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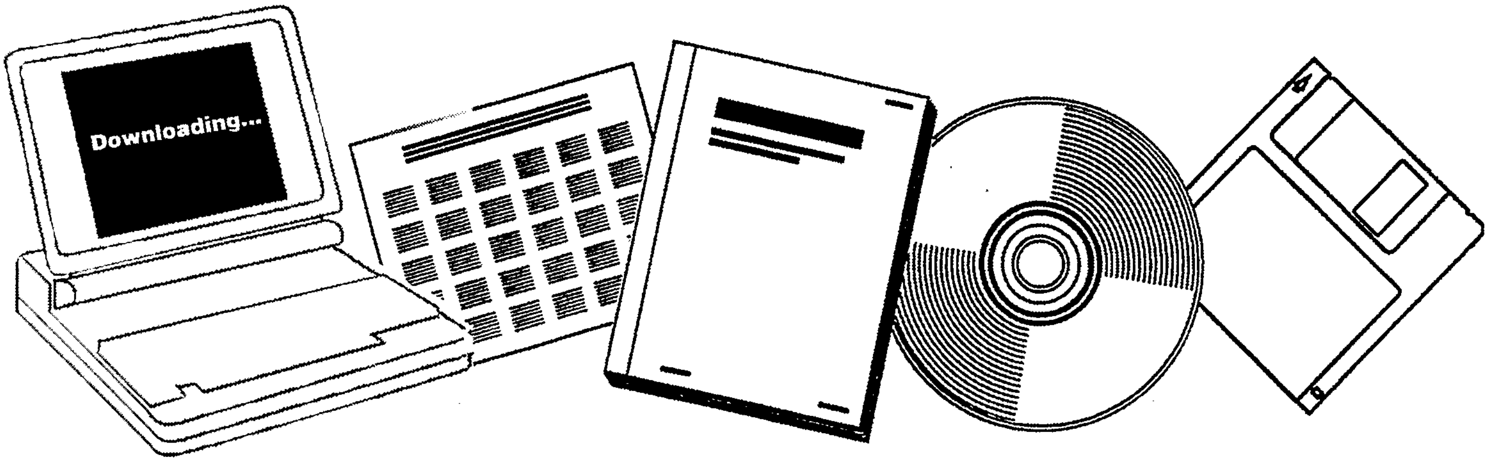
CATALYTIC SYNTHESIS OF GASEOUS HYDROCARBONS. QUARTERLY REPORT, SEPTEMBER--NOVEMBER, 1975

CARNEGIE-MELLON UNIV.
PITTSBURGH, PA

DEC 1975



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MASTER

Quarterly Report for the
Period September-November, 1975

Dr. Anthony L. Dent

CARNEGIE-MELLON UNIVERSITY
PITTSBURGH, PENNSYLVANIA 15213

Report Date - December, 1975

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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

Patent Cleared
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TABLE OF CONTENTS

List of Tables

List of Figures

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 second quarterly period, work has been devoted primarily to the areas of equipment assembly (Task I), preliminary catalyst screening tests (Task II), and preliminary mechanistic studies (Task IV). In the area of the first task, improved temperature flexibility of CRU-1 has been achieved by a modification of the reactor's furnace and preheater. CRU-2's electrical components have been completed and installed, as well as the panel mounting and testing of the three non-dispersive infrared analyzers and the assembly of the gas-chromatographic system.

In the area of Task II, a training program utilizing olefin hydrogenation was undertaken to prepare for the initial tests of a typical Fischer-Tropsch catalyst in CRU-1 which is scheduled for the next quarter. In the area of Task IV, poor quality infrared spectra of nickel aerosols has prompted a detailed modeling of the aerosol-generation method. In addition, considerable effort has been devoted to unraveling the complex olefin hydrogenation data reported in the first quarterly report.

In conclusion, despite several unexpected delays in equipment fabrication for CRU-2 in University shops, and unusually lengthy delivery periods by manufacturers, the project is proceeding without 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 $(CO + 3H_2 \underset{cat}{\rightleftarrows} CH_4 + H_2O)$ 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.

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 second quarterly period, work has been devoted to: (a) the completion of the assembly of two (2) catalytic reactor units which will be employed in work described in Tasks II, III, and IV; (b) preliminary work for Tasks II and IV.

In the area of Task I, a redesign and modification of catalytic reactor-1's (CRU-1) preheater and reactor furnace became necessary to improve the temperature flexibility of that unit. As a result, temperatures of 400-500°C required for catalyst reduction more easily are attainable. The Berty internally recycled catalytic reactor arrived from Autoclave Engineers; the necessary electrical components for its heating jacket have been fabricated, and the unit has been installed in CRU-2. In addition, the Mine Safety Appliances' NDIR analyzers for carbon monoxide, methane and carbon dioxide arrived; the analyzers have been panel mounted in a cabinet which also contains a 3-point mV recorder. With the exception of the CO_2 analyzer, which shows exceptionally poor sensitivity, the unit is operating according to manufacturer's specifications. Finally, all of the components required for the complete analysis of product gas by gas chromatography have arrived from Varian and are being assembled.

In the area of Task II, the hydrogenation of olefins over a kieselguhr supported nickel catalyst was employed to train operators in the safe techniques of catalyst reduction by hydrogen, reactant gas blending, and product analyses. While mass-transfer effects proved to dominate the surface reactions in these studies, the indications were that such effects would be unimportant in the much slower Fischer-Tropsch synthesis to be studied.

In the area of Task IV, a greater effort has been devoted to modeling the nickel-aerosol generation method in an effort to understand the poor quality infrared spectra obtained, and to unraveling the complex reactions involved in the hydrogenation of olefins over nickel catalysts. An all-glass cell which facilitates collection of BET samples has been fabricated.

In conclusion, despite several unexpected delays in equipment fabrication in University shops, and prolonged delivery of equipment by several manufacturers, no major changes in milestone scheduling are warranted.

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 apparatus constitutes the assignment of the first task (Task I). While much of this work was accomplished during the first quarterly period, the remainder was undertaken during this second period. In addition, preliminary work was initiated in Task II, as well as the continuation of preliminary work for Task IV. 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 the third period. Due to delays either in receipt of equipment from suppliers, for example, the Berty CSTR purchased from Autoclave Engineers, arrived eight weeks beyond their revised delivery date, and the Valco automatic gas sampling valves arrived ten weeks beyond Varian's assured delivery date, or backlogs in Mellon Institute's Instruments Shop, many of the items originally scheduled for completion during the second quarter had to be rescheduled for later dates. This was most notable with respect to CRU-2 components. Nonetheless, we were able to complete all of the scheduled subtasks related to CRU-1 and the analytical system. These are described in greater detail below.

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

Subtasks

Item No.	(No. Weeks to Complete Subtask)+	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 Schedule of Remaining Task I Projects

Item No.	(No. Weeks to Complete Subtaks)[+]	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.

1. Catalytic Reactor Unit-1

Catalytic Reactor Unit-1 (CRU-1) is essentially a fixed-bed reactor system designed for Fischer-Tropsch and methanation catalysts screening tests. It should, therefore, be capable of operating in the temperature range from 100 to 400°C and a pressure range from 0 to 200 psig. The original design consisted of a gas-delivery system employing very fine metering valves (operated at sonic flow conditions) capable of blending seven gas streams to feed a fixed-bed, 1-inch, tubular reactor. This reactor was temperature controlled by boiling Dowtherm. After several preliminary trials involving prolonged runs at 400°C to achieve adequate catalyst reduction, severe erosion of the reactor tube was observed as well as noticeable deterioration of the Dowtherm. In addition, temperatures above 400°C were difficult to maintain. Fortunately, a 3-zoned 2-1/2 in. diameter tube furnace became available from another project in the laboratory at this time. Consequently, the decision was made to evaluate this furnace for stable operation. The system was modified to accommodate this furnace. Figure 1 shows details including positions of the thermocouples. Each of the three zones are 8-inches in length and controlled by a temperature controller; the first two zones are used for preheating the feed gas to reaction temperature before entering the third zone or catalyst bed. These zones are packed with ceramic beads to provide adequate turbulence and gas heat-up. The third zone controls the temperature of the catalyst bed (which has a maximum bed volume of 90 cm^3). Thermocouples are placed at regularly spaced intervals within the reactor tube as well as at four positions on the skin of the reactor. Heat transfer calculations based on the usual correlations for forced convection in packed circular tubes* provided an indication of the length of the preheat zone required for specified conditions of skin temperature and desired bed temperatures. These calculations and subsequent experiments, wherein the temperature profiles through the preheat and catalyst bed zones were measured, indicated that the 16-inch preheat zone was more than adequate to maintain an isothermal bed. In addition, these tests indicated that steady-state temperature profiles were established within twenty minutes of a step-change increase in the furnace temperatures. Temperatures of 450°C could be achieved within thirty minutes when the initial temperature was room temperature.

Table 3 shows the results of a study in which the performance of the seven sonic-nozzle flow controllers were evaluated. Column 2 indicates the total flow rates while compositions are given in columns 3-7. The last column gives the relative peak areas based on carbon monoxide. The results indicates that the greatest scatter in the data resulted from the nitrogen data. However, all of the results show less than a five percent deviation from the mean values, thus, indicating that good flow control can be achieved over a range of flow rates in a reproducible manner.

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*See for example, R.B. Bird, W.E. Stewart and E.N. Lightfoot, Transport Phenomena, J. Wiley and Sons, Inc., New York (1960), pp 396-412.

FIGURE 1. CRU- 1 REACTOR and FURNACE

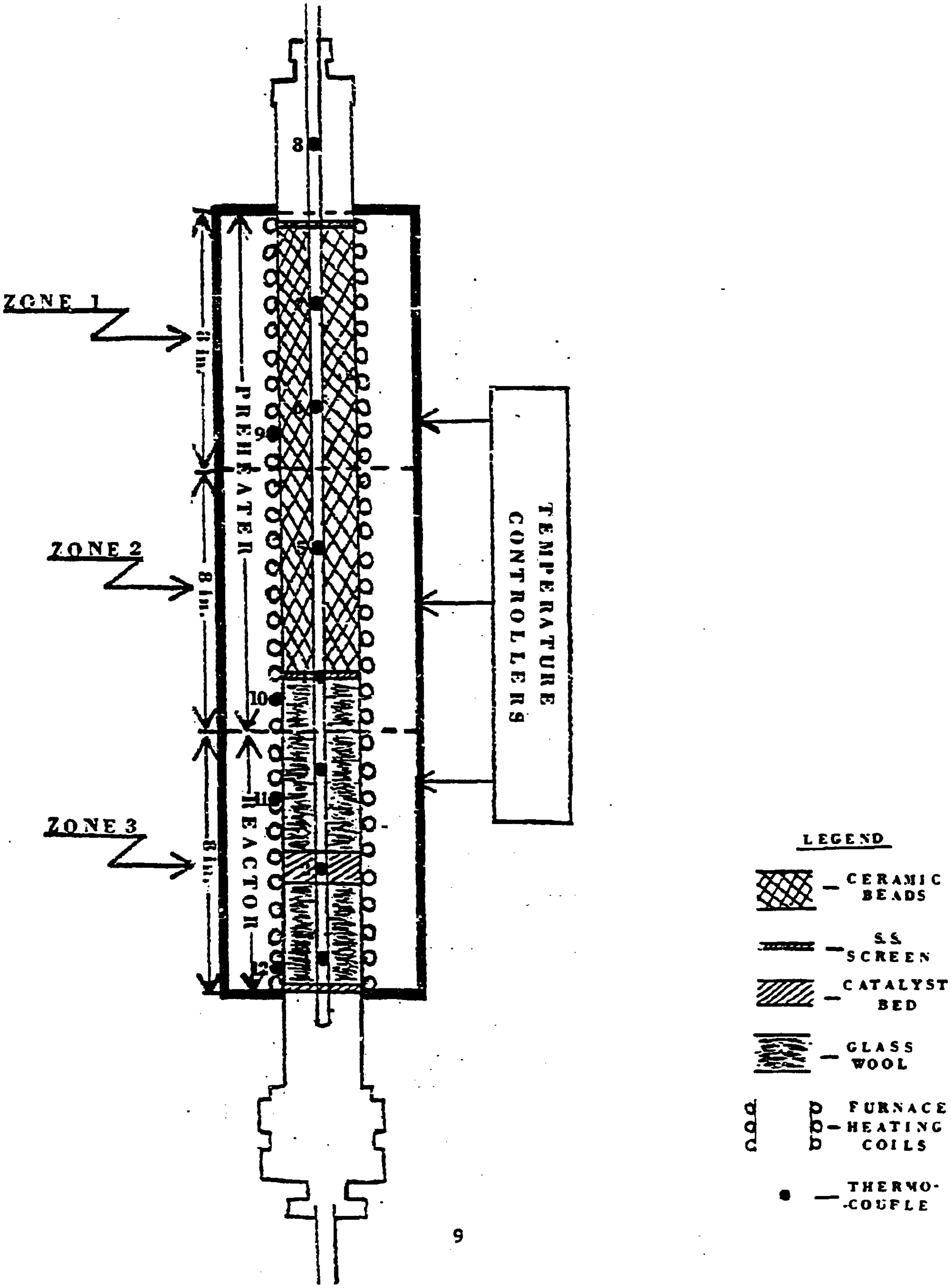


Table 3 Evaluation of Sonic Nozzles for Flow Measurement by Gas Chromatography[a]

Run #	Total Flow Rates (cm^3/min)	Mole % Component					Peak Area Rates[b] Relative to CO		
		H_2	AR	N_2	CO	He	H_2/CO	Ar/CO	N_2/CO
1	1741.3	22.28	27.59	16.71	22.81	10.61	0.0273	1.238	0.737
2	1741.3	22.28	27.59	16.71	22.81	10.61	0.0276	1.258	0.835
3	1741.3	22.28	27.59	16.71	22.81	10.61	0.0271	1.253	0.824
4	1556.6	24.92	30.87	19.00	25.52	—	0.0269	1.233	0.814
5	1556.6	24.92	30.87	19.00	25.52	—	0.0276	1.236	0.812
6	1915.8	20.25	25.08	15.19	20.73	18.75	0.0281	1.244	0.849
7	1915.8	20.25	25.08	15.19	20.73	18.75	0.0277	1.250	0.820
8	2960.7	13.10	16.23	9.83	13.42	47.42	0.0284	1.252	0.874
							<0.0276> ± 1.6%	<1.240> ± 0.7%	<0.821> ± 4.8%

---

[a] Gas chromatography done on Perkin-Elmer Model 154C using a 50:50 mixture of molecular sieves 13X and 5A at 100°C. Carrier gas was helium at 60cc/min. Peak integration accomplished using the Varian CDS-101 data analyzer. Sample size = 2cm^3.

[b] Relative flow ratios (Xi/CO) are constant at H_2/CO = 0.977; Ar/CO = 1.210; and N_2/CO = 0.733.

2. Catalytic Reactor Unit-2

Whereas, work on CRU-1 is proceeding at the expected rate, work on CRU-2 has lagged, somewhat, behind schedule. This is due in part to delays by suppliers but more so by a backlog of work scheduled for completion by the Mellon Institute Instruments Shop. The major piece of equipment, the Berty CSTR reactor, finally arrived and is being installed. This unit contains a 3-kilowatt heated jacket. Since the Nanmac temperature controllers cannot handle this high wattage, a mercury relay switch had to be fabricated to provide the necessary temperature control. This system has been installed and is being tested.

The gas delivery system which will be common for both reactor units has been installed. This unit consists of high-pressure gas manifolds which allow two or three gas cylinders to be connected in parallel. In this manner test runs of several days duration can be accomplished. For convenience and safety the gas cylinders were installed along one wall of the laboratory; 1/4-inch stainless-steel tubing runs overhead to connect these cylinders to the gas delivery panel. In Figure 2, this unit is located in the center of the photograph. Gases can be distributed to both reactors from this panel.

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 which were outstanding arrived during this period. The three NDIR analyzers for CO_2, CH_4 and CO were sent immediately to Mellon Institute for panel mounting in a unit which contains the analyzers and a 3-point-10 millivolt recorder. In Figure 2, the unit is located on the far left. Currently the unit is being tested with several blends of gases. The carbon dioxide analyzer appears to be less responsive than its specifications indicate that it should be. This problem will be examined further during the next quarterly period. Training of personnel on these instruments is otherwise in progress.

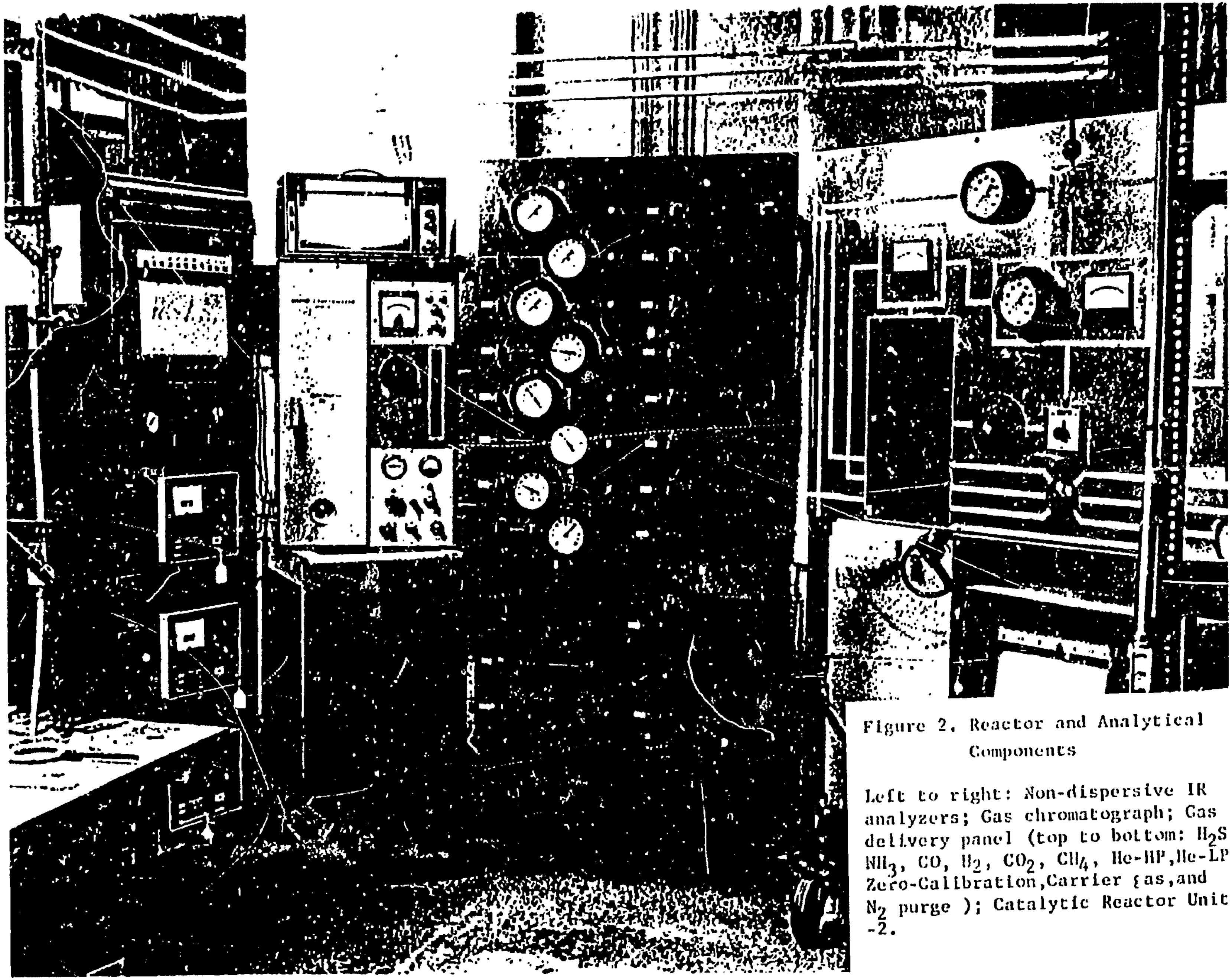


Figure 2. Reactor and Analytical Components

Left to right: Non-dispersive IR analyzers; Gas chromatograph; Gas delivery panel (top to bottom: H_2S NH_3, CO, H_2, CO_2, CH_4, He-HP, He-LP Zero-Calibration, Carrier gas, and N_2 purge); Catalytic Reactor Unit -2.

4. Task I - Work Forecast for Third Quarter

Table 2 summarizes the work that is scheduled for the next quarterly period. The major emphasis will be placed on getting CRU-2 back on schedule and the training of personnel to use the various pieces of equipment safely.

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. Figure 3 presents in block diagram format the alternatives for synthesis gas from a coal gasification process. It should be emphasized that the Fischer-Tropsch route offers several alternatives for the use of a coal derived synthesis gas. The primary goal of this project is to alter the typical product distribution indicated by the solid lines of Figure 4 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. Since continual feedback will be required to achieve this goal, work from this point onward must proceed in a manner as outlined in Figure 5 which shows the circuitous routes that the work must follow.

Work in this task began as scheduled during the second quarterly period. To insure safety of operation as well as facility of reactant gas blending and product analyses, preliminary studies involving olefin hydrogenation were undertaken. These studies included the simultaneous hydrogenation of ethylene and propylene over a thoria promoted nickel catalyst. Figure 6 summarizes the results of those studies and points out the fact that care must be exercised to avoid the limitations of mass-transfer effects during fast reactions. Despite the small volume of catalyst (1.2 cm^3) and high space velocities (131,000 to 262,000 hr^{-1}) the reactor behaved as an integral rather than a differential reactor. The lower catalyst activities involved in Fischer-Tropsch synthesis should enable us to overcome the difficulty experienced in these preliminary test runs.

2. Task II - Forecast for Third Quarter

During the next quarter, an iron based catalyst will be tested in CRU-1. Test runs will initially be run on conditions closely resembling commercial F-T systems (3600 hr^{-1}; 100 psig and 240°C). Additional tests will be conducted at both higher temperatures and space velocities to determine the effect on product distribution. These results will then be used to compare other catalyst formulations over comparable temperature and pressure ranges.

FIGURE 3

CATALYTIC SYNTHESIS OF GASEOUS HYDROCARBONS

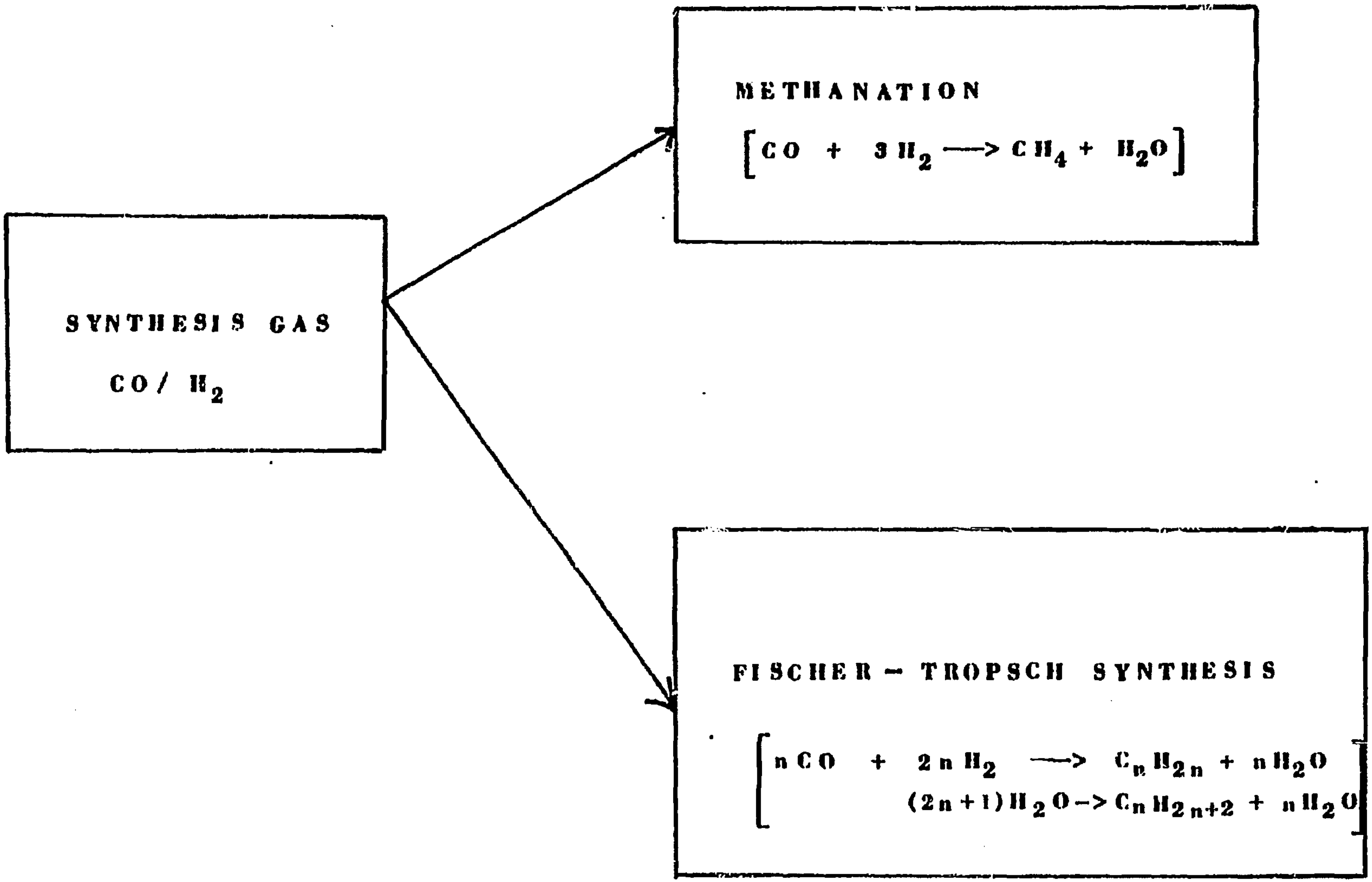


FIGURE 4 **Product Distribution**

vs.

Length of Hydrocarbon Chain

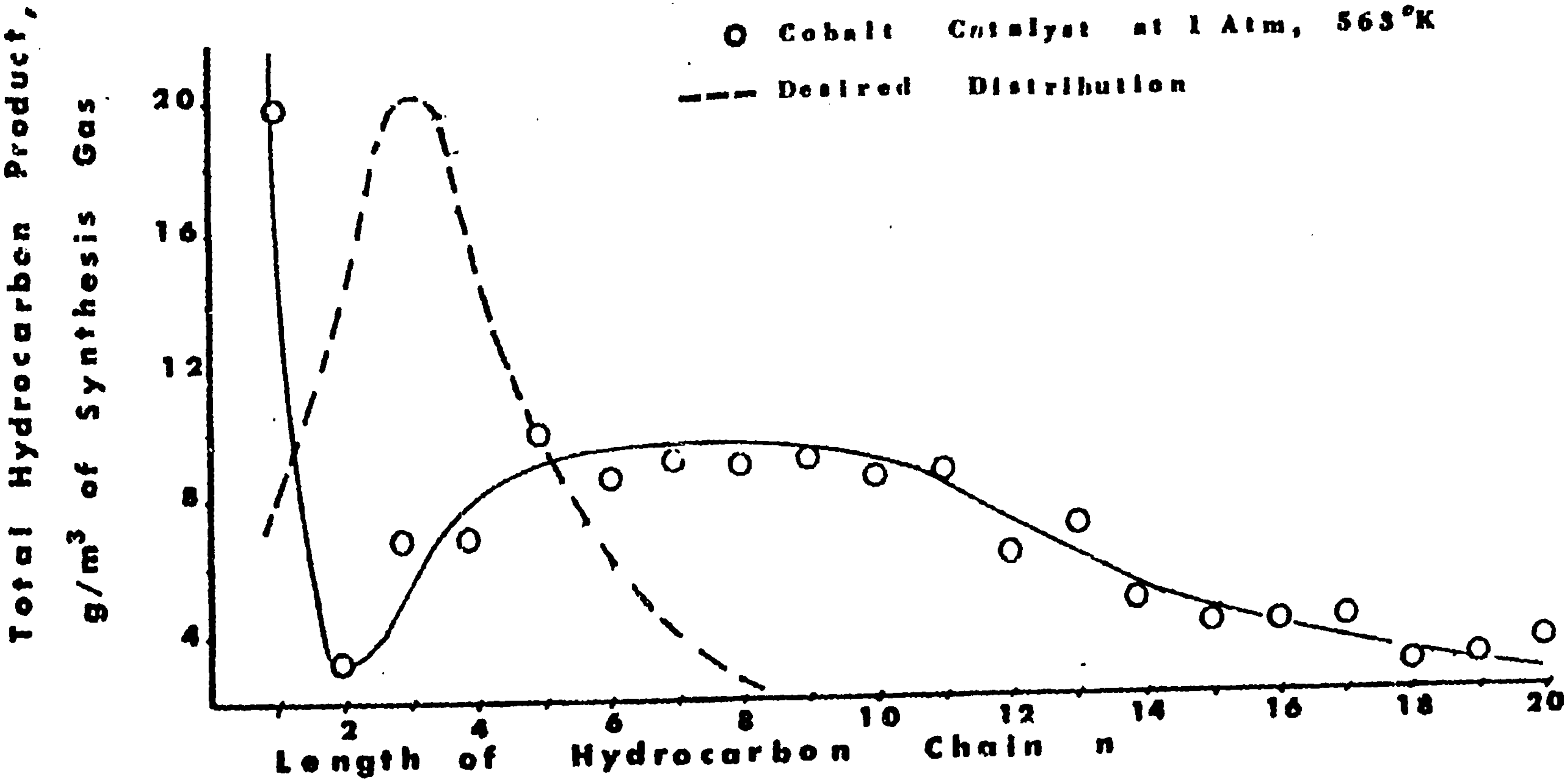


FIGURE 5. SCHEMATIC OF "CATALYST DEVELOPMENT FOR SYNTHESIS OF GASEOUS HYDROCARBONS"

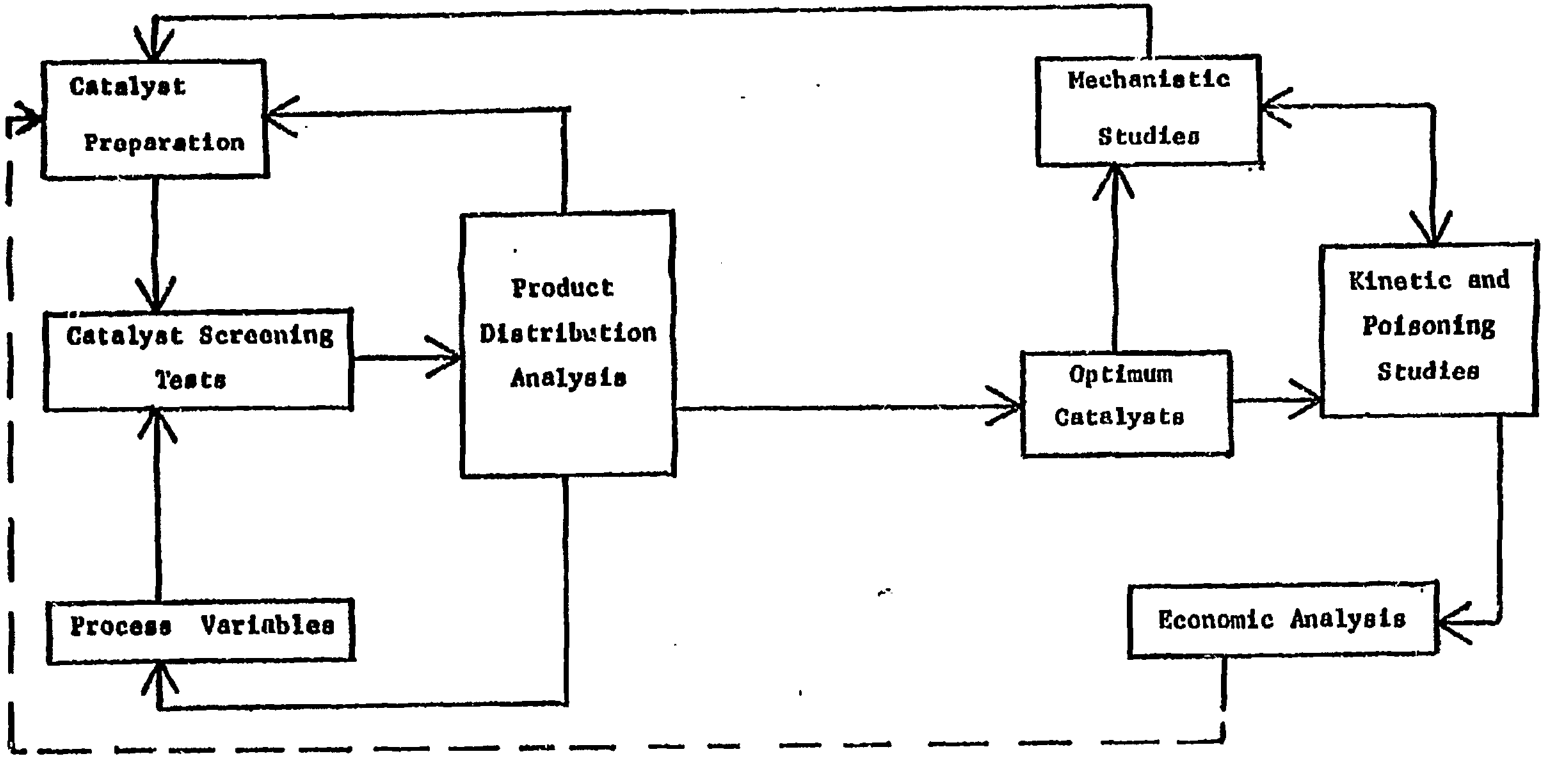
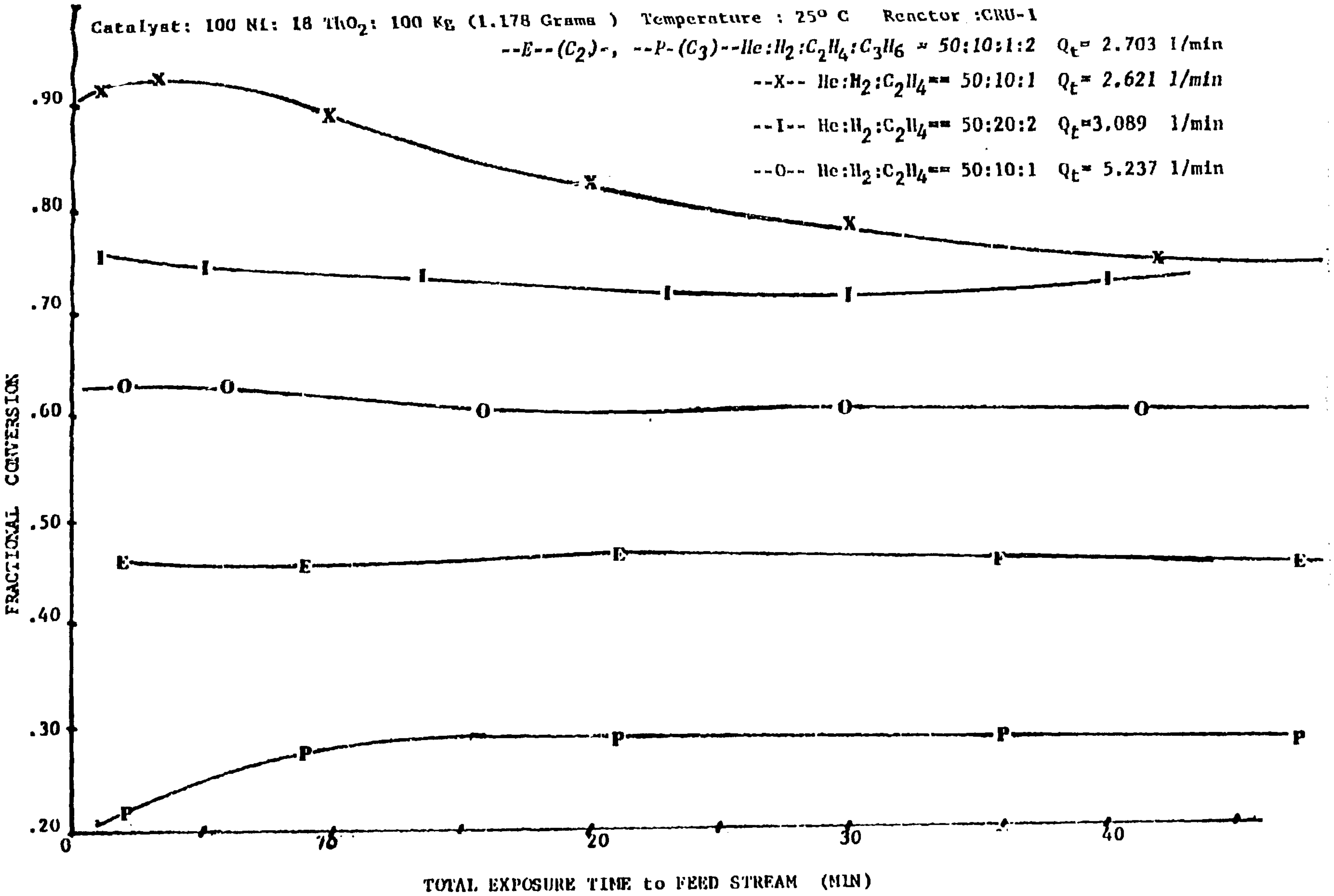


FIGURE 6 OLEFIN HYDROGENATION OVER A NICKEL CATALYST



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 indicated in Figure 4, 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 second period and indicate what future experiments are planned. However, a quick review of the technique might prove more informative.

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. Aerosol Characterization

The surface area of a number of aerosol samples have been measured by the BET method using argon adsorption at -195°C and by CO and H_2 chemisorption. The values range from 14 m^2/g to 63 m^2/g in a manner that suggests a correlation between generation rates and aerosol surface area. The higher the generation rate the lower the surface area. These studies were made possible by the fabrication of a new sample collection cell shown in Figure 7. This is an all-glass cell containing a fine grade, fritted-glass tube through which the aerosol is drawn by a vacuum pump. Collection, therefore, is obtained without exposure to the environment. A number of electron micrographs of aerosol samples taken under various conditions also have been measured and will be described in the next quarterly period.

3. Catalytic Hydrogenation Studies

To establish the catalytic activity of the nickel aerosol, a study of ethylene hydrogenation was undertaken. At 25°C 4:1 and 1:1 hydrogen: ethylene mixtures were hydrogenated in a sample cell similar to the one shown in Figure 7 containing 7 mg Ni. Analyses of the data show that this nickel is quite active. Pre-exposure of this catalyst to hydrogen produces a 3-fold increase in activity which decays with subsequent pulses of the reaction mixture to the initial values. In addition, an apparent increase in activity to a steady-state value occurs with subsequent pulses of the reaction mixture. These studies coupled with a literature review of ethylene hydrogenation over nickel catalysts appear to suggest a mechanism which involves acetylenic species on the surface. Since the analysis is incomplete at this time, further details will be delayed until the next quarterly period.

4. Summary and Task Forecasts

To date we have moved closer towards developing an infrared technique for studying unsupported metal catalysts. We have been able to correlate particle size to aerosol generation rates. However, significant problems still plague this system. These problems will be addressed during the next period. In addition we are approaching a mechanism for ethylene hydrogenation which embodies all of the known facts about this complex reaction. More time is needed to complete this model. Also, we have undertaken a model of the aerosol generation system which should predict the necessary controls which must be exercised to achieve stable infrared spectra.

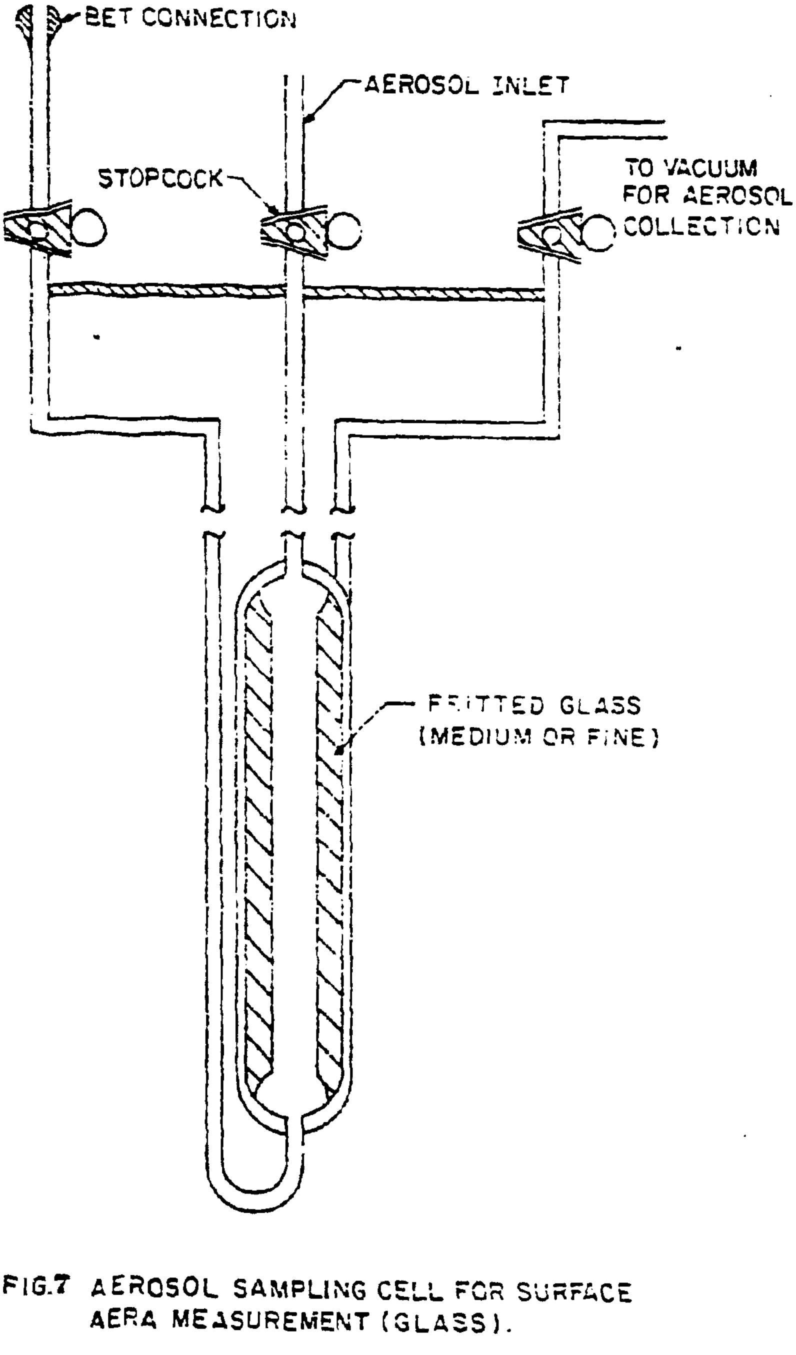


FIG.7 AEROSOL SAMPLING CELL FOR SURFACE AERA MEASUREMENT (GLASS).

IV. CONCLUSIONS

Throughout the previous section we have stated the work accomplished in this contract. In Task I, one reactor unit has been remodeled to provide greater temperature flexibility. While progress on the second reactor unit has lagged behind schedule due to several unforeseen equipment delays, it appears that we will be back on schedule by the end of the next period. The analytical system has been delivered and is nearing completion with the exception of the noted problem associated with the CO_2 analyzer. Preliminary work in Task II has been encouraging to the point that we anticipate completing the evaluation of the first catalyst during the early stages of the next period. While problems still exist in Task IV, several measures of success are noteworthy. A greater understanding of the aerosol-infrared technique has been achieved.

During the second quarter, the Principal Investigator reviewed two research proposals for ERDA and participated in the joint ERDA-NSF/RANN - EPRI Principal Investigators Conference held at Salt Lake City, Utah on October 22-23, 1975 in compliance with Task VIII of the contract.

V. 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

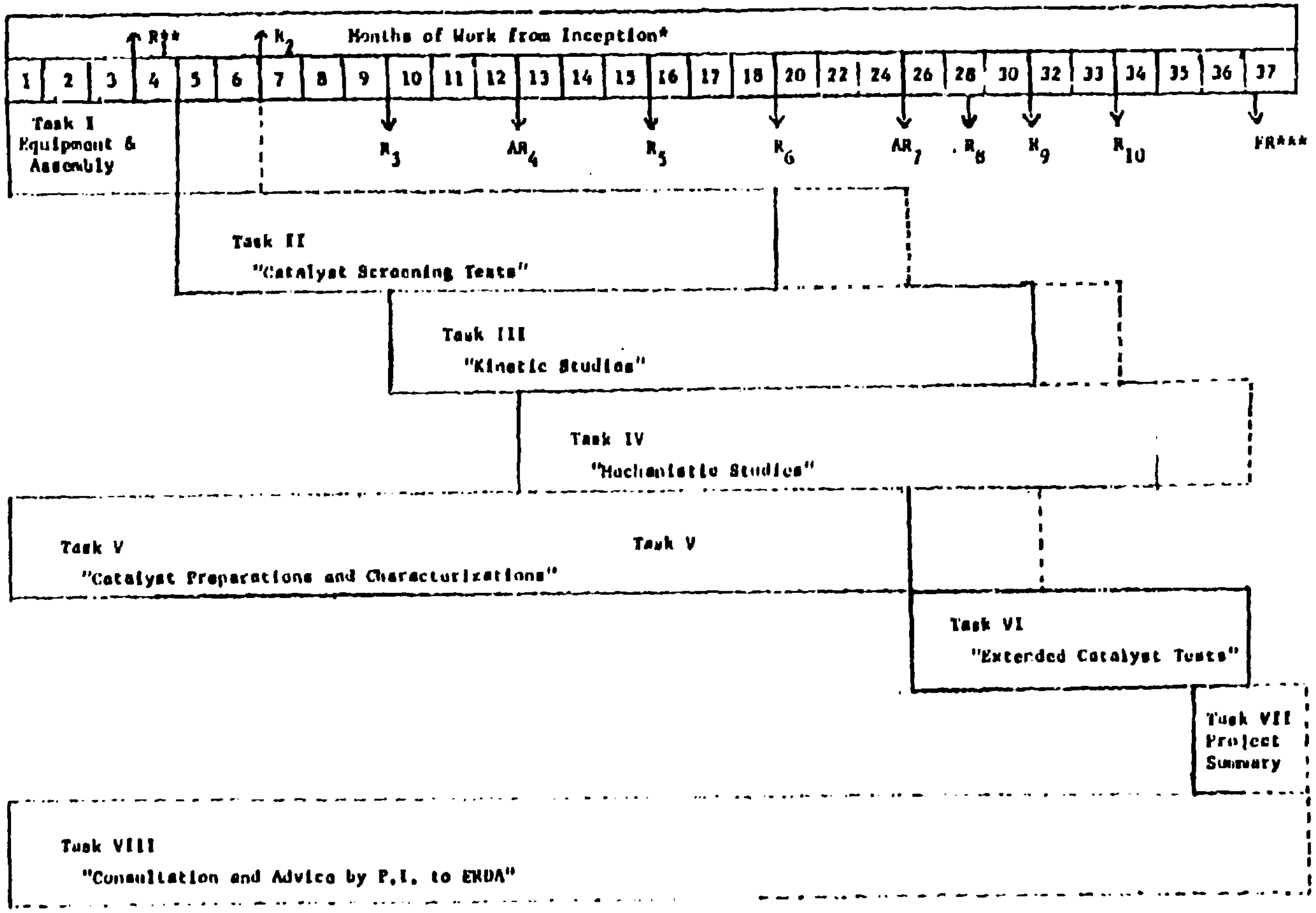
The data obtained from Tasks 1 through 6 shall be summarized and interpreted in the final report on the contract. This final report shall include the advantages and disadvantages of each catalyst system, the economics of production of SNG and SLPG from coal-derived synthesis gas using different catalyst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