III. CHRONOLOGICAL SUMMARY OF PROGRESS

A. Pilot Plant Installation

The project status during July-September, 1976 involved an overlap with Phase III of Contract No. E(49-18)-1505 which included completion of Liquid Phase Methanation (LPM) Pilot Plant construction.

During July, 1976, work continued on the repair of defective welds and was completed on August 6. A hydrostatic test was performed on August 10 and witnessed by personnel from Chem Systems and Davy Powergas. After the hydrostatic tests on August 11 and 12, all vessels and piping were drained. All piping blanks were removed and the piping was reconnected.

Chem Systems personnel inspected the pilot plant, exclusive of the control room, upon completion of hydrostatic testing on August 11, 1976. A number of discrepancies and omissions were noted and transmitted to Davy Powergas for immediate rectification. Re-insulation of the process piping began on August 16. By the end of August, this work and paint retouching were completed.

The construction phase of the LPM pilot plant was completed and thorough inspection was carried out by Chem Systems on September 9-10, 1976. Two items were found incomplete and were to be installed after relocation to the gas gasification pilot plant. Disassembly of the pilot plant began on September 15 and was completed on September 20, with the skid modules ready for shipment to the designated demonstration site.

Chem Systems personnel interviewed several vendors during the July 14, 1976 visit to the ICI Corp. shop with respect to the various services necessary to relocate the pilot plant to the still to be designated demonstration site. Each vendor was asked to submit detailed bid proposals to Chem Systems by August 6.

Quotations for crating, rigging and truck shipment of the LPM pilot plant to one of the proposed demonstration sites were received by Chem Systems and reviewed. The final destination was not known at that time and no immediate action was taken since additional proposals might be required.

A spare parts list recommended by DPG was thoroughly reviewed but no further action taken since final destination of the pilot plant might determine the need for additional parts.

Quotations for chemical cleaning were also received and reviewed by Chem Systems during August. Vendor recommendations were that cleaning should not begin until the plant was ready for start-up since equipment would only rust again.

In early September, 1976, IGT's HYGAS Plant in Chicago, Illinois, was selected by ERDA and AGA as the first demonstration site for the LPM Pilot Plant.

Five trailers were delivered to ICI Corp. on September 20 and by September 22, all skid sections and the control house had been loaded on low-boy trailers. By September 28 all preparatory work for shipment was completed. On September 29, the five trailers left the ICI Corp. yard for the Chicago destination. Requests for quotations on all essential pilot plant spare parts were sent out at the end of September to all appropriate vendors.

All the skid sections had arrived in Chicago by the first week in October, 1976 and were unloaded in IGT's parking lot. After the LPM skid modules were moved to their designated location within the HYGAS Plant, reassembly work started. IGT contractors performed the necessary mechanical, electrical and instrumentation work. By the end of December, 1976, practically all of this work was completed.

Due to the extremely cold winter being experienced in Chicago, it was decided to provide additional steam tracing and insulation. The major process vessels were opened and internals inspected. There was little evidence of rusting and therefore it was decided to dispense with chemical cleaning. The spare parts list was completed, orders placed, and by the end of December, 1976, most had arrived in Chicago. Outstanding orders were expedited.

All materials and equipment for the analytical system were specified and ordered. This system was to be assembled in Chem Systems' Hackensack laboratories and, when completed, delivered to Chicago.

It was decided that shakedown and operation of the LPM Pilot Plant would be done with a hydrogen stream from a steam-methane reformer if synthesis gas from the HYGAS Plant was not available. The reformer could provide up to 2 MM SCFD of hydrogen containing an hydrogen/carbon dioxide ratio of 6/1. A revised experimental program was prepared for this hydrogen stream based on runs in Chem Systems' bench scale unit with a gas simulating the 6/1 hydrogen/carbon dioxide feed gas.

During the period January-March, 1977, reassembly and installation of the LPM Pilot Plant was essentially completed. Additional steam tracing was added to various sections of the plant to insure continuity of operation during the winter conditions. Because of the extremely cold weather experienced in Chicago, the steam tracing could not be commissioned until early in February, 1977. Meanwhile other items were attended to. The electrical system was commissioned with relays and alarm circuits checked out. Leak testing was conducted and any leaks encountered were eliminated.

The analytical system was designed and installed. The gas cylinder storage shed was completed and sample lines from the shed to the control room were installed. The gas chromatograph and integrator were installed and procedures for operation of the sampling and analytical system were prepared.

A motorized lift mechanism for the reactor nuclear gauge level device was designed and installed. This allowed for easier movement of the nuclear source and detector up and down the length of the reactor. Reactor bed densities could be measured and read out on both a locally mounted indicator and an indicator in the control room.

During the first shake-down runs, a problem was encountered with a misaligned flange on the hydrogen exchanger. This could not be repaired satisfactorily so the entire unit was removed from the system and returned to the vendor for repair. This exchanger is used to minimize the load on the electrical heater during the time when the catalyst is reduced with hydrogen. Therefore, temporarily removing it from the system did not hinder progress on reassembly of the pilot plant.

As oil was circulated through the system, first cold and then hot, blockages due to ice formation were removed. Instruments and controllers were commissioned. The seal flush system for the process oil circulating pumps was put into service.

Spare parts that had been previously ordered were received and a complete inventory prepared. A copy was given to IGT since it was their responsibility to replenish items used.

Pressure testing with nitrogen was started in the beginning of December, 1976. Several leaks were discovered and tightened up. Leaking valves were removed, greased and repacked, where necessary. Many lines to and from instruments had ice blockages which were steamed out. Process liquid was charged to the system via the oil make-up drum. The hydrocarbon liquid used is designated Freezene-100 and has a very low pour point (-35°F) to allow operation even with very low ambient temperatures.

Leak testing with nitrogen was completed during January, 1977. Leaks and blockages encountered were remedied. Early in January, a cold oil flow test throughout the entire system was started. The main circulating oil pumps were commissioned. Ice blockages around the process oil filters were cleared. Flow and level controllers in the oil system were commissioned. The process oil heater was turned on for the first time. However, the heater controller was not functioning due to a burned out SCR which was repaired.

During the first week in February, the process oil was heated to 200°F and nitrogen flow initiated through both the hydrogen reduction system and the synthesis gas feed line. A five day round-the-clock continuous run was started the second week in February to test integrated operation with oil and gas flows. All systems were commissioned. System pressure was held at 100 psig and the process oil slowly heated to 438°F. Heat losses in the unit prevented heating to any higher temperature. This was attributed to several uninsulated flanges in the major vessels and an excessive flow of cold process oil to the wear ring of the circulating oil pumps.

The unit was shut down on the fifth day to repair some leaks and insulate the exposed flanges. The system was quickly restarted and a second continuous shake-down run begun. The oil temperature quickly reached 560°F. System pressure was increased to 300 psig and several more leaks were detected at flanges, valves and other fittings. It was decided not to increase pressure any further until the leaks were repaired and hence the unit was shut down again. During this shutdown, the demister vessels was opened for inspection and it was discovered that the internals were missing. A replacement was quickly ordered from the vendor. The unit was run temporarily without any mist eliminator.

Another continuous shakedown run was made with system pressure at 600 psig and oil temperature at 460^{0}F. A few new leaks were encountered at the higher pressure.

During the first week in March, 1977, the pilot plant was prepared for the first experimental run. The reactor density measurement device was calibrated with the assistance of a Texas Nuclear representative. The reactor was then charged with catalyst and inert material at the bottom.

This completed all work in the task of start-up and pre-operational testing of the LPM Pilot Plant.

B. Experimental Program At the HYGAS Pilot Plant

During the second week of March, 1977, the catalyst loaded in the LPM reactor was reduced with hydrogen at 800°F. The bed was cooled to 550°F and hot process oil slowly introduced into the reactor. The entire system was stabilized with oil circulation and a small nitrogen flow. This is a "stand-by" condition for feeding synthesis gas to the unit. Due to difficulties encountered by IGT, neither HYGAS synthesis gas nor steam-methane reformer gas was available by the end of March. The LPM Pilot Plant logged close to 600 hours in a stand-by condition; 500°F and 100 psig. During this time, liquid only fluidization tests were performed. Results confirmed the empirical fluidization models developed during earlier Process Development Unit operation.

On April 4, 1977, synthesis gas from the HYGAS Pilot Plant became available. This was fed to the LPM reactor for only three hours when a severe upset occurred in IGT's acid gas removal system. A large quantity of sulfur laden diglycol amine (DGA) was carried over with the synthesis gas and passed through the LPM reactor and the rest of the LPM unit. The feed gas was stopped as rapidly as possible and the stand-by conditions reestablished until the extent of damage could be ascertained. The DGA also got into the analytical system destroying chromotographic columns and necessitating a thorough cleanup of the sampling system.

On April 11, 1977, the LPM unit was able to accept synthesis gas from IGT's catalytic steam-methane reformer. This gas had a hydrogen/carbon monoxide ratio of 9.5. Process variable scans were performed over a 24-hour period. Analyses of the data obtained appeared to indicate approximately a 40 percent loss in catalyst activity from that measured prior to the DGA upset. Since both the HYGAS plant and the hydrogen unit were scheduled to shut down, it was decided to also shut down the LPM plant and dump the catalyst. This was accomplished by first flooding the reactor with water. Catalyst samples were sent to Chem Systems' laboratory for analysis.

The LPM Pilot Plant ran for 44 hours when the feed gas supply was interrupted due to problems in the steam-methane reforming unit. The LPM unit remained under stand-by conditions for the next five days.

Feed gas was resumed on May 22, 1977. After an additional 14 hours of operations, a fire occurred while placing a clean process oil filter on stream. The fire started when hot oil escaped from a vent valve which was inadvertantly left wide open. The fire was extinguished after about 15 minutes by closing the vent valve. Damage to the unit was slight with the major losses being several pressure measuring devices, instrument air lines, and insulation. Run #2 was terminated during the fire and the unit was rapidly depressurized to minimize the extent of the fire.

Analysis of the data taken during the 60 hours of synthesis gas feed indicated basic agreement with bench scale and PDU results on the effect of gas flow rate and hydrogen/carbon monoxide ratio. The catalyst activity leveled off after the first 20 hours and thereafter remained constant. The kinetic rate constant was approximately 1/3 lower than values determined in BSU and PDU runs with the same catalyst. Several explanations were proposed for this observation: 1) inadequate catalyst reduction procedures in the pilot plant, 2) a poor batch of catalyst, and 3) hydrodynamic effects in the larger diameter pilot plant reactor. Catalyst samples were sent to Chem Systems' laboratory to test the above possibilities.

After Run #2 was terminated, the catalyst was dumped from the reactor without water flooding and found to be similar to that found at the end of the PDU runs. The reactor and entire unit was flushed with water to remove all residual catalyst which may have accumulated downstream when the unit was rapidly depressurized during the fire.

The entire LPM plant was cleaned out and other maintenance tasks performed. The demister internals were installed. Additional surface thermocouples were welded to pipes at various locations around the circulating process liquid system. A new shipment of 1,500 gallons of Freezene-100 process oil was received and stored in the oil make-up drum. The repaired hydrogen exchanger was returned by the vendor.

On May 2, 1977, a meeting was held between Chem Systems and IGT to review scheduling and synthesis gas feed requirements. It was decided that for Run #2, the hydrogen/carbon monoxide ratio of the steam-methane reformer would be lowered, if possible, from its normal 10/1 value to a 4-5/1 ratio. Chem Systems requested a 30-day uninterrupted supply of steam-methane reformer gas for a short-term continuous run.

Preparations for Run #2 were made at the beginning of May, 1977. The pilot plant was flushed and cleaned with water, dried, and then filled with process oil. On May 5, the second charge of catalyst was loaded into the LPM reactor. The reactor was heated up and the catalyst was reduced at 800°F for four hours with a hydrogen stream containing 1.5% CO. Following reduction, the catalyst was cooled to 550°F and process oil flow started into the reactor. The system pressure was raised to 500 psig and a series of liquid-only fluidization tests performed.

Synthesis gas from the steam-methane reformer was introduced into the system on May 14, 1977. The hydrogen/carbon monoxide ratio was gradually lowered from 10/1 to 6.5/1. During the first few hours of operation, the process oil flow was switched from a set of filters to the spare. A small oil leak developed at a pipe flange and caught fire. This was quickly extinguished and the leaky flange tightened.

Meetings were held with Chem Systems, IGT, and ERDA personnel to discuss the fire, future prevention and overall safety of the filter changing operation. It was decided to relocate the filters to a more accessible location. In addition, piping was to be added for venting and for refilling with fresh oil from the oil make-up drum.

By the end of June, 1977, these modifications were well along towards completion. Other maintenance items were also accomplished. The suction lines of the process oil circulating pumps were opened and the inlet basket strainers removed, cleaned and reinserted. The impeller and wear ring of one of the pumps were inspected and found to be in excellent condition.

The hydrogen exchanger was installed. New transmitters to replace those damaged in the fire were received and installed. A leaky flange under the reactor separator was removed and a new one ordered. The reactor separator was inspected and cleaned out.

LGT's annual turnaround was begun in July, 1977. Maintenance and modification work were performed and the pilot plant was readied for Run #3. Work performed included relocating the main process oil filters to make them more accessible, revising the oil filter piping, testing and radiography, instrument inspection and recalibration, and other routine maintenance and inspection items.

During the week of August 8, 1977, the entire system was flushed and drained twice, dried with nitrogen, and pressure tested to 500 psi. The pumps were thoroughly tested, and improvements were made on the analytical systems.

On Monday, August 22, the inerts were charged to the reactor up to the top of the oil sparger. The charging operation took place in a reactor half filled with cold Freezene-100 oil. After inerts loading, 2320 lbs

(10.8 ft^3) of INCO catalyst batch #087 H were charged, yielding a bed height of 4.7 feet. After charging, the circulating oil system was started, by-passing the reactor. Attempts to initiate cold flow into the reactor failed, but after heating the oil to 250°F, a breakthrough occurred and oil flow commenced.

Run #3 began on August 22, 1977, and contained 70 hours of successful operation on HYGAS product. A limited process variable scan was conducted to determine catalyst activation energy, fluidization parameters and the effects of other process variables on catalyst activity.

During the initial 12 hours of operation, both main oil filters plugged and the system had to be run on filter by-pass. When these filters were cleaned out, a total of 455 lbs of catalyst were removed, or approximately 20 percent of the original charge.

At 1630 hours on August 27, 1977, IGT interrupted HYGAS feed due to a blockage in their unit. The LPM Pilot Plant was switched over to HP nitrogen and bed fluidization tests were performed until August 30, when oil flow was terminated.

Feed gas to the LPM unit during Run #3 had an hydrogen/carbon monoxide ratio of 2.7 to 3.1 and contained small amounts of carbon dioxide and ethane as well as approximately 12 percent nitrogen and 28 percent methane. Methanation product had a methane concentration ranging up to 64 percent. CO conversions ranged up to 96 percent and selectivity to methane ranged from 85 percent at 651°F to 96 percent at 600°F. The remainder were mostly carbon dioxide. Calculations of the kinetic rate constant, the activation energy, and the catalyst activity as a function of reaction time indicate agreement with the LPM kinetic model and result in a kinetic rate constrant of 0.13×10^{-6} lb-mol/(atm-lb catalyst-sec) at 650°F. The catalyst seemed to maintain its activity throughout the run.

The pilot plant was prepared for Run #4. On September 19, 1977, all remaining INCO catalyst was charged to the reactor, which was full of oil at 350°. Approximately 2450 lbs. of catalyst were added. On September 23, oil was slowly bled into the reactor. The oil temperature dropped to 275°F and took about six hours to reach 530°F. The oil flow rate was brought up to 0.11 ft/sec very carefully. Feed gas from the steam-methane reformer containing 13% CO was begun at 1600 hours at 2000 SCFH. System pressure was raised from 80 psig to 500 psig over the next half hour, which was evidently too rapid, because it was discovered that the main circulating oil pump seals were leaking excessive flush oil into the system and the process was cooling down rapidly. At 1700 hours gas flow was stopped, the reactor isolated, and the oil system cooled while depressurizing to 80 psig.

After the spare pump was repaired on September 24, 1977, the system was reheated and repressurized. Steam-methane reformer gas was introduced into the reactor at 1600 hours on September 25.

Reactor temperature was increased to 650°F over a six-hour period and the feed gas flow rate was gradually increased to 39,000 SCFH over a 24-hour period. During the next 20 hours, four points from the process variable scan were completed plus a duplicate of the standard condition. The filters were plugging at a rapid rate, however, and by hour #44, the second and third filters were plugged and the system had to be placed on oil-filter by-pass while the filters were cleaned. 920 lbs. of catalyst were removed from the filters, or 33 percent of the original bed. Before the filter cleanout could be completed, a fire developed at a leaking flange on the circulating oil cooler. After 46 hours of reaction time, feed gas was terminated and shutdown of the unit began. Inspection revealed no visible damage caused by the fire.

Upon completion of the shutdown, all lines were flushed to remove catalyst deposits. A total of 1825 pounds of catalyst were removed from the system other than the reactor, which implied that only 40 percent of the original catalyst bed remained at the end of the run.

The catalyst activity dropped only 20 percent even though 60 percent of the catalyst was carried out of the reactor. The magnitude of the rate constants were similar to those obtained in Run #3, but only 25 - 30 percent of those obtained in the laboratory. This evidence indicates that the hydrodynamics in the reactor was far from ideal. Evidently, the gas was spouting through the bed and some of the catalyst never contacted the gas.

To remedy this problem, reactor modifications including internal baffles, sparger redesign and distribution plates were discussed at a meeting held on October 3, 1977 at the Fairchild Research Center. It was decided to modify the reactor internals before preparing the pilot plant for the next run. DOE personnel were briefed on the flow distribution problems in the LPM reactor in another meeting on October 13.

Several alternatives were considered to improve the flow distribution. By the end of October, it was decided to go ahead with a screen catalyst support and also modify the gas and oil spargers. This would eliminate the use of inerts at the bottom of the reactor.

This modification called for redrilling the gas sparger with 1/8" holes to improve gas distribution. The oil sparger was eliminated in favor of an oil disperser which was to be inserted through the oil inlet pipe. This disperser also connected to a plug for a catalyst withdrawal hole in the support screen.

The support screen was ordered on November 18, 1977 with 0.004-inch slot widths for gas and oil distribution and a 2.5-inch hole in the center for catalyst removal. It was received at IGT on December 28, 1977 and work orders were immediately issued for installation of the screen and reassembly of the bottom head of the reactor.

Simultaneously, other alternatives to the screen support design were investigated in case the screen failed to improve flow distribution during the next run. One such alternative, designed by CSI,[5] was sent to fabricators for estimates. A prototype of this design was built for the PDU and tested prior to installation at the pilot plant.

At the pilot plant, catalyst was cleaned from all low spots. The reduction heater, H-102, and the main circulating oil heater, H-101, were opened for inspection. Two surface thermocouples, found detached, were braised onto the heater surface and the bundles were reinstalled. The circulating oil cooler, E-103, was also opened for inspection.

The bottom of the reactor was disassembled early in October, 1977. After cleaning out catalyst and inerts, work began on modifying the oil inlet line and the gas sparger in preparation for the catalyst support screen. Other pilot plant maintenance work was carried out at the same time.

A complete list of flanges to be insulated with removable flange shields, for safety and hot bolt tightening during start-up, was transmitted to IGT. Operating instructions were updated to include a hot bolt tightening checklist.

Meetings and discussions with IGT and DOE personnel were held regarding the strategy, timetable and costs of LPM reactor modifications as well as the need for additional operators during future runs. Also, it was proposed to DOE that the pilot plant remain at IGT until the development phase and experimental program were completed.

At the beginning of January, 1978, the catalyst support screen was inspected and installed. Designs for the assembly of the catalyst removal plug and surrounding piping were finalized, the piping was fabricated, and the entire reactor bottom head assembly was reinstalled by January 22. Other mechanical work was performed, including relocating some cooling water piping, installing lighting near the main process filters, replacing insulation, and installing a differential pressure gauge across the reactor.

The pilot plant was pressure tested for pre-startup during the last week in January. On February 7, 1978, Calsicat Ni-230S catalyst was charged to the reactor for Run #5.

Run #5 was successfully completed in February. Twenty-five hours of reaction time were achieved on HYGAS synthesis gas before the HYGAS pilot plant was shut down because of mechanical problems. Reactor conditions ranged up to 650°F, 500 psig, 135 GPM oil flow and 15,000 SCFH feed gas flow. Catalyst activity was comparable to previous pilot plant runs with Calsicat Ni-230S, namely 0.5×10^{-6} lb-mol/(sec-lb catalyst-atm).

Catalyst reduction began on February 11 with reduction temperatures maintained above 800°F for 20 hours. The oil system was started on February 13, heated to 500°F and introduced into the five-foot-high catalyst bed. HYGAS synthesis gas was introduced into the reactor on February 23 after completion of some liquid-only fluidization studies.

On February 24, when HYGAS shut down, it was decided to shut down the LPM pilot plant because a high rate of catalyst attrition had been observed during the entire 329 hours of operation. The high catalyst breakup rates were suspected to have been caused by the weakened physical structure of the catalyst due to its long-term outdoor storage at IGT. This suspicion was later verified in a PDU run at the Fairchild Research Center.

The unit was cleaned out and prepared for Run #6. A batch of catalyst #038-A, 1/8" tablets, was shipped to the pilot plant. Personnel from Process Operators, Inc. arrived at the pilot plant on March 20 and began manning the unit with one person per shift for the duration of Run #6.

On March 24, 1978, 860 pounds of catalyst #038-A were loaded into the reactor, and catalyst reduction began with a mixture of hydrogen and nitrogen on March 30. A liquid-only fluidization study was carried out on April 3-4 and then the unit remained in a standby mode until steam-methane reformer gas became available on April 18.

Reactor conditions were brought up to 500 psig, 650°F, 35,000 SCFH of feed gas and 150 gpm of oil flow where the initial catalyst activity was 1.1 x 10^{-6} lb-mol/(sec-lb catalyst-atm). This was substantially higher than that observed in earlier pilot plant runs. Some cracking of the oil occurred when the reactor temperature rose above 650°F. Due to the high catalyst activity, some temperature cycling occurred while attempts were being made to line out the process conditions. Before steady conditions could be reached, feed gas was interrupted after ten hours of methanation in order to supply hydrogen for HYGAS startup.

During the subsequent period of oil-only flow, the process oil filters were plugging in approximately 15-hour intervals. An attempt to restart feed gas on April 20 had to be discontinued after 2.5 hours due to filter plugging. Evidently, the catalyst binder was not strong enough at this point to withstand LPM process conditions.

On April 24, steam-methane reformer gas feed was started at 300 psig, 600°F and 30,000 SCFH while by-passing the main process oil filters. While the initial catalyst rate constant was 0.8×10^{-6} lb-mol/(sec-lb catalyst-atm), it increased to 4.0 x 10^{-6} in ten hours and CO conversion approached 100 percent.

On April 25, HYGAS product was substituted in place of reformer feed. Again, the initial catalyst rate constant was low (1.2×10^{-6}), but after 20 hours it had increased to 5.0×10^{-6}. The enhanced catalyst activity, which was based upon the catalyst loading prior to initiation of filter by-passing, was caused by the breakup of catalyst particles into fines that circulated as a slurry throughout the oil system. Since the LPM Pilot Plant was not designed for slurry operation, accumulation of catalyst fines in the seal flush system eventually caused all the oil pump seals to fail and the unit had to be shut down.

At the end of the run, no integral catalyst particles were found in the reactor. Therefore, the efficient methanation results can be attributed to slurry operation. Based upon the estimated slurry concentration in the circulating oil, the catalyst rate constant within the reactor was approximately 40×10^{-6} at the end of the run.

Run #6 was terminated after 645 hours on-stream, which included 24 hours of methanation on HYGAS product and 30 hours on steam-methane reformer gas. The results were better than all previous pilot plant runs. Each time feed gas was restarted, the rate constant was initially low and then gradually increased as more catalyst became reslurried. The initial catalyst activity, which occurred in a packed bed, was higher than the activities previously observed in the fluidized beds at the pilot plant. Less backmixing apparently took place in the packed bed mode of operation.

During May, 1978, the pilot plant was cleaned out and internals were fabricated for the reactor to reduce backmixing. These internals consisted of vertical stainless steel tubes which were plugged at the upper end. The unconnected vertical surface area was designed to reduce the reactor equivalent diameter without compartmentalizing. In addition, a new catalyst support plate containing bubble caps with non-return valves was fabricated. The former catalyst support screen was utilized as a catalyst retention screen covering most of the reactor cross-sectional area above the vertical tubes.

The reactor modifications were completed by June 11, 1978, and the circulating oil pump seals were replaced. On June 21, 2200 pounds of INCO-J catalyst were loaded into the reactor. Since this type of catalyst does not require reduction, Run 7 began immediately with the introduction of steam-methane reformer gas. Most of the 32 hours of methanation consisted of operation at 30,000 SCFH feed gas, 150 GPM oil flow, 500 psig and 600°F. CO conversion ranged from 48 to 65 percent. The catalyst rate constant started out initially at 0.13×10^{-6} lb mol/(atm-lb catalyst-sec) and dropped to 0.06×10^{-6} by the end of the run.

The drop in catalyst activity was accompanied by a loss in expanded catalyst bed height. Evidently, the INCO-J catalyst was being carried out of the reactor in a manner similar to previous experiences with other INCO catalysts (Runs #3 and 4), despite the inclusion of baffles and a catalyst retention screen within the reactor. Because of the small diameter of INCO-J particles (250-500 microns), these solds cause bubble coalescence in a three-phase fluidized system. The vertical baffles were probably not sufficient to restrict bubble growth and spouting occurred which carried catalyst out of the reactor. For a larger diameter catalyst particle, such as Calsicat Ni-230S, which would operate in the range where bubbles are broken up rather than colesced, the vertical baffles in the reactor might have reduced backmixing as intended even though they did not reduce backmixing with INCO-J.

On June 22, 1978, the main circulating oil filter by-pass valve was found to be partially open. After closing it, the differential pressure across the inboard filter rose rapidly. The outboard filter was heated up and brought on stream. Both the inboard filter and the filter by-pass were shut off. Standard operating procedures for cooling down the inboard filter were carried out, and the filter was opened for cleanout. A leak developed through the filter discharge valves into the filter cavity.

Attempts to stop the leak failed and a fire started at this filter when the oil overflowed the filter cavity. Details of the events leading up to and including the fire have been covered in a separate "Report of Fire." Clean-up and coordination of the fire investigation was begun on June 26. Representatives of DOE, IGT and CSI formed a fire investigation committee. Meanwhile, the pilot plant was completely drained of oil and entrained catalyst. All utility lines leading to the LPM unit were blocked off and isolated. The LPM unit was inerted, awaiting repair.

As a result of the fire at the LPM Pilot Plant in June, 1978, a preliminary estimate was made of the cost to repair the unit. On September 27, a team from Argonne National Laboratories made a visual metallurgical inspection of the vessels in the burn area.

The fire investigation committee dismantled the suspect filter inlet and discharge valves. Solids deposits were found which caused the leak that resulted in the fire. On August 7, the committee issued its report which detailed the results of the investigation and recommendations for future operation.

Based upon a directive from DOE to temporarily suspend the experimental program at the pilot plant for a period of four to six months, all activities were discontinued except securing the unit for short-term shutdown. Catalyst and oil were removed from the equipment where possible, the unit was reassembled and all vessels were dried with nitrogen. Files and delicate instruments were shipped to the Fairchild Research Center for temporary storage.

The report of the preliminary inspection of the vessels damaged in the fire at the LPM Pilot Plant was received from Argonne National Laboratories. This report covered observations and recommendations based on a visual metallurgical inspection. No major damage was observed. Copies were forwarded to DOE.

C. Laboratory Support Work

As part of the LPM Pilot Plant development, evaluation of commercial catalysts for use in the pilot plant and commercial size plants were performed. Using the bench scale unit, several formulations of the CRG-A catalyst, prepared by LDI Catalyst Company, were tested.

During July, 1976, two runs were made and both were terminated due to plugs which had developed. In both cases, the catalyst was found in goods shape. The reactor was modified for future use to prevent plugging from occurring.

A third run was made in August, 1976 with CRG-A tablets and Witco 40 mineral oil at 500 psig and 316-340^{0}C and a 3/1 hydrogen/carbon monoxide ratio. The observed reactivity of the catalyst was good during the one-day run, and the catalyst looked in good condition.

Two additional runs were made during August. The first used operating conditions similar to the previous run and resulted in the same reactivity after the first day. The reactivity dropped slightly on the next day before a plug developed on the third day.

The second run used an extrudate form of the catalyst and the same operating conditions of the previous two runs. A much higher activity was observed and the catalyst was found to be in good condition after the one-day run.

A 90-hour run was made with the tableted form of catalyst and 3/1 hydrogen/carbon monoxide feed gas. Initially, the reactivity was 5-6 x 10^{-6} g-mol/(atm-g catalyst-sec) and it slowly decreased to 4.5 x 10^{-6} over the first 18 hours. In the next four hours, there was an unexplained rapid loss in activity and the reactivity equilibrated at 1 x 10^{-6} for the next 65 hours.

During September, 1976, an 80-hour run was performed with the extrudate form of the catalyst and a 3/1 hydrogen/carbon monoxide feed gas. The reactivity equilibrated at 5×10^{-6} after approximately 50 hours and the run was voluntarily terminated after 80 hours. The catalyst was found to be in good condition.

The excellent behavior of the catalyst during the previous run can be taken as evidence that a poisoning-type failure was responsible for the sudden activity loss experienced after 18 hours on-stream with the prior run.

Three runs were made in the Process Development Unit (PDU). The first run tested CRG-A tablets (3/32" dia. x 3/32") with a 2/1 hydrogen/carbon monoxide feed gas and Witco-40 mineral oil. The catalyst activity stabilized after about 20 hours and remained constant for the 92 hours of operation. The results were comparable to those obtained earlier with the same system in the bench scale unit. The second run tested a CRG-A extrudate (same dimensions) and ran for 68 hours. The catalyst activity stabilized at a rate practically twice that of the tablets. In the middle of the second run, the process liquid was switched from Witco-40 to Freezene-100, another Witco product with a lower pour point (-35°F). No adverse effects were observed and a large supply was ordered for use in the LPM Pilot Plant. The third PDU run tested an Engelhard catalyst with Freezene-100. The catalyst activity was lower than the CRG-A tablets, but entirely consistent with a previous bench scale unit run with this catalyst.

The bench scale unit was run with a synthesis gas feed simulating the hydrogen/carbon monoxide gas that would be obtained from the HYGAS reformer and used in the LPM Pilot Plant. The results could be correlated with the basic LPM/S kinetic model and from that a revised experimental program was planned for the LPM Pilot Plant in the event synthesis gas from the HYGAS Plant was not available.

Several process oil samples from the pilot plant were analyzed for sulfur content at Chem Systems' Fairfield Laboratories. The results indicated less than 2 ppm sulfur, which was the lower limit of the analytical technique used.

A new catalyst, INCO-H, specifically prepared for the LPM process, was tested in the BSU (bench scale unit) in July, 1977. The catalyst is a finely divided (0.25 - 0.5 mm), spherical, nickel-based catalyst. It is about 3 - 4 times denser than typical methanation catalysts, with a bulk density of 3 - 3.5 gm/cm^3. Experiments indicated that the material is cost competitive with existing catalysts. In addition, the material has been shown to possess superior physical properties, requires no activation procedure, and is not pyrophoric under normal ambient atmospheric conditions. A variable scan was performed with this catalyst in order to check the operating characteristics prior to full scale testing in the pilot plant. The results were sufficiently promising to warrant full-scale testing. These tests took place during LPM Pilot Plant Run #3 in late August, 1977.

During the initial INCO-H pilot plant series, nearly 30 percent of the catalyst bed was carried over the first few hours on-stream. A series of fluidization tests were performed in the PDU in order to provide some insight into the start-up problems encountered. These experiments showed that the high viscosity of the Freezene-100 at ambient temperature caused catalyst particles to be smoothly elutriated from the reactor. These problems can be alleviated by simply preheating the oil to about 300°F, since the viscosity drops by almost two orders of magnitude over this temperature range. This procedure was successfully demonstrated at the pilot plant during the second start-up with INCO-H.

A series of liquid and liquid-gas fluidization runs were performed in order to determine the operating characteristics of INCO-H. The minimum fluidization velocities for this catalyst are similar to the velocities for the Calsicat Ni-230S. The liquid-gas fluidization data, however, show marked differences from all other catalysts. The bed expansion ratio is virtually independent of gas velocity up to approximately 0.2 ft/sec.

Tests were performed on the pilot plant batch of Calsicat Ni-230S catalyst in order to determine whether its poor performance in the pilot plant was due to incomplete reduction and activation.

In mid-July, 1977, a 200-gram sample of Calsicat Ni-230S used in the pilot plant was loaded in the BSU and rigorously reduced with hot hydrogen purge gas for 24 hours. A process variable scan was carried out which resulted in an equilibrated activity value of 1×10^{-6}, which was only 60 - 70 percent of the value previously measured with this catalyst. In September, three more process variable scans were performed, but this time, catalyst activities were much higher, approximately 5×10^{-6}. It was determined that the last three runs were indicative of true catalyst behavior, and that the results from the first bench scale run are suspect. These activity levels are 5 - 8 times higher than those obtained in the pilot plant runs, and this confirms that reduction procedure is not a serious problem but rather the poor gas distribution in the reactor is the major cause of lower catalyst activity.

Two catalysts, INCO D and INCO E, are modifications of the INCO H catalyst previously tested in both the bench scale and pilot units. The primary differences between the catalysts are particle size and the method and severity of the activation procedures. Both catalysts were tested in the BSU over a temperature range of 550 - 620^{0}F and with feed gas mixture of 3 - 9 H_2/CO molar ratio. The results for the two variable scans compare favorably with the results for the INCO H catalyst tested in August, 1977.

Two runs were conducted in the bench scale unit using an improved Grace CRG-A (3/32" extrudates) catalyst. This material was from the same production run as a batch sent to the pilot plant for future runs.

In BSU Run #9, reduction was carried out at 880° as recommended by the manufacturer. The initial activity was 7 - 9 x 10^{-6} g-mol/(sec-g catalyst-atm) or 2 - 3 times more active than any other catalyst candidate. The unit had to be shut down after the fifth day of operation due to a plug which formed in the reactor.

The same conditions were repeated with a fresh batch of catalyst in BSU Run #10. During the thirty-hour run, an equilibrated activity level of 2 x 10^{-6} g-mol/(sec-g catalyst-atm) was recorded and the activation energy of 18,750 cal/g-mole was also higher than usual.

Three runs were attempted in the PDU with the same Grace CRG-A catalyst. In PDU Run #10, the catalyst was reduced at 800°F due to problems in the temperature control system. An equilibrated activity of 2 x 10^{-6} g-mol/(sec-g catalyst-atm) was observed during the 60-hour run which was much lower than the BSU results, but comparable to PDU results with other catalysts. Catalyst attrition also seemed normal.

A second charge of Grace extrudates was loaded into the PDU and reduced at 890°F in PDU Run #11. Filter and reactor plugging became a problem after only a few hours of operation and the run was terminated. In PDU Run #12, the reduction temperature was held to 850°F, but rapid plugging still occurred and the run was again terminated.

Evidently, this Grace catalyst exhibits unusually high activity when high reduction temperatures are used, but physical strength of the catalyst is sacrificed. At normal reduction temperature, the catalyst activity is also normal and the physical strength of the extrudate is good.

PDU Runs #14 and #15 were performed using Grace 3/32" O extrudates. In every run, the initial catalyst activity was 2.45 ± 0.1 x 10^{-6} g-mol/(sec-atm-g catalyst). This gradually declined to an equilibrium activity value of 1.70 ± 0.1 x 10^{-6} g-mol(sec-atm-gm-catalyst). The catalyst particles held up well throughout the runs although there was evidence of some particle breakage. On the basis of these results, the Grace catalyst was deemed to be a possible candidate for further testing in the pilot plant.

During March, 1978, the PDU operated with catalyst samples obtained from the LPM Pilot Plant. Run #16 was conducted using Calsicat Ni-230S 3/32" spheres, while Run #17 used catalyst #038-A 1/8" Dia. x 8/8" cylindrical tablets. Both runs used the test design bubble cap for introduction of gas and oil into the reactor. Run #16 comprised 28 hours of accumulated reaction time and an additional 20 hours of liquid-only fluidization. Catalyst activity for Run #16 was 1.75 x 10^{-6} g-mol/(g catalyst-atm-sec). The catalyst breakup and attrition rates for this run were similar to those experienced during Run #5 in the pilot plant. When the reactor was emptied at the end of the run, visual examination of the catalyst showed evidence of particle breakage, confirming that its physical strength had deteriorated during its long outdoor storage at IGT.

Run #17 was conducted with #038-A tablets. Catalyst activity was 1.30 x 10^{-6} g-mol/(g catalyst-atm-sec) over the course of the run. The run had to be terminated, however, because of massive system-wide plugging caused by a catalyst breakup. This breakup had created a granular, mud-like sludge that permeated the entire system. The reasons for this disintegration of the catalyst are unknown.

Upon completion of PDU Run #17, it was discovered that oil heater elements had melted down and shorted to the heater shell. A new heater assembly was fabricated and installed along with an improved heater control system. Simultaneously, the process oil filter was reinstalled in a more accessible location along with a new second filter to permit continuous filter usage during future runs. By the end of June, the PDU was ready for operation, but did not operate during the remainder of the contract period.

D. Rates of Carbon Formation Experimental Program

During the period July - September 1977, detailed equipment take-off lists were completed and all remaining items were ordered for the multiple fixed-bed reactor system. Several of the long-lead delivery items were received during this period.

Construction of the test unit assembly began in October, 1977. The assembly is subdivided into five identical reactor systems plus a master control panel.

Initially, one reactor system was completed as a prototype for the other four units. In addition, feed gas lines from the trailer to the reactor skid, as well as the reactor skid itself, were completed. A modular unit for two gas booster compressors was also constructed.

By the end of December, 1977, the four duplications of the prototype reactor system were completed and construction of the analytical unit adjacent to the reactor skid was started.

The construction of electrical and analytical systems was completed in early February, 1978. Each component was then carefully checked for leaks and malfunctions prior to conducting any experimental work.

C.F. Braun was contacted to perform a series of computer calculations to establish the thermodynamic carbon formation boundaries in the C-H-O system for both graphite and non-equilibrium carbon. This information was later received in the form of computer printouts and used to determine the feed gas composition for the experimental runs.

A meeting held on January 11, 1978, defined the overall scope of the experimental program and updated the program time schedule. Some important conclusions from this meeting are summarized below:

- Among the many variables involved in determining a set of experimental conditions for methanation, particularly important ones are feed gas composition, operating pressure and temperature, catalyst type, test duration and amount of steam injected.

- Gases simulating three different coal gasification process sources would be used to represent different regions in the atomic C-H-O boundaries of both graphite and nonideal carbon formation. In formulating the feed gas composition, however, it is necessary to shift the proportions of CO, CO_2, and CH_4 depending upon the carbon oxide limitations. The atomic C-H-O distribution remains unchanged.

- Tests were to be carried out at 600, 900 and 1200°F (a high-temperature catalyst might be necessary at 1200°F). The pressures would be 500 and 1000 psi, with duration of 500 hours.

- Two different catalysts would be tested: one is from Harshaw (Ni-104T) and the other from United Catalyst (G-87 P, 1/8" extrudates).

- Steam injection is needed to bring the feed gas composition out of the nonideal carbon or graphite forming regions. This steam injection reduces the atomic C-H-O fraction until it moves outside the graphite formation boundary.

The first series of exploratory runs was conducted to check out the stability and performance of each reactor and of the entire system as a whole. Four reactors were loaded with catalyst and raised to 315°C and 500 psig with a feed of 6.7 liters/min. A standard operating procedure for each reactor unit was developed through this series of runs.

A second series of runs was conducted with 4 percent and 6 percent CO feed gas in order to measure the temperature profile in detail and to learn to control the temperature rise. The third series of preliminary runs was designed to increase the space velocity to the desired level of 10,000 v/v-hr. An attempt was made to determine the operating procedure for steam injection.

These preliminary runs established that several procedures would have to be implemented in future runs, including limiting the feed carbon oxide content to 4 percent, removing insulation from the reaction zone to minimize the exotherm temperature, maintaining the inlet temperatures above the methanation ignition temperature and instituting effective startup procedures.

The experimental program was begun with Lurgi gas, modifying the gas such that its CO content was 4 percent but maintaining its atomic C-H-O fraction. A summary of all runs completed during the course of this study is shown in Table III-D-1.

Runs 1, 2, 3

The first three standard runs with Lurgi Gas/G-87P catalyst at 35 atm, 480°C and 500 hours were begun in March, 1978. Temperature profiles indicated that the reaction took place mainly in the upper fifth of the catalyst bed. Spent catalyst was analyzed for carbon, surface area, pore volume and x-ray diffraction. Most carbon was formed in the top quarter of the beds in Run 1 (no steam addition) and Run 2 (5 percent steam addition). These runs operated in the carbon forming region. In Run 3, which operated outside the carbon forming region with 30 percent steam injection, carbon formed in all catalyst bed sections. This result was unexpected and, therefore, was re-examined with a second catalyst at a later date.

TABLE III.D.1
SUMMARY OF RUNS COMPLETED IN THE RATES OF CARBON FORMATION EXPERIMENTAL PROGRAM

RUN NO.	GAS	CATALYST	TEMP. (C)	PRESS (ATM)	STEAM (%)	TIME (HOURS)
1	Lurgi	G-87P	480	35	0	500
2	Lurgi	G-87P	480	35	5	500
3	Lurgi	G-87P	480	35	30	500
4	Lurgi	G-87P	315	35	0	500
5	Lurgi	G-87P	315	35	5	300
5A	Lurgi	G-87P	315	35	5	215
5B	Lurgi	G-87P	315	35	5	510
6	Lurgi	G-87P	480	69	0	500
7	Lurgi	G-87P	480	69	5	500
8	Lurgi	G-87P	480	35	3.85	100
8A	Lurgi	G-87P	480	35	3.85	0
8B	Lurgi	G-87P	480	35	3.85	25
8C	Lurgi	G-87P	480	35	3.85	50
8D	Lurgi	G-87P	480	35	3.85	100
9	Lurgi	G-87P	480	35	3.85	310
10	Lurgi	G-87P	480	35	3.85	580
11	Lurgi	G-87P	480	35	3.85	900
12	Lurgi	G-87P	480	35	3.85	1200
12A	Lurgi	G-87P	480	35	3.85	1105
13	Lurgi	G-87P(Regen.)	480	35	3.85	500
14	Lurgi	Ni-104T	480	35	30	510
15	Lurgi	Ni-104T	480	35	0	500
16	Lurgi	Ni-104T	480	35	5	500
17	Lurgi	Ni-104T	480	35	3.85	96
18	Lurgi	Ni-104T	480	35	3.85	280
18A	Lurgi	Ni-104T	480	35	3.85	305
19	Lurgi	Ni-104T	480	35	3.85	570
20	Lurgi	Ni-104T	480	35	3.85	1200
21	Lurgi	Ni-104T	480	35	3.85	620
22	Lurgi	Ni-104T	315	35	0	500
23	Lurgi	Ni-104T	315	35	5	500
24	Lurgi	G-87P (T)	480	35	0	505
25	Lurgi	G-87P (T)	480	35	5	505

Runs 14, 15, 16

Runs 14-16, initiated in July, 1978 and completed in August, 1978, were designed as standard conditions to study the effect of steam dilution on the Lurgi Gas/Ni-104T catalyst combination. Near equilibrium conversion was obtained for all three runs. Although only one run operated outside the region thermodynamically favorable to graphite formation, all three produced equivalent amounts of carbon. In sharp contrast to similar tests with G-87P catalyst, the carbon level with Ni-104T was negligible after 500 hours of methanation. This implies that the physical and chemical characteristics of the catalyst may be as important as the feed gas composition relative to theoretical equilibrium carbon formation boundaries.

Runs 24, 25

The main objective of these two standard runs was to determine whether catalyst physical properties are as important as chemical properties in carbon formation. Two runs were initiated with a tableted version of United Catalyst G-87P (3/16" dia x 1/8"). Run 24, without steam addition is similar to the conditions of Run 1 while Run 25, with 5 percent steam addition, duplicated the conditions of Run 2. The temperature profile appeared normal with the hot spot located one inch from the top of the catalyst bed. The conversion was nearly at equilibrium throughout the run. Both spent catalysts had a slight silvery appearance indicating that this version of the catalyst forms only minor amounts of carbon, over an order of magnitude lower than the extrudate form.

Runs 4, 5, 5a, 5b

These runs were designed to study the effect of low temperature operation with G-87P catalyst. They were conducted at 35 atm, 315^{o}C and 500 hours. The reactors were loaded with 90 percent inerts and 10 percent catalyst to control the temperature rise and, therefore, the gas space velocity was 10 times greater than in Runs 1-3. Runs 5, 5a and 5b also had 5 percent steam injection. The first three of these runs exhibited decreasing catalyst activity with time. Analyses for trace contaminants yielded no abnormalities. Therefore, it was assumed that accelerated aging took place due to the high gas space velocities. Carbon was formed in all sections of the catalyst beds in these runs, but more carbon seemed to be present in the top sections. Comparing Runs 4 and 5 with Runs 1 and 2 for the effect of temperature, the average total carbon content was 3.3 percent in Run 4 (135°C, no steam injection) versus 5.8 percent in Run 1 (480°C, no steam injection). With 5 percent steam injection, the carbon content was 3.7 percent in Run 5 at 315°C versus 5.7 percent in Run 2 at 480°C. However, a direct comparison may be invalid because Runs 4 and 5 did not operate a full 500 hours due to premature catalyst deactivation.

Run 5b was started on September 23, 1978 to duplicate the conditions of Runs 5 and 5a with the exception that the preheat zone prior to the catalyst bed was maintained about 20°C to 30°C higher, at about 285°C. This run showed that conversion was very sensitive to the inlet and initial catalyst bed temperature. This lends support to the hypothesis that the apparent deactivation is strongly related to an increase in catalyst initiation temperature.

Runs 22, 23

Runs 22-23 were initiated in August, 1978 to study carbon formation at low temperature on Ni-104T catalyst. Both runs were completed on September 21, 1978. In contrast to Runs 4-5 with G-87P catalyst, the Ni-104T runs deactivated only slightly in 500 hours. Conversions averaged 50-70 percent of equilibrium during these runs.

Runs 6, 7

Runs 6 and 7 were conducted with Lurgi Gas/G-87P catalyst at 69 atm, 480°C and 500 hours to study the effect of higher pressure. Run 7 included 5 percent steam addition. Spent catalyst samples were analyzed for carbon content and a comparison with Runs 1 and 2 indicate the effect of pressure. With no steam injection, the average total carbon content was 3.5 percent in Run 6 at 69 atm versus 5.8 percent in Run 1 at 35 atm. With 5 percent steam injection, the carbon content was 4.3 percent in Run 7 at 69 atm. versus 5.7 percent in Run 2 at 35 atm.

Based upon these results, it appears that increased operating pressure reduces the level of carbon deposition, with all other circumstances the same. However, operating difficulties that occurred during these runs make these findings somewhat tentative.

Runs 8, 8a, 8b, 8c, 8d, 9, 10, 11, 12, 12a

These runs were designed to study cumulative carbon formation as a function of time on-stream over the period of 0-1,200 hours with Lurgi Gas/G-87P catalyst at 35 atm, 480°C and 3.85 percent steam. Additional tests were conducted in order to repeat runs which experienced operating problems.

Run 8 through Run 12 were scheduled to operate for periods of 100, 300, 600, 900 and 1,200 hours with G-87P catalysts. Shortly after completing Runs 8 and 9, a failure of the booster compressor system resulted in 100 percent steam flow to the reactors of Runs 10, 11 and 12, Up to that time, all five reactors exhibited extremely stable operation, as evidenced by their temperature profiles and the constant near equilibrium conversion. When Runs 10, 11 and 12 were restarted, the temperature profile for Run 10 exhibited a marked shift in the hot-spot temperature, indicative of catalyst deactivation.

This was quite similar to the circumstances of Run 7, previously described. What was unusual, however, is the fact that Runs 11 and 12 were not similarly affected. When this original series of runs was completed, the catalysts were analyzed for carbon levels and crystallographic structure. Catalysts from runs 10, 11 and 12 exhibited reduced surface area, previously attributed to 100 percent steam operation. In addition, carbon deposition levels for samples from Runs 10 (600 hours) and 12 (1200 hours) were unusually low and were of an amorphous nature, not the crystalline structure detected in the samples from Runs 8, 9, and 11.

In an attempt to clarify these anomalies, data from Run 2 were used in place of Run 10, while Run 12 was repeated, as Run 12a. Additional runs were also performed, Runs 8a, 8b, 8c, and 8d, in order to obtain data for operating times of less than 100 hours. All the supplementary runs gave near equilibrium conversion. It appears that there is a short induction period of about 100 hours during which the carbon level slowly increases from 0.5 percent to 0.87. At that time, the rate rapidly accelerates, and by 300 hours the carbon level has increased to over 5 percent. The carbon level continued to regularly increase, reaching almost 10 percent after 900 hours. Then, for an as yet unexplained reason, since the repeat Run 12a ran without mishap, the carbon level at 1200 hours was only 2 percent.

Runs 17, 18, 18a, 19, 20, 21

A total of six runs, Run 17 through 21 and Run 18a, were conducted, over the range of 100 to 1200 hours duration with Ni-104T catalyst, to study cumulative carbon formation as a function of time on-stream. All operated without mishap, yielding near equilibrium conversion at all times. The reactor temperature profiles were extremely stable throughout the runs. However, while unloading the reactor contents of Run 18 the inlet section was found to be severely sintered. It was also apparent from the 2000^{o}A nickel crystallite size that the reactor must have experienced an extremely high temperature period of operation. In spite of this, the catalyst still maintained its high level of activity. Nevertheless, this run was repeated, as Run 18a.

In all runs, carbon deposition levels were quite low, essentially equivalent to the freshly reduced catalyst carbon levels. Physical and crystallographic analyses corroborate existing evidence that this catalyst is particularly stable under these operating conditions.

Run 13

This Run was designed to test the ability to regenerate in-situ a spent catalyst containing carbon. Portions of spent catalyst from Runs 2, 8 and 9 were collected and well mixed prior to loading into the reactor. The catalyst was then oxidized for 16 hours at 250°C after which the oxidized catalyst appeared gray, similar to fresh catalyst, and seemed structurally weak and easily crushable. The carbon level on the oxidized catalyst was determined to be 2.5 percent.

The catalyst was reloaded into the reactor and Lurgi feed gas was introduced. The hot spot temperature remained exceptionally stable throughout the run and analysis of the effluent indicated that equilibrium was attained at all times.

Thus, it appears that controlled oxidation can be utilized to remove deposited carbon without altering catalyst activity, but some questions remain as to the effect of multiple regeneration cycles on the particle physical properties.