CHAPTER IV

EXPERIMENTS

Two phases of experimentation were performed: (1) justification experiments, and (2) kinetic experiments. The kinetic experiments constituted the major part of experimental work conducted in this research. Numerous initial experiments were performed to justify the operating conditions for the kinetic experiments. Both phases of experiments were carried out in the same fixed-bed microreactor system. Additional work included catalyst preparation and characterization, product analysis, and computer computations for thermodynamic equilibrium determination and nonlinear regression fits to kinetic models.

IV-1. Fixed-bed Microreactor System.

The schematic flow diagram of the reacting system is sketched in Figure 4.1. Cylinder gases from Air Products and Chemicals, equipped with 400 psig Veriflo single stage regulators, were used to simulate the synthesis gas for the feed. The manifold provided hydrogen (99.995%), carbon monoxide (98.0%), ethylene (93.0%), carbon dioxide (99.8%) and methane (93.0%) as constituent gases. Helium

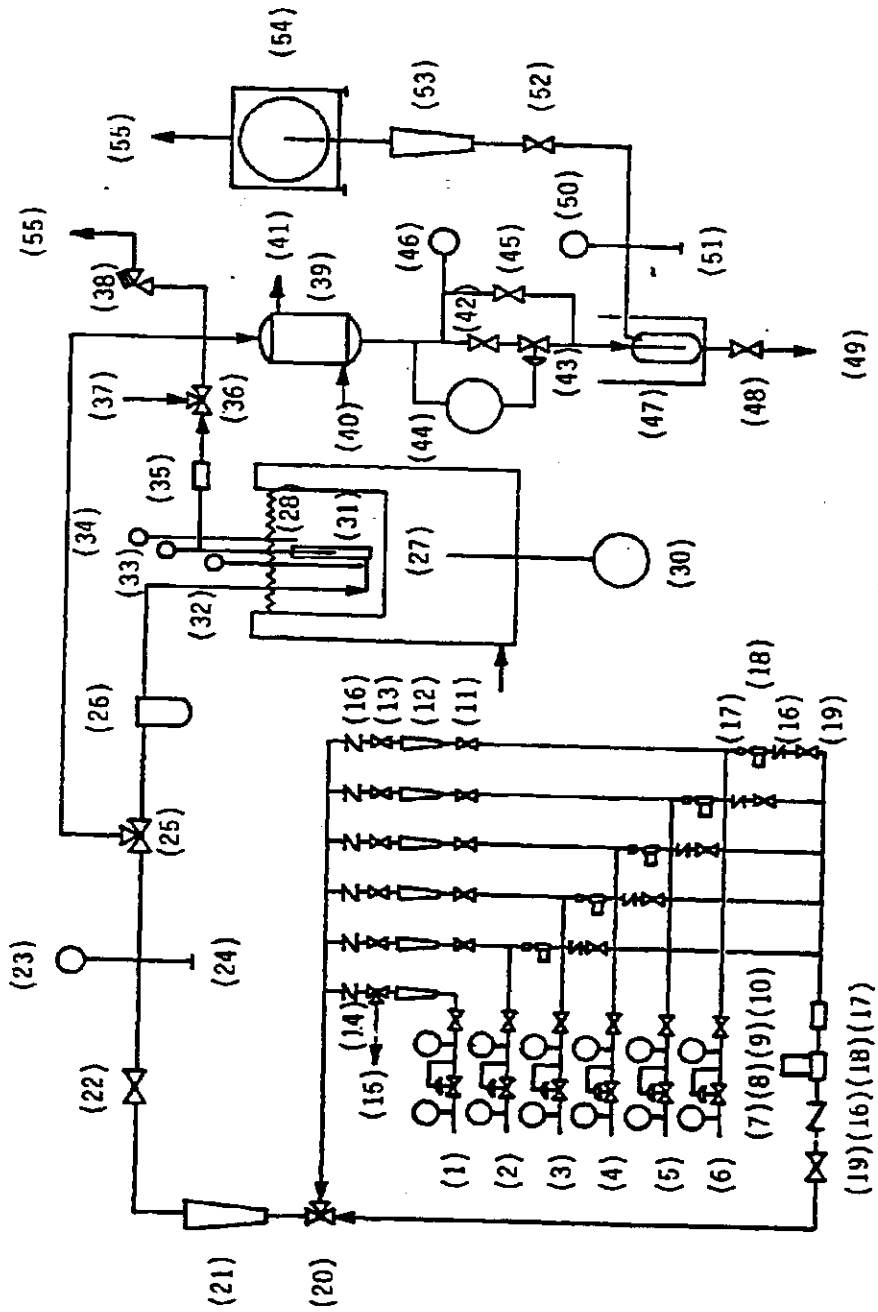

Figure 4.1. Microreactor System - Schematic.

Index for Figure 4.1

(1) Helium from gas cylinder

(2) Carbon dioxide from gas cylinder

(3) Ethylene from gas cylinder

(4) Hydrogen from gas cylinder

(5) Methane from gas cylinder

(6) Carbon monoxide from gas cylinder

(7) Inlet pressure gauge of regulator

(8) Regulator

(9) Outlet pressure gauge of regulator

(10) Outlet valve of regulator

(11) Inlet valve of rotameter

(12) Rotameter

(13) Metering valve of rotameter

(14) 3-way valve

(15) To catalyst sampling section of fluidized-bed minireactor system

(16) Check valve

(17) On-line filter

(18) Mass flow controller

(19) Outlet ball valve for mass flow controller

(20) 3-way valve

(21) Inlet rotameter

(22) Inlet valve

(23) Inlet pressure gauge

(24) To gas chromatograph

Index for Figure 4.1 (Continued.)

(25) 3-way valve

(26) Filter

(27) Fluidized-bed heater

(28) Sand

(29) Air

(30) Temperature indicator and controller

(31) Fixed-bed microreactor

(32) Thermocouple

(33) Thermocouple

(34) Thermocouple

(35) On-line filter

(36) 3-way valve

(37) Product from fluidized-bed minireactor system

(38) Adjustible rupture release

(39) Condenser

(40) Inlet of chilled water

(41) Oulet of chilled water

(42) Valve

(43) Pressure controller valve

(44) Pressure recorder and controller

(45) Valve

(46) Pressure gauge

(47) Trap

(48) Valve

(49) Liquid product

Index for Figure 4.1 (Continued.)

(50) Pressure gauge

(51) To gas chromatograph

(52) Outlet valve

(53) Rotameter

(54) Wet test meter

(55) To vent

(99.998%) was also used as a purge gas. The gases were metered by individual Aalborg rotameters (FM032-41) or Brooks mass flow controllers (Model 5850) and fed into a common feed line through a 3-way Whitey brass ball valve. A Nupro C series check valve was placed in each individual gas line before it joined the common feed line to prevent back mixing of feed into the pure gases in case of a sudden pressure drop in one cylinder or a surge of pressure in the reactor. A high pressure filter (Linde SG6098) was installed on the feed line prior to entering the reactor to remove possible impurities, especially moisture and oils in the feed gas. A by-pass line was piped for the purpose of calibration and maintenance. A photograph of the system is shown in Figure 4.2.

The microreactor itself was made of a 0.25 by 0.035 inches 304W stainless steel tubing, 4 inches in length. A Swagelok stainless steel union elbow connected the reactor and feed line. An extension tubing of the same type, about 6 inches long, was attached to the top of the reactor by a Swagelok bulkhead union. The other end of the extension tube was connected to a Swagelok union tee. One end of the union tee was hooked up with a 1/4 to 1/16 in. Swagelok reducer through which a thermocouple was placed. The other end joined the product line. The extension tube was used to support and suspend the

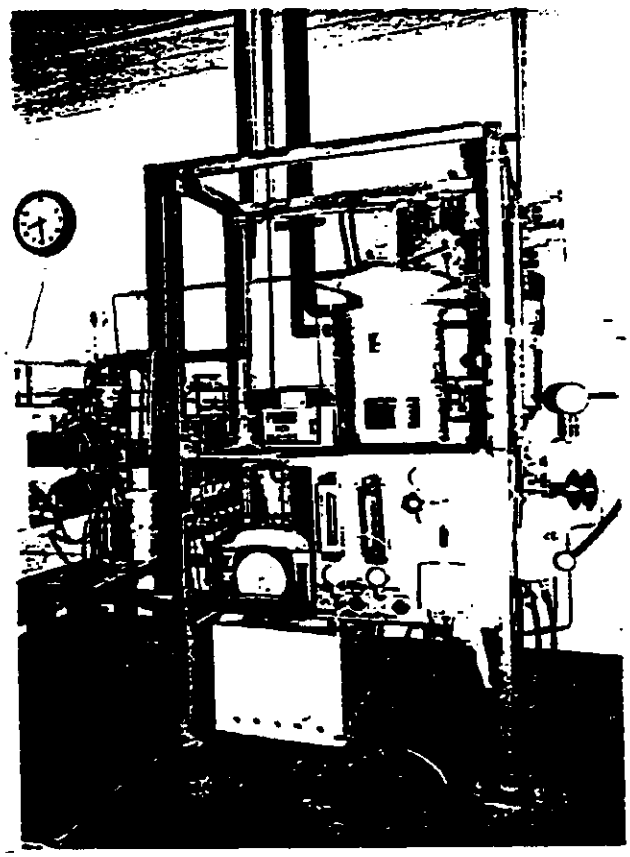

Figure 4.2. Microreactor System - Photograph.

reactor in a fluidized sand bath heater. An Alpha K type thermocouple, 1/16 by 12 inches, passes through the extension tube to the middle of the catalyst bed of the microreactor. The whole microreactor assembly is shown in Figures 4.3 and 4.4. Heating and maintaining the isothermal condition of the reactor was accomplished by a Teche Tecam fluidized bath (Model SBS-4) with an automatic temperature controller (TC4D) [213].

The outlet side of the reactor was provided with a compact in-line Nupro microfilter (4F-7 microns) to remove any possible catalyst particles carried over in the product stream, a Whitey 3-way ball valve (SS-83 x T4) to access another fluidized-bed minireactor system, and a Nupro adjustable in-line relief valve (4CA series) with a Fike rupture disc (497 psia at 70 °F) attached to the end. The product stream passed through the inner tube of a condenser. The condenser was fabricated by fitting a one-foot piece of 2-inch O.D. Sch. 40 stainless steel pipe around a piece of 1/4-inch stainless steel tubing. The pipe was threaded with 1/2-inch NPT threads on both ends and capped with hexagonal screw caps. The caps were drilled in the center to allow the insertion of 1/4-inch center tubing. The cooled vapor and condensed liquids then passed into an ice or acetone/dry ice cooled trap where liquid products were separated from the vapor and collected at the bottom of the trap through a

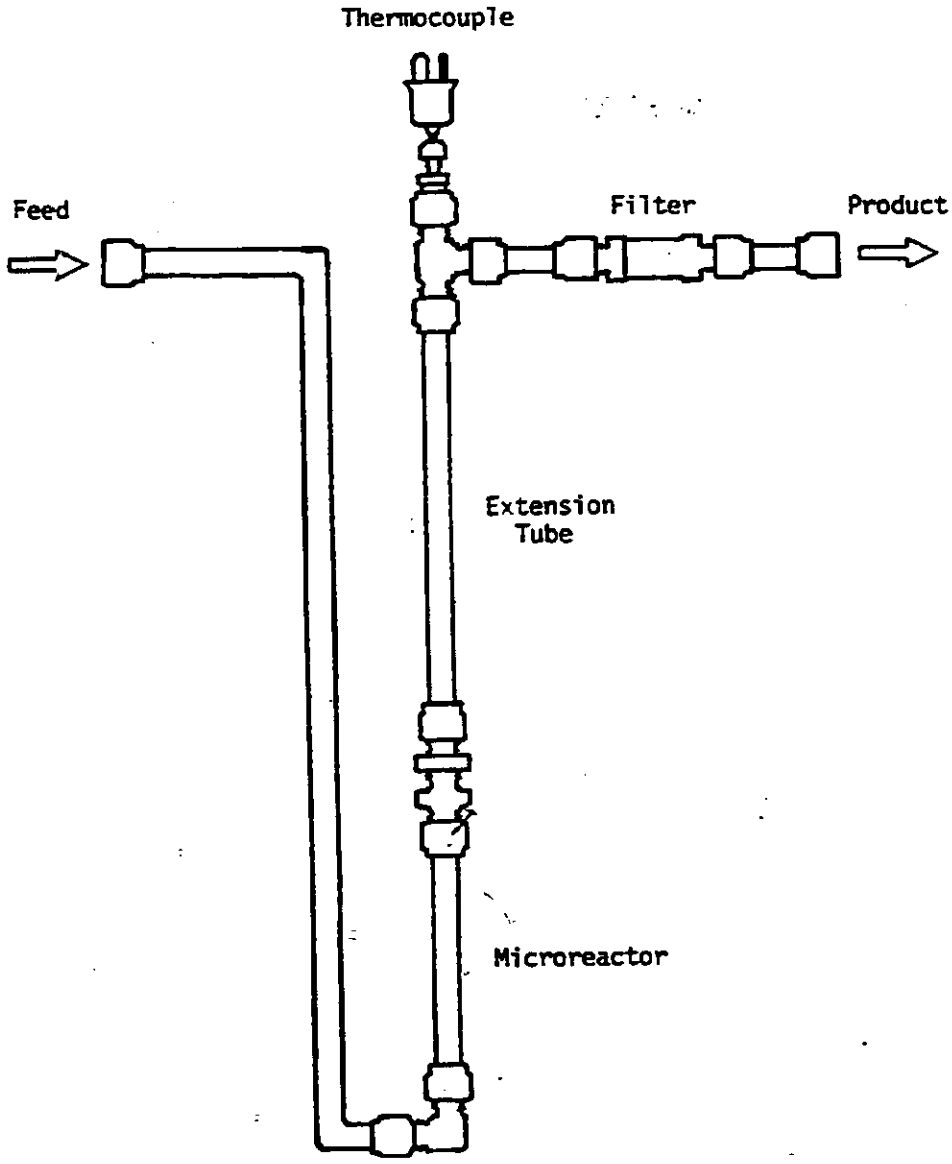

Figure 4.3. Fixed-bed Microreactor Assembly - Schematic.

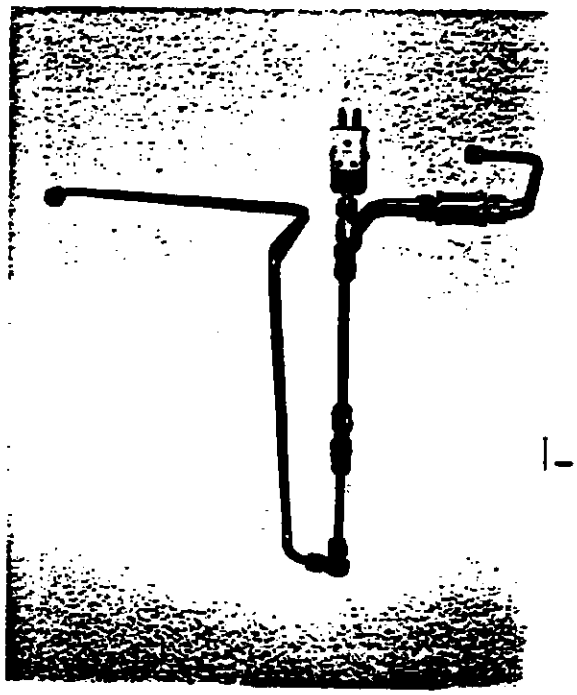

Figure 4.4. Fixed-bed Microreactor Assembly - Photograph.

Swagelok valve. The gaseous product flowed through an outlet rotameter, then a GCA/Precision wet testmeter, and finally to the vent. Details of construction of the condenser and trap are given in Figures 4.5 and 4.6.

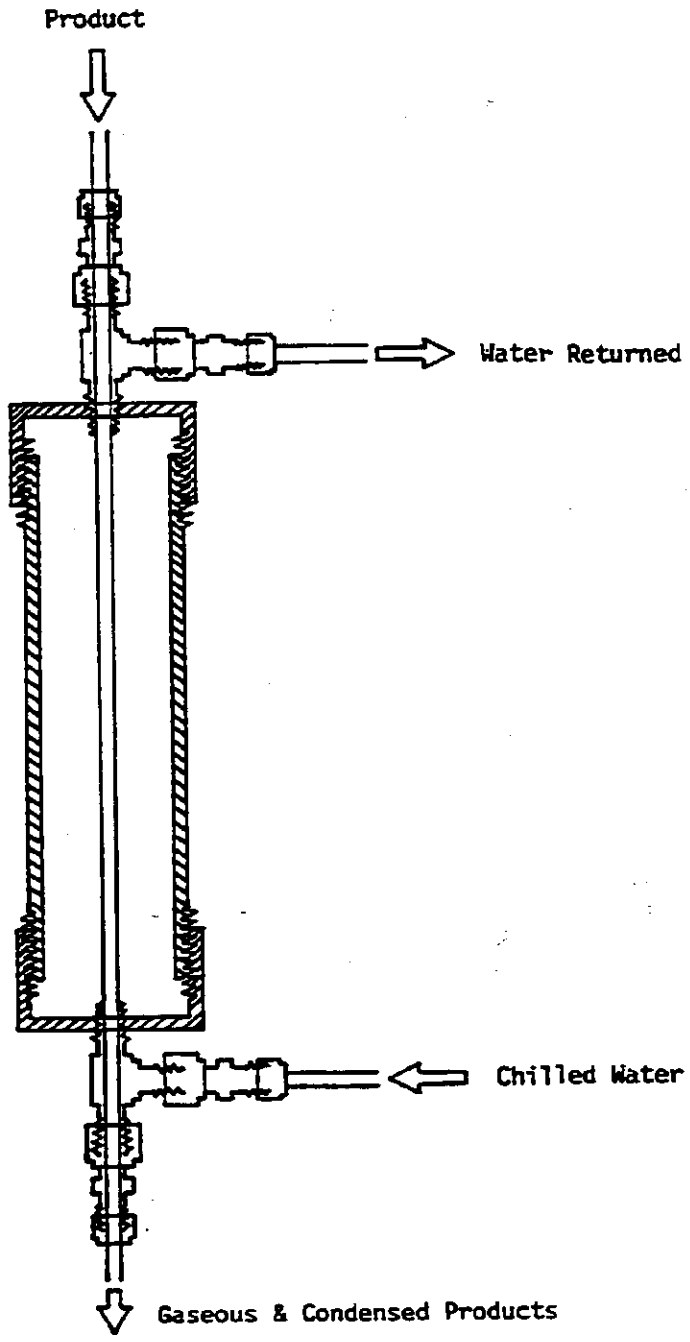

Figure 4.5. Condenser.

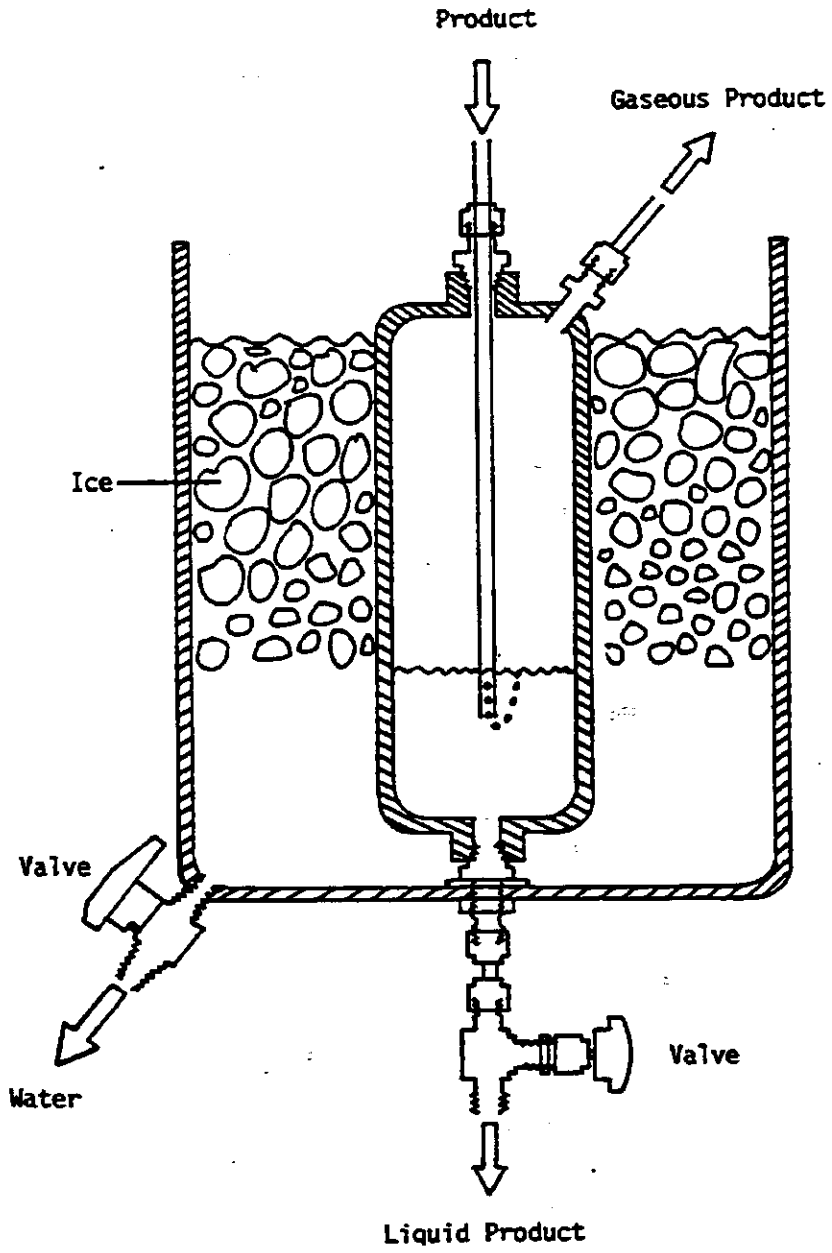

Figure 4.6. Trap.

IV-2. Operating Procedure.

Weighed fresh catalyst was poured through a small funnel into the reactor with the bottom end assembled and stuffed with pyrex wool. The reactor was connected to the extension tube by tightening the Swagelok nut onto the bulkhead union. The assembly was then attached to the by-pass line and pressurized with helium to check for leaks. Pressure control was maintained by a Westinghouse /Veritrak Model 55CC PID compact controller located in the central control room. The control loop also consisted of a Veritrak gauge pressure transmitter (Model 75PG1), a Foxboro 69TA-2R current-to-air transducer and an air-to-close Research/ Badger meter control valve (Model 78s) [88,235,236]. After passing the leak test, the pressure was relieved, the reactor assembly removed from the by-pass line, immersed into the partially fluidized sand bath and connected with both feed and product lines. The entire system was then pressurized and rechecked for leaks. After correcting any more leaks, the system was ready for an experimental run.

Prior to starting any experimental run, it was also necessary to hook up the temperature recorder (Yokogawa/Hybrid Recorder ER250 Model 4088) [248], an on-line analytical gas chromatograph (Carle Model 111) [48] along with a digital integrator (SP 4270) [204], chilled

water from a Application Engineering chiller (Model WC-5-D) flowing through the shell side of the condenser, and with ice or acetone/dry ice in place. The system was gradually pressurized and swept by helium. When the system reached normal operational pressure, i.e., 140 psig, the heaters of the fluidized sand bath were then turned on with proper flow rate of air to maintain stable fluidization of sand [213]. The temperature controller was initially set at the temperature of catalyst reduction, i.e., 675°K for cobalt/alumina catalyst [219]. As the catalyst bed registered steady reduction temperature, helium was quickly replaced by a proper amount of hydrogen (about 2.70 grams of H_2 per hour per gram of catalyst). The reduction continued for at least four hours until no more visible water could be collected. The temperature controller was then reset at desired reaction temperature and the reactor was allowed to cool down.

When the reactor reached and held the pre-set temperature steadily (usually after an hour of cooling), the feed component gases were admitted and adjusted until steady flows of desired composition were obtained. Meanwhile the reactor temperature was carefully watched so as to avoid any possible overshooting. Gaseous product sampling could start as early as 20 minutes after the reaction commenced and continued at 20-minute

intervals. During the run, liquid products were periodically removed from the trap, collected in small sample vials and sealed, and stored in a refrigerator for later analyses. Most experiments were usually operated for seven to eight hours after a steady state had been reached, before switching to the next condition. At the end of each run, the reactant feed gas was replaced with helium, the heater was shut off and the reactor pressure was relieved. After the reactor had been thoroughly flushed, the system was shut down by closing all the valves and turning off the instruments, chilled water, air supply, and finally helium gas. A photograph of the control panel is shown in Figure 4.7.

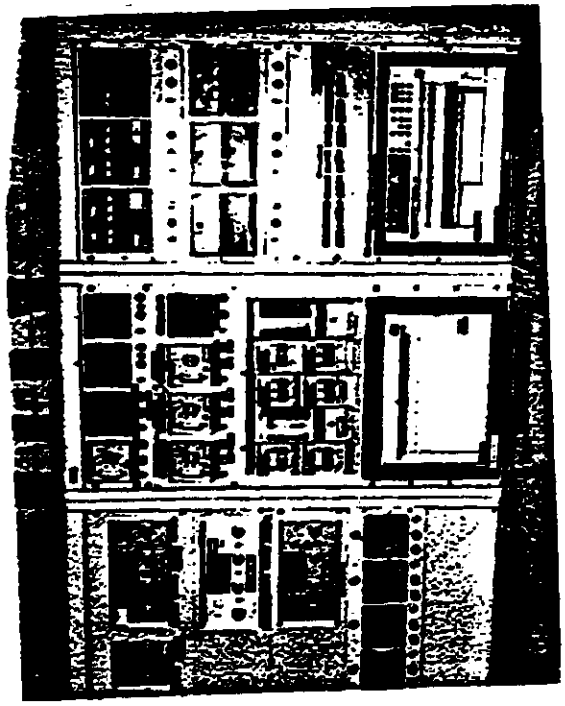

Figure 4.7. Control Panel.

IV-3. Laboratory Safety.

Safety deligence is a fundamental requirement in the project laboratory. A general guideline for laboratory safety requirements has been filed in the laboratory manual [9].

The most possible serious hazard in the laboratory is fire. Almost all the chemicals used in the experiments, such as hydrogen, carbon monoxide, methane and ethylene in the gas streams, liquid product and solvents, are highly flammable. Therefore, caution must be exercised when dealing with them, e.g., securely ground appropriate equipment, eliminate spark sources, no smoking in the laboratory etc.

Carbon monoxide gas is a deadly poison. Good ventilation of the laboratory is an absolute necessity. Cobalt catalyst is a very fine cluster powder. Breathing or surface contact can cause illness to the lungs or eyes. Thus, appropriate protection equipment (mask, safety glasses) is required when working with them.

Another type of possible hazard is explosions due to overpressuring. Caution should be exercised to avoid possible build-up of excessive pressure. Rupture disks should be installed to protect the equipment and

inspected periodically. Steam lines should be properly insulated to avoid burns.

IV-4. Experimental Design.

A key to the success of an experimental program is to utilize a sound experimental design. The procedure of the experimental design in this research can be outlined as below.

The first step is to clearly establish the objective of the experiment. In this kinetic study, the goal is to obtain a sufficient amount of legitimate experimental data which will fit the kinetic models (rate equations) derived from various reaction mechanisms proposed previously. Following the convention given in the previous chapter (of theory), the rate equation is defined as the variation of measured number of gram-moles of the sum of three active reactant species (i.e., hydrogen, carbon monoxide and ethylene) converted per unit gram of the Co_3O_4/Al_2O_3 catalyst per unit hour, with reaction temperature and the partial pressures of species in measurable amounts in the product streams at steady state conditions.

However, component mass flow rates in the feed and the operating conditions (amount and size of catalyst, temperature and total pressure) are the truly manipulable variables in the experiments. The experimental design is further simplified by fixing the catalyst conditions and operating pressure. The number of the manipulating

variables is reduced to four: the mass flow rates of three active reactants (H_2, CO and C_2H_4) and operating temperature. The mass flows of methane and carbon dioxide are relatively fixed.

Prior to the execution of any experiment, the reaction system along with auxiliary equipment, and the analytical gas chromatograph (GC) must be set up and checked for the proper operation and accuracy. The rotameters are calibrated on process gases using a wet testmeter. The calibration of the gas chromatograph is also performed using standard gases, and the component weight response factors for the thermal conductivity detector (TCD) of GC are determined.

In the next step, a base point is chosen as a reference, which corresponded to the mid scales of the rotameters. Experiments are then carried out at this base point for a couple of times to verify the stability of the operation and the consistency of experimental data. Equipment and procedures are modified to correct any problems if necessary.

After successful runs of the base point have been accomplished, the levels of the manipulating variables will be varied so as to cover the entire ranges allowed by the experimental equipment. The differential operation requirement, namely, the sum of the three

active reactant conversions must be less or equal to 5%, will be imposed for all kinetic experiments in order to utilize a simple component mass conservation equation to interpreter the experimental data. The kinetic experiments are also subject to satisfying the justified operating conditions determined by the initial phase of experimentation. For the experiments in the justification phase, the requirement of differential operation will be relaxed to about 10% instead, so that wider range of operating conditions can be observed.

IV-5. Kinetic Justification Experiments.

Transport phenomena can seriously interfere with the reaction and complicate the analysis for the reaction system, if caution is not taken to eliminate or minimize the effects in kinetic investigations. Gradients between the fluid and the solid may be minimized by sufficient turbulence. With the tubular flow reactor, this requires a sufficient high flow velocity. For a given catalyst, the internal gradients (inside the pores of catalyst particle) can be eliminated by crushing the catalyst to reduce its dimensions [92,93].

Therefore, experiments for determining proper operation conditions for kinetic experiments should include studies of temperature, mass velocity and particle size [189,190]. Figure 4.8 illustrates the general guideline for justification experiments for a kinetic study. All experiments were carried out in the same fixed-bed microreactor by the same procedures as described previously. Catalyst activity was checked periodically by a long experimental run at the base point and the variation of the conversion of reactants was observed.

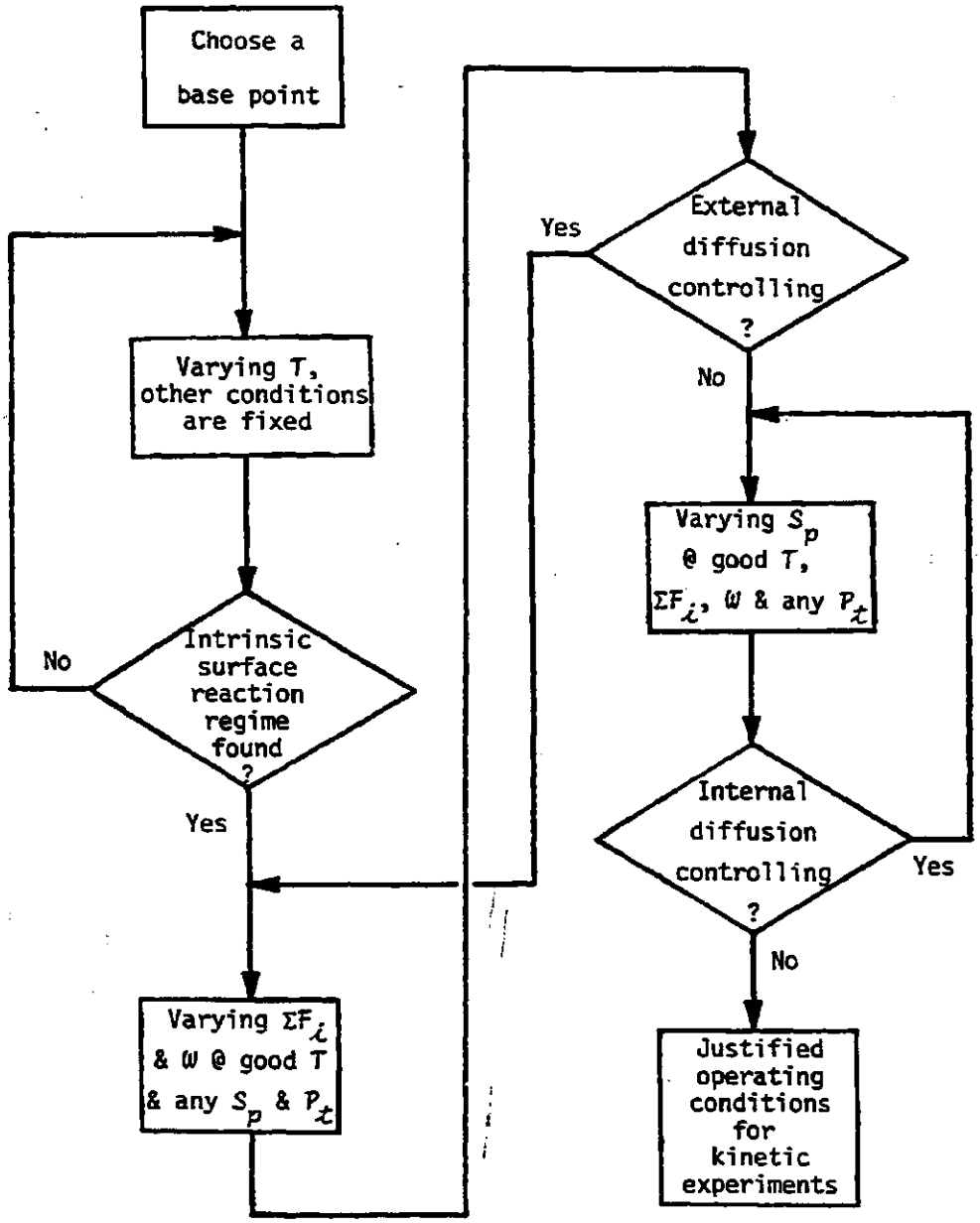

Figure 4.8. Study Plan for Kinetic Justification Experiments.

Notations for Figure 4.8

F_i : i-component mass flow rate in feed, $\frac{gms}{hr}$,

P_t : total pressure, kP_a,

S_p : mean particle size of catalyst, cm,

T : reaction temperature, °K,

W : mass of catalyst, gms.

IV-6. Kinetic Experiments.

The kinetic experiments were carried out according to the general direction described in the previous section (IV-4) of experimental design. The operating conditions were set inside the safety regime determined by the result of the kinetic justification experiments. 1.0 gram catalyst of 60-150 mesh was used and total operating pressure was set at 140 psig throughout the kinetic experiments. Only those experiments executed under the differential condition, i.e., less than 5% of conversion of reactants, were retained for further analysis.

IV-7. Catalyst Preparation and Characterization.

The cobalt/alumina catalyst used in this study was prepared by a typical impregnation method [9]. Standard cobalt nitrate solution was obtained by physically mixing 600 gms of Hall cobalt nitrate flakes ($Co(NO_3)_2 \cdot 6H_2O$) with 250 ml of deionized water. A standard cobalt nitrate solution (5400 ml) was then poured onto 20,455 gms of ALCOA F-1 activated alumina. After thorough mixing, the catalyst was left to dry in the oven overnight at 75 °C. The catalyst was then calcined in the Solid State Laboratory tube furnace the next day for four hours at 450 °C with 4 cu.ft. per hour of dry air (Figure 4.9). Approximately 45 lb of catalyst was recovered and ground. The catalyst was then screened and separated according to mesh size. The weight percentage of cobalt in the final form of the catalyst was calculated to be 11.62 wt%.

A Philips X-ray diffractometer, Type 42267/0 (shown in Figure 4.10), from the Chemistry Department, was employed to identify the compound in the catalyst and to measure the mean crystallite size [242]. Some operational parameters are listed in Table I.5 of Appendix I. The catalyst was packed in an aluminum sample holder of 1 cm by 2 cm by 1 mm and covered with transparent tape to avoid spillage in the rotary scanning. The diffraction

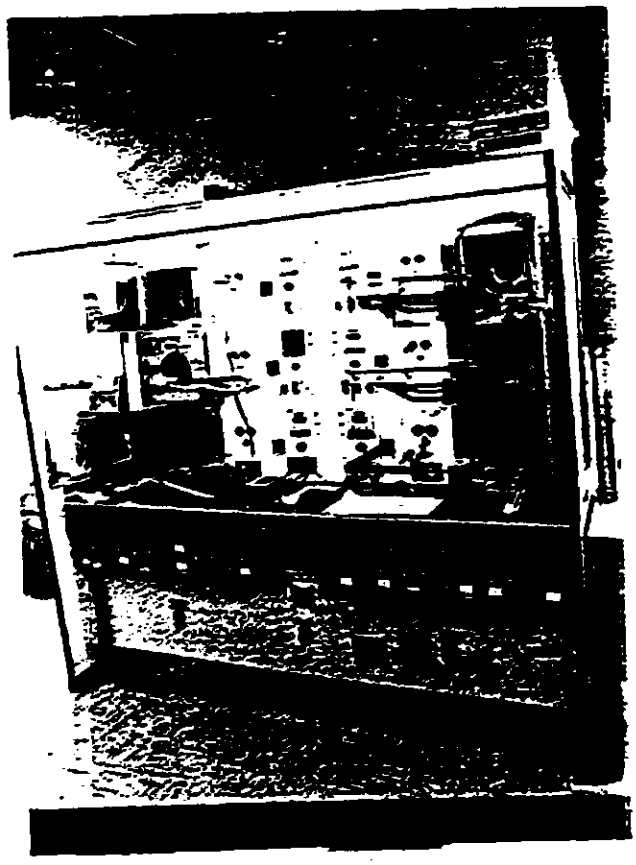

Figure 4.9. Furnace Chamber.

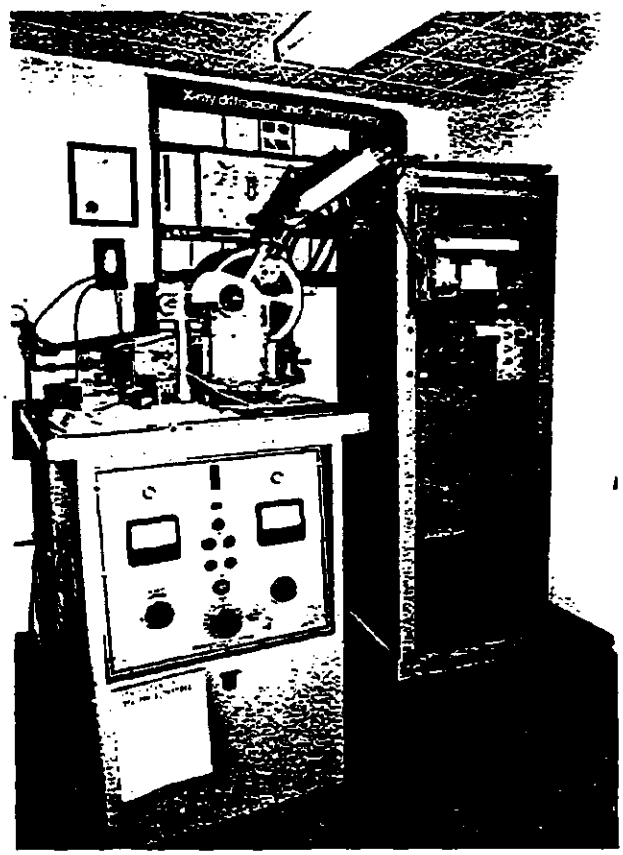

Figure 4.10. Philips X-Ray Diffractometer (Type 42267/0).

pattern of the catalyst was transformed into d-spacings and compared with tabulated values filed by the Joint Committee on Powder Diffraction Standards (JCPDS) of the American Society for Testing and Materials (ASTM).

The same instrument was also used to measure the broadening of the peak of (311) plane of the catalyst at θ=36.83°. With ALCOA F-1 activated alumina (80-200 mesh) as the internal standard (same 311 face-centered cubic index at 38.2°), the mean particle size of the catalyst can be estimated according to the Scherrer equation [66,131];

$$t = \frac{0.9\lambda}{B\cos\theta} \qquad (4.1)$$

Here t is the volume-averaged crystallite diameter, λ is the X-ray wavelength, B is the broadening of diffraction peak measured at half of its maximum intensity (in radians) and θ is the Bragg's angle corresponding to the peak.

A Phillips X-ray fluorescence spectrometer (Model PW1410-60K) shown in Figure 4.11 and located in the Chemistry Department, was employed to measure the bulk concentration of active species (cobalt) in the catalyst

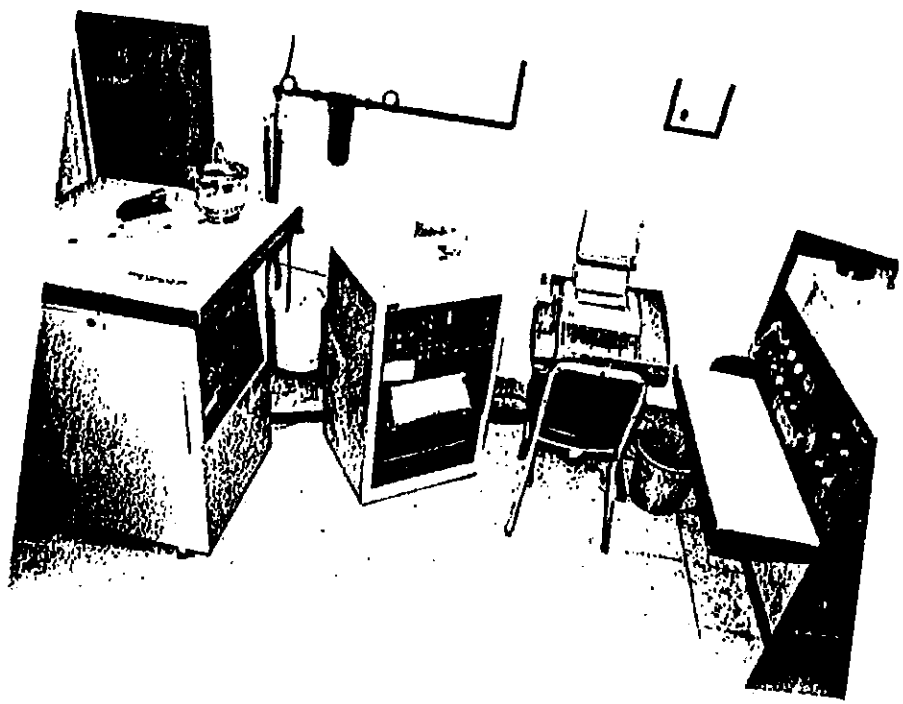

Figure 4.11. Philips X-Ray Fluorescene Spectrometer (Model PW1410-60K).

[243]. Operation parameters of this equipment are given in Table 1.6 of Appendix 1. Standard of 0.2 grams were prepared by mixing proper amounts of Baker cobalt oxide and MCB activated alumina. The standards were further blended with 0.4 gm of Brinkmann avicel microcrystalline cellulose and packed into discs in a stainless steel mold under 3,000 lb force by a hydraulic jacket. Scanning a standard locates three Bragg's angles (2θ) of the most sensitive plane and two backgrounds (one before and one after). Measured intensities of radiation from LIF (200) crystal were fed into an on-line PDP minicomputer to calculate the correct relative intensities from which a calibration curve was established and catalysts of unknown compositions thus were compared. Calibration curves for cobalt scanning are shown in Figures F.1 and F.2 in Appendix F. Sample experimental results are shown in Table F.2.

A conventional volumetric adsorption apparatus with two manifolds was fabricated and installed in the project laboratory (see Figures 4.12 and 4.13), and was used to measure the amount of hydrogen uptaken by cobalt in a fresh catalyst sample at room temperature [145]. Weighed catalyst was first loaded into the mid section of the sample cell shown in Figure 4.14. The sample cell was then connected to a catalyst pretreatment unit (Figures 4.15 and 4.16) where reduction of catalyst was conducted.

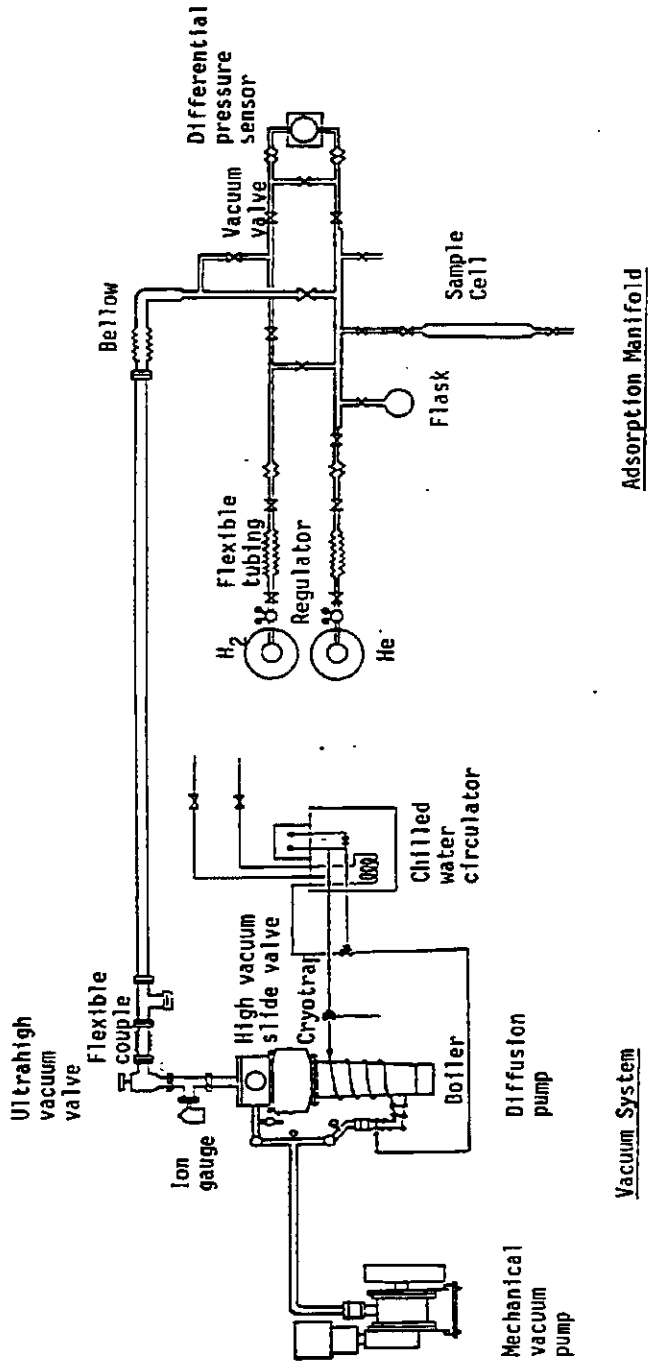

Figure 4.12. Adsorption Apparatus - Schematic.

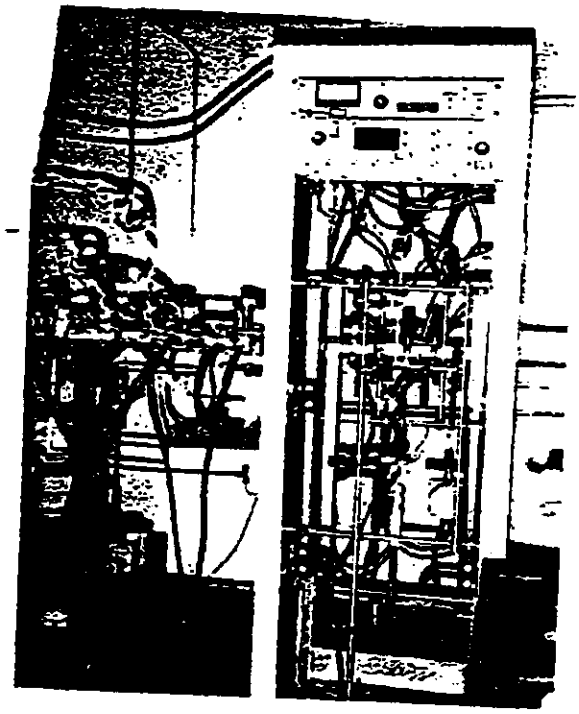

Figure 4.13. Adsorption Apparatus - Photograph.

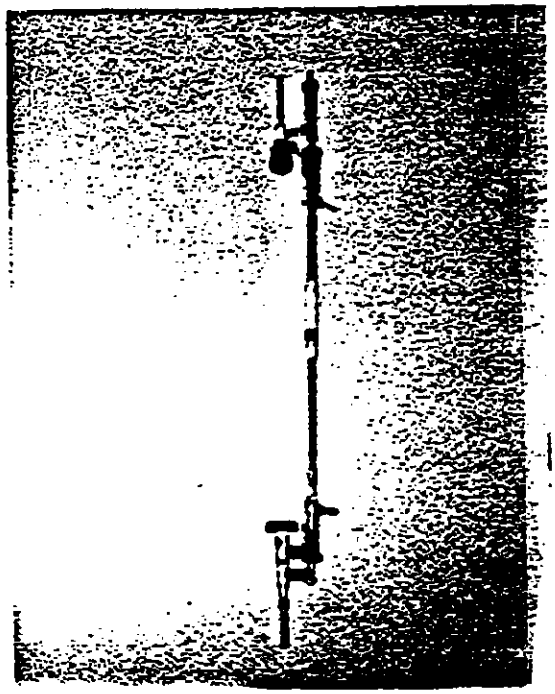

Figure 4.14. Catalyst Sample Cell.

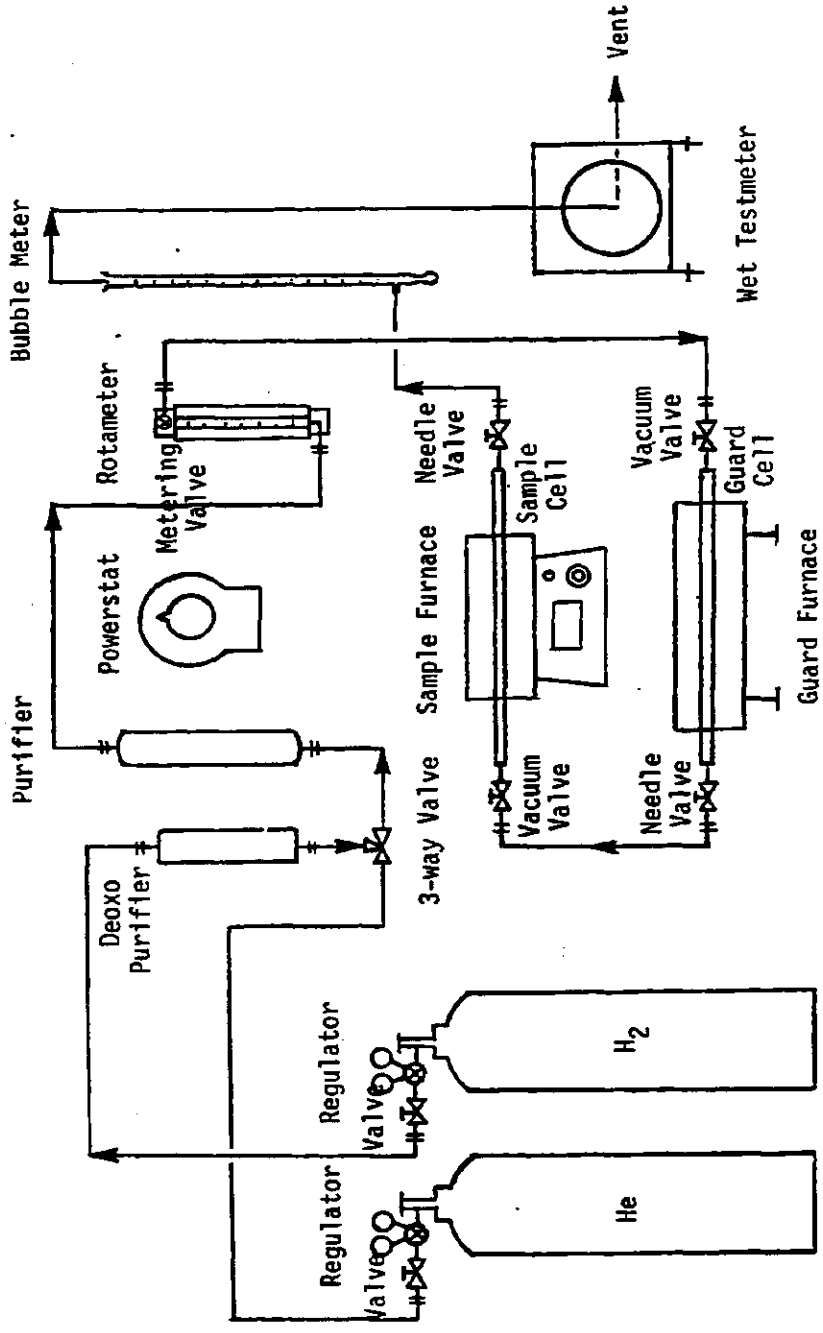

Figure 4.15. Catalyst Sample Pretreatment Unit - Schematic.

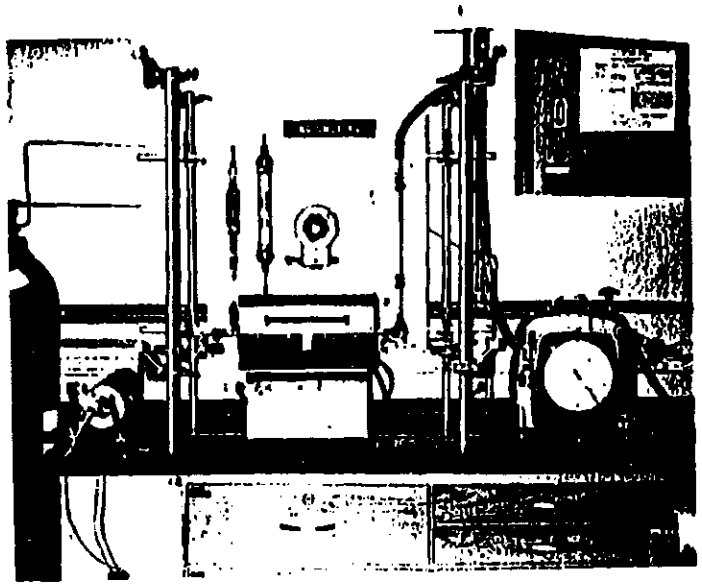

Figure 4.16. Catalyst Sample Pretreatment Unit - Photograph.

The reduction was started by manually adjusting the heating rate about 10 °C/min with ultra-pure hydrogen (99.999%) from Air Products at 0.012 cubic foot per minute (28.6 °C and 1 atm) until 400 °C and then held at this temperature overnight. At the end of the reduction period (about 20 hours), the tube furnace (Linberg 55035) was turned off and both inlet and outlet vacuum valves (Kontes 826510) of the sample cell were sealed. The sample cell was then carefully removed from the catalyst pretreatment unit and attached to the adsorption manifold through a Cajon ultratorr union (SS-6-UT-6).

A 1/2 inch by 4 feet heating tape was wrapped around the sample cell outside the catalyst bed and adjusted by a variable Powerstat transformer to 390 °C. The outgassing of the catalyst was continued for an hour. The transformer was then turned off and the sample cell was isolated and cooled down. The adsorption manifold was filled with a sufficient amount of ultra-pure helium (99.998%) and the pressure was recorded by a MKS 170M series instrument consisting of a 3-channel selector (34C), a digital readout (27E) and an electronics unit (6C) with a Baratron temperature-controlled differential sensor (310CH-1000) [159]. The measured quantity of helium was then expanded into the sample cell to determine the dead volume of the sample cell. After evacuation, the sample cell was again isolated from the

manifold and the proper amount of pure hydrogen was admitted into the manifold. The hydrogen was later expanded through the vacuum valve into the sample cell.

The uptake of hydrogen by the active cobalt in the fresh catalyst at room temperature is actually obtained by the usual adsorption isotherm procedure, namely, repeatedly evacuating the manifold and sample cell, isolating the sample cell, admitting an appropriate quantity of hydrogen into the manifold, recording the pressure, expanding the hydrogen into the sample cell, waiting until equilibrium (usually 45 minutes) and recording the final pressure [86,145,162]. Another technique which admits hydrogen at rather high temperature and then allows it to cool to room temperature can lead to the maximum uptake of hydrogen [181].

From the amount of adsorbate adsorbed by the adsorbent, the number of accessible surface atoms, N_S, of the adsorbent can be calculated by [162]:

$$N_S = \frac{N_{Avo} V_m X_S}{V_{mol}} \qquad (4.2)$$

provided the stoichiometric factor, X_S (the average number of surface metal atoms covered by each molecule of adsorbate), is known. V_m is the measured volume of chemisorbed monolayer, V_{mol} is the molar volume of the adsorbate, and N_{Avo} is the Avogardro number. To calculate the surface area of active metal, A_S, it is necessary to know the site density, n_S (the average number of metal atoms per crystal surface area), as follows:

$$A_S = \frac{N_S}{n_S} \qquad (4.3)$$

IV-8. Product Analysis.

IV-8.1. Gas Product.

Although the products of the modified Fischer-Tropsch reactions are complex, most components (>C_4) can be condensed and separated from the gaseous product. A Carle analytical gas chromatograph (Model 111), shown in the middle of Figure 4.17, equipped with a hydrogen transfer system and automatic programming base allowed for analysis of gaseous product in either a single run, repetitive runs, or short or long runs with automatic sequencing. Coupled with a Spectra-Physics integrator (SP-4270), plotting and calculation of a sample analysis can be completed within a 15-min interval for a short run or 45-min for a long run. Some operational conditions of the Carle GC are given in Table I.3 in Appendix I.

IV-8.2. Liquid Products.

Water-insoluble organic products were analyzed by a Hewlett-Packard 5710A gas chromatograph equipped with a flame ionization detector (FID). The GC is shown in Figure 4.18. The C_{5+} hydrocarbons were separated by a 1/8 inch by 6 feet 3% Dexsil 300 on 100/120 Supelco high temperature column. All samples were diluted to 10 mg/cc with carbon disulfide before injection into the column. FID response factors for C_{5+} hydrocarbons were

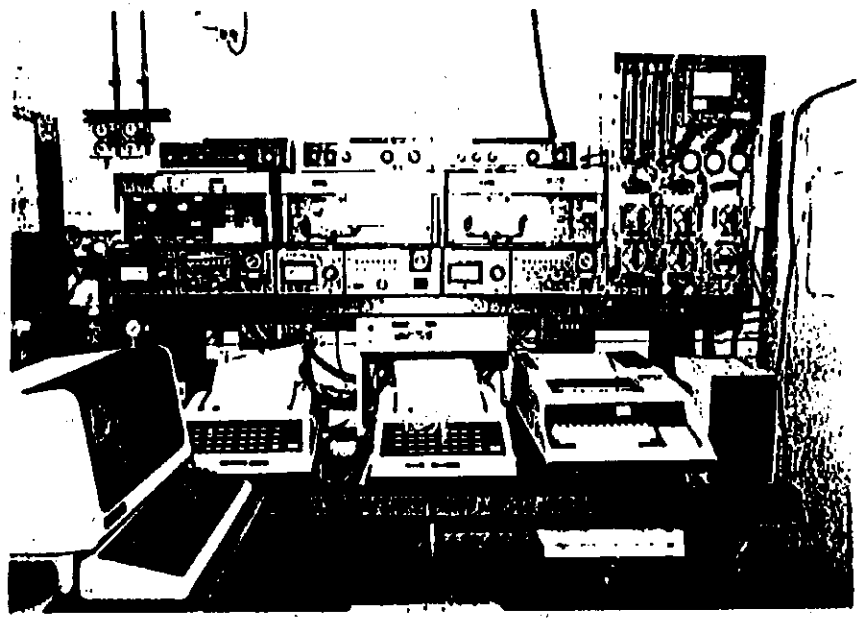

Figure 4.17. On-line Carle Analytical Gas Chromatographs and Spectra-Physics Digital Integrators.

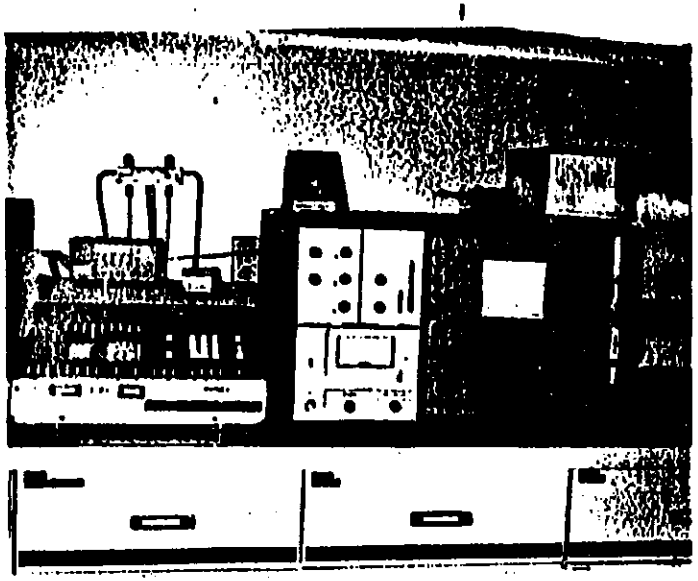

Figure 4.18. Hewlett-Packard FID Gas Chromatograph (Model 5710A).

essentially the same and taken to be 1.0, hence the normalized peak areas would be directly proportional to the weight composition of the sample [249]. Some operational settings for this GC are given in Table I.2 of Appendix I [113].

Water-soluble liquid product analysis was performed on another Hewlett-Packard 5730A gas chromatograph (Figure 4.19) equipped with a thermal conductivity detector (TCD). A 1/8 inch by 6 feet Poropak Q column was used to separate the water and alcohols and a 5A molecular sieve column was also installed in parallel as a reference column. Table I.3 in Appendix I lists major operation parameters [113].

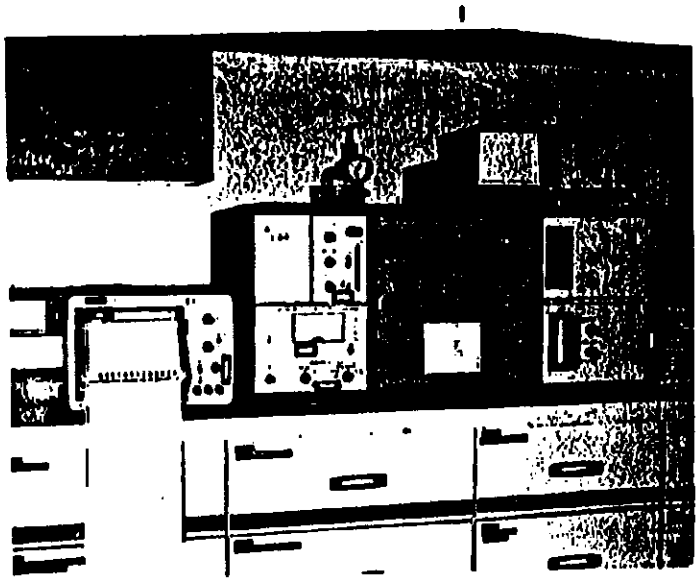

Figure 4.19. Hewlett-Packard TCD Gas Chromatograph (Model 5730A).

IV-9. Computer Computation.

The sequence of steps in the data reduction process utilized in the experimental work of this research can be summarized as follows.

1. Determine the component weight response factors for the TCD of the GC.
2. Obtain the peak areas of the GC chromatogram for each species, by the digital integrator.
3. Measure the amount of steady flow of gas product by wet testmeter.
4. Measure average amounts of liquid products collected in between two samplings and determine the specific densities.
5. Feed all the above information about product streams plus known amounts of feed components by corresponding rotameters, into the computer to perform the calculation of the material balance. Component rates, mole fractions in product, and percentage conversions are also determined by the calculations.

As usual, these response factors are obtained through the standard calibration procedure [45,87,146,227,249]. by:

$$f_i = \left(\frac{W_i}{W_{CO_2}}\right)\left(\frac{A_{CO_2}}{A_i}\right) \qquad (4.4)$$

where f_i is the TCD weight response factor for component I, W_i and W_{CO_2} are weights of component I and carbon dioxide (reference), and A_{CO_2} and A_i are the peak areas measured from the gas chromatograms.

The University IBM computer system (370) was employed to perform most data reduction and analysis. Fortran programs GC, THERMODY, and MODEL6B were developed with the incorporation of routines available from various sources [125,187]. Program GC was used to calculate the material balance. Program THERMODY computed the equilibrium conversions based on the method of steepest descent to minimize the total Gibbs free energy of a mixture subject to the conservation constraints of atomic elements [13]. Figure 4.20 shows the logic of this program. Kinetic models from theoretical derivations were fitted by Program MODEL6B using the Marquardt nonlinear regression method [151]. All three computer software programs are listed in Figures K.1 through K.3 of Appendix K.

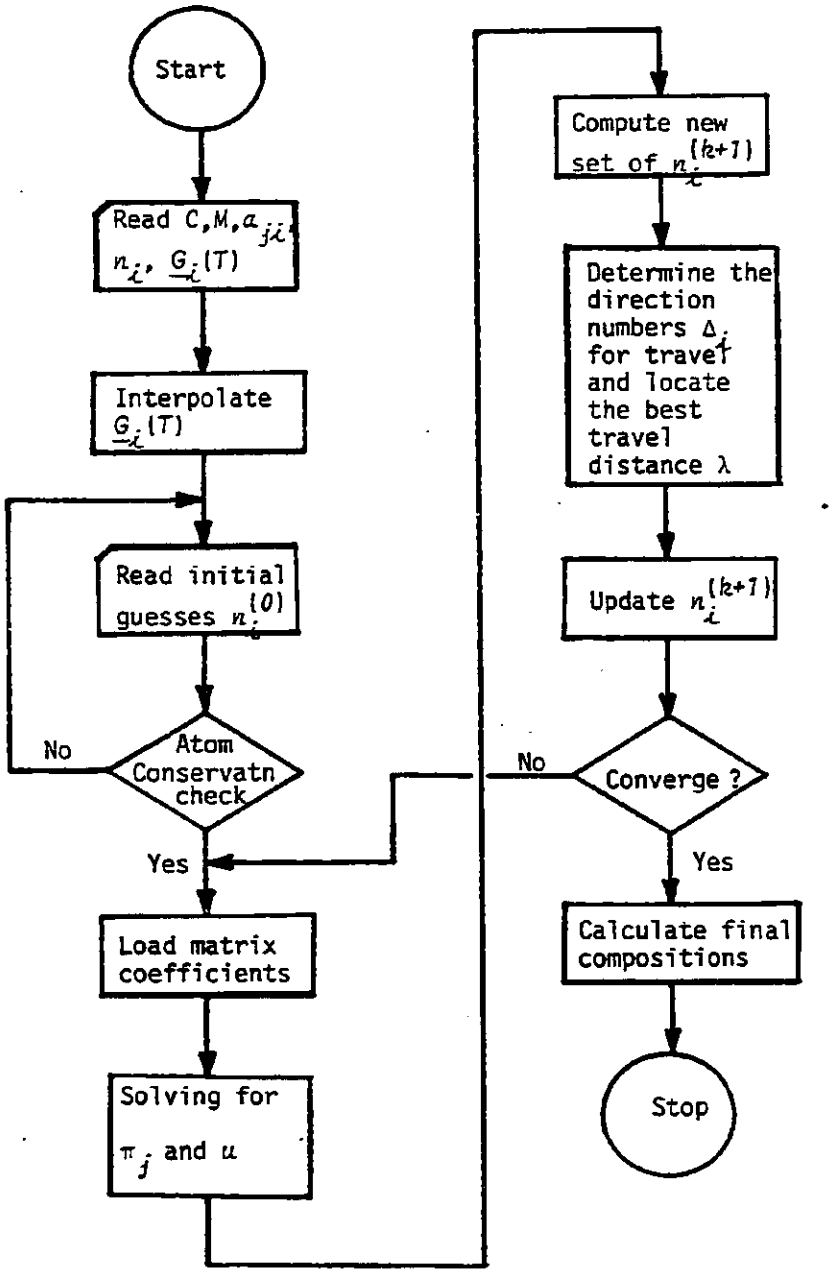

Figure 4.20. Logic Algorithm for Program THERMODY.

Notations for Figure 4.20.

a_{ji} : number of gm-atoms of atomic element j in a mole of component molecule i,

b_j : total number of gm-atoms of atomic element j in the reacting mixture,

C : total number of components in the reacting system,

$\underline{G}_i^0$: standard molar Gibbs free energy of formation of component i,

$\underline{G}_i(T)$: molar Gibbs free energy of formation of component i at temperature T,

k : k^{th} iteration,

M : total number of atomic elements present in the reacting mixture,

n_i : moles of component i in feed,

$n_i^{(k)}$: moles of component i in product after k^{th} iteration,

$n^{(k)}$: total number of moles in the reacting mixture after k^{th} iteration,

$u \triangleq \dfrac{n^{(k+1)}}{n^{(k)}} - 1$,

π_j : Lagrange multiplier of atomic element j,

Δ_i : direction number in i direction,

λ : distance of travel.