



The catalytic desulfurization of Wyoming fuel oil
by Bradley L Munro

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
© Copyright by Bradley L Munro (1952)

Abstract:

The primary purpose of this investigation was to compare various destructive hydrogenation catalysts at various operating conditions to determine the most effective catalyst and operating conditions with which to reduce the sulfur content of a petroleum distillate from 2.1 to less than 0.5 percent without carbon-to-carbon fissure.

The various destructive hydrogenation catalysts which were investigated were molybdena alumina, cobalt molybdate, molybdenum sulfide and tungstic oxide, A nickel oxide catalyst was briefly investigated at destructive hydrogenation operating conditions* The three to six hour tests were performed with 850 to 1000 grams of catalyst in a fixed bed reactor at reactor pressures of 300 and 500 psig, temperatures between 375 and 430°C, space velocities between 0.75 and 1.3 grams oil per gram catalyst per hour and hydrogen-to-oil ratios between 0.2 and 1.2 liters exit gas per gram of oil. Cobalt molybdate, molybdenum sulfide, and molybdena alumina catalysts produced effluent oil containing less than 0.5 percent sulfur. Cobalt molybdate and molybdenum sulfide displayed nearly similar catalyst activity which was greater than the activity of molybdena alumina.

The secondary purpose of this investigation was to determine the duration of effective catalyst activity of molybdenum sulfide at operating conditions of 500 psig and 410°C* Molybdenum sulfide was capable of reducing the effluent oil sulfur content to less than 0.5 percent for an operating period in excess of 2000 hours with only a 35 percent decline in catalyst activity.

THE CATALYTIC DESULFURIZATION
OF WYOMING FUEL OIL

by

BRADLEY L. MUNRO

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

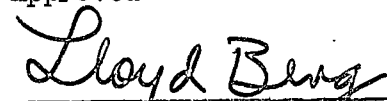
for the degree of


Master of Science in Chemical Engineering

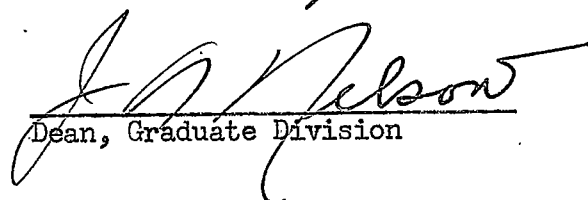
at

Montana State College

Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

Bozeman, Montana
August, 1952

LIBRARY MONTANA STATE COLLEGE
BOZEMAN
AUG 21 1952

N 378
M 926 c
Cop. 2

TABLE OF CONTENTS

	page
Abstract.	3
Introduction.	4
Equipment, Materials and Methods.	8
Equipment	8
Materials	10
Methods	10
Sample Calculations	13
Thermodynamic Calculations.	16
Discussion of Results	20
The effect of operating conditions upon desulfurization with various destructive hydrogenation catalysts at super atmospheric pressure.	20
The effect of operating conditions upon the Life Study Run of molybdenum sulfide catalyst	23
Conclusion	28
Literature Cited.	30
Acknowledgment.	31
Appendix.	32

ABSTRACT

The primary purpose of this investigation was to compare various destructive hydrogenation catalysts at various operating conditions to determine the most effective catalyst and operating conditions with which to reduce the sulfur content of a petroleum distillate from 2.1 to less than 0.5 percent without carbon-to-carbon fissure.

The various destructive hydrogenation catalysts which were investigated were molybdena alumina, cobalt molybdate, molybdenum sulfide and tungstic oxide. A nickel oxide catalyst was briefly investigated at destructive hydrogenation operating conditions. The three to six hour tests were performed with 850 to 1000 grams of catalyst in a fixed bed reactor at reactor pressures of 300 and 500 psig, temperatures between 375 and 430°C, space velocities between 0.75 and 1.3 grams oil per gram catalyst per hour and hydrogen-to-oil ratios between 0.2 and 1.2 liters exit gas per gram of oil. Cobalt molybdate, molybdenum sulfide, and molybdena alumina catalysts produced effluent oil containing less than 0.5 percent sulfur. Cobalt molybdate and molybdenum sulfide displayed nearly similar catalyst activity which was greater than the activity of molybdena alumina.

The secondary purpose of this investigation was to determine the duration of effective catalyst activity of molybdenum sulfide at operating conditions of 500 psig and 410°C. Molybdenum sulfide was capable of reducing the effluent oil sulfur content to less than 0.5 percent for an operating period in excess of 2000 hours with only a 35 percent decline in catalyst activity.

INTRODUCTION

The increased utilization of high sulfur content crude petroleum found in West Texas, Wyoming, Montana, and California has caused an ever increasing petroleum refining problem. Some crude petroleum stocks contain as much as 4 to 5 percent sulfur and the reduction or elimination of this objectionable constituent from refined petroleum products is necessary. Sulfur may occur in crude petroleum and various refined fractions as one or more of the following forms: elemental sulfur, mercaptans, hydrogen sulfide, carbon disulfide, thiophenes, thiophanes, thioalcohols, organic sulfides, disulfides, polysulfides, and sulfates (6). The principal objections to sulfur compounds in refined products are their actual or potential corrosiveness, disagreeable odor, deleterious effect on color stability, unfavorable influence on tetra-ethyl lead susceptibility and oxidation characteristics (6).

A literature survey of the various petroleum treating methods disclosed that a number of schemes are available to convert immediately corrosive sulfur compounds such as mercaptans into less objectionable sulfur compounds. These methods for treating a motor fuel would not accomplish a reduction in sulfur content and the potential corrosiveness of the fuel would still be present. Other treating methods for removal of sulfur from gasoline and naphtha distillates take advantage of the relatively acidic type sulfur compounds. Alkaline solutions will remove some sulfur compounds acidic in nature while activated bauxites will cause the decomposition of certain sulfur compounds (8).

The above methods of desulfurization are effective for distillates

boiling below 400°F and only slightly effective for heavier distillates of the 400 to 700°F boiling range. The use of a solvent extraction method to remove sulfur containing molecules in a high sulfur content, high boiling distillate would not be practical because a high proportion of the oil molecules contains sulfur and a high loss of product would result. The use of an activated bauxite or Fullers earth type catalyst would be effective in decomposing only the less stable sulfur compounds while it would have little effect upon the cyclic-type sulfur compounds. Koski (7) reported a 50 percent decrease in sulfur content of a fuel oil in the boiling range of 440 to 650°F with the use of bauxite and acid-activated bauxite catalysts.

The recent interest in the utilization of distillates heavier than gasoline for Diesel engines, gas turbines, and jet aircraft motors has increased the need for effective refining methods of high sulfur content fuel oil distillates. A fuel of high sulfur content used in high-speed Diesel engines causes formation of deposits on the cylinders and wear of various parts of the engine (8). The combustion products of sulfur also cause weakening and corrosion of the vital parts of gas turbines and jet engines.

The bond energy for a carbon-to carbon bond (58.6 K cal/mol) is only slightly higher than a carbon-to-sulfur bond (54.5 K cal/mol). Therefore, a contact agent used for desulfurization of heavy distillates, without carbon-to-carbon fission, must be very selective to take advantage of the slight difference in bond energy. Certain contact agents such as NiO which form stable sulfides on contact with sulfur-bearing hydrocarbons are very effective until the contact agents are converted to the sulfide form which displays little catalytic desulfurization activity. Therefore, frequent

and costly regeneration methods are a serious disadvantage in reclaiming the expensive chemical reagent type contact agent.

Desulfurization has been accomplished by the use of destructive hydrogenation contact agents which do or do not form metal sulfides. Examples found in the literature point toward those metals in Groups VI and VIII of the Periodic table with particular emphasis upon chromium, cobalt, iron, molybdenum, nickel and tungsten as being the most effective agents for destructive hydrogenation and desulfurization.

Destructive hydrogenation reactions are carried out at temperatures at which incipient carbon-to-carbon cracking occurs at moderate to high hydrogen pressures and with a catalyst containing an oxide or sulfide of an element in Groups VI and VIII of the Periodic table.

Previous work has been done in the investigation of desulfurization agents to reduce the sulfur content by more than 75 percent in a fuel oil with a boiling range of 440 to 650°F. Haas (5) and Fischbach (3) performed tests on various nickel oxide contact agents and discovered that the active desulfurization life of the catalyst was short and regeneration was difficult. Koski (7) investigated the use of less expensive contact agents such as bauxite and alumina at less drastic operating conditions, but results disclosed that a maximum of only 50 percent sulfur removal could be accomplished.

The investigation of destructive hydrogenation catalysts at super-atmospheric pressures with a variety of catalysts to indicate a possible approach toward more complete desulfurization was reported by Koski (7) as well as in this work. The catalysts investigated were molybdena alumina,

cobalt molybdate, tungstic oxide, nickel oxide, and molybdenum sulfide. Of this group of catalysts the most promising was MoS_2 on the basis of activity and patentability. The variables of hydrogen-to-oil ratio, pressure, space velocity, and temperature which effect the performance of the various catalysts were briefly studied. An extensive catalyst life study was performed on the molybdenum sulfide catalyst to give additional data on the variables of hydrogen-to-oil ratio, and space velocity. Green (4) reported on additional investigations of MoS_2 catalyst and the effects of pressure, air oxidation regeneration, and dilution of hydrogen with hydrocarbon gases.

EQUIPMENT, MATERIALS AND METHODS

EQUIPMENT

The two reactors that were used for the investigation were designed for use at pressures up to 900 psig. The essential difference of the reactors was the volume of the catalyst bed.

The large volume pressure reactor which was used for short operating periods with catalyst charges of nearly 1000 grams is illustrated in Figure 1. An excellent detailed description of the construction of this reactor was given by Crecelius (2). The reactor was used with a hydrogen gas supply tank fitted with a high-pressure regulator, an oil charge piston pump, an effluent oil receiver, and an exhaust gas blow-down system which contained a caustic wash and a wet test meter.

The small volume pressure reactor which was used for the catalyst life study with a catalyst charge of 100 grams is illustrated in Figure 2. The reactor consisted of a 16 inch length of $1\frac{1}{2}$ inch extra-strong black pipe fitted with a $1\frac{1}{2}$ to $3/4$ inch reducer at the top and a $1\frac{1}{2}$ to $1/2$ inch reducer at the bottom. Extra-strong pipe and fittings were used throughout the reactor system which was under pressure. The top of the reactor was fitted with a union, two crosses, and an assembly of valves for hydrogen inlet, oil inlet, oil feed-line bleed, air inlet for regeneration, blowout-disk exhaust system, and thermowell tube. The thermowell tube was a $1/4$ inch black pipe which extended from the cross at the top of the reactor along the vertical axis of the reactor to within one inch of the bottom. The thermowell was capped at the bottom end and provided room for insertion of three thermocouples. The hot junctions of the thermocouples were placed at any desired

position in the thermowell.

At the bottom or discharge end of the reactor were fitted a $\frac{1}{2}$ inch pipe union, a tee, pressure gage, and a small-volume Grove spring-loaded back-pressure valve which was capable of controlling back pressures between 0 and 1000 psig. A Mason-Neilan small-volume air-to-close regulator valve was substituted for the Grove valve during the latter half of the catalyst life study run. A Fisher Wizard proportional controller was used to supply the correct control pressure to the Mason-Neilan valve diaphragm. The Fisher Wizard was supplied with compressed air at 20 psig from the laboratory compressed air system.

The pressure gage was connected through an oil-sealed pig tail to the tee fitting above the back pressure valve. The vapors passing through the back pressure valve were condensed in a water-cooled copper tube condenser and were collected in a one-liter Erlenmeyer flask. The non-condensable exhaust gases were passed in series through two gas scrubbing flasks containing sodium hydroxide solution to remove the hydrogen sulfide present in the exhaust gases. The sweetened gas was metered through a wet test meter manufactured by the Precision Scientific Company.

The heating elements for the reactor consisted of three 33-foot lengths of beaded Nichrome coils supplied with current from three 110-volt Powerstat autotransformers. The coils were wound upon the reactor over a layer of asbestos tape and insulated with an additional covering of asbestos tape and a one-inch layer of magnesia mud.

The oil feed system consisted of a two cylinder adjustable stroke piston pump and an oil reservoir.

The design of the reactor made it necessary that catalyst and preheat media be charged to the reactor through the bottom while the reactor was in an inverted position. Preheat media consisted of either 1/4 inch diameter steel or Alundum (aluminum oxide) balls.

The iron-constantan thermocouples for temperature measurements were used in conjunction with a Leeds and Northrup indicating potentiometer.

MATERIALS

The principal materials used for the desulfurization studies were a #3 fuel oil, compressed hydrogen, and various catalysts.

The #3 grade fuel oils produced by the Husky Oil Company from Oregon Basin, Wyoming crude oil contained 2.09 to 2.19 percent sulfur. Additional inspection data of the oils are listed in Table I.

The catalysts investigated were cobalt molybdate, molybdena-alumina, tungstic oxide, nickel oxide and molybdenum disulfide. The code letters and composition of the various catalysts may be found in Table II.

The hydrogen used in this research was obtained from the Whitmore Oxygen Company of Salt Lake City, Utah.

METHODS

The oil charge pump was designed with an adjustable piston stroke length to give any desired oil pumping rate as a means of controlling the space velocity.

The pressure of the reactor was maintained at the desired value by adjustment of the back pressure valve and supply pressure from the hydrogen tank regulator. With the hydrogen supplied at a slightly higher pressure

than the control setting of the back pressure valve, gas flow was maintained through the reactor and the exit gas metering system. During the life study run the wet test meter which measured the amount of exit gas was read every 15 minutes and the value was recorded. Close control of the gas rate was maintained during the operation by this means.

The temperature of the reactor was maintained by beaded Nichrome resistance elements supplied with the proper quantity of current from auto-transformers. An average temperature was determined by means of two thermocouples placed in the thermowell at the catalyst section. These average temperatures determined at 15 minute intervals were in turn averaged for each eight hour sample period.

The pressure reactor was placed in operation by applying current to the resistance coils while hydrogen gas was allowed to flow through the reactor. When the temperature of the catalyst chamber reached 300°C the reactor was pressurized to the desired operating pressure and the gas throughput was adjusted and maintained. When the catalyst temperature reached 380°C the oil pump was turned on to charge oil to the reactor and the heating element current was adjusted to maintain the proper reactor temperature. All recorded readings were begun at the time the reactor conditions became constant.

The operation of the large volume reactor was essentially the same as the catalyst life study reactor. The total operating periods for the large volume reactor seldom exceeded a total of six hours with effluent oil sample periods at either 15, 30, or 60 minute intervals. Temperature measurements were taken at 5-minute intervals with the arithmetic average computed for

the recorded sample periods. The exit gas metering system for the large volume reactor consisted of two wet test meters arranged in parallel to meter accurately large volumes of exit gas.

The collected effluent oil samples were weighed and 10 to 15 gram portions of oil were removed from each sample for sulfur content determination. Dissolved H_2S gas was removed from the 10-15 gram portions of oil by washing with a 10 percent sodium hydroxide solution followed by a water wash. The sulfur content was determined by a modified lamp sulfur method (1) using approximately 2.0 equivalents of sodium carbonate to absorb the sulfur dioxide from the lamp combustion gases. One tenth normal HCl was used to neutralize the remaining sodium carbonate solution by titration with a brom-phenol indicator.

SAMPLE CALCULATIONS

1. A typical Short Duration Run

Run 95

V-2 KGEM

Oil = #3 Fuel Oil (2.09% S)

Reactor Pressure, 300 psig.

Catalyst = 889.5 Gm. Harshaw MoS₂ Mo-X-L321-42 T-1/8"

October 6, 1951
Barometer 640.1 mm Hg

Time Minutes	Sample No.	Sample Weight (grams)	Percent sulfur in Effluent oil	Average Temperature °C	Liters Exit Gas at 22°C
0-60	1	621.5	.442	408	721
60-120	2	761.0	.360	406	1390
120-180	3	742.5	.386	410	2135
180-240	4	827.0	.493	404	2780
		<u>2952.0</u>			

Oil charged 3261.0 grams

Calculation of Space Velocity

$$\frac{3261.0 \text{ gram (oil charge)}}{(889.5 \text{ gram catalyst}) (4 \text{ hour})} = 0.917 \text{ Gram Oil/Gram Catalyst/Hour}$$

Calculation of Exit Gas Liters STP per Minute

Gas metered in Wet Test Meter; therefore, assume gas saturated with water vapor.

Vapor pressure H₂O at 22°C = 19.8 mm Hg

640.1 - 19.8 = 620.3 mm Hg dry gas

Corrected to STP of 760 mm Hg and 0°C

$$\frac{620.3}{760.0} \times \frac{273}{(273 + 22)} \times \frac{721 \text{ liters/hr}}{60 \text{ minute/hr}} = 9.07 \text{ liters STP/minute}$$

Calculation of Liters Exit Gas STP per Gram of Charge Oil

Total exit gas flow 2780 liters

Total exit gas flow STP 2085 liters

Charge oil weight 3261 grams

$$\frac{2085 \text{ liters STP}}{3261 \text{ grams oil}} = 0.640 \text{ Liters Exit Gas STP/Gram Oil}$$

Calculation of Composite Sulfur Content

Sample Weight	Percent Sulfur	Grams Sulfur
621.5	0.442	2.75
761.0	0.360	2.74
742.5	0.386	2.87
827.0	0.493	4.08
<u>2952.0</u>		<u>12.44</u> Total

$$\frac{12.44 \times 100}{2952} = 0.422 \text{ Percent Sulfur}$$

Calculation of Oil Charge Weight Losses

3261.0	Weight Charge oil
2952.0	Weight effluent oil
309.0	Gram Charge loss

$$\frac{309 \times 100}{3261.0} = 9.47 \text{ Percent Loss}$$

Weight Basis

2. A Typical Two Day Entry During MoS₂ Catalyst Life Study Run

V-2 KGBM

LSR

November 26, 27, 1951

Oil = #3 Fuel Oil (2.14% S)

Catalyst = 100 gm. Harshaw MoS₂ Mo-X-L321-42

Reactor Pressure, 500 psig.

Hour	Sample No.	Sample Weight Grams	Percent Sulfur in Effluent Oil	Average Temperature °C	Liters Exit Gas
232	29	549.5	.420	411	1012
240	30	555.5	.398	410	1040
248	31	551.0	.467	411	860
256	32	549.5	.453	412	929
264	33	557.5	.435	411	869
272	34	545.5	.426	411	952
		<u>3308.5</u>			

Calculation of Charge Weight Percent Loss

Charge oil weight : 37397 grams
Effluent oil weight : 34790 grams
2606 grams loss

$$\frac{2606 \times 100}{37397} = 6.97 \text{ Percent Weight Losses between November 16 and December 8, 1951}$$

Calculation of Space Velocity

Sample weight includes approximately 93 percent of the charge oil weight due to 6.97 percent losses.

$$\frac{549.5 \text{ sample weight}}{.93} = 591 \text{ Grams Charge Weight}$$

$$\frac{591 \text{ gram oil}}{(100 \text{ gram catalyst})(8 \text{ hours})} = 0.739 \text{ Gram Oil/Gram Catalyst/Hour}$$

Calculation of Liters Exit Gas STP per Gram of Charge Oil

The factor to correct the observed wet test meter reading to STP of 760 mm Hg and 0°C averages 0.75 at the average barometric pressure and metering temperature.

$$\frac{(1012 \text{ liters gas})(.75)}{591 \text{ gram charge oil}} = 1.28 \text{ Liters Gas STP/Gram Oil}$$

Calculation of Grams of Sulfur Removed from Oil per gram of Catalyst per Eight Hour Sample

Charge oil weight = 591 grams at 2.14% Sulfur
Effluent oil = 549.5 grams at 0.42% Sulfur

$$\begin{aligned} 591.0 \times 0.0214 &= 12.6 \\ 549.5 \times 0.0042 &= \underline{2.3} \\ &10.3 \text{ grams sulfur removed} \end{aligned}$$

$$\frac{10.3 \text{ grams sulfur removed}}{100 \text{ grams catalyst}} = 0.103 \text{ Grams Sulfur Removed/Gram Catalyst/Sample}$$

THERMODYNAMIC CALCULATIONS

In postulated desulfurization reactions the sulfur compounds release the sulfur atoms from the oil by carbon-to-sulfur bond fracture at the proper temperature in the presence of the catalytic agent. The resultant free sulfur atoms are removed from the distillate by combining with the multi-valent catalytic agent to form a higher metal sulfide. Upon the conversion of the catalytic agent to a higher metal sulfide further desulfurization would cease and regeneration would be necessary. Therefore, desulfurization reactions were carried out in the presence of an excess of hydrogen to hydrogenate the unsaturated sulfur free hydrocarbon molecules and to react with the relatively unstable high metal sulfide contact agent to reform the low sulfide and hydrogen sulfide. The sulfur thus removed from the petroleum appears as hydrogen sulfide and can be easily removed from the effluent gases and oil.

The thermodynamics of the reactions of desulfurization, hydrogenation and decomposition of metal sulfide catalyst were studied to support the postulated mechanism involved in the reaction of sulfur compounds, hydrogen, and molybdenum sulfide catalyst. Thermodynamic calculations were performed on four specific reactions which are as follows:

1. $C_4H_4S(g) + 4H_2(g) \rightarrow C_4H_{10}(g) + H_2S(g)$
2. $2MoS_3 \rightarrow 2MoS_2 + S_2(g)$
3. $MoS_2 + C_4H_4S(g) + 3H_2 \rightarrow MoS_3 + C_4H_{10}(g)$
4. $MoS_3 + H_2(g) \rightarrow MoS_2 + H_2S(g)$

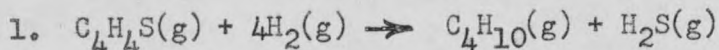
The first reaction is concerned with the overall conversion of thiophene and hydrogen to a saturated hydrocarbon and hydrogen sulfide. The

decomposition of molybdenum trisulfide in the second reaction is of interest because a great deal of elemental sulfur was evolved upon heating 96 percent molybdenum trisulfide.

A postulated decomposition mechanism was studied to determine the effect of pressure and temperature in curbing the undesirable evolution of elemental sulfur from a fresh catalyst. The third and fourth reactions deal directly with the postulated role which molybdenum sulfide catalyst plays in transferring the sulfur from the oil to hydrogen sulfide.

Thiophene was used as the sulfur bearing compound in these reactions because a large part of the sulfur contained in the #3 fuel oil was probably in the form of thiophenic type sulfur compounds. The boiling point of pure thiophene (84°C) is far lower than the boiling range of fuel oil. Thermodynamic data was not available for high molecular thiophenic compounds therefore thiophene was used to obtain some data to indicate the ease of effecting similar reactions with the higher boiling compounds.

Data and Equations for Thermodynamic Calculations



ΔH at 298°K = -62,400 cal/mol

ΔF at 298°K = -41,300 cal/mol

$T_{N.E.} = 882^{\circ}K = 609^{\circ}C$

$\Delta F_T = -58914 - 9.2 T \ln T + 12.3 \times 10^{-3}T^2 - 6.5 \times 10^{-6}T^3 + 3.5T$

$K_{eq} = \frac{-\Delta F}{RT}$
 $\ln \gamma = \frac{9PT_c}{128 P_c T} \left(1 - 6 \frac{T_c}{T^2}\right)$

$K\gamma = \frac{\gamma_{C_4H_{10}} \gamma_{H_2S}}{\gamma_{C_4H_4S} \gamma_{4H_2}}$

$$K_N = \frac{K_{eq}}{K P^{\Delta N}} = K_{eq} P^3 = \frac{x^2(5-3x)^3}{(1-x)(4-4x)^4}$$



$$\Delta H \text{ at } 298^\circ\text{K} = 41,440 \text{ cal/mol}$$

$$\Delta F \text{ at } 298^\circ\text{K} = 25,690 \text{ cal/mol}$$

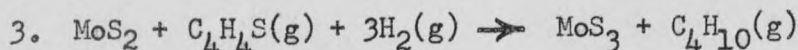
$$T_{NE} = 784^\circ\text{K} = 511^\circ\text{C}$$

$$\Delta F_T = 45580 + 13.24 T \ln T + 2.13 \times 10^{-3} T^2 - 143T$$

$$K_N = \frac{K_{eq}}{K P^{\Delta N}} = \frac{K_{eq}}{K \gamma P}$$

$$K_{eq} = \frac{-\Delta F}{RT}$$

$$K = \frac{\gamma_{\text{MoS}_2}^2 \gamma_{\text{S}_2}}{\gamma_{\text{MoS}_3}^2} = \frac{4x^3}{(2+x)(2-2x)^2}$$



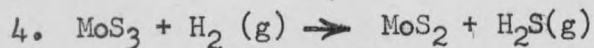
$$\Delta H \text{ at } 298^\circ\text{K} = -21,330 \text{ cal/mol}$$

$$\Delta F \text{ at } 298^\circ\text{K} = -36,640 \text{ cal/mol}$$

$$T_{NE} = 715^\circ\text{K} = 442^\circ\text{C}$$

$$\Delta F_T = 2.43T \log_{10} T + .0125T^2 - 0.661 \times 10^{-5} T^3 - 61,730 + 75T$$

$$K_N = \frac{x^2(5-3x)^3}{(1-x)^2(3-3x)^3} = \frac{K_{eq} P^3}{K \gamma}$$



$$\Delta H \text{ at } 298^\circ\text{K} = 440 \text{ cal/mol}$$

$$\Delta F \text{ at } 298^\circ\text{K} = -4,660 \text{ cal/mol}$$

$$T_{NE} = 25.6^\circ\text{K} = -247.4^\circ\text{C}$$

$$\Delta F_T = 2800 + 18.75 T \log_{10} T - 0.00076T^2 - 0.801 \times 10^{-7} T^3 - 71T$$

$$K_N = \frac{x^2}{(1-x)^2} = \frac{K_{eq}}{K \gamma}$$

The calculated results of the above equations are listed in Table III. The effect of increasing the reaction temperature from 250 to 1000°C causes a rapid reduction in percent conversion at all pressures between one and 100 atmospheres for the reaction which yields butane and hydrogen sulfide from thiophene and hydrogen. The increase of pressure from one to 100 atmospheres would cause an increase in percent conversion from 94.7 to 99 percent at 375°C. Therefore, higher values of percent conversion with high reaction rates would be achieved at 10 to 50 atmospheres of pressure and temperatures of 375 to 500°C.

The decomposition of MoS_3 to MoS_2 was nearly complete at 1000°C and one atmosphere pressure. At pressures above 50 atmospheres and temperatures below 375°C less than 5 percent conversion was possible.

In the reaction of MoS_2 , thiophene and hydrogen to yield MoS_3 and butane, the percent conversion was slightly increased by an increase of pressure while a rapid decline in percent conversion was calculated at increasing temperatures between 375° and 500°C. Temperatures below the neutral equilibrium temperature of 442°C would give increasing percent conversion.

The effect of pressure upon the conversion of MoS_3 and hydrogen to MoS_2 and H_2S would be very slight while increase of temperatures between 25 and 1000°C would cause only a decrease of 98.1 to 94.4 percent conversion at one atmosphere to indicate that the reaction would be highly favorable at any chosen operating condition.

DISCUSSION OF RESULTS

The Effect of Operating Conditions Upon Desulfurization with Various Destructive Hydrogenation Catalysts at Super-Atmospheric Pressures.

The catalysts employed in the investigation were cobalt molybdate, molybdena alumina, tungstic oxide, nickel oxide and molybdenum sulfide. The operating conditions of the various three-to-six-hour tests were reactor pressures of 300 and 500 psig, temperatures of 375 to 430°C, space velocities of 0.75 to 1.3 grams of oil per gram of catalyst per hour and hydrogen rates of 2 to 12 standard liters per minute. A #3 grade fuel oil containing 2.10 percent sulfur constituted the charge oil to the reactor system illustrated in the schematic diagram in Figure 1.

Figure 3 shows the effect of space velocity upon desulfurization. Data for these curves are found in Table IV from a number of runs made with two types of molybdena alumina and molybdenum sulfide catalysts. The general effect of increasing the space velocity or reducing the contact time was to reduce the desulfurization. The data from testing the molybdenum sulfide catalyst (Table IV) were obtained with the small volume reactor system as illustrated in Figure 2. One generalization that can be drawn from the plot of desulfurization versus space velocity is the similarity of rate of change of desulfurization with space velocity for molybdenum-containing catalysts.

The relationship of temperature to desulfurization is indicated in Figure 4 from data tabulated in Table V concerning tests made at reactor pressures of 300 and 500 psig. The molybdena alumina catalyst Mo-0201 contained 5.6 percent SiO_2 while the molybdena alumina Mo-0602 contained no silica. Nearly linear relationships of desulfurization and temperature were displayed

by each of the molybdena alumina catalysts at an operating pressure of 300 psig. The space velocity of the selected data of Table V varies between 0.850 and 0.943 grams oil per gram catalyst per hour with the exception of the value of 1.26 grams oil per gram catalyst per hour for the molybdena alumina Mo-0201 catalyst. Thus, the relatively high space velocity of the molybdena-alumina Mo-0201 catalyst gave the false impression of a lower catalyst activity than the molybdena alumina Mo-0602 catalysts. Molybdenum sulfide at operating pressures of 300 and 500 psig displayed nearly similar relationships between desulfurization capacity and temperature with a slightly higher activity at the higher operating pressure. Cobalt molybdate catalyst at 500 psig would give slightly higher activity than molybdenum sulfide at 500 psig yet there was not sufficient operating data on cobalt molybdate at various temperatures to make any broad statements. Figure 4 also indicates that the molybdenum sulfide was more active than the molybdena alumina Mo-0201, Mo-0602, and tungstic oxide catalysts. The curve of desulfurization versus temperature for molybdenum sulfide at 500 psig gave additional information that the relation of desulfurization versus temperature was not linear and that increasing temperature above 410°C has little effect on desulfurization. Koski (7) found the same relationship for molybdena alumina catalyst at 300 psig. Thus, these data point to about 400 to 410°C as the optimum temperature to investigate that catalyst to obtain maximum desulfurization without the danger of excessive cracking and coke formation to cause the decrease of the catalyst activity.

The effect of reactor pressure upon desulfurization is presented in Figure 5 and Table VI. Higher pressures increased desulfurization which

was substantiated by the thermodynamic calculations on the postulated desulfurization mechanisms. The greatest effect of pressure change on desulfurization was displayed by the molybdena alumina Mo-0602 catalyst and the least effect by molybdena alumina Mo-0201 which contains 5.6 percent silica. Three short duration runs did not furnish sufficient data to substantiate the slightly negative effect of pressure upon desulfurization with molybdena-alumina Mo-0201 catalyst. The effect of a pressure increase upon desulfurization was similar with molybdenum sulfide and tungstic oxide catalysts. Green (4) reported more detailed study of the effect of pressures from atmospheric to 500 psig with molybdenum sulfide catalyst to furnish more conclusive data from continuous reactor operation.

Figure 6 shows the effect of on-stream time and desulfurization. Data for these curves are found in Table VII for the two types of molybdena alumina, nickel oxide, and molybdenum sulfide. Nickel oxide displayed a very rapid pattern of deactivation during two-five hour runs. The first run involved operation with a fresh catalyst charge of 10 percent nickel oxide on alumina for five hours followed by an air oxidation regeneration of the catalyst. The second run was performed at nearly the same conditions to yield nearly identical curves for both runs. The data indicated that nickel in the presence of sulfur bearing oil forms a stable sulfide which is relatively inactive in removing further sulfur from the oil. Upon air regeneration an active nickel oxide or sulfate was formed which was capable of accomplishing nearly the same degree of desulfurization over a five hour period as a fresh nickel oxide catalyst. The exhaust air regeneration gas contained sulfur dioxide to give further indication that a nickel oxide

was formed upon regeneration.

The additional curves of desulfurization versus on-stream time for molybdenum sulfide and molybdena alumina found in Figure 6 were drawn to lend some support to the hypothesis that a molybdenum sulfide was the active desulfurizing agent. The curves of the two types of fresh molybdena alumina catalyst indicate increased activity during the respective first runs of the catalysts. Additional use of the metal oxide catalyst caused the improvement of the catalyst activity where as the activity of molybdenum sulfide was initially high. In the air regeneration of molybdena alumina catalysts the burn off gases contained sulfur dioxide thus indicating the occurrence of an active sulfide catalyst formed from an oxide catalyst of slightly lower activity.

The data obtained from the short four to five hour runs indicated that desulfurization to a product containing less than 0.5 percent sulfur was possible by destructive hydrogenation at pressures of 300 and above, temperatures above 390°C, space velocities less than one gram oil per gram catalyst per hour and hydrogen to oil ratios of about one liter hydrogen per gram charge oil. The most promising catalysts were cobalt molybdate, molybdena alumina and molybdenum sulfide while tungstic oxide and nickel oxide were somewhat inferior.

The Effect of Operating Conditions Upon the Life of Molybdenum Sulfide Catalyst.

From the results of the short run catalyst tests additional data were desired concerning the catalyst activity over extended operating periods. A schematic diagram of the apparatus for the catalyst life study is ill-

ustrated in Figure 2. The catalyst containing approximately 15 percent molybdenum disulfide impregnated on alumina was chosen for the life study because that catalyst appeared to have activity comparable to any other molybdenum or cobalt molybdate catalysts previously tested. The molybdenum sulfide catalyst had an additional feature in that it was not extensively patented.

The catalyst life study run extended for a total of 2010 operating hours to produce approximately 37 gallons of treated fuel oil with a sulfur content less than 0.5 percent. During the run the catalyst treated 1233 grams of oil per gram of catalyst at an average space velocity of 0.613 grams of oil per gram of catalyst per hour. The overall oil charge losses were 6.26 percent on weight basis or 4.36 percent on volume basis at an average hydrogen-to-oil ratio of 1.60 liters of exit gas per gram of oil. The reactor pressure was maintained at 500 psig. with hydrogen gas and the operating temperature was controlled at an average of 410°C throughout the run.

The life study run was divided into five operating periods caused by four shut-downs. At intervals as frequent as 200 and as long as 500 operating hours carbon and coke deposits were formed in the preheat section of the reactor causing excessive flow resistance and pressure differential through the reactor. The four shut-downs necessitated the removal of the catalyst and carbon covered preheat material followed by recharging the reactor unit with clean preheat material and replacing the original catalyst. Experience proved that following each shut-down the catalyst responded somewhat differently from the previous period and reactor operating

conditions such as space velocity and hydrogen throughput had to be changed to maintain an effluent oil containing less than 0.5 percent sulfur.

The data of Table VIII are plotted in Figure 7 to give a graphic picture of the average results obtained and the conditions used during the life study. Table VIII contains the arithmetic averages for approximately one hundred hour periods of grams of sulfur removed from the oil per gram of catalyst per eight hours, the exit gas-to-oil ratio, space velocity, and percent sulfur in the effluent oil. The calculated average values of grams of sulfur removed from the oil per gram of catalyst per eight hours, the exit gas-to-oil ratio, and space velocity were plotted versus on-stream time in Figure 7 with the occurrence of the various shut-downs indicated in conjunction with the numbered operating periods. The overall trend of the sulfur removal indicated that the catalyst lost approximately 35 percent activity by comparing the initial 400 hours with the final 400 hours of the run. The plot of space velocity indicated the same pattern as does the sulfur removal plot. It will be noted that following the first shut-down, period #2 displayed a sharp decrease in catalyst activity yet the activity in periods #3 and #4 resumed nearly the same level of activity as period #1. During period #1 the reactor preheat material consisted of 1/4 inch steel balls and following the first shut-down 1/4 inch alundum ceramic balls were substituted for the steel balls which were thought to have catalyzed cracking and coke formation in the preheat section. The resumed level of activity in periods #3 and #4 with alundum preheat balls discounts the fact that low catalyst activity found in period #2 was caused primarily by a change in the preheat material. The charge oil used for the first 87

hours of period #5 was treated at the Husky Oil Company refinery by passing #3 fuel oil through a bed of sand at $^{\circ}\text{C}$ to remove the unstable gum and coke forming compounds. Inspection data for the sand treated oil are found in Table I. The catalyst was unable to reduce the sulfur content of the sand treated oil below 0.5 percent despite a 15 percent reduction of the space velocity and a 19 percent increase of the hydrogen-to-oil ratio. The virgin #3 fuel oil was used again after 87 hours of unsuccessful use of sand treated oil. The catalyst activity did not improve with the use of #3 fuel oil indicating a low level of catalyst activity. Green (4) reported that the use of air regeneration upon molybdenum sulfide catalyst restored the activity to a level higher than fresh catalyst.

The plot of the gas-to-oil ratio versus on-stream time is presented in Figure 7. This plot indicated the need of a higher hydrogen gas throughput necessary to desulfurize the same quantity of oil when the catalyst becomes deactivated.

The data listed on Table IX and plotted in Figure 8 show the relationship between space velocity and percent sulfur in the effluent oil. The term space velocity is inversely proportional to the contact time of oil on the catalyst, therefore with longer contact times or lower space velocities the sulfur content of the effluent oil is lower. The curves of Figure 8 were obtained from the curves which most nearly characterized the plots of all the samples for desulfurization versus space velocity in the individual operating periods. Inspection of Figure 8 would reveal that the curves for the first three periods indicated similar slopes except that a different range of activity was displayed by the three periods. Periods #1 and #3

had nearly identical activities while the period #2 curve was shifted to the left to indicate reduced activity. The curves of period #4 and #5 display greater slopes which indicate the increased effectiveness of space velocity upon the sulfur content of the effluent oil. The curve of period #5 corresponds only to the data obtained during the use of sand treated charge oil. Figure 8 indicates the greatly reduced activity between periods #4 and #5. In general during the life study run a reduction of space velocity by 0.1 gram oil per gram catalyst per hour would effect the reduction of about 0.05 percent sulfur in the effluent oil.

The relationship of liters exit gas-to-oil ratio and desulfurization for the various periods of the life study run is presented in Table X and Figure 9. The curves of Figure 9 were obtained from the curves which most nearly characterized the plots of all the values of desulfurization versus gas-to-oil ratios for each operating period. The plots characterizing the various operating periods in Figure 9 reveal that a definite relationship of increased gas-to-oil ratios would yield a reduced sulfur content in the effluent oil. The slopes of periods #1 and #3 were nearly alike with a reduced slope on the curve of period #2 which characterized a period of low activity when a large change in gas-to-oil ratio had little effect on the desulfurization. Operating period #5 was divided into two curves, one representing the use of sand treated oil and the other representing the use of #3 fuel oil. It was noted that the #3 fuel oil required a lower gas-to-oil ratio to effect the same reduction in sulfur content than did the sand treated oil. Period #4 required far less gas than period #5 for the same sulfur reduction but more than periods #1 and #3.

CONCLUSION

All the molybdenum containing catalysts studied displayed nearly the same relationship of desulfurization and space velocity. An average increase in space velocity of 0.1 gram oil per gram catalyst per hour would cause a decrease of nearly 0.1 percent sulfur in the effluent oil. The effect of temperature increase above 410 to 420°C caused little increase of desulfurization for molybdenum-containing catalysts. Temperature changes below 400°C effect a much greater change in desulfurization per degree temperature variation. The activity of molybdenum sulfide and cobalt molybdate catalysts were nearly identical while the molybdena alumina catalysts were somewhat less active. Tungstic oxide catalyst displayed the least activity under operating conditions comparable to those used for molybdenum sulfide and cobalt molybdate. The increase of reactor pressure from 300 to 500 psig gave approximately 0.1 percent reduction in sulfur content when using molybdenum and tungsten catalysts.

The catalyst of nickel oxide impregnated on alumina gave the highest initial activity but decreased rapidly and following the treatment of four grams oil per gram catalyst the effluent oil had a sulfur content of approximately 1.0 percent. One air regeneration treatment restored the catalyst to nearly the same initial activity with a similar rate of decrease during a second-five hour run.

The oxide type molybdenum catalyst displayed an increase in activity following the first three to five hours of desulfurization service while the molybdenum sulfide catalyst displayed high uniform activity throughout the same initial period indicating that the sulfide type molybdenum catalyst

was the more active desulfurization agent and that the oxide type catalyst experienced some form of sulfiding which yielded a more active catalyst.

The data obtained from the molybdenum sulfide catalyst life study run indicated that the catalyst experienced a 35 percent loss of activity following an operating period in excess of 2000 hours to treat 1200 grams of oil per gram catalyst. During the life study run an approximate increase in space velocity of 0.1 grams oil per gram catalyst per hour reduced the effluent oil sulfur content by 0.05 percent while an increase of the exit gas-to-oil ratio of approximately 0.2 liters per gram of oil reduced the sulfur content by 0.1 percent.

In conclusion, it was possible to obtain an effluent oil containing less than 0.5 percent sulfur throughout an operating period in excess of 2000 hours while using a molybdenum sulfide catalyst under destructive hydrogenation conditions of 500 psig and 410°C.

LITERATURE CITED

- (1) A.S.T.M. Standards on Petroleum Products and Lubricants, American Society for Testing Materials, Philadelphia, p. 272 (1941).
- (2) Grececius, R. L., M.S. Thesis, Montana State College, (1949).
- (3) Fischbach, R. J., M. S. Thesis, Montana State College, (1952).
- (4) Green, K. J., M. S. Thesis, Montana State College, (1952).
- (5) Haas, P. A., M. S. Thesis, Montana State College, (1951)
- (6) Kalichevsky, V. A. and Stagner, B. A., "Chemical Refining of Petroleum" (Text) Reinhold Publishing Corporation, New York, (1942).
- (7) Koski, O. H., M. S. Thesis, Montana State College, (1951).
- (8) Sachanen, A. N., "Conversion of Petroleum" (Text) Reinhold Publishing Corporation, New York, (1948).

ACKNOWLEDGEMENT

The author wishes to thank the Husky Oil Company of Cody, Wyoming for their courtesy in sponsoring the work on this problem and for supplying the fuel oil and materials used throughout the project.

APPENDIX

	page
Table I Fuel Oil Inspection Data	34
Table II Catalysts.	35
Table III Thermodynamics	36
Table IV Desulfurization versus Space Velocity with Molybdenum Catalysts	38
Table V Desulfurization versus Temperature with Various Catalysts.	39
Table VI Desulfurization versus Pressure with Various Catalysts.	40
Table VII Desulfurization versus On-Stream Time with Various Catalysts.	41
Table VIII Desulfurization Characteristics of Molybdenum Sulfide Catalyst During Life Study Run	42
Table IX Desulfurization versus Space Velocity During Various Operating Periods of the MoS ₂ Catalyst Life Study Run.	43
Table X Desulfurization versus Liters Exit Gas Per Gram Oil During Various Operating Periods of the MoS ₂ Catalyst Life Study Run	45
Figure 1 Diagram of Hydrogenation Equipment for Large Volume Super-atmospheric Work	47
Figure 2 Diagram of Hydrogenation Equipment for Small Volume Super-atmospheric Work for Life Study Run.	48
Figure 3 The Effect of Space Velocity Upon Desulfurization with Molybdenum Catalysts	49
Figure 4 The Effect of Temperature Upon Desulfurization with Various Catalysts.	50
Figure 5 The Effect of Reactor Pressure Upon Desulfurization.	51
Figure 6 The Effect of Operating Time Upon Desulfurization	52

APPENDIX (continued)

	page
Figure 7 Plot of Grams Sulfur Removal, Liters Exit Gas per Gram Oil, and Space Velocity versus On-stream Time for Life Study of MoS ₂ Catalyst.	53
Figure 8 The Effect of Space Velocity Upon Desulfurization for the Operating Periods of MoS ₂ Catalyst Life Study	54
Figure 9 The Effect of Exit Gas to Oil Ratio Upon Desulfurization for the Operating Periods of MoS ₂ Catalyst Life Study	55

TABLE I
FUEL OIL INSPECTION DATA

	Charge Stock No. 3 Oil	Charge Stock Sand Treated No. 3 Oil	Life Study Run Effluent Oil Using No. 3 Oil charge Stock
A.P.I. at 60°F	30.6	30.5	34.0
Sp. GR. at 60°F	0.8729	0.8735	0.8550
d 60°F (Calc.)	0.8709	0.8715	0.8530
Average Mol. Wt.	222	222	208
U.O.P. K Factor	11.5	11.5	11.6
Bromine No.	7.57	9.24	4.44
% Olefin	10.5	12.8	5.7
Wt. % Sulfur	2.223	2.181	0.460
Wt. % H ₂ in Oil	10.9	10.9	11.2
A.S.T.M. Distillation	<u>°F</u>	<u>°F</u>	<u>°F</u>
I.B.P	425	385	197
5%	504	499	443
10%	520	519	478
20%	536	536	506
30%	548	547	520
40%	558	555	532
50%	567	566	543
60%	575	575	555
70%	584	584	566
80%	594	595	582
90%	611	613	601
95%	625	631	624
E. P.	652	651	650
Recovered	99.0 %	99.0 %	99.0 %
Residue	0.8 %	0.8 %	0.8 %
Loss	0.2 %	0.2 %	0.2 %

TABLE II
CATALYSTS

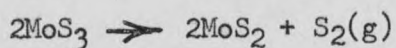
Producer: Harshaw Chemical Co.

Catalyst and Composition	Identification Code
Cobalt Molybdate	CoMo-0201 T-1/8"
MoO ₃ 9.5%	
CoO 3.0%	
SiO ₂ 5.0%	
Graphite 2.0%	
Al ₂ O ₃ Balance	
Molybdena Alumina	Mo-0201 T-1/8"
MoO ₃ 10.4 - 11.0%	
SiO ₂ 5.6%	
Al ₂ O ₃ Balance	
Molybdena Alumina	Mo-0602 T-1/8"
MoO ₃ Approx. 10.0%	
Al ₂ O ₃ Balance	
Nickel Oxide	Ni-0301 T-1/8"
NiO Approx. 10%	
Al ₂ O ₃ Balance	
Tungstic Oxide	Wo-0101 T-1/8"
WoO ₃ Approx 10%	
Al ₂ O ₃ Balance	
Molybdenum Sulfide	Mo-X-L321-42 T-1/8"
MoS ₂ 15%	
Al ₂ O ₃ Balance	

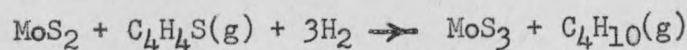
TABLE III
THERMODYNAMICS



Temp. °C	% Conversion at 1 ATM Press	% Conversion at 10 ATM Press	% Conversion at 50 ATM Press	% Conversion at 100 ATM Press
25	100	100	100	100
100	100	100	100	100
250	99.6	99.9	100	100
375	94.7	98.5	99.5	99.6
500	70.0	92.7	97.2	97.5
1000	0.5	2.0	19.0	27.0



Temp. °C	% Conversion at 1.0 ATM Press	% Conversion at 50 ATM Press
25	0	0
100	0	0
250	0.95	0.7
375	12.0	5.0
500	35.0	30.
1000	95.5	75.



Temp. °C	% Conversion at 1 ATM Press	% Conversion At 10 ATM Press	% Conversion at 50 ATM Press	% Conversion at 100 ATM Press
25	100	100	100	100
100	100	100	100	100
250	99.6	99.9	100	100
375	97.2	99.3	99.9	99.7
500	0.7	18.0	72.0	71.0
1000	0	0.9	2.6	2.6

TABLE III (continued)
THERMODYNAMICS



Temp. °C	% Conversion at 1 ATM Press	% Conversion at 10 ATM Press	% Conversion at 50 ATM Press	% Conversion at 100 ATM Press
25	98.1	98.2	98.3	98.5
100	98.0	98.1	98.2	98.3
250	97.8	97.9	98.0	98.1
375	96.9	97.0	97.2	97.5
500	96.7	96.7	96.7	96.7
1000	94.4	94.4	94.5	94.6

TABLE IV
DESULFURIZATION VS. SPACE VELOCITY
WITH MOLYBDENUM CATALYSTS

Catalyst and Reactor Pressure PSIG	Percent Sulfur in Effluent Oil	Space Velocity grams Oil per gram catalyst per hour	Average Temp. °C	Ratio Liters Exit Gas per gram Oil	On-Stream Time in Hours
Molybdena Alumina Mo-0201 300	.925 .484	1.26 0.841	398 412	.490 .630	6 12
Molybdena Alumina Mo-0602 500	.473 .578	.764 1.011	402 399	.435 .244	6 8
Molybdenum Sulfide Mo-X-L321-42 500	.738 .671 .493 .493	1.24 1.28 0.98 0.835	410 408 413 410	0.55 0.87 1.16 1.19	31 34 40 44

TABLE V
DESULFURIZATION VS. TEMPERATURE
WITH VARIOUS CATALYSTS

Catalyst and Reactor Press. PSIG	% Sulfur in Effluent Oil	Average Temp °C	Liters Exit Gas per min.	Space Velocity Grams Oil per gram cat. per hr.	On-Stream Time
Molybdena	1.054	379	7.85	1.26	1
Alumina	0.940	392	11.90	↓	5
Mo-0201	0.855	400	9.67	↓	6
300	0.710	428	7.20	↓	2
Molybdena	0.709	393	4.34	0.926	1.5
Alumina	0.656	404	4.17	0.926	2.5
Mo-0602	0.573	427	3.19	0.927	0.5
300	0.665	397	4.32	0.926	2.0
Cobalt	0.315	410	9.67	0.943	3.5
Molybdate	0.383	405	8.95	0.943	4.0
300	0.454	401	7.85	0.943	5.5
Tungsten	0.761	406	8.95	0.862	1
Wo-0101	0.816	398	8.58	↓	2
500	0.811	403	8.08	↓	3
Molybdenum	0.412	409	9.27	.917	2
Sulfide	0.429	405	8.32	↓	4
300	0.547	395	9.50	↓	6
Molybdenum	0.355	412	10.87	.917	11
Sulfide	0.365	410	11.47	.850	13
500	0.332	421	9.91	.855	15
	0.463	398	10.80	.855	16
	0.655	390	9.53	.855	18

TABLE VI
DESULFURIZATION VS. PRESSURE
WITH VARIOUS CATALYSTS

Catalyst	% Sulfur in Effluent Oil	Reactor Pressure PSIG	Average Temp °C	Ratio Liters Exit Gas Per Gram Oil	Space Velocity grams oil per gram catalyst	On-Stream Time in Hours
Molybdena Alumina Mo-0201	.484	300	412	0.630	0.841	12
	.493	500	414	0.603	0.888	16
Molybdena Alumina Mo-0602	.734	300	399	0.278	0.924	3
	.583	500	399	0.244	1.011	8
Tungsten Wo-0101	.797	500	402	0.643	0.862	3
	.852	300	406	0.757	0.821	9
Molybdenum Sulfide	.442	300	414	0.839	0.917	9
	.378	500	415	0.705	0.850	15

TABLE VII
DESULFURIZATION VS. ON-STREAM TIME
WITH VARIOUS CATALYSTS

Catalyst and Space Velocity Grams Oil per grams Catalyst per Hour.	On-Stream Time (Minutes)	Percent Sulfur in Effluent Oil	Average Temp. °C	Exit Gas Liters per Minute	On-Stream Time in Hours
Molybdenum Sulfide Mo-X-L321-42	0-60	.442	408	9.07	1
	60-120	.360	406	8.41	2
	120-180	.386	410	9.39	3
	180-240	.493	404	8.24	4
0.917					
Nickel Oxide Ni-0301	0-60	.282	395	8.22	1
	60-120	.478	402	6.83	2
	120-180	.753	399	8.97	3
	180-240	.864	398	4.47	4
0.817	240-300	.957	397	7.53	5
Nickel Oxide Regenerated	0-60	.298	412	6.11	1
	60-120	.624	407	10.43	2
	120-180	.761	404	6.05	3
	180-240	.865	402	11.61	4
0.863	240-300	.895	398	11.60	5
Molybdena Alumina Mo-0602	0-30	.765	400	4.50	0.5
	30-60	.653	398	4.50	1.0
	60-90	.772	392	4.80	1.5
	90-120	.724	402	4.43	2.0
	120-150	.730	401	4.80	2.5
0.924	150-180	.768	400	2.63	3.0
Molybdena Alumina Mo-0201	0-60	1.054	379	7.85	1
	60-120	0.710	428	7.20	2
	120-180	1.039	398	7.34	3
	180-240	0.995	393	9.65	4
	240-300	0.940	392	11.90	5
	300-360	0.855	400	9.67	6
1.26					

TABLE VIII
DESULFURIZATION CHARACTERISTICS OF
MOLYBDENUM SULFIDE CATALYST DURING LIFE STUDY RUN

Hours Operating Time	Average Grams Sulfur Removed per Gram Catalyst per 8 hours.	Average Space Velocity Grams Oil per Gram Catalyst per Hour.	Average Ratio Liters Exit Gas (S.T.P.) Per Gram Oil	Average % Sulfur content of Effluent oil
0-91	.0985	.701	1.213	0.412
91-200	.1200	.887	1.017	0.453
200-312	.1037	.746	1.160	0.430
312-402	.1022	.736	1.226	0.440
402-498	.0851	.646	1.500	0.509
498-602	.0724	.531	1.645	0.464
602-699	.0677	.486	1.890	0.405
699-795	.0870	.613	1.505	0.380
795-899	.1071	.788	1.260	0.466
899-996	.0968	.687	1.460	0.505
996-1092	.0906	.683	1.364	0.515
1092-1196	.0920	.671	1.455	0.450
1196-1292	.0930	.680	1.460	0.461
1292-1396	.0888	.659	1.540	0.473
1396-1492	.0890	.650	1.555	0.456
1492-1584	.0708	.553	1.853	0.648
1584-1696	.0674	.485	2.100	0.580
1696-1792	.0570	.428	2.230	0.495
1792-1896	.0616	.449	2.200	0.444
1896-2010	.0664	.475	2.240	0.416

TABLE IX
DESULFURIZATION VS SPACE VELOCITY DURING
VARIOUS OPERATING PERIODS OF THE MoS₂ CATALYST LIFE STUDY RUN

On-Stream Time in Hours	% S	Space Velocity Grams Oil per gram Catalyst per Hour	Liters Exit Gas	Liters Exit Gas Per Gram Oil	Grams S Removed per gram Catalyst per 8 Hours
<u>Period No. 1</u>					
24	.407	.709	988	1.305	.0999
56	.398	.679	955	1.32	.0959
112	.475	.857	888	0.971	.1165
184	.525	.887	909	0.962	.1169
232	.420	.739	1012	1.28	.1031
320	.452	.804	865	1.01	.1105
378	.326	.568	877	1.445	.0834
<u>Period No. 2</u>					
410	.641	.796	1008	1.263	.0952
466	.346	.361	956	2.56	.0525
506	.478	.567	891	1.518	.0767
554	.442	.532	843	1.533	.0735
562	.490	.536	832	1.50	.0723
602	.474	.501	923	1.78	.0680
618	.298	.315	971	2.985	.0469
<u>Period No. 3</u>					
683	.282	.474	1004	2.05	.0681
715	.336	.518	870	1.625	.0748
739	.354	.548	863	1.523	.0794
755	.389	.608	973	1.547	.0861
787	.418	.683	954	1.350	.0958
843	.476	.803	958	1.151	.1089
867	.496	.836	1041	1.202	.1120
915	.444	.755	1065	1.361	.1042
<u>Period No. 4</u>					
956	.580	.734	1020	1.538	.0937
972	.489	.690	999	1.40	.0931
1020	.516	.691	972	1.363	.0909
1180	.424	.639	1048	1.590	.0890
1196	.394	.579	934	1.556	.0822

TABLE IX (continued)
 DESULFURIZATION VS SPACE VELOCITY DURING
 VARIOUS OPERATING PERIODS OF THE MoS₂ CATALYST LIFE STUDY RUN

On-Stream Time in Hours	% S	Space Velocity Grams Oil per gram Catalyst per Hour	Liters Exit Gas	Liters Exit Gas Per Gram Oil	Grams S Removed per gram Catalyst per 8 Hours
1204	.351	.589	977	1.604	.0852
1420	.451	.619	944	1.475	.0944
1476	.398	.610	857	1.543	.0971
<u>Period 5 Sand Treated #3 Fuel Oil</u>					
1500	.706	.651	1287	1.910	.0807
1508	.726	.632	1092	1.670	.0775
1512	.670	.632	513	1.570	.0800
1520	.754	.660	998	1.46	.0792
1528	.746	.633	975	1.49	.0767
1536	.670	.550	1114	1.97	.0700
1544	.625	.503	1049	2.02	.0655
1552	.584	.485	1100	2.19	.0648
1560	.599	.464	911	1.86	.0627
1568	.575	.445	958	2.08	.0600
1576	.615	.457	981	2.08	.0600

TABLE X
 DESULFURIZATION VS LITERS EXIT GAS PER GRAM OIL DURING
 VARIOUS OPERATING PERIODS OF THE MoS₂ CATALYST LIFE STUDY RUN

On-Stream Time in Hours	% S	Liters Exit Gas Per gram Oil	Liters Exit Gas	Space Velocity Grams Oil per gram Catalyst per Hour	Grams Sulfur Removed per gram Catalyst per 8 hour.
Period No. 1					
64	.400	1.22	957	.735	.1040
112	.475	0.971	888	.857	.1165
120	.435	1.10	1130	.960	.1331
128	.360	1.36	1165	.805	.1163
192	.551	0.774	767	.928	.1207
288	.426	1.178	913	.726	.1012
320	.452	1.01	865	.804	.1105
352	.390	1.19	931	.734	.1040
378	.326	1.445	877	.568	.0834
Period No. 2					
418	.564	1.073	920	.829	.1070
442	.521	1.46	986	.654	.0863
498	.480	1.465	928	.613	.0828
514	.428	1.904	1048	.533	.0743
538	.477	1.785	946	.514	.0697
546	.517	1.34	760	.548	.0724
562	.490	1.50	832	.536	.0723
570	.471	1.82	993	.527	.0718
578	.447	1.975	1004	.508	.0690
Period No. 3					
715	.336	1.625	870	.518	.0748
723	.369	1.63	927	.550	.0784
739	.354	1.523	863	.548	.0794
763	.454	1.24	871	.680	.0932
795	.424	1.383	961	.670	.0935
811	.465	1.20	948	.761	.1039
915	.444	1.361	1065	.755	.1042
931	.498	1.115	865	.750	.1000

TABLE X (continued)
 DESULFURIZATION VS LITERS EXIT GAS PER GRAM OIL DURING
 VARIOUS OPERATING PERIODS OF THE MoS_2 CATALYST LIFE STUDY RUN

On-Stream Time in Hours	% S	Liters Exit Gas per gram Oil	Liters Exit Gas	Space Velocity Grams Oil per gram Catalyst per hour	Grams Sulfur Removed per gram Catalyst per 8 hour
-------------------------------	-----	---------------------------------------	--------------------	--	--

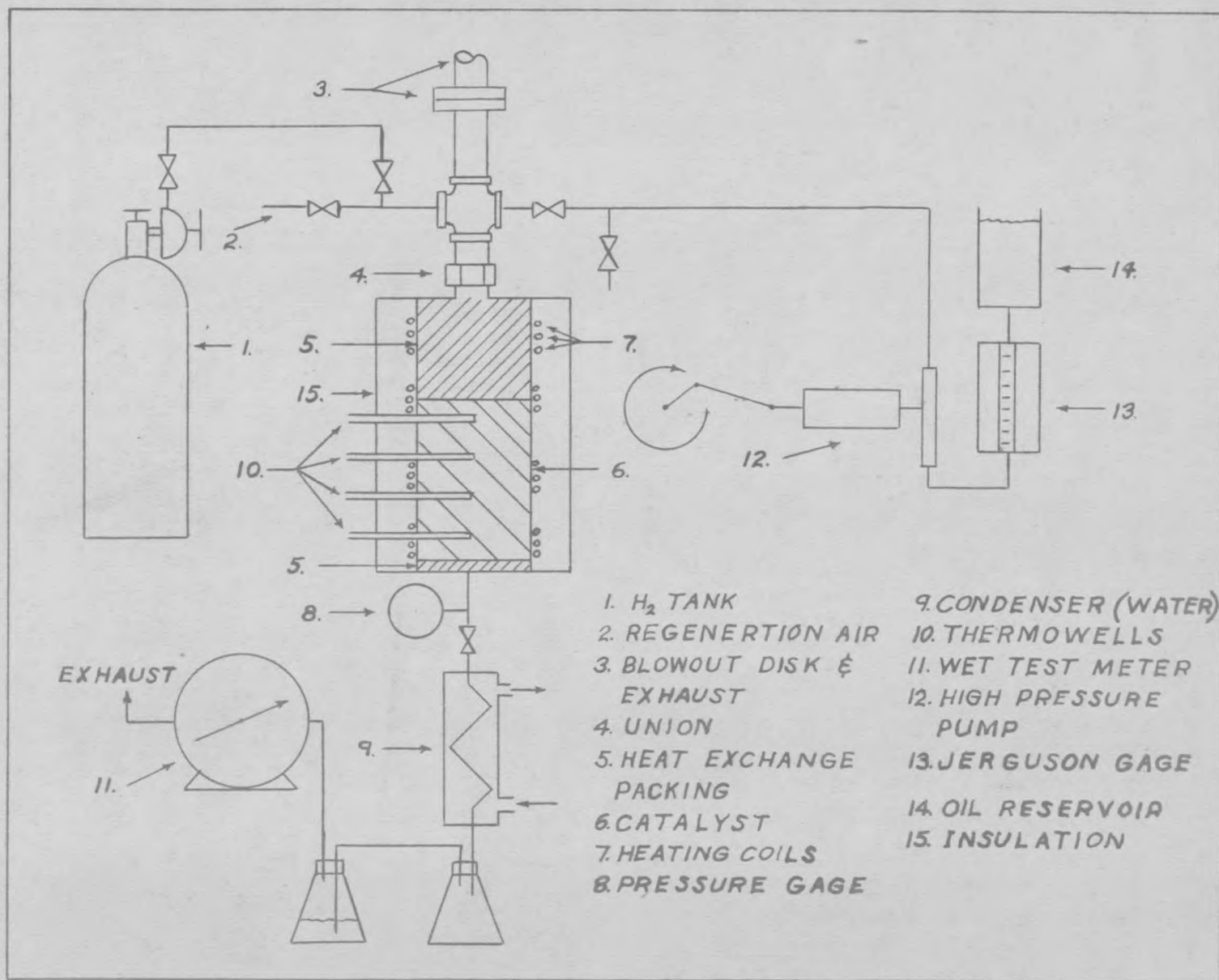
Period No. 4

964	.606	1.20	948	.764	.0960
1052	.520	1.35	958	.687	.0898
1156	.566	1.255	915	.705	.0908
1300	.464	1.486	1043	.679	.0930
1380	.476	1.418	982	.669	.0904
1396	.436	1.556	1034	.644	.0808
1412	.446	1.55	1027	.642	.0983
1420	.451	1.475	944	.619	.0842
1452	.429	1.755	1163	.642	.0883
1492	.441	1.728	1200	.673	.0920

Period No. 5

1632	.663	1.528	913	.577	.0717
1656	.607	1.92	971	.484	.0614
1752	.558	2.04	897	.424	.0543
1776	.363	2.52	1138	.435	.0622
1800	.439	2.31	979	.410	.0561
1832	.525	2.17	1022	.456	.0596
1840	.315	2.53	1107	.422	.0618
1872	.480	2.095	1052	.486	.0655
1944	.461	2.18	1037	.461	.0626
1952	.384	2.34	1108	.456	.0645

Figure 1. Diagram of Hydrogenation Equipment for Large Volume Super-atmospheric Work



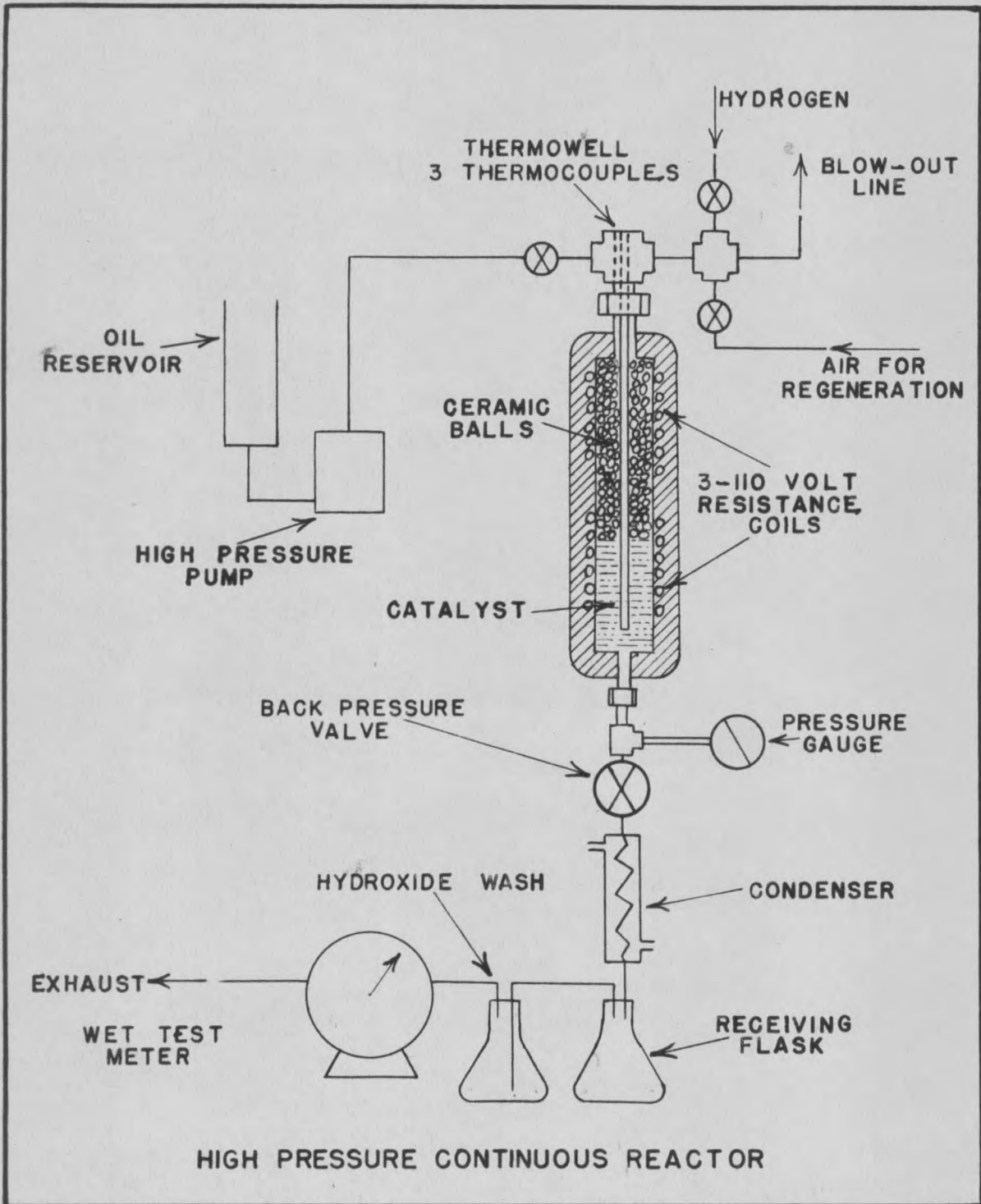


Figure 2. Diagram of Hydrogenation Equipment for Small Volume Super-atmospheric Work for Life Study Run

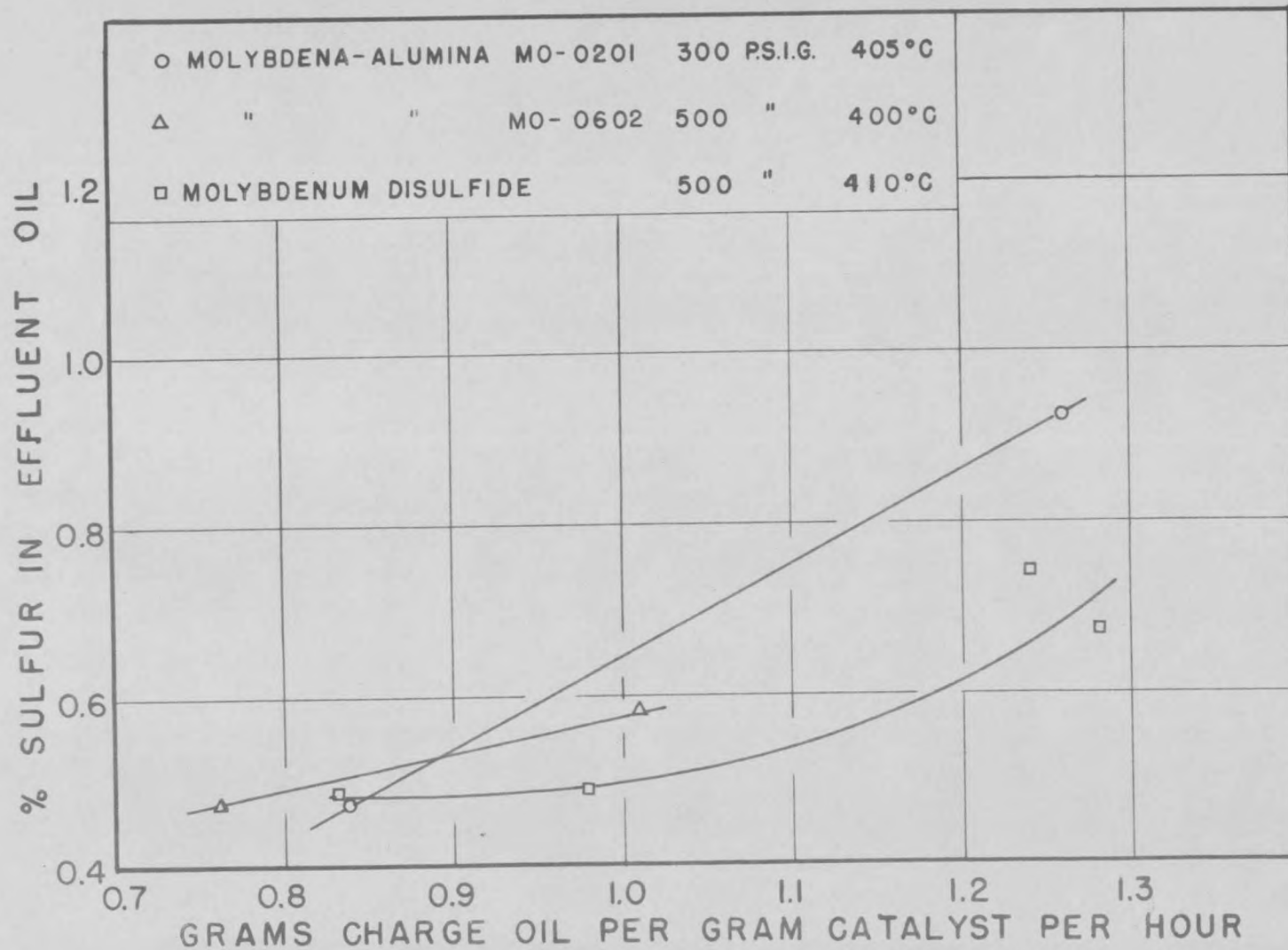


Figure 3. The Effect of Space Velocity Upon Desulfurization with Molybdenum Catalysts

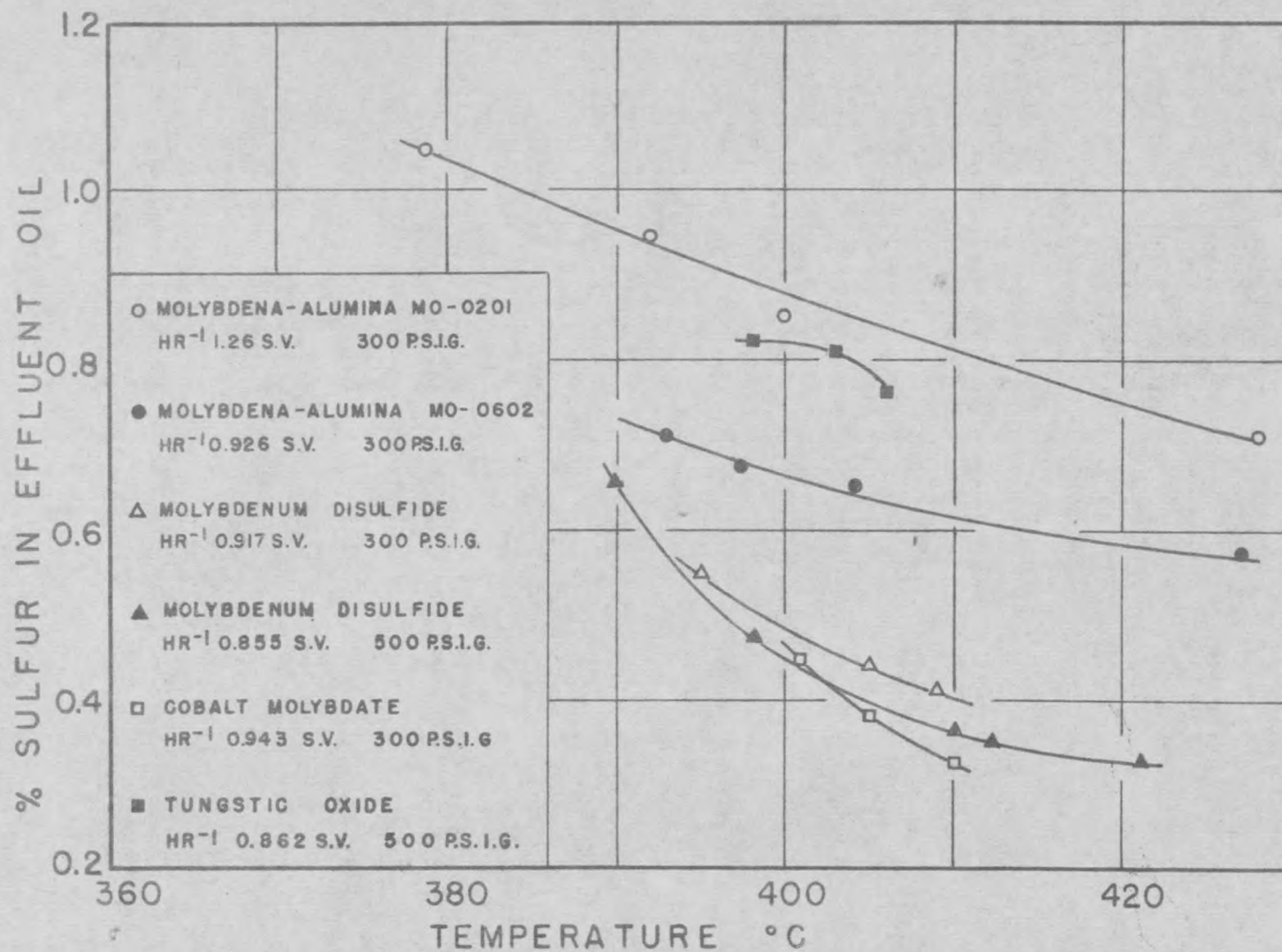


Figure 4. The Effect of Temperature Upon Desulfurization with Various Catalysts

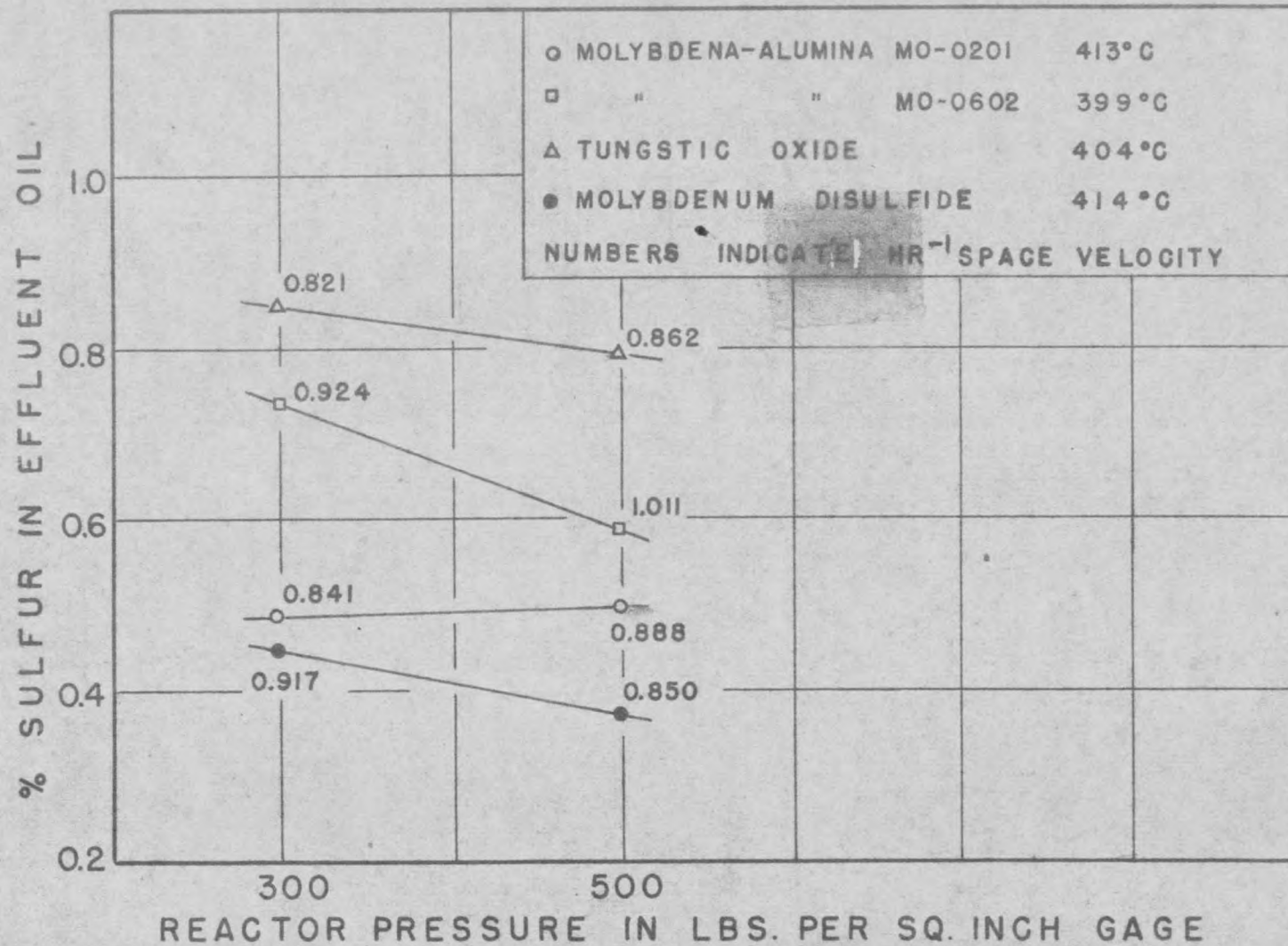


Figure 5. The Effect of Reactor Pressure Upon Desulfurization

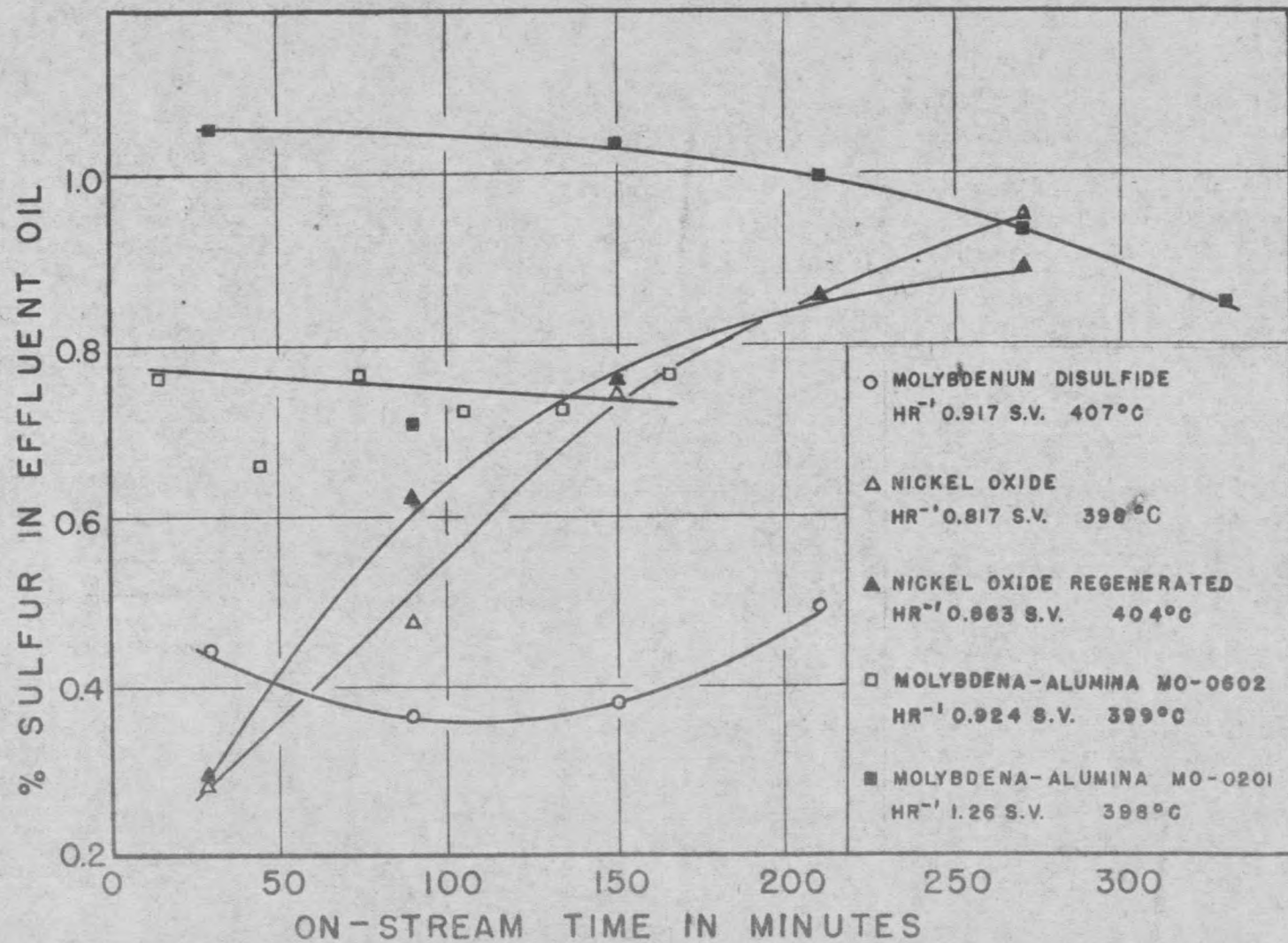


Figure 6. The Effect of Operating Time Upon Desulfurization

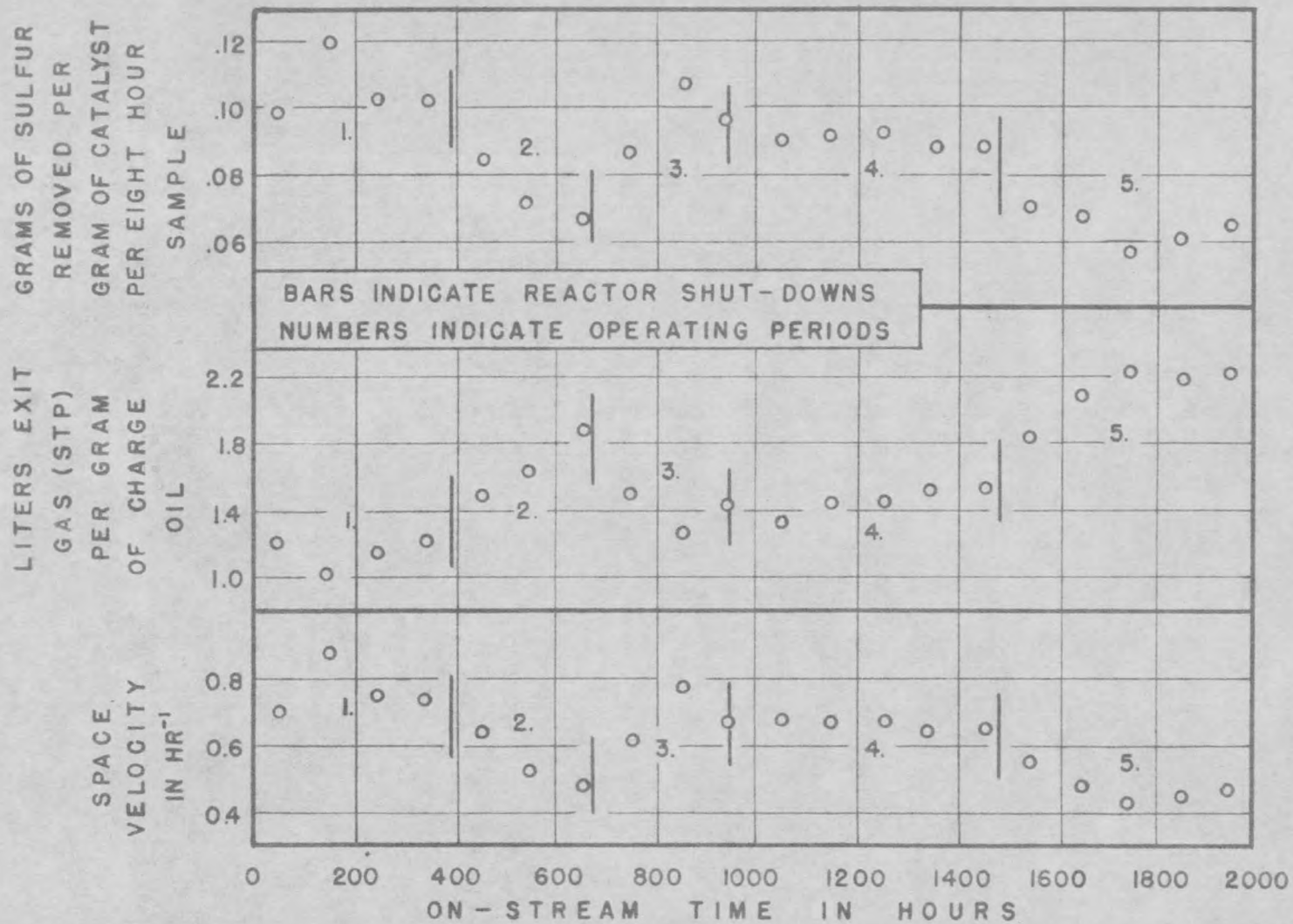


Figure 7. Plot of Grams Sulfur Removal, Liters Exit Gas per Gram Oil, and Space Velocity versus On-stream Time for Life Study of MoS₂ Catalyst

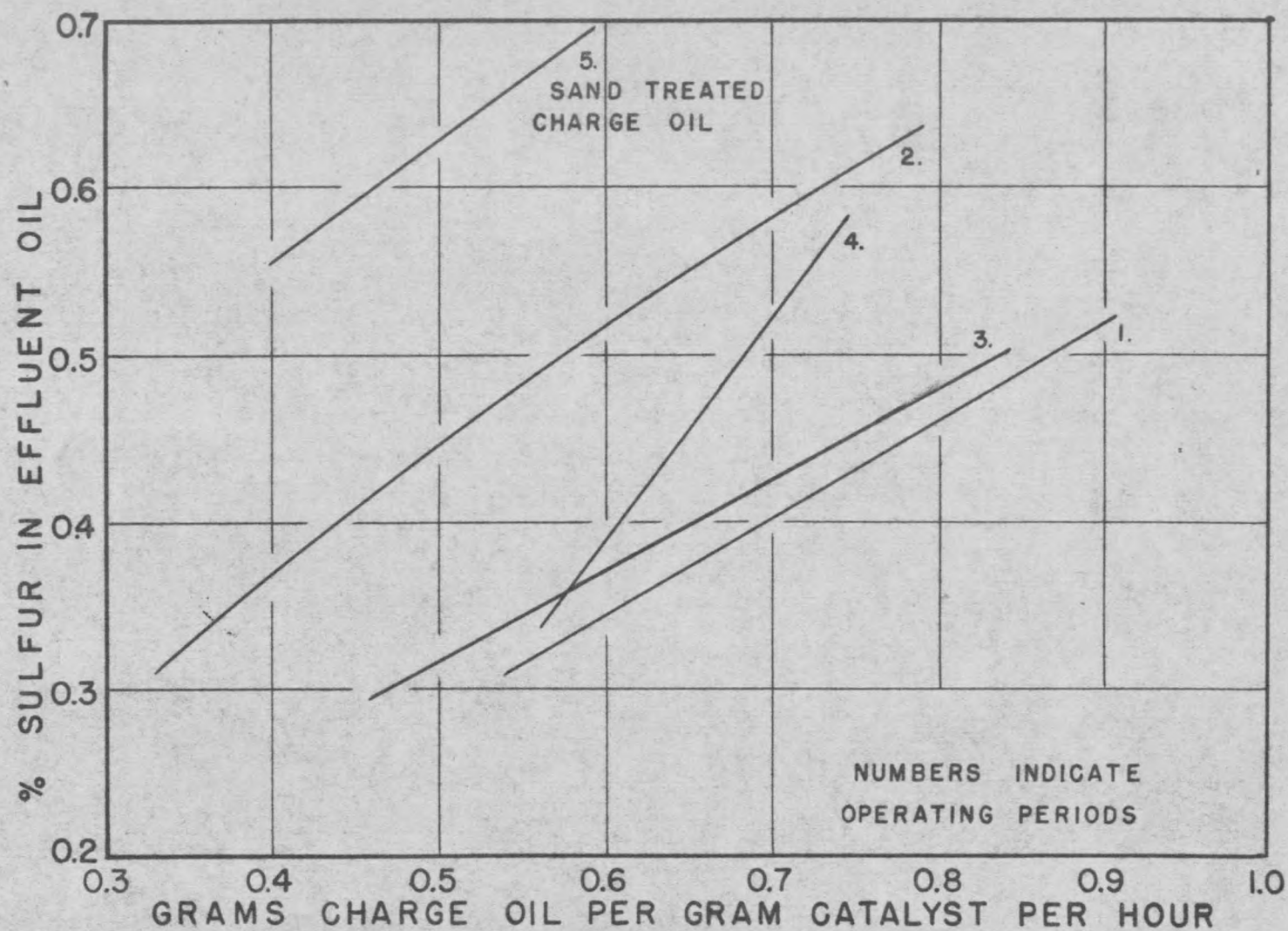
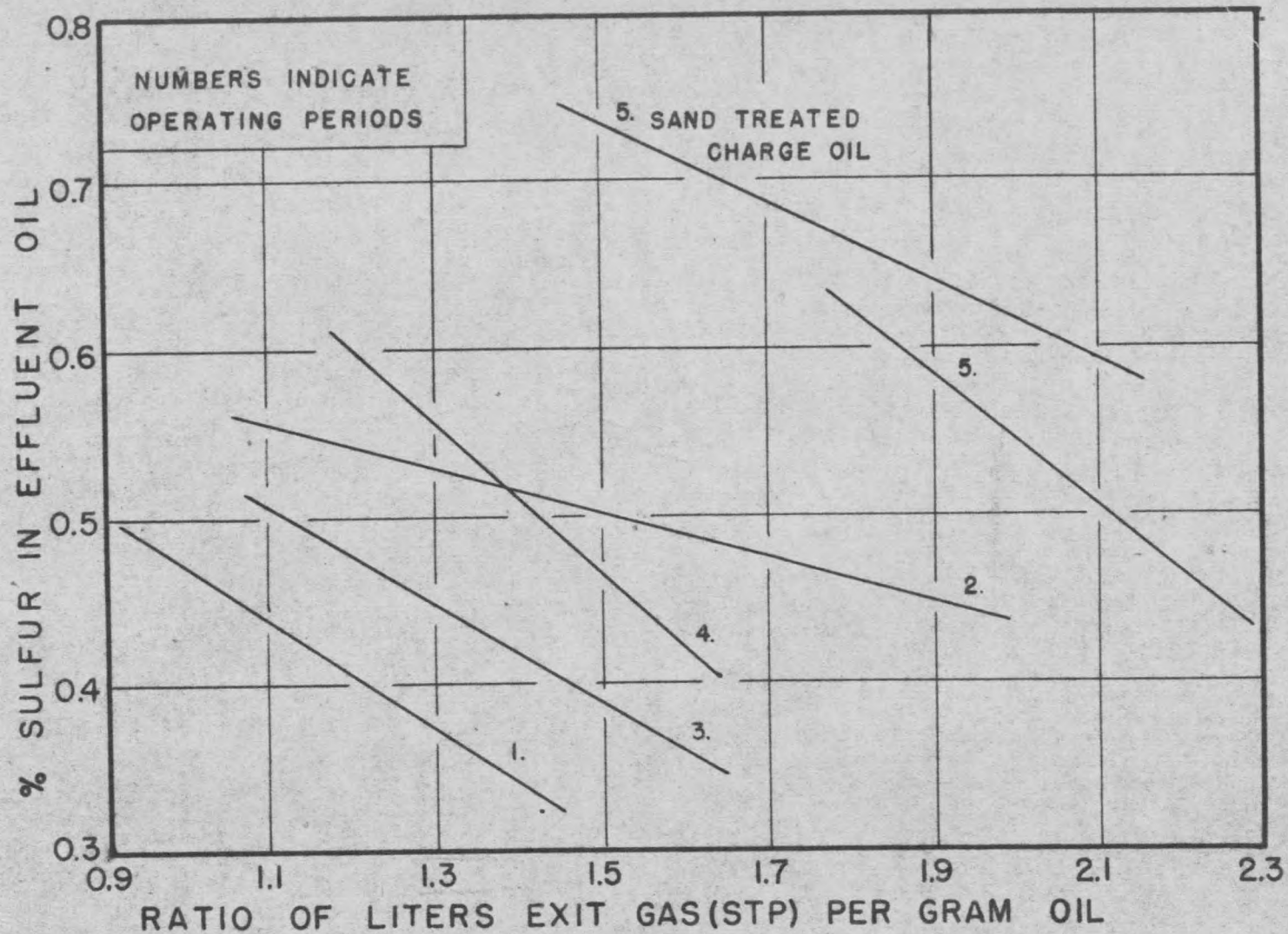


Figure 8. The Effect of Space Velocity Upon Desulfurization for the Operating Periods of MoS₂ Catalyst Life Study

103333



55

Figure 9. The Effect of Exit Gas to Oil Ratio Upon Desulfurization for the Operating Periods of MoS₂ Catalyst Life Study



3 1762 10015048 9

N378
M926c cop. 2 103333

AUTHOR
Munro, Bradley L.

TITLE The catalytic desulfurization
of Wyoming fuel oil.

DATE DUE	BORROWER'S NAME
	<i>[Handwritten signature]</i>
31 0 '58	Robert W. Jones 612 30 12 41 B. 11-36-58 <i>[Handwritten notes]</i>
	(7-7264)
	notice
	called
APR 27 58	<i>[Handwritten mark]</i>
	N378 M926c cop. 2

21

103333