EXECUTIVE SUMMARY

Slurry phase Fischer-Tropsch technology was successfully demonstrated in DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas. Earlier work at LaPorte, with iron catalysts in 1992 and 1994, had established proof-of-concept status for the slurry phase process. The third campaign (Fischer-Tropsch III), in 1996, aimed at aggressively extending the operability of the slurry reactor using a proprietary cobalt catalyst. Due to an irreversible plugging of catalyst-wax separation filters as a result of unexpected catalyst fines generation, the operations had to be terminated after seven days on-stream. Following an extensive post-run investigation by the participants, the campaign was successfully completed in March-April 1998, with an improved proprietary cobalt catalyst.

These runs were sponsored by the U. S. Department of Energy (DOE), Air Products & Chemicals, Inc., and Shell Synthetic Fuels, Inc. (SSFI). A productivity of approximately 140 grams (gm) of hydrocarbons (HC)/ hour (hr)-liter (lit) of expanded slurry volume was achieved at reasonable system stability during the second trial (Fischer-Tropsch IV). The productivity ranged from 110-140 at various conditions during the 18 days of operations. The catalyst/wax filters performed well throughout the demonstration, producing a clean wax product. For the most part, only one of the four filter housings was needed for catalyst/wax filtration. The filter flux appeared to exceed the design flux. A combination of use of a stronger catalyst and some innovative filtration techniques were responsible for this success. There was no sign of catalyst particle attrition and very little erosion of the slurry pump was observed, in contrast to the Fischer-Tropsch III operations.

The reactor operated hydrodynamically stable with uniform temperature profile and gas hold-ups. Nuclear density and differential pressure measurements indicated somewhat higher than expected gas hold-up (45 - 50 vol%) during Fischer-Tropsch IV operations. The high gas hold-up was confirmed by a dynamic gas disengagement test conducted at the end of the run. Heat transfer in the reactor was better than expected. Heat, mass and elemental balance calculations indicated excellent closure. After the initial learning curve with system dynamics, the plant was restarted very quickly (24 hours and 17 hours) following two plant trips. This demonstrates the ease and flexibility of the slurry technology.

In-situ reduction of catalyst pre-cursor was completed successfully during F-T IV operations. Water measurements proved to be inaccurate due to wax/oil contamination of the analytical system. However, the reduction appeared to proceed well as close to expected syngas conversion was obtained at the beginning of the run. The selectivity to wax was lower than expected, with higher methane selectivity. Returning to the baseline condition indicated a productivity decline from 135-140 to 125-130 gm HC/hr-lit. of reactor volume in two weeks of operation. This may be a result of some catalyst loss from the reactor as well as initial catalyst deactivation.

Significant quantities of product and samples were collected for further processing and analysis by the participants. Gas, liquid and solid phase mixing were studied as planned at two operating conditions using radioactive materials. A large amount of data were collected by ICI Tracerco using 43 detectors around the reactor. The data are being analyzed by Washington University as part of the Hydrodynamic Program with DOE.

INTRODUCTION

Domestic development of a slurry-phase Fischer-Tropsch (F-T) process is of considerable interest to Department of Energy's Indirect Liquefaction program. The Federal Energy Technology Center (FETC) sponsors the Indirect Liquefaction program as part of its Coal Liquefaction program. The overall goal of the Coal Liquefaction program is to develop a 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. In addition, several industrial companies have an interest in developing the technology for remote gas conversion.

During October 1996, operations were carried out at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, to evaluate further improvements to the slurry process for Fischer-Tropsch synthesis. Earlier work at LaPorte in 1992 and 1994, had established proof-of-concept status for the slurry phase process. The first campaign in 1992 was a 19-day demonstration of the technology at 1 T/D product scale and addressed scale-up issues such as catalyst activation, catalyst performance and hydrodynamics (1). 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 (2). A very high level of reactor productivity (more than five times the F-T I productivity) was demonstrated for slurry phase Fischer-Tropsch synthesis in 1994 (3). Reactor productivity of 136 grams of HC/hr - liter of slurry volume was achieved, which was within the target of 120-150. The productivity was constrained by mass transfer limitations, due to slurry thickening. With an improved catalyst, if carbon formation can be avoided, there appeared to be significant room for further improvements.

The third campaign, in 1996, aimed at aggressively extending the operability of the slurry reactor using a SSFI proprietary catalyst. This demonstration had significant industrial backing. In addition to DOE, this run was sponsored by Air Products and Chemicals and Shell Synthetic Fuels, Inc. Preliminary results from this run were presented earlier at a DOE’s Contractors Review Conference and an AIChE meeting (4, 5). Due to an irreversible plugging of catalyst-wax separation filters as a result of unexpected catalyst fines generation, the operations had to be terminated after seven days on-stream. Following an extensive post-run investigation by the participants, the campaign was successfully completed with an improved SSFI proprietary catalyst in March-April 1998 (Fischer-Tropsch IV). A paper discussing the evolution of the technology through the four pilot plant campaigns was presented at the 1998 International Pittsburgh Coal Conference (6). Key issues such as catalyst-wax separation, reactor productivity improvements, reactor temperature control, and in-situ activation were addressed. The paper only included preliminary results from the F-T III and IV, as detailed analysis was pending. This report provides details and final analysis for the two runs.

OBJECTIVES

The principal objective of these runs was to conduct Fischer-Tropsch synthesis in a large diameter bubble column and demonstrate:

(1) Sustainable high productivity - a space time yield of 150 grams hydrocarbon per hour per liter of reactor volume;
(2) Activity and selectivity of SSFI's proprietary catalyst;
(3) Catalyst-wax separation by external cross-flow filtration; and
(4) In-situ reduction of catalyst pre-cursor.

The runs would also allow the participants to study other issues such as:

(1) Large scale fluid dynamics,
(2) Erosion,
(3) Catalyst stability, and
(4) Catalyst attrition.

ENGINEERING AND MODIFICATIONS (F-T III)

Process Description

Simplified process flow diagrams for Fischer-Tropsch III are given in Figures 1 and 2. The operation of the AFDU for Fischer-Tropsch is described as follows (refer to Fig. 1): Carbon monoxide, hydrogen and nitrogen are blended and compressed using the 01.10 compressor to obtain desired fresh synthesis gas composition and flow. The fresh feed is then mixed with recycle feed from the 01.20 recycle compressor. High pressure hydrogen is used to supplement the fresh feed. The high pressure hydrogen may be compressed using the recycle compressor if its pressure is not adequate. The combined feed gas is 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, water and carbon dioxide. The heat of reaction is absorbed by the slurry medium and then rejected to an internal heat exchanger. Heavier hydrocarbon fraction of the product (heavy wax) is liquid at reaction conditions and accumulates in the reactor. The reactor effluent is first sent through the 27.11 cyclone separator to remove entrained slurry and then 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. Condensed hydrocarbon and water are separated from the vapor phase in the 22.10 separator. After analysis, part of the uncondensed vapor is sent to the flare as a purge stream, most of this stream is recycled using the 01.20 recycle compressor. The liquids from the 22.10 are de-pressurized and sent to vessels 22.11, 22.15 and 22.16 in sequence. The product from the 22.16 is sent to a tank trailer in batches, periodically.

The excess slurry from the reactor is drained into the 27.15 slurry degasser. Following degassing, the slurry is cooled by about 36°F in the 21.70 catalyst-wax slurry cooler. The slurry is then pumped using the 10.62 catalyst-wax circulation pump to the 22.62 cross flow filter for wax removal. The product wax from the filter is collected in the 28.30 prep tank and then drained into trailer or drums and sampled periodically. After filtration, the concentrated slurry is sent back to the reactor. The liquid level in the reactor is measured by the nuclear density gauge DIC-585 and is controlled by position of the control valve which directly controls wax withdrawal from the filters. In the reactor, particles are kept fully suspended by the upward liquid flow (also in the absence of gas flow), as the liquid velocity is well beyond the particle settling velocity.

A liquid level is maintained in the 27.12 slurry carryover surge tank which receives slurry from the 27.11 cyclone separator. Excess liquid from the 27.12 is sent to the 27.10 reactor using the 10.52.02 carryover oil pump. The light wax from the 22.14 separator is de-pressurized into the 27.13 tank. Light wax in the 27.13 tank is circulated around using the 10.60 pump and kept warm by flowing it through the 21.85 heat exchanger. Heavy wax in the 28.30 prep tank is circulated around by the 10.52.01 pump. The pressurized wax is used to back-flush the 22.62 filters when needed. Waxes from the 27.13 and the 28.30 are drained into trailer or drums.

Flows and compositions are measured at various strategic points in the process including feed and product gas.

Bubble Column Reactor

The 27.10 bubble column reactor is 28.3' top to bottom and 22.5" inside diameter. The maximum slurry level is about 20' with the remainder being vapor disengagement space. A goal of 150 grams HC/liter reactor vol - hr of HC productivity, which was same as F-T II, was set. The heat exchanger, which was installed prior to F-T II (3), was evaluated for F-T III and found adequate. The 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. Detailed drawings of the heat exchanger were included in the Fischer-Tropsch II topical report (3). The external surface area of the U-tubes is 217.7 ft^2 based on 36 ft length. The heat exchanger occupies 9.6% of the reactor cross-section. The reactor is fitted with a number of thermocouples, located at various elevations. A nuclear density gauge is mounted on an external track and spans the space occupied by the internal heat exchanger. The maximum temperature for the reactor is $315^{o}C$ at the maximum pressure of 1000 psig. Operations at higher temperature are feasible by lowering the operating pressure.

Analytical Set-up

Two of the AFDU gas chromatographs (GCs) are set up with two flame ionization detectors (FIDs) each, for both hydrocarbon and alcohol analysis. The hydrocarbon analysis uses DOE-FETC's methods (7). Both the GCs are dedicated to product gas analysis, measuring concentrations of C_1-C_8 hydrocarbons. Two other GCs are set up with two thermal conductivity detectors (TCDs) each. These GCs measure 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}) analysis were performed by SSFI. Samples from 22.11 and 22.16 liquid (HC + aqueous phase), 22.14 light wax, 28.30 heavy wax as well as spent slurry from 27.10 were taken and shipped to SSFI.

Water analyzers were added to measure water production during the reduction of catalyst pre-cursor. This included adsorbent tubes for periodic analysis and Panametric instruments for instantaneous measurements.

Catalyst-wax Separation System

The catalyst-wax separation has been recognized as a challenge. No single proven technology exists in the public domain. An external system of tangential (cross) flow filters was used at LaPorte based on SSFI’s pilot plant experience. Filtration was preferred at reactor pressure to avoid catalyst attrition that may occur if a control valve is used to reduce the pressure. The existing filtration system at LaPorte was designed for low pressure, with limited capacity. So, the entire filtration system was redesigned and replaced. The new system was rated at higher pressure (1000 psig) and higher temperature (600°F), with significantly higher capacity. It included four new cross-flow filters in series, a catalyst-wax slurry circulation pump, a slurry cooler and a slurry degasser. A layout of the filtration system is shown in Figure 3. The sketch is not to scale but does show an approximate elevation of the equipment. The degasser was installed close to the top of the reactor to obtain almost the same liquid level in the two vessels. The slurry cooler was located at a level near the bottom of the reactor. The pump and the filters were installed at the ground level. There was no back-up system for filtration. If the filtration did not work as designed, the reactor would have to be shut down. An extra charge of catalyst was available on site for another start-up if the problem could be identified and addressed.

27.15 Slurry Degasser

The degasser was used to separate gas and solid-liquid from the three-phase reactor slurry. The degasser would protect the slurry pump from gas and minimize any further reaction in the loop. The degasser diameter was based on the liquid velocity to be half the bubble rise velocity. A tubular vessel with 8” internal diameter and 8 ft tall was specified. A sketch of the vessel is shown in Figure 4. The instrumentation on the vessel included three thermocouples and a differential pressure transmitter to measure the liquid level, which was maintained at 5 ft level. A cone head was used for the bottom to avoid slurry accumulation. The layout of the degasser was very important (see Figure 3). Liquid level in the degasser was maintained at the same level as the reactor through nozzle T1 and a 3" pipe. A new nozzle was installed and used to return the gas back to the reactor. In case of gas shut down, valve NV-1752-S on nozzle T1 will close and valve NV-1751-S on nozzle P will open to provide continuous liquid flow to the pump. The bypass line with two shut-off valves (NV-1756-S and 3553-S) was provided for start-up. If the degasser does not degas adequately, the pump and filter will see gas in the slurry which could affect their performance.

21.70 Slurry Cooler

Slurry cooling of 36°F was desired to significantly lower the reaction rate. Utility oil exiting from the reactor heat exchanger was used on the shell side to cool the slurry (Figure 2). Use of cooler oil going into the reactor heat exchanger was avoided so that the reactor temperature stability will not be impacted. HTRI (Heat Transfer Research Institute) heat exchanger simulations were performed for the slurry cooler. Oil temperatures based on realistic calculations (2.14 MMBtu/hr heat load) for the reactor heat exchanger were specified. A conservative heat load (2.50 MMBtu/hr) on the reactor heat exchanger would lead to an under-design of this heat exchanger. If the reactor heat exchanger worked much better than designed, the oil would be hotter than expected. In that case, the cooler would not have adequate capacity. The cooler was not substantially over-designed to keep slurry inventory/residence time in the filtration system to a minimum. A horizontal multi-pass flow heat exchanger with segmental baffles on the shell side was specified. It contained 8” internal diameter single pass shell with 6 cross passes and 10 tubes with 3 passes, 11.5 ft long and 0.527” internal diameter.

10.62 Slurry Pump

Due to an anticipated long delivery time for the slurry pump, a process specification for the pump was quickly issued. A centrifugal pump was chosen based on SSFI's experience. The centrifugal pump is more reliable in operation compared to a disc type pump considered which has lower catalyst attrition rate. SSFI's testing showed acceptable level of catalyst attrition. The high temperature, high pressure service was considered severe. There was no back-up for this pump. In case of mechanical problems, the reactor would have to be shut down and the pump repaired on site. A design flow rate of 26 gpm was specified with a head of 107.5 psi. A variable speed motor was utilized to allow flow rate changes during the run.

22.62 Cross-flow Filters

The cross flow filter system consisted of four 10' filters (four parallel elements in each) in series. The elements were 1/2" ID, 5/8" OD, 1 micron grade stainless steel. A tangential velocity of 9 ft/sec would be maintained through the elements. The elements would be back-flushed with clear wax, as needed. The filters were designed for 62 gph of filtrate wax which was the anticipated maximum production rate. The design flux through the elements was 0.059 gpm/ft^2, which was a conservative number based on SSFI's experimental work. The total filtration area of the system was 20.9 ft^2, about 20% higher than required. The filtration performance depended on the catalyst strength. Laboratory testing at SSFI indicated that the catalyst was much harder than those used in F-T I and II. The F-T III catalyst was a supported catalyst which is typically more resistant to attrition. Differential pressure measurements capabilities were installed for individual filter housings. This was necessary to control pressure drop across each filter separately as significant pressure drop was expected for the 40 ft of total length due to the slurry flow through the inside of the elements. The trans-membrane pressure drop would be controlled by throttling manual valves.

Miscellaneous Modifications

Preliminary heat and mass balance calculations indicated that at high conversion (~80%) and high pressure (750 psig), the dew point for water (~235°C) was very close to the operating temperature (240-250°C). The heat exchanger tubes were expected to be significantly colder (170°C), where water could condense out. Water condensation would be an obvious problem for catalyst activity. Hence, it was decided to reduce per-pass conversion to 40% with a recycle of unconverted syngas. The Fischer-Tropsch train was connected to the existing 01.20 recycle compressor to allow the recycle. It was decided not to modify the system for light HC/water separation due to funding limitations.

Miscellaneous changes include:

(1) Differential Pressure (DP) taps and transmitters on the 27.10 Reactor,
(2) Radial thermocouples in the reactor,
(3) Erosion test pieces,
(4) Removal of once -thru connections for the reduction of catalyst pre-cursor.
(5) Relocation of water analysis sample port for catalyst activation from the reactor outlet to the 22.14 vapor-liquid separator outlet to avoid significant hydrocarbon condensation in the water analyzer which could cause interference.

The reactor was modified to accommodate SSFI’s proprietary sparger and optical fiber probe. The probe was installed to measure radial bubble size distribution. A number of signals were connected to SSFI's high speed data acquisition system.

Mass balances were generated using ASPEN simulator based proprietary kinetic and mass balance information available from SSFI. Close agreement was obtained with SSFI's gross predictions and more detailed mass balance information was generated for design purpose.

New instrumentation needing specification included slurry/wax flow meters, differential pressure transmitters, and automatic shut-off valves. In addition, specifications were developed for two new relief valves (PSV-236A/B and PSV-1766) and a rupture disc (PSE-1769).

Hazards Reviews

A Preliminary Hazards Review (PHR) was conducted on February 15, 1996. Mass and energy balances were performed in preparation for the examination of various safety devices and a review of existing relief devices was initiated. Operability reviews were conducted both internally and with SSFI personnel. Automatic shutdown and flush scenarios were developed and engineered.

A Design Hazards Review (DHR) was conducted on May 10, 1996, following completion of P&ID (Piping & Instrumentation Diagram) development. The modifications were divided into six different nodes, and a HAZOP was conducted on each node. The review of existing relief devices was also completed. For a 100% hydrogen case during reduction, two relief devices were found to be inadequate for this run. The reduction outlet gas was rerouted to bypass one vessel, while the other device was replaced.

A number of issues identified during the Design Hazards Review were followed up:

(1) A deadhead condition in the 10.62 pump would result in over-pressure of downstream piping and the 22.62 filters. It was confirmed that the speed control for the pump will not increase the deadhead pressure beyond 150 psi differential. Due to power limitations, the pump speed can only be increased to a maximum of 110% of the current design, which would result in a deadhead pressure differential of 142.5 psi. With PSV-1766 on the 27.15 Slurry Degasser set at 850 psig, the deadhead pressure of the 10.62 pump will not exceed the design pressure of 1000 psig. PSV-1766 is rated for a fire case on the filtration system as well as line blockage on reactor outlet requiring relief of all feed gases (fresh feed compressor, recycle feed compressor and high pressure H_2) at 850 psig.

(2) Three failure cases were considered for PSE-335A/B on the 28.30 Slurry Prep Tank: Vapor passing through fully open LV-203, valve 3611, and liquid flowing through failed open PV-644. The existing disks were found to be sufficiently sized for all three cases.

(3) The relief case for PSV-749A/B on the 27.13 Tank when LV-688 fails open was considered. The relief valves were found to be insufficiently sized for the maximum flow allowed by the existing trim on LV-688. It was decided to purchase a new trim for LV-688 to restrict the flow to the level the relief valves could handle.

A Design Verification Review (DVR) was held on September 10, 1996. All Process hazard review items were completed prior to the review and no new action items resulted. Following the meeting, OSHA PSM safety documentation was issued. Operator training was conducted by process and plant personnel on September 24 and an Operational Readiness Inspection (ORI) was conducted on the 25th of September, prior to the start-up. 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. Open items were completed before commencement of the October demonstration and an approval was given for start-up.

Metallurgical Review

A metallurgical review was conducted to discuss material compatibility for F-T III. A concern was raised about hydrogen attacking carbon in the carbon-steel particularly at H_2 partial pressures higher than 100 psig and temperature higher than 500°F. It was confirmed that stainless steel is being used in the reactor area where these conditions may be reached. Another concern was presence of acids in the water phase corroding the liquid product vessels (22.10, 22.11, 22.15 and 22.16), which are all carbon-steel. SSFI provided the following water phase pH and corrosion rate data:

(1) Analysis of the water produced in the autoclave unit with the SSFI proprietary catalyst yielded pH values ranging from 3.37 to 3.43. Acid corrosion rates at this pH range and at temperatures below 50°C are considered negligible for the total run time.

(2) For the 22.10 vessel, the acid corrosion rate will be negligible due to the low temperature (38°C). In addition, the presence of carbon monoxide will inhibit corrosion at this low temperature.

(3) For the 22.11, 22.15, and 22.16 vessels, on the basis of the low temperature maintained in these vessels (38°C), the acid corrosion rate can be neglected relative to the total run time anticipated.

It was decided to monitor the pH of the liquid while it was temporarily stored in these vessels.

Environmental Reviews

The planned modifications were documented and sent to Radian Corporation to evaluate their impact on air emission. Radian evaluated the proposed modifications and operation to check if we needed a new exemption for this run or a letter documenting these changes was sufficient. Emission calculations were completed for a material balance case corresponding to maximum production and emissions. Both exemption and non-attainment estimates were made and transmitted to Radian. Although there was a net decrease in emissions compared to F-T II, there were instances of individual increases in component emissions. For example, F-T III had higher hourly CO emissions from process equipment because the CO concentration was higher in the reactor effluent due to lower conversion. Also, Volatile Organic Components (VOCs) were higher for hydrocarbon (HC) loading fugitives due to the catalyst selectivity difference. Upon recommendation from Radian, an exemption application for the air emission permit was drafted. Now that the AFDU was an independent facility for air emissions purposes, a significant margin was added to each component for future flexibility, while staying below the exemption limitations. The exemption application was completed and submitted to TNRCC (Texas Natural Resource Conservation Commission). An approval for the exemption was received from TNRCC in July 1996.

Reactor Cleaning

Some heat exchanger tube fouling was noticed through opened nozzles in the 27.10 reactor. There appeared to be a thin coating of the Fischer-Tropsch II catalyst on some spots. It was not known how widely the coating was spread. Industrial cleaning vendors were contacted and proposals obtained from two companies. Rust Industrial Cleaning Services was chosen to run lab tests on the spent slurry from F-T II. Tests indicated successful break down of the slurry using alkaline degreasing solution. On August 15, 1996, the 27.10 reactor was cleaned by Rust. Alkaline degreasing solution was used followed by a water rinse. Limited success was achieved cleaning the tubes. While the degreasing solution drained from the reactor appeared dirty, visible fouling remained on the tube. More cleaning was expected to occur when the reactor was exposed to hot oil during the "carbonyl burnout" before the start of the run.

DEMONSTRATION RUN PLAN (F-T III)

A run plan was developed by the participants to achieve the objectives discussed earlier. A summary of the plan is shown in Table 1. The plan included a process variable scan at nine different conditions. Key parameters to be studied were feed compositions, recycle ratio, and conversion levels. The fresh feed range was from a H_2/CO ratio of 1.72 to 2.07. The recycle ratio varied from 0.8 to 3.3, resulting in a wide range of H_2/CO ratios between 0.65 and 2.07 in the reactor feed. Operating pressure was to be held constant at 710 psig for all but one condition (Run 15.6), when it would be reduced to 520 psig to achieve a high velocity of 0.85 ft/sec. A high productivity of 150 gm HC/lit-hr was targeted at all conditions except the start-up condition (Run 15.1). Reactor temperature levels were chosen to achieve CO conversions per pass in the range of 17-57 %. The target plant CO conversion was 80% at all the conditions with the exception of one (Run 15.7) for which the target was 90%. This matrix of process variables spanned through a large range and approached the plant limits of recycle compression and heat removal capacity. In addition, a high catalyst loading of 42.6 wt% perhaps pushed the slurry F-T technology to its limit. An activity check (Run 15.10) was planned at the end of the process variable scan. A 3-day tracer study would follow to look at gas, liquid, and possibly solid phase mixing at two different conditions. This would be followed by a 2-day dynamic gas disengagement study. At the end of the 30-day operating campaign, a 3-day filter study was planned without syngas operations. The objective of the filter study was to evaluate effects of operating parameters such as trans-membrane differential pressure, slurry velocity, slurry viscosity, and catalyst concentration on filtrate flux. It was decided to use a heavier medium as start-up fluid. Shell's commercial Callista 158 wax would be used.

PRE-RUN SET-UP AND TESTING (F-T III)

All new equipment (27.15 Slurry Degasser, 21.70 Slurry Cooler, 10.62 Catalyst/Wax Slurry Pump, 22.62A/D Cross-Flow Filters and associated instrumentation) was installed and tested. The optical fiber probe and the high-speed data logger provided by SSFI were installed and function tested. The 27.10 Reactor was pressure-tested to check the nozzle installed for the vapor return from the 27.15. Instrumentation check-out and calibration was complete. The gas sampling system was modified to the Fischer-Tropsch mode of operation. A significant amount of time and effort was spent in troubleshooting a data transfer problem between the distributed control system (DCS) and the data acquisition system (DAS). Replacement hardware was installed for the DAS, and new DCS software was put in place so that signals will be available at the minimum frequency needed for process analysis. Nuclear density gauge calibration was completed on 10/4/96, and a nitrogen plant test was performed. Following maintenance on the 10.62 pump, synthesis gas was introduced on 10/8/96 as part of a hot function test (carbonyl burn-out) and final plant check-out.

RESULTS AND DISCUSSION (F-T III)

Start-up wax (Callista-158) was charged to and melted in the slurry preparation tank on 10/10/96. SSFI's proprietary catalyst precursor (CMT-25) was loaded to the slurry preparation tank to make a 41.2 wt% slurry, and the slurry was then transferred to the reactor. A Run Chronology for F-T III is included in Appendix A.

Catalyst Activation

Please note that the word “catalyst” is conveniently used in this report both for the inactive pre-cursor as loaded in the reactor and its activated form. The calculation basis for mass balance purposes is the oxide form unless otherwise indicated.

Catalyst drying began at 20:00 hours on 10/11/96. Reactor temperature was ramped up with a flow of 100% nitrogen to drive the physical water out of the catalyst. Water concentrations were monitored in the system and drying was essentially complete at 23:00 hours on 10/12/96. At that point, hydrogen was brought in to begin catalyst activation using SSFI’s proprietary procedure. In-situ catalyst activation was well controlled using gas recycle. The water concentration level was maintained below the maximum allowed at all times. Water concentrations were monitored using both instantaneous Panametric instruments and accumulated measurements via P_2O_5 tubes. At 07:00 hours on 10/14/96, about 80% of the reduction appeared to be complete based on both the measurement techniques. The activation was considered complete at 12:00 hours on 10/14/96 and the reactor was cooled down to set up for hydrocarbon synthesis.

Further analysis of the activation results indicated an error in the calculations of the accumulated water amount in the P_2O_5 tubes. Applying the correction resulted in significant disagreement between the Panametric and the adsorption measurements. At the end of the activation period, the Panametric indicated 90% completion while the P_2O_5 suggested only 40% completion (see Figure 5). In addition to the calculation error in accumulated water quantity, increasing methane production was also responsible for a decision to terminate activation which may have been premature. Estimated water partial pressures during activation are shown in Figure 6. A multiplier of 0.44 was used to correct the Panametric data based on P_2O_5 data.

Process Variable Study

The filter system was brought on-line prior to introduction of CO. After initial start-up challenges, the filters operated normally through the night. CO was brought in at 20:00 hours on 10/14/96 and, adjustments were made to bring the plant to the conditions of run AF-R15.1. This was a low productivity condition, designed to allow streamlining of the system. As the productivity appeared to be lower than expected at the target reactor temperature of 211°C, temperature was increased during the night. During the temperature adjustment, a sharp rise in temperature was experienced. Reactor temperature reached 275° C for a short time and the reactor was quickly cooled down. The reactor was then brought back in control at about 225°C. Precise reactor temperature control was a challenge initially with temperature swinging between 220 and 230°C. It appeared that the reactor was extremely temperature sensitive and difficult to hold stable at low conversion levels of 10-12%. The control improved somewhat later as the plant operators became more familiar with the system dynamics, and the catalyst apparently lost some of its initial activity.

We had to delay moving to the next, higher productivity condition until a product stewardship issue was resolved. It appeared that neither SSFI nor Air Products could accommodate the aqueous and light hydrocarbon product cut, and output of this product could not increase until this issue was resolved. The product stewardship issue was subsequently resolved, with SSFI agreeing to accommodate the aqueous and light hydrocarbon product cut. The initial condition, AF-R15.1, was completed at 10:00 on 10/19/96. Preliminary heat and mass balances for two data periods during this condition indicated hydrocarbon productivity of about 45 gm HC/lit reactor vol. - hr at a reactor temperature of 227°C compared to an expected productivity of 75. Due to low conversion levels, the data were not very accurate. However, it appeared that the alpha of the catalyst was lower than expected (high methane, low wax).

The next condition, AF-R15.2, was begun at 13:00 on 10/19/96. As the temperature rose, productivity increased significantly. There was also evidence of additional CO_2 evolution at higher temperature. It is not clear as to the source of the additional CO_2. With significant rise in productivity, there was a large increase in the pressure drop across the filters and the filters were not able to keep up with the wax production. Backflushing the system seemed to increase the pressure drop further. The reactor temperature was reduced to lower the productivity. It was assumed that catalyst fines, perhaps created by the slurry pump, were gradually plugging the filter elements. The longitudinal as well as membrane differential pressures (DP) had been rising since two days on-stream. The longitudinal DPs are shown in Figure 7. The longitudinal DPs for each pair of filters increased from about 12 psi to 25-30 psi for a slurry circulation flow in approximately the same range. The membrane DPs for each filter are shown in Figures 8 and 9. The membrane DPs started in 0-20 psi range and ended up in the 30-70 psi range for the same flux. A membrane DP of about 100 psi was required to get a slightly higher flux. The unit was held on a stand-by until filter issues could be resolved. Mott Metallurgical was contacted to see if arrangements could be made to replace the current elements with a smaller filter grade (i.e. 0.2 microns instead of 1 micron). In addition, Sundstrand was contacted to see if modifications could be made so that the slurry velocity through the discharge throat of the pump could be reduced.

Several attempts were made to backflush the catalyst/wax filters without a significant improvement in filter performance. As the plant could not run without filtering the product wax out of the reactor slurry, it was shut down after being on a stand-by for a day. Immediately prior to that, a shut down test was performed on the reactor to look at dynamic gas disengagement and axial catalyst concentration profile. The nuclear density readings were constant along the length of the reactor in the two phase slurry, indicating axial uniformity. The plant was cooled, purged, and partially drained overnight on 10/21/96 so that the filters could be examined internally. Examination of the filters could provide some clues about the cause of the plugging problem. If the plugging was caused by a buildup of the filter cake, and particle size distribution tests confirmed that catalyst attrition was not a problem, we would have some hope of mechanically cleaning the filters and restarting. However, if the catalyst had broken down, penetrated into the annular region of the filter, and plugged, a replacement filter with a smaller micron grade was not available within the current time window.

After cooling down, the reactor slurry was drained and the reactor was flushed with oil. Flush oil from the filter system was also drained; it did not show significant solid content. The filters were taken apart on 10/23/96. Although no plugging was visible, backflushing with steam pushed out significant quantities of solids. It was difficult to judge whether the solids came from a cake on the slurry side (inside) of the filters or from the filter membrane annulus. Overnight, the filters were kept on a longitudinal steam flush through the slurry side. A nitrogen purge was maintained from the clean wax (shell) side. Mechanical cleaning was attempted on 10/24/96 with a nylon brush to clean the filter elements from inside. Looking inside through a boroscope showed that the brush action was only scraping the layer partially and just moving the material around. We returned to steam backflushing, as it was the only method that had worked. High pressure steam and nitrogen were used to get higher temperature and pressure on the elements. Backflushing of filters C and D continued overnight. With limited steam supply, having all four on line at the same time at lower steam flow and pressure was not desirable. Filters A & B were backflushed with steam and nitrogen overnight on 10/25/96. Inspection of the filters with boroscope indicated that most of the filter cake was flushed out.

The system was put together and a hot oil flush was conducted late on 10/26/96 to remove residual water from the system. Some of the stickiness observed with the solids could be due to agglomeration of particles caused by condensate from steam. The flush oil was then replaced with clean oil and a flux test was conducted on all the filters. The test revealed a significantly higher pressure drop across the membranes than expected. The pressure drop was in the range of 10 to 40 psi at a flux of 1 lb/min compared to an expectation of 0.1 psi for a new clean element. The longitudinal pressure drops were lower than observed during the run. It seemed that while the filter cake was removed, the membrane remained blocked with particles. Samples taken from the clean wax side appeared to contain fines indicating breakthrough.

Particle size distribution results on various samples from the filter system were received from SSFI laboratories on 10/26/96. The analysis showed a bi-modal distribution indicating particle breakdown. The particle size ranged from 0.5 to 100 micron with peaks at 3 and 35 microns. This compares with the fresh catalyst particle size range of 10 to 100 micron with a single peak at 35 microns. According to Mott Metallurgical, a 1 micron membrane can only retain 100% of the particles above ~3 micron particles.

The clean oil test clearly showed that the existing elements did not have adequate capacity for a high productivity condition. The particle size distribution provided an explanation of membrane blockage due to smaller than expected particle size. With replacement filters not immediately available, the participants decided to terminate the run at that point and regroup for a second trial later.

The data gathered during the Fischer-Tropsch III run were analyzed in detail. Even though, the run had to be terminated after seven days on-stream, significant achievements were accomplished to advance the learning process for the F-T slurry technology as discussed in the following sections.

Mass Balance

Some simplifying assumptions were made for mass and elemental balance. The 22.10 Separator hydrocarbon to aqueous phase ratio was assumed to be constant during the run. The value of the ratio was determined to be 0.256 HC/Aqueous by volume based on density measurements during transfer of liquid from the 22.16 day tank to the liquid trailer. Nitrogen was used as an internal standard to correct less accurate gas flow meter measurements. Nitrogen balance across the reactor was used to correct the product flow rate first. Plant nitrogen balance was then used to adjust the purge-1 flow rate. The 01.20 Compressor discharge flow was finally corrected using either feed nitrogen or product nitrogen balance (redundant).

A run-time table, which summarizes the cross-reference between run numbers, actual times and on-stream times, is given in Table 2. Mass balance was performed for two data periods during the run AF-R15.1. A summary of the results is given in Table 3. Heat and mass balances as well as flow correction factors are summarized in Table 4, elemental balances are shown in Table 5. The closures are considered adequate for the pilot scale, considering the fact that the conversion levels were low. Detailed data for each period are included in Appendix B.

When conditions were changed to high productivity (run AF-R15.2), significantly higher conversions and heat of reaction were observed. Although accurate calculations were difficult, as conditions were transient during this two hour period, productivities in the range 100 to 200 gm HC/lit reactor vol. - hr were estimated. Also, heat of reaction consistent with the above productivities (1.8 to 3.1 MMBtu/hr) was observed during the period.

Catalyst Inventory

Catalyst inventory in the reactor throughout the run was estimated. The details are given in Table 6. The initial catalyst load was 1043 lbs. With several reasonable assumptions made for catalyst loss as shown in the table, an end of the run catalyst inventory of 852 lbs was calculated for the reactor. This was higher than a catalyst inventory of 792 lbs estimated from the dynamic gas disengagement test conducted at the end of the run.

Catalyst Concentration and Gas Hold-up Estimates

Catalyst concentrations in the reactor were estimated based on nuclear density gauge (NDG) and differential pressure (DP) readings as well as slurry and wax density measurements in the filter loop. The comparison between the three methods is shown in Table 7 and Figure 10. The concentrations were estimated to be in 38-44 wt% range during Run AF-R15.1.

The average gas hold-up, calculated from the DP readings, was in the range of 36 to 37 vol% during run 15.1. The gas hold-up calculated from the NDG readings was somewhat higher (41-43 vol%), as expected (see Table 7 and Figure 11). Gas hold-up was also measured using the optical fiber probe during catalyst drying and early activation. Gas hold-up indicated by the probe was generally lower than that estimated by the other methods. Unfortunately, the probe stopped functioning in the middle of the activation, perhaps because of excessive slurry thickening due to inadequate maintenance of slurry level. Gas hold-up profile based on NDG data at different reactor height is shown in Figure 12. The gas hold-up appeared uniform axially in the reactor.

Dynamic Gas Disengagement and Reactor Temperature Control

Differential pressure data were acquired on the SSFI proprietary fast data logger during the dynamic gas disengagement (DGD) test conducted at the end of the run. The variation of the gas hold-up as a function of time during the test is shown in Figure 13. The curves do not show two distinct slopes that may be associated with two classes of bubbles. With a high initial liquid level and a low gas hold-up, the final liquid level was above the top-mid section at 18.2 ft reactor height. This resulted in nearly zero final gas hold-ups in both the sections. The gas hold-up and catalyst concentration at the end of the run were also verified. The DGD results indicated somewhat lower gas hold-up and catalyst concentration (see Table 7 and Figures 10-11). Nuclear density readings taken in the two phase slurry during the dynamic gas disengagement test were fairly constant along the length of the reactor, indicating the catalyst was uniformly distributed axially.

Measurements were also made to evaluate the response time of the revised reactor temperature control system. With the re-alignment of the utility oil system carried out prior to the run, the control system was judged to be adequate for the high productivity condition of run AF-R15.2.

Heat Balance and Heat Transfer in the Reactor

Heat loss from the reactor was estimated at about 35,000 Btu/hr from data obtained during drying. Heat balance during the run AF-R15.1 was in the 96 to 97% range based on the heat of reaction. Heat transfer coefficients were calculated based on the data obtained for the run AF-R15.1. The measured overall coefficient (U) was estimated to be 94 Btu/hr-ft2-°F as compared to the prediction of 90. Measured slurry-side coefficient was estimated at 305 Btu/hr-ft2-°F compared with the prediction of 264. The predicted slurry-side coefficient is based on Deckwer correlations (8). The results are tabulated in Table 8 and plotted in Figure 14. The heat transfer in the reactor was better than expected.

Reactor Performance

The reactor showed excellent temperature uniformity and even gas and catalyst distribution. Axially, the temperatures ranged from 225 to 228°C during the operations at the start-up condition (Run # AF-R15.1). The radial variation was only 0.4°C. SSFI's proprietary sparger appeared to work well. There was only a small amount of catalyst sedimentation on the reactor bottom and no catalyst was found in the gas feed line. Also, no erosion was evident in the reactor as indicated by erosion pieces.

Filtration Loop

The degasser functioned as designed. It effectively removed gas from the slurry going to the slurry pump when proper level in the reactor was maintained. The slurry cooler provided sufficient cooling; there was no evidence of any reaction in the filter loop. The slurry pump provided steady head and flow in the filtration loop. No erosion was found in the loop. However, an inspection of the pump showed erosion marks and browning on the surface of the bowl suggesting that perhaps higher temperatures were reached on the surface. Also, part of the wall separating the discharge throat and the bowl was eroded away resulting in retreat and sharpening of the so called "cut water" wall. The filters under-performed during the run. A filtrate flux of only 0.0045 gpm/ft^2 was achieved during Run 15.1 compared to the design flux of 0.059 gpm/ft^2.

Catalyst Stability

The actual CO conversion rate per unit of catalyst (gmole CO converted / liter of catalyst particle volume / hr) was calculated for the two mass balance periods. Autoclave data obtained by SSFI under kinetically limited conditions were used to generate a kinetic expression based on hot reactor outlet gas phase composition. Continuous Stirred Tank Reactor (CSTR) behavior was assumed for the autoclave. The pre-exponential term was made run-hour dependent as to reflect initial deactivation. Predictions of the CO conversion rate in the LaPorte reactor were derived in the same way as for the autoclave. The ratio of actual / predicted CO conversion rate is shown in Figure 15. The data indicate lower than expected initial activity for the catalyst. The catalyst appeared stable during the short period of condition AF-R15.1. Catalyst productivities were calculated at 200°C based on an activation energy calculated from autoclave data. A reference temperature was used to compare activities obtained at different temperatures. The results are shown in Table 9. After correcting for CO_2 selectivity, a stable productivity is observed expressed in Normal liter CO/liter catalyst/hr at 200°C.

Liquid/Wax/Slurry Analysis

A number of liquid, wax and slurry samples were collected during the run for various analyses. The analytical work, including corresponding data analysis, was performed by SSFI.

1. Product Water:

The results of the water phase analysis are given in Table 10. The pH of about 3 is normal for cobalt catalyst and is caused by small amounts of organic acids dissolved in the water. Cobalt was not detectable by the method applied (ICP). The trailer sample showed some iron, probably a result of corrosion by organic acids. The Total Organic Content (TOC) of about 0.96%w carbon is mainly caused by lower alcohols dissolved in the water. Ethanol can be considered as an average in terms of alcohol carbon number.

2. Hydrocarbons:

The results of the hydrocarbon analysis are summarized in Table 11, details are included in Appendix C. In the light and heavy wax, no cobalt was detectable by the ICP method. The H/C ratio was as expected. The light wax does not have an impact on the mass balance as very small quantity of light wax was produced during the run.

3. Slurry:

The results of the slurry sample analysis are summarized in Table 12. SSFI proprietary Pyrolysis Combustion Mass-spectrometric Elemental (PCME) analysis was conducted to estimate free carbon or carbon as coke on the catalyst. Samples #9-12 show high residue content in PCME analysis, suggesting that the sedimented part of the original sample was used for the analysis. Samples #13-15 show residue content close to expectation. The particle size distribution data are plotted in Figure 16 and show a substantial reduction in average particle size accompanied by high fines formation right from the first sample. This is fully in line with the observed filter plugging during the run.

4. Light Hydrocarbon Product:

The carbon distribution of the light hydrocarbon product is shown in Figure 17. A relatively light product with a heavy tail is observed. The two shoulders between C_{20} and C_{30} are probably caused by presence of some flush oil, Ethylflo-164 (now known as Durasyn-164). The type distribution of the light hydrocarbon product is shown in Figure 18. The high 1-alcohol content of C_4-C_6 is caused by flashing effects. The boiling point of the corresponding alkanes and alkenes is lower, causing these to end up to a larger extent in the gas phase. Olefinicity goes through a maximum at C_8 and decreases at higher carbon numbers. The 1-Alcohols above C_{16} were below the detection limit. Iso-alkanes increase with increasing carbon number. Apart from a natural increase of branching with carbon number, this can be caused by both attributing all unidentified GC peaks to iso-alkanes and the presence of some of the light components of Ethylflo-164. The calculated elemental oxygen content from alcohols is 0.52%w.

5. Wax Products:

The carbon distribution of the wax samples is shown in Figure 19. The light and heavy wax show a clear difference in carbon distribution reflecting the “overhead” character of the light wax. The presence of Ethylflo-164, as witnessed by the sharp peaks at C_{27} and C_{34}, is very clear. The Ethylflo peaks influence the overall product distribution, the physical properties of the waxes and the alpha values. Reliable alpha values can only be determined at carbon numbers below 20 and above 40.

6. Carbon Distribution for Total Product:

The flow and gas composition data for the mass balance period AF-R15.1C were used in combinations with carbon distributions of heavy wax and light hydrocarbon product (trailer) to estimate carbon distribution of the total product. The results are shown in Figure 20. As expected, the Ethylflo peaks are clearly visible. The AFS (Anderson-Flory-Schulz) alpha plot is shown in Figure 21. It shows a valley around C_{20}. This might be caused by light wax still building up in the separators (the light wax shows a maximum around C_{20}). The plot shows low alpha (0.8) up to C_{20} and higher alpha from C_{40} onwards (0.91-0.95).

POST FISCHER-TROPSCH III INVESTIGATIONS

A plan of action described below was developed and followed prior to a second trial:

- Investigate catalyst particle breakdown in laboratory. While it was suspected that the particle breakdown occurred in the pump, it needed to be proven. Based on the findings, the slurry pump design may need re-evaluation.

- Conduct additional filter tests. It was suggested the F-T III spent slurry be tested with 0.2 micron elements. Future run plan should include back-up filter elements.

- Improve catalyst activation procedure. While the activation was controlled well, there was evidence that it was not complete. Better water measurement techniques were required to decide when the activation is complete.

Spent slurry and a filter element bundle were shipped to SSFI for testing. The slurry pump was shipped to the manufacturer (Sundstrand) for evaluation.

Slurry Pump

A meeting was held with Sundstrand personnel on January 9, 1997 to discuss their post Fischer-Tropsch III run observations of the slurry pump and develop a plan to improve its performance. Following is a summary of the discussion:

- The throat could be opened up from 0.328" to a maximum of 0.446". This would reduce the throat velocity by almost a factor of 2: from 83.5 ft/sec to 45.2 ft/sec at 22 gpm (9 ft/sec in the filter element). We could reduce the throat velocity further to 30.1 ft/sec by operating at 14.7 gpm (6 ft/sec in the filter element). Higher throat diameter would mean we would have to operate at lower pump speed which would decrease the efficiency. This was not a problem at LaPorte, as we had enough horsepower. According to Sundstrand, our application involved too low a flow for the head requirement. Scale-up to a higher flow for commercial application would improve the efficiency.

- There was no need to increase the impeller clearances at the top or the bottom from bowl erosion point of view. The clearance between the impeller and the bottom bowl was measured at 0.055", which was within specification. The clearance may have opened up about 0.004". The clearance between the impeller and the top cover was measured at 0.050", which was within the normal range of 0.040-0.060".

- Sundstrand suggested considering alternative harder materials for pump internals instead of the current 316 SS (ASTM A351 grade CF8M - both bowl and impeller were made of this material): Duplex steel (CD4MCU) or heat treated carbon-steel. The current pump had no coating on the internals. Sundstrand did not favor coating because if the coating is broken through, it leaves a rough surface for significant erosion.

- Sundstrand suggested use of bellow seals in the lower position to prevent leakage during the operation. Other suggestions included use of differential pressure regulator to maintain the seal pressure 50 psi above the suction pressure; pressure rating of the lower seal at the full pressure; and use of a block valve to stop process fluid from going into the buffer system. The valve can trip on a buffer pump trip or a differential pressure trip. A normally closed solenoid valve connected with the pump circuit could be used. We already had a check valve to prevent pressure on the buffer pump.

- There was no evidence of damage in the largest diameter of the bottom bowl. All the damage was on the angled portion where it was close to the spinning impeller. Sundstrand was surprised at the extent of damage on the bottom bowl and only one scratch on the top cover. Typically, they see a lot more damage at the top compared to the bottom.

Testing at SSFI

SSFI followed up several possible causes of filter problems during F-T III: (1) Strength of their proprietary catalyst used in F-T III vs. strength of their improved proprietary catalyst. (2) Effect of liquid medium on catalyst attrition. (3) Effect of pumping velocity on attrition. (4) Use of different type of filter elements. The initial laboratory test results were inconclusive for (1), (2) and (3). The improved catalyst appeared to be stronger when slurried with water. However, in oil, the two catalysts showed similar attrition. Also, surprisingly, no effect of pumping velocity on attrition was evident. For filtration, the plan was to test three types of filter elements (sintered metal, ceramic membrane and woven metal) in parallel with activated improved catalyst in wax. A Sundstrand centrifugal pump would be used in these tests to evaluate erosion.

Commissioning of the filter loop in SSFI's pilot plant was completed and slurry pump/filtration tests started during May 97. SSFI's improved proprietary catalyst was activated in-situ in wax. Initially, the slurry circulation was started at high pump velocity to generate fines and test the pump for erosion. A more erosion resistant material - manganese alloy was utilized for pump internals. Reliable and steady operation was obtained with only a small sign of erosion. Also, very limited catalyst attrition was observed.

For filtration, woven metal filter elements were tested. These elements were most promising as they are uniform. Successful filtration was achieved with flux rate at twice the design rate at low membrane and longitudinal differential pressures.

ENGINEERING AND MODIFICATIONS (F-T IV)

As a result of successful filtration tests, the F-T IV modifications were kicked-off. The modifications included new filter elements, new element bundle arrangement, rebuilding the slurry pump and individualizing the filtration control. A simplified process flow diagram for Fischer-Tropsch IV is given in Figure 22. Other improvements included purchase of significant hardware and software to the Bailey control system to fix the data acquisition glitch and upgrade the system, and a cooling water pump to boost the cooling water pressure. In preparation of installing alternate filter elements, four filter housings from LaPorte were shipped to SSFI.

10.62 Slurry Pump

The slurry pump modification involved new internals (diffuser and cover plate) made up of manganese alloy, opening the throat to 0.446”, use of a differential pressure regulator to maintain proper differential pressure between process and buffer fluid, and installation of a shut-off valve on the buffer system.

22.62 Cross-flow Filters

The cross flow filter system consisted of four 10' filters (four parallel elements in each) in series. The new filter elements were woven metal elements, 14 mm ID, 10 ft long, 10 micron grade stainless steel. A tangential velocity of 8.7 ft/sec, corresponding to 26 gpm of pump flow, would be maintained through the elements. The elements would be back-flushed with clear wax, as needed. For 61 gph of filtrate wax production rate, the design flux through the elements required would be 0.044 gpm/ft^2. The total filtration area of the system was 23.1 ft^2. With expectation of lower wax production associated with the new catalyst and higher filter capacity as measured by SSFI, it appeared that there was a 100% spare capacity. So it was decided to put only two housings on-line initially, and withdraw wax from only one of them. For additional back-up, 16 extra elements were purchased and constructed into 4 additional bundles. The new bundle arrangement would allow easier on-site replacements of bundles, if the four bundles in service got plugged. Four control valves were installed on the product wax line to improve filtration control by achieving an individual control of each housing. These valves replaced the existing manual throttle valves. The single existing larger control valve (LV-203) was also removed.

Other miscellaneous items addressed in preparation for F-T IV are described below:

- A hazard review was conducted in January 98. Safety analysis and documentation were completed to support the Flowsheet Change Notices (FCNs) required for the process hazards review.

- A meeting was held between ICI Tracerco, Air Products and Washington University personnel to discuss improvements in tracer techniques and plan for a study during F-T IV. Tracerco agreed to several suggestions to improve the quantitative methods.

- An alternate oil was evaluated for the utility oil system to improve heat transfer. Better heat transfer in the reactor tubes translates into improved reactor temperature control. Therminol-59, a heat transfer fluid used in the Kingsport reduction vessel, was found to be superior to the current Drakeol-10. The log mean delta T (LMTD) reduced by about ~15%. The improvement is due to better heat transfer properties: higher thermal conductivity, lower viscosity and higher density. The only negative effect is due to lower heat capacity. After consultation with SSFI, it was decided to switch the oil at the cost of ~$9,000.

- Proprietary kinetic information was received from SSFI and the LaPorte flow sheet was simulated to generate mass balances.

DEMONSTRATION RUN PLAN (F-T IV)

Meetings were held between the participants to define scope and develop a run plan consistent with available funding for the second trial. The run plan was similar to the Fischer-Tropsch III plan. It consisted of 18-days on syngas including four process conditions, a baseline check-back, a tracer study at two conditions and a day on dynamic gas disengagement (see Table 13). Slurry concentration of approximately 25 wt% was planned compared to the F-T III concentration of about 40 wt%. Lower concentration was chosen to improve slurry transport and filterability. Also, the improved catalyst had a somewhat lower density than the F-T III catalyst. A space-time yield of 150 was targetted throughout the run.

PRE-RUN SET-UP AND TESTING (F-T IV)

Initial set-up and calibration activities for the F-T IV demonstration began at LaPorte in February 98. This included the analytical set-up, the data-acquisition system and the nuclear density measurements. Final preparations were completed in March. The new DCS control stations were programmed, and communications between the distributed control system (DCS) and the data acquisition system (DAS) were successfully tested. Nuclear density gauge calibration on the reactor was completed, and calibration of a radial nuclear density device for chordal scans was performed by ICI Tracerco. A hot function test of the unit without catalyst was performed on 21-22 March. This test was performed with both nitrogen and synthesis gas at the conditions for reactor operation. This provided a final check of the equipment and instrumentation systems.

RESULTS AND DISCUSSION (F-T IV)

SSFI's improved proprietary catalyst (MDC), start-up wax (Callista-158) as well as some flush Durasyn-164 oil were mixed in the prep tank to make a 26.8 wt% slurry. The slurry was then transferred to the reactor and catalyst drying began at 19:00 hours on 03/23/98. A Run Chronology is included in Appendix D.

Catalyst Activation

The reactor temperature was ramped up with a flow of 100% nitrogen to drive the physical water out of the catalyst. Water concentrations were monitored in the system using both instantaneous Panametric instruments and accumulated measurements via zeolite-5A tubes. Initially, plugging was experienced at a pressure regulator on the sample line for the reactor off-gas. Start-up wax was found in the regulator upon cleaning. The problem was addressed by inserting a knock-out pot up-stream of the regulator as well as increasing the reactor operating pressure.

The drying was essentially complete at 22:00 hours on 3/24/98. At that point, hydrogen was brought in to begin catalyst activation using SSFI's proprietary improved activation procedure. Monitoring of the water concentration continued, but water measurements proved to be difficult due to wax/oil contamination of the analytical system. The contamination problem may have been associated with higher operating pressure compared to F-T III. The activation, however, appeared to proceed well, as the expected methane production was observed. The activation procedure was completed at 14:00 hours on 3/28/98. The activation was terminated after exceeding the on-stream time required in the autoclave at the activation conditions.

The calculated extent of reduction is given in Figure 23. The zeolite tubes show a 1200% reduction which is obviously erroneous due to wax/oil contamination. The panametric measurements indicate about 40% reduction. Estimated water partial pressures during activation are shown in Figure 24. A multiplier of 2.05 was used to correct the panametric data based on expectations from a typical 80% activation.

Process Variable Study

The filter system was brought on-line with the reactor and a slurry sample taken through from the filter system. CO was then introduced to the process at 14:15 on 3/28/98. The start-up with syngas included a series of intermediate steps to reach the first operating condition (Run AF-R16.1). Over Day 1 of the start-up, the plant was stabilized at approximately half the target productivity. Temperature control was satisfactory at stable operating conditions and low productivity, but proved challenging during transient moves to higher productivity conditions. As a result, we relied on the automatic temperature control scheme, with some tuning modifications, and made a series of small steps to the operating conditions. During this period, the productivity increased from about 65 gm HC/hr-lit. of reactor volume to above 120 gm HC/hr-lit. of reactor volume. The reactor operated hydrodynamically stable with uniform temperature and gas hold-ups. The catalyst/wax filters performed well, producing a clean wax product. For the most part, only one of the four filter housings was needed for catalyst/wax separation. The plant lined out at condition AF-R16.1 at midnight on 01 April with a productivity of approximately 140 gm HC/hr-lit. of reactor volume. At that point the heat load in the reactor caused the automatic temperature control to oscillate significantly (see Figures 25 and 26). As more than 90% of the productivity goal was achieved, and the productivity was within the success criteria of 120-150, it was decided not to push any further and risk unacceptable system instability. As a result, the baseline condition was defined, and a steady data collection period began.

On 02 April, the plant tripped out due to high temperature on a vapor-liquid separator. A cooling water exchanger in the product separation area vapor-locked, causing the high gas temperature which tripped the compressor. Gas flows to the reactor were re-established shortly thereafter, but the resulting upset in pressure and temperature had already quenched the reaction. In addition, the upset caused some plugging problems in the catalyst/wax circulation system which were rectified after a few hours of troubleshooting. In the restart, we still needed only one of the four filter housings, demonstrating the robust character of the new filter design. We returned to the sequence of startup steps to get back to the baseline condition. However, we were able to move much more quickly through the sequence because of the confidence gained in the system stability during the initial startup. The baseline condition was reached within 24 hours after the plant trip. Stable operation was achieved and the conditions were held constant for about two days to collect data. The productivity was approximately 135-140 gm HC/hr-lit. of reactor volume during this period. By bringing the plant back to the high productivity condition within 24 hours, another significant milestone for the slurry phase technology was achieved. The automatic temperature control oscillations were smaller than during the previous 6 hour operating period at this condition on 02 April. The filter system operations continued with one filter housing, yielding clean wax product. Close to expected catalyst productivity obtained at the beginning of the run indicated successful in-situ catalyst activation. The wax selectivity appeared to be lower than expected while the methane production was slightly higher.

As the start-up had taken longer than expected, several discussions were held between the representatives of the participants on-site to modify the run plan. The goal was to get quality information from this run in the on-stream time available while making sure that the important needs of each participant were met. It was decided to skip the operating condition AF-R16.2 and spend the same amount of time originally planned at the rest of the conditions.

At 05:00 on 05 April, the transition to high velocity condition (AF-R16.3) began. The recycle ratio was gradually increased ratio from 1.2 to 3.0. During the transition to condition AF-R16.3 on 06 April, operating limitations were encountered that required redefinition of the test condition. It appeared that wax loss from the reactor was exceeding the wax production, resulting in decreasing slurry level in the reactor. To correct this situation, the reactor temperature was reduced by 8°F, and the recycle flow was reduced to maintain the high productivity target. The final recycle ratio for the redefined AF-R16.3 was approximately 2:1. On 07 April, gamma scans were conducted by ICI Tracerco to get flow profile information at the high velocity condition. At 08:45 on 07 April the GC computer stopped communicating with the overall data acquisition computer because of a memory limitation on the acquisition computer. No data were lost, except during brief troubleshooting periods, but the data reduction process required hand input of the GC data for a 15 hour period. The operating time at AF-R16.3 was extended to have 12 hours of continuous data after the restoration of communication between the GC and the acquisition computers. Stable data for a 36 hour period was obtained. The productivity was approximately 130 gm HC/hr-lit. of reactor volume during this period.

At 13:00 on 08 April, the transition to run condition AF-R16.4 began. This test applied a high fresh feed H2/CO ratio of 2.18 which is approximately equal to the consumption ratio and was expected to result in more difficult plant control. Therefore, the target reactor productivity was reduced to 120 gm HC/hr-lit. of reactor volume. The condition was reached at 08:00 on 09 April. However, an upset in the high pressure H_2 supply caused a reactor temperature excursion to 518°F at 13:45. By 18:00, condition AF-R16.4 was reached again. Data collection continued until 07:00 on 10 April. A stable productivity of 110-115 gm HC/hr-lit. of reactor volume was achieved at this condition.

Transition to the baseline condition (AF-R16.5) was smooth and quick, as the new condition was reached in 7 hours. The plant operations were stable during 33 hours of data collection period. The catalyst activity as well as selectivity to wax showed some decline relative to the initial catalyst performance two weeks earlier, as the productivity dropped about 7% (from 135-140 range to 125-130 range) while the methane selectivity increased. A suspected restriction in a slurry line caused the plant to shut down in the morning of 4/12/98. After performing maintenance on the slurry pump, the plant was brought back on-stream at the baseline condition in 17 hours. The quick re-start demonstrates the ease and flexibility of the slurry technology.

Tracer Study

After the process variable scan, gas, liquid and solid phase mixing were studied at two operating conditions using radioactive materials. ICI Tracerco set up 43 detectors around the reactor during the last day of the process variable study. The first tracer run was conducted on April 14 at the baseline condition (AF-R16.6). Argon-41 was injected into the inlet gas line for the vapor residence time distribution study. In addition, two injections of radioactive manganese oxide were made in the reactor slurry to study liquid phase mixing. Solid injections were also done with radioactive manganese doped catalyst support to evaluate solid mixing. The first tracer runs were completed at midnight on April 14.

After switching to the high velocity condition (AF-R16.7) overnight, the second tracer runs were conducted on April 15. The injections began at 19:20 on April 15 and concluded at 01:20 on April 16. The large amount of data collected by ICI Tracerco are being analyzed by Washington University as part of the Hydrodynamic Program with DOE. After the second tracer runs, a dynamic gas disengagement test was conducted at the high velocity condition (AF-R16.8) to estimate the gas and solid hold-up as well as extract bubble size information.

Immediately after the dynamic gas disengagement test, syngas was purged from the plant with N_2, and shutdown activities commenced. ICI Tracerco returned onsite in the afternoon of April 16 to insure that the radioactive levels were low enough to begin draining the system.

Mass Balance

Assumptions similar to F-T III data analysis were made for mass and elemental balance. The 22.10 Separator hydrocarbon to aqueous phase ratio was assumed to be constant during the run. The value of the ratio was determined to be 0.722 HC/Aqueous by volume based on density measurements during transfers of liquid from the 22.16 day tank to the liquid trailer. Nitrogen was used as an internal standard to correct less accurate gas flow meter measurements similar to F-T III. With the wax flow meter not operating properly due to degassing at low pressure, instantaneous wax production data were not available. The average production rate was calculated based on amount of wax drained from the system for operation during a particular length of time.

A run-time table, which summarizes the cross-reference between run numbers, actual times and on-stream times, is given in Table 14. Mass balance was performed for twelve different data periods during the run. A summary of the results is given in Table 15. Heat and mass balances as well as flow correction factors are summarized in Table 16, elemental balances are shown in Table 17. The closures are quite good for the pilot scale, given the number of components involved in some of the streams. Detailed data for each period are included in Appendix E.

Catalyst Inventory

Catalyst inventory in the reactor throughout the run was estimated. The details are given in Table 18. The initial catalyst load was 501 lbs. With several reasonable assumptions made for catalyst loss as shown in the table, an end of the run catalyst inventory of 337 lbs was calculated for the reactor. This was higher than a catalyst inventory of 304 lbs estimated from the dynamic gas disengagement test conducted at the end of the run.

Catalyst Concentration and Gas Hold-up Estimates

Catalyst concentrations in the reactor were estimated based on nuclear density gauge (NDG) and differential pressure (DP) readings as well as slurry density measurements in the filter loop. The comparison between the three methods is shown in Table 19 and Figure 27. The concentrations were estimated to be in 24-30 wt% range.

The average gas hold-up, calculated from the DP readings, was in the range of 41 to 49 vol% during the run. The gas hold-up calculated from the NDG readings was somewhat higher (45-53 vol%), as expected (see Table 19 and Figure 28).

Dynamic Gas Disengagement

Differential pressure data were acquired on the SSFI proprietary fast data logger during the dynamic gas disengagement test conducted at the end of the run. The variation of the gas hold-up as a function of time during the test is shown in Figure 29. The curve does not show two distinct slopes that may be associated with two classes of bubbles. With a relatively higher gas hold-up compared to F-T III, the final liquid level was in the top-mid section at 11.3 ft reactor height. As a result, the gas hold-up in that section leveled of at a positive value after going through a dip. The gas hold-up and catalyst concentration at the end of the run were verified. The DGD results indicated somewhat lower gas hold-up and catalyst concentration (see Table 19 and Figures 27-28). The NDG readings taken along the length of the reactor during the DGD test showed only a small variation suggesting fairly uniform axial distribution of the catalyst.

Heat Balance and Heat Transfer in the Reactor

Heat loss from the reactor was estimated at about 50,000 Btu/hr from data obtained during the 2-phase hot function test. Heat balance during the run was in the 96 to 102% range based on the heat of reaction. Heat transfer coefficients were calculated based on the data obtained during the run. The results are tabulated in Table 20 and plotted in Figure 30. The heat transfer in the reactor was significantly better than expected.

Reactor Performance

The reactor operated hydrodynamically stable with uniform temperature profile and even gas and catalyst distribution. Nuclear density and differential pressure measurements indicated somewhat higher than expected gas hold-up (45 - 50 vol%). The high gas hold-up was confirmed by the DGD test conducted at the end of the run. SSFI's proprietary sparger appeared to work well. The reactor bottom was found to be clear of large amount of catalyst sedimentation upon inspection following the shut-down.

Catalyst-wax Separation

The catalyst/wax filters performed well throughout the demonstration, producing a clean wax product. For the most part, only one of the four filter housings was needed for filtration. The filter flux appeared to exceed the design flux. An average filtrate flux of 0.031 gpm/ft^2 was demonstrated during Run 16.1, compared to the design flux of 0.044 gpm/ft^2. However, the system showed significant higher capacity, as the filtrate was withdrawn intermittently during the run. The average flux was calculated based on amount of wax drained from the system, since instantaneous flux data were not available. With the slurry being recycled back from the filtration loop, the upward liquid velocity through the reactor was about 0.024 ft/sec.

Catalyst Stability

The actual CO conversion rate per unit of catalyst (gmole CO converted / liter of catalyst particle volume / hr) was calculated for the twelve mass balance periods. As in the case with the F-T III data analysis, kinetic expressions based on autoclave data obtained by SSFI were used for comparison. The ratio of actual / predicted CO conversion rate is shown in Figure 31. It appears that conditions 16.1, 16.4 and 16.5 have a similar ratio indicating that the initial catalyst deactivation rate in the LaPorte reactor was similar to that in the autoclave. The ratio is about 0.76-0.77, which is much higher than the F-T III value of 0.43-0.44. The ratio being lower than 1.0 can be explained by either a less than optimal activation of the catalyst precursor in the LaPorte reactor vs in the autoclave or presence of some mass transfer limitation.

For the high gas velocity condition (16.3), the ratio of actual vs predicted CO conversion rate dropped to 0.63. This can be explained by an increase in mass transfer limitation or more back-mixing.

Catalyst productivities were calculated at 200°C based on an activation energy calculated from autoclave data. The results are shown in Table 21. The results are corrected for CO_2 selectivity, and the productivity is expressed in Normal liter CO/liter catalyst/hr at 200°C. The productivities reflect the effect of the actual H_2 and CO concentration. This is apparent in the results of condition 16.4, where high H_2/CO ratio results in highest productivity. Conditions 16.1 and 16.5 (check-back) give activities in the same range indicating the absence of fast deactivating. These data are not corrected for initial deactivation.

Liquid/Wax/Slurry Analysis

An estimated 1,875 gallons of wax, 16,915 gallons of light hydrocarbon liquids and 23,428 gallons of water were made during the run. Significant quantities of the product were collected for further processing by the participants. In addition, a number of liquid, wax, and slurry samples were taken for analysis. The analytical work, including corresponding data analysis, was performed by SSFI. An overview of the samples chosen for analysis is given in Table 22.

1. Product Water:

The results of the water phase analysis are given in Table 23. Like F-T III, a pH of about 3 was obtained, which is normal for cobalt catalyst. The Total Organic Content (TOC) of about 1.69%w carbon is mainly caused by lower alcohols dissolved in the water. Ethanol is considered as an average in terms of alcohol carbon number.

2. Hydrocarbons:

The results of the light hydrocarbon analysis are summarized in Table 24, details are included in Appendix F. The oxygen content is mainly caused by 1-alcohols. The calculated oxygen content from GC was 0.62%w. The results of the wax analysis are summarized in Table 25, with details included in Appendix F. The wax density shows little variation over the samples. The cobalt content of 3 ppm is considered low.

3. Slurry:

The results of the slurry sample analysis are summarized in Table 26. The PCME data show no fixed carbon, in other words, no free carbon or carbon as coke on the catalyst. Taking a separate sample from the slurry samples appeared difficult in view of the residue contents which strongly deviated from the expected 25%w. The larger sub-samples taken for de-waxing showed solids contents which are much closer to 25%w. The samples taken from the reactor after shutdown indicate high solids contents for both methods, which is not surprising since these samples were already highly concentrated and further sedimentation is not possible.

The particle size distribution data are plotted in Figure 32. The particle size of the catalyst in the slurry samples is hardly different from that of the fresh catalyst precursor and, more importantly, constant in time. Moreover, the production of fines is very limited and seems to occur mainly at the start-up. These data suggest very good mechanical properties of the catalyst, which is consistent with the excellent filtration performance observed and represents a large improvement over F-T III. The relatively large particle size of the reactor bottom sample suggests sedimentation during the shutdown phase when the slurry recycle was not operating.

4. Light Hydrocarbon Product:

The carbon distribution of the light hydrocarbon product is shown in Figure 33. There is very little difference between the products of the various conditions. The products show a heavy tail, which is also reflected by the deposits in the product and the greasy character of some samples. The heavy tail is related to an ineffective phase separation in the reactor, probably accompanied with some entrainment. Due to the heavy tail, capillary column analysis was not possible for all samples except for the drum sample. As a result, high temperature GC (HT-GC) had to be applied. The fraction less than C_{10} is not correctly measured by HT-GC. Therefore, some reconstruction of data was carried out using the $<C_{10}$ fraction of the drum sample. The Samples 22.11-18 and 22.11-19 show presence of some Durasyn-164 oil. This is probably a result of the Durasyn additions to the filtration loop on April 12, 1998, following operational problems.

The type distribution of the light hydrocarbon product is shown in Figure 34. The high alcohol content of the C_3-C_6 fraction is caused by flashing effects. The boiling point of the corresponding alkanes and alkenes is lower causing these to end up to a larger extent in the gas phase. Olefinicity passes through a maximum at C_6 and decreases at higher carbon numbers. Alcohols above C_{17} were below the detection limit. Iso-alkanes increase with increasing carbon number. Apart from a real increase of branching with increasing carbon number, this can also be caused by attributing all unidentified GC-peaks to iso-alkanes.

5. Wax Products:

The carbon distribution of the wax samples is shown in Figure 35. The alpha-values for the waxes as such are not reliable at carbon numbers below 40 due to separation effects. A carbon distribution for the Durasyn-164 oil could not be generated due to the high degree of branching. Direct information from the chromatogram (not shown) indicated a sharp maximum around C_{27} and a smaller maximum around C_{34}. The Callista-158 start-up wax has a broad maximum around C_{34}. The waxes are relatively light F-T waxes with hardly any material above C_{90}. During the run, a small shift to heavier wax is observed, as indicated by a shift in the maximum of the carbon distribution as well as the generation of more material in the C_{70} range. Sample 22.62-27 (condition 16.6, 14 April 1998) seems to contain a relatively large amount of Durasyn-164 oil. This is consistent with the observation in the light HC product discussed above and probably due to the same Durasyn-164 additions on April 12, 1998, following operational problems. Alpha values of 0.88-0.90 are observed in the C_{40}-C_{80} range.

6. Carbon Distribution for Total Product:

Carbon distributions for the following separate samples were available:

- Wax: HT GC (short column) for samples 22.62-14, 22.62-20, 22.62-22, 22.62-25 and 22.62-27.
- Light Hydrocarbons: HT GC (short column) for samples drum sample, 22.11-12, 22.11-18, 22-11-19.
- Light hydrocarbons after removal of heavy tail: capillary column for drum sample.

The light hydrocarbon samples all had a heavy tail, which did not allow capillary column analysis. The samples were greasy, not allowing removal of the heavy tail by sedimentation in a refrigerator. The exception was the drum sample, where removal of the heavy tail appeared possible. The HT-GC method does not produce correct concentrations for the C_9- fraction. However, the distributions of the light hydrocarbons as determined by HT-GC seemed very much alike for the four light hydrocarbons samples. It was, therefore, decided to correct the carbon distributions of the light hydrocarbons samples by imposing the C_9- fraction as determined for the drum sample on each of the four samples. This was done by using the C_{10} concentration as a scaling factor, followed by re-normalization.

The total carbon distributions were then calculated by combining:

- hydrocarbon concentrations in the purge gas and purge gas flow,
- corrected carbon distribution of the light hydrocarbon product and production rate of light hydrocarbon product, and,
- carbon distribution of the wax and production rate of the wax.

The total carbon distributions thus obtained were re-normalized. Subsequently, the AFS (Anderson-Flory-Schulz) plots were constructed and alpha values (chain growth probability) were determined. Also, a product based C_5+ selectivity was calculated which can deviate slightly from the gas phase derived C_5+ selectivity. Since the carbon distributions of the light hydrocarbon product were all very similar, it was decided to use the results of adjacent condition where no analysis was available.

This lead to the following combinations:

F-T IV Condition #	Wax sample used	Light HC sample used
16.1C	22.62-14	drum sample
16.3D	22.62-20	22.11-12
16.4A	22.62-22	22.11-12
16.5C	22.62-25	22.11-18

The total product carbon distribution results as well as the AFS alpha plots are shown Figures 36-43. Apart from the high methane production, the carbon numbers with the largest weight fractions were C_5 and C_6. Condition 16.1C (Figure 37) shows a single alpha with the usual undershoot for C_2 and overshoot for C_1. The average alpha value for C_{10}-C_{80} was 0.865. Condition 16.3D alpha plot (Figure 39) shows a slight bend at around C_{35} with alpha values of about 0.82 below C_{35} and about 0.88 above C_{35}. The average alpha value for C_{10}-C_{80} was 0.858. Condition 16.4A alpha plot (Figure 41) is straight with a hump at C_{60}-C_{90}. The wax concentrations in this range are very low; the hump may, therefore, be an artifact. The average alpha value for C_{10}-C_{80} was 0.880. Both the total carbon distribution and the alpha plots for condition 16.5C (Figures 42-43) show a hump at C_{27-28} caused by the presence of some Durasyn. The average alpha value for C_{10}-C_{80} is 0.890.

The above analysis was performed on the overall plant basis. The alpha values and the selectivities presented here are slightly different than shown in the run reports (Appendix E), which were calculated based on the reactor balance. However, since the mass balance closures were excellent, the differences are negligible.

CONCLUSIONS AND RECOMMENDATIONS

The slurry phase Fischer-Tropsch technology was successfully demonstrated:

- A productivity of approximately 140 gm HC/hr-lit. of reactor volume was achieved at reasonable system stability during the second trial. As this was more than 90% of the goal of 150, and within the success criteria of 120-150, it was decided not to push any further and risk unacceptable system instability. The productivity ranged from 110-140 at various conditions during the 18 days of F-T IV operations.

- The catalyst/wax filters performed well throughout the F-T IV demonstration, producing a clean wax product. For the most part, only one of the four filter housings was needed for catalyst/wax filtration. The filter flux appeared to exceed the design flux. A combination of use of a stronger catalyst and some innovating filtration techniques were responsible for this success. There was no sign of catalyst particle attrition and very little erosion of the slurry pump was observed. This was in contrast to the F-T III operations, when the run had to be terminated after seven days on-stream, as the filter membranes apparently plugged with catalyst fines.

- The reactor operated hydrodynamically stable with uniform temperature profile and gas hold-ups. Nuclear density and differential pressure measurements indicated somewhat higher than expected gas hold-up (45 - 50 vol%) during F-T IV operations. The high gas hold-up was confirmed by a dynamic gas disengagement test conducted at the end of the run.

- Heat transfer in the reactor was better than expected. Heat, mass and elemental balance calculations indicated excellent closure.

- After the initial learning curve with system dynamics, the plant was restarted very quickly (24 hours and 17 hours) following two plant trips. This demonstrates the ease and flexibility of the slurry technology.

- In-situ catalyst activation was completed successfully during F-T IV operations. Water measurements by the zeolite tube system proved to be inaccurate due to wax/oil contamination. However, the activation appeared to proceed well as close to expected syngas conversion was obtained at the beginning of the run. The selectivity to wax was lower than expected, with higher methane selectivity. Calculation error in accumulated water quantity as well as increasing methane production lead to a decision to terminate activation prematurely during F-T III operations. The results confirmed that the P_2O_5 adsorption is a better water measurement technique than Panametric measurements.

- Returning to the baseline condition indicated a productivity decline from 135-140 to 125-130 gm HC/hr-lit. of reactor volume in two weeks of operation. This may be a result of some catalyst loss from the reactor as well as initial catalyst deactivation.

- Significant quantities of product and samples were collected for further processing and analysis by the participants.

- Gas, liquid and solid phase mixing were studied as planned at two operating conditions using radioactive materials. A large amount of data were collected by ICI Tracerco using 43 detectors around the reactor. The data are being analyzed by Washington University as part of the Hydrodynamic Program with DOE.

Although the technology was successfully demonstrated, it is worthwhile to recommend actions that would improve the operations at the LaPorte facility:

- More accurate water measurement using P_2O_5 adsorption is needed to improve the monitoring of catalyst activation step.

- To improve the reactor temperature control for the existing LaPorte reactor would require significant modifications in the utility oil loop, including a larger capacity heater and a larger capacity cooler. This is particularly true because there is no room to add significantly more heat transfer area in the LaPorte reactor. Alternately, a boiling water system can be used. However, it will add significant complexity to the operations.

- The interruption in data communication was an isolated event, which can be prevented in future. However, it should be noted that the data acquisition system needs upgrading to catch up with technological advances in this area. The current system was installed in 1992 and is extremely primitive.

- Plant trips and upsets are incidental occurrences in this type of demonstration unit. Facility upgrading can certainly reduce some of these interruptions.

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