DIRECT DIGITAL CONTROL
OF A BUTANE HYDROGENOLYSIS
CHEMICAL REACTOR

DIRECT DIGITAL CONTROL OF A BUTANE HYDROGENOLYSIS CHEMICAL REACTOR

by

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ABSTRACT:

A catalytic tubular reactor has been built and interfaced to a minicomputer located at some distance from the actual process equipment. Software has been written to control and monitor the hydrogenolysis of butane within this reactor. The principal aims of this thesis are to describe the process equipment, to detail the structure of the real-time control and monitor software developed for use on a Supernova minicomputer and to demonstrate that the process may indeed be controlled by direct digital control. Finally, in view of the success of the study, a recommendation to explore the applicability of modern control theory is made, particularly, the formulation of an optimal control and changeover policy and the development of multivariable control.

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To CHARLIE,

A TRUE FRIEND

1- INTRODUCTION

Current socio-economic pressures are forcing the process industries to continuously evaluate the efficiency of their production. On one hand, they must maximize corporate profits yet on the other they must minimize the social damage they inevitably will cause. One must encroach on the other. Several controls must be co-ordinated so that corporate profits may be maximized and social damage minimized. As it becomes more difficult to satisfy these opposing extreme requirements, engineers seek out improved methods of controlling, scheduling and optimizing process operations. Up till twenty years ago, analog systems had been developed to at least improve process profitability. However, as it became clear that no analog system could adequately implement complex control schemes or on-line optimization techniques, digital computers for process control were developed. In the least, these machines were able to duplicate the equivalent analog control systems. But digital computers may also be used to log data and schedule process operations. And beyond this, an entire process could be optimized when on-line to meet current company goals. However, processing companies would have a great deal of trouble trying to justify the installation of a huge digital computer to perform all these functions simultaneously. Fortunately, there is an alternative. A supervisory computer may be connected to a number of smaller computers dedicated to the control of specific units of a process plant. In this way, the control scheme of the entire plant is split into its basic parts. The supervisory computer is then used to optimize the operating conditions of the whole plant.

Within this thesis, it will be shown how a minicomputer is used to manage the direct digital control of a complex process. However, the true purpose of this work is to establish a base on which the applicability of multivariable control, non-linear control and optimal changeover policies of a complex process could be investigated. At the same time, startup and shutdown techniques could be developed. These modern control techniques would be implemented using a minicomputer.

Before all this advanced control theory can be applied to a process, four objectives must be reached. These are the construction of a reasonably complex process, the interfacing of the process to a digital control minicomputer, the formulation of a real-time monitor and control package designed to control * the entire process and finally to demonstrate the operation of the process under direct digital control. This thesis will serve to explain how these goals have been reached and to demonstrate that there is basis for future investigation into the applications of modern control theory.

It was necessary to build a piece of equipment that was complex enough to offer many challenging technical and engineering problems. The hydrogenolysis of butane was selected as the process for this study. According to the kinetics of the reaction (1, 2 **), the process exhibits severe nonlinearities over a wide range of operating conditions. Since the rate of this reaction is a function of three independent variables *** for a given reactor and catalyst bed, it was believed that this process was adequately complex for the purposes of this and future projects. To have used any process that was more complex would have smothered the project with excessive technical difficulties.

* For the present, only univariable control has been considered since much development work is required before anything more complex can be formulated. Our prime purpose is to show that the process can indeed be controlled by DDC.

** These numbers refer to references listed in the bibliography.

To ensure that the reactor used in this study would be reasonably sensitive to changes in the operating conditions, the non-linear characteristics of the reaction must be well accentuated. This could be achieved by building a fairly large reactor and choosing an adequate catalyst size and concentration.

Before the reactor could be operated under computer control, the entire process needed to be interfaced to the control computer and the software performing the monitoring and controlling tasks written. Once the process was assembled, the process interfaced to the computer and the necessary software written, tests on the process equipment were begun. In order to obtain an approximate steady-state model of the reactor, a full factorial design was carried out. To demonstrate that the process may be controlled by direct digital control, a series of step response experiments were carried out.

*** The kinetics of the butane hydrogenolysis reaction are presented in Appendix D. For a given reactor and catalyst bed, catalyst temperature and the partial pressures of butane and hydrogen govern the reaction rate. If catalyst activity changes with time, the effect is considered to be process drift.

2- GENERAL INFORMATION ON DIRECT DIGITAL CONTROL

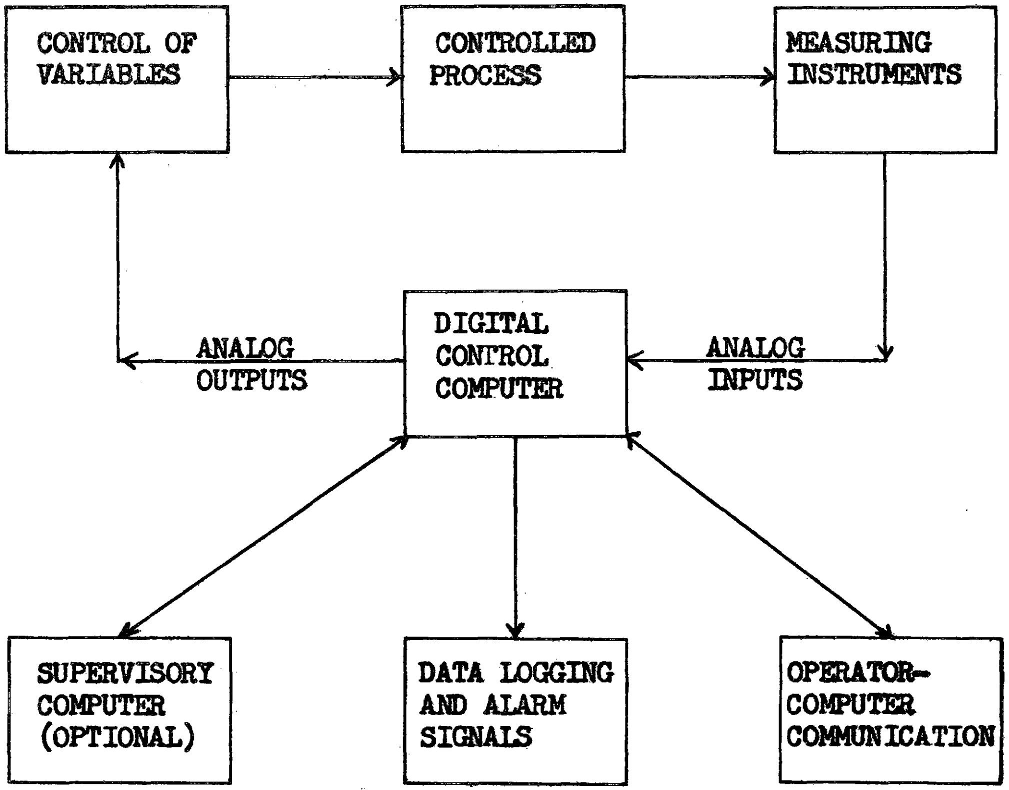
2.1 Justification of DDC

The configuration of a typical direct digital control system is given in Figure 1. Process conditions are sensed by the measuring elements and transmitted signals are quantized for use by the computer. Control action is then computed on the basis of these and past measurements. The set points and characteristics of the control algorithm are supplied either by an operator or by a supervisory computer optimizing the entire process. The principal feature of a digital control system is its flexibility. Unlike an analog control system which requires a large amount of hardware relocation (and perhaps acquisition) to implement a control reconfiguration, a digital control system may be restructured by simply reconfiguring the control software. This would minimize down time since all of the software can be prepared off-line. Also, complex control algorithms can be implemented much more readily with software.

The digital control system represented in Figure 1 may be used to simply replace an equivalent analog control system or else to implement extremely complex control strategies. However, it is not simple to justify the installation of a digital control system (20, 23). Such systems

FIGURE 1

BASIC STRUCTURE OF A DIRECT DIGITAL CONTROL SYSTEM

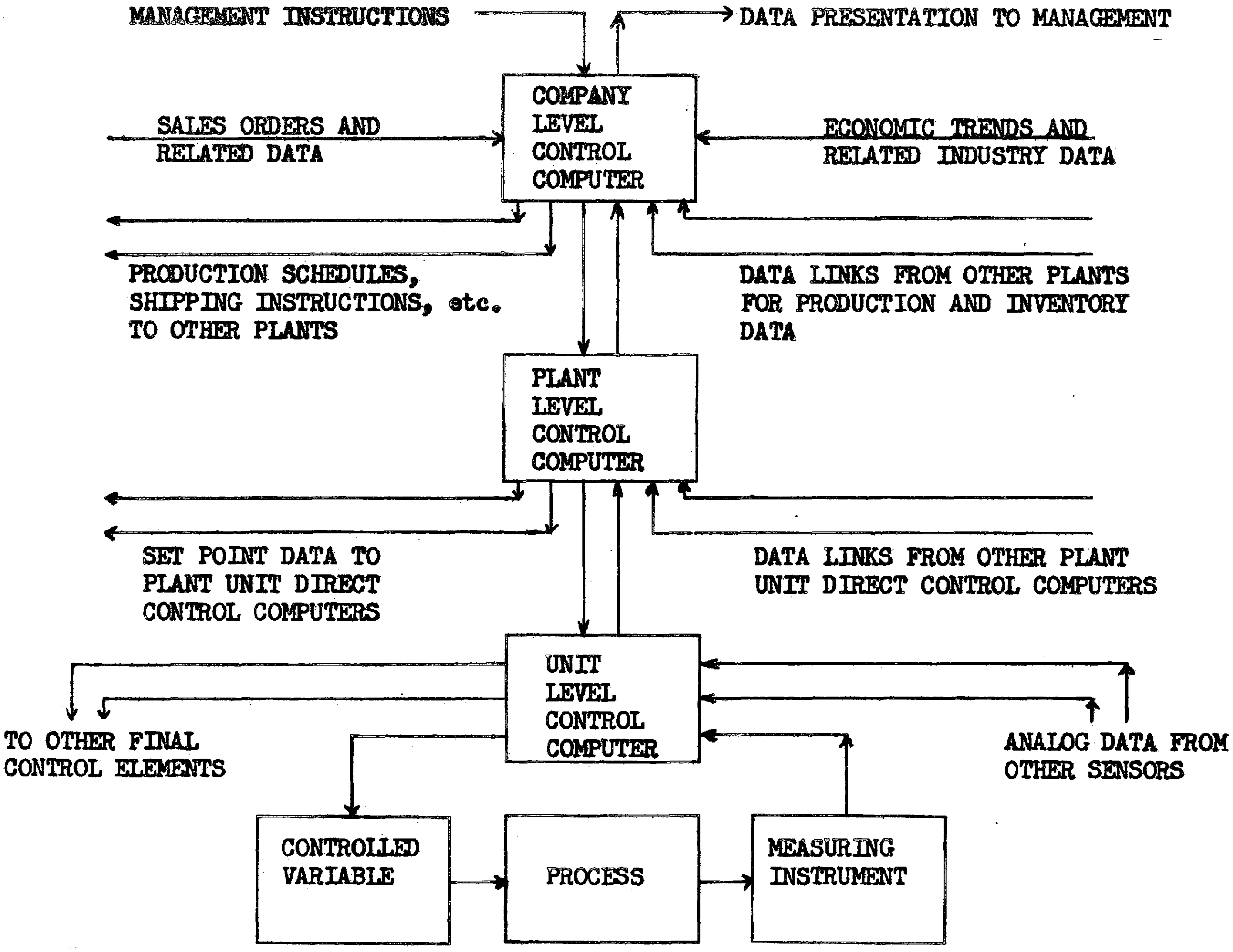


are costly to install; software costs may be four times the cost of the actual hardware. There is also a great expense in training people to service the highly sophisticated digital equipment. Overall, one can expect that a digital control system will cost more than an analog control system. However, there are many benefits that may result from the use of a digital control system. Accurate data logs of the process variables are automatically available. From the data, updated process models may be developed and based on these models highly sophisticated control schemes may be implemented by simple reconfiguration of the control software. Though there is promise that digital control schemes can be an improvement over analog control systems, there must be strong evidence indicating that a digital control system will pay for itself through increased process efficiency and profitability.

Though this thesis is primarily concerned with the application of control theory using direct digital control, the value of such work may be explained by illustrating how direct digital control is used in the process industries (4). Figure 2 represents the hierachy of control as it may exist within any processing company. It is the lowest level

FIGURE 2

HIERARCHY OF CONTROL IN A PROCESS INDUSTRY



we are interested in. A direct digital control computer is used to control a complex unit of a given plant. Advanced control techniques are implemented at this level. Above this, a supervisory computer is used to optimize the operations of the entire plant by adjusting the operating set points of the individual plant units. The objectives of each plant are formulated by the highest level computer. Management instructions, current economic trends, inventory data, sales orders and like managerial information are used to set the objectives of each plant. Thus the control of an entire corporation may be decentralized so that the actual control of each individual unit is an independent operation. The control computer of each unit needs only to know what is entering the unit and what the operating set points are so that it may compute appropriate control action.

2.2 Survey of the Literature

The application of digital computers to the control of complex processes has been increasing rapidly over the last twenty years. Several industries such as pulp and paper, steel making and power generation have been developing direct digital control to a high degree of sophistication. However, the chemical industry has been slow to avail itself to this new technology. Reports from people involved in the implementation of DDC of chemical processes indicate that only fundamental control techniques have been applied, although there have been notable exceptions (19). It may be that most progress in DDC has simply been unreported for reasons of secrecy.

Until now, few academics have attempted to apply control theory to real chemical processes. The high cost of the equipment required for such studies and the amount of time that must be sacrificed to develop operating software and to maintain the equipment have been major obstacles to the advancement of such research. However, with the advent of the minicomputer, more people are able to venture into this new field of research. The low cost and reliability of the minicomputer makes the field more attractive to independent researchers.

Recently, reports on the application of modern control theory have appeared in the journals. Jarvis and Wright (13) have used a minicomputer to implement optimal changeover policies on an analog simulation of a liquid extraction column. Wood and Pacey (16) have applied combined feedforward and feedback control of a binary distillation unit. Newell and Fisher (14) have achieved optimal control of a double effect evaporator unit interfaced to a medium sized computer using multivariable integral control. Multivariable feedforward control of this same unit was done by Newell, Fisher and Seborg (15). Bacher and Kaufman (22) have also used a medium sized computer to control a batch reactor.

As more people interface control computers to complex processes, the gap between the theory and application of modern control theory to chemical processes will be rapidly narrowed.

3- DESCRIPTION OF THE APPARATUS

The three basic components of the apparatus will be described in the following pages. They are the control computer, the process equipment and the computer-process equipment interface. The computer is located in the Chemical Engineering Control Laboratory some fifty feet from the process equipment which was built in the Chemical Engineering Unit Operations Laboratory. Electrical connections between the two sites were made through an electrical conduit which linked the Control Laboratory to various parts of the Unit Operations Laboratory.

3.1 The Control Computer

Clearly, the control computer is a major component of the apparatus. The machine used for this study was a 16K Supernova digital computer manufactured by Data General Corporation. Its cycle time is 300 nanoseconds and the machine instruction set is based on a word length of 16 bits. Interfaced to the computer are 16 channels of analog input multiplexed into a single 10 bit analog to digital converter (A/D), 6 10 bit digital to analog converters (D/A), 16 relay outputs, 16 contact sense inputs, 2 teletypes, 1 line printer, 1 high speed paper tape punch, 1 high speed paper tape reader, 1 256K fixed head disk and 1 160K cassette tape recorder.

Although all the peripherals mentioned above could be supported under the structure of the real-time operating system supplied by the computer manufacturer (10), devices such as the disk, cassette and reader were not used for process control and monitor. However, these devices were extremely useful during the period of software development. The details of the software package that was developed for this control study have been outlined in another chapter.

3.2 The Process Equipment

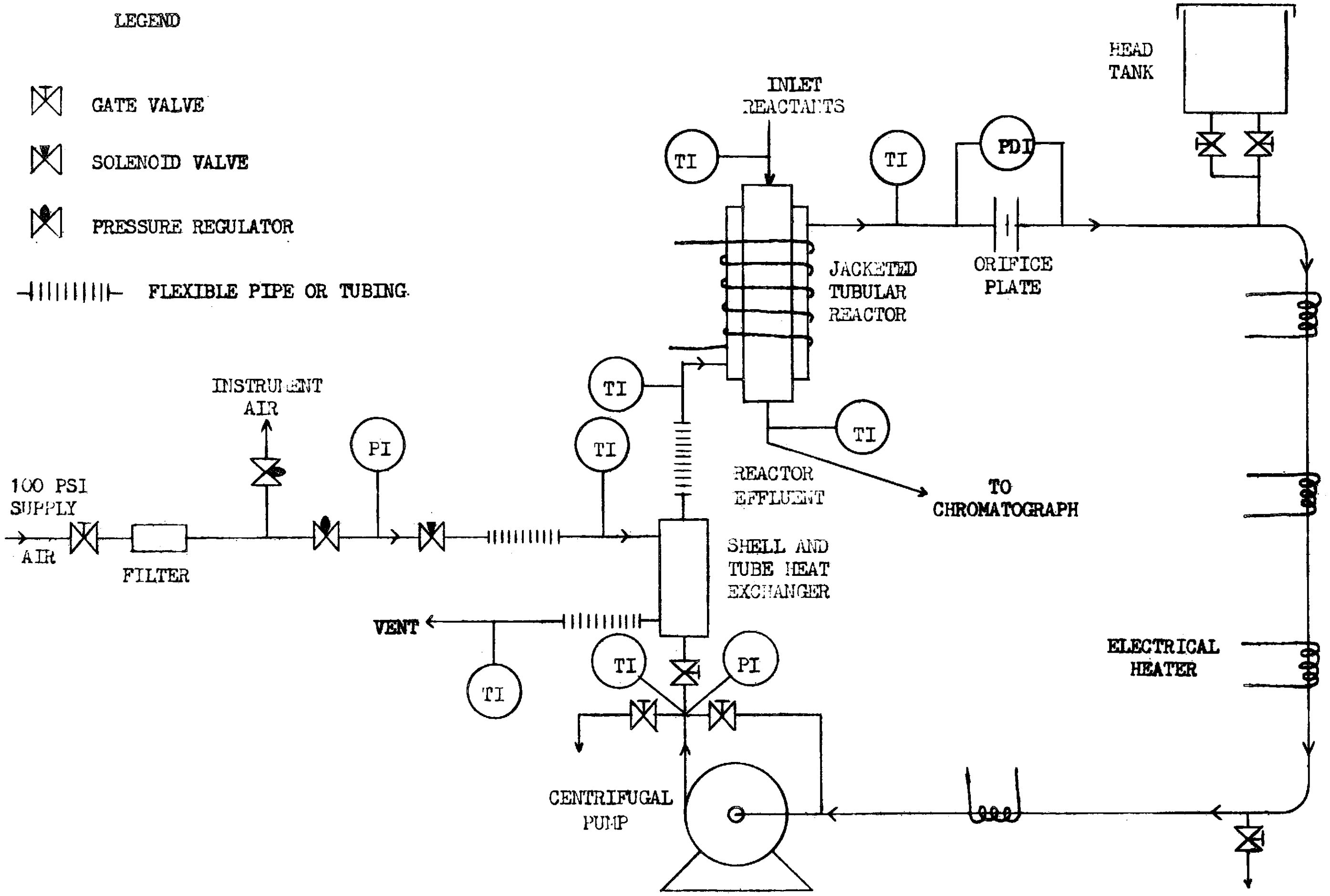
Figures 3 and 4 are schematic illustrations of the process equipment. As represented, the apparatus may be considered to be built up of two basic systems; the coolant flow system and the reactant flow system. The former will be described first.

The coolant flow system is illustrated by Figure 3. The coolant, Sun No. 21 heat transfer oil is continuously circulated by a Sihi Model ZLLE 4017/155Q centrifugal pump equipped with special high temperature gland and gasket materials. The oil flows through the tube side of an American Standard Model 200-8 single pass heat exchanger, through the jacket of the tubular reactor, then across a 5/8" orifice plate located downstream of the reactor outlet. A head tank has been mounted above the vertical section of the return piping.

Five electrical resistance heaters were used to heat the coolant flow system. The overall rating of these heaters was about 5.8 kw. The heaters were made up of lengths of .010" x .625" Kanthal electrical resistance strips embedded in a layer of HiloSet refractory cement. Three of these heaters were mounted side by side on the vertical section of the return piping. Another was located

FIGURE 3

COOLANT FLOW SYSTEM



on the horizontal section at the pump inlet; the fifth was mounted on the reactor jacket itself. Each heater was powered by a 1200 watt low voltage, high current AC source. Power was transmitted along number 6 gauge type TWH stranded cables.

To eliminate stresses on the heat exchanger body, special flexible pipe was connected to the outlet ports. The oil inlet port was fixed to the pump; a length of flexible high pressure hose was connected to the inlet air port. This need to have the entire heat exchanger assembly floating was apparent after the first high temperature run. Expansion stresses as well as stresses due to poor piping alignment tended to pry apart the heat exchanger flanges. This resulted in serious oil leaks around the gaskets.

The head tank provided a simple means of keeping the coolant system topped with oil. It also doubled as an expansion chamber for the oil whenever the apparatus was brought up to operating temperature. In order to minimize the oxidation of coolant oil, it was necessary that the head tank remain at ambient temperature. Since the head tank was sufficiently removed from the main circulation network and that the tubes leading to it were small enough to inhibit convection currents, no special cooling was required. Because of these reasons, it was possible to heat the oil near to its recommended upper temperature limit.* The oil capacity of the system is approximately three imperial gallons.

One Hundred (100) psig air was used as a source for both instrument and cooling air. The air was first filtered in a Norgren Model 12-002-020 air filter. Then Norgren Model 11-002-061 air regulators were used to obtain desired air pressures. The air to the heat exchanger was finally controlled by an ASCO Model 8210 D2 normally closed solenoid valve.

Five copper-constantan thermocouples were installed at various locations in the coolant system. The temperature of the oil and of the air entering and leaving the heat exchanger was measured. The fifth thermocouple was located just at the outlet of the reactor jacket.

The pressure of the oil leaving the pump was indicated by a pressure gauge. The pressure drop across the orifice plate was measured using a differential pressure gauge.

The reactant flow system has been represented in Figure 4. In order to make the reactant flow system versatile, several flow paths were designed into it. These

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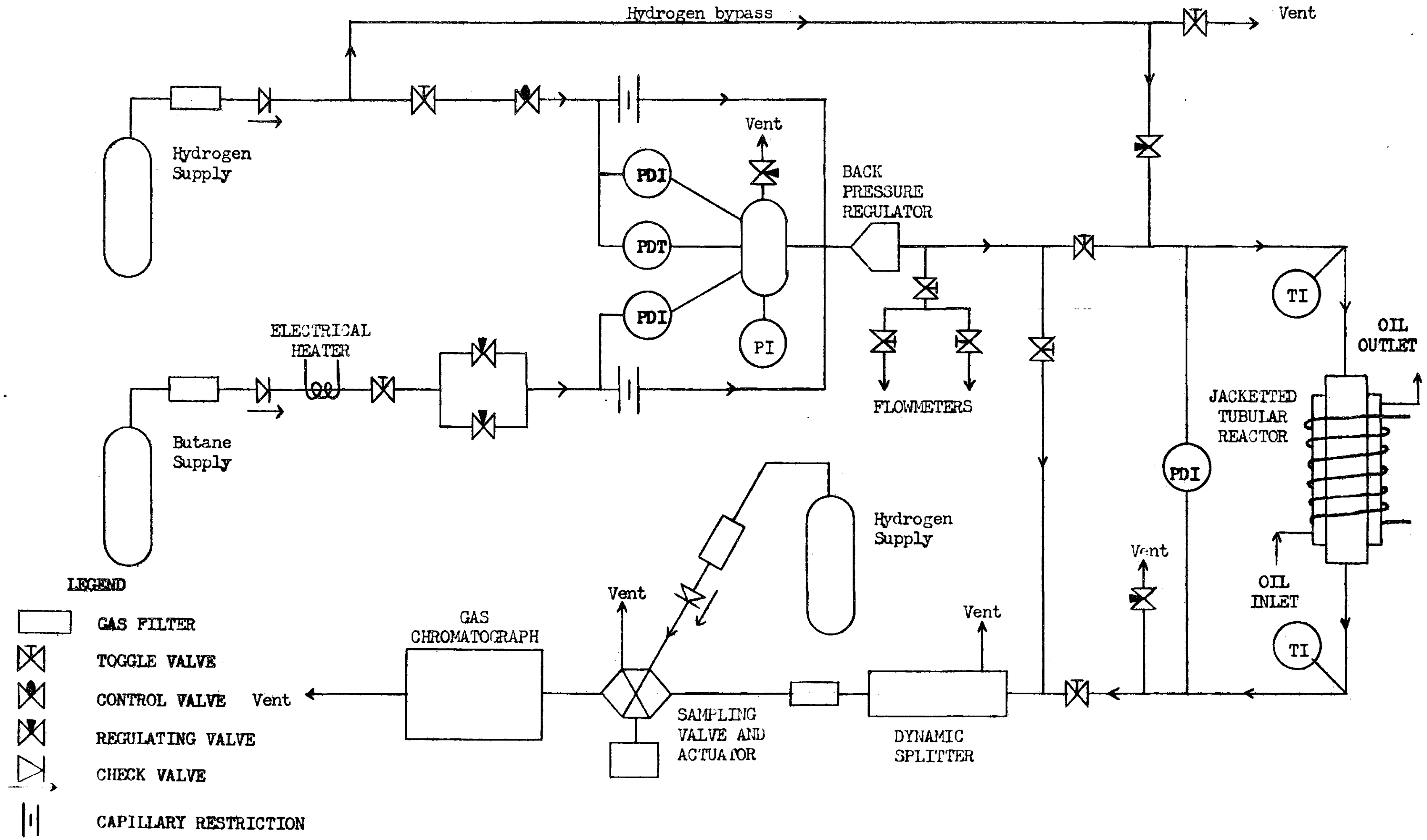
* Sun No. 21 heat transfer oil is recommended for service in closed systems operating at temperatures below 600°F.

FIGURE 4

REACTANT FLOW SYSTEM



numerous flow paths served to direct butane and hydrogen mixtures to any one of three locations: the flowmeters, the reactor or the gas chromatograph.

Pure n-butane purchased from the Matheson Gas Products Co. is first filtered then heated before reaching the throttling valves.** The gas flowrate is then determined from measurements of the pressure drop across a calibrated capillary. A Fairchild-Hiller Model 10BP back pressure regulator was used to maintain the flow capillary exit pressure constant at 450 mm Hg above atmospheric pressure.

The hydrogen gas which was purchased from Canadian Liquid Air was metered in a fashion similar to the above description except that a Research Control Valve (linear characteristics, Cv = .006) was used for the throttling and that a Foxboro Model E13 DM differential pressure transmitter was used to monitor the pressure drop across a calibrated capillary. A bypass direct to the reactor inlet has been included to assist in the purging of the system before startup.

** Heating of the gas was necessary in order to prevent the liquification of n-butane across the throttling valves. This was achieved by wrapping the gas line with an electrical heating tape.

Downstream of the back pressure regulator, several flow paths are possible. The metered gas mixture may flow directly to the chromatograph (Varian Model 90P-3) for analysis or to some external metering device or to the reactor itself. Whenever a gas stream is directed towards the chromatograph, a dynamic splitter is used to take a continuous sample, thereby venting most of the admitted gas. This sample of the gas is in turn sampled in 1cc units by an electrically actuated chromatograph sample valve (Carle Gas Sampling Valve, Model No. 2014 and Carle Valve Actuator, Model No. 4200). Each sample is then analysed for its butane content.

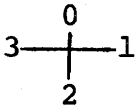
N-butane flow rates were restricted to 10 to 40 cc/sec at STP while the hydrogen flow rates were at least four times the butane rates with an upper limit of 160cc/sec at STP.

A schematic of the reactor itself has been included in Figures 3 and 4. A more detailed illustration of the reactor is given in Figure B-1 of Appendix B. The reactor was made of two concentric sections of type 316 stainless steel pipe. The inner pipe was Schedule 40 1½" pipe and the outer pipe was Schedule 10 2" pipe. The annular spacing was 1/8". An 11" deep catalyst bed rests on a disk near the bottom of the inner pipe. The disk is supported by a tube carrying thermocouple wires to the outside of the reactor. Ten chromel-alumel thermocouples were located at various positions throughout the bed. The actual positioning of these thermocouples is given in Table 1. Gases entering the reactor are distributed over the catalyst bed by a porous stainless steel disk (Type H, pore size: 5 microns, Pall Trinity Micro Corporation). The flow through the reactor is counter-current to the flow in the annulus.

The reactor design needs several improvements. For instance, the thermocouples should be brought up through the annulus and positioned through the reactor wall rather than locating them from within the reactor. This would position the thermocouples much more accurately, hence ensure reliable temperature profiles of the reactor bed. Instead of using fine screen to support the catalyst bed, a cintered disk similar to the one used to distribute gases over the bed should be used. This change would enable control studies using finer catalysts. The ends of the reactor tube should be flanged to permit easy access to the reactor interior. Also the reactor jacket should be fabricated in such a way that it may be removed to allow thermocouple relocation.

TABLE 1

Thermocouple Distribution Inside Reactor

Vertical Position Above Bed Bottom (Inches)	Radial Position 	Radial Distance From Axis (Inches)
10	3	3/8
9	1	3/4
8	0	9/16
7	2	9/16
6	3	3/8
6	1	3/4
4	2	1/2
3	3	1/2
2	1	1/2
1	0	9/16
0	Bed Bottom	

The nickel on silica gel catalyst that was used is described in Appendix A. Because pure catalyst produced almost 100% conversion of the butane and prevented control of the reactor, it was diluted to 20% with inert carrier. This catalyst concentration was then found to be satisfactory for control studies, giving a wide range of potential operating conditions (i.e. a range of butane conversions). The reactor was filled with 344cc of the diluted catalyst.

3.3 The Control Computer-Process Equipment Interface

Only a small number of process measurements and controls have been used for this study. 17 thermocouples, 1 differential pressure transmitter, 1 gas chromatograph, 1 E/P transducer and associated control valve, 1 solenoid valve and 1 sampling valve actuator were used.

The ten chromel-alumel thermocouples positioned inside the reactor as well as the two copper-constantan thermocouples located at the reactor inlet and outlet were simply monitored by a twelve point Honeywell Electronik recorder placed near the reactor itself. However, the other five copper-constantan thermocouples were used with Acromag thermocouple transmitters. These devices produce a 10 to 50 milliamp current into a 200 ohm load resistance at the computer interface. The voltage drop across the load resistor is used as input to an A/D converter.

For a specified range of differential pressure, the differential pressure transmitter generates a 10 to 50 milliamp signal into a 200 ohm load resistance at the computer interface.

Prior to transmission, millivolt level signals from the chromatograph detector were amplified by a Burr Brown Model 3620 differential-input instrumentation amplifier with a gain of 1000.

Digital to analog converter signals were transmitted directly to the E/P transducer actuating the hydrogen flow control valve.

The solenoid valve and the sampling valve actuator were operated with power switched by the computer relays.

All transmitter signals between the computer and the process equipment were carried in individually twisted pairs of wires (Belden type 8775 and 8778 cables) running in a 6" square conduit.

A separate six conductor shielded cable (Belden type 8426) was used to carry 110 volt AC voltage, interfacing the solenoid valve and sampling valve actuator to the computer relays.

4- REAL-TIME MONITOR AND CONTROL PACKAGE

4.1 Fundamentals of Real-Time Data Processing

The instruction set of the Supernova minicomputer is structured in such a way that the manipulation of data is handled by two distinct classes of operations: register to register (including memory to register and vice versa) operations and input-output (I/O) data transfer operations. The former execute at high speed (of the order of microseconds) whereas the I/O operations typically range from about 50 microseconds (for A/D conversions) to the order of fractions of a second (for teletype operation). Logically simple programs requesting I/O operations may be written to instruct the computer to wait in turn for each data transfer to be completed before proceeding with the programmed sequence. (It is important to realize that the computer operation is serial in nature, i.e. only one instruction is executed at a time). This method of programming effectively reduces the processing speed of the minicomputer to the speed of the input-output device in operation. In fact, data transfers between computer and buffer associated with any device are done at high speed; it is the transfer of data between the buffer and the device that requires the relatively large amounts of time during which the central processing unit (CPU) is idle. A much more efficient mode of operation is required when several peripheral devices are involved and particularly in real-time data processing where the execution of certain tasks is directly tied to the time of day. Each peripheral device is capable of receiving instructions from the CPU to initiate an I/0 operation, carrying it out without interference from the CPU and then signalling the CPU that the operation has been completed. The signal generates an interrupt which is in fact a request for service from the device to the CPU. In order to keep the device in operation, the CPU must acknowledge the interrupt and initiate the next data transfer. However, before the interrupting device can be serviced, whatever program had been executing in the CPU must be set aside in such a way that the CPU can proceed from the point of interruption after the interrupting device has been serviced.

In order to take full advantage of processor speed, some type of operating system is required to handle the servicing of interrupts and the scheduling of real-time data processing operations. Such an operating system must be based on two priority structures. Firstly, it is possible to define a device priority. A device like the analog to digital converter is much faster than the teletype, for example. It is clear that the faster device should be serviced first even if interruption of the slower device servicing routine is required. Thus, the faster device must be given a higher priority so that it will not be delayed by the slower ones. It is also possible to define task priority in real time. This type of priority makes it possible to schedule tasks in real time: tasks running at low priority may be interrupted by higher priority tasks. The lower priority task may not resume operation until the higher priority task has been completed or is temporarily suspended (pending data transfer or passage of time). Thus two types of priorities may be considered when servicing an interrupt: device priority and task priority in real time.

The real-time operating system (RTOS, ref. 10) supplied by the computer manufacturer employs the device and task priority schemes outlined above. The operating system is, in effect, used to schedule all the tasks requesting run time. Task scheduling will be based on the task priority in real time and device servicing will follow the device priority structure that has been established within the operating system.

Real-time data processing is necessary whenever I/O activity is to parallel plain processor duty. For example, in order to support both data logging and control calculations simultaneously, a real-time operating system must be used to schedule the various tasks.

In the context of this work, a network will refer to a particular combination of equipment service and software service. The equipment implies the computer and its peripherals (but not the process equipment). The software refers to the real-time operating system and the programs based on the operating system. These programs have been written so that no direct interaction exists between any two. (This can only be if each program is complete within itself. For this reason, these programs will be referred to as network functions.) Any interaction that does exist occurs through the status of special flags. Thus, it is possible to synchronize tasks without actually linking programs together.

The software has been set up to perform two widely different tasks. On one hand, the software is used to establish communication between the operator and the network.

On the other, it manages the control of the process equipment according to the conditions specified by the operator. Evidently, the latter task has priority since it is directly tied to real time. The former will only be scheduled for run time whenever the control task has been temporarily suspended.

Figures 5 and 6 illustrate the structure of the network. Figure 5 details the linkages between the functions that manage operator-network communication. Function EXECT is continuously expecting operator input from the console. Upon transmission of the correct recognition code, a number of network functions may be initiated by the operator. For example, inputting the string LOGON on the console will initiate the logging function, and the operator may select which of three devices will be used to obtain the hardcopy record. The "time of day" which is generated by the CLOCK function is used by LOGON for interval timing. Functions may be terminated as easily by calling up the ENDAL or ENDJB functions. Figure 6 illustrates the various links between the interface support functions and the process control functions. Input analog data is sampled regularly by the

FIGURE 5

STRUCTURE OF OPERATOR-NETWORK COMMUNICATION SOFTWARE

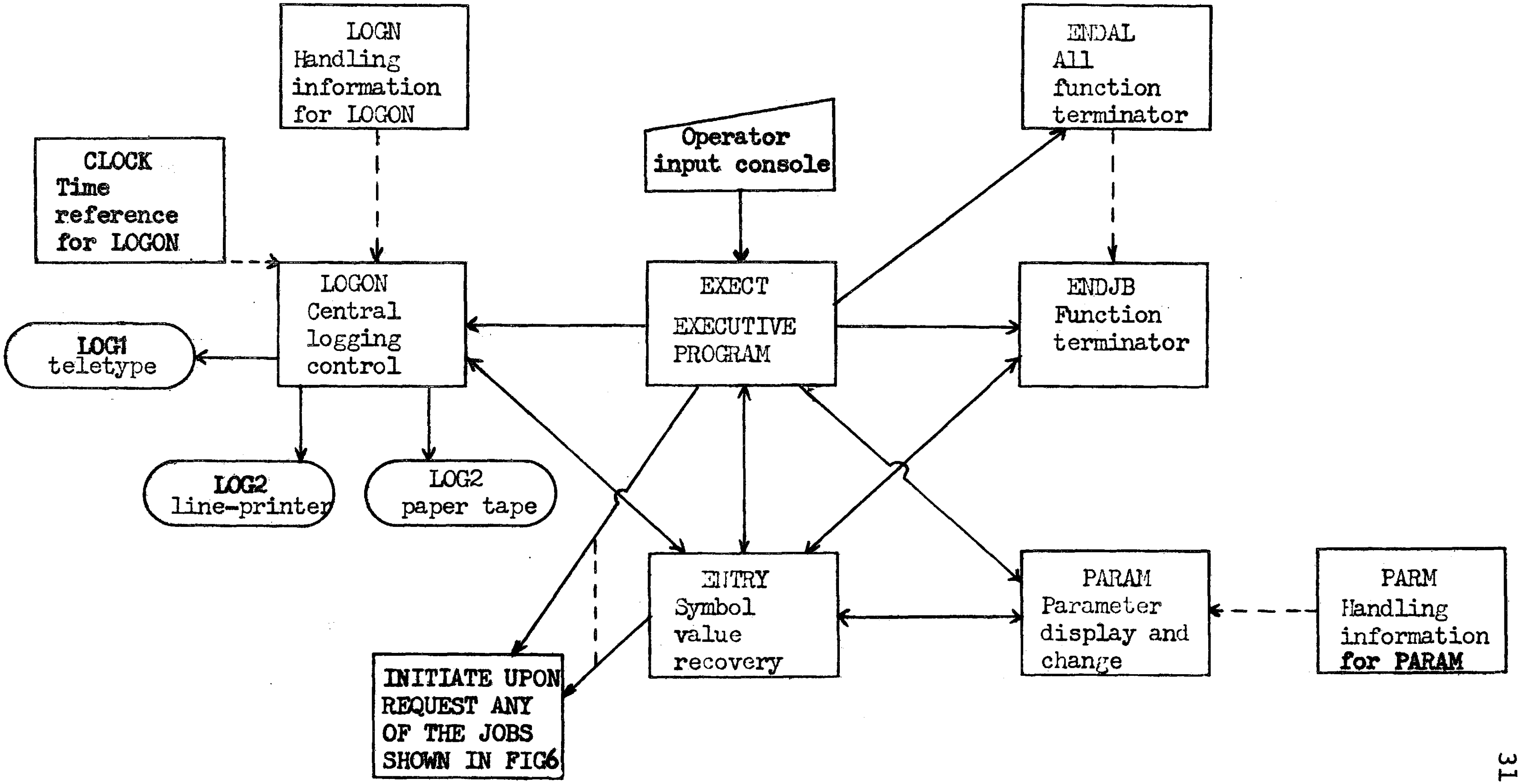
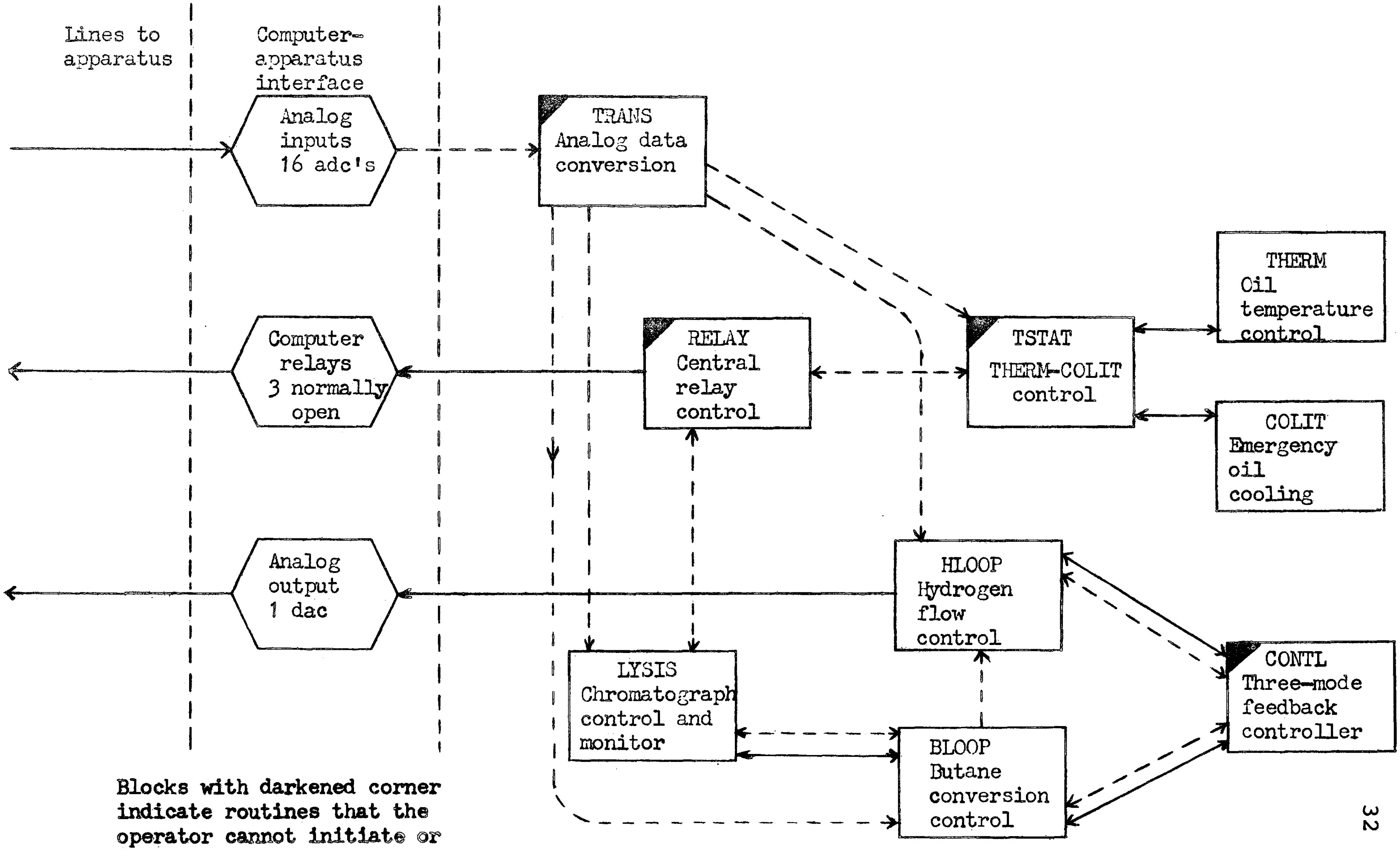


FIGURE 6

STRUCTURE OF THE DIRECT DIGITAL CONTROL SOFTWARE



Blocks with darkened corner indicate routines that the operator cannot initiate or terminate.

TRANS function. Any routines requiring process measurements refer to TRANS for that data. The RELAY function continuously examines a number of relay status flags and sets the relays accordingly. Both TSTAT and LYSIS use the RELAY facility. TSTAT monitors the THERM (on-off oil temperature control) and COLIT (rapid oil cooling) flags to determine the type of oil temperature control requested. The reactor effluent is analysed every thirty seconds using a gas chromatograph actuated and monitored by LYSIS. The hydrogen flowrate and the butane conversion are controlled by HLOOP and BLOOP respectively.

Only a small fraction of the processor time is required to operate the network. For this reason, the computer is able to support several peripheral devices and calculate control strategies simultaneously. For example, data logging on three devices and parameter display on the console are not slowed by the oil temperature control, the hydrogen flow control, the butane conversion control and the gas chromatograph support. It is the extreme speed of the processor and the structure of the real-time task scheduler that make it possible to create this impression.

The software package developed for this work may be divided into four distinct sections:

1 - Basic network functions

2 - Operator-network communication routines

3 - Control functions

4 - General purpose routines.

All of the programs that will be described shortly have been formulated to conform to the syntax of the real-time operating system (10, 11). All I/0, sampling and control loop timing and task scheduling was managed using the RTOS command set.

The functions of the first section are used to support much of the I/0 activity created by the functions of the second and third sections. Operator-network communication functions are listed under section two. All control functions are included in section three and a number of utility programs are classified in section four. Brief descriptions and logic diagrams of each of the programs of sections one, two and three will be given. Since routines in section four are logically simple, no flow diagrams are included with the written comments.

Listings of the actual programs have been compiled in a manual (26) detailing the use of the monitor and control package.

4.2 Basic Network Functions

Four programs fit into this category. They are:

- CLOCK
- TSTAT
- TRANS
- RELAY

These four routines are basic to the network because of their special duties: they are essential to the operation of the network. TRANS and RELAY maintain the analog to digital converter and relays respectively. CLOCK is a routine that permits the timing of the logging functions; TSTAT is a program that supports the two functions entitled COLIT and THERM (to be described in another section).

CLOCK

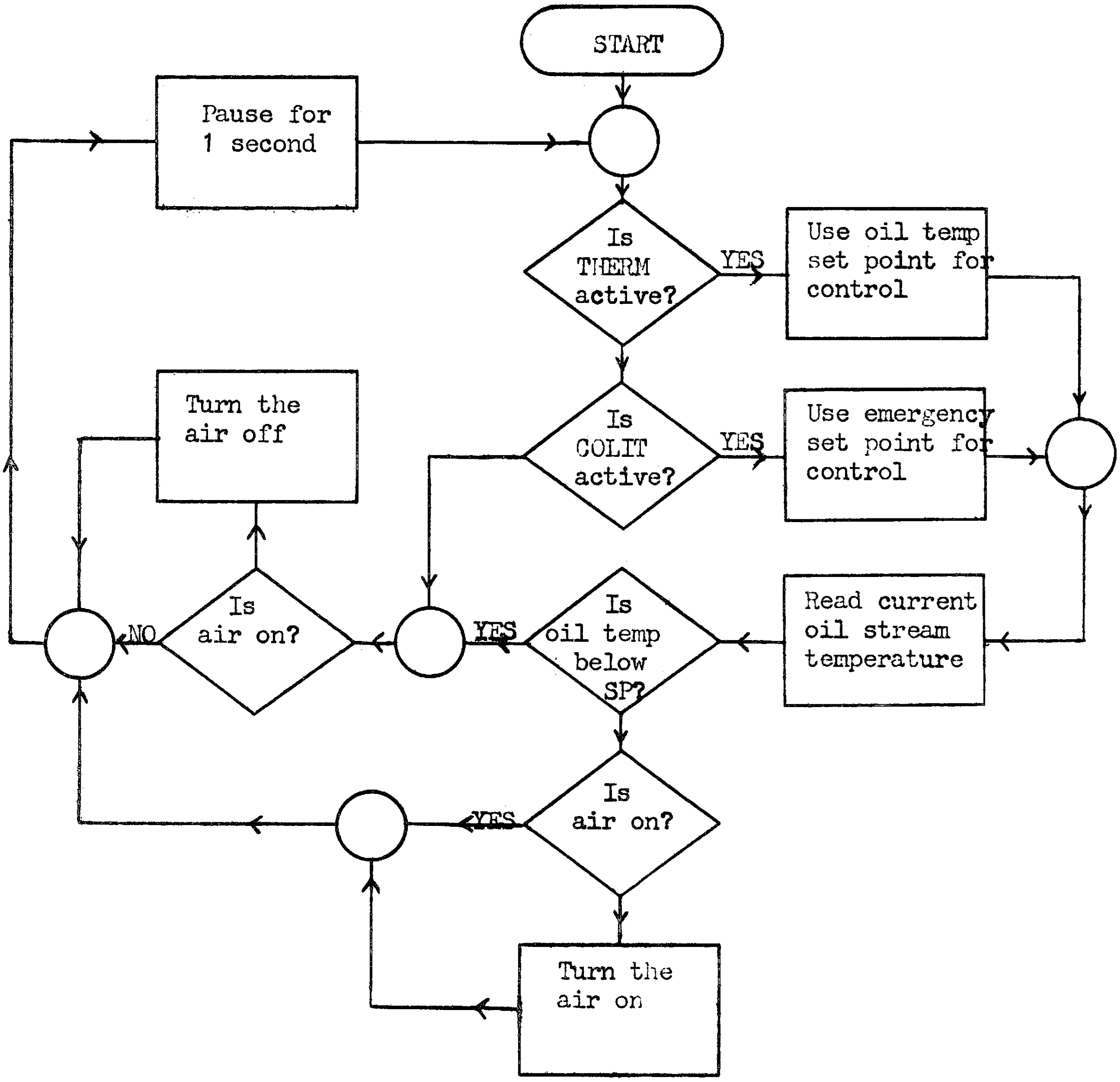
In general, data logging is done at regular time intervals. The interval is normally split into two parts: the data output and a time delay. Once a data record is complete, there must be a way of calculating the time delay for the current logging interval. The only way to do this is to know the exact times at which the data record began and ended. With these times and the intended duration of each time interval, the time delay before the next logging interval may be calculated. The routine that enables the logging program to know the "time of day" is entitled CLOCK. The CLOCK routine increments a "time" register every hundreth of a second. It is the "time" register that is examined to obtain the time at which the start and end of data records occur.

<u>TSTAT</u> (see Figure 7)

Control of the oil stream temperature is achieved in one of two possible ways. Either there is thermostat control of the temperature about a set point (THERM), or else the entire oil system is cooled as rapidly as possible to room temperature (COLIT). In both cases, air is used as the coolant. In order that the operator may choose one control over another, the routine TSTAT has been formulated. Due to the nature of the THERM and COLIT functions (see the description of these in a later section), only one of the two may be requested at any one time. A request for one of the control functions is made via two special status flags. These are examined once

FIGURE 7

STRUCTURE OF TSTAT



every second by TSTAT and based on their values, either THERM or COLIT control is taken. By simply altering the value of these status flags, the type of control may be changed.

TRANS (see Figure 8)

To simplify the input of analog data, signals of all of the sixteen analog to digital converter channels were sampled one every tenth of a second. This high sampling rate was necessary to monitor the chromatograph signals and for the sake of convenience, it was simpler to read all sixteen A/D channels at once rather than setting up several monitoring loops with different sampling rates. Following this, most of the information was directly converted to engineering data. The conversion of raw data to engineering data is not required within TRANS. (This part may be removed and data conversion carried out only where required.) For example, thermocouple and fluid flow data were directly translated into temperatures and fluid flowrates using predefined calibration expressions. However, some of the data could not be directly converted. For instance, the interpretation of chromatographic signals required a separate routine entitled LYSIS.

FIGURE 8

STRUCTURE OF TRANS

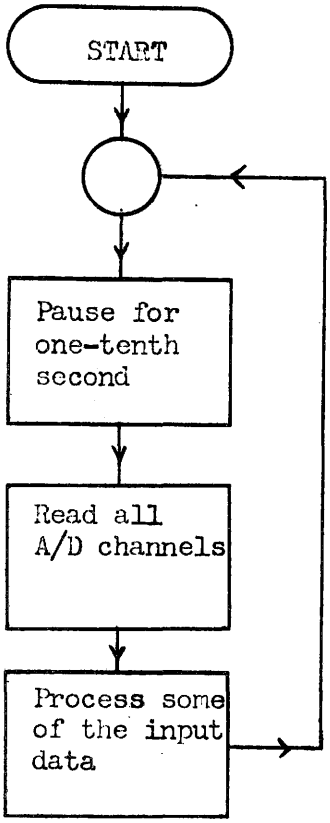
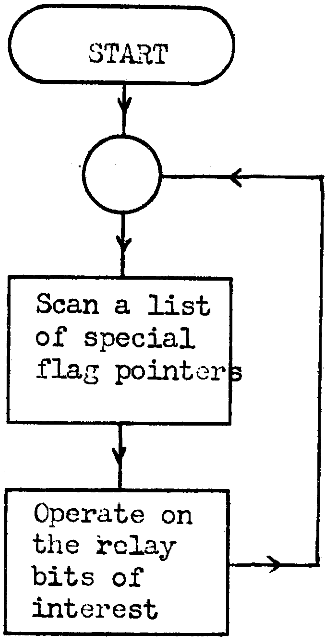


FIGURE 9

STRUCTURE OF RELAY



RELAY (see Figure 9)

Programs such as TSTAT and LYSIS (to be detailed later) use the computer relays to switch a solenoid valve and a gas sampling valve, respectively. Since the relay instruction of the assembler language for the Supernova in effect changes the status of all relays, it was necessary that some method of keeping track of the status of all relays be devised. To accomplish this, RELAY was written. Each routine that uses at least one relay has defined two locations in which a mask pattern and a corresponding status pattern are found. On each pass of RELAY, all these defined locations are examined and if the status pattern indicates a change in the relay pattern since the last pass, then appropriate commands adjust the relay pattern to match the status pattern. In this way, the status of certain relays will change by simply modifying the appropriate status patterns.

4.3 Operator-Network Communication Routines

The following routines are classified within this section:

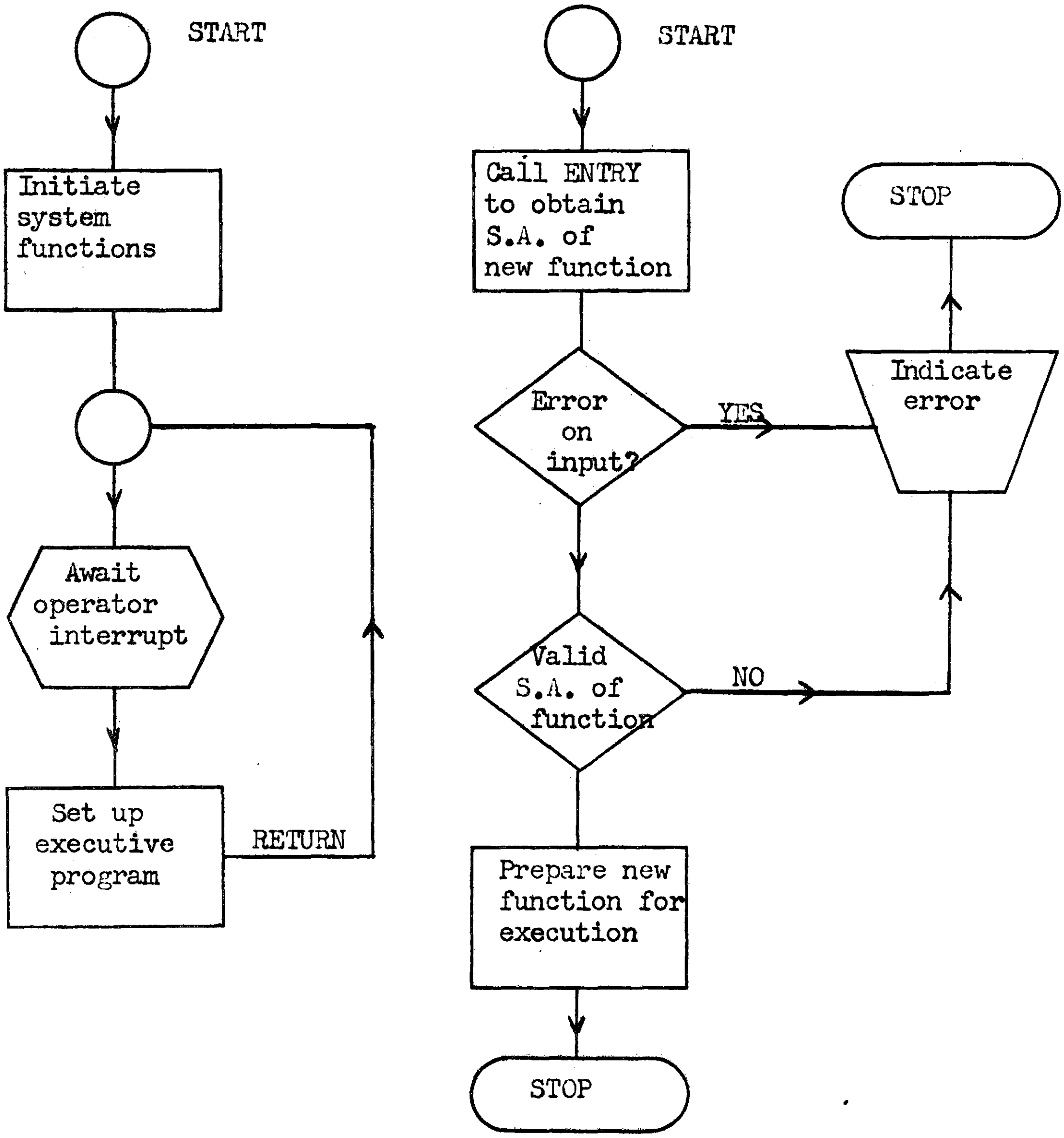
- EXECT
- ENTRY
- ENDJB
- ENDAL
- LOGON and LOGN
- PARAM and PARM

In brief, these routines establish links between the operator and the network itself. LOGON is used to log data on hardcopy equipment; PARAM serves to display and if desired, to alter various parameter values; ENDJB and ENDAL permit the operator to terminate a number of network functions. EXECT and ENTRY are the heart of the entire communication facility.

EXECT (see Figure 10, (a) and (b))

In any flexible control and monitor network, the initiation of new functions must be possible. To achieve this flexibility, EXECT was written. It is labelled the executive function. The first thing EXECT is programmed to do is initiate the CLOCK, TSTAT, TRANS and RELAY

FIGURE 10



(a)
STRUCTURE OF EXECT

(b)
STRUCTURE OF EXECUTIVE PROGRAM

S.A.: starting address

functions previously described. Once this initialization is complete, the program awaits commands from the operator. The software is written to interpret a special command character on the control console as an operator interrupt. When the correct code is transmitted, the operator is requested by ENTRY (see next program description) to input on the console the one to five character name of the function he wishes to initiate. (By this time, the executive function has returned to await another operator interrupt). If the function name is recognized as a system symbol, then a table within EXECT itself is examined to be certain that the recovered symbol value is indeed the starting address of an operator creatable function. If the symbol value is also present within this table, then the function identified by the operator request is initiated. Otherwise, an error is indicated.

ENTRY (see Figure 11)

Frequently it is necessary to determine the value of some symbol defined in the symbol table.* For this

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* As programs are loaded into core, network symbols are saved in a symbol table. In order to conserve memory and to simplify symbol encoding, the symbol is represented by a radix 50 code.

FIGURE 11

STRUCTURE OF ENTRY

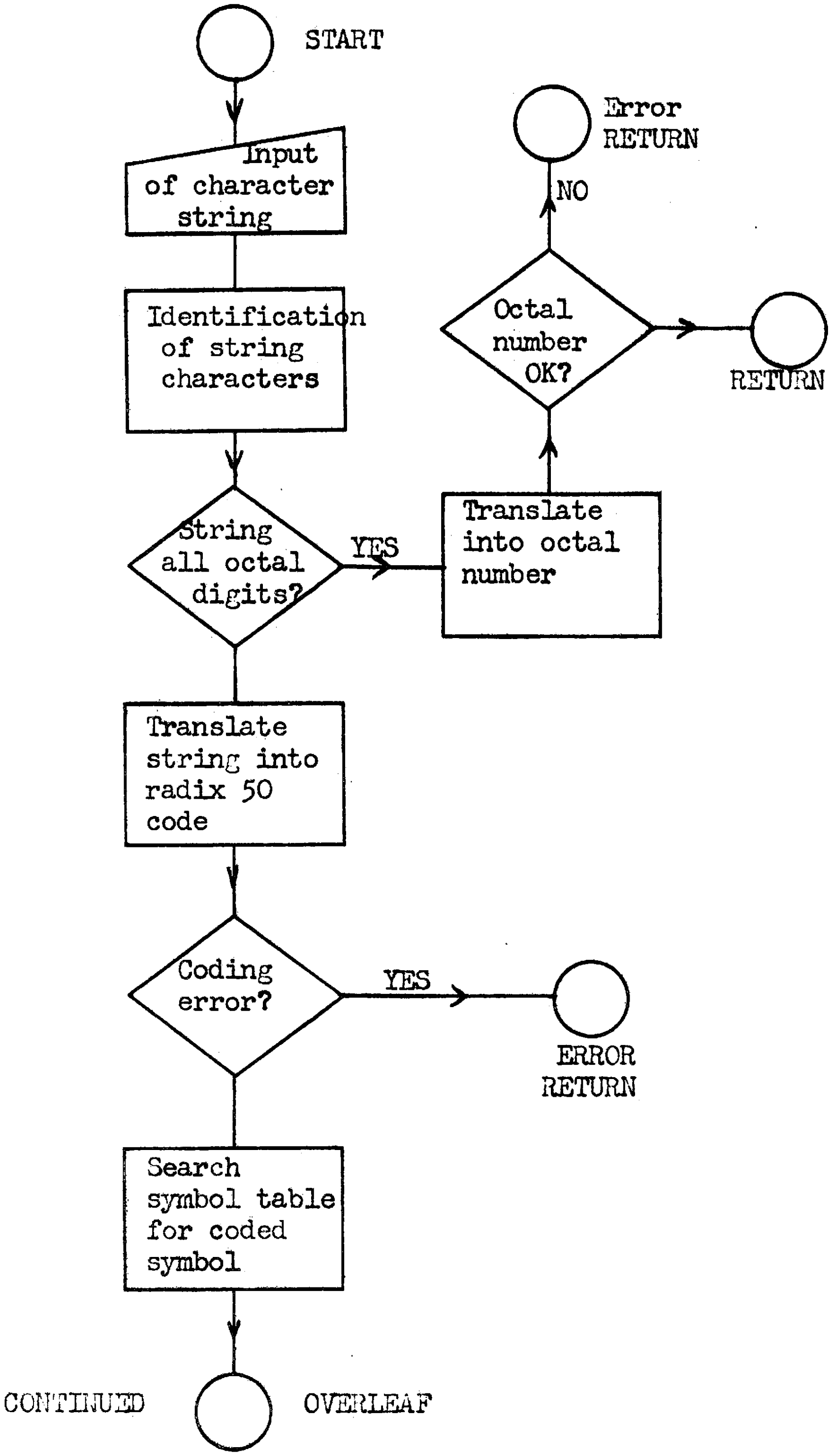
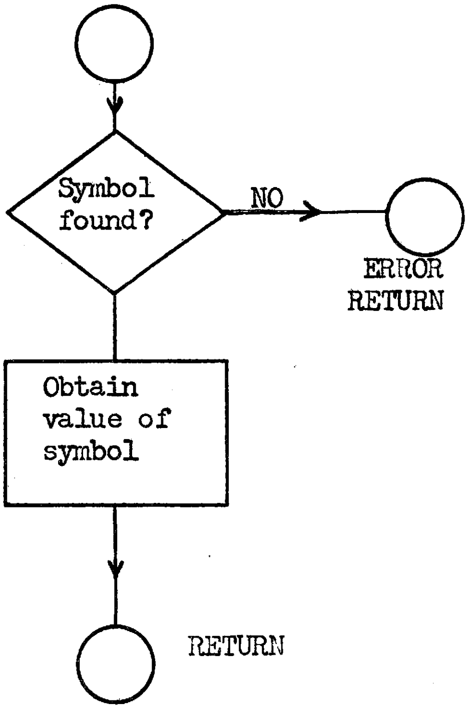


FIGURE 11 (continued)



purpose, the routine entitled ENTRY was written. It requests a string of up to five alpha-numeric characters. The string may be either numeric, alphabetic or a combination of both. If the entire string is made up of octal digits, then it is considered to be an octal number and the number is returned to the calling program. Otherwise, the string is assumed to be a network symbol and it is translated into a radix 50 code. By this encoding, it is possible to uniquely represent a five character string by two sixteen bit words. Having encoded the character string, the symbol table is searched to determine if the symbol is defined therein. If it is, its value is recovered and returned to the calling program. For inputs of less than five characters, a delimiter terminates input and initializes the translation. If only a delimiter is input, ENTRY simply returns to the calling program with a null.

ENDJB (see Figure 12)

Whereas EXECT is used to initiate certain functions, from time to time, it is necessary to terminate these active functions. To do this, each executable job under

FIGURE 12

STRUCTURE OF ENDJB

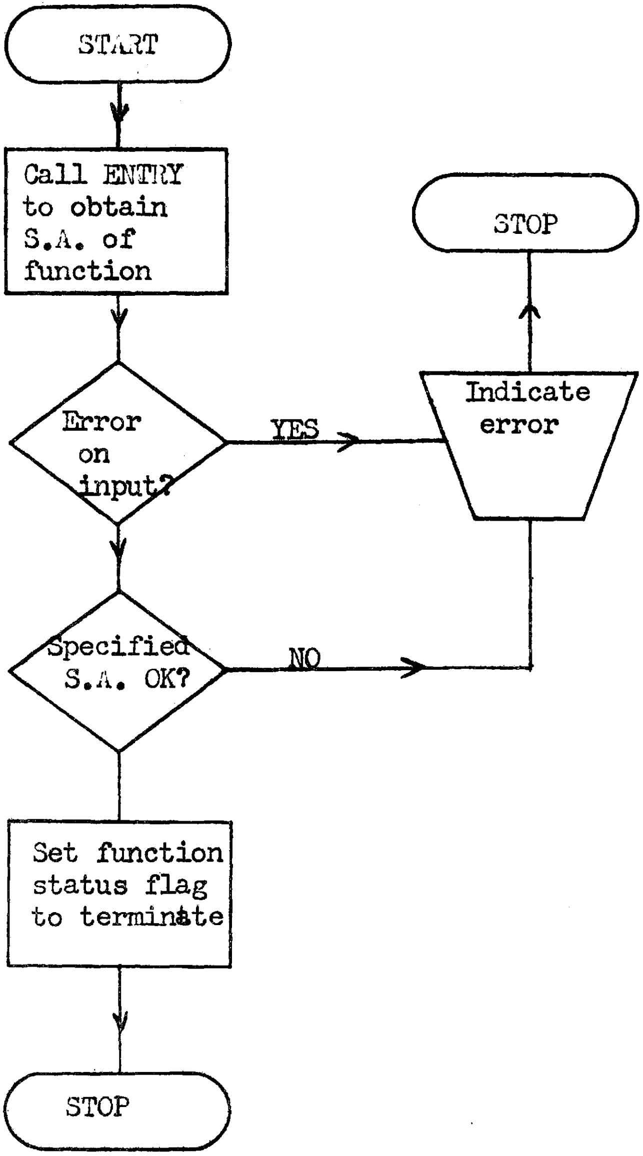
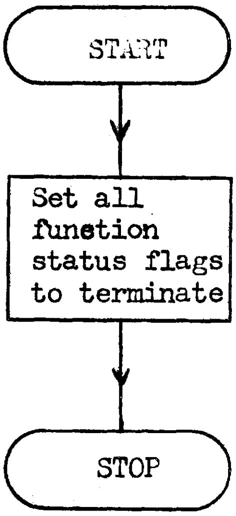


FIGURE 13

STRUCTURE OF ENDAL



operator control has a status flag. With ENDJB, it is possible to selectively terminate an active function simply by setting its status flag to the deactivate mode.

ENDAL (see Figure 13)

This routine's purpose is similar to that of ENDJB. The only difference rests in the fact that all operator controlled function status flags are put into the deactivate mode.

LOGON and LOGN (see Figure 14)

These two sister programs have been formulated in such a way that the logging of process variables in real time is possible. LOGON which is the actual controlling program of the two has two basic sections. The first part communicates with the operator through the console to obtain the list of variables to be logged. Up to thirty different variables may be monitored simultanteously on three output devices. The devices are a teletype, a line-printer and a high speed paper tape punch. The time interval at which data are to be logged is specified by the operator in tenths of a second and each output device

FIGURE 14

STRUCTURE OF LOGON

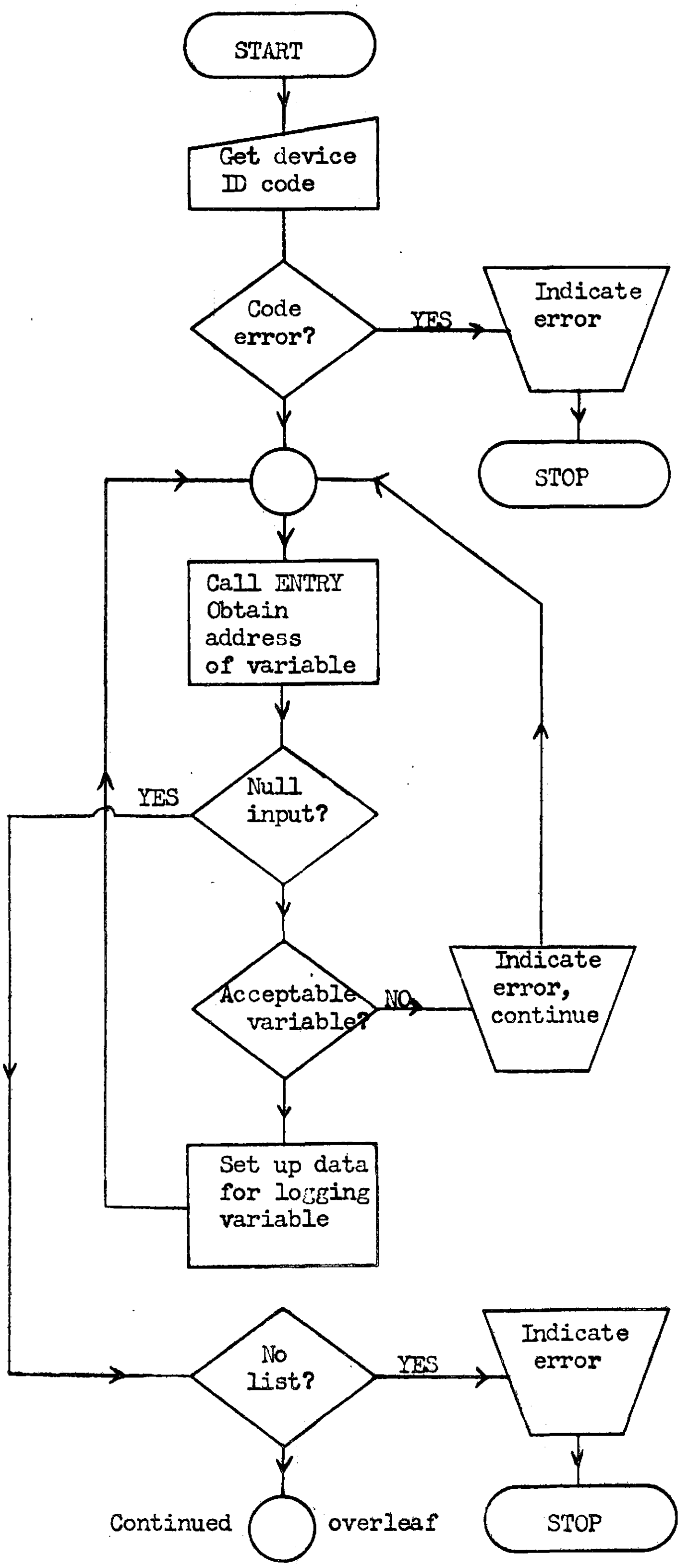
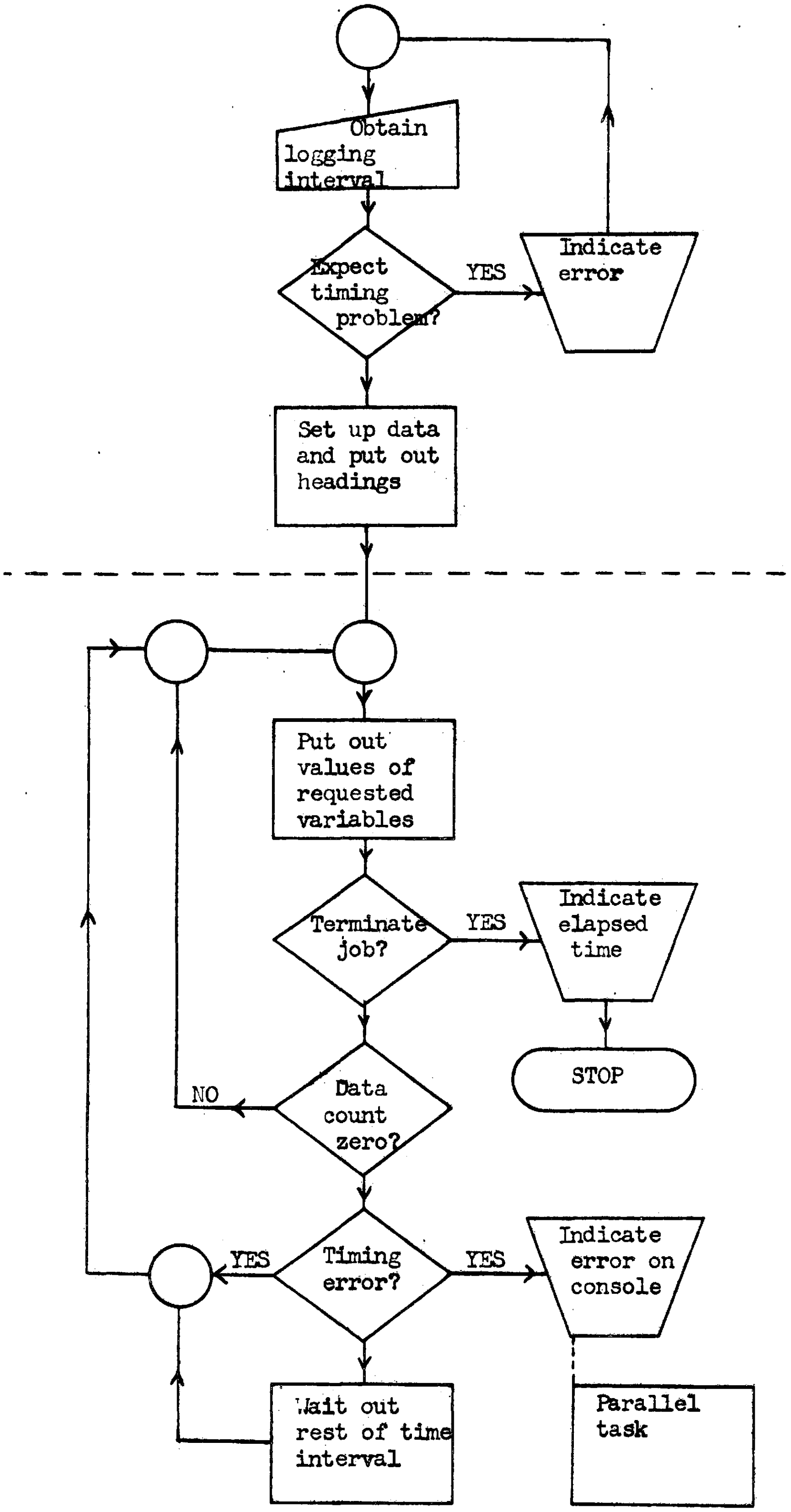


FIGURE 14 (continued)



may proceed at different time intervals. Having provided the necessary information, the second part of LOGON is initiated. This part is truly composed of three sections, each being dedicated to driving one of the output devices. Since these are nearly identical functions, most of the programming is reentrant {see definition of reentrant in the description of CONTL, Section 4.4} save for those parts where the hardware device is actually driven. Column headings, lines, data and page spacing are automatically controlled. The three output functions may be terminated at any time by the operator using ENDAL or ENDJB.

It is necessary to declare in LOGN those variables that are to be logged. Of course, the symbol names for these variables must be declared somewhere else as entry points. The appropriate column headings must also be listed.

PARAM AND PARM (see Figure 15)

These are sister programs which permit the operator to display and alter the value of a number of different types of parameters. Once PARAM is initialized, the program requests a control loop number. By definition, loop zero

FIGURE 15

STRUCTURE OF PARAM

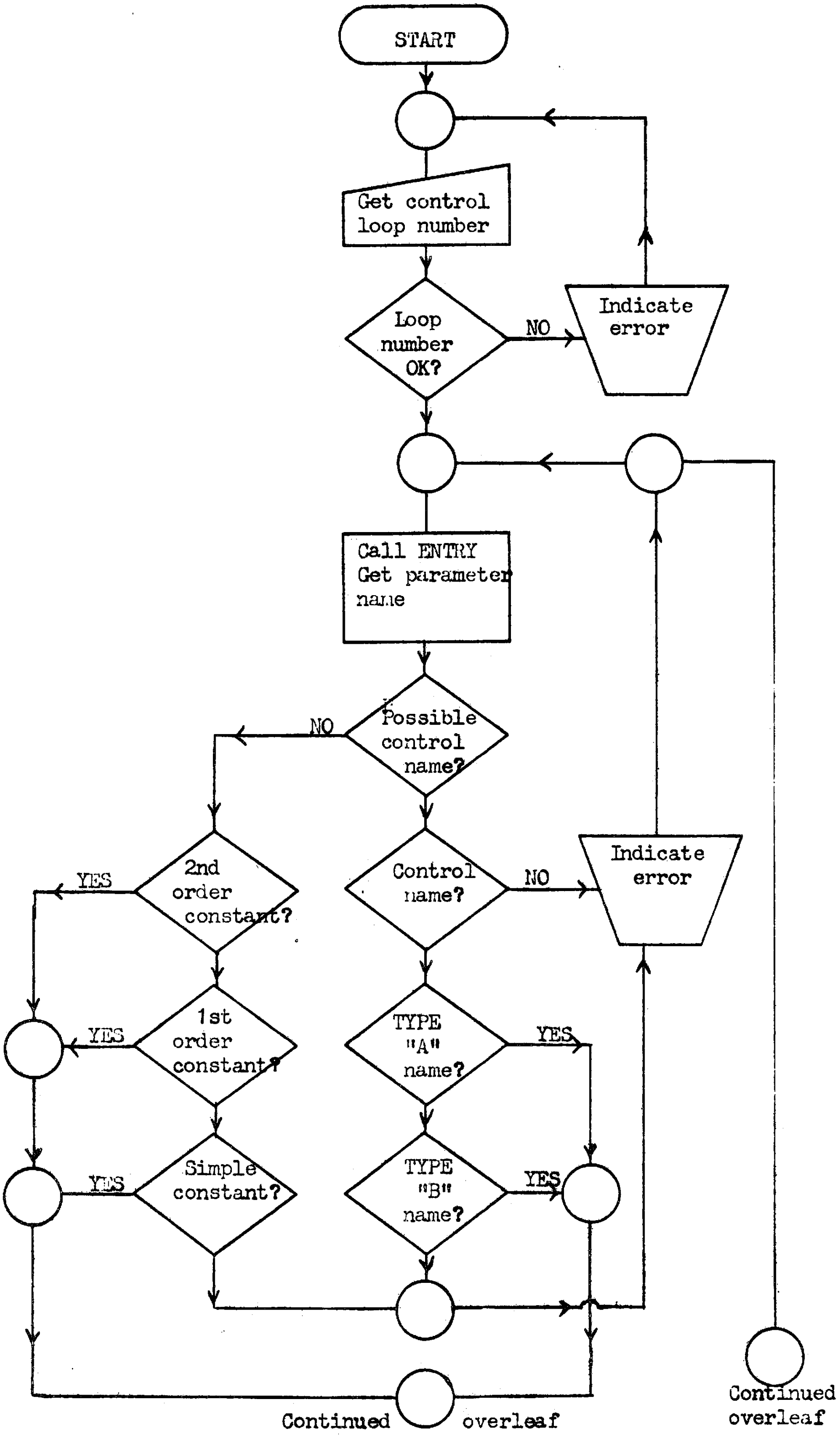
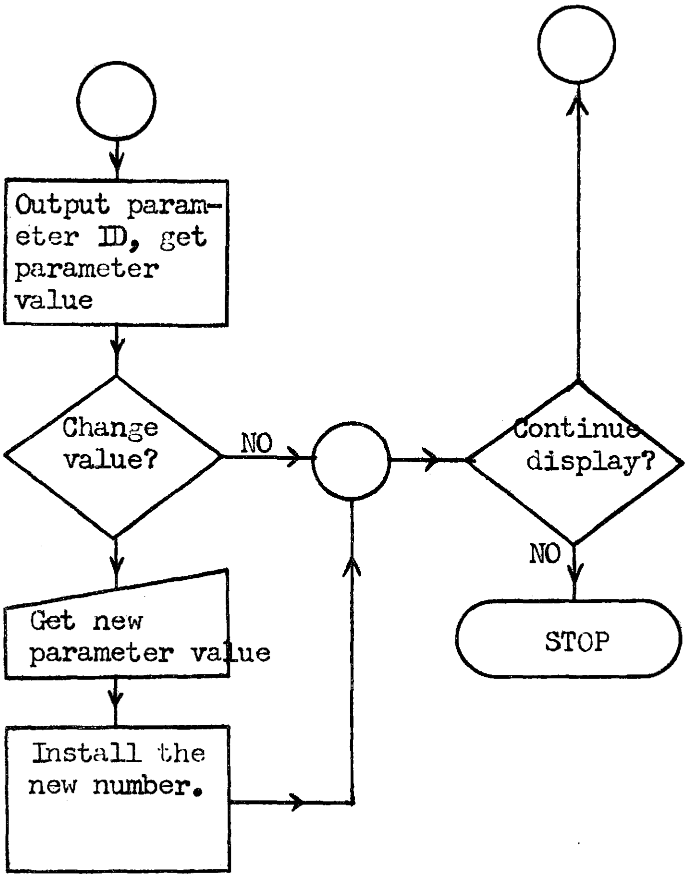


FIGURE 15 (continued)



implies that parameter names to follow do not define quantities in a controller data block. This means that parameters to be displayed are constants that are used in various calculations. For positive loop numbers, the number refers to a specific controller data block. Only parameters defined within a data block may be displayed for this case.

Having selected a loop number (hence a parameter type), the operator may examine one or more of the parameters defined within that type.

PARM is a support program that supplies all the necessary information for PARAM. The various types of parameters are sectioned into blocks to prevent uncontrolled access of information. The descriptive captions for the parameters are also found within this program.

4.4 Control Functions

The programs that achieve control of the various parts of the process equipment are briefly described within this section. They are:

- THERM and COLIT
- CONTL
- HLOOP
- BLOOP

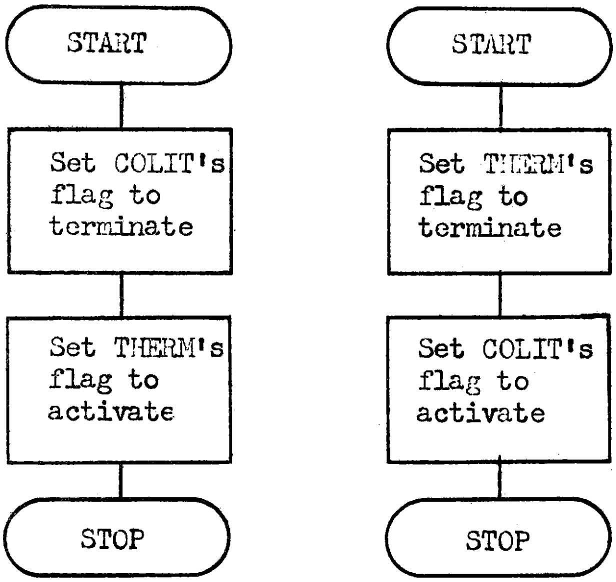
In conjunction with TSTAT, THERM and COLIT are used to establish control of the oil stream temperature. CONTL is a general three mode (PID) position type feedback controller subroutine. It is used by HLOOP to achieve control of the hydrogen flow and by BLOOP to regulate the conversion of butane of the reactor feed stream.

THERM and COLIT (see Figure 16)

These routines actually come under the control of TSTAT previously described. They indicate to TSTAT which mode of control is to be used on the oil temperature. When the THERM function is requested, on-off control of the oil temperature at the reactor inlet is achieved by appropriate

FIGURE 16

STRUCTURE OF THERM AND COLIT



use of the cooling air. When the oil is too hot, the air is turned on until the correct temperature has been reached. The other function (called COLIT) is an emergency function which overrides the thermostat duty and just keeps cooling the oil until it reaches room temperature. THERM and COLIT complement each other: when one is on, the other must be off. A request for THERM for example occurs when the THERM status flag is up and the COLIT status flag is down. With EXECT, the status flags may be altered so that a request for COLIT occurs. TSTAT cycles once every second so that reasonable thermostat control is achieved without much overshoot and chatter on the control.

CONTL (see Figure 17)

By their very nature, some routines must be reentrant. A routine is said to be reentrant if it may be used simultaneously by several calling programs without ever causing the results of one calculation to affect the results of another. CONTL is a three-mode proportional-integral-derivative (PID) position type feedback controller routine capable of providing either direct or cascade control action. Hence, if this routine is to be used simultaneously within many control loops, it must be reentrant . In CONTL, this is achieved by defining a data block for each control loop.

FIGURE 17

STRUCTURE OF CONTL

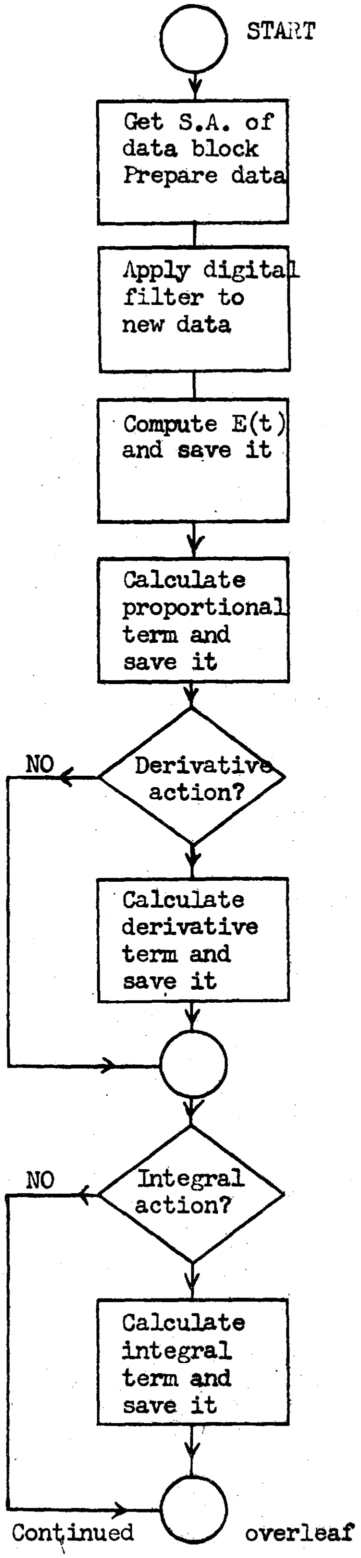
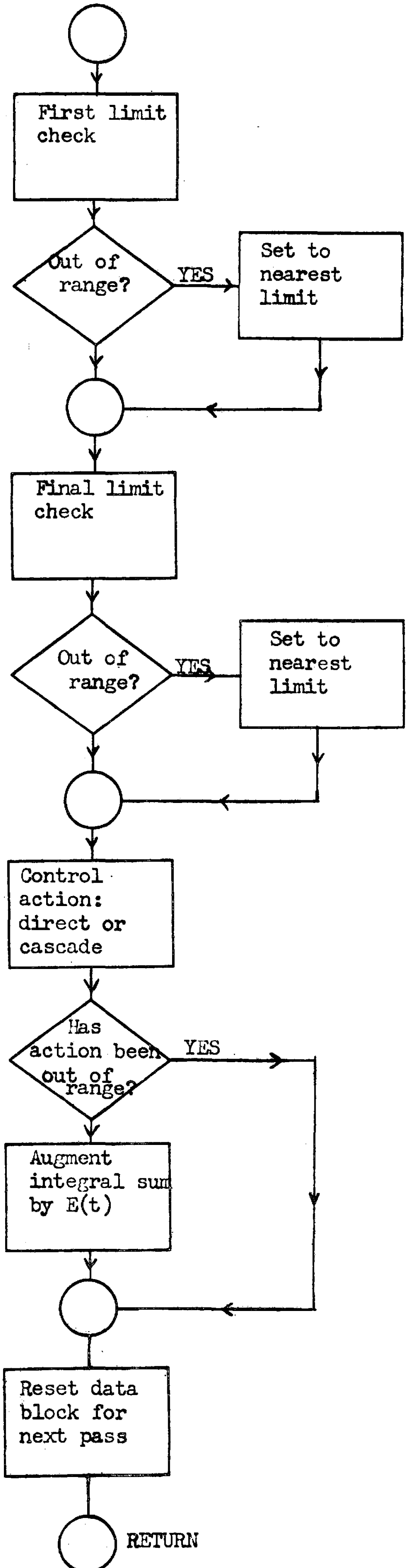


FIGURE 17 (continued)



Each controller data block is 36 words long. The first 16 are used by CONTL itself to store certain quantities such as a return address to the calling program, three past errors, a loop counter and storage locations for intermediate results. The remaining 20 locations are used to store the following data particular to a controller block:

- filter constant (0 to 1000)
- address from which raw data will be taken (in A/D units)
- set point in A/D units
- proportional gain (positive)
- derivative gain (non-negative)
- integral gain (non-negative)
- scale factor and direction of action (non-zero)
- time interval (positive) - any units
- address of limit checking routine
- flag indicating direct or cascade control action
- destination of control action: either a D/A channel or the address of the cascaded data block

- mean value of control output - D/A or A/D units depending on type of control action
- address of data used to convert set point from A/D units to engineering units
- address of the equation that used the above data
- address of data used to convert set point from engineering units to A/D units
- address of the equation that uses the above data
- address of data used to convert mean output value from A/D-D/A units to engineering units
- address of equation that uses the above data
- address of data used to convert mean output value from engineering units to A/D-D/A units
- address of equation that uses the above data

Since each data block defines all the data and storage space required by the control algorithm, it is easy to see how several control loops may utilize the CONTL program simultaneously.

The feedback controller algorithm used in CONTL is given by the following relation:

$$P_n = P_m + K_c * \varepsilon(n\Delta t) + K_i * \Delta t^n * \sum_{j=1}^{n} \varepsilon(j\Delta t)$$
$$+ K_d * \frac{\Delta\varepsilon}{\Delta t}$$

where

$$\frac{\Delta\varepsilon}{\Delta t} = \frac{\varepsilon(n\Delta t) + 3 * \varepsilon((n-1)\Delta t) - 3 * \varepsilon((n-2)\Delta t) - \varepsilon((n-3)\Delta t)}{6 * \Delta t}$$

n = $t/\Delta t$, the number of time intervals

t = total time elapsed, any units

Δt = time interval between successive variable measurements, any units

ε = deviation of variable measurement from set point, (set point - measurement), A/D units

K_c = proportional gain, any units

K_d = derivative gain, any units ($K_c * \tau_d$); τ_d: derivative time

K_i = integral gain, any units (K_c/τ_i); τ_i: integral time

P_m = mean value of the output control, A/D or D/A units

P_n = value of output control, A/D or D/A units

The above equation is the discretized form of the continuous PID control algorithm. Variable measurements are taken at regular time intervals Δt. The derivative has been approximated by a central difference and a summation has replaced the integral term. Derivative and integral times are included in the K_d and K_i respectively.

A first order digital filter has also been incorporated into the CONTL routine. It is of the following form:

$$R'_n = (1-B)*R_n + B*R'_{n-1}$$

where B = the filter constant, $0 \leq B < 1$

R_n = current variable measurement

R'_{n-1} = last filtered measurement

R'_n = current filtered measurement

When $B = 0$, there is no filtering action. This filter is used before computing the control action.

Controllers containing integral action and subject to bounded control action will be eventually driven off scale whenever a sustained deviation is imposed. For example, this could occur when there are large set point changes. The term "reset-windup" is used to described the result of integrating a large error term over a long period of time (27). The integral sum becomes so large that even a change in the sign of the error (implying that the response has overshot the set point) does not show its effect on the control output until the integral sum has been sufficiently reduced. This effect frequently causes large oscillations within the control loop and may lead to loop instability. To correct this natural defect of the PI controller operating a bounded final control element, the integral sum is not augmented by the $(\varepsilon(n\Delta t)\Delta t)$ increment for the current pass if the increment will drive the proposed control action outside some specified range. Thus the absolute value of the integral sum will remain relatively small, permitting the controller to bring the system to steady state much more rapidly.

Also available is the option to maintain control action within certain limits. For each control loop a separate "limit checking" routine must be provided. It is within this routine that the decision is made on whether or not to augment the integral sum.

CONTL has been written on the basis that all incoming variable measurements and set points are in A/D units lying in the range 2 to 10 volts (146_8 to 777_8). The control action may be either cascade or direct. If cascade control (set point change) is intended, then the result of the control calculation will lie in the range 2 to 10 volts (146_8 to 777_8). If direct control of a final control element is intended, then the result of the control calculation will lie in the rande 1 to 9 volts (63_8 to 714_8). This convention was used because the machine's integer arithmetic could cope with any control situation using these units, irrespective of the actual engineering units of the process measurements.

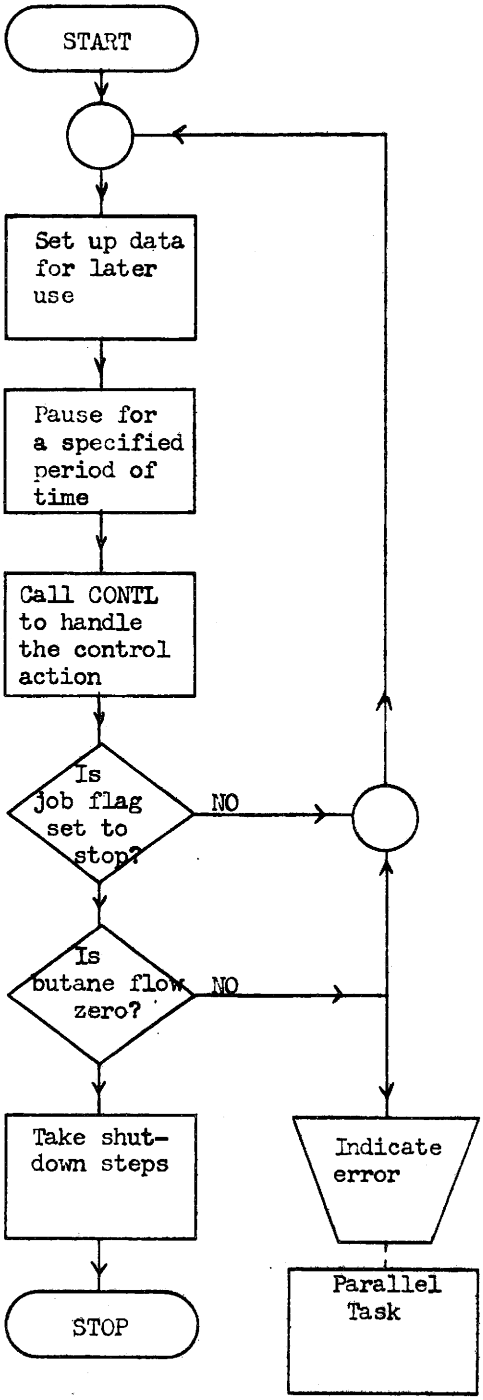
HLOOP (see Figure 18)

At regular intervals, the control of the hydrogen gas flowrate is attempted. Program CONTL is called and the information required by CONTL is located within a data block present within HLOOP itself. After control action is taken (which is to adjust the position of a control valve), the output signal is translated into a valve position. Then, a new cycle is begun.

The operator may terminate HLOOP by using either ENDJB or ENDAL. However, if the system believes that there still is butane gas entering the reactor, then the terminate command will be ignored and a message indicating this will be output on the console.

FIGURE 18

STRUCTURE OF HLOOP



Also present within HLOOP is a limit checking routine to test the acceptability of proposed control action. If necessary, a correction is made and depending on the outcome of the check, the appropriate load-no-load flag is set. At this point, the short subroutine returns command to CONTL and the control algorithm is completed.

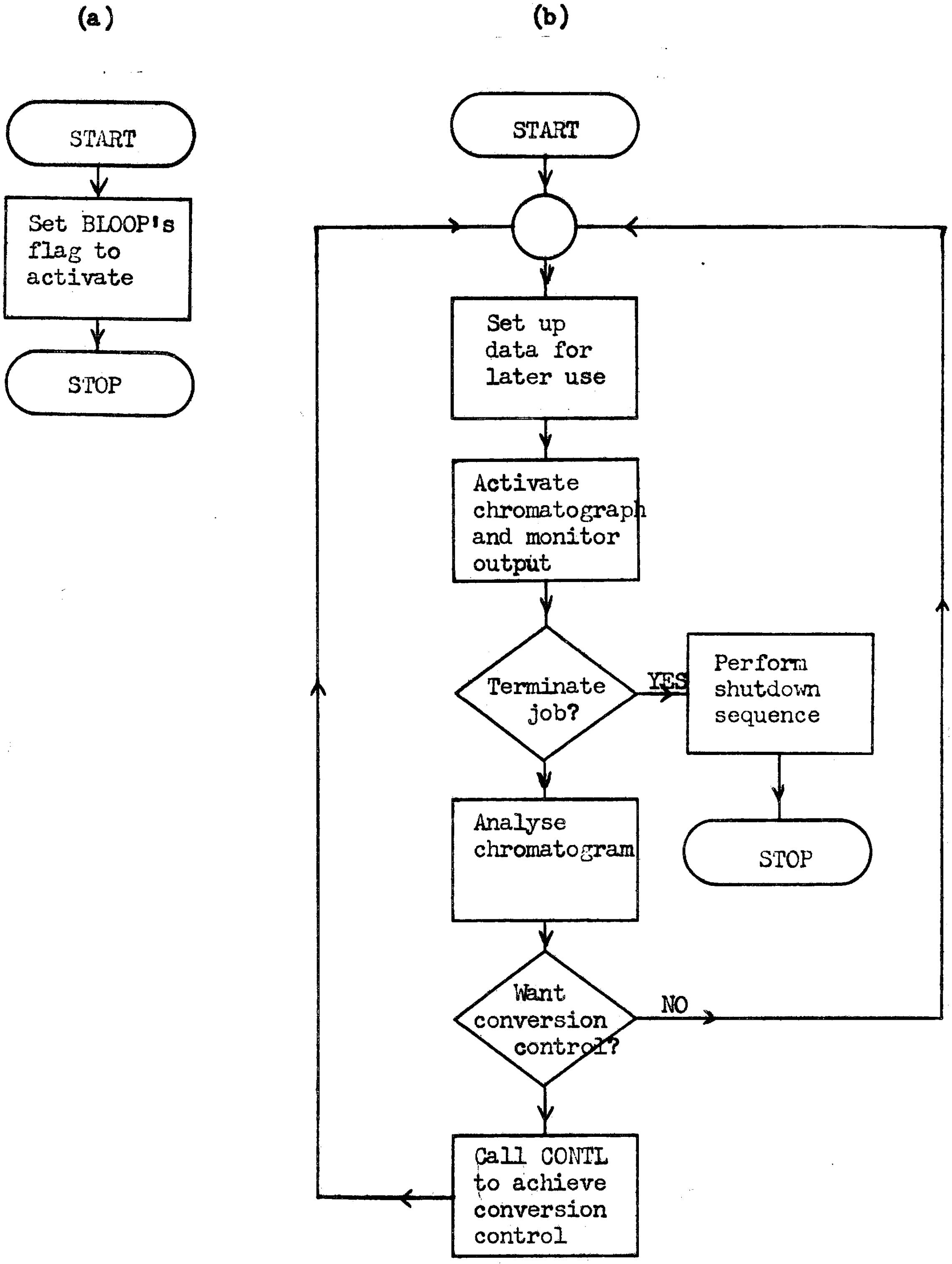
<u>BLOOP</u> (see Figure 19)

There are two sections within BLOOP. The first serves to inform the second whether or not there is to be an attempt to control the conversion of the butane entering the reactor. The control action is to change the set point of the hydrogen flow control loop. The second part of this program manages the chromatographic duties and translates all transmitted information into a butane conversion. This routine (called LYSIS) then calls CONTL if butane conversion control is intended. If not, LYSIS simply returns to continue its normal duties. Also present within BLOOP is a limit checking routine used to verify proposed cascade control action

After each cycle of LYSIS (which takes 30 seconds), an updated value of the butane conversion is available for logging or control action. At any time it is possible to

FIGURE 19

STRUCTURE OF BLOOP AND LYSIS



end the operation of BLOOP and LYSIS with ENDAL or ENDJB.

4.5 General Purpose Routines

The routines to be described below are but simple routines that perform specific functions. They are named:

- EQUNS
- RTIOT
- RTDB
- RTBD

EQUNS

There are three basic parts within this routine. Each serves to evaluate a certain type of algebraic expression. The first is a linear equation, the second a quadratic equation and the third an inverse quadratic. The coefficients of the expressions have all been scaled so that integer arithmetic may be used. The coefficients that apply to the quadratic and the inverse quadratic equations may be the same.

These short programs were found to be essential in establishing calibration curves for non-linear elements. A capillary flowmeter and associated instrumentation is such an element. Also, relations such as these have permitted the simplified structure of the software establishing communication between the network and the operator. This is because the operator may converse with the network in engineering units without ever having to worry about translating this information into the internal number scale. This then permitted the formulation of general reentrant routines useful in many sections of the network.

RTIOT

Actually, this routine is a collection of eight different and separate routines. Six serve to perform all the I/0 for the system. The other two are byte manipulating routines used exclusively by the routines entitled RTDB and RTBD described below. It simply was convenient to combine all these routines under one title.

RTDB

This routine is a single precision ASCII decimal to binary convert used for the simultaneous translation of input information from two different teletypes. The logic within this routine is basically that supplied by Data General Corporation, except that it has been modified to function in a real-time environment.

RTBD

This routine is exactly the inverse of RTDB. It is a single precision binary to ASCII decimal convert. It may be used to output on two teletypes, a line-printer, and a high speed paper tape punch, all of these devices being driven at the same time if required. This routine is also a modified version of the software supplied by Data General Corporation.

5- ON-LINE STREAM ANALYSIS

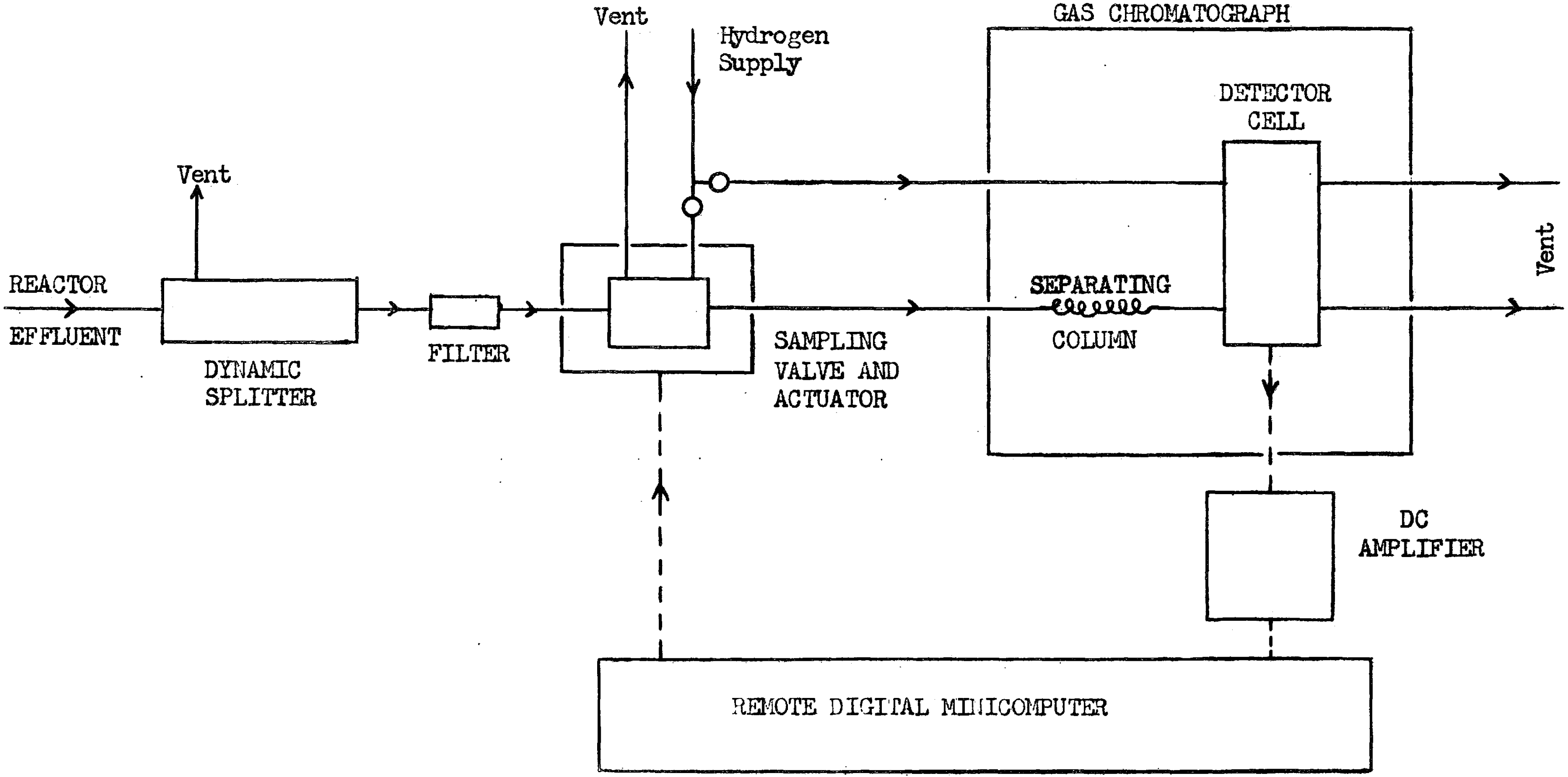
A model 90P-3 Varian gas chromatograph was used to determine the butane composition of the reactor effluent. Both sample injection and detector signal interpretation were performed by the minicomputer. Figure 20 represents the actual analytical installation used within the butane conversion control loop.

The reactor effluent enters a dynamic splitter which permits only a fraction of the total gas flow to proceed towards the chromatograph. This continuous sample is then filtered before entering a two position sampling valve.* This valve was mechanically coupled to an electrical valve actuator. When signalled by the computer the valve actuator rotates in one of two possible directions, conforming to the port arrangement of the sampling valve. That is, when the valve is in the clockwise position, it will be turned to its counterclockwise position, and vice versa. The injected sample is then eluted in a column of 50/80 Porapak S before passing into the thermal conductivity cell. The column was made of an 18" length of 1/4" type 316 stainless steel tubing. It was held at 150°C whereas the detector was held at 180°C. A filament current of 140ma was used. Hydrogen

* Carle Micro Gas Sampling Valve-No. 2014 fitted with two 1cc sample loops. The valve was held in an isothermal oven at 50°C.

FIGURE 20

SCHEMATIC OF THE GAS ANALYSIS EQUIPMENT



was used as the carrier and reference gas. The flow rate of each was 2cc/sec. The signals from the detector cell had been adjusted so that a butane peak lying between 2 and 10 millivolts was produced for samples of 0 to 20% butane. A D.C. amplifier was used to amplify these signals one thousandfold. These higher level signals, ranging from 2 to 10 volts, could then be interpreted by the computer.

A short program was written in order to use the Supernova to assist in calibrating the chromatograph. The program was used to activate the chromatograph valve, sample and analyse the detector output and record all data on paper tape. From the data it was possible to establish a linear relationship between the butane composition of the injected sample and the butane peak height.

The data also indicated that the butane peak would occur some 23 seconds after sample injection. Consequently, a 30 second analysis time was used for the butane conversion control loop. For further details, refer to Appendix 'C'.

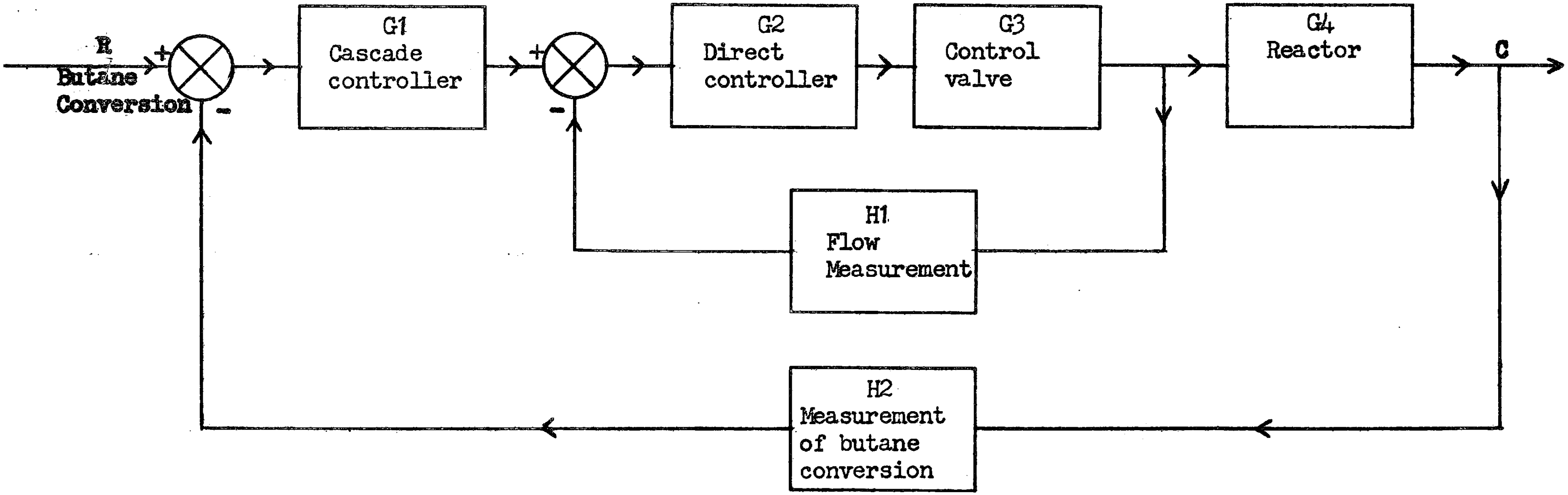
6- OVERALL CONTROL STRATEGY

For this study, a simple control scheme was implemented in order to determine whether the butane hydrogenolysis reaction could be controlled. Figure 21 illustrates the control loops that were built around the reactor. The computer was used to monitor both the hydrogen flowrate and the butane conversion. The hydrogen flowrate was determined every tenth of a second; however, the chromatographic analysis of the reactor effluent took thirty seconds. Control of these variables was achieved by the minicomputer using the PI algorithm outlined previously. Control action on the hydrogen flowrate was made once every second; control of the butane conversion was attempted every thirty seconds by adjusting the set point of the hydrogen flow controller.

The inner control loop (hydrogen flow control) was tuned using Ziegler-Nichols techniques. With the control loop closed and the integral and derivative action of the controller inactive, the proportional gain was slowly increased until the hydrogen gas flowrate began to oscillate about the set point. This procedure was used at several

FIGURE 21

CONTROL LOOPS OF THE BUTANE CONVERSION CONTROL



$$\frac{C}{R} = \frac{G1*G2*G3*G4}{1 + G2*G3*(H1 + G1*G4*H2)}$$

set points. From the series of "ultimate gains" and "ultimate periods" which resulted from these tests, preliminary values of K_c and K_i (K_c/τ_i) were 5.40 and 3.00 respectively. With these controller settings, the flow loop was very unstable. (This instability may be due to the non-linearity of the flow element.) For this reason, the values of K_c and K_i were reduced ending finally at 2.15 and 1.80 respectively. At these settings, the flow controller was able to handle any set point change within the range of the feedback measuring device, restoring steady state about the new set point within ten seconds.

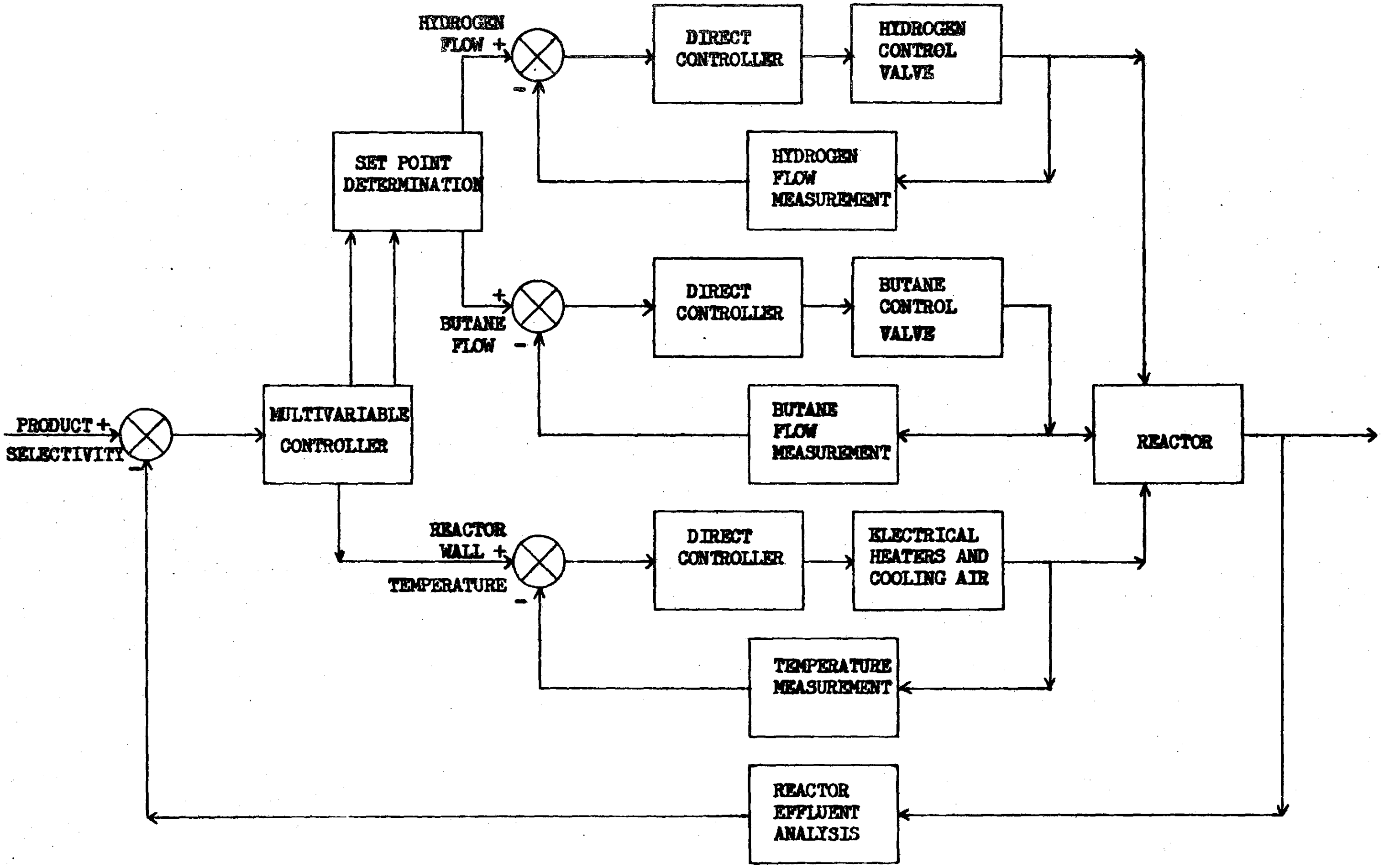
With the inner control loop satisfactorily tuned, several attempts to use process response techniques to arrive at controller settings for the outer loop (butane conversion control) were unsuccessfully attempted. Although step changes in the set point of the inner loop (hydrogen flow control) lead to significant changes in the reactor performance, it was not possible to obtain a reasonable trace of the actual response. This was because the time required to analyse a sample of the reactor effluent was nearly equal to the time constant of the reactor itself. Without any estimates of the controller settings, a number of tests were conducted to study the stability of the reactor. It was found that a small controller gain and a low reset rate were necessary to maintain process stability. The butane conversion controller K_c and K_i settings that were found to maintain the reactor system stable at all feasible set points were 0.220 and 0.025 respectively.

The temperature of the oil stream was maintained at a fixed level using on-off control. Electrical heaters were kept at their upper limit and compressed air was used for cooling whenever required.

We currently have only used a single variable cascade control scheme to achieve control of the conversion of the butane entering the reactor. However, multivariable control using other variables may be employed to arrive at tighter control. For instance, to achieve control on the selectivity of one of the reactor products, control of the reactor wall temperature, total feed rate and feed ratio (hydrogen to butane) would be feasible. The schematic of a possible control scheme is presented in Figure 22. These three control variables would provide an enormous range of operating conditions, hence a wide variety of control objectives would be feasible. This and other potential multivariable control studies will be the subject of future work with the reactor system.

FIGURE 22

POSSIBLE MULTIPLE LOOP CONTROL FOR BUTANE SELECTIVITY CONTROL



7- PROCESS COMMISSIONING AND EXPERIMENTAL RESULTS

Before the set of experiments proving that the reactor could be controlled over a wide range of operating conditions, a number of preliminary equipment checks, instrument calibrations and software verifications were required.

The coolant oil system was brought up to temperature a number of times before all the problems with it were corrected. For example, leaky pipe joints were tightened and failing gland and gaskets of the centrifugal pump were replaced. It was during these high temperature equipment checks that it was discovered that the heat exchanger body had to be floated using sections of flexible pipe.

In order to monitor the various thermocouples located in the coolant oil system, the differential pressure across the hydrogen flow capillary and the composition of the reactor effluent, a number of instruments required calibration.

Thermocouple transmitters were used to amplify and transmit the copper-constantan thermocouple signals.

An attempt to use a pair of stepping relays to multiplex the reactor's ten chromel-alumel thermocouples to a single transmitter failed due to the unreliability of the mechanisms. Development work is continuing on a solid state switching device which when connected to the computer could be used to multiplex a number of low level thermocouple signals into a single transmitter. In this way, only a few transmission lines would be required to carry the signals to the computer. Since it was not possible to transmit these ten thermocouple signals to the computer, they were simply recorded on a Honeywell Electronik 12 point chart recorder.

Since the hydrogen flow capillary and the gas chromatograph are to be monitored and controlled by the control computer when the reactor is in operation, it is mandatory that the calibration of these devices be done with the assistance of the computer. In doing the calibrations this way, a device's calibration curve will include instrumentation non-linearities, which of course would have to be accounted for otherwise. Also, the reliability of all instrumentation associated with a sensing element is verified by testing the instruments under conditions similar to those which will exist when control of the process is attempted. The details of the calibration procedures and the calibration curves for these two devices as well as the thermocouple transmitters are given in Appendix C. The calibration of these instruments must be done frequently and must be done off-line. For this reason, it would be extremely useful if one could devise a method of calibrating the instruments when on-line.

A number of problems had to be overcome before the signals from the various transmitters were of satisfactory quality for accurate interpretation. First, a problem characteristic of most grounded systems is the occurrence of ground loops. These ground loops arise when an instrument is connected to two different grounds. The potential difference or common mode voltage (see ref. 8 and 9 for detailed descriptions of this problem) between the two grounds invariably distorts the transmitter signals, unless the proper type of instruments are used to transmit or to monitor the signals. The second problem, characteristic of long transmission lines is the induction of noise. Frequently the noise will completely mask out the important signals if improper transmission lines are used. For most installations requiring some distance between transmitter and receiver, the use of twisted shielded pairs of conductors is essential.

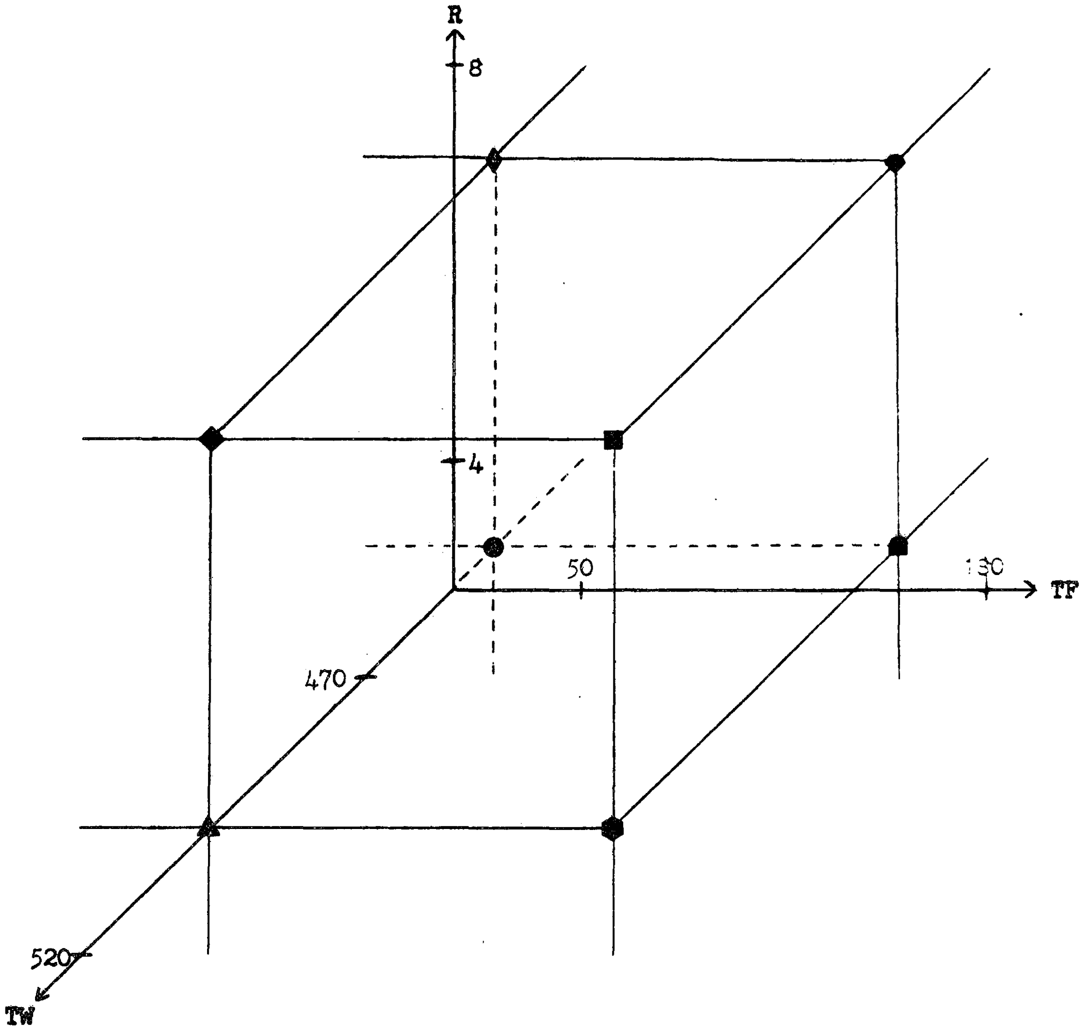
The nickel on silica gel catalyst used in this work was prepared and conditioned in the manner described in Appendix A. A coarse catalyst was used because the support screen near the base of the reactor was unable to retain fine particles. Though the nickel content of the catalyst was only 4.6% by weight, this concentration of active nickel was far too great. For a wide range of reactor wall temperatures, total feed flowrate and feed ratio, the butane was completely hydrogenolized. In an attempt to reduce the activity of the catalyst bed, the pure catalyst was diluted to 20% with inert carrier. At this lower nickel concentration, it was found that the reactor could be operated over a wide range of conditions without completely reacting the butane.

Once the reactor could be operated at various steady state conditions, a full factorial design was carried out so that an approximate steady state reactor model could be formulated. The design was done over three independent variables: reactor wall temperature (TW), feed ratio (R) and total feed flow (TF). Based on preliminary test work, the operating limits for the design were selected. These operating conditions have been represented in Figure 23 and Table 2. To the eight corner operating conditions, four replicate experiments were scheduled for the centre point. These replicates were required to detect possible changes in catalyst activity over the duration of the design.

To minimize the effect of changing catalyst activity during a day's operation, the design experiments were blocked into four separate pairs. On any one of the four days in which the experiments were carried out, a blocked pair of experiments and a replicate experiment were performed. The order in which the experiments were done was determined by random selection. Table 2 gives the actual sequence in which the experiments were conducted.

FIGURE 23

EXPERIMENT DESIGN



	TF	R	TW
■	180	8	520
●	50	4	470
⬟	180	8	470
▲	50	4	520
⬛	180	4	470
◈	50	8	520
⬢	180	4	520
♦	50	8	470

TF = Total Feed Flow, cc/sec

R = Feed Ratio, Hydrogen to Butane, unitless

TW = Reactor Wall Temperature, °F

TABLE 2

Schedule of Factorial Design Experiments

	Design Conditions				Operating Conditions			
	$\overline{TF}$	$\overline{TW}$	$\overline{R}$	Experiment No.	TF	TW	R	C
Day 1	0	0	0	1	115	495	6	78
	-1	-1	-1	2	50	470	4	99
	+1	+1	+1	3	180	520	8	87
Day 2	-1	+1	-1	4	50	520	4	98
	+1	-1	+1	5	180	470	8	18
	0	0	0	6	115	495	6	87
Day 3	-1	+1	+1	7	50	520	8	95
	+1	-1	-1	8	180	470	4	59
	0	0	0	9	115	495	6	90
Day 4	-1	-1	+1	10	50	470	8	76
	+1	+1	-1	11	180	520	4	92
	0	0	0	12	115	495	6	89

0	refers to the centre point conditions
-1	refers to the minimum setting of the variable
+1	refers to the maximum setting of the variable
TF	total feed flow, cc/sec at STP
TW	reactor wall temperature, ^{o}F
R	feed ratio, hydrogen to butane, unitless
C	% conversion of butane
$\overline{TW}$	normalized reactor wall temperature
$\overline{TF}$	normalized total feed flowrate
$\overline{R}$	normalized feed ratio, hydrogen to butane

The reactor model that resulted from the factorial design is given below:

$$\begin{aligned}\text{Percent conversion of butane} = {} & 82.4 - 14.0 * \overline{TF} + 15.0 * \overline{TW} \\ & - 9.00 * \overline{R} + 10.5 * \overline{TF} * \overline{TW} \\ & - 2.50 * \overline{TF} * \overline{R} + 7.00 * \overline{TW} * \overline{R} \\ & + 2.00 * \overline{TF} * \overline{TW} * \overline{R}\end{aligned}$$

where: $\overline{TW}$ = reactor wall temperature, $-1 \leq \overline{TW} \leq +1$

$\overline{TF}$ = total feed flowrate, $-1 \leq \overline{TF} \leq +1$

$\overline{R}$ = feed ratio, hydrogen to butane, unitless, $-1 \leq \overline{R} \leq +1$

This relationship is of course only correct when discussing the behaviour of the reactor used in this study. The actual performance of the reactor depends very much on the amount of catalyst forming the bed, and to a lesser extent on the physical properties of the reactor itself.

The above relationship indicates a number of clear tendencies relating the three independent variables to the reactor performance. These have been summarized in Table 3. These trends, though quite simple confirm the properties of the butane hydrogenolysis reaction as described by the reaction kinetics given in Appendix 'D'.

From this crude model of the reactor, it is clear that it exhibits severe non-linearities. The reactor wall

TABLE 3

Summary of Reactor Behaviour

Butane conversion decreases with an increase in TF
Butane conversion decreases with an increase in R
Butane conversion decreases with a decrease in TW

Hot spot temperature decreases with a decrease in TW
Hot spot temperature decreases with an increase in R

has the greatest effect on the reactor per- though the effects of the other two variables cannot be neglected. The magnitude of the coefficients of the second order terms indicates a strong coupling between the independent variables. In order to illustrate the extreme effects which exist within the reactor, Figures 24 and 25 have been included. The great variations in the behaviour of the system point out the suitability of this system for the study of optimal changeover policies, non-linear control algorithms and multivariable control theory. Figure 24 illustrates the extreme thermal gradients in the axial direction and suggests the presence of equally great radial gradients. Figure 25 illustrates the exact opposite situation: the flatter temperature profile demonstrates the more moderate properties of the system. In view of the kinetics of the butane hydrogenolysis reaction, (see Appendix D) one expects a high hot spot temperature (735°F) for the higher reactor wall temperature (520°F). It was necessary to use the highest flowrate possible (180 cc/sec at STP) and the greatest feed ratio (8) so that the rapid temperature rise in the axial direction could be illustrated (Figure 24). Lower feed ratios and feed rates would cause the hot spot

FIG. 24 REACTOR TEMPERATURE PROFILE

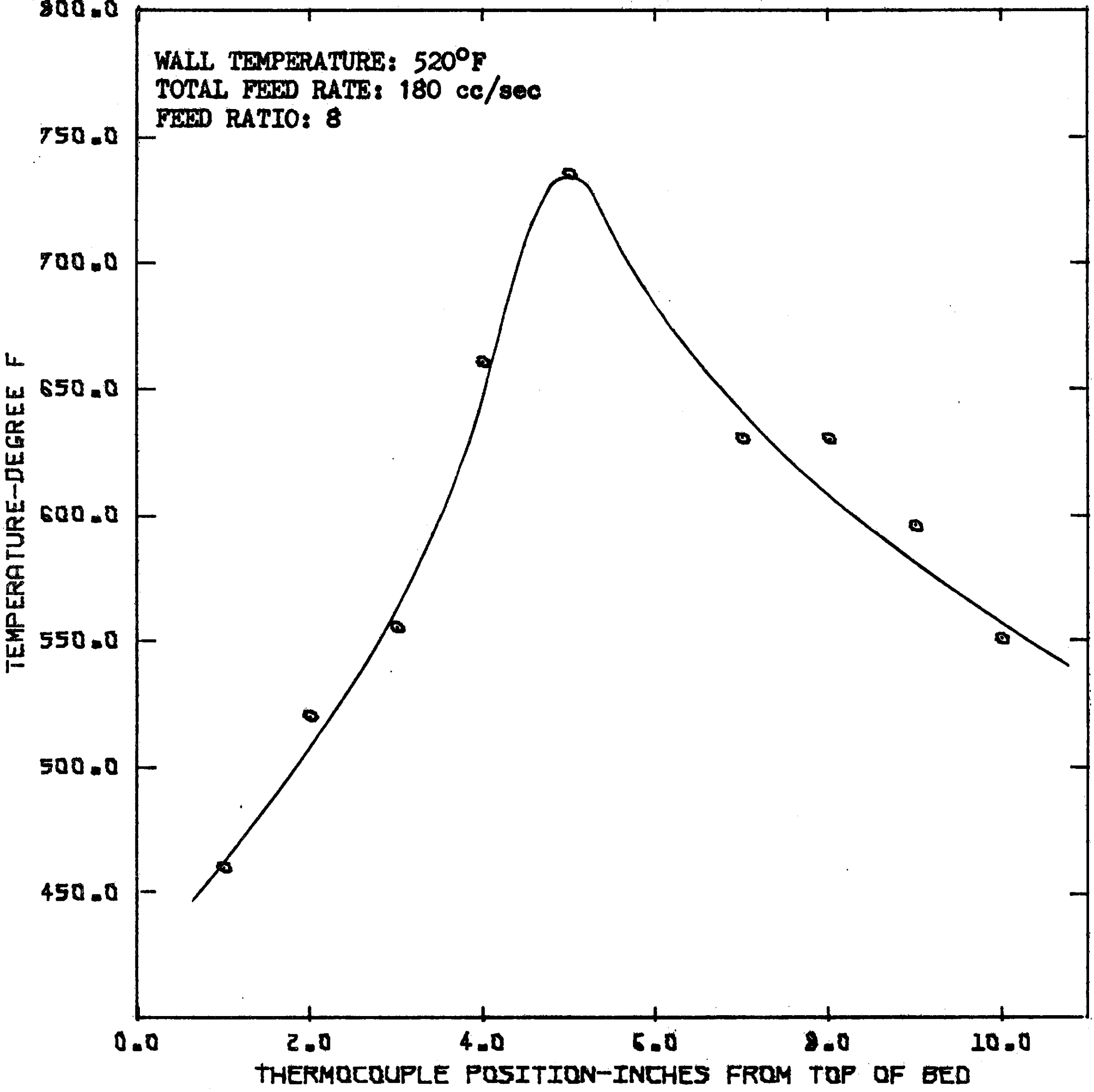
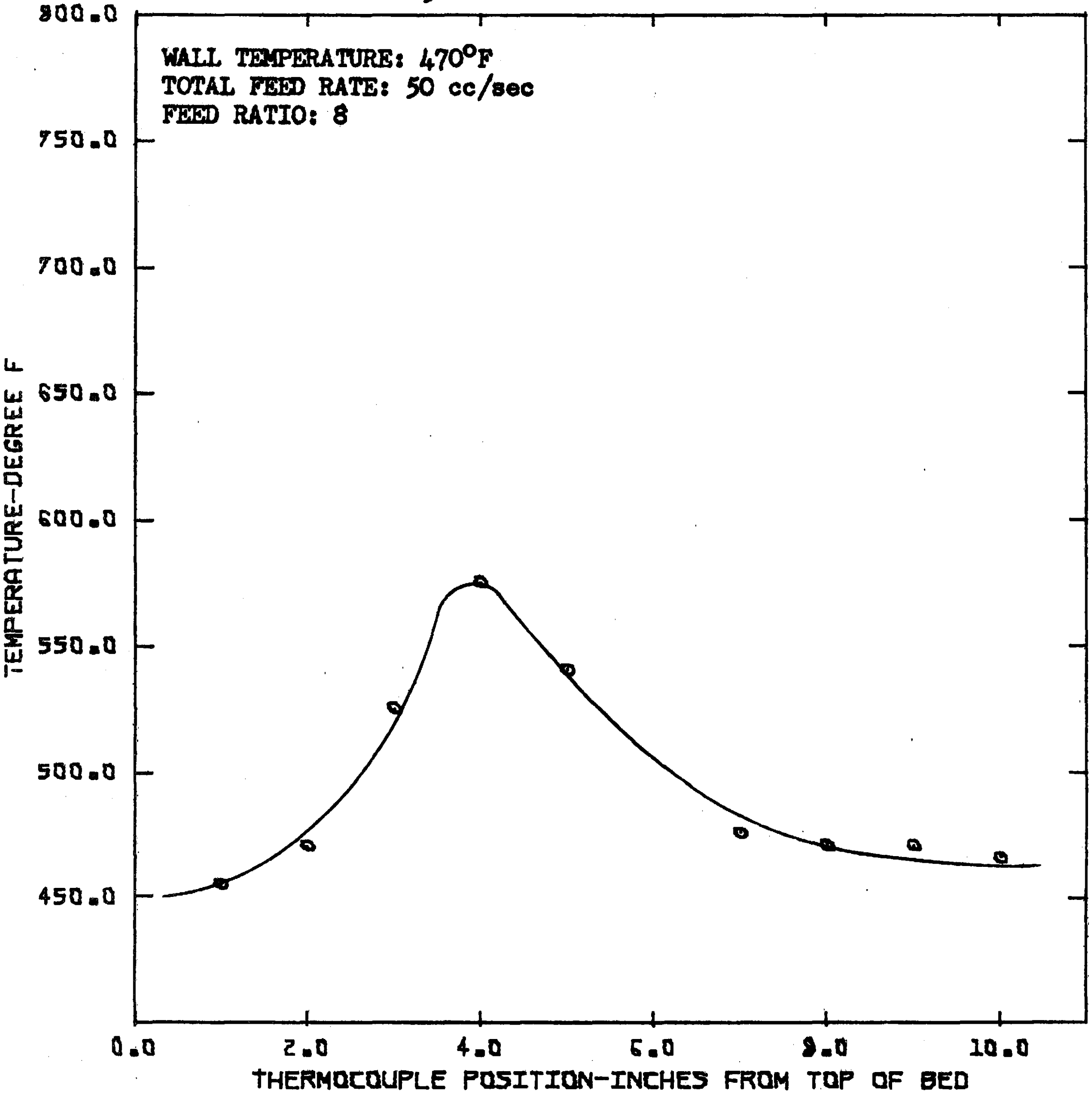

WALL TEMPERATURE: 520°F
TOTAL FEED RATE: 180 cc/sec
FEED RATIO: 8

FIG. 25 REACTOR TEMPERATURE PROFILE



to move switfly up the bed. In order to satisfactorily represent the bed temperature profile (Figure 25) with the lower wall temperature (470^{o}F), the lowest feed rate (50 cc/sec) was used since large feed rates tended to flatten out the profile so that little temperature rise occurred.

Closed loop step response experiments were carried out after the hydrogen flowrate and the butane conversion control loops were properly tuned. The controller settings have been provided in Chapter 6. The response curves for the closed loop system were obtained following step changes in the set point of the butane conversion cascade control loop. The results of the response tests are illustrated in figures 26, 27 and 28. As indicated by the figures, the cascade controller is able to cope with the large set point changes that were introduced as disturbances. In all cases, steady-state was restored within five minutes.

The sensitivity of the reactor increases as control at lower butane conversion is attempted. In each of the three figures, two step changes are represented. From an initial steady-state, a step up in the set point is made followed by a larger step down. Examination of the figures

FIG. 26 CONTROL ACTION AND RESPONSE VS TIME

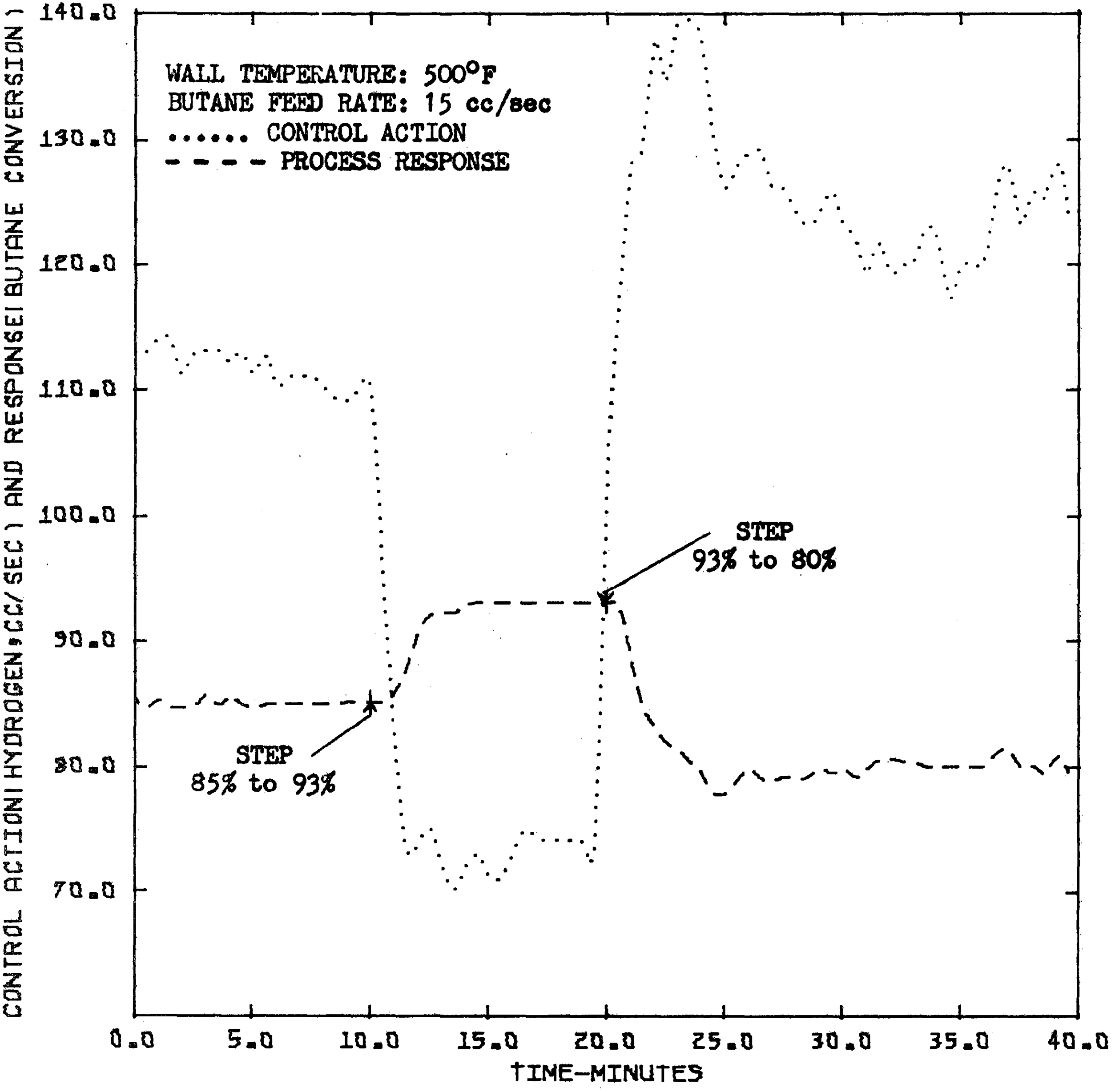


FIG. 27 CONTROL ACTION AND RESPONSE VS TIME

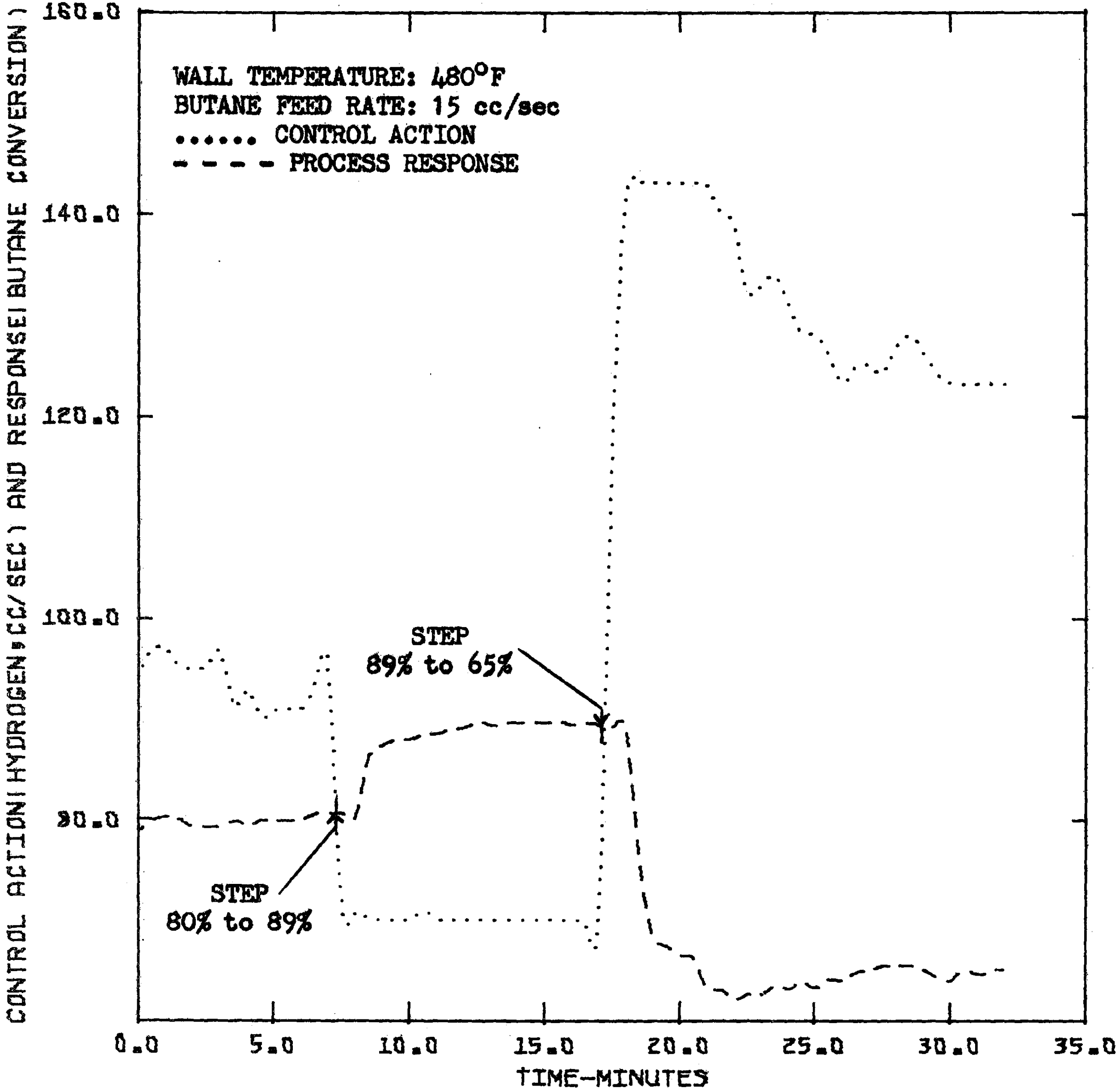
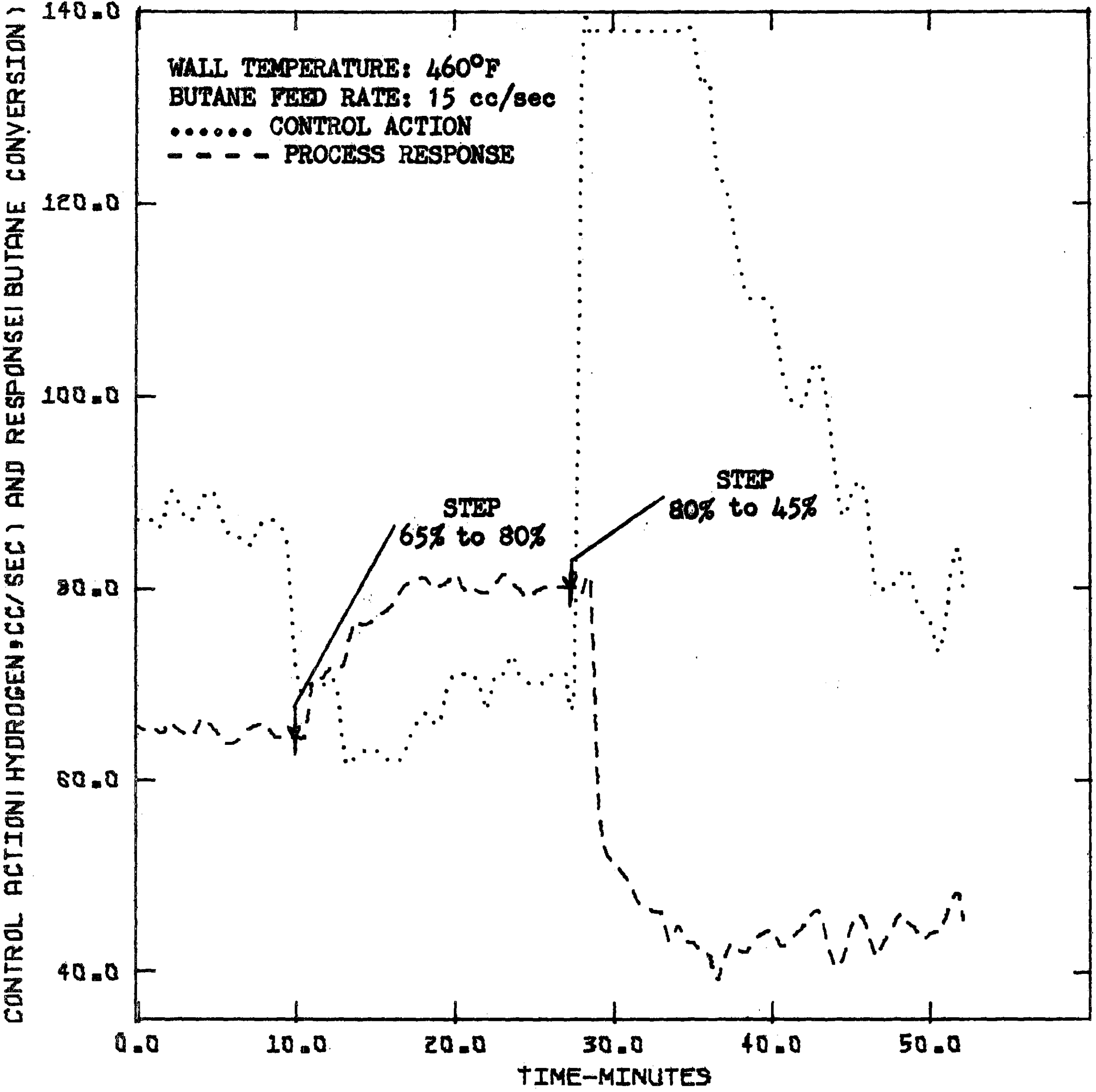


FIG. 28 CONTROL ACTION AND RESPONSE VS TIME



will indicate that greatest stability occurs at high wall temperatures. A mere drop of 20°F in the wall temperature markedly reduces the stability of the system. The most stable operating condition is represented in Figure 26. We notice that the control action is maintaining the process near to its set point. In Figure 27, we notice that there is a little more difficulty in holding the process at its set point. In Figure 28, the system sensitivity is clearly indicated. The increased oscillations that follow reductions in the reactor wall temperature may be attributed to fluctuations in the wall temperature itself. However, it is more plausible that variations in the hydrogen flowrate are more important at the lower wall temperatures. This is because the hydrogen flowrate rapidly affects the rate of reaction, particularly at low reaction temperatures. The oscillations in the conversion of butane manifest these slight fluctuations.

Although the reactor was quite sensitive at the reduced wall temperatures, the PI controller used in this study was able to maintain the reactor near its operating set point.

8- CONCLUSIONS AND RECOMMENDATIONS

The three prime objectives have been achieved:

(a) a process suitable for statistical modelling and direct digital control studies has been assembled,

(b) an interface between the apparatus and the computer has been installed,

(c) a simple real-time monitor and control package has been developed.

To these achievements, we must add:

(d) the development of a simple model to approximately describe the reactor behaviour at steady state,

(e) the actual computer control of the apparatus using the real-time software package.

It has been shown that the hydrogenolysis reaction may be controlled even though the reactor response to changes in operating conditions is more rapid than the analysis of the reactor effluent. The monitor and control package was found to be simple to use yet versatile enough to offer the operator several operating options.

The experiments on the reactor have proven its non-linear characteristics. Having established that the process can be controlled by simple DDC, it seems reasonable that studies leading to multi-variable control, optimal changeover policies and statistical modelling of the process are worthwhile. However, before it will be possible to investigate these research topics, it will be necessary to consider the following:

- the butane flow should be controlled
- on-off control of the oil temperature may be adequate, but the use of a regulatory controller should be considered
- an improved reactor design is necessary in order to obtain accurate temperature profiles of the reactor bed
- the analytical procedure must be extended to measure all hydrocarbon species, hence determine selectivities as well as conversion. However, total analysis time must be short.

- solenoid valves should be installed throughout the apparatus so that computer controlled startup and shutdown is possible.
- the computer hardware and software should be developed to facilitate on-line calibration of transmitters.
- improved communication software should be developed to increase network efficiency and versatility.
- remote multiplexing units should be acquired so that more temperatures may be monitored by the computer.
- the equipment interface should be altered in such a way that line noise and ground loops will either be eliminated or at least their effects minimized.

BIBLIOGRAPHY

1- Orlickas, A., Hoffman, T.W., Shaw, I.D. and Reilly, P.M., Canadian Journal of Chemical Engineering, Vol. 50, October, 1972, p. 628-36

2- Shaw, I.D., Hoffman, T.W., Orlickas, A., Reilly, P.M., Canadian Journal of Chemical Engineering, Vol. 50, October, 1972, p. 637-43

3- Crane Co., Technical Paper No. 410-C, p. 3 - 14

4- Williams, T.J. and Ryan, F.M., Progress in Direct Digital Control, Instrument Society of America, Pittsburgh, 1969

5- Macmillan, R.H., Higgins, T.J. and Naslin, P., Progress in Control Engineering, Vol. 3, Heywood Books, London, 1966

6- Murrill, P.W., Automatic Control of Processes, International Textbook Co., Scranton, Penn., 1967

7- Smith, C.L., Digital Computer Process Control, Intext Educational Publishers, Scranton, Penn., 1972

8- Williams, T.J., A Manual for Digital Computer Applications to Process Control, Purdue University Press, Lafayette, Indiana, 1966

9- Savas, E.S., Computer Control of Industrial Processes, McGraw Hill, New York, 1965 (Chapter 10)

10- Data General Corporation, Real Time Operating System Reference Manual, 1971

11- Data General Corporation, How To Use the Nova Computers, 1971

12- Perry's Chemical Engineers' Handbook, Perry, J.H., Chilton, C.H., Kirkpatrick, S.D., McGraw Hill, Table 5-2, New York, 4th Ed., 1963

13- Jarvis, R.C.F., Wright, J.D., Canadian Journal of Chemical Engineering, Vol. 50, #4, August 1972, P. 520 - 528

14- Newell, R.B., Fisher, D.G., Automatica, Vol. 8, #3, May 1972, p. 247 - 262

15- Newell, R.B., Fisher, D.G. and Sebarg, D.E., American Institute of Chemical Engineers' Journal Vol. 18, #5, September 1972, p. 976 - 984

16- Wood, R.K., Pacey, W.C., Canadian Journal of Chemical Engineering, Vol. 50, #3, June 1972, p. 376 - 384

17- Lees, M.J., Australian Computer Journal, Vol. 3, #4, p. 146 - 149, November 1971

18- Routley, J.H., Proceedings, IEEE, Vol. 116, #9, p. 1585 - 1588, 1969

19- Chemical Engineering, Vol. 76, #12, June 1969

20- Hileman, J.R., Chemical Engineering, Vol. 79, #12, May 1972, p. 61 - 66

21- Proceedings, IEEE, Vol. 58, #1, January 1970

22- Bacher, S., Kaufman, A., Industrial and Engineering Chemistry, Vol. 62, #1, January 1970, p. 53 - 61

23- Brown, G.C., Control and Instrumentation, Vol. 3, #7, August 1971, p. 39 - 41

24- Shah, M.J., Stillman, R.E., Industrial and Engineering Chemistry, Vol. 62, #12, December 1970, p. 59 - 75

25- Choquette, P., Norton, A.R.M. and Watson, C.A.G., Proceedings, IEEE Vol. 58, #1, January 1970, p. 10 - 16

26- Tremblay, J.P., Monitor and Control Manual, McMaster University, 1973

27- Shinskey,F.G., <u>Process-Control Systems</u>, McGraw-Hill, New York, 1967

APPENDIX A

CATALYST PREPARATION

A-1 General

The catalyst used in this study was similar to the one on which the kinetics of the butane hydrogenolysis reaction were determined. Basically, they were nickel on silica gel. However, the differences between them lie with the nature of the carriers themselves. The silica gel used for the kinetic studies ranged in size from 70 microns up to 297 microns; one gram of this material could absorb 0.81 cc of water. With this type of porosity, it was then possible to prepare a 10% nickel on silica gel catalyst. On the other hand, silica gel ranging in size from 0.71 mm up to 1.4 mm was obtained for the control studies. Unfortunately, one gram of this material could only absorb 0.33 cc of water. Due to this considerably lower porosity it was only possible to prepare a 4.6% by weight nickel on silica gel catalyst.

Clearly, the catalysts are significantly different.

They are different in size and in nickel content, and it is possible that these changes will alter the accuracy of the existing reaction model. But off hand, it is difficult to predict the sensitivity of the model to these parameters.

The silica gel used in the control studies was manufactured by Davison Chemicals and supplied through the Fisher Scientific Company. This material was a refrigeration grade (GRADE 408, manufacturer's code PA400) and was reported to have a particle distribution between 12 and 28 mesh. The material was screened to be within 0.71 mm and 1.4 mm using 25 mesh and 14 mesh screens.

The nickel coating on the silica gel was obtained by impregnating the dried carrier with an aqueous solution of nickel nitrate. (Fisher certified N-62 nickel nitrate crystals were purchased from the Fisher Scientific Company.) The carrier was then dried and then fired in a muffle furnace. The final reduction of the nickel was achieved within the tubular reactor using hydrogen gas.

A-2 Procedure

Since it was apparent that it would be difficult to prepare a 10% nickel on silica gel catalyst, it was decided to get the greatest nickel content possible. To manage this, it would be necessary to impregnate the silica gel with a saturated solution of nickel nitrate. Of course, all this was to be done at room temperature if no special apparatus was to be acquired.

Approximately 500 ml of a saturated solution of nickel nitrate was prepared. This solution was first filtered and a 50 ml sample taken to determine the true solute concentration. The solution was found to be 41.9% $Ni(NO_3)_2 \cdot 6H_2O$ by weight or to contain 65 gm of the solute per 100 cc of solution. Three ten gram samples of the dried silica were "titrated" with this solution: it was found that one gram of the dry carrier could absorb 0.37 cc of the solution. From this, it was estimated that 250 cc of the solution would be absorbed by 676 grams of the dried silica gel. Indeed, this was found to be exact. The impregnated carrier was then dried at 200°F for two hours, at 300°F for one hour, then fired at 700°F for twelve hours. A Lucifer electric muffle funace was used to fire the carrier. Since the amount of nitrogen oxides to be driven off was quite small, it was considered safe to vent the furnace gases directly to the atmosphere.

The catalyst prepared by the above procedure was near enough to 4.6% nickel on silica gel.

A-3 Note on Catalyst Conditioning

The catalyst prepared according to the procedure detailed above will not initiate the butane hydrogenolysis reaction unless it is conditioned for use. For this work, there was little need to maintain a close control on the conditioning temperature. This is because the activated catalyst was to be conditioned at temperatures far beyond the capacity of the coolant system. Tests have shown that the hot spot temperature within the reactor may reach 1000°F for a particular set of feed rates, feed ratios and jacket temperatures. Since the initial conditioning was carried out at 570°F only, it was clear that tight control on the quality of conditioning was not extremely important. Whenever the reactor was operated, the catalyst activity was somewhat altered.

In the light of this information, the initial conditioning of the catalyst was carried out in the following way. For four hours the catalyst bed within the reactor was maintained at 570°F. At the same time hydrogen gas was circulated through the bed at the rate of 15cc/sec. Following this period of treatment, it was found that the catalyst was active enough to initiate the reaction.

APPENDIX B

BASIC TECHNICAL DATA

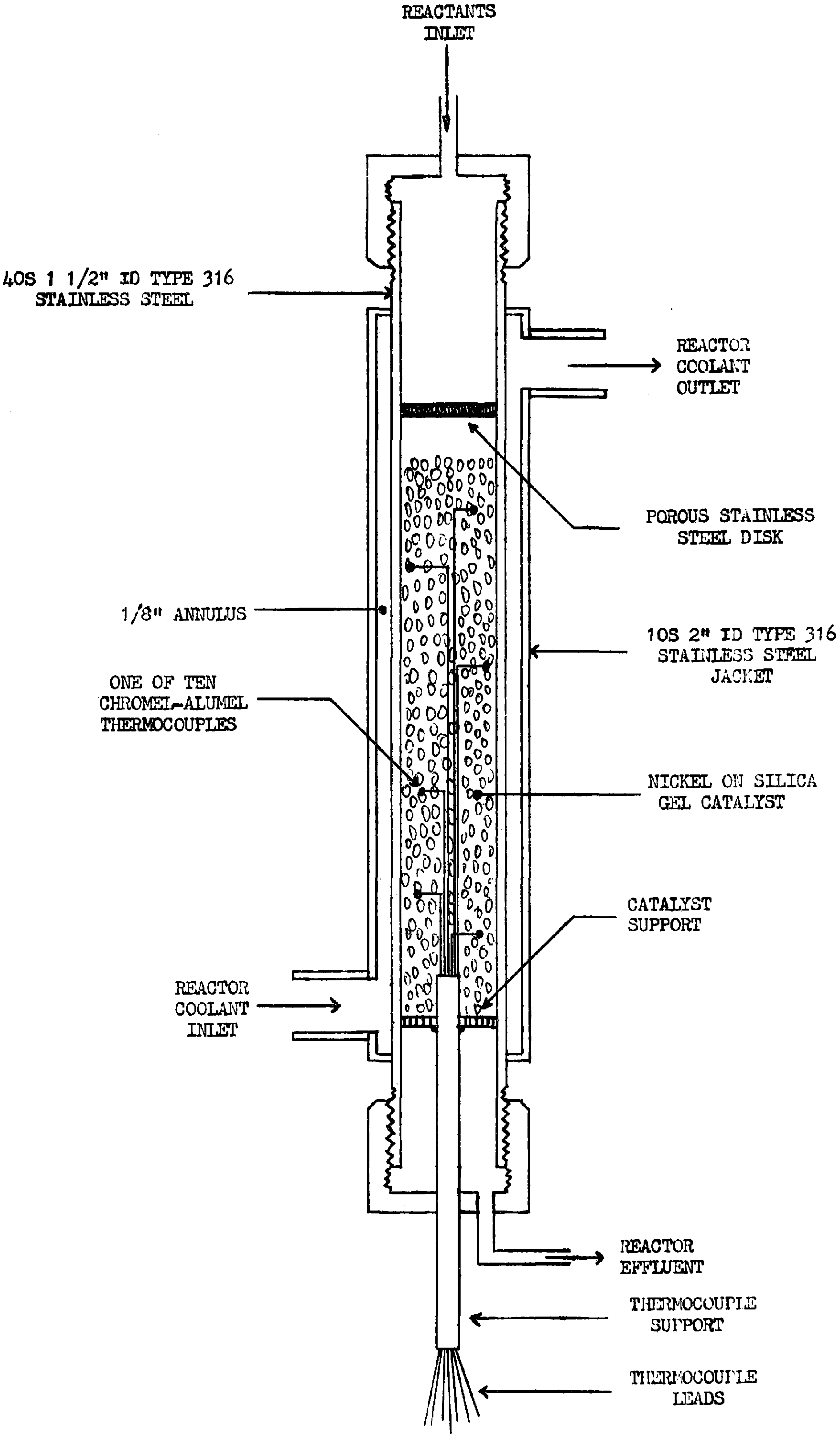
B-1 General

(a) Thermocouples: All thermocouple material was purchased from the Thermo Electric Company. Both copper-constantan and chromel-alumel thermocouples were used. The latter type was used exclusively within the reactor. All thermocouples contacting the process equipment were prepared from ceramo wire sheathed in stainless steel. In all, 10 chromel-alumel and 7 copper-constantan thermocouples were installed in strategic locations.

(b) Reactor: A schematic of the reactor that was used in this study is given in figure B-1. The reactor was formed from two concentric type 316 stainless steel pipes. The inner

FIGURE B-1

SCHEMATIC OF REACTOR



was Schedule 40 1½" pipe and the outer Schedule 10 2" pipe. These sizes then provided a 1/8" annulus. Pipe caps were used to seal the inner pipe ends. All gas connections were made through these caps. At the top, the reactant mixture was distributed over the catalyst bed by a porous stainless steel disk. (pore size: 5 microns, Type H, Pall Trinity Micro Corp.) The catalyst bed rested on a screen supported by a perforated stainless steel disk. This disk was in turn supported by 3/8" OD stainless steel tube that also served to guide the thermocouple leads into the reactor. Ten ceramo type chromel-alumel thermocouples were located at various points throughout the bed. The actual location of these thermocouples is given in Table 1. The flow of reactants is countercurrent to the flow of oil in the reactor jacket.

B-2 Coolant Flow System

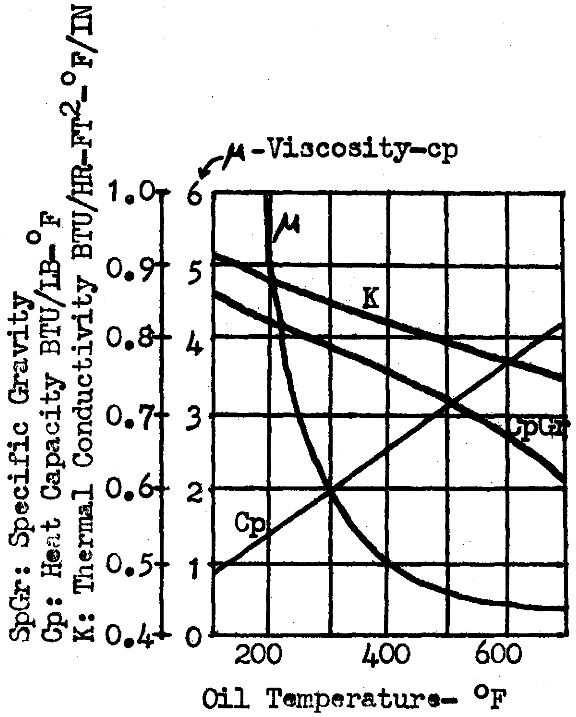
(a) Coolant: Sun No. 21 heat transfer oil was purchased from the Sun Oil Company. The oil is recommended for service within closed circulating systems with operating temperatures less than 600°F. A summary of the oil's thermal properties is given in the figure B-2.

(b) Pump: The pump used to circulate the coolant was acquired from SIHI Pumps Company. It is a centrifugal pump (Model ZLLE 4017/155Q) flexibly coupled to a 1HP, 1750 RPM induction motor. The gaskets and the gland (which is water cooled) were made of special high temperature materials.

(c) Heat Exchanger: A model 200-8 single pass shell and tube heat exchanger was obtained from the American Standard Co. The 28 8" long 1/4" OD tubes provided the unit with an effective heat transfer area of 1.2 ft^2.

FIGURE B-2

PHYSICAL PROPERTIES OF SUN OIL 21



(d) Orifice: A 5/8" orifice plate was used to estimate the oil flow rate in the coolant system. The calculations to be presented are based on information taken from references 3 and 4. The distance upstream from the orifice plate to the nearest fitting was measured to be twelve pipe diameters. According to reference 3, the minimum distance upstream to the nearest fitting which is a contraction is about ten pipe diameters. Based on this rule, it was felt that a fairly accurate estimate of the oil flow rate in the system may be calculated knowing all relevant quantities defined in reference 4. The following calculations are for a 5/8" orifice in a Schedule 40 1" black pipe. Heat transfer oil is the fluid being circulated.

ESTIMATION OF THE OIL FLOWRATE IN THE COOLANT FLOW SYSTEM

$d_o =$ 0.625 inches

$d_i =$ 1.049 inches

$d_o/d_i = 0.6$

$\Delta p =$ 70 inches water(2.5 psi)

Assume turbulent flow: $C \sim 0.65$

from monograph, find $q = 0.031$ ft.^{3}/sec.

$$\text{Fluid velocity} = \frac{\text{fluid flow rate}}{\text{X sectional area}} = \frac{0.031}{.006} = 5.2\ \frac{\text{ft.}}{\text{sec.}}$$

Fluid Properties at 500°F

$\rho = 44.9$ lbm/ft.^{3}

$\mu = 0.6$ cp

$$R_e = \frac{Dv\rho}{\mu} = \frac{\{\frac{1.049}{12}\}\ (5.2)\ (44.9)}{(.6)\ (6.72 \times 10^{-4})} = 50620$$

Verify C and find it to be correct.

Hence, the oil circulation rate is about 1.86 ft.^{3}/min. which implies that the minimum fluid velocity anywhere in the system is 5 ft./sec.

SYMBOL DEFINITION

d_o = orifice diameter

d_i = pipe ID

Δp = pressure drop across orifice

ρ = fluid density

μ = fluid viscosity

R_e = Reynolds Number

C = orifice coefficient

(e) Pressure Gauges: Two pressure gauges were bought from the U.S. Gauge Co. One in the range 0 to 60 psig was installed on the pump outlet and the other 0 to 160 psig was used to measure the pressure of cooling air.

One model 120 differential pressure gauge was purchased from the Mid West Co. It was connected across the orifice flowmeter. It ranged from 0 to 150 inches of water.

(f) Flexible Pipe: Two one foot sections of 1" ID pipe were purchased from Flexonic Co. One was used in the oil stream downstream of the heat exchanger. The other was connected to the hot air outlet port of the heat exchanger. These flexible sections prevented the transmission of the stresses to the heat exchanger body.

(g) Electrical Heaters: Five electrical heaters were fabricated from resistance strip produced by the Kanthal Corporation. Lengths of 5/8" x 0.010" strips were imbedded in a layer of Hiloset refractory cement mounted on a section of pipe. The refractory cement was obtained from the Kaiser Refractories Co. Three heaters rated at 1170 watts each were mounted side by side on a length of 1½" Schedule 40 black pipe. A heater rated at 1200 watts was wrapped around the reactor jacket. An 1100 watt heater was mounted near the pump inlet on a 1" Schedule 40 black pipe. Overall, 5.8 kilowatts of heating power was built into the coolant flow system.

B-3 Reactant Flow System

(a) Reactants: The hydrogen gas used in this work was purchased from Canadian Liquid Air. The pure n-butane had been acquired from the Matheson Gas Co.

(b) Tube & Fittings: Throughout, 1/4" OD copper tube was used except downstream of the reactor where type 316 stainless steel tubing was used. All tube fittings, check valves and gas filters were Swagelok type purchased from the Niagara Valve and Fitting Co.

(c) Pressure Gauges: Three manometers were used to measure the pressure of the gases at different points. The back pressure maintained by the back pressure regulator was measured with a mercury manometer. The other manometers filled with Meriam oil were used to determine the pressure drop across the capillary flowmeters. Finally, a model 120 differential pressure gauge manufactured by the Mid West Co. was used to indicate the Pressure drop across the reactor bed.

(d) Valves: Both toggle and regulating valves have been used. These were purchased from the Niagara Valve and Fitting Co. Basically, the toggle valves were used in locations that required only on-off control. The regulating type were either used to throttle flows or simply produce a variable flow restriction.

(e) Control Valve: A control valve (linear characteristics, $C_V = 0.006$) was used to throttle the flow of hydrogen to the reactor. A Fisher Governor type 546 E/P transducer was used to activate the valve.

(f) Gas Chromatograph: A model 90P-3 Varian chromatograph was used to analyse the reactor effluent for its butane composition.

(g) Sampling Valve and Actuator: A model 2014 Carle sampling valve and a model 4200 Carle valve actuator were purchased for use with the chromatograph. The valve could be moved to a clockwise or anticlockwise position thereby injecting two samples in one full cycle. The actuator was electrically driven and was used to move the sampling valve from one position to another.

(h) Back Pressure Regulator: A Fairchild-Hiller model 10-BP back pressure regulator was used to maintain constant the downstream pressure of the capillary flowmeters. The back pressure was maintained at 450 mm of mercury above atmospheric pressure.

APPENDIX C

CALIBRATION OF INSTRUMENTS

C-1 Chromatograph: Ideally, the butane hydrogenolysis reaction is equimolar and only butane, propane, ethane, methane and hydrogen remain at equilibrium. Since this study was only interested in the butane content of the reactor effluent, on-line analysis by gas chromatography was greatly simplified. Elution of a butane-propane-ethane-methane-hydrogen mixture in a column of Porapak S would yield four different peaks if reference was made to hydrogen. The butane peak would be the last to diffuse through the column and the height of this peak could be directly related to the butane content of the gas stream.

In view of this fact, the gas chromatograph was calibrated in the following manner. Employing the same configuration of the analytical equipment as described in Chapter 5, gas mixtures of known composition were introduced into the dynamic splitter and the responses of the detector cell were related to the butane content of the mixture. These mixtures were prepared in a large bottle which was first purged, then evacuated and filled with various amounts of hydrogen, butane and propane. The mixtures' composition was established on the partial pressure of each component. Since the minicomputer was to be used to perform on-line analysis of the reactor effluent, it was decided that calibration of the chromatograph would be done with the computer. A special real-time program was written to schedule sample injection and chromatogram interpretation. A sample chromatogram of a calibration mixture is given in figure C-1.

Eight different mixtures were prepared and used to calibrate the chromatograph. Figure C-2 summarizes the results obtained from the calibration work.

FIG. C-1 CHROMATOGRAM FOR SAMPLE WITH 14 PERCENT BUTANE

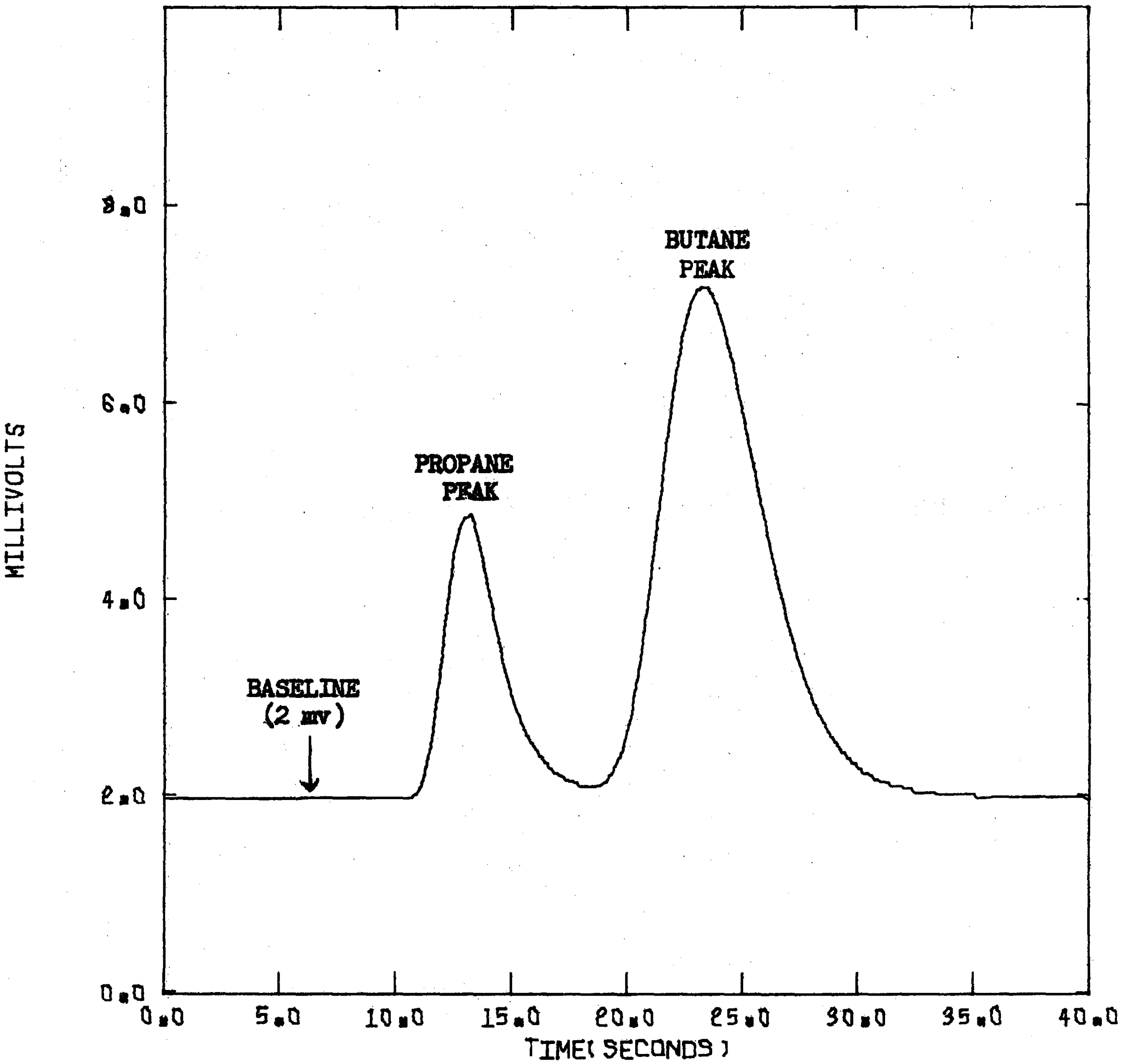
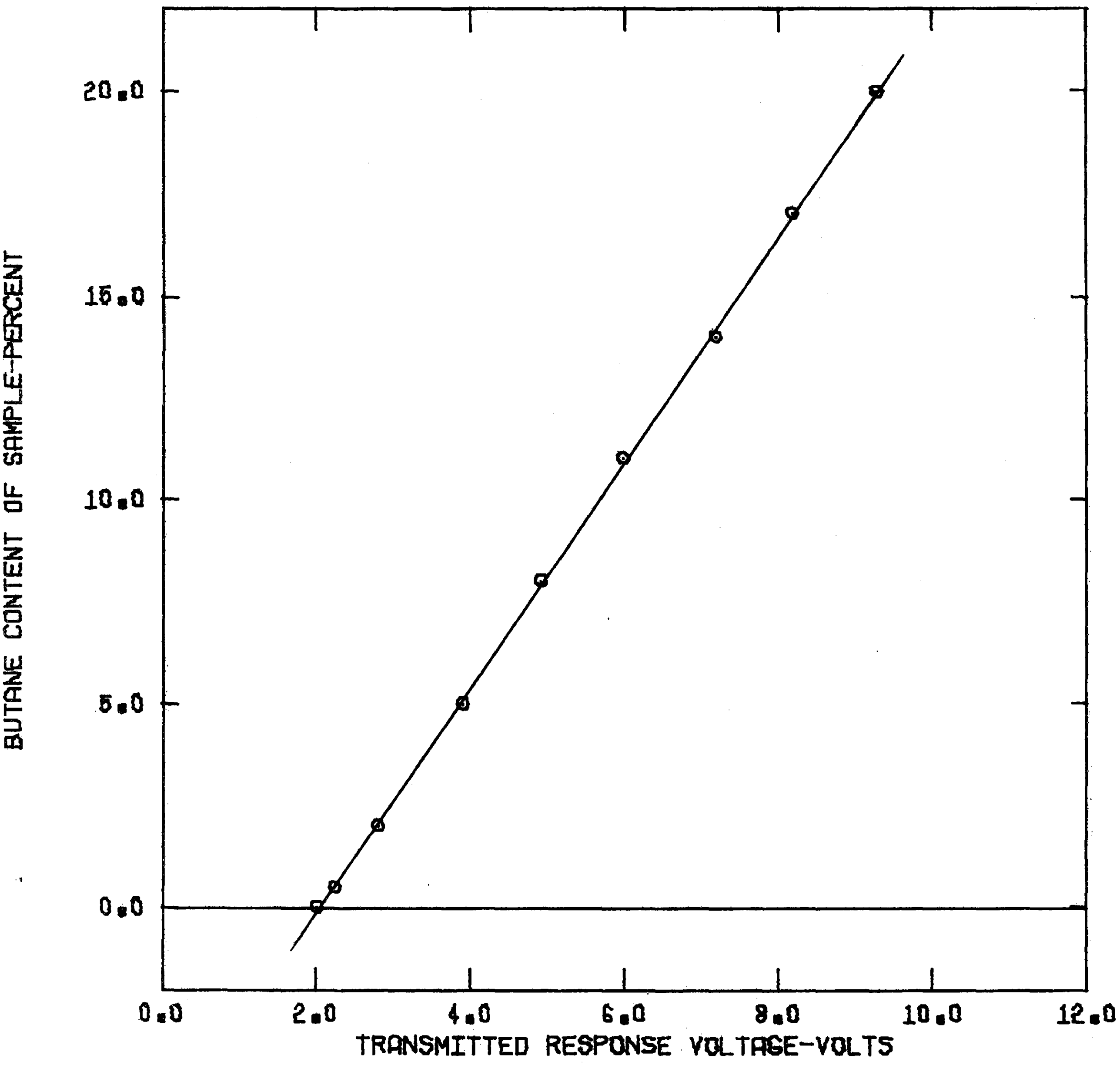


FIG. C-2 GAS CHROMATOGRAPH CALIBRATION



The chromatograph operating conditions that yielded the calibration data were the following:

- column length: 18" of ¼" OD type 316 stainless steel tubing
- column packing: 50/80 Porapak S
- oven temperatures: 150°C
- detector temperature: 180°C
- carrier flow: 2cc/sec hydrogen
- filament current: 140ma
- attenuation: 2
- sample valve temperature: 50°C
- zero level signal: 2 mv

C-2 Thermocouple Transmitters: Five Acromag copper-constantan transmitters were used to transmit temperature data to the computer. Based on a millivolt input and suitable settings of the zero and span of the device, the input signal is converted to a milliamp current ranging from 10 to 50 ma. If the voltage drop across a 200 ohm resistance is measured, then a 2 to 10 volt signal may be obtained. Unfortunately, the thermocouple transmitters that were used for this work were not the type to properly handle grounded thermocouple signals. Because of this, the upper range of the transmitter's output was always saturated. Following a great deal of investigation, it was found that the transmitters could only properly generate voltages between 2 and 9 volts and that this signal had to be measured differentially at the computer end.

In any event, the transmitters were calibrated to measure temperatures from 32^{o}F to 532^{o}F (i.e., 2 to 9 volts). Ice water was used to set the zero reference and an isothermal bath of Hitec salt at 532°F to set the span. For the purposes of this study, a linear relationship was assumed between the temperature and the measured output voltage.

C-3 Hydrogen Capillary, Differential Pressure Transmitter, Control Valve

An industrial type Foxboro Model E13 DM differential pressure transmitter was used to monitor the flow of hydrogen gas through a capillary flowmeter. The instrument outputs a linear signal from 10 to 50 ma for differential pressures of 0 to 100 inches of water. This current will produce a 2 to 10 volt drop across a 200 ohm resistance.

A Research (normally closed) Control Valve was used to maintain a certain flow of hydrogen gas. In response to a voltage lying between 1 and 9 volts from the computer, a Fisher Governor Type 546 E/P transducer regulated the pneumatic signal (3 to 15 psi) to the control valve.

Using a computer program written expressly for this purpose, a signal was transmitted to the transducer which then activated the control valve. A certain gas flow resulted from this valve position. The pressure drop across the flow capillary was then indicated by the differential pressure transmitter. The actual gas flowrate was determined using a flowmeter.

From this it was possible to relate a valve position to a flow rate and a flow rate to a pressure drop across the flow capillary. Second order curve fits of the data presented in figures C-3 and C-4 were found to be accurate enough for this study.

FIG. C- 3 HYGROGEN CAPILLARY CALIBRATION

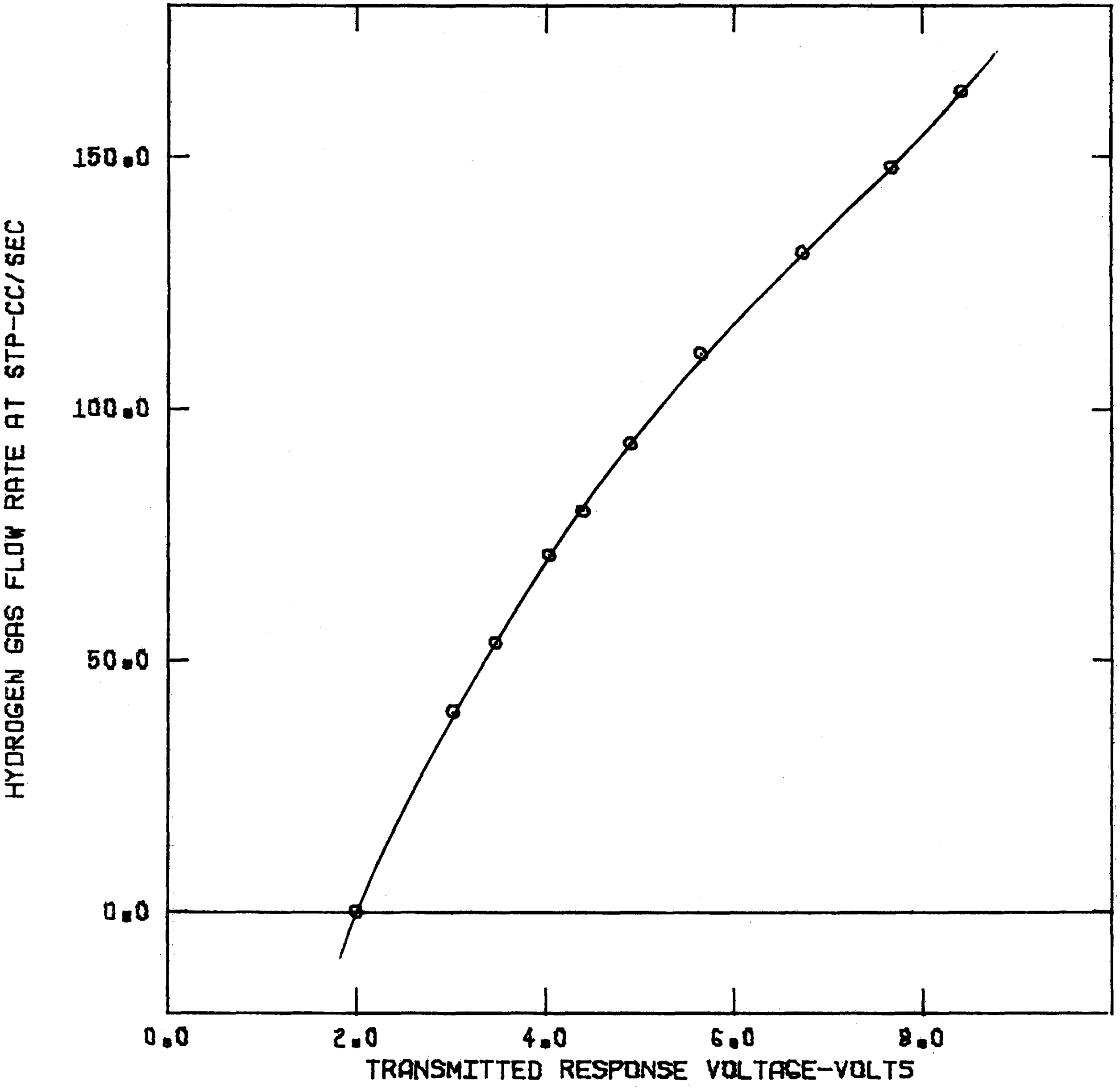
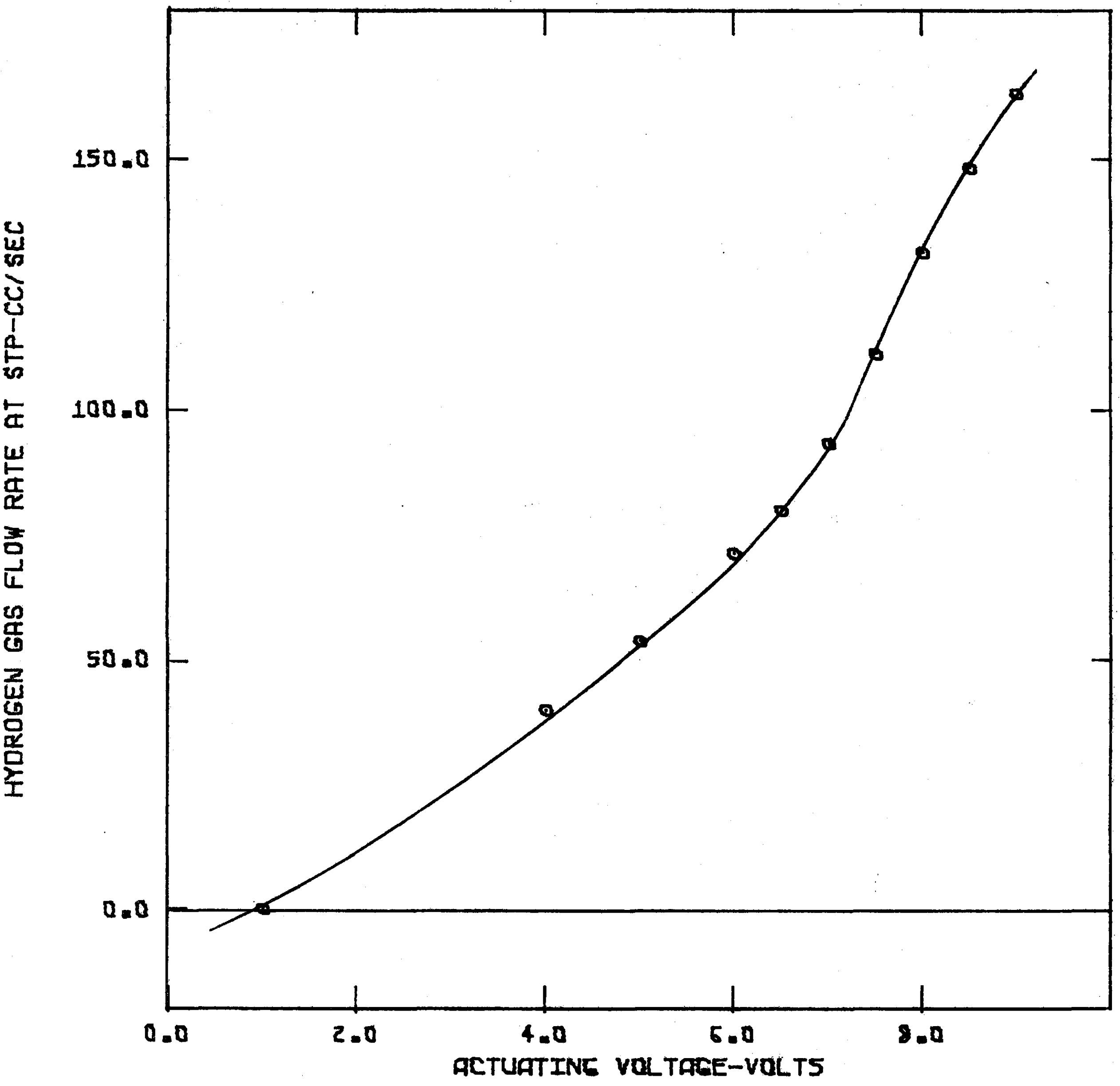
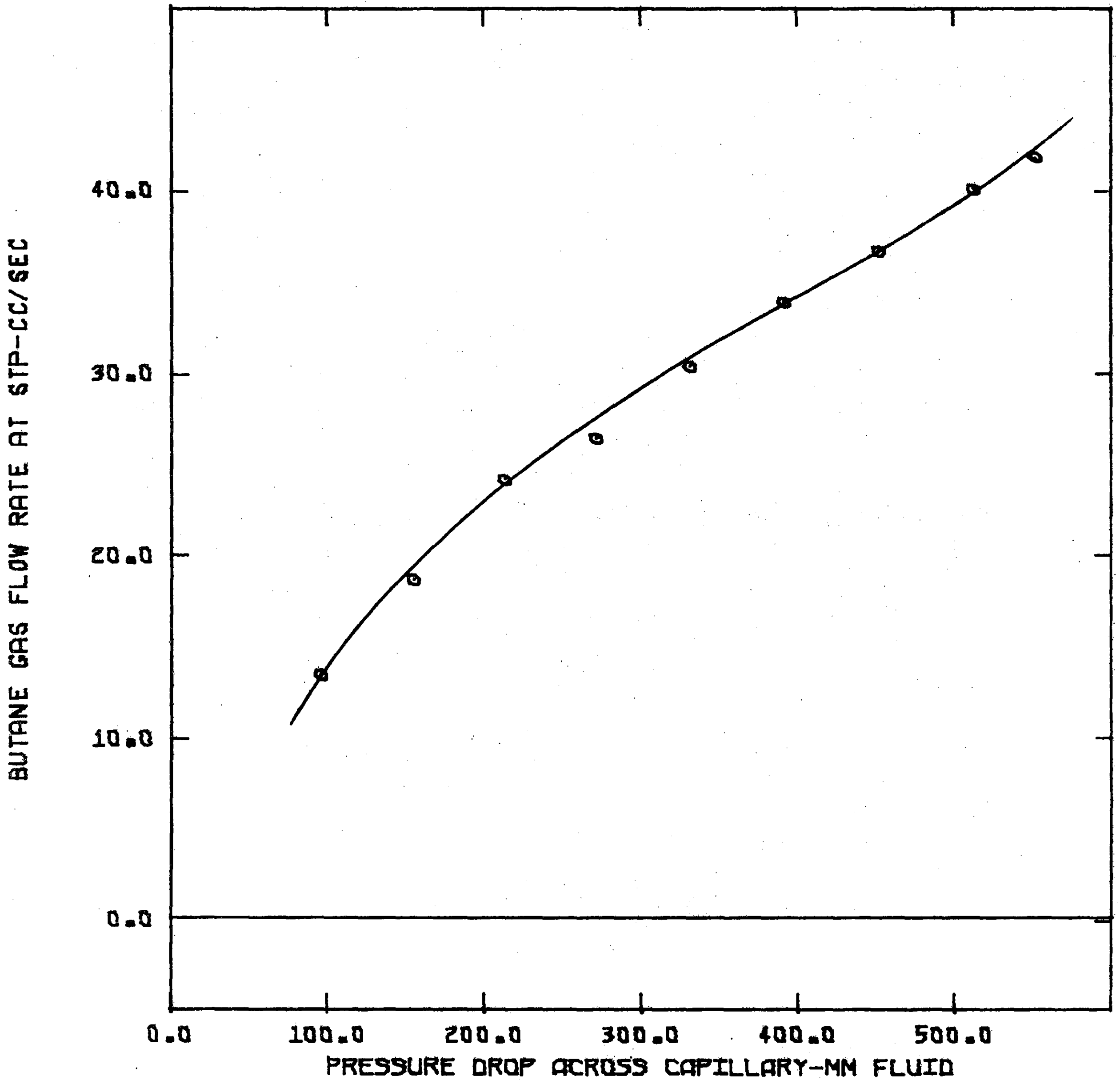


FIG. C-4 HYDROGEN CONTROL VALVE CALIBRATION



C-4 <u>Butane Capillary</u>: The flow of butane gas was not under control or supervision by the computer. Calibration was achieved manually. The flow of butane through a flow capillary was related to the pressure drop across it. The relationship is presented graphically in figure C-5.

FIG. C-5 BUTANE FLOW CAPILLARY CALIBRATION



APPENDIX D

BUTANE HYDROGENOLYSIS KINETICS

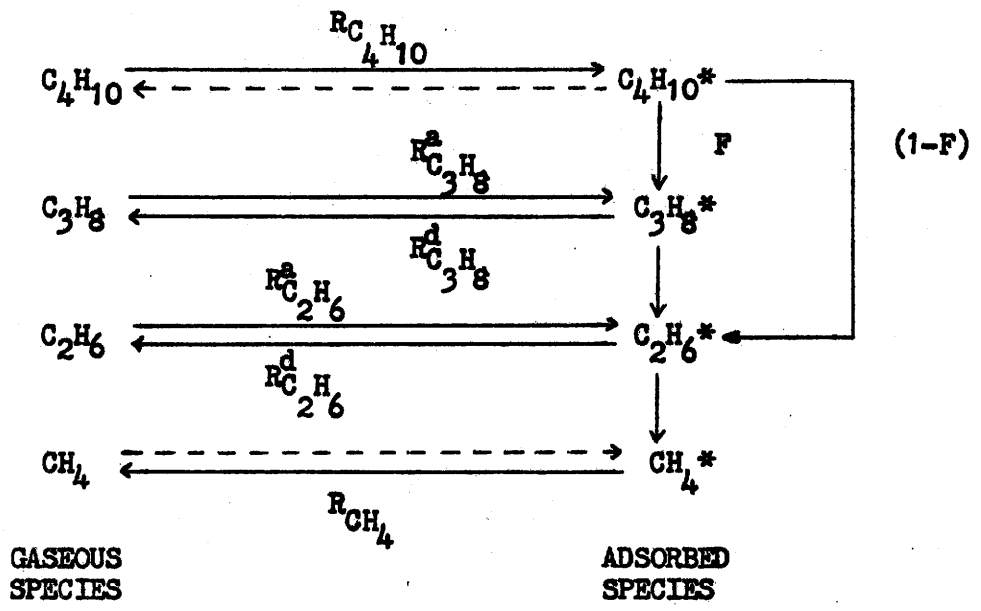
D-1 General

The kinetics of the n-butane hydrogenolysis reaction on a nickel on silica catalyst have been modelled by Orlikas (1) and Shaw (2) . The fundamental work done by Orlikas was improved by Shaw. They have postulated a mechanism for the reaction and it is represented by figure D-1. This mechanism is based on the following assumptions:

- butane and propane are absorbed in the catalyst surface and reaction takes place entirely as a surface-catalyzed reaction
- the reaction products from these reactions may react further or be desorbed.
- because of low probability of breaking two or three carbon bonds simultaneously, reactions converting butane and propane to methane are assumed not to occur.

FIGURE D-1

OVERALL REACTION SCHEME FOR THE HYDROGENOLYSIS OF BUTANE



$R_{C_4H_{10}}$ = rate of cracking of butane

$R^a_{C_3H_8}$ = rate of adsorption of propane

$R^d_{C_3H_8}$ = rate of desorption of propane

$R^a_{C_2H_6}$ = rate of adsorption of ethane

$R^d_{C_2H_6}$ = rate of desorption of ethane

R_{CH_4} = rate of production of methane

F = fraction of $C_4H_{10}*$ that cracks to C_3H_8*

$\longrightarrow$ Reaction Paths Considered

$\dashrightarrow$ Assumed = 0

The formal mechanistic model based on these assumptions has been established and is presented below. From a number of treatments with actual experimental data, the parameters have been estimated to yield the best fit.

D-2 Reaction Rates of the Reaction Species

Net rate of disappearance of butane

$$R_{C_4H_{10}} = \frac{k}{k_o} \cdot A \cdot P^{m'}_{C_4H_{10}} \cdot P^{n'}_{H_2}$$

where $A = k_B \cdot \exp\{-\Delta E_B/RT\}$

Net rate of appearance of propane

$$R_{C_3H_8} = \frac{F \cdot R_{C_4H_{10}} - \frac{k}{k_o} \cdot B \cdot P^{m''}_{C_3H_8} \cdot P^{n''}_{H_2}}{1 + C}$$

where $B = k_{P1} \cdot \exp\{-\Delta E_{P1}/RT\}$

$C = k_{P2} \cdot \exp\{-\Delta E_{P2}/RT\}$

Net rate of appearance of ethane

$$R_{C_2H_6} = \frac{(2-F) \cdot R_{C_4H_{10}} - R_{C_3H_8} - \frac{k}{k_o} \cdot D \cdot P^{m'''}_{C_2H_6} \cdot P^{n'''}_{H_2}}{1 + G}$$

where $D = k_{E1} \cdot \exp\{-\Delta E_{E1}/RT\}$

$G = k_{E2} \cdot \exp\{-\Delta E_{E2}/RT\}$

Net rate of appearance of methane

$$R_{CH_4} = 4 \cdot R_{C_4H_{10}} - 3 \cdot R_{C_3H_8} - 2 \cdot R_{C_2H_6}$$

Net rate of disapearance of hydrogen

$$R_{H_2} = 3 \cdot R_{C_4H_{10}} - 2 \cdot R_{C_3H_8} - R_{C_2H_6}$$

where

F = fraction of butane which reacts to propane

$\frac{k}{k_o}$ = catalyst activity (dimensionless)

k_B = frequency factor for butane (moles-sec^{-1}-volume of reactor^{-1}-atm$^{(m'+n')}$)

ΔE_B = activation energy for rate of butane cracking (cal-gm mole^{-1})

m' = exponent on butane partial pressure

n' = exponent on hydrogen partial pressure in the butane rate expression

$P_{C_4H_{10}}$ = partial pressure of butane (atm)

P_{H_2} = partial pressure of hydrogen (atm)

k_{P1} = pre-exponential factor in propane rate expression (moles-sec^{-1}-volume of reactor^{-1}-atm$^{-(m''+n'')}$)

k_{P2} = pre-exponential factor in propane rate expression (dimensionless)

ΔE_{P1}, ΔE_{P2} = activation energies in propane rate expression (cal-gm mole^{-1})

m" = exponent on propane partial pressure

n" = exponent on hydrogen partial pressure in the propane rate expression

$P_{C_3H_8}$ = partial pressure of propane (atm)

k_{E1} = pre-exponential factor in ethane rate expression (moles-sec^{-1}-volume of reactor^{-1}-atm$^{-(m"'+n"')}$)

k_{E2} = pre-exponential factor in ethane rate expression (dimensionless)

ΔE_{E1}, ΔE_{E2} = activation energies in ethane rate expression (cal-gm mole^{-1})

m"' = exponent on ethane partial pressure

n"' = exponent on hydrogen partial pressure in the ethane rate expression

$P_{C_2H_6}$ = partial pressure of ethane (atm)

R_i = rate of disappearance or appearance of component i (gm moles-sec^{-1}-volume of packed bed^{-1})

T = reacting temperature (degree Kelvin)

R = universal gas law constant (atm-cm^{-3}-gm mole^{-1}-$^oK^{-1}$)

D-3 Values of the Kinetic Parameters

$\frac{k}{k_o} = 1.6 \quad F = 0.9$

(a) Butane rate expression:

$k_B = 10^{15.6}$

$\Delta E_B = 5.1 \times 10^4$

$m' = 1$

$n' = -2.34$

(b) Propane rate expression:

$k_{P1} = 10.6$

$k_{P2} = 12.2$

$\Delta E_{P1} = 4.0 \times 10^4$

$\Delta E_{P2} = 3.0 \times 10^4$

$m'' = 1$

$n'' = -2.15$

(c) Ethane rate expression;

$k_{E1} = 10^{4.52}$

$k_{E2} = 10^{6.81}$

$\Delta E_{E1} = 2.6 \times 10^4$

$\Delta E_{E2} = 1.6 \times 10^4$

$m''' = 1$

$n''' = -2.21$