



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
© Copyright by Franklin C Silvey (1953)

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.

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 no 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.

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

at

Montana State College

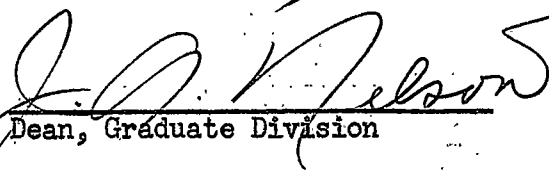
Approved:



Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

Bozeman, Montana
August, 1953

RECEIVED
MONTANA STATE COLLEGE
LIBRARY

N378
Si39c
cop. 2

TABLE OF CONTENTS

	Page
Abstract.	3
Introduction.	4
Thermodynamic Calculations.	6
Equipment	7
Materials	10
Methods	10
Sample Calculations	13
Discussion of Results	15
Summary	19
Literature Cited.	20
Acknowledgment.	21
Appendix.	22

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.

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 no 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.

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

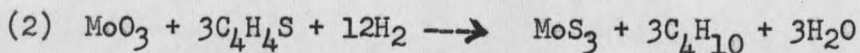
catalysts under mild conditions and found that a maximum of 50 percent sulfur removal could be achieved. Using destructive dehydrogenation catalysts, such as molybdenum sulfide, as desulfurization agents in the presence of a hydrogen atmosphere, Green (3) and Munro (7) reported successful desulfurization, 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.



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 practical 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 $1/2$ 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 $1/4$ 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 $1/2$ inch pipe union. The condenser consisted of a 21 inch length of $1/2$ 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 $1/2$ 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 $\frac{3}{4}$ 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
		<u>3768</u>				

Oil Charged = 3893 grams

Calculation of Average Space Velocity

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

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

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

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

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 = $781 \times 2.090 = 16.31$
Grams Sulfur in Effluent Oil = $755 \times 0.561 = 4.23$
Grams Sulfur Removed = $\underline{12.08}$

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

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
<u>756</u>	<u>0.725</u>	<u>5.48</u>
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, GMR-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 ft³ per barrell which is somewhat lower than values determined in previous studies. The results of the GMR-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.

APPENDIX

	Page
Table I Thermodynamic Calculations for the reaction: $\text{MoO}_3 + 3\text{H}_2\text{S} \longrightarrow \text{MoS}_3 + 3\text{H}_2\text{O}$	23
Table II Thermodynamic Calculations for the reaction: $\text{MoO}_3 + 3\text{C}_4\text{H}_4\text{S} + 12\text{H}_2 \longrightarrow \text{MoS}_3 + 3\text{C}_4\text{H}_{10} + 3\text{H}_2\text{O}$	23
Table III General Thermodynamic Data.	24
Table IV Number 3 Fuel Oil Inspection Data	24
Table V Catalysts	25
Table VI Tabulated Data for Molybdenum Oxide Sulfiding Run One	26
Table VII Tabulated Data for Molybdenum Oxide Sulfiding Run Two	27
Table VIII Tabulated Data for Molybdenum Oxide Sulfiding Run Three	28
Table IX Tabulated Data for Sulfided Catalyst Study Run One.	29
Table X Tabulated Data for Molybdenum Oxide Sulfiding Run Four.	30
Table XI Tabulated Data for Molybdenum Oxide Sulfiding Run Five.	32
Table XII Tabulated Data for Cobalt Molybdate Run One	38
Table XIII Recycle Gas Analyses.	42
Figure 1 Diagram of Reactor.	43
Figure 2 Effect of On-Stream Time on Desulfurization for Molybdenum Oxide Catalysts.	44
Figure 3 Effect of On-Stream Time on Desulfurization for Molybdenum Oxide Catalysts.	45
Figure 4 Desulfurization and Percent Hydrogen in Recycle Gas vs On-Stream Time for 16% Molybdenum Oxide Catalyst.	46
Figure 5 Critical Hydrogen Content of Recycle Gas for 16% Molybdenum Oxide Catalyst	47
Figure 6 Effect of On-Stream Time on Desulfurization for Cobalt Molybdate Catalyst	48

