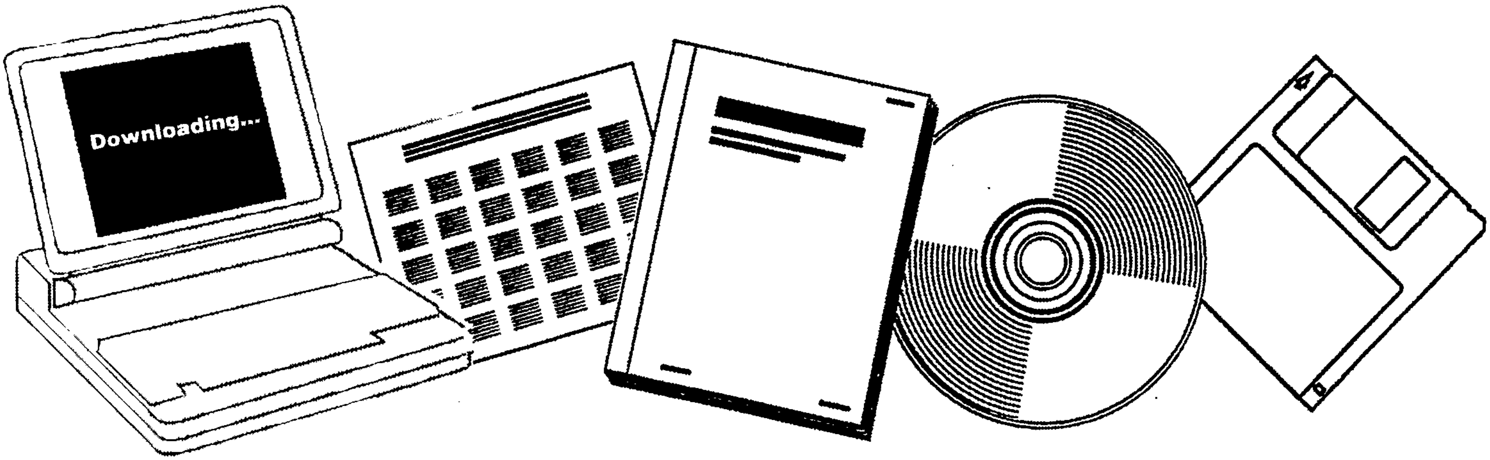
CATALYTIC SYNTHESIS OF GASEOUS HYDROCARBONS. QUARTERLY REPORT, DECEMBER 1975--FEBRUARY 1976

CARNEGIE-MELLON UNIV.
PITTSBURGH, PA

MAR 1976



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CATALYTIC SYNTHESIS OF GASEOUS HYDROCARBONS

Quarterly Report for the Period
December, 1975-February, 1976

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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 syntheses. To accomplish the first objective, two versatile catalytic reactor units (CRU-1 and CRU-2) will be employed to screen a variety of iron-, cobalt- and nickel-based catalysts. Careful attention will be given to product selectivity. To accomplish the second objective, infrared spectroscopic techniques will be coupled with traditional mechanistic studies. The role of poisons in affecting the concentration and nature of surface intermediates will be investigated.

During this third quarterly period, work has been devoted primarily to the areas of equipment assembly (Task I), catalyst screening tests (Task II), and preliminary mechanistic studies (Task IV). In the area of the first task, the second catalytic reactor unit (CRU-2) was completed and two of the three non-dispensive infrared analyzers were calibrated. The problem with the CO_2 analyzer was traced to an error in shipment by MSA.

In the area of Task II, three catalyst tests were completed on an iron-based Fischer-Tropsch catalyst (100 Fe:5 Cu:30 CaO:100 Kgh, alkali free). The results provided valuable training experience as well as an assessment of the performance of CRU-1. Modifications in the unit are underway to make the unit more convenient to operate. In the area of Task IV electron micrographic studies determined that the reason for the poor quality infrared spectra of nickel aerosol was due to greater coagulation of the aerosol particles than anticipated. Modeling of the aerosol-generation technique is being continued.

In conclusion, the completion of CRU-2 and the experiences gained in the initial catalyst tests on CRU-1 should speed the return of this research program to the original Task schedules.

. 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 ($CO + 3H_2 \underset{Cat}{\rightarrow} CH_4 + H_2O$) 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 C_2-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.

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 third quarterly period, work has been devoted to: (a) the completion of the assembly of Catalytic Reactor Unit-2; (b) preliminary tests on an iron-based Fischer-Tropsch catalyst with CRU-1 for Tasks II and III; and (c) background studies for Task IV.

In the area of Task I, CRU-2 assembly was completed and the unit has been pressure-tested. The unit is now ready for catalyst testing. In addition, the problem encountered with the CO$_2$ NDIR analyzer was traced to an incorrectly sensitized instrument (carbon monoxide instead of carbon dioxide). The instrument is in the process of being replaced.

In the area of Task II, three test runs were completed on CRU-1 using an iron-based, alkali-free, Fischer-Tropsch catalyst (100 Fe:5 Cu: 30 CaO:100 Kgh). The runs were approximately 48 hours in duration and served to provide experience in operating the unit as well as assessing the performance of the unit and the catalysts. Problems encountered with plugging of the reactor by solid paraffins during the first run and with ineffective trays during the next two runs prompted the modification of the unit. These modifications will make the unit more convenient to operate and are in progress.

In the area of Task IV, electron micrographs of nickel aerosol powder were examined. The results showed that the two methods of sample collection gave equivalent results which suggests that the samples collected for catalytic experiments are representative of the nickel aerosol. These two samples were observed to have individual particle sizes which were quite close to those determined from the BET adsorption data, which indicates that the particles are non-porous. In addition, it was observed that significant necking of the individual particles produces aggregates which greatly impair our ability to observe infrared spectra.

In conclusion, the completion of CRU-2 and the experiences gained from operating CRU-1 should accelerate the return of this research program to the original tasks schedules.

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 intermediate formed during the catalytic reactions on these catalysts; and e) measuring catalysts 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 equipment constitutes the assignment of the first task (Task I). While much of this work was accomplished during the first two quarterly periods, the remainder was completed during this third period. Preliminary work in Task II, which began during the second quarterly period, was continued; an iron-based Fischer-Tropsch catalyst was tested in three runs. In addition, background work involving the characterization of nickel aerosol-generated powders for Task IV was continued. For a complete description of the various tasks and the corresponding timetable, see Appendix A.

A. Task I - Equipment Assembly and Testing

Table 1 summarizes the work accomplished in Task I during the first quarterly period. Column 3 describes the subtasks that were involved and column 2 represents the number of weeks involved with each of these subtasks.

Table 2 summarizes the work accomplished in Task I during the second quarterly period and that scheduled for this third period. We noted delays in accomplishing several subtasks due to either unexpected delays in receipt of equipment from suppliers or to a backlog of work in the Mellon Institute's instruments shop. As a result, these subtasks were rescheduled for the third quarterly period.

Table 3 summarizes the work accomplished during this third quarter and that scheduled for the fourth period. Upon comparison with Table 2, it is seen that the delays noted earlier have propagated through this period such that the integration of the analytical package (NDIR's and gas

Table 1 First Quarter Task I Projects: Equipment Assembly and Testing

Item No.	(No. Weeks to Complete Subtask)[+]	Subtasks Description
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 CSTCR 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 NDIR 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.

Table 2 Second Quarter Task I Projects: Equipment Assembly and Testing

Item No.	(No. Weeks to Complete Subtask)[+]	Subtasks Description
1	((4[*],[**]))	Design and fabrication of electrical components of CRU-2.
2	((8[**]))	Panel mounting of MSA NDIR analyzers, recorder and programmed sequencing times.
3	((6[**]))	Electrical overhaul and panel mounting of temperature recorders.
4	2	Complete shakedown of CRU-1 at "reaction test" conditions.
5	2	Redesign and modification of CRU-1's reactor and preheater system.
6	1	Temperature retest of CRU-1 prior to catalyst reduction.
7	2	Assembly and modifications of gas chromatographic analytical system.
8	2	Installation of common gas delivery system for CRU-1 and CRU-2.
9	1	Panel mounting of temperature recorders.
10	(3)	Completion of fabrication of CRU-2 piping system.
11	(3)	Pressure and temperature tests of CRU-2.
12	(1)	Further evaluation of NDIR analyzers to unravel CO_2 problem.
13	(1)	Flow controller calibrations for CRU-2.
14	(2)	Complete shakedown of CRU-2.
15	(2)	Integration of analytical package with CRU-1 and CRU-2.
Total # Wks	24	

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

[*] Half of this work was performed by Mellon Institute's Instruments Shop personnel.

[**] These subtasks were performed by Mellon Institute's Instruments Shop personnel and are not counted as part of the total number of weeks devoted to the task.

Table 3 Schedule of Remaining Task I Projects

Item No.	(No. Weeks to Complete Subtask)[+]	Subtasks Description
1	3	Completion of fabrication of CRU-2 piping system.
2	3,(1)	Pressure and temperature test of CRU-2.
3	1	Solution to CO_2 NDIR analyzer "problem".
4	1,(2)	Flow controller calibrations for CRU-2.
5	1,(2)	Complete shakedown of CRU-2.
6	(1)	Modification of CRU-1 flow system for greater operational convenience.
7	1,(1)	Modification of CRU-1 condensers and traps network.
8	(1)	Modifications to gas chromatographic system.
9	(2)	Integration of analytical package with CRU-1 and CRU-2.
Total # Wks	20	

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

chromatography) must await the next quarterly period. However, all of the other subtasks were accomplished, and are described in greater detail below. As a result of work undertaken in Task II, several modifications to CRU-1 are required and have been scheduled for the fourth quarter. These are shown in Table 3 also.

1. Catalytic Reactor Unit-2

In the second quarterly report, we indicated that whereas work on CRU-1 was progressing at the expected rate, work on CRU-2 lagged behind schedule. Therefore, a major effort during this third period involved bringing this second unit back onto schedule. As a result of those efforts, the fabrication of CRU-2 has been completed and the unit is ready for operation. Figure 1 is a schematic of CRU-2 with the gas delivery system. Figure 2 is a diagram of the traps and condenser network for this unit and Figure 3 is a photograph of the unit during the early stages of assembly. The gas cylinders shown in the background (Figure 3) are connected via overhead piping to the gas delivery panel (see Figure 1).

The purpose of the network of traps and condensers (Figure 2) is to remove water and other liquid products from the gas stream prior to its entrance either to the non-dispersive infrared (NDIR) analyzers which monitor concentrations of carbon monoxide, methane and carbon dioxide or to the gas chromatograph which measures the concentrations of C_1-C_5 hydrocarbons produced during the reaction. A detailed drawing of trap #2 is shown in Figure 4. The final design is the result of lessons learned from operation of CRU-1 (to be discussed later). The trap consists of a one-liter Whitey sample cylinder (Crawford Fitting Company) fitted with a bored-through, 1/2-inch male run tee through which a 1/4-inch stainless-steel tube is placed. The end of the tube is bent in such a manner as to ensure impingement of the gas stream on the inner wall of the cylinder thereby improving cooling efficiency and vapor-liquid separation. Liquid product removal is achieved at the bottom of the cylinder which also contains a thermocouple for temperature measurement. Leak testing of the assembled traps was accomplished by immersing the cylinders in a tube of water, pressurizing with helium to 400 psig for a period of 12 hours. The assembly was considered to be leak tight when the pressure drop over this period was less than 2 psig. Often the male run tees required silver soldering to achieve leak tightness.

The reactor indicated in Figure 1 (not shown in Figure 3) is an internally recycled catalytic reactor obtained from Autoclave Engineers. A diagram of the reactor is shown in Figure 5. This reactor system consists of a magnetically driven impeller located directly under a variable volume catalyst bed. As the impeller rotates, gas is recycled through the bed at a rate proportional to the rotation of the impeller. In this manner, continuous stirred tank reactor (CSTR) conditions can be achieved. Thus, kinetic modeling is greatly simplified for this unit as well as reduction of the temperature rise in the catalyst bed due to the exothermicity of the Fischer-Tropsch reactions.

This unit has been successfully tested and is ready for catalyst testing following prolonged temperature tests at operating pressures and completion of the calibration of the flow controllers.

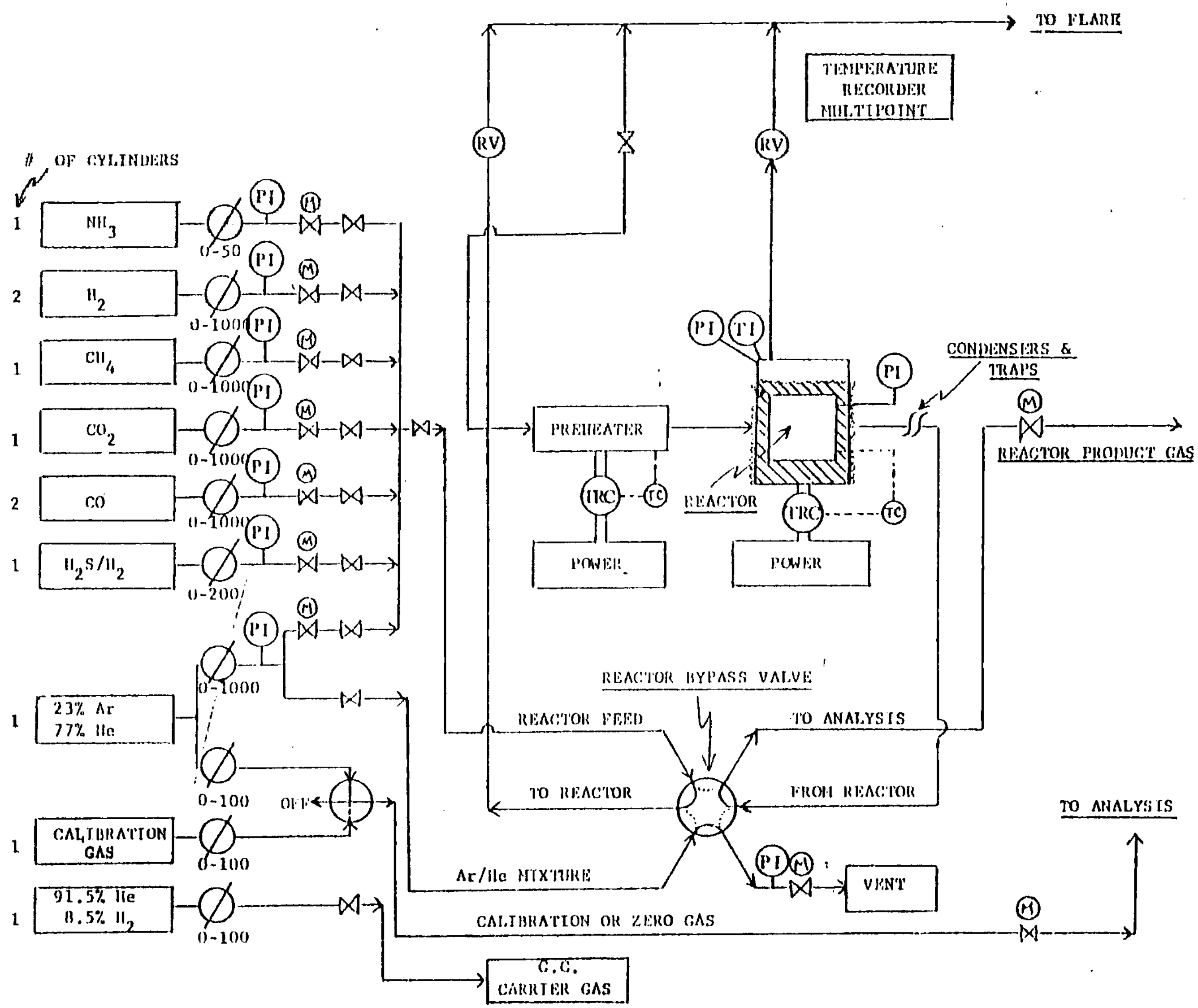
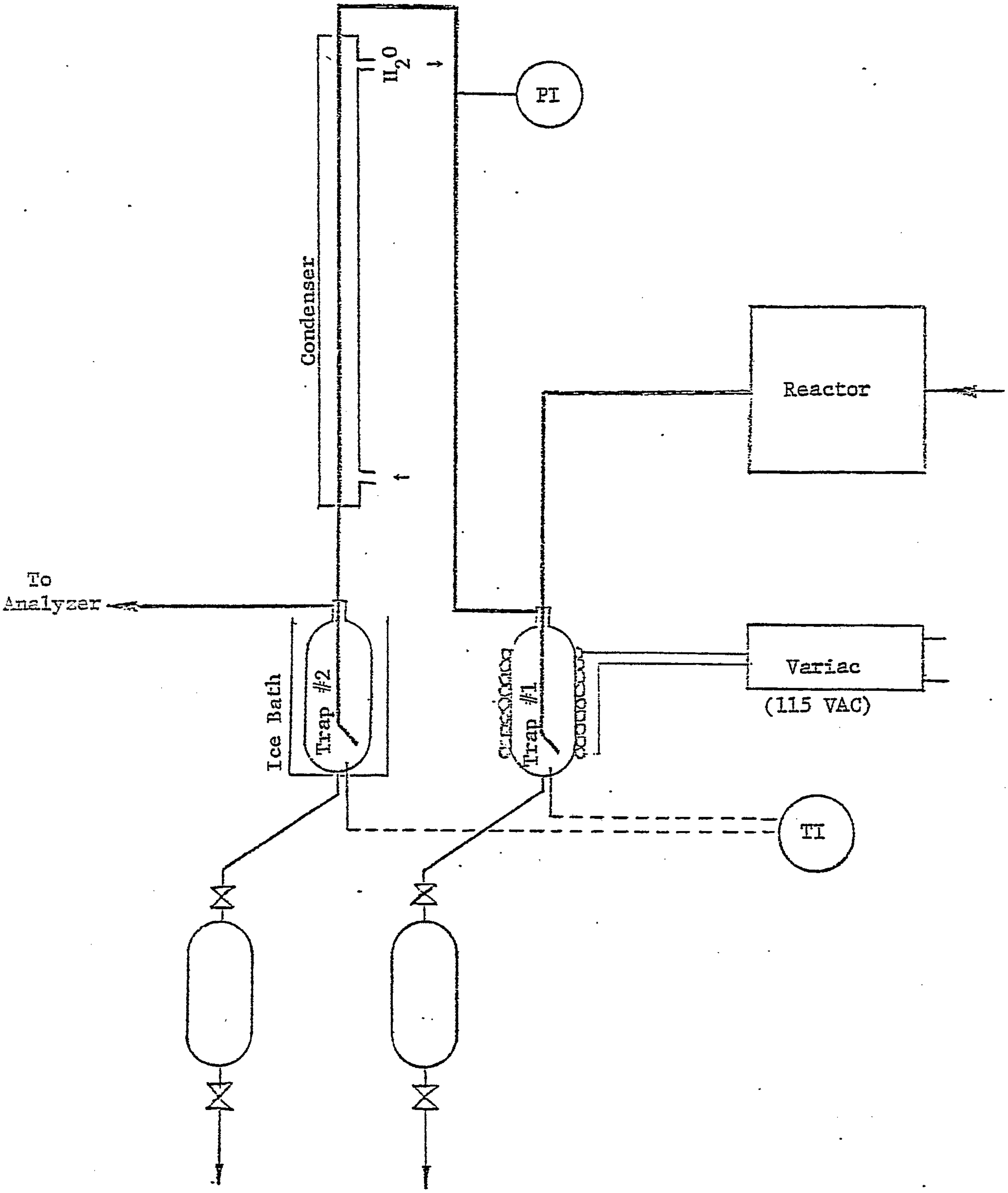


Figure 1 - Catalytic Reactor Unit-2

Figure 2. Traps and Condenser Network for GRU-2



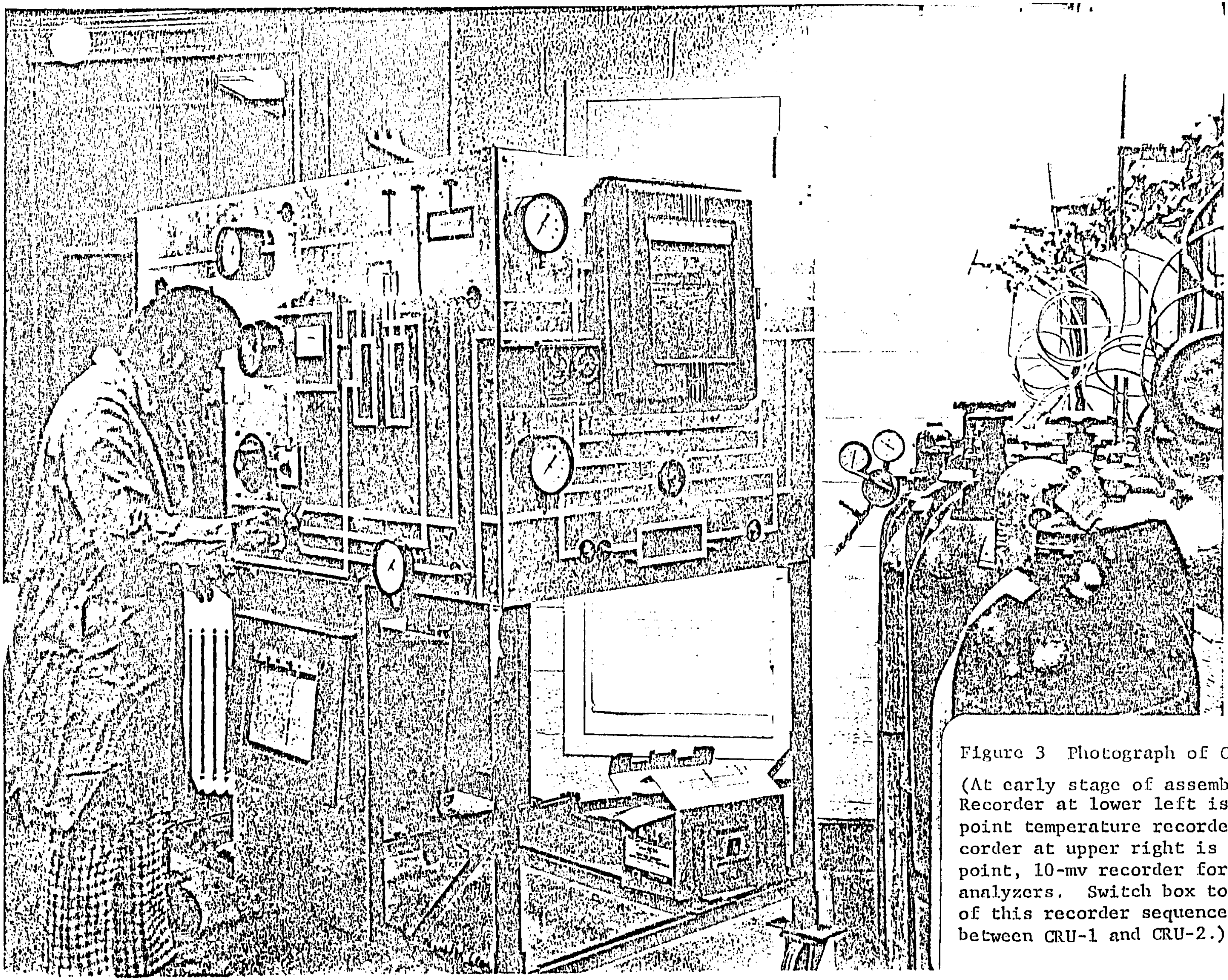


Figure 3 Photograph of CRU-2

(At early stage of assembly. Recorder at lower left is a 12-point temperature recorder; recorder at upper right is a 3-point, 10-mv recorder for NDIR analyzers. Switch box to left of this recorder sequences time between CRU-1 and CRU-2.)

Figure 4 Schematic of Trap Design

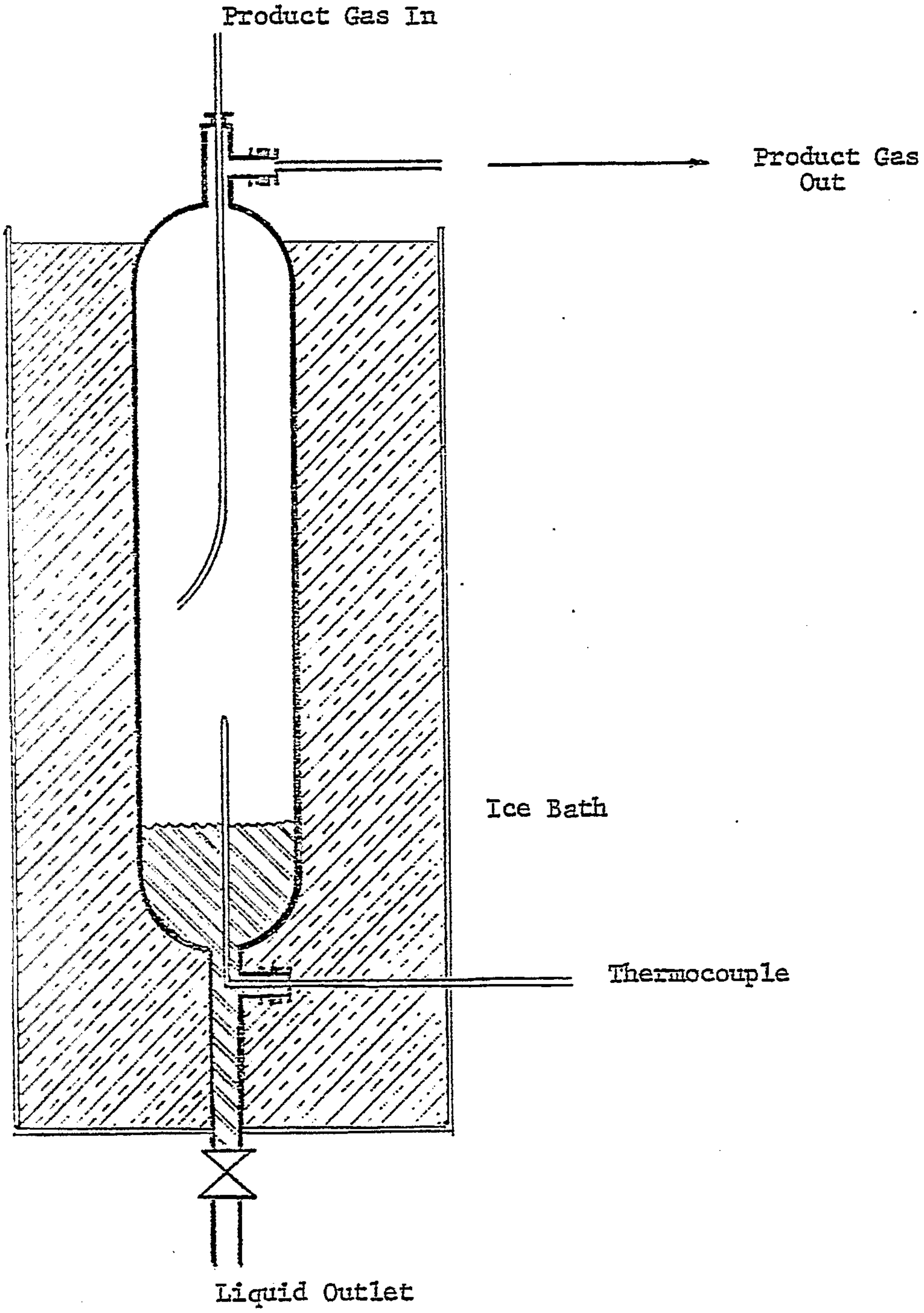
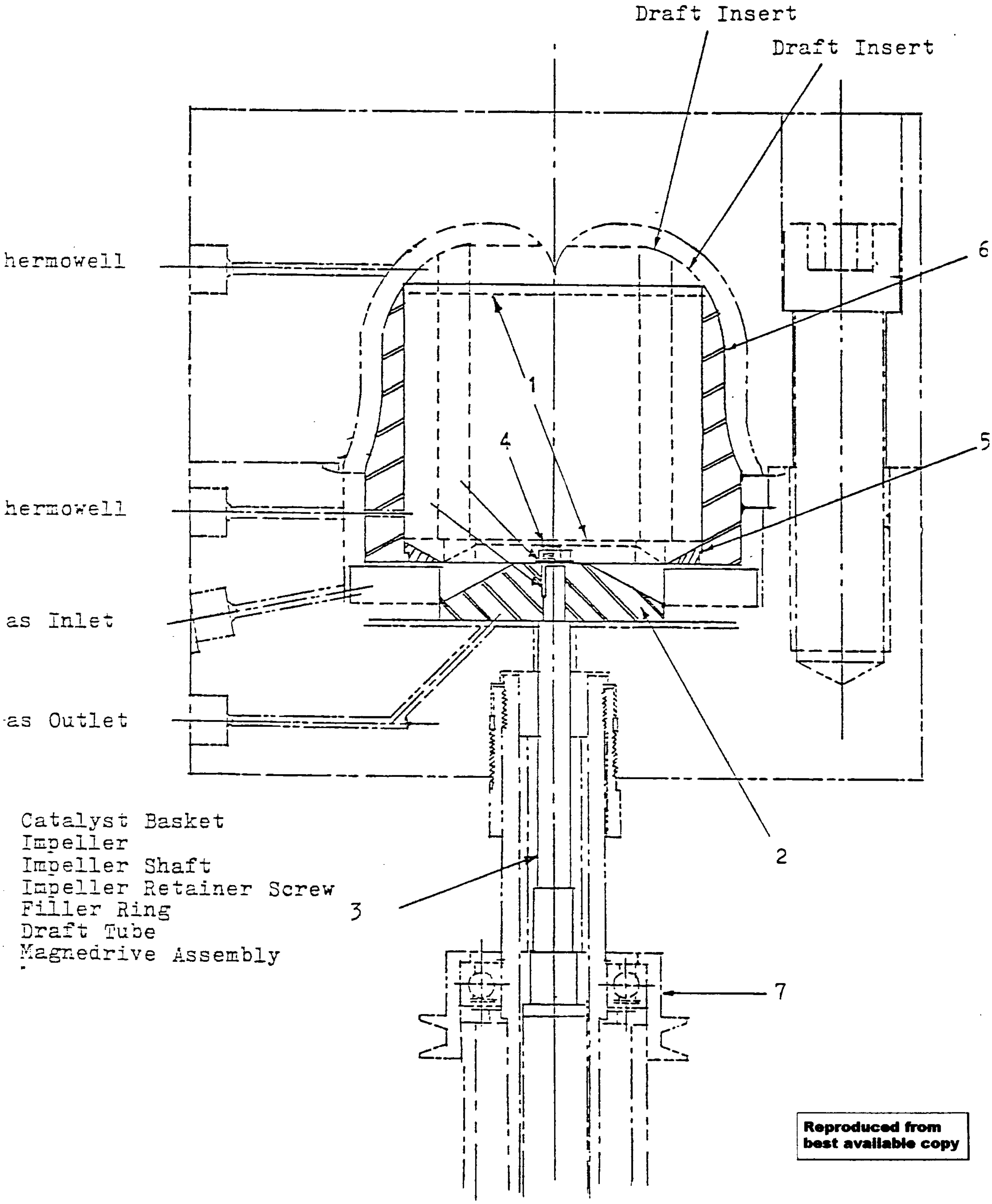


Figure 5 Internally Recycled Catalytic Reactor



2. Catalytic Reactor Unit-1

Following the first catalyst screening test (discussed later) in CRU-1, it was apparent that several modifications were required. These modifications consisted of improving the condenser system to remove a greater amount of the liquid products from the gas stream and a simplification of the flow system to improve operating convenience. These modifications have begun and will be completed during the next quarter.

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. This package was described in detail in the first quarterly report. All of the components arrived during the second period and were panel mounted into a mobile unit by Mellon Institute's instruments shop. This unit is shown in Figure 6.

In the second quarterly report, we noted that the carbon dioxide analyzer appeared to be less responsive than its specifications predicted it should have been. Further investigation established that the unit had been incorrectly sensitized. In fact, the unit shipped was actually a carbon monoxide analyzer. This unit was subsequently replaced by Mine Safety Appliances. However, the replacement unit also proved to be unsatisfactory since it was sensitized for 0-100 millivolts, whereas the specifications stipulated a sensitivity of 0-10 mv (to be compatible with the 3-point, 10 mv recorder housed in the unit). This second unit is expected to be replaced in the very near future. The methane and carbon monoxide analyzers were tested thoroughly by blends of synthesis gas using the gas-delivery system of CRU-2.

4. Task I - Summary and Work Forecast for Fourth Quarter

Table 3 summarizes the work that is scheduled for the next quarterly period. Several modifications of CRU-1 will be undertaken to improve the operation of that unit and, thereby, facilitate the Task II assignment scheduled for continuation.

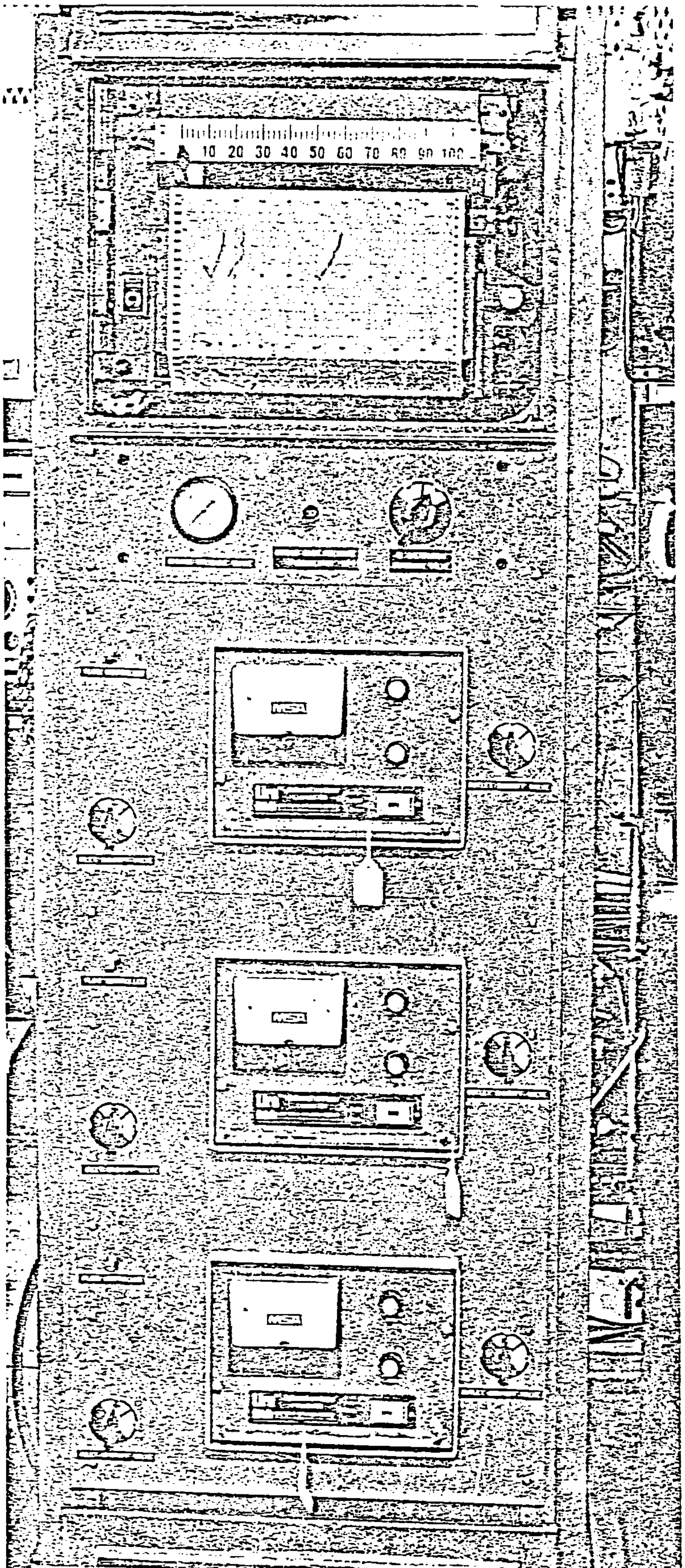


Figure 6 NDIR Analyzers

(10 mv Recorder at top of Panel; below are CH_4, CO and CO_2 analyzers, respectively.

B. Task II - Catalysts Screening Tests

1. Introduction

Task II represents the most important task in this research project -- the development of catalysts for the synthesis of gaseous hydrocarbons. The primary goal of this project is to alter the typical product distribution indicated by the solid lines of Figure 7 to that indicated by the dotted curve. This will be accomplished by a careful analysis of the process variables including catalyst choice, reactor temperature and pressure, and H_2/CO ratio.

Work on this task began as scheduled during the second quarterly period. To ensure safety of operation as well as facility of reactant gas blending, reactor control and product analyses, preliminary studies involving olefin hydrogenation over a thoria promoted nickel catalyst preceded the experiments involving hydrogenation of carbon monoxide. These studies proved to be a useful method of training new personnel in catalytic research.

Since the studies of Franz Fischer and Hans Tropsch during the 1920's in which they reported[1] that alkalized iron turnings at 100-150 atm of hydrogen plus carbon monoxide and at 400-500°C catalyzed the production of oxygenated and aliphatic hydrocarbons, considerable efforts have been devoted to understanding this synthesis and to improving its efficiency. Excellent reviews by Storch, Anderson and Golumbic[2] and by Greyson[3] summarize much of the earlier work in this field; recent reviews by Mills and Steffgen[4] and by Vlasenko and Yuzefovich[5] update the literature on this subject. Lee, Feldkirchner and Tajbl[6] and Vannice[7] have discussed kinetic studies over a number of catalysts. Some features which were obtained from an analysis of this vast quantity of information that have a direct bearing of the objectives of this research are summarized below.

a. Pressure Effect:

(1) For iron and cobalt catalysts, the average molecular weight of hydrocarbon products increases with operating pressure up to 15 or 20 atm.

(2) For iron and cobalt catalysts, the fraction of olefins decreases slightly with increases in the operating pressure.

b. Temperature Effect:

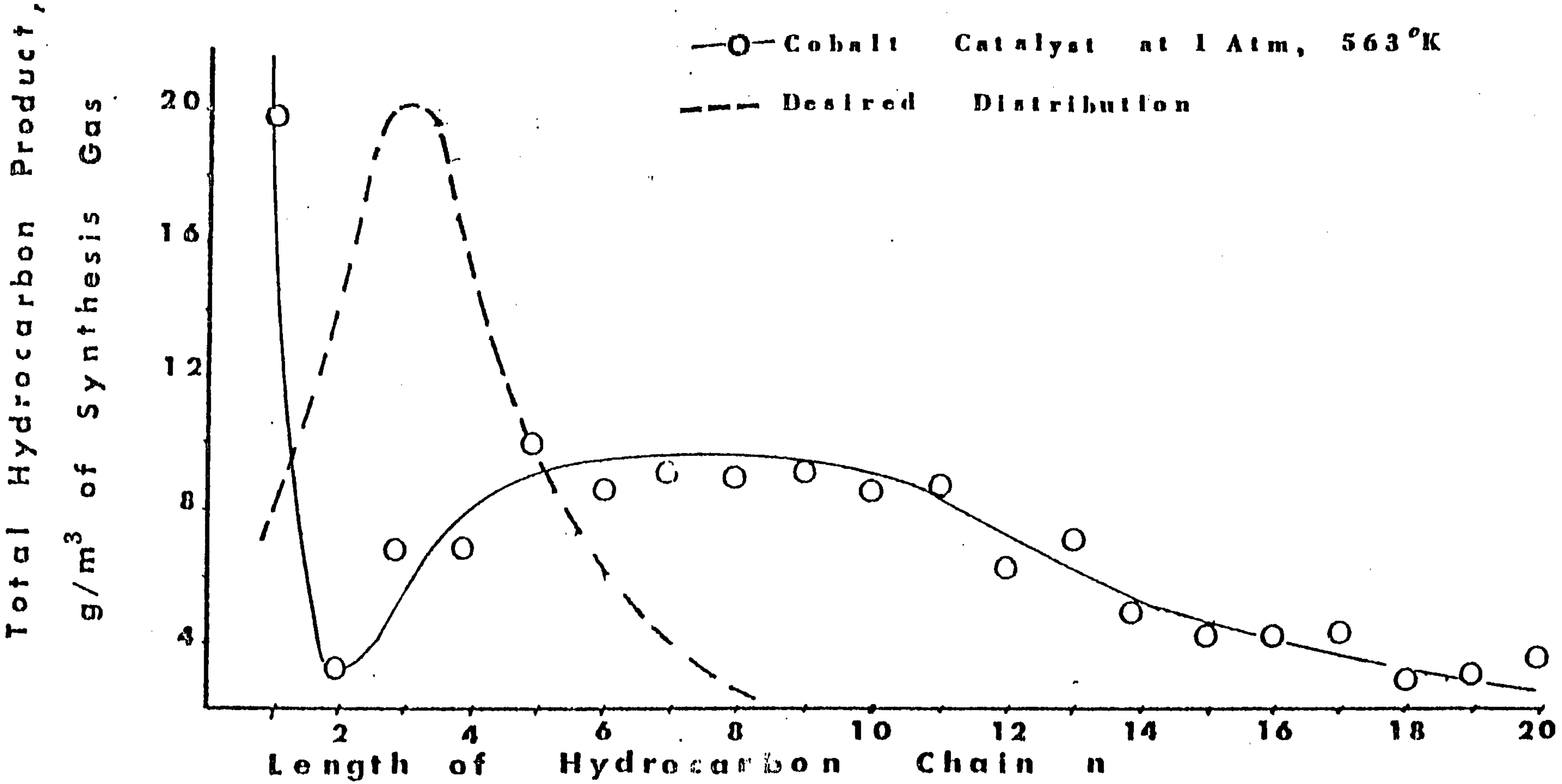
(1) For iron catalysts, the fraction of olefins increases with the operating temperature, whereas for cobalt catalysts, the olefin fraction doesn't change much with temperature.

(2) For iron and cobalt catalysts, the average molecular weight of hydrocarbon products decreases with increasing temperatures.

FIGURE 7 Product Distribution

vs.

Length of Hydrocarbon Chain



c. H_2/CO Ratio Effect:

(1) For cobalt catalysts, the fraction of solid paraffins is greater with a 2:1 than with a 1:1 ratio.

(2) For iron catalysts, the fraction of light hydrocarbons (C_1-C_4) is greater with 2:1 than with a 1:1 ratio.

While there are considerably more aspects of the work reported in the literature which are important to the studies proposed for this work, the above features will serve to orient our catalyst screening program. It must be kept in mind, however, that the objectives of past Fischer-Tropsch researches focused on the production of liquid hydrocarbons from hydrogen and carbon monoxide mixtures, and, therefore, the catalysts were modified accordingly to produce the product distributions indicated by the solid line of Figure 7. Therefore, such generalizations as noted above will serve merely as guidelines for future work on this project.

2. Catalyst Screening Tests

Table 4 summarizes the results of three test runs on catalyst number Fe-Cu-CaO-Kg-SZ-7. This typical Fischer-Tropsch type catalyst has the nominal composition of 100 Fe:5 Cu:30 CaO:100 kieselguhr and was prepared by the coprecipitation of the nitrates of iron, copper and calcium (slurried with kieselguhr) by the addition of a boiling solution of ammonium carbonate so as to be alkali free. Care was taken during subsequent washings to remove traces of nitrates to ensure that the catalyst remained alkali free. A similar catalyst (Fe-Cu-CaO-Kg-SZ-8) containing potassium carbonate is scheduled for water studies to test alkali effects.

Reduction of the catalyst in CRU-1's fixed-bed reactor was achieved in hydrogen at 20 psig and 450°C at a space velocity of 800 hr^{-1} for two days. Following reduction, the catalyst was cooled to 150°C under a hydrogen pressure of 40 psig. Synthesis was started at this temperature by stepwise increasing the carbon monoxide and helium pressures after a six-hour period until the final desired composition was achieved. This conditioning period is similar to that of Dry and coworkers[8] to stabilize iron catalysts.

The primary objective of the initial run was to train the research associate in the manipulation of a Fischer-Tropsch reactor. As anticipated, several problems were encountered during the course of this run. The main problem was pressure instability due to plugging of the lines downstream from the reactor by solid paraffins. The cause of this problem was insufficient heating and insulation of the exit lines; correction was achieved during operation by infrared heaters. However, as a result of these "corrections", the cooling system was inadequate to remove all of the liquid products from the gas stream. Obviously, this resulted in condensation in unexpected places, thus causing greater pressure instability. The run was terminated at that point and the unit was disassembled and inspected. Most of the problems were corrected prior to runs 2 and 3.

Table 4 Results of Screening Test on an Iron Catalyst[a,b]

Run No.	H_2:CO:He	Space Velocity $cm^3/hr^{-1}/cm^{d,c}$ of Catalyst[c]	Temperature	Conversion Based on CO[d]	% CH_4 in Product[e]	% CO_2 in Product[e]	Comments
1[f]	2:1:7	2727	240°C	60.5%	0.9%	0.27%	Considerable waxes and heavy liquids formed
2[g]	2:1:7	6080	250°C	15.6%	0.4%	0.05%	C_{10}^{+} paraffins, alcohols and ketones
3[g]	4:1:0	6480	240°C	19.5%	0.4%	0.04%	Greatest amt H_2O, alcohols, C_1-C_{16}-HC's

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[a] Catalyst: 100 Fe:5Cu:30 CaO:100 kieselguhr (~ 100 mesh size)

[b] Reactor Pressure = 100 psig; total reaction time ≈ 48 hours

[c] Total Flow Rate = 3 liters/min.

[d] Conversion (x) defined as:

$$x = \frac{([CO] + [CO_2]_{in} - ([CO] + [CO_2])_{out}}{([CO] + [CO_2])_{in}}$$

[e] Percentages based on NDIR analyses

[f] 45.95 grams of catalyst used

[g] 21.06 grams of catalyst mixed with 42.12 grams of alumina

In runs 2 and 3, it became apparent that occasional checks of the stability of the feed composition by gas chromatographic or NDIR analysis required interruption of the flow through the reactor. Since this caused some discontinuity in the state of the catalyst's surface conditions of undetermined nature, it was decided to modify the flow system at this point. In addition to the above noted inconveniences, it also became apparent that the traps were not operating as designed. As a result, the gas chromatographic analyses required considerably longer time for completion than desirable due to the slow elution of the higher molecular weight hydrocarbons. Thus, modification of the traps to those described in Figure 4 also is planned. While these modifications are scheduled for early during the next period, a schematic of the modified CRU-1 was completed and is shown in Figure 8. When completed, the unit will contain two multiport valves similar to those installed on CRU-2 to greatly facilitate convenience of operation.

3. Task II's Summary and Forecasts for Next Quarter

As indicated above, actual catalysts testing began during this quarter. Three runs on iron-based standard Fischer-Tropsch type catalysts (prepared to be alkali free) were completed. The result of these three runs was to indicate necessary modifications in CRU-1. These modifications, as indicated above, will improve greatly its convenience of operation and simplify product analyses by GC. They have been scheduled and appear in Table 3. However, during the next quarter the major effort will be devoted to further tests with this iron catalyst to verify the generalization as outlined. Table 5 summarizes these planned experiments.

C. Background Work for Task IV - Mechanistic Studies

The objective of this task is to obtain a fundamental understanding of the hydrogenation of carbon monoxide reaction. As noted earlier, mixtures of hydrogen and carbon monoxide react to form methane under one set of conditions (methanation) or higher hydrocarbons (alkanes, olefins and alcohols) -- the Fischer-Tropsch synthesis under another set of conditions. Since the catalysts are similar in many respects, the initial reaction intermediates, i.e. similar reaction mechanisms, must be common to both systems. Therefore, studies involving the characterization of reaction intermediates and surface species should be useful in understanding both reaction systems. Such studies, therefore, must involve techniques which permit the elucidation of relevant surface species. The coupling of infrared spectroscopic techniques with traditional mechanistic studies offers the greatest potential for providing the needed information. Techniques are being developed to facilitate such studies for both supported and unsupported metal catalysts under this task.

To date the major effort has been devoted to developing a technique to study unsupported metal catalysts by infrared spectroscopy. Since the details of this aerosol-bed technique for a nickel catalyst were reported in the first quarterly report, we will focus on work accomplished during this third period and indicate what future experiments are planned. However, a quick review of the technique might prove more informative.

Figure 8 Modified Catalytic Reactor Unit-1

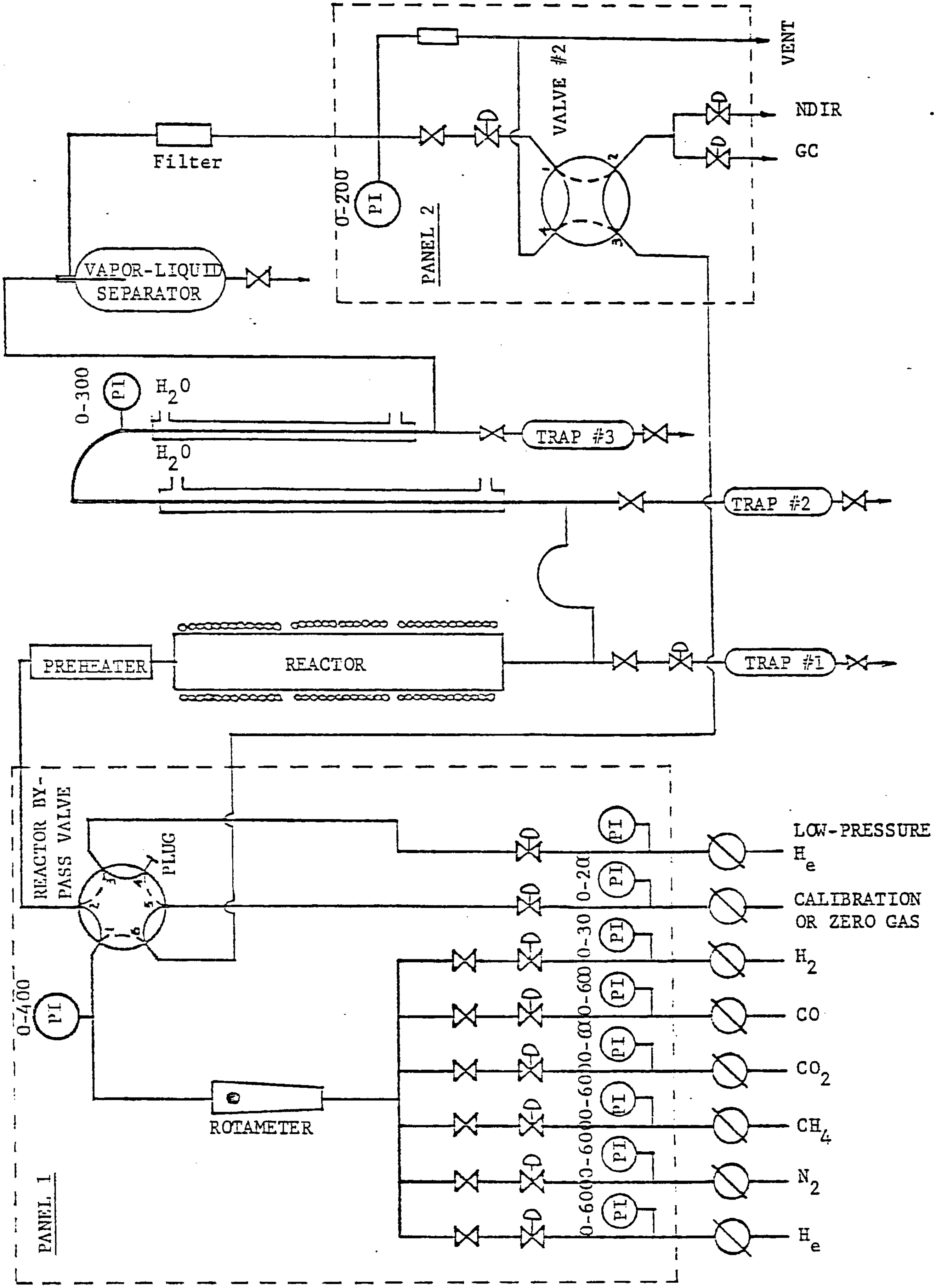

Table 5 Scheduled Test Runs with Iron Catalysts

Composition H_2:CO:He	Space Velocity[a] hr^{-1}	Temperature °C
2:1:7	6000	275
		300
		240
	9000	275
		300
3:1:6	6000	240
		275
		300
	9000	275
		300

1. A System for Studies of Nickel Aerosols in the Infrared

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. Adsorbate gases can be injected into the aerosol just prior to entrance to the infrared cell. 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_2, CO_2, 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.

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.

To date, this project has evolved to the stage where all of the earlier problems associated with removing 16-kilowatts of heat from the 2-liter vaporization chamber have been solved. As a result, we can generate aerosol routinely for any desired period. We have noted, however, that during several prolonged runs (2 to 3 hours of aerosol generation) the operating characteristics of the torch changed noticeably. The effect of these slight changes have been to produce drastic changes in the background spectrum. The overall effect is to produce a poor quality spectrum which makes interpretation difficult if not impossible. We have traced the source of these problems to uncontrollable oscillations in the current supplied by the two welding machines which operate the plasma torch. Since we have been able to establish a strong correlation between the operating current level and the aerosol generation rates, we currently are exploring methods to exercise greater control over this behavior. A complete analysis of the system's operating characteristics is in progress. While this system's of aerosol fluctuations has limited infrared studies, it has not prevented us from characterizing the catalytic properties of the aerosol. These are described in the next section.

2. Physical Characterization of the Aerosol Particles

Physical characterization consisted of electron microscope examination of the particles and surface area measurements using physical adsorption of argon at liquid nitrogen temperature (77°K). The surface area measurements were reported in the second quarterly report and are summarized in Figure 9 as a function of the generation rate of the aerosol. These data are the results of several experiments obtained at a high torch-gas flow rate (60 SCFH, ϴ) and at a low torch-gas flow rate (29 SCFH, A), and they suggest a means of producing a range of surface areas of unsupported nickel powders by this technique.

The Debye-Scherrer electron diffraction pattern was obtained from a sample of material which had been exposed to the atmosphere for several months. The sample still retained its typical intense black color, indicating it was not completely transformed to nickel oxide which is grey in color. However, the electron diffraction pattern definitely indicated the presence of nickel oxide. This is illustrated by Table 6 where the first eight rings in the pattern are assigned to line numbers (corresponding to lattice planes). The measured interplanar spacings were calculated from the radius of the rings.

Figures 10, 11 and 12 are electron micrographs of the nickel aerosol powder during this same generation run. The BET surface area of this material was 44.2 m^2/g which is equivalent to a spherical diameter of 153 Å. Figure 10 which has a magnification of 25,000X (1 cm = 0.4 microns) indicates that the particles cluster in a "tree branch" configuration with an approximate size of 1-2 microns per aggregate (longest length). This will be detrimental to infrared studies of the aerosol. Figure 11 represents an 8-fold magnification (1 cm = 500 Å) of this same sample. Here the individual particles can be observed to have a size close to that predicted by the BET measurements. (No statistical analysis was employed to confirm this.) This material was collected by a point-to-plane electrostatic precipitation (P-T-P) technique which directly sampled the nickel aerosol.

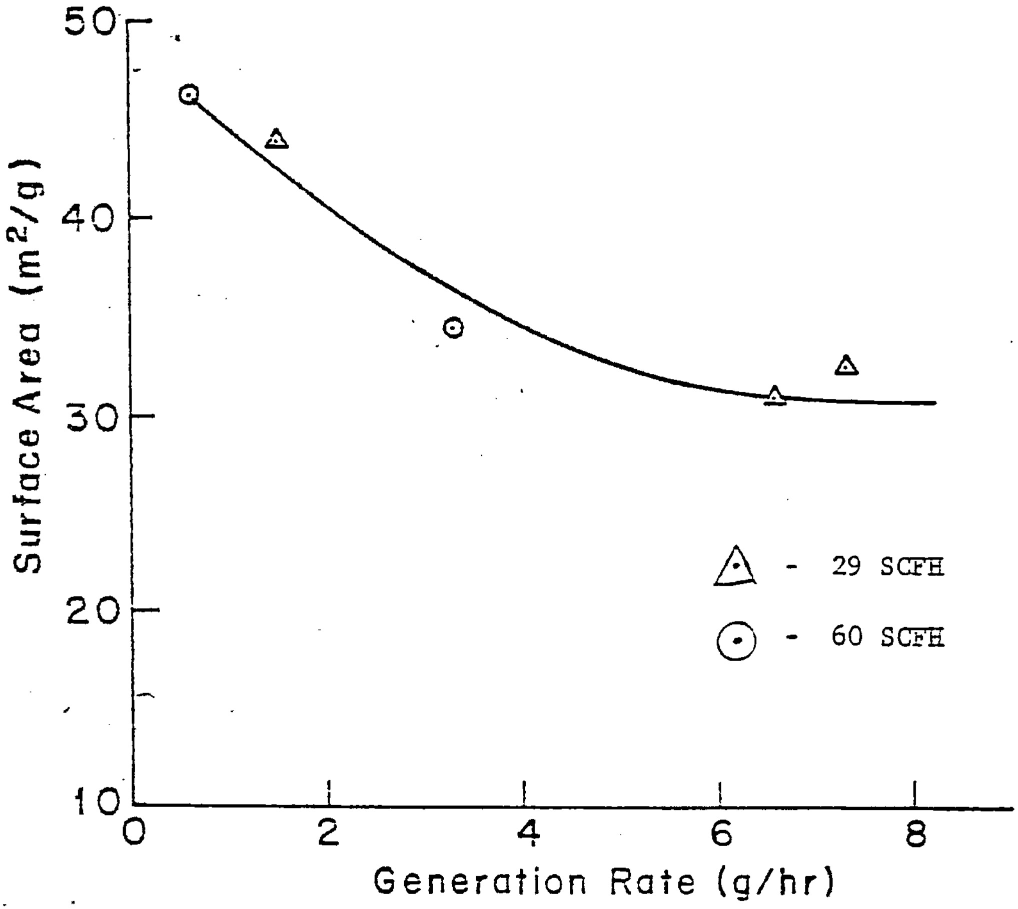

FIG. 9 SURFACE AREA VS. GENERATION RATE

Table 6 Debye Scherrer Electron Diffraction Data[d]

Line No.(a)	Interplanar(b) Spacing Calc. NiO	Interplanar Spacing (Measured)	Interplanar(c) Spacing Calc. Ni	Interplanar Spacing (Measured)
1	4.20			
2	2.97	3.17		
3	2.42		2.03	
4	2.10		1.76	1.77
5	1.88			
6	1.71			
7	1.59			
8	1.48	1.51	1.25	
9	1.40			
10	1.33			
11	1.27	1.28	1.06	1.08
12	1.21		1.02	
13	1.16			
14	1.12			
15	1.08	1.08		
16	1.05		0.881	.881
17	1.02			
18	0.99			
19	0.96		0.808	.804
20	0.94	.92	0.788	

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[a] $N = (h^2 + k^2 + \ell^2)$

[b] $d = 3.524\ N^{-1/2}$ NiO is simple cubic

[c] $d = 4.195\ N^{-1/2}$ Ni is face centered cubic and only line numbers corresponding to this structure are tabulated

[d] All spacing in Angstrom units.

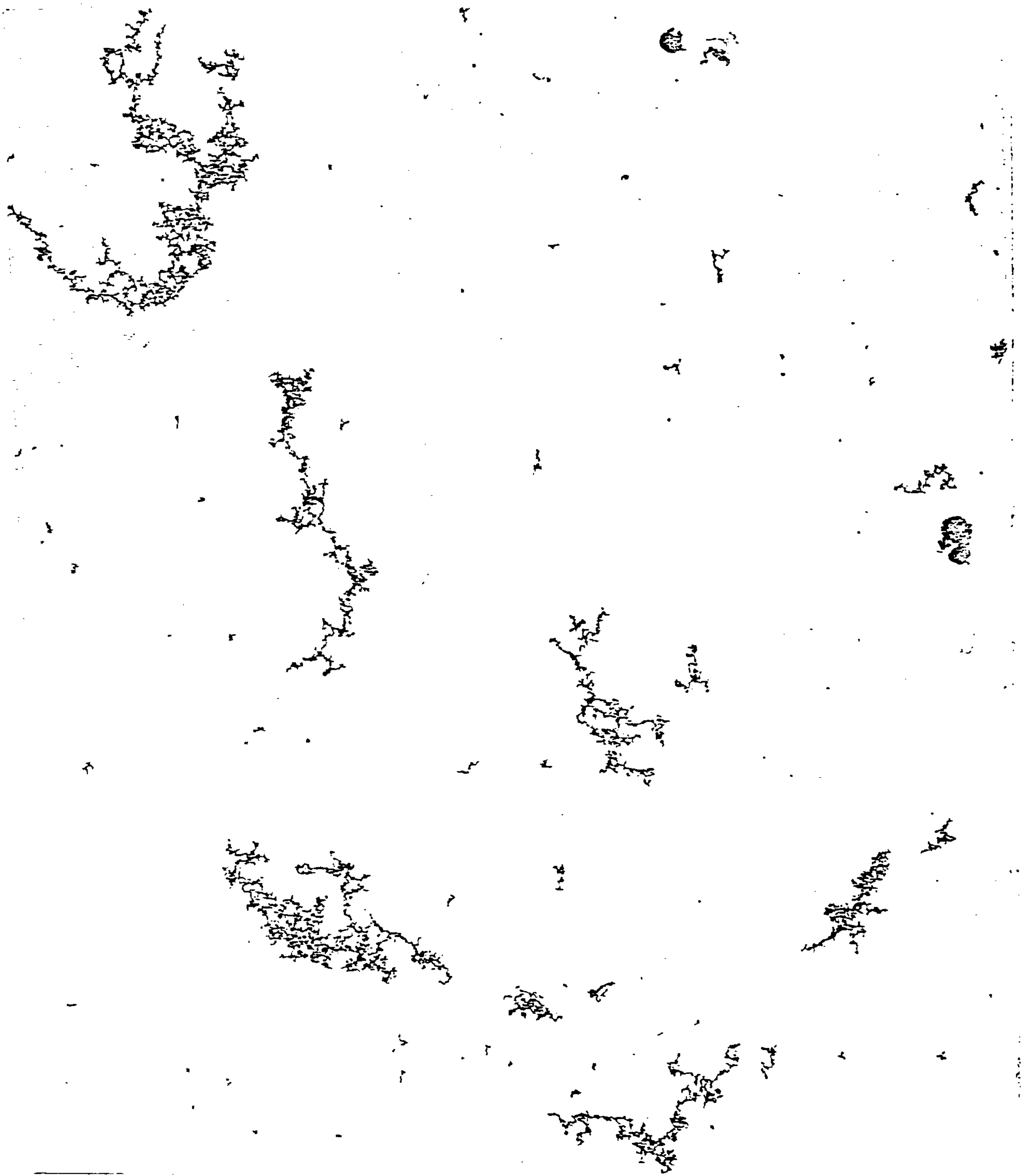

Figure 10 Electron Micrograph of Particles Collected by P-T-P Electrostatic Precipitation Magnification 25,000X

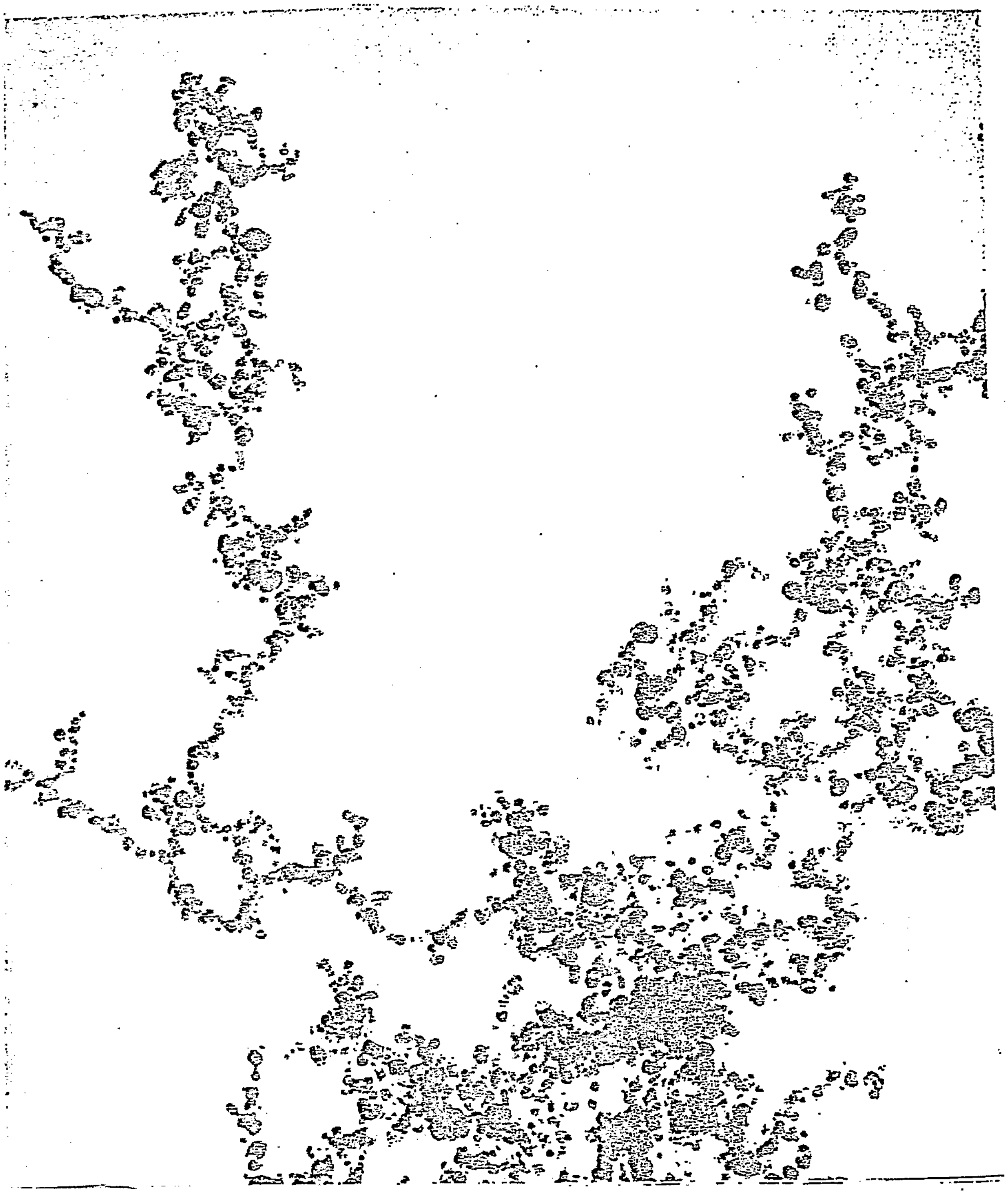

Figure 11 Electron Micrograph of Particles Collected by P-T-P Electrostatic Precipitation Magnification 200,000X

Figure 12   Electron Micrograph of Particles Collected by Forced Coagulation Magnification 200,000X

On the other hand, Figure 12 which also has a magnification of 200,000X (1 cm = 500 Å) was collected (during the same run) on a "Millipore membrane" (Millipore Co.) by drawing the aerosol through the membrane with the aid of a vacuum pump. The micrograph shows that this "forced" coagulation method produces layers of the material which must be fractured into pieces, but the sample features are similar to the P-T-P sample. Both figures show that there is significant necking between individual particles, thus indicating at least some growth by coagulation. This coagulation probably occurs during the very early stages of particle generation.

3. Catalytic Hydrogenation Studies

We reported earlier that the catalytic activity of the aerosol generated nickel powder had been studied by ethylene hydrogenation at room temperature. Analysis of the data show that this nickel is quite active catalytically. Since an extensive literature review of ethylene hydrogenation is still in progress, the significance of these results have not been assessed fully. Therefore, we will delay further discussion until the next quarterly period.

4. Summary and Task Forecasts

In summary, the electron micrographs have indicated that: (1) the method of sample has no effect on the aerosol powder which implies that the samples collected for catalytic experiments by forced coagulation (i.e., "Millipore" membranes) should be representative of the aerosol; (2) the observed individual particle size (~ 150 Å) is quite comparable to that calculated from the BET adsorption data, indicating that the material is non-porous; and (3) significant necking between individual particles produce aggregates about 1-2 microns in size which will significantly reduce the infrared transmission of the aerosol. Unless deaggregation can be achieved, the prospects for infrared studies are seriously jeopardized. On the other hand, considerable progress towards an infrared technique for studying unsupported metal catalysts has been made. The front portions of the unit have been completed and a fundamental understanding of how the system works is becoming more apparent. For example, Figure 9 indicates that a range of surface areas and, equivalently, particle sizes can be produced by judicious choice of operating conditions. This opens up the possibility of investigations of catalyst activity as a function of particle size for this material, which should be very interesting.

During the next quarter, the ethylene hydrogenation analysis will be completed and design of a system for studying the hydrogenation of benzene will be undertaken.

IV. CONCLUSIONS

Throughout the previous sections, we have stated the work accomplishments during this quarterly period. In Task I, Catalytic Reactor Unit-2 (CRU-2) was completed and pressure tested. A problem associated with the CO_2 NDIR analyzer was traced to an error in the calibration and shipment of the instrument by MSA. A new instrument has been promised for delivery within a week. In Task II, three runs on an iron-based, alkali free, Fischer-Tropsch catalyst provided needed experience in manipulation of CRU-1 and also indicated the need for minor modifications to make the unit more convenient to operate. A greater understanding of the nature of the arc-vaporized nickel aerosol was achieved through an electron micrographic study of the nickel powder.

This research program has returned to the originally proposed schedule for completion of tasks.

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VI. APPENDIX A - CONTRACT TASKS

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

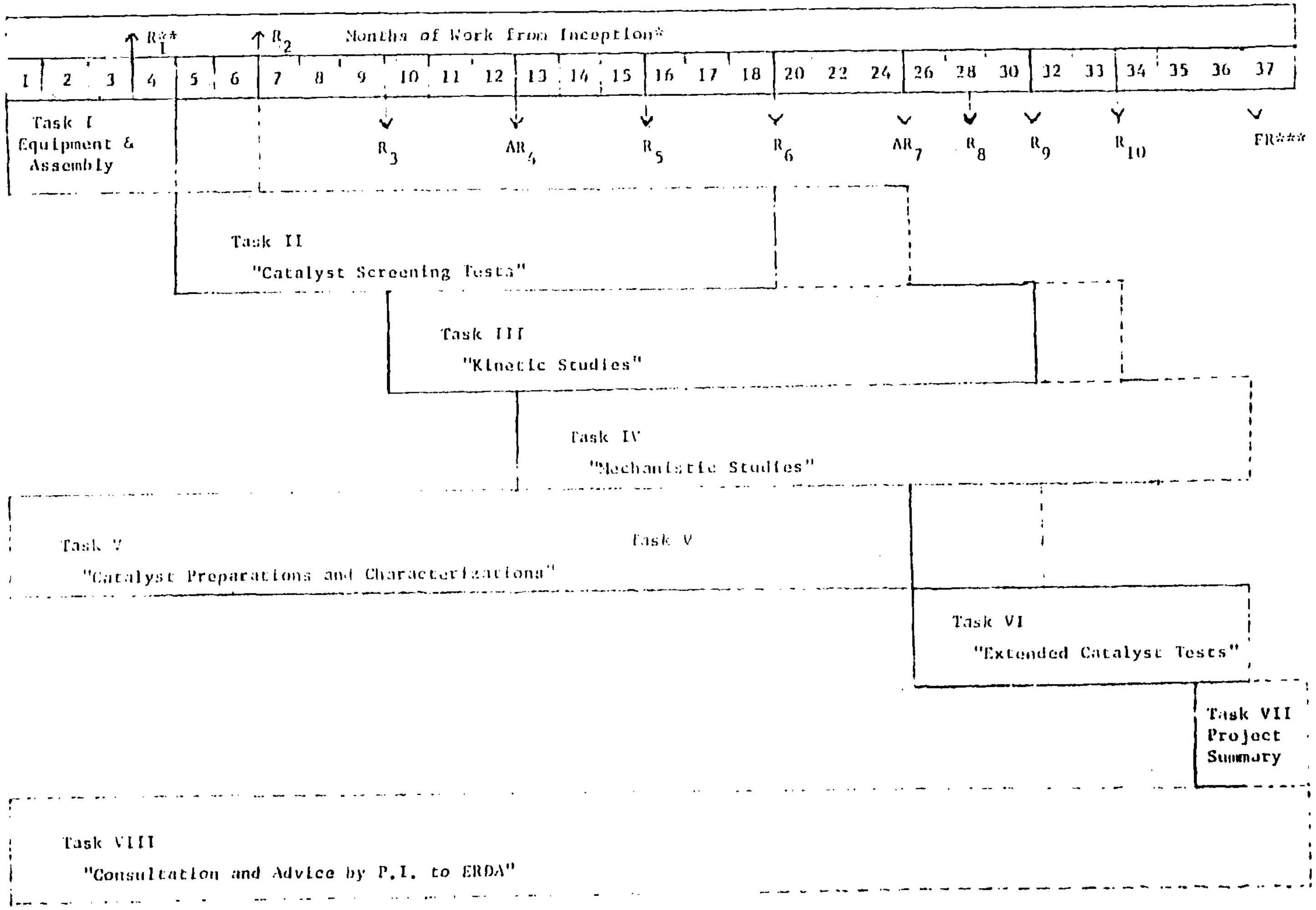
The data obtained from Tasks 1 through 6 shall be summarized and interpreted in the final report on the contract. This final report shall include the advantages and disadvantages of each catalyst system, the economics of production of SNG and SLPG from coal-derived synthesis gas using different catalyst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