from 0.19 to 0.36 ft/sec. The demonstration was conducted at a pilot scale of 5 T/D. Catalyst activation with CO/N_2 proceeded well. Initial catalyst activity was close to the expectations from the CAER autoclave runs. CO conversion of about 85% was obtained at the baseline condition. The catalyst also showed good water-gas shift activity and a low α.

At high productivity conditions, reactor productivity of 136 grams of HC/hr - liter of slurry volume was demonstrated, which was within the target of 120-150. However, mass transfer limitations were observed at these conditions. To alleviate these limitations and prevent excessive thickening, the slurry was diluted during the run. This enabled operations under kinetic control later in the run. But, the dilution resulted in lower conversion and reactor productivity. The catalyst activity declined steadily during the run, with carbon formation suspected to be the cause. The gas hold-up declined significantly earlier in the run and was much lower than expected (~ 10 vol%) during most of the run. Slurry thickening with time on-stream appeared to be the reason for the low gas hold-up. The gas hold-up estimates were confirmed by shutdown tests.

A new reactor internal heat exchanger, installed for high productivity conditions, performed well above design, and the system never limited the performance. As expected, the reactor temperature control needed manual intervention. The control can be improved by realigning the utility oil system.

EXECUTIVE SUMMARY

Liquid Phase Fischer-Tropsch (LPFT) technology was demonstrated in DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas. This run, conducted in May-June 1994, was a second demonstration run in a bubble column at the AFDU. The 10-day run demonstrated a very high level of reactor productivity for LPFT, more than five times the previously demonstrated productivity (1). The productivity was constrained by mass transfer limitations, perhaps due to slurry thickening as a result of carbon formation on the catalyst. With a cobalt catalyst or an improved iron catalyst, if the carbon formation can be avoided, there is significant room for further improvements.

The run was sponsored by the U. S. Department of Energy (DOE), Air Products & Chemicals, Inc., and Shell Oil. Analytical methods developed by DOE at the Pittsburgh Energy Technology Center (PETC) were used to set up chromatographs for gas analysis (C_1-C_8). Liquid hydrocarbons (C_5-C_{20}) and wax samples (C_{12}-C_{50}) were shipped to PETC for analysis. Four different trial batches of precipitated iron catalysts were prepared by UCI, tested at Air Products for sedimentation, and tested at the Center for Advanced Energy Research (CAER) - University of Kentucky, DOE-PETC, Exxon Chemicals, UOP, and Texas A&M for activity. An unsupported catalyst composition was selected by the participants based on the activity, selectivity and stability of the catalyst. A catalyst having low wax selectivity was required since the AFDU has limited catalyst-wax separation capability. An external slurry loop with a porous metal filter was planned to separate limited quantities of wax from slurry if needed. A cross-flow filter test was conducted at Mott Metallurgical with the unsupported catalyst, which was first activated in CAER's bubble column. The test proved to be extremely successful with a 0.2 micron filter element. The small size element was necessary as the slurry contained some catalyst fines. The filtrate was clear with expected flux rate for the small pore size.

The reactor was operated with 0.7 H_2/CO synthesis gas in the range of 2400 - 11700 sl/hr-kg Fe, 175 - 750 psig and 270 - 300°C. The inlet gas velocity ranged from 0.19 to 0.36 ft/sec. The demonstration was conducted at a pilot scale of 5 T/D. Catalyst activation with CO/N_2 proceeded well. Initial catalyst activity was close to the expectations from the CAER autoclave runs. CO conversion of about 85% was obtained at the baseline condition. The catalyst also showed good water-gas shift activity and a low α.

At high productivity conditions, reactor productivity of 136 grams of HC/hr - liter of slurry volume was demonstrated, which was within the target of 120-150. However, mass transfer limitations were observed at these conditions. To alleviate these limitations and prevent excessive thickening, the slurry was diluted during the run. This enabled operations under kinetic control later in the run; however, the dilution resulted in lower conversion and reactor productivity. The catalyst activity declined steadily during the run, with carbon formation suspected to be the cause due to severe operating conditions. The gas hold-up declined significantly earlier in the run and was much lower than expected (~ 10 vol%) during most of the run. Slurry thickening with time on-stream appeared to be the reason for the low gas hold-up. The gas hold-up estimates were confirmed by shutdown tests.

A new reactor internal heat exchanger, installed for high productivity conditions, performed well above design, and the system never limited the performance. As expected from reactor temperature control analysis by Shell and Air Products, the reactor temperature control needed manual intervention. The control can be improved by realigning the utility oil system.

INTRODUCTION

The Pittsburgh Energy Technology Center (PETC) sponsors an Indirect Liquefaction program as part of DOE's Coal Liquefaction program. The overall goal of the Coal Liquefaction program is to develop the scientific and engineering knowledge base with which industry can bring economically competitive and environmentally acceptable advanced technology for the manufacture of synthetic liquid fuels from coal into the marketplace when needed. The specific area of interest for this project was to provide a second demonstration of slurry-phase Fischer-Tropsch (F-T) synthesis, showing significant improvements over the initial run (1). The F-T process converts synthesis gas to liquid hydrocarbons suitable as feedstock for transportation fuels.

The test run was conducted at DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas, which has been operated by Air Products and Chemicals, Inc, for slurry phase methanol, DME, water gas shift, F-T, isobutylene and isobutanol synthesis (2, 3, 4). The scale-up of the technologies involves demonstration in a 22.5" (ID) diameter slurry bubble column reactor based on laboratory bench scale investigations. The chemistry of Fischer-Tropsch Synthesis as well as advantages of conducting F-T in a slurry phase were discussed in a report on the initial F-T demonstration (1).

This demonstration had significant industrial backing. In addition to DOE, this run was sponsored by Air Products and Chemicals and Shell Oil. A final partners' meeting was held at LaPorte on 10 May 1994 prior to the run. The catalyst qualification and run plan were discussed and approved.

OBJECTIVES

The main objective of this run was to demonstrate liquid phase F-T technology at a pilot scale (5 T/D product) in a bubble column reactor and address scale-up issues such as:

- Reactor productivity
- Catalyst activation
- Catalyst performance
- Hydrodynamics

Significant differences from the initial demonstration included:

- Higher productivity (5-6 times F-T I)
- Higher pressure / Higher space velocity
- Higher catalyst concentration
- Constant catalyst inventory in the reactor

ENGINEERING AND MODIFICATIONS

The AFDU was modified to handle higher heat of reaction associated with higher reactor productivity. Major modifications included a new internal heat exchanger for the reactor and addition of a heat exchanger in the cooling (utility oil) system.

New Internal Heat Exchanger for 27.10 Reactor

A goal of 150 grams HC/liter reactor vol - hr of F-T productivity was set, which was about 3.6 times the existing productivity limit of 42 grams HC/liter - hr. The current limit was based on a heat exchanger capacity of 900,000 BTU/hr. The new goal required a heat exchanger capacity of 3.3 MMBtu/hr. Hence, significantly higher heat exchanger area was needed. In addition, higher oil velocity and lower oil temperature were also required. The new heat exchanger consists of 22 vertical 3/4" U-tubes with an internal header. Twelve of the U-tubes are near the wall and ten are near the center (see Figures 1 and 2). The external surface area of the U-tubes is 217.7 ft^2 based on 36 ft length. The design basis for heat exchanger assumes 80% CO conversion with 150 lbmole/hr reactor feed ($H_2/CO = 0.7$) and 33 wt% slurry at 518°F, 750 psig and 8600 sl/hr-kg Fe (0.24 ft/sec).

The new heat exchanger tube bundle was installed with the 27.10 reactor in place. Some tubes were moved slightly to create adequate room for the nuclear density gauge (NDG) scan. Also, both the source and the detector for the NDG had to be moved about 2" as they were originally off-centered to accommodate the old tube bundle. Subsequent NDG scans resulted in readings close to expected.

Modifications to Utility Oil System

In addition to the modification on the existing air cooler (21.40) that was underway for the oxygenates, use of an existing heat exchanger (21.20) was planned to remove additional heat from oil with cooling water. The 21.20 heat exchanger was reviewed for this application. A process specification was issued to purchase two rupture discs for the 21.20. The rupture discs protect the cooling water system in case of a tube rupture in the 21.20.

Process Description

Process flow diagrams for the run are shown in Figures 3 and 4. The operation of the AFDU is described as follows: Carbon monoxide, hydrogen and nitrogen are blended and compressed in the 01.10 compressor to obtain desired synthesis gas composition and flow. The feed gas is then preheated in the 21.38 feed/product economizer and the 02.61 feed gas steam heater. The preheated feed gas is introduced to the bottom of the slurry reactor, 27.10. The synthesis gas flows upward through the slurry and is partially converted to hydrocarbons, carbon dioxide and water. The heat of reaction is absorbed by the slurry medium and then rejected to an internal heat exchanger. The heavy wax product is liquid at reaction conditions and accumulates in the reactor. The reactor effluent is cooled using the 21.38 economizer to condense light waxes which are separated in the 22.14 separator. The reactor effluent is subsequently chilled against cooling water in the 21.65 hairpin exchangers. The condensed hydrocarbon and water are separated from vapor phase in the 22.18 separator. The uncondensed vapor is analyzed, depressurized and sent to the flare. The liquids from the 22.18 are depressurized and sent to vessels 22.11, 22.15 and 22.16 in sequence. The product from the 22.16 is then sent to a tank trailer.

The liquid level in the reactor is controlled using signals from a nuclear density gauge. Due to low wax selectivity of the catalyst, the liquid level in the reactor was expected to drop, as the wax vaporization rate was expected to exceed the wax production rate. The liquid level would be then maintained in the reactor by recycling light wax from the 22.14 separator. In the unexpected case of higher wax production rate, the excess slurry from the reactor would be drained into the 27.13 slurry holding tank, filtered in the 22.60 cross-flow filters, and the concentrated slurry would be returned to the reactor. Excess light and heavy wax is collected in the 28.30 prep tank and then drained into drums and sampled. Flows and compositions are measured at various strategic points in the process including feed and product gas.

The 27.10 bubble column reactor is 28.3' top to bottom and 22.5" inside diameter (1). The maximum slurry level is about 20 ft with the remainder being vapor disengagement space. The new internal heat exchanger occupies 9.6% of the reactor cross-section.

Catalyst-wax Separation System

As a result of a cross-flow filter test at Mott (see Cross-Flow Filter Test Section), 0.2 micron filter elements were installed to the existing filter system (1). The filters were designed for 4 gph of filtrate wax which was twice the anticipated maximum production rate with the low α catalyst. The design flux through the elements was 0.02 gpm/ft^2. A new 10.60 pump with higher temperature rating was installed for filter system. The existing pump (diaphragm pump) did not perform well during the F-T I run near the design temperature. The new pump is a progressive cavity pump which can handle the abrasive slurry in a smooth pumping motion which will not crush the catalyst particles or allow the particles to damage the pump.

Analytical Set-up

Two of the AFDU GCs were set up with two FIDs each for both hydrocarbon and alcohol analysis. The hydrocarbon analysis used DOE-PETC's methods (5). Both the GCs were dedicated to product gas analysis, measuring concentrations of C_1-C_8 hydrocarbons. Two other GCs were set up with two TCDs each. These GCs measured H_2, CO, N_2, and CO_2 in both feed and product gas streams. Liquid (C_5-C_{20}) and wax (C_{12}-C_{50}) analyses were performed by DOE-PETC. Samples from 22.11 and 22.16 liquid (HC + aqueous phase), 22.14 light wax as well as spent slurry samples were taken and shipped to PETC for composition analysis.

Hazards Reviews

Hazards reviews were conducted to evaluate safety issues associated with the F-T operation. A preliminary hazards review (PHR), a design hazards review (DHR), and a design verification review (DVR) were conducted at various stages of the project. The

Fischer-Tropsch part of the plant was divided into several sections and each section was reviewed in detail with a What-If analysis in accordance with OSHA-PSM (Process Safety Management). Several action items were generated and were followed up prior to the Design Verification Review as follows:

(1) A temperature rise in the reactor after an emergency shut down was estimated using ASPENPLUS simulations. A worst case scenario, when cooling with the internal heat exchanger is not available, was considered. An emergency trip (e.g. high temperature alarm due to absence of cooling) would shut off the compressor and vent the system. The syngas inventory upstream of the reactor would pass through the reactor, react and release significant amount of heat as the system depressurizes. Assuming 100% CO conversion, the reactor rises to 720°F at 15 psig. The current reactor rating was 700°F at 1007 psig. The Equipment Engineering group rerated the reactor at 750°F. The new rating including the new internal heat exchanger is 750°F at 985 psig. Hence, the reactor would be within the rating during the shutdown.

(2) Possible entrainment of liquid out of the 15.91 Knockout Drum was also reviewed. For the maximum flow through the 15.91, the required diameter of the vessel is estimated to be 14", which is much lower than the actual 6 ft diameter of the 15.91. Hence, no entrainment of liquid is expected out of 15.91.

(3) A meeting was held with ICI Tracerco to discuss a tracer study for F-T II. Two primary issues were discussed: Radioactivity of the product wax and liquid level control with the Nuclear Density Gauge during the tracer study. Radioactivity of the product wax was not a major issue due to dilution in the reactor as well as the rest of the plant. A 10-hour elapsed time was needed after the last liquid injection prior to draining the wax. This time constraint was acceptable as the wax drain was scheduled on a daily basis. Concentration of radioactive powder in the filters was a concern. Assuming a worst case scenario of all radioactive material depositing on one filter, 36 hours were required after injection for the material to decay to the regulatory limit. Hence, no maintenance on the filters was to be permitted for 36 hours after the last liquid injection. For the liquid level control, it was decided to leave the Nuclear Density Gauge at the normal controlling reactor height. The gauge would be shut off for 10-15 minutes during the injections as cross-interference was expected.

(4) Mass and energy balances were performed in preparation for the examination of various safety devices. Existing relief devices were evaluated for the F-T II conditions. The devices were found to be adequate for the F-T service.

(5) The analysis of the blast pressure, radiation and toxic effects was completed for worst case flows by Corporate Safety. The radiation heat calculations indicated that the existing flare will provide an acceptable radiation heat level to operators at grade.

Operator training was conducted by process and plant personnel and all documentation was completed as per OSHA PSM. An Operational Readiness Inspection (ORI) was conducted prior to the start-up, reviewing the revisions and preparations for the run.

The scope of the ORI included review of the equipment, piping and instrumentation to be used for the run. The plant was found in satisfactory condition and an approval was given for start-up.

Environmental Reviews

Calculations were performed to check air emissions for F-T II. The maximum new case was within the current permit limitation. However, since the maximum new case exceeded the F-T case described in the permit, an exemption application was necessary. Air emission estimates were completed and an exemption application was filed with TNRCC (Texas Natural Resource Conservation Commission). An approval was received from TNRCC for the F-T exemption application.

Reactor Temperature Stability

An analysis of reactor temperature stability for Fischer-Tropsch Synthesis at the AFDU was conducted (see Volume II, Appendix A). The analysis indicated that at the high productivity condition, a small disturbance to the system will require the entire utility oil heater capacity to automatically control the system. The automatic control can be greatly improved by placing the heaters downstream of the oil coolers. In the present configuration, the coolers dampen the response of the heaters. This did not affect our ability to control temperature during F-T I, as the magnitude of heat of reaction was much smaller. Due to funding and timing constraints, it was decided not to install the above improvement in the system at the current time. This was certainly not a safety issue, as there are three independent high temperature shutdown thermocouples in the reactor. At high productivity, the reactor temperature control would be monitored closely. For a large disturbance to the system, the 21.40 cooler would be controlled manually, as done in the past.

CATALYST DEVELOPMENT

One of the recommendations from the initial F-T demonstration was a need for more catalyst development with a goal of minimizing catalyst loss from the reactor. Hence, a modest catalyst development effort began aimed at higher attrition resistance and larger particle size (~70 microns, average). Also, the goal was to keep the α low to minimize or eliminate the need for catalyst-wax separation.

United Catalyst, Inc (UCI) was contracted to prepare six batches (~ 10 lbs each) of precipitated iron catalyst with different supports, alkaline level and calcination temperatures. Physical and chemical properties of the catalysts are summarized in Table 1. All of the supported catalysts had average particle size under 25 microns, the unsupported catalyst average size was about 65 micron. The attrition resistance of all the catalysts was found to be excellent based on Fluid Bed Attrition Tests (FBAT) conducted at UCI. The FBAT involves fluidizing the material with air, and measuring attrition rate of particles larger than 16 microns for 15 hours. As attrition resistance was acceptable for all the catalysts, lower temperature (370°C) calcined catalysts were selected for further testing, as higher activity was expected with those catalyst. Two silica supported (#3 and #7), one kaolin supported (#11) and one unsupported (#8) catalyst were tested further.

Activity Tests

CAER, UOP, Texas A&M and Exxon Chemicals conducted activity testing on the four selected catalysts. The following catalyst activation procedure and test conditions were use:

Catalyst Activation Procedure

- Use Drakeol-10 as start-up fluid.
- Heat up in N_2 to 200°C.
- Switch to syngas ($H_2/CO = 0.7$, 25% N_2) at 200°C. Maintain 150 psig pressure and 2000 sl/hr kg-Fe space velocity. Heat up to 280°C at about 7°C/hr heat up rate. Maintain 280°C for 12 hrs. Monitor the exit gas for CO, H_2, N_2, CO_2 and CH_4 during the entire activation.

Test Conditions

- Maintain the following conditions for one week;
  Feed Gas: $H_2/CO = 0.7$ (Add N_2, as needed, as an internal standard)
  Reactor Temperature: 265°C
  Reactor Pressure: 200 psig
  Space Velocity: 2500 sl/hr kg-Fe

- Monitor exit gas composition (at least CO, H_2, N_2, CO_2, CH_4, C_2, $C_2^=$, C_3, $C_3^=$) as well as accumulation rates in hot and cold traps for an estimate on catalyst activity, selectivity as well as liquid/wax production rate.

Activity test results indicated that catalyst # 11, which was supported by kaolin, had the best activity. Both methane and wax selectivity appeared low indicating good selectivity towards middle range hydrocarbons. Catalyst # 3, which was silica supported with about 1% K_2O, appeared to be the second best in activity. However, it had very high methane selectivity. The unsupported iron oxide catalyst (# 8), showed very little activity. This was a surprise and probably due to the activation procedure used. Catalyst # 7, a silica supported catalyst with 2% K_2O, also indicated low activity. It appeared that in comparison to catalysts studied during the initial Fischer-Tropsch demonstration (1), the above catalysts had lower activity due to calcination which was employed to improve the mechanical integrity of the catalysts.

Further development work, including more appropriate activation procedures, was conducted. Activation using CO, instead of a mixture of CO and H_2, was investigated. Activity results from CAER for all four catalysts are shown in Figure 5. Results indicate substantial activity improvements with CO activation instead of syngas activation. It appears that the calcined catalysts are harder to activate and are susceptible to hydrothermal sintering when activated in the presence of hydrogen. Even though the conversion dropped during the test with catalyst #11 at CAER, a stable run was obtained with that catalyst at Exxon Chemicals. The conversion decline at CAER was probably due to loss of oil from the reactor during the runs shown in Figure 5. With low wax selectivity, the wax production in the reactor was not keeping up with the oil loss through vaporization.

Sedimentation Tests

Sedimentation tests were conducted for the four selected catalysts. The purpose of these tests was to compare slurry properties of the new catalysts to that of demonstrated catalysts. The sedimentation tests are qualitative and were developed during the Liquid Phase Methanol program. These tests have been successfully used in differentiating catalyst for their slurry properties. Currently, the tests are limited to testing catalysts in their oxidic form.

The sedimentation tests show a collective effect of particle properties such as size, density, shape and orientation, and interference from neighboring particles. Fluid viscosity and density also affect the sedimentation rate. Fast settling rate and tighter packing are preferred slurry properties. Smaller packing volume is also desirable from a volumetric productivity point of view, since it allows loading of more catalyst on a weight basis into a fixed reactor volume.

The tests are conducted with 19 grams of catalyst and 77.85 grams of Drakeol-10 oil in a 100 ml graduated glass cylinder. The catalyst and oil are shaken to mix and then the catalyst is allowed to settle. The separation line between the concentrated and the dilute phase is noted visually.

Results of these tests with the four Fischer-Tropsch catalysts are compared with two methanol catalysts in Figure 6. Catalyst # 8 and 11 show settling rates similar to a demonstrated methanol catalyst (F21/-43) and hence are considered acceptable. Catalyst # 3 and 7 have settling rates closer to methanol catalyst # F51/-27, which did not qualify for the slurry phase. Since these tests are qualitative, catalysts are not qualified or disqualified on the basis of these tests alone. Instead, this information is added to other information available on the catalyst for making a decision on catalyst selection.

Catalyst Scale-up

Two catalysts were selected for further development based on activity test results, settling test results, physical properties as well as ease of preparation: Catalyst # 11 (Kaolin Supported) and # 8 (Unsupported). UCI prepared about 20 lbs of each catalyst with the catalyst particle size specification of 80% above 20 microns, 0% below 5 microns and a target of 70 micron median particle size. A target α of about 0.65 was agreed upon to minimize the wax production rate.

UCI was successful in achieving the desired 70-75 micron average particle size for the two catalysts (new batch # 1185-75/Kaolin Supported and # 1185-78/Unsupported). The Fluid Bed Attrition Tests (FBAT) performed at UCI on the two catalysts indicated very good attrition resistance (about 1% loss in 15 hrs.). Settling tests conducted at Air Products indicated good slurry properties for both the catalysts. Activity tests were conducted at CAER for the two catalysts. C_{28} hydrocarbon was used as start-up medium instead of Drakeol-10 to reduce the liquid loss from the reactor. The results are shown in Figures 7-10. Excellent activity and stability was observed for both the catalysts (85 - 90 % CO conversion). The unsupported catalyst appeared to have a lower α compared to the kaolin supported catalyst (Figures 8 and 10). On the basis of lower α and a more uniform particle size distribution, the unsupported catalyst (UCI # 1185-78) was selected for the LaPorte run.

A CSTR test with a heavy wax as a slurry medium was conducted at CAER to better define the α of catalyst. C_{50} polyethylene wax from Allied Signal was stripped under vacuum and then loaded into reactor to practically eliminate liquid loss from the reactor. This would also eliminate the C_{28} peak interference experienced with the use of C_{28} liquid. Results of the test are shown in Figures 11-13. A low α (0.67 - 0.72) of the catalyst along with excellent catalyst activity were confirmed. With such a low α, the liquid level in the reactor would rise very little, if any, at 270°C and higher. This was an important experiment, as a low α (< 0.71) would allow a successful LaPorte operation with a constant catalyst inventory, even if filtration proved to be difficult.

CATALYST ACTIVATION AT CAER

A catalyst-wax separation filter test was planned at Mott Metallurgical with activated catalyst to check the filtration design parameters. Several batches of the unsupported Fe catalyst were activated at CAER. Generating representative activated catalyst for a filter test proved to be as difficult as anticipated. Activation runs conducted in stirred autoclaves indicated catalyst breakdown. The breakdown appeared to be mechanical due to the stirrer as it was observed even under nitrogen flow. So further activations were conducted in a 2" ID bubble column. Initial activation was conducted with a 98° C/hr heat-up rate, 25 wt% catalyst concentration and 100% CO as a reductant at 175 psig pressure and 1400 sl/hr-kg Fe space velocity. The activation appeared to be significantly better than the stirred autoclave, with minimum particle attrition. However, the reactor inlet plugged due to excessive carbon formation.

Subsequently, the catalyst was activated at milder conditions than previously: lower heat-up rate (~ 7°C/hr), lower catalyst concentration (15 wt%), ~25% N_2 with CO for activation. The temperature ramp during the activation is shown in Figure 14. Compared to the previous activation, the space velocity was increased (6000 sl/hr-kg Fe) and the pressure was reduced (85 psig) to increase the linear velocity to 0.14 ft/sec. Perhaps the reactor inlet plugging during the first run was caused by catalyst settling due to the low linear velocity used (0.02 ft/sec). Since the previous run resulted in almost 200% of theoretical carbiding, a limit of 120% carbiding was set. CO_2 concentration in the effluent as a function of on-stream time is shown in Figure 15. The CO_2 concentrations were much lower than the previous run with the CO_2 concentration showing a single peak and returning to the baseline after 30 hours. The total carbiding amounted to 112% of theoretical (Figure 16). From an operational point of view, this was a highly successful activation. There were no upsets or plugging problems through the run.. A sample of the carbided sample was analyzed by SEM. It appeared that some of the particles did breakdown to fines. However, the attrition was lower than that observed in the autoclave. Three more activations were conducted at the same conditions. Surprisingly, all the additional three activations appeared to result in even lower attrition.

CAER also conducted a fixed bed activation, which showed no particle breakdown. A CSTR test with the same activation procedure as the bubble column procedure showed good catalyst activity (~85% CO conversion).

CROSS-FLOW FILTER TEST

As planned, a cross-flow filter test was conducted with the activated unsupported catalyst at Mott Metallurgical on November 16-18, 1993. Details of the test are included in Volume II, Appendix B. The bubble column activated catalyst was tested. The catalyst, which was slurried in Ethylflow C_{30} oil, was passivated in the bubble column after the activation. The test proved to be extremely successful. Initially, a 1 micron filter element was tested. Filtration was conducted at 130-145 °F with the C_{30} oil to simulate the wax viscosity at 250-300 °F. In service, this did not handle the catalyst fines present in the feed material. Particle breakthrough was evident in the filtrate. To improve the performance, a smaller pore size element (0.2 micron) was tested next. The filtrate was clear with expected flux rate for the small pore size. The filtration continued successfully with this element for the duration of the test. The results are summarized in Figure 17. The flux rate remained extremely stable at about 0.02 gpm/ft^2 throughout the two and a half days of testing. No backflush was needed during the entire test. On Day 2, due to slow heat up, the flux was somewhat lower after starting up. With a faster heat-up rate on Day 3, the system reached the expected flux quickly. It appeared that temperature maintenance was critical as viscosity is a strong function of temperature in the low temperature range. A different shut down procedure was implemented between days of operation during this test. The slurry was drained from the system and stored in bottles overnight. It appears that during the F-T I filter test at Mott, overnight stirring at relatively high speed in the reservoir may have caused the particles to break down. During the current test, effects of various process parameters were briefly studied. This included the effects of backflush, linear velocity and pressure. Expected system behavior was observed during these experiments.

The results of the filter test indicated a successful slurry separation. A smaller pore filter element (0.2 micron) exhibited a stable performance with a finer catalyst. As expected, the flux rate with the smaller micron grade is lower (15% of the design flux for 1 micron element). However, the flux rate was adequate for use with the low α catalyst. Installing the 0.2 micron filter element in the existing LaPorte system gave a capability of filtering up to 4 gph of product wax. Obviously, a high α catalyst would require significantly higher (~ 9 times) filter area.

CATALYST QUALIFICATION

Following the confirmation of low α of the catalyst at CAER and a successful filter test at Mott, 2000 lbs of the unsupported iron oxide catalyst was ordered from UCI. Since this was a development catalyst, UCI first produced 500 lbs of catalyst (UCI # 1185-149) to check if the material can be produced according to the specification. Results from tests conducted at UCI on a composite sample are compared with the specifications in Table 2. The chemical and physical properties of the catalyst were close to the specifications.

Activity tests from CAER indicated that the catalyst performance was similar to the earlier bench scale preparation (UCI # 1185-78). CO conversion was stable for 150 hours in 85-90% range (Figure 18), with α_2 of 0.68-0.72 (Figure 19). The C_1 - C_4 make was similar to that for Catalyst # 78. Hence, the catalyst was certainly acceptable on the basis of activity, selectivity and stability. Activity test conducted at DOE-PETC showed significant loss in conversion. It appeared that the hollow stirrer shaft in the autoclave plugged, causing the decline in conversion. Another run conducted later at PETC with a second 500 lbs batch sample indicated catalyst performance similar to CAER (Figures 20-21).

Particle size distribution calculated by CAER on the basis of SEM analysis indicated particle size in the 10-80 micron range (Figure 22). Tests conducted by DOE using Microtrac (Laser Diffraction) confirmed the large particle size initially (69 microns average), but showed lower particle size in subsequent analysis. Either the large particles were breaking down, or they were settling out over a period of time. Tests conducted at Air Products in Microtrac confirmed the above trend. It appeared that the initial particle size was large as indicated by tests at UCI. However, size reduction was likely due to catalyst handling.

Atomic Adsorption tests conducted at DOE indicated the composition comparable to that reported by UCI. DOE also measured the density to be close to UCI's reported density. Settling test conducted at Air Products indicated acceptable settling characteristics, with settling rate similar to catalyst # 78 (Figure 23).

In summary, the catalyst activity, selectivity and stability were as expected. The chemical composition and density were close to the specifications. The initial particle size was large; however, the catalyst could get finer due to handling. With the α being low, filtration problems were not expected. Based on the above information, it was decided to go ahead with the catalyst production. UCI completed 1500 lbs of the catalyst manufacture and six drums of the catalyst were received at LaPorte. Physical and chemical data on the entire batch are given in Table 3.

STARTING SLURRY MEDIUM

Since one of the goals of the catalyst development effort was to achieve a low α, it was desirable to start up the reactor system with wax. Low wax production rates would require a very long time to reach a steady state. Two alternatives were considered: process slurry from F-T I LaPorte run at Kerr-McGee's pilot plant using supercritical extraction, or use Shell's intermediate product wax. In order to keep the project costs down, it was decided to start up with Shell's wax. The catalyst performance should be independent of starting medium so long as it does not contain any contaminants. Composition of the wax is given in Table 4.

DEMONSTRATION RUN PLAN

A run plan for the F-T II run is summarized in Table 5. A 15-day run was planned. The run included operating conditions of interest for all the partners. Aggressive conditions such as 44 wt% slurry concentration, high productivity with 3.3 MMBtu/hr heat of reaction and high linear velocity of 0.45 ft/sec were planned. Charging extra catalyst (44 wt% vs. 33 wt% originally planned) would give flexibility to achieve high production rates even if the filtration system had to be put on line for higher than expected wax production. The viscosity of the slurry at 44 wt% concentration was considered acceptable based on data obtained by Shell with fresh catalyst (Figures 24-25). The viscosity was measured using Haake Dynamic Viscosity Meter which is a rotating disc type machine. A high conversion (80%) was expected at most of the conditions. A repeat run was planned at the end of the process variable study to check for catalyst stability. A one-day tracer study was also planned towards the end of the run to evaluate liquid and vapor mixing in the reactor. If filters were not needed during the run, they would be tested after shut down for catalyst-wax separation. Run Authorizations for the demonstration (# 41, 42 and 43) are included in Appendix C.

RESULTS AND DISCUSSION

Start-up wax from Shell (1110 lbs), flush liquid Ethylflow (162 lbs) and UCI Catalyst L-3950 # 1185-149 (985 lbs) were mixed to make a 44 wt% slurry in the slurry preparation tank. The slurry was preheated to 121°C (250°F) in the tank and then transferred to the reactor. A Run Chronology is included in Appendix D.

Catalyst Activation (F-T II)

The catalyst activation procedure is given in Table 6. The activation began with 100% nitrogen flow. CO was introduced to the reactor slowly when the reactor reached 149° C (300°F). An 11°C (20°F) temperature rise was observed with the introduction CO. This heat of adsorption was anticipated based on the experience during F-T I. The reactor temperature was ramped up and CO_2 production was monitored. The temperature ramp, the effluent CO_2 concentration, and calculated cumulative CO_2

production are plotted as function of activation time in Figures 26-28. The initial spike in CO_2 concentration was perhaps due to a lower flow rate during start-up. Between 182°C (360°F) and 216°C (420°F), a peak in CO_2 concentration was observed. This is similar to what was observed in a bubble column activation at CAER and may be due to reduction of CuO at a lower temperature. The major peak of CO_2 in effluent started at 216°C (420°F). The CO_2 production trend was very similar to that observed at CAER. The activation was stopped after 12 hours on-stream at 270°C (518°F), when 128% of theoretical carbiding was complete. The 120% target was exceeded as the CO_2 concentration was slowly coming down to the baseline.

Process Variable Study (F-T II)

The reactor temperature was reduced to 240°C under CO/N2 feed gas. H2 was brought in to begin Fischer-Tropsch synthesis. The operating conditions were adjusted to conditions of Run No. AF-R11.1. The initial catalyst activity was lower than expected, CO conversion was 35% vs. 80% expected based on autoclave data. The low α nature of the catalyst was confirmed. In order to improve performance, a number of operating parameters were varied (see Table 7). The temperature was first increased from 265°C to 270°C, with little improvement in performance. Unsteady nuclear density readings and reactor temperatures were observed. To increase mixing, the gas velocity was increased by reducing the reactor pressure. Further mixing was imposed by introduction of additional N_2 in the feed. The reactor temperatures appeared to be more steady but the nuclear density readings seemed to be getting worse with very large swings.

The slurry was then diluted by operating the reactor at the maximum height, N_2 was backed out, and the gas velocity was reduced by increasing the pressure to 300 psig. This was an effort to reduce gas slugging and channeling. Both reactor temperature and nuclear density readings became steadier; however, the catalyst performance showed a decline. The CO conversion declined from 35% (at 10 hrs on-stream) to 26% (at 33 hrs on-stream) even when the temperature was increased from 265°C to 270°C and the pressure increased from 200 to 300 psig. This showed a clear evidence of major loss in catalyst performance. Next, the syngas composition was switched from 0.7 H_2/CO to 2.0 H_2/CO. The objective was to remove some carbon that may have deposited on the catalyst. The catalyst performance did not show any improvements. Higher CH_4 and lower CO_2 were observed as expected with the higher H_2 concentration in the feed gas. However, the syngas conversion did not increase. Even increasing the reactor temperature to 288°C did not show any effect.

$CO/H_2/CO_2/CH_4$ concentrations in the product gas as well as reactor and utility oil temperatures during the two days of operation are shown in Figures 29-31. CO_2 and CH_4 showed continuous decline while CO and H_2 increased. The difference between utility oil in and out temperatures narrowed. Also, the two utility temperatures came closer to the average reactor slurry temperature. These trends indicate decline in heat of reaction which is consistent with the GC results.

When the slurry temperatures were being ramped to 300°C (572°F), temperatures at some locations in and around the reactor reached near 329°C (625°F), tripping a shut down alarm. The plant depressurized automatically and was purged with nitrogen. The plant was started up after 45 minutes, but another high-temperature alarm tripped the plant again. It appeared that there was some catalyst in the reactor outlet. At that point, it was decided not to start up the plant again, as all the available data indicated that the slurry was not productive in the operating range of the bubble column. The reactor was cooled under nitrogen and the slurry was drained. The slurry was found to be highly viscous and was extremely difficult to flow even at 150°C. The reactor was then filled with Drakeol-10, heated to 200°C overnight and drained. Even the flush oil appeared unusually viscous when drained.

Analytical/Autoclave Investigations

A list for possible causes of the lower performance was generated as follows: excessive slurry concentration, carbon build-up in the slurry, chemical poisoning, and/or poor catalyst activation. Spent slurry samples were shipped to Air Products (Allentown), Shell (Amsterdam), CAER and PETC. Extensive analytical and activity testing were conducted to determine the cause of deactivation. The analytical work included: Dynamic viscosity of the slurry; Pyrolysis Combustion Mass-spectrometric Elemental (PCME) analysis to determine carbon in the slurry, as well as on the catalyst; C/Fe ratio; oxidation state of Fe; elemental analysis (Cl, S, Ni, Fe, Cu, K); particle size distribution, surface area, and pore volume.

Conclusions from these tests are summarized as follows: No chemical poisons were found (No net chloride or sulfur pickup). No significant carbon build-up was observed in the slurry. The spent catalyst was mostly Fe_3O_4, with some Fe_5C_2. However, significant amount of carbon was found on the catalyst. It appeared that the carbon on the particles acted as binder to agglomerate.

The spent catalyst average particle size was 3-7 microns. It had adequate surface area, which may indicate good activity. Viscosity of the spent slurry was found to be much higher than the fresh slurry. Several autoclave tests were conducted at CAER and PETC to check performance in the range of 25-30 wt% slurry concentration. This range represented lower concentration than the F-T II LaPorte operation but higher concentration than previous autoclave tests with the UCI catalyst. The activation procedure was altered to reduce CO exposure time by switching to CO at a higher temperature and increasing the heat up rate. Also, the activation would be terminated after reaching 100% of theoretical carbiding. Autoclave tests were successful with the new activation procedure for both 25 wt% and 29 wt% slurry, although the 29 wt% slurry required higher stirrer speed (1100 vs 750 RPM) to achieve good activity.

Based on the above information, it appeared that the main cause of the lower catalyst performance during F-T II was the increase in slurry viscosity due to carbon formation at high slurry concentration. After activation, the slurry was too viscous to be mixed adequately in the bubble column. The viscosity also caused the gas to channel and slug, as indicated by the nuclear density measurements during the run. Following discussions between Air Products, Shell, PETC, and CAER personnel, it was decided to make a run with 29 wt% slurry concentration. The goal of 120-150 grams HC/ hr-liter of reactor volume would be achievable after concentrating during the run to 33 wt%. A run plan for this second run (F-T IIA) is given in Table 8.

Catalyst Activation (F-T IIA)

The reactor was reloaded with Drakeol-10 and operated under syngas to check out the system. The system appeared normal. Drakeol-10 (1175 lbs) and UCI catalyst (480 lbs) were then charged to make up 29 wt% slurry. Drakeol-10 was used as a slurry medium to simplify slurry handling. The slurry was heated up in the reactor under 100% N_2 flow. The activation procedure is given in Table 9. At 220°C (428°F), CO was introduced to the reactor slowly. A 11°C (20°F) temperature rise, associated with the heat of adsorption, was observed with the introduction CO. The reactor temperature heat up was continued at 17°C/hr (30°F/hr) and CO_2 production was monitored. The temperature ramp, effluent CO_2 concentration and calculated cumulative CO_2 production are plotted as function of activation time in Figures 32-34. An initial spike in CO_2 concentration attributed to a lower flow rate during start-up observed similar to F-T II. Also, a peak in CO_2 concentration probably due to reduction of CuO was observed at low temperature. The major peak of CO_2 in the effluent occurred at the final temperature of 270°C (518°F). The CO_2 production trend was very similar to that observed at CAER. However, the activation appeared to be slower than the autoclave. The activation was stopped after 12 hours on-stream at 270°C. The carbiding was about 92% complete based on Fe_5C_2 formation. The CO_2 concentration in the effluent had leveled off at about 1.5% when the activation was halted.

Process Variable Study (F-T IIA)

At the end of the activation, H2 was introduced to begin a process variable study for F-T synthesis. The operating conditions were adjusted to conditions of Run No. AF-R12.1 (baseline). The catalyst activity was close to expectations (Table 10). For example, the CO conversion was 84.7 % compared to about 79 % in the CAER autoclave. The CO_2 selectivity was 44.9% indicating good water gas shift activity. As expected, the C_1-C_5 selectivity was very high (64.7 mole% C on CO_2-free basis), consistent with the low α of the catalyst. The reactor productivity was 41.4 grams HC/hr-liter of reactor volume. Toward the end of this data period, a significant decrease in gas hold-up was observed. The gas hold-up decreased from 24 vol% to 7-10 vol%. Also, a drop-off in CO conversion was observed. The slurry appeared to be showing some signs of thickening up. As a result, it was decided to move immediately to high productivity conditions (Run No. AF-R12.2), which was the main objective of the run. The catalyst activity was slightly lower than expected at the new conditions (Table 10). The CO conversion was 54.2%, and the CO_2 selectivity was 43.7% indicating good water gas shift activity. The reactor productivity was 136.4 grams HC/hr-liter of reactor volume, within the target of 120-150 grams HC/hr-liter. This productivity is more than five times what was achieved during F-T I (25 grams HC/hr-liter). The C_1-C_5 selectivity remained high (62.6 mole% C on CO_2-free basis). The reactor performance was stable with excellent temperature profile and steady nuclear density readings. The gas hold-up, however, remained surprisingly very low - about 9 vol%.

In order to increase reactor productivity, several changes were made in the operating conditions. Results at these conditions are summarized in Table 11. Temperature was first increased from 302°C (576°F) to 312°C (593°F, Run No. AF-R12.3A). Surprisingly, conversion did not increase with the temperature increase. It appeared that mass transfer resistance was limiting the performance. The reactor productivity at this condition was 136.1 grams HC/hr-liter of reactor volume. Due to concerns about accelerated carbon formation at high temperature, the temperature was dropped to 297 °C (567°F) after spending 8 hrs at the high temperature (Run No. AF-R12.3B). The CO conversion at these conditions was 42%. Thus, significant deactivation had occurred at high temperature. Next, the H2/CO ratio in the feed was increased from 0.72 to 1.27, while holding the CO feed rate constant (Run No. AF-R12.3C). The objective here was to increase the gas velocity while increasing the reactor productivity. The reactor productivity increased from 97.6 to 114.9 grams HC/hr-liter. The conversion remained the same, but the CO_2 selectivity was lower, as the shift reaction was suppressed. Because of concerns about oxidizing the catalyst with higher water partial pressure in the reactor, the H_2 flow was reduced to the previous level after an hour (Run AF-R12.3D). A shutdown test was then conducted to confirm earlier gas hold-up estimates. The gas hold-up was found to be about 6%. The reactor slurry was diluted next by increasing the reactor height from 17.8 ft to 20.3 ft (Run No. AF-R12.3E). The conversion increased from 40.3% to 48%, and the reactor productivity increased from 104.3 to 111.7 grams HC/hr-liter. The gas hold up remained the same.

To improve the slurry properties, it was decided to remove some slurry from the reactor and replace it with Drakeol-10. A large change was necessary to dilute and create room for larger hold-up. The reactor was cooled down and a third of the slurry was drained. The reactor was brought back on-stream at the 20 ft slurry height (Run No. AF-R12.3F). The slurry concentration dropped from 23 wt % to 14.4 wt%. The initial CO conversion was about 30%, which was consistent with a kinetic space velocity effect (Table 12). However, the conversion declined steadily through this data period to 21%. The CO_2 selectivity was low (29%), indicating a significant drop off in shift activity as well. The slurry properties showed some improvements after dilution. The nuclear density readings were more stable, but the gas hold-up remained low - about 9 vol%. The dilution seemed to have stabilized the slurry, however, the catalyst activity continued to decline steadily.

Operating conditions were changed to go to a higher linear velocity condition (0.36 ft/sec inlet, Run No. AF-R12.4). The CO conversion averaged about 15% (Table 12), which is lower than expected. The shift activity continued to decline as indicated by the low CO_2 selectivity (20%). The nuclear density readings showed some instability. The gas hold-up increased to about 13 vol%. The operating conditions were then returned to the baseline condition (Run No. AF-R12.5A) to estimate the extent of catalyst deactivation. The feed flow rate was not changed from the initial baseline condition to maintain the linear velocity. So, the space velocity was 33% higher due to the earlier dilution. The CO conversion averaged only 10%, indicating severe catalyst deactivation. Also, the CO_2 selectivity was low (22%), indicating low shift activity. The slurry properties appeared acceptable. The nuclear density readings were stable and the gas hold-up was estimated at 7 vol%. Since the catalyst performance was very low at 270°C, it was decided to increase the reactor temperature to 309°C (Run No. AF-R12.5B). If the catalyst was kinetically controlled, the conversion would increase significantly. The CO conversion did increase dramatically to about 44%. The CO_2 selectivity also increased to 46%, indicating good shift activity at these conditions. The gas hold-up was estimated to be about 6 vol%. At the end of the mass balance period,