The catalytic desulfurization of Wyoming fuel oil
by Franklin C Silvey

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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This investigation was conducted to determine the applicability of molybdenum oxide and cobalt molybdate as desulfurization agents in the catalytic desulfurization of a number three fuel oil produced from a high-sulfur-containing Oregon Basin, Wyoming crude oil. The desulfurization studies were carried out in a pilot plant unit capable of holding 100 grams of catalyst, operated at a pressure of 500 psig and a temperature of 415°C. A space velocity of approximately 1.0 grams of oil per gram catalyst per hour and recycled "catforming" gas as a desulfurization atmosphere were employed in all the desulfurization studies. To meet specifications, the effluent oil was to contain less than 0.5 percent sulfur.

When a number three fuel oil was desulfurized using a molybdenum oxide catalyst and a recycle gas hydrogen content above the critical value, successful desulfurization was accomplished for 495 hours without air regeneration. Air regeneration had ho noticeable effect on the original activity of the molybdenum oxide.

The critical hydrogen content of the recycle gas was found to be a function of and increased with catalyst on-stream time.

Cobalt molybdate was used successfully as a desulfurization agent for 864 hours of continuous operation with no air regeneration. This catalyst showed a considerably higher activity and a longer catalyst life than the molybdenum oxide.

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Master of Science in Chemical Engineering

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Montana State College

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Bozeman, Montana
August, 1953

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ABSTRACT

This investigation was conducted to determine the applicability of molybdenum oxide and cobalt molybdate as desulfurization agents in the catalytic desulfurization of a number three fuel oil produced from a high-sulfur-containing Oregon Basin, Wyoming crude oil. The desulfurization studies were carried out in a pilot plant unit capable of holding 100 grams of catalyst, operated at a pressure of 500 psig and a temperature of 415°C. A space velocity of approximately 1.0 grams of oil per gram catalyst per hour and recycled "catforming" gas as a desulfurization atmosphere were employed in all the desulfurization studies. To meet specifications, the effluent oil was to contain less than 0.5 percent sulfur.

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The critical hydrogen content of the recycle gas was found to be a function of and increased with catalyst on-stream time.

Cobalt molybdate was used successfully as a desulfurization agent for 864 hours of continuous operation with no air regeneration. This catalyst showed a considerably higher activity and a longer catalyst life than the molybdenum oxide.

INTRODUCTION

With the increased demand for heavier distillates for use in Diesel engines, gas turbines and jet aircraft motors, and the depletion of high quality low sulfur crudes, petroleum refiners have been forced to turn to crude stocks with high sulfur contents. Such crudes can be utilized only if an economical method for reducing the sulfur content can be devised.

Sulfur has been found to occur in crudes and refined fractions as elemental sulfur, mercaptans, hydrogen sulfide, thiophenes, thiophanes, thioalcohols, organic sulfides, disulfides, and polysulfides (9). The objection to sulfur compounds in refined products are their actual or potential corrosive action on metal surfaces, reduction of the effectiveness of tetra-ethyl lead addition, detrimental effect on color stability, disagreeable odor and undesirable oxidation characteristics.

The literature contains numerous processes for treating light distillates. These generally remove the simple sulfur compounds by absorption or extraction or convert the sulfur to a less objectionable form without reducing the total sulfur content. The methods used for light distillates are not applicable to heavier fractions since they do not affect the more complex sulfur compounds found in heavy distillates, do not reduce the potential corrosiveness due to sulfur or cause excessive charge losses if extraction methods are used.

The most successful means of reducing the sulfur content of heavy fractions to meet required specifications with minimum losses is catalytic decomposition. Koski (5) studied the effect of bauxite and alumina catalysts under mild conditions and found that a maximum of 50 percent sulfur removal could be achieved. Using destructive dehydrogenation catalysts, such as molybdenum sulfide, as desulfurization agents in the presence of a hydrogen atmosphere, Green (3) and Munro (7) reported successful desulfurization, long catalyst life and easy catalyst regeneration. The mechanism of desulfurization in the presence of hydrogen is destructive dehydrogenation which converts the sulfur compound to a hydrocarbon and hydrogen sulfide. Hartwig (4) studied the effect of using a hydrogen rich gas, such as the off-gas from a "catforming" up-grading process, as a desulfurization atmosphere with a molybdenum sulfide catalyst. His results are comparable to those of Green (3) and Munro (7). Using the off-gas from a "catforming" unit eliminates the necessity of constructing a hydrogen plant in conjunction with the desulfurization process.

The purpose of this research was to study the effect of recycling "catforming" gas, using molybdenum oxide and cobalt molybdate catalysts on the desulfurization of number three fuel oil. The maximum allowable sulfur content for number three fuel oil was to be 0.5 percent.

THERMODYNAMIC CALCULATIONS

Tabulated thermodynamic data and calculations are presented in Tables I - III of the appendix.

Two reaction mechanisms were postulated for the conversion of molybdenum oxide to molybdenum sulfide during the desulfurization of a number three fuel oil. Either or both of these reactions may take place.

(1) $MoO_3 + 3H_2S \longrightarrow MoS_3 + 3H_2O$

(2) $MoO_3 + 3C_4H_4S + 12H_2 \longrightarrow MoS_3 + 3C_4H_{10} + 3H_2O$

These reactions were considered since the conversion of the oxide to the sulfide may be due to the hydrogen sulfide present in the recycle gas or the sulfur in the fuel oil. Although thiophene is not present in number three fuel oils, it was considered in the absence of thermodynamic data on higher alkyl thiophenes and should approximate the results that would be obtained with higher alkyl thiophenes.

The following free energies show that reaction (1) is feasible at 400°C while reaction (2) is not.

Reaction	F at 25°C Cal/mol	F at 400°C Cal/mol
1	-32,930	-12,660
2	-27,350	+61,040

The thermodynamic calculations of four mechanisms postulated for the desulfurization of fuel oil by molybdenum sulfide catalyst are given by Green (3). The results of these calculations help to confirm the postulated mechanism for desulfurization but are not of much value when used to fix the proper conditions under which the overall reaction should be run since the equilibrium constants are all very high in the paractical operating range.

EQUIPMENT

A diagram of the reactor is shown in Figure 1. The reactor consisted of a 16 inch length of $1\frac{1}{2}$ inch extra-strong black iron pipe fitted with a $1\frac{1}{2}$ to 3/4 inch reducer at the top and a $1\frac{1}{2}$ to $\frac{1}{2}$ inch reducer at the bottom. The top of the reactor was fitted with a union, two crosses, and an assembly of valves for feed gas inlet, oil inlet, oil feed-line bleed, an inlet for regeneration, blowout-disk exhaust system, and thermowell tube. The thermowell tube was a $\frac{1}{4}$ inch black iron 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 tube was capped at the bottom, and three thermocouples were inserted from the top. The hot junctions of the thermocouples could be adjusted to any desired position in the thermowell.

At the bottom of the reactor a condenser was connected with a $\frac{1}{2}$ inch pipe union. The condenser consisted of a 21 inch length of $\frac{1}{2}$ inch pipe with a 3 inch pipe as a water jacket. Below the condenser were fitted a cross, two tees, a pressure gage, a Jerguson receiver, a Mason-Neilan small volume air-to-close regulator valve and a 23 inch length of $\frac{1}{2}$ inch pipe which served as an overflow standpipe. A Fisher-Wizard proportional controller was used in connection with the Mason-Neilan valve to maintain the correct pressure in the system.

The condensed vapors were removed from the Jerguson receiver and collected in a one liter Erlenmyer flask. The non-condensable exhaust gases entrained in the effluent oil were passed through two scrubbing flasks in series containing a concentrated sodium hydroxide solution to remove the hydrogen sulfide. The sweetened gas was metered in a wet test meter manufactured by the Precision Scientific Company.

The recycle system consisted of a surge tank, a compression tank, and a feed tank. A number two gas cylinder served as the surge tank and was fitted at the top with a 3 inch length of 3/4 inch pipe, a cross, a pressure gage and two valves. The compression tank was a number two gas cylinder. At the top of the compression tank were a small sight glass, a cross, pressure gage and two valves used to isolate the tank from the recycle system. A $\frac{1}{2}$ inch standard black iron pipe was welded to the bottom of the compression tank. Fitted to the $\frac{1}{2}$ inch pipe through a $\frac{1}{2}$ to $\frac{1}{4}$ inch reducing elbow was a length of $\frac{1}{4}$ inch pipe which connected the compression tank to the compression pump. On the $\frac{1}{4}$ inch pipe was a tee one side of which was connected to a two cylinder adjustable stroke high pressure Hills-McCanna piston pump, the other side was fitted with a valve for returning the compression oil to the oil storage reservoir. The oil storage reservoir was a five gallon oil barrell. The feed tank was a number two gas cylinder fitted at the top with a cross and a pressure gage and with a valve at the bottom. All connections between tanks in the recycle system were made with high pressure steel tubing.

The heating elements for the reactor consisted of three 33 foot lengths of beaded Nichrome wire supplied with current from three 110-volt Powerstat variacs. The coils were wound around 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.

One-eighth inch alundum balls were used as the preheat medium. The catalyst bed was located below the preheat section and below the catalyst bed was another layer of alundum balls supported by a wire screen.

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

Auxilliary equipment included a Fisher Flowrator, a Brooks Rotameter, and gas cylinders with pressure regulators. Iron-constantan thermocouples were used in conjunction with a Leeds and Northrup indicating potentiometer for temperature measurement.

Analysis of recycle gas samples was made in a low temperature fractionation column.

MATERIALS

The materials used for the desulfurization studies were a number three fuel oil, compressed hydrogen, methane, "catforming" gas, and various catalysts.

The number three fuel oils, produced by the Husky Oil Company from Oregon Basin, Wyoming crudes, contained from 2.09 to 2.176 percent sulfur. Additional inspection data of the oil are listed in Table IV.

The catalysts investigated were 10% molybdenum oxide, 16% molybdenum oxide and cobalt molybdate; all on alumina. The code letters and compositions of these catalysts may be found in Table V.

The hydrogen gas used in this research was obtained from the Whitmore Oxygen Company of Salt Lake City, Utah. The methane gas and "catforming" gas used in the studies were obtained from the Matheson Company of East Rutherford, New Jersey. The composition of the "catforming" gas was 89 percent hydrogen, 3.5 percent methane, 1.5 percent ethane, 2.5 percent propane and 3.5 percent propylene.

METHODS

The desulfurization unit was put into operation by applying current to the heating coils. When the temperature in the catalyst bed reached 300°C, "catforming" gas flow was started and the reactor was pressurized by adjusting the back pressure valve. When the catalyst temperature reached 380°C, the oil to be desulfurized was charged to the reactor by the oil pump and the heating coil current was adjusted to maintain the proper reactor temperature. Recorded readings were not made until the reactor conditions became constant.

Recycling the "catforming" gas was accomplished by compressing the gas flowing from the reactor through the back pressure valve and returning it to the feed tank. When the pressure in the surge and compression tanks reached 300 psig, the compression tank was isolated from the system and the compression pump was started. Oil was pumped into the bottom of the compression tank until the pressure was equal to the pressure in the feed tank. Having reached equal pressures, the valve between the compression tank and the feed tank was opened and the compression continued. When the pressure in the feed and compression tanks had reached 600 psig, the compression pump was turned off and the valve between the feed and compression tanks was closed. The oil in the compression tank was forced out by opening the valve between the compression tank and the oil storage tank. After the oil had been removed from the compression tank, the pressures in the surge and compression tanks were equalized and the compression cycle was completed.

The "catforming" gas flow rate was measured by means of a Fisher Flowrator and was controlled by a high pressure needle valve. Gas flow through the reactor was maintained by supplying the "catforming" gas at a pressure higher than the reactor pressure setting of the back pressure valve. The reactor pressure was controlled by supplying the proper amount of air pressure to the diaphragm of the back pressure valve.

The temperatures at the top and bottom of the catalyst bed and in the preheat section were controlled by varying the current in the beaded Nichrome heating coils. The temperature in the preheat section was maintained at approximately 95°C below the catalyst bed temperature. The temperatures at the top and bottom of the catalyst bed were recorded at 30 minute intervals and these readings were averaged over a period of eight hours.

The effluent oil was removed continuously from the Jerguson receiver at a rate which maintained a continuous liquid seal in the receiver. Samples of the effluent oil were taken at eight hour intervals. The space velocity was controlled by adjusting the pumping rate of the oil charge pump. Space velocity calculations for the sample intervals were based on the weight of charge oil and the weight of catalyst in the reactor.

The samples of the effluent oil were weighed and a portion of the oil removed from each sample for sulfur content determination. The dissolved hydrogen sulfide gas was removed from the portion by washing with a 10 percent solution of sodium hydroxide followed by two distilled water washes. The sulfur content was determined by a modified lamp sulfur method (1) in which a sodium carbonate solution was used to absorb the sulfur dioxide from the lamp combustion gases. The excess sodium carbonate was titrated with dilute hydrochloric acid with brom-phenol blue indicator.

SAMPLE CALCULATIONS

A TYPICAL SHORT DURATION RUN

MoS-III

V-3 JHFS
Oil - Husky #3 Fuel Oil (2.09% S)
Catalyst - 100 Grams Harshaw Mo-0203 T 1/8-160A-2-1
Reactor Pressure - 500 Psig

Sample Number	Total Hours	Sample Weight Grams	Percent Sulfur Per Samp.	Average Temp. °C	Liters STP Makeup Gas	Liters STP Bleed-off Gas
1	8	755	.561	415	0	7.6
2	16	741	.584	414	0	7.6
3	24	755	.666	416	74.9	7.2
4	32	761	.691	415	25.1	6.9
5	40	756	.725	413	41.7	6.8
		3768				

Oil Charged = 3893 grams

Calculation of Average Space Velocity

$$\frac{\text{(3893 grams oil charged)}}{\text{(100 grams catalyst)(40 hours)}} = 0.973 \text{ grams oil/gram cat./hour}$$

Calculation of Average Gas Consumption

Total Liters (STP) Make-up Gas = 141.7
Total Liters (STP) Bleed-off Gas = 36.1
Total Liters (STP) Consumed = 105.6

$$\frac{\text{105.6 Liters Consumed}}{\text{3893 Grams Oil}} \times \frac{\text{1000 grams}}{\text{Kilogram}} = 27.1 \ \frac{\text{Liters Consumed}}{\text{Kilogram Oil}}$$

$$27.1 \ \frac{\text{Liters}}{\text{Kgm}} \times \frac{1 \text{ ft}^3}{28.316 \text{ liters}} \times \frac{3.78 \text{ Kgm}}{1 \text{ gal}} \times .871 \times \frac{42.0 \text{ gal}}{\text{bbl}} = 129.8 \text{ ft}^3\text{/bbl}$$

Calculation of Weight Percent Loss

Charge Oil Weight = 3893 grams
Effluent Oil Wt. = 3768 grams
125 grams loss

$$\frac{125}{3893} \times 100 = 3.21\%$$

Calculation of Grams Sulfur Removed From Oil Per Gram of Catalyst Per Eight Hour Sample

For Sample One

Charge Oil = 781 Grams at 2.09% Sulfur
Effluent Oil = 755 Grams at 0.561% Sulfur

Grams Sulfur in Charge Oil = 781 x 2.090 = 16.31
Grams Sulfur in Effluent Oil = 755 x 0.561 = 4.23
Grams Sulfur Removed = 12.08

$$\frac{12.08 \text{ Grams Sulfur Removed}}{100 \text{ Grams Catalyst}} = 0.1208 \text{ Grams Sulfur Removed/Gm. Cat.}$$

Calculation of Composite Sulfur Percent

Sample Weight	Percent Sulfur	Grams Sulfur
755	0.561	4.23
741	0.584	4.32
755	0.666	5.02
761	0.691	5.26
756	0.725	5.48
3768		24.31

$$\frac{24.31}{3768} \times 100 = 0.645\% \text{ Sulfur}$$

DISCUSSION OF RESULTS

The catalysts employed in the investigations were 10 percent molybdenum oxide, 16 percent molybdenum oxide and cobalt molybdate. The operating conditions of the various runs were a reactor pressure of 500 psig, an average temperature of 415°C, space velocities of approximately 1.0 grams of oil per gram of catalyst per hour, and "catforming" gas recycle rates of approximately 147 standard liters per hour.

Several molybdenum oxide studies were made to determine the applicability of this catalyst as a desulfurization catalyst. The results of these runs are shown in Figures 2 and 3 on which calculated composite sulfur contents are plotted versus catalyst on stream time.

The data for the first molybdenum oxide study, MOS-I, are shown in Table VI. Using a 16 percent molybdenum oxide catalyst, the results of the MOS-I run were in no way comparable to the molybdenum sulfide studies made by Hartwig (4), or to similar runs performed by the Husky Oil Company. The sulfur content of the effluent oil exceeded 0.5 percent after only 40 hours of on-stream operation, so the run was discontinued.

Considering the possibility of incorrect designation of the composition of the catalyst used in the MOS-I run, a second molybdenum oxide study using a 10 percent molybdenum oxide catalyst was made. The data for this run are shown in Table VII. In the MOS-II run the sulfur content of the effluent oil exceeded 0.5 percent after only 32 hours of operation. This run indicated that the compositions of the catalysts were properly designated.

A third molybdenum oxide study, using a 16 percent molybdenum oxide catalyst obtained from the Husky Oil Company, did not produce specification oil during any part of the run and was discontinued after 40 hours of operation. The data for this run, MOS-III are shown in Table VIII.

A molybdenum sulfide catalyst was prepared by sulfiding a 16 percent molybdenum oxide catalyst with hydrogen sulfide at 300°C. Using this catalyst, the sulfided catalyst study run, SCS-I, was made. The sulfur content of the effluent oil exceeded 0.5 percent after 8 hours of the run, and the catalyst was regenerated with an air burn-off after 40 hours of operation. When the run was continued after the catalyst regeneration, a space velocity of 0.5 was used for the first 16 hours of operation and then increased to approximately 1.0 for the remainder of the run. The sulfur content of the effluent oil was correspondingly low at the low space velocity but exceeded 0.5 percent soon after the space velocity reached 1.0. The gas rate was increased from 147 to 157 standard liters per hour at sample number 13. This increased rate did not have any noticeable effect on the sulfur content of the effluent oil. The SCS-I run was discontinued 108 hours after the catalyst regeneration. Tabulated data for this run are shown in Table IX.

The MOS-IV run, using a 16 percent molybdenum oxide catalyst, was started with pure hydrogen as feed gas on a one pass basis and changed to "catforming" gas on recycle when the hydrogen supply became exhausted after 8.5 hours of operation. In this run the charge oil was started through the reactor at 100°C and the reactor temperature was allowed to increase slowly over a period of 11 hours to 415°C. During this same period the space velocity was increased from 0.57 to 0.87. After the first 11 hours, the space velocity was slowly increased to approximately 1.0 and held at this rate for the remainder of the run. For the first seven samples, excluding sample number one, specification oil was produced. However, as soon as the unit was switched to "catforming" gas on recycle and the space velocity increased, the sulfur content in the effluent oil began to rise. At the end of 335 hours of operation, the MOS-IV run was discontinued. The tabulated data for this run are shown in Table X.

Gas analyses of samples of the recycle gas used in the molybdenum oxide studies are shown in Table XIII. Analysis of the recycle gas at the end of the MOS-IV run showed a hydrogen content of 76 percent. Hartwig (4) found that specification oil was produced using a recycle gas containing 81.1% hydrogen. This indicated that if the molybdenum sulfide and oxide catalysts have similar properties, the preceding molybdenum oxide studies were made with a deficiency of hydrogen in the recycle gas.

For the MOS-V run, the recycle gas was enriched to 87.5 percent hydrogen and the unregenerated catalyst from the preceding run, MOS-IV, was used. Data for the MOS-V run are shown in Table XI. Since the sulfur content of the effluent oil remained over 0.5 percent for the first 92.5 hours of the run, the catalyst was air regenerated. Using the regenerated catalyst and an initial space velocity of 0.346, the MOS-V run was continued. The space velocity was increased slowly to approximately 1.0 and continued at this rate for the remainder of the run. During the remainder of the run, specification oil, which yielded a calculated composite sulfur content of 0.418, was produced for 495 hours of continuous operation.

Satisfied that molybdenum oxide was comparable to molybdenum sulfide as a desulfurization catalyst, the catalyst was regenerated with an air burn-off and the MOS-V run was continued to determine the critical hydrogen content in the recycle gas. For the first 72 hours of the continued run, "catforming" gas was used as make-up gas until it was evident that the catalyst was responding normally. When normal catalyst response was established, methane gas was substituted as make-up gas for 120 hours until the sulfur content of the effluent oil exceeded 0.5 percent. When specification oil was no longer produced, the methane was replaced, and pure hydrogen gas was used as make-up gas for the remainder of the run. Samples of the recycle gas were taken at frequent intervals during the run and their analyses are shown in Table XIII. The results of this study are shown on Figure 4, where percent sulfur for each sample and the hydrogen content of the recycle gas are plotted versus hours on-stream time. Using Figure 4, the critical hydrogen content of the recycle gas can be evaluated at several different periods during the run. These values are shown on Figure 5, where percent hydrogen is plotted versus catalyst on-stream time for an operating space velocity of 1.0. The critical hydrogen content was found to increase with catalyst on-stream time.

The data for the cobalt-molybdate comparison run, CMR-I, are shown in Table XII. This run was operated for 864 hours under the same conditions used for the preceding molybdenum oxide studies. Specification oil was produced for the entire run and the calculated composite sulfur content was found to be .1082. The highest sulfur content for a single sample was only 0.206 percent. The gas consumption averaged 201 ft^3 per barrell which is somewhat lower than values determined in previous studies. The results of the CMR-I run, as shown in Figure 6, in which percent sulfur for each sample and composite sulfur percent are plotted versus catalyst on-stream time, clearly shows that cobalt molybdate catalyst exhibited considerably higher activity than the molybdenum oxide catalysts studied previously.

SUMMARY

A catalyst containing 16 percent molybdenum oxide can be successfully employed as a desulfurization agent using "catforming" gas on recycle. The results indicate that this catalyst will produce a calculated composite sulfur content of less than 0.5 percent for a period of 495 hours without an air regeneration from a number three fuel oil originally containing 2.176 percent sulfur.

Air regeneration does not produce a noticeable effect on the original activity of molybdenum oxide.

The critical hydrogen content of the recycle gas, utilized with a 16 percent molybdenum oxide catalyst operated at a space velocity of approximately 1.0, was found to increase with catalyst on-stream time. As shown in Figure 5, the critical hydrogen content increased from 66% at 160 hours on-stream to 88% at 536 hours on-stream.

The presence of a small amount of cobalt oxide with the molybdenum oxide greatly increased the activity and extended the catalyst life.

LITERATURE CITED

(1) A.S.T.M. STANDARDS ON PETROLEUM AND LUBRICANTS, American Society for Testive Materials, Philadelphia, Pa., p 272 (1941).

(2) Glasstone, Samuel, THERMODYNAMICS FOR CHEMISTS, D. Van Nostrand Company, Inc., New York, N. Y., Fourth Printing (1949).

(3) Green, K. J., M. S. Thesis, Montana State College (1952).

(4) Hartwig, J. R., M. S. Thesis, Montana State College (1953).

(5) Koski, O. H., M. S. Thesis, Montana State College (1952).

(6) Lange, N. A., HANDBOOK OF CHEMISTRY, Sixth Edition, Handbook Publishers, Inc., Sandusky, Ohio, (1946).

(7) Munro, B. L., M. S. Thesis, Montana State College (1952).

(8) Perry, J. H., CHEMICAL ENGINEERS HANDBOOK, McGraw-Hill Publishing Company, New York, N. Y., Third Edition (1950).

(9) Sachanen, A., CONVERSION OF PETROLEUM, Reinhold Publishing Company, New York, N. Y., Second Edition, (1948).

(10) United States Bureau of Mines Bulletin No. 406.

(11) United States Bureau of Mines Bulletin No. 477.

ACKNOWLEDGMENT

The author wishes to thank the Husky Oil Company of Cody, Wyoming for sponsoring this research work and for supplying the fuel oil used throughout the project.

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TABLE I
THERMODYNAMIC CALCULATIONS FOR THE REACTION

$$MoO_3 + 3H_2S \dashrightarrow MoS_3 + 3H_2O$$

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

Temperature		ΔF	K_{eq}
°C	°K		
25	298	-32,930	$10^{24.1}$
100	373	-31,820	$10^{18.7}$
200	473	-30,320	10^{14}
300	573	-28,830	10^{11}
350	623	-28,080	$10^{9.8}$
400	673	-27,350	$10^{8.9}$

TABLE II
THERMODYNAMIC CALCULATIONS FOR THE REACTION

$$MoO_3 + 3C_4H_4S + 12H_2 \dashrightarrow MoS_3 + 3C_4H_{10} + 3H_2O$$

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

Temperature		ΔF cal/mol	K_{eq}
°C	°K		
25	298	-12,660	$10^{9.3}$
100	373	4,340	$10^{-2.5}$
200	473	27,040	$10^{-12.5}$
300	573	38,540	$10^{-14.7}$
350	623	61,040	$10^{-21.4}$
400	673	72,540	$10^{-23.5}$

TABLE III
GENERAL THERMODYNAMIC DATA*

Compound	H_{f298} K cal/mol	S^o_{298} E.U./mole
$MoO_3(S)$	-180.39	18.7
$MoS_3(S)$	-61.48	15.9
$H_2S(g)$	-4.77	49.15
$H_2O(g)$	-57.80	45.11
$C_4H_4S(g)$	27.82	69.3
$C_4H_{10}(g)$	-29.81	74.21
$H_2(g)$	0	31.21

*Data obtained from the following sources: U.S. Bureau of Mines Bulletin No. 406 (10), U.S. Bureau of Mines Bulletin No. 477 (11), Glasstone (2), Lange (6), Perry (8).

TABLE IV
NUMBER 3 FUEL OIL INSPECTION DATA

A.P.I. at 60°F	30.6	Bromine No.	7.57
Sp. Gr.	0.8729	% Olefin	10.5
d. 60°F (calc)	0.8709	Wgt. % Sulfur	2.223
Ave. Mol. Wt.	222	Wgt. % H_2 in Oil	10.9
U.O.P. K factor	11.5		

A. S. T. M. Distillation

I.B.P.	425 °F
5%	504
10%	520
20%	536
30%	548
40%	558
50%	567
60%	575
70%	584
80%	594
90%	611
95%	625
E.P.	652
Recovered	99.0%
Residue	0.8%
Loss	0.2%

TABLE V
CATALYSTS

Producer: Harshaw Chemical Co.

Catalyst and Composition	Identification Code
Molybdenum Oxide 16% MoO_3 Al_2O_3 Balance	Mo-X-L739-21-3T-3/8"
Molybdenum Oxide 10% MoO3 Al_2O_3 Balance	Mo-X-L739-21-1T-3/8"
Molybdenum Oxide 16% MoO_3 Al_2O_3 Balance	Mo-0203 T 1/8"-160-A-2-1
Cobalt Molybdate MoO_3 - 9.5% CoO - 3.0% SiO_2 - 5.0% Graphite - 2.0% Al_2O_3 - balance	Co-Mo-0201-T-3/16"

TABLE VI

TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN (MOS-I)

Harshaw Mo-X-L 739-21-3-T 3/8" was used at 500 Psig
Husky #3 Fuel Oil + catforming gas on recycle
Composite sulfur percent = .483
Percent loss (weight basis) = 3.16

Samp. No.	Total Hours	Sample wt. gms.	% S per Samp.	Space vel. gms oil/ gm cat/hr	Liters Recycle Gas/gm oil	Gms. S removed/gm cat/hr	cu. ft. consumed/ bbl oil cumulative Average	Ave. Temp °C	Composite S %
1	8	715	.337	.924	1.420	.1249	-	415	.337
2	16	723	.439	.935	1.401	.1188	141	414	.389
3	24	788	.438	1.015	1.285	.1295	78	415	.407
4	32	786	.479	1.014	1.300	.1262	185	416	.426
5	40	786	.511	1.014	1.300	.1237	138	415	.443
6	48	785	.518	1.013	1.295	.1229	107	414	.456
7	56	782	.523	1.010	1.297	.1220	143	416	.466
8	64	785	.514	1.013	1.295	.1232	150	415	.472
9	72	779	.564	1.003	1.306	.1183	130	410	.483

TABLE VII
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN TWO (MOS-II)

Harshaw Mo-X-L 739-21-1-T 3/8" was used at 500 Psig.
Husky #3 Fuel Oil and catforming gas on recycle
Composite Percent Sulfur = .523
Percent loss (weight basis) = 1.28

Samp. No.	Total Hours	Sample Wt.Gms.	% S per Samp.	Ave. Temp. °C	Space Vel. Gms oil/ Gm Cat./Hr	Liters Recycle Gas/Gm Oil	Gms. S Removed/Gm Cat/Hr.	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	8	737	.336	415	.932	1.408	.1310	-	.336
2	16	729	.427	415	.923	1.420	.1230	-	.382
3	24	793	.478	416	1.003	1.381	.1298	-	.416
4	32	779	.516	415	.987	1.329	.1248	11.5	.442
5	40	810	.526	414	1.025	1.279	.1289	32.5	.459
6	48	800	.552	415	1.012	1.295	.1252	94.5	.476
7	56	831	.536	417	1.052	1.249	.1314	75.3	.484
8	64	879	.568	415	1.112	1.209	.1363	105.7	.496
9	72	852	.608	414	1.079	1.215	.1285	136	.509
10	80	786	.581	416	.996	1.316	.1208	129	.517
11	88	780	.597	415	.988	1.328	.1184	160	.523

TABLE VIII
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN THREE (MOS-III)

Harshaw Mo-0203 T 1/8" 160 A-2-1 was used at 500 Psig.
Husky #3 Fuel Oil and catforming gas on recycle.
Composite Percent Sulfur = .645
Percent loss (weight basis) = 3.21

Samp. No.	Total Hours	Sample Wt. Gms.	% S Per Samp.	Ave. Temp. °C	Space Vel. Gms oil/ Gm Cat./Hr	Liters Recycle Gas/Gm Oil	Gms. S Removed/Gm Cat/Hr.	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	8	755	.561	415	.977	1.352	.1208	-	.561
2	16	741	.584	414	.958	1.392	.1147	-	.573
3	24	755	.666	416	.977	1.345	.1124	105.7	.603
4	32	761	.691	415	.983	1.325	.1116	107.5	.626
5	40	756	.725	413	.978	1.342	.1084	129.8	.645

TABLE IX
TABULATED DATA FOR SULFIDED CATALYST STUDY RUN (SCS-I)

Harshaw Mo-0203 T 1/8" 160 A-2-1 Sulfided with H_2S
Husky #3 Fuel Oil, catforming gas on recycle, 500 Psig reactor pressure
Composite Percent Sulfur = .580
Percent loss (weight basis) = 2.72

Samp. No.	Total Hours	Sample Wt.Gms.	% S Per Samp.	Ave. Temp. °C	Space Vel. Gms Oil/ Gm Cat/Hr	Liters Recycle Gas/Gm Oil	Gms. S Removed/Gm Cat/Hr.	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	8	740	.457	415	.957	1.391	.1262	-	.457
2	16	749	.527	415	.971	1.352	.1226	212	.493
3	24	750	.546	416	.972	1.351	.1213	124.2	.512
4	32	747	.557	416	.968	1.358	.1201	78.3	.521
5	40	735	.585	415	.952	1.380	.1161	54.9	.534
6	48	380	.342	415	.493	2.680	.0693	157	.342
7	56	461	.345	414	.597	2.205	.0816	126.5	.344
8	64	761	.443	416	.985	1.332	.1309	104.1	.391
9	72	787	.557	416	1.018	1.289	.1262	137.2	.445
10	80	799	.608	415	1.033	1.275	.1243	118.6	.486
11	88	784	.631	416	1.016	1.292	.1204	125.8	.508
12	96	783	.634	414	1.012	1.295	.1196	111.6	.534
13	104	822	.598	414	1.063	1.511	.1380	122.1	.546
14	112	852	.621	415	1.102	1.478	.1410	131.0	.554
15	120	842	.715	415	1.091	1.492	.1316	135.5	.572
16	128	822	.708	415	1.065	1.528	.1291	139.4	.586
17	136	826	.604	415	1.069	1.520	.1382	141.8	.577
18	144	855	-	415	1.108	1.468	-	149.8	.579
19	148	356	.605	413	.923	1.761	.0589	168.0	.580

Catalyst regenerated with air after sample five.

TABLE X

TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FOUR (MOS-IV)

Harshaw Mo-0203-T-1/8" 160A-2-1 was used at 500 Psig.
Husky #3 Fuel Oil and Catforming gas on recycle or hydrogen with no recycle.
Composite Percent Sulfur = 0.609. Percent loss (weight basis) = 2.66

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	6	333	1.732	221.5	.570	*790	1741	-
2	11	427	.248	415.5	.869	*391/1.500	1760/1140	.248
3	19	628	.174	415	.808	1.631	835	.204
4	27	638	.356	414.5	.820	1.569	710	.250
5	35	716	.422	415	.919	1.429	588	.308
6	43	732	.477	414.7	.940	1.393	493	.348
7	51	734	.462	414.2	.942	1.431	472	.372
8	59	744	.541	415.5	.954	1.373	415	.399
9	67	763	.589	415	.979	1.338	436	.426
10	75	766	.554	415	.984	1.370	394	.441
11	83	779	.552	415	1.000	1.302	358	.455
12	91	775	.630	414.5	.996	1.317	354	.471
13	99	735	.637	414.7	.944	1.396	356	.486
14	107	737	.647	414.5	.948	1.390	347	.500
15	115	763	.658	415	.980	1.360	337	.512
16	123	762	.706	415	.978	1.348	331	.516
17	131	769	.690	415.5	.988	1.341	310	.536
18	139	742	.712	414	.952	1.410	291	.538
19	147	740	.638	415	.951	1.387	286	.544
20	155	762	.523	415.5	.978	1.371	293	.542
21	163	761	.716	414	.976	1.335	308	.559
22	171	762	.686	416.5	.978	1.353	293	.568
23	179	780	.684	416	1.001	1.340	278	.574
24	187	762	.686	413.5	.978	1.348	294	.580
25	195	753	.571	414	.966	1.380	308	.579

TABLE X (cont'd)

TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FOUR (MOS-IV)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
26	203	761	.636	416	.976	1.356	295	.581
27	211	761	-	414.5	.976	1.343	289	.587
28	219	762	.740	413	.978	1.310	295	.594
29	227	767	.672	415	.986	1.330	297	.598
30	235	763	.783	415	.980	1.336	304	.600
31	243	747	.726	415	.961	1.403	317	.604
32	251	771	.631	414.5	.989	1.323	319	.605
33	259	763	.604	417	.979	1.338	317	.606
34	267	755	.595	416	.971	1.365	307	.606
35	275	751	.616	414.5	.964	1.365	318	.606
36	283	792	.582	416	1.018	1.296	309	.606
37	291	746	.627	416	.958	1.391	296	.606
38	299	775	.616	418.5	.996	1.349	287	.606
39	307	737	.685	416.5	.948	1.395	294	.608
40	315	811	.604	415	1.041	1.280	286	.608
41	323	740	.552	416	.951	1.387	298	.608
42	331	726	.630	414.5	.932	1.405	299	.609
43	335	357	.590	416.5	.917	1.463	294	.609

*For sample #1 and 2.5 hours of sample #2 these numbers are liters feed gas.

TABLE XI
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS V)

Harshaw Mo-0203-T-1/8 160-A-2-1 (Previously on MOS IV 355 Hrs)
Reactor Pressure-500 Psig Husky #3 Fuel Oil Catforming & Hydrogen Mixture on Recycle
Composite Percent Sulfur Percent Loss (weight basis) = 3.52
Sample 14 thru 75 = .418
Sample 75 thru 143 = .506
Catalyst regenerated with air after samples 13, 75, and 144

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	5	334	1.880	227	.682	2.100	580	-
2	10	524	1.002	410.5	1.070	1.361	429	-
3	18	756	.690	414	.965	1.477	406	-
4	26	789	.636	416.5	1.007	1.460	418	-
5	34	810	.660	416	1.003	1.400	383	-
6	42	811	.728	416	1.040	1.438	369	-
7	50	817	.713	414	1.043	1.429	356	-
8	58	366	.397	415.5	.467	3.240	431	-
9	66	758	.625	415	.970	1.500	455	-
10	74	700	.670	415	.892	1.619	404	-
11	82	701	.637	414	.894	1.642	423	-
12	90	692	.663	414	.882	1.663	411	-
13	92.5	221	.649	413	.902	1.588	430	-
14	99.5	234	.336	415	.346	4.830	394	.336
15	107.5	406	.169	415	.526	2.780	364	.231
16	115.5	419	.129	414	.543	2.710	337	.191
17	123.5	453	.156	417	.588	2.490	314	.180
18	131.5	629	.213	414.2	.815	1.800	294	.190
19	139.5	644	.224	416	.835	1.770	308	.191
20	147.5	649	.273	416.5	.843	1.749	303	.212
21	155.5	648	.263	414	.840	1.760	286	.221

TABLE XI (continued)

TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS-V)

Samp. No.	Total Hours	Sample Wt. Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
22	163.5	651	.249	414.5	.845	1.755	281	.225
23	171.5	795	.379	416.5	1.030	1.439	303	.246
24	179.5	865	.456	415	1.121	1.320	295	.275
25	187.5	746	.308	415	.965	1.519	304	.278
26	195.5	741	.354	415	.960	1.530	295	.285
27	203.5	733	.361	414	.950	1.550	286	.292
28	211.5	734	.354	415.5	.951	1.540	285	.297
29	219.5	743	.363	416.5	.964	1.490	294	.301
30	227.5	735	.366	414	.951	1.540	312	.306
31	235.5	716	.357	414.5	.926	1.580	314	.309
32	243.5	720	.394	415	.931	1.575	328	.314
33	251.5	746	.422	413.5	.966	1.520	334	.320
34	259.5	734	.348	413.5	.952	1.550	332	.322
35	267.5	723	.360	415	.937	1.568	340	.323
36	275.5	728	.418	414.5	.945	1.559	334	.328
37	283.5	759	.389	417	.982	1.510	326	.331
38	291.5	772	.393	416.5	1.000	1.468	333	.334
39	299.5	768	.477	415	.994	1.495	329	.340
40	307.5	771	.445	414	.997	1.468	326	.345
41	315.5	761	.418	417.5	.986	1.496	323	.347
42	323.5	717	.399	414.5	.931	1.580	330	.349
43	331.5	740	.443	415	.958	1.518	325	.353
44	339.5	749	.436	416	.971	1.505	316	.355
45	347.5	727	.436	414.5	.944	1.551	315	.358
46	355.5	786	.457	415.5	1.018	1.438	327	.362
47	363.5	734	.453	416	.952	1.538	325	.365
48	371.5	806	.491	414	1.042	1.382	317	.369
49	379.5	755	.475	415	.979	1.495	329	.373
50	387.5	792	.464	416	1.026	1.430	321	.376

TABLE XI (continued)
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS-V)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
51	395.5	758	.475	415	.983	1.490	319	.379
52	403.5	780	.467	416	1.010	1.438	324	.382
53	411.5	784	.520	416	1.016	1.438	344	.385
54	419.5	834	.561	415.5	1.072	1.350	337	.390
55	427.5	815	.505	413.5	1.042	1.415	330	.393
56	435.5	753	.453	415.5	.976	1.512	334	.395
57	443.5	745	.470	415	.966	1.518	327	.397
58	451.5	750	.442	414.5	.972	1.538	323	.398
59	459.5	757	.484	416	.981	1.491	324	.400
60	467.5	764	.484	413	.991	1.490	322	.402
61	475.5	752	.452	414.5	.974	1.521	333	.402
62	483.5	698	.638	390	.905	1.561	332	-
63	491.5	735	.458	414.5	.953	1.578	327	.404
64	499.5	750	.514	415	.972	1.525	342	.406
65	507.5	739	.447	416	.958	1.528	336	.404
66	515.5	774	.516	416.5	1.003	1.458	337	.407
67	523.5	764	.456	416	.991	1.481	337	.408
68	531.5	752	.486	416	.975	1.520	335	.409
69	539.5	753	.496	416	.976	1.480	334	.411
70	547.5	729	.480	416	.945	1.555	334	.412
71	555.5	762	.488	416	.988	1.452	330	.413
72	563.5	734	.527	415	.952	1.538	334	.416
73	571.5	795	.459	415	1.030	1.402	329	.417
74	579.5	727	.475	415.5	.942	1.559	326	.417
75	587.5	759	.485	415	.984	1.492	333	.418
76	595.5	668	.199	416	.868	1.692	190	.199
77	603.5	713	.255	416	.926	1.560	238	.228
78	611.5	785	.298	414	1.020	1.429	213	.253
79	619.5	722	.297	418	.951	1.553	241	.264

TABLE XI (continued)

TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS-V)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
80	627.5	773	.312	416	1.005	1.461	231	.276
81	635.5	759	.317	415	.988	1.472	299	.284
82	643.5	752	.326	415	.979	1.500	319	.289
83	651.5	751	.337	414	.978	1.516	275	.295
84	659.5	756	.346	415	.983	1.502	320	.302
85	667.5	763	.341	415	.993	1.480	319	.305
86	675.5	738	.343	416	.960	1.529	285	.308
87	683.5	735	.347	416	.957	1.538	348	.311
88	691.5	780	.380	417	1.014	1.449	331	.317
89	699.5	743	.371	417	.966	1.521	344	.320
90	707.5	757	.391	415	.984	1.492	332	.325
91	715.5	749	.374	415	.975	1.508	385	.328
92	723.5	752	.431	413	.979	1.501	397	.335
93	731.5	762	.465	416.5	.990	1.544	469	.342
94	739.5	758	.524	415	.986	1.495	471	.351
95	747.5	739	.493	416	.961	1.529	486	.358
96	755.5	753	.521	415	.979	1.508	493	.367
97	763.5	712	.528	416	.926	1.600	499	.373
98	771.5	717	.575	416	.932	1.596	476	.381
99	779.5	709	.551	415	.923	1.591	472	.389
100	787.5	722	.602	416	.939	1.555	477	.397
101	795.5	716	.573	416	.931	1.576	476	.403
102	803.5	725	.582	415	.942	1.558	467	.409
103	811.5	751	.591	417	.976	1.511	472	.416
104	819.5	743	.659	415	.966	1.535	461	.424
105	827.5	748	.633	416	.972	1.525	470	.431
106	835.5	742	.622	415.5	.965	1.538	462	.437
107	843.5	726	.704	415	.944	1.490	445	.445

TABLE XI (continued)
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS-V)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
108	851.5	742	.652	415.5	.965	1.521	443	.452
109	859.5	724	.604	417	.943	1.559	433	.457
110	867.5	729	.611	415	.949	1.549	419	.462
111	875.5	737	.638	415	.957	1.535	412	.466
112	883.5	513	.585	415	.669	2.200	424	.468
113	891.5	683	.568	415	.889	1.652	412	.470
114	899.5	713	.612	414.5	.928	1.540	425	.474
115	907.5	734	.553	417.5	.955	1.495	414	.476
116	915.5	708	.605	415	.922	1.592	402	.478
117	923.5	731	.575	415	.950	1.561	394	.481
118	931.5	735	.568	415.5	.957	1.537	398	.483
119	939.5	732	.585	415	.951	1.542	388	.486
120	947.5	738	.567	415	.961	1.529	389	.488
121	955.5	719	.564	416	.935	1.570	388	.488
122	963.5	732	.545	415	.951	1.542	379	.490
123	971.5	757	.548	415.5	.984	1.498	385	.491
124	979.5	742	.542	415.5	.965	1.521	385	.492
125	987.5	734	.568	415	.955	1.552	377	.493
126	995.5	780	.483	415.5	1.014	1.462	387	.493
127	1003.5	776	.545	415.5	1.009	1.455	381	.494
128	1011.5	793	.542	415	1.030	1.425	379	.496
129	1019.5	769	.504	416	1.000	1.468	375	.496
130	1027.5	779	.485	417.5	1.012	1.450	367	.496
131	1035.5	771	.566	415	1.002	1.470	369	.497
132	1043.5	794	.570	415	1.031	1.425	370	.498
133	1051.5	769	.566	415	1.000	1.475	371	.499
134	1059.5	790	.572	415	1.029	1.429	369	.501
135	1067.5	781	.558	415	1.015	1.445	359	.502
136	1075.5	779	.526	415.5	1.012	1.450	353	.503

TABLE XI (continued)
TABULATED DATA FOR MOLYBDENUM OXIDE SULFIDING RUN FIVE (MOS-V)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
137	1083.5	772	.530	415	1.002	1.470	359	.504
138	1091.5	781	.542	414.5	1.015	1.445	353	.503
139	1099.5	792	.544	416	1.030	1.425	364	.503
140	1107.5	744	.531	415	.968	1.525	359	.504
141	1115.5	795	.537	417	1.032	1.422	369	.504
142	1123.5	791	.481	419	1.029	1.429	367	.504
143	1131.5	767	.584	415.5	.997	1.472	364	.506
144	1133.0	155	-	412.5	1.072	1.369	358	-

TABLE XII
TABULATED DATA FOR COBALT MOLYBDATE RUN (CMR-I)

Harshaw Co-Mo-0201-T-3/16 was used at 500 Psig
Husky #3 Fuel Oil and catforming gas on recycle.
Composite Percent Sulfur = .1082 Percent loss (weight basis) = 2.87

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
1	8	535	.156	418.5	.694	2.118	330	.156
2	16	535	.0986	414.5	.694	2.110	165	.127
3	24	717	.0637	414.5	.930	1.589	143	.102
4	32	767	.0536	420	.995	1.470	98	.0874
5	40	773	.0354	414	1.000	1.470	255	.0753
6	48	778	.0725	415.5	1.008	1.450	231	.0747
7	56	793	.0830	416	1.028	1.430	259	.0761
8	64	700	.0758	415	.906	1.629	222	.0761
9	72	686	.0756	416.5	.889	1.625	190	.0761
10	80	747	.0981	415	.970	1.522	216	.0783
11	88	760	.0874	415	.986	1.480	218	.0792
12	96	759	.0794	415	.981	1.459	198	.0792
13	104	773	.0700	415	1.000	1.476	242	.0784
14	112	754	.0617	416	.976	1.496	240	.0772
15	120	770	.0873	415	.996	1.480	241	.0779
16	128	765	.0942	415	.990	1.485	257	.0789
17	136	778	.0926	414.5	1.010	1.460	239	.0802
18	144	783	.101	415.5	1.015	1.440	232	.0816
19	152	836	.117	416	1.083	1.350	222	.0832
20	160	793	.102	415	1.027	1.219	208	.0847
21	168	753	.0942	415	.976	1.344	196	.0852
22	176	728	.119	415	.945	1.548	213	.0866
23	184	754	.113	413	.977	1.502	208	.0877
24	192	740	.0886	417	.958	1.531	197	.0877

TABLE XII (continued)
TABULATED DATA FOR COBALT MOLYBDATE RUN (CMR-I)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed/ Bbl Oil Cumulative Average	Composite Sulfur %
25	200	731	.0785	414.5	.949	1.549	210	.0872
26	208	747	.0754	415	.969	1.515	201	.0869
27	216	796	.0835	415.5	1.031	1.430	197	.0869
28	224	767	.115	416	.994	1.484	206	.0882
29	232	809	.0501	415	1.049	1.371	206	.0869
30	240	786	.0286	415	1.020	1.455	206	.0848
31	248	779	.0864	415.5	1.010	1.450	212	.0850
32	256	790	.0805	415	1.025	1.440	215	.0848
33	264	788	.0795	416.5	1.021	1.442	207	.0846
34	272	789	.0754	417.5	1.022	1.436	210	.0843
35	280	794	.0623	416.5	1.029	1.436	211	.0838
36	288	797	.0834	416.5	1.031	1.420	213	.0836
37	296	797	.0702	416.5	1.031	1.410	214	.0833
38	304	793	.0945	417	1.026	1.433	218	.0835
39	312	805	.1047	415	1.044	1.404	217	.0830
40	320	822	.0922	416.5	1.064	1.381	219	.0843
41	328	795	.1225	415.5	1.030	1.425	221	.0853
42	336	835	.142	417	1.083	1.369	215	.0869
43	344	789	.139	415.5	1.022	1.462	220	.0882
44	352	811	.148	415	1.051	1.389	214	.0895
45	360	799	.135	414.5	1.037	1.445	212	.0906
46	368	776	.154	416	1.008	1.456	220	.0918
47	376	821	.144	416	1.065	1.376	220	.0925
48	384	787	.164	415	1.020	1.452	219	.0942
49	392	791	.159	416.5	1.025	1.436	218	.0954
50	400	802	.139	415	1.039	1.420	221	.0965
51	408	817	.145	414	1.061	1.391	224	.0976
52	416	877	.124	415	1.071	1.375	228	.0982
53	424	836	.145	415.5	1.082	1.362	230	.0992

TABLE XII (continued)
TABULATED DATA FOR COBALT MOLYBDATE RUN (CMR-I)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed BBl Oil Cumulative Average	Composite Sulfur %
54	432	854	.133	417	1.108	1.333	228	.0999
55	440	789	.151	415	1.022	1.450	227	.1008
56	448	809	.128	414.5	1.049	1.400	224	.1015
57	456	728	.138	415.5	.943	1.556	222	.1021
58	464	769	.148	415	.996	1.475	222	.1026
59	472	789	.116	415	1.016	1.430	220	.1028
60	480	790	.103	415.5	1.024	1.440	215	.1030
61	488	786	.157	415.5	1.020	1.450	220	.1038
62	496	830	.137	414.5	1.075	1.416	215	.1043
63	504	741	.0683	415.5	.961	1.530	211	.1042
64	512	753	.1252	416	.975	1.505	211	.1042
65	520	777	.1038	414.5	1.005	1.460	206	.1042
66	528	773	.1057	415.5	1.001	1.465	209	.1042
67	536	759	.1467	414.5	.983	1.500	207	.1048
68	544	774	.1429	419.5	1.001	1.470	205	.1055
69	552	740	.109	416	.960	1.540	204	.1055
70	560	727	.115	417	.943	1.561	204	.1057
71	568	724	.1105	414	.938	1.571	203	.1057
72	576	762	.1496	416.5	.988	1.380	203	.1062
73	584	743	.1195	417	.963	1.531	203	.1065
74	592	754	.1176	416	.976	1.505	202	.1065
75	600	785	.128	415.5	1.018	1.455	204	.1069
76	608	801	.122	415.5	1.038	1.410	201	.1071
77	616	802	.115	416	1.040	1.375	199	.1072
78	624	793	.127	415.5	1.025	1.432	197	.1074
79	632	790	.111	414.5	1.024	1.425	198	.1074
80	640	813	.130	415	1.055	1.400	197	.1078
81	648	800	.117	414	1.030	1.428	195	.1080
82	656	791	.120	416.5	1.020	1.442	196	.1075

TABLE XII (continued)
TABULATED DATA FOR COBALT MOLYBDATE RUN (CMR-I)

Samp. No.	Total Hours	Sample Wt.Gms.	Percent Sulfur Per Samp.	Ave. Temp. °C.	Space Vel. Gms Oil/ Gm Cat/Hr.	Liters Recycle Gas/Gm Oil	Cu. Ft. Consumed Bbl Oil Cumulative Average	Composite Sulfur %
83	664	811	.119	415	1.042	1.408	196	.1078
84	672	769	.085	416	.990	1.490	195	.1078
85	680	754	.080	415	.969	1.530	193	.1072
86	688	784	.120	416	1.009	1.450	194	.1072
87	696	782	.206	415	1.006	1.467	193	.1082
88	704	843	.099	415.5	1.084	1.360	196	.1082
89	712	764	.087	415	.984	1.485	195	.1080
90	720	760	.062	415	.978	1.509	193	.1072
91	728	755	.066	416	.972	1.526	198	.1070
92	736	773	.063	415	.995	1.476	195	.1065
93	744	760	.077	415.5	.979	1.509	195	.1062
94	752	786	.135	415	1.012	1.450	196	.1065
95	760	775	.089	415	.997	1.472	196	.1068
96	768	765	.1312	416.5	.985	1.500	197	.1068
97	776	755	.1312	415	.972	1.511	197	.1070
98	784	774	.1042	415.5	.995	1.492	196	.1070
99	792	764	.1213	414.5	.984	1.494	196	.1069
100	800	755	.141	416	.972	1.525	197	.1072
101	808	773	.1325	414	.995	1.476	197	.1077
102	816	770	.1108	416	.990	1.483	197	.1078
103	824	757	.1158	416	.975	1.515	197	.1078
104	832	769	.1202	414	.990	1.487	201	.1079
105	840	771	.1222	415.5	.992	1.480	201	.1079
106	848	767	.1183	415	.988	1.510	201	.1081
107	856	804	.1174	415	1.035	1.408	201	.1082
108	864	749	.1125	416	.965	1.530	201	.1082

TABLE XIII
RECYCLE GAS ANALYSES

Run Designation	Hours on Run	% H_2	% CH_4	% C_2^+
MOS-III	40	80.8	15.7	3.5
SCS-I	148	79.2	16.8	4.0
MOS-IV	335	76.0	17.3	6.7
MOS-V	0	87.5	6.0	6.5
MOS-V	92.5	87.0	7.8	5.2
MOS-V	184	85.6	8.3	6.1
MOS-V	256	87.0	9.8	3.2
MOS-V	373	86.0	11.1	2.9
MOS-V	475	82.9	11.2	5.9
MOS-V	588	82.2	13.5	4.3
MOS-V	680	81.6	14.1	4.3
MOS-V	750	65.5	30.0	4.5
MOS-V	822	58.6	27.6	13.8
MOS-V	922	72.2	23.3	4.5
MOS-V	970	75.4	21.2	3.4
MOS-V	997	77.6	18.1	4.3
MOS-V	1062	82.1	13.8	4.1
MOS-V	1095	84.0	12.4	3.6
MOS-V	1114	86.4	10.7	2.9
MOS-V	1133	88.1	8.2	3.8

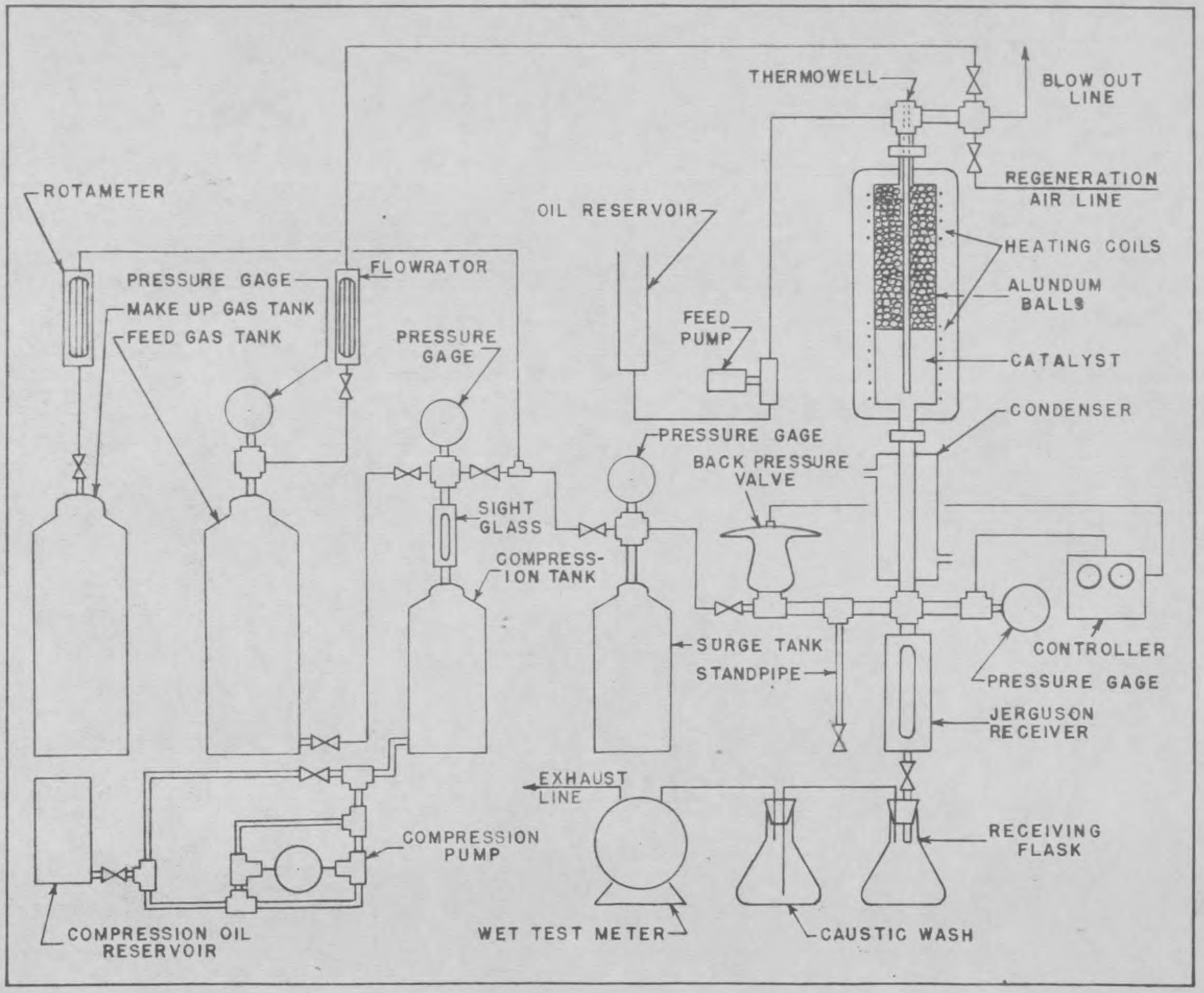

Figure 1. Reactor Diagram

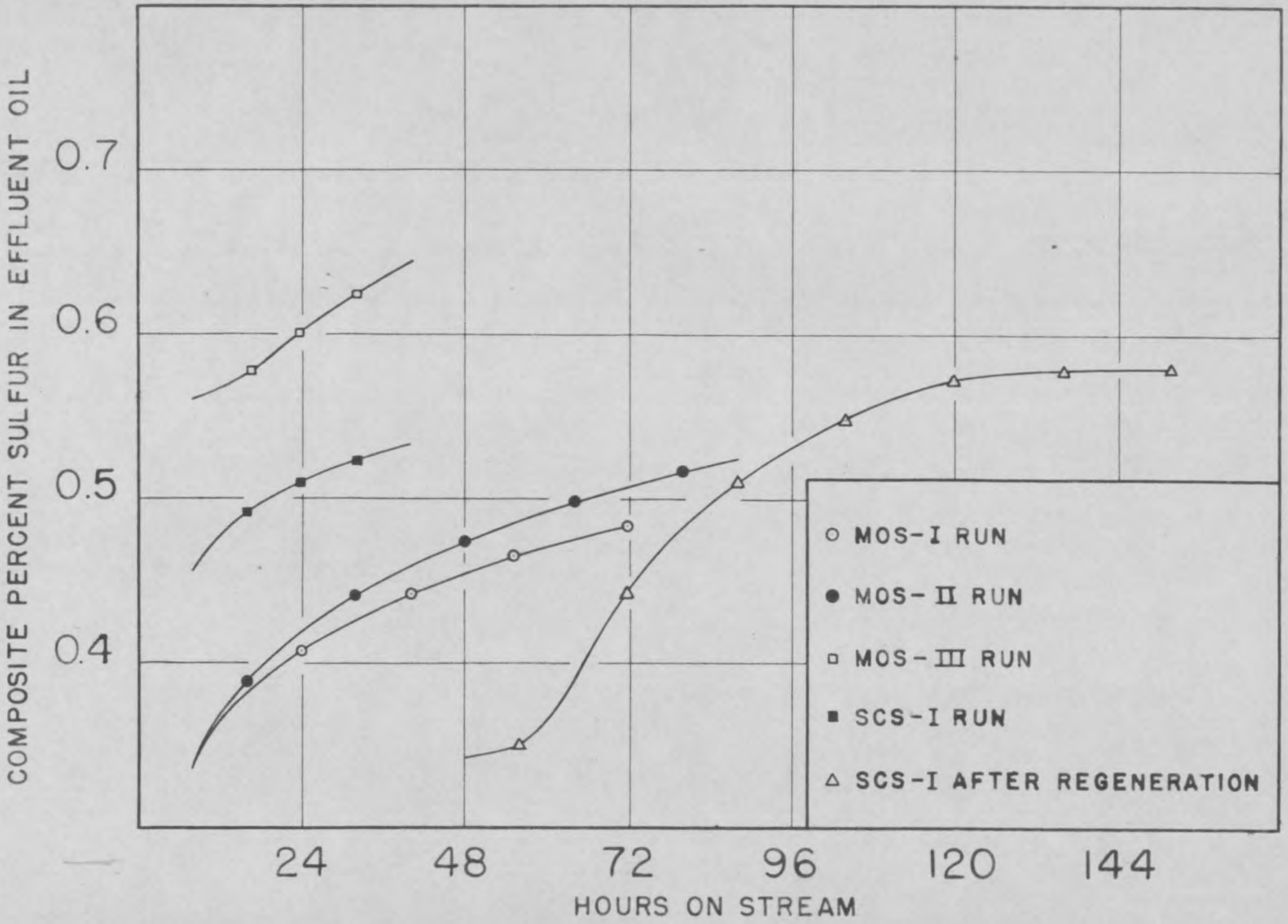

Figure 2. Effect of On-Stream Time on Desulfurization for Molybdenum Oxide Catalysts

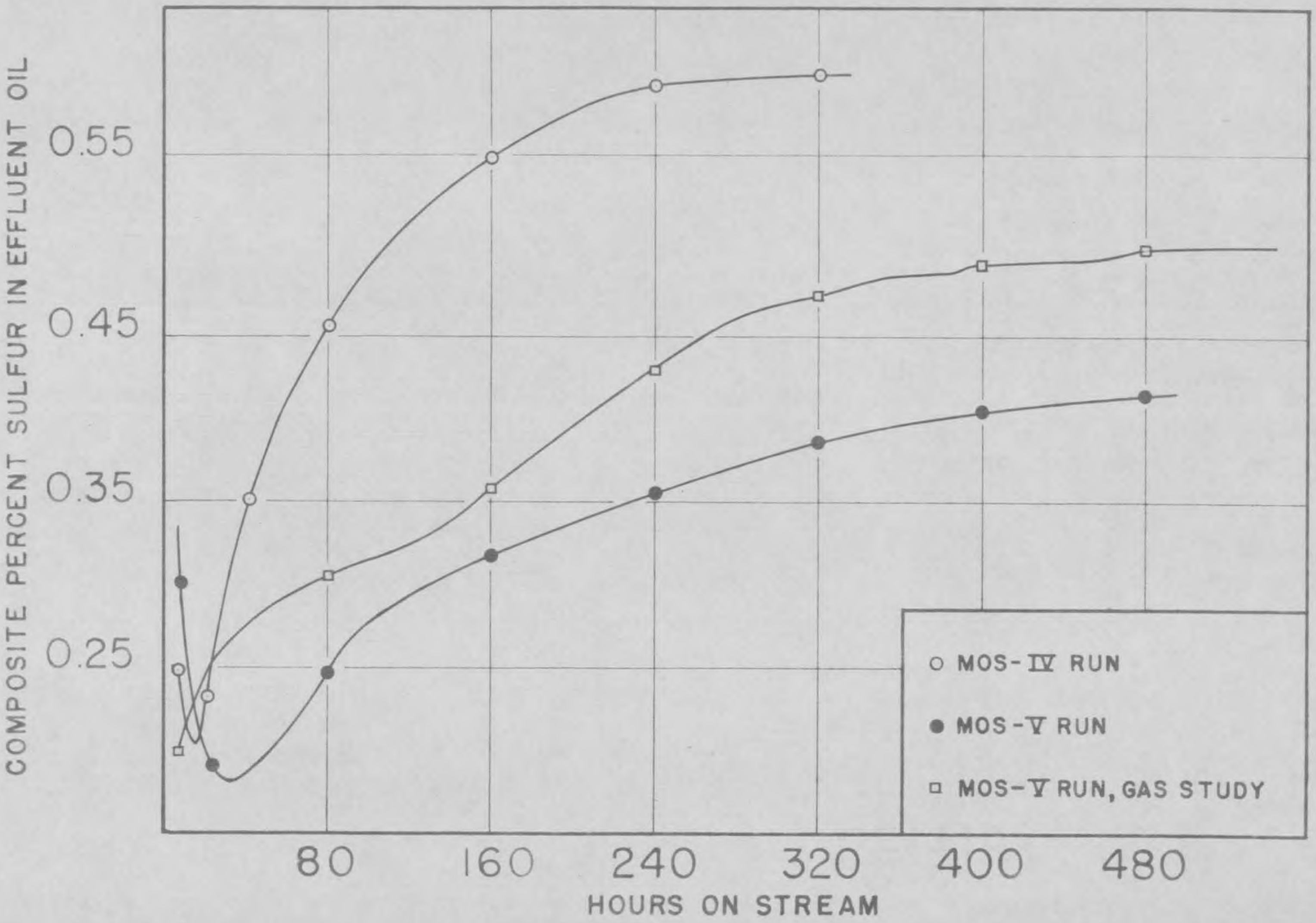

Figure 3. Effect of On-Stream Time on Desulfurization for Molybdenum Oxide Catalysts

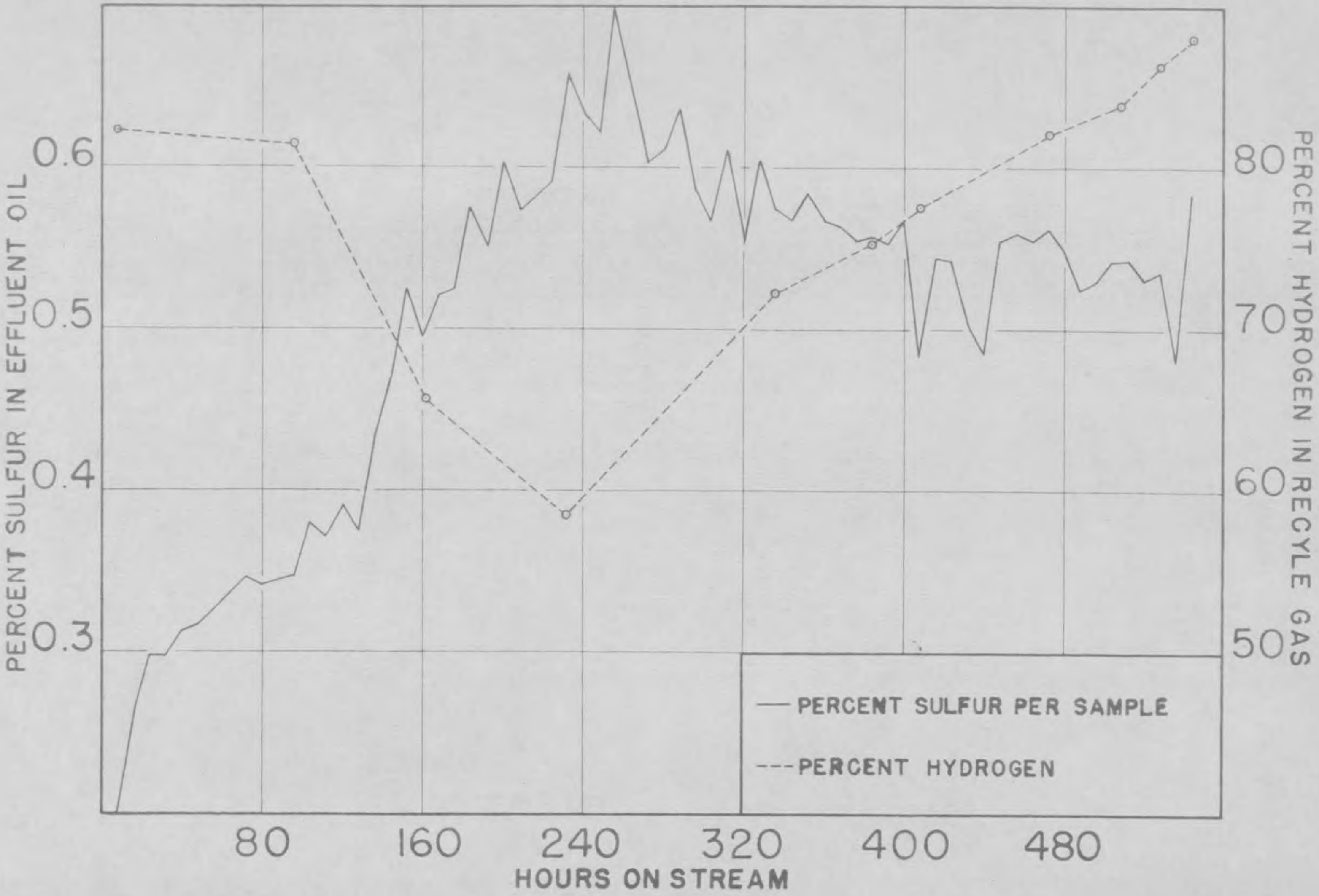

Figure 4. Desulfurization and Percent Hydrogen in Recycle Gas vs On-Stream Time for 16% Molybdenum Oxide Catalyst

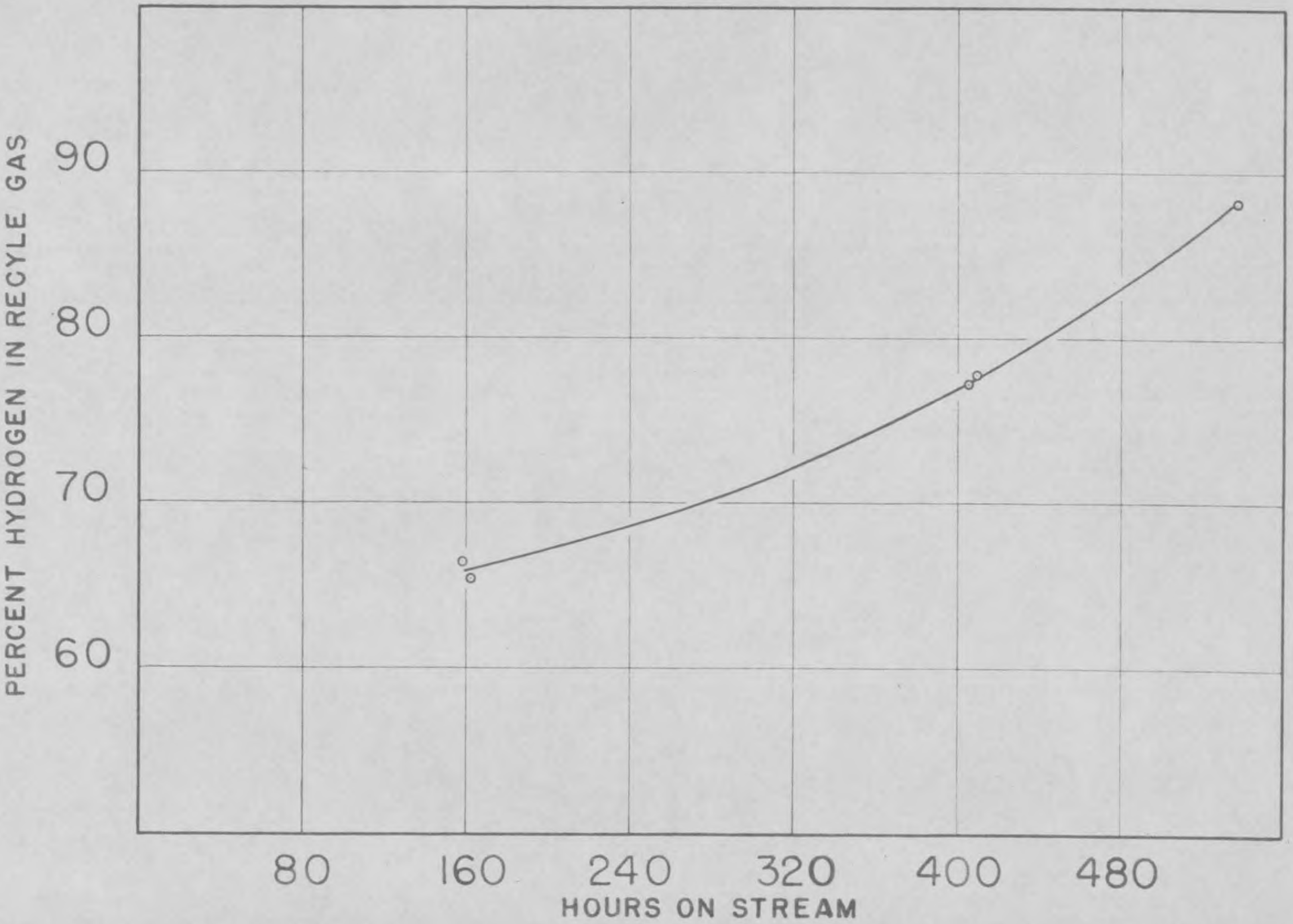

Figure 5. Critical Hydrogen Content of Recycle Gas for 16% Molybdenum Oxide Catalyst

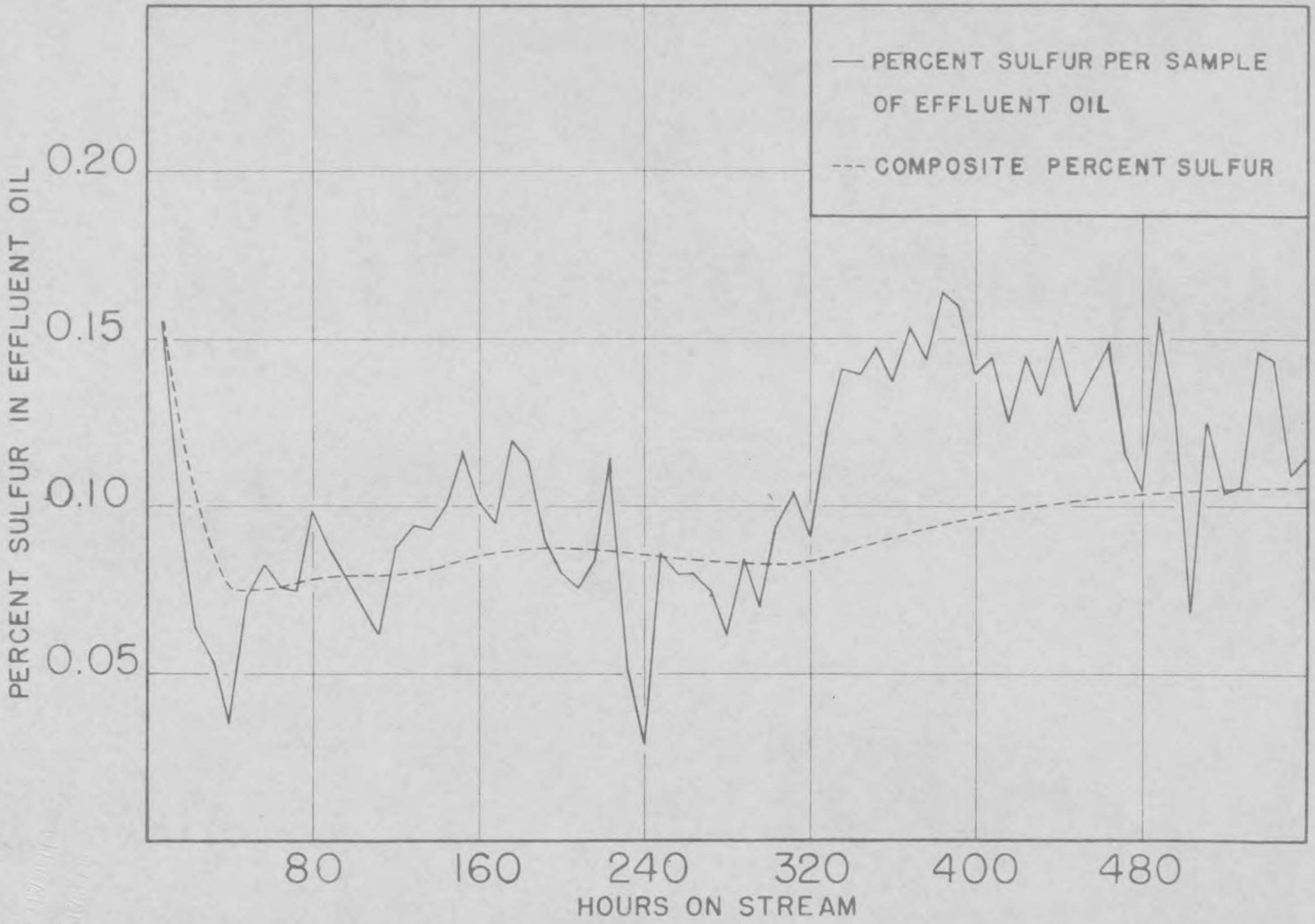

Figure 6. Effect of On-Stream Time on Desulfurization for Cobalt Molybdate Catalyst

	NAME AND ADDRESS
[illegible]	Dale P. [illegible] 401 S [illegible]
	Dale P. [illegible]
APR 27 '59	John [illegible]
MAR 13 '61	INTERLIBRARY LOAN /
	[illegible]
[illegible]	Wm. Hlunkal 578 N. Block
11-25 Ⓖ 27 CW	[illegible]-yuh Kim, 91'
11-13-86	Andrea Doo QUAD D
[illegible]	[illegible]

[redacted]