



Catalytic hydrodesulfurization of fuel oil
by Kenneth J Green

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at Montana State College
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Abstract:

This investigation was conducted to determine operating variables in the catalytic hydrodesulfurization of number one and number three fuel oils obtained from a high-sulfur-containing Oregon Basin, Wyoming crude. Desulfurization was carried out in pilot plant equipment capable of holding 100 ml of catalyst and operable at pressures up to 500 psig. The catalysts investigated were cyclocel (activated bauxite) and molybdenum oxide and sulfide. The variables temperature, pressure, and space velocity were studied using hydrogen or hydrogen-methane gas mixtures. Desulfurization was considered satisfactory when the sulfur content of number three oil was reduced from 2.2 percent to below 0.5 percent and of the number one oil from 1.1 percent to below 0.5 percent.

When number three fuel oil was desulfurized over cyclocel the percent sulfur of the product oil increased from an initial 1.1 to 1.9 after 100 hours. Cyclocel was air regenerated after desulfurization of number three fuel oil and the catalyst regained its original activity. Number one fuel oil was desulfurized to below 0.5 percent sulfur content for a total time of 178 hours and there was no noticeable deactivation of the catalyst.

The effect of pressure during desulfurization of number three fuel oil using molybdenum sulfide catalyst indicated that increased pressure affected increased sulfur removal from the oil. Number three fuel oil with less than 0.5 percent sulfur content was produced at 500 psig and 300 psig, but could not be produced at 200 psig or below.

Hydrogen-methane gas mixtures were used during desulfurization of number three fuel oil over molybdenum sulfide. When the percent methane in the mixture was increased the sulfur removal from the oil decreased. Oil with less than 0.5 percent sulfur content was produced using hydrogen-methane mixtures which contained five percent, 15 percent, and 25 percent methane respectively, but could not be produced at space velocities above 0.45 using a mixture containing 40 percent methane. No appreciable carbon deposition on the catalyst was found during this study.

The effect of carbon burn-off from molybdenum sulfide was studied after desulfurization with a heavy gas oil. The gas oil was used in a deliberate attempt to make carbon lay-down on the catalyst. After burning the carbon off with air the activity of the catalyst doubled (as measured by grams of sulfur removed per gram of catalyst).

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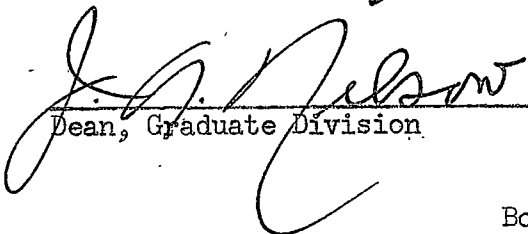
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Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

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ABSTRACT

This investigation was conducted to determine operating variables in the catalytic hydrodesulfurization of number one and number three fuel oils obtained from a high-sulfur-containing Oregon Basin, Wyoming crude. Desulfurization was carried out in pilot plant equipment capable of holding 100 ml of catalyst and operable at pressures up to 500 psig. The catalysts investigated were cyclocel (activated bauxite) and molybdenum oxide and sulfide. The variables temperature, pressure, and space velocity were studied using hydrogen or hydrogen-methane gas mixtures. Desulfurization was considered satisfactory when the sulfur content of number three oil was reduced from 2.2 percent to below 0.5 percent and of the number one oil from 1.1 percent to below 0.5 percent.

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The effect of pressure during desulfurization of number three fuel oil using molybdenum sulfide catalyst indicated that increased pressure affected increased sulfur removal from the oil. Number three fuel oil with less than 0.5 percent sulfur content was produced at 500 psig and 300 psig, but could not be produced at 200 psig or below.

Hydrogen-methane gas mixtures were used during desulfurization of number three fuel oil over molybdenum sulfide. When the percent methane in the mixture was increased the sulfur removal from the oil decreased. Oil with less than 0.5 percent sulfur content was produced using hydrogen-methane mixtures which contained five percent, 15 percent, and 25 percent methane respectively, but could not be produced at space velocities above 0.45 using a mixture containing 40 percent methane. No appreciable carbon deposition on the catalyst was found during this study.

The effect of carbon burn-off from molybdenum sulfide was studied after desulfurization with a heavy gas oil. The gas oil was used in a deliberate attempt to make carbon lay-down on the catalyst. After burning the carbon off with air the activity of the catalyst doubled (as measured by grams of sulfur removed per gram of catalyst).

I INTRODUCTION

With the depletion of high quality low sulfur crudes, petroleum refiners have been forced to turn to crudes with higher sulfur content. A large variety of sulfur compounds have been found in petroleum. Elemental sulfur, hydrogen sulfide, mercaptans, thioethers, disulfides, and thiophenes, have been found in the various fractions.

It was the purpose of this research to determine the conditions for the catalytic desulfurization of number one and number three fuel oils. The maximum allowable sulfur specification for fuel oil was to be 0.5 per cent.

Sulfur compounds in kerosene and fuel oil may give rise to objectionable odor, corrosive action on metals, poor stability, and are responsible for acrid fumes on burning (3). A considerable number of methods are in existence for the removal of sulfur from light distillates. A few of these methods which are in commercial use are the Unisol process, the Solutizer and Tannin Solutizer processes, hypochlorite treatment, Gray desulfurization, and treatment with bauxite catalysts. In addition to these processes, hydrogen sulfide can be removed by caustic scrubbing, and certain other sulfur compounds are removed during sulfuric acid treatment. Generally speaking, sulfur compounds are distributed in larger percentages in the higher boiling petroleum fractions. When the above methods are used to desulfurize high boiling petroleum fractions the sulfur compounds are either not removed to the desired percentage or the losses are excessive. One method used to remove a large portion of the sulfur compounds in higher boiling fractions, without excessive charge losses, is catalytic decomposi-

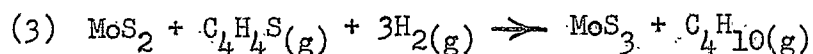
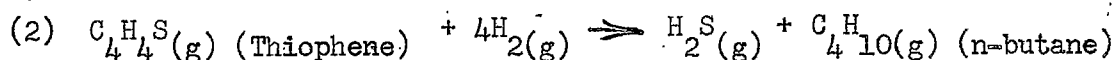
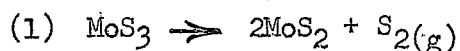
tion in the presence of hydrogen. The mechanism of desulfurization in the presence of hydrogen is one of destructive dehydrogenation, whereby the sulfur compound is converted to a hydrocarbon and hydrogen sulfide. Three catalysts which have been used for hydrodesulfurization of petroleum are cobalt molybdate (2), molybdenum oxide (6), and molybdenum sulfide (6).

Any desulfurization process used commercially must be economical. In an attempt to find an economical process, Koski (4), and Munro (6), made an initial study on the following catalysts: Bauxite, molybdenum sulfide, molybdenum oxide, tungstic oxide, nickel oxide, cobalt molybdate, and chromic oxide. In addition an extensive study on the life of molybdenum sulfide catalyst was made (6). This life study was discontinued after 2010 hours of successful desulfurization of number three fuel oil. Because of its long life the following conditions using molybdenum sulfide were studied and the results are reported in this thesis: (1) Effect of pressure; (2) effect of using mixtures of hydrogen and methane; (3) effect of the desulfurization of a heavy gas oil; (4) effect of air regeneration. In addition hydrodesulfurization using cyclocel catalyst was studied.

II THERMODYNAMIC CALCULATIONS

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

Four reaction mechanisms were postulated for desulfurization of fuel oil by molybdenum sulfide catalyst. All or some of these reactions may occur in the overall desulfurization.



The first reaction was considered because sulfur was produced when the catalyst was heated. The calculations from reaction number two provide information about the ease of destructive hydrogenation of sulfur compounds. Thiophene boils at 84°C and is not present in number three fuel oil, but higher alkyl thiophenes with higher boiling points are present. Thiophene was considered in the absence of thermodynamic data on higher alkyl thiophenes. Results calculated from thiophene should, in most cases, approximate the results that would be obtained from higher alkyl thiophenes.

In the third reaction the sulfur compounds in the oil convert MoS_2 to MoS_3 . In the fourth reaction MoS_3 is reacted with hydrogen and reduced to MoS_2 and $\text{H}_2\text{S}(\text{g})$. The catalyst, according to the mechanism, acts as a carrier of sulfur from the oil to the H_2S that is expelled.

All of these reactions are thermodynamically possible at the operating conditions of 410°C and 34 atmospheres. The following free energies will, to some degree, show the feasibility of these reactions.

Reaction	F at 25°C Cal/mol	F at 375°C Cal/mol
1	+25,700	+9,575
2	-41,300	-14,560
3	-36,640	-21,330
4	-4,660	-9,341

The results of the calculations are tabulated in Tables I-V. The calculations help to confirm the postulated mechanism for desulfurization. The calculations are not, however, of much value when used to fix the proper conditions under which the overall reaction should be run. This is because the equilibrium constants are all very high in the practical operating range.

Practical desulfurization of fuel oil must be carried out at temperatures below incipient carbon to carbon cracking if the product oil is to have the same boiling point range as the charge oil. The energy between a carbon to carbon bond (58.6 KCal/mol) is only slightly higher than that for a carbon to sulfur bond (54.5 KCal/mol). From this analysis it is evident that any thermal cracking of the carbon to sulfur bond would be accompanied by considerable carbon to carbon cracking. This is substantiated by data (8) on the thermal cracking of sulfur stocks which showed that 75 per cent of the sulfur remained in the residue. The temperature for catalytic desulfurization of fuel oil must therefore be below thermal cracking temperatures and the catalyst must be selective in its action.

III. EQUIPMENT, METHODS, AND MATERIALS

A. EQUIPMENT

A schematic diagram of the reactor is shown in Figure 1. The reactor consisted of a 16 inch length of one-and-one-half inch O. D. extra strong black pipe reduced with reducing couplings to three-fourth inch at the top and one-half inch at the bottom. The top of the reactor was fitted with a union, two crosses, and an assembly of valves for hydrogen inlet, oil inlet, oil feed bleed line, and air for regeneration. A thermowell tube extended from the cross at the top down the vertical axis of the reactor to within one inch of the bottom. The thermowell tube was made from $\frac{1}{4}$ inch black pipe. The tube was capped at the bottom, and three thermocouples were inserted from the top. The hot junctions of the thermocouples were adjustable to any desired position in the reactor.

The bottom of the reactor was fitted with a one-half inch union and a tee. There was a pressure gage and a valve fitted from the tee. During part of the investigation a Grove spring loaded back pressure valve was used. A Mason-Neilan air-to-close valve, controlled by a Fisher Wizard Controller, was used during the remainder of the investigation.

The heating elements consisted of three 33 foot lengths of beaded Nichrome wire which were supplied with current from 110 volt auto transformers. The coils were wound on the reactor over a layer of asbestos tape. Another layer of asbestos tape was wound over the wire and an inch layer of magnesia mud was placed over the final layer of asbestos tape.

One-eighth inch alundum balls were used as the pre-heat medium. The pre-heat section extended for 10 inches from the top of the reactor. The

catalyst bed was located below the pre-heat section and below the catalyst bed a layer of alundum balls extended to the bottom of the reactor.

Auxiliary equipment consisted of a high pressure piston type pump, Precision Scientific wet test meters, water cooled copper tube condensers, hydrogen cylinders with pressure regulators, receiver flasks, and alkali scrubbers. Iron-constantan thermocouples were used in conjunction with a Leeds and Northrup indicating potentiometer for temperature measurement.

Analysis of the exit gas was made in a low temperature fractionation column.

B. METHODS

Control and measurement of process variables were conducted as summarized in the following paragraphs.

1. Sampling and Space Velocity: Samples were taken at eight-hour intervals. Space velocity calculations were made over the eight hour sampling periods and were based on the weight of charge oil and the weight of catalyst. Space velocity was controlled by pump adjustments.

2. Temperature: Temperatures were measured with iron constantan thermocouples in conjunction with a Leeds and Northrup indicating potentiometer. Thermocouples were placed near both ends of the catalyst section, and one was placed mid-way in the pre-heat section. The temperature in the pre-heat section was maintained at approximately 90°C below the temperature in the catalyst section. Temperatures were controlled by adjustment of the power input to the heating elements with auto-transformers. An average of the two temperatures in the catalyst section was recorded at 15-minute intervals and these readings were averaged over a period of eight hours.

3. Hydrogen Rate: Hydrogen rate was maintained by control of the pressure differential across the reactor. The actual hydrogen input was not measured but a relative hydrogen rate was measured by metering the volume of exit gases. As seen by gas analysis data the build up of non-condensable hydrocarbons in the exit gas was not more than 3.5 per cent per cycle. Before the exit gases were measured, hydrogen sulfide was removed by a caustic wash. Exit gas meter readings were recorded every 15 minutes, and the total exit gas over an eight-hour period was used to calculate the hydrogen-to-oil ratio.

4. Pressure: The pressure was controlled by proper adjustment of the back pressure valve on the reactor.

5. Air Regeneration: The catalyst was heated to 450°C and air was passed over it. Once the regeneration had begun the temperature was maintained below 550°C by proper adjustment of the air rate.

6. Sulfur Analysis: Sulfur content of the oil was determined by the lamp method (1). This method involves the combustion of a weighed sample of oil and the absorption of the sulfur dioxide produced in a known amount of alkali. The excess alkali is determined by titration with a suitable acid and indicator. The gas oil used in the regeneration study run was too viscous to be analyzed directly by the lamp method so a modification of this method was used. The gas oil was diluted with an approximately equal weight of number one fuel oil which had a known sulfur content. The diluted gas oil was then analyzed by the conventional method. The per cent sulfur in the gas oil was calculated from the analysis of the mixture.

C. MATERIALS

The following catalysts were used in this study:

1. Bauxite (Cyclocel).

10/30 mesh. Code number SB-2446-51. Produced by the Porocel Corporation.

2. Molybdenum Sulfide.

This catalyst consists of 15 per cent MoS_3 impregnated on alumina and pelleted into one-eighth inch pellets. Code number Mo-x-1321-42. Produced by the Harshaw Chemical Company.

Three commercial grades of oil were used. A.S.T.M. distillation data for these oils are presented in Table VI.

1. Number three fuel oil.

- a. Boiling point range, 460-660°F.
- b. Specific gravity, 0.875.
- c. Sulfur content, 2.19 per cent.

2. Number one fuel oil.

- a. Boiling point range, 204-495°F.
- b. Specific gravity, 0.832.
- c. Sulfur content, 1.09 per cent.

3. Gas oil.

- a. Boiling point range, 580-750°F.
- b. Specific gravity, 0.925.
- c. Sulfur content, 2.85 per cent.

IV SAMPLE CALCULATIONS

Data for the following calculations were taken from the mixture study run Table XIII. Number three fuel oil which contained 2.19 per cent sulfur and one-hundred grams of catalyst were used.

Sample No.	Total Sample Time Hr.	Sample Weight Grams	% Sulfur	Liters Exit Gas	Ave. Temp. °C
22	8	533	0.340	1022	410

A. Calculation of Space Velocity:

Assume weight loss of charge oil is seven per cent. Per cent loss was calculated from data obtained over periods of two to four days. Calculation is based on weight of charge oil.

$$\frac{533}{(1.0 - .07) \times 8 \times 100} = 0.716$$

= grams oil (per gram of catalyst) per hour.

B. Calculation of Exit Gas to Oil Ratio:

It was assumed that all exit gases metered were saturated with water vapor.

Data:

Room temperature	= 24°C
Barometric pressure	= 641 mm Hg
Vapor pressure of water at 24°C	= 22.4 mm Hg
Partial pressure of exit gas	= 641.4 - 22.4
	= 619 mm Hg

$$\frac{619}{760} \times \frac{273}{273 + 24} \times \frac{1022 \times (1.0 - .07)}{533} = 1.34$$

1.34 = Liters exit gas
at S. T. P. per
gram charge oil

C. Calculation of Grams of Sulfur Removed Per Gram of Catalyst Per

Eight Hours:

$$\frac{533 \times 0.0219 - 533 \times .0034}{(1.0 - 0.07)} \times \frac{100}{100} = .1074$$

This value was calculated on the assumption that all of the oil reported as per cent loss was free from sulfur. The per cent error in this figure has a maximum value of 4.13.

D. Calculation of Per Cent Losses:

Data:

Kgm influent oil	= 20.916
Kgm effluent oil	= 19.3635
Specific gravity of number three oil at 70°F	= 0.875
Specific gravity of product oil at 70°F	= 0.850
$\frac{20.916 - 19.3635}{20.916} \times 100$	= 7.43 per cent
	= loss on weight basis
$\frac{20.916 - \frac{19.3635}{0.850}}{0.875} \times 100$	= 4.6 per cent
$\frac{20.916}{0.875}$	= loss on volume basis

V. DISCUSSION OF RESULTS

A. DESULFURIZATION OF FUEL OILS USING CYCLOGEL AS A CATALYST

This study was made to obtain information on catalyst life, and the effect of hydrogen rate on desulfurization with cyclocel catalyst. Both number one and number three fuel oils were used.

Tabulated data for this run are presented in Table VII.

The effect of desulfurization on catalyst life is shown in Figure 2. Number three fuel oil was first passed over the catalyst for 160 hours. During this time the reaction conditions were kept constant, and the sulfur content of the effluent oil increased from 1.22 per cent at eight hours to 1.945 per cent at 160 hours. The catalyst was then regenerated with air, and number three fuel oil was again passed over the catalyst. After air regeneration the sulfur content of the effluent oil increased from 1.29 per cent at eight hours to 1.80 per cent at 120 hours.

As seen in Figure 2 the rate of decrease in activity was about the same before and after the first air regeneration. The near coincidence of the two curves (Figure 2) which show catalyst activity as a function of time, indicates that the first air regeneration did not alter the level of sulfur removal.

After desulfurization of number three fuel oil the catalyst was regenerated with air a second time. Number one fuel oil was then desulfurized over the catalyst. As seen in Figure 2 number one fuel oil was desulfurized for 168 hours with no noticeable deactivation of the catalyst. Charge losses were 2.38 weight per cent for number three fuel oil and 1.23 weight per cent for number one fuel oil. The charge losses indicate that

more cracking occurred during number three fuel oil desulfurization which undoubtedly caused more carbon deposition on the catalyst. For this reason number three fuel oil probably caused deactivation of the catalyst, while number one fuel oil did not. Number three fuel oil is more susceptible to cracking since it is heavier than number one fuel oil. Temperature, space velocity, and pressure were kept constant for desulfurization of both number one and number three fuel oils.

Figure 3 shows the effect of hydrogen rate on desulfurization of number one fuel oil. The hydrogen rate, down to a certain critical point, has very little effect on sulfur removal. The point where hydrogen rate begins to effect sulfur removal was not determined experimentally, but was found by extrapolation of the curve in Figure 3. The level of sulfur removal dropped abruptly when the use of hydrogen was discontinued. The catalyst, however, did effect some sulfur removal when hydrogen was not used. Temperature and space velocity were not studied as process variables.

B. THE EFFECT OF PRESSURE ON THE DESULFURIZATION OF FUEL OIL USING MOLYBDENUM SULFIDE CATALYST

The effect of pressure on the desulfurization of number three fuel oil was studied at 500, 300, 200, 100, and zero psig using a MoS_2 catalyst. Tables VIII and IX and Figure 4 show the effect of pressure on sulfur removal. Each pressure was investigated for an on-stream-time of 64 to 96 hours. The investigation at each pressure was discontinued when the percent sulfur in the effluent oil remained constant for 20 to 50 hours.

The decrease in the activity of the catalyst as a function of time was neglected during this study.

Figure 4 and Table IX show the decrease in sulfur removal when pressure was decreased. Oil with less than 0.5 per cent sulfur content was produced at 500 psig with a space velocity of 0.85 and at 300 psig with a space velocity of 0.70. At 200 psig, and below, oil with less than 0.5 per cent sulfur content could not be produced at space velocities above 0.5.

This study clearly shows that increased reaction pressures, at the temperatures used, give greater sulfur removal.

C. THE EFFECT OF METHANE-HYDROGEN MIXTURES ON FUEL OIL DESULFURIZATION USING MOLYBDENUM SULFIDE CATALYST

When fuel oil is desulfurized, using molybdenum sulfide catalyst, methane and ethane are formed. Data have shown that the build-up of methane and ethane in the exit gases is less than three per cent per pass. Because hydrogen is relatively expensive and the separation of light hydrocarbons from hydrogen is difficult, it is desirable that the exit gases be recycled. The purpose of this study was to determine the build-up of hydrocarbons per cycle and how much methane can be tolerated in the recycle gas.

The following gas mixtures were obtained from the Matheson Chemical Company.

Approximate Analysis:

- a. 5% CH₄, 95% H₂
- b. 15% CH₄, 85% H₂
- c. 25% CH₄, 85% H₂
- d. 40% CH₄, 60% H₂

A test was made on each of the mixtures at 500 psig. A run was then made on the five per cent and 15 per cent mixtures at 300 psig, and on the 25 per cent, and 40 per cent mixtures at 200 psig. The tests under 500 psig were run 16 to 24 hours and are inconclusive because it sometimes takes 30 to 50 hours for the catalyst to come to conditions of constant sulfur removal. Number three fuel oil was used exclusively in this study.

A plot of sulfur removal versus per cent methane in the mixtures is shown in Figure 5. Complete tabulated data, analysis of exit gas and a summary of the effect of gas mixtures on desulfurization are presented in Tables X-XIII.

Figure 5 shows a decrease in sulfur removal as the percent methane in the gas mixtures was increased. The decrease of sulfur removal was small when five per cent and 15 per cent methane mixtures were used, but the decrease became proportionally larger when mixtures containing 25 per cent and 40 per cent methane were used.

An increase in the percentage of methane in the mixture effectively lowers the partial pressure of hydrogen in the reaction. As seen previously in the pressure study run, a decrease of pressure gave a decrease in sulfur removal. Both the pressure study run and the mixture study run substantiated the importance of the partial pressure of hydrogen in the desulfurization reaction.

By adjustment of the space velocity, oil with less than 0.5 per cent sulfur content was produced at 500 psig using gas mixtures which contained five per cent, 15 per cent, and 25 per cent methane. When a mixture containing 40 per cent methane was used, oil with less than 0.5 per cent

sulfur content could not be produced at space velocities above 0.5. Space velocities below 0.5 were not investigated.

The analysis of the exit gas is tabulated in Table XI. When 100 per cent hydrogen was charged the build up of methane and ethane was generally over three per cent per pass. When gas mixtures containing methane were used the build up of methane and ethane ranged from 0.1 per cent to 2.5 per cent, with an average of about one per cent.

All exit gas samples were collected over a period of approximately one hour and were taken when the gas flow was constant.

D. THE EFFECTS OF GAS OIL DESULFURIZATION AND AIR REGENERATION ON MOLYBDENUM SULFIDE CATALYST

In the work done on molybdenum sulfide catalyst, regeneration of the catalyst was never needed. Since there is always a possibility of deactivation of the catalyst, information concerning air regeneration was desired. A heavy gas oil with a specific gravity of 0.925 and a sulfur content of 2.85 per cent was passed over the catalyst to see if some deactivation due to carbon lay-down might occur. After treatment with gas oil, number three fuel oil was passed over the catalyst to evaluate activity on the basis of previous data obtained with number three fuel oil. The conditions used for gas oil and number three fuel oil desulfurization were the same. Data from this study are tabulated in Table XIII.

The sequence of operations followed during this study is as follows:

1. Gas oil was charged for 160 hours.
2. Number three fuel oil was charged for 71 hours.
3. Gas oil was charged for 96 hours.

4. Number three fuel oil was charged for 64 hours.
5. Catalyst was air-regenerated.
6. Number three fuel oil was charged for 88 hours.

Gas oil was first passed over the catalyst for 160 hours and no deactivation occurred as evidenced by the sulfur content of the effluent gas oil. Number three fuel oil was then passed over the catalyst and the percent sulfur in the effluent oil gave proof that the catalyst had not been deactivated. Gas oil was again passed over the catalyst and after a period of 96 hours there was no change in the sulfur content of the effluent gas oil.

After the second treatment with gas oil, number three fuel oil was again passed over the catalyst. This time the desulfurization with number three fuel oil indicated that the catalyst had the lowest level of sulfur removal (as measured by grams sulfur removed per gram of catalyst) of any molybdenum sulfide catalyst tested.

The catalyst was then air-regenerated at temperatures varying between 440 and 550°C. During the regeneration the odor of sulfur dioxide was noted in the exit gases.

After air regeneration number three fuel oil with a sulfur content of 0.02 per cent was produced when a space velocity of about 0.4 was used. The space velocity was gradually increased to about one and the per cent sulfur in the oil increased to about 0.15. This increase in activity is shown graphically in Figure 6. The activity of the catalyst, as measured by grams of sulfur removed per gram of catalyst, doubled after air regeneration.

Previous to air-regeneration the best results had been obtained at a space velocity of 0.9 which resulted in an effluent oil with a sulfur content of 0.45 per cent. After air regeneration number three fuel oil was desulfurized for an on-stream time of 88 hours with no apparent deactivation of the catalyst. As seen in Figure 6 the rate of increased sulfur removal had just begun to level off when the run was ended.

The charge losses, on a weight basis, were 6.23 per cent for the gas oil and 5.68 per cent for number three fuel oil. This indicates that more cracking occurred during gas oil desulfurization.

VI SUMMARY

The results indicate that cyclocel catalyst can be air-regenerated without apparent effect on catalyst activity. Number one fuel oil was desulfurized using cyclocel for an on stream time of 175 hours, and during this time the catalyst did not decrease in activity.

Sulfur removal with molybdenum sulfide catalyst decreased with decreased reactor pressure. Number three fuel oil with a sulfur content of less than 0.5 per cent was produced at 500 psig, and 300 psig, but could not be produced at 200 psig or below, with liquid hourly space velocities above 0.5.

When gas mixtures were used which contained hydrogen and methane the sulfur removal, using molybdenum sulfide catalyst, decreased with increases in the concentration of methane. Number three fuel oil with a sulfur content of less than 0.5 per cent was produced with hydrogen-methane mixtures which contained five per cent, 15 per cent, and 25 per cent methane. With a mixture containing 40 per cent methane, oil with less than 0.5 per cent sulfur content could not be produced. Using molybdenum sulfide the maximum build-up of methane and ethane in the exit gas was 3.5 per cent per pass.

Air regeneration of molybdenum sulfide was very successful. The catalyst activity, as measured by grams of sulfur removed per gram of catalyst, doubled after air regeneration.

VII ACKNOWLEDGEMENT

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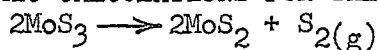
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IX APPENDIX

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Table I	Thermodynamic Calculations for the Reaction: $2\text{MoS}_3 \rightarrow 2\text{MoS}_2 + \text{S}_2(\text{g})$ 26
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TABLE I

THERMODYNAMIC CALCULATIONS FOR THE REACTION:



$$\Delta H_{298} = 41.44 \text{ KCal/Mol}; \Delta S_{298} = 52.81 \text{ Cal/Mol}$$

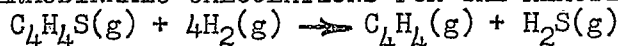
$$\Delta H_T = 45,580 - 13.24T - 2.13 \times 10^{-3}T^2 = \text{Cal/Mol}$$

$$\Delta F_T = 45,580 + 13.24T \ln T + 2.13 \times 10^{-3}T^2 - 143.0T = \text{Cal/Mol}$$

Temp. °C	Pressure Atm.	Free Energy F Cal/Mol	Equilibrium Constant K _{eq}	Percent Conversion
25	1	25,700	1.3×10^{-19}	0
100		22,075	1.25×10^{-13}	0
250		14,962	5.61×10^{-7}	0.95
375		9,575	5.88×10^{-4}	12.0
500		4,352	.0592	35.
1000		-12,970	165	95.5
25	50			0
100				0
250				0.7
375				5.0
500				30.0
1000				75.0

TABLE II

THERMODYNAMIC CALCULATIONS FOR THE REACTION:



$$\Delta H_{298} = -62.40 \text{ KCal/Mol}; \Delta S_{298} = -70.78 \text{ Cal/Mol}$$

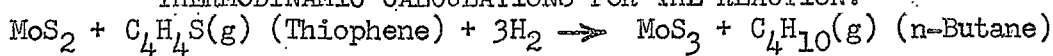
$$\Delta H_T = -58,914 - 9.21T - 12.24 \times 10^{-3}T^2 = 13.07 \times 10^{-6}T^3 = \text{Cal/Mol}$$

$$\Delta F_T = -58,914 + 3.5T + 12.25 \times 10^{-3}T^2 - 6.53 \times 10^{-6}T^3 + 9.21T \ln T = \text{Cal/Mol}$$

Temp. °C	Pressure Atm	Free Energy F Cal/Mol	Equilibrium Constant K _{eq}	Percent Conversion
25	1	-41300	2.59×10^{30}	100
100		-35900	1.0×10^{21}	100
250		-24500	1.78×10^{10}	99.6
375		-14560	8.035×10^4	94.75
500		-4590	20	70.0
1000		+37600	4.13×10^{-7}	0.5
25	10			100
100				100
250				99.9
375				98.5
500				92.7
1000				2.0
25	50			100
100				100
250				100
375				99.5
500				97.2
1000				19.0
25	100			100
100				100
250				100
375				99.6
500				97.5
1000				27.0

TABLE III

THERMODYNAMIC CALCULATIONS FOR THE REACTION:



$$\Delta H_{298} = -62,840 \text{ Cal/Mol}; \Delta S_{298} = -87.92$$

$$\Delta H_T = -61,730 - 1.057T - .0125T^2 + 1.322 \times 10^{-5}T^3$$

$$\Delta F_T = -61,730 + 1.057T \ln T + .0125T^2 - .661 \times 10^{-5}T^3 + 75T$$

Temp. oC	Pressure Atm.	Free Energy F Cal/Mol	Equilibrium Constant K _{eq}	Percent Conversion
25	1	-36,640	5.02×10^{26}	100
100		-33,140	2.10×10^{19}	100
250		-25,000	2.5×10^{10}	99.6
375		-21,330	1.35×10^7	97.2
500		12,240	$.323 \times 10^{-3}$	0.7
1000		49,970	$.317 \times 10^{-8}$	0
25	10			100
100				100
250				99.9
375				99.3
500				18.0
1000				.09
25	50			100
100				100
250				100
375				99.9
500				72.0
1000				2.6
25	100			100
100				100
250				100
375				99.7
500				71.0
1000				2.55

TABLE IV
THERMODYNAMIC CALCULATIONS FOR THE REACTION:
 $\text{MoS}_3 + \text{H}_2(\text{g}) \rightarrow \text{MoS}_2 + \text{H}_2\text{S}(\text{g})$

$$\Delta H_{298} = 440 \text{ Cal/Mol}; \quad \Delta S_{298} = 17.14 \text{ Cal/Mol}$$

$$\Delta H_T = 2,800 - 8.147T + .00076T^2 - .01602 \times 10^{-5}T^2$$

$$\Delta F_T = 2,800 - 8.147T \ln T - .00076T^2 - .801 \times 10^{-7}T^3 - 71T$$

Temp. °C	Pressure Atm.	Free Energy F Cal/Mol	Equilibrium Constant K _{eq}	Percent Conversion
25	1	-4660	2580	98.1
100		-5800	2450	98.0
250		-8,019	2200	97.8
375		-9,341	1400	96.9
500		-10,816	1080	96.7
1000		-14,448	290	94.4
25	10			98.2
100				98.1
250				97.9
375				97.0
500				96.7
1000				94.4
25	50			98.3
100				98.2
250				98.0
375				97.2
500				96.7
1000				94.5
25	100			98.5
100				98.3
250				98.1
375				97.5
500				96.7
1000				94.6

TABLE V
GENERAL THERMODYNAMIC DATA***

Compound	Critical Pressure Atm	Critical Temp °K	Heat of Formation H _f KCal/Mol 298°K	Entropy Cal/Mol 298°K	Heat Capacity C _p Cal/Mol/°K
H ₂ (g)	12.8	33.2	0	31.21	$6.947 + .200 \times 10^{-3}T + .04808 \times 10^{-5}T^2$
C ₄ H ₄ S(g) (Thiophene)	48	690	27.82	69.3	$-7.017 + 100 \times 10^{-3}T - 63.25 \times 10^{-6}T^2$
H ₂ S(g)	88.9	373.4	-4.77	49.15	$7.20 + 3.6 \times 10^{-3}T$
C ₄ H ₁₀ (g) (n-Butane)	36	426.1	-29.81	74.21	$-7.017 + 100 \times 10^{-3}T - 63.25 \times 10^{-6}T^2$
S ₂ (g)	234**	1313	11.48	54.41	$3.58 + 0.3 \times 10^{-3}T$
MoS ₂	--	--	-56.27	15.1	$19.7 + 3.15 \times 10^{-3}T$
MoS ₃	--	--	-29.81	15.9	$*28.1 + 5.43 \times 10^{-3}T$

*Calculated by analogy with available heat capacities of SnS and SnS₂. An assumption was made that the difference in heat capacities between SnS and SnS₂ would be the same as the difference between MoS₂ and MoS₃.

**Calculated by Meissner and Redding's method of parachors.

***Data obtained from following sources: U.S. Bureau of Mines Bulletin No. 406 (9), Perry (7), Lange (5), Hodgman (3)

TABLE VI
A. S. T. M. DISTILLATION DATA

Percent Over	Husky #3 Fuel Oil	Husky #1 Fuel Oil	Husky Gas Oil
First Drop	460°F	204°F	580°F
5%	500	264	629
10	518	294	637
20	534	315	667
30	546	332	680
40	556	347	692
50	566	362	702
60	576	377	709
70	586	396	718
80	600	420	727
90	621	452	741
Final Temp.	660	495	750
% Recovery	98	98.7	92.0
% Sulfur	2.19	1.09	2.85

TABLE VII
TABULATED DATA FOR CYCLOCEL STUDY RUN (CSR)

Cyclocel catalyst used at atmospheric pressure.
Husky #3 oil used from samples #1-#35.
Husky #1 oil used from samples #36-#62
Air regenerations after samples #20 and #35
Maximum charge losses were 2.38% on weight basis.

Sample No.	Total Hours	Sample Weight Grams	Percent Sulfur	Average Temp. °C	Space Velocity Grams Oil Per Gram Catalyst Per Hour	Liters Exit Gas Per Gram Oil	Grams Sulfur Removed Per Gram Of Catalyst Per Eight Hours
1	8	997.0	1.22	396	1.31	0.797	0.108
2	16	911.0	1.39	400	1.20	0.813	0.083
3	24	834.5	1.555	398	1.10	0.947	0.0635
4	32	817.0	1.54	403	1.075	0.895	0.0628
5	40	765.0	1.62	400	1.005	0.947	0.525
6	48	743.5	1.646	400	0.997	1.040	0.0492
7	56	811.0	1.66	402	1.07	1.00	0.0523
8	64	712.0	1.65	400	0.937	1.26	0.0467
9	72	770.0	1.705	401	1.010	0.970	0.0461
10	80	748.0	1.735	400	0.985	0.978	0.0429
11	88	754.5	1.76	400	0.992	0.925	0.0412
12	96	748.0	1.80	400	0.984	1.115	0.0380
13	104	756.0	1.832	401	0.994	0.980	0.0358
14	112	779.0	1.87	400	1.023	1.150	0.0342
15	120	788.5	1.878	400	1.007	1.035	0.0282
16	128	796.5	1.897	400	1.017	0.994	0.0270
17	136	801.5	1.955	400	1.024	1.010	0.023
18	144	822.0	1.724	400	1.05	1.052	0.0420
19	152	820.5	1.905	400	1.049	0.990	0.0275
20	160	825.0	1.945	400	1.051	1.095	0.0237
21	168	743.0	1.19	403	0.951	1.08	0.078
22	176	803.5	1.286	401	1.025	0.967	0.0766
23	184	790.5	1.374	400	1.010	0.972	0.0681
24	192	767.0	1.408	400	0.980	1.040	0.0635
25	200	811.0	1.421	400	1.037	0.945	0.0668
26	206	585.5	1.394	400	0.975	1.065	0.0665
27	214	784.5	1.580	400	1.002	1.09	0.0518
28	222	800.0	1.600	400	1.020	1.06	0.0510
29	230	787.5	1.628	400	1.007	0.99	0.0478
30	238	748.0	1.643	400	0.955	1.115	0.0445
31	246	804.0	1.680	400	1.028	0.975	0.0450
32	254	801.0	1.712	400	1.028	1.075	0.0426
33	262	805.0	1.73	400	1.030	0.974	0.0409

TABLE VII (continued)
TABULATED DATA FOR CYCLOCEL STUDY RUN (CSR)

Sample No.	Total Hours	Sample Weight Grams	Percent Sulfur	Average Temp. °C	Space Velocity Grams Oil Per Gram Catalyst Per Hour	Liters Exit Gas Per Gram Oil	Grams Sulfur Removed Per Gram of Catalyst Per Eight Hours
34	270	815.0	1.772	400	1.042	0.975	0.0380
35	278	822.0	1.80	401	1.053	1.141	0.0360
36	286	749.5	0.348	401	.954	1.07	0.0551
37	294	759.0	0.327	401	.965	1.06	0.0574
38	302	776.5	0.346	400	.988	.990	0.0573
39	310	773.0	0.415	402	.985	.963	0.0517
40	318	756.0	0.375	399	.964	1.01	0.0537
41	326	779.5	0.357	400	.995	.88	0.0567
42	334	748.0	0.350	401	.955	.995	0.0548
43	342	790.5	0.367	400	1.01	.651	0.0566
44	350	797.0	0.350	399	1.015	.611	0.0585
45	358	787.5	0.381	400	1.005	.672	0.0554
46	366	767.0	0.377	400	0.990	.665	0.0553
47	374	798.0	0.374	400	1.017	.564	0.0567
48	382	783.5	0.363	406	1.000	.662	0.0566
49	390	780.5	0.379	400	0.995	.690	0.0551
50	398	764.5	0.387	401	0.975	.620	0.0533
51	406	830.5	--	400	1.06	.317	--
52	414	821.0	.403	400	1.046	.279	0.0560
53	422	850.5	--	400	1.083	.276	--
54	430	811.5	.410	399	1.035	.393	0.0549
55	438	837.0	--	400	1.065	.355	--
56	446	833.0	.409	401	1.060	.363	0.0562
57	454	950.5	.405	396	1.210	'	0.645
58	462	810.5	.582	385	1.030	'	0.0406
59	470	769.5	.550	400	0.980	No	0.0411
60	478	581.5	.558	400	0.742	H ₂	0.0305
61	486	652.5	.510	401	0.831	Used	0.0374
62	494	754.5	.532	401	0.963	'	0.0418

