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 first year, work has been devoted primarily to project start-up. This has included the areas of: (a) equipment design, assembly and testing (Task I); (b) catalyst preparation, physical and chemical characterization (Task V); and (c) catalyst screening tests (Task II). In addition a fourth area of work has involved preliminary mechanistic studies (Task IV).

In the area of Task I, two catalytic reactor units (CRU) have been constructed and put into operation. CRU-1 contains a fixed-bed, tubular reactor, whereas, CRU-2 employs a Berty internally recycled reactor. An analytical package consisting of gas chromatographs and three MSA non-dispersive infrared analyzers permit monitoring of the gaseous product streams from the two CRUs on a continuous time-shared basis. Liquid products can be collected throughout the run and analyzed by infrared spectroscopy and gas chromatography.

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

Following the pressure and temperature tests on the two CRUs, two series of test runs were initiated. An iron-based Fischer-Tropsch catalyst (100 Fe:5 cu: 30 CaO:100 Kghr, alkali free) was tested in CRU-1, and a zirconia-promoted, cobalt-based, Fischer-Tropsch catalysis was analyzed in CRU-2. The results of these runs formed the basis for comparisons for later planned catalyst studies as well as provided the necessary training experience for the research associates.

In the final area (Task IV), considerable progress has been made towards developing a new infrared technique to observe unsupported metal catalysts during mechanistic studies. To date, generation of a nickel aerosol by sophisticated arc vaporization methods has been reduced to a routine

procedure. Unfortunately, actual infrared observations have not been achieved due to a particle aggregation and/or deposition in the IR cell. This is the final roadblock which must be overcome. However, BET results obtained on aerosols produced at different conditions strongly suggests a correlation between the surface area of the nickel and the generation rate of the aerosol. In addition, the ethylene hydrogenation activity of this catalyst was unusually high by comparison to other nickel catalysts. These two features have stimulated additional work on this system to characterize better the catalyst and the process for producing these catalysts.

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

I. OBJECTIVE AND SCOPE OF WORK

To meet the needs of the increasing energy demand and to satisfy the corresponding environmental constraints, coal gasification has been proposed as a means of producing clean fossil fuel. Such processes become increasingly more important when the projections that petroleum oil resources will be effectively depleted within the next twenty years are taken into account. Likewise, it should be recognized that the depletion of petroleum oil resources also means that the petrochemical industry must look elsewhere to obtain their feed-stocks. While there are several American processes for conversion of coal to synthetic natural gas (SNG) at varying stages of development, there are, however, none available for the production of synthetic liquefied petroleum gas (SLPG). Fortunately, however, SLPG appears to be obtainable by a modification of the methanation step of the SNG processes. Unfortunately, the methanation step ($CO + 3H_2 \xrightarrow[Cat]{} CH_4 + H_2O$) 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 DURING THE FIRST YEAR

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 first year, work has been devoted to: (a) the design, fabrication and assembly of two catalytic reactor units (CRU) which will be employed in work described in Tasks II, III and IV; (b) to preparation and characterization of catalysts by physical and chemical methods (Task V); (c) to catalyst screening tests using an iron-based and a cobalt based Fischer-Tropsch catalyst; and (d) to preliminary mechanistic work for Task IV.

In the area of Task I, one catalytic reactor unit (CRU-1) was completed and calibrated during the first quarterly period. The modified version of this unit consists of a 1-inch stainless-steel, tubular reactor which is temperature controlled by a three-zone, electric furnace. Calibrated sonic nozzles provide flow control and blending of as many as six gases to the reactor. A multiport valve allows switching of the feed gas from the reactor directly to the analytical system with simultaneous replacement by purge gas (helium). A second multiport valve permits analysis of the product gas on calibration gases. Several temperature-controlled traps permit separation and collection of liquid products during the reaction period.

CRU-2 is similar in design to the unit described above with the major exception being the reactor. This unit contains a Berty internally-recycled, catalytic reactor supplied by Autoclave Engineers. Temperature and pressure tests were completed on this unit during the third quarterly period.

The analytical package for the two units involves gas chromatography (GC) and non-dispersive infrared (NDIR) analysis Each reactor has its own Parkin-Elmer Model 154 GC with an automatic gas sampling valve. Gas sample injection and peak analysis are controlled by a Varian "CDS 101 Data Analyzer." In addition, three NDIRs monitor continuously the product stream for methane, carbon monoxide and carbon dioxide. An Industrial Timer Corporation Dual Trol Timer controls the period during which the product streams from the two reactors are analyzed by the NDIRs when the units are operated simultaneously. Three-point 10-mV recorders provide a permanent record of the performance of each CRU, respectively. Liquid products can be analyzed by the usual IR and GC methods.

Initial work for Task II began during the second quarterly period. Following a training program which served to instruct the research associates in the safe techniques of catalysts reduction by hydrogen, reactant gas blending, and product analyses, actual catalyst screening tests were undertaken in the first month of the third quarter with CRU-1. A total of ten runs were conducted on an iron-based Fischer-Tropsch catalyst (100 Fe:5 Cu: 30 CaO: 100 kghr, alkali free) over a temperature range of 200-350°C and at three H_2/CO ratios and at 100 psig. Helium was used to dilute the feed gases (10% CO in all runs) in order to minimize the exothermicity of the reaction. An apparent activation energy of 12.1 kcal/mole was obtained for this series. During the fourth quarterly period, three runs were completed on a commerical zirconia-promoted, cobalt-based Fischer-Tropsch catalyst using CRU-2. The feed gas composition and temperature range of these tests were similar to those described for the iron catalysts. When this series is completed, we will have established the basis of comparisons for later tests on these catalysts.

In the area of Task V, several iron, cobalt and nickel based catalysts have been prepared in the laboratory or obtained from commercial suppliers. These include catalysts supported on kieselguhr and on alumina. The majority of these catalysts were prepared in the manner prescribed typically for Fischer-Tropsch catalysts. In many cases, a second formulation was prepared which is identical except for the precaution of keeping the sample alkali free. In this manner the role of the alkali in product selectivity can be assessed. In addition, the total surface area of some of these catalysts have been determined by BET adsorption methods. For many of the catalysts, chemical analyses of the actual metal contents have also been completed. These characterizations should provide greater understanding of the catalytic activities which will be obtained during the screening tests (Task II).

The final area of work (Task IV), involved preliminary studies associated with the mechanistic studies planned for Task IV. In this area, the major effort during the first half of the year was devoted towards developing an infrared technique to study unsupported metal catalysts. The catalyst in this scheme exists as a nickel aerosol (helium provides the gas phase) or smoke which is produced in one portion of the system by an arc-vaporization process and is transported to another portion of the system -- the long-path-length infrared cell where spectral observations occur. To date, generation of the nickel aerosol has been reduced to a routine procedure. However, infrared spectral observations have been hampered by what appears to be a deposition of the aerosol onto the interval optics of the IR cell as a result of particle-particle aggregation. In addition, electron micrographs of the 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 explains our inability to observe infrared spectra.

Despite this difficulty, other aspects of the work have continued. "Clean" aerosol samples have been collected by designing an all-glass cell which contains a fritted-tube through which the helium can be removed and on which the nickel powder is deposited. Collection of large samples facilitated BET surface-area measurements, whereas collection of smaller samples provide a membrane, micro-catalytic reactor for assessment of activity of the catalysts.

During the first two quarters, the hydrogeneration of ethylene was studied over such a catalyst. The results suggested an unusually high catalytic activity for the material in comparison to other nickel catalysts reported in the literature. Following an extensive literature review of ethylene hydrogenation over nickel, tentative conclusions were reached about the reaction mechanism as well as about the performance of the membrane, micro-catalytic reactor. Acetylenic residues appear to account for the time dependence of reaction rate changes and their formation should be retarded by going to lower temperature. Another point of equal importance to the high catalytic activity is the correlation of the BET surface area of the deposited nickel catalyst with the generation rate of the aerosol. This suggests that even smaller sized, catalyst particles can be prepared, and, thus, structure sensitivity studies can be investigated with this system. To summarize the progress during the first year, we have accomplished the following:

1. Completed the design, assembly, calibration and shakedown of catalytic-reactor unit-1 (CRU-1) with its tubular reactor.
2. Completed the design, assembly, calibration and shakedown of catalytic-reactor unit-2 with its internally recycled reactor.
3. Completed the combined analytical package which involved GC and NDIR analysis of feed, product and calibration streams.
4. Prepared a substantial number of catalysts in the laboratory of known, analyzed composition for testing in Task II.
5. Obtained additional commercial catalysts for testing in Task II.
6. Characterized several of the catalysts from 4 and 5 by BET surface area measurements and also by chemical analyses for actual metal content.
7. Completed 10 test runs on an iron-based F-T catalyst using CRU-1.

8. Completed 3 test runs on a cobalt-based F-T catalyst using CRU-2.

9. Reduced the complicated generation of nickel aerosol catalysts to a routine procedure.

10. Developed a method of collecting the aerosol which ensures that it remains in an uncontaminated state.

11. Established that the nickel aerosol generated by arc vaporization has substantial activity for ethylene hydrogenation and a high surface area.

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

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

As previously stated, the objectives of this research program are to develop improved catalyst systems for the preparation of gaseous hydrocarbons from coal-derived mixtures of carbon monoxide and hydrogen, and to develop a fundamental understanding of the reaction mechanisms associated with catalytic methanation and Fischer-Tropsch synthesis. This will be accomplished in this project by pursuing several aspects of the problem which include: (a) catalysts preparation and characterization of their physical properties; (b) evaluation of these catalysts for the synthesis of C_2-C_4 hydrocarbons in a screening test; (c) conducting kinetic studies to obtain rate expressions to predict product yields for the most promising catalyst formulations; (d) investigation of the mechanism of formation and types of reaction 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 the third period. Preliminary work in Task II, which began during the second quarterly period, has continued; an iron-based Fischer-Tropsch catalyst was tested in 10 runs, using CRU-1. A cobalt-based, commercial Fisher-Tropsch catalyst was tested in 3 runs using CRU-2 during the fourth quarterly period. The major portion of the catalyst preparation and characterization was completed during the first quarterly period. 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 the third period. We noted that delays occurred 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 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	

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*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 summarizes the work accomplished during the third quarter and that scheduled for the fourth period. As a result of work undertaken in Task II, several modifications to CRU-1 were required to make the unit more convenient to operate. These modifications were completed during the fourth quarter and are shown in Table 3 in parenthesis.

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 450°C and a pressure range from 0 to 200 psig. The original design consisted of a gas-delivery system capable of blending seven gas streams to feed a fixed-bed, 1-inch, tubular reactor (see Figure 1). It should be noted that cylinder gases rather than a coal-derived synthesis gas is blended *in situ* for these studies. The individual gases are metered by flow-controller valves. [These valves are "Swagelok" S-series very fine metering valves fitted with micrometer handles to permit reproduction by setting. (A double S-series valve is used for greater control on the hydrogen line.) These valves can be operated in either subsonic or sonic flow modes. In the sonic flow mode of operation, the flow rate, Q, is independent of the downstream pressure and is given by:

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

where Q = flow in std. liters per min.

C_V = valve flow coefficient

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

T_1 = absolute temperature of flowing gas, °K

P_1 = inlet pressure (psia)

Equation 1 is a simplification of the more exact equation:

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

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

M = molecular weight of gas

R = gas constant

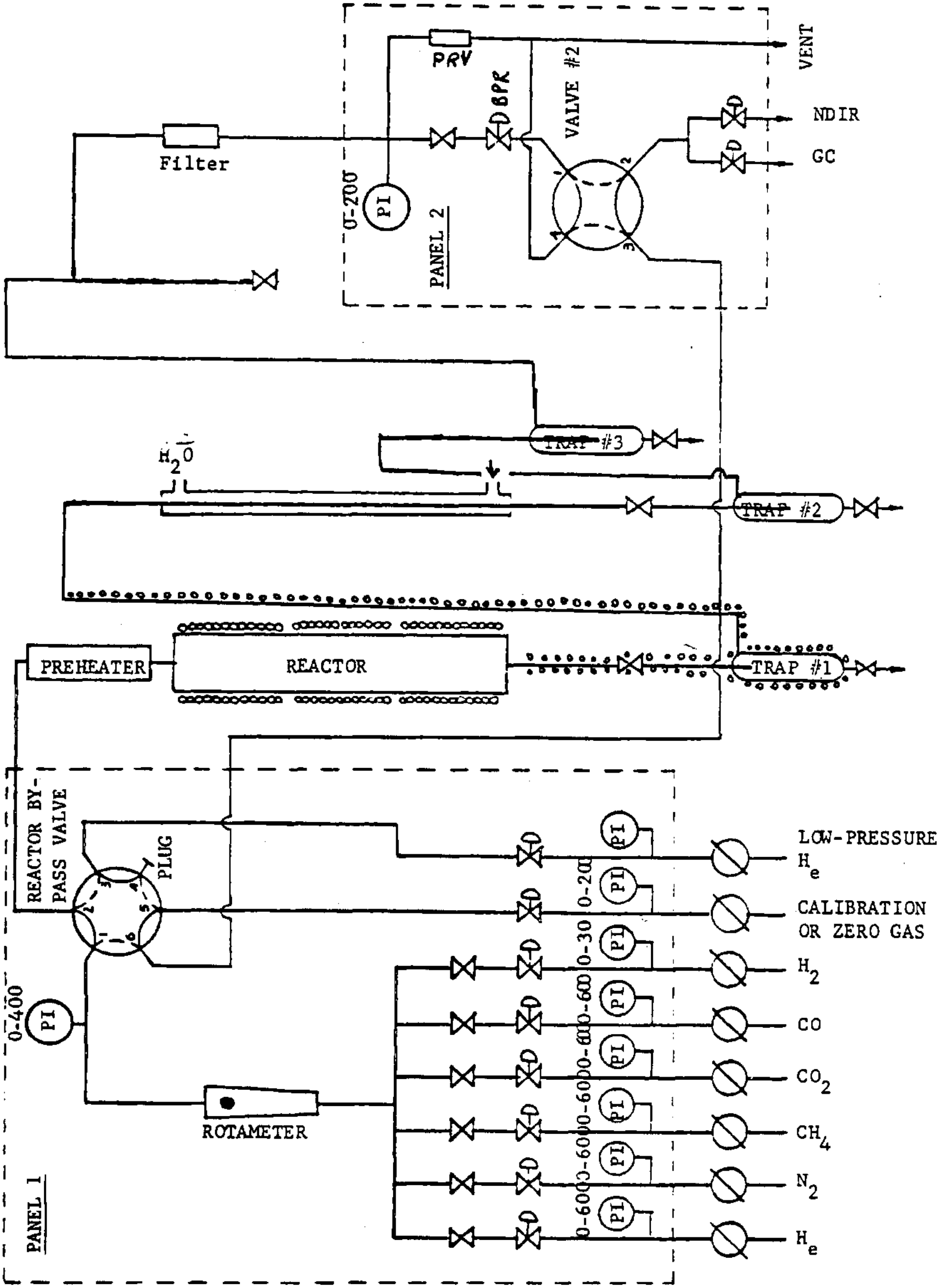
γ = ratio of heat capacities, C_P/C_V of flowing gas. (γ = 1.40 for air).

Table 3 Third and Fourth Quarter 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 were completed during the fourth quarterly period.

Figure 1 Modified Catalytic Reactor Unit-1



When the critical pressure condition defined as

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

is exceeded, these equations can be used. Calibration was achieved by determining C_v values as a function of the number of turns open of the valve stem when the flow rates were measured by a gas bubble meter or a 0.1 CFM per revolution wet-test meter. Table 4 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.]

As shown in Figure 1, the blended feed gases are sent to a 6-port Swagelok valve where it can be sent either to the reactor or by-passed to a 4-port valve downstream. During feed gas by-pass, helium is sent to the reactor as a purge gas. In series with the reactor are three temperature controlled traps which serve to segregate the liquid products into heavy oils, water and oxygenated compounds, and light oils. The product gas leaving the reactor flows to a 4-port valve where it is sent either to the NDIR-GC bypass for analysis or vented. It can be seen from Figure 1 that calibration of the NDIR analyzers or the GC can be achieved at any time during the test run by simply diverting the product gas to vent.

Originally the reactor for CRU-1 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 2 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.

Table 4. 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> ± 1.8%	<1.246> ± 0.7%	<0.821> ± 4.8%

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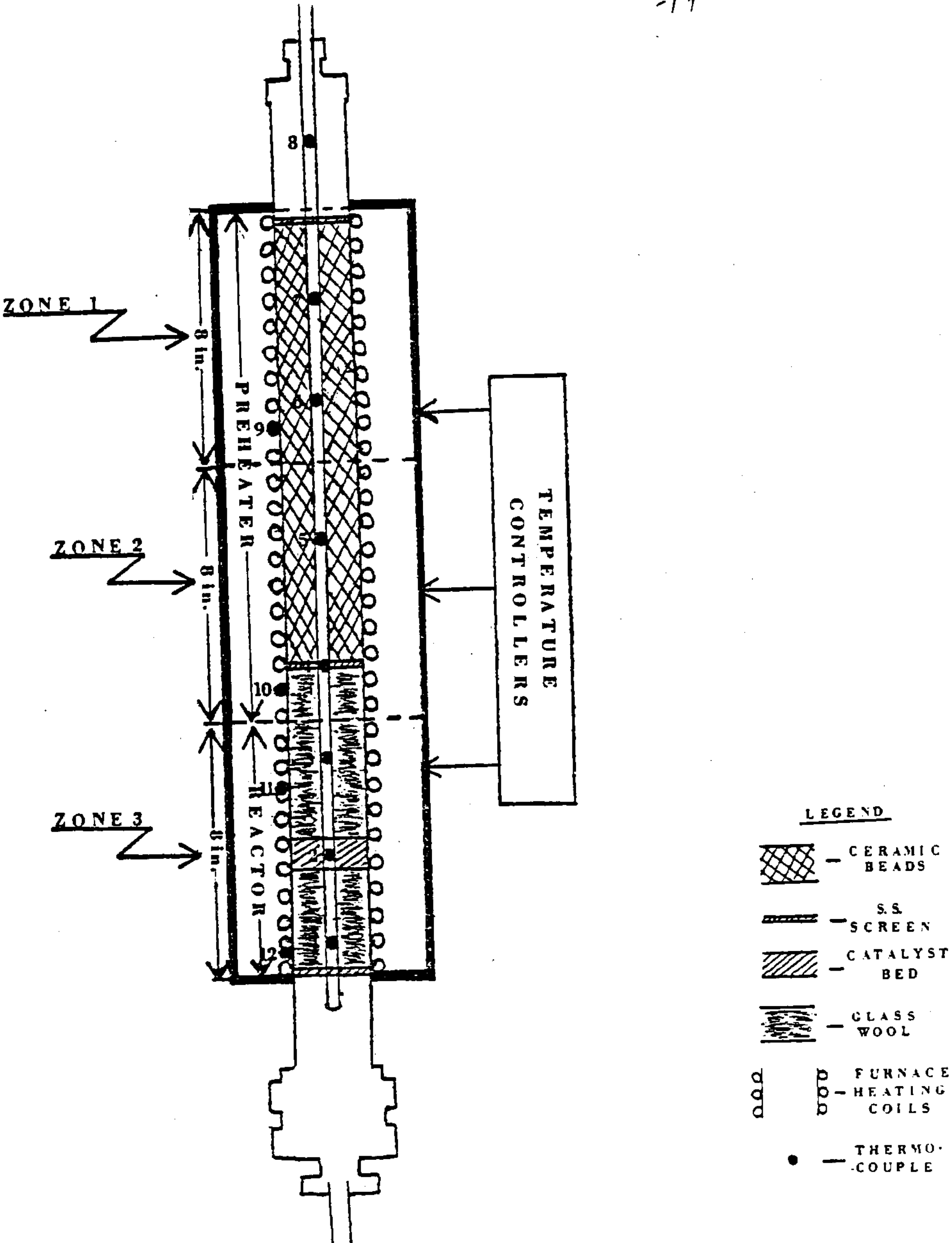
[a] Gas chromatography done on Perkin-Elmer Model 154C using a 50:50 mixture of molecular sieves 13X and 5A at 100°C. Carrier gas was helium at 60cc/min. Peak integration accomplished using the Varian CDS-101 data analyzer. Sample size = 2cm^3.

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

FIGURE 2. CRU- 1 REACTOR and FURNACE



2. Catalytic Reactor Unit-2

Figure 3 is a diagram of CRU-2 and the gas delivery system which supplies both units. Figure 4 is a diagram of the traps and condension network for this unit and were described in detail in quarterly report #3. The unit is shown on the right of the photograph in Figure 5 in its early stages. As noted in previous quarterly reports, the principal difference between the two units are the reactors. Whereas, CRU-1 contains a fixed-bed catalytic reactor controlled by a three-zone electric furnace. The reactor indicated in Figure 3 (not shown in Figure 5) is an internally recycled catalytic reactor obtained from Autoclave Engineers. A diagram of the reactor is shown in Figure 6. 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.

Whereas, work on CRU-1 proceeded according to schedule, progress on CRU-2 often lagged behind the expected rate. This was due in part to delays by the suppliers but more so by a backlog of work scheduled for completion by the Mellon Institute shops. However, testing of the unit was completed during the third quarterly period so that Task II studies could be initiated during the fourth 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 on the extreme left in Figure 5.

When the two units are operated simultaneously, an Industrial Timer Corporation Dual Trol timer (mounted on CRU-2) controls the period during which the product streams from the two reactors are analyzed. Typically each product stream is analyzed for a 20-minute period. The timer then activates two solenoid valves which switches to the flow from the other reactor. Figure 7 illustrates how this is achieved.

Figure 3 - Catalytic Reactor Unit-2

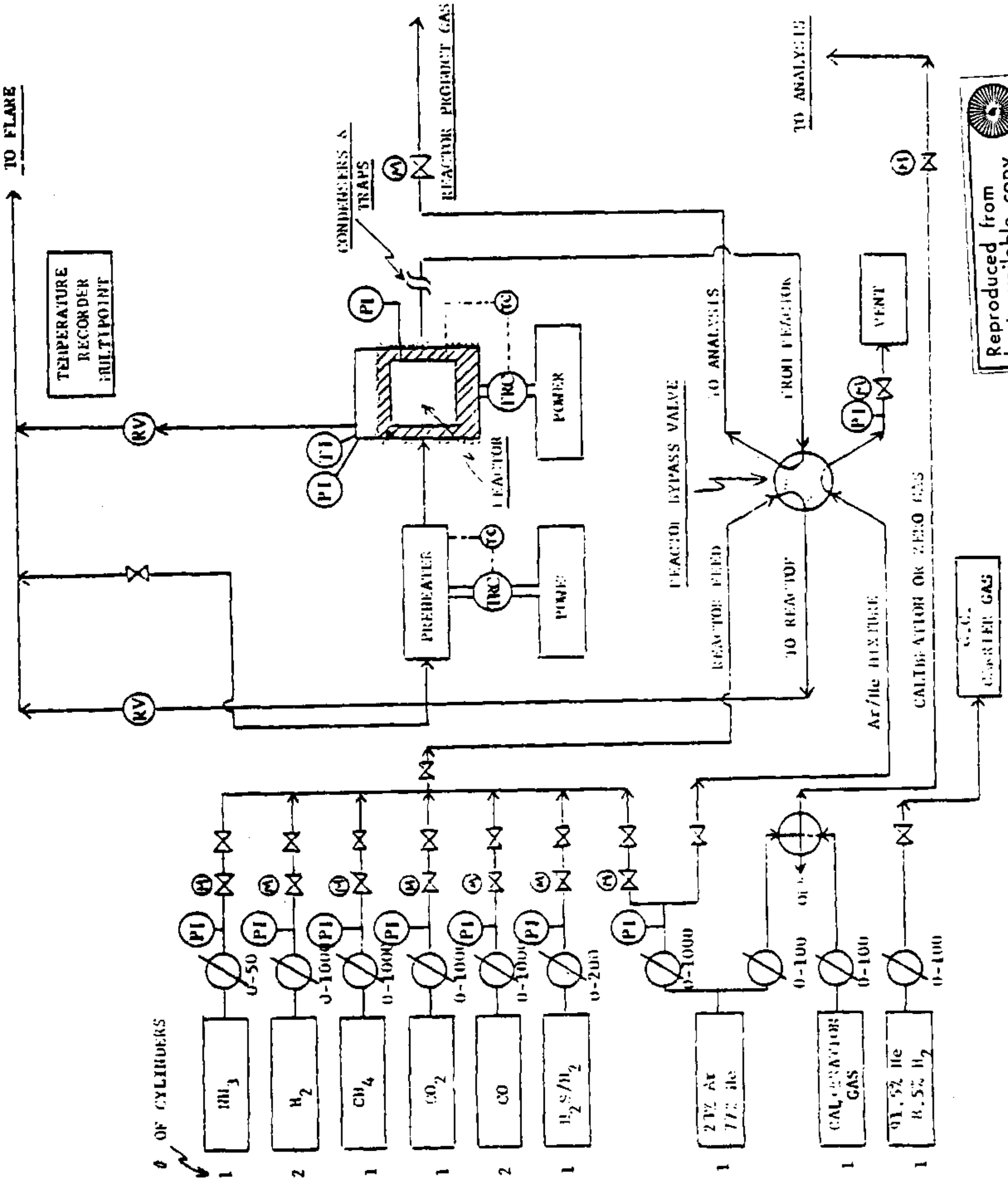
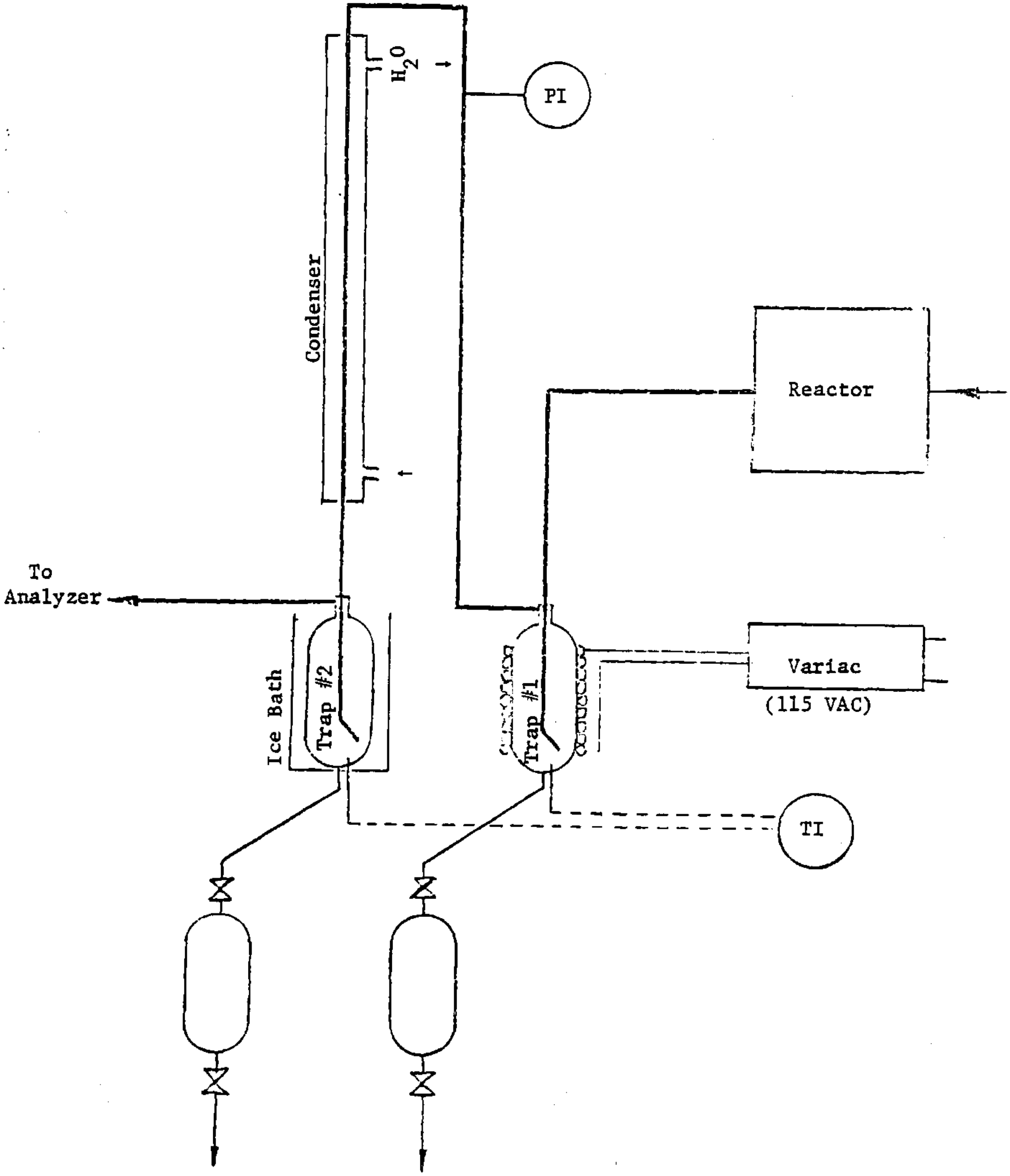


Figure 4 Traps and Condenser Network for CRU-2



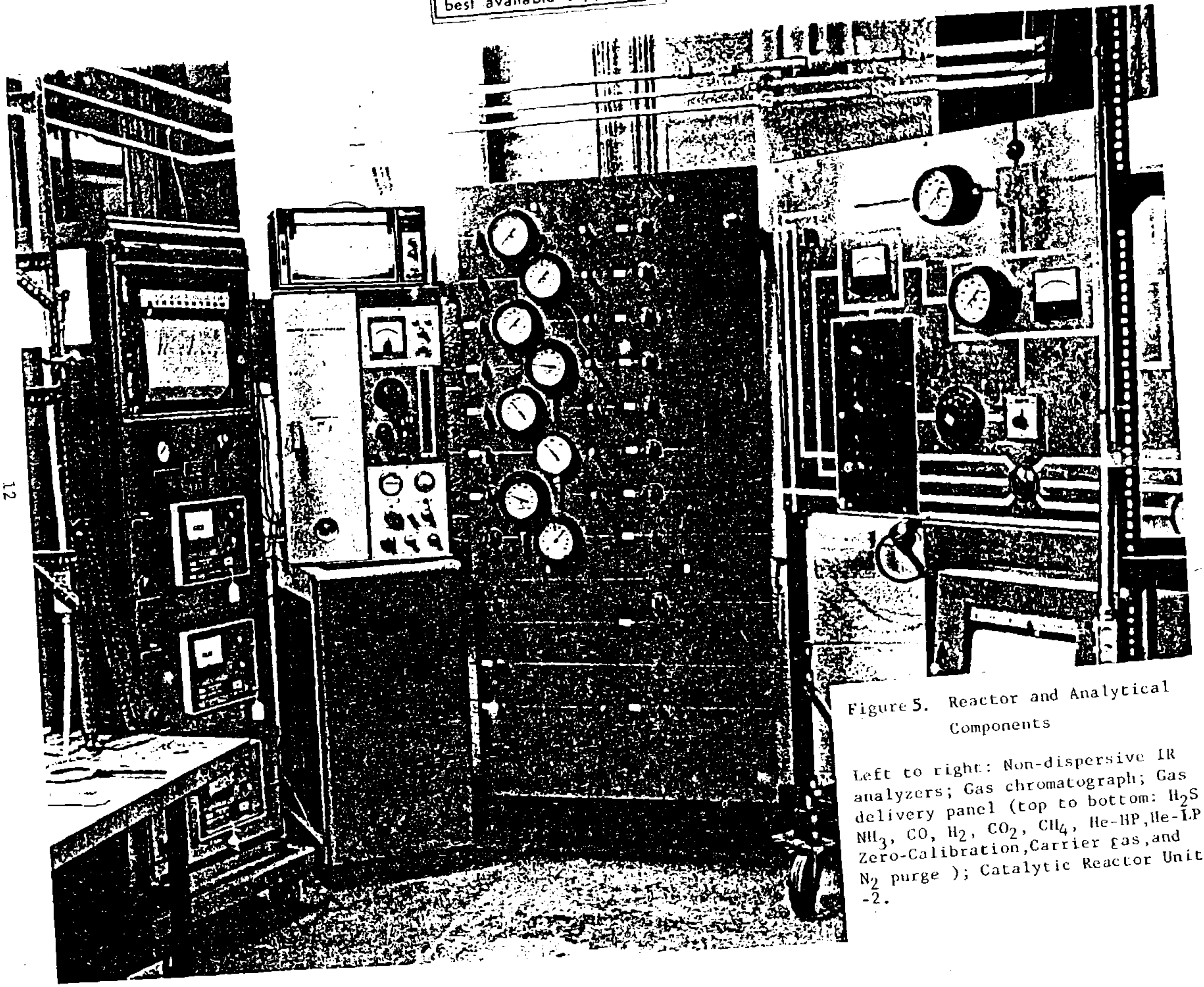
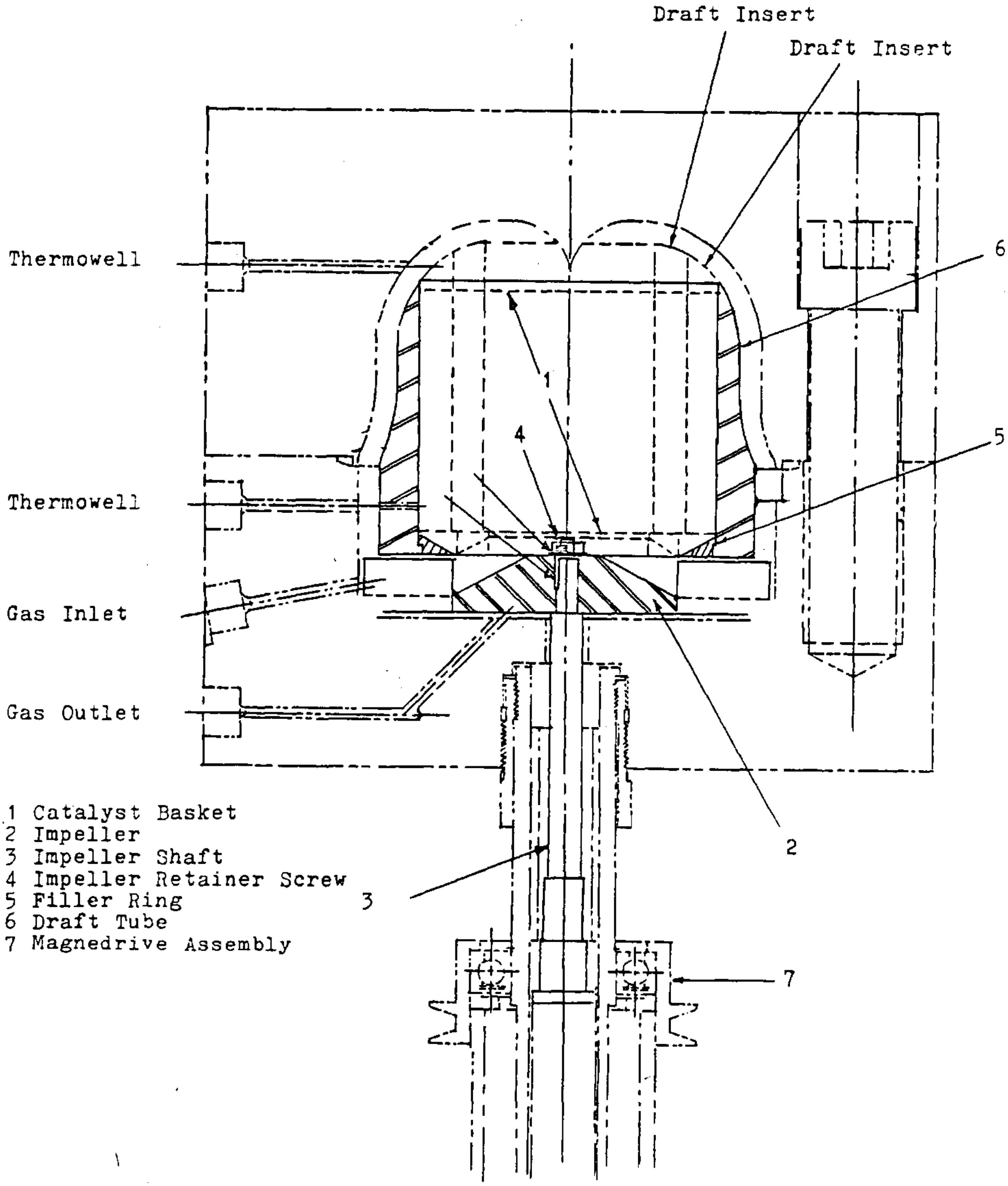


Figure 5. Reactor and Analytical Components

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.

Figure 6. Internally Recycled Catalytic Reactor



1 Catalyst Basket
2 Impeller
3 Impeller Shaft
4 Impeller Retainer Screw
5 Filler Ring
6 Draft Tube
7 Magnedrive Assembly

Figure 7. Analytical System