



Reduction of sulfur dioxide to elemental sulfur
by John D Bryan

A THESIS Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree
of Master of Science in Chemical Engineering
Montana State University
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Abstract:

The reduction of sulfur dioxide to elemental sulfur was investigated using coal char and methane as reducing agents. Since high temperatures were required when using coal char, methane was found to be more favorable as the reducing agent.

The reduction of sulfur dioxide with methane (natural gas) was carried out in a fixed-bed catalytic reactor containing 400 grams of alumina catalyst.

The possibility of increasing yields by following the sulfur dioxide-methane reaction with a reaction between the hydrogen sulfide formed and unreacted sulfur dioxide was investigated. The low yields of sulfur that were obtained indicated that sulfur formed in the first reaction was converted to other products and that the second reaction was probably inhibited by certain components of the gas mixture.

It was determined that operating without a preheat increased yields slightly and that the reaction products should be cooled as soon as possible after they have left the catalyst bed.

A temperature gradient was detected throughout the catalyst bed and the influence of this gradient was found to be quite critical. Best results were obtained when the upper portion of the reaction zone was operated as low as possible without dropping the lower portion of the zone below 560°C, the optimum temperature for producing sulfur. It was concluded that with close temperature control, conversions up to 80 percent might be expected with fresh catalyst.

A mole ratio of 3.6 moles of methane per mole of sulfur dioxide and a feed rate of 8 gram-moles of gas mixture per hour per 400 grams of catalyst appeared to be optimum conditions.

The catalyst activity was shown to decrease approximately linearly with respect to the hours the catalyst had been in use.

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John D. Bryan

A THESIS

Submitted to the Graduate Faculty

in

Partial Fulfillment of the Requirements

for the Degree of

Master of Science in Chemical Engineering

at

MONTANA STATE COLLEGE

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July, 1957

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ABSTRACT

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The possibility of increasing yields by following the sulfur dioxide-methane reaction with a reaction between the hydrogen sulfide formed and unreacted sulfur dioxide was investigated. The low yields of sulfur that were obtained indicated that sulfur formed in the first reaction was converted to other products and that the second reaction was probably inhibited by certain components of the gas mixture.

It was determined that operating without a preheat increased yields slightly and that the reaction products should be cooled as soon as possible after they have left the catalyst bed.

A temperature gradient was detected throughout the catalyst bed and the influence of this gradient was found to be quite critical. Best results were obtained when the upper portion of the reaction zone was operated as low as possible without dropping the lower portion of the zone below 560°C, the optimum temperature for producing sulfur. It was concluded that with close temperature control, conversions up to 80 percent might be expected with fresh catalyst.

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The catalyst activity was shown to decrease approximately linearly with respect to the hours the catalyst had been in use.

INTRODUCTION

In recent years a great deal of apprehension has been felt because of the limited amount of sulfur available to the United States. In the early part of the 1950's a serious sulfur shortage was realized and steps were taken to overcome this shortage. Since then, new mines have been discovered, old mines reopened, and more and more by-product sulfur has been produced. At the present time the sulfur shortage is not as pressing as it was, but there is still not an unlimited supply.

At present the main sources of sulfur in the United States are:

1. The Frasch process for recovering sulfur from elemental sulfur deposits.
2. Pyrites which is in general a trade name for iron sulfide minerals containing between 25 and 50 percent sulfur.
3. Sulfates which, although a large potential source, are a costly source.
4. By-product sulfur.

Most experts seem to agree that the Frasch process is about as well developed as it will ever be, so unless new sulfur deposits are found, no increase in the sulfur production can be obtained there.

Pyrites, although still present in large quantities, has the disadvantage of high shipping costs as compared to pure sulfur.

This leaves, then, as the most likely source of additional sulfur reserves, the by-product sulfur. The petroleum industry, in particular, has been producing more and more byproduct sulfur in recent years. This sulfur has been recovered from the hydrogen sulfide present in natural

gas and refinery gases by applying different modifications of the Claus process. Basically, this process involves oxidizing a portion of the hydrogen sulfide to sulfur dioxide, and then reacting the two substances together to form sulfur plus water.

Another large source of by-product sulfur, potentially capable of producing as much as three-fourths of the total sulfur requirements (2), are the stack gases from various smelters in the United States.

Those smelters which are treating sulfide ores for the recovery of metals such as copper, lead, or zinc, produce large quantities of sulfur dioxide. The sulfur dioxide is formed when the sulfide ores are roasted or oxidized to convert the metal sulfide to the metal oxide. In this oxidation process the sulfur from the metal sulfide reacts with excess oxygen to produce sulfur dioxide. The concentration of sulfur dioxide in the various waste gases in a smelter varies, but the introduction in recent years of the Fluosolids roaster is said to produce gases having a higher concentration of sulfur dioxide (2).

The fact that large amounts of sulfur are available in these smelter waste gases, coupled with the fact that the removal of the sulfur from these gases would increase the value of the gases as a fuel and help to alleviate the problem of air pollution, makes these stack gases appear to be an attractive source of sulfur.

The fact that 70 percent of all the sulfur consumed is used in the production of sulfuric acid (5) indicates that it might be more desirable to recover sulfur dioxide from the smelter gases rather than elemental

sulfur. The sulfur dioxide could then be converted to sulfuric acid without going through the oxidation of sulfur. However, the problem of stockpiling and transportation make the production of elemental sulfur from the smelter gases appear attractive. The problem resolves, then, to that of converting the sulfur dioxide in the smelter gases to elemental sulfur.

A review of previous work done on the reduction of sulfur dioxide to form elemental sulfur was made by Davis (3). His survey illustrates that coke, natural gas, and carbon monoxide were used as reduction agents, and that bauxite and vanadium pentoxide were employed as catalysts. In addition to the work reviewed by Davis, a semi-commercial unit to reduce sulfur dioxide has been operated in Garfield, Utah (4). The process involved burning natural gas with air containing 5 to 8 parts by volume of sulfur dioxide at 1250°C. It was shown that natural gas had to be available at 12 cents per thousand cu. ft. for the process to be economically feasible.

The reduction of sulfur dioxide using hydrogen at 300°C over an iron, nickel, or cobalt oxide catalyst has been patented by Boswell (1).

The last known commercial unit to be in operation was at a smelter located at Trail, British Columbia. This unit, with a capacity of 150 tons of sulfur per day, reduced the sulfur dioxide to sulfur over a bed of incandescent coke.

The restriction to date on processes involving the reduction of sulfur dioxide to elemental sulfur has been the cost of the reducing agent.

This report is an investigation of the possibilities of producing elemental sulfur from sulfur dioxide. The use of coal char, which can be obtained cheaper than coke, and natural gas as reducing agents was studied.

EQUIPMENT DESIGN AND CONSTRUCTION

A. Flow Sheet

In order to investigate the reduction of sulfur dioxide using natural gas as the reduction agent, a fixed-bed, catalytic reactor was operated at atmospheric pressure. A block flow diagram of the process is shown in Fig. 1, and a detailed flow sheet of the unit is shown in Fig. 2. Figure 2 illustrates that the sulfur dioxide and natural gas were each metered through orifices and passed to the top of the reactor. The gases were introduced to the mixing section of the reactor, containing alundum balls, and then passed on down over the catalyst bed. The reacted gases from the catalyst bed were carried to a constant-temperature condenser where the sulfur was condensed. The liquid sulfur, together with the remaining gases, passed from the constant-temperature condenser to the bottom of the sulfur receiver where the sulfur solidified and was collected in a cup. The remaining gases were carried through a glass-wool filter to remove any entrained sulfur particles that might have remained, and then passed to a water-cooled condenser where the water vapor was condensed. The remaining gases were then discharged through a vent line to the atmosphere.

Duplicate equipment was provided for all the units which were positioned after the constant temperature condenser in the process. That is, two sulfur receivers and two water condensers were used in such a manner that one set could be used during the line-out period, then the other set could be connected into the process for the actual run.

B. Design and Specifications of Component Parts

Reactor: The reactor, constructed of 2-inch, schedule 40, black-iron pipe, was 27 in. in length and was capped at each end with standard cast iron pipe caps. The thermowell was constructed of $\frac{1}{4}$ -in. standard black-iron pipe, welded closed at the top, which passed through the center of the reactor. A stainless-steel screen was placed near the bottom of the reactor to act as a support for the catalyst bed, and a metal baffle was placed at the top of the reactor to mix the incoming gases and prevent their impinging directly on the top of the thermowell. Details of the construction of the reactor appear in Fig. 3.

Heat was provided to the reactor from three nichrome coils, each of which supplied heat to approximately one-third of the reactor. The resistance of the three coils from top to bottom was 24.5, 20, and 24.5 ohms, respectively.

The nichrome coils, strung with ceramic beads, were wrapped around the reactor over a layer of asbestos tape. The coils were then covered with a second layer of asbestos tape, and the reactor was covered with a layer of 85 percent magnesia. The top cap of the reactor was the only part not insulated. This facilitated more rapid filling and inspection

of the reactor.

Constant-temperature Condenser: The construction of the constant-temperature condenser is illustrated in Fig. 4. The temperature of the condenser was adjusted to condense and maintain the sulfur in a liquid form. The temperature was controlled by boiling an ethylene glycol-water mixture.

The center tube, constructed of $\frac{1}{2}$ -in. thin-wall electrical conduit, was 30 in. in length and was packed with ceramic beads to give a larger heat transfer area for the hot gases. The condenser jacket was constructed of a 26-in. length of 1-in. diameter thin-wall electrical conduit. Heat was provided to boil the ethylene glycol-water mixture by a nichrome coil wound around the lower portion of the condenser. A coolant reservoir was connected to the jacket surrounding the center tube so that the boiling mixture was being constantly circulated. A water-cooled condenser was fastened to the top of the coolant reservoir to condense the vapors formed by the boiling mixture.

Sulfur Receiver: The sulfur receiver was constructed of a 13-in. length of $2\frac{1}{4}$ -in. diameter glass tubing (See Fig. 5). A 9-in. length of 1-in. diameter glass tubing extended from the top of the receiver to carry the gases and sulfur to the lower part of the receiver where a removable aluminum-foil cup collected the sulfur. Glass wool was packed between the two glass tubes to act as a filter for any sulfur particles that might have been entrained in the gases. The top and bottom of the receiver were closed with two large rubber stoppers. The top stopper contained a glass

tube that served as a gas outlet for the sulfur receiver.

Water Condenser: The water condenser was constructed from a 36-in. long water-cooled glass condenser with a 3/8-in. center tube.

Water Receiver: A one-liter Erlenmeyer flask, attached to the bottom of the water condenser, served as a water receiver.

Vent Line: The vent line was $\frac{1}{2}$ -in. saran tubing.

Sulfur Dioxide Feed: Two small steel tanks of about 3000-gm. capacity were used as feed tanks.

Sulfur Dioxide Metering: A glass venturi-type orifice was calibrated and used in conjunction with a water-filled manometer.

Natural Gas Metering: A glass venturi-type orifice was calibrated and used in conjunction with a Bacharach inclined manometer filled with diesel oil.

Sulfur Dioxide Metering Valve: Ideal-Aerosmith needle valve.

Natural Gas Metering Valve: Hoke brass blunt-spindle needle valve.

Autotransformers: One 220-volt and three 110-volt Powerstats.

Thermocouples: Three iron-constantan.

Temperature Indicator: Leeds and Northrup 18-point indicating potentiometer.

PROCEDURE AND MATERIALS

Procedure

Reactor Assembly: The reactor was placed in position and 400 gm. of catalyst were poured in to form as uniform a bed as possible. This resulted in a 12-in. catalyst bed. Alundum balls were added until the

reactor was full, and the baffle plate was placed in position. The top cap was then screwed onto the reactor, feed lines were attached, the thermocouples were connected, and the heating coil leads were plugged in.

The constant-temperature condenser was next connected to the reactor and secured in place. Cooling water lines to the various condensers were then attached.

Start-up: Powerstats for the heating coils of the reactor were adjusted to their proper settings and turned on. The sulfur receiver and water receiver to be used in the run were weighed, the weights were recorded, and the receivers were placed in position. Cooling water to the condensers was turned on and all lines were checked for leaks.

The reactor was heated to temperature for a three- to four-hour period, then the natural gas flow was started. A 5-liter beaker, filled with hot water to prevent water from condensing in the sulfur receiver was placed around the sulfur receiver and an electric hot-plate was placed under the beaker to keep the water boiling. The constant-temperature condenser was brought to temperature.

When the temperatures in the reactor reached a point about 20°C below the desired temperatures, the sulfur dioxide flow was started. It was determined that the temperatures in the catalyst bed would rise about 20°C after the reaction started.

Operation: Temperatures were controlled by adjusting the power input to the heating coils with the powerstats. Natural gas and sulfur dioxide flow rates were controlled by maintaining the desired manometer

readings for each. In addition, the sulfur dioxide feed bottle was weighed before and after each run to check the amount of sulfur dioxide used in each run. When the line-out period was completed, the duplicate sulfur receiver, water condenser, and sulfur dioxide feed bottle were turned on stream and readings were recorded at 10-min. intervals until the run was completed.

Shut-down: To complete a run the sulfur dioxide flow was stopped, and power to the reactor coils, constant-temperature condenser coil, and the hot-water bath was turned off. The natural gas was left flowing for a short period to flush the system and then turned off. The sulfur dioxide tank was weighed and the amount used during the run was obtained by difference. The sulfur receiver was weighed and the amount of sulfur formed was also obtained by the difference in weight.

Materials

The sulfur dioxide used was commercial grade, obtained from the Matheson Company of Joliet, Illinois.

Natural gas containing 91 percent methane, 6 percent ethane, and 3 percent propane was obtained from the lines of the local utility company.

One-eighth-inch extruded activated alumina catalyst manufactured by the Harshaw Chemical Company was used in this work.

One-fourth-inch alundum balls were used as packing in the mixing section of the reactor.

One-fourth-inch ceramic beads were used for packing in the constant-temperature condenser.

DISCUSSION OF RESULTS

Reduction of Sulfur Dioxide Using Char as the Reducing Agent.

In order to investigate the formation of sulfur from sulfur dioxide some work was done using coal char as a reducing agent. Since the thermodynamics of several postulated reactions between sulfur dioxide and coal char (carbon) to form sulfur indicated the results could be favorable (See Table I), several experimental runs were made.

The reactor was charged with coal char and runs were made using both sulfur dioxide and a methane-sulfur dioxide mixture. An attempt was made to make the runs at 600°C, the highest temperature it was felt the equipment could withstand for any extended period of time. When the methane-sulfur dioxide mixture was passed over char at temperatures between 565°C and 594°C, no sulfur was recovered. When only sulfur dioxide was passed over the char bed, small amounts of sulfur were recovered. With a temperature of 595°C and a feed rate of 2.54 moles of sulfur dioxide per hour, a 14.8 percent yield of sulfur was obtained and when a temperature of 593°C and a feed rate of 1.97 moles of sulfur dioxide were used, a 14.3 percent yield of sulfur was obtained. The thermodynamic calculations indicated that higher temperatures would result in better conversion to sulfur, but it was felt that the high cost of building high-temperature equipment was not warranted.

The possibility of passing sulfur dioxide through a fluidized bed of char was also investigated. By carrying out the reduction of sulfur dioxide in a fluidized char bed, the inherent advantages of a fluidized bed,

good mixing and temperature control, could be realized. Work was done to investigate the fluidization characteristics of char using four different mixtures of char sized between 20 and 100 mesh (Table II). Although the mixture having the smallest particle size could be fluidized, the coal char did not exhibit good fluidization properties. There was a marked tendency for slugging to occur, and under no conditions was it possible to obtain a good fluid condition.

In view of the poor fluidization characteristics of the coal char and the high temperatures that were indicated to be necessary when using a fixed char bed, it was felt that char did not appear as favorable as natural gas as a reducing agent. Therefore, the investigation was diverted to get more complete information on the reduction of sulfur dioxide with natural gas.

Reduction of Sulfur Dioxide Using Methane as the Reducing Agent.

A. Two Reaction Zones in Series:

Previous work carried out by Davis (3) indicated that sulfur could be obtained by reducing sulfur dioxide with methane. In view of the fact that hydrogen sulfide as well as sulfur is formed in this reaction, it was proposed to increase the sulfur yield by reacting the hydrogen sulfide with unreacted sulfur dioxide in a second reaction zone. A series of runs was set up to carry out these two reactions in series. The first runs were made with two catalyst beds in series in one reactor. Later runs were made carrying the two reactions out in series but in separate reactors.

An attempt was made to hold the temperature of the first reaction zone in the range of 550°C and that of the second reaction zone at 350°C . Previous work done by Davis (3) had indicated that the reaction between sulfur dioxide and methane at 550°C resulted in a 53 percent yield of sulfur and also resulted in an off-gas containing hydrogen sulfide and sulfur dioxide in a ratio of 2 to 1, which is what is required for the reaction between hydrogen sulfide and sulfur dioxide to form sulfur. A temperature of 350°C was chosen as the temperature of the second reaction zone since the reaction is carried out commercially at approximately that temperature.

The attempt to run the two reactions -- methane with sulfur dioxide and hydrogen sulfide with sulfur dioxide -- in one reactor was unsuccessful since the length of the reactor and arrangement of the heating coils prevented the attainment of the desired temperatures in the two reaction zones. When the catalyst beds were positioned in separate reactors and the temperatures of the two reaction zones held at 553°C and 378°C , respectively, only a 2.4 percent yield of sulfur was obtained. Since both of the reactions under consideration were known to produce sulfur, this low yield indicated that the second reaction, that between hydrogen sulfide and sulfur dioxide, was probably being inhibited by one or more of the other components of the gas mixture. It further indicated that there was some conversion of the sulfur formed in the first reaction to other products, and this was later substantiated by the results of a study made on catalyst bed position.

B. Catalyst Bed Position and Preheat Temperatures.

In the work carried out with two reaction zones, the possibility of sulfur being converted to other products after leaving the catalyst bed was recognized. A series of runs was undertaken in which a single catalyst bed was moved to various positions in the reactor to determine the effect of the bed position in the reactor. Since the study of bed position indicated sharply decreasing yields as the bed was moved upward in the reactor (Table III and Fig. 6), it became necessary to determine whether the decreased yields were due to the shorter preheat section which resulted as the catalyst bed was moved upward or from a conversion of the sulfur to other products occurring in the packed zone below the bed. A series of runs was then made to determine the effect of preheat on the sulfur recovery.

Figure 7 and Table IV illustrate that when the catalyst bed was at the bottom of the reactor, the conversion to sulfur increased slightly as the preheat was decreased. When operating with a preheat of 523°C, a sulfur yield of 50.4 percent was obtained. When the coil supplying heat to the preheat section was shut off, the temperature in the preheat section dropped to 228°C and a sulfur yield of 65.3 percent was obtained. Although a slight increase in yield seems to be indicated when the reaction is carried out without a preheat section, the preheat section seems to have little effect on the sulfur recovery other than to insure that the incoming gases were thoroughly mixed when they reached the catalyst bed. The results of this preheat

study coupled with the results of the study on catalyst bed position lead to the conclusion that there must have been a conversion of sulfur to other products, and that the reaction products should be removed from the reactor and cooled as soon as possible after they are formed.

C. Temperature

Following the study on preheat, a series of runs was made with the coil on the preheat section turned off, in order to determine the effect of reaction temperature on the sulfur yield. The results appear in Table V and are graphically illustrated in Fig. 8. A maximum conversion of about 65 percent was obtained at an average bed temperature of 546°C . This conversion was only three percent higher than that reported by Davis (3), but the temperature at which the maximum sulfur yield occurred was 17°C lower than he reported. This deviation in optimum temperatures led to an investigation of temperature gradient throughout the catalyst bed.

Up to this point in the investigation the average temperature in the catalyst bed had been determined by using two thermocouples spaced at about 4-in. intervals in a 12-in. catalyst bed. In order to study more thoroughly the temperature gradient, a third thermocouple was inserted into the bed and the three thermocouples were spaced at about 3-in. intervals. Under this arrangement it became evident that the temperature in the central portion of the catalyst bed was higher than at either end. A temperature gradient of this

type is quite common with exothermic reactions. In view of this temperature gradient it is apparent that the temperature of 546°C found to be the optimum in Fig. 8 was not the true average, and the actual temperature was higher than that being measured. There is a possibility that the optimum temperature, 563°C , reported by Davis (3) was nearly correct since he was operating with preheat temperatures of about 510°C . This preheat would probably move the high-temperature spot up the reaction zone and into the vicinity of the point where he was actually measuring the temperature. When operating without the preheat, however, the maximum temperature occurred below the first thermocouple and was not detected by the thermocouple.

A more intensive examination of how temperature gradients across the catalyst bed might influence sulfur yields was next undertaken. Before making this study, however, the unit was revised to allow for a line-out period prior to the actual run. Previously, the erratic line-out period had been an integral part of the run, and in runs of short duration the error introduced by not having steady-state conditions throughout the run could be of considerable magnitude.

Data for the runs carried out during the temperature-gradient study are shown in Table VI. For this discussion the temperatures as measured by the top, middle, and bottom thermocouples will be referred to as T_1 , T_2 , and T_3 , respectively. The data in Table VI

indicate a trend toward an increase in sulfur recovery if the temperature in the upper part of the reaction zone is held down and that in the lower portion held in the region of 560°C . Figure 9 indicates the relationship between the sulfur yield and the temperature of the lower part of the reaction zone when T_1 was held between 525°C and 531°C . It illustrates that the conversion to sulfur increased from about 64 percent to 81 percent as the average of T_2 and T_3 increased from 535°C to 560°C . Figure 10, a similar plot, shows that when T_1 was held between 533°C and 540°C , the conversion to sulfur began to decrease when the average of T_2 and T_3 exceeded 560°C . Figure 11 shows percentage conversion versus T_1 with the average of T_2 and T_3 held between 557°C and 565°C . It indicates that the sulfur recovery can be increased by lowering T_1 .

There is a limit, however, to how low the temperature in the upper portion of the bed can be reduced without also reducing the temperature in the remaining part of the bed below the desired temperature. With the reactor used in this study, this limit was about 525°C . When T_1 was reduced below 525°C , the sulfur yields decreased, but this decrease in yield can be attributed to reduced temperatures throughout the entire reaction zone. The influence of temperature appears to be quite critical on the conversion to sulfur. Since precise temperature control of the various zones was difficult, some of the difficulties in reproducing results can probably be accounted for by this critical effect of temperature.

The overall picture that results from this study indicates that temperatures in the range of 560°C are most favorable for the maximum conversion to sulfur.

Figure 12 shows the overall average temperature of the reaction bed versus the conversion to sulfur, and includes all the runs listed in Table VI. The optimum temperature for conversion to sulfur is indicated to be 549°C . Much of the variation in sulfur yields can be accounted for by the different temperature distributions that resulted in similar average temperatures. Figures 13 and 14 are the same as Fig. 12 with the exception that they use T_2 and the average of T_2 and T_3 , respectively, in place of the overall average temperature. Either of these curves probably gives a better picture of the actual optimum temperature. In both cases this optimum falls in the region of 560°C . It appears reasonable to assume from this study that single-pass yields up to 80 percent might be expected with very close temperature control.

It should be pointed out that the conversion of 70 to 80 percent which were obtained consistently in this investigation are 10 to 20 percent higher than those reported by Davis. Most of this increase can be attributed to closer temperature control and removal of the erratic line-out period from the actual run.

D. Feed Rate

The influence of the feed rate to the reactor is illustrated in Fig. 15 and Table VII. The maximum conversion to sulfur, 78

percent, was obtained at about 8 gram-moles of feed per hour. The conversion is shown to have dropped to 60 percent at 10 gram-moles per hour and to 32 percent at 6 gram-moles per hour. A more extensive study of this particular variable would be desirable to define more clearly the influence of feed rate on the conversion of sulfur dioxide to sulfur.

E. Mole Ratio

The data appearing in Table VIII, when presented graphically in Fig. 16, illustrates the influence of the mole ratio of methane to sulfur dioxide on the sulfur recovery. A ratio of 3.7 moles of methane to one mole of sulfur dioxide is seen to have given a maximum percentage conversion to sulfur of 74 percent. In the range of the operating conditions that were studied, the effect of mole ratio on the reduction to sulfur seems to be less than that of temperature and feed rate. The sulfur recovery is shown to decrease to 54 percent at a mole ratio of methane to sulfur dioxide of 2, and to decrease to 66 percent at a ratio of 5 moles of methane to 1 mole of sulfur dioxide.

F. Catalyst Activity

In the course of these investigations a decrease in the maximum conversion to sulfur was observed. This decrease was found to be due to a loss of catalyst activity. The rate of loss of catalyst activity is shown in Fig. 17 which was plotted using the data in Table IX.

If the assumption is made that Fig. 17 illustrates a linear relationship between catalyst activity and the hours the catalyst had been in use, the method of least squares can be used to fit a linear equation to this data. This results in the equation

$$y = 74.7 - 0.116x$$

where

y = percentage conversion to sulfur, and

x = hours that the catalyst had been in use.

Examination of this expression leads to the conclusion that for every 10 hours the catalyst was used, the reduction to sulfur was decreased by 1.16 percent. It is further illustrated that a maximum conversion to sulfur of 74.7 percent can be expected with fresh catalyst. The data used to develop this expression were taken from runs made at similar average temperatures, mole ratios, and feed rates. Since the average temperatures were not all obtained under what appears to be the optimum temperature distribution throughout the catalyst bed, and since these runs were taken from a long series of runs made at a great variety of conditions, it should be pointed out that this expression does have limitations.

It does offer an indication of how catalyst life influences the conversion to sulfur, however, and in an attempt to present the results on a more comparable basis, the slope of the equation was used to correct some of the conversions obtained in this study to the conversions that would theoretically have been obtained if the

catalyst had been used zero hours. Figures 9 through 16 were all plotted using these corrected values for conversion of sulfur dioxide to sulfur.

SUMMARY

Coal char was investigated as a reducing agent for sulfur dioxide. Several runs were made over a fixed bed of char, and work was done to determine the fluidization characteristics of char. Since high temperatures were indicated to be required when using a fixed bed, and since the char seemed to have poor fluidization characteristics, natural gas appeared to be more favorable than char as a reducing agent.

The work done on carrying out two reactions, a reaction between methane and sulfur dioxide followed by a reaction between hydrogen sulfide and unreacted sulfur dioxide, in series, resulted in very small sulfur yields. These low yields indicated that the sulfur formed in the first reaction was being converted to other products and that the second reaction, that between hydrogen sulfide and sulfur dioxide, was probably inhibited by the other components in the mixture of gases.

It was determined that yields dropped sharply when the catalyst bed was moved up the reactor. Since the effect of removing preheat increased the yield slightly, the decrease in yields as the catalyst bed was moved up was attributed to a conversion of sulfur to other products in the packed zone below the catalyst bed. It was concluded that the reaction products should be cooled as soon as possible after they leave the catalyst bed.

The influence of temperature on the conversion to sulfur when operating without preheat was investigated. The initial results led to an investigation of a possible temperature gradient through the catalyst bed. With the addition of a third thermocouple into the catalyst bed it was determined that the central part of the reaction zone was at a higher temperature than either end. The erratic line-out period was removed from the actual run and an intensive study was undertaken to determine how the temperature gradient influenced the sulfur yields.

The influence of temperature was found to be quite critical, and best results were obtained when the upper part of the reaction zone was operated as low as possible consistent with maintaining the lower portion of the zone at about 560°C . It was concluded that with close temperature control and the removal of the line-out period from the actual run, sulfur recoveries up to 80 percent might be expected when using fresh catalyst.

The optimum feed rate seemed to be at 8 gram-moles of feed per hour when using 400 gm of catalyst. More data would have been desirable, however, to fix more accurately the feed rate.

The mole ratio of the reactants appeared to have less influence on the sulfur recovery than either temperature or feed rate, but a maximum sulfur conversion was obtained at a mole ratio of 3.7 moles of methane to 1 mole of sulfur dioxide.

The catalyst activity was shown to decrease approximately linearly with respect to time. When a linear relationship was assumed, an ex-

pression was developed which approximated this decrease in conversion to sulfur due to loss of catalyst activity as being 1.16 percent for each 10 hours the catalyst was in use.

ACKNOWLEDGMENT

The author wishes to thank the Engineering Experiment Station at Montana State College for sponsoring this research project, and Professors H. A. Saner, Lloyd Berg, and R. L. Nickelson for their suggestions and criticisms.

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APPENDIX

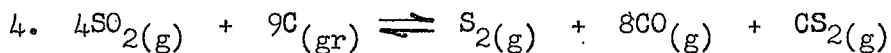
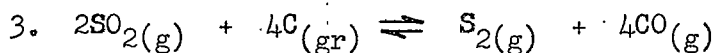
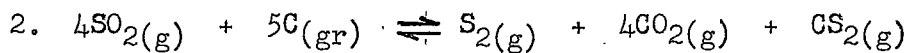
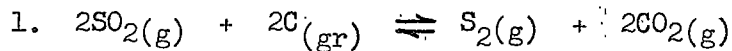
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THERMODYNAMIC INVESTIGATION OF COAL CHAR AS REDUCING AGENT

The following four reactions were postulated as possible mechanisms in the reduction of sulfur dioxide to sulfur using coal char (considered to be graphite carbon) as the reducing agent:



The results of the thermodynamic calculations in investigating these reactions appear in Table I. All values for the equilibrium constants were calculated at 500°C.

TABLE I

Reaction	ΔF_{298} (cal/mole)	Temperature of Neutral Equilibrium (°K)	K_{eq}
1	-25,540	-435	8.9×10^{11}
2	-54,170	-464	7.95×10^{24}
3	31,500	563	1.26×10^7
4	59,830	549	1.26×10^{15}

TABLE II

Particle Size of Samples Used in Fluidization Tests

<u>Sample No.</u>	<u>Screen Mesh</u>	<u>Weight Fraction Retained</u>
1	- 20 + 28	0.10
	- 28 + 35	0.60
	- 35 + 48	0.15
	- 48 + 65	0.05
	- 65 +100	0.05
	-100	0.05
2	- 20 + 28	0.10
	- 28 + 35	0.50
	- 35 + 48	0.20
	- 48 + 65	0.10
	- 65 +100	0.05
	-100	0.05
3	- 20 + 28	0.15
	- 28 + 35	0.40
	- 35 + 48	0.20
	- 48 + 65	0.10
	- 65 +100	0.10
	-100	0.05
4	- 20 + 28	0.05
	- 28 + 35	0.40
	- 35 + 48	0.30
	- 48 + 65	0.10
	- 65 +100	0.10
	-100	0.05

TABLE III

Effect of Bed Position on Sulfur Recovery

Run No.	Average Temp. °C	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	Inches From Reactor Bottom to Catalyst Bed	% SO_2 Converted to S
BP - 1	548	3.57	1.75	8.01	0	50.40
BP - 2	540	3.68	1.70	7.96	5	41.60
BP - 3	535	3.64	1.72	7.98	5	37.60
BP - 4	544	3.58	1.75	8.01	10	5.95
BP - 5	536	3.70	1.69	7.95	10	0.62
BP - 6	540	3.62	1.73	7.99	2	51.20

TABLE IV

Effect of Preheat on Sulfur Recovery

Run No.	Ave. Temp. °C	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	Preheat Temperature °C	% SO_2 Converted to S
BP - 1	548	3.57	1.75	8.01	523	50.4
Pr - 1	550	3.70	1.69	7.95	476	64.0
Pr - 2	550	3.60	1.74	8.00	425	62.0
Pr - 3	550	3.50	1.79	8.05	349	58.0
Pr - 4	550	3.41	1.84	8.10	255	64.0
Pr - 5	547	3.60	1.74	8.00	228	65.3

TABLE V

Effect of Temperature on Sulfur Recovery

(Temperatures read with two thermocouples)

Run No.	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	Ave. Temp. $^{\circ}\text{C}$	% SO_2 Converted to S
TA - 1	3.54	1.77	8.03	563	20.65
TA - 2	3.57	1.75	8.01	527	54.00
TA - 3	3.55	1.76	8.02	540	62.50
TA - 4	3.44	1.82	8.08	556	37.10
TA - 5	3.52	1.78	8.04	518	52.50
TA - 6	3.57	1.76	8.02	555	44.00
TA - 7	3.60	1.74	8.00	552	55.70
Pr - 5	3.60	1.74	8.00	547	65.30

TABLE VI

Effect of Temperature Gradient on Sulfur Recovery

(Temperatures read with three thermocouples)

Run No.	Mole Ratio CH_4/SO_2	Moles SO_2 per hr. ²	Total gram-moles per hr.	T ₁ ¹	T ₂	T ₃	Average T ₁ , T ₂ , T ₃	Average T ₂ , T ₃	% SO_2 Converted to S	Hrs. on Catalyst	% ² Conversion (corrected)
TB - 1	4.05	1.55	7.81	536	555	549	547	552	73.5	3.5	73.9
TB - 2	3.67	1.71	7.97	540	560	555	552	557	73.0	7.0	73.8
TB - 3	3.80	1.65	7.91	524	550	551	541	551	62.2	10.5	63.4
TB - 4	3.79	1.65	7.91	515	536	530	527	533	41.7	14.0	43.3
TB - 5	3.58	1.75	8.01	536	566	564	555	565	47.1	17.5	49.1
TB - 6	3.48	1.80	8.06	545	568	562	558	565	67.6	21.0	70.0
TB - 7	3.51	1.79	8.05	526	545	535	535	540	67.0	24.5	69.9
TB - 8	3.75	1.67	7.93	539	570	570	560	570	67.2	28.0	70.5
TB - 9	3.71	1.69	7.96	530	561	558	550	560	77.5	31.5	81.2
TB - 10	3.47	1.81	8.07	520	543	536	533	540	60.6	35.0	64.7
TB - 11	3.62	1.73	7.99	535	566	564	555	565	69.5	38.5	74.0
TB - 12	3.59	1.75	8.01	525	552	539	535	545	63.1	45.5	68.4
TB - 13	3.68	1.70	7.96	531	562	548	547	555	70.7	49.0	76.4
TB - 14	3.82	1.64	7.90	548	573	545	555	559	66.5	52.5	72.6
TB - 15	3.60	1.74	8.00	492	515	492	500	504	33.7	56.0	40.2
TB - 16	3.56	1.76	8.02	526	549	521	532	535	57.7	59.5	64.6
TB - 17	3.71	1.69	7.95	533	556	528	539	542	62.2	63.0	69.5
FR - 6	3.48	1.80	8.06	524	564	558	549	561	68.7	86.0	78.7
MR - 8	3.76	1.66	7.92	535	560	556	550	558	62.1	115.5	75.5

¹ T₁, T₂, and T₃ are the temperatures in °C at the top, middle, and bottom of the catalyst bed, respectively.

² See Section F, Catalyst Activity, under Discussion of Results, page 21.

TABLE VII

Effect of Feed Rate on Sulfur Recovery

Run No.	Ave. Temp. °C.	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	% SO_2 Converted to S	Hrs. on Catalyst	% Conversion (corrected)
FR - 1	544	3.84	2.04	9.865	58.4	68.5	66.4
FR - 2	554	3.63	2.16	9.980	53.4	71.0	61.7
FR - 3	548	3.18	1.48	6.180	39.6	75.0	48.2
FR - 4	551	3.46	1.36	6.060	15.3	78.0	24.4
FR - 5	547	3.78	2.07	9.895	49.6	80.5	59.0
FR - 6	549	3.48	1.80	8.060	68.7	86.0	78.7
TB -13	547	3.68	1.70	7.960	70.7	49.0	76.4

TABLE VIII

Effect of Mole Ratio on Sulfur Recovery

Run No.	Ave. Temp. °C.	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	% SO_2 Converted to S	Hrs. on Catalyst	% Conversion (corrected)
MR - 1	546	4.51	1.42	7.95	55.6	91.5	66.2
MR - 2	550	2.67	2.14	7.85	47.6	94.0	58.5
MR - 3	547	4.86	1.37	8.03	58.6	96.5	69.8
MR - 4	547	5.19	1.28	7.94	52.8	99.0	64.3
MR - 5	546	2.16	2.48	7.82	51.3	101.0	63.0
MR - 6	545	3.65	1.72	7.98	58.4	110.0	71.2
MR - 7	553	2.14	2.49	7.83	45.2	112.5	58.3
MR - 8	550	3.76	1.66	7.92	62.1	115.5	75.5

TABLE IX

Effect of Catalyst Activity on Sulfur Recovery

Run No.	Ave. Temp. °C.	Mole Ratio CH_4/SO_2	Moles SO_2 per hr.	Total gram-moles per hr.	% SO_2 Converted to S	Hrs. on Catalyst
TB - 2	552	3.67	1.71	7.97	73.0	7.0
TB - 8	560	3.75	1.67	7.93	67.2	28.0
TB - 9	550	3.71	1.70	7.96	77.5	31.5
TB - 11	555	3.62	1.73	7.99	69.5	38.5
TB - 14	555	3.82	1.64	7.90	66.5	52.5
FR - 6	549	3.48	1.80	8.06	68.7	86.0
MR - 6	545	3.65	1.72	7.98	58.4	110.0
MR - 8	550	3.76	1.66	7.92	62.1	115.5

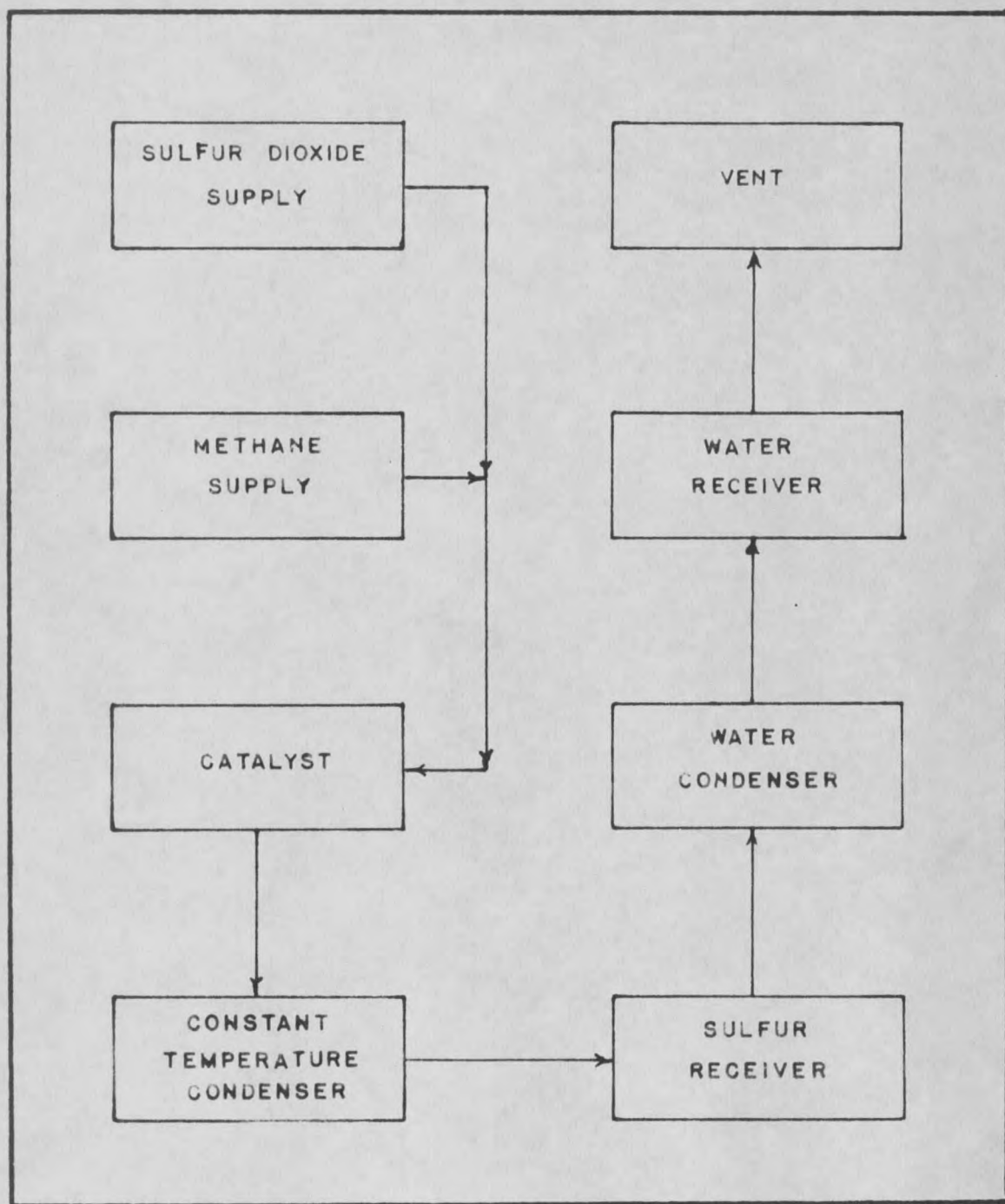


FIG.1 BLOCK FLOW DIAGRAM

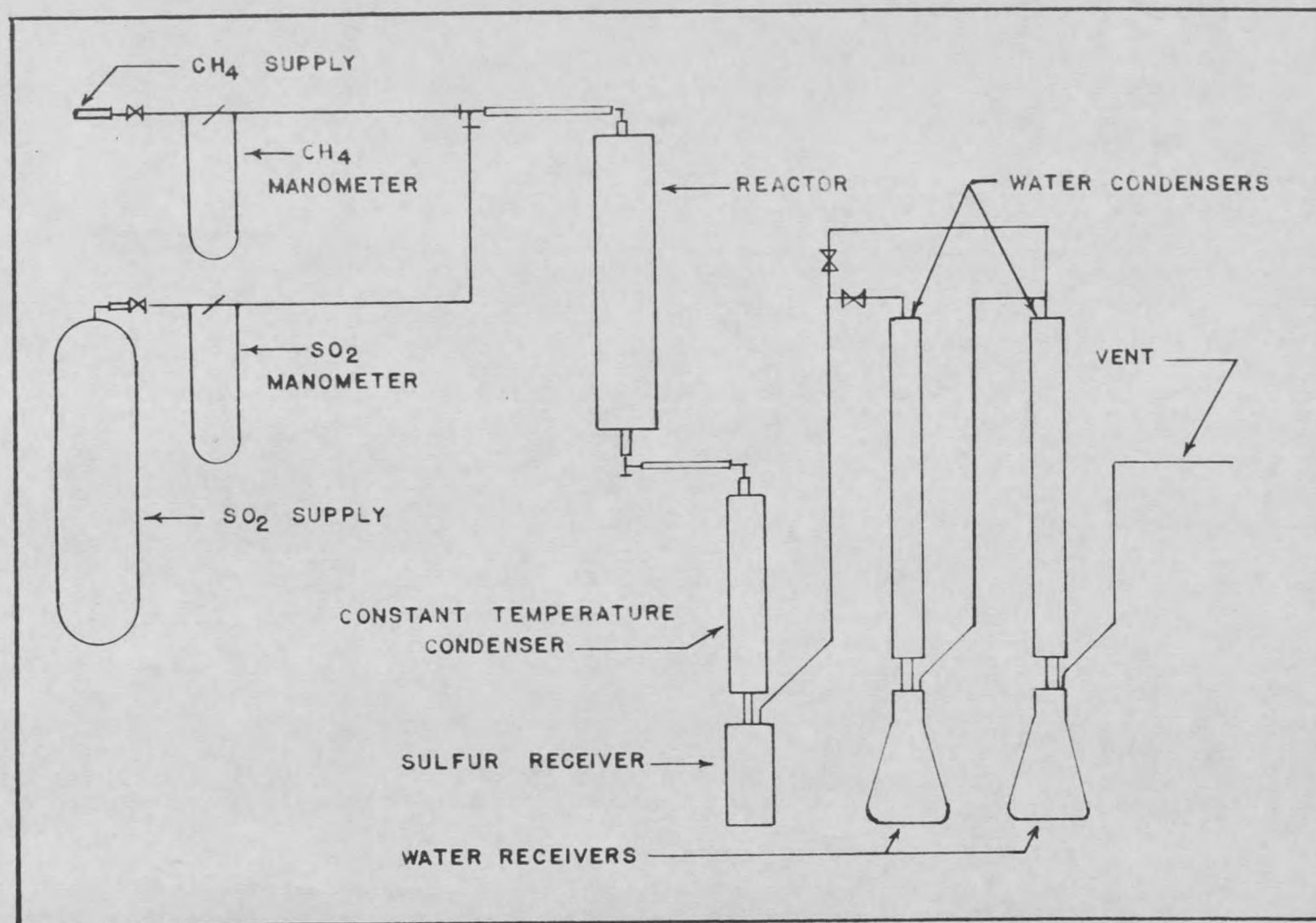


FIG 2 DIAGRAM OF SULFUR DIOXIDE REDUCTION UNIT

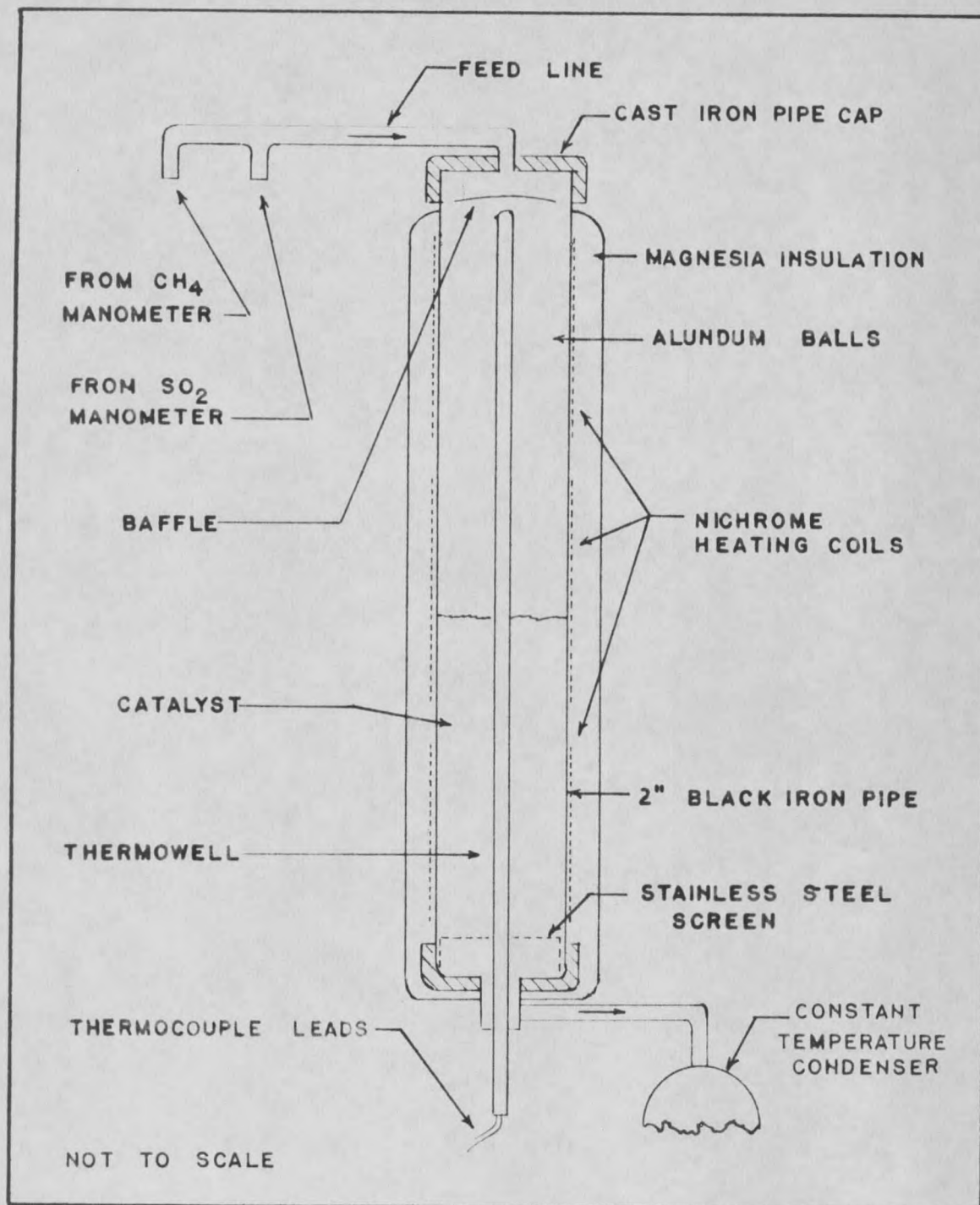


FIG 3 DIAGRAM OF REACTOR

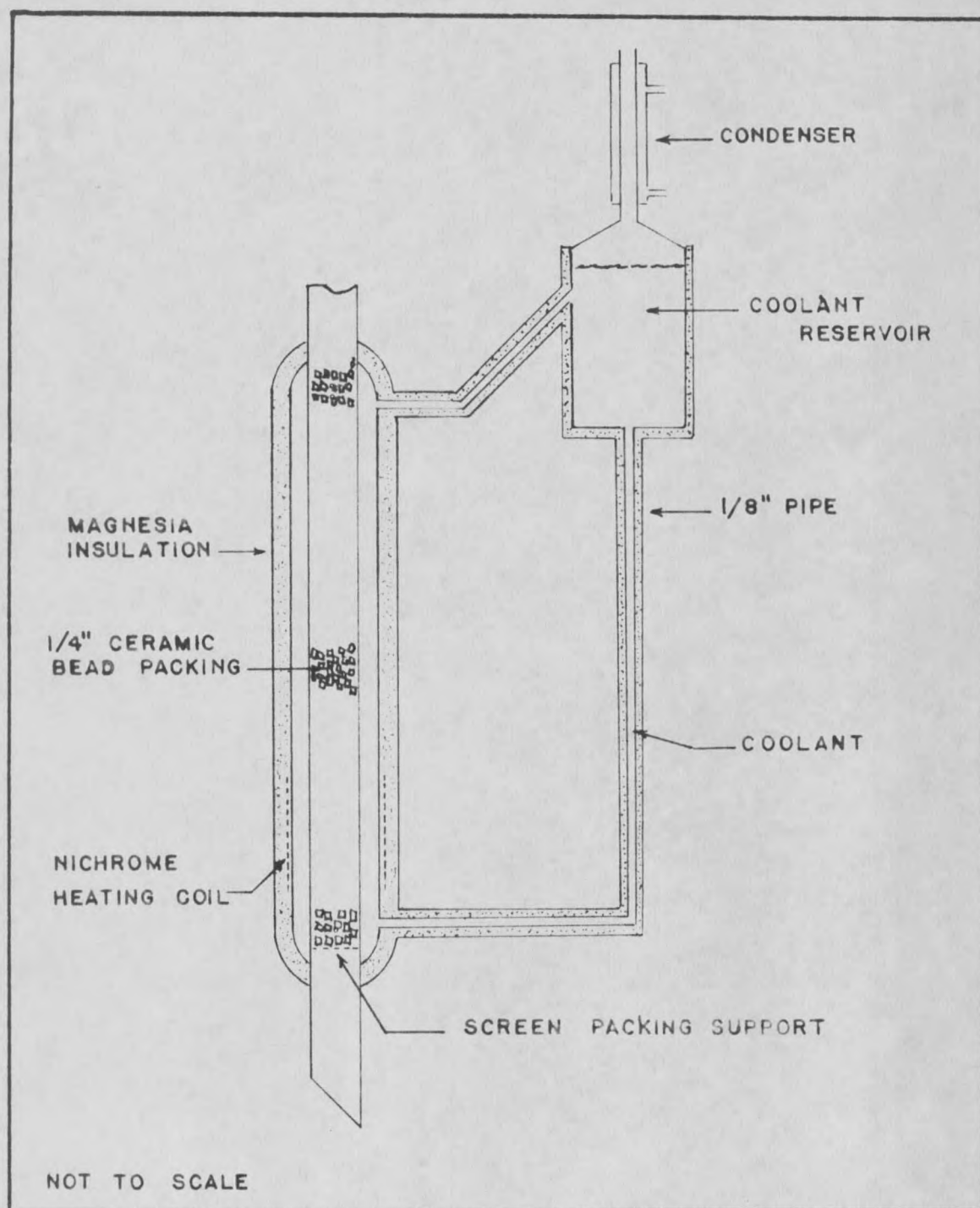


FIG 4 DIAGRAM OF CONSTANT-TEMPERATURE CONDENSER

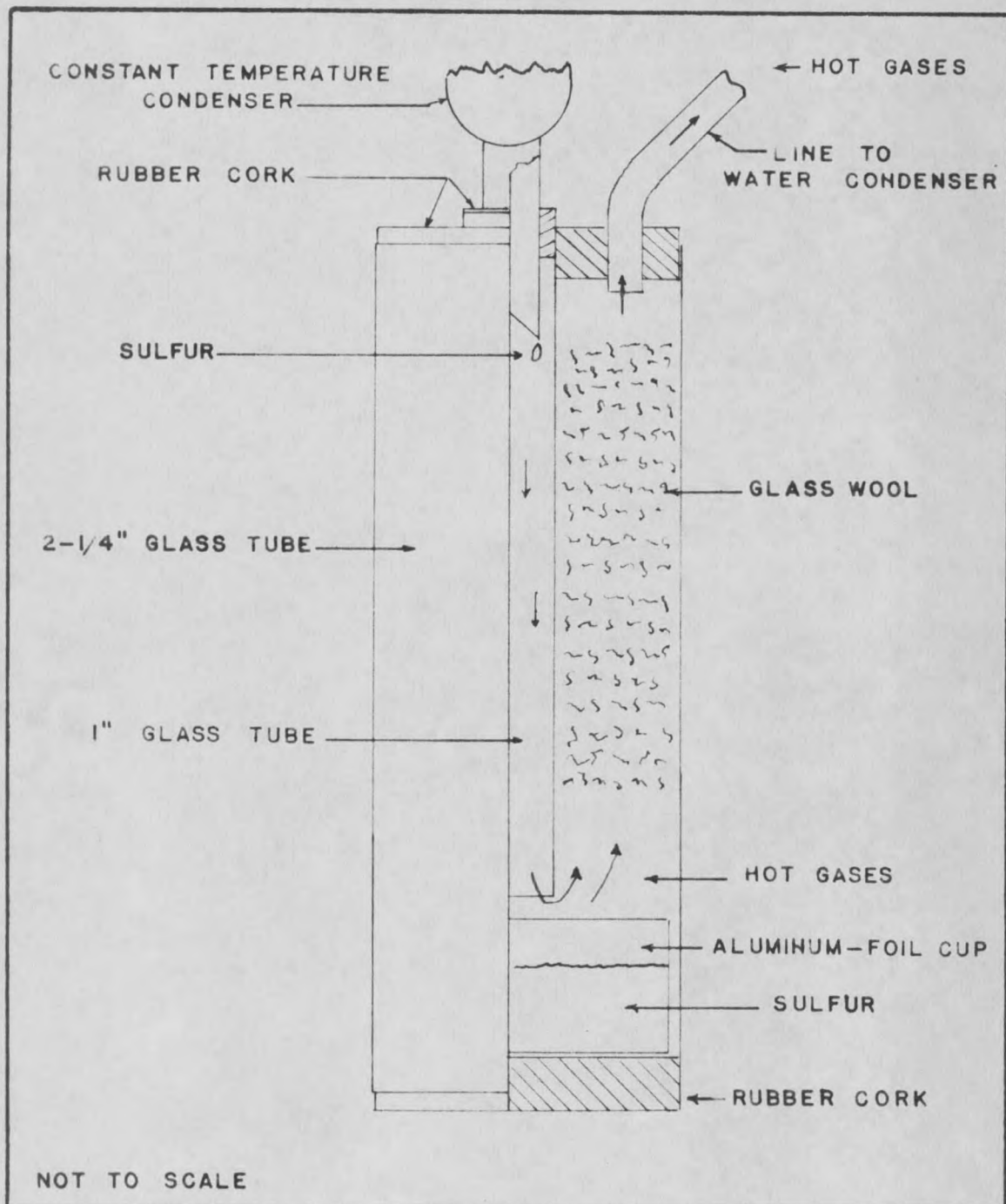


FIG 5 DIAGRAM OF SULFUR RECEIVER

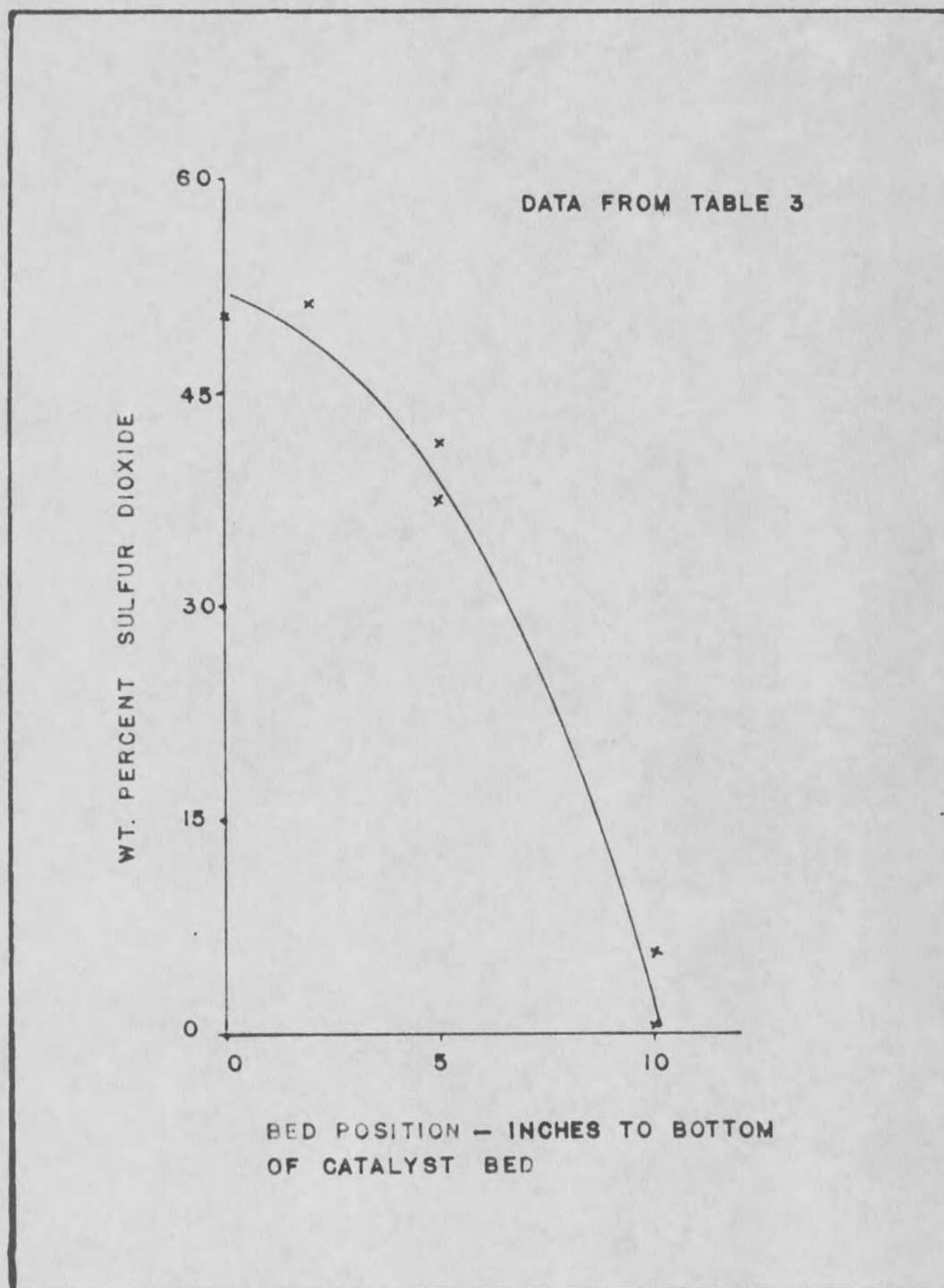
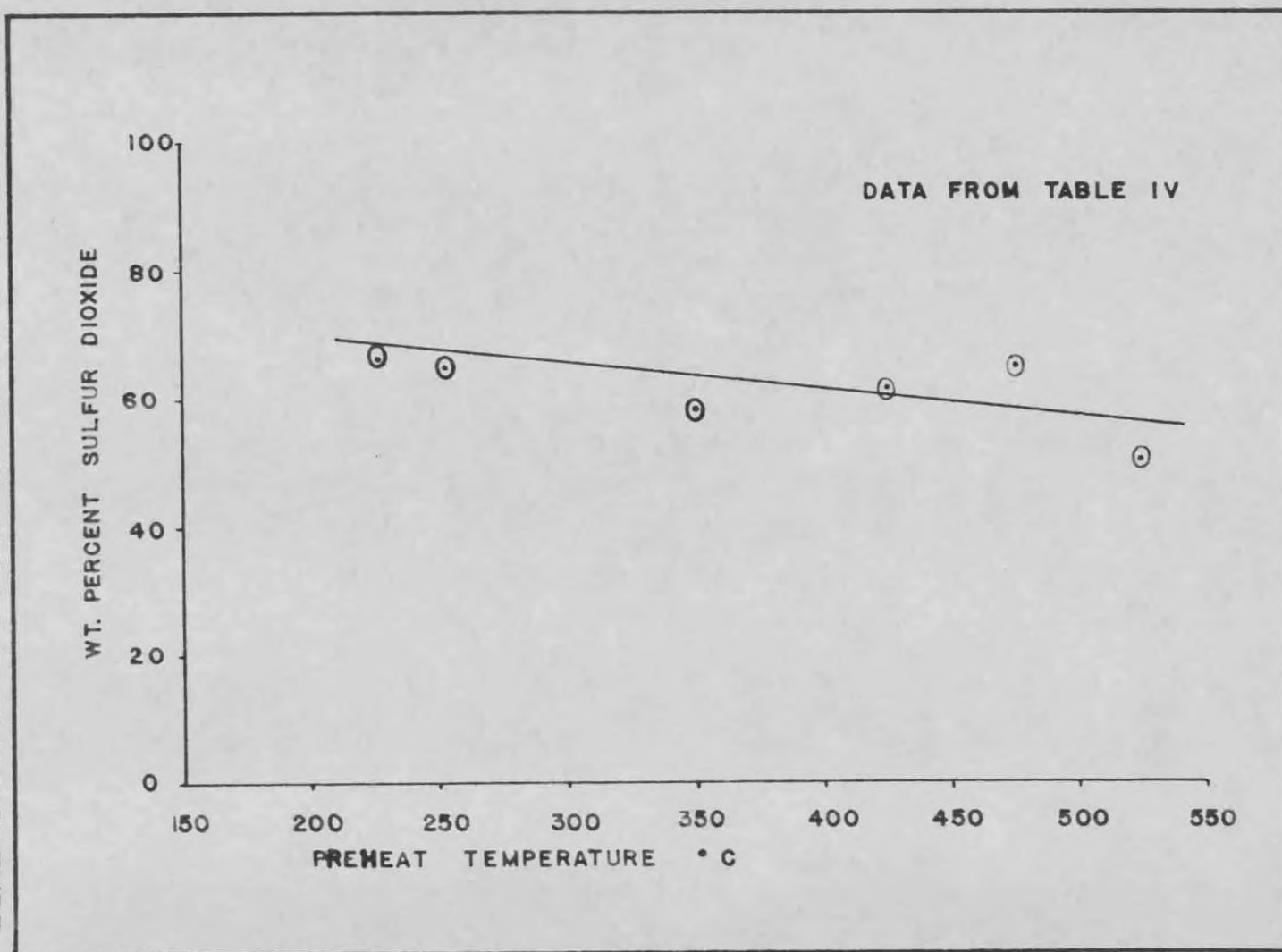


FIG 6 PERCENT YIELD VS BED POSITION

FIG 7 PERCENT YIELD VS PREHEAT TEMPERATURE



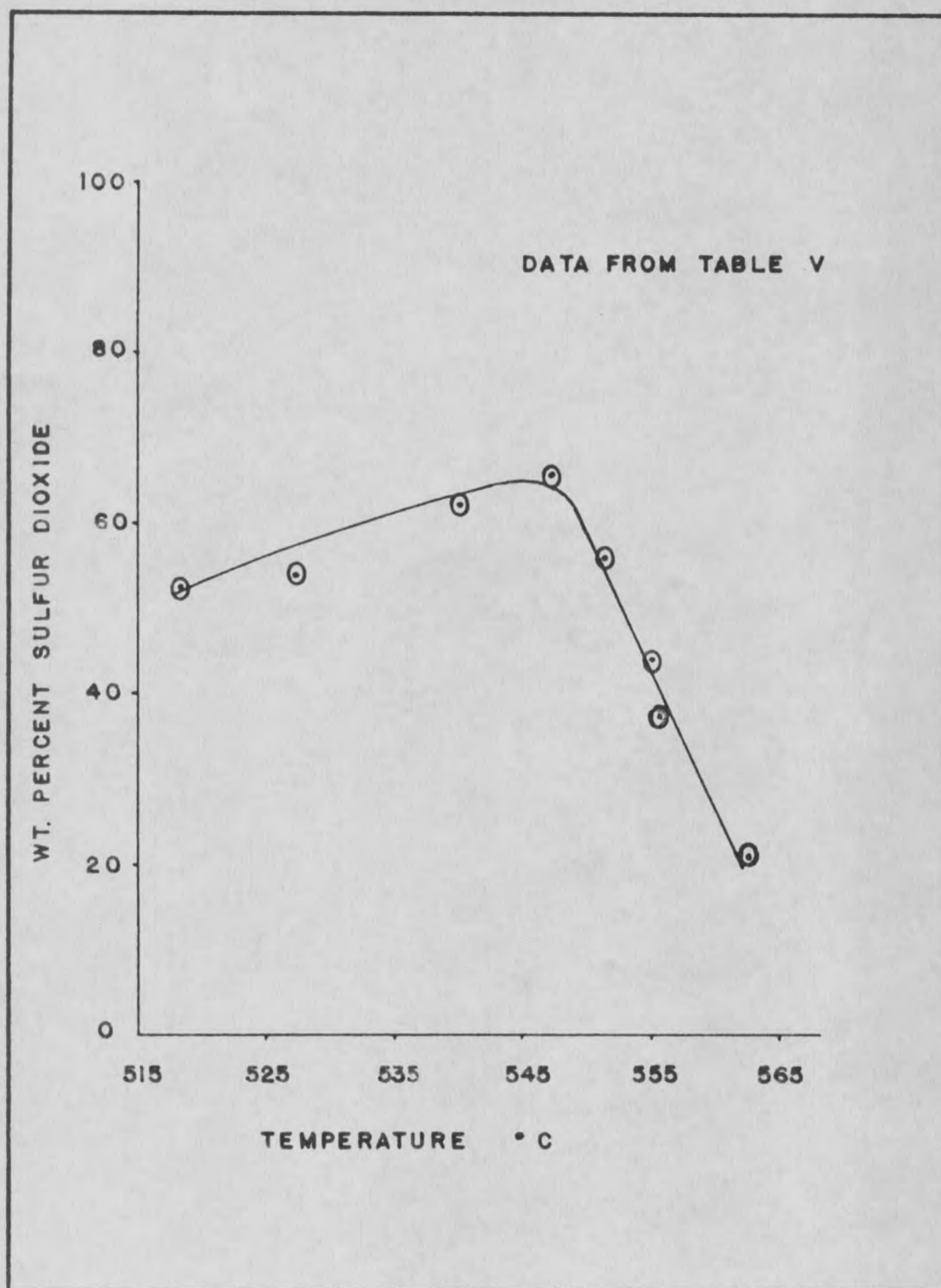


FIG 8 PERCENT YIELD VS TEMPERATURE

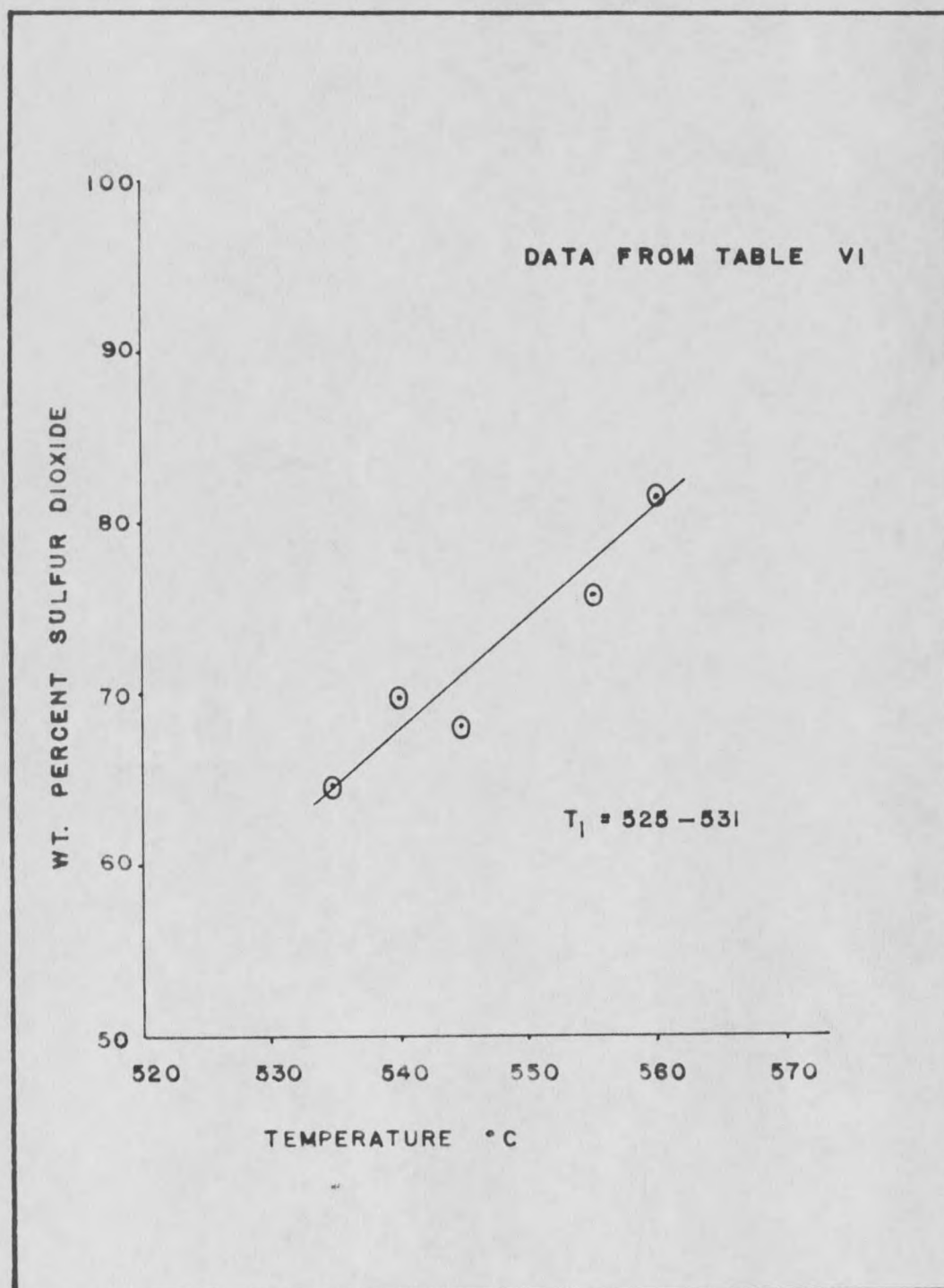


FIG 9 PERCENT YIELD VS AVERAGE OF T_2 AND T_3

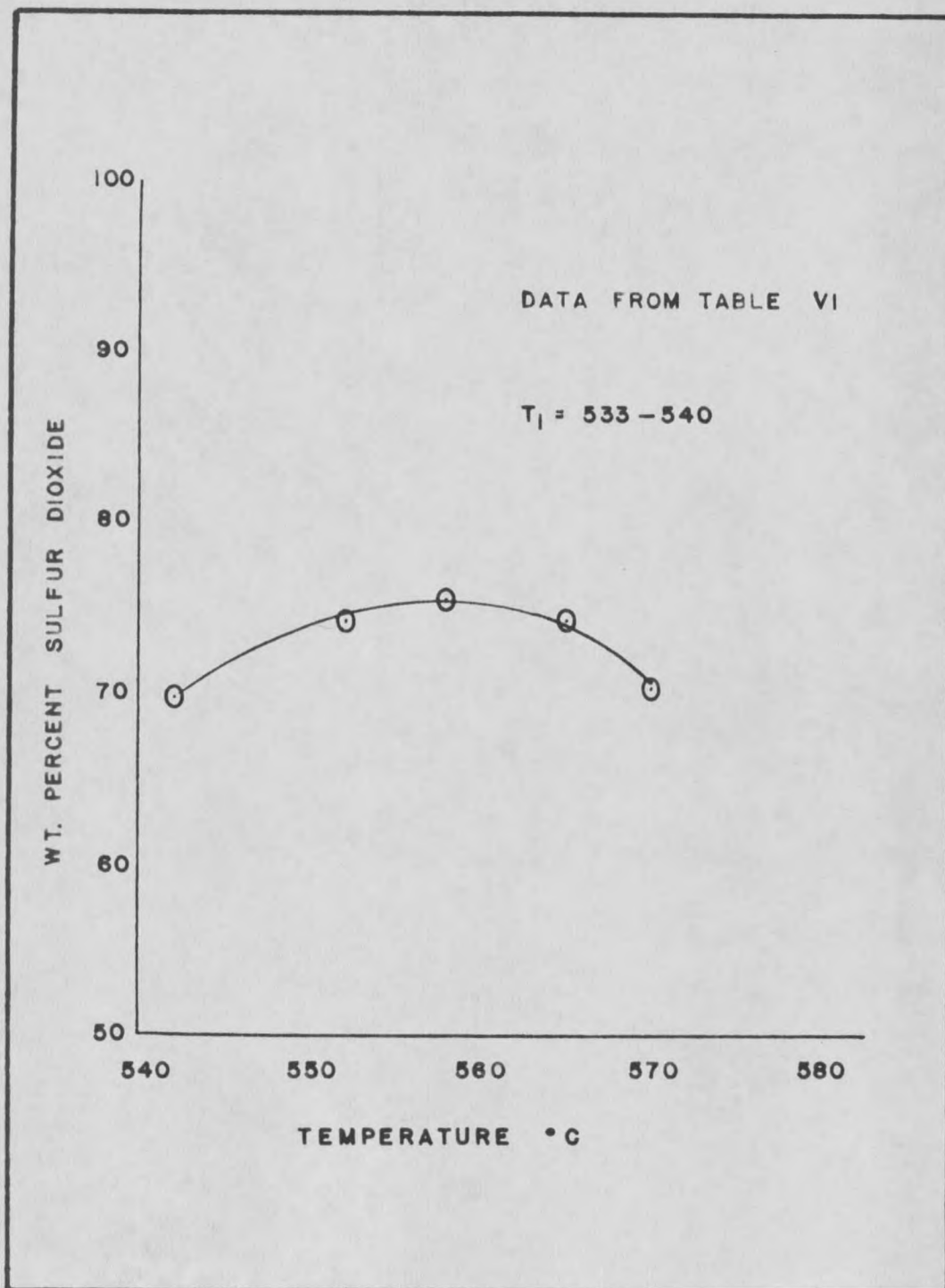
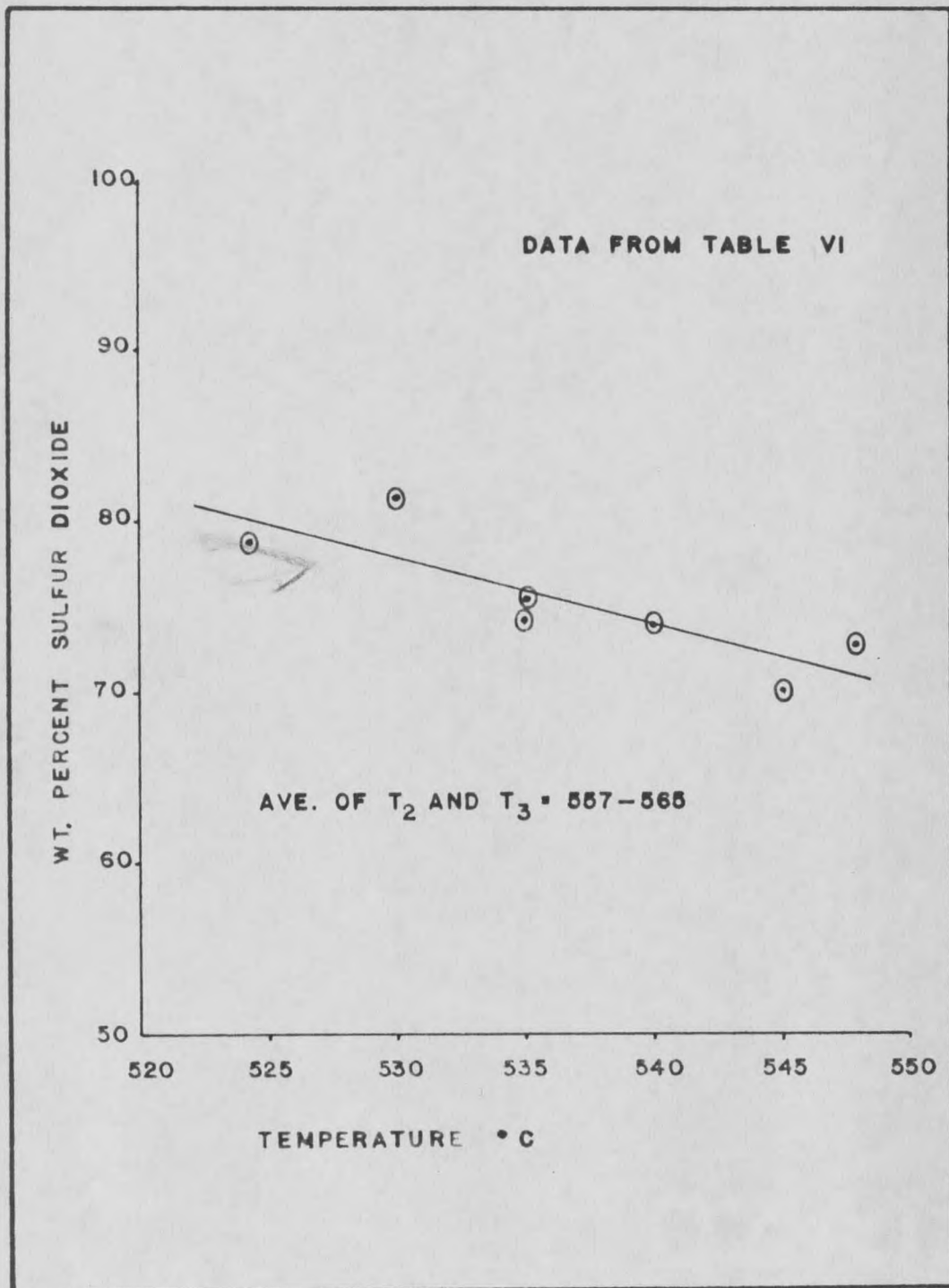


FIG 10 PERCENT YIELD VS AVERAGE OF T_2 AND T_3

FIG II PERCENT YIELD VS T_1

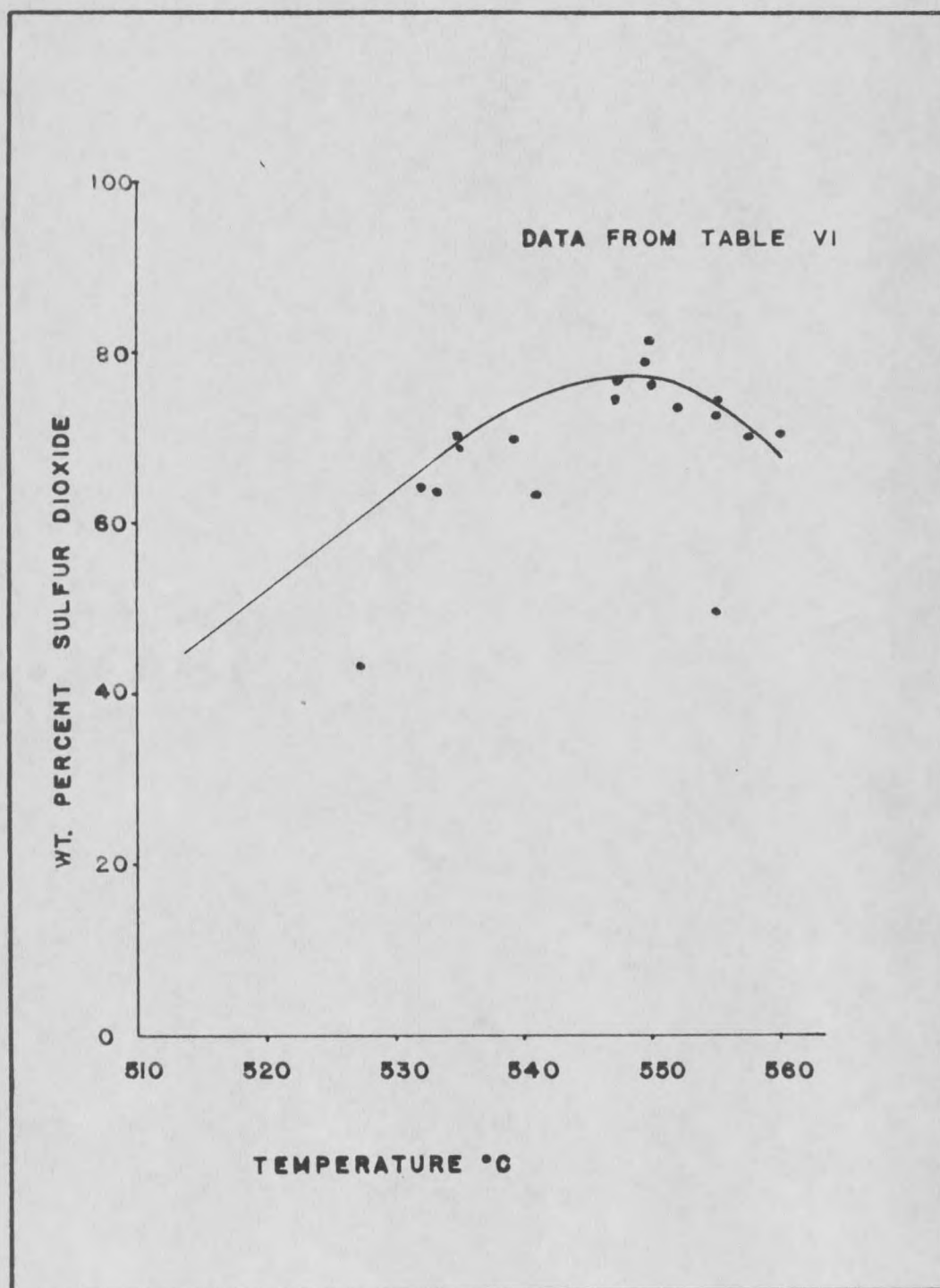
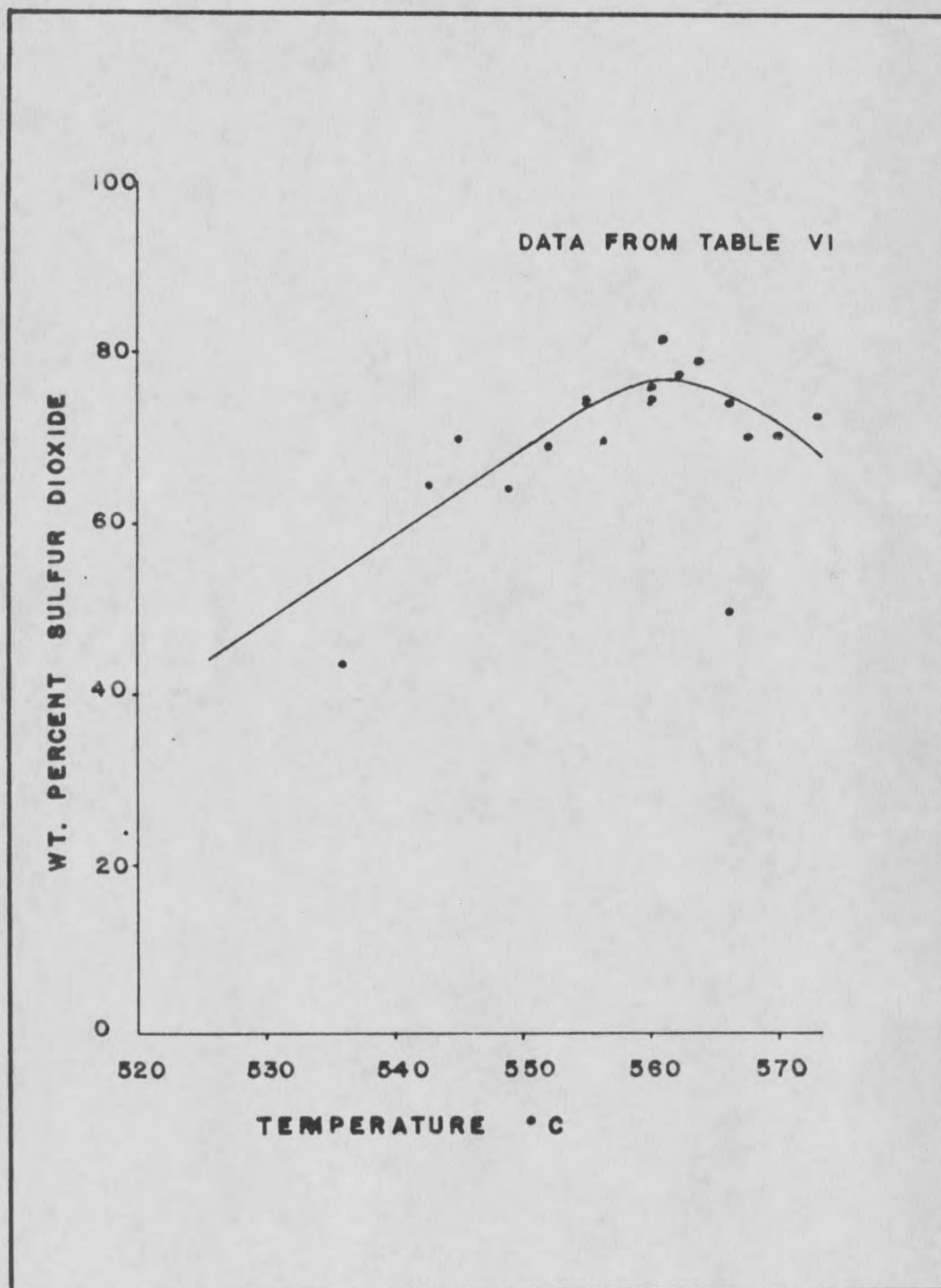


FIG 12 PERCENT YIELD VS AVERAGE TEMPERATURE

FIG 13 PERCENT YIELD VS T_2

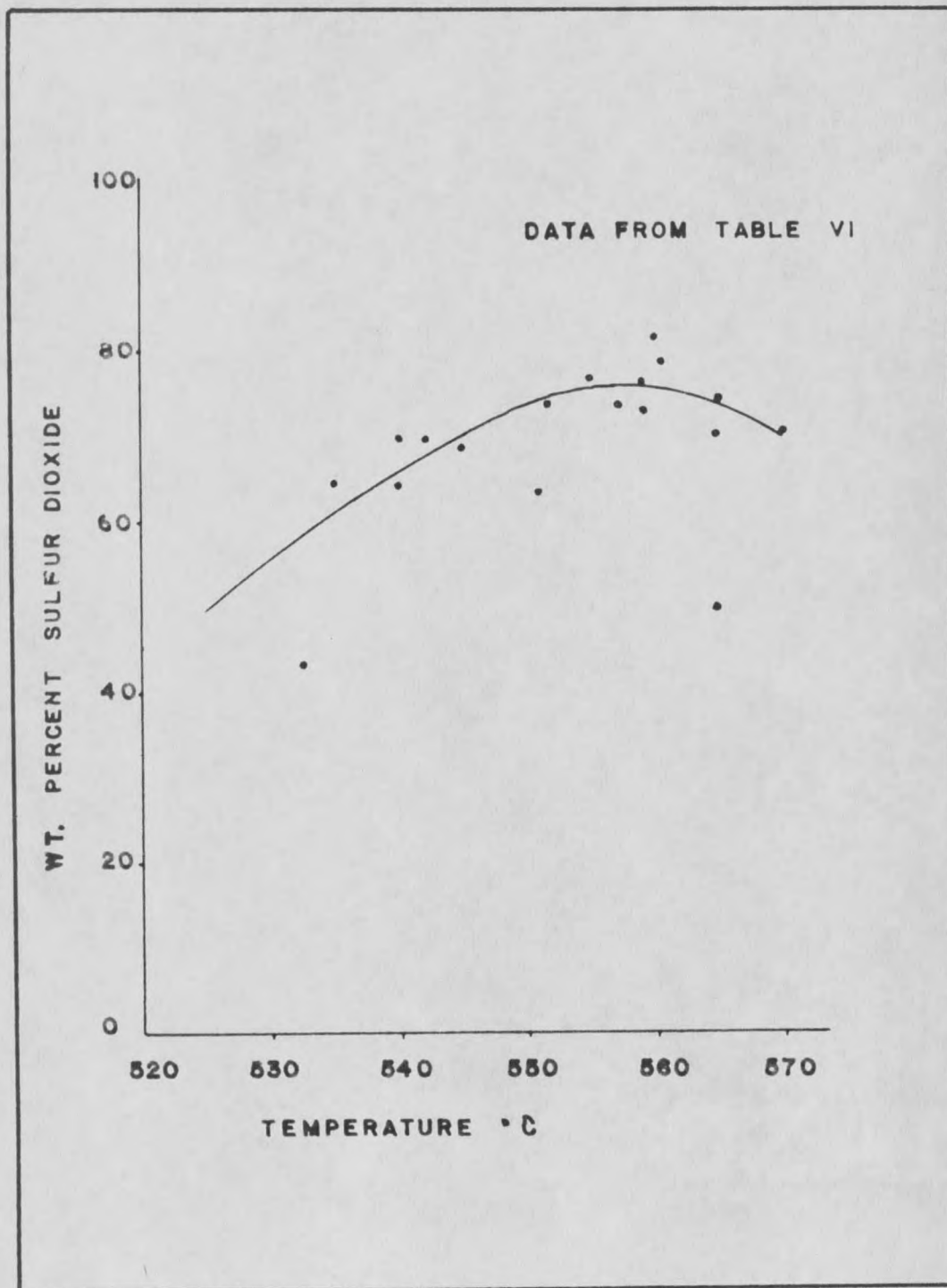


FIG 14 PERCENT YIELD VS AVERAGE OF T_2 AND T_3

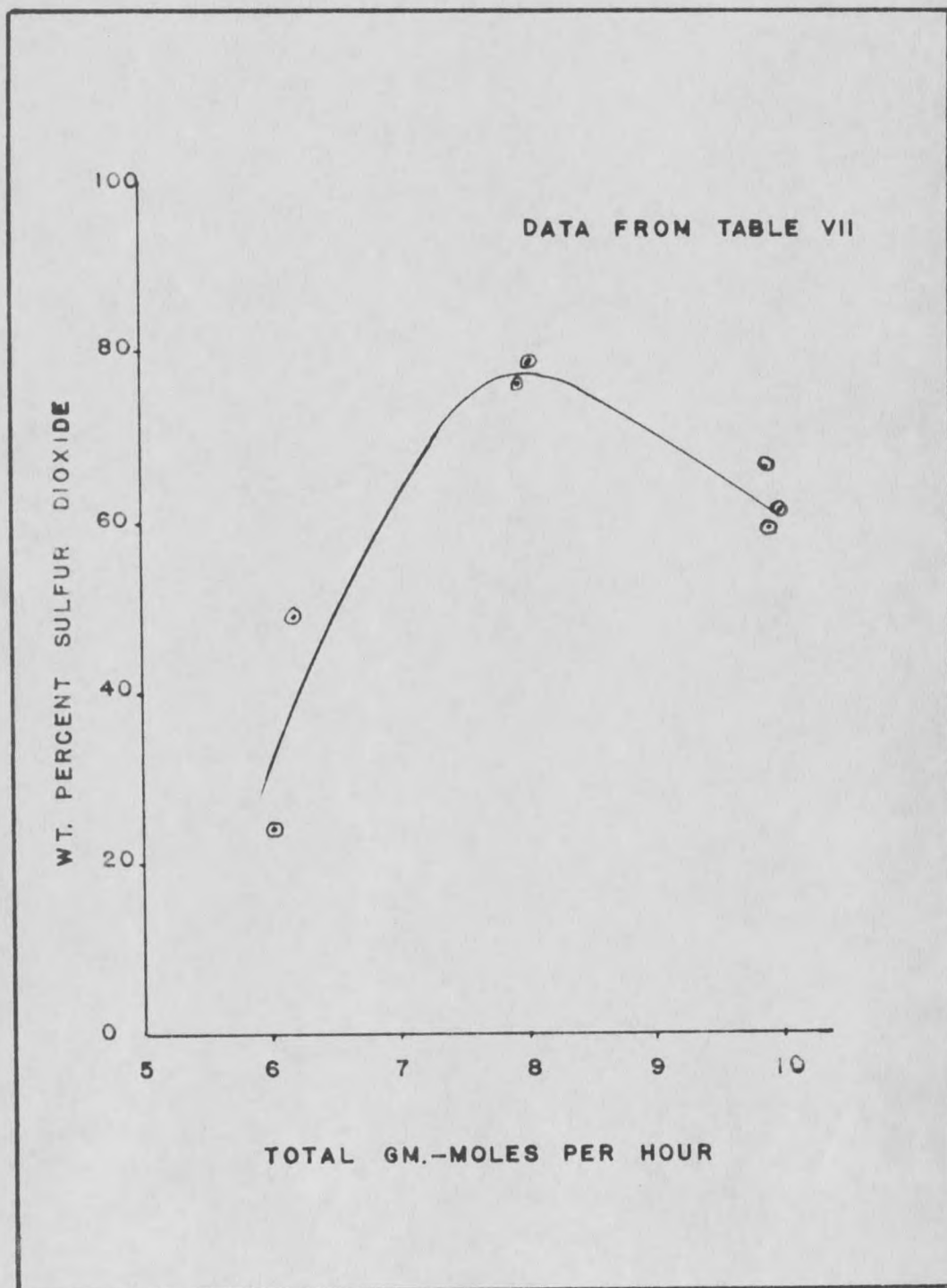


FIG 15 PERCENT YIELD VS FEED RATE

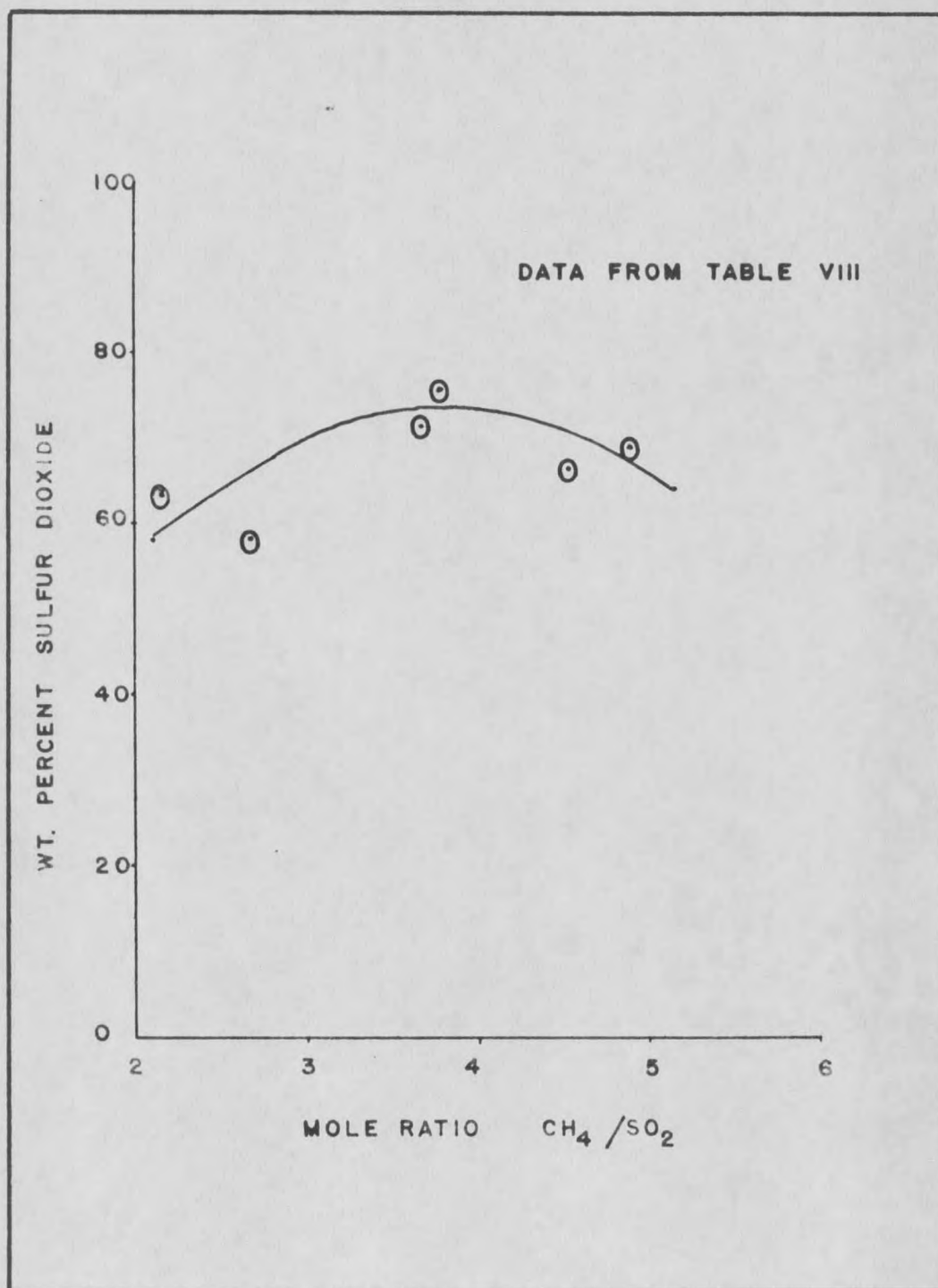
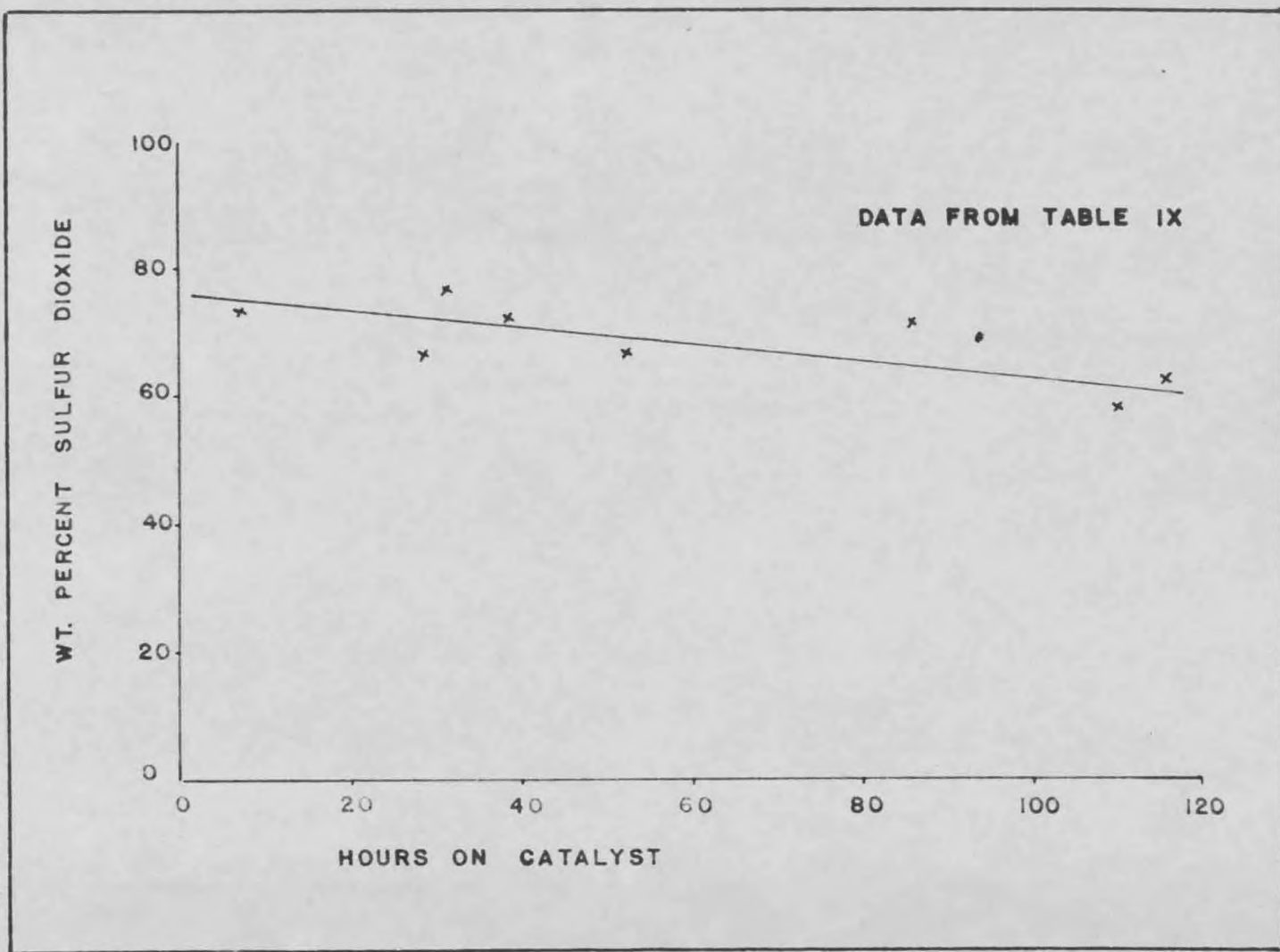


FIG 16 PERCENT YIELD VS MOL RATIO

FIG 17 PERCENT YIELD VS ON-STREAM HOURS





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Bryan, J. D.

Reduction of sulfur dioxide
to elemental sulfur.

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