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LIQUID PHASE METHANATION/SHIFT PROCESS DEVELOPMENT

Final Technical Report, September 1, 1980—November 30, 1981

May 12, 1982

Work Performed Under Contract No. AC21-80MC14384

Chem Systems Research & Development Group
Fairfield, New Jersey

TECHNICAL INFORMATION CENTER
UNITED STATES DEPARTMENT OF ENERGY

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FINAL TECHNICAL REPORT
SEPTEMBER 1, 1980 - NOVEMBER 30, 1981
LIQUID PHASE METHANATION/SHIFT
PROCESS DEVELOPMENT

SUBMITTED TO:

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1.0 ABSTRACT

This final technical report covers the work performed between September 1, 1980 and November 30, 1981 relating to Chem Systems' Liquid Phase Methanation/Shift Process. The program, carried out at Chem Systems Research Center located in Fairfield, New Jersey, included two tasks: (1) a continuation of experimental study on rates of carbon formation in methanators, and (2) evaluation of the hydrodynamics of a three-phase fluidized bed for the process.

Under the current program (DOE Contract No. DE-AC21-80MC14384), work was performed on (1) the rate of carbon formation, and (2) the hydrodynamics study.

The work performed on Task I - Rates of Carbon Formation - can be summarized as follows.

A total of 44 runs were completed covering testing of five (5) commercially available catalysts. All catalysts were tested at 900°F, 1000 psig and 10,000 hr⁻¹ VHSV. The shifted methanation feed gas consisted of 63% H₂, 19% CO, 2% CO₂ and 16% CH₄. To determine the effects of steam, twenty (20) of the scans had 15% steam injected into the feed gas. Each test ran for 100, 300, 600 or 1200 hours with continuous effluent sampling and temperature profile monitoring. At each of the termination points, a catalyst sample was taken from the hot spot section of the bed for analysis.

Results show that carbon was deposited on the catalyst under the methanation conditions studied. The rate of carbon deposition was found to be primarily a function of catalyst properties and not of the thermodynamics of the methanation reaction system. In spite of heavy carbon deposition, the catalytic behavior for these systems generally remains unaffected. Physical plugging of the catalyst bed is the limiting condition of the process and not catalyst deactivation. In this respect, a controlled oxidation of the carbon deposits is a viable method of extending catalyst life.

Steam injection proved to have a detrimental effect on the catalysts' crush strength but generally resulted in lower carbon levels.

The work performed on Task 2 - Hydrodynamics Study - can be summarized as follows.

The hydrodynamics and design of a cold-flow test unit for a three-phase, liquid-fluidized bed for Liquid Phase Methanation/Shift was evaluated. This report includes a historical overview of the LPM/S Process along with a survey of the pertinent technology concerning the three-phase reaction system. The cold-flow unit process design, equipment take-off lists, construction cost and timing schedule are included. As a second potential application, the unit was designed for hydrodynamic studies of a liquid-entrained system for Liquid Phase Methanation/Shift.

2.0 OBJECTIVES AND SCOPE

The objective of this work is to acquire further data on the development of the Liquid Phase Methanation/Shift Process. This was accomplished by (1) continuing the experimental study on rates of carbon formation in methanators and by (2) evaluating the hydrodynamics of a three-phase fluidized bed for Liquid Phase Methanation/Shift.

2.1 Introduction

Methanation is a unit process step common to all developed and the majority of developing high BTU gas technologies. It is normally carried out in two distinct steps; bulk methanation and a polishing or finishing methanation.

The bulk methanation steps vary greatly from process to process. These include reactor designs consisting of adiabatic beds, packed tubes, adiabatic coated plates, fluidized beds and liquid fluidized beds. Other variations include operating temperatures between 600°F and 1400°F and hydrogen to carbon monoxide ratios in the feed of between 3.5:1 to 1:1.

The polishing methanation steps do not vary as greatly since they all operate at relatively low temperatures (<750°F) due to equilibrium constraints on achieving high CO conversion. All will normally employ adiabatic bed reactors since this design can handle the lower heat release of this step in a single pass. However, the composition of gases to this polishing step will vary depending on whether or not the bulk methanation step employed an integrated shift step in its reaction.

A constraint to the design of all types of methanators has been the avoidance of operation in carbon forming regions, as predicted from thermodynamic considerations. This thermodynamic carbon forming region is itself only approximately known since the calculation of it is dependent on the form and the associated free energy of the type of carbon formed. At high temperatures, graphite appears to be the correct choice of carbon type while at temperatures below 850°F a non-ideal fiber-like carbon,

commonly referred to as Dents carbon can form which has a significantly different free energy, and hence allowable operating region, than graphite carbon.

Although a significant amount of calculations have been performed on the equilibrium between C, H and O to establish regions in which coke formation may be a problem, the formation of coke is not basically governed by thermodynamics, but rather by kinetic considerations. The gas composition can be such that thermodynamic theory predicts the formation by one reaction and its removal by another. Thus, the question of whether there is a net build-up of carbon is a kinetic one. The generally accepted methanation mechanism involves a balance between carbidic carbon deposition by dissociation of CO followed by its removal by hydrogenation to form methane. If carbon removal is not sufficiently fast, a build-up will occur in a short period of time. It should be remembered that though carbon formation is thermodynamically possible, its rate of formation might be so low in some regions as to be negligible. Furthermore, the presence of some components such as steam and CO₂ could have an accelerating or inhibiting effect on the rate of carbon formation. Finally, from an operational point of view, if carbon does form at some design conditions, just how bad an effect will this have? What is the rate of carbon lay down and how does it distribute? How does the porosity, pressure drop and reactivity of the catalyst change with time and will this trend reverse if one switches to a non-carbon forming region?

Chem Systems became involved with these questions when we started to study the polishing methanation step to follow our integrated shift- methanation process. From a limited study of four 1000 hour runs, it was surprisingly found that steam had a kinetically moderating effect on the system. Under identical conditions, carbon laydown on the catalyst was suppressed in the presence of steam. Similarly, we found that one could operate in a trouble-free manner with high CO₂ concentrations in the feed though the literature indicated this was not possible, and also that feed H₂/CO ratios could be below 3:1. It was also observed that when carbon formation did occur, it did not cause shutdown of the system but led to "hot spot" transfer down the bed with an increased pressure drop.

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In 1976, Chem Systems proposed to carryout a study on the rates of carbon formation in methanation which would answer the questions raised above. The results of this study would be applicable to both bulk and polishing methanation processes.

This current program (Contract No. DE-AC 21-80 MC 14384) is a continuation of the Liquid Phase Methanation/Shift Program (Contract No. EX-76-C-01-2036) which was completed on November 30, 1978. The primary concern of the initial program was investigation of the rates of carbon formation during methanation as a function of dry feed gas composition, steam level, operating temperature and pressure, and the effect of this carbon deposition on catalyst activity and selectivity. Comparisons with predictions based on thermodynamic equilibria were made.

While many objectives of the original experimental program had been satisfied, a number of conditions were observed which raised additional questions with regard to rates of carbon formation during methanation. It was readily apparent from the experimental results that thermodynamic equilibria data are of little use in predicting carbon formation, the type of carbon or the rate at which it forms. It was apparent, for a given feed gas/catalyst combination operating at conditions which had previously resulted in carbon formation, that there are circumstances which can completely alter the experimental behavior, such that carbon will not be formed, e.g., treatment with 100 percent steam.

The most important variable in determining the level of carbon formation is the catalyst itself. Under identical operating conditions, one catalyst (Girdler G-87P extrudates) formed extremely high levels of carbon, up to 10 percent, while another (Harshaw Ni-104T) lost some carbon originally present in the tablets. The different behavior could be attributed to the difference in catalyst carrier (G-87P uses alpha-alumina, while the Ni-104T uses kieselguhr). However, a tableted version of the G-87P, of the same chemical composition as the extrudate, formed virtually no carbon under the same reaction conditions. Therefore,

these differences in behavior arise from much more subtle sources, which involve not only gross physical and chemical properties, but also fine structure details as well.

Based upon the results obtained and observations made throughout the experimental program, a set of guidelines was developed that formed the basis of this continuing effort to further refine our understanding of the formation of carbon during methanation.

First, the experimental program was modified to include as many different methanation catalysts as possible, while at the same time, reducing the number of experiments with each catalyst/feed gas pair to a select group of operating conditions. Experience shows that catalysts which have a propensity to form carbon, will do so under a wide range of operating conditions. Furthermore, these experiments included some on-stream time variation in order to quantify the rates of carbon formation. This increased the understanding of the role that the fine structure, as detailed by pore volume distribution, carrier composition, nickel crystallite size and dispersion, etc., play in carbon formation. Efforts also concentrated on catalyst treatments, which have been shown to modify catalyst reaction behavior, such as steam treatment.

In conjunction with these experiments, it was necessary to use specific analytical methods to better define the morphological changes occurring on the catalyst. These include carbon analysis, BET surface area, mercury pore volume, x-ray diffraction scans and nickel surface area. These analyses will enable understanding of the fine structural changes and to determine the nature of the formed carbon-graphite or amorphous.

The results of the initial study also warranted work in the area of carbon removal by in-situ controlled oxidation and its cumulative effect on structure properties as well as reactivity related characteristics. This was accomplished by way of an accelerated regeneration test scan.

At the time, because of the problems encountered in our Liquid Phase Methanation pilot plant, apparently related to reactor hydrodynamics, we also added a task concerned with preparing an engineering design for a cold-flow model of our Liquid Phase Methanation pilot plant three-phase fluid-bed reactor. As a secondary use, the model was also designed for hydrodynamic studies of slurry systems, as well.

2.2 Task A - Rates of Carbon Formation

One of the key steps in producing substitute natural gas is the catalytic methanation of coal-derived synthesis gases^(1,2). Ultimately, success of the methanation depends on the catalyst stability and process conditions which favor economic operation over long periods of time. Probably the most serious deactivation problem in methanation is carbon formation on the catalyst surface. These carbon deposits foul the surface of the catalyst and plug its pores. Reactor voids can also become plugged. This fouling causes a drop in catalyst activity, physical destruction of catalyst pellets and a significant increase in pressure drop through the reactor. There is concern for this problem since two of the economically necessary features of most reactor designs, low hydrogen usage and high exit temperatures, also constitute favorable carbon formation conditions.

There are several important reactions which occur during methanation. These include:

For the practical operation of a methanation reactor, Reaction 4 would have to be avoided. The carbon formed would plug the reactor and render it inoperative. Operation of the unit would have to take place where carbon (graphite) is not a thermodynamically stable phase.

Enthalpy calculations, shown graphically in Figure 1, indicate that all of the above reactions are exothermic. Also, the free energy and K_p values for these reactions, as depicted in Figures 2 and 3, are shown to be very sensitive to temperature. The equilibrium constants were used to calculate the composition of the exit gas from the methanators by solving the equilibrium relationships for Reactions 1 and 2 simultaneously.

A comparison between the actual and theoretical equilibrium compositions of the effluent gases is shown in Table 1. As indicated all are within experimental error of the theoretical 99% CO conversion.

From an equilibrium point of view, it would be beneficial to increase the H_2 partial pressure. This would reverse the shift reaction and simultaneously push the methanation reaction closer to completion. The activation energy for methanation from CO and H_2 over nickel has been found to be approximately 23.5 kcal/mol⁽⁴⁾.

Several studies suggest that the dominant mechanism is the dissociation of CO, followed by the rehydrogenation of the surface carbon atoms to methane⁽⁵⁾. The removal of the absorbed oxygen is accomplished by reaction with another molecule of CO. The overall process which produces the active surface carbon that is to be hydrogenated is described as the disproportionation of CO or the Boudouard reaction.

This mechanism has been proposed by several researchers⁽⁶⁻¹¹⁾, but other mechanisms have also been offered. These involve the direct hydrogenation of CO⁽²⁾, intermediate molecular CO⁽¹²⁾ or both CO and H_2 ⁽¹³⁾ on the catalyst surface.

The temperature range in which the dissociation of CO produces active surface carbon is very narrow. The surface carbon formed from the dissociation of absorbed CO above 700°K was found to have negligible reactivity in methanation and to deactivate the catalyst with the formation of bulk Ni₃C or graphitic carbon structures⁽¹⁴⁾. Below 450°K, the rate of CO dissociation to produce active carbon is too slow to produce this carbon in high enough concentrations. Thus, the temperature dependence of the nature of the CO and the carbon chemical bonds introduce a narrow range of conditions for methane production. This was also noted by Wentrick, et al⁽¹⁵⁾ who observed a first-order formation of surface carbon when their nickel catalyst was exposed to pulses of CO. This surface carbon exhibited high reactivity toward hydrogen with quantitative conversion to methane. Analysis indicated that the surface carbon was bonded to the nickel as a carbidic surface species which converted to graphitic carbon of very low reactivity towards hydrogen at temperatures above 675°K.

Beeckman and Froment⁽¹⁶⁾ describe catalyst deactivation by coke deposition in terms of two mechanisms: site coverage and pore blockage. The blockage was due to coke growing from a precursor covering an active site.

In addition to carbon formation, loss of methanation activity of supported nickel catalysts was attributed to growth in nickel particle size. A mechanism involving the formation, diffusion and subsequent decomposition of Ni(CO)₄ was proposed by Shen, et al⁽¹⁷⁾ to explain the observed nickel particle size growth. Due to high pressure requirements of commercial reactor designs⁽¹⁸⁾, an increase in CO pressure is inevitable. With an increasing CO pressure the possibility of forming volatile nickel carbonyl is enhanced.

2.3 Task B - Hydrodynamic Study

The task of designing a cold-flow hydrodynamic unit was added to this present DOE contract. This was a support effort to the then operating CSI Liquid Phase Methanation pilot plant facility located at IGT in Chicago. A brief historical review will be included to put this task in its proper perspective.

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The development program for the Liquid Phase Methanation (LPM) process was initiated in 1973. In the LPM process, an inert hydrocarbon liquid is used to fluidize the catalyst and simultaneously absorb the heat generated by the highly exothermic methanation reaction. This results in optimal control of the reaction temperature. Near total conversion (95%) of high concentration carbon monoxide feed streams (25 v/o) can be achieved in a single pass through the reactor and hence obviate the need for recycle of unconverted synthesis gas.

3.0 SUMMARY OF TECHNICAL PROGRESS

This final report represents the work performed during the calendar period September 1, 1980 through November 30, 1981.

3.1 Task A - Rates of Carbon Formation

The five commercially available catalysts listed in Table 2 were tested simultaneously at equivalent conditions. Nominal reaction conditions for all the runs are presented in Table 3. Samples of the spent catalysts for the tests were analyzed. The results are shown in Table 4 and 5 and graphically in Figures 107 through 146.

3.2 Task B - Hydrodynamic Study

The task of designing a cold-flow hydrodynamic unit was added to this DOE contract as a support effort to the then operating CSI Liquid Phase Methanation pilot plant facility. Presented is a historical review of the LPM Process along with a survey of the pertinent technology concerning the three-phase reaction system. The cold-flow unit process design, equipment take-off lists, construction cost and timing schedule are included in the text.

4.0 DETAILED DESCRIPTION OF TECHNICAL PROGRESS

4.1 Task A - Rates of Carbon Formation

4.1.1 Experimental Equipment

During the first few months of the program, the multiple fixed-bed reactor system designed and constructed under DOE Contract No. EX-76-C-01-2036 was refurbished and modified. This system is depicted in Figures 4 and 5 along with the control panel and booster compressor diagrams in Figures 6 and 7, respectively. Modifications to the system include - high/low temperature and pressure alarm systems - capillary tube water injector to prevent pulse feeding of steam - and a regeneration gas mixing station.

The reactor design incorporates a removable multi-section catalyst basket which can be positioned inside the reactor pipe. In each of the baskets, a provision is provided to allow for a central thermowell. Contained inside the thermowell are three traveling thermocouples used in obtaining the temperature profile along the catalyst bed.

The tubular reactor consists of a three (3) foot long 316 SS, one inch Schedule 80 pipe with a male weld connection welded to each end. Feed gas enters the top of the reactor through 1/4" SS tubing. Water, when utilized, is injected into this 1/4" tubing through 1/16" SS capillary tubing. The feed gas then passes through a 6" long alumina sphere packed preheater section before entering the catalyst bed. The effluent passes through a 1/2" SS union tee to 1/4" tubing where it is diverted through a heat exchanger and a drain pot to the analytical system.

Five separately wired one-inch band heaters supply heat to each reactor. The controlling thermocouples are placed between the heaters and the reactor skin. These heaters are controlled by three individual zone controllers. The zones consisted of the preheater, hot-spot zone and the remaining catalyst bed. The reactors are insulated with one (1) inch of fiberglass Temp-Mat and two (2) inches of fiberglass pipe insulation (Microlok 650-AP).

4.1.2 Experimental Procedures

The experimental program was modified from the contract work statement during the first few months of the program in two ways. The first modification being the dilution of the feed gas with four (4) parts N_2 in order to lower the reactable CO_x concentration to 4%. This allows for improved temperature control of the highly exothermic methanation reaction. The composition of the feed gas in terms of C-H-O values is: 14.8% C - 76.0% H- 9.2% O. Operating the reactors at 1000 psig total pressure is thermodynamically equivalent to 200 psig for comparison of the mixture composition point with the carbon formation isotherms shown in Figures 8 and 9. In any event, the isotherms are relatively insensitive to pressure at pressures greater than 100 psig. Thermodynamically, this feed gas composition is slightly outside the graphite formation region.

The second contract modification involved the catalyst regeneration studies. Rather than performing a single regeneration after 1200 hours on-stream, a series of regenerations after each 300 hours of a 1200 hour scan were carried out. Regenerating in this manner will accelerate the aging effects that the regeneration cycles have on the catalyst.

The catalysts used for the duration of this experimental test program are listed in Table 2. These were chosen on the basis of nickel concentration (35-60%). These catalysts were diluted with inert alumina spheres (RHODIA SCS-9 2/4 mm), to a ratio of 1 catalyst to 1.5 inert V/V, in order to provide better hot-spot temperature control. The catalysts were activated by treating with H_2 in order to reduce the NiO to the active Ni form. The diluted catalysts were charged into the reactor baskets and placed inside the reactor. The system was then purged with N_2 at a flow of 40 liters/hour to flush it free of oxygen. Once the system was thoroughly purged, (≈ 10 min), the heaters were turned on and the reactor temperatures were controlled at $200^{\circ}F$. When the system stabilized at this temperature, the N_2 purge was turned off. The system was then purged with H_2 at a flow of 100 liters/hour. The reactors were kept at $200^{\circ}F$ for 1 hour after the start of the H_2 purge. The temperature was increased at a rate of $100^{\circ}F$ per hour to ultimately obtain a minimum

catalyst bed temperature of 600°F while keeping the hot spot below 850°F. At these final conditions, the catalyst would be fully reduced in 18 hours.

At the termination of the reduction, the system was flushed with N₂ and brought to run pressure (1000 psig) and temperature (900°F). At this time, the shifted methanation feed gas was slowly fed to the reactors at the rate of 400 liters/hour, which gave the desired VHSV of 10,000 hr⁻¹.

When the desired feed gas flow rate was obtained, the run was started. The feed gas and the reactor effluents were sampled automatically in the sequence - Feed, Effluent 1, Effluent 2, Effluent 3, Effluent 4 and Effluent 5. This sequence allowed every effluent to be sampled and analyzed at a rate of one time every two hours.

Typical GC chromatograms of the standard gas, feed gas and the reactor effluents are shown in Figures 10 through 16, respectively.

The theoretical product gas equilibrium composition was calculated (see Table 1) for comparison purposes with the effluent gas composition. The equilibrium composition was obtained by solving the equilibria relationships of reactions (1) and (2) simultaneously.

A comparison between the actual and theoretical equilibrium compositions of the effluent gases showed that all are within experimental error of the theoretical 99% CO conversion.

Also completed during the course of this project was a catalyst regeneration study using a single catalyst (UCI-CI50-4-03) throughout the test.

If air is passed over a coked catalyst hot enough to initiate combustion, a hot spot will develop due to the burning gases. As the coke is burned, the hot spot will move down the catalyst bed as a discrete layer. By

limiting the rate of oxygen supplied to the reactor, it is possible to control the catalyst temperature within a desired limit to a temperature runaway and permanent catalyst damage.

There are several techniques which can be employed to moderate the hot spot and decrease the chances of catalyst damage. One common method, and the one utilized in this study, is to reduce the O_2 concentration in the incoming gases to about 2%. This tends to thicken the hot spot and greatly reduces the peak temperature. The inert gases also aid in removing the heat of reaction. If desired, the overall rate of burning can be increased by recirculating the gases and increasing the pressure to 2 to 10 atmospheres. For this study the following regeneration procedure was used.

Fresh UCI-CI50-4-03 catalyst was loaded into each reactor and reduced in the usual way. The system was put on-stream for 300 hours and then shut down. The catalyst was unloaded and a representative sample was taken. The coked catalyst was then reloaded into the reactors. With a helium purge, the system was brought to 250°F at atmospheric pressure. Oxygen was then bled into the helium stream at the 1 to 2 percent level in order to burn off the deposited carbon under controlled conditions. The temperature was increased slowly in order to maintain a maximum hot spot somewhat lower than the nominal reaction temperature of 900°F. The catalyst bed was held at these conditions for 16 hours. The effluent gases were sampled automatically every half hour and analyzed for CO_2 and O_2 .

A sample of the regenerated catalyst was taken for total analysis. Its appearance was similar to the fresh catalyst in color but contained cracks throughout.

The regenerated catalyst was reloaded into the reactors and re-reduced with H_2 in the standard manner. On completion of the reduction, the system was flushed with N_2 and pressurized. Feed gas flow was started and the second 300-hour cycle of the regeneration test began.

This cycling was continued until the catalyst had logged a total of 1200 hours at methanation conditions. This gave a total of four 300 hour cycles and three controlled oxidative regeneration cycles.

4.1.3 Experimental Results and Discussions

All of the planned test scans were completed during the course of this work. Each scan will be presented briefly below in terms of the actual running of the experiment and the individual catalysts. The result of each of these scans will then be discussed.

The first test completed was the 100 hour scan without steam injection. This proceeded with some minor mechanical difficulties. After initial startup of the unit, only Reactor 1 was yielding acceptable results, i.e., 98+% CO conversion. The composition of the effluent from Reactors 2 through 4 was virtually unchanged from the feed gas, while the effluent from Reactor 5 showed about 60% conversion of CO. These zero and low conversion values were suspected to be due to gas leakage through a ΔP gauge, allowing the feed to completely (partly in the case of Reactor 5) by-pass the catalyst bed. This was remedied by capping off the reactor ΔP gauge. After this modification and re-reduction of the catalyst, the gas analysis was indicating essentially 100% CO conversion for all of the reactor effluents.

The CO conversion in all reactors remained virtually constant throughout the entire run. The slight differences in CO concentration from sample to sample are attributed to the statistical variations in the analytical system. The lower CO conversion obtained in Reactor 1 (98% opposed to 100%) was due to a slight gas leakage across the reactor ΔP gauge. This problem was corrected when the run terminated.

The temperature profiles for the 100 hour scan without steam are presented in Figures 17 through 21. These profiles show that over the 100 hour period, the activity of the catalysts remained unaffected by carbon deposition. This is apparent since the hot spot (main reaction zone) did not travel down the catalyst bed during the run as it would if catalyst

activity decreased due to coke accumulation on its surface. In all cases, the hot spot measured 1 to 2 inches into the catalyst bed and remained there for the entire duration of the run.

Figures 22 through 26 show the variation of component concentration versus time on stream for the five 100 hours scans. As seen in Figure 22 (Reactor 1), the CO concentration never decreased to less than 0.06 mole percent. This was due to a slight gas leakage through the reactor ΔP gauge allowing unreacted feed gas to be mixed with the effluent gas causing an increase in the CO concentration. This problem was rectified before proceeding to other tests. All of the CO concentrations are virtually 0% indicating essentially 100% CO conversion. The small amounts of CO present during the early portion of the tests are due to residual CO within the system.

The concentration of CH_4 , H_2 and CO_2 , as depicted in Figures 22 through 26, is virtually constant. The minor fluctuations are due to statistical variations within the analytical systems.

For the second five tests (300 hour without steam), fresh batches of catalyst were loaded into each reactor. During the catalyst reduction, two temperature controllers failed, causing full power to be supplied to the heaters of one reactor. When the problem was discovered, the catalyst bed had been heated to $750^{\circ}C$ ($1382^{\circ}F$) which is well above the recommended reduction temperature of $850^{\circ}F$ for the catalysts.

At this point, it was decided to recheck each of the individual controllers and heaters of the entire reactor system. Several heaters were found to be faulty and were replaced. In addition, the controlling thermocouples were repositioned around the reactor skin to enable better control of the temperature profile. The reactors were reinsulated with one (1) inch of fiberglass temp-mat and two (2) inches of fiberglass pipe insulation (Micro Lok 650-AP).

The reactors were then heated to reduction temperature ($600^{\circ}F$ min.) and the reduction continued. After the reduction was completed and all five (5) reactors were put on-stream, it was found that the over-heated

catalyst yielded only 66% CO conversion while the other four (4) catalysts were yielding 99 to 100% CO conversion. This overheated batch of catalyst was dumped from the reactor, and a fresh batch was loaded and reduced. On restarting, the fresh batch of catalyst yielded 99 to 100% CO conversion. It should be noted that during the early part of the runs, the temperature controllers are adjusted in order to fine tune the temperature profiles. This accounts for the differences between the earliest profiles and those taken later in the run.

The temperature profiles for the 300-hour scan without steam injection are shown in Figures 27 through 31. A hot spot is evident, but due to catalyst dilution and the new controlling thermocouples positioning, a quasi-isothermal catalyst bed was obtainable. The CO conversion over four of the five catalysts was 99 to 100% as indicated by the reactor effluent gas compositions shown in Figures 32 through 35. The conversion level for the fifth catalyst (Harshaw Ni-0104) was only 97% (Figure 36).

The temperature profiles for the third test scan (100 hour time test with 15% steam injection) are shown in Figures 37 through 41. The CO conversion over each of the five catalysts was 99 to 100 percent. This is indicated by the reactor effluent gas compositions shown in Figures 42 through 46. Temperature profiles for the fourth test scan (300-hour time test with 15% steam injection) are shown in Figures 47 through 51. The CO conversion during each of these tests are also 99 to 100 percent as depicted by the reactor effluent gas compositions in Figures 52 through 56.

In addition, as the results in Figure 52 show, (300-hour time test with 15% steam - United Catalyst Inc., - G87-S) instances occurred during which the concentrations of the CO_2 and H_2 rapidly decreased, while that of CH_4 increased. This was due to two (2) short-term water pump failures (at 50 and 125 hours) during the test. With the loss of co-fed water, the water gas shift reaction equilibrium shifts to $(\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2)$ the left. That is, there is a decrease in CO_2 and H_2 concentrations and an increase in CO concentration. However, at the same time, because of the lower water concentration, the methanation reaction $(\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O})$ shifts to the right, with a resultant increase in CH_4 concentration.

The temperature profiles for the 600-hour time test without steam injection are shown in Figures 57 through 61. The CO conversion over each of the five catalysts was between 98 and 100 percent as is depicted in Figures 62 through 66. The 600-hour time test with 15% steam injection temperature profiles are presented in Figures 67 through 71. The concentration versus time curves are shown in Figures 72 through 76. These indicate that in all cases, CO was at least 98% converted.

Figures 57 through 61 and Figures 67 through 71 show a maximum hot spot temperature of 485-495°C. The temperature profiles along the catalyst beds are very stable with little downward migration. This suggests that after 600 hours, the catalyst activity has not decreased significantly.

The 1200-hour time test without steam injection temperature profiles are shown in Figures 77 through 81. The CO conversion over each of the five catalysts was between 98 and 100 percent as depicted in Figures 82 through 86. Early in this test run, the product gas analysis from Reactor 4 (Harshaw Ni-3210) began to show a slowly increasing CO level. Initially, this was thought to be due to a gradual loss in catalyst activity, possibly as a result of carbon deposition. However, it was later recognized that there was a minor malfunction in the analytical system. After making the necessary adjustments, the measured product gas CO level again fell to the expected 0.01 v/o level.

The 1200 hour - 15% steam scan temperature profiles are shown in Figures 87 through 91. These profiles indicate a hot spot temperature of 485-500°C. The profile along the catalyst bed is very stable with no forward movement of the hot spot. The CO conversion over each of the catalysts was 99 to 100% as shown in Figures 92 through 96. It can be seen from these figures that there were instances during which the concentrations of CO₂ and H₂ decreased, while that of CH₄ increased. This was due to several intermittent water pump failures. As mentioned earlier, the loss of co-fed water causes the water gas shift reaction equilibrium ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) to shift to the left,

thereby decreasing the concentrations of CO_2 and H_2 and increasing the CO concentration. Simultaneously, due to the lower H_2O concentration, the equilibrium of the methanation reaction ($\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$) shifts to the right. This shift increases the CH_4 concentration.

Temperature profiles for each of the four regeneration cycle scans using the UCI-C150-4-03 catalyst are presented in Figures 97 through 100. As seen, the hot spot was always located in the first quarter of the catalyst bed. This indicates that the active catalyst can be successfully oxidized and re-reduced to its previous high activity. This is supported in the component concentration curves shown in Figures 101 through 104, which indicate that the CO conversion was 98 to 100% complete throughout the entire test. Figure 105 depicts the effect that a controlled in-situ oxidative regeneration has on the crush strength of the catalyst. Initially, the catalyst loses a significant amount of strength, from 7.75 kg to 1.3 kg during the first 300 hours. After three regenerations and 900 additional hours on-stream, the crush strength decreased to 0.6 kg. This is compared in Figure 106 to the crush strength of the same catalyst after 1200 hours of continuous running under similar conditions without any regeneration. This indicates that the in-situ oxidation of the surface carbon from the catalyst does not reduce the strength of the catalyst any more than normal operation. From a strength point of view, this would seem to be a potential method of increasing effective catalyst life in a reactor.

The following synopsis pertains to the individual tested catalysts. A general discussion will follow. The pertinent catalyst results are presented in summary in Tables 6 through 11.

Harshaw Ni-3210

As shown in Figure 107 and Table 6, the nickel crystallite size increased in the absence of steam at a gradual rate from its initial $65 \text{ \AA}$ to $85 \text{ \AA}$. When steam was injected, the nickel crystals grew to $127 \text{ \AA}$. With this increase in Ni crystallite size a decrease in the nickel surface area is

expected. This is verified in Figure 108 and Table 7 which show the decrease in nickel surface area from $74 \text{ m}^2/\text{g}$ for the fresh catalyst to $54.3 \text{ m}^2/\text{g}$ without steam and $37.8 \text{ m}^2/\text{g}$ with steam injection. Also seen (Figure 109 and Table 8) is the overall decrease in catalyst surface area from the initial $159.0 \text{ m}^2/\text{g}$ to $74.0 \text{ m}^2/\text{g}$ and $49.7 \text{ m}^2/\text{g}$ without and with steam injection, respectively. The mercury pore volume (Figure 110 and Table 9) showed an increase from 0.14 cc/g to 0.27 cc/g in the absence of steam and to 0.23 cc/g in the presence of steam. An increase in carbon content is shown in Figure 111 and Table 10. The carbon content seems to stabilize near the 300-hour mark, indicating that about 300 hours are required for the carbon to reach equilibrium on the catalyst surface. At this point, the rate of carbon formation is equal to the rate of carbon utilization to form methane. The carbon present as graphite is due to the organic binder utilized during pelletization of the catalyst.

Figure 112 illustrates the change in catalyst strength with time. It is noted that the strength of the catalyst remained essentially constant throughout the test. The presence of water increased the crush strength. This seems to be due to a morphological change in the CaCO_3 support material. As time progressed, the crystallite size of the CaCO_3 increased. This increase was more pronounced in the presence of steam indicating that an increase in support crystallite size may strengthen the support material.

UCI-G87-S

The nickel crystallite size (Figure 113; Table 6) increased slightly when steam was not injected from $100 \text{ \AA}$ to $320 \text{ \AA}$. When steam was injected, the growth of the crystals were greatly accelerated to a final size of $1322 \text{ \AA}$. The catalyst surface area (Figure 114; Table 8) decreased rapidly from $72 \text{ m}^2/\text{g}$ to $30 \text{ m}^2/\text{g}$ in 100 hours and then stabilized at $40 \text{ m}^2/\text{g}$ for the remaining time. In the presence of steam, the initial rapid decrease followed the same path to $30 \text{ m}^2/\text{g}$ but continued to decrease gradually to $15 \text{ m}^2/\text{g}$ where it stabilized. The surface area of the

nickel (Figure 115; Table 7) decreased from 20 m²/g to 15 m²/g without steam injection and to 5 m²/g with steam injection. The pore volume (Figure 116; Table 9) both with and without steam injection decreased from 0.49 to 0.58 cc/g during the first 100 hours. It stabilized at this point when steam was not injected but continued to decrease gradually to 0.38 cc/g when steam was injected.

The carbon content (Figure 117; Table 10) increased from the initial 0.2 to 1.2 wt% in 100 hours and stabilized at about 1.3 wt% when steam was not injected. With steam injection, the initial increase in carbon was to 1.7 wt% in 100 hours with a gradual decrease in 1.2 wt% at the end of the run. The crush strength (Figure 118) decreased significantly during the first 100 hours from 10.8 kg to 4.3 and 4.7 kg for the scans with and without steam injection, respectively. These continued to decrease with time on-stream to 1.5 kg and 3.3 kg at the end of the run with and without steam, respectively.

Harshaw Ni-0104

The nickel crystallite size (Figure 119; Table 6) increased slightly from 60 Å to 100 Å without steam injection and to 120 Å with steam injection. The overall catalyst surface area (Figure 120; Table 8) decreased gradually from 140 m²/g to 55 m²/g and 52 m²/g in the absence and presence of steam, respectively. The nickel surface area (Figure 121; Table 7) increased from 45 m²/g to 58 m²/g in 100 hours and then stabilized at 48 m²/g when steam was not injected. With steam injected, the surface area of the nickel increased sharply to 78 m²/g in the first 100 hours and then decreased and stabilized at 40 m²/g for the remainder of the test. The pore volume (Figure 122; Table 9) showed only a slight increase from 0.14 cc/g to 0.2 cc/g without steam and 0.16 cc/g with steam. When steam was not injected, the carbon content (Figure 123; Table 10) increased from 4.1 to 5.5 wt%. With steam, the carbon increased to 5.4 wt% after 300 hours and then stabilized at 4.6 wt% for the remainder of the test. The crush strength (Figure 124) decreased slightly from 4.7 kg to 3.75 kg without steam and to 2.9 kg with steam injection.

UCI-C150-4-03

The nickel crystallite size (Figure 125; Table 6) of this catalyst increased from the initial 30 Å to 140 Å when steam was not injected. With steam, the crystals increased to 240 Å. The surface area (Figure 126; Table 8) decreased rapidly in 100 hours from 175 m²/g to 55 m²/g where it stabilized. When steam was injected, the surface area decreased slowly during the entire test to 35 m²/g. The nickel surface area (Figure 127; Table 7) decreased rapidly in 100 hours from 38 m²/g to 15 m²/g then increased to and stabilized at 36 m²/g for the remainder of the test. In the presence of steam, a rapid increase in nickel surface area to 55 m²/g was noted at the 300-hour point with a gradual decrease and stabilization at 20 m²/g at the test's termination. The pore volume (Figure 128; Table 9) showed a rapid increase in 100 hours from 0.2 cc/g to 0.38 cc/g and then stabilized at 0.36 cc/g. When steam was injected, the pore volume rapidly increased to 0.34 cc/g in 100 hours and stabilized itself in that area for the remainder of the run. The carbon content (Figure 129; Table 10) increased from the initial 2.5 wt% to 3.5 wt% gradually when steam was not injected. In the presence of steam, however, the overall carbon content decreased to 2.2 wt%. The crush strength (Figure 130) of the catalyst decreased rapidly from 7.7 kg to 1.2 kg at 100 hours of operation both with and without steam addition. After this initial drop, there was little change in strength. At the 1200 hour point the crush strength was 0.4 and 1.0 kg with and without steam, respectively.

Katalco CRG-F

Without steam injection, the nickel crystallite size (Figure 131; Table 6) of this catalyst increased from the initial 20 Å to 140 Å. This increase was much greater in the presence of steam where the crystals grew to 290 Å. The catalyst's surface area (Figure 132; Table 8) decreased slowly from 135 m²/g to 70 m²/g without steam and to 35 m²/g when steam was injected. The nickel surface area (Figure 133; Table 7), however, increased from 23 m²/g to 35 m²/g in 100 hours and remained there for

the duration of the test. When steam was injected, the nickel surface area increased from the initial 23 m²/g to 55 m²/g in 100 hours and then decreased to 17 m²/g at the 1200-hour point. The pore volume (Figure 134; Table 9) was essentially constant, increasing from 0.3 cc/g to 0.35 cc/g and 0.34 cc/g with and without steam injection. The carbon content (Figure 135; Table 10) increased slightly from 2.4 to 3.7 wt% when steam was not present. When steam was injected, the carbon content showed an increase to 3.5 wt% at 300 hours but then slowly decreased and stabilized at 3.0 wt%. The crush strength (Figure 136) decreased slightly during the course of the study from 2.6 kg to 1.4 kg. In the presence of steam, the catalyst crush strength was decreased to 0.4 kg.

In all cases, an increase in nickel crystallite size was noted. This increase was more pronounced in the presence of steam. This may have been due to sintering of the nickel if the surface temperature of the catalyst was allowed to exceed 600°C. Since the reaction was carried out at <500°C, it is safe to assume that very little growth was due to excessive temperature.

One possibility is the formation of Ni(CO)₄ by the following reaction:

The product Ni(CO)₄ molecules can leave the metal particle and diffuse through the gas phase and/or over the catalyst support. These species can then decompose to metallic Ni on either a nearby Ni particle or a Ni particle on a catalyst granule downstream. This type of growth seems unlikely for this system since the partial pressure of CO in the feed gas was kept very low.

What may be responsible for the observed nickel crystallite growth is known as steam poisoning. This involves a catalyst deactivation - activation cycle proceeding via the following reaction:

This type of catalyst poisoning (due to reduction in active Ni concentration) is a known occurrence at high steam to H_2 ratios.

In the present case, this type of catalyst deactivation would occur when a significant portion of the H_2 present in the feed gas is consumed during methane production. From a study of the temperature profiles, the bulk conversion takes place in the upper portion of the catalyst bed. With a decrease in H_2 concentration, the reaction would shift to the right. With the resultant increase in inactive NiO, the catalyst activity would decrease in the upper portion of the bed. On decreasing the catalysts' activity, the conversion of the feed gas would be reduced resulting in an increase of H_2 in the initial portion of the catalyst bed. This would tend to shift the reaction back to the left. By doing this, the inactive NiO is harshly reduced to the active Ni form. It is known that if a Ni catalyst is activated by reducing with H_2 , the resulting crystallite size of the active Ni would depend extensively on the degree of reduction severity. A reduction occurring under the nominal reaction conditions is considered to be very harsh.

Although the crystallite size of the Ni particles increased during each of the test scans, at no time did this increase affect the overall catalyst activity. In all cases and throughout each run, the conversion of CO was always 98-100% complete. These high conversions are realized due to the overall length of the catalyst bed (12 inches). Since the reaction is occurring mainly in the upper 2 to 3 inches of the bed, the remaining 9 to 10 inches is simply a catalyst reservoir functioning as a polisher to obtain the equilibrated effluent gas mixture.

The increase in pore volume is also enhanced in the presence of steam. An increase in the size of catalyst pores is usually associated with a composition change in the support material. This change may be due to the hydration of the support, usually Al_2O_3 , or a structural change from the α to γ or other form of Al_2O_3 . Any change of this type can greatly effect the pore volume.

The surface area of the catalyst and that of the nickel both decreased during each of the scans. This is expected with the increased Ni crystallite size and pore volume.

Carbon was deposited on all the catalysts under the methanation conditions studied. The amount of carbon that was determined to be on the surface of the catalysts may not be indicative of the total carbon formed but rather the bulk non-methane forming carbon. A high activity toward carbon formation was found to be associated with the catalysts with the higher Ni surface area. The incorporation of steam into the system reduced the overall carbon content. The more dilute catalysts, i.e., those of lesser Ni concentration, were more resistant to carbon formation. This is probably due to a stronger interaction of the nickel with the support material. From these findings, one can see that the rate of carbon deposition was primarily a function of the catalyst properties and not of the thermodynamics of the methanation reaction system. In spite of heavy carbon deposition, the catalytic behavior of these systems remained unaffected. The limiting condition would be the physical plugging of the catalyst bed and not catalyst deactivation. In this respect, the controlled oxidation of the carbon deposits might be a viable method of extending catalyst life.

With the formation of carbon deposits during methanation, a disintegration of catalyst pellets due to internal stresses produced by the increased concentrations of the strong carbon filaments was also expected. This was found to be true except in the case of the two Harshaw catalysts tested. The strength of these catalysts remained unchanged throughout the entire test scan.

4.1.4 Conclusions and Recommendations

- Based on observations of measured temperature profiles, the reaction hot spot is always near the top of the catalyst bed. This indicates that very short catalyst contact times are required for nearly complete conversion of CO. The remainder of the catalyst bed only serves as a catalyst reservoir. Any future work should be performed with a catalyst bed operated in the kinetic regime utilizing a differential fixed-bed reactor. This will enable swifter evaluation of the parameters suspected of influencing the deactivation of the catalyst.
- This study showed that an active catalyst can be carefully oxidized and re-reduced to obtain its original high activity. Future work should include a study to determine if a deactivated catalyst (due to carbon) can be regenerated and re-reduced to its initial high activity.
- In all but one case, a decrease in catalyst crush strength was noted. If the crush strength of the catalyst is significantly decreased during operation, it will be pulverized under its own weight causing plugging of the reactor and shutdown. Future work should include an investigation of the effects of process variables on the catalysts' crush strength.
- Future work should include a study which will concentrate on the development of a promoted nickel catalyst which would be more resistant than nickel to carbon formation under carburizing conditions.
- Deactivation may be temperature dependent, and future experiments should include a study of the temperature dependence of catalyst sintering under strong reducing conditions.

4.2 Task B - Hydrodynamic Study

4.2.1 Introduction

The cold flow hydrodynamic test unit was designed to be a diverse, highly instrumented test facility. All components are to be selected based on proven performance in similar operating pilot plants. To provide the maximum in serviceable information, all process variables are to be monitored and controlled by industrial type, state-of-the-art instrumentation.

An ebullated bed consists of a reactor whose catalyst contents are fluidized by bulk upward liquid flow. The liquid velocity should only be sufficient to expand the catalyst bed to 1.5-2 times its settled height, but should not elutriate the smaller particles from the reactor. The feed gas is sparged into the fluidized catalyst mass where it diffuses through the liquid phase and reacts at the catalyst surface. The exothermic heat of reaction is absorbed by the flowing liquid, primarily as sensible heat. The product gas and liquid only, pass from the reactor to a vapor/liquid separator. The separated liquid is cooled by generating high pressure steam, prior to recycle back to the reactor inlet.

In contrast, for the entrained reactor, the bulk liquid phase contains a uniformly distributed fine catalyst particle ($< 100 \mu$) suspension. The liquid flow rate must be set to maintain proper flow dynamics and temperature control.

These reactors fall into the general category of plug-flow reactors (as compared to CSTR or fully back-mixed reactors). Deviations from plug-flow ideality for these systems have been historically modelled by superimposing an axial dispersion (diffusion) mechanism over the plug-flow case. The obvious effect of back-mixing in such reaction systems is a reduction in overall reactor productivity due to a global lower average concentration of reacting species. In addition, for the ebullated bed case, the relative phase motions within the reactor affect the ability to

establish a well defined solids level interface within the reactor. When this behavior becomes the dominant characteristic, the catalyst cannot be readily contained within the reactor. Further, the rates of catalyst attrition depend very heavily on the dynamics of phase mixing. Both these conditions were strongly evident during the pilot plant experimental program.

The key assumption in the axial dispersion model is that the reactants move under plug-flow conditions while simultaneously diffusing along the axis of flow. A mass balance on a differential element of the fluid (with no reaction term) results in Fick's second law of diffusion,

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2}$$

In this equation D_L is the axial diffusivity, c is the reactant concentration, x is the distance along the axis of flow and t is time. The value of the axial diffusivity can be determined for a given system using any of several experimental techniques, e.g., tracer analysis. (19-22)

The effect of axial dispersion is quantified by the dimensionless Peclet number defined as:

$$Pe = \frac{u \cdot L}{D_L}$$

where u is a relative or absolute velocity in the direction of flow, L is the length of the reactor in the direction of flow and D_L is the axial diffusivity.

For a true plug-flow reactor the axial diffusivity approaches zero while the Peclet number approaches infinity. For the other limiting case, a true backmixed reactor with infinite mixing, the axial diffusivity approaches infinity while the Peclet number approaches zero.

The performance of a chemical reactor with respect to conversion and selectivity depends on the intrinsic kinetics of the various chemical reactions, various physical rate processes such as interphase, and inter and intra particle heat and mass transfer. The effects of these physical rate processes on the reactor performance have been shown to depend on the dynamics of the various phases involved. While there are numerous publications about backmixing in liquid-gas bubble columns and in solid-fluid systems,⁽²³⁻²⁷⁾ much less material has been published on three-phase ebullated bed/liquid entrained systems⁽²⁸⁻³⁰⁾.

Experimental data on Peclet numbers due to axial dispersion in chemical reactors are also very limited. Most of the work has been limited to single phase packed bed reactors. Moreover, data on such systems are only reliable when applied to systems resembling those of the experimental studies⁽³¹⁾.

At the present time an extensive effort is being directed toward the measurement and evaluation of backmixing in multiphase systems through residence time distribution (RTD) studies⁽³²⁻³³⁾ (from which Peclet numbers can be calculated). One major problem encountered is that separate RTD measurements are required to evaluate the mixing characteristics of each phase. Although there are numerous methods available to obtain RTD data in complex multiphase systems, measurement problems have been encountered by all recent investigators. Flow maldistribution of the phases can especially impede evaluation of RTD data.

In most RTD models, radial mixing is assumed to be complete. Under many conditions this may not be correct. At the present time there are no applicable criteria that would define the set of reactor conditions under which the assumptions of complete radial mixing are valid. The establishment of any governing criteria would need to consider all phases and all possible flow regimes within the reactor.

Basic to the operation of a three-phase reactor system is the need to properly distribute the respective phases within the vessel. For small diameter columns the design of the gas distributor has been shown to have a significant effect on the Peclet number. Data on large diameter three-phase columns is presently unavailable. Liquid phase maldistribution also remains a problem. A liquid fluidized bed is known to have poor liquid redistribution. This could have a significant impact on the LPM reactor design.

Reactor modelling ultimately combines the RTD analysis with the reaction kinetics in conjunction with heat and mass transfer effects in order to describe a given chemical reactor system. Unless simplifying assumptions are made, the mathematics describing the performance of a three-phase system become very complex, even though the phase mixing phenomenon may be described by a simple axial diffusion model. Furthermore, the RTD data reported in available literature has generally been limited to small scale apparatus. Since the prevailing flow regimes in small and large equipment may differ, there is a real need for experimental data from large diameter reactor systems. At the present time experimental data for commercial reactors is generally confidential and unavailable in the open literature.

The cold flow hydrodynamic unit can be operated as either a liquid fluidized reactor or a liquid entrained (slurry) reactor. In the liquid fluidized mode, the process liquid velocity is controlled over a narrow range in order to fluidize a fixed quantity of catalyst particles within the confines of the reactor. For liquid entrained operations, smaller catalyst particles are intentionally suspended in the process liquid and are circulated throughout the liquid circulation loop. The process flows and physical dimensions of the hydrodynamic unit broadly resemble that of the Liquid Phase Methanation pilot plant.

A conceptual process flow diagram of the cold flow hydrodynamic unit is shown in Figure 147. For the sake of clarity, only the cocurrent liquid/gas upflow mode of operation has been shown. By properly

structuring inlet and outlet piping, alternate flow configurations can be readily established, e.g., liquid and gas cocurrent upflow or liquid downflow - gas countercurrent upflow.

It is anticipated that the hydrodynamic test unit would be constructed of materials that are compatible with a range of organic solvents. The process liquids will be selected to have properties similar to those of the hot process liquids.

Solvents of differing physical properties would be used in the determination of the density, viscosity and surface tension effects on the hydrodynamic character of the process fluid.

4.2.2 Liquid Fluidized Mode

For liquid-fluidized operation in the cocurrent gas/liquid upflow mode (the design configuration of the pilot plant), liquid is introduced through the bottom of the reactor (TW-100) by means of a distributor device that insures a uniform gas bubble distribution throughout the reactor cross-section. The process liquid enters the reactor below the gas distribution device and serves both to fluidize the catalyst bed and under reaction conditions remove the exothermic heat of reaction. Superficial liquid velocity would be controlled over a narrow range in order to expand the catalyst bed over a fixed length, yet contain the catalyst particles within the reactor.

Separation of the solids from the liquid/gas continuous phase occurs in the upper portion of the reactor in a region above the expanded catalyst bed. The liquid and gas streams are taken overhead as a two-phase system for subsequent liquid disengagement in the vapor/liquid separator (VT-100). The process liquid is recirculated through feed pump (CP-100) to the bottom reactor inlet. The gas passes through a demister (VT-101) located on top of the vapor-liquid separator in order to de-entrain any liquid droplets. The gas can either be vented to the atmosphere or fed back to the feed gas compressor (GC-100).

The gas compressor will be equipped with a water cooled aftercooler (HE-100). The gas then flows into a surge tank in order to damp out pressure (or flow) fluctuations prior to passing to the reactor gas distribution system.

4.2.3 Liquid Entrained Mode

In the liquid entrained gas/liquid upflow configuration gas and slurry are co-fed to the bottom of the reactor (TW-100). Gas is introduced through a suitable distribution device while the slurry is introduced below the gas distributor. Catalyst particle size and process liquid flows would be selected so as to intentionally suspend the catalyst in the process liquid and circulate the solids throughout the liquid circulation loop. By design the catalyst solids and process liquids must remain a homogeneous mixture everywhere within the liquid circulation loop. Gas/solids/liquids are taken overhead out of the reactor to the V/L separator (VT-100) where phase separation between gas and slurry phases occurs. The separated slurry phase is recirculated to the reactor inlet through Pump (CP-100). As in the liquid entrained mode of operation, the gas phase passes through a demister (VT-101) to de-entrain any liquid droplets. The gas can then be vented or recycled back to the compressor.

4.2.4 Process Equipment

Reactor

The reactor used for the hydrodynamic study would be constructed of a combination of flange-connected glass and metal sections. The column dimensions (identical to the LPM pilot plant reactor) will be 22 inches inside diameter by 15 feet long. The reactor piping connections at the top and bottom will be flexible. The bottom metal spool piece is designed to support the entire cold flow reactor assembly. Each metal spool piece would be constructed so as to allow for the introduction of sample probes, pressure taps, and other instrumentation as required. The

sample probes would be constructed and operated so as to obtain slurry concentration data along the radial and axial direction. A Plexiglass or Lexan shield would be used to enclose the glass column for personnel protection. Sections of the plastic shield would be made removable to allow access to the various sample and pressure taps. Finally, an x-ray source and detector will be mounted so as to traverse the length of the reactor. Such an x-ray source/detector system has been successfully used in the LPM Pilot Plant to monitor the fluid dynamics of the system. Alternately, a series of fixed source/detector pairs may be mounted along the vertical length to obtain the density profile.

Pumps and Compressors

A rotary screw air compressor with a water cooled aftercooler would be used for supplying gas. The present design requires a compressor capable of up to 100 SCFM at 100 psig outlet pressure. The compressor discharges into a surge tank to damp out pressure and flow fluctuations.

Magnetically coupled centrifugal pumps will be selected for the slurry feed and circulation loop. These pumps are magnetically coupled to their motor so as to eliminate problems of liquid or gas leakage across a dynamic seal. In addition, these pumps do not require a seal flush flow. The present design requires a pump capable of 220 gpm maximum flow at 75 feet total dynamic head.

Catalyst Recovery Filter

A plate and frame filter press is included in the design to be used in determining solids holdup within the column. Additional use would be made of the filter in recovering "used" catalyst upon completion of testing.

Vessels

The slurry feed tank (VT-102) was sized (300 gallons) to hold the entire contents of the cold flow hydrodynamic test unit. It is baffled at 90° and supplied with an agitator to maintain the catalyst slurry in

suspension. Liquid inventory can be monitored by placing the unit on a weigh cell or by using a ΔP cell. If a ΔP cell is used, an inert purge gas must be supplied to the high side of the cell to prevent plugging by catalyst. A slurry feed pump (CP-102) is used to transfer the slurry to the main test unit circulating loop.

The slurry preparation tank (VT-103) has a capacity of 100 gallons and was sized for slurry addition and makeup in multiple batches. It is also baffled at 90° and supplied with an agitator. Inventory control would be accomplished by placing the unit on a weigh cell. Slurry is transferred from the vessel to the feed tank or the main circulation loop through the slurry transfer pump (CP-101).

4.2.5 Experimental Techniques

Test methods for determining hydrodynamic system characteristics can be categorized as being either external or internal monitoring techniques. External techniques are preferential in that they do not interfere with established flow patterns. Internal methods involve the insertion of devices through the test cell wall, consequently inducing flow disturbances downstream of the sample location.

External Methods

Sonic probes and gamma-ray scan techniques have been used to obtain data on the average bulk density in multiphase systems. Gamma-ray techniques make use of differential absorption of radiation by various materials. Being an external technique, it is an excellent method for determining the average density of a multiphase system without creating a flow disturbance. Chem Systems has used a movable density gauge in their LPM program which could traverse the length of the reactor and give point bed density measurements directly. These measurements combined with fluidized bed height measurements give a direct evaluation of the relative liquid, gas and solid phase volume fraction.

Sonic techniques are alternate external methods for determining densities of multiphase systems, using sound rather than radiation. In single-phase systems, phase-time and dual-path sonic probes (which measure sonic impedance) can be used to determine density. These devices can also be used in two-phase, liquid-solid slurry systems, provided that the sonic impedance of the two-phase mixture is a very weak function of slurry concentration. These devices can not be used when a bulk gas phase is present because discrete gas bubbles give rise to interfering sonic reflections. A Doppler shift sonic probe makes use of these sonic reflections. It can measure vertical bubble rise velocity or slurry velocity.

Internal Methods

Several tracer testing methods are known for determining residence time distributions, flow rates and relative phase volumes in multiphase reactors. The techniques employed involve use of a tracer component with an internal or external monitoring device. External detection systems are preferred as they will not interfere with established flow patterns.

In general, flow patterns can be studied by injecting a tracer into a vessel inlet stream and observing the subsequent concentration profile at the outlet. At steady state, methods used consist of injecting a continuous tracer into the inlet of a studied interval and measuring the upstream concentration. For large diameter columns, problems are encountered in obtaining a homogeneous dispersion of the tracer. Further, attempts to obtain an average sample profile across the column can be difficult without disturbing the original flow patterns within the column. When continuous sample withdrawal is employed, sample time effects may distort the measured response. Unsteady state methods of measuring residence time distributions consists of injecting a momentary tracer pulse at the reactor inlet and measuring the response function at the outlet. Pulse injection methods are preferred to step or frequency response methods since inputs requiring large quantities of tracer are impractical on large units. Pulse injection techniques are simple, inexpensive, and require only small quantities of tracer material.

In performing a tracer study, proper tracer selection is extremely important. The hydrodynamic response must be characteristic of the flowing phase and not a function of the tracer component. Any tracer employed should be miscible and have physical properties similar to the bulk fluid phase. The tracer must not be transferrable to the other phases of the system. All tracers under consideration should be accurately detectable in low concentrations to minimize disturbances in the established reactor flow patterns.

To enable tracer detection in fast moving streams, the data recording equipment must offer exceptional sensitivity with a minimal detection response time. For simplicity and accuracy, the response of this equipment should be linear.

Gas, liquid or solid tracers can be injected into a flow system to determine the responses for each phase. For the gas phase, a tracer gas injected into a multi-phase reactor would have its concentration measured by a thermal conductivity or infrared absorption cell. Alternately, a radioisotope is substituted. In using gas phase tracers, absorption into the liquid phase precludes an accurate determination of the gas phase mixing and holdup without an independent measurement of tracer content in other phases. The differing rise velocities of individual bubbles further complicate the detector response. Because of these inherent difficulties in using gas phase tracers, only qualitative data concerning gas phase mixing are available in the literature.

The use of liquid tracers are well accepted industrial practices. Problems associated with their use are the familiar ones of sampling induced errors when internal techniques are used. External techniques employed include the use of dyes coupled with high speed photography and radioactive tracer methods. Unfortunately, photographic techniques relying on photochromatic dyes or particle luminescence cannot be used if the color change is obscured by the catalyst particles. In larger diameter columns wall effects can also obscure the events from photographic interpretation.

For the solid phase, a magnetic tracer can sometimes be used. The concentration of a solid phase tracer may be measured by a capacitance probe if the dielectric constant of the tracer material is substantially different than that of the solid phase. In general, for solid phases, a suitable radioactive tracer is often the most convenient to use. If proper precautions are observed, a radioactive tracer has a distinct advantage over other tracers in that the tracer detection devices can be mounted externally. In this way, no disturbances in the established flow patterns resulting from the presence of probes or sampling devices are encountered. The use of a radioactive tracer permits the time distribution function of a rapidly moving phase to be accurately determined, since scintillation detectors can be interfaced with high speed recorders or with multi-channel analyzers with data storage capabilities.

The use of radioactive tracer technology for hydrodynamic studies should never be promoted simply because it is "glamorous" and novel, nor neglected because of difficulties real or imaginary. The use of alternate methods should always be the first consideration. However, when these have proved to be inadequately sensitive or cumbersome, one must seriously consider radioactive tracers.

4.2.6 Construction Cost Estimate and Schedule

The overall construction program cost and fabrication schedule for the hydrodynamic test unit is detailed in the following sections. The total field cost plus engineering charges is estimated to be \$268,580. This cost does not include a contingency fee or any user fees. A breakdown of the total cost indicates a purchased equipment cost of \$166,580 with a manpower component of \$102,000.

The cost estimate was prepared for a hydrodynamic unit capable of simulating the Liquid Phase Methanol pilot plant reactor loop. This test unit was designed to operate in either a liquid fluidized or liquid entrained mode of operation. The field cost estimate was developed by

piecing out all major process equipment items and then applying overall component factors to arrive at an installed cost (Table 1). A detailed equipment list for all major process items is presented in Section 4.2.7. The list delineates the design specifications for each item, including materials of construction, as well as an estimated purchased price on a 3rd quarter 1981 basis. Prices were obtained from either a vendor quote, catalog price list or by direct comparison to recent purchase. Instrumentation costs were derived from the instrument specification sheets (Section 4.2.7) and amount to \$34,920 of the total and are not a factored quantity. This represents a minimum in instrumentation required to operate the unit. It does not include sophisticated data acquisition equipment nor does it include instrumentation required in utilizing radioactive tracer techniques. Also omitted is a combustible vapor alarm required if flammable light hydrocarbon liquids are to be utilized in simulating the actual reactor loop oil properties.

Working from vendor and potential fabricator quoted delivery times, an estimated construction schedule was proposed (Table 2). Overall construction time is approximately 8 months. A portion of the major process equipment and instrumentation can be ordered based on the specifications of the attached major equipment and instrument specification sheets. However, detailed engineering drawings are still required for the vessel supports, major vessels and control panel layout.

The following material highlights the program accomplishments achieved by Chem Systems.

Bench Scale Unit Program

- Experimental work was performed in a bench-scale unit (1 inch x 6 feet). Several catalysts were found suitable for the liquid fluidized system. At least two different types of hydrocarbon liquids; one a paraffinic material, and the other an aromatic liquid, were found to perform acceptably. A kinetic model was developed which could predict reaction rate and catalyst activity over a wide range of process conditions.

Process Development Unit Program

- A larger Process Development Unit (PDU) was designed and built. The liquid fluidized reactor in the PDU is 4 inches diameter by 8 feet long and represented a fifty-fold scale-up from the bench-scale reactor.
- Three-phase fluidization studies were conducted in the PDU using a gamma-ray nuclear device which was used to measure bed densities along the length of the reactor. A correlation was developed which predicts catalyst bed expansion and gas holdup over a wide range of process conditions.
- Process variable scans were performed in the PDU investigating the effect of temperature, pressure, space velocity and gas composition. Results corroborated the kinetic model developed from bench-scale data.
- The use of a liquid-fluidized reactor was extended to synthesis gas feeds containing hydrogen to carbon monoxide ratios lower than three to one (designated Liquid Phase Methanation/Shift (LPM/S)).

Experiments under LPM/S conditions were performed in both the bench-scale unit and PDU. Process variable scans were conducted, and a modified kinetic model developed to describe the results.

Pilot Plant Program

- A larger scale pilot plant was designed and constructed. The reactor was 2 feet in diameter by 15 feet long and capable of handling two million SCFD of synthesis gas (a 100 fold scale-up over the smaller PDU). The pilot plant was installed and operated at IGT's HYGAS test facility, in Chicago, Illinois.

- Feed gases were used with H_2/CO molar ratios ranging from 2.2 to 9.5 and flow rates up to 1.3 million SCFD. Reactor conditions ranged up to 750 psig and 675°F with a variety of circulating oil flow rates. Conversions of CO as high as 100% were observed. Catalyst rate constants were determined and the LPM kinetic model was verified over a wide range of process conditions for three different catalysts.
- Unfortunately, one objective that was not met during the pilot plant program was the determination of the larger scale reactor hydrodynamics. In fact, it was obvious that the fluid flow behavior in the 2 foot diameter reactor was quite different from the flow behavior in the smaller 4 inch PDU reactor. This was predominantly a result of large scale backmixing. Attempts were made to quantify the scale of backmixing, but the program was terminated (for other reasons) before sufficient data could be obtained.

4.2.7 Equipment and Instrumentation Lists

Major Equipment List

Following is a major equipment list of all major process equipment required for a cold-flow unit simulation of the Ebulated Bed/Liquid Entrained Methanol Pilot Plant. Sizes, materials of construction and purchased costs on a 3rd quarter, 1981 basis are shown. The major equipment items are listed alphabetically by section and are numbered the same as appears on the process flowsheets.

MAJOR EQUIPMENT LIST
FOR HYDRODYNAMIC TEST UNIT

		Cost; \$ <u>(3rd Quarter, 1981)</u>
CP-100	Main slurry circulation pump (1) 270 gpm x 75.0 head, 25 H.P., CS	6,050
CP-101	Slurry transfer pump (1) 10 gpm x 50 ft head, 3 H.P., CS	1,550
CP-102	Slurry feed pump (1) 10 gpm x 50 ft head, 3 H.P., CS	1,550
CP-103	Liquid transfer pump (1) 10 gpm x 50 ft head, 3 H.P., CS	1,300
CP-104	Slurry transfer pump (1) 10 gpm x 150 ft head, 5 H.P., CS	1,850
F-100	Main slurry filter (1) Sparkler type plate/frame 5990 25 ft ² , CS/CS	5,990
F-101	Final liquid filter (1) pipeline filter with metal element, CS	260
GC-101	Rotary screw gas compressor (1) 110 ACFM @ 100 psig, 30 H.P., SF-1.15 includes: air/oil receiver, ASME coped 150 psig, oil filter, air inlet filter, minimum pressure valve, high temperature	

MAJOR EQUIPMENT LIST
FOR HYDRODYNAMIC TEST UNIT

Cost; \$
(3rd Quarter, 1981)

	shutdown switch, automatic blow-down valve, oil cooler, safety relief valve, Nema T frame motor, magnetic motor starter, hour meter, discharge pressure gauge, oil sump pressure gauge, constant speed unloading control, modulating control	9,800
HE-100	Compressor after cooler 91) shell/tube: CS/CS, 25 ft ²	720
HE-101	Slurry cooler/heater (1) shell/tube: CS/CS, 15 ft ²	520
HT-100	Liquid storage tank (1) 750 gal CS	3,500
TW-100	Hydrodynamic test unit (1) 22" O x 20' T-T, 4 glass sections, 3 CS sections with sample probes and instrumentation taps, top head, bottom head with sparger assembly	26,010
VT-100	Vapor/slurry separator (1) 300 gal, CS	2,950
VT-101	Demister (1) 8" yard pipe x 15" 8" entrainment packing, CS	720

MAJOR EQUIPMENT LIST
FOR HYDRODYNAMIC TEST UNIT

		Cost; \$ <u>(3rd Quarter, 1981)</u>
VT-102	Slurry feed tank (1) 500 gal, CS, 5 H.P. agitator	10,960
VT-103	Slurry prep. tank (1) 100 gal CS, 3 H.P. agitator	9,300
VT-104	Compressor discharge surge tank (1) ASME air receiver, 240 gal CS	1,070
VT-105	Absorbent drier (1) ASME coped external heater type desiccant supports, pressure gauges, temperature gauges, relief valves, purge controls, pre-filter, post filter	5,360

		TURBINE FLOWMETERS				SHEET <u>1</u> OF <u>1</u>		
						SPEC. NO.	REV.	
		NO	BY	DATE	REVISION			
						CONTRACT	DATE	
						REQ. - P.O.		
						BY	CHK'D	APPR.
METER	1	Tag Number	FI-100		FI-101			
	2	Service	Vapor		Vapor			
	3	Meter Location						
	4	Line Size	1"		2"			
	5	End Connections	1"NPT		2"NPT			
	6	Body Rating	--		--			
	7	Nominal Flow Range	2-20 ACFM		40-400 ACFM			
	8	Accuracy	± 5%		± 5%			
	9	Linearity	± 1% F.S.		± 1% F.S.			
	10	K Factor, Cycles per Vol. Unit	6000		6000			
	11	Excitation	--		--			
	12	Materials: Body	MFR STD		MFR STD			
	13	Support	"		"			
	14	Shaft	"		"			
	15	Flanges	"		"			
	16	Rotor	"		"			
	17	Bearings: Type	MFR STD		"			
18	Bearing Material	MFR STD		"				
19	Max. Speed	25 CPS		25 CPS				
20	Min. Output Voltage	30 MV		30 MV				
21	Pickoff Type	MAGNETIC		MAGNETIC				
22	Enclosure Class	CL J Grp D		CL J Grp D				
FLUID DATA	24	Fluid	GAS		GAS			
	25	Flow Rate: Min. Max.	2ACFM 20ACFM		40ACFM 400ACFM			
	26	Normal Flow	12 ACFM		240 ACFM			
	27	Operating Pressure	100 PSIG		5 PSIG			
	28	Back Pressure	--		--			
	29	Operating Temp. Max. Min.	400°F 120°F		400°F 120°F			
	30	Operating Specific Gravity	VARIABLE		VARIABLE			
	31	Viscosity Range	VARIABLE		VARIABLE			
32	Percent Solids & Type	NONE		NONE				
SECONDARY INSTR.	34	Secondary Instr. Tag No.	FI-100		FI-101			
	35	Preamplifier	YES		YES			
	36	Function	Indicator/IL		Indicator/IL			
	37	Mounting	RACK		RACK			
	38	Power Supply	110 VAC		110 VAC			
	39	Scale Range	0-100%		0-100%			
	40	Output Range	0-10 VDC		0-10 VDC			
OPTIONS	41	Totalizer Type	RESET		RESET			
	42	Compensation	NO		NO			
	43	Preset Counter	NO		NO			
	44	Enclosure Class						
	45	Strainer Size & Mesh	MFR STD		MFR STD			
	46							
	47							
	48							
	49	Manufacturer						
	50	Meter Model No.						
	51	Secondary Instr. Model No.						
Notes:								

G COMPANY _____
E Address _____
N PERSON & Position _____
E Address _____
R Address of Installation _____
A Number of Systems _____ Delivery Required _____
L **ESSENTIAL INFORMATION; *Important information which may have a significant effect on the measurement.
Tag Nos. RDI-100, 101, 102, 103, 104

M Purpose of gauge: ☒ Density Control/Indication and/or ☐ Mass Flow of dry solids, ☐ Mass Flow of total fluid
E **Density Span 0.4 to 1.8 ☒ SGU (g/cc), ☐ % by wt solids, ☐ % by vol solids, ☐ lb/ft³, ☐ lb/gal
A ☐ °Baume'L, ☐ °Baume'H, ☐ °API, ☐ °Twaddell, ☐ gms/liter, ☐ metric tons/cubic meter
S
U *Nominal operating density 0.9g/cc; Typical operating range 0.8 to 1.0
R
E **ACCURACY REQUIREMENTS (in % of Density Span) TBD
M Precision ± _____ % at _____ % confidence level; Nonlinearity ± _____ %; Max drift _____ %/week
E Other Accuracy requirements _____
N STANDARDIZATION: STD Block - ☒ Yes, ☐ No; Pipe Status for STD - ☒ Empty, ☐ H₂O, ☒ Process
T On Scale Cal plates (Only) ☐ Yes, ☐ No; Other _____
D
A RESPONSE TIME CONSTANT: (Min) TBD Sec, (Max) _____ Sec, (Nom) _____ Sec
T *Material temperature compensation required ☒ Yes, ☐ No; If Yes: Material temp coef UNK. SGU (g/cc)/°C at _____ °C
A Material Temperature range 60 to 120 ☐ °C, ☒ °F, Nominal 80 ☐ °C, ☒ °F
Meter Scale Calibration Required ☐ (0-10 Standard), ☒ other Digital

P M Material Name _____
R A Material is a: ☐ Solution, ☒ Slurry, ☐ Other _____
O T
C E Liquid Phase of Slurry or Solvent: Name WITCO 40 MINERAL OIL Chemical Formula PARAFFINIC
E R *Liquid gravity 0.75 to 0.85 SGU (g/cc), _____ Hydrogen Content _____ %
S I Content of material with atomic number greater than 50 ALL
S A
L Solid Phase of Slurry or Solute: Name METHANOL CATALYST Chemical Formula _____
*Solids gravity 1.1 to 1.3 SGU (g/cc), _____ Hydrogen Content _____ %
*Content of material(s) with atomic number greater than 50 ALL
Material is: - ☐ Corrosive, ☒ Abrasive, or ☒ Builds up on inside of pipe
Is there air or gas entrainment or entrapment at the point of measurement? ☒ Yes, ☐ No Attach detailed explanation

G COMPANY _____
E Address _____
N PERSON & Position _____
E Address _____
R Address of Installation _____
A Number of Systems _____ Delivery Required _____
L **ESSENTIAL INFORMATION; *Important information which may have a significant effect on the measurement.
Tag Nos. FI-100

M Purpose of gauge: ☐ Density Control/Indication and/or ☐ Mass Flow of dry solids, ☒ Mass Flow of total fluid
E **Density Span 0.4 to 1.8 ☒ SGU (g/cc), ☐ % by wt solids, ☐ % by vol solids, ☐ lb/ft³, ☐ lb/gal
A ☐ °Baume'L, ☐ °Baume'H, ☐ °API, ☐ °Twaddell, ☐ gms/liter, ☐ metric tons/cubic meter
S
U *Nominal operating density 0.9g/cc; Typical operating range _____ to _____
R
E **ACCURACY REQUIREMENTS (in % of Density Span) TBD
M Precision $\pm$ _____ % at _____ % confidence level; Nonlinearity $\pm$ _____ %; Max drift _____ %/week
E Other Accuracy requirements _____
N STANDARDIZATION: STD Block - ☒ Yes, ☐ No; Pipe Status for STD - ☒ Empty, ☐ H₂O, ☒ Process
T On Scale Cal plates (Only) ☐ Yes, ☐ No; Other _____
D
A RESPONSE TIME CONSTANT: (Min) TBD Sec. (Max) _____ Sec. (Nom) _____ Sec
T *Material temperature compensation required ☒ Yes, ☐ No; If Yes: Material temp coef UNK SGU (g/cc)/°C at _____ °C
A Material Temperature range 60 to 120 °C, ☒ °F, Nominal 80 °C, ☒ °F
Meter Scale Calibration Required ☐ (0-10 Standard), ☒ other Digital

P M Material Name _____
R A Material is a: ☐ Solution, ☒ Slurry, ☐ Other _____
O T
C E Liquid Phase of Slurry or Solvent: Name WITCO 40 MINERAL OIL Chemical Formula Paraffinic
E R *Liquid gravity 0.75 to 0.85 SGU (g/cc), _____ Hydrogen Content _____ %
S I ALL
S A Content of material with atomic number greater than 50 _____
L Solid Phase of Slurry or Solute: Name METHANOL CATALYST Chemical Formula _____
*Solids gravity 1.1 to 1.3 SGU (g/cc), _____ Hydrogen Content _____ %
*Content of material(s) with atomic number greater than 50 ALL
Material is: - ☐ Corrosive, ☒ Abrasive, or ☒ Builds up on inside of pipe
Is there air or gas entrainment or entrapment at the point of measurement? ☒ Yes, ☐ No Attach detailed explanation

**Pipe ID 4 ☒ in, ☐ mm; OD 4 in, ☐ mm; Schedule No. 40
 **Wall Material STEEL **Thickness in, ☐ mm
 **Pipe Liner Material N.A. **Pipe Liner Thickness in, ☐ mm
 Pipe Position: ☐ Vertical, ☒ Horizontal, ☐ Measurement not being made on a pipe (attach explanation)

	GAUGE HEAD (ELEMENT)	ELECTRONICS (TRANSMITTER)
LOCATION:	☒ Indoor, ☐ Outdoor	☒ Indoor, ☐ Outdoor
ENCLOSURE:	☒ Explosion Proof, ☐ Nema <u> </u>	☐ Nema <u> </u> , ☒ Panel Mount, ☐ Explosion Proof
TEMPERATURE:	<u>60</u> to <u>120</u> ☐ °C, ☒ °F	<u>60</u> to <u>120</u> ☐ °C, ☒ °F

Power Available 110 ± VAC @ 60 Hz ± Hz
 Cable length required from density measuring heads to electronic unit 50 ☒ ft, ☐ m

MASS FLOW DATA: What is signal from flow meter? 4 to 20 ☐ volts, ☒ milliamps, ☐ Hz.

If Hz give details of signal _____

Can negative side of signal line be grounded? ☐ Yes, ☒ No; Flow Rate 200 gpm

OUTPUTS: Density ☐ 1-5mA, ☐ 4-20mA, ☐ 10-50mA, ☐ Other _____

Mass Flow ☐ 1-5mA, ☒ 4-20mA, ☐ 10-50mA, ☐ Other _____

Totalized Mass Flow - ☐ Total Dry Solids, ☐ Total Mass; ☐ Contact Closure and/or ☐ Pulse

Other _____

COMMENTS

PLEASE MAIL THIS FORM TO:

**Texas Nuclear
Division**

OR

Ramsey Engineering Company
Box 9267
Austin, Texas 78766 USA
Telephone (512) 836-0801
Telex 77-6413

LEVEL INSTRUMENTS (CAPACITANCE TYPE)				SHEET ____ OF ____	
			NO	BY	DATE	REVISION	SPEC. NO.	REV.
							CONTRACT	DATE
							REQ.	P.O.
				BY	CHK'D	APPR.		
GENERAL	1	Tag Number	LIC -100					
	2	Service	SLURRY					
	3	Line No./Vessel No.	VT-100					
	4	Application	SLURRY LEVEL					
	5	Function	TRANSMIT					
	6	Fail-Safe	LOW					
PROBE	7	Model Number						
	8	Orientation	VERTICLE					
	9	Style	KROD					
	10	Material	316SS					
	11	Sheath	N.A.					
	12	Insertion Length	TBD					
	13	Inactive Length	TBD					
	14	Gland Size & Mat'l.	TBD					
AMPLIFIER	16	Conduit Connection	1/2" EMT					
	17	Location	LOCAL					
	18	Enclosure	XP					
	19	Conduit Connection	1/2" EMT					
SWITCH	20	Power Supply	115 VAC					
	21	Type	MED STD					
	22	Quantity and Form	2-SPOT					
	23	Rating: Volts/Hz or dc	120	60 HZ				
	24	Amps/Watts/HP	1					
	25	Load Type	NON INDUCTIVE					
	26	Contacts Open	On	Incr.				
	27	Close	Level	Decr.				
TRANS.	28	Output	4-20MA					
	29	Range	2"					
	30	Enclosure Class	XP					
OPTIONS	31	Compensation Cable	25'					
	32	Local Indicator	NA					
	33	I/P Transducer	NA					
	34	Signal Lights	NA					
	35							
SERVICE	36	Upper Fluid	VAPOR					
	37	Dielectric Constant	AIR					
	38	Lower Fluid	VARIES					
	39	Dielectric Constant	--					
	40	Pressure Max.	Normal	30 PSIA	PSIA			
	41	Temp. Max.	Normal	120°F	180°F			
	42	Moisture	NA					
	43	Material Buildup	UNKNOWN					
44	Vibration	UNKNOWN						
45	Manufacturer							
46	Model Number							
Notes:

PRESSURE INSTRUMENTS				SHEET <u>1</u> OF <u>2</u>	
						SPEC. NO.	REV.
		NO	BY	DATE	REVISION	CONTRACT	DATE
						REQ.	P.O.
						BY	CHK'D
						APPR.	
1		Tag No. <u>PI-100, PE-100</u> Service <u>FEED GAS</u>					
GENERAL	2	Function	Record ☒ Indicate ☒ Control ☐ Blind ☐ Trans ☐ Other _____				
	3	Case	MFR STD ☒ Nom Size _____ Color: MFR STD ☐ Other _____				
	4	Mounting	Flush ☐ Surface ☐ Yoke ☒ Other _____				
	5	Enclosure Class	General Purpose ☐ Weather proof ☐ Explosion proof ☒ Class <u>D</u>				
	6	Power Supply	For Use In Intrin. Safe System ☐ Other _____				
	7	Chart	117V 60Hz ☒ Other ac _____ dc _____ Volts Strip ☐ Roll ☒ 4" Fold ☒ Circular _____ Time Marks _____				
	8	Chart Drive	Speed <u>MFR STD</u> Power <u>117V 60 HZ</u>				
	9	Scales	Type <u>HORIZONTAL</u> Range 1 <u>0-100</u> 2 <u>0-100</u> 3 <u>0-100</u> 4 _____				
	XMTR	10	Transmitter Output	4-20 mA ☒ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____ For Receiver See Spec Sheet _____			
CONTROLLER	11	Control Modes	P=Prop (Gain) I=Integral (Auto-Reset) D=Derivative (Rate) Sub: s=Slow f=Fast P ☐ PI ☐ PD ☐ PID ☐ If ☐ Df ☐ Is ☐ Ds ☐ Other _____				
	12	Action	On Meas. Increase Output: Increases ☐ Decreases ☐				
	13	Auto-Man Switch	None ☐ MFR STD ☐ Other _____				
	14	Set Point Adj.	Manual ☐ External ☐ Remote ☐ Other _____				
	15	Manual Reg.	None ☐ MFR STD ☐ Other _____				
	16	Output	4-20mA ☐ 10-50mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____				
ELEMENT	17	Service	Gage Press. ☐ Vacuum ☐ Absolute ☒ Compound ☐				
	18	Element Type	Diaphragm ☒ Helix ☐ Bourdon ☐ Bellows ☐ Other _____				
	19	Material	316 SS ☒ Ber. Copper ☐ Other _____				
	20	Range	Fixed ☒ Adj. Range _____ Set at _____ Overrange protection to <u>150 PSIA MIN.</u>				
	21	Process Data	Press: Normal <u>110PSIA</u> Max <u>135PSIA</u> Element Range _____				
	22	Process Conn.	1/2 in. NPT ☐ 1/2 in. NPT ☒ Other _____ Location: Bottom ☒ Back ☐ Other _____				
	23	Alarm Switches	Quantity _____ Form <u>SDSL</u> Rating <u>1 amp</u>				
	24	Function	Press ☒ Deviation ☐ Contacts To <u>NC</u> on Inc Press.				
OPTIONS	25	Options	Filt-Reg. ☐ Sup Gage ☐ Output Gage ☐ _____ Charts _____ Diaph Seal ☐ Type _____ Diaph _____ Bot Bowl _____ Conn _____ Capillary: Length _____ Mtl. _____ Other _____				
	26	MFR & Model No.					

Notes:

[illegible]

Notes:

		RECEIVER INSTRUMENTS				SHEET _____ OF _____		
		NO	BY	DATE	REVISION	SPEC. NO.	REV.	
						CONTRACT	DATE	
								REQ.
						BY	CHK'D	APPR.
1	Tag No	DI-100		Service	SLURRY DENSITY			
GENERAL	2	Function	Record ☒ Indicate ☒ Control ☐ Blind ☐ Integ ☐ Deviation ☐ Other _____					
	3	Case	MFR STD ☒ Nom Size _____ Color: MFR STD ☒ Other _____					
	4	Mounting	Flush ☐ Surface ☐ Rack ☒ Multi-Case ☐ Other _____ For Multiple Case, See Spec. Sheet _____					
	5	Enclosure Class	General Purpose ☐ Weather Proof ☐ Explosion-Proof ☐ Class _____ For Use in Intrinsically Safe System. ☒ Other _____					
	6	Power Supply	117 V 60Hz ☒ Other ac _____ dc ☐ _____ Volts					
	7	Chart	Strip ☐ Roll ☐ 4" Fold ☒ Circular _____ Time Marks _____ Range _____ Number _____					
	8	Chart Drive	Speed _____ Power _____					
	9	Scales	Type _____ Range 1 _____ 2 _____ 3 _____ 4 _____					
	CONTROLLER	10	Control Modes	P = Prop (Gain), I = Integral (Auto Reset), D = Derivative (Rate), Sub: s = Slow, f = Fast P ☐ PI ☐ PD ☐ PID ☐ If ☐ Df ☐ Is ☐ Ds ☐ _____ Other _____				
11		Action	On Meas. Increase Output: Increases ☐ Decreases ☐ _____					
12		Auto-Man Switch	None ☐ MFR STD ☐ Other _____					
13		Set Point Adj.	Manual ☐ External ☐ Remote ☐ Other _____					
14		Manual Reg	None ☐ MFR STD ☐ Other _____					
INPUTS	15	Output	4-20 mA ☐ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____					
	16	Input Signals	4-20 mA ☒ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____					
	17	No. of Inputs	1 ☒ 2 ☐ 3 ☐ 4 ☐ _____					
ALARMS	18	Power for XMTRS	External ☐ This Inst ☒ No. of Independent Supplies _____ For Transmitters. See Spec Sheet. _____					
	19	Alarm Switches	Quantity _____ Form <u>SPST</u> Rating <u>5A</u>					
	20	Function	Meas. Var. ☐ Deviation ☒ Contacts To _____ On Meas _____ Other _____					
	21	Options	Filter-Reg ☐ Supply Gage ☐ Charts ☐ Int. Illumination ☐ Other _____					
	22	MFR & Model No.	_____					
Notes:								

		DIFFERENTIAL PRESSURE INSTRUMENTS				SHEET <u>1</u> OF <u>2</u>		
		NO		BY	DATE	REVISION	SPEC. NO.	REV.
							CONTRACT	DATE
							REQ.	P.O.
						BY	CHK'D	APPR.
	1	Tag No. DPT-100	Slurry Service					
GENERAL	2	Function	Record ☒ Indicate ☒ Control ☐ Blind ☐ Trans ☐ Integ ☐ Other _____					
	3	Case	MFR STD ☒ Nom Size _____ Color: MFR STD ☒ Other _____					
	4	Mounting	Flush ☐ Surface ☐ Yoke ☒ Other _____					
	5	Enclosure Class	General Purpose ☐ Weather proof ☐ Explosion proof ☒ Class _____					
	6	Power Supply	For use in Intrinsically Safe System? Other _____					
	7	Chart	117V 60 Hz ☒ Other ac _____ dc ☐ Volts _____					
	8	Chart Drive	12 in. Circ. ☐ Other <u>2-Fold</u> Range <u>0-100</u> No. _____					
	9	Scale	24 hr Other _____ Elec. ☒ Spring ☐ Other _____					
				Type _____ Range: 1 _____ 2 _____ 3 _____				
XMTR	10	Transmitter Output	4-20 mA ☒ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____ For Receiver, See Spec Sheet _____					
CONTROLLER	11	Control Modes	P=Prop (Gain), I=Integral (Auto Reset), D=Derivative (Rate) Sub: s=Slow, f=Fast If ☐ Df ☐ P ☐ PI ☐ PD ☐ PID ☐ Is ☐ Ds ☐ Other _____					
	12	Action	On Meas. Increase Output: Increases ☐ Decreases ☐					
	13	Auto-Man Switch	None ☐ MFR STD ☐ Other _____					
	14	Set Point Adj.	Manual ☐ External ☐ Remote ☐ Other _____					
	15	Manual Reg.	None ☐ MFR STD ☐ Other _____					
	16	Output	4-20 mA ☐ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____					
UNIT	17	Service	Flow ☐ Level ☐ Diff. Pressure ☒ Other _____					
	18	Element Type	Diaphragm ☒ SS Bellows ☐ Mercury ☐ Other _____					
	19	Material	Body _____ Element <u>Alloy</u> _____					
	20	Rating	Overrange <u>1060"</u> H ₂ O _____ Body Rating <u>3000</u> _____ psig					
	21	Diff. Range	Fixed ☐ Adj. Range <u>150-850"</u> H ₂ O _____ Set At _____					
	22		Elevation _____ Suppression _____					
	23	Process Data	Fluid <u>Slurry</u> _____ Max Temp. <u>120</u> F _____ Max. Press. <u>100</u> PSIG					
	24	Process Conn.	1/2 in. NPT ☒ Other _____					
25	Alarm Switches	Quantity <u>1</u> _____ Form <u>SPST</u> _____ Rating <u>1AMP</u> _____						
26	Function	Meas. Var. ☐ Deviation ☒ Contacts To <u>NC</u> _____ on Inc. Meas.						
	27	Options	Pressure Element ☐ Range _____ Material _____ Temp. Element ☐ Range _____ Type _____ Filt Reg. ☐ Sup. Gage ☐ Output Gage ☐ _____ Charts Valve Manifold _____ Cond. Pots ☐ Adj. Damp ☐ Integral Sq. Rt. Ext. ☐ Integrator _____ Other _____					
	28	MFR & Model No.						
	Notes:							

		POTENTIOMETER INSTRUMENTS				SHEET ____ OF ____		
						SPEC. NO.	REV.	
		NO	BY	DATE	REVISION	CONTRACT	DATE	
						REQ.	P.O.	
						BY	CHK'D	APPR.
	1	Tag No.	TI-100		Service			
GENERAL	2	Function	Record ☐ Indicate ☒ Control ☐ Blind ☐ Transmit ☒ Other _____					
	3	Type	Auto Bal. ☒ Man Bal. ☐ Galv ☐ Other _____					
	4	Case	MFR STD ☒ Norm Size _____ Color: MFR STD ☒ Other _____					
	5	Mounting	Flush ☒ Surface ☐ Rack ☐ Multi-Case ☐ Other _____ For Multiple Case Spec, See Sheet _____					
	6	Enclosure Class	Gen Purp ☒ Weather Proof ☐ Explosion-Proof ☐ Class _____ Other _____					
	7	Power Supply	117V 60 Hz ☒ Other _____					
	8	Chart	Strip ☐ Circ ☐ Time Marks ☐ Range _____ No _____ Chart Speed: _____ Change Gears _____					
	9	Scale	Type _____ Range 1 _____ 2 _____					
	10	Printout	No. of Points _____ Sec Per Point _____ Full Travel Speed _____ Print Character and Color _____ Point Select ☐					
	11	Selector Switches	No. and Form _____ In Case ☐ External ☐ Switch Cabinet Specs _____					
	XMTR	12	Trans. Output	4-20 mA ☒ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____ Input-Output Isolation ☒ For Receiver See Sheet _____				
13		Control Modes	P = Prop (Gain), I = Integral (Auto Reset), D = Derivative (Rate), Sub: s=Slow f=Fast I _f ☐ D _f ☐ P ☐ PI ☐ PD ☐ PID ☐ I _s ☐ D _s ☐ Other _____					
CONTROLLER	14	Action	On Meas. Increase Output: Increases Decreases					
	15	Auto-Man Switch	None ☐ MFR STD ☐ Specify _____					
	16	Set Point Adj.	Manual ☐ External ☐ Remote ☐ Specify _____					
	17	Manual Reg.	None ☐ MFR-STD ☐ Other _____					
INPUT	18	Output	4-20 mA ☐ 10-50 mA ☐ 21-103 kPa (3-15 psig) ☐ Other _____					
	19	Thermocouple Type	J(1C) ☒ K(1CA) ☐ T(1CC) ☐ E(1CHR-CON) ☐ Other _____					
	20	Other Input	Ref Junction Comp. ☒ Lead Resistance (Galv) _____ Resistance Temp Sensor ☐ Calibration _____ Other _____					
ALARM	21	Alarm Switches	Quantity <u>1</u> Form <u>SPST</u> Rating <u>1 AMP</u>					
	22	Function	Meas. Var. ☒ Deviation ☐ Contacts to <u>NC</u> measure _____ Other _____					
	23		Front Adj. ☒ Back Adj. _____					
OPTIONS	24	T/C Burnout Drive	None ☐ Upscale ☒ Downscale ☐					
	25	Accessories	Case Illuminator ☐ Charts _____ Filter Reg. ☐ Other _____					
	26	MFR. & Model No.	_____					
Notes:								

[illegible]

ISA FORM S20.41a

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6.0. PATENTABLE INVENTIONS

No patentable inventions were conceived during the course of this project.

7.0 APPENDIX

7.1 Tables 1 Through 15

7.2 Figures 1 Through 147

TABLE 1

SHIFTED METHANATION FEED, CALCULATED EQUILIBRIUM,
AND TYPICAL PRODUCT GAS COMPOSITIONS

<u>Component</u>	<u>Feed; v/o</u>	Equilibrium ⁽¹⁾ <u>Calculated</u> <u>Effluent; v/o</u>	<u>Typical</u> <u>Effluent</u>
Hydrogen	13.30	2.07	1.77
Argon	5.17	5.84	5.92
Nitrogen	73.96	83.54	84.20
Methane	3.39	8.11	7.86
Carbon Monoxide	3.72	0.04	0.01
Carbon Dioxide	<u>0.46</u> 100.00	<u>0.40</u> 100.00	<u>0.23</u> 99.99

⁽¹⁾ Dry Basis; at 1000 psig and 900°F

TABLE 2

LISTING OF NICKEL CATALYSTS

<u>Manufacturer</u>	<u>Catalyst</u>	<u>Nominal Composition</u>	<u>Reactor</u>
United Catalyst Inc.	G87-S 1/4 x 1/8 Spheres	40% Ni; calcium aluminate	1
United Catalyst Inc.	C150-4-03 1/8 x 1/8 Tablets	60% Ni; alumina	2
Katalco Corp.	CRG-F 1/8 x 1/8 Tablets	60% Ni; proprietary	3
Harshaw	Ni-3210 Lot #133 3/16 Tablets	35% Ni; proprietary	4
Harshaw	Ni-0104 Lot #972 1/8 Tablets	60% Ni; kieselguhr	5

TABLE 3NOMINAL REACTION CONDITIONS

Test Length, Hr	100	300	600	1,200
Maximum Temperature, °F	900	900	900	900
Total Pressure, psi	1,000	1,000	1,000	1,000
Space Velocity, Hr ⁻¹	10,000	10,000	10,000	10,000
Gas Type*	Shifted, methanation feed gas (63% H ₂ , 19% CO, 2% CO ₂ , 16% CH ₄)			
Steam Addition, Mol%	0; 15	0; 15	0; 15	0; 15

*Gas will be diluted with 4 parts N₂

TABLE 4

CATALYST CHARACTERISTICS

<u>Scan Description</u>	<u>Catalyst*</u>	<u>Surface Area; m²/g</u>	<u>Pore Volume 29.2A; cc/g</u>	<u>%C</u>	<u>XRD Ni Surface Area; m²/g</u>
Virgin	A	72.0	0.49	0.18	19.7
Reduced	B	174.0	0.21	2.55	37.0
	C	134.0	0.29	2.33	23.4
	D	159.0	0.14	3.53	74.0
	E	138.0	0.14	4.10	37.0
100 Hour w/o Steam	A	32.0	0.57	1.18	14.4
	B	52.0	0.38	2.78	15.4
	C	66.0	0.34	2.70	34.0
	D	61.0	0.16	4.61	47.0
	E	75.0	0.21	4.63	58.0
100 Hour with Steam	A	32.0	0.58	1.68	14.5
	B	111.0	0.34	4.18	47.4
	C	107.0	0.32	2.75	54.5
	D	131.0	0.19	5.33	120.0
	E	92.7	0.17	4.09	77.3
300 Hour w/o Steam	A	36.0	0.57	1.20	18.0
	B	64.0	0.34	2.80	32.1
	C	53.0	0.24	1.38	36.8
	D	139.0	0.17	5.37	77.3
	E	89.0	0.14	5.12	49.0
300 Hour with Steam	A	27.5	0.59	1.51	18.0
	B	89.5	0.33	4.16	54.0
	C	91.5	0.34	3.47	53.0
	D	67.0	0.20	6.29	47.0
	E	81.0	0.18	5.39	47.4
600 Hour w/o Steam	A	36.0	0.58	1.62	14.3
	B	83.0	0.34	4.42	33.5
	C	143.0	0.59	3.26	36.6
	D	82.0	0.23	5.81	67.6
	E	73.0	0.34	4.10	61.5

*Catalyst A = UCI-G87-S
 B = UCI-C150-4-03
 C = Katalco CRG-F
 D = Harshaw Ni-3210
 E = Harshaw Ni-0104

TABLE 4 (CONTINUED)

CATALYST CHARACTERISTICS

<u>Scan Description</u>	<u>Catalyst*</u>	<u>Surface Area; m²/g</u>	<u>Pore Volume o 29.2A; cc/g</u>	<u>%C</u>	<u>XRD Ni Surface Area; m²/g</u>
1200 Hour w/o Steam	A	40.0	0.60	1.27	14.5
	B	60.0	0.36	3.30	33.7
	C	67.0	0.36	3.62	33.7
	D	74.0	0.27	5.15	54.5
	E	56.0	0.20	5.48	47.4
1200 Hour with Steam	A	14.0	0.38	1.13	3.6
	B	30.6	0.34	2.23	19.7
	C	35.0	0.34	2.87	16.4
	D	49.7	0.23	2.47	37.8
	E	52.0	0.16	4.67	40.0

*Catalyst A = UCI-G87-S
 B = UCI-C150-4-03
 C = Katalco CRG-F
 D = Harshaw Ni-3210
 E = Harshaw Ni-0104

TABLE 5

Virgin Reduced CatalystCatalyst *XRD** Data

A	1.	NiO ($\sim 58\%$) MCS = 39 Å
	2.	Ni ($\sim 42\%$) MCS = 103 Å
	3.	γ -Al ₂ O ₃ MCS = 41 Å
	4.	α -Al ₂ O ₃ ·H ₂ O (?)
B	1.	NiO ($\sim 79\%$) MCS = 40 Å
	2.	Ni ($\sim 21\%$) MCS = 27 Å
	3.	C (Graphite) MCS = 582 Å
	4.	α -Al ₂ O ₃ ·H ₂ O (?)
C	1.	NiO ($\sim 80\%$) MCS = 31 Å
	2.	Ni ($\sim 20\%$) MCS = 41 Å
	3.	C (Graphite) MCS > 1323 Å
D	1.	Ni MCS = 65 Å
	2.	CaO MCS = 817 Å
	3.	C (Graphite) MCS > 1000 Å
E	1.	NiO ($\sim 56\%$) MCS = 34 Å
	2.	Ni ($\sim 44\%$) MCS = 58 Å
	3.	C (Graphite) MCS > 1000 Å

*Catalyst A - UCI-87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F
 D - Harshaw Ni-3210
 E - Harshaw Ni-0104

**MCS = Mean Crystallite Size

TABLE 5 (CONTINUED)
100 Hour w/o Steam Test

Catalyst*XRD** Data

A	1. Ni MCS = 335 Å^o 2. γ-Al₂O₃ MCS = 67 Å^o 3. α-Al₂O₃ (10%) MCS > 2000 Å^o 4. CaCO₃ MCS = 1428 Å^o 5. 12CaO·7Al₂O₃ (?)
B	1. Ni MCS = 312 Å^o 2. γ-Al₂O₃ MCS = 58 Å^o 3. C (Graphite) MCS = 1323 Å^o 4. α-Al₂O₃·H₂O (?)
C	1. Ni MCS = 143 Å^o 2. γ-Al₂O₃ MCS = 45 Å^o 3. C (Graphite) MCS = 1003 Å^o 4. α-Al₂O₃·H₂O (?)
D	1. Ni MCS = 84 Å^o 2. C (Graphite) MCS > 1000 Å^o 3. CaCO₃ (?)
E	1. Ni MCS = 83 Å^o 2. CaCO₃ MCS = 800 Å^o 3. C (Graphite) MCS > 1000 Å^o

*Catalyst A - UCI-87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F
 D - Harshaw Ni-3210
 E - Harshaw Ni-0104

** MCS = Mean Crystallite Size

TABLE 5 (CONTINUED)

100 Hour with Steam Test

<u>Catalyst*</u>	<u>XRD** Data</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 330 Å^o 2. γ-Al₂O₃ MCS = 68 Å^o 3. α-Al₂O₃ (<10%) MCS > 2000 Å^o 4. CaCO₃ MCS = 1428 Å^o
B	<ol style="list-style-type: none"> 1. Ni MCS = 101 Å^o 2. γ-Al₂O₃ MCS = 51 Å^o 3. C (Graphite) MCS > 2000 Å^o
C	<ol style="list-style-type: none"> 1. Ni MCS = 88 Å^o 2. γ-Al₂O₃ MCS = 47 Å^o 3. C (Graphite) MCS > 2000 Å^o
D	<ol style="list-style-type: none"> 1. Ni MCS = 40 Å^o 2. CaCO₃ MCS = 1285 Å^o 3. C (Graphite) MCS > 2000 Å^o 4. α-Al₂O₃ (?)
E	<ol style="list-style-type: none"> 1. Ni MCS 62 Å^o 2. C (Graphite) MCS = 1136 Å^o

*Catalyst A - UCI-87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F
 D - Harshaw Ni-3210
 E - Harshaw Ni-0104

**MCS = Mean Crystallite Size

TABLE 5 (CONTINUED)

300 Hour with Steam Test

<u>Catalyst*</u>	<u>XRD** Data</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 268 Å⁰ 2. γ-Al₂O₃ MCS = 63 Å⁰ 3. α-Al₂O₃ (<10%) MCS > 2000 Å⁰ 4. CaCO₃ MCS = 1397 Å⁰
B	<ol style="list-style-type: none"> 1. Ni MCS = 89 Å⁰ 2. γ-Al₂O₃ MCS = 53 Å⁰ 3. C (Graphite) MCS = 780 Å⁰
C	<ol style="list-style-type: none"> 1. Ni MCS = 90 Å⁰ 2. γ-Al₂O₃ MCS = 63 Å⁰ 3. C (Graphite) MCS = 980 Å⁰
D	<ol style="list-style-type: none"> 1. Ni MCS = 100 Å⁰ 2. CaCO₃ MCS = 980 Å⁰ 3. C (Graphite) MCS = 1250 Å⁰
E	<ol style="list-style-type: none"> 1. Ni MCS = 101 Å⁰ 2. C (Graphite) MCS = 1600 Å⁰

*Catalyst A - UCI-87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F
 D - Harshaw Ni-3210
 E - Harshaw Ni-0104

**MCS = Mean Crystallite Size

TABLE 5 (CONTINUED)

300 Hour w/o Steam Test

<u>Catalyst *</u>	<u>XRD** Data</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 268 Å^o 2. γ -Al₂O₃ = 71 Å^o 3. α -Al₂O₃ > 2000 Å^o 4. CaCO₃ MCS = 1385 Å^o 5. 12 CaO·7Al₂O₃ (?)
B	<ol style="list-style-type: none"> 1. Ni (~60%) MCS = 90 Å^o 2. NiO (~40%) MCS = 43 Å^o 3. C (Graphite) MCS = 1380 Å^o
C	<ol style="list-style-type: none"> 1. Ni (~72%) MCS = 94 Å^o 2. NiO (~28%) MCS = 39 Å^o 3. C (Graphite) MCS = 980 Å^o
D	<ol style="list-style-type: none"> 1. Ni MCS = 62 Å^o 2. CaCO₃ MCS = 1120 Å^o 3. C (Graphite) MCS = 870 Å^o
E	<ol style="list-style-type: none"> 1. Ni MCS = 98 Å^o 2. C (Graphite) MCS > 2000 Å^o

*Catalyst A - UCI-87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F
 D - Harshaw Ni-3210
 E - Harshaw Ni-0104

**MCS = Mean Crystallite Size

TABLE 5, (CONTINUED)
600 Hour Without Steam Test

Catalyst*XRD Data**

A

1. Ni MCS = 335 Å⁰
2. γ -Al₂O₃ MCS = 56 Å⁰
3. CaCO₃ MCS = >2000 Å⁰
4. α -Al₂O₃ (?)
5. 12CaO·7Al₂O₃

B

1. Ni MCS = 143 Å⁰
2. α -Al₂O₃ MCS = 52 Å⁰
3. C (Graphite) MCS = 1001 Å⁰

C

1. Ni MCS = 131 Å⁰
2. α -Al₂O₃ MCS = 44 Å⁰
3. C (Graphite) MCS = 510 Å⁰
4. CaCO₃ MCS = >2000 Å⁰

D

1. Ni MCS = 71 Å⁰
2. CaCO₃ MCS = >2000 Å⁰
3. C (Graphite) MCS = >2000 Å⁰

E

1. Ni MCS = 78 Å⁰
2. CaCO₃ MCS = >2000 Å⁰
3. C (Graphite) MCS = >2000 Å⁰
4. Ni₃(OH)₄Si₂O₅ (?)
5. SiO₂ (α -quartz) (?)
6. SiO₂ Al₂O₃ (?)

*A - UCI-G87-S
 B - UCI-C150-4-03
 C - Katalco CRG-F

D - Harshaw Ni-3210
 E - Harshaw Ni-0104

**Mean Crystallite Size

TABLE 5 (CONTINUED)

600 Hour With Steam Test

<u>Catalyst*</u>	<u>XRD**</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 264 Å^o 2. CaCO₃ MCS = >2000 Å^o
B	<ol style="list-style-type: none"> 1. Ni MCS = 192 Å^o 2. δ-Al₂O₃ MCS = 91 Å^o 3. C (Graphite) MCS = 1320 Å^o
C	<ol style="list-style-type: none"> 1. Ni MCS = 247 Å^o 2. δ-Al₂O₃ MCS = 94 Å^o 3. C (Graphite) MCS = 1320 Å^o
D	<ol style="list-style-type: none"> 1. Ni MCS = 114 Å^o 2. CaCO₃ MCS > 2000 Å^o 3. C (Graphite) MCS > 2000 Å^o
E	<ol style="list-style-type: none"> 1. Ni MCS = 148 Å^o 2. δ-Al₂O₃ MCS = 87 Å^o 3. C (Graphite) MCS = 1020 Å^o

*A - UCI-G87-S

B - UCI-C150-4-03

C - Katalco CRG-F

D - Harshaw Ni-3210

E - Harshaw Ni-0104

**MCS = Mean Crystallite Size

TABLE 5 (CONTINUED)

1200 Hour w/o Steam Test

<u>Catalyst*</u>	<u>XRD Data**</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 330 Å 2. γ-Al₂O₃ MCS = 57 Å 3. CaCO₃ MCS > 2000 Å 4. α-Al₂O₃ MCS > 2000 Å 5. 12 CaO·7 Al₂O₃ (?)
B	<ol style="list-style-type: none"> 1. Ni MCS = 143 Å 2. γ-Al₂O₃ MCS = 64 Å 3. C (Graphite) MCS > 2000 Å
C	<ol style="list-style-type: none"> 1. Ni MCS = 143 Å 2. γ-Al₂O₃ MCS = 54 Å 3. C (Graphite) MCS = 1000 Å 4. CaCO₃ MCS > 2000 Å
D	<ol style="list-style-type: none"> 1. Ni MCS = 88 Å 2. CaCO₃ MCS > 2000 Å 3. C (Graphite) MCS > 2000 Å
E	<ol style="list-style-type: none"> 1. Ni MCS = 101 Å 2. CaCO₃ MCS > 2000 Å 3. C (Graphite) MCS > 2000 Å

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw - Ni-3210

E = Harshaw - Ni-0104

**Mean Crystallite Size

TABLE 5 (CONTINUED)

1200 Hour With Steam Test

<u>Catalyst*</u>	<u>XRD Data**</u>
A	<ol style="list-style-type: none"> 1. Ni MCS = 1322 Å⁰ 2. CaCO₃ MCS = >2000 Å⁰
B	<ol style="list-style-type: none"> 1. Ni MCS = 244 Å⁰ 2. δAl₂O₃ (distorted) MCS = 97 Å⁰ 3. C (Graphite) MCS = 1320 Å⁰
C	<ol style="list-style-type: none"> 1. Ni MCS = 292 Å⁰ 2. γ-Al₂O₃ (~85%) MCS = 66 Å⁰ 3. α-Al₂O₃ (~15%) MCS = >2000 Å⁰ 4. C (Graphite) MCS = >2000 Å⁰
D	<ol style="list-style-type: none"> 1. Ni MCS = 127 Å⁰ 2. CaSiO₃ MCS = >2000 Å⁰ 3. C (Graphite) MCS = >2000 Å⁰ 4. CaCO₃ MCS = >2000 Å⁰
E	<ol style="list-style-type: none"> 1. Ni MCS = 120 Å⁰ 2. CaCO₃ MCS = >2000 Å⁰ 3. C (Graphite) MCS = >2000 Å⁰ 4. Ni₃(OH)₄Si₂O₅ (?) 5. SiO₂ (α-quartz) (?)

*A - UCI-G87-S

B - UCI-C150-4-03

C - Katalco CRG-F

D - Harshaw Ni-3210

E - Harshaw Ni-0104

**mean crystallite size

TABLE 6

INCREASE IN NICKEL CRYSTALLITE SIZE (A) WITH TIME

Catalyst*	Steam Level (Mol %)	Scan Description				
		Virgin Reduced	100 Hour	300 Hour	600 Hour	1200 Hour
A	0	103	335	268	335	330
	15	---	330	268	264	1322
B	0	27	312	90	143	143
	15	---	101	89	192	244
C	0	41	143	94	131	143
	15	---	88	90	247	292
D	0	65	84	62	71	88
	15	---	40	100	114	127
E	0	58	83	98	78	101
	15	---	62	101	148	120

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 7DECREASE IN NICKEL SURFACE AREA (m²/g) WITH TIME

<u>Catalyst*</u>	<u>Steam Level (Mol %)</u>	<u>Scan Description</u>				
		<u>Virgin Reduced</u>	<u>100 Hour</u>	<u>300 Hour</u>	<u>600 Hour</u>	<u>1200 Hour</u>
A	0	19.7	14.4	18.0	14.3	14.5
	15	---	14.5	18.0	18.2	3.6
B	0	37.0	15.4	32.1	33.5	33.7
	15	---	47.4	54.0	25.0	19.7
C	0	23.4	34.0	36.8	36.6	33.7
	15	---	54.5	53.0	19.4	16.4
D	0	74.0	47.0	77.3	67.6	54.5
	15	---	120.0	47.0	42.1	37.8
E	0	37.0	58.0	49.0	61.5	47.4
	15	---	77.3	47.4	32.4	40.0

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 8

DECREASE IN CATALYST SURFACE AREA (m²/g) WITH TIME

<u>Catalyst*</u>	<u>Steam Level (Mol %)</u>	<u>Scan Description</u>				
		<u>Virgin Reduced</u>	<u>100 Hour</u>	<u>300 Hour</u>	<u>600 Hour</u>	<u>1200 Hour</u>
A	0	72.0	32.0	36.0	36.0	40.0
	15	---	32.0	27.5	16.7	14.0
B	0	174.0	52.0	64.0	83.0	60.0
	15	---	111.0	89.5	45.0	30.6
C	0	134.0	66.0	53.0	143.0	67.0
	15	---	107.0	91.5	41.0	35.0
D	0	159.0	61.0	139.0	82.0	74.0
	15	---	131.0	67.0	48.0	49.7
E	0	138.0	75.0	89.0	73.0	56.0
	15	---	92.0	81.0	35.0	52.0

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 9

INCREASE IN PORE VOLUME (cc/g) WITH TIME

<u>Catalyst*</u>	<u>Steam Level (Mol %)</u>	<u>Scan Description</u>				
		<u>Virgin Reduced</u>	<u>100 Hour</u>	<u>300 Hour</u>	<u>600 Hour</u>	<u>1200 Hour</u>
A	0	0.49	0.57	0.57	0.58	0.60
	15	---	0.58	0.59	0.58	0.38
B	0	0.21	0.38	0.34	0.34	0.36
	15	---	0.34	0.33	0.34	0.34
C	0	0.29	0.34	0.24	0.59	0.36
	15	---	0.32	0.34	0.36	0.34
D	0	0.14	0.16	0.17	0.23	0.27
	15	---	0.19	0.20	0.22	0.23
E	0	0.14	0.21	0.14	0.34	0.20
	15	---	0.17	0.18	0.15	0.16

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 10
INCREASE IN CARBON CONTENT (WT%) WITH TIME

<u>Catalyst*</u>	<u>Steam Level (Mol %)</u>	<u>Scan Description</u>				
		<u>Virgin Reduced</u>	<u>100 Hour</u>	<u>300 Hour</u>	<u>600 Hour</u>	<u>1200 Hour</u>
A	0	0.18	1.18	1.20	1.62	1.27
	15	---	1.68	1.51	1.10	1.13
B	0	2.55	2.78	2.80	4.42	3.30
	15	---	4.18	4.16	3.20	2.23
C	0	2.33	2.70	1.38	3.26	3.62
	15	---	2.75	3.47	2.90	2.87
D	0	3.53	4.61	5.37	5.81	5.15
	15	---	5.33	6.29	4.30	2.47
E	0	4.10	4.63	5.12	4.10	5.48
	15	---	4.09	5.39	5.00	4.67

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 11
CHANGE WITH CRUSH STRENGTH (Kg) WITH TIME

<u>Catalyst*</u>	<u>Steam Level (Mol %)</u>	<u>Scan Description</u>				
		<u>Virgin Reduced</u>	<u>100 Hour</u>	<u>300 Hour</u>	<u>600 Hour</u>	<u>1200 Hour</u>
A	0	10,818	4716	4200	3436	3312
	15	---	4241	2960	3322	1562
B	0	7,753	1115	1141	935	1031
	15	---	1167	1439	463	444
C	0	2,628	2088	2463	1629	1438
	15	---	2033	902	1102	427
D	0	6,101	3325	5742	5464	9775
	15	---	6460	8348	6128	6965
E	0	4,693	7312	2809	3208	3740
	15	---	3620	3930	2549	3161

*Catalyst A = UCI-G87-S

B = UCI-C150-4-03

C = Katalco CRG-F

D = Harshaw Ni-3210

E = Harshaw Ni-0104

TABLE 12

Characteristics of UCI Catalyst C150-4-03During Regeneration Test Scans

<u>Description</u>	<u>Total Hours On Stream</u>	<u>Surface Area; m²/g</u>	<u>Pore Volume 0 >29.2 Å; cc/g</u>	<u>%C</u>	<u>XRD Ni Surface Area; m²/g</u>
Cycle 1	300	64.0	0.34	3.6	30.6
Regeneration 1		--	--	1.7	--
Cycle 2	600	57.0	0.36	2.3	23.2
Regeneration 2		--	--	1.8	--
Cycle 3	900	55.0	0.38	2.4	25.0
Regeneration 3		--	--	1.7	--
Cycle 4	1200	51.0	0.36	2.4	25.0

TABLE 13

XRD Data For Regeneration Tests
Using UCI Catalyst C150-4-03

<u>Cycle</u>	<u>Total Hours On Stream</u>	<u>XRD Data*</u>
1	300	<ol style="list-style-type: none"> 1. Ni MCS = $157 \overset{\circ}{\text{A}}$ 2. $\delta\text{-Al}_2\text{O}_3$ MCS = $58 \overset{\circ}{\text{A}}$ 3. C (Graphite) MCS = $1320 \overset{\circ}{\text{A}}$
2	600	<ol style="list-style-type: none"> 1. Ni MCS = $207 \overset{\circ}{\text{A}}$ 2. $\delta\text{-Al}_2\text{O}_3$ MCS = $64 \overset{\circ}{\text{A}}$ 3. C (Graphite) MCS = $860 \overset{\circ}{\text{A}}$
3	900	<ol style="list-style-type: none"> 1. Ni MCS = $192 \overset{\circ}{\text{A}}$ 2. $\delta\text{-Al}_2\text{O}_3$ MCS = $70 \overset{\circ}{\text{A}}$ 3. C (Graphite) MCS = $807 \overset{\circ}{\text{A}}$
4	1200	<ol style="list-style-type: none"> 1. Ni MCS = $192 \overset{\circ}{\text{A}}$ 2. $\delta\text{-Al}_2\text{O}_3$ MCS = $94 \overset{\circ}{\text{A}}$ 3. C (Graphite) MCS > $2000 \overset{\circ}{\text{A}}$

*MCS = Mean Crystallite Size

TABLE 14

COMPONENT SUMMARY OF INSTALLED COST FOR
COLD-FLOW HYDRODYNAMIC UNIT

Cost; \$ (3rd Quarter, 1981)

1. Purchased Equipment	89,460
2. Equipment Setting	4,500
3. Piping	73,800
4. Steel	5,400
5. Instrumentation	42,420
6. Electrical	16,100
7. Paint	<u>900</u>
Total Field Cost	232,580
Engineering	<u>36,000</u>
Total	268,580

TABLE 15

PILOT PLANT CONSTRUCTION SCHEDULE

TASK	MONTHS											
	1	2	3	4	5	6	7	8	9	10	11	12
<ul style="list-style-type: none"> • Detailed Engineering Design • Order/Receive Process Equipment • Skid Fabrication • Vessel Fabrication • Skid Piping • Electrical Wiring • Order/Receive Instrumentation and Control Equipment • Control Panel/Motor Control Panel Fabrication 	■	■										
		■	■	■	■	■	■					
		■	■									
			■	■	■	■	■					
				■	■	■	■	■				
					■	■	■					
		■	■	■	■	■	■					
		■	■	■	■	■	■	■

FIGURE 2

FREE ENERGIES OF METHANATOR REACTIONS³

$-\Delta G_R; \text{Kcal}$

50
40
30
20
10
-10

TEMPERATURE; $^{\circ}\text{K}$

FIGURE 4

SCHEMATIC DIAGRAM OF REACTOR ASSEMBLY CARBON FORMATION STUDY IN METHANATION

FIGURE 5

CARBON FORMATION REACTOR SYSTEM CONTROL PANEL

CARBON FORMATION BOOSTER CONTROL PANEL

FIGURE 8

Atomic C-H-O Boundaries
for Graphite and Non-Ideal Carbon Formation

Source: C. F. Braun

Temperature: 900°C

Pressure : 515 PSIA

FIGURE 9
Atomic C-H-O Boundaries
for Graphite and Non-Ideal Carbon Formation

Source: C. F. Braun

Temperature: 900°F

Pressure : 1015 PSIA

FIGURE 10

CARBON STUDY GAS STANDARD

DATE 13 Nov 80

TIME 1046

SAMPLE NO. 5.

PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.90	39489
2	Ar	4.68	127982
3	N ₂	5.25	1705408
4	CH ₄	7.16	66636
5	CO	9.45	90836
6	CO ₂	13.48	11140
7	--	14.16	140
TOTAL			2041631

CALIBRATION

NO.		TIME	FACTORS
1	H ₂	3.90	3152.
2	Ar	4.68	25550.
3	N ₂	5.25	22720.
4R	CH ₄	7.16	20760.
5	CO	9.45	23900.
6	CO ₂	13.48	27850.
		14.16	140.1

FIGURE 11

CARBON STUDY FEED GAS

DATE 11 Nov 80

TIME 1046

SAMPLE NO. 5.

PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.90	41540
2	Ar	4.68	132360
3	N ₂	5.27	1668096
4	CH ₄	7.17	67262
5	CO	9.53	87084
6	CO ₂	13.49	12484
TOTAL			2008826

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.90	13.270
2	Ar	4.68	5.211
3	N ₂	5.27	74.000
4R	CH ₄	7.17	3.260
5	CO	9.53	3.668
6	CO ₂	13.49	0.453
TOTAL			99.850

FIGURE 12

REACTOR #1 EFFLUENT
CATALYST: UCI-G87-S

DATE 26 Nov 80
TIME 1611
SAMPLE NO. 11.
PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.92	5452
2		4.36	5
3	Ar	4.68	151752
4	N ₂	5.18	1894496
5		6.23	147
6	CH ₄	7.07	168448
7		11.32	75
8	CO ₂	13.48	6736
9		12.16	118
TOTAL			2227229

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.92	1.585
2	Ar	4.68	5.974
3	N ₂	5.18	83.790
4R	CH ₄	7.07	7.923
6	CO ₂	13.48	0.218
TOTAL			98.310

FIGURE 13

REACTOR #2 EFFLUENT
CATALYST: UCI-C150-4-03

DATE 25 Nov. 80
TIME 2203
SAMPLE NO. 45.
PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.92	6043
2	Ar	4.67	150756
3	N ₂	5.19	1743520
4		6.60	35
5	CH ₄	7.06	167736
6	CO ₂	13.48	5618
7	C ₂	14.16	168
TOTAL			2073876

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.92	1.742
2	Ar	4.67	5.994
3	N ₂	5.19	82.400
4R	CH ₄	7.06	7.987
6	CO ₂	3.48	0.196
			<u>98.310</u>

FIGURE 14

REACTOR #3 EFFLUENT

CATALYST: CRG-F (KATALCO)

DATE 25 Nov. 80
TIME 1623
SAMPLE NO. 28.
PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.92	5179
2	Ar	4.67	150580
3	N ₂	5.19	1721536
4	CH ₄	7.06	167120
5		8.67	8
6		8.78	1
7		12.50	1
8	CO ₂	13.48	6103
9	C ₂	14.16	162 TT
10		15.45	1
TOTAL			2050691

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.92	1.493
2	Ar	4.67	5.987
3	N ₂	5.19	81.360
4R	CH ₄	7.06	7.958
6	CO ₂	3.48	0.213
TOTAL			97.010

FIGURE 15

REACTOR #4 EFFLUENT

CATALYST: Ni-3210 (HARSHAW)

DATE 25 Nov. 80
TIME 843
SAMPLE NO. 5.
PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.91	17695
2	Ar	4.68	144224
3	N ₂	5.19	1715936
4	CH ₄	7.07	151288
5	CO ₂	13.47	9323
6	C ₂	14.16	71
7		15.98	2952
TOTAL			2041489

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.91	5.099
2	Ar	4.68	5.734
3	N ₂	5.19	81.090
4R	CH ₄	7.07	7.204
6	CO ₂	13.47	0.326
TOTAL			99.450

FIGURE 16

REACTOR #5 EFFLUENT

CATALYST: Ni-0104 (HARSHAW)

DATE 25 Nov. 80
TIME 1303
SAMPLE NO. 18.
PROGRAM NO. 1

NO.		TIME	AREA
1	H ₂	3.92	6651
2	Ar	4.68	149072
3	N ₂	5.19	1711136
4	CH ₄	7.07	162760
5	CO ₂	13.48	11284
6	C ₂	14.16	156
7		15.06	17
TOTAL			2041076

VB

EXTERNAL STANDARD

NO.		TIME	PCT CONC
1	H ₂	3.92	1.917
2	Ar	4.68	5.927
3	N ₂	5.19	80.870
4R	CH ₄	7.07	7.750
6	CO ₂	3.48	0.395
TOTAL			96.850

VB

FIGURE 17

TEMPERATURE PROFILE OF RUN 215-6-1-1

482°C; 1000 psig; 0% Steam

Catalyst - UCI-687 S

FIGURE 18

TEMPERATURE PROFILE OF RUN 215-8-2-2

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

FIGURE 19

TEMPERATURE PROFILE OF RUN 215-8-3-3

482°C; 1000 psig; 0% Steam

Catalyst - Katalco CRG-F

FIGURE 20

TEMPERATURE PROFILE OF RUN 215-8-4-4

482°C; 1000 psig; 0% Steam

Catalyst - Harshaw Ni-3210

FIGURE 21

TEMPERATURE PROFILE OF RUN 215-8-5-5

482°C; 1000 psig; 0% Steam

Catalyst - Marshaw Ni-0104

FIGURE 22

Component Concentration vs. Time For Run 215-6-1-1

482°C; 1000 psig; 0% Steam

Catalyst - UCI - G87 S

○ - CH₄

● - H₂

▲ - CO₂

x - CO

SEMI-LOGARITHMIC 4 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.

Concentration (Mole Percent)

Time (Hours)

FIGURE 23

FIGURE 24

Component Concentration vs. Time For Run 215-8-3-3

482°C; 1000 psig; 0% Steam

Catalyst - Katalco CRG-F

FIGURE 25

FIGURE 26

FIGURE 27

TEMPERATURE PROFILE OF RUN 215-15-1-1
 482°C; 1000 psig; 15% Steam
 Catalyst - UCI-687 S

FIGURE 28

TEMPERATURE PROFILE OF RUN 215-15-2-2
 482°C; 1000 psig; 15% Steam
 Catalyst UCI-C150-4-03

FIGURE 29

TEMPERATURE PROFILE OF RUN 215-15-3-3

482°C; 1000 psig; 15% Steam

Catalyst KATALCO CRG-F

FIGURE 30

TEMPERATURE PROFILE OF RUN 215-15-4-4

482°C; 1000 psig; 15% Steam

Catalyst Harshaw Ni-3210

FIGURE 31

TEMPERATURE PROFILE OF RUN 215-15-5-5

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-0104

FIGURE 32

COMPONENT CONCENTRATION VS. TIME FOR

RUN 215-15-1-1

482°C; 1000 psig; 15% Steam

Catalyst - UCI-GB7 S

FIGURE 33

FIGURE 34

COMPONENT CONCENTRATION VS. TIME FOR
RUN 215-15-3-3

482°C; 1000 psig; 15% Steam

Catalyst - KATALCO CRG-F

- - H₂
- - CH₄
- ▲ - CO₂
- X - CO

FIGURE 35

COMPONENT CONCENTRATION VS. TIME
FOR RUN 215-15-4-4

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-3210

FIGURE 36

COMPONENT CONCENTRATION VS. TIME

FOR RUN 215-15-5-5

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-0104

FIGURE 37

Temperature Profile of Run 215-11-1-1

482°C; 1000 psig; 0% Steam

Catalyst - UCI - 687 S

Hours on Stream

● - 19 hours

○ - 66 hours

△ - 162 hours

□ - 307 hours

FIGURE 38

Temperature Profile of Run 215-11-2-2

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

Hours on Stream

- - 19 hours
- ⊙ - 66 hours
- △ - 162 hours
- ⊠ - 307 hours

FIGURE 39

Temperature Profile of Run 215-11-3-3

482°C; 1000 psig; 0% Steam

Catalyst - Katalco CRG-F

Hours on Stream

- - 19 hours
- - 66 hours
- △ - 162 hours
- - 307 hours

FIGURE 40

Temperature Profile of Run 215-13-4-4

482°C; 1000 psig; 0% Steam

Catalyst - Harshaw Ni-3210

Hours on Stream

• - 7 hours

○ - 101 hours

□ - 250 hours

FIGURE 41

Temperature Profile of Run 215-11-5-5

482°C; 1000 psig; 0% Steam

Catalyst - Harshaw Ni-0104

Hours on Stream

● - 19 hours

○ - 66 hours

△ - 162 hours

□ - 307 hours

FIGURE 42

Component Concentration vs. Time For Run 215-11-1-1
432°C; 1000 psig; 0% Steam
Catalyst UCI-G87-5

FIGURE 43

FIGURE 44

FIGURE 45

FIGURE 46

FIGURE 47

TEMPERATURE PROFILE FOR RUN 215-17-1-1

482°C; 1000 psig; 15% Steam

Catalyst UCI-G87 γ

- - 16 Hours
- - 150 Hours
- △ - 250 Hours
- - 300 Hours

FIGURE 48

TEMPERATURE PROFILE FOR RUN 215-17-2-2

482°C; 1000 psig; 15% Steam

Catalyst UCI-C-150-4-03

- - 16 Hours
- - 150 Hours
- △ - 250 Hours
- - 300 Hours

FIGURE 49

TEMPERATURE PROFILE FOR RUN 215-17-3-3

482°C; 1000 psig; 15% Steam

Catalyst KATALCO-CRG-F

- - 16 Hours
- - 150 Hours
- △ - 250 Hours
- - 300 Hours

FIGURE 50

TEMPERATURE PROFILE FOR RUN 215-17-4-4

482°C; 1000 psig; 15% Steam

Catalyst Harshaw Ni-3210

- - 16 Hours
- - 150 Hours
- △ - 250 Hours
- - 300 Hours

FIGURE 51

TEMPERATURE PROFILE FOR RUN 215-17-5-5

482°C; 1000 psig; 15% Steam

Catalyst Marshaw Ni-0104

FIGURE 52

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-17-1-1

482°C; 1000 psig; 15% Steam

Catalyst-UCI-G87 S

FIGURE 53

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-17-2-2

482°C; 1000 psig; 15% Steam

Catalyst - UC1-G150-4-03

FIGURE 54

FIGURE 85

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-17-4-4

482°C, 1000 psig, 15% Steam

Catalyst - Harshaw Ni-3210

FIGURE 56

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-17-5-5

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-0104

FIGURE 57

FIGURE 58

FIGURE 59

FIGURE 60

FIGURE 61

FIGURE 62

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-22-1-1

482°C; 1000 psig; 0% Steam

Catalyst UCI-G87-S

FIGURE 63

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-22-2-2

482°C; 1000 psig; 0% Steam

Catalyst UCI-C150 4-03

FIGURE 67

FIGURE 68

FIGURE 69

FIGURE 70

FIGURE 71

FIGURE 73

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-24-2-2

482°C; 1000 psig; 15% Steam

Catalyst - UCI-C150-4-03

FIGURE 76

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-24-5-5

482°C, 1000 psig; 15% Steam

Catalyst - Harshaw Ni-0104

FIGURE 77

TEMPERATURE PROFILE OF RUN 215-18-1-1

482°C; 1000 psig; 0% Steam
Catalyst - UCI-687-S

FIGURE 78

TEMPERATURE PROFILE OF RUN 215-18-2-2

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

FIGURE 79

TEMPERATURE PROFILE OF RUN 215-18-3-3

482°C; 1000 psig; 0% Steam

Catalyst - Katalco CRG-F

FIGURE 80

TEMPERATURE PROFILE OF RUN 215-18-4-4

482°C; 1000 psig; 0% Steam

Catalyst - Harshaw NH-3210

FIGURE 81

TEMPERATURE PROFILE OF RUN 215-18-5-5

482°C; 1000 psig; 0% Steam

Catalyst - Harshaw Ni-0104

FIGURE 82

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-18-1-1

482°C; 1000 psig; 0% Steam

Catalyst - UCI 687-S

● - H_2
○ - CH_4
▲ - CO_2
✱ - CO

COMPONENT CONCENTRATION, MOLE PERCENT

0.1

0.01

200

400

TIME; HOURS

800

1000

1200

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

9

10.0

10.0

2

3

4

5

6

7

8

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FIGURE 83

FIGURE 84

FIGURE 85

FIGURE 86

FIGURE 87

TEMPERATURE PROFILE FOR RUN 215-21-1-1

482°C; 1000 psio; 15% steam

Catalyst - UCI 87-S

FIGURE 88

TEMPERATURE PROFILE FOR RUN 215-21-2-2

482°C; 1000 psig; 15% Steam

Catalyst - UCI - C150-4-03

FIGURE 89

TEMPERATURE PROFILE FOR RUN 215-21-3-3

482°C; 1000 psig; 15% Steam

Catalyst - Katalco CRG-F

FIGURE 90

TEMPERATURE PROFILE FOR RUN 215-21-4-4

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-3210

FIGURE 91

TEMPERATURE PROFILE FOR RUN 215-21-5-5

Hours on Stream

482°C; 1000 psig; 15% Steam

Catalyst - Harshaw Ni-0104

- 75 hours
- 200 hours
- △ 450 hours
- 775 hours
- 1000 hours
- ▽ 1150 hours

FIGURE 92

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-21-1-1

482°C; 1000 psig; 15% Steam

Catalyst - UCI-87-S

FIGURE 94

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-21-3-3

482°C; 1000 psig; 15% Steam
Catalyst - Katalco-CRG-F

FIGURE 96

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-21-5-5

482°C, 1000 psig, 15% Steam

Catalyst - Harshaw Ni-0104

FIGURE 97

FIGURE 98

FIGURE 99

FIGURE 100

FIGURE 101

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-28-1-2 (CYCLE ONE)

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C-150-4-03

COMPONENT CONCENTRATION; MOL PERCENT

FIGURE 102

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-21-1-2 (CYCLE TWO)

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

COMPONENT CONCENTRATION; MOL PERCENT

TOTAL TIME ON STREAM; HOURS

FIGURE 103

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-32-1-2 (CYCLE THREE)

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

FIGURE 104

COMPONENT CONCENTRATION VS. TIME FOR RUN 215-33-1-2, (CYCLE FOUR)

482°C; 1000 psig; 0% Steam

Catalyst - UCI-C150-4-03

FIGURE 105

FIGURE 106

FIGURE 107

FIGURE 108

FIGURE 109

FIGURE 110

FIGURE 111

FIGURE 112

FIGURE 113

FIGURE 114

FIGURE 115

FIGURE 116

FIGURE 117

FIGURE 118

FIGURE 119

FIGURE 120

FIGURE 121

FIGURE 122

FIGURE 123

FIGURE 124

FIGURE 125

FIGURE 126

FIGURE 127

FIGURE 128

FIGURE 129

FIGURE 130

FIGURE 131

FIGURE 132

FIGURE 133

FIGURE 134

FIGURE 135

FIGURE 136

FIGURE 137

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 138

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 139

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 140

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 141

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 142

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 143

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 144

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 145

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 146

EQUIVALENT PORE DIAMETER (MICRONS) = 175/PSI

FIGURE 147