Reduction of sulfur dioxide to elemental sulfur using methane as the reducing agent
by Willard F Davis

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:
An investigation was conducted to determine what effect temperature, mol ratio of feed, and total mols of feed would have on the reduction of sulfur dioxide with methane using a semi-continuous flow fixed-bed catalytic process unit.

Sulfur dioxide was reduced with methane over 400 grams of catalyst while operating conditions were varied between the following limits; temperature — 525°to 595°C., mol ratio of methane to sulfur dioxide — 1.32 to 7.14, total mols of feed per hour — 6.06 to 9.09.

When operating at a mol ratio of 3.6 and 8.0 total mols of feed, a temperature of 562°C. gave a maximum conversion to sulfur of 62 percent with fresh catalyst but after extended catalyst use a temperature of 550°C. gave a maximum yield of 58 percent. In both cases a decrease in conversion to sulfur was accompanied by an increase in the percent sulfur dioxide converted to other products at temperatures above 562°and 550°C., and by an increase in percent sulfur dioxide which was unreacted at temperatures below 562°and 550°C.

A 3.6 mol ratio of methane to sulfur dioxide produced a 62 percent maximum reduction to sulfur when temperature and total mols of feed were held constant at 562°C. and 8.0 mols, respectively. A decrease in reduction to sulfur was accompanied by an increase in percent sulfur dioxide converted to other products at mol ratios greater than 3.6 and an increase in percent sulfur dioxide which passed unreacted when mol ratios less than 3.6 were used.

The rate of feed which appeared most favorable for conversion to sulfur when used with a temperature of 562°C. and a mol ratio of 3.6 was 8.4 total mols per hour and feed rates both greater and less than this value gave a sharp reduction in percent conversion to sulfur accompanied by a corresponding sharp increase in percent sulfur dioxide converted to other products.

It is believed that greater ultimate yield of sulfur may be obtained by operating at a temperature below 560°C, and a mol ratio less than 3.6 with subsequent recycle of the unreacted sulfur dioxide.

Extended use of the catalyst produced a definite change in its activity as indicated by a decrease in maximum, conversion to sulfur from 62 to 58 percent, while the temperature at which these maximums occurred shifted from 562°C. for fresh catalyst to 550°C. for catalyst which had been in service for 160 hours.

Time required to stabilize operating conditions was felt to be a source of experimental error since it was included in the actual run.

REDUCTION OF SULFUR DIOXIDE TO ELEMENTAL SULFUR USING METHANE AS THE REDUCING AGENT

by

WILLARD F. DAVIS

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Approved:

Lloyd Berg
Head, Major Department

H. Albert Saner
Chairman, Examining Committee

Leon D. Thomas
Dean, Graduate Division

Bozeman, Montana
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TABLE OF CONTENTS

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ABSTRACT

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Sulfur dioxide was reduced with methane over 400 grams of catalyst while operating conditions were varied between the following limits: temperature -- 525° to 595°C., mol ratio of methane to sulfur dioxide -- 1.32 to 7.14, total mols of feed per hour -- 6.06 to 9.09.

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A 3.6 mol ratio of methane to sulfur dioxide produced a 62 percent maximum reduction to sulfur when temperature and total mols of feed were held constant at 562°C. and 8.0 mols, respectively. A decrease in reduction to sulfur was accompanied by an increase in percent sulfur dioxide converted to other products at mol ratios greater than 3.6 and an increase in percent sulfur dioxide which passed unreacted when mol ratios less than 3.6 were used.

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It is believed that greater ultimate yield of sulfur may be obtained by operating at a temperature below 560°C. and a mol ratio less than 3.6 with subsequent recycle of the unreacted sulfur dioxide.

Extended use of the catalyst produced a definite change in its activity as indicated by a decrease in maximum conversion to sulfur from 62 to 58 percent, while the temperature at which these maximums occurred shifted from 562°C. for fresh catalyst to 550°C. for catalyst which had been in service for 160 hours.

Time required to stabilize operating conditions was felt to be a source of experimental error since it was included in the actual run.

INTRODUCTION

A. Background

In the years following World War II, and particularly the years 1950 to 1952, there developed in the sulfur market a "tight" situation in which industrial supplies were sufficient to meet consumer needs for only three to seven months. This was not considered a healthy condition and steps were taken by various Government agencies to remedy the situation. During this period prices of sulfur ranged from $21 to $24 per ton at the mines to as much as $100 to $200 per ton on the export market.

The upswing of the value of sulfur led to increased effort in the search for additional sources of this commodity. Old mines were reopened and new deposits of sulfur ores were surveyed and developed, but these gave only a 30 to 40 year reserve at present consumption rates. The high market value of elemental sulfur made recovery of this material as a by-product from fuels and stack gases economically attractive. The need for removal of sulfur from industrial gases to improve their utility as fuel or to reduce air pollution encouraged this type of sulfur production, but the greatest impetus was given by the sulfur shortage. Many companies that consume sulfur, particularly those in the petroleum industry, saw an opportunity to improve their individual supply positions by installing equipment to recover sulfur from their waste gases. These plants gave a 35 percent increase in the recovered-sulfur output.

Since 1952 extensive deposits of elemental sulfur have been located and developed in Mexico and mining methods have been improved in other

parts of the world and, as a result, the price of sulfur has taken a sharp drop, thus removing much of the incentive for the expenditures of capital on sulfur reclamation equipment at this time. The existing reserves of sulfur are not unlimited and the time will come when other sources will have to be developed to supplement the natural deposits.

In the metallurgical industry many of the ores of iron, copper, silver, lead, and other metals are found and mined as the respective sulfides in varying forms. One of the methods used for recovering these metals from their ores, which has been in use for centuries and is still used extensively today, involves converting the sulfide ore to its corresponding oxide and then reducing to the metal with carbon or some other material.

To convert the metallic sulfides to oxides, the ores are literally burned, or sintered, at relatively high temperatures in an air atmosphere. Part of the oxygen from the air replaces the sulfur in the ore, thus forming metallic oxides, and the displaced sulfur then reacts with sufficient quantities of the remaining oxygen to form sulfur dioxide or sulfur trioxide. These sulfur compounds, being gaseous, enter the flue-gas stream and pass to the stack where they are dissipated into the atmosphere.

Most smelters have for sometime recovered enough sulfur dioxide from their stack gases to manufacture the sulfuric acid required in their own plant and in the immediate area. To attempt to supply a market located any distance from the plant is prohibited by the high cost of transporting

the acid. Some plants have found it profitable to install fertilizer plants and other related processes wherein additional amounts of sulfuric acid can be used. These processes are generally seasonal in nature and at best use only a small portion of the sulfur dioxide which is produced in the smelting operation. If some economical method were available by which this wasted sulfur dioxide could be converted to elemental sulfur, a new source of revenue would be available to the smelters and a valuable contribution would be added to our sulfur reserves.

B. Previous Work

In considering the problem of reduction of sulfur dioxide to obtain elemental sulfur, the literature was consulted to determine what previous work, if any, had been done along these lines. No survey was made on work which appeared in the literature prior to 1929. It was found that considerable work had been done on the problem, both in the United States and in other countries.

Arthur J. Caddick (1) carried out experiments in which a bed of incandescent coke was used to produce elemental sulfur from gases of varying sulfur dioxide content. Caddick's results indicated that there was a maximum recovery of sulfur and a minimum consumption of coke when the feed gases contained seven percent sulfur dioxide by volume. In an experiment in which steam was injected with the SO_2, Caddick reported the recovery of 74.14 percent of the sulfur content, with a consumption of 1.12 tons of coke and 0.08 tons of steam per ton of recoverable sulfur.

In experiments carried out by the Russians, (5), sulfur dioxide was reported to react well with methane at 900°C. over a bauxite catalyst to form sulfur, hydrogen sulfide, water, and carbon monoxide. At higher temperatures hydrogen and carbon monoxide were formed, while at lower temperatures the methane was reported to react incompletely. When using a methane to sulfur dioxide ratio of 0.43 and a temperature of 900°C., their yield of sulfur, based on methane, was 89.2 to 96.5 percent.

J. W. Beckman (3) reduced sulfur dioxide in the presence of a "simple" catalyst by passing a mixture of sulfur dioxide and natural gas or carbon monoxide through a cylindrical chamber which contained the contact mass, and which was electrically heated to maintain the contact mass at 427° to 470°C. The sulfur produced was condensed from the discharge gases and was collected as a liquid. The reduction reaction was found to be exothermic.

The reduction of sulfur dioxide was reported to be catalyzed by bauxite (7) (5) or vanadium pentoxide (2), and the catalytic action of bauxite was reported to be improved by the addition of iron or manganese compounds (1).

A smelter located at Trail, British Columbia, (4), operated a plant which utilized an incandescent bed of coke to reduce the sulfur dioxide from their stack gases to elemental sulfur. This plant was operated on a commercial scale.

After studying the information found in the literature and considering the various reducing agents which were readily available, it was decided that preliminary studies of the reduction of sulfur dioxide would

be made using natural gas as a source of methane and activated alumina as a catalyst.

This paper is a discussion of the experimental reduction of sulfur dioxide by methane and the effects on that reduction produced by varying temperature, mol ratio of reactants, and total mols of reactants passed per hour.

THERMODYNAMIC CONSIDERATIONS

A. Methods

In considering the reduction of sulfur dioxide with methane, it was felt that some preliminary study of the thermodynamic aspects of the problem should be carried out. To do this, a number of reaction equations involving sulfur dioxide and methane were postulated. These equations were chosen to give various reaction products and to test how some of the products might possibly be expected to behave in the presence of sulfur dioxide. The suggested reactions were set forth as only a portion of those which could be written. It is possible that the reduction is by a reaction which has not been presented. The six reactions which were considered are:

(1) $2SO_{2(g)} + CH_{4(g)} \rightarrow S_{2(g)} + CO_{2(g)} + H_2O_{(g)}$

(2) $4SO_{2(g)} + 3CH_{4(g)} \rightarrow CS_{2(g)} + 2CO_{2(g)} + 4H_2O_{(g)} + 2H_2S_{(g)}$

(3) $5SO_{2(g)} + 3CH_{4(g)} \rightarrow CS_{2(g)} + 3/2\ S_{2(g)} + 2CO_{2(g)} + 6H_2O_{(g)}$

(4) $3SO_{2(g)} + 2CH_{4(g)} \rightarrow \frac{1}{2}S_{2(g)} + 2H_2S_{(g)} + 2CO_{2(g)} + 2H_2O_{(g)}$

(5) $SO_{2(g)} + CS_{2(g)} \rightarrow 3/2\ S_{2(g)} + CO_{2(g)}$

(6) $SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3/2\ S_{2(g)} + 2H_2O_{(g)}$

In these equations the first four deal with reaction between methane and sulfur dioxide, while the last two suggest some possible reactions between sulfur dioxide and some of the products obtained in the first four equations.

Data from Table I was used to calculate a change of enthalpy at standard conditions (ΔH_{298}) by subtracting the total heats of formation (ΔH_{F298}) of the reactants from the total heats of formation of the products. Similarly, the change in entropy (ΔS_{298}) was calculated by subtracting the sum of S^{o}_{298} of the reactants from the S^{o}_{298} of the products. A temperature of neutral equilibrium (T_{NE}), at which the equilibrium constant (K_{eq}) equals one, was calculated by dividing the ΔH_{298} of an equation by its corresponding ΔS_{298}. These respective values of ΔH_{298} and ΔS_{298} were then used to calculate the change in free energy (ΔF) for each of the postulated reactions at temperatures of 298°, 400°, 600°, 1000°, and 1500°K, using the equation

$$\Delta F_T = \Delta H_{298} - T(\Delta S_{298})$$

where

T = temperature being studied, in degrees Kelvin, (°K).

A more rigorous determination of the values of ΔF was not attempted, since heat capacities for some of the products formed were not available.

Equilibrium constants (K_{eq}) were calculated for each reaction at each of the temperatures, using the equation

$$\log_{10} K_{eq(T)} = \frac{-\Delta F}{2.3\ RT}$$

where

T = temperature in °K.

R = gas constant (1.987)

ΔF = change in free energy at temperature T.

A sample of these calculations is given in Table II along with the calculated values of ΔH_{298}, ΔS_{298}, ΔF_T and $K_{eq(T)}$ for each of the postulated reactions.

B. Conclusions:

In the first five suggested reactions the $\Delta F_{(T)}$ values are all negative and the $K_{eq(T)}$ equilibrium values are all greater than one, indicating that if these were the reactions involved, they should proceed toward the right at reasonable operating temperatures. Reaction six has a positive $\Delta F_{(T)}$ value in the lower temperature range but changes to a negative value at 811°K. (538°C.), which might indicate that the reaction was questionable. The recovery of the sulfur as a liquid rather than a gas might have given more favorable values for $\Delta F_{(T)}$.

The values obtained for these suggested reactions indicated that a reduction reaction should take place between sulfur dioxide and methane in the temperature range considered, and that experimental studies of the problem were justified.

EQUIPMENT DESIGN AND CONSTRUCTION

A. Flow Sheet

In preparing for research investigations of the reduction of sulfur dioxide with methane at various temperatures, mol ratios, and space velocities, a semi-continuous-flow, fixed bed, catalytic process unit was designed and built. The early operation of the unit necessitated design changes in which the original units were replaced or modified to overcome specific operating problems as they were encountered. A block flow diagram of the unit as it emerged in its final form is shown in Fig. 1, and a detailed flow sheet of the unit is shown in Fig. 2. As this unit was set up, sulfur dioxide and methane were metered by orifices and manometers from their respective sources into a pipe which carried them to the top of the reactor. The mixed gases then passed down through the preheat section containing one-half inch Berl saddles and then over the catalyst bed. The hot reacted gases then passed to the constant-temperature condenser where the sulfur vapor was condensed to the liquid state, after which the liquid sulfur and the partially cooled gases passed down the center of the sulfur receiver to a cup in the bottom where the sulfur was collected. The remaining gaseous materials then passed upward through a glass-wool filter where any entrained sulfur particles were removed. From the sulfur receiver the gases were carried to a water cooled condenser where most of the water they contained was condensed out and collected in the water receiver. After the water was removed, the gases went to the low temperature condenser where any unreacted sulfur dioxide was collected,

and they then passed out the vent line to the atmosphere.

B. Design and Specifications of Component Parts

Reactor: The reactor was made from a 27-inch length of 2-inch, schedule 40, black-iron pipe. Standard cast-iron pipe caps were used to close the ends. See Fig. 3 for details of reactor construction. Three nichrome coils were spaced along the length of the reactor to supply the outside heat necessary to maintain any desired reactor temperature. The resistance of the top coil was such that it would draw 9 A.C. amperes when connected to a 220-volt power supply. The resistances of the middle and bottom coils were such that they drew 5.5 and 4.5 A.C. amperes, respectively, when connected to a 110-volt power supply. A single layer of asbestos tape was wrapped the full length of the reactor, then the ceramic bead-strung heating coils were wound into place, covered with a second layer of asbestos tape, and finally insulated with about one inch of 85 percent magnesia. To permit filling and inspection of the reactor, the top cap was not insulated, but the bottom cap and the exit gas line were covered with the one-inch magnesia layer. A $\frac{1}{4}$-inch standard black-iron pipe, welded closed at the top end, was passed through the center of the bottom cap to serve as a thermowell in the reactor. A metal baffle was placed in the top of the reactor to mix and diffuse the feed gases and to prevent their impinging directly upon the end of the thermowell. A stainless-steel screen was placed in the bottom of the reactor to serve as a catalyst support and give an open space for free gas passage to the outlet opening.

Sulfur Condenser: A water-cooled condenser made of metal was first tried, but the sulfur solidified in the tube and soon plugged it, thus stopping the flow of gases. An insulated 3/8-inch glass tube approximately 24 inches in length was then tried, but it also plugged with solidified sulfur. A constant-temperature condenser was then built which would condense the sulfur and maintain it in a liquid state until it was delivered to the sulfur receiver. Details of the condenser are shown in Fig. 4. The center tube was made from a 30-inch length of $\frac{1}{2}$-inch diameter thin-wall electrical conduit. A 26-inch section of 1-inch diameter thin-wall electrical conduit was used for the condenser jacket and was secured in place by brazing at each end. Inlet and outlet connections for coolant were provided by brazing sections of $\frac{1}{4}$-inch black-iron pipe into holes drilled at the top and bottom of the condenser jacket. The center tube was packed with $\frac{1}{4}$-inch ceramic electrical insulating beads to give a greater contact surface for the hot gases and to coalesce the fine particles of sulfur which were suspended in the gas stream. A ceramic-bead-strung nichrome heating coil was wound on the lower portion of the condenser to provide sufficient heat to constantly boil the coolant in the condenser. Approximately 400 watts of heat was found to be sufficient power to maintain boiling. A $\frac{1}{4}$-inch standard pipe was used to connect the coolant outlet to the top of a one-quart coolant reservoir, and another section of pipe was used to connect the bottom of the reservoir to the inlet, or bottom, of the condenser. A water-cooled glass condenser was connected to the top of the coolant reservoir to condense and return to

the system any vapors formed by the boiling in the condenser. A 3/4-inch layer of 85 percent magnesia was used to insulate the condenser, reservoir and lines of the unit. An ethylene-glycol-water solution, adjusted to boil at 317°F., was used as the heat transfer medium in the condenser.

Sulfur Receiver: A 300-ml. Florence flask, to which a side arm had been attached, was first used as a sulfur receiver, but difficulties were encountered in that the sulfur could not be removed, and some sulfur particles were entrained in the gases and subsequently settled out in the lines. To overcome these difficulties a sulfur receiver was constructed from a 13-inch section of $2\frac{1}{4}$-inch diameter glass tubing. Two large rubber corks were used to close the ends, the top one being bored to take a nine-inch section of one-inch diameter glass tubing which extended down into the receiver to carry the gases and any entrained sulfur particles to the lower section of the receiver. The lower section of the receiver held a small, easily removed, aluminum-foil cup in which the liquid sulfur collected and solidified. From the bottom the gases passed upward through glass wool loosely packed between the concentric walls of the two glass tubes where any entrained sulfur particles were filtered out. A second small hole in the top cork, fitted with a glass tube, served as an outlet for the gases passing to the water condenser. When in operation, the sulfur receiver was surrounded by a boiling water bath to prevent any water from condensing in it. See Fig. 4-A for details of sulfur receiver.

Water Condenser: A 36-inch long water-cooled glass condenser having a 3/8-inch center tube was used to remove most of the water vapor from

the gases.

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

Cold Condenser: A 600-ml. distillation flask with the gas inlet tube extending nearly to the bottom was immersed in an acetone-dry-ice bath as a first trial low-temperature condenser. The small amount of water vapor present in the gases being cooled collected in the inlet tube in the form of ice and soon stopped the flow of gases. An attempt to insulate the inlet tube was made by wrapping it with a 3/16-inch layer of glass wool followed by a second glass tube, with the annular spaces at the ends closed with bored corks. This afforded little relief from the formation of ice and the tube soon plugged. A nichrome heating coil was then wound on the inlet tube, followed by a glass-wool insulation and a second tube, but ice still formed in the section covered by the cork at the lower end and plugged the tube. A larger flask with more room in the neck was secured. A new inlet tube was constructed in which a nichrome heating coil was spaced at 3/16-inch per turn along its entire inside surface and the outside was insulated by a 3/16-inch layer of glass wool covered by a second tube. Details of condenser construction are shown in Fig. 5. Approximately 12 volts applied by an autotransformer was sufficient to prevent formation of ice in the tube.

Vent Line: One-half-inch saran tubing.

Sulfur Dioxide Feed: Feed was started from a 150-pound supply in a steel tank, but in order to obtain a more accurate determination of feed

to the reactor, a steel tank of 2,500-gram capacity was filled from the large tank and used as a feed supply. This tank was small enough to be weighed on the laboratory balance to determine the amount used during each run.

Sulfur Dioxide Metering: A glass venturi-type orifice was used in conjunction with a water-filled manometer. Calibration was done by weighing the feed bottle to determine the amount passed in unit time.

Methane Metering: A glass venturi-type orifice was used in conjunction with a diesel-oil-filled Bacharach inclined manometer. Calibration was done with a Precision Scientific 20-cu.ft. Wet Test Meter.

Sulfur Dioxide Metering Valve: Ideal-Aerosmith needle valve.

Methane Metering Valve: Hoke brass blunt-spindle needle valve.

Low-Temperature Bath: Solid carbon dioxide and acetone in a four-liter vacuum bottle.

Autotransformers: One 220-volt Powerstat for the top reactor coil, two 110-volt Powerstats for the middle and bottom reactor coils, one 110-volt Powerstat for the constant temperature condenser, and one 110-volt Powerstat for the low temperature condenser.

Thermocouples: Three iron-constantan.

Quick-disconnect: One six-pole, self-aligning disconnect for thermocouple leads.

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

PROCEDURES AND MATERIALS

Procedures

Reactor Assembly: With the reactor supported in upright position, the inside of the reactor was inspected to be sure the stainless steel screen was in position at the bottom. Next, 400 grams of catalyst were carefully poured in so that a uniform bed was obtained. This gave a catalyst bed 13 inches in depth. The remaining space was filled with $\frac{1}{2}$-inch Berl saddles which were dropped in a few at a time, after which the metal baffle plate was put into place in the top and the cap screwed on. A graphite-in-oil thread dressing was used to prevent seizure of the threads. The reactor was then set in place and the feed lines connected to it. Heating coil leads were plugged into their respective powerstats and the thermocouple disconnect was secured in its socket.

The constant-temperature condenser was then secured in place and connected to the reactor, after which it was filled with coolant and the coolant condenser was fitted into place. Cooling-water lines and heating-coil powerstat were then connected to it.

Start-up: Cooling water to the two water-cooled condensers was turned on. Powerstats for the heating coils of the reactor and the constant-temperature condenser were turned on and adjusted to their proper settings. A clean sulfur receiver, water receiver, and low-temperature-condenser flask were each weighed and placed in the unit, and their respective weights were recorded. All lines were connected and all connections were checked to make sure they were gas-tight. A five-liter

beaker was placed around the sulfur receiver and filled with hot water. An electric hot-plate was placed under it to keep the water boiling. Small pieces of dry-ice were added to the acetone bath of the low-temperature condenser until the bath temperature dropped to that of the dry ice, after which an excess of dry ice was added. The low-temperature-condenser powerstat was turned on and adjusted to 12 volts.

The reactor was heated to temperature over a three-hour period. When the temperature of the preheat section reached 510°C., the methane flow was started through the system. Sulfur dioxide flow was started and the powerstats were adjusted to operating settings when the two catalyst temperatures were 20 degrees below the desired operating temperature, since it was found that these two temperatures would rise 20 degrees and start to level off in the first 10 minutes after the sulfur dioxide flow was started.

Operation: Temperatures were controlled by adjusting the power input to the reactor heating coils with the powerstats. The preheat section was held at 510° to 515°C. except when it became necessary to change it to control a difficult temperature situation in the catalyst bed. An attempt was made to hold the two catalyst temperatures the same, and this temperature was determined by the conditions of operation. Methane and sulfur dioxide flow were regulated by adjusting their control needle-valves to give the desired manometer readings. The sulfur dioxide supply bottle was weighed before and after each run and the weight used during the run was obtained by the difference. Enough dry ice was periodically added to

keep it in excess in the acetone bath of the low-temperature condenser. Readings were taken and adjustments were made at 10-minute intervals during the run.

Shut-down: To shut the unit down, the valve on the sulfur dioxide tank was closed, and power to the reactor heaters, constant-temperature condenser and the hot-water bath were turned off. Methane was left flowing for 10 minutes to sweep all of the sulfur dioxide from the unit. The power to the low-temperature condenser was turned off and the flask was removed from the acetone bath and weighed, then corked and connected to the vent line to permit any sulfur dioxide which had been collected to boil away. The flask was then weighed again and the amount of sulfur dioxide collected was obtained by the difference between this weight and the weight at the end of the run. The difference between the flask's final weight and its weight at the start of the run gave the amount of water which had collected in it. The sulfur and water receivers were weighed and the amount of material contained in each was obtained by difference.

Materials

The sulfur dioxide used in this research was a commercial grade, obtained from Matheson Company of Joliet, Illinois.

Methane used as a reducing agent for the sulfur dioxide was obtained from the natural gas lines of the local utility company.

Pelletized activated alumina catalyst manufactured by the Harshaw Chemical Company was used for this study. One-eighth-inch extruded

pellets were used.

The material used for packing in the preheat section was $\frac{1}{2}$-inch ceramic Berl saddles.

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

EXPERIMENT DESIGN

A series of runs was made to obtain data regarding the reduction of sulfur dioxide with methane and to study the effect variations in temperature, mol ratio of reactants, and total mols of reactants passed per hour had on the reaction. The first runs made were of a purely exploratory nature and were made at conditions which a study of the materials involved had indicated might be favorable to the reaction. After several runs had been made, the data was arranged into groups in which only one of the operating conditions varied. This was done in an attempt to find trends in the effects exerted by variation in operating conditions. When these trends were ascertained additional runs were made in the range which appeared most favorable in an attempt to more closely pinpoint the conditions giving the greatest reduction to sulfur.

Conditions found to give favorable reactions were then used to set up runs in which each variable was studied individually. After enough data had been collected to plot rough curves of the effect of each variable, the length of the runs was extended from two hours to three-and-one-half hours to minimize the effect of experimental error introduced by line-out time, (time required to stabilize operating conditions), and an extensive study was made in which only one operating condition was varied while the other two were held at the previously determined optimums. A maximum percent reduction to sulfur was sought as the desirable result.

In the series of runs made to check the effect of temperature, the results obtained did not correspond with results obtained from runs made

at the beginning of the test which were made under identical operating conditions. To check a possible change in catalyst activity due to extended use, the catalyst was removed and replaced with fresh material, after which another series of runs was made. In this series, temperature was varied while other conditions were held at the same values used for the previous temperature study.

In this study, temperature was varied between 525°C. and 595°C., mol ratio of methane to sulfur dioxide was varied between one and seven, and total feed was varied from six to ten mols per hour. A 400-gram catalyst bed was used for the runs.

DISCUSSION OF RESULTS

A. Temperature

A definite effect was found to be exerted on the reaction by temperature. The plot of data obtained when using fresh catalyst, shown in Fig. 6, gives a maximum of 62 percent conversion of sulfur dioxide to sulfur per pass in the range of 560° to 565°C. Above this temperature range the reduction to sulfur drops off rapidly with a corresponding rapid increase of sulfur dioxide which was converted to other materials. Temperatures below 560°C. gave a sharp decrease in conversion to sulfur and increase in percent sulfur dioxide unreacted, but the decrease in sulfur dioxide converted to other products was small. At 525°C. there was 41.5 percent of the sulfur dioxide recovered unreacted as compared with two percent at 565°C. The sulfur dioxide converted to other products dropped from approximately 36 percent at 565°C. to 28 percent at 525°C.

When the catalyst had been in service for 160 hours the maximum percent conversion of sulfur dioxide to sulfur had decreased to 58 percent and this maximum had shifted from the 560° to 565°C. range for new catalyst to 550°C. Above 560°C. the percent reduction to sulfur dropped off very rapidly, as shown in Fig. 7, and was less than ten percent at 575°C. as compared to 52 percent for fresh catalyst at this temperature. At 525°C. the sulfur dioxide which remained unreacted was 29.5 percent for used catalyst and 28.0 percent for fresh catalyst.

B. Mol Ratio

A mol ratio of methane to sulfur dioxide of 3.6 gave the greatest percent sulfur dioxide reduced to sulfur on a single pass basis. Above this mol ratio reduction to sulfur dropped off very rapidly to four percent at mol ratios of five or greater, as shown in Fig. 8. For mol ratios less than 3.6 conversion to sulfur dropped off very rapidly to 15.5 percent at 1.32 mol ratio, while the percent sulfur dioxide which remained unreacted increased very rapidly from eight to sixty percent as the mol ratio was decreased from 3.6 to 1.32. A greater ultimate yield of sulfur might possibly be realized by operating at lower mol ratios and recycling the unreacted sulfur dioxide as is shown in Fig. 11.

C. Total Mols of Feed

A plot of data obtained by varying total mols of feed per hour, Fig. 9, indicates that a maximum conversion to sulfur was obtained with 8.4 mols of feed per hour using 400 grams of catalyst. No extensive study was made using this value for an operating condition and slightly higher yields of sulfur might have been obtained using it in conjunction with a mol ratio of 3.6 and a temperature of 565°C. Fresh catalyst might also have given better results, since the catalyst used to obtain this data had been in service in excess of 125 hours.

D. Theoretical Recycle of Unreacted Sulfur Dioxide

A comparison of the graph showing percent sulfur dioxide reduced to sulfur per pass versus temperature, Fig. 6, with a graph of ultimate yield

of sulfur versus temperature, Fig. 10, indicates that a slight increase in ultimate yield of sulfur might be effected by performing the reduction at 555°C. and recycling the unreacted sulfur dioxide rather than using a single pass operation at 563°C. Similarly, a comparison of the graph of percent conversion to sulfur per pass versus mol ratio, Fig. 8, with the graph of ultimate yield of sulfur versus mol ratio, Fig. 11, indicates that a considerable increase in ultimate yield of sulfur could be obtained over single pass operation by using a methane to sulfur dioxide mol ratio of 2.7 and recycling the unreacted sulfur dioxide.

E. Catalyst Activity

The data for the two temperature studies, shown in Tables IV and V and plotted in Figs. 6 and 7, indicate that the catalyst had a definite change in activity with extended use. A comparison of these two series reveals that the fresh catalyst gave a maximum reduction to sulfur which was four percent higher than the catalyst which had been in service more than 160 hours. The maximum yield for the fresh catalyst was obtained using an operating temperature of 562°C., but 551°C. gave the best yields of sulfur after extended catalyst use. An increase in temperature above 562°C. with a fresh catalyst gave a corresponding decrease in yield which appeared to be a nearly straight line function, while a very sharp drop in reduction to sulfur accompanied a temperature increase from 560° to 570°C. in runs with catalyst which had been in use more than 160 hours. At 525°C. the fresh catalyst gave only 30.5 percent reduction to sulfur but after

extended use the conversion to sulfur was 41.0 percent at the same temperature. The sulfur dioxide which was converted to other products was virtually the same for fresh and used catalyst at 525°C., but the percent converted to products other than sulfur increased much more rapidly for the used catalyst at temperatures above 560°C. This indicates that with extended catalyst use there was a shift in activity which favored increased reduction to sulfur at temperatures below 560°C. and a sharp increase in products other than sulfur at temperatures greater than 560°C.

F. Lineout

No provision was made to separate lineout time (time required to stabilize operating conditions) from the rest of the run; consequently, this will present a definite source of experimental error. An average of 20 minutes was required to bring operating conditions to the desired level, but some runs required as long as one hour for lineout. This tends to make the experimental error greater for some runs than for others.

SUMMARY

Temperature was found to affect reduction to sulfur and highest yields obtained per pass were 62 percent reduction to sulfur at 562°C. with fresh catalyst and 58 percent reduction to sulfur at 550°C. with catalyst which had been in service 160 hours.

A mol ratio of methane to sulfur dioxide of 3.6 gave the highest sulfur yields for single pass operation but a greater ultimate yield appeared to be possible on a recycle basis at lower mol ratios.

The feed rate which appeared to give the best sulfur recovery was 8.4 total mols per hour using 400 grams of catalyst, but no extensive studies were made using this value.

A slight increase in ultimate yield might be realized by operating at lower temperatures and recycling the unreacted sulfur dioxide. The greatest increase in ultimate yield made possible by recycle seemed to be when operating at a mol ratio of methane to sulfur dioxide of 2.7.

A change in catalyst activity appears to accompany extended catalyst use. The change favored the formation of more gaseous products and less sulfur above 560°C. At temperatures below 560°C., catalyst which had been used extensively gave greater sulfur recovery and less unreacted sulfur dioxide than was obtained with fresh catalyst at the same temperatures.

Lineout time was believed to introduce experimental error into the data since no provision was made for separating it from the actual run.

BIBLIOGRAPHY

(1) Brit. Pat. No. 427,999 May 3, (1935)

(2) Can. Pat. No. 301,554 July 1, (1930)

(3) Eng. Mining J. 131 7, (1931)

(4) Ind. Eng. Chem. 32 910-14 (1940)

(5) J. Chem. Ind. (Moscow) 2 33-7, (1934)

(6) Olaf A. Hougen and Kenneth M. Watson, Chemical Process Principles, John Wiley & Sons, Inc., Part One 71-2, (1952).

(7) U. S. Pat. No. 1,771,480, Official Gazette 396-5, 973, July 29, (1930)

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APPENDIX

APPENDIX (continued)

TABLE I

THERMODYNAMIC DATA

Compound	H_{f298} Kcal	S^{o} 298 E.U.	T_c $^{o}K.$	P_c Atm.
$SO_{2(g)}$	-70.96	59.24	430.3	77.7
$S_{(Rombic)}$	0.0	7.62	- - -	- - -
$S_{2(g)}$	31.02	54.41	1313.2	234.5*
$C_{(gr)}$	0.0	1.36	- - -	- - -
$CO_{(g)}$	-26.42	47.30	134.4	34.6
$CO_{2(g)}$	-94.05	51.06	304.1	72.9
$CS_{2(g)}$	22.08	57.1	546.2	76.0
$CH_{4(g)}$	-17.89	44.5	191.1	45.8
$H_2S_{(g)}$	- 4.815	49.15	373.5	88.9
$H_2O_{(g)}$	-57.80	45.11	647.3	218.2

* Calculated by Parachors from Hougen and Watson (6).

TABLE II

SAMPLE CALCULATIONS AND CALCULATED VALUES
of ΔH_{298}, ΔS_{298}, T_{NE}, ΔF_T, and K_{eq} for REACTION EQUATIONS

(1) $$2SO_{2(g)} + CH_{4(g)} \rightarrow S_{2(g)} + CO_{2(g)} + 2H_2O_{(g)}$$

ΔH_{298} $\quad 2(-70.96) - 17.89 \rightarrow 31.02 - 94.05 + 2(-57.80)$

$$\Delta H_{298} = -18.32 \text{ Kcal}$$

ΔS_{298} $\quad 2(59.24) + 44.5 \rightarrow 54.41 + 51.06 + 2(45.11)$

$$\Delta S_{298} = 32.71 \text{ E.U.}$$

$$T_{NE} = \frac{\Delta H}{\Delta S} = \frac{-18820}{32.71} = -555^{\circ}K$$

$$\Delta F_{298} = \Delta H_{298} - T(\Delta S_{298}) = 18820 - 298(32.71) = 18820 - 9740$$
$$= -28560 \text{ cal} = -28.56 \text{ Kcal}$$

$$\text{Log}_{10} K = \frac{-\Delta F}{2.3\ RT} = \frac{28560}{(2.3)(1.987)(298)} = 28.5$$

$$K_{eq} = 6.80 \times 10^{20}$$

$\Delta H_{298} = -18.82$ Kcal

$\Delta S_{298} = 32.71$ E.U.

$T_{NE} = -555^{\circ}K.$

Temp. $^{\circ}K$	ΔF Kcal	K_{eq}
298	-28.56	6.8×10^{20}
400	-31.90	2.46×10^{17}
600	-38.37	8.92×10^{13}
1000	-51.53	1.78×10^{11}
1500	-67.92	7.60×10^{9}

TABLE II (continued)

SAMPLE CALCULATIONS AND CALCULATED VALUES

of ΔH_{298}, ΔS_{298}, T_{NE}, ΔF_T, and K_{eq} for REACTION EQUATIONS

(2) $4SO_{2(g)} + 3CH_{4(g)} \rightarrow CS_{2(g)} + 2CO_{2(g)} + 4H_2O_{(g)} + 2H_2S_{(g)}$

$\Delta H_{298} = -74.74$ Kcal

$\Delta S_{298} = 68.50$ E.U.

$T_{NE} = -1090^{\circ}K.$

Temp. $^{\circ}K.$	ΔF Kcal	K_{eq}
298	-95.14	3.98×10^{69}
400	-102.14	6.30×10^{55}
600	-115.84	1.26×10^{42}
1000	-143.24	1.58×10^{31}
1500	-177.54	6.30×10^{25}

(3) $5SO_{2(g)} + 3CH_{4(g)} \rightarrow CS_{2(g)} + 3/2\ S_{2(g)} + 2CO_{2(g)} + 6H_2O_{(g)}$

$\Delta H_{298} = -73.148$ Kcal

$\Delta S_{298} = 13.78$ E.U.

$T_{NE} = -5300^{\circ}K.$

Temp. $^{\circ}K.$	ΔF Kcal	K_{eq}
298	-77.25	3.98×10^{56}
400	-78.66	7.95×10^{42}
600	-81.41	3.80×10^{29}
1000	-86.93	8.93×10^{18}
1500	-93.83	4.46×10^{13}

TABLE II (continued)

SAMPLE CALCULATIONS AND CALCULATED VALUES

of ΔH_{298}, ΔS_{298}, T_{NE}, ΔF_T, and K_{eq} for REACTION EQUATIONS

(4) $3SO_{2(g)} + 2CH_{4(g)} \rightarrow \frac{1}{2}S_{2(g)} + 2H_2S_{(g)} + 2CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H_{298} = -49.16$ Kcal

$\Delta S_{298} = 51.13$ E.U.

$T_{NE} = -961^{\circ}K.$

Temp. $^{\circ}K.$	ΔF Kcal	K_{eq}
298	-64.40	1.26×10^{47}
400	-69.61	7.95×10^{37}
600	-79.86	1.00×10^{29}
1000	-100.29	7.95×10^{21}
1500	-125.76	1.78×10^{18}

(5) $SO_{2(g)} + CS_{2(g)} \rightarrow 3/2\ S_{2(g)} + CO_{2(g)}$

$\Delta H_{298} = 1.43$ Kcal

$\Delta S_{298} = 16.32$ E.U.

$T_{NE} = 88^{\circ}K.$

Temp. $^{\circ}K.$	ΔF Kcal	K_{eq}
298	-3.43	3.24×10^{2}
400	-5.10	6.03×10^{2}
600	-8.37	1.12×10^{3}
1000	-14.89	1.74×10^{3}
1500	-23.07	2.29×10^{3}

TABLE II (continued)

SAMPLE CALCULATIONS AND CALCULATED VALUES
of ΔH_{298}, ΔS_{298}, T_{NE}, ΔF_T, and K_{eq} for REACTION EQUATIONS

(6) $SO_{2(g)} + 2H_2S_{(g)} \dashrightarrow 3/2\ S_{2(g)} + 2H_2O_{(g)}$

ΔH_{298} = 11.58 Kcal

ΔS_{298} = 14.28 E. U.

T_{NE} = 811°K.

Temp. °K.	ΔF Kcal	K_{eq}
298	7340	4.26×10^{-5}
400	5870	7.42×10^{-2}
600	3020	8.15×10^{-1}
1000	-2690	3.86
1500	-9810	2.69×10

TABLE III

OPERATING CONDITIONS AND PRODUCT YIELD

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
E-1	649.4	174	4.6	1.15	94.25	4.58	7.77
E-2	443.5	343	2.92	.58	96.5	2.28	8.52
E-3	581.8	375	30.9	45.1	24.0	1.91	8.90
E-4	583.9	329	27.4	18.85	53.85	2.85	7.89
E-5	594.9	128	18.75	1.56	79.7	3.83	8.79
E-6	563.2	316	41.8	32.9	75.3	2.83	9.43
E-7	524.7	326	15.95	62.20	21.95	2.73	9.52
E-8	566.9	256	55.5	14.45	30.1	2.95	7.89
E-9	579.4	239	27.6	0.4	72.0	3.93	9.22
E-10	559.7	274	43.1	14.95	42.0	4.27	9.07
E-11	562.1	227	42.25	0.44	57.3	3.63	8.19
E-12	575.9	278	33.69	0.366	67.3	4.72	9.91
E-13	575.7	217	51.6	.461	47.94	3.78	8.12
E-14	550.6	235	42.6	Not Determined		3.5	8.25
E-15	566.9	329	54.1			3.74	8.14
E-16	560.2	218	57.74	.46	41.8	3.77	8.12
E-17	560.5	282	37.6	21.3	41.1	1.98	6.55
E-18	573.2	565	18.05	67.85	14.1	0.9	8.53
E-19	569.6	229	44.55	33.65	21.8	1.3	4.11
E-20	574.5	204	33.32	0.49	66.19	1.92	3.53
E-21	573.2	315	42.5	29.85	27.65	1.98	7.34
E-22	568.9	165	13.35	0.6	86.05	4.42	5.98
E-23	570.8	314	39.5	24.5	36.0	1.99	7.33
MR-1	558.9	370	52.5	11.1	36.4	3.62	8.23
MR-2	559.2	513	57.3	11.9	30.8	3.62	8.23
MR-3	566.6	363	56.7	15.14	28.16	3.23	8.00
MR-4	562.9	480	49.2	30.4	20.4	2.47	8.14
MR-5	564.5	598	38.4	42.2	19.2	1.87	7.94

TABLE III (continued)

OPERATING CONDITIONS AND PRODUCT YIELD

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
MR-6	565.9	763	26.0	59.9	14.1	1.32	7.91
MR-7	564.4	330	63.0	1.8	35.2	3.8	8.28
MR-8	563.3	360	54.4	0.0	45.6	4.05	8.14
MR-9	563.1	333	34.3	0.6	65.1	4.44	8.08
MR-10	561.0	328	33.6	0.2	66.2	4.51	8.06
MR-11	562.4	243	4.12	0.41	95.5	6.44	8.06
MR-12	563.3	313	5.12	0.32	94.56	4.69	7.96
MR-13	563.6	220	4.55	0.91	94.54	7.14	7.98
MR-14	564.1	350	48.00	0.0	52.00	4.14	8.02
MR-15	564.5	340	35.3	0.3	64.4	4.32	8.03
MR-16	562.8	330	32.8	0.0	67.2	4.34	8.08
MR-17	564.5	308	3.9	0.0	96.1	4.83	7.99
TM-1	563.3	383	39.2	0.2	60.6	4.12	8.76
TM-2	563.4	386	43.5	0.5	56.0	4.2	8.73
TM-3	552.2	463	52.3	0.0	47.7	3.87	9.90
TM-4	562.5	347	31.1	0.0	68.9	3.65	7.03
TM-5	562.3	347	61.7	2.6	35.7	4.1	5.17
TM-6	560.3	304	8.55	0.66	90.8	3.46	6.06
TM-7	562.5	429	57.3	0.7	42.0	3.68	8.97
T-1	553.6	408	57.8	.24	41.96	3.44	8.08
T-2	542.8	399	56.2	6.01	37.8	3.6	8.00
T-3	535.0	384	49.5	6.77	43.7	3.65	7.98
T-4	524.3	381	41.0	29.9	29.1	3.68	7.96
T-5	582.6	394	3.56	.51	96.	3.56	8.02
T-6	571.0	390	10.25	0.25	89.50	3.6	8.00

TABLE III (continued)

OPERATING CONDITIONS AND PRODUCT YIELD

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
T-7	562.0	380	52.00	0.0	48.00	3.72	8.03
T-8	525.5	400	30.5	41.5	28.0	3.67	7.97
T-9	574.	382	54.	0.0	46.0	3.68	7.97
T-10	584.9	397	34.8	0.5	64.7	3.61	7.99
T-11	565.	390	61.5	2.0	36.5	3.60	8.00
T-12	545.	385	52.	16.6	31.4	3.64	7.98

TABLE IV

PERCENT YIELDS WITH VARYING TEMPERATURE
(Fresh Catalyst)

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
E-5	594.9	128	18.75	1.56	79.7	3.83	8.79
E-13	575.7	217	51.60	.46	47.94	3.78	8.12
T-8	525.5	400	30.50	41.5	28.0	3.67	7.97
T-9	574.0	382	54.00	0.0	46.0	3.68	7.97
T-10	584.9	397	34.80	0.5	64.7	3.61	7.99
T-11	565.0	390	61.50	2.0	36.5	3.60	8.00
T-12	545.0	385	52.00	16.6	31.4	3.64	7.98

TABLE V

PERCENT YIELDS WITH VARYING TEMPERATURE
(Catalyst Used 160 Hours)

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
T-1	553.6	408	57.8	.24	41.96	3.44	8.08
T-2	542.8	399	56.2	6.01	37.8	3.6	8.00
T-3	535.0	384	49.5	6.77	43.7	3.65	7.98
T-4	524.3	381	41.0	29.9	29.1	3.68	7.96
T-5	582.6	394	3.56	.51	96.	3.56	8.02
T-6	571.0	390	10.25	0.25	89.50	3.6	8.00
T-7	562.0	380	52.00	0.0	48.00	3.72	8.03

TABLE VI

PERCENT YIELDS WITH VARYING MOL RATIO

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
MR-2	559.2	513	57.3	11.9	30.8	3.62	8.23
MR-4	562.9	480	49.2	30.4	20.4	2.47	8.14
MR-5	564.5	598	38.4	42.2	19.2	1.87	7.94
MR-6	565.9	763	26.0	59.9	14.1	1.32	7.91
MR-8	563.3	360	54.4	0.0	45.6	4.05	8.14
MR-9	563.1	333	34.3	0.6	65.1	4.44	8.08
MR-10	561.0	328	33.6	0.2	66.2	4.51	8.06
MR-11	562.4	243	4.12	0.41	95.5	6.44	8.06
MR-12	563.3	313	5.12	0.32	94.56	4.69	7.96
MR-13	563.6	220	4.55	0.91	94.54	7.14	7.98
MR-14	564.1	350	48.00	0.0	52.00	4.14	8.02
MR-15	564.5	340	35.3	0.3	64.4	4.32	8.03
MR-16	562.8	330	32.8	0.0	67.2	4.34	8.08
MR-17	564.5	308	3.9	0.0	96.1	4.83	7.99

TABLE VII

PERCENT YIELDS WITH VARYING TOTAL MOLS OF FEED

Run No.	Average Temp. °C.	Grams SO_2 Used	% SO_2 Converted to S	% SO_2 Unreacted	% SO_2 to Other Products	Mol Ratio CH_4/SO_2	Total Mols per Hr.
TM-3	552.2	463	52.3	0.0	47.7	3.87	9.90
TM-4	562.5	347	31.1	0.0	68.9	3.65	7.03
TM-6	560.3	304	8.55	0.66	90.8	3.46	6.06
TM-7	562.5	429	57.3	0.7	42.0	3.68	8.97
T-1	553.6	408	57.8	.24	41.96	3.44	8.08

TABLE VIII

PERCENT SULFUR DIOXIDE CONVERTED TO SULFUR
DIVIDED BY PERCENT SULFUR DIOXIDE REACTED AT VARIOUS MOL RATIOS

Run No.	% SO_2 to Sulfur	% SO_2 Reacted	$\frac{\%\ SO_2 \text{ to Sulfur}}{\%\ SO_2 \text{ Reacted}} \times 100$	Mol Ratio CH_4/SO_2
MR-2	57.3	88.10	65.1	3.62
MR-4	49.2	69.60	70.6	2.47
MR-5	38.4	57.80	66.4	1.87
MR-6	26.0	40.10	64.8	1.32
MR-8	54.4	100.00	54.4	4.05
MR-9	34.3	99.40	34.5	4.44
MR-10	33.6	99.80	33.7	4.51
MR-11	4.12	99.59	4.14	6.44
MR-12	5.12	99.68	5.14	4.69
MR-13	4.55	99.09	4.58	7.14
MR-14	48.00	100.00	48.00	4.14
MR-15	35.3	99.7	35.4	4.32
MR-16	32.8	100.0	32.8	4.34
MR-17	3.9	100.0	3.9	4.83

TABLE IX

PERCENT SULFUR DIOXIDE CONVERTED TO SULFUR
DIVIDED BY PERCENT SULFUR DIOXIDE REACTED AT VARIOUS TEMPERATURES

Run No.	Average Temp. °C.	% SO_2 to Sulfur	% SO_2 Reacted	$\frac{\%\ SO_2 \text{ to Sulfur}}{\%\ SO_2 \text{ Reacted}} \times 100$
E-5	594.9	18.75	98.44	19.05
E-13	575.7	51.60	99.44	51.90
T-8	525.5	30.50	58.50	52.10
T-9	574.0	54.00	100.00	54.00
T-10	584.9	34.80	99.50	35.00
T-11	565.0	61.50	98.00	62.80
T-12	545.0	52.00	83.40	62.40

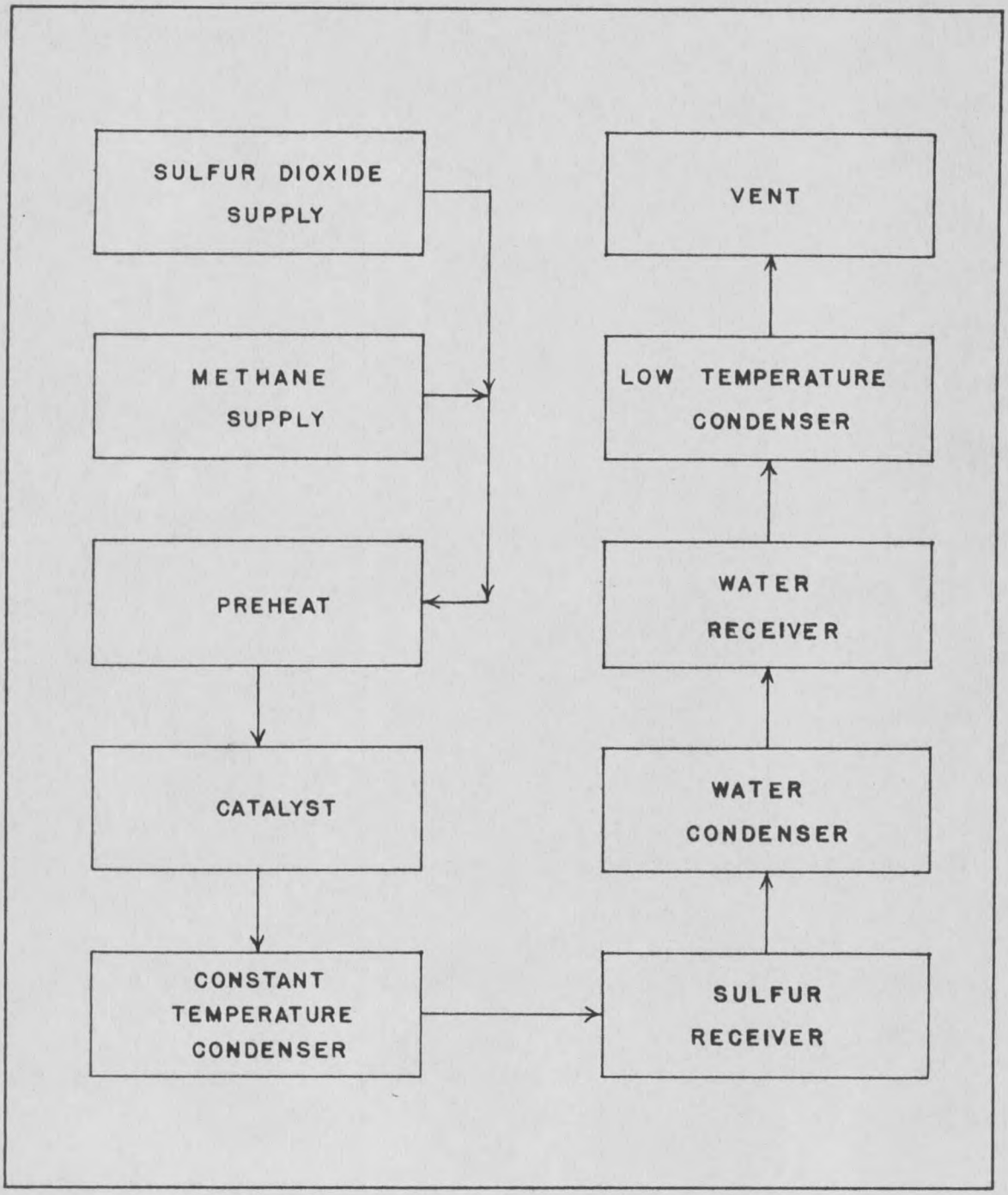

FIG. 1. BLOCK FLOW DIAGRAM

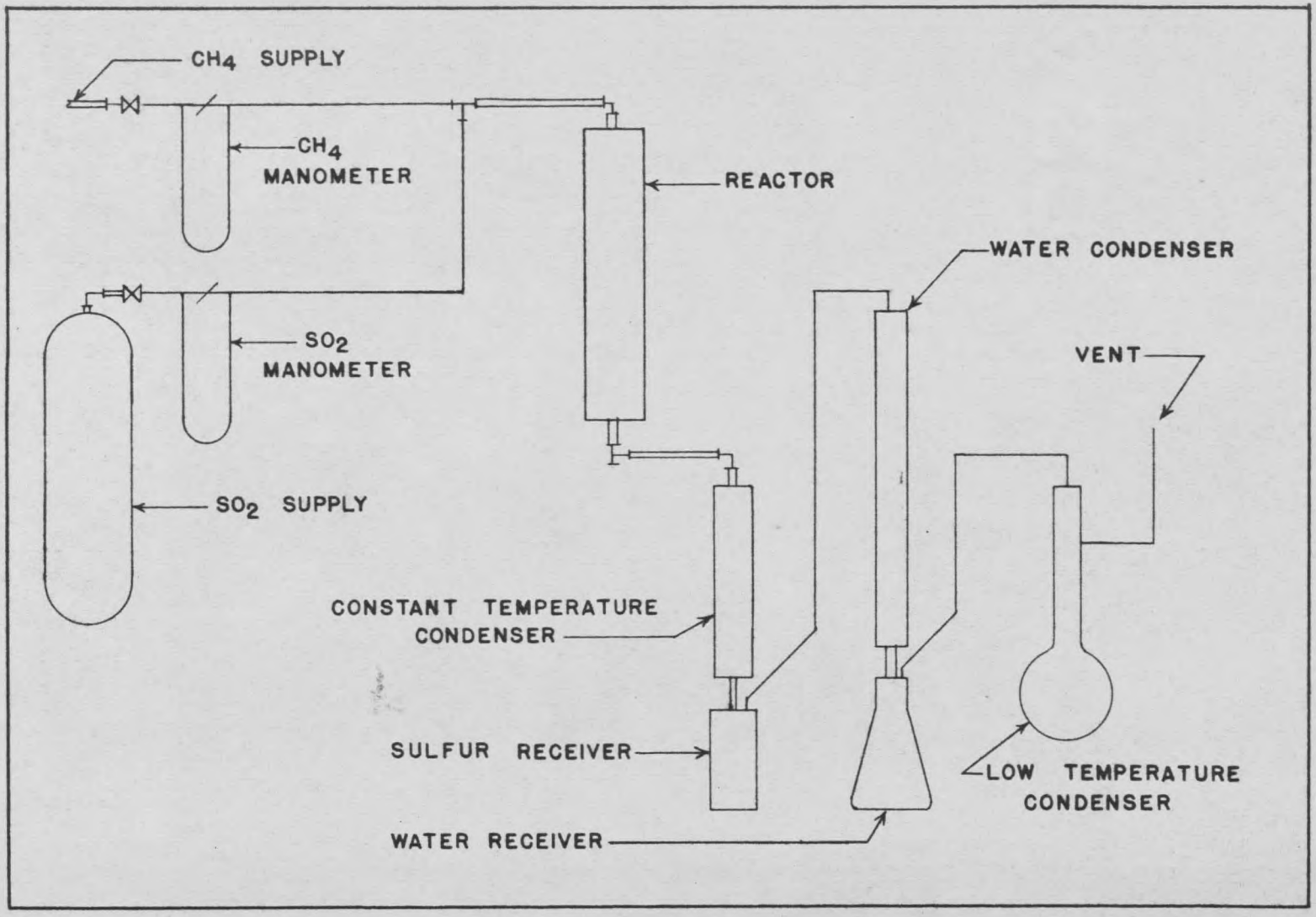

FIG. 2 DIAGRAM OF SULFUR DIOXIDE REDUCTION UNIT

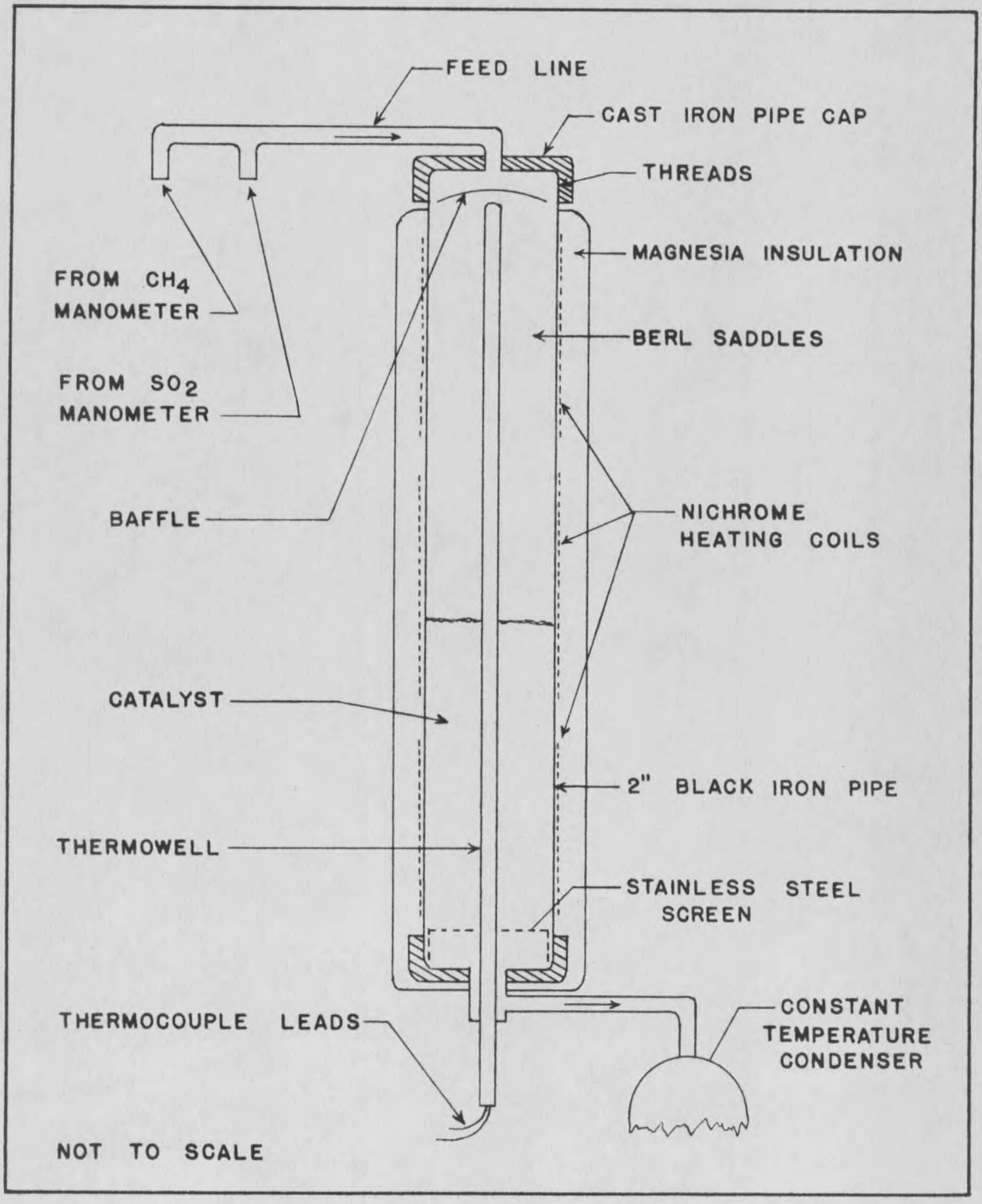

FIG. 3. DIAGRAM OF REACTOR

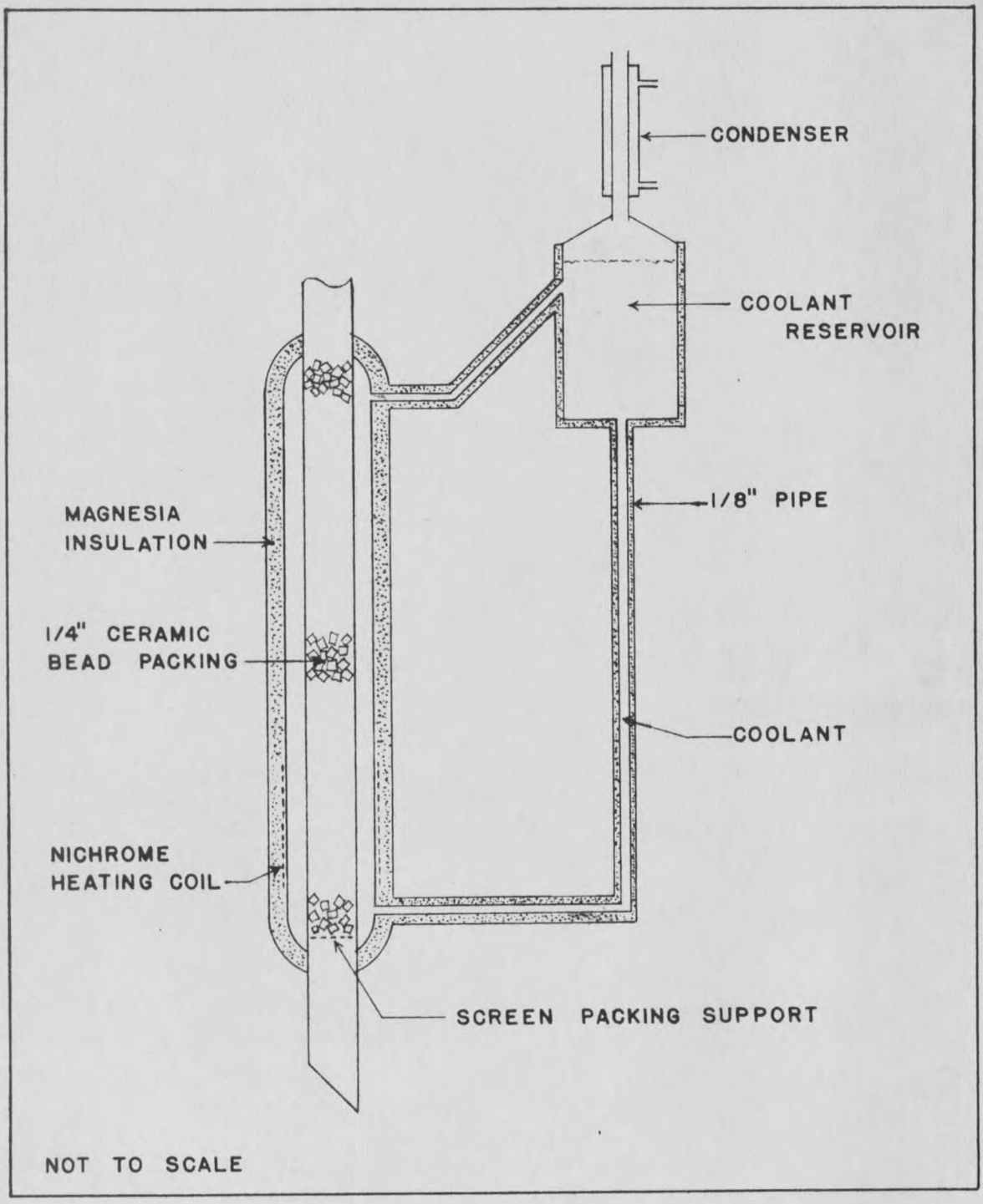

FIG. 4. DIAGRAM OF CONSTANT TEMPERATURE CONDENSER

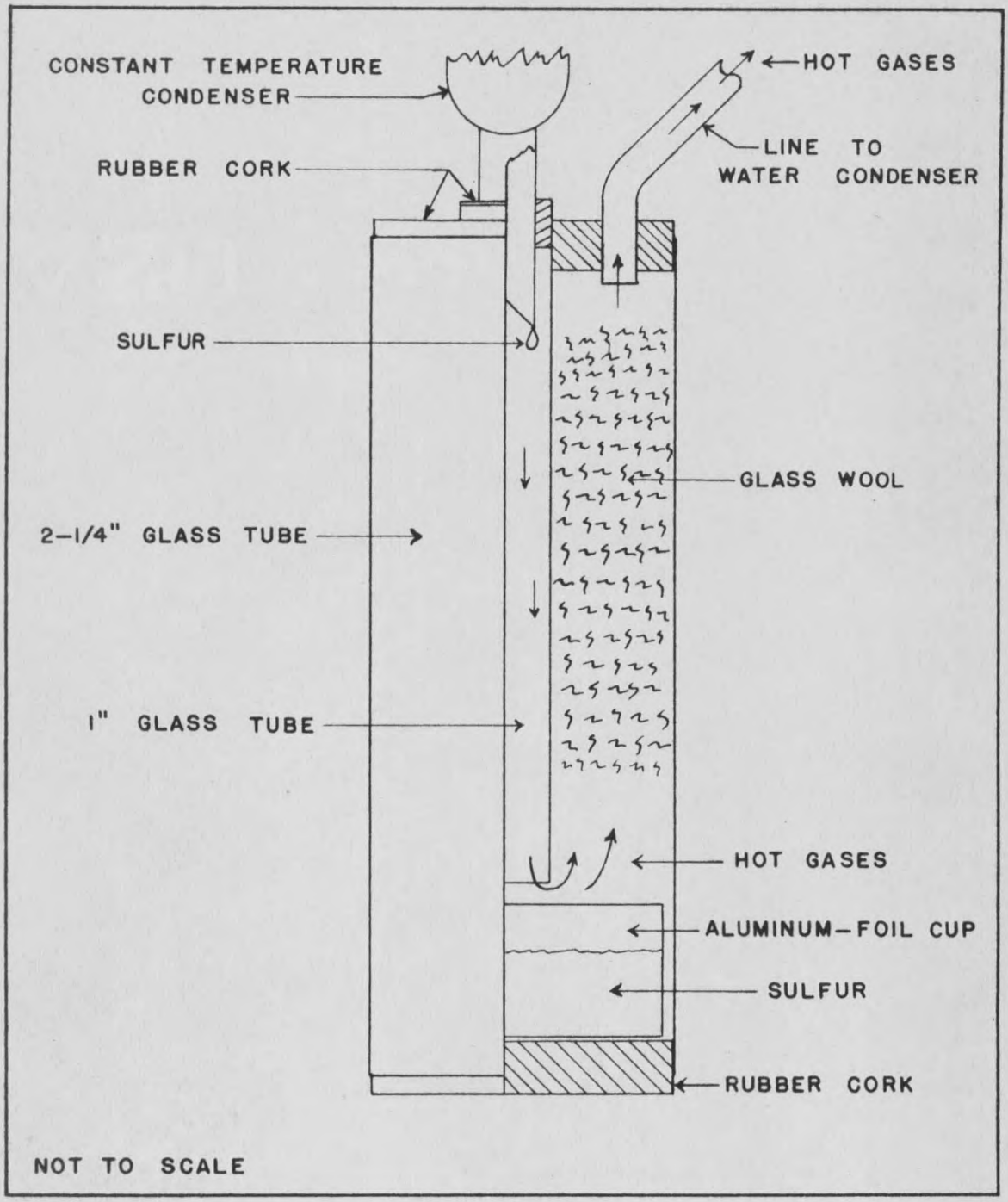

FIG. 4-A. DIAGRAM OF SULFUR RECEIVER

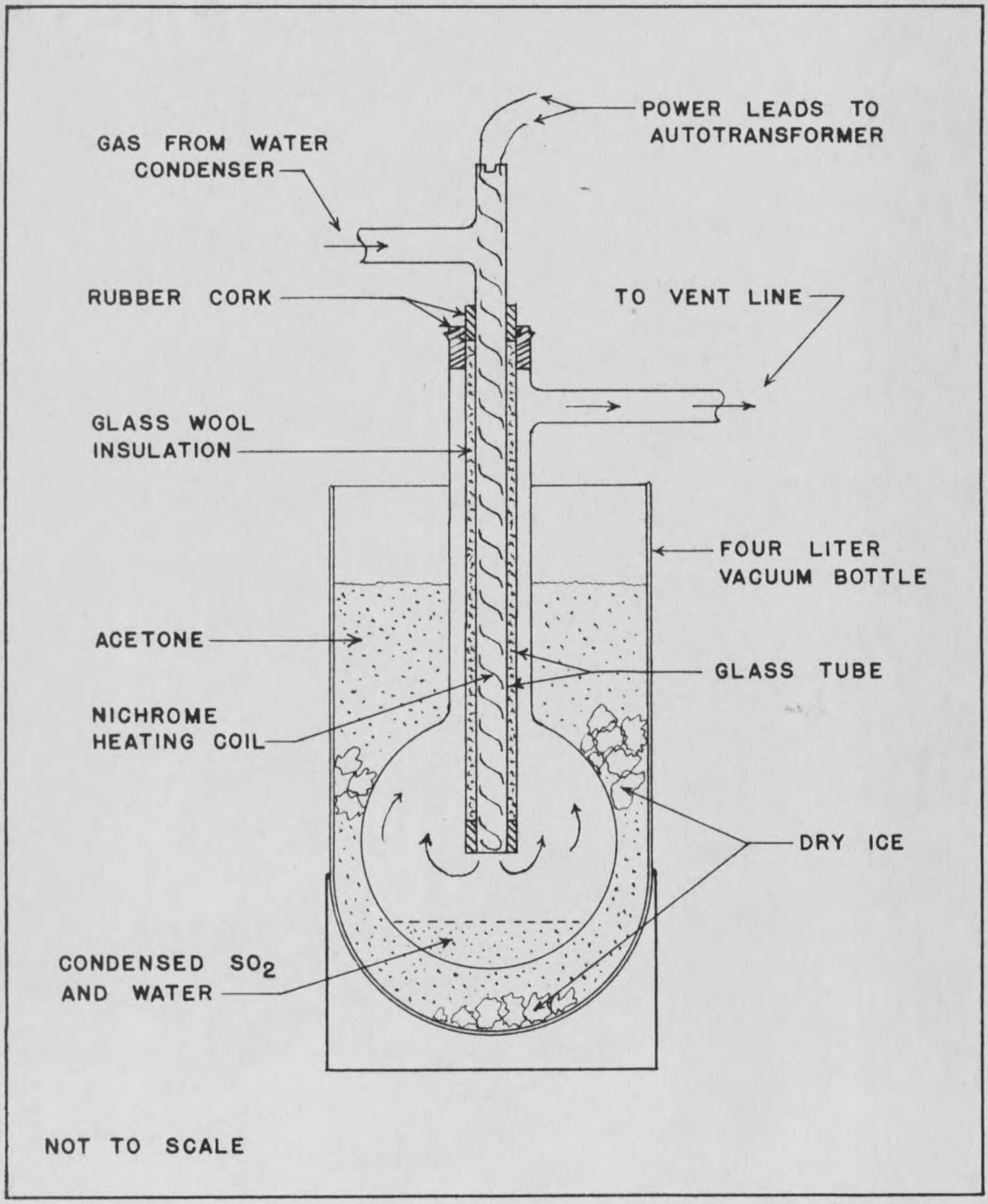

FIG. 5. DIAGRAM OF LOW TEMPERATURE CONDENSER

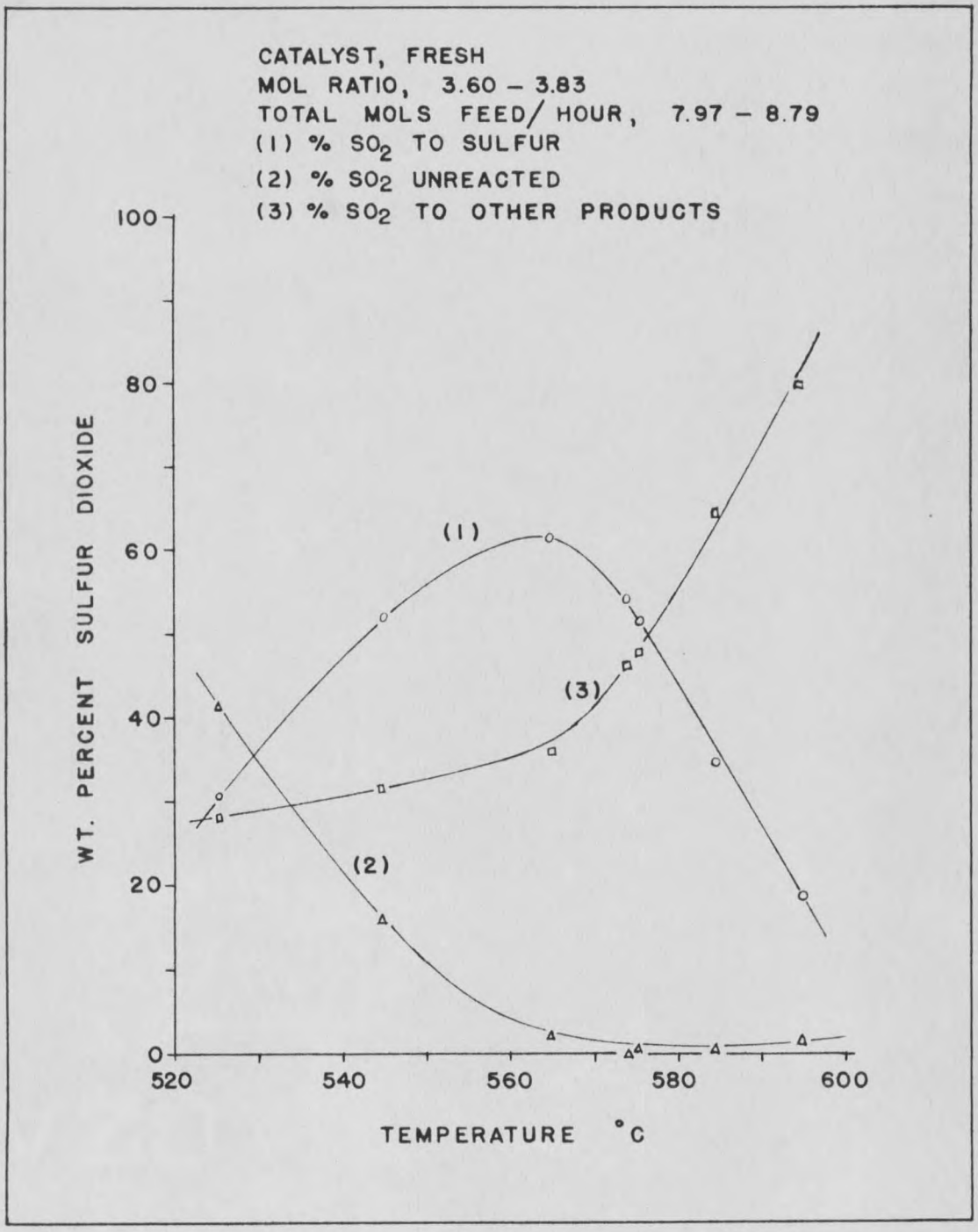

FIG. 6. PERCENT YIELD WITH VARYING TEMPERATURE WHEN USING FRESH CATALYST

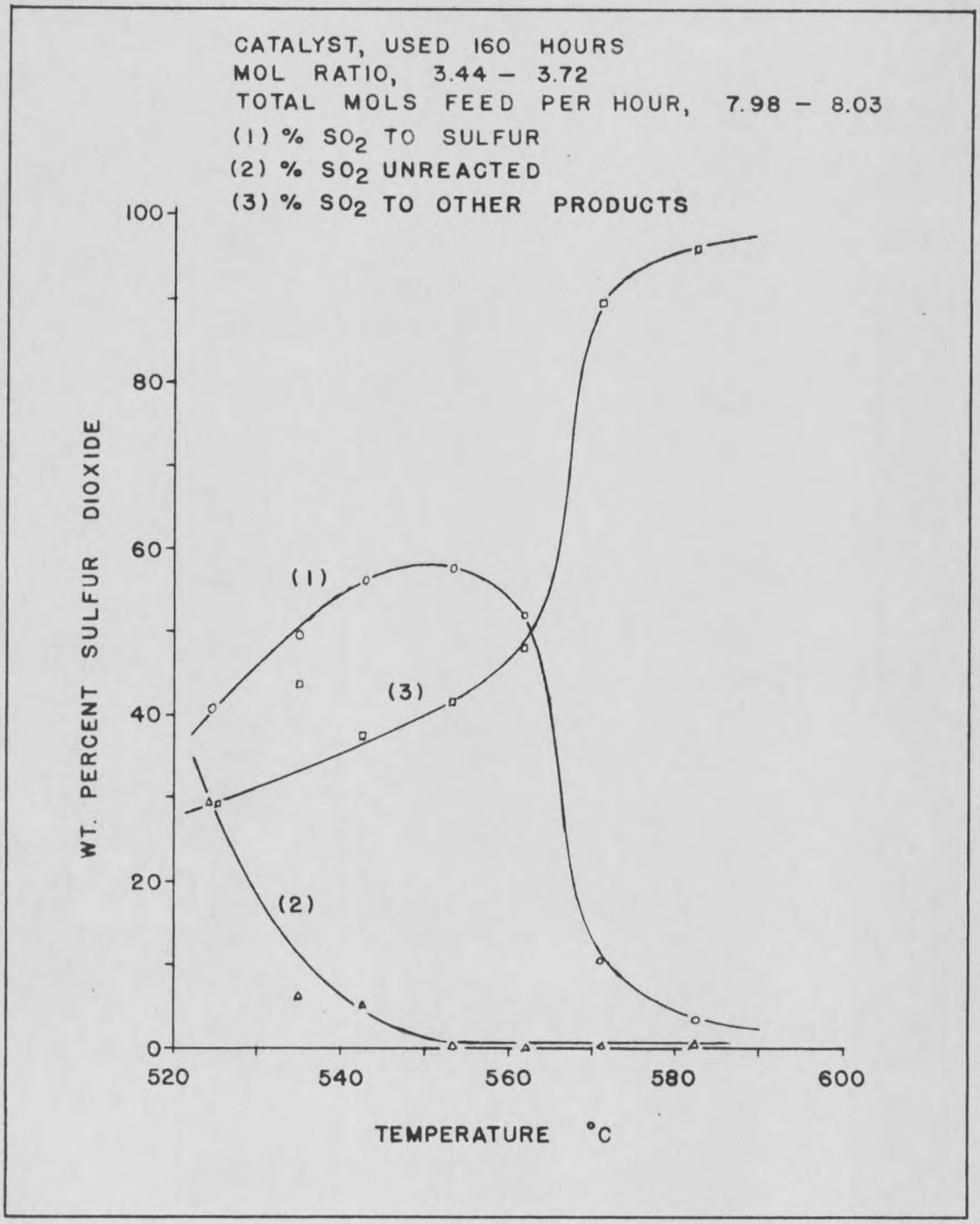

FIG. 7. PERCENT YIELD WITH VARYING TEMPERATURE WHEN CATALYST USED MORE THAN 160 HOURS

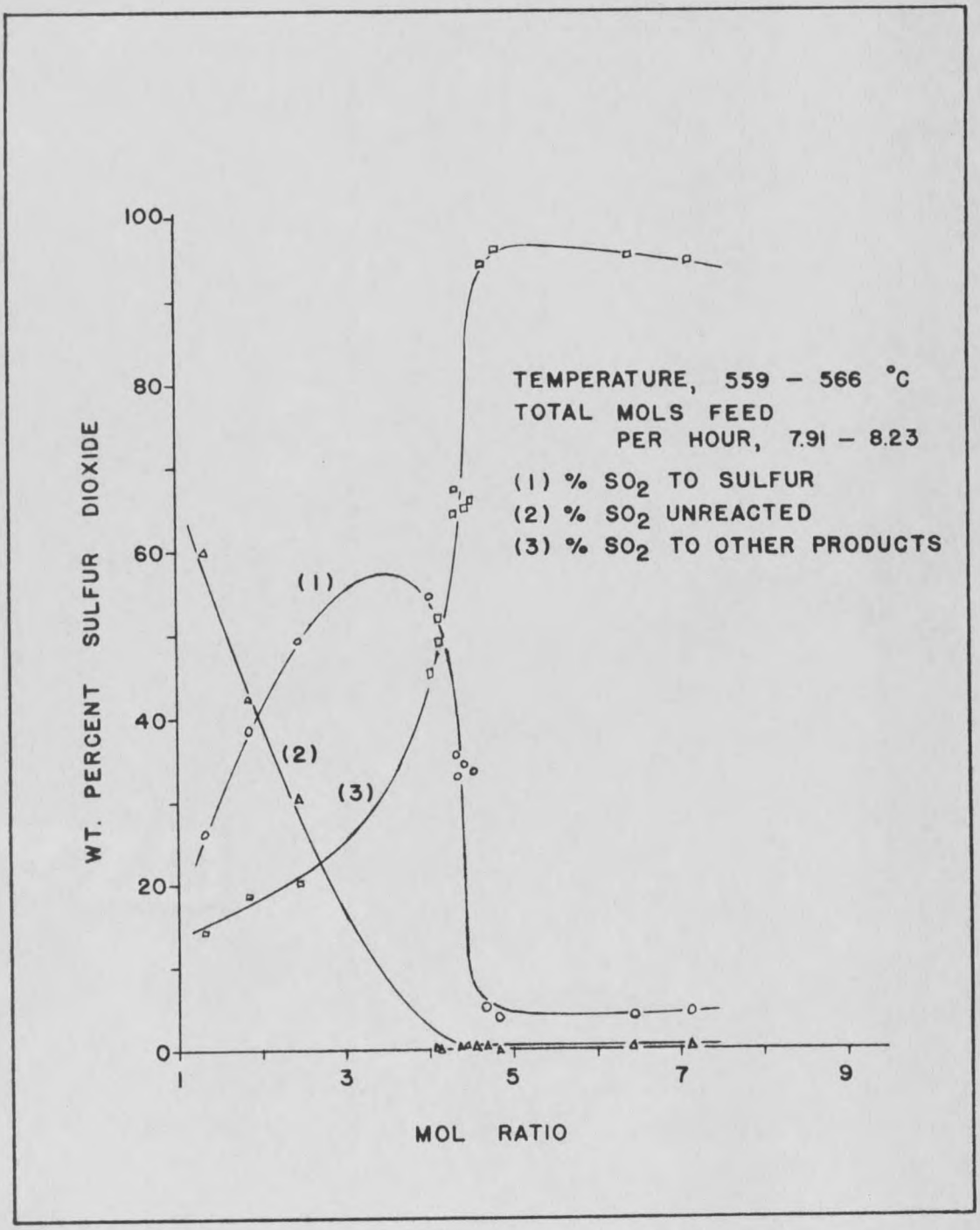

FIG. 8. PERCENT YIELD WITH VARYING MOL RATIO

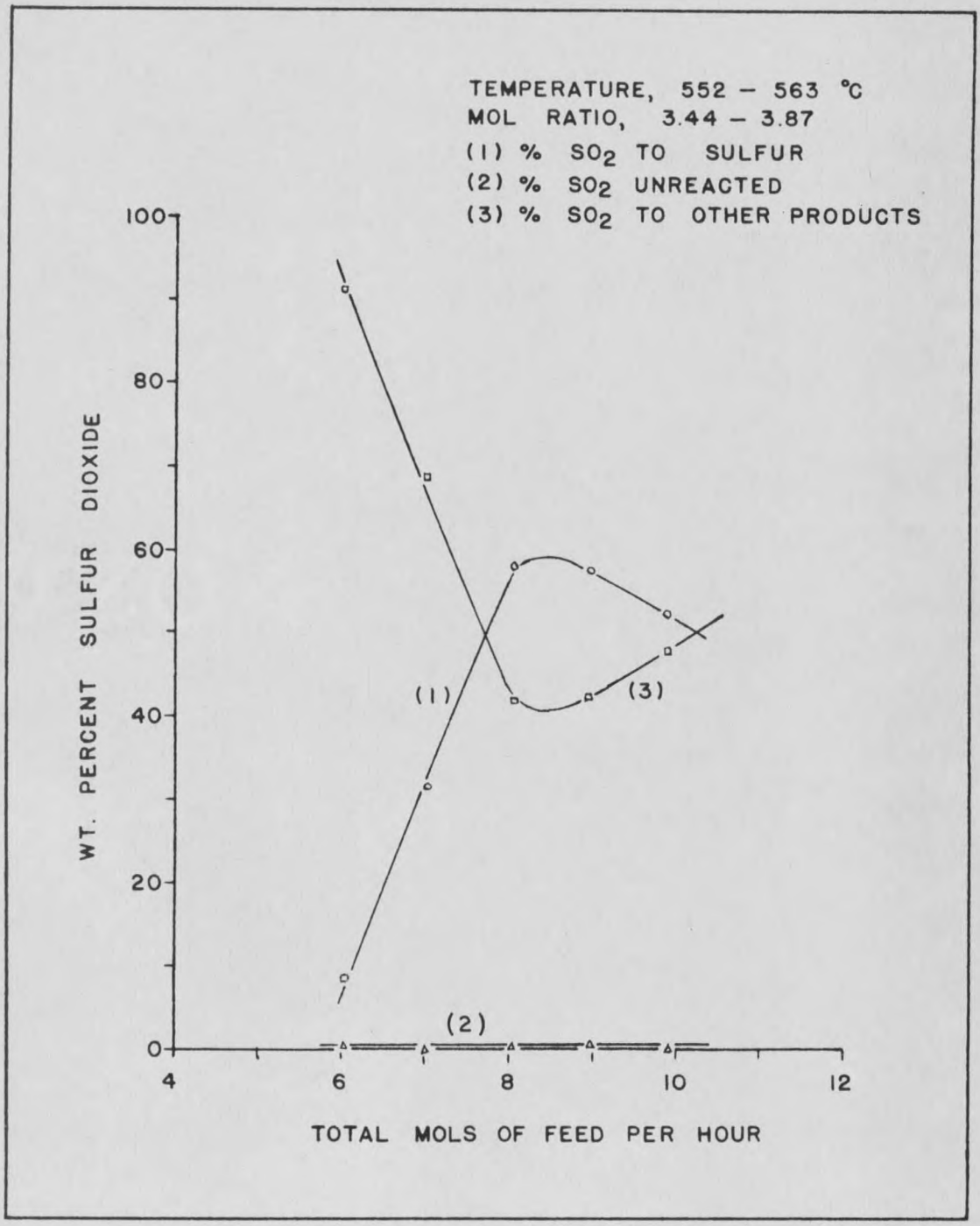

FIG. 9. PERCENT YIELD WITH VARYING TOTAL MOLS OF FEED PER HOUR

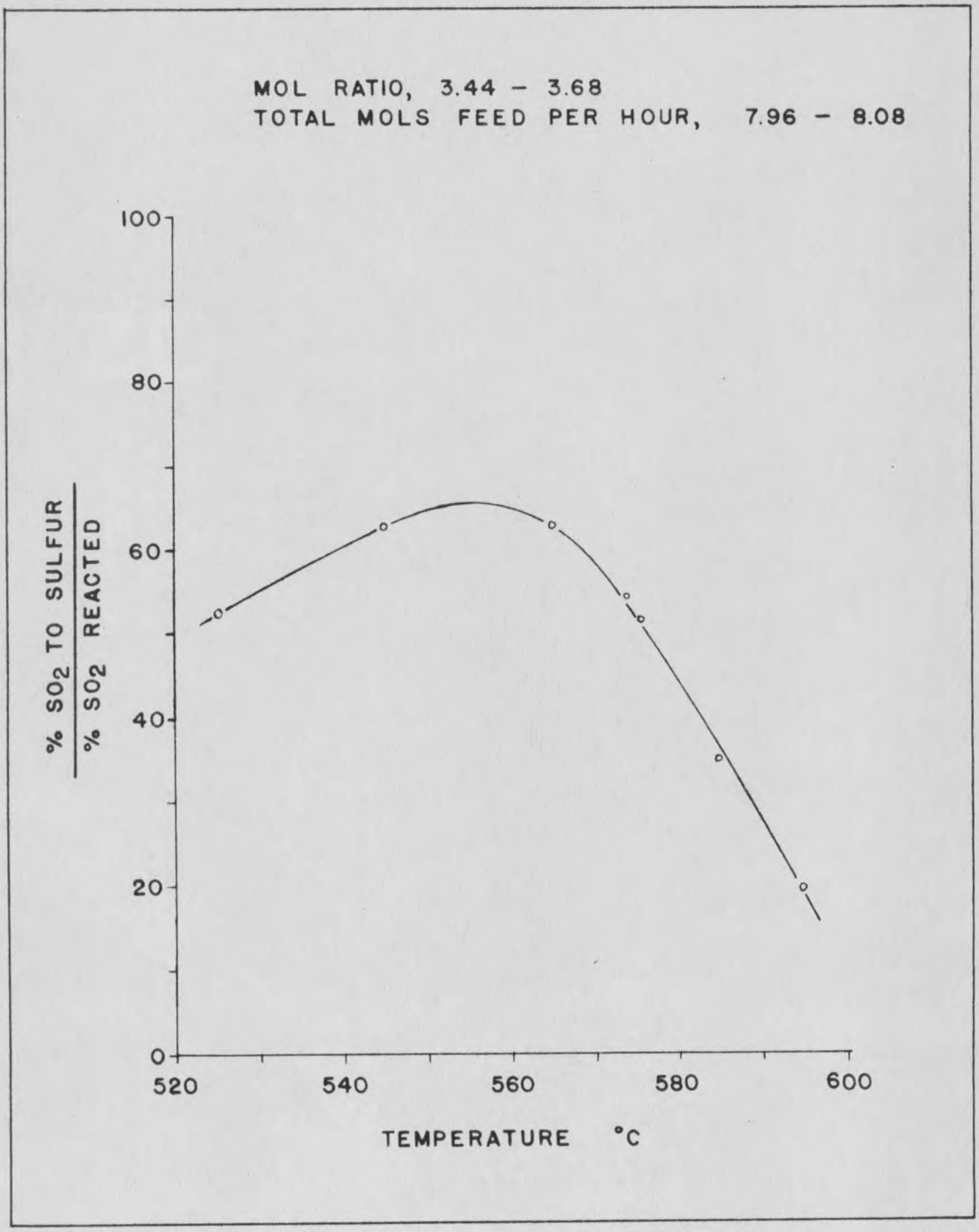

FIG. 10. ULTIMATE YIELD OF SULFUR WITH VARYING TEMPERATURE

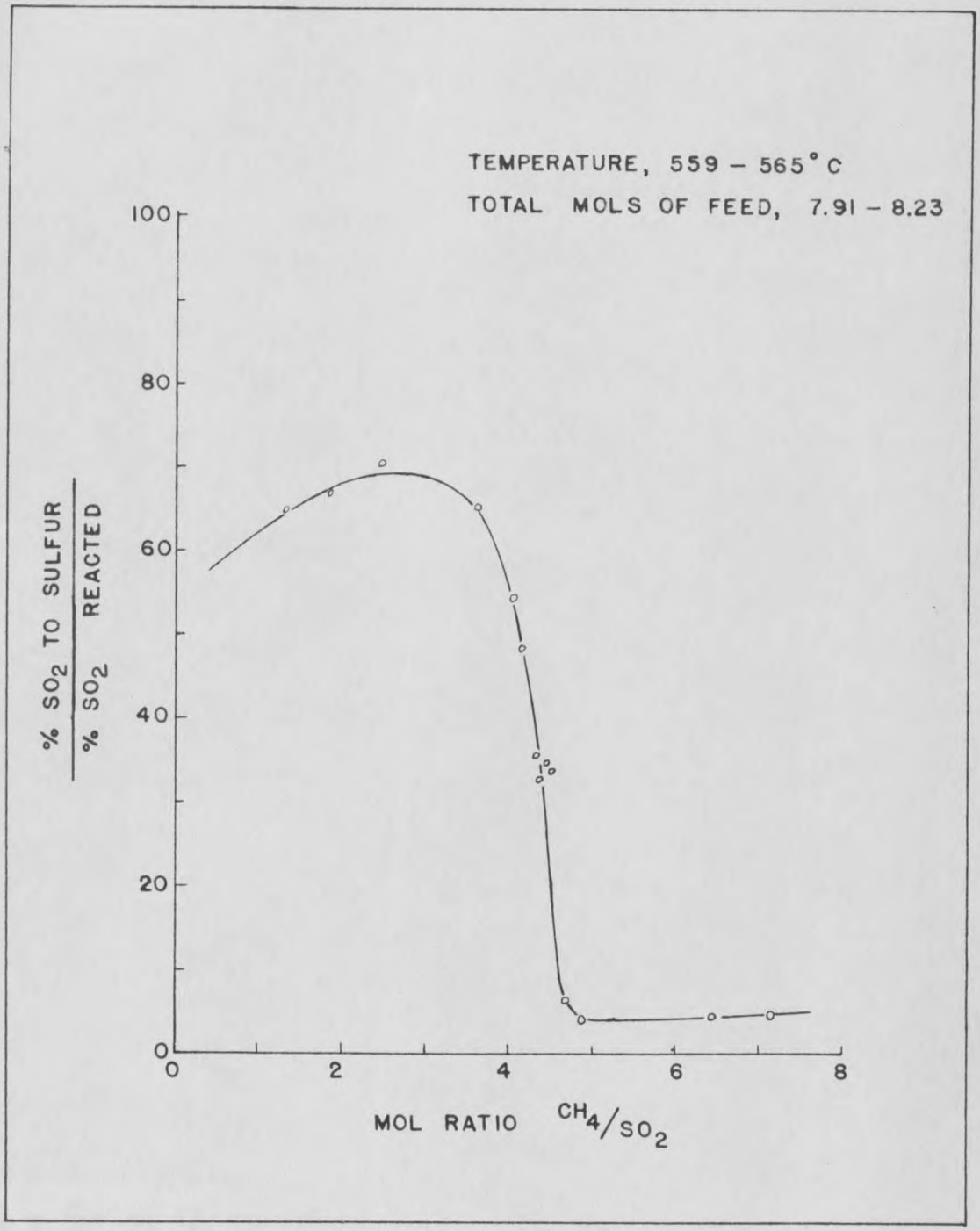

FIG. II. ULTIMATE YIELD OF SULFUR WITH VARYING MOL RATIO

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