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GAMMA IRRADIATED CATALYTIC DEHYDROGENATION OF BUTENE-2 TO BUTADIENE-1,3

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Project 2581

THE DOW CHEMICAL COMPANY
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PREFACE

This report is presented as a result of investigations and evaluations of the dehydrogenation of butene-2 to butadiene 1-3 as affected by gamma irradiation.

The work upon which this report is based was undertaken at the request of Alden W. Hanson, Director, Nuclear and Basic Research Laboratories. L. R. Drake, Assistant Director, Nuclear and Basic Research Laboratories, and D. E. Harmer, of the Nuclear and Basic Research Laboratories of The Dow Chemical Company have been of great assistance to the authors in completing the work described in this report.

The authors wish to acknowledge gratefully the cooperation of the Phoenix Memorial Laboratory in making available space and radiation facilities for the completion of this work. Particular appreciation is due H. J. Gomberg, Assistant Director, Michigan Memorial Phoenix Project, and A. H. Emmons and W. Dunbar of the Phoenix Memorial Laboratory staff.

Alan Christman and Roberto Trevino, graduate engineering students at the University of Michigan contributed greatly to the construction of the equipment and the completion of the experimental work reported herein. Alfred Anderson, Robert Dunn, and John Payne, engineering students at the University, assisted in the construction of experimental equipment and facilities.

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ABSTRACT

Equipment was constructed for the conduct of the catalytic dehydrogenation of butene-2 over Dow Type B catalyst as influenced by gamma irradiation from MTR fuel elements and cobalt-60.

The equipment after construction and test operation was installed in the Phoenix Memorial Laboratory for operation under irradiation conditions. Equipment design and construction was conducted so that the entire pilot plant facility could be moved from the site of construction to the site required for irradiation in order to fulfill space and facility requirements during the construction and test operation period.

Results of catalytic dehydrogenation runs, both with and without irradiation, are presented for the range of temperatures of 575 to 650°C; space velocities in the vicinity of 300 standard volumes of butene feed per volume of catalyst per hour; steam ratios of 20 to 21 parts of steam per part of butene; and for a cycle time of one hour, comprising 28 minutes of dehydrogenation, 2 minutes of purge steaming, 28 minutes of burnoff, and concluding with 2 minutes of purge steaming.

Some indications were available from the data that irradiation accelerated the deterioration of the Dow Type B dehydrogenation catalyst. These indications cannot be confirmed at this writing, however. No significant difference was observed in the conversions or selectivities of dehydrogenation of butene-2 to butadiene 1-3 as affected by the presence or absence of gamma radiation for the doses and dose rates studied.

1.0 INTRODUCTION

In September of 1956, the Engineering Research Institute, University of Michigan, was contacted by the Nuclear and Basic Research Laboratories of The Dow Chemical Company relative to the conduct of sponsored research work. Discussions among the personnel of the two organizations resulted in The Dow Chemical Company's sponsoring a research contract with the Engineering Research Institute. Subsequently, among the many reactions which were of mutual interest to the two organizations, the Engineering Research Institute was directed to concentrate efforts upon the study of the catalytic dehydrogenation of butene-2 to butadiene 1-3 over Dow Type B catalyst, as affected by gamma irradiation.

Complete experimental facilities for this particular reaction were not available at the University of Michigan and efforts were immediately concentrated upon the design and construction of a suitable pilot plant embodying all of the necessary special requirements. Because of the great interest in irradiation work at the University of Michigan, space is at a premium in the immediate vicinity of the irradiation facilities. Consequently, it was decided to construct the pilot plant at the North Main Street, Ann Arbor, facilities of the Engineering Research Institute and to move the entire pilot plant to the Phoenix Memorial Laboratory upon completion of construction.

The program of construction was substantially completed by the end of January, 1957. Test operations without radiation were completed and the pilot plant moved to the Phoenix Memorial Laboratory in March, 1957. The experimental program of butene dehydrogenation in the presence of radiation was completed at the end of June, 1957. The portable pilot plant and supporting spare parts and small tools were returned to The Dow Chemical Company at the conclusion of the experimental work.

2.0 EXPERIMENTAL PROGRAM

The Dow Chemical Company have for many years conducted research on the catalytic dehydrogenation of butenes to butadiene 1-3, which is required as a raw material in the production of synthetic rubber. The Dow Chemical Company are presently engaged in the manufacture of a highly selective catalyst, the Dow Type B catalyst, for conducting the dehydrogenation of butene-2 to butadiene 1-3.

As a consequence of the interest which The Dow Chemical Company have in the butadiene production program, it was decided that the Engineering Research Institute should concentrate its studies in the field of radiation effects upon chemical reactions upon the irradiation of the catalytic dehydrogenation of butene over Dow Type B catalyst under conditions which were similar to those used in Dow's standard test #5 for evaluating manufactured lots of the Dow Type B catalyst. The standard test #5 of The Dow Chemical Company is used to evaluate the activity and service life of lots of Dow Type B catalyst.

The experimental pilot plant constructed at the University of Michigan was therefore designed to operate under temperatures, space velocities, steam to hydrocarbon ratios, and production and burnoff cycle times similar to those employed in the standard test #5.

Consequently, the experimental conditions of operation for studying the butene dehydrogenation were rather firmly established prior to the initiation of any experimental work. The unique feature of the experimental program is that the catalytic dehydrogenation was conducted under industrial conditions during irradiation. In particular irradiated reaction studies were conducted under continuous flow conditions at temperatures ranging from 575 to 650°C, employing a catalytic bed with continuous charging of raw materials and continuous withdrawal of product.

The method employed for analysis of product gases was that of gas phase chromatography using a wet-screened celite carrier and 2-5 hexanedione as stationary phase (2). This method provided indications of air, methane, carbon monoxide, carbon dioxide, lower hydrocarbons, butane, butene-1, trans-butene-2, cis-butene-2, and butadiene-1-3.

Phillips pure grade mixed butene-2 was the only charge stock employed. Dow Type B catalyst, Lot 36, was used as furnished by D. E. Harmer. Distilled water was used throughout these investigations for conversion to required diluent steam.

Initial efforts upon completion of the pilot plant were devoted to checking the performance of the catalytic dehydrogenation in the absence of radiation. These efforts were undertaken to establish baselines of comparison for evaluating the performance of the pilot plant with those data available from previous experimental investigations of The Dow Chemical Company. After some six weeks of intermittent operation in the absence of radiation, it was mutually agreed by The Dow Chemical Company and the University of Michigan that the pilot plant displayed consistent performance and irradiation work should be started.

The irradiation program at the Phoenix Memorial Laboratory was somewhat more flexible in regard to the application of radiation than were the process conditions of operation. In general, the effort was to run the standard test #5, modified in certain respects, first without radiation and then with radiation, and to observe any differences which might be apparent due to the radiation. Some unexpected effects were observed, such as, in certain cases, rapid coking of the catalyst. Initial runs at the Phoenix Memorial Laboratory were with 4 MTR fuel elements only, and later runs employed the 3,000 curie cobalt-60 source in addition to the 4 MTR fuel elements. Various combinations of variables were tried with and without radiation, either for considerable periods under each condition or under alternating radiation and no radiation conditions. Various indications of the experimental data were followed as they appeared in the attempt to derive generalizations of the effect of radiation upon the reaction under study.

3.0 EXPERIMENTAL EQUIPMENT

3.1 General Design Criteria

The experimental equipment required for the butene dehydrogenation work studied under this contract was constructed at the University of Michigan. The Dow Chemical Company lent to the University of Michigan for the purposes of the study several vital pieces of equipment, including a Brown 8-Point Temperature Recorder, two Milton Roy pumps, and a gas chromatography unit for continual analysis of the product gas streams.

In Figures 1, 2, and 3 appear photographs of the pilot plant as construction had been concluded at the construction shops at the University of Michigan. As can be seen from the photographs, the pilot plant employed certain features of design which were necessary due to the unique requirements of this particular program of investigation. The necessity of constructing the pilot plant at one location and then moving the entire facility bodily to another location for the radiation work was imposed by space requirements in the vicinity of the radiation source. The requirement of portability dictated lightness and rigidity, compactness, and accessibility of the experimental equipment. From these requirements arose the use of the Dexion slotted galvanized steel angle for the construction of the control panel and reactor support. The placement of all the control equipment upon one panel occupying one plane only was dictated by space requirements adjacent to the radiation source. This point can be further appreciated by referring to Figure 4, a photograph of the control panel in place in the space available on the west side of a gamma radiation room in the Phoenix Memorial Laboratory. About one foot was left clear behind the panel for access and about three feet in front of the panel for operation. It was decided to construct the control panel in an open style, that is, without any panel board covering the rack, in order to permit ready access to the equipment for inspection, replacement, or repair. The layout of equipment on the control panel was governed by the grouping of related operations and accessibility of components. In addition, all of the process, instrument, and power lines were required to leave the right end of the panel and pass through a highly restricted chute with an offset through the wall of the radiation cave. This chute, although open throughout, provided the required radiation shielding due to the offset angles in its construction, so that no direct radiation or intolerable amounts of scattered radiation could pass through the chute.

The requirement of grouping all lines and passing them through one common opening necessitated an extreme compactness in the wiring, piping and tubing layouts. The passage of all power wiring adjacent to the thermocouple wiring was believed to be sufficient basis for running all thermocouple wiring through a braided, tinned-copper shielding which was grounded at both ends to minimize the effects of alternating current pickup upon the thermocouple performance. The reactor rack in its final location is shown in Figure 5 in location over the storage well for the radiation source. The reactor

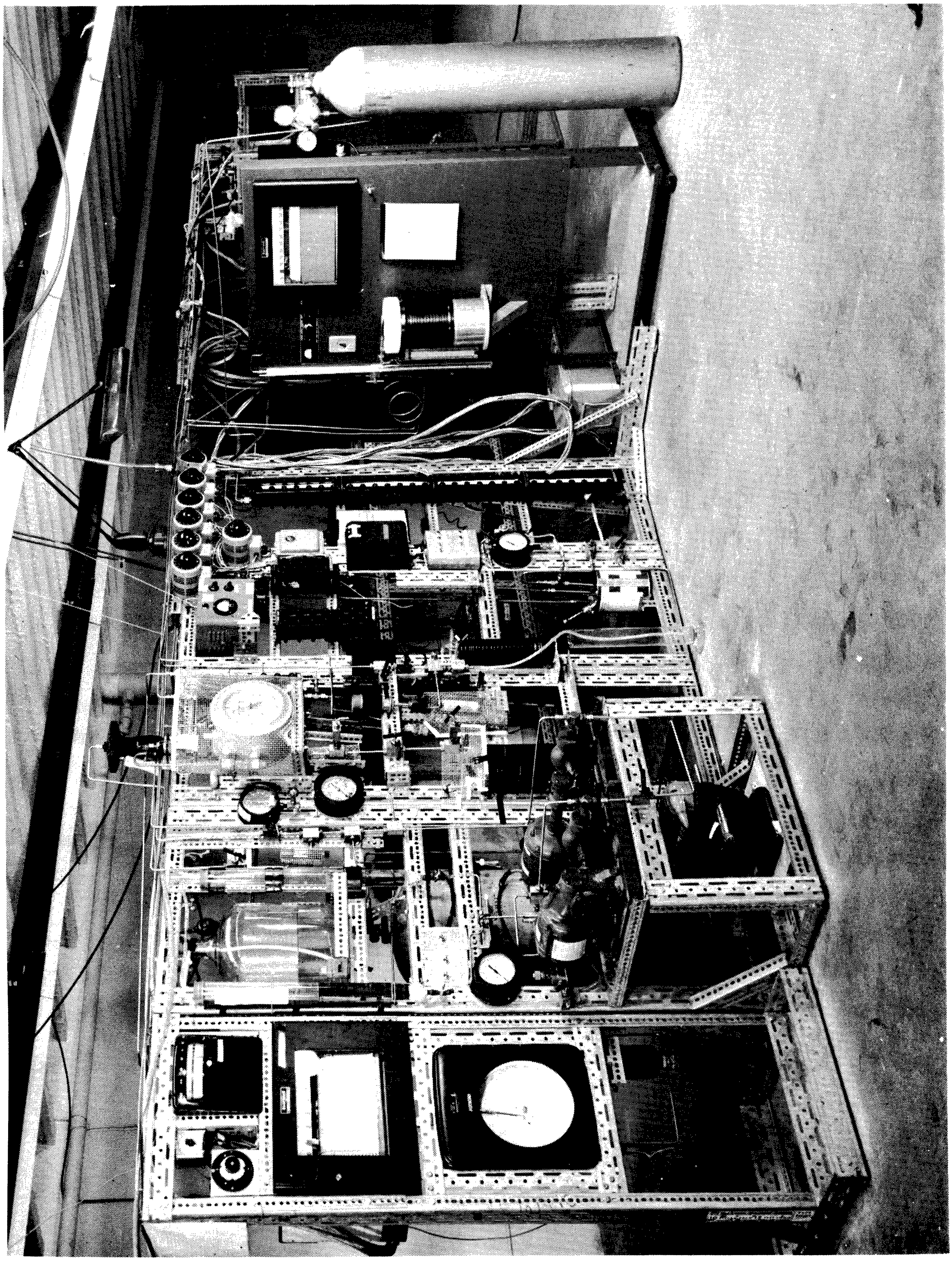

FIGURE 1 - CONTROL PANEL AT NORTH MAIN STREET

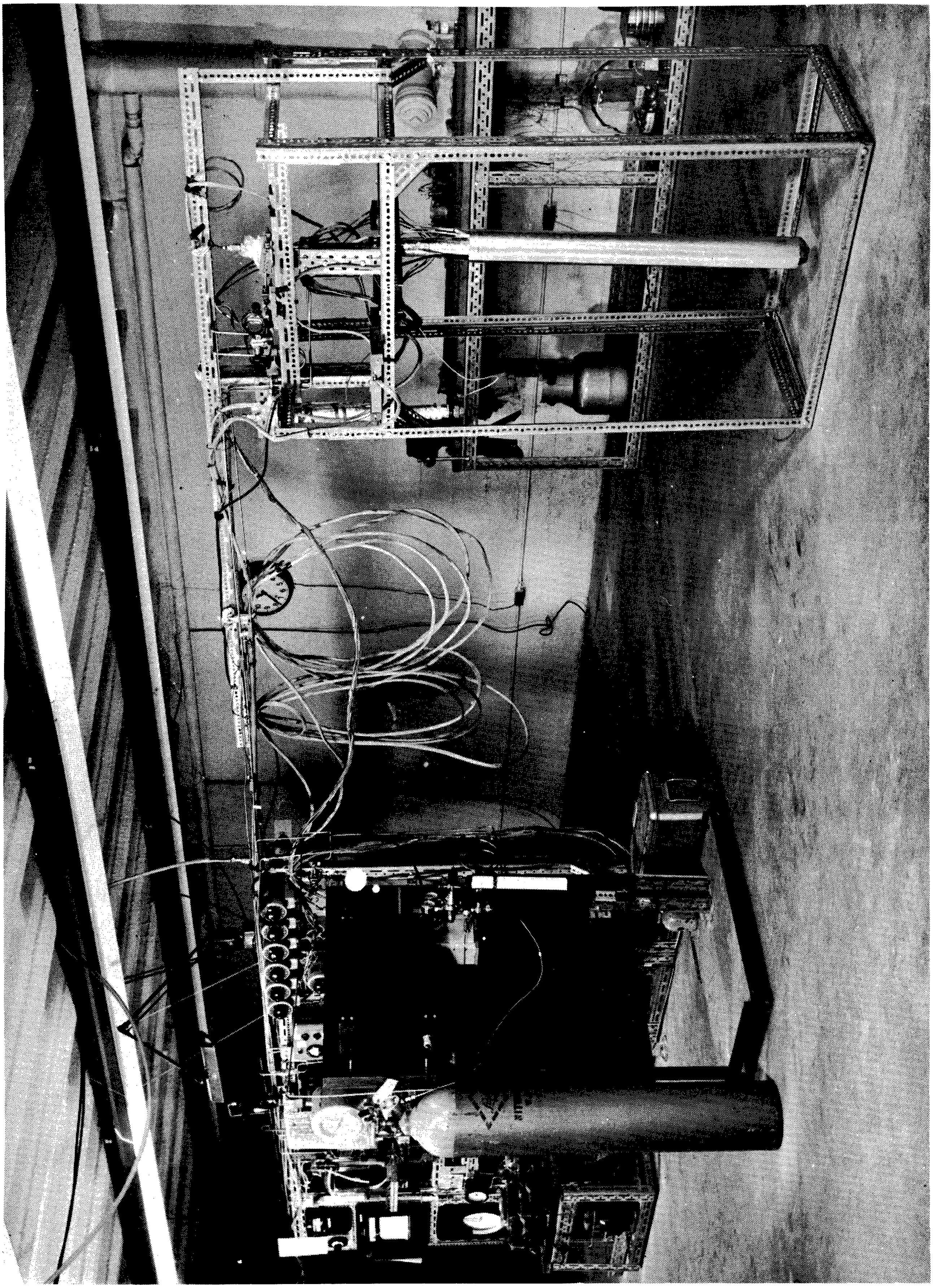

FIGURE 2 - REACTOR ASSEMBLY AT NORTH MAIN STREET

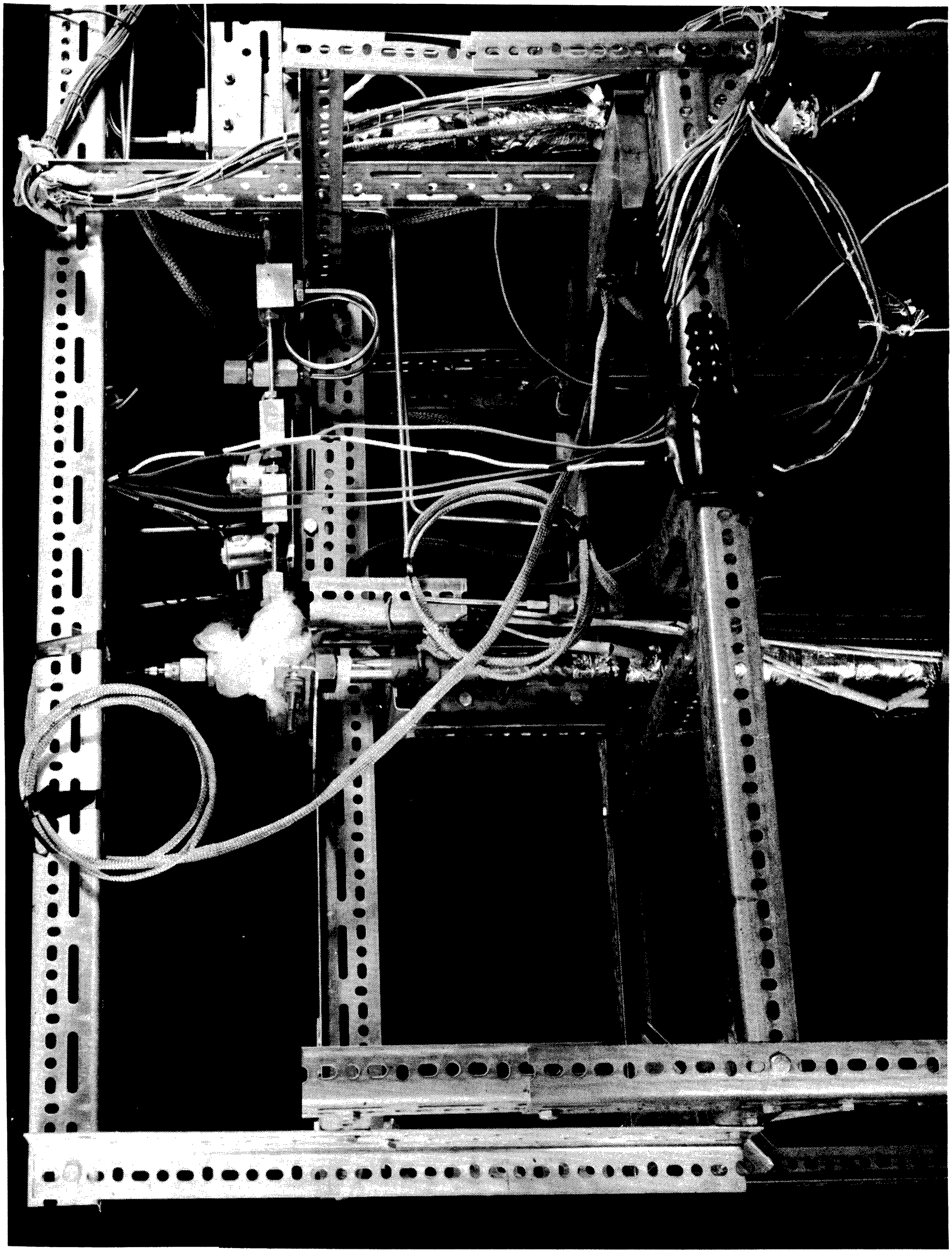

FIGURE 3 - REACTOR DETAILS AT NORTH MAIN STREET

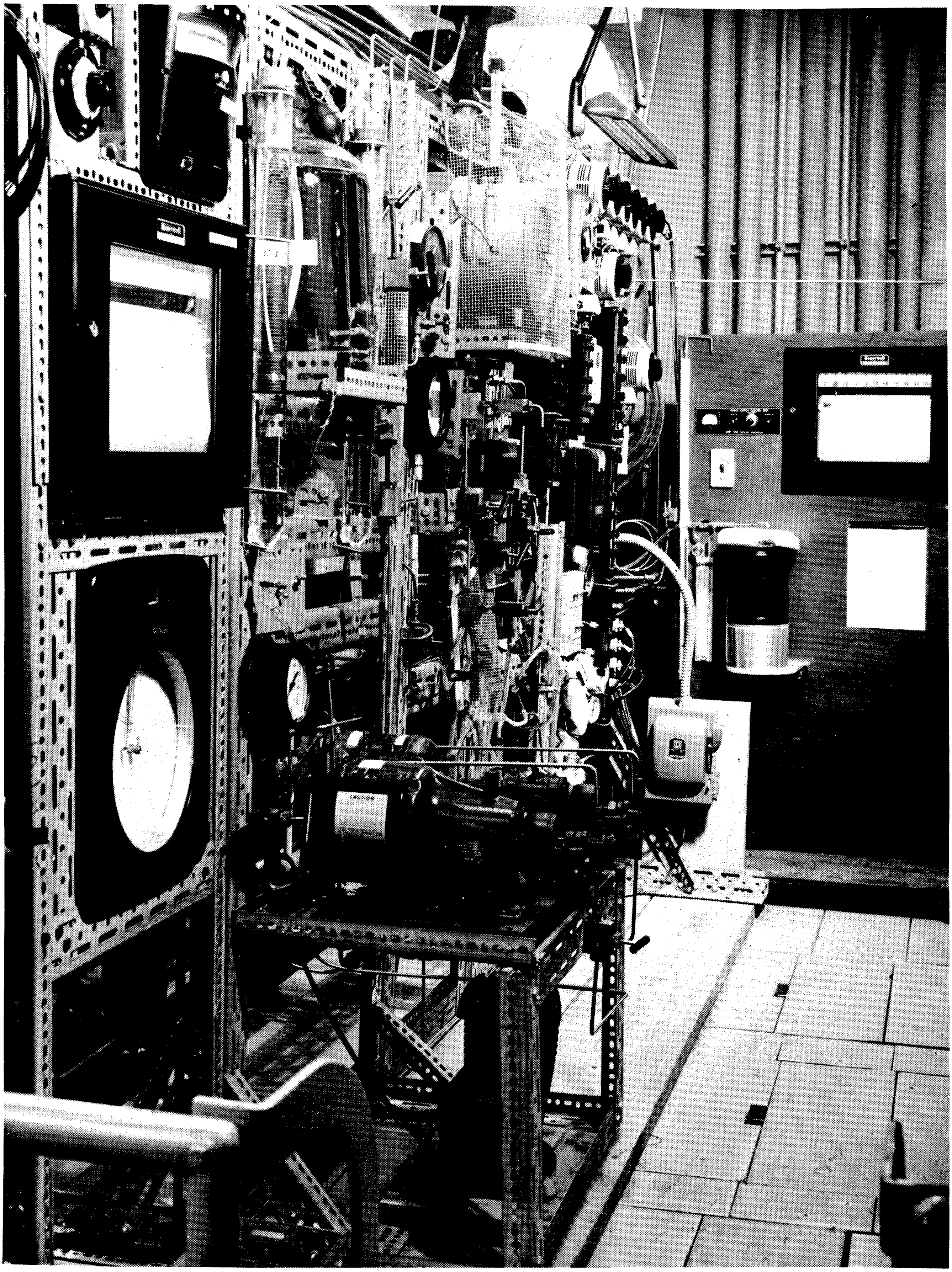

FIGURE 4 - CONTROL PANEL AT PHOENIX MEMORIAL LAB

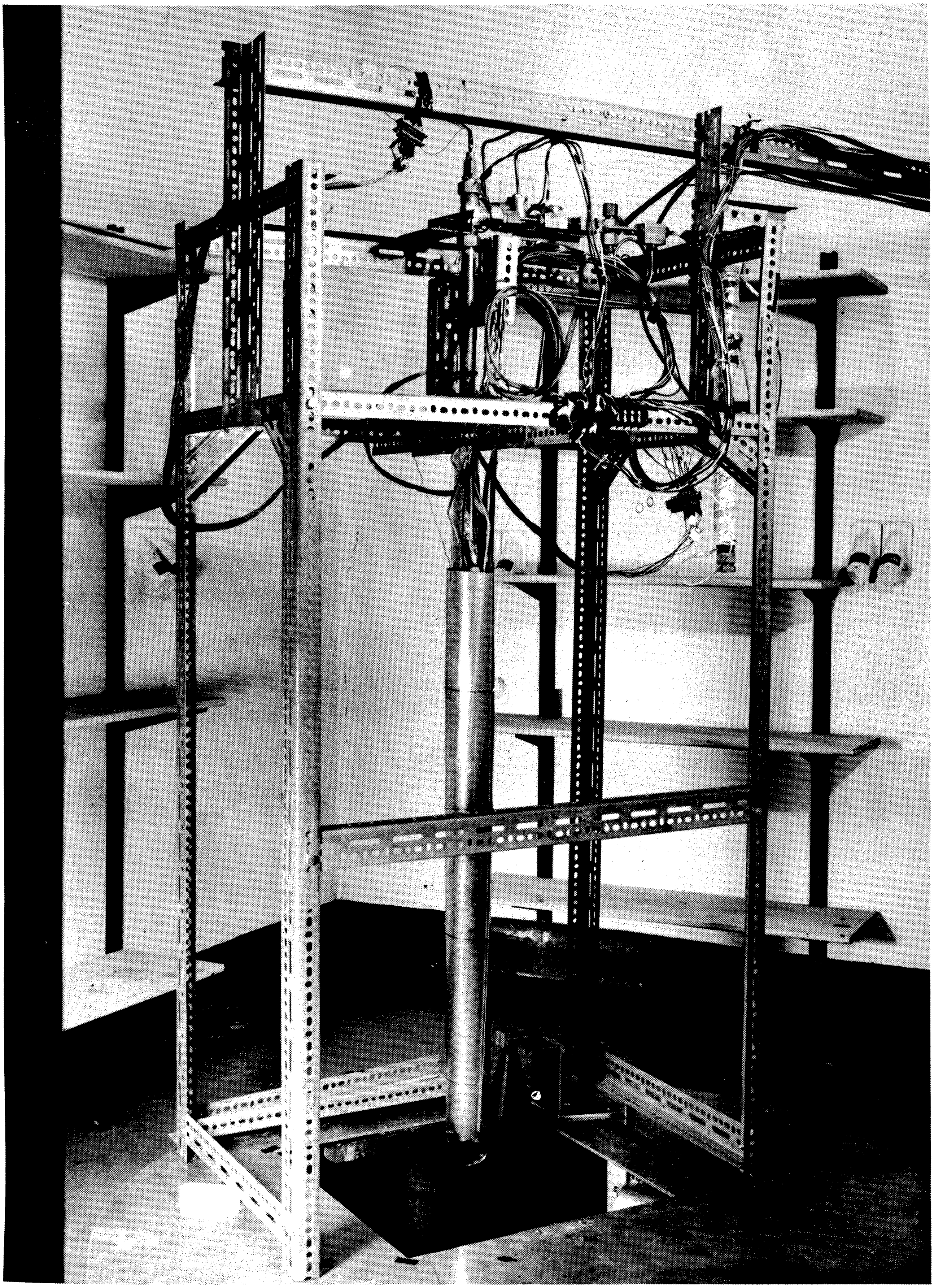

FIGURE 5 - REACTOR IN PHOENIX MEMORIAL LAB. IRRADIATION ROOM

was in competition with many other experiments for utilization of the source, which rises out of the well and surrounds the reactor, as shown in the figure. Consequently, it was necessary to move the reactor rack from the well whenever the source was not being used in order that others might use the space. As a means of circumventing this difficulty and also maintaining an orderly appearance and accessibility to all parts of the irradiation room, all of the process lines, instrument and power wiring were run on one beam cantilevered from the reactor rack as shown and terminating in the entire group of lines which drop directly down into the opening of the access chute through the shielding wall.

A flow diagram of the experimental unit is shown in Figure 6. The flow diagram was entirely conventional and follows closely the type of related units presently employed by the Gas Laboratory of The Dow Chemical Company. Figure 7 shows the power wiring diagram for the pilot plant and Figure 8 shows the thermocouple wiring diagram for the pilot plant.

No special difficulties were encountered when the pilot plant was moved from the North Main Street shops to the Phoenix Memorial Laboratory. No joints were found to have leaked during the transportation of the pilot plant. However, it was necessary to make connections to the new utility sources in the Phoenix Memorial Laboratory and to add some lengths of tubing line to pass through the shielding chute.

3.2 Reactor Vessel

Limitations of time and unavailability of special 446 welding rod led to the adoption of a reactor design which could be fabricated quickly and cheaply in order to avoid delaying the commencement of investigative work. The reactor consisted of a piece of 3/4" IPS 446 pipe which was turned down to 1.00" outside diameter on each end. This procedure permitted closing each end of the reactor by means of compression-type tubing fittings. The fittings employed were of carbon steel, cadmium plated as manufactured by the Weatherhead Company and bore the trade name Ermeto. The bottom fitting was located 5" below the bottom heating winding and the top fitting was located 13" above the top heating winding. The reactor was left bare between the termination of the heating windings and the fittings on each end in order to provide the maximum amount of cooling and prevent the overheating of the end fittings. During operation the top or inlet fitting was never observed to rise above 100°C and the bottom fitting did not rise above 225°C. Both of these temperatures were well within the operating limits of the materials of construction.

3.3 Influence of Radiation Source Upon Reactor Design

The design and construction of the reactor to operate at a temperature of 650°C at locations within one to 1-1/2 inches of aluminum clad source of radiation posed problems requiring special consideration. It was necessary to prevent overheating of the fuel elements and

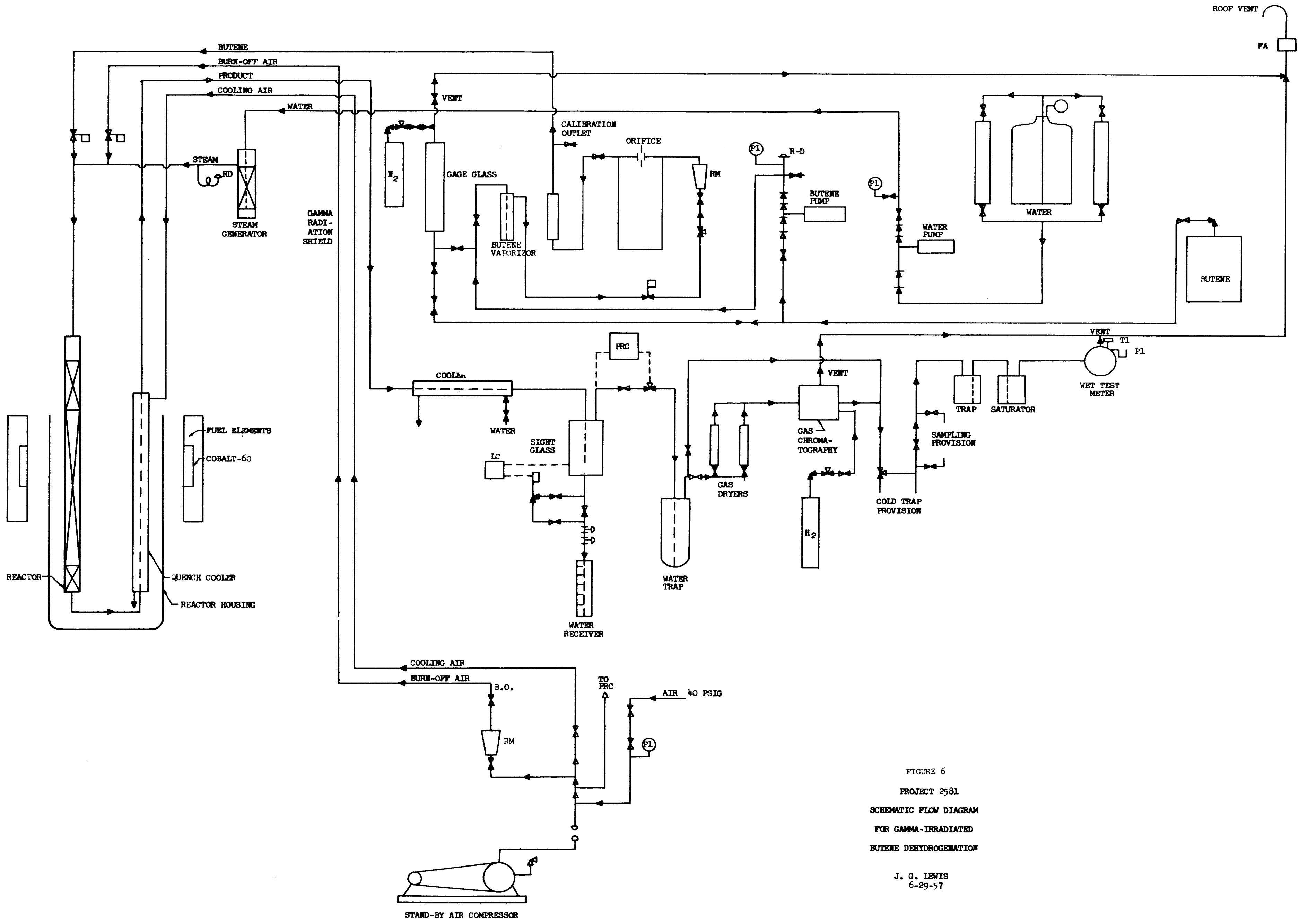

FIGURE 6

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SCHEMATIC FLOW DIAGRAM

FOR GAMMA-IRRADIATED

BUTENE DEHYDROGENATION

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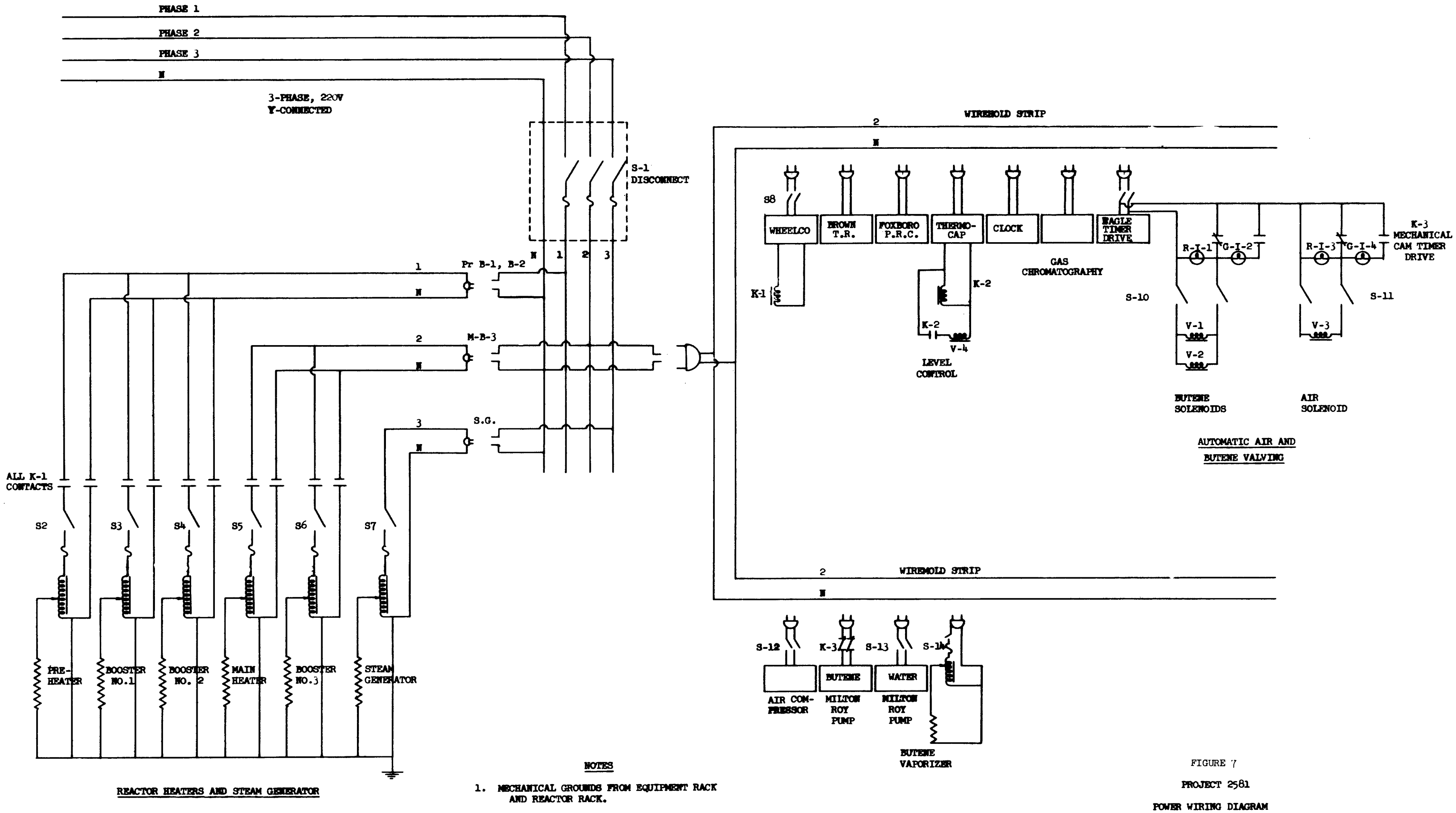

NOTES

1. MECHANICAL GROUNDS FROM EQUIPMENT RACK AND REACTOR RACK.
2. EAGLE TIMER CONTACTS ARE CLASSIFIED AS NORMALLY CLOSED, BUT MECHANICALLY DRIVEN, SO THAT NOT ALL ARE CLOSED AT ANY ONE TIME.

FIGURE 7

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POWER WIRING DIAGRAM

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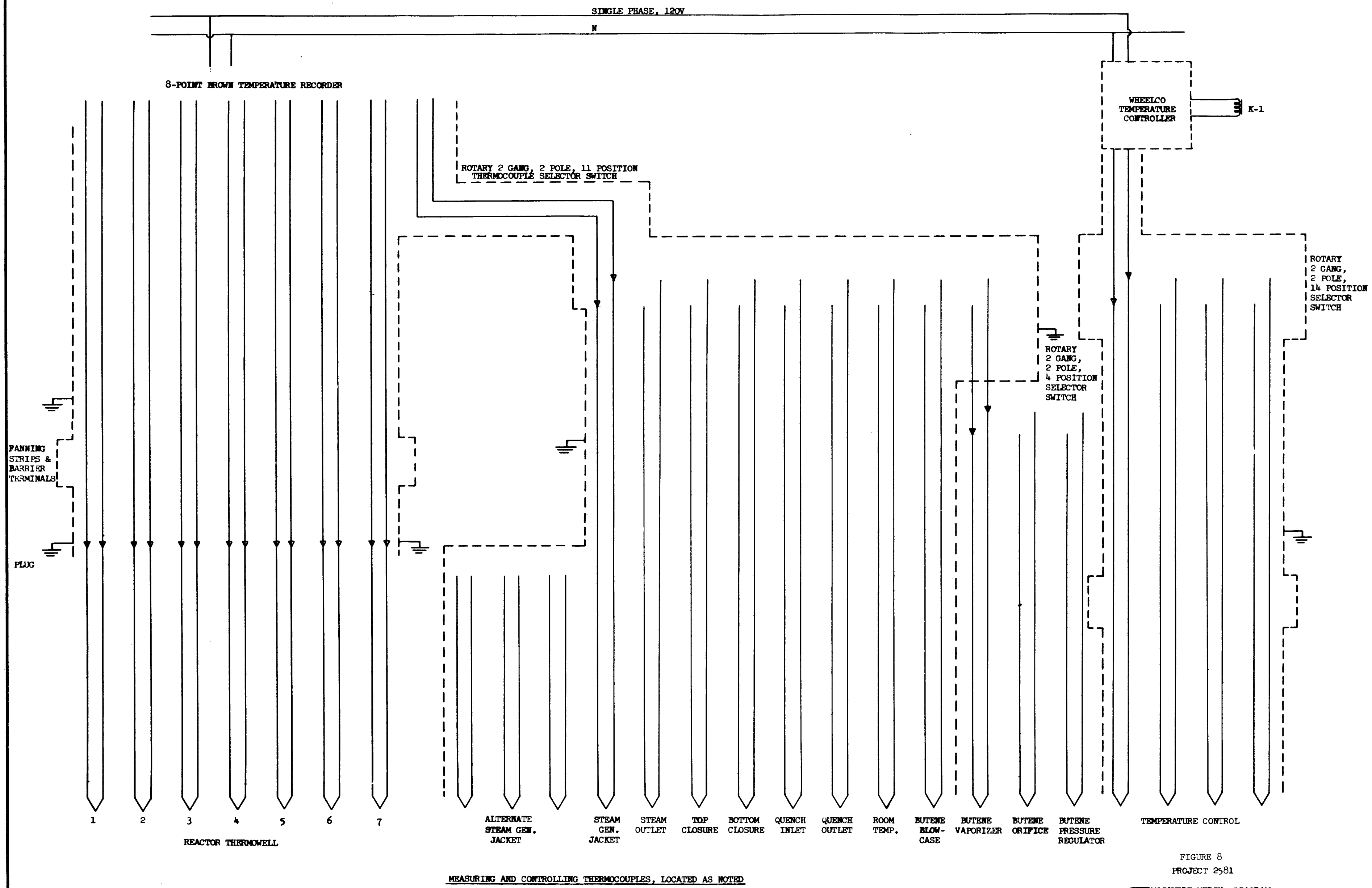

FIGURE 8
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THERMOCOUPLE WIRING DIAGRAM

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possible rupturing or parting of the seams of the aluminum cladding surrounding the cobalt rods. This problem was met by surrounding the reactor, together with the associated power wiring, quench cooler, and measuring and control thermocouples, by means of the 4" diameter sheet aluminum housing. This housing fitted with about 1/4" clearance on all sides within the rack holding the radiation source. Consequently, the reactor had to be centered accurately over the location at which the fuel elements would rise from the source when operated by remote control. It was believed necessary to reduce the temperature of the products as they left the reactor as rapidly as possible in order to avoid undesirable secondary reactions of the products. This was accomplished by passing a stream of air through a jacket surrounding the outlet tube from the reactor. This cooler was then located immediately adjacent to the reactor inside the aluminum sheet housing described above. The air, as it exited from the bottom of the quench cooler, was allowed to pass upward around the outside of the reactor, helping to reduce the temperature of the exterior of the reactor insulation, the measuring and control thermocouples, and power wiring leads passing into the reactor insulation from the outside.

3.4 Reactor Heaters

In addition to preventing the overheating of the gamma source due to the close proximity of the high temperature reactor operation, it was necessary to design and construct the reactor in such a way that it would maintain a uniform temperature throughout its length by means of heating elements which would absorb minimum amount of gamma radiation from the source. The heater design employed is shown in Figure 7, Power Wiring Diagram in schematic form. The actual heater windings were made of 20 gauge chromel A-wire insulated with asbestos, jacketed on the outside with 302 stainless braid. This wire was wrapped over a copper sheet which had previously been wrapped around the 446 pipe reactor. The copper sheet was of some assistance in maintaining uniform temperature along the length of the reactor. The use of the self-insulated heating wire permitted much lower dead times in response to controller signals from the temperature controller than would be possible when using a layer of insulating material wrapped upon the reactor and also around the outside of the heating elements. This design also absorbed a minimum of gamma radiation.

A similar design of heaters was employed for the steam generator required to vaporize the distilled water charged from the control rack and used as a diluent and heat transfer medium within the reaction bed.

The initial installation of heating elements worked quite well. Temperatures were controlled automatically within ± 1°C, employing a Wheelco type of proportioning controller connected to four 16-gauge iron constantan thermocouples, any one of which could be selected by means of a rotary selector switch. One of the initial experiments in the Phoenix Memorial Laboratory under radiation resulted in coking the catalyst badly. High temperatures were applied to the windings in order to raise the temperature of the reaction, which was evidently being lowered by the water gas reaction. Under these conditions several of the heating elements burned out. These were replaced without the copper sheet over the reactor and under the heating wires. These heaters did not perform very well. Close temperature control and uniform temperature control among the various heaters was not possible. This assembly was re-wound, employing an additional copper sheet under the windings. This assembly was employed for the remainder of the experimental work and appeared to work reasonably well. Good temperature control was possible, using the system as designed if the reaction was behaving in such a way that large endothermic or exothermic effects were not observed.

3.5 Measurement of Reaction Temperatures

The measuring thermocouples were placed inside an SAE 4130 steel tube, heliarc welded closed at the bottom. It was decided to try the double glass-wrapped silicon-impregnated thermocouple wire for this application within the thermo-well although the manufacturer of this wire does not recommend its use above a temperature of 900°F. It was found that the thermocouples standardized using the freezing points of Bureau of Standards samples of pure metals in graphite containers as reference points would operate well so long as they were not subjected to mechanical disturbance. If the thermocouples were withdrawn from the thermowell after being heated to 650°C or were subjected to undue jarring or disturbance, such as when changing catalyst, then it was necessary to replace the entire set of thermocouples. An improved design of thermocouples could have been employed. However, within the limitations of the time and manpower available it was not deemed desirable to divert effort to this end.

It was desired to read about 16 temperature points, whereas only 8 positions were available in the Brown recorder. It was decided to record continually the 7 points within the reactor thermowell. The four control couples were hooked directly to the Wheelco and constituted no problem, because they did not compete for a recorder space with the other points measured. However, the remaining points were connected to point #8 in the Brown recorder through a Leeds and Northrup 11-position rotary double pole thermocouple selector switch. Thus, it was possible to stop the recorder on point #8, read the other nine points as desired, and then start the recorder chart to continue the automatic logging.

3.6 Butene Metering System

The metering of the butene into the system under controlled conditions represented considerable problems. A reason for these problems evidently lay in understandings between The Dow Chemical Company and the University of Michigan during starting of the project. The option was left to the University of operating some of the proposed reactions under high pressure. Consequently, the entire pilot plant was designed to run at a pressure of 400 psig, the probable limiting pressure due to creep considerations of the 446 reactor at 650°C for 10,000 hours of operation. For pressure operation, 1/4" stainless steel AISI 304 lines were employed. These lines were too small to permit flow of the required quantities of gases for operation at atmospheric pressure without back pressures of the order of about 3 to 5 lbs/sq. in. gauge. Consequently, a wet test meter could not be employed under these pressures for metering the feed gas at 1 atmosphere.

One of the early methods of attempting to meter butene was the use of a Brooks rotameter. This rotameter had the proper characteristics with regard to flow range for metering butene in liquid form. It was initially believed that the combination of the sight glass for measuring integral quantities of butene liquid charged together with the instantaneous reading on the liquid butene rotameter would be adequate to provide control of the system. It was found, however, that particles of paint and other foreign matter continually dissolved out of the system and caused the float to stick in the rotameter. In addition, the rotameter has a vent at the bottom of the sight glass which allowed the pressure-space of the rotameter to fill with liquid butene during operation. A further difficulty encountered because of the low pressure of operation was that the liquid butene flashed to the vapor form upon passing through the metering valve into the lower pressure of the reaction system. A steady flow of the butene could not be maintained under flashing flow conditions.

A system was then devised to meter the butene in the liquid state inside a Penberthy 4 section gauge glass under nitrogen pressure. The liquid butene was charged to a vaporizer, which admitted the vaporized butene through a solenoid valve into an orifice constructed of a hypodermic needle and read by means of a manometer. This system was not satisfactory because of liquid-level-surging in the gauge glass.

It was then decided to pump the liquid butene through a Milton Roy pump. The pump was connected to the contacts on the Eagle signal timer governing the burnoff operations. The liquid butene discharged from the pump went to a vaporizer. From the vaporizer it went through a solenoid valve to a pressure regulator. The vapor was discharged from the pressure regulator at about 6 lbs/sq.in. gauge. The butene vapor then passed through a rotameter, into the orifice described above, through a metering valve, and finally to a second part of the vaporizer. The second part of the vaporizer re-heated the vapor for charging to the system.

The last system described represents a compromise between a design of the overall unit for high pressure operation and its utilization for atmospheric operation. If one were to employ the system for high pressure operation, it would be necessary to put in more high pressure components, such as a high pressure alloy steel regulator and gauge glass and a better device than the orifice and manometer employed. Perhaps one could use a gauge capable of withstanding high static pressure but reading inches of water directly in a bourdon type element over an orifice placed in the line. However, operation of the equipment at high pressure was not easily possible under this setup. The principal reason for this was the desire to conduct the atmospheric runs first. In addition, it would have been necessary to supply high pressure air to the system, and such a source of air was not readily available.

Compressed air was not available from existing utilities provisions on the North Main Street site during startup operations of the initial six weeks. Consequently, a small DeVilbiss paint spray compressor was purchased in order to supply air during this period. The Phoenix Memorial Laboratory had building air supply which was used for experiments in that location.

It is believed that the unit could be run more advantageously at 1 atmosphere pressure if the sizes of the lines were reviewed and increased where necessary to values which would permit backpressures within the limits of the type of metering equipment it would be desired to use.

3.7 Product-Handling System

The let-down pot which received product from the reactor was a single section Penberthy alloy steel gauge glass. Gas was removed from the top of this gauge glass and sent through the trap and drier to a gas chromatography unit, where samples were taken and analyzed periodically. The remaining gas was vented through a system comprising provision for cold traps, provision for a gas sampling bulb, backflow trap, water saturator, wet test meter, and a vent line which terminated in the roof in a flame arrestor and vent hood.

Water was removed from the bottom of the separation pot through a manifold. This manifold included a solenoid valve for regulation of the water level within the let-down pot. However, the solenoid valve caused large surges in current whenever activated. These surges caused blips to appear on the gas chromatography chart whenever the valve was activated. Consequently, the valve was not employed during the majority of the operations because it was not desired to divert the necessary man-power to the alteration of the system. If desired, however, a valve such as a Skinner low pressure solenoid could be hooked directly to the level controller, possibly even without the use of an intermediate relay. Such a system would reduce the starting current from a solenoid valve. The valve employed was designed to open under 3,000 lbs/sq.in. pressure and consequently, had much heavier solenoids than were required for the job. The level regulator proper was a capacitance bridge known as a Thermocap relay. This device operated on the signal of variable capacitance between a probe inserted into the bottom of the separation pot and the pot itself. Fluid within the pot influenced this capacitance and gave an index of liquid level. The probe was 1/4" copper tube, silver-soldered shut on the top end and surrounded by a 3/8" teflon rod. Upon startup the capacitance between the probe and the separation pot was so great that it was not possible to balance the instrument. In order to reduce the capacitance between probe and ground, a small capacitor was inserted in the series in the line between the probe and the capacitance bridge. The unit operated quite satisfactorily then, except for the excessive starting current in the solenoid valve as described above.

3.8 Some Start-Up Considerations

Before raw materials were charged to the unit, all parts were blown free with air in order to remove scale, dirt and other gross contamination. After removal of the large particulate contamination occurring as a result of construction, the entire system was flushed with several gallons of acetone. The acetone removed quantities of oil, grease, and other foreign matter. The cleaning with acetone was continued throughout the entire system until the acetone came out of the system as clean as it was charged. Upon the conclusion of this cleaning operation, it was found necessary to replace the seats in all of the Skinner solenoid valves. These seats were evidently of butyl rubber. The rubber may have been attacked by acetone to a much greater extent than it would be normally by the liquid butene. In any event, neoprene plugs were cut and used to replace the butyl rubber inserts with which the valves were shipped.

4.0 RESULTS OF EXPERIMENTAL WORK

The results of the experimental work are summarized in Table I.

Data and calculated results are presented in chronological order of runs. It can be seen that the controls of temperature and space velocity are subject to variation. Conversions varied over a rather wide range, from low values approximating 5% to high values on the order of 45%. Generally, conversions were in the range of 15-30%. Selectivities were usually in excess of 90%. Lower selectivities were, almost without exception, indicative of catalyst failure.

The pressure of operation was generally in the range of 3-5 psig. These pressures are somewhat higher than those normally used by Dow and were a consequence of the use of lines sized for higher pressure operation and hence, too small to pass desired flow rates at atmospheric pressure.

In all, six charges of catalyst were placed in the reactor. Each charge was introduced in order to replace a batch which had begun to function unsatisfactorily. Malfunctioning of the catalyst was indicated in each case by greatly reduced conversions and selectivities. The sixth charge of catalyst was still functioning satisfactorily at the conclusion of experimental work.

Discharged batches of catalyst were black in color near the bottom of the bed. Flow of reactants was downward through the reactor. Usually the top of the bed was nearly normal in color when removed.

Incomplete burn-off of carbon was suspected as a strongly contributing variable in causing catalyst to behave poorly. During the last few runs the burn-off gases were tested for carbon dioxide by barium hydroxide solution. Generally a noticeable turbidity occurred in about one to two minutes at the end of the burn-off period. Orsat analysis of the same stream using potassium hydroxide solution indicated a maximum concentration of about 1% of carbon dioxide near the beginning of the burn-off period.

A record of batches of catalyst used and irradiation to which these batches were subjected is provided in Table II.

The rate of catalyst failure reported in Table II is considered to be excessive. As indicated above, tests were conducted to assess the adequacy of burn-off procedures as one suspected element in rate of catalyst failure. In addition, analyses were made of the AISI 4130 thermocouple well in the reactor. Nickel content of this thermowell was found (1) by D. E. Harmer to be 0.1 ± 0.01%, a level regarded as too low to accelerate catalyst failure. No analysis was made of the reactor vessel, which was AISI 446 3/4" IPS schedule 80 pipe, purchased from Rolled Alloy, Inc., Detroit, Michigan.

TABLE I

1957 Date & Run	Temp.	Pressure		S.V.	H_2O / C_4	Dose Rate*	% Conversion	% of Select.
		H_2O	C_4					
March 25 - (First day of operation in Phoenix Laboratory)								
325-1B	~575	6.0	10.0	--	--	No Rad.	~ 25.0	~100.0
March 28								
328-1B	653-658	4.0	4.0	272	18.6	No Rad.	37.0	95.0
328-2B	646	3.5	3.5	259	19.5	No Rad.	32.0	95.0
328-3B	650	--	--	267	19.0	No Rad.	33.0	95.0
328-4B	650	3.5	4.0	267	19.0	No Rad.	36.0	95.0
March 29								
329-1B	650	3.5	4.0	281	17.9	No Rad.	~ 32.0	~ 95.0
329-2B	646	3.5	4.0	277	18.1	No Rad.	34.0	~ 95.0
329-3B	647	3.5	4.0	294	17.1	No Rad.	35.0	~ 95.0
329-4B	646	3.5	4.0	277	18.1	No Rad.	34.0	~ 95.0
329-5B	645	3.5	4.2	300	16.7	No Rad.	35.0	~ 95.0
April 1								
401-1B	642-652	3.5	4.0	266	18.2	No Rad.	41.0	93.0
401-2B	650-655	3.3	4.0	255	18.7	No Rad.	38.0	93.0
401-3B	648-652	3.0	4.0	266	18.0	No Rad.	35.5	94.0
401-4B	648-651	3.0	4.0	261	18.2	No Rad.	35.0	94.0
401-5B	645-652	3.0	4.0	260	18.9	No Rad.	35.0	94.0
April 2								
402-1B	646-653	3.5	4.0	262	18.6	No Rad.	33.0	94.0
402-2B	644-650	3.0	4.0	262	18.7	No Rad.	39.2	93.5
402-3B	642-649	3.0	4.0	255	20.2	No Rad.	41.0	94.0
402-5B	645-651	3.2	4.0	275	18.2	No Rad.	40.4	92.0
NOTE: The runs were made with the source up, but reactor not over the well.								
April 3								
403-1B	645-655	3.6	4.0	262	19.6	No Rad.	30.7	94.5
403-2B	648-654	3.5	4.0	270	18.9	No Rad.	37.7	86.0
403-3BR	634-645	3.2	4.0	262	19.6	60	47.2	85.0
April 4								
404-1BR		3.5	4.0	263	19.5	60	Data Unavailable	
404-2BR		4.0	4.0	262	19.6	60		
404-3BR		--	--	261	19.6	60		
April 5								
405-1B	600-650	5.0	5.0	240	21.3	No Rad.	?	-0-
405-2B	625-675	4.5	4.5	287	17.9	No Rad.	16.8	49.0
405-3B	620-645	--	--	--	--	No Rad.	9.9	91.0

* Dose Rates are in Kilorep per hr., measured in air at axial mid-plane position of source. No estimates made of influence of absorption, scatter, or dose rate variations with position in source.

TABLE I (Continued)

1957 Date & Run	Temp.	Pressure		S.V.	$\frac{H_2O}{C_4}$	Dose Rate	% Conversion	% of Select.
		H_2O	C_4					
May 2								
502-1B	575-625	5.0	6.0	311	19.7	No Rad.	12.4	100.0
502-3B	550-575	--	--	296	20.6	No Rad.	10.5	100.0
502-5B	580	4.7	4.8	288	21.2	No Rad.	9.9	100.0
502-7B	550-580	4.2	4.8	296	20.6	No Rad.	9.9	100.0
502-8B	570-580	4.5	5.0	278	22.0	No Rad.	10.0	100.0
502-9B	574-576	4.5	5.0	278	22.0	No Rad.	7.9	100.0
May 3								
503-1B	550-575	4.5	4.5	294	21.0	No Rad.	7.2	100.0
503-2B	550-560	4.5	4.5	269	22.8	No Rad.	7.5	100.0
May 6								
506-1B	575-585	4.2	4.5	296	21.1	No Rad.	9.7	100.0
506-3B	565-570	4.0	4.5	291	21.4	No Rad.	8.6	100.0
506-5B	575	--	--	295	21.2	No Rad.	8.9	100.0
506-6BR	~550-600	4.2	4.6	302	20.6	60	-0-	--
506-8BR	575	4.0	4.5	300	20.7	60	8.9	100.0
May 7								
507-1BR	560-575	4.5	4.5	--	--	60	9.9	100.0
507-3BR	575-580	5.1	5.0	281	22.3	60	< 5.0	100.0
507-5BR	575-585	5.0	5.4	316	19.8	60	< 5.0	100.0
507-6BR	575-585	--	--	313	20.0	60	< 5.0	100.0
507-8BR	565-570	5.0	5.2	335	18.7	60	6.5	100.0
507-9BR	565-570	5.0	5.2	335	18.7	60	10.0	100.0
May 8								
508-1BR	590-600	4.5	5.0	280	22.4	60	9.2	100.0
508-3BR	595-602	4.5	5.0	327	19.2	60	11.7	100.0
508-4BR	595-600	4.5	5.0	327	19.2	60	12.2	100.0
May 9								
509-1BR	593-7	4.3	5.6	325	19.3	60	7.0	100.0
509-2BR	591-2	5.0	5.7	325	19.3	60	10.0	100.0
509-4BR	594	5.0	5.7	312	20.1	60	11.4	100.0
509-6BR	598-603	4.5	5.7	305	20.4	60	11.6	100.0
509-7B	596	5.0	5.6	310	20.2	No Rad.	11.5	100.0
May 10								
510-1B	616-626	4.6	5.8	325	19.1	No Rad.	9.4	100.0
510-3B	621	5.1	5.7	298	19.8	No Rad.	12.3	100.0
510-5B	620	4.6	5.7	298	19.9	No Rad.	13.2	100.0
510-7BR	621	4.7	5.7	330	18.9	60	13.1	100.0
510-9BR	626	4.5	5.8	298	19.8	60	13.1	100.0

TABLE I (Continued)

1957 Date & Run	Temp.	Pressure		S.V.	$\frac{H_2O}{C_4}$	Dose Rate	% Conversion	% of Select.
		H_2O	C_4					
May 13								
513-1BR	616-19	4.0	5.5	291	21.4	60	5.85	89.0
513-3BR	611-13	4.0	5.5	313	19.8	60	13.6	100.0
513-5BR	615-19	4.0	5.7	320	19.5	60	14.0	100.0
513-7B	650	4.0	5.7	317	19.7	No Rad.	16.5	100.0
513-9B	647	4.5	5.7	320	19.5	No Rad.	16.6	100.0
May 14								
514-1B	648-9	4.5	5.7	300	20.9	No Rad.	10.8	100.0
514-3B	642	4.5	5.7	300	20.9	No Rad.	15.8	100.0
514-5B	645-6	4.2	5.7	328	19.0	No Rad.	16.7	100.0
514-7BR	646	4.2	5.7	318	20.0	60	16.0	100.0
514-9BR	5.0	5.7	Chart off rollers					100.0
May 15								
515-1BR	645-50	4.5	5.4	280	22.3	60	9.3	100.0
515-3BR	649	5.0	5.7	334	18.8	60	15.4	100.0
515-5BR	645-54	5.0	5.6	310	20.0	60	12.5	100.0
May 16								
516-1BR	645-55	4.2	5.6	290	21.0	60	11.2	100.0
516-2BR	647-8	4.2	5.6	294	20.6	60	12.3	100.0
516-4BR	648-9	4.2	5.6	318	19.4	60	13.2	100.0
516-6BR	648-50	4.8	5.8	325	19.8	60	13.0	100.0
516-8BR	645-6	5.0	5.8	325	19.8	60	11.6	100.0
May 17								
517-1BR	639-40	4.5	5.8	293	21.8	60	9.4	100.0
517-3BR	638-45	4.5	5.8	304	20.4	60	12.4	100.0
517-5B	642-7	4.6	5.7	313	19.8	No Rad.	13.1	100.0
517-7B	645-6	4.4	5.7	310	20.1	No Rad.	12.9	100.0
517-8B	645-6	4.5	5.7	327	19.1	No Rad.	13.8	100.0
May 20								
520-1B	648-50	4.5	5.0	278	22.8	No Rad.	20.0	100.0
520-3B	643-7	5.5	5.0	297	21.1	No Rad.	18.3	100.0
520-4B	645-8	4.8	5.1	310	20.3	No Rad.	17.0	100.0
520-4B'	650	4.8	5.1	310	20.3	No Rad.	18.0	100.0
May 23								
523-1B	540-60	4.5	6.0	266	23.2	No Rad.	27.1	97.4
523-3B	555-60	4.5	6.5	311	20.0	No Rad.	27.9	97.8
523-5B	545-50	4.5	6.5	295	21.8	No Rad.	28.0	96.0
523-7B	620-25	3.0	6.5	295	21.8	No Rad.	28.4	97.0
523-8B	550-53	3.0	6.5	300	20.8	No Rad.	33.7	97.0
May 28								
528-1BR	475-575	12.0	12.0	273	21.7	60	14.9	80.0

TABLE I (Continued)

1957 Date & Run	Temp.	Pressure		S.V.	$\frac{H_2O}{C_4}$	Dose Rate	% Conversion	% of Select.
		H_2O	C_4					
May 29								
529-1B	520-70	--	--	315	19.9	No Rad.	12.5	61.0
529-2B	565-95	--	--	340	18.4	No Rad.	14.0	~ 5.0
June 5								
605-2B	350-560	5.0	11.5	320	19.6	No Rad.	10.9	-0-
605-3B	550-605	5.0	10.5	310	20.2	No Rad.	18.0	-0-
June 11								
611-1B	630-640	5.5	5.7	400	15.6	No Rad.	24.66	94.5
611-3B	640-660	5.2	5.4	265	25.2	No Rad.	34.05	96.8
611-5BR	570-660	5.5	6.5	291	21.7	300	31.2	92.5
611-6BR	665-695	6.0	6.5	365	17.3	300	36.3	93.5
June 12								
612-1BR	570-660	6.2	6.2	166	~38.0	300	38.4	32.4
612-3BR	612-628	5.5	6.3	370	17.0	300	30.5	31.1
612-5BR	610-650	5.0	--	425	14.8	300	50.0	-0-
612-6BR	630-655	3.2	6.9	386	16.3	300	19.1	62.0
June 13								
612-1B	620-663	6.0	7.6	280	22.4	No Rad.	42.2	91.0
613-3B	635-650	6.0	6.0	361	17.3	No Rad.	31.3	95.2
June 14								
614-2B	641-645	4.1	6.0	308	20.5	No Rad.	23.33	97.2
614-4BR	647-655	4.5	6.1	357	17.7	300	31.45	97.8
614-6BR	652-661	--	--	374	16.9	300	32.25	97.0
614-7BR	646-654	5.2	6.6	323	19.6	300	34.05	98.0
614-9BR	645-652	4.5	6.4	308	20.5	300	29.0	~100.0
614-11BR	650-655	5.0	6.4	287	22.0	300	32.0	~100.0
614-13BR	645-650	4.1	6.4	294	21.5	300	22.3	~100.0
June 17								
617-1BR	615-625	~5.0	--	227	27.8	300	~ 14.1	
617-3BR	646-653	~5.0	--	333	18.9	300	22.66	95.5
617-5BR	646-655	5.0	5.8	335	18.8	300	23.16	95.8
617-7BR	651-657	5.0	6.2	338	18.6	300	20.0	98.0
June 18								
618-1BR	620-30	5.5	6.0	240	26.2	300	14.05	97.4
618-3BR	643-48	6.0	6.3	217	29.1	300	19.7	97.4
618-5BR	640-45	--	--	248	25.4	300	19.36	97.7
618-7BR	645-50	4.5	6.1	298	21.2	300	19.87	97.7
618-8BR	648-54	5.0	6.0	325	19.4	300	19.51	97.7
618-10BR	644-49	5.2	6.1	318	19.8	300	19.89	97.5
618-12B	645-47	5.0	5.5	302	20.8	No Rad.	19.12	97.8

TABLE I (Continued)

1957 Date & Run	Temp.	Pressure		S.V.	$\frac{H_2O}{C_4}$	Dose Rate	% Conversion	% of Select.
		H_2O	C_4					
June 19								
619-1BR	655-60	3.5	6.0	300	21.0	300	16.0	98.5
June 20								
620-1BR	645-49	5.5	7.0	238	26.5	300	13.7	--
620-2BR	645-51	4.5	6.8	304	20.7	300	18.0	--
620-4BR	647-49	4.8	6.9	288	21.8	300	19.3	--
620-5BR	640-50	--	--	300	21.0	300	21.0	--
620-6B	646-49	4.5	6.9	325	19.4	No Rad.	17.4	--
620-8B	637-40	4.5	7.0	311	20.2	No Rad.	16.3	--
June 21								
621-1BR	648-52	~4.5	--	304	20.7	300	< 10.0	--
621-3B	655-57	4.5	--	315	20.0	No Rad.	15.5	~100.0
621-5BR	647-53	4.5	--	307	20.5	300	16.2	
621-7B	648-52	4.5	--	316	19.9	No Rad.	16.9	
621-9BR	644-47	4.2	6.9	317	19.8	300	15.7	
621-10B	635-40	5.0	6.9	390	16.2	No Rad.	14.8	
621-12BR	645-47	4.5	6.9	295	21.3	300	15.2	
621-13B	640-48	5.0	6.9	311	20.2	No Rad.	16.2	

TABLE II

CONDITIONS OF CATALYST USE

Batch No.	Date Charged	Date Discharged	Hours of Radiation		Max. Rep in Air, Thousands	
			During Runs	With Reactor Cold		
1	2-7-57	4-9-57	*			
2	4-10-57	4-22-57				
3	4-22-57	5-23-57				
4	5-24-57	6-6-57				
5	6-7-57	6-12-57	8.25	None	2,500	None
6	6-13-57	Not Removed	34	49	10,000	15,000

* Accurate log of cold reactor irradiation kept only for batches 5 and 6.

5.0 SUMMARY AND CONCLUSIONS

An experimental program was conducted comprising the construction and operation of required pilot plant equipment to investigate the dehydrogenation of butene-2 over Dow Type B catalyst in the presence of gamma radiation.

Measurements of conversion and selectivity to butadiene-1,3 were made, using gas chromatography as the analytical method. Experimental conditions approximated those of the usual industrial process for butadiene-1,3 manufacture. Temperatures were 575-650°C; pressures were 3-5 psig; space velocities were 260-400 standard volumes of butene-2 per hour per volume of catalyst; steam to butene-2 ratios were 14.8 to 29.1; and maximum radiation dose rates were 60,000 or 300,000 rep per hour in air.

Conversions were observed to vary between 5.9 and 51.8% of the butene charged. Usual conversions were in the range of 10-30%. Selectivities were generally in excess of 95%. Lower selectivities were generally accompanied by low conversions, poor temperature control, on occasion by other operating abnormalities, and were considered to provide sufficient reason to replace the catalyst.

Preliminary indications were that exposure to radiation accelerated loss of catalyst activity. However, later work did not support this view.

On the basis of the data available from the experiments conducted under this program, no effect of gamma irradiation could be detected upon the dehydrogenation of butene-2 to butadiene-1,3 over Dow Type B catalyst.

6.0 BIBLIOGRAPHY

1. Harmer, D. E., Private Communication, June, 1957.

2. "Vapor-Liquid Partition Chromatography," The Dow Chemical Company, MLS.55.36, January 26, 1956.