EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL LIQUEFACTION REACTOR. FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

AUG 1983
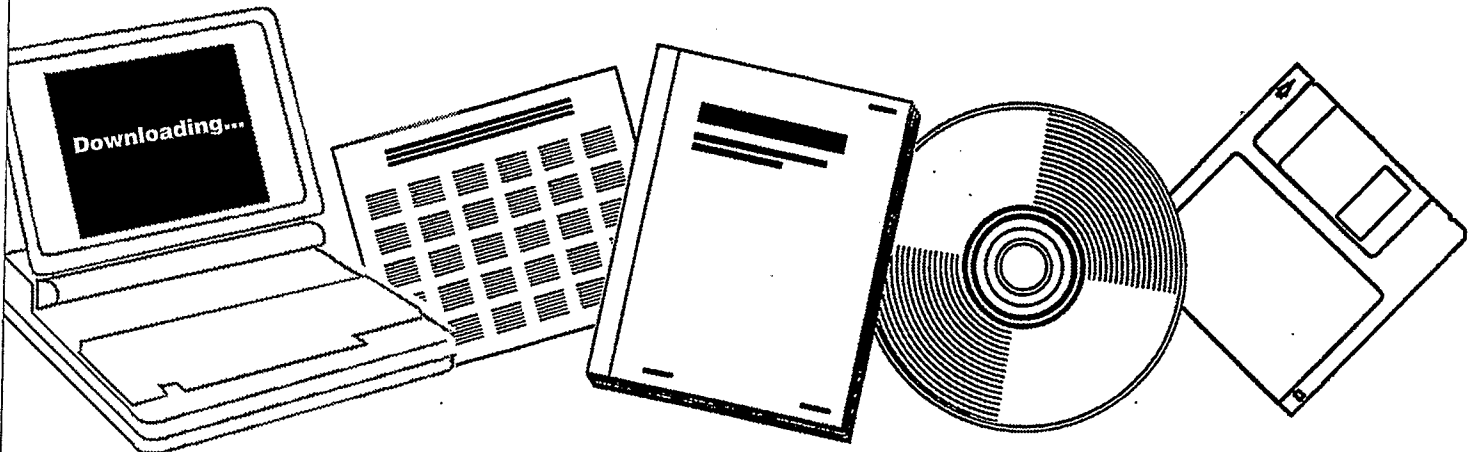
AN EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES
IN AN ADIABATIC COAL LIQUEFACTION REACTOR

Final Report

S. Bhattacharjee
M. McMahon
Y. T. Shah
J. W. Tierney

Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

August, 1983

Summary:

Many industrially important three phase hydroprocessing reactions are highly exothermic. The rational design of any three phase slurry reactor requires fundamental understanding of its thermal behavior. In the first phase of this project an adiabatic CSTR slurry reactor was designed, constructed and operated at the Gulf Research and Development laboratories. Ignition and quench were demonstrated for coal liquefaction. Under normal feed conditions for SRC-II operation, repeated ignition and quench behavior were demonstrated. No stable steady state was found in the vicinity of 450°C (and below 475°C). Ignition occured at a feed temperature of about 415°C. The low steady states observed occured at conditions of no heat generation, presumably at low or no reaction of hydrogen. Some evidence of a preheater effect on reactor ignition was indicated but not systematically studied.

Data on the first phase of the project indicated that a small scale batch reactor can be made to operate in an adiabatic mode by using proper compensation for heat losses. However, a major difficulty with the reactor was the long time to reach steady state. In the second phase of this project a modified version of the reactor was designed and built in the laboratories of the Chemical and Petroleum Engineering Department of the University of Pittsburgh. This reactor shows a significant improvement in the degree of adiabaticity achieved and is more versatile. It can be used to measure the heat effects for complex hydroprocessing reactions. Fischer-Tropsch reaction was used as a case study and, in preliminary test, operation values for thermal requirements were found to agree with calculated values.

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1. Introduction:

The rational design of any three phase slurry reactor requires a fundamental knowledge of the kinetics of the reaction, the hydrodynamics of the reactor and the thermal behavior of the reactor. The kinetics and hydrodynamics of three phase slurry reactors, have been studied (Shah, 1981) but few experimental bench scale or pilot scale studies have been reported which elucidate the exothermic nature and behavior of the reactors. There are substantial difficulties in designing and operating a small scale reactor in adiabatic mode because of the high surface area to volume ratio in a small scale reactor. Yet for large commercial reactors, the reverse is true and adiabatic operation will result unless heat exchange is provided. A small scale reactor designed to operate adiabatically was contructed and operated at Gulf Research and Development and was described in previous reports (Shah, 1982a,b). Although adiabatic operation was demonstrated there are some serious limitations in the operation of the reactor: the only control of reactor temperature is the feed temperature, and this results in long times to reach equilibrium; the placement of thermocouples for measurement of temperature gradient in the insulation surrounding the reactor is critical because of poor thermal conductivity of the insulation; and the use of a simple analog control system does not provide the versatility desired.

A new reactor was designed with the following features.

(1) A cooling coil is provided for the reactor. This permits removal of large amounts of heat and more importantly, allows the heat removal to be exactly measured. Furthermore, the reactor can be operated in an isothermal mode by measuring and controlling the amount of heat removed. This should result in short times to reach steady state.

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(2) The insulated reactor is placed in a thick copper vessel and a zero temperature gradient is maintained between the reactor wall and the copper vessel. Because of the high thermal conductivity of the copper, the thermocouple placement is less critical.

(3) A digital computer is incorporated in the system to record important process variables at frequent intervals, to provide control signals for the adiabatic heaters and to control the flow of coolant.

A detailed description of the reactor is given in the next section. It has been built in the Chemical and Petroleum Engineering Department laboratories and some preliminary test data taken on this system are reported.

2. Reactor Design

A detailed schematic diagram of the reactor is given in Figure 1. The reactor is a standard 1 liter autoclave manufactured by Autoclave Engineers Inc. The reactor has a 7.62 cm inside diameter and an internal height of 24.1 cm. The vessel is equipped with a variable speed mechanical stirrer which is driven by a magnetic coupling. A special 1-in diameter and 12-in long extension for the stirring shaft has been made in our shop to provide extra room for the insulation and heating tapes placed around the shaft. Feed gases are sparged through a 1/8 inch sparger at the bottom of the reactor and product gases and vapors are removed at the top of the reactor.

The reactor and its contents can be heated to the initial reactor temperature by a 51-in long, 1/4-in diameter and 1500 W tubular heater (manufactured by Chromalox Inc.) which is wrapped around the body of the reactor. A cooling coil is also provided inside the reactor where house air, available at 100 psig can be used as coolant.

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Figure 1   Cross Section of Adiabatic Container

for Slurry Reactors

Six Thermocouples
on Copper Vessel

Ring
Heaters

Shaft
Extension

Drum

Six Thermocouples
on Reactor Body

Ceramic
Heaters

Copper
Pipe

Tubular
Heater

Copper
Plate

Reactor

Insulation

Insulation

Insulation

Ring Heaters

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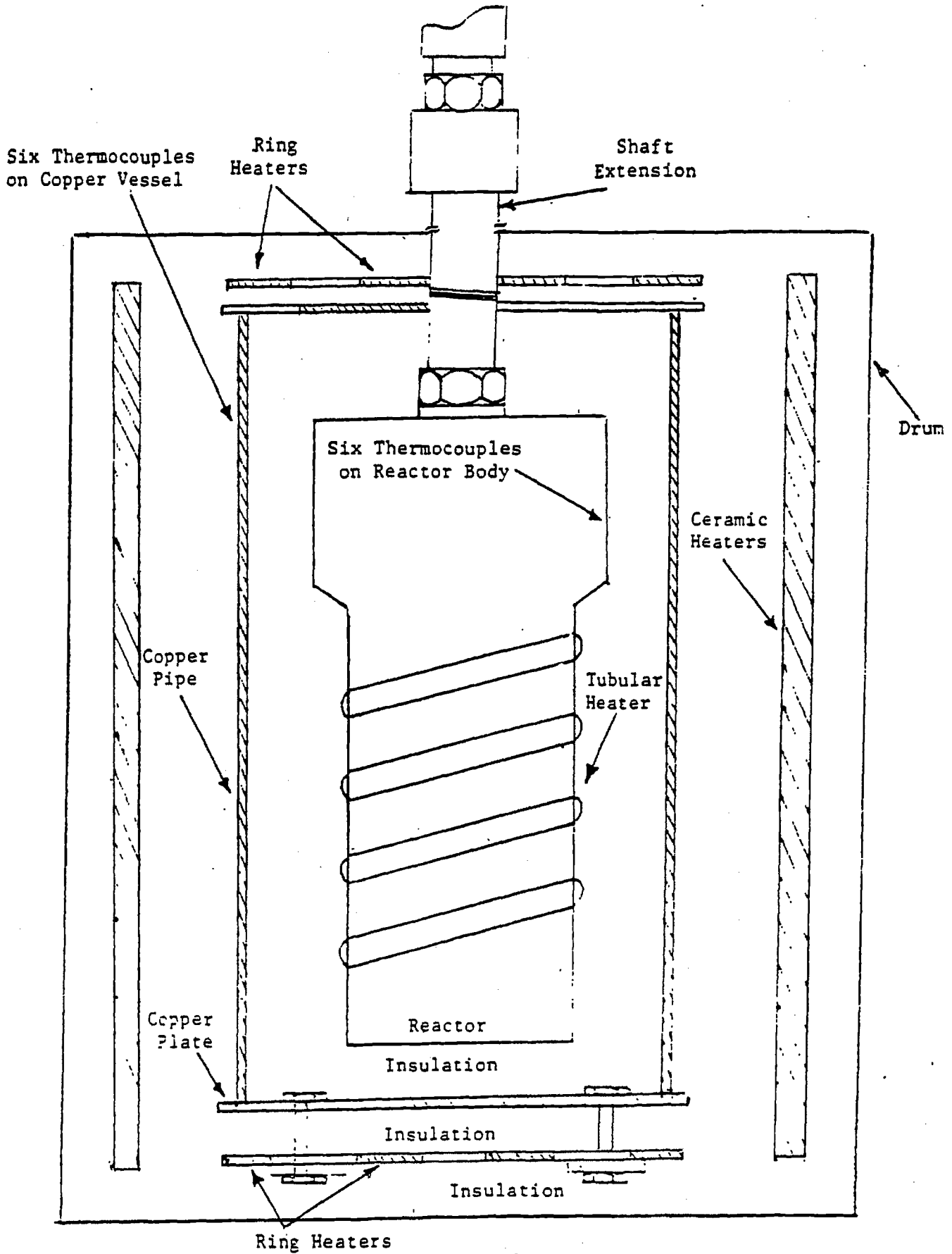
The autoclave is then put inside a 15-in long, 10-in o.d. and 1/4-in thick copper pipe and Fiberfrax bulk fiber insulation is packed in between the copper pipe and the reactor. Four quarter-circle ceramic heaters 18-in long, 12-in radius of curvature and each 1000 W (manufactured by Electrode Heat System Inc.) were placed around the copper pipe. The space in between the copper pipe and the ceramic heaters is filled with 3/8-in diameter aluminum balls for effecient and uniform heat transfer from the heaters to the copper pipe.

The bottom of the copper vessel is closed with a 11-in diameter and 1/4-in thick copper plate which is screwed on the wall of the copper pipe. Beneath the copper plate there are two ring heaters (a small one of 6 19/32-in o.d., 41/2-in i.d. and 500 W and a larger one of 10 31/32-in o.d., 8 1/2-in i.d. and 1000 W) which are tightly clamped with the bottom copper plate.

The top of the copper pipe is similarly covered with another copper plate of 11-in diameter and 1/4-in thickness. Two slots are provided on the top copper plate as shown in Figure 1, to take out the feed and product gas lines, coolant inlet and outlet lines, thermocouple extension wires and the lead wires of the tubular heater wrapped around the skin of the reactor. Two ring heaters (a small one of 6 1/8-in o.d., 3-in i.d. and 660 W and a larger one of 10 31/32-in o.d., 8 1/2-in i.d. and 1000 W) are placed on the top copper plate. Thermocouples are placed around the reactor body and on the copper vessel at the positions shown in Figure 2. One thermocouple and two tape heater (each of 400 W) are placed on the shaft extension to minimize the heat loss through the shaft. No insulation is placed around the ceramic heaters to achieve a better control on the temperature of the copper vessel.

The whole assembly consisting of the reactor, the copper enclosure around the reactor (copper pipe and the top and bottom copper plates) and heaters

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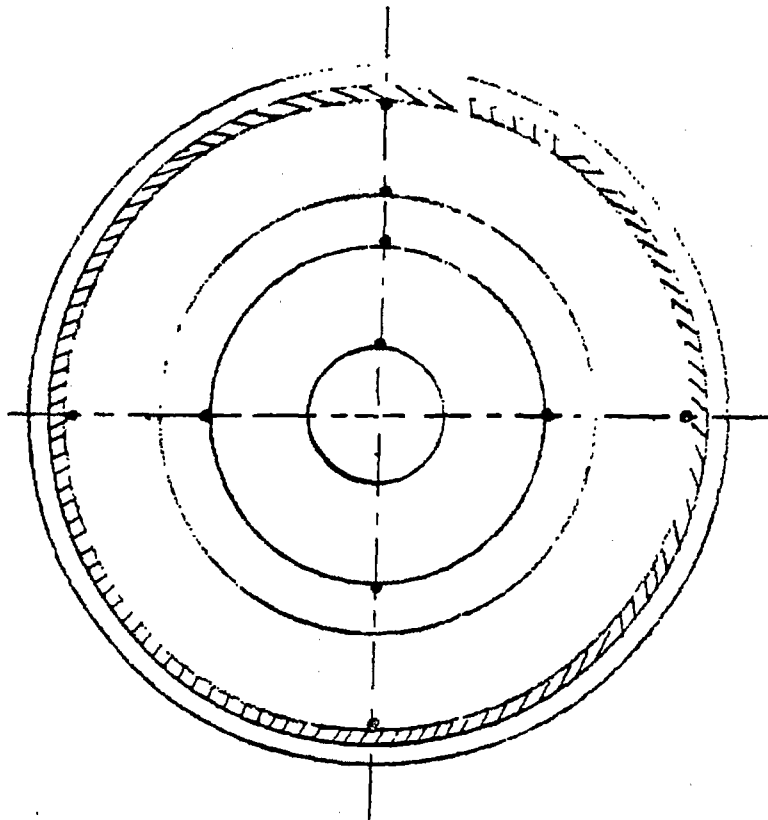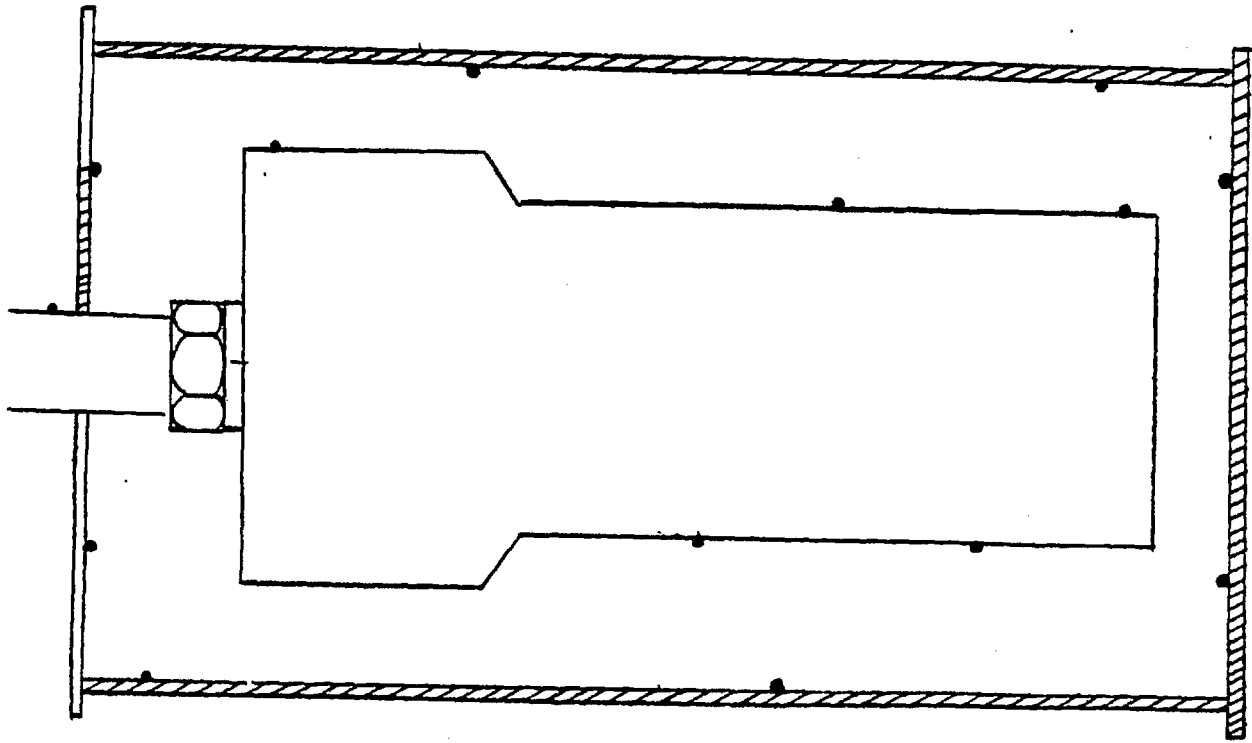
FIGURE 2.   Positions of Thermocouples Around the Reactor and the Copper Vessel

(four side heaters around the copper pipe, two at the bottom and two at the top) is placed inside a 20-in diameter and 30-in tall drum. A Fiberfrax Durablanket is wrapped around the outside surface of the drum to minimize the heat loss from the system.

3. Process Flow Diagram

Figure 3 is a process flow diagram for the slurry reactor unit which has been constructed. The system is shown with a gas feed of CO and H_2. With little modification, it can be used for other low or medium pressure gas-solid reactions. The gases are metered through calibrated valves and then enter a preheater to be heated to the reaction temperature. They then enter the reactor through a sparger in the bottom of the reactor. Product gases are removed from the reactor through an outlet line at the top of the reactor. Heat can be removed through a cooling coil which uses air as a coolant. House air at 100 psig enters through a pressure reducing valve, passes through a knockout drum to remove any liquid or solid and then passes through a two micron filter before entering a mass flow meter which is equipped with an integral control valve. The flow rate is controlled by the computer or by a manual set point potentiometer.

Liquid and gas leaving the reactor pass through a high temperature, high pressure gas-liquid separator with sight glass. Liquid samples are then removed through high pressure collection vessels. The gaseous product then goes through a back-pressure regulator and then through a water cooled condenser (to remove most volatile hydrocarbons) before it finally goes through a wet gas meter to measure the flow rate of the product gases. Provision is made to collect gas samples. Product gases are then analyzed by a Perkin-Elmer Sigma 1 chromatograph and is described in more detail in Section 6.

FIGURE 3. Process Flow Diagram
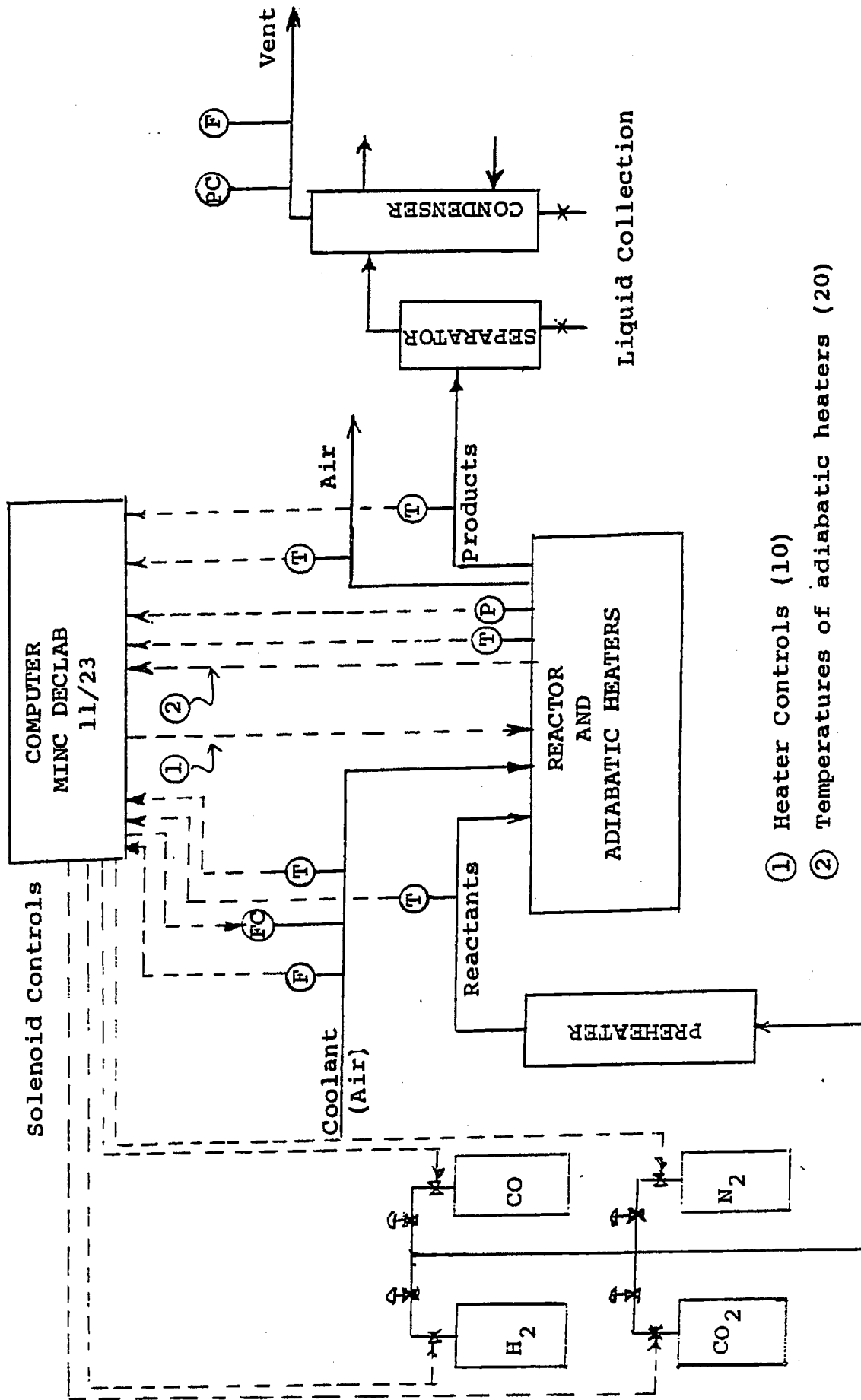
① Heater Controls (10)

② Temperatures of adiabatic heaters (20)

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4. Data Acquisition and Control:

A digital computer (MINC/DECLAB-23) is interfaced with the system to record important process variables at frequent intervals and to provide the control function needed for the coolant flow and direct digital control of the external heaters so as to maintain a zero temperature gradient between the reactor and the surrounding copper vessel. The computer system is comprised of processor and memory device options and various peripheral devices through which both analog and digital signals are accepted from or transmitted to the experimental unit. Real time programming is employed for acquisition of data from the thermocouples placed on the reactor, copper vessel and on the various process lines, flow rate of the coolant (0-5V output from the mass flow meter), and the reactor pressure (0-5V output from the pressure transducer). These analog data are digitized through an A/D converter and processed by the computer to generate the following.

a) Direct digital control of each of the nine adiabatic heaters (including the one on the shaft) which in turn is directly connected to a solid state relay. Each relay is turned on and off by the computer, which uses the temperature measurements made on the reactor and on the copper vessel to determine the state of each relay. A total of 18 on-off signals can be provided from the computer.

b) Provide surpervisory control of the cooling air flow rate by establishing a set-point for the control valve.

c) Monitor reactor temperature and pressure and initiate an emergency shut-down procedure in critical situations.

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5. Fischer-Tropsch Reaction

In general, reactions of F-T synthesis can be approximately represented by

$$nCO + 2n\ H_2 \rightarrow CnH_2n + nH_2O \qquad (1)$$

and two important side reactions are

$$CO + H_2O = CO_2 + H_2 \text{ (Water gas shift reaction)} \qquad (2)$$

$$2CO \rightarrow C\ (s) + CO_2 \text{ (Boudouard reaction)} \qquad (3)$$
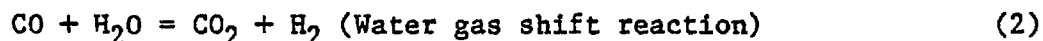
Most products from the F-T reaction are unbranched parrafins and olefins. The molecular weights range from 16 (methane) to 20000, and are strongly dependent on the catalyst, operating conditions and reactor type. The molecular weight distribution for the F-T reaction is generally found to follow a "Schultz-Flory" distribution (Madon, 1979; Satterfield and Huff, 1982). Some investigators (Satterfield and Huff, 1982) insist that the oxygenated compounds of significance must be included if the above equations are to hold good. Especially in the low carbon number range, where oxygenates are more common, their exclusion from the data can cause errors.

The product distribution in F-T synthesis depends significantly on the nature of the catalyst. Numerous catalysts have been used for the F-T reaction and a number of good reviews are available (Haggin, 1981, Shah, 1976, Anderson, 1956). Catalysts include Fe, Co, Ni and Ru. Promoters consist of Th, Mg, Al or K-oxides which are added mainly to stablize and create a high surface area. The energetic promoters which increase reaction rates via molecular effects are also used. Most catalysts used in either fixed bed or fluidized bed can also be used in slurry reactors if they are reduced to small enough size for suspension in slurry.

The catalyst used in this study is a commercial ammonia synthesis, fused-iron catalyst from United Catalyst, Inc. of Louisville, KY and designated as C73-1-01 and supplied as granules. The catalyst used in all the experiments reported here come from the batch #0656-S. The catalyst was first crushed, pulverized and then the cut between -150 and +250 mesh was chosen for our use. Typical catalyst properties, supplied by the manufacturer, are given in Table 1.

Fischer-Tropsch liquid supplied by Gulf Research and Development Co. is used as the liquid carrier. It is a relatively inexpensive parraffin that is characteristics of products formed by Fischer-Tropsch synthesis and it has a low volatility under reaction conditions (5% evaporation loss at $200^{\circ}C$). Typical properties of the solvent supplied by the manufacturer, is given in Table 2.

No commercial F-T process in slurry reactor exists today. However the process has been under development for a number of years in Europe and is considered ready for commercial production. The largest demonstration plant is the Rheinpressen-Koppers plant in 1951. The description of this process can be found in the paper by Thompson et al. (1981). Experiments done by a number of workers have generated the following conclusions.

(a) The rate of reaction is comparatively lower in slurry reactor than other reactors due to the presence of liquid.

(b) The best selectivity towards liquids is found with the slurry reactor system due to good temperature control and direct contact between liquid and catalyst particles.

(c) The slurry reactor offers greater flexibility in operation than a fixed bed reactor.

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Table 1: Typical Chemical and Physical Properties of the
Ammonia Synthesis Catalyst.
(Supplied by United Catalyst Inc.)

Catalyst Type   C73-1-01
         Size   -150 +250 Mesh
         Density lbs/cuft   170 ±10

Chemical Analyses (weight percent):

Fe	30-37	CaO	0.7-1.2
Fe_2O_3	65-68	SiO_2	<0.4
Free Fe	<0.5	P	<0.015
Total Fe	67-69	S	<0.001
Al_2O_3	2.0-3.0	Cl	<0.002
K_2O	0.5-0.8	Fe^{++}/Fe^{+++}	.45-.65

Table 2: Properties of the Liquid Carrier

Viscosity Index	136
Pour Point, ^{o}C	$<$-54
Flash Point, ^{o}C	243.3
Fire Point, ^{o}C	268
Flash Autogenous Ignition ^{o}C	360
Evaporation Loss, Wt.% 6.5 Hrs. @ 204.4 ^{o}C (400°F)	5.4
Total Acid No. (D974)	0.03
Specific Gravity, 15.6/15.6^{o}C (60/60°F)	0.8285
Water PPM	8
Appearance, 24 Hr., 0°C (32°F)	Bright
Bromine Index	824
C_{20} —	.06
C_{30} —	28.04
C_{40} —	53.22
C_{50} —	15.58
C_{60} —	3.11

6. Experimental Procedure:

Prior to start up, the reactor is internally cleaned by scrubbing all parts with THF (tetrahydrofuran) to remove any wax or carbon build-up. The reactor is then half-filled with THF and the reactor head placed back into the autoclave body to dissolve any organic material. They are then rinsed thoroughly with distilled water followed by acetone and allowed to dry overnight.

After cleaning the reactor 500 cc. of Fischer-Tropsch liquid (properties given in Table 2) and a predetermined amount of -150 to +250 mesh catalyst particles are charged to the reactor. The cover is then rebolted and the whole reactor is put inside the copper enclosure and the inlet and outlet lines are reconnected. The reactor is then pressure tested at 3.9 MPa. The space between the reactor and the copper vessel is filled with insulation and the top copper plate is placed back again. The thermocouples are reconnected and the reactor is ready for operation.

In all the experiments reported here, the catalyst was reduced in the slurry phase. After charging the solvent and catalyst, hydrogen is introduced to the reactor at a rate of approximately 300 cc/min and the reactor is heated up slowly with the help of tubular heaters to approximately 250°C and maintained there for at least 24 hours. Then the temperature is increased to 350°C and the catalyst is reduced at this temperature for at least 24 hours. During this reduction period, liquid starts collecting in the gas-liquid separator at a rate of approximately 25 ml/hr which is periodically flushed back to the reactor at a regular at interval of 2 hours.

After the catalyst has been reduced with hydrogen, the reactor is ready for synthesis runs. The regulator on the premixed gas cylinders are opened and the gas is allowed to flow through the bypass line. The upstream pressure

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of the gas is set at the desired value with the help of the back pressure regulator and the flow is allowed to stabilize for at least half hour. Concurrently the reactor is heated to the reaction temperature (typically in between $230^{\circ}C - 270^{\circ}C$) and the stirrer speed is fixed at approximately 600 rpm. At least four to five hours before this operation, the adiabatic heaters are switched on and the computer is allowed to raise the temperature of the copper vessel and the stirrer shaft to the reactor skin temperature. The extent of adiabaticity of the reactor is evaluated by measuring the rate of fall of temperature of the slurry inside the reactor. Once this has been established, the synthesis gas is taken off from the bypass line and allowed to flow through the reactor. The rate of flow of the product gas is recorded every half hour while the temperature profile of the reactor body, copper shell and the slurry temperature is continuously monitored by the computer.

The residual gas contains significant quantities of lower hydrocarbons (C_1-C_5) in addition to water. A fixed volume of the gas is taken out through a septum installed in the line after the back-pressure regulator and then injected into a Perkin-Elmer Sigma 1 Gas Chromatographic system equipped with a thermal conductivity detector. The column used is a 6 ft long and 1/4-in diameter 80/100 chromosorb manufactured by SUPELCO Inc. During analysis the injector and detector temperature are maintained at $150^{\circ}C$. A temperature programming of initial temperature of $40^{\circ}C$, initial time of 3 minutes and a final temperature of $150^{\circ}C$ is attained at a ramp rate of $11^{\circ}C/min$ and maintained at the final temperature of $150^{\circ}C$ for 8 minutes. The flow rate of helium carrier is 25 cc/min and the inlet pressure is maintained at 80 psig. Hydrogen, carbon monoxide, carbon dioxide and C_1-C_4 hydrocarbons are well separated in the column and a sample gas chromatogram is shown in Figure 4. Calibration curves of peak area versus amount injected for major Fischer-

Figure 4   Sample Gas Chromatogram

Retention Time	Component
1.55	H_2
2.38	CO
4.13	CH_4
7.54	CO_2
11.19	C_2H_6
12.87	C_3H_8
14.51	H_2O
19.12	nC_4
19.78	iC_4

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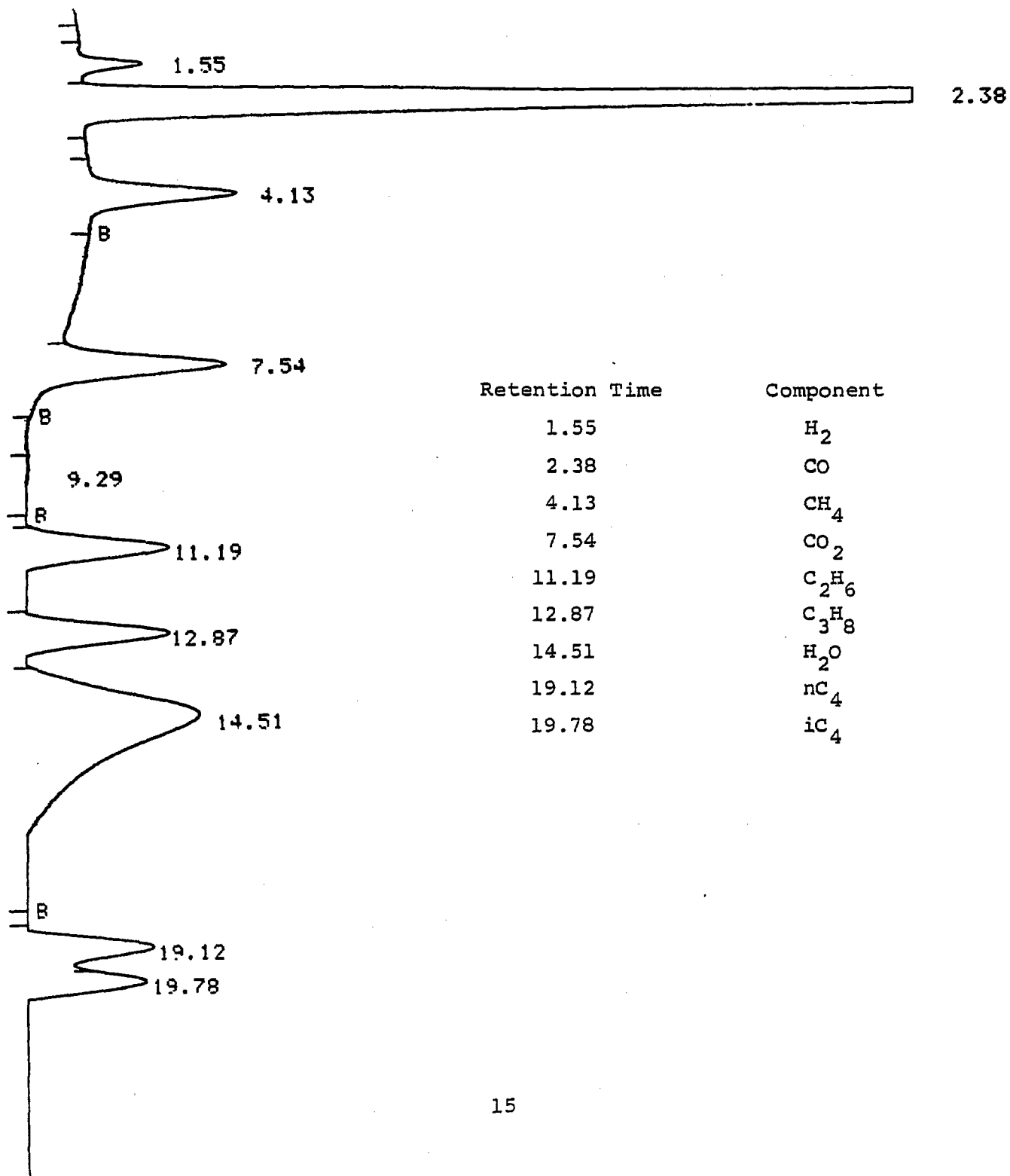
Tropsch components revealed that all gas chromatographic responses, except that for hydrogen, are linear and passed through the origin. However, we express all our conversion data in terms of total amount of carbon monoxide converted, which could be measured very accurately.

7. <u>Preliminary Runs to Test the Adiabaticity of the Reactor</u>:

The general principle of maintaining adiabaticity in the reactor has been described in Section 2. Direct digital control of the adiabatic heaters is maintained by interfacing the system to the MINC/DECLAB 23 computer. A series of runs were made to determine how effectively the control system maintained adiabatic operation. An inert gas, N_2, was fed to the reactor at the same rate as synthesis gas. If the system were completely adiabatic there would be no change in reactor temperature with time. The reactor was initially brought up to reaction temperature with the tubular heater and then the copper vessel was heated to within $5^\circ C$ of the average reactor skin temperature. Once a steady state temperature profile was established (about 2-3 hours), the following measurements were made.

a) The change in temperature with time was recorded. This measures the extent of adiabaticity of the reactor.

b) A known amount of heat was added using the tubular heater and the change in temperature was recorded.

To analyze the results, a reactor energy balance can be written as

$$Q' = m\ C_p \frac{dT}{dt} + Q_{loss} \tag{1}$$

where Q' =   Heat supplied through the tubular heater or rate of heat

                generation due to reaction (Cal /hr)

$m\ C_p$ =   Reactor thermal capacity (Cal/$^\circ$C)

Q'_{loss} =   Rate of heat loss from the reactor (Cal/hr)

     Since Q' and dT/dt can be measured experimentally, the heat loss (Q_{loss}) and thermal capacity of the reactor ($m\ C_p$) can be calculated. The temperature response of the system for three different rates of heat addition (0, 10 W and 2.5 W) is shown in Table 3 and Figures 5,6,7. A plot Q' against $\frac{dT}{dt}$ gives a straight line and is shown in Figure 8. A linear regression gives an estimate of the slope (mc_p) equal to 2184.4 cal/$^\circ$C and intercept (Q_{loss}) equal to 5619.6 cal/hr and a correlation coefficient equal to 1.0 indicating that the data can be well correlated by a straight line. These data enable us to determine mc_p and Q'_{loss} of the system. The experimental value of thermal capacity and agrees well with a value of 2170 cal/$^\circ$C calculated using the mass and heat capacity of the reactor body, the solvent and the catalyst. Preliminary experiments indicate that using the temperature change of the reactor we can measure the amount of heat added to or generated inside the reactor. The system responds rapidly to changes and the rate of temperature rise is very uniform for a fixed rate of heat addition to the system (Figure 6 and Figure 7). With no heat addition, there was a heat loss of 6.5 W, and in future experiments we plan to reduce this heat loss to zero by adjusting the adiabatic heater controls.
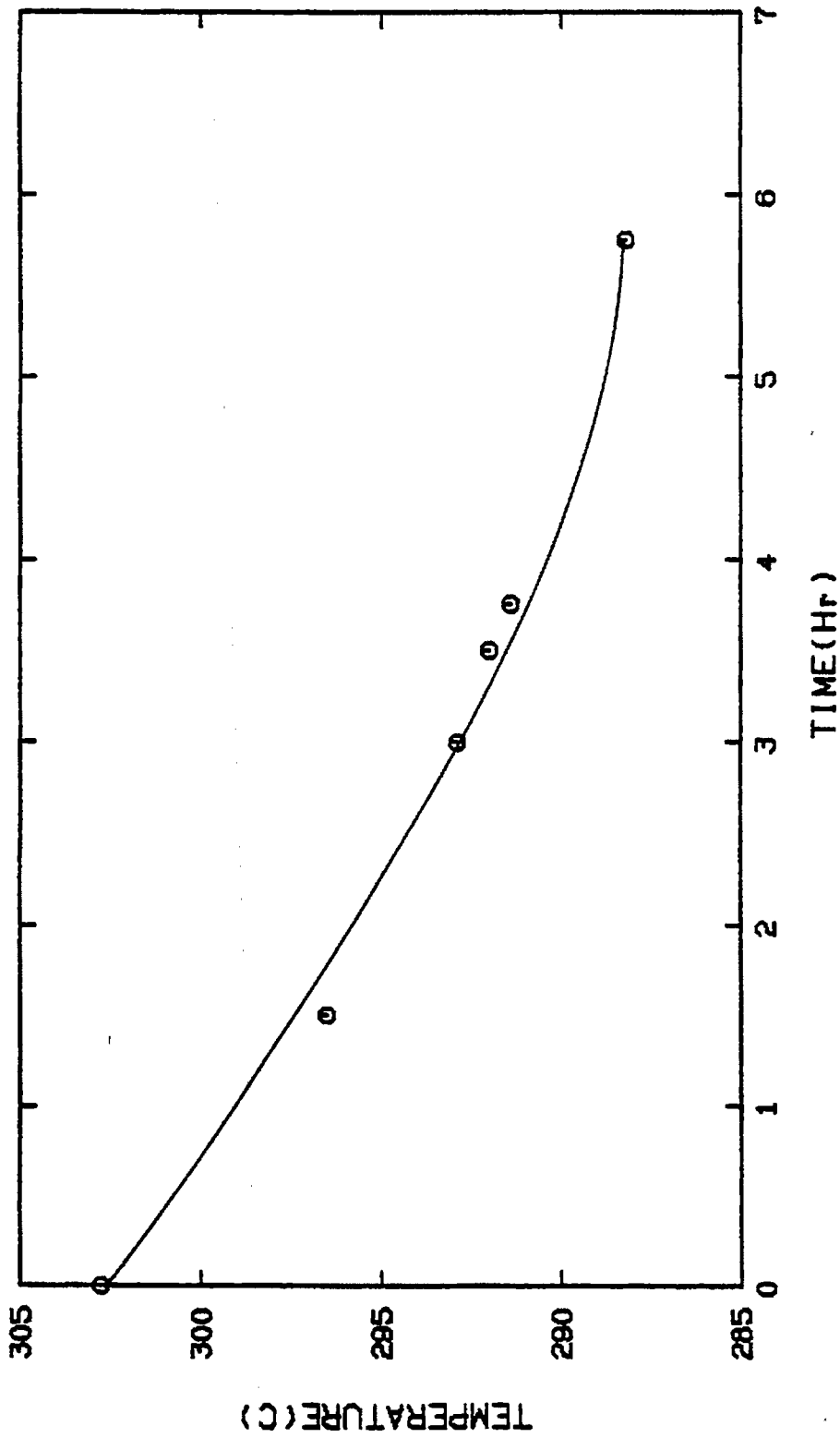
TEMPERATURE RESPONSE OF THE REACTOR FOR Q'=0

FIGURE 5
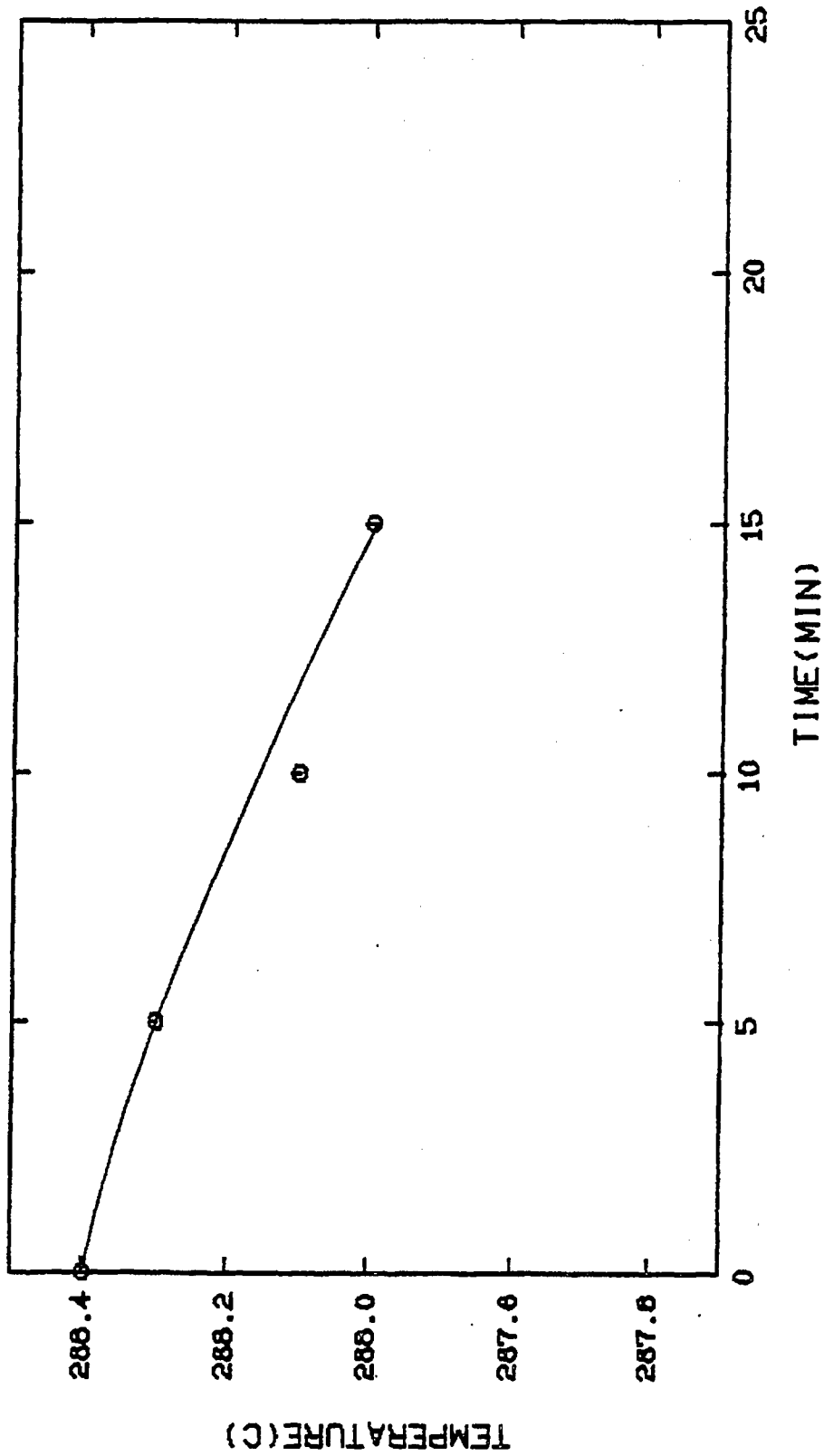
TEMPERATURE RESPONSE OF THE REACTOR FOR Q'=2.5W

FIGURE 6

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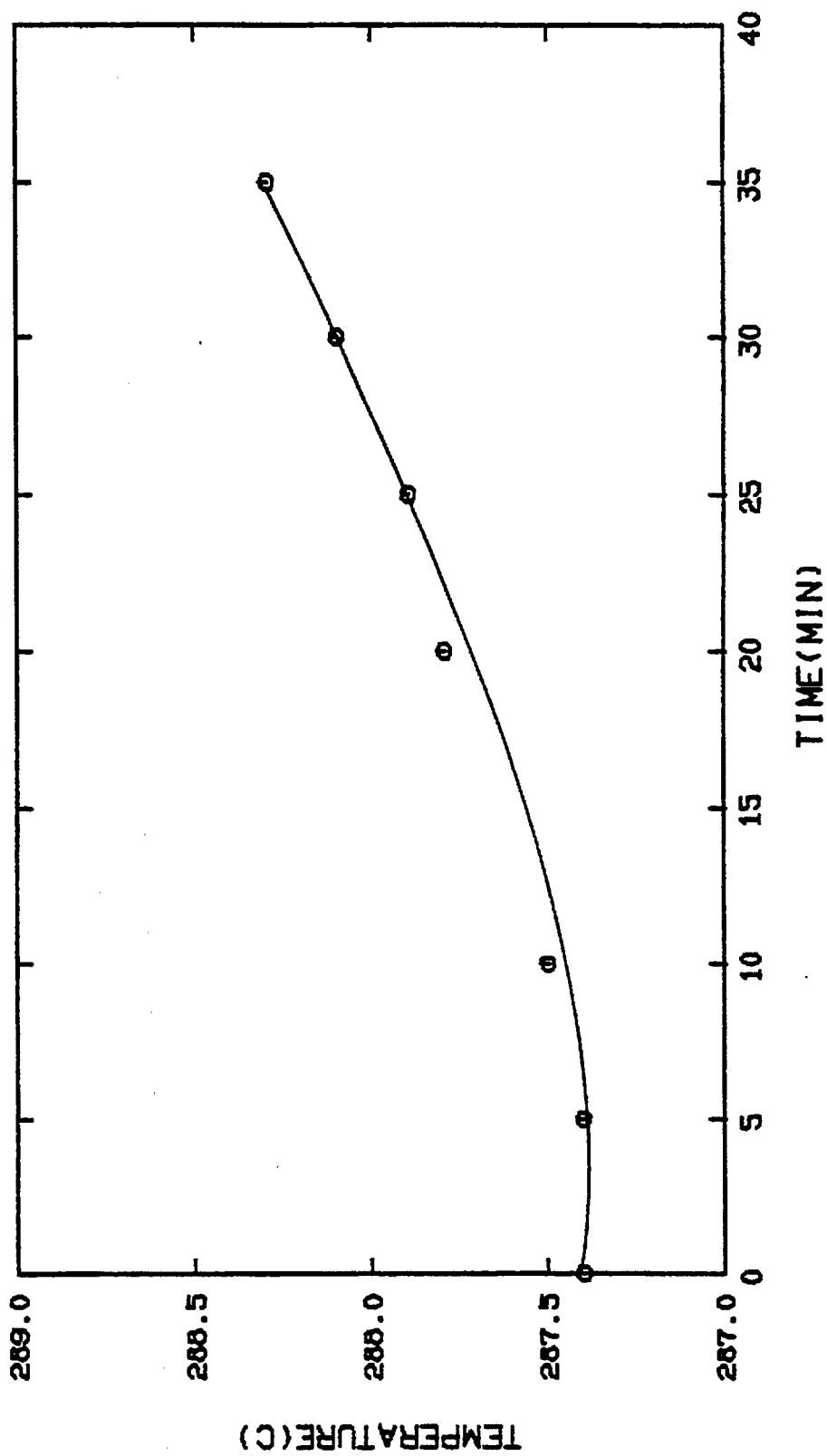
TEMPERATURE RESPONSE OF THE REACTOR FOR Q'=10W

FIGURE 7

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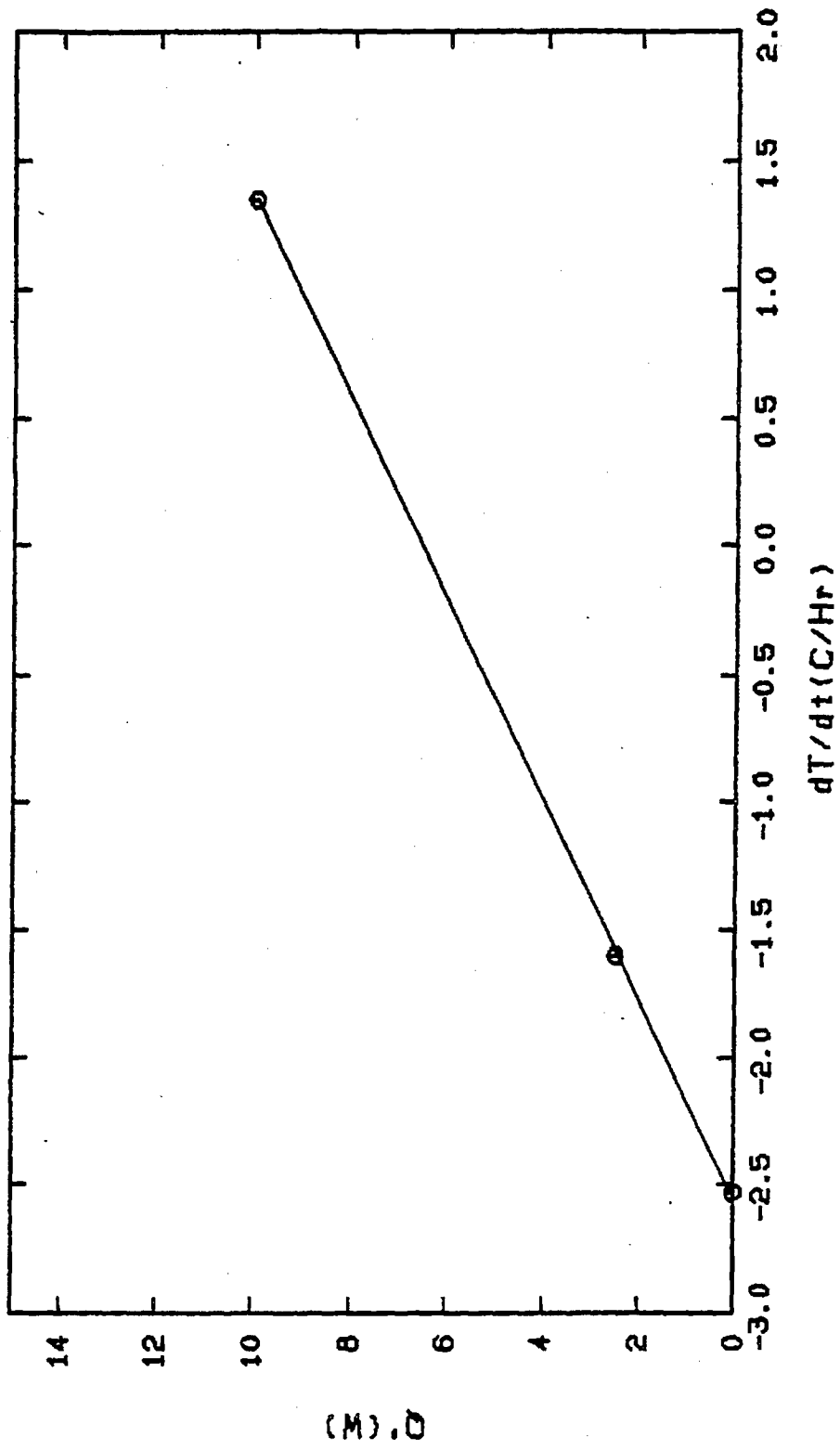
PLOT OF Q' vs. dT/dt UNDER DIFFERENT CONDITIONS

FIGURE 8

8. Preliminary Runs to Evaluate the Thermal Requirement for F-T Reaction:

We have seen in section 7 that any heat addition to the reactor results in a steady rise in temperature and the rate of rise in temperature is directly proportional to the amount of heat added to the system. The same idea can be extended to the cases where reaction is involved and equation 1 can be modified as

$$Q'_R + Q'_t = (mC_p) \frac{dT}{dt} + Q'_s + Q_\ell \qquad (2)$$

where

$\qquad Q'_R \qquad$ = Rate of heat generation due to reaction (Cal/hr)

$\qquad Q'_t \qquad$ = Rate of addition of heat to the reactor through the tubular heater (Cal/hr)

$\qquad Q'_s \qquad$ = Sensible heat removed from the system by the feed gas (Cal/hr)

$\qquad Q'_\ell \qquad$ = Rate of loss of heat from the reactor (Cal/hr)

Therefore by recording the rate of temperature rise of the reactor during reaction, the temperatures of the feed and product gases and using equation 2, we should be able to estimate the value of Q'_R or the amount of heat generated in the system during reaction. The value Q'_R calculated this way is not the heat of reaction but is a combination of the heat of reaction, heat of solution and the sensible and latent heats involved because the feed and products are not exactly at the same state. However, the value of Q'_R is an important parameter for the design of commercial scale reactors because this is the actual amount of heat which must be removed from the reactor to operate at a steady state. Two sets of experiments on F-T reaction were carried out

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and the process conditions are tabulated in Table 4. In experiment set 1, 2.5W of heat was constantly supplied to the reactor through the tabular heater to make up for the loss of heat to the system and in set 2, no heat was supplied externally and therefore, the heat effect observed was entirely due to reaction. The rate of change of temperature of the reactor under these two condition (i.e. Q'_t = 0 and 2.5W) but without any reaction have been reported in Table 3 and therefore the rates of change of temperature of the reactor only due to reaction can be easily calculated and are shown in Table 4 and Figure 9 for experiment #1 and Table 5 and Figure 10 for experiment #2. From a knowledge of the integral average value of rise in temperature of the reactor due to reaction and conversion we can calculate the heat generated per unit mole of carbon monoxide converted during reaction and they are reported in Table 3. For only hydrocarbon formation by F-T reaction, the heat of reaction is approximately 39 kcal/mol of CO converted, which is approximately 10 kcal/mol higher than the values of 21.1 and 27.7 which were experimentally observed. This might be due to the fact that a substantial amount of carbon monoxide has been consumed by the water gas shift reaction - which is highly thermodynamically favorable at the temperature and pressure of Fischer-Trospch reaction. Furthermore, the accuracy in the estimation of rate of heat generation depends on the degree of accuracy in the measurement of Q_t and Q_s which in turn depends on how accurately we can measure the feed and product gas temperatures. The heat to the tubular heater (Q'_t) was supplied through 0-32V constant DC supply source having less than 0.1% ripple and therefore could be measured accurately. There is, however, uncertainty involved in measuring the gas phase temperature. This is because we were using stainless steel sheath thermocouples which can be in error because of conduction from process lines. We plan to circumvent this problem by using bare ungrounded

Table 3:   Table of Q′ versus dT/dt under Different Condition

Experiment	Q′ (W) added through tubular heater	$\frac{dT}{dt}$ ($^{\circ}$C/hr)	Thermal Requirement For Reaction Kcal/mol of CO Converted
No Reaction	10.0	1.35	
No Reaction	2.5	−1.6	
No Reaction	0.0	−2.53	27.7
Reaction	0.0	−0.08	
Reaction	2.5	0.20	21.1
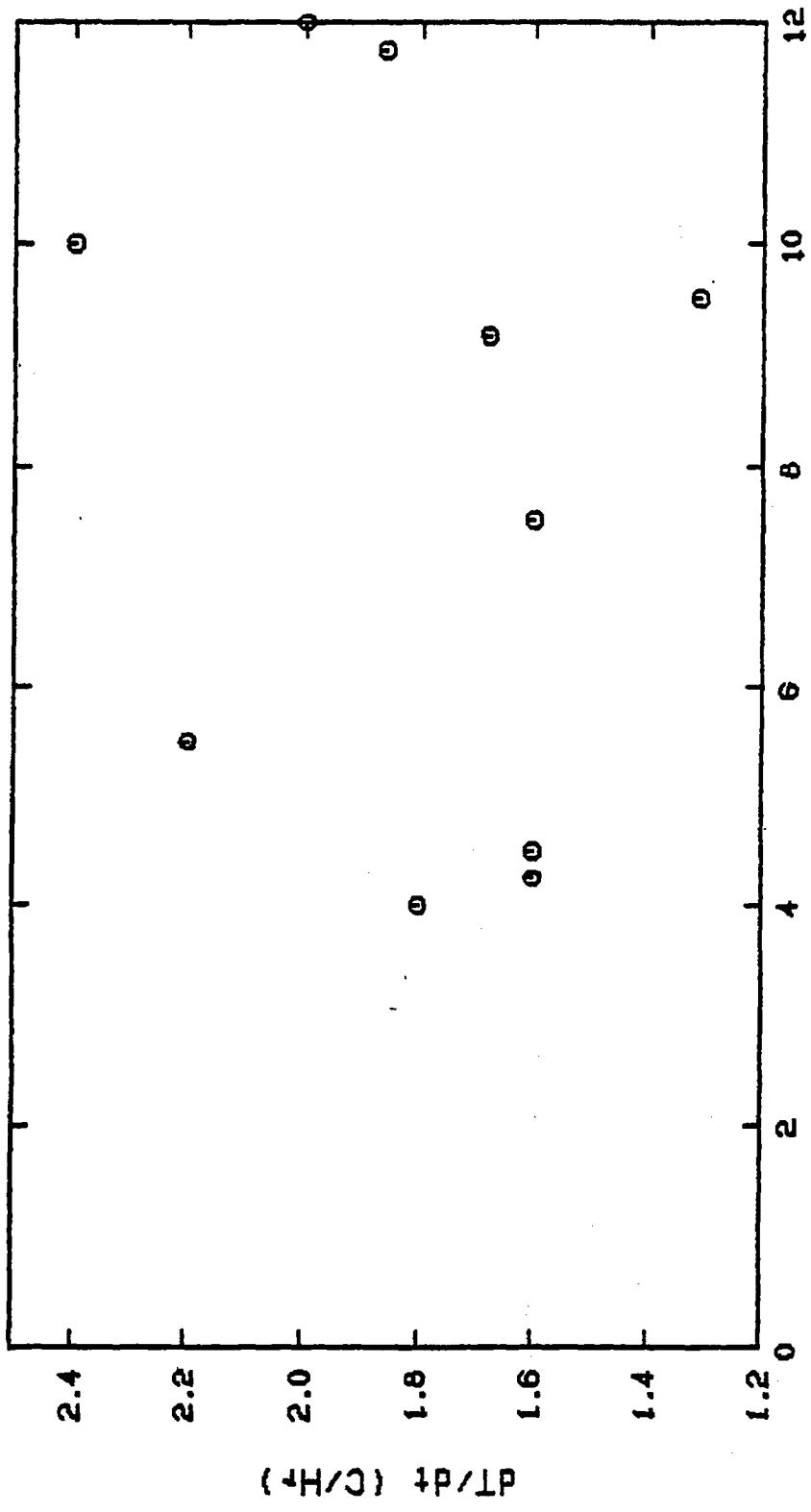
THERMAL EFFECT OF F-T REACTION WITH Q'=2.5W

FIGURE 9
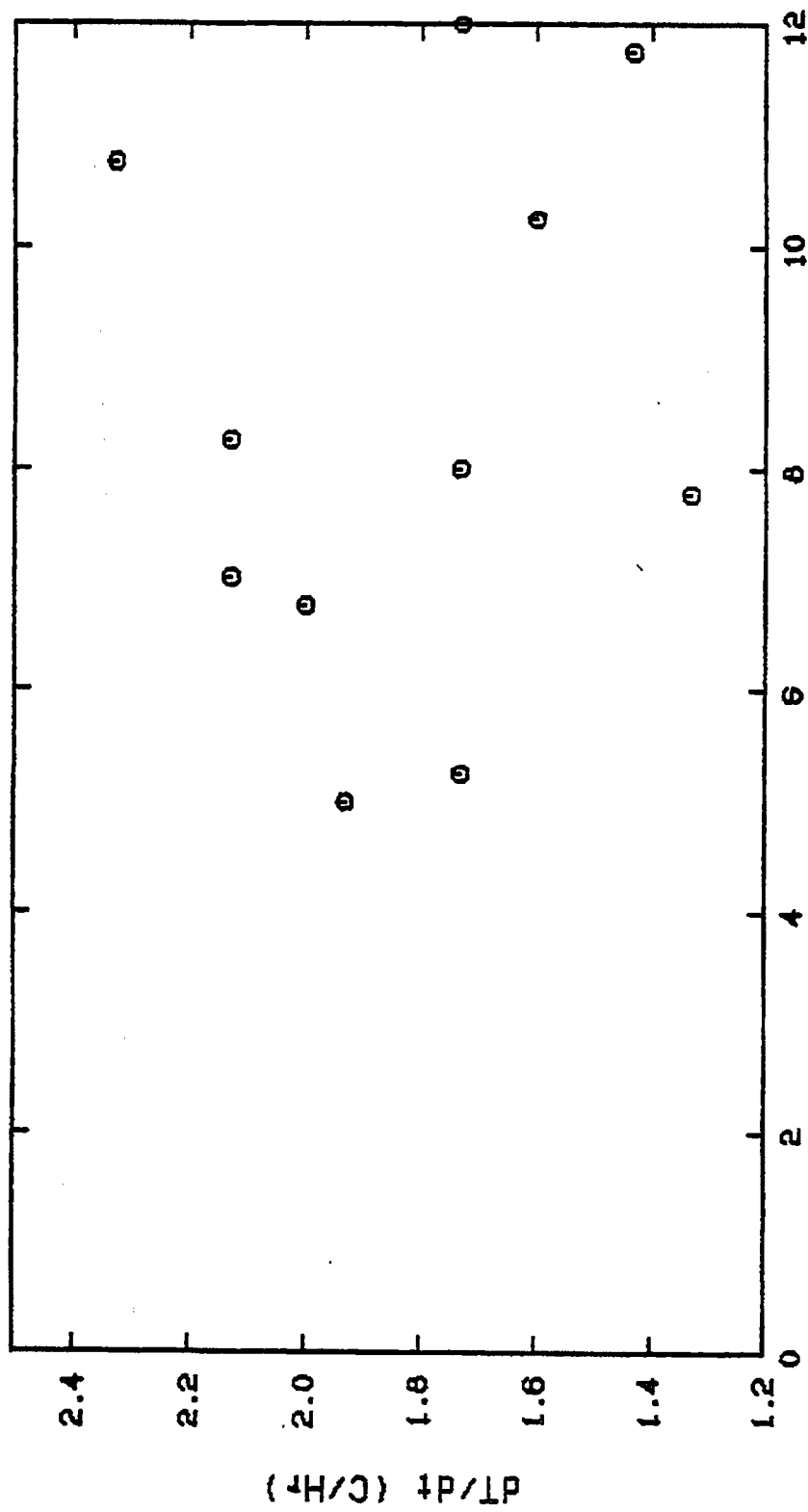
THERMAL EFFECT OF F-T REACTION WITH Q'=0W

FIGURE 10

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.020" diameter thermocouples which can be inserted through the 1/8" process lines before and after the feed and product enters and leaves the reactor.

Conversion of Carbon Monoxide and Hydrogen

Two sets of Fischer-Tropsch reaction were carried out, each of which lasted for a total time of twelve hours. The experimental conditions and the rate of conversions of carbon monoxide and hydrogen are listed in Table 4. In both the cases studied, periodic oscillations in the conversion of carbon monoxide and hydrogen were observed. Experiment #1 (i.e. from 1-1 to 1-6) was carried out at a time-average temperature of 268.9°C. The lowest conversion of carbon monoxide was 14.54% while the highest observed was 47.44%. Conversion of hydrogen varied between 20.95 and 58.55%. Similarly for experiment #2 (i.e. 2-1 to 2-7) the conversion of carbon monoxide varied between 12.25 and 42.8% whereas that for hydrogen varied between 19.2 and 54.7%. This kind of oscillatory behavior during Fischer-Tropsch synthesis has been observed experimentally by Tsotsis (1982) and Pikios and Luss (1977) have concluded from a more simplified theoretical model that surface heterogeneity can induce such sustained kinetic oscillations. In future we plan to take more data for confirm this behavior.
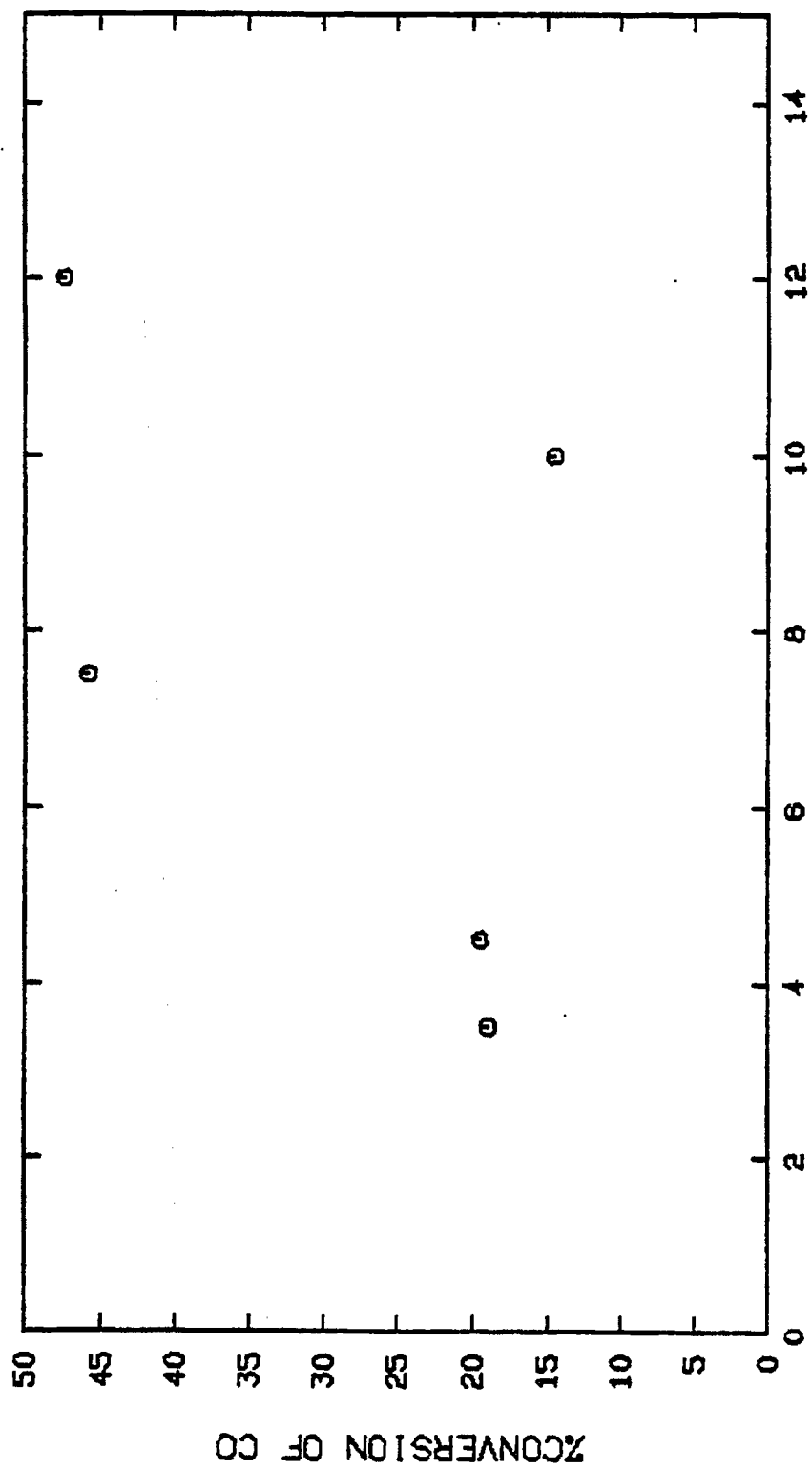
CONVERSION OF CO(Q'=2.5W)

FIGURE 11
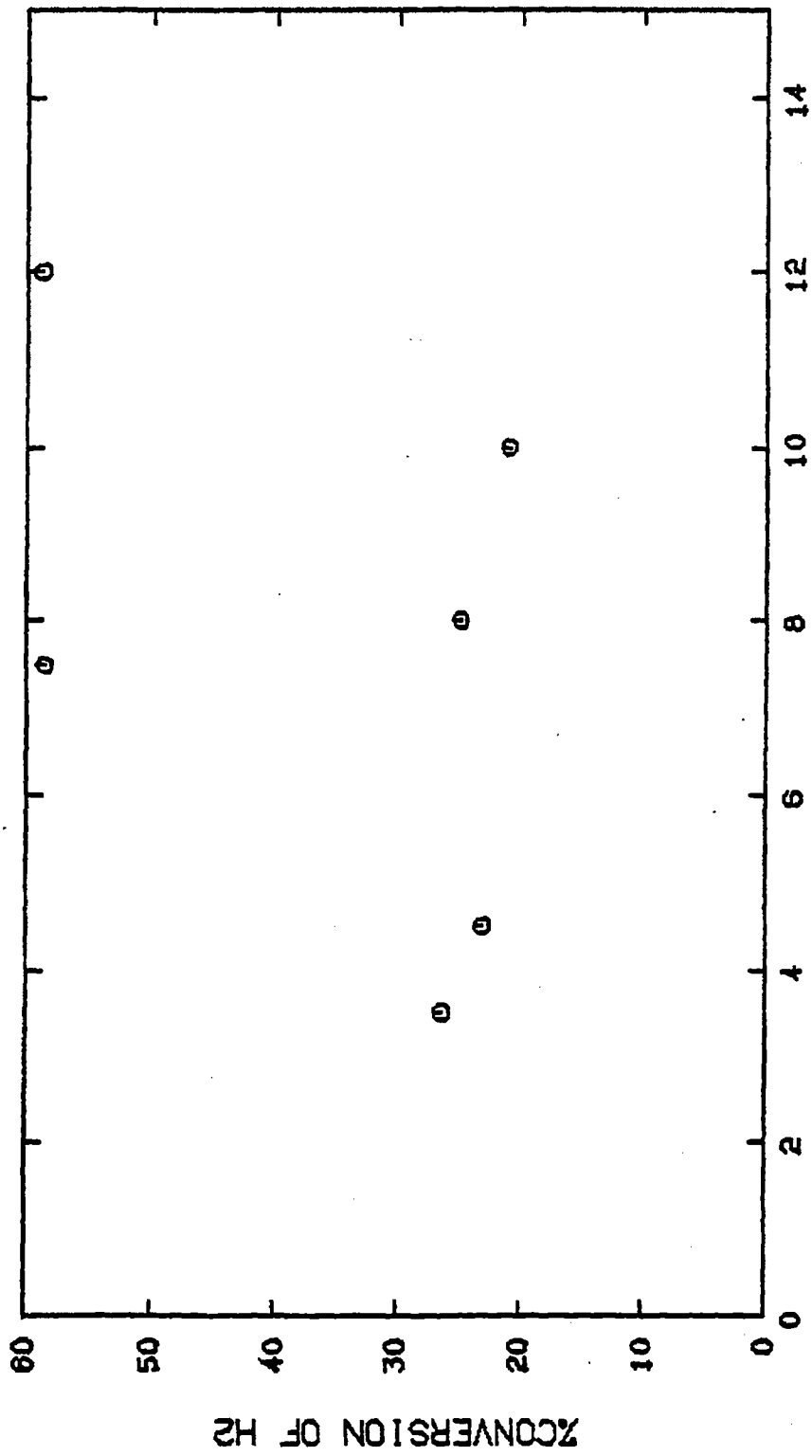
TIME ON STREAM (Hr)

CONVERSION OF H2(Q'=2.5W)

FIGURE 12
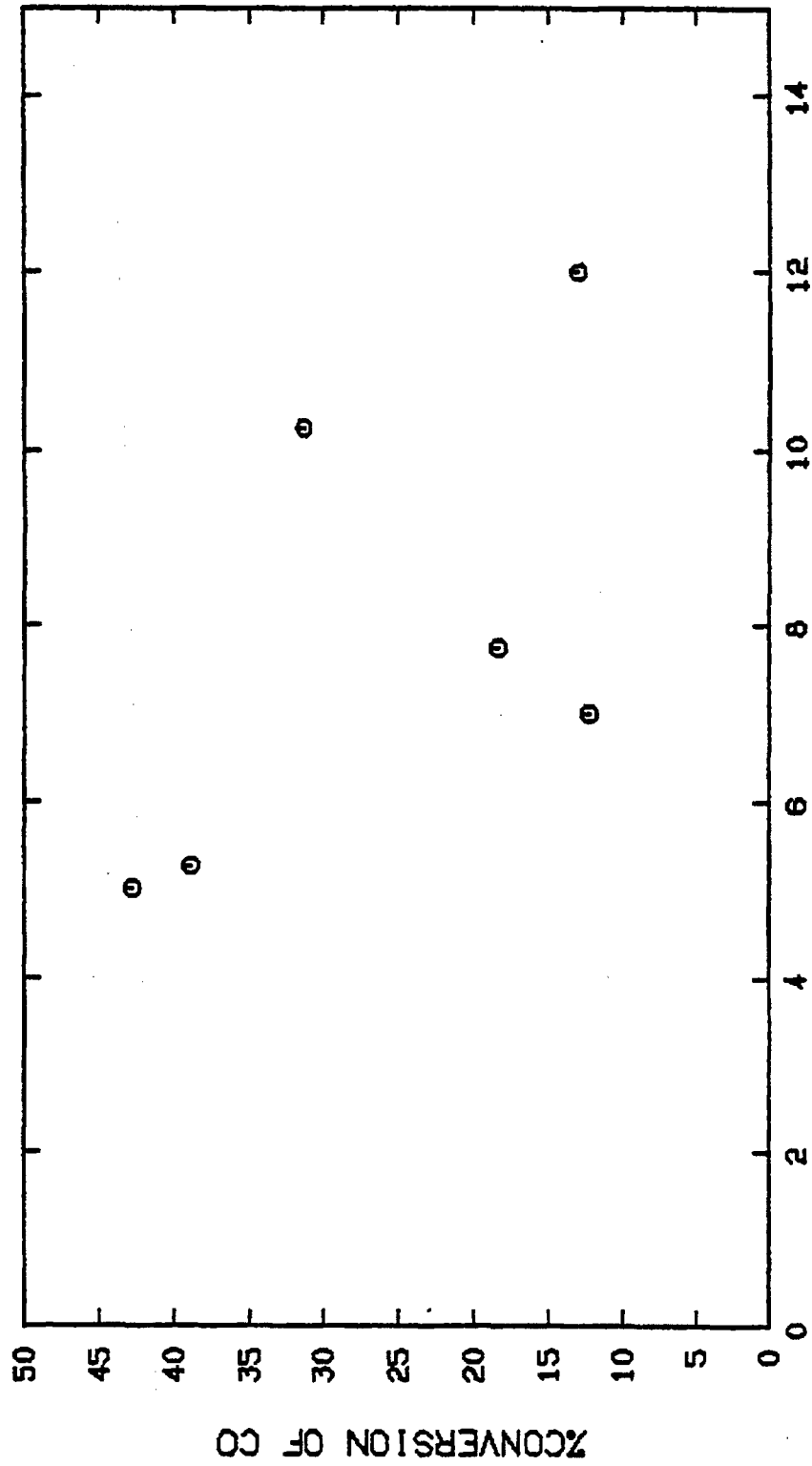
%CONVERSION OF H2

TIME ON STREAM (Hr)

CONVERSION OF CO(Q'=OW)

FIGÙRE 13

30
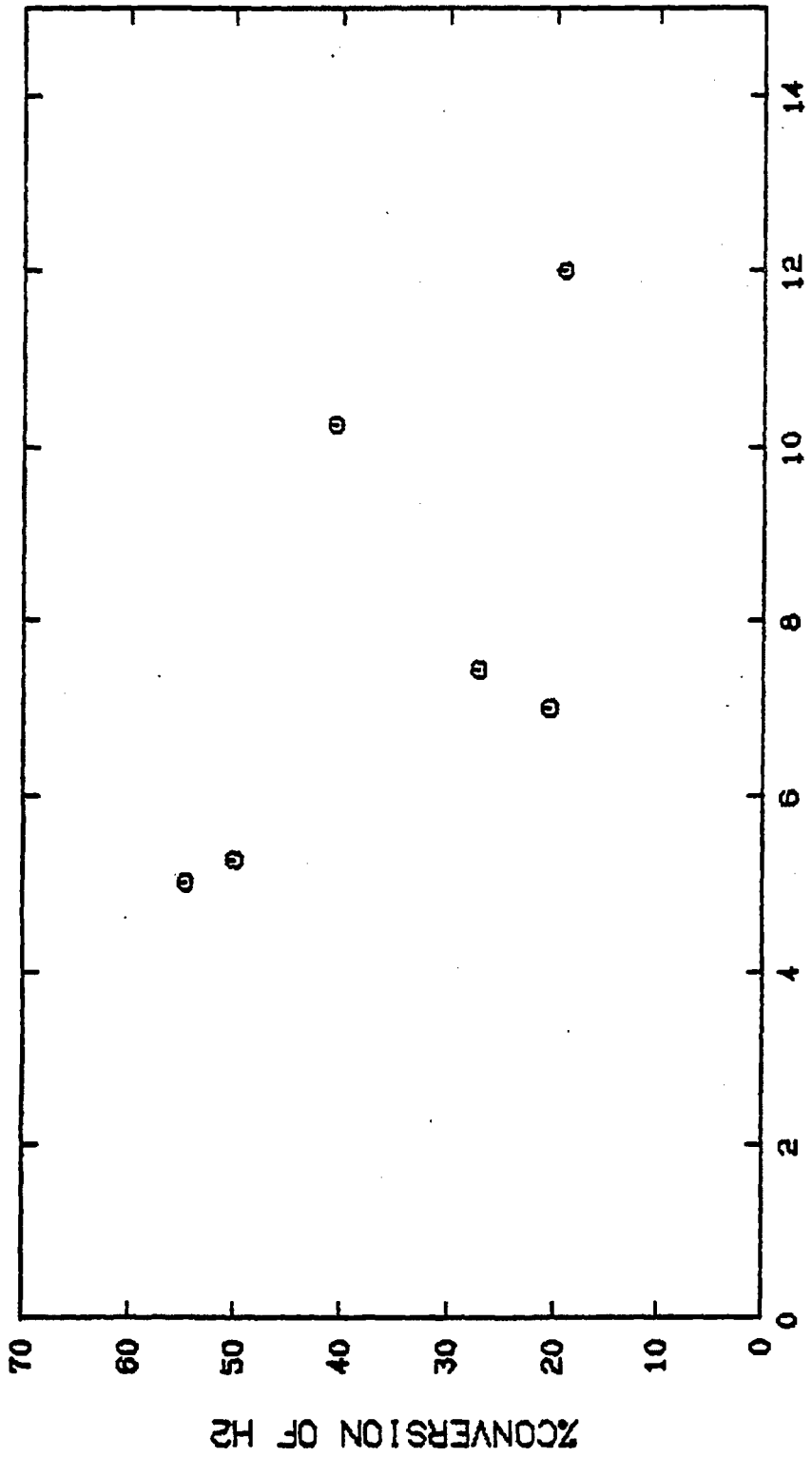
TIME ON STREAM (Hr)

CONVERSION OF H2(Q'=0W)

FIGURE 14

%CONVERSION OF H2

31

Table 4: Reaction Condition for F-T Reaction

Solvent = 500 ml. Catalyst = 80 gms. Catalyst loading = 160 g/l. Inlet $H_2:Co$= 1:1, Pressure = 996 kPa, Density of Catalyst = 2.9 gm/cc

Run #	Inlet Flow Rate (scc/min)	Temperature of the Slurry (°C)	Outlet Flow Rate (scc/min)	Space Velocity (hr^{-1})	% Conversion of CO	% Conversion of H_2	Run time (hr)
1-1	707.9	268.3	685.08	1539.7	19.0	26.4	3.5
1-2	707.9	269.0	679.6	1539.7	19.56	23.1	4.5
1-3	707.9	269.0	671.5	1539.7	45.87	58.6	7.5
1-4	707.9	269.0	668.9	1539.7	19.01	25.0	8.0
1-5	707.9	269.4	668.9	1539.7	14.54	20.95	10.0
1-6	707.9	269.4	668.9	1539.7	47.44	58.85	12.0
2-1	577.1	268.6	541.1	1255.2	42.8	54.7	5.0
2-2	577.1	267.8	544.5	1255.2	38.9	50.1	5.25
2-3	577.1	266.9	536.98	1255.2	12.25	20.45	7.00
2-4	577.1	266.0	534.27	1255.2	18.4	27.2	7.45
2-5	577.1	263.8	534.27	1255.2	31.3	40.7	10.25
2-6	577.1	263.7	534.27	1255.2	14.26	20.1	10.75
2-7	577.1	262.4	532.9	1255.2	12.98	19.2	12.0

Table 5: Thermal Effect of Fischer-Troposch Reaction with Q' = 2.5W

Run#	Time on Stream (hrs)	Temperature of Slurry (°C)	Rate of Temperature Rise due to Reaction (°C/hr)	% Conversion of CO
1-1	3.5	268.3		19.0
	4.0	268.4	1.8	
	4.25	268.4	1.6	
1-2	4.50	268.4	1.6	19.56
	5.50	269.0	2.2	
1-3	7.50	269.0	1.6	45.87
	9.16	269.1	1.68	
	9.50	269.0	1.31	
1-5	10.00	269.4	2.4	14.54
	11.75	269.6	1.86	
1-6	12.00	269.7	2.0	47.44

Table 6: Thermal Effect of Fischer-Troposch Reaction with $Q' = 0$

Run #	Time on Stream (hrs)	$T(^oC)$	Rate of Temperature rise due to reaction $(^oC/hr)$*	% Conversion of CO
2-1	5.00	2680	1.93	42.8
2-2	5.25	267.8	1.73	38.9
	6.75	267.0	2.00	
2-3	7.00	266.9	2.13	12.25
2-4	7.75	266.0	1.33	18.42
	8.00	265.8	1.73	
	8.25	265.7	2.13	
2-5	10.25	263.8	1.60	31.33
2-6	10.75	263.7	2.33	14.26
	11.75	262.6	1.43	
2-7	12.00	262.4	1.73	12.98

*During adiabatic run without reaction temperature dropped @ 2.53^o C/hr

10. Conclusion and Recommendation:

Preliminary test runs have indicated that a three phase slurry reactor can be made to operate close to adiabatically by making proper compensation for radial and axial heat losses from the system. A reliable estimate of the reactor thermal capacity under operating conditions has been evaluated from the reactor temperature response data. Fischer-Tropsch reaction was carried out in this slurry reactor and the extent of conversion based on carbon monoxide was evaluated from gas chromatographic analysis. Based on these data, time-average rate of heat generation during reaction was estimated and found to agree with the calculated values.

As a result of these preliminary runs, we have identified some problems and plan to correct them as follows. Firstly, the temperature profiles around the copper enclosure and in the reactor itself are not uniform and there is 10-15°C difference in temperature between the top and bottom part of the copper vessel and 5-10°C between the top and bottom of the reactor. We plan to eliminate this difference in temperature by more refined tuning of the P-I control algorithum employed for maintaining adiabaticity of the reactor. Another problem is the uncertainity involved in measuring the feed and product gas temperature and the coolant air inlet and outlet temperatures. We have discussed this problem in section 8 and mentioned how do we plan to circumvent this problem in our future experiments. Preliminary data show the existence of oscillation of conversion of carbon monoxide and hydrogen during F-T reaction and we plan to explore this phenomenon in more detail by taking more data points.

Bibliography

1. Anderson, R. B., "Catalysis, Vol. IV, P. Emmett, Ed. Reinhold, N.Y. (1956)

2. Haggin, J., "Fischer-Tropsch: New Life for Old Technology", C&E News, Oct. 26, p22 (1981)

3. Huff, G. A., "Ph.D. Thesis", MIT (1982)

4. Madon, R. J., "On the Growth of Hydrocarbon Chairs in the Fischer-Troposch Synthesis", Jl. of Catalysis, 57, p. 183 (1979)

5. Piklos, C. A. and Luss, D., "Isothermal Concentration Oscillations on Catalytic Surfaces," CES, Vol. 22, p19, (1977).

6. Satterfield, C. N. and Huff, G. A., "Carbon Number Distribution of Fischer-Troposch Products formed on an Iron Catalyst in a Slurry Reactor", Jl. of Catalysis, 73, p. 187 (1982)

7. Shah, Y. T., "Reaction Engineering in Direct Coal Liquefaction", Addison-Wesley Publ., Reading, MA (1981)

8. Shah, Y. T. and Perrota, A. J., "Catalysts for Fischer-Troposch and Isosynthesis", I & EC Prod. Res. Devel., 15, p. 123 (1976)

9. Shah, Y. T., An Experimental Study of the Multiple Steady States in an Adiabatic Coal Liquefaction Reactor, Work Performed under Contract No. DE-FG-22-80PC30243, Annual Progress Report submitted to DOE, Sept. (1982a)

10. Shah, Y. T., ibid. Feb. (1983)

11. Thompson, G. J., et al., "Comparison of reactor Systems for Indirect Liquefaction via Fischer-Tropsch Technology," presented at Second World Congress of Chemical Engg., Montreal, Canada, Oct. 4-9 (1981).

12. Tsotsis, T. T., et. al., "Reaction Rate Oscillations during Fischer-Tropsch Synthesis on Fe-precipitated Nu-1 Zeolite-Type Catalysts," AIChE, Vol. 28, No. 5, p847 (1982).

APPENDIX

Reactor Digital Control System

A DECLAB-11/MINC digital computer is used for data acquisition, data manipulation, process monitoring and on-line control. The computer has 128K bytes of random access memory and two hard disks. It regularlarly takes the following process readings:

• Temperatures indicated by 40 thermocouples installed on the reactor, the copper vessel, and the key points in the system.

• Flow rate of the coolant, a 0-5 V output from the mass flow meter.

• Reactor pressure, a 0-5 V output from a pressure transducer.

These values will be used by the computer to generate the following:

• A process operating record which will be stored on the disk.

• Process alarms. Rapid rises in temperature and/or pressure or high levels of these variables will trigger alarms at the terminal. At critical levels, solenoids will be activated to shut off the H_2-CO feed and quench the reactor with N_2.

• Control set-point for the coolant flow. The coolant control system is analog, but the set point is provided by the computer. The coolant set-point can be controlled by reactor temperatures.

• Control of adiabatic heaters. Each of the eight heaters used to maintain no heat loss from the reactor is controlled by a solid state relay. Each relay is turned on and off by the computer, which uses temperature measurements made on the reactor and ont he copper vessel to determine the state of each heater. The heaters located on the stirrer shaft extension, the gas feed, coolant lines, and product lines are controlled in a similar way to keep the temperatures of these tubes the same as the reactor temperature. A total of 18 on-off signals can be provided from the computer.

The above tasks are incorporated in a real-time executive program. The FORTRAN program is comprised of two distinct parts, a synchronous and an asynchronous portion. In the synchronous protion, tasks are performed in a sequence specified by the ordering of the programming steps. The frequency in which the tasks are completed is determined by the speed of the computer and cannot be controlld by the user. Tasks included in the asynchronous portion, however, are performed at a frequency specified by the user. The asynchronous portion is accessed through interrupts generated by the real-time clock module MNCKW. Upon generation of an interrupt, the computer exits the synchronous portion and processes the asynchronous programming steps. The computer returns to the previous position in the synchronous portion upon completion of the asynchronous tasks.

A flow chart of the MAIN routine of the synchronous portion is presented in Figure A-1. Parameters are initialized, common blocks are defined and an external data output file is opened. A series of library routines are called which control the action of the A/D and real-time clock modules.

In order to maximize computational efficiency and enhance the clarity of the programming techniques employed, the desired tasks are programmed into six distinct subroutines. Flow charts for the subroutines are presented in Figures A-2 through A-7.

A series of counters are used to determine when the subroutines are called. The counters are incremented in the asynchronous interrupt service routine (ISR) (Figure A-2). Since the ISR is accessed at a specified frequency, the individual subroutines are executed at a fixed frequency as well. A/D sampling sweeps are triggered in the ISR as well. Upon completion of an A/D sampling sweep, a second asynchronous routine, known as a completion routine (CSR), is executed. In the CSR, data are transferred from the A/D

storage buffer to the main storage buffer and the A/D buffer is cleared for future use.

In subroutine JOB1, digital signals controlling the ON/OFF cycling of the adiabatic heaters are output via the MNCDO module. The desired signals are stored in the vector IHTR. The library routine DOUT allows control of the NCDO module in the FORTRAN program. The frequency at which the adiabatic heater status is updated is set by the parameter J1MAX.

Due to inherent fluctuations present int he mV signal conversions of the A/D module DT2764, readings are averaged over a period of time to ensure reliable measurements. In subroutine JOB3, readings of the sampled channels are averaged over the time between successive calls to the subroutine. The readings are converted to temperature, pressure and flow rate measurements through application of calibration data. The data are output to the video display terminal and storage file. J3MAX determines the frequency at which the subroutine is called.

The adiabatic heating rates are updated in the adiabatic control subroutine JOB4. Average temperatures are computed for the various portions of the reactor and the copper vessel – extended shaft system. Set point deviations are calculated, and the errors are substituted into control algorithms for the various adiabatic heaters. The velocity form of the P-I control aligorithm is used to establish the desired changes in the adiabatic rates. Heating rates are represented as a percentage of the maximum input rate (100 % on-time).

The subroutine SETHT converts the percentage heating rates into 16 bit integer representations. The subroutine SETWRD combines the integer rates for the individual heaters into a single 16 bit integer for each time interval.

These values are stored in the IHTR vector and are output to the relays in JOB1.

Air flow through the internal cooling coils is used to control the reactor temperature as heat is generated by the exothermic chemical reaction. A velocity form of the PI control algorithm is employed to calculate the change in the coolant flow required to correct the set point deviation. The updated coolant flow is converted to an integer representation and is output to the flow control valve via the D/A module DT2767. The library routine IDAC allows the D/A hardware to be activated from the FORTRAN program. The resulting output is scaled from 0-5 V and serves as a set point for the analog control valvel.

The subroutine JOB6 allows the user to interact with the program and make desired changes. For example, the user can switch between manual and sutomatic control of the adiabatic heaters and coolant air flow. The subroutine also enables changes in the various control parameters to be enacted "on-line." Termination of the program is initiated in JOB6. Improvements in the interactive capabilities of the program are implemented as necessary.
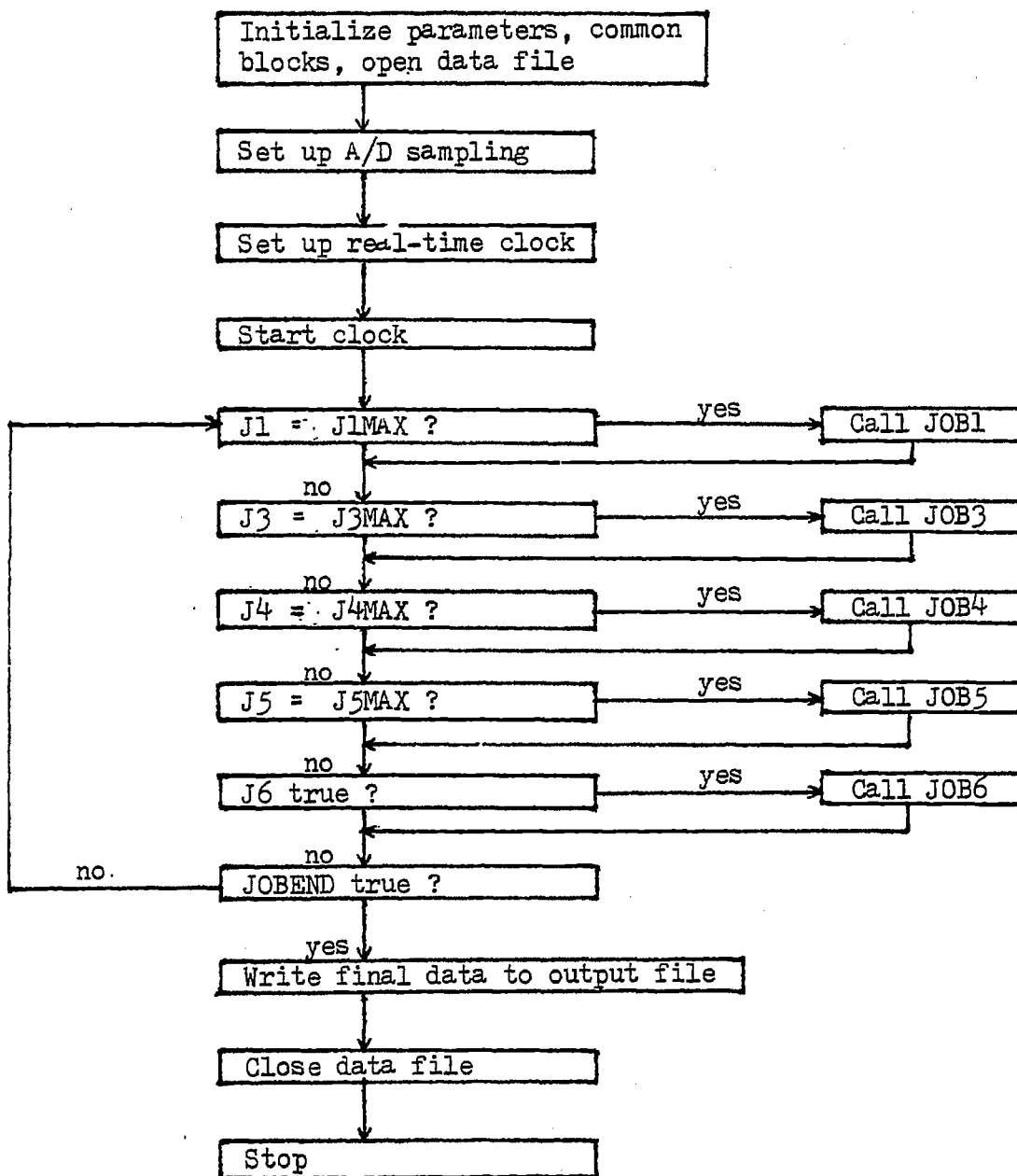
Figure A1: Synchronous portion (MAIN)

Interrupt Service Routine :

Increment parameters INT,J1,J2,J3,J4,J5

Desire access to JOB6 ? —— yes —→ Turn off clock

↓ no

Reset clock

Turn off relays

Trigger A/D sweep ←— yes —— J2 = J2MAX ?

J6 = true

↓ no

J2 = 0 ——————→ Continue

Return

Completion Routine :

Increment available sub-buffers

Return
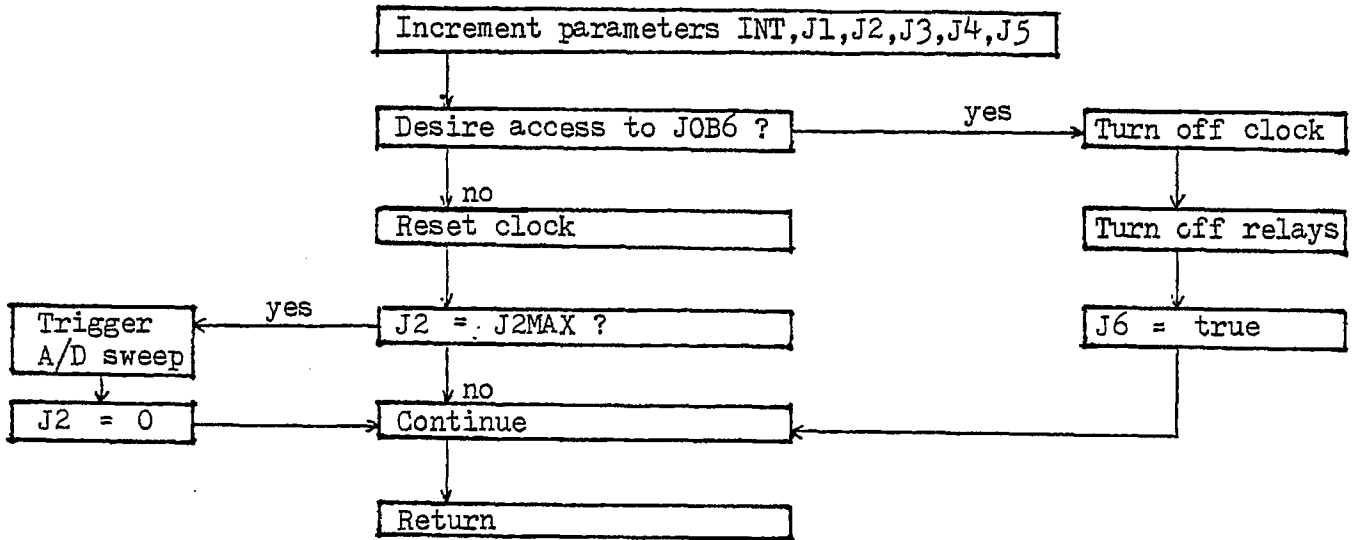
Figure A2 : Asynchronous Portion
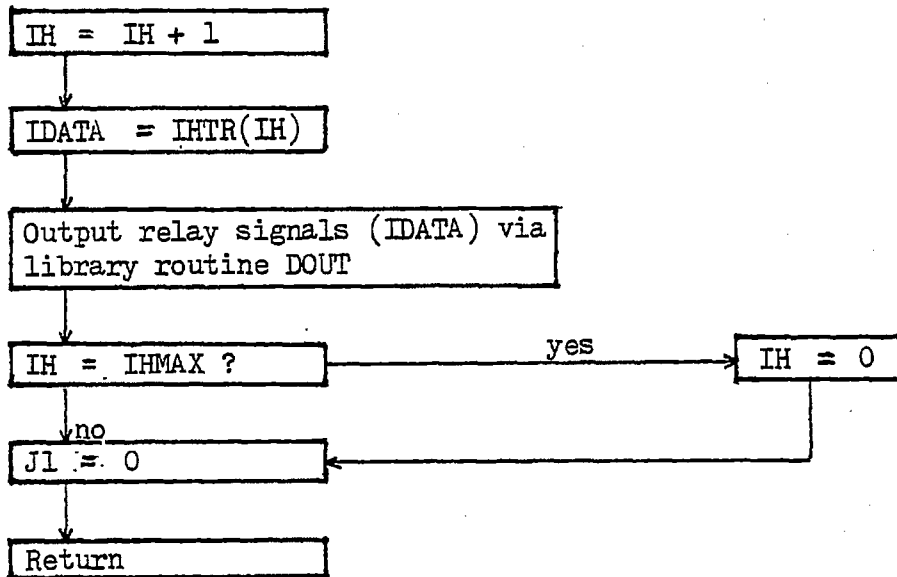
Figure A3: Subroutine JOB1
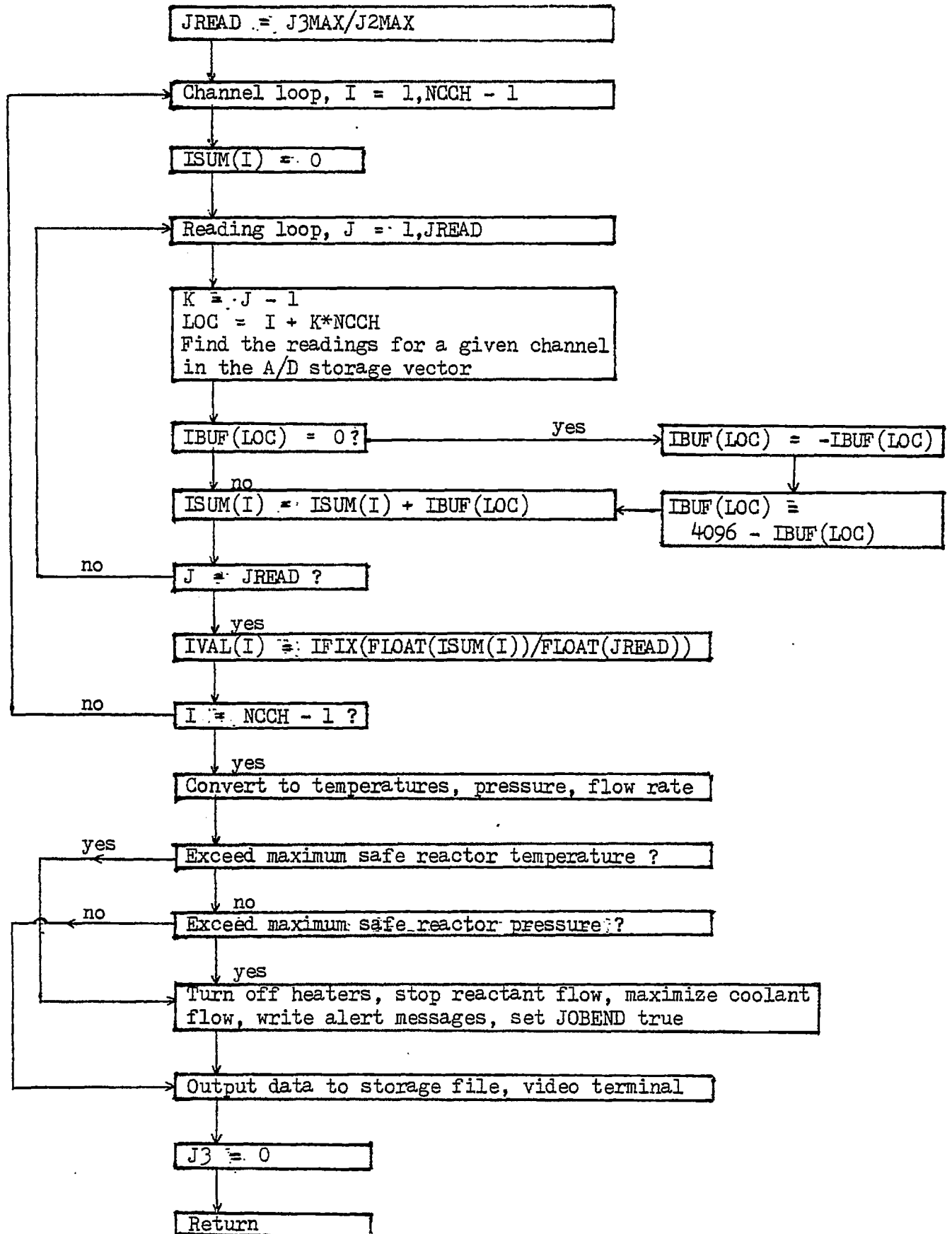
Figure A4: Subroutine JOB3

```
┌─────────────────────────────────────────────┐
│ Compute average temperatures for the         │
│ reactor and the copper cylinder              │
└─────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────┐
│ Compute deviations from the set point for    │
│ the cylinder, top plate, bottom plate, shaft │
└─────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────┐
│ Compute necessary change in heat rate via    │
│ the P-I velocity algorithm                   │
│   ΔQ  =  Kc*((E - Eold) + (TSAMP/TI)*E)       │
└─────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────┐
│ Add change in heat rate to previous heat rate│
│   Q = Q + ΔQ                                 │
└─────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────┐
│ Convert heat rate to a % of maximum heat rate│
│   PCT = (Q/QMAX)*100                          │
└─────────────────────────────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────────────┐
│ Convert calculated percentage to an integer representation│
│ via the routine SETHT                                  │
└───────────────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────────┐
│ Combine individual heating words for each     │
│ heater into a single word for all heaters    │
│ for each time interval using the routine SETWRD│
└─────────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────┐
│ J4 = 0          │
└─────────────────┘
                    │
                    ▼
┌─────────────────┐
│ Return          │
└─────────────────┘
```

Figure A5: Subroutine JOB4

```
┌────────────────────────────────────────────────────┐
│ Compute deviation of the reactor                   │
│ temperature from the set point                     │
└────────────────────────────────────────────────────┘
                    │
                    ↓
┌────────────────────────────────────────────────────┐
│ Compute change in CFR set point via                │
│ the P-I velocity algorithm                         │
│   ΔM = K_c*((E - E_old) + (TSAMP/T_I)*E)           │
└────────────────────────────────────────────────────┘
                    │
                    ↓
┌────────────────────────────────────────────────────┐
│ Add change in set point to previous set point      │
│    M = M + ΔM                                      │
└────────────────────────────────────────────────────┘
                    │
                    ↓
┌────────────────────────────────────────────────────┐
│ Convert calculated setting to an integer           │
│ value via calibration data                         │
└────────────────────────────────────────────────────┘
                    │
                    ↓
┌────────────────────────────────────────────────────┐
│ Output integer setting to the flow control         │
│ valve via the library routine IDAC                 │
└────────────────────────────────────────────────────┘
                    │
                    ↓
┌────────────────────┐
│ J5 = 0             │
└────────────────────┘
                    │
                    ↓
┌────────────────┐
│ Return         │
└────────────────┘
```
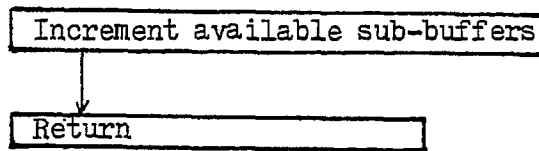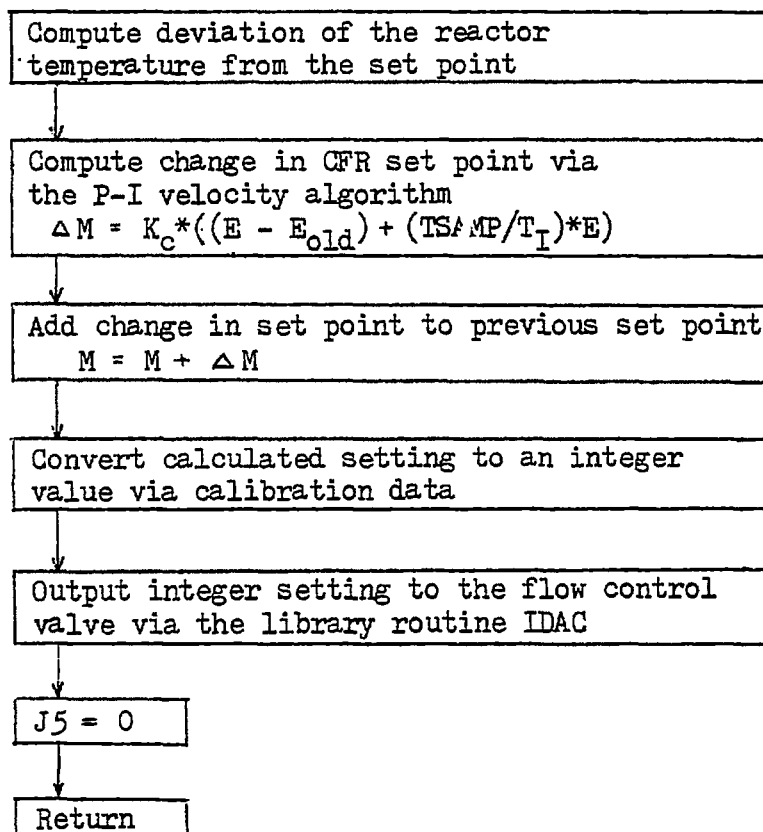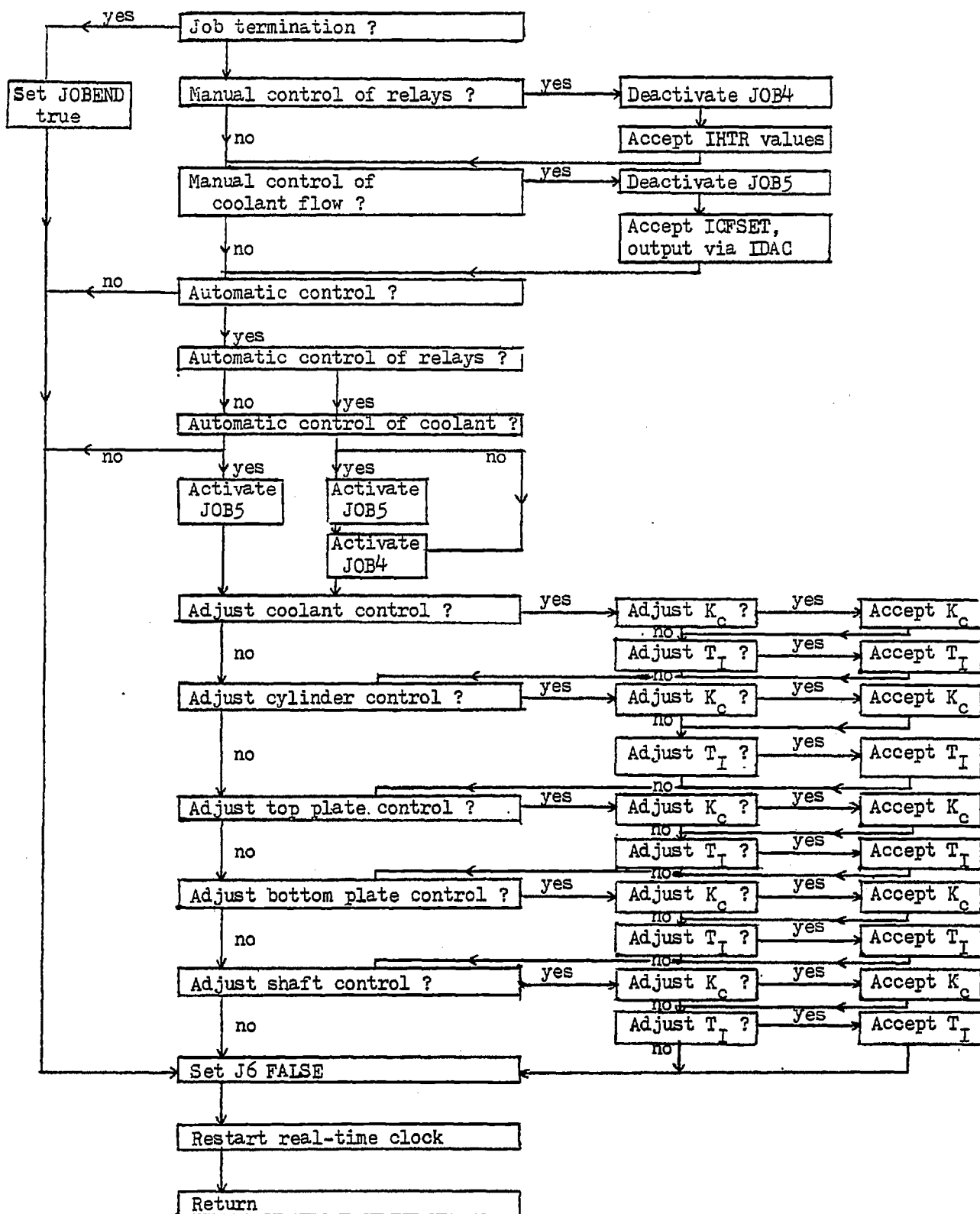
Figure A6: Subroutine JOB5

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Figure A7: Subroutine JOB6

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