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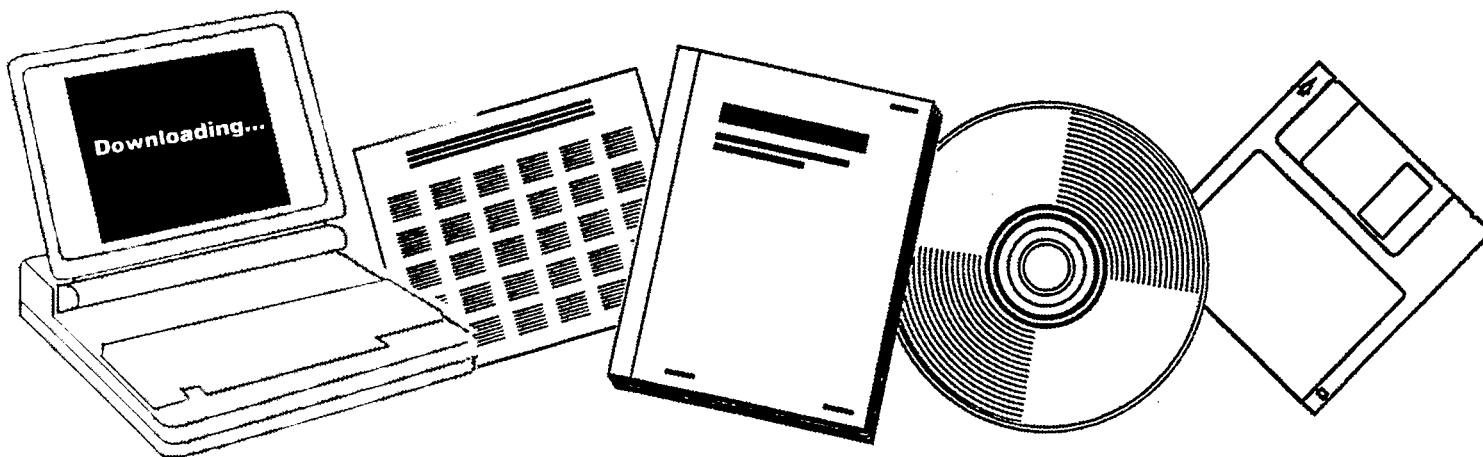
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## CATALYTIC SYNTHESIS OF GASEOUS HYDROCARBONS. QUARTERLY REPORT, MAY--AUGUST 1975

CARNEGIE-MELLON UNIV.  
PITTSBURGH, PA

AUG 1975



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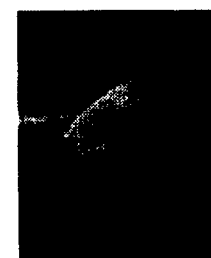
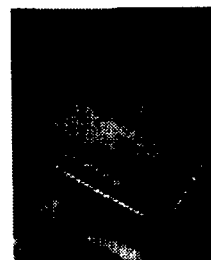
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OF  
GASEOUS HYDROCARBONS

Quarterly Report for the  
Period May-August, 1975

Dr. Anthony L. Dent

CARNEGIE-MELLON UNIVERSITY  
PITTSBURGH, PENNSYLVANIA 15213

Report Date - August, 1975

PREPARED FOR THE UNITED STATES  
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Under Contract No. E(49-18)-1814

MASTER



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### Abstract

The objectives of this research program are to develop improved catalyst systems for preparation of gaseous hydrocarbons from coal-derived mixtures of carbon monoxide and hydrogen, and to develop a fundamental understanding of methanation and Fischer-Tropsch synthesis. To accomplish these goals the work will be divided into several tasks as follows:

(1) Task No. I - Equipment Assembly; (2) Task No. II - Catalyst Screening Tests; (3) Task No. III - Kinetic Studies; (4) Task No. IV - Mechanistic Studies; (5) Task No. V - Catalyst Preparations and/or Characterizations; (6) Task No. VI - Extended Catalyst Tests; (7) Task No. VII - Project Summary; and (8) Task No. VIII - Consultation and Advice by P.I. to ERDA.

A timetable for these tasks has been developed which represents a more realistic approach to managing the project. During this initial quarterly period, work has been devoted largely to the areas of Tasks I, IV, and V.

In the area of Task I, one catalytic reactor unit (CRU-1) has been completed and its flow system has been calibrated. This unit has been operated for several lengthy periods at reaction temperatures and pressures. A second catalytic reactor unit (CRU-2) has been designed, equipment specified and items purchased. This unit will have features similar to CRU-1 with several improvements in its flow diagram. Reactant and product gas analysis for both units will be achieved by a combination of gas chromatography and infrared non-dispersive analyzers (NDIR). NDIR analyzers have been ordered from Mine Safety Appliances for carbon monoxide, carbon dioxide and methane. Complete analysis will be achieved by gas chromatographic analyses of the two reactor streams. A Varian CDS-101 Chromatography Data System unit has been ordered to control the GC's. Delivery is scheduled for early September.

In the area of Task V, several iron, cobalt and nickel based catalysts have been prepared or obtained from commercial suppliers. These include catalysts supported on kieselguhr and on alumina. The total and metal surface areas of some of these catalysts have been determined by BET methods. For some of the catalysts, chemical analyses of the actual metal contents have also been completed. These characterizations should provide greater understanding of the catalytic activities which will be obtained during the screening tests (Task II).

In the third area (Task IV), considerable progress has been made towards developing an infrared technique to study unsupported metal catalysts. To date, generation of a nickel aerosol by sophisticated arc vaporization methods has been reduced to a routine procedure and characterization of the aerosol by BET surface area measurements and ethylene hydrogenation activity have been accomplished. The BET results indicate that the surface area of this nickel aerosol is approximately 14 square meters per gram based on argon adsorption. More surprisingly, the activity for ethylene hydrogenation, tentatively, appears to be a factor of  $10^4$  greater than that reported by Bond. Further studies are in progress. However, the major emphasis in these studies continues to be the observation of adsorbed species via infrared techniques.

In conclusion, the project is proceeding according to schedule with no significant changes in milestone scheduling.

## I. OBJECTIVE AND SCOPE OF WORK

To meet the needs of the increasing energy demand and to satisfy the corresponding environmental constraints, coal gasification has been proposed as a means of producing clean fossil fuel. Such processes become increasingly more important when the projections that petroleum oil resources will be effectively depleted within the next twenty years are taken into account. Likewise, it should be recognized that the depletion of petroleum oil resources also means that the petrochemical industry must look elsewhere to obtain their feed-stocks. While there are several American processes for conversion of coal to synthetic natural gas (SNG) at varying stages of development, there are, however, none available for the production of synthetic liquefied petroleum gas (SLPG). Fortunately, however, SLPG appears to be obtainable by a modification of the methanation step of the SNG processes. Unfortunately, the methanation step ( $\text{CO} + 3\text{H}_2 \xrightarrow{\text{Cat}} \text{CH}_4 + \text{H}_2\text{O}$ ) is one of the two least understood steps of the coal-to-gas process.

This research program, therefore, has as its objectives the production of synthetic liquefied petroleum gases, and a fundamental understanding of catalytic methanation. Thus, work will be developed along these two major areas. The first area, catalyst development for producing  $\text{C}_2$ - $\text{C}_4$  hydrocarbons, has as its objectives the development and characterization of catalysts with high selectivity and defining the relevant process variables. We anticipate carrying this project to the pilot-plant stage whereby an economic assessment can be made. The second area involves fundamental studies of the hydrogenation of carbon monoxide with the objective of understanding the nature of the surface reactions involved. It should be noted that the hydrogenation of carbon monoxide under one set of conditions leads predominately to methane, whereas under another set of conditions it leads to higher hydrocarbons, Fischer-Tropsch synthesis. The processes must be similar, i.e., involve the same surface intermediates. We anticipate achieving an understanding of how catalysts or process variables can be modified to effect the two processes economically.

For the first area, two reactor units will be employed to evaluate potential catalysts and to obtain kinetic and mechanistic data. In addition to testing potential commercial catalysts, laboratory catalyst preparations of a number of catalysts will be undertaken to establish standards for comparison. Both types of catalysts will be analyzed for total metal and active metal content. More complete kinetic studies will be conducted on the most promising catalysts from the preliminary evaluations.

In the second area the emphasis will be placed on achieving a fundamental understanding of the hydrogenation of carbon monoxide reaction. To accomplish this understanding, infrared spectroscopic techniques will be coupled with traditional mechanistic studies to obtain information about the nature of surface intermediates. Investigations of both supported and unsupported metal catalysts will be undertaken.



For the infrared studies two different systems will be employed. The usual "pressed disk" technique will be employed for supported metal catalysts. However, a novel approach to the unsupported catalyst studies will be explored. This new approach involves passing infrared radiation through a long-path-length cell containing the catalyst in a metal-aerosol form. Comparison of the catalytic activity and surface properties as well as characterization of the surface intermediates will constitute the major work effort in this area.

The key feature of this proposed study is a combination of several techniques, notably, infrared spectroscopic techniques with kinetic measurements to simultaneously measure reaction rates, surface intermediates and reaction products. The use of isotopic tracers in connection with these techniques should greatly increase our understanding of these reactions.

As previously stated, the objectives of this research program are to develop improved catalyst systems for preparation of gaseous hydrocarbons from coal-derived mixtures of carbon monoxide and hydrogen, and to develop a fundamental understanding of methanation and Fischer-Tropsch synthesis. To accomplish these goals the work will be divided into several tasks (see Appendix A) with each task covering a definite time period. Therefore, the work's progress can easily be assessed by monitoring the movement through the schedule of tasks as indicated during quarterly technical and progress reports.

## II. SUMMARY OF PROGRESS TO DATE

Work under this contract (E(49-18)-1814) began in May, 1975 with a division of work into eight (8) tasks:

1. Task No. I - Equipment Assembly
2. Task No. II - Catalyst Screening Tests
3. Task No. III - Kinetic Studies
4. Task No. IV - Mechanistic Studies
5. Task No. V - Catalyst Preparations and/or Characterizations
6. Task No. VI - Extended Catalyst Tests
7. Task No. VII - Project Summary
8. Task No. VIII - Consultation and Advice by P.I. to ERDA

The timetable for these tasks is detailed in Appendix A to this report and represents a more realistic approach to managing the project. During this initial quarterly period, work has been devoted to: (a) the design and/or assembly of two (2) catalytic reactor units which will be employed in work described in Tasks II, III, and IV; (b) preliminary work for Task IV; and (c) preparation and characterization of catalysts (Task V).

In the area of Task I, one catalytic reactor unit (CRU-1) has been completed and its flow system has been calibrated. This unit consists of a 1-inch stainless steel tubular reactor which is temperature controlled by a boiling Dowtherm jacket. The reactor is capable of operating in a temperature range from 100 to 400°C and a pressure range from 0 to 200 psig. Flow measurement and control is achieved through the use of very fine needle valves (Swagelok S-series or double-S-series) operated at sonic flow conditions. This unit has been operated for several lengthy periods at reaction temperatures and pressures.

A second catalytic reaction unit (CRU-2) has been designed, equipment specified and items purchased. This unit will have features similar to CRU-1 with several improvements in its flow diagram. CRU-2 will have the flexibility of operating one of three types of reactors; a) tubular reactor, b) fluidized bed reactors, and c) stirred tank catalytic reactor (Carberry reactor or CSTCR). A CSTCR unit has been ordered from Autoclave engineers; delivery is scheduled for early September. The tubular and fluidized-bed reactors will be constructed inhouse.

Reactant and product gas analysis for both units will be achieved by a combination of gas chromatography and infrared non-dispersive analyzers (NDIR). Non-dispersive infrared analyzers have been ordered from Mine Safety Appliances (MSA) for carbon monoxide, carbon dioxide and methane. The effluent gas from both reactors will flow through a series of switching valves which will operate on a time-sequencing program. This will permit continuous analysis via NDIR when one or both reactor units are in operation. Complete analysis will be achieved by gas chromatographic analyses of the two streams. To facilitate these analyses, a Varian CDS-101 Chromatography Data System unit has been ordered. This unit performs automatic gas sampling as well as integration of the chromatographic peaks. Delivery is scheduled for early September.

Since the two CRU's will require measurement of temperature at several locations on the systems, we have decided to use multipoint temperature recorders to monitor the systems. Thus, two 12-point temperature recorders have been purchased.

In the area of Task V, several iron, cobalt and nickel based catalysts have been prepared in the laboratory or obtained from commercial suppliers. These include catalysts supported on kieselguhr and on alumina. In addition, the total surface area and metal surface area of some of these catalysts have been determined by BET adsorption methods. For some of the catalysts, chemical analyses of the actual metal contents have also been completed. These characterizations should provide greater understanding of the catalytic activities which will be obtained during the screening tests (Task II).

The third area of work involved preliminary studies associated with the mechanistic studies planned for Task IV. In this area, considerable progress has been made towards developing an infrared technique to study unsupported metal catalysts. To date, generation of a nickel aerosol by sophisticated arc vaporization methods has been reduced to a routine procedure and characterization of the aerosol by BET surface area measurements and ethylene hydrogenation activity have been accomplished. Because of the nature of the nickel aerosol, a substantial effort was involved in obtaining a "clean" sample of the material. After several iterations we settled upon two methods of sample collection -- one involved passing the aerosol through pyrex glass traps filled with glass spirals and the other involved collection of the aerosol on a millipore membrane filter. Both methods give catalysts which can be maintained in an uncontaminated state for subsequent investigations. The BET results indicate that the surface area of this nickel aerosol is approximately 14 square meters per gram based on argon adsorption. More surprisingly, the activity for ethylene hydrogenation, tentatively appears to be a factor of  $10^4$  greater than that reported in Bond's book, Catalysis by Metals. Further studies along these lines are in progress which include establishing a "proper reactor" to measure the activity of these catalysts with assurances that mass-transport effects are not dominating the results; activity studies at several temperatures; and attempts to further increase the specific surface area of this catalyst. However, the major emphasis in these studies continues to be the observation of adsorbed species via infrared techniques.

To summarize the progress to date, we have accomplished the following

1. Established a realistic timetable for the tasks associated with this research program.
2. Completed design, assembly, and calibration of Catalytic-Reactor Unit 1 (CRU-1).
3. Completed "shake-down" tests of CRU-1.
4. Completed design and ordering of equipment for Catalytic-Reactor Unit 2.
5. Completed specifications and purchases of an analytical package for both CRU-1 and CRU-2 which employs gas chromatographic and non-dispersive infrared analyses of both reactant and product gases.
6. Purchased a "Corberrry type" stirred tank catalytic-reactor unit to be used for Task II work.
7. Prepared a substantial number of catalysts in the laboratory for testing in Task II.
8. Obtained additional commercial catalysts for testing in Task II.
9. Characterized several of the catalysts from 7 and 8 by BET surface area measurements.

10. Completed chemical analyses for actual metal content in the catalysts.
11. Reduced the complicated generation of nickel aerosol catalysts to be used for infrared studies of unsupported metals to a routine procedure.
12. Developed a method of collecting the aerosol which ensures that it remains in an uncontaminated state.
13. Established that the nickel aerosol generated by arc vaporization has substantial activity for ethylene hydrogenation and a high surface area.

Reference to Table A1 indicates that the project is proceeding according to schedule. Except as noted above, there are no significant changes in milestone scheduling.

### III DETAILED DESCRIPTION OF TECHNICAL PROGRESS

As previously stated, the objectives of this research program are to develop improved catalyst systems for the preparation of gaseous hydrocarbons from coal-derived mixtures of carbon monoxide and hydrogen, and to develop a fundamental understanding of the reaction mechanisms associated with catalytic methanation and Fischer-Tropsch synthesis. This will be accomplished in this project by pursuing several aspects of the problem which include: a) catalysts preparation and characterization of their physical properties; b) evaluation of these catalysts for the synthesis of  $C_2$ - $C_4$  hydrocarbons in a screening test; c) conducting kinetic studies to obtain rate expressions to predict product yields for the most promising catalyst formulations; d) investigation of the mechanism of formation and types of reaction intermediates formed during the catalytic reactions on these catalysts; and e) measuring catalytic activity for extended periods on the most promising catalyst to obtain an economic assessment of the process. The above studies require the use of several types of reactor systems. For example, the screening test will be conducted in tubular plug-flow reactors and a "Carberry-type" stirred catalytic reactor. Since a wide spectrum of products, e.g., methane, ethane, ethylene, propane, propylene, carbon dioxide, hexanes, etc., is anticipated, there is a critical need for monitoring the individual yields as well as the total conversion of carbon monoxide. This will be accomplished by the use of NDIR's to continuously monitor methane, carbon dioxide and carbon monoxide, and gas chromatography to monitor all products on an intermittent basis, e.g., every thirty minutes.

The design, purchase, and assembly of the necessary apparatus constitutes the assignment of the first task (Task I); whereas, subject (a) above constitutes the assignment for Task V. Since these tasks represent the logical starting points for this research, they will be presented in detail below. In addition, some preliminary work on subject (c) above will be reported. For a complete description of the various tasks associated with this project and the corresponding timetable, see Appendix A.

## A. Task I - Equipment Assembly

Table I summarizes the work accomplished and forecast for Task I. Column 2 of this table indicates the number of weeks involved with each subtask. The numbers in parentheses represent times for work which is forecast for the next quarterly period. It should be noted that, whereas, work involving assembly of CRU-2 will continue beyond the fourth month, CRU-1 will be available during this same period to begin work under Task II.

### 1. Catalytic Reactor Unit - 1

Figure 1 represents a process flow diagram for CRU-1. The reactor unit is designed to operate in the temperature range from 100 to 400°C and a pressure range from 0 to 200 psig. To understand its operation, we will follow the gases as they travel through the reactor. It should be noted that cylinder gases rather than a coal-derived synthesis gas will be blended in situ for these studies. Figure 1 shows that the individual gases are passed through charcoal traps and are metered by flow-controller valves. These valves are Swagelok S-series very fine metering valves containing micrometer handles to permit reproduction of setting. A double S-series valve is used for the hydrogen line. These valves can be operated in either subsonic or sonic flow modes. In the sonic flow mode of operation, the flow rate, Q, is independent of the downstream pressure and is given by:

$$1) \quad Q = 287.08 \times P_1 \times C_v \left( \frac{1}{(SG) \times T_1} \right)^{1/2}$$

where Q = flow in std. liters per min.

$C_v$  = valve flow coefficient

SG = specific gravity of gas (air @ 1 atm and 20°C = 1.00)

$T_1$  = absolute temperature of flowing gas, °K

$P_1$  = inlet pressure (psia)

Equation 1 is a simplification of the more exact equation:

$$2) \quad \dot{m} = C_v \times P_1 \left[ 2g_c \left( \frac{M}{RT_1} \right) \left( \frac{\gamma}{\gamma + 1} \right) \left( \frac{2}{\gamma + 1} \right)^{2/(\gamma-1)} \right]^{1/2}$$

where  $\dot{m}$  = mass flow rate

M = molecular weight of gas

R = gas constant

$\gamma$  = ratio of heat capacities,  $C_p/C_v$  of flowing gas. ( $\gamma = 1.40$  for air)

Table 1 Task 1: Equipment Assembly

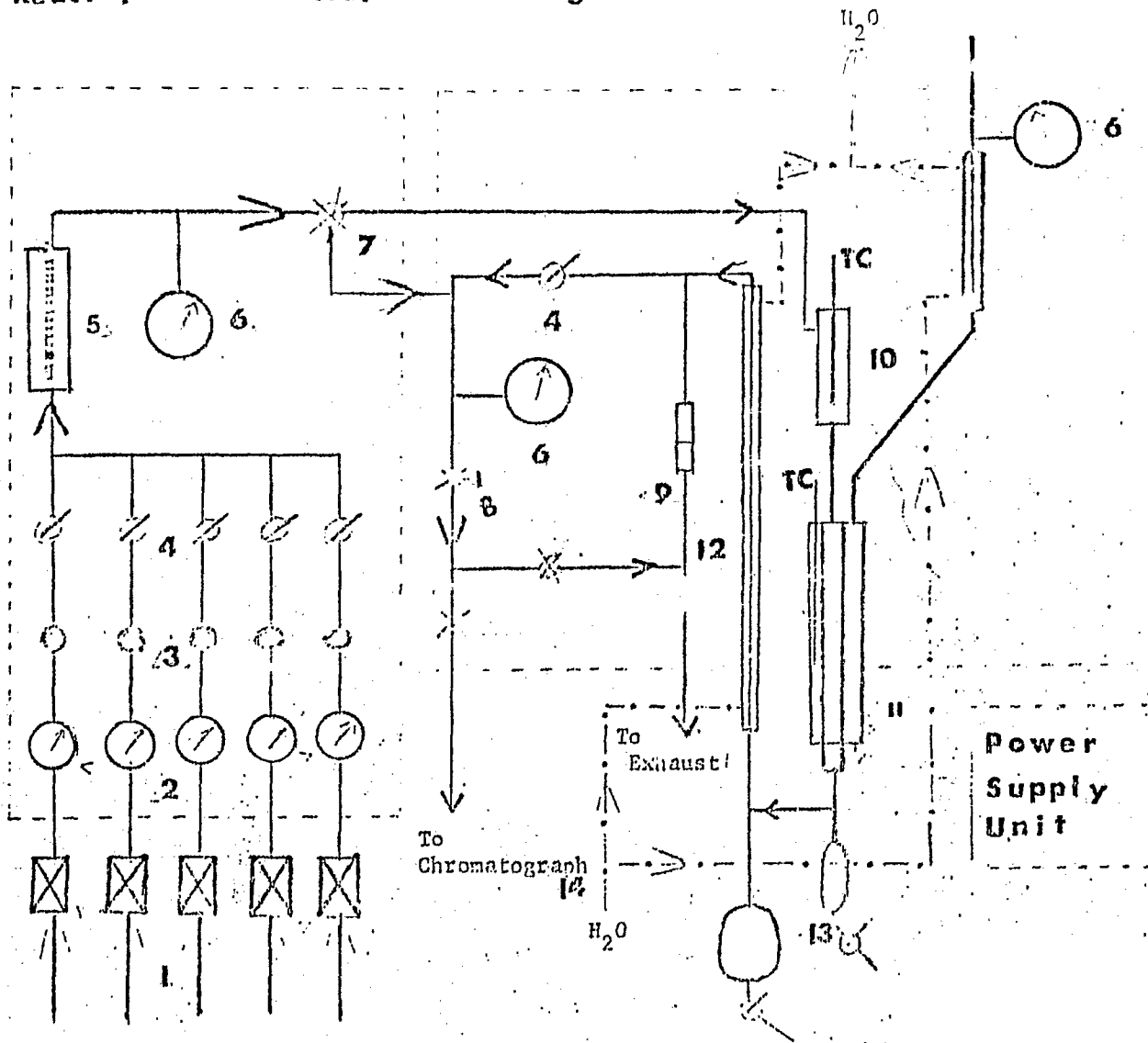
Subtasks

| <u>Item No.</u> | <u>(No. Weeks<br/>to Complete<br/>Subtask)</u> <sup>+</sup> | <u>Description</u>   |
|-----------------|---|--|
| 1               | 3   | Design and assembly of CRU-1   |
| 2               | 1   | Pressure testing of CRU-1  |
| 3               | 2   | Flow calibration of needle valves for CRU-1  |
| 4               | 2   | Temperature testing of CRU-2   |
| 5               | 2   | Redesign of Dowtherm circulation loop and preheater for CRU-1  |
| 6               | 1   | Temperature retest of CRU-1  |
| 7               | 3   | Design and equipment specification for CRU-2   |
| 8               | 1   | Consultation with vendors and order placements for CRU-2   |
| 9               | 1   | Design of analytical package for dual system analysis  |
| 10              | 0.5   | Consultation with Varian, Hewlett-Packard, and MSA salesmen prior to ordering analytical package           |
| 11              | 0.5   | Literature evaluation of Autoclave Engineers CSTC and consultation with AE salesmen prior to placing order |
| 12              | (2)   | Fabrication of CRU-2 components  |
| 13              | (1)   | Pressure and temperature test of CRU-2   |
| 14              | (1)   | Flow controller calibrations for CRU-2   |
| 15              | ((3))*  | Panel mounting of MSA NIR analyzers, recorder and programmed sequencing timers                             |
| 16              | ((1))*  | Panel mounting of temperature recorders  |
| 17              | (2)   | Complete shakedown of CRU-2  |
| 18              | (1)   | Integration of analytical package with CRU-1 and CRU-2.  |
| Total # Wks     |   | 24   |

\*These subtasks will be performed by Mellon Institute's Instruments shop personnel.

+Items in parentheses represent work which has been scheduled but which has not been completed.

# Reactor Unit No. 1 High Pressure System



## LEGEND

1. Charcoal Traps
2. Inlet Pressure Gauges
3. Flow Controllers
4. On-Off Valve
5. Rotameter
6. Pressure Gauge  
a - Inlet  
b - reactor  
c - Noetherm
7. 3-Way Valve
8. Back-Pressure Regulation Valve
9. Pressure Relief Valve
10. Preheater
11. Reactor
12. Condensor
13. Trap
14. Cooling Water Lines

When the critical pressure condition defined as

$$3) \left( \frac{P_2}{P_1} \right)_{\text{critical}} = \left( \frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)}$$

is exceeded, these equations can be used. Table 2 gives values of the critical pressure ratios for the gases employed in these studies.

Table 2 Critical-Pressure Ratios for Various Gases

| <u>Gas</u>      | <u><math>\gamma (= C_p/C_v)</math></u> | <u><math>(P_2/P_1)_{\text{critical}}</math></u> |
|-----------------|--|---|
| Helium          | 1.667                                  | 0.487   |
| Hydrogen        | 1.402                                  | 0.528   |
| Carbon Monoxide | 1.407                                  | 0.527   |
| Carbon Dioxide  | 1.311                                  | 0.544   |
| Methane         | 1.279                                  | 0.550   |

From this table and Eqs. 1 or 2, we can calculate the flow rates when the  $C_v$  valves are known. This approach was used in reverse to calibrate the valves. Various pressures were chosen in such a manner as to ensure that Eq. 3 was satisfied, and a curve of  $C_v$  versus number of turns of valve stem was plotted. A gas bubble meter and a 0.1 CFM per revolution wet-test meter were used to obtain the flow calibration data. Figures 2a, 2b, 2c, and 2d are the results of these calibrations. Figures 2a and 2b indicate that Eq. 1 adequately describes the system as anticipated, however, Figures 2c and 2d imply that the  $C_v$  values are pressure dependent for hydrogen and helium. We have not attempted to account for this dependency, since the actual calibration curves for the desired inlet pressures are available. The reproducibility and accuracy of flow measurement with these valves were found to be about  $\pm 1\%$ .

If we continue to follow the gas by Figure 1, we see that it passes next through individual shut-off valves into a mixing region. As shown by Figure 1,\* the gas enters a 3-way valve (7) where it is sent either to the preheater (10) and reactor (11) or is by-passed to the exit line. By-passing permits analysis of the reactant gas mixture by GC or NDIR. As the gas emerges from the reactor, it is passed through a heat exchanger (12) to condense water and higher molecular weight gases into a tray (13). At this stage the gas is sent to the exhaust line where a portion of it is diverted through a gas sampling valve for GC analysis. Reactor pressure is maintained by a back-pressure needle valve (8). The main stream passes through the three NDIR analyzers to the exhaust. An adjustable pressure-relief valve (9) has been installed to prevent overpressurization of the reactor.

\*Numbers refer to items listed on Figure 1.



Figure 2a - Carbon Monoxide

Valve #5

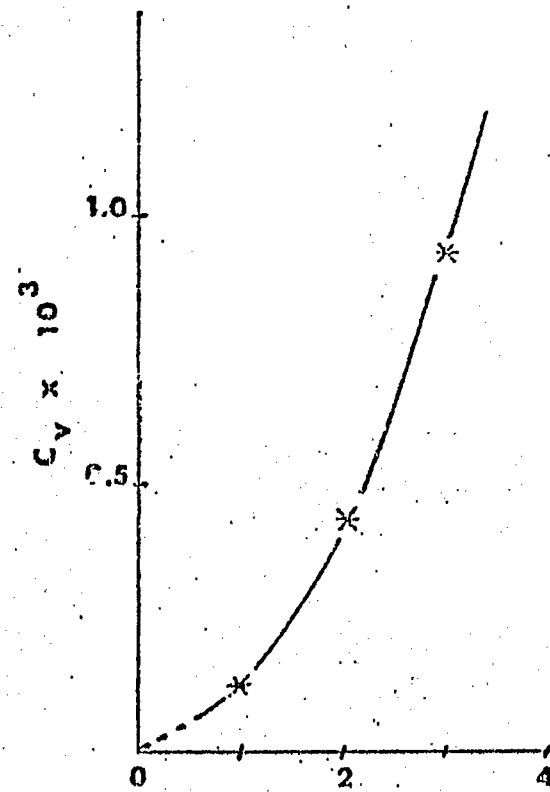
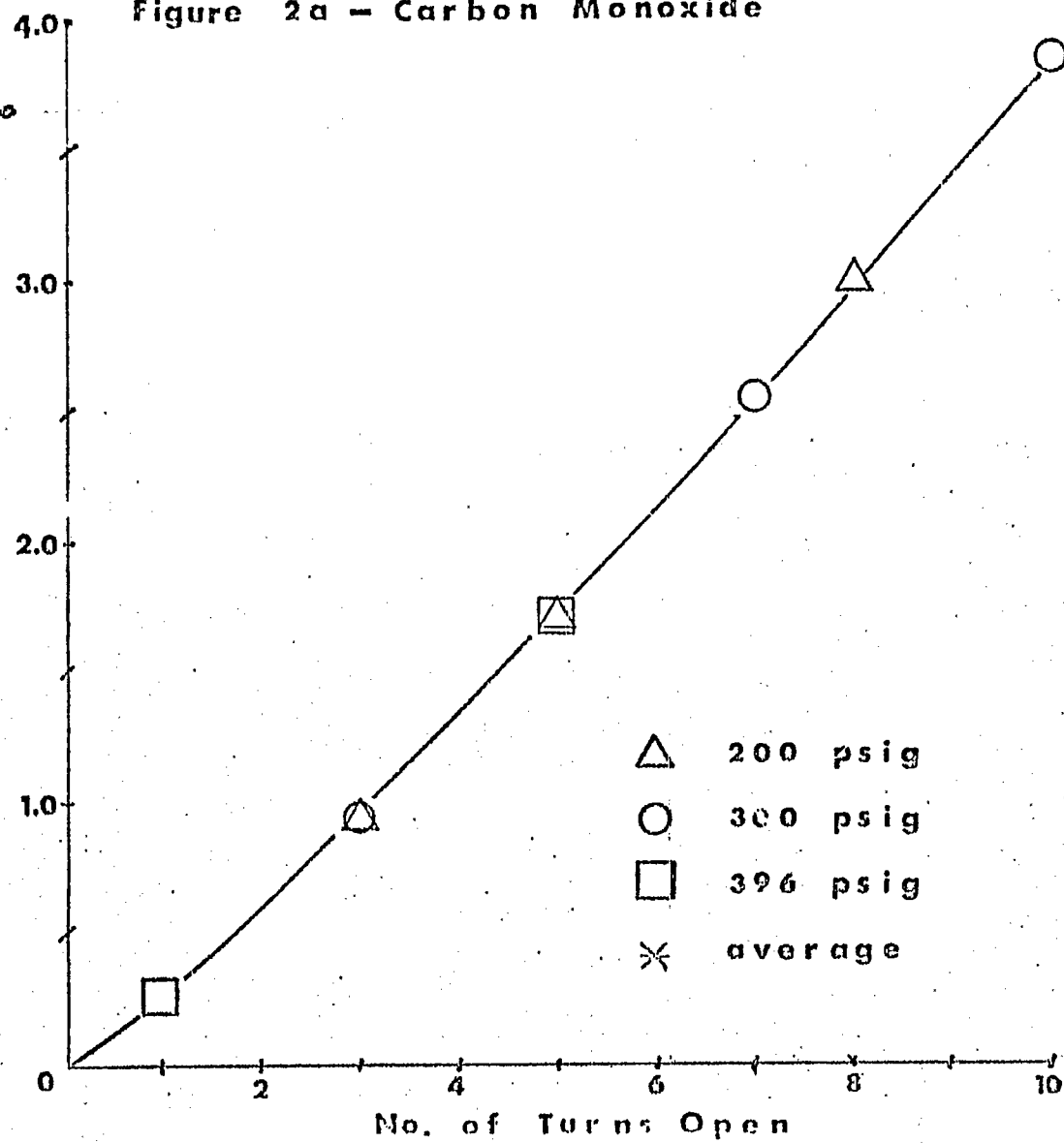


Figure 2b - Methane

Valve #3

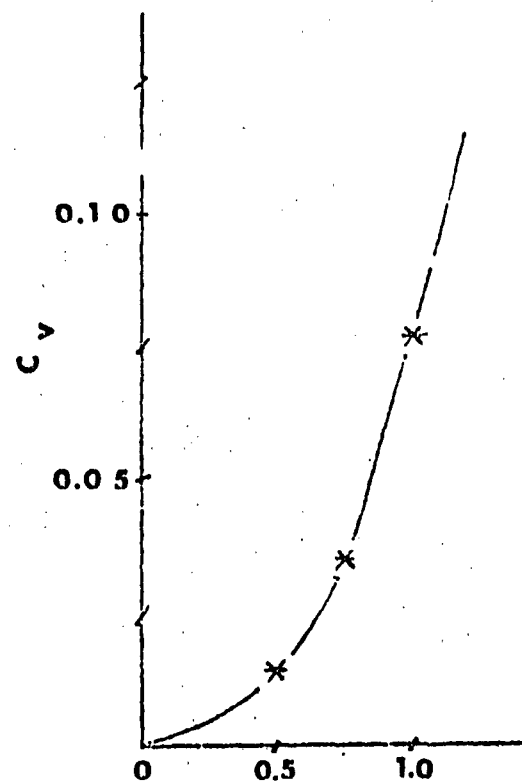
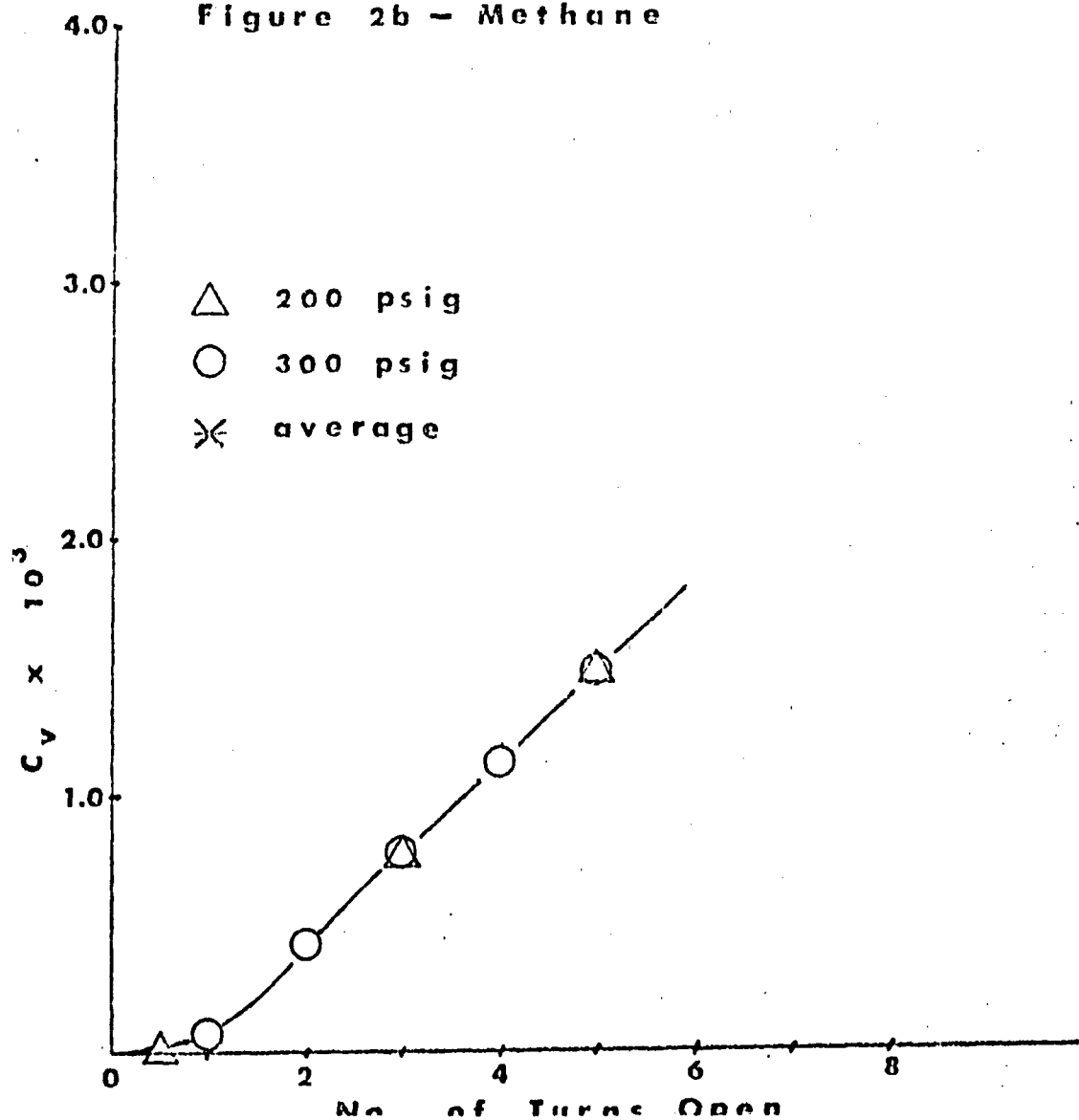


Figure 2c - Helium

Valve #1

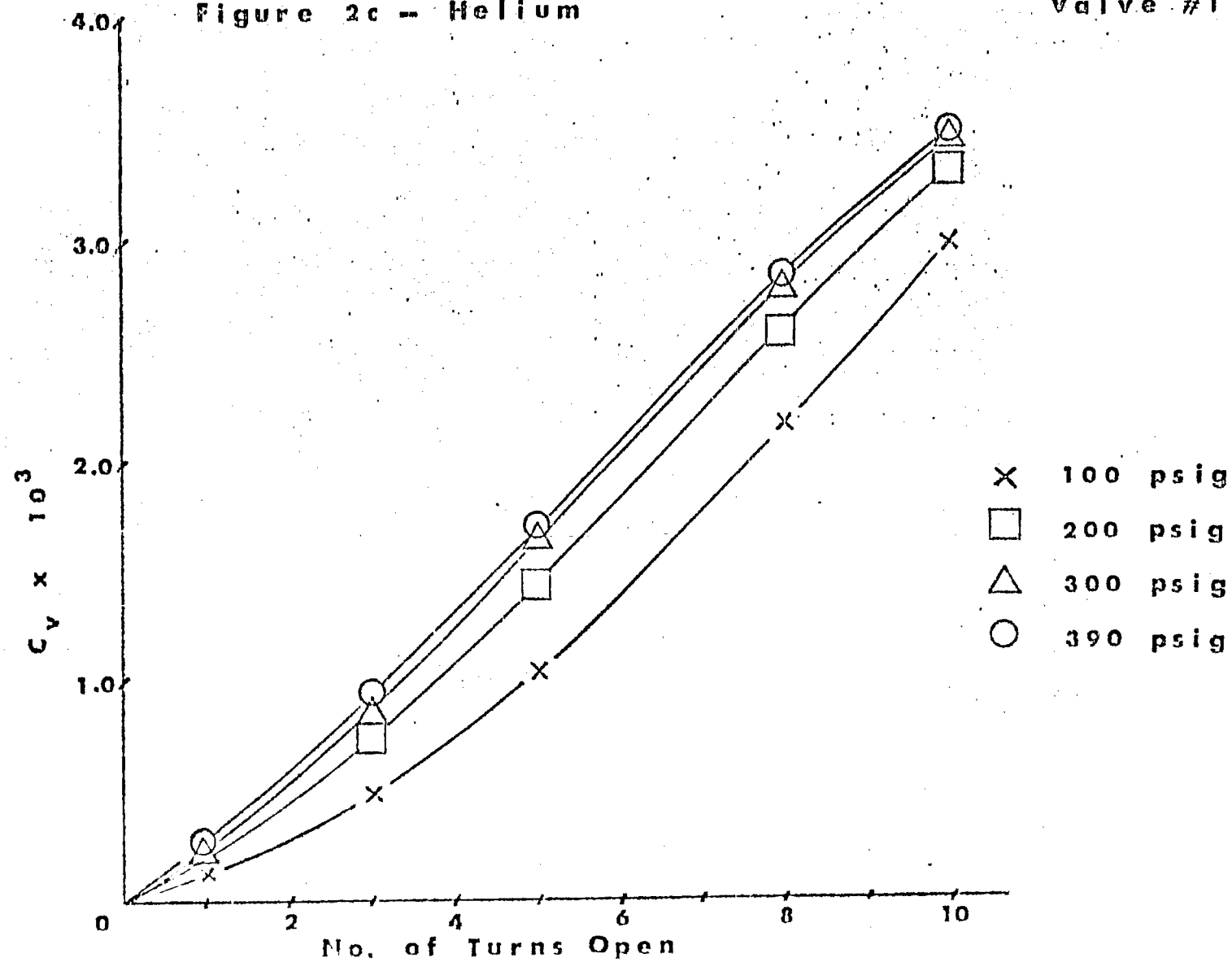
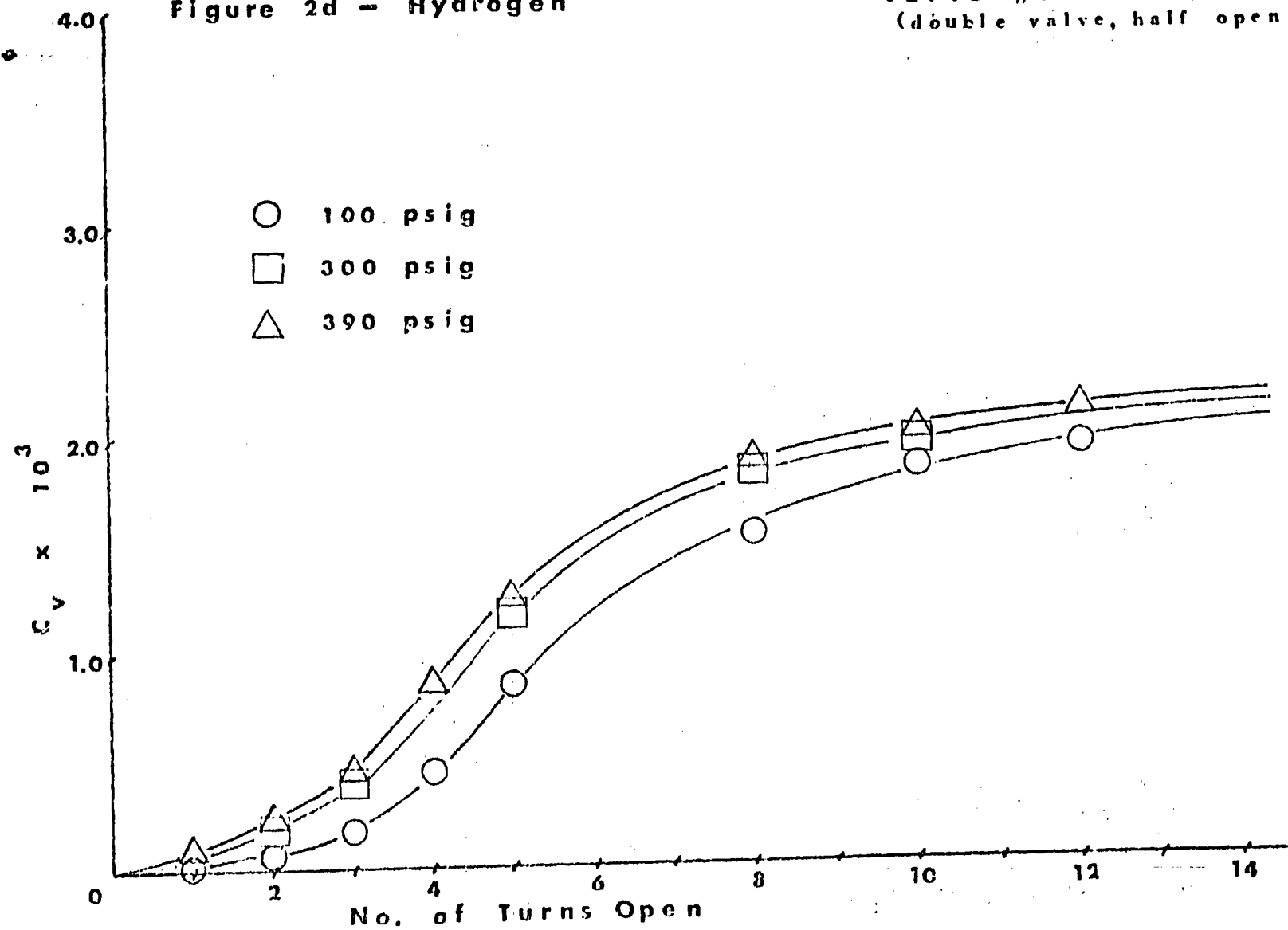


Figure 2d - Hydrogen

Valve #6  
(double valve, half open)



It was indicated earlier that CRU-1 employs a tubular reactor. Greater details of that reactor are shown in Figure 3. Here it should be noted that the 1-inch stainless-steel tubular reactor is surrounded by a Dowtherm heating jacket which permits temperature control of the exothermic reactions which occur in Fischer-Tropsch synthesis. The unit contains sufficient overflow volume to permit operation over a wide range of temperatures. The thermowell contains four thermocouples located at varying depths in the catalyst bed. These temperatures as well as those for the preheater, Dowtherm circulation loop, and Dowtherm jacket will be monitored by a Honeywell 12-point temperature recorder. The temperature of the Dowtherm jacket, circulation loop and preheater are individually controlled by Nanmac (Model PC-1, type K) temperature controllers.

Liquid samples will be collected in 300-ml S.S. sample bombs (13). These samples, subsequently, can be cooled and analyzed by gas chromatography to complete the product analysis.

As indicated by items 2 and 4 of Table 1, some time was devoted to pressure and temperature testing of CRU-1. Since carbon monoxide and hydrogen represent safety and health hazards, care was exercised to ensure that the system was leak tight. The unit was charged with helium to 200 psig and static-pressure tested for a period of forty-eight hours. The system was deemed leak tight when the pressure drop over this period of time was less than 5 psi. Similarly, the system was tested for isothermal operation across the length of the catalyst bed. This test consisted of measuring the temperature of a flowing gas mixture -- 77% He, 8% N<sub>2</sub>, 15% H<sub>2</sub> -- at 1-inch intervals along the reactor length in the catalyst bed region. When the inlet and outlet temperature differed by less than 2°C, the unit was considered to be isothermal. Additional insulation material and heating of the Dowtherm circulation loop was used to achieve this condition. This was accomplished after a partial redesign of the Dowtherm circulation loop as indicated by items 6 and 7 of Table 1. This unit has been operated for several days at reaction conditions. Thus, as implied by Table 1, CRU-1 has been made completely operational. A nickel-thoria-kieselguhr catalyst has been loaded into the reactor for the first series of studies which will be described later.

## 2. Catalytic Reactor Unit - 2

Concurrent with the installation of CRU-1, work also began on the design of a second unit. This unit, as shown in Figure 4, will have many of the features of CRU-1. However, its operation has been simplified by the use of three 6-point valves (59, 99 and 102 on diagram) which permit the reactor to be by-passed while the reactant-gas mixture is being analyzed. However, in this case a helium-argon mixture of the same molecular density is fed to the reactor (58) to maintain constant temperature and pressure profiles. All of the components for this unit have been received and are, currently, being assembled.

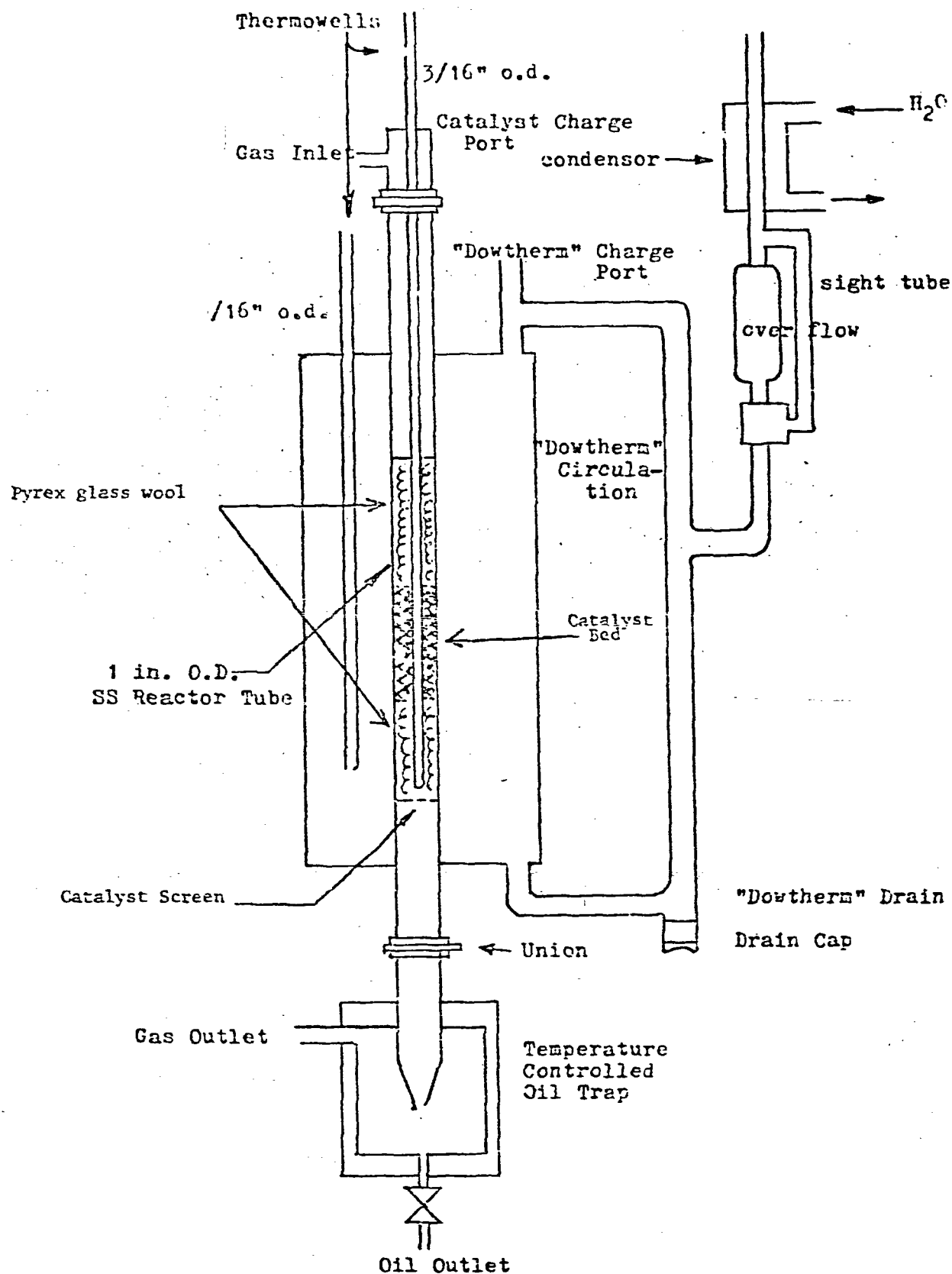


Figure 3 Fixed Bed Catalyst Reactor

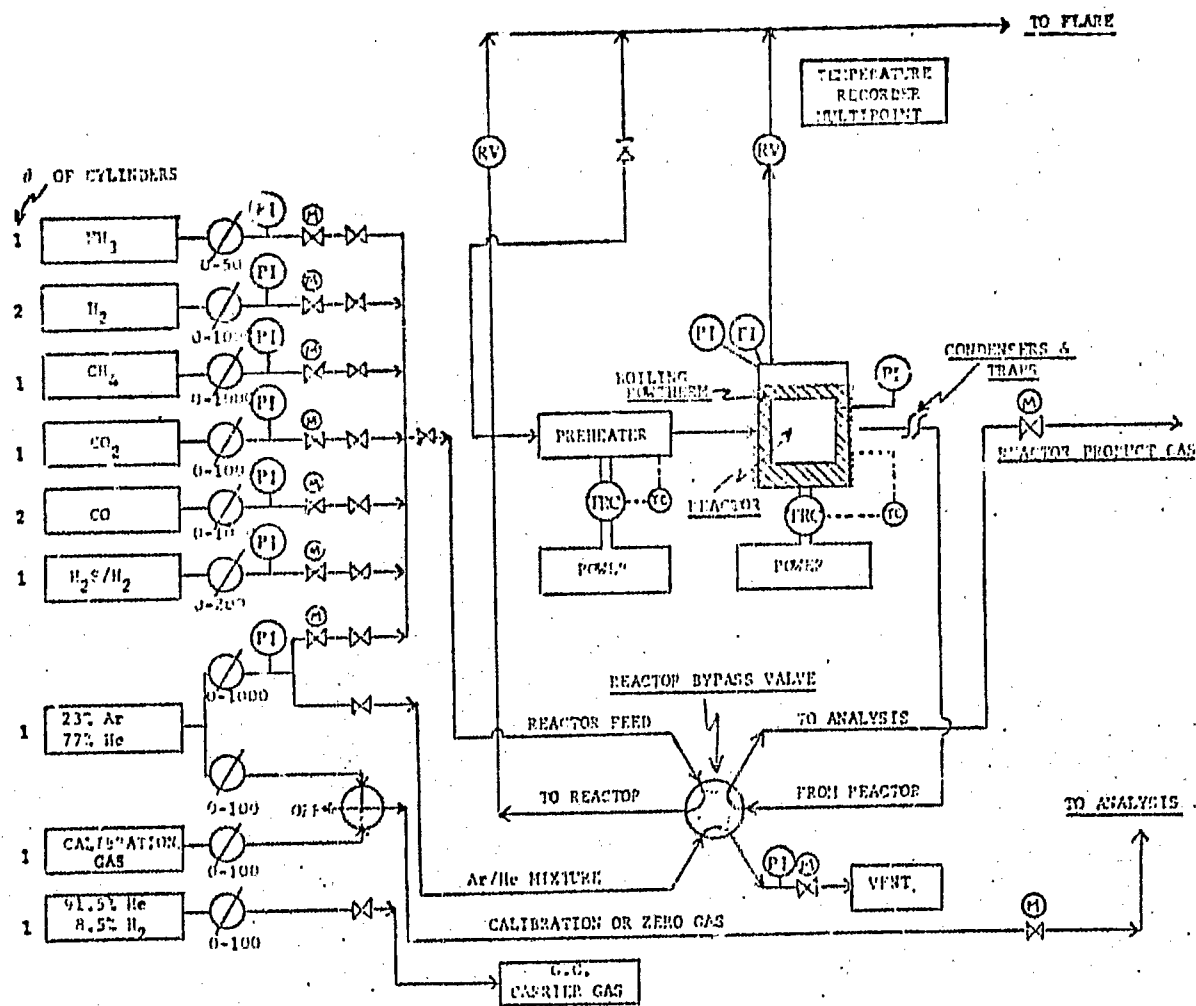


Figure 4 - Catalytic Reactor Unit-2

As was previously indicated, CRU-2 will have the flexibility of accepting three types of catalytic reactors. In addition to the tubular reactor installed in CRU-1, this unit will be fitted for the Carberry stirred catalytic reactor which is on order from Autoclave Engineers\*. A diagram of the reactor is shown in Figure 5. This reactor system consists of a magnetically driven basket which can contain various amounts of catalyst. The spinning basket causes internal recycling of the gas such that continuous stirred tank reactor (CSTR) conditions are achieved. Thus, kinetic modeling is greatly simplified for this unit.

The third type of reactor which will be used with this unit is a fluidized-bed reactor. This unit which has yet to be designed will permit a comparison of the behavior of the catalysts as a function of reactor designs. It should also be useful for extended-life studies to test the physical durability of the catalysts as well as their catalytic activity.

Work on CRU-2 will proceed according to the schedule presented in Table 1.

### 3. Analytical Package for Product Analysis

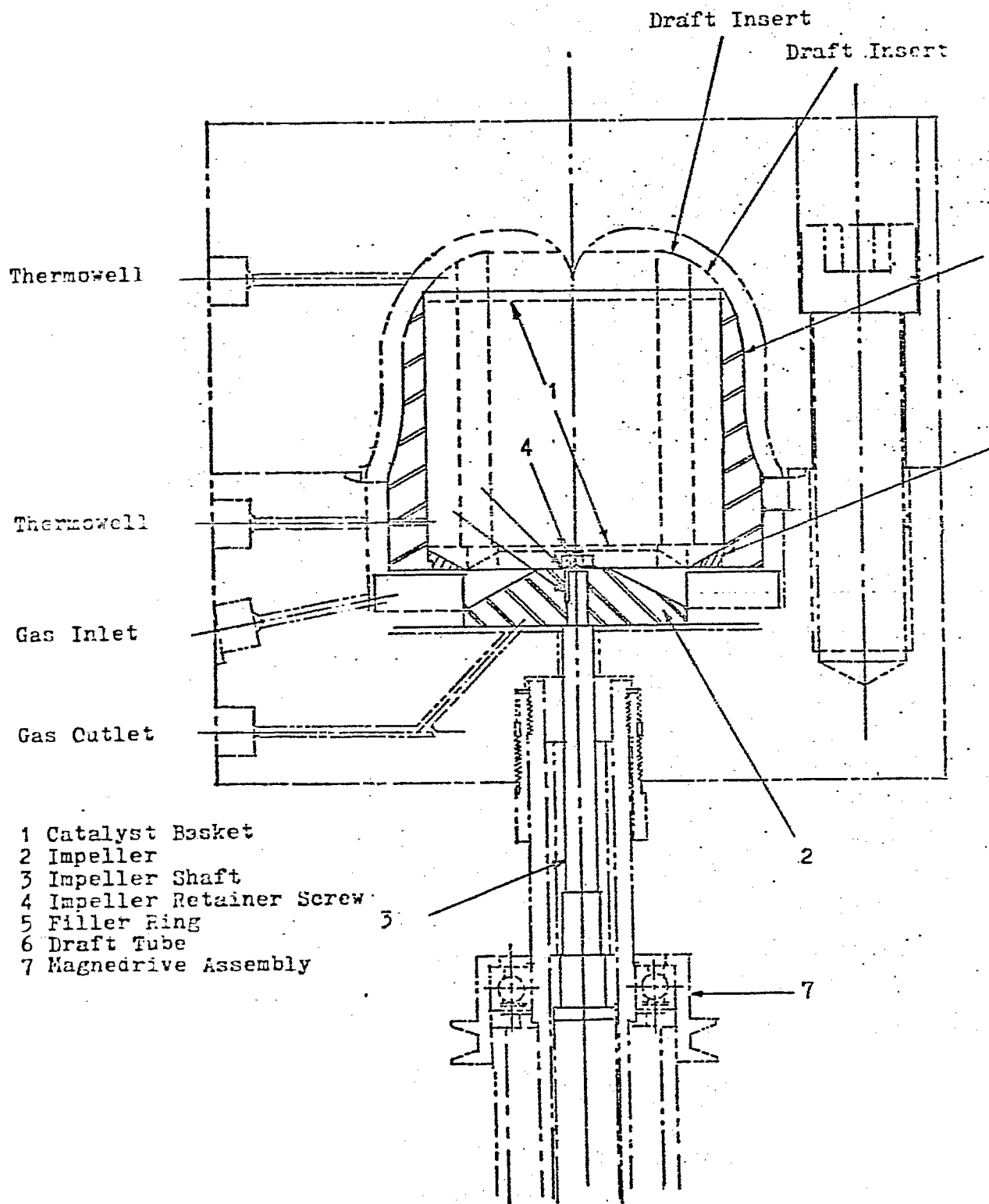
One of the key features of the proposed research program is the careful attention to the details of the product distribution for the various catalysts which will be investigated. To this end both continuous and intermittent analyses will be obtained to document the performance of a catalyst. Continuous analyses will be performed for carbon monoxide, carbon dioxide and methane using MSA non-dispersive infrared analyzers (NDIR). Intermittent analyses of the complete product spectrum will be achieved by gas chromatographic analyses. Because of budgetary restrictions on the contract, it became apparent that replication of the analytical portion of the two systems was not feasible. Therefore, considerable effort was devoted to developing an analytical package which would be compatible to both systems and achieve the goal of continuous monitoring of each reactor. After considerable consultation with salesmen from Varian Associates, Hewlett-Packard, and Mine Safety Appliances, we decided upon the analytical package summarized in Figure 6 and Table 3. Figure 6 is a schematic of the flow of product, reactant, calibration gases, or zero gases through the analytical network\*\*. When both systems are in operation the analysis proceeds in the following manner. Product gas from CRU-2 is by-passed to exhaust through a back-pressure regulator (A) and is flared (B). Valves (C) and (D) are operated by a timer to open automatically during the period in which PGI is being analyzed. A small portion of this gas is diverted to the GC calibration valve (E) where it is further regulated (F) and sent to the gas chromatographic system. The major portion of this gas passes through the infrared calibration valve (G) and is split equally between the three NDIR analyzers.

\*Delivery has been scheduled for early September.

\*\*The reactant gas stream will be analyzed periodically for reassurance of constant composition by both G.C. and NDIR.



Figure 5 Internally Recycled Catalytic Reactor



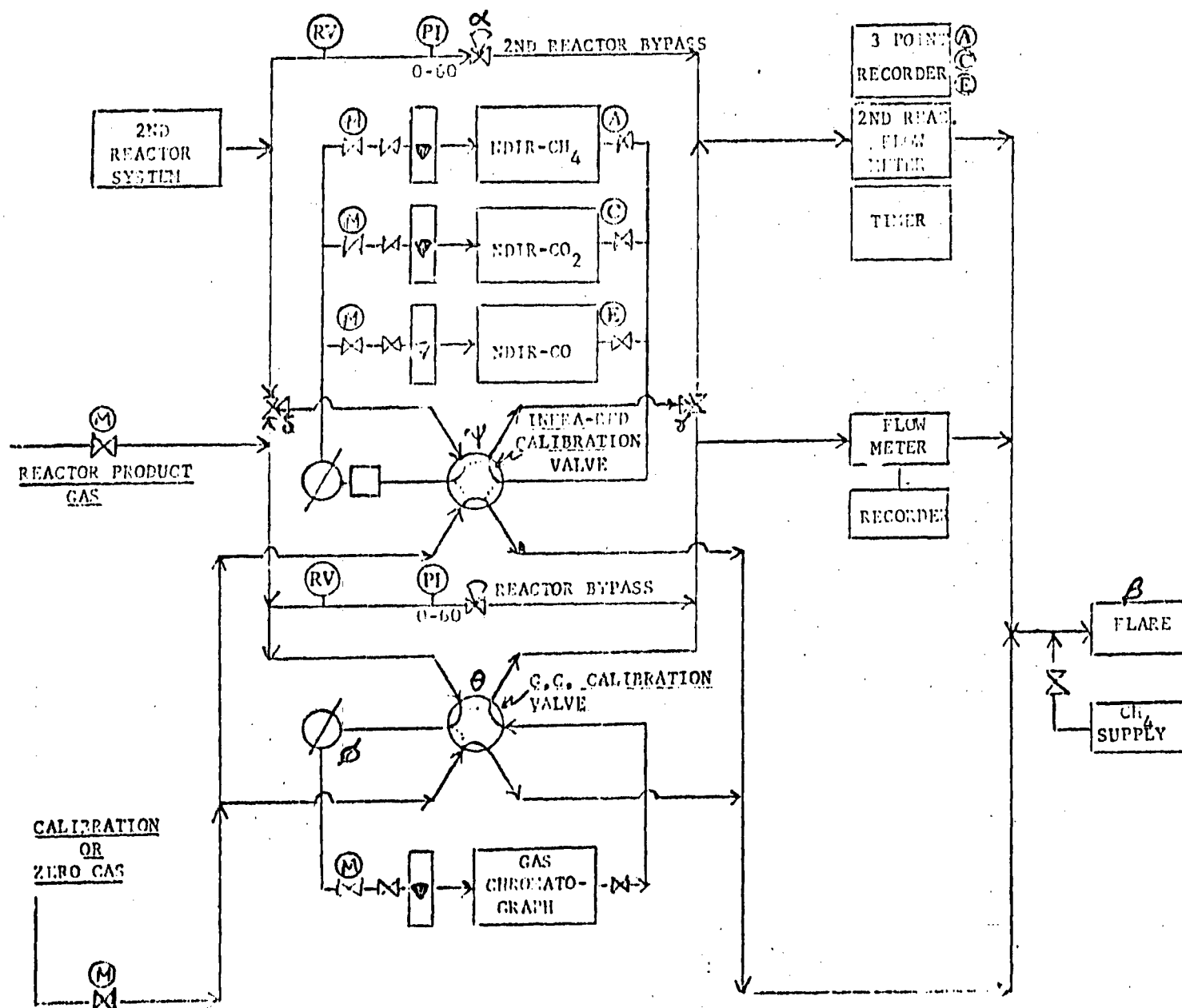


Figure 6 Analytical System

Table 3 Analytical Package for Product Analysis

| <u>No.</u> | <u>Gas</u>                   | <u>Method of Analysis</u>             | <u>Comments</u>  |
|------------|------------------------------|---------------------------------------|--|
| 1          | Carbon Monoxide              | NDIR <sup>a</sup> and GC <sup>b</sup> | Continuous and intermittent using molecular sieve column   |
| 2          | Carbon Dioxide               | NDIR <sup>c</sup> and GC              | Porapak GC column  |
| 3          | Hydrogen                     | GC <sup>b</sup>                       | Intermittent analysis, may prove difficult to measure on molecular sieve column                                    |
| 4          | Methane                      | NDIR <sup>d</sup> and GC              | Same as 1  |
| 5          | Ethane                       | GC <sup>b</sup>                       | Alumina or Porapak column  |
| 6          | Ethylene                     | GC <sup>b</sup>                       | Same as 5  |
| 7          | Propane                      | GC <sup>b</sup>                       | { BIS (2-methoxyethyl) adipate on<br>chromosorb F and DC 200 silicone<br>oil/chromosorb column                     |
| 8          | Propylene                    | GC <sup>b</sup>                       |  |
| 9          | Butane                       | GC <sup>e</sup>                       |  |
| 10         | Butenes                      | GC                                    | Same as 7; repeat analysis on separate sample using propylene carbonate on firebrick to obtain isomeric separation |
| 11         | Pentanes                     | GC                                    | Same as 7  |
| 12         | Pentenes                     | GC                                    | Same as 10   |
| 13         | C <sub>6</sub> 's and higher | GC                                    | Same as 7 but with back-flush of column  |

<sup>a</sup>MSA Lira Infrared Analyzer Model 303 tuned for 0-10% and 0-60% CO.

<sup>b</sup>Perkin-Elmer Model 154 Gas Chromatograph with two 10-port automatic gas sampling valves installed.

<sup>c</sup>MSA Lira Infrared Analyzer Model 303 tuned for 0-20% CO<sub>2</sub>.

<sup>d</sup>MSA Lira Infrared Analyzer Model 303 tuned for 0-20% CH<sub>4</sub>.

<sup>e</sup>Varian Aerograph GC with a 10-port automatic gas sampling valve installed.

The output from the NDIR's is preserved on a 3-point Honeywell recorder, (116). At the start of the operation, the product gas may be replaced by a calibration gas on a zero gas to facilitate adjustment of the NDIR's. At the end of the sampling period, e.g., ten minutes, the timer automatically switches sampling to CRU-2. This sequencing is repeated for the desired period of operation.

The gas chromatographic system consists of two Perkin-Elmer Model 154 modified instruments containing 10-port automatic gas sampling valves. The valve operations are controlled by a Varian Model CDS-101 Chromatography Data System processor which controls the sample injection and integrates the resulting chromatogram as area percent of each component. This system will be tested thoroughly on synthetic mixtures prior to its application to the present work. (Delivery of this unit is tentatively scheduled for early September.) To economize laboratory space, the MSA NDIR analyzers and their 3-point recorders will be panel mounted in a portable cabinet.

#### 4. Task I - Work Forecast for Second Quarter

Table 1 summarizes the work that is scheduled for the next quarterly period. The list of outstanding equipment is summarized in Table 4. Assuming that everything arrives as scheduled, the next quarter will be devoted largely to the assembly of CRU-2 and the analytical package. Each system will require considerable testing and training of personnel.

Table 4 Outstanding Equipment

| <u>Item No.</u> | <u>Description</u>  | <u>Supplier</u>        |
|-----------------|---|------------------------|
| 1               | CO - NDIR   | MSA                    |
| 2               | CH <sub>4</sub> - NDIR  | MSA                    |
| 3               | Carberry type<br>stirred catalytic<br>reactor                           | Autoclave<br>Engineers |
| 4               | CDS-101 Chromato-<br>graphy data system                                 | Varian Associates      |
| 5               | Two 10-port auto-<br>matic gas sampling<br>valves with air<br>actuators | Varian Associates      |

## B. Task V - Catalysts Preparation and Characterization

In the original proposal for this work, we emphasized the fact that the major effort in the development of Fischer-Tropsch catalysts was directed towards producing liquids, e.g.,  $C_5^+$  hydrocarbons. However, based on the work summarized by Storch, Columbia and Anderson (Fischer-Tropsch and Related Synthesis, 1951), there appears to be considerable evidence to support the belief that with the appropriate choice of catalyst and reaction conditions, the Fischer-Tropsch process could be modified to produce gaseous hydrocarbons. This work will seek to establish those necessary process variables and to develop suitable catalysts.

The table below list some of the F-T catalysts that have been reported in the literature which show high selectivity for the  $C_1$ - $C_4$  hydrocarbon fraction. It should be emphasized that the F-T synthesis process has been optimized to produce gasoline and diesel fuels and, therefore, these catalysts represent the "undesirables" for that process.

Table 5 Potential Catalysts

| <u>Catalyst</u>   | <u>Remarks</u>  |
|---|---|
| $Fe_3O_4$ - $MgO$ - $K_2O$                                  | Fused ammonia catalysts<br>~ 43% $C_2$ - $C_4$ yield after<br>$H_2$ reduction, yield in-<br>creases to ~50% after<br>nitriding pretreatment |
| 100 Fe:10 Cu:100 kieselguhr                                 | ~39% $C_2$ - $C_4$ yield at 7.8 atm<br>1:1 $H_2/CO$   |
| 100 Fe:20 Cu:0.2 $K_2CO_3$                                  | Precipitated from chloride,<br>at 280°C ~69% $C_2$ - $C_4$ yield  |
| 100 CO:18 $TiO_2$ :100 kieselguhr                           | Precipitated with $(NH_4)_2 CO_3$<br>gives higher yields of $C_2$ - $C_4$   |
| 100:Ni:18 $TiO_2$ :100 kieselguhr                           | at 178°C ~33% $C_1$ - $C_4$ yield   |
| $Fe_3O_4$ - $K_2CO_3$ , sintered                            | ~30% $C_1$ - $C_4$ yields   |
| 100 Alan Wood Magnetite -<br>16 water glass - 0.5 $K_2CO_3$ | ~44% $C_2$ - $C_4$ yield but overall<br>low activity  |

Anderson and coworkers have described a number of catalysts which are active for the Fischer-Tropsch synthesis. They studied the selectivity of many iron catalysts, and their results can be summarized in terms of the operating variables of temperature, pressure and gas composition as follows:

1. Increased temperatures cause :
  - a) decrease in average molecular weight of hydrocarbon products;
  - b) decrease in production of oxygenated organic compounds;
  - c) either increased or constant amounts of olefins to be formed.
2. Increased pressures cause increases in the average molecular weight of hydrocarbons.
3. Increase in  $H_2/CO$  ratio causes:
  - a) increase in usage ratio ( $H_2/CO$ );
  - b) decrease in average molecular weight of product;
  - c) decrease in olefin content of products.
4. Increase in particle size causes:
  - a) decrease in catalyst activity;
  - b) increase in gaseous products.

These results imply that our catalyst screening tests should be conducted at high temperatures and  $H_2/CO$  ratios and at low pressures on catalysts with large pore volumes and/or low areas.

#### 1. Catalyst Preparations

With the above concepts in mind, we have prepared a number of catalysts which may be useful to the stated objectives. These catalysts were prepared according to recipes presented in Storch's book. In some cases modifications were employed to facilitate ease of preparation or to obtain a series of well characterized catalysts. Table 6 is a summary of the catalysts that have been prepared in this laboratory. Table 7 is a summary of commercial catalysts that have been obtained for evaluation in this work. A seven digit alpha numeric system is used to designate the various catalysts. (The first term identifies the major metal component, the second term refers to minor metal content, the third and fourth terms identify promoters, the fifth term refers to the support, the sixth term identifies the catalyst preparer by initials, and the last term indicates the chronological ordering of the catalysts. Whenever a quantity is missing, it is omitted from the sequence.) For example, Fe-Cu-CaO-Kg-SZ-8

Table 6 Summary of Laboratory Catalysts

| <u>Item No.</u> | <u>Catalyst Designation</u>                                  | <u>Catalyst Composition</u>  | <u>Comments</u>  |
|-----------------|--|--|--|
| 1               | Fe-Cu-K <sub>2</sub> O-SZ-1                                  | 100 Fe:10 Cu:1 K <sub>2</sub> CO <sub>3</sub>  | Precipitated with Na <sub>2</sub> CO <sub>3</sub>                                    |
| 2               | Fe-SZ-2  | Fe   | Precipitated by K <sub>2</sub> CO <sub>3</sub>                                       |
| 3               | Fe-SZ-3  | Fe   | Precipitated by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub><br>to be alkali free |
| 4               | Fe-Cu-K <sub>2</sub> O-SZ-4                                  | 100 Fe:0.3 Cu  | Precipitated by Na <sub>2</sub> CO <sub>3</sub>                                      |
| 5               | Fe-Fe-Cu-K <sub>2</sub> O-SZ-5                               | 75 Fe <sup>+2</sup> :25 Fe <sup>+3</sup> :20 Cu:<br>1 K <sub>2</sub> CO <sub>3</sub> | Precipitated by Na <sub>2</sub> CO <sub>3</sub><br>ex chlorides                      |
| 6               | Fe-Fe-Cu-SZ-6  | 75 Fe <sup>+2</sup> :25 Fe <sup>+3</sup> :20 Cu                                      | Precipitated by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub><br>to be alkali free |
| 7               | Fe-Cu-CaO-Kg-SZ-7  | 100 Fe:5 Cu:30 CaO:100 Kg  | Precipitated by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub><br>to be alkali free |
| 8               | Fe-Cu-CaO-Kg-SZ-8  | 100 Fe:5 Cu:30 CaO: 100 Kg   | Precipitated by Na <sub>2</sub> CO <sub>3</sub>                                      |
| 9               | Fe-K <sub>2</sub> O-CaO-Al <sub>2</sub> O <sub>3</sub> -SZ-9 | 100 Fe: 1 K <sub>2</sub> O:1.6 CaO:<br>5 Al <sub>2</sub> O <sub>3</sub>              | Fused at 950°C for 1 hr.   |
| 10              | Fe-Cu-K <sub>2</sub> O-Dol-SZ-10                             | 100 Fe: 5 Cu:75 Dolomite:<br>3 K <sub>2</sub> CO <sub>3</sub>                        | Precipitated by Na <sub>2</sub> CO <sub>3</sub>                                      |
| 11              | Fe-Cu-K <sub>2</sub> O-ZnO-SZ-11                             | 100 Fe:5 Cu:75 ZnO: 6 K <sub>2</sub> CO <sub>3</sub>                                 | Precipitated by Na <sub>2</sub> CO <sub>3</sub>                                      |
| 12              | Fe-Cu-Al <sub>2</sub> O <sub>3</sub> -RD-1                   | 100 Fe:10 Cu:100 Al <sub>2</sub> O <sub>3</sub>                                      | Alumina impregnated  |
| 13              | Fe-Cu-Al <sub>2</sub> O <sub>3</sub> -RD-2-Cal               | 100 Fe:10 Cu:100 Al <sub>2</sub> O <sub>3</sub>                                      | Same as 12, but calcined at<br>1000°C for 1 hr.                                      |
| 14              | Fe-Cu-Kg-RD-3  | 100 Fe:10 Cu:100 Kg  | Precipitated by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>                      |
| 15              | Fe-Cu-Kg-RD-4-Cal  | 100 Fe:10 Cu:100 Kg  | Same as 14, but calcined at<br>1000°C for 1 hr.                                      |

Table 6 (Contd.)

| <u>Item No.</u> | <u>Catalyst Designation</u>                                   | <u>Catalyst Composition</u>                                    | <u>Comments</u>   |
|-----------------|---|--|---|
| 16              | Fe-Cu-K <sub>2</sub> O-RD-5                                   | 100 Fe:20 Cu:0.2 K <sub>2</sub> CO <sub>3</sub>                | Precipitated by Na <sub>2</sub> CO <sub>3</sub>   |
| 17              | Fe-Cu-K <sub>2</sub> O-RD-6-Cal                               | 100 Fe:20 Cu:0.2 K <sub>2</sub> CO <sub>3</sub>                | Same as 16, but calcined at 1000°C for 1 hr.  |
| 18              | Fe-Cu-K <sub>2</sub> O-Kg-RD-7                                | 100 Fe:10 Cu:0.2 K <sub>2</sub> CO <sub>3</sub> :100 Kg        | Precipitated by Na <sub>2</sub> CO <sub>3</sub> ex chlorides                                      |
| 19              | Ni-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -RD-1     | 100 Ni:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Alumina impregnated   |
| 20              | Ni-ThO <sub>2</sub> -Kg-RD-4                                  | 100 Ni:18 ThO <sub>2</sub> :100 Kg                             | Precipitated by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>                                   |
| 21              | Ni-ThO <sub>2</sub> -Kg-RD-6-Cal                              | 100 Ni:18 ThO <sub>2</sub> :100 Kg                             | Same as 20, but calcined at 1000°C for 1 hr.  |
| 22              | Ni-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -RD-3-Cal | 100 Ni:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Same as 19, but calcined at 1000°C for 1 hr.  |
| 23              | Ni-ThO <sub>2</sub> -Kg-RD-7                                  | 100 Ni:18 ThO <sub>2</sub> :100 Kg                             | Precipitated by Na <sub>2</sub> CO <sub>3</sub>   |
| 24              | Ni-ThO <sub>2</sub> -Kg-RD-8-Cal                              | 100 Ni:18 ThO <sub>2</sub> :100 Kg                             | Same as 23, but calcined at 1000°C for 1 hr.  |
| 25              | Ni-PE-12  | Unsupported Nickel   | Ex carbonate  |
| 26              | Ni-TB-10  | Arc-Vaporized Nickel   | Prepared by Dent-Bierl-arc vaporization process.  |
| 27              | Ni-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -SZ-12    | 100 Ni:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Co-precipitated Al <sub>2</sub> O <sub>3</sub> by K <sub>2</sub> CO <sub>3</sub>                  |
| 28              | Co-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -SZ-13    | 100 Co:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Co-precipitated Al <sub>2</sub> O <sub>3</sub> by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> |
| 29              | Co-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -RD-1     | 100 Co:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Alumina impregnated   |
| 30              | Co-ThO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -RD-2-Cal | 100 Co:18 ThO <sub>2</sub> :100 Al <sub>2</sub> O <sub>3</sub> | Same as 29, but calcined at 1000°C for 1 hr.  |
| 31              | Co-ThO <sub>2</sub> -Kg-RD-3                                  | 100 Co:18 ThO <sub>2</sub> :100 Kg                             | Precipitated by K <sub>2</sub> CO <sub>3</sub>  |
| 32              | Co-ThO <sub>2</sub> -Kg-RD-4-Cal                              | 100 Co:18 ThO <sub>2</sub> :100 Kg                             | Same as 31, but calcined at 1000°C for 1 hr.  |



Table 7 List of Commercial Catalysts

| <u>Item No.</u> | <u>Catalyst Designation</u>                 | <u>Description</u>   | <u>Supplier</u> |
|-----------------|---|--|-----------------|
| 1               | Ni 203T                                     | ~58% nickel on kieselguhr, 1/8"x1/8" pellets, reduced.           | Calsicat        |
| 2               | Ni 230T                                     | ~60% on alumina, 1/8"x1/8" pellets, reduced.                     | Calsicat        |
| 3               | Ni-G-52                                     | 33% nickel on refractory support 3/16"x3/16", reduced.           | Chemetron Corp. |
| 4               | Ni-Cu-Al <sub>2</sub> O <sub>3</sub> -GT312 | 11% Ni and 1% Cu on gamma alumina, 3/16"x1/8"                    | Chemetron Corp. |
| 5               | Fe-G-3A                                     | chromium-promoted iron oxide, CO conversion catalyst, 3/8"x3/16" | Chemetron Corp. |
| 6               | Fe-G-82                                     | triple-promoted iron oxide, ammonia synthesis catalyst, granules | Chemetron Corp. |
| 7               | CO-ZrO <sub>2</sub> -Kg-G-67                | 60% cobalt, zirconium promoted supported on kieselguhr, powder   | Chemetron Corp. |
| 8               | CO-Kg-G-61                                  | 60% cobalt on kieselguhr powder                                  | Chemetron Corp. |
| 9               | CO-La-900                                   | lanthanum cobalt oxide powder                                    | Molycorp.       |
| 10              | Fe-Mag-8                                    | Alan Wood Magnetite  | PERC, ERDA      |

identifies an iron-copper catalyst promoted by calcium oxide and supported on kieselguhr which was prepared by Susan Zloinick as her eighth catalyst. Note that many of the catalysts are repeats with minor variations in method of preparation. For example, the pair, Fe-SZ-2 and Fe-SZ-3 differ only in that the latter is alkali free. This and similar combinations will permit us to evaluate the effects of alkali and support, e.g.,  $K_2O$  content and alumina versus kieselguhr, on the product distribution. We anticipate evaluating these catalysts during Task II's tenure.

## 2. Catalysts Characterization by Surface Area Measurements

Over the years, knowledge of the total surface area and active metal surface areas have come to be recognized as absolute necessities in understanding processes at the surface of a catalyst. While the BET method using nitrogen or argon at  $-195^{\circ}C$  has become the standard technique for measuring the amount of physically adsorbed material in a monolayer and hence the total surface area, techniques for measuring the active metal surface area are less well established. The two prevailing approaches have been: a) to measure the amount of hydrogen adsorbed at room temperature or at  $100^{\circ}C$  at a sufficient pressure to ensure saturation of the surface; and b) to measure the difference between the amount of carbon monoxide totally adsorbed and the amount of nitrogen physically adsorbed on top of the chemisorbed CO. Physically adsorbed CO is removed by degassing at  $-78^{\circ}C$ . Unfortunately, often the two methods yield different values for the metal area. Several explanations have been presented to account for these differences.

An attempt to obtain the total (TSA) and metal surface areas (MSA) of a number of the catalysts designated for Task II studies was initiated prior to the inception of this contract. However, since the work was continued under this contract, the results will be reported here. A standard multipurpose vacuum system was used for this work. Both methods described above were employed and the results are presented in Table 8. Consider the first entry in this table which is a commercial nickel on kieselguhr catalyst. The results from the CO- $N_2$  method at  $-195^{\circ}C$  indicate that the metal surface area is  $60 \text{ m}^2/\text{g}$ . However, hydrogen adsorption at room temperature gives a value about one-third of this amount. The difference may be in part due to the one-point method (suggested by Sinfelt and coworkers) for determining the chemisorbed amount of hydrogen in a monolayer. More importantly, these two values should serve as a bracket about the actual total metal surface area and is, therefore, sufficient for design purposes.

Table 8 Surface Area Comparison by  
CO and H<sub>2</sub> Chemisorption

| <u>Catalyst</u>              | <u>Total SA<br/>(m<sup>2</sup>/g)</u> | <u>Method of Measuring TSA</u>             | <u>MSA via CO<sup>a,b,c</sup><br/>Chemisorption<br/>(m<sup>2</sup>/g)</u> | <u>MSA via H<sub>2</sub><sup>b</sup><br/>Chemisorption<br/>(m<sup>2</sup>/g)</u> |
|------------------------------|---------------------------------------|--|---|--|
| Ni-203T                      | 121.1                                 | N <sub>2</sub> on chemisorbed CO at -195°C | 60.1  | 20.1   |
| Fe-Cu-Kg-RD-3                | 12.4                                  | N <sub>2</sub> on chemisorbed CO at -195°C | 3.1   | 7.2  |
| Fe-Mag-8                     | 2.1                                   | N <sub>2</sub> on chemisorbed CO at -195°C | 0.9   | 0.1  |
|                              | 1.8                                   | Argon at -195°C                            |   |  |
| Ni-PE-12                     | 5.7                                   | N <sub>2</sub> on chemisorbed CO at -195°C | 4.0   | 1.9  |
|                              | 5.6                                   | Argon at -195°C                            |   |  |
| Ni-TB-10                     | 8.8                                   | Argon at -195°C                            | 2.82  | 0.9  |
|                              | 8.9                                   | N <sub>2</sub> on chemisorbed CO at -195°C |   |  |
| Kieselguhr                   | 4.4                                   | N <sub>2</sub> at -195°C                   | —   | 0.06   |
| CO-ThO <sub>2</sub> -Kg-RD-3 | 27.8                                  | N <sub>2</sub> at -195°C                   | ---   | 4.8  |

<sup>a</sup> Dotted line indicates not measured.

<sup>b</sup> CO chemisorption at -195°C, H<sub>2</sub><sub>ads</sub> at room temperature and 100 mm unless otherwise stated.

<sup>c</sup> Surface area determined from difference in carbon monoxide and nitrogen volumes adsorbed per gram at the relative pressure, P/P<sub>0</sub>, equals 0.1.

### 3. Chemical Analyses of Some Catalysts

Another problem associated with making comparisons of the performance of a number of catalysts is establishing the bases for such a comparison. In addition to the total and active metal surface areas, one would like to know the amount of metal present in the catalysts. Due to uncertainty in completeness of precipitation and solubility of the various components of promoted dual-metal catalysts, we decided to undertake a chemical analysis of the catalysts that were prepared in the laboratory. Table 9 shows the partial results of that work. It indicates that the catalysts have nominally the percentage of components as expected. It does, however, offer the advantage of knowing more precisely what the actual concentrations of species are. Thus, comparisons can be made more intelligently from these data.

### 4. Summary and Work Forecast

As indicated by Tables 6, 7, 8, and 9, the preliminary work on catalyst preparations have been completed. Until a substantial number of these catalysts have been tested, the only work that is needed in this area is the completion of the surface area measurements and chemical analyses. This should be completed during the next quarter.

Table 9 Chemical Analysis of Laboratory Catalysts

| <u>Item No.</u> | <u>Catalyst Designation</u>      | <u>Measured Principal Component</u> | <u>Expected Principal Component</u> | <u>Measured Minor Component</u> | <u>Expected Minor Component</u> |
|-----------------|----------------------------------|-------------------------------------|-------------------------------------|---------------------------------|---------------------------------|
| 1               | Fe-Cu-K <sub>2</sub> O-SZ-4      | 60.0% Fe                            | 68.1% Fe                            | 2.2% Cu                         | 2.0% Cu                         |
| 2               | Fe-Cu-C <sub>A</sub> O-Kg-SZ-8   | 30.5% Fe                            | 35.8% Fe                            | 3.7%                            | 1.8% Cu                         |
| 3               | Fe-SZ-3                          | 62.6% Fe                            | 69.9% Fe                            | --                              | --                              |
| 4               | Fe-Cu-K <sub>2</sub> O-SZ-1      | 57.5% Fe                            | 63.9% Fe                            | 18.5% Cu                        | 6.4%                            |
| 5               | Fe-Cu-K <sub>2</sub> O-ZnO-SZ-11 | 38.8% Fe                            | 43.4% Fe                            | 5.1% Cu                         | 2.2%                            |
| 6               | Fe-Fe-Cu-K <sub>2</sub> O-SZ-5   | 53.7% Fe                            | 60.9% Fe                            | 12.7% Cu                        | 12.2% Cu                        |

### C. Background Work for Task IV - Mechanistic Studies

A complete understanding of the processes involved in heterogeneous catalysis requires, first, a knowledge of the nature of the chemical reactants at the gas-solid interface, i.e., the structure of the adsorbed species, and secondly, a knowledge of how these species interact to form products, i.e., the role of the reactive intermediates. The application of infrared spectroscopy to surface chemistry represents a major advance towards answering these two fundamental questions. There are many examples in the scientific literature demonstrating the utility of this technique in providing answers in the former area-adsorption. There are, however, considerably fewer examples with respect to the latter case. This lack stems largely from the experimental limitations imposed by the technique.

Two methods will be used in this work to remove some of the more serious limitations and thereby develop an infrared technique to study heterogeneous reactions under dynamic conditions similar to actual industrial conditions. The first method involves passing infrared radiation through a "fluidized bed" of the catalytic material. (The term "fluidized bed" is used to describe a reactor wherein the catalyst is suspended in the gas phase medium by Brownian motion, hence, an aerosol-bed.) The second method involves the pressed disc technique wherein the catalyst sample is pressed into a very thin wafer. This wafer is then fixed in the I.R. beam by a metallic (or quartz) support within an infrared cell. Spectra are then obtained first on the catalyst in an active state in the absence of reactant gases and subsequently in their presence. Work to date has concentrated on developing the aerosol-bed technique.

#### 1. A System for Studies of Nickel Aerosols

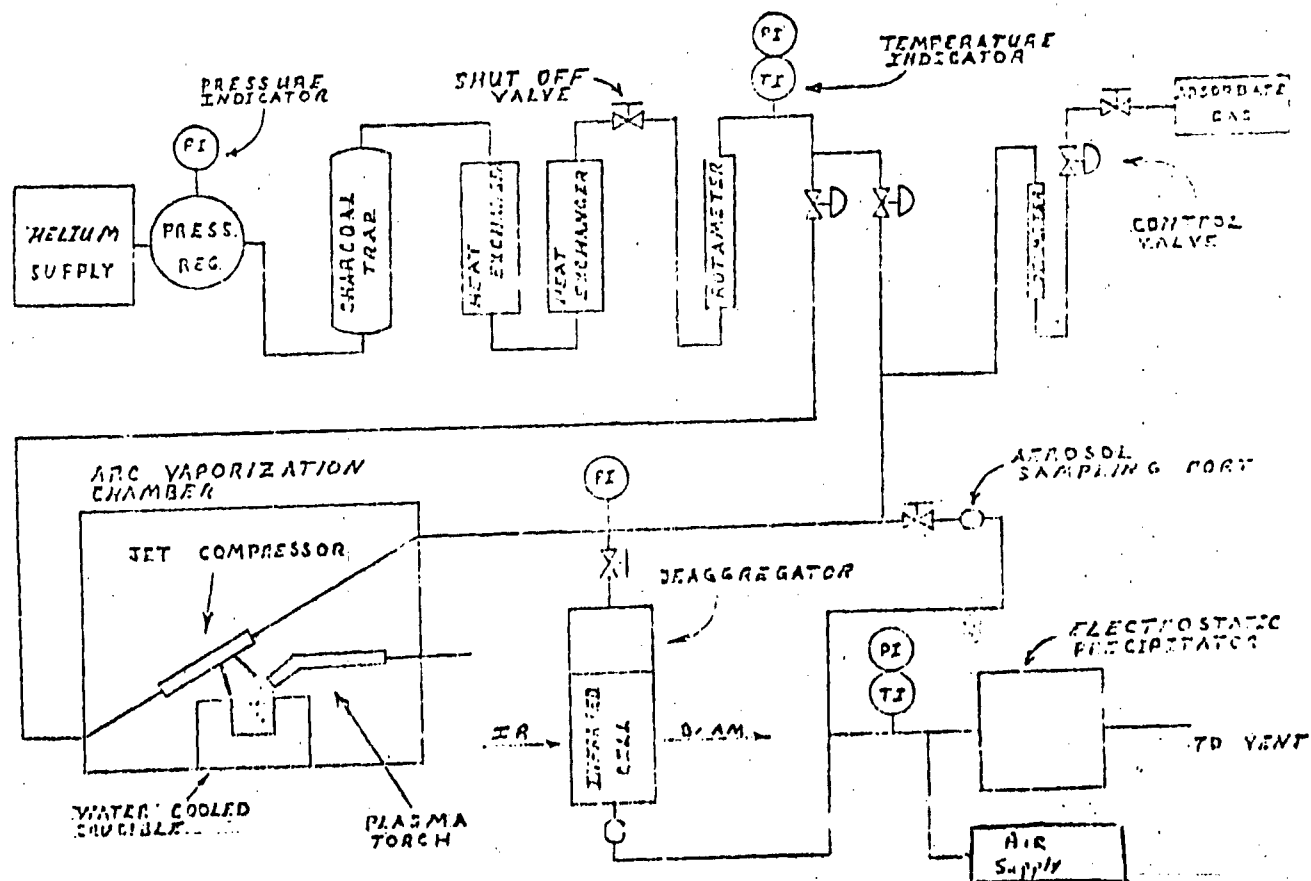
Since nickel is the most effective methanation catalyst, we have initiated our studies using this material. Briefly, the aerosol-bed technique involves generation of the catalyst by arc-vaporization techniques, gas-phase transfer of the aerosol to a long-path-length infrared cell where observations of surface reactions are made, and removal of the aerosol from the system by electrostatic precipitation. Arc vaporization, which is the most sophisticated of the several unit operations involved in this process, is employed as a means of generating a clean metal surface of sufficiently small particle size so as to permit infrared transmission through the bed. In this process, the metal, e.g., nickel, is vaporized at temperatures in excess of 4000°K by transfer of a high intensity electrical arc to the surface of a plug of the metal which serves as the electrode for the circuit. Since the metal is well above its boiling point, vaporization occurs at a rate proportional to the amount of heat transferred to the surface. Hence, a dense gas of metal atoms is produced. In this case these nickel atoms or atom-clusters are rapidly quenched within the vaporization chamber, and are swept through the system by the helium carrier gas. As the nickel aerosol emerges from the vaporization chamber, it passes through two heat exchangers where its temperature is adjusted as desired. The aerosol then passes into a 40 meter Wilkes long-path-length IR cell which is modified to retard deposition of the nickel

particles on the mirror surfaces. Because nickel in such finely divided states represents a potential health and safety hazard, the aerosol is cleaned by passage through two electrostatic precipitators in parallel before venting the gas. Figure 7 is a schematic diagram of the process. As indicated by the diagram, adsorbate gases can be injected into the aerosol just prior to entrance to the infrared cell. Rotameters on the helium and adsorbate line permit measurement and adjustment of the gas concentrations at will. Spectral observations are made first in the absence of adsorbate gases, i.e., background conditions, then in the presence of adsorbate gases, e.g., CO, H<sub>2</sub>, CO<sub>2</sub>, or mixtures of these gases. An equivalent concentration of adsorbate gases in the reference beam of the Beckmann IR 12 infrared spectrophotometer used for these studies permits compensation for the gas phase effects. Thus, the difference between these two spectra represents the spectrum of adsorbed species, assuming of course that the background remains constant over this period. In this manner, a number of mechanistic studies will be conducted with the objective of characterizing the reaction intermediates at the surface of the catalyst.

To date this project has evolved to the stage where all of the earlier problems associated with removing 16 kilowatts of heat from the two-liter vaporization chamber have been solved. As a result, we can generate aerosol routinely for periods of several hours. Unfortunately, we do have an unforeseen problem. Because of the limited supply of electrical power to our wing of the building and the high power consumption involved with operation of the welding machines, we are limited to a work schedule involving night and weekend operations.

This system has several advantages and disadvantages associated with it. Among its advantages is the removal of the catalyst support and consequently the opportunity to observe low frequency infrared vibrations, typically in the region where surface-to-adsorbates bonds are expected to absorb. These observations would be unobtainable otherwise. Because of the manner of operation which is essentially plug flow through the reactor, one is always observing a fresh surface. This surface may contain adsorbed species depending upon whether or not adsorbate gases were introduced into the aerosol stream. This means that a re-examination of the catalyst in the manner associated with pressed-disk IR samples is not permissible. This places a stringent requirement on the rate of aerosol generation -- it must be constant, and on the particle size distribution in the aerosol -- it too must be constant. Tests of the generation rate during two-hour periods of operation showed that the rate of aerosol generation varies by less than 5 percent over this period, and therefore, may be considered constant. Particle size measurement has presented a problem and will be discussed next.

FIGURE 7  
"AEROSOL CATALYST PROCESS FLOW DIAGRAM"





## 2. Aerosol Characterization

Particle sizes can only be obtained indirectly, for example, by measurement of the total surface area. However, since the surface area is actually the important parameter for both catalyst activity and infrared transmission, this is sufficient. We have observed that the nickel powder generated in this process will spontaneously ignite upon exposure to the atmosphere. This fact coupled with the desire to establish the catalytic activity of the aerosol led us to design a sample collector and reactor which satisfied the need to sample the aerosol without exposure to the environment.

Our first attempts at this were unsuccessful. We found that a pyrex trap containing glass wool quickly was plugged by the aerosol. Replacement of the glass wool by glass spirals proved to be more successful. Figure 8 shows a schematic of this sample collector. Surface area measurements on samples collected in this manner indicated that the catalyst had an area of approximately  $14 \text{ m}^2/\text{g}$ . This value is much lower than a previously obtained value of  $42 \text{ m}^2/\text{g}$  collected in a much different manner. These results suggest that we are not collecting the entire particle size distribution of the aerosol but, rather, only the larger particles. As a result, the collector will be redesigned. However, since we had a known quantity of catalyst whose surface area was also known, we decided to investigate the catalytic activity.

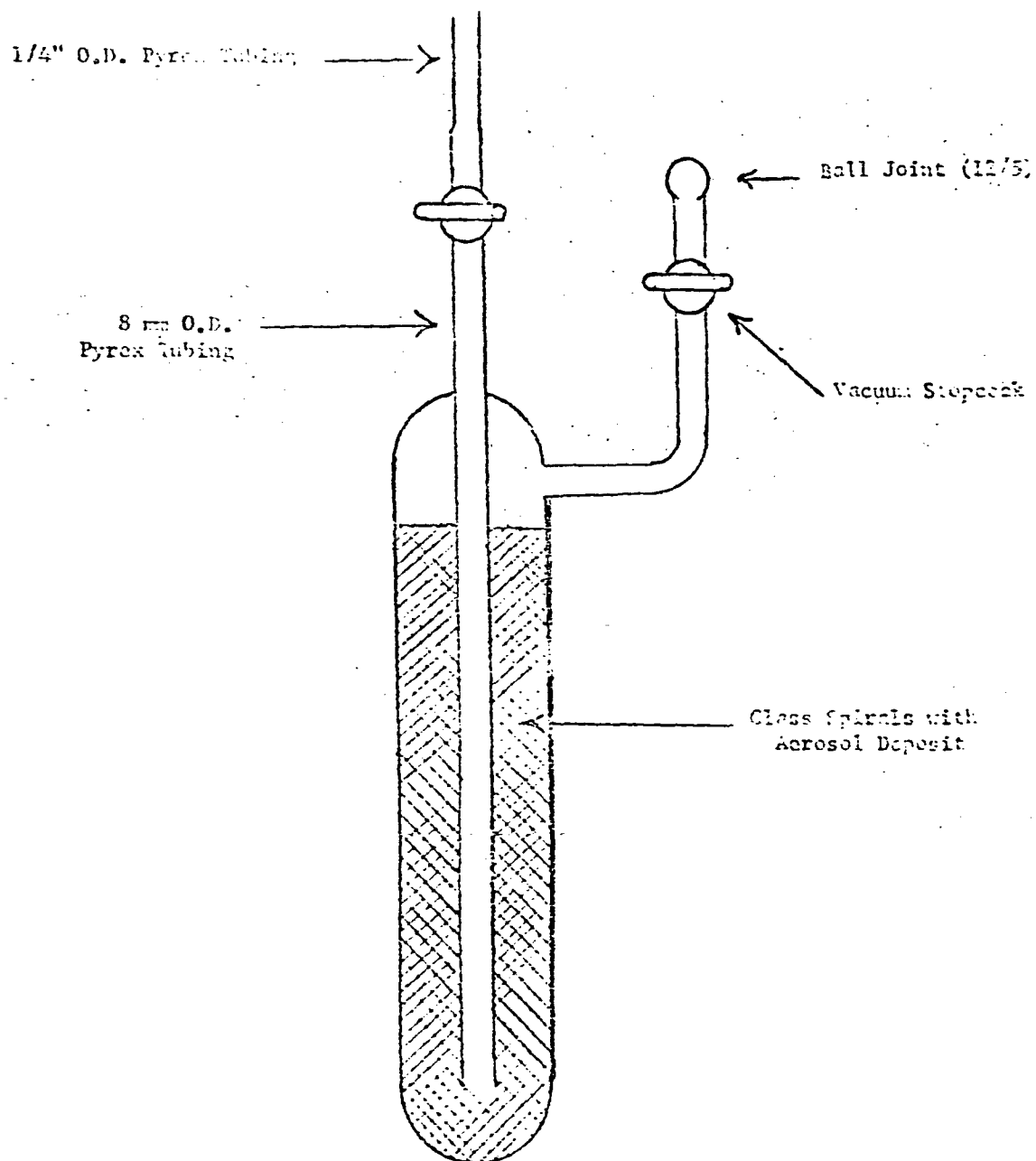
## 3. Preliminary Catalytic Studies

This unit behaved much like a batch reactor. Subsequent reaction measurements in this reactor indicated that the catalyst had a very high activity for catalytic hydrogenation. A 4:1 hydrogen:ethylene mixture at 400 mm Hg was admitted to the reactor for a one minute period at  $27^\circ\text{C}$ . Analysis of the hydrocarbon fraction was accomplished by gas chromatographic separation on an alumina column. Based on a comparison with data presented in Bond's book (Catalysis by Metals) the rate approaches a factor of  $10^4$  greater than previously reported catalysts. It should be stressed that these results are tentative and work is in progress to confirm these initial observations.

## 4. Infrared Studies of Nickel Aerosols

To date, we have made only one complete test of the infrared cell which was designed for this system. During that test, an initial decrease in transmission occurred which invalidated the test. It was later established that this transmission loss was due to deposition of large nickel particles on the field mirror of the cell. We have attempted to correct this problem by installing a large settling tank in series prior to the IR cell. Additional tests of this system has been scheduled for the forthcoming quarter. Despite the problems which occurred during this test, our understanding of the system was increased markedly. As a result, future tests should prove to be more successful.

Figure 8 Glass Spiral Reactor with Aerosol Deposit



## 5. Summary and Task Forecasts

To summarize this section we have mastered the difficult task of generating a clean, fine-particle-size aerosol for infrared studies. In addition, we have initiated experiments to establish the catalytic reactivity of this form of nickel catalyst and to make comparisons with conventional types of nickel catalysts. We have designed a sample collection unit which should prove useful for future measurements of surface areas and catalyst activities.

During the next quarter, we anticipate that making infrared tests on the system using a number of adsorbate gases, e.g., CO, CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub>, will occupy the major portion of our time. The remaining available time will be devoted to completion of the catalyst's characterization by conducting ethylene hydrogenation studies at several temperatures and by careful measurement of the surface area of the nickel powder collected in such a manner which will ensure its aerosol character. Table 10 summarizes the work accomplished for this task and gives the tentative schedule for the work which has been planned for the next quarter.

Table 10 Task IV Mechanistic Studies - Background Work

| <u>Item No.</u> | <u>No. Weeks of Work*</u> | <u>Description of Subtasks</u>  |
|-----------------|---------------------------|---|
| 1               | 4                         | Final modifications of aerosol generation system.   |
| 2               | 3                         | Test runs of the aerosol system to establish generation rates.  |
| 3               | 2                         | Test run of the complete system and subsequent repairs on the Wilkes cell.                              |
| 4               | 1                         | Design and fabrication of a sample collection cell.   |
| 5               | 1                         | Aerosol sample collection and surface area measurement.   |
| 6               | 1                         | Preliminary catalyst activity measurements using ethylene and hydrogen.                                 |
| 7               | (3)                       | Detailed catalytic activity measurements of the C <sub>2</sub> H <sub>4</sub> -H <sub>2</sub> reaction. |
| 8               | (2)                       | Surface area measurements of the aerosol powder in the redesigned cell.                                 |
| 9               | (7)                       | Extensive test runs on the complete system to obtain infrared data.                                     |

\*Numbers in parenthesis refer to work forecasted for the next quarter.

#### IV. CONCLUSIONS

Throughout the previous sections we have stated the work accomplished in this contract. In Task I, one reactor unit has been completed and a second unit has been designed. In Task V, a considerable number of catalysts have been prepared, a number of which have been characterized. In Task IV, much of the preliminary background work for mechanistic studies have been completed. We conclude, therefore, that the work is proceeding according to schedule and in some areas is slightly ahead of schedule.

### Appendix A

The investigation of catalytic syntheses of gaseous hydrocarbons shall proceed according to the following tasks:

#### 1. Task No. 1

a. Equipment and apparatus shall be assembled and integrated for the study of catalytic synthesis of hydrocarbons by means of gas chromatography and in situ high-pressure infrared spectrometry. Catalyst systems employing both fixed- and fluidized-bed mode of operation shall be provided.

b. Simultaneously with this effort the Principal Investigator shall ascertain in greater detail through discussions with catalyst manufacturers and users, the catalysts currently being employed for gaseous hydrocarbon synthesis, and the principal problems with use of such catalysts.

#### 2. Task No. 2

Screening tests shall be developed for evaluation of catalyst formations used in synthesis of  $C_1$ - $C_4$  hydrocarbons. The adequacy of the tests shall be verified using catalysts known to be effective for such reactions. The tests shall be used to evaluate new catalyst preparations that offer the possibility of improved effectiveness and resistance of poisoning and sintering under the conditions of synthesis of various gaseous hydrocarbons from carbon monoxide-hydrogen mixtures.

#### 3. Task No. 3

The most promising catalyst formulations obtained from Task 2 will be used for kinetic studies. Data obtained from the studies will be used to develop equations for predicting product yields of gaseous hydrocarbons as a function of temperature, pressure,  $H_2/CO$  ratio, and other experimental parameters. The data will also be interpreted in terms of possible reaction mechanisms, to serve as a guide for more detailed studies (Task 4).

#### 4. Task No. 4

Studies shall be carried out on the mechanism of formation and types of reaction intermediates formed during the catalytic synthesis of gaseous hydrocarbons using the apparatus and approaches described in Task 1. In addition, catalyst poisoning and mass transfer effects will be assessed via a gas chromatographic pulsed tracer technique.

5. Task No. 5

Alternative catalyst preparation approaches will be undertaken, involving (a) the Michalko technique for imbedding catalytically active metals at a controlled depth within a catalyst pellet, and (b) development of catalyst formulations for simultaneous shift conversion and methanation.

6. Task No. 6

Tests of long-term activity, poisoning, and regeneration of catalysts shall be carried out in laboratory apparatus, and evaluations of the most promising candidates shall be conducted in a fluidized-bed reactor.

7. Task No. 7

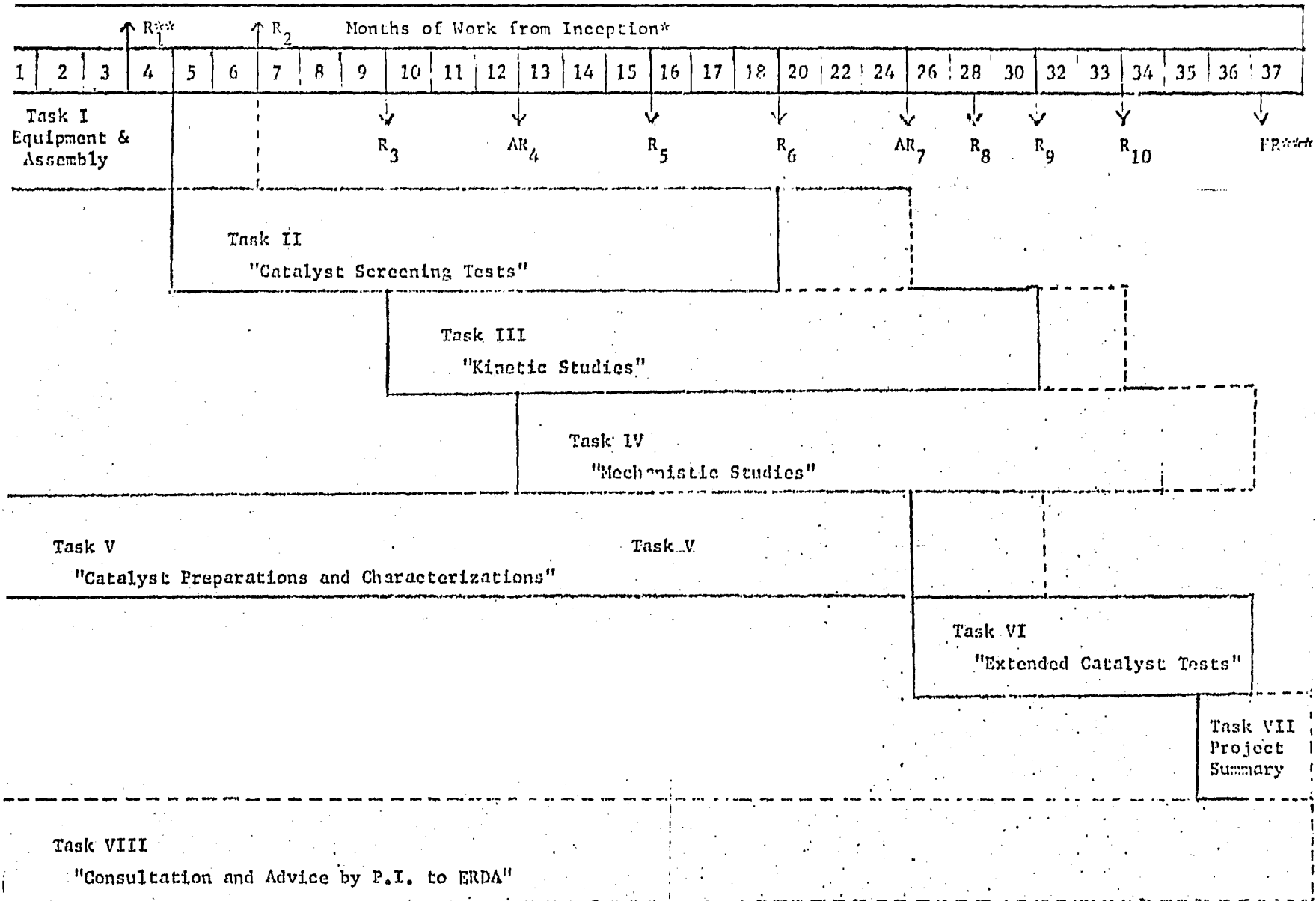
The data obtained from Tasks 1 through 6 shall be summarized and interpreted in the final report on the contract. This final report shall include the advantages and disadvantages of each catalyst system, the economics of production of SNG and SLPG from coal-derived synthesis gas using different catalyst formulations, and recommendations for additional research in the field of catalytic synthesis of gaseous hydrocarbons.

8. Task No. 8

The Principal Investigator shall furnish consultation and advice on subject related to his expertise, at such times and places as mutually agreed upon.

These tasks shall proceed according to the following tentative schedule.

Table A1 Tasks Schedules



\* - The dashed lines indicate possible overruns or extended periods of work in a given task.

\*\* - Technical report due dates. \*\*\* - Final report.

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