



The catalytic hydrodesulfurization of fuel oils
by Howard C Hooper

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Montana State University
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Abstract:

Desulfurization studies utilizing a No. 3 fuel oil and a vacuum heavy gas oil (from Husky Oil Company, Cody, -Wyoming) containing 2.176 percent sulfur and 3.18 percent sulfur respectively were carried out on Harshaw's (Harshaw Chemical Company) molybdenum oxide and cobalt molybdate catalysts, -A critical hydrogen content (minimum amount of hydrogen present in a recycle gas necessary to produce an oil containing less than 0.5 percent sulfur) for cobalt molybdate after 1568 hours of operation on No, 3 fuel oil was less than 40 volume percent hydrogen.

Cobalt molybdate and molybdenum oxide catalysts were compared as to activity and life, In every case the cobalt molybdate catalyst proved superior to the molybdenum oxide catalyst, -Preliminary desulfurization studies were made on a crude tower overhead containing 0,874 percent sulfur from Continental Oil Company at Billings, Montana, The oil was desulfurized to less than 0,163 percent sulfur during 128 hours of operations, The catalyst used was Harshaw's Cobalt molybdate. The recycle gas for desulfurization contained less than 35 volume percent hydrogen.

Two oils containing 0.600 percent sulfur and 1,28 percent sulfur from Farmers Union Central Exchange at Laurel, Montana, were desulfurized with Union Oil Company's cobalt molybdate 3/16" catalyst to less than 0,109 and 0.534 percent sulfur respectively. The recycle gas contained less than 18 volume percent hydrogen, -Data was collected on the effect of regeneration of an activated bauxite (Cyclocel) catalyst after desulfurizing an oil blend containing' approximately 0,8 percent sulfur. Regeneration decreased catalyst life, but seemed to increase the initial catalyst activity.

All research was carried out in bench scale equipment.

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FOX RIVER

ABSTRACT

Desulfurization studies utilizing a No. 3 fuel oil and a vacuum heavy gas oil (from Husky Oil Company, Cody, Wyoming) containing 2.176 percent sulfur and 3.18 percent sulfur respectively were carried out on Harshaw's (Harshaw Chemical Company) molybdenum oxide and cobalt molybdate catalysts.

A critical hydrogen content (minimum amount of hydrogen present in a recycle gas necessary to produce an oil containing less than 0.5 percent sulfur) for cobalt molybdate after 1568 hours of operation on No. 3 fuel oil was less than 40 volume percent hydrogen.

Cobalt molybdate and molybdenum oxide catalysts were compared as to activity and life. In every case the cobalt molybdate catalyst proved superior to the molybdenum oxide catalyst.

Preliminary desulfurization studies were made on a crude tower overhead containing 0.874 percent sulfur from Continental Oil Company at Billings, Montana. The oil was desulfurized to less than 0.163 percent sulfur during 128 hours of operations. The catalyst used was Harshaw's cobalt molybdate. The recycle gas for desulfurization contained less than 35 volume percent hydrogen.

Two oils containing 0.600 percent sulfur and 1.28 percent sulfur from Farmers Union Central Exchange at Laurel, Montana, were desulfurized with Union Oil Company's cobalt molybdate 3/16" catalyst to less than 0.109 and 0.534 percent sulfur respectively. The recycle gas contained less than 18 volume percent hydrogen.

Data was collected on the effect of regeneration of an activated bauxite (Cyclocel) catalyst after desulfurizing an oil blend containing approximately 0.8 percent sulfur. Regeneration decreased catalyst life, but seemed to increase the initial catalyst activity.

All research was carried out in bench scale equipment.

INTRODUCTION

About 35 percent of all crude in the United States may be considered high in sulfur (above 0.5 percent) with nearly all of the high sulfur crude coming from California and West Texas. Gulf coast crudes are usually low in sulfur, while the Mid Continent area has about 25 percent of its production classified as high sulfur crude (1).

Sulfur may occur in petroleum as free sulfur, hydrogen sulfide, mercaptans, sulfides, disulfides, cyclic sulfides, and thiophenes (2).

Elemental sulfur and its compounds in petroleum products are undesirable in the following respects:

1. Have undesirable odor
2. Are corrosive or are potentially corrosive
3. Have poor color stability
4. Give off acrid fumes when burned

Many successful and economic processes have been developed to either remove or convert sulfur compounds found in light distillates to less objectionable forms. Generally these processes are either extractive or absorptive and do not remove the more complex refractory compounds found in heavier distillates.

Husky Oil Company at Cody, Wyoming, is manufacturing petroleum products from a high sulfur Wyoming (Mid Continent) crude oil. Husky's No. 3 fuel oil contains between 2.0 and 2.2 weight percent sulfur.

For the past four years Husky Oil Company has sponsored research projects concerned with reducing the sulfur content of their No. 3 fuel oil

to 0.5 weight percent or less.

The first work was done by P. A. Haas in 1950-1951 (3). He investigated the use of nickel oxide as a catalyst for desulfurization of fuel oil. Various nickel oxide catalysts were tested under specified conditions of temperature, space velocity, hydrogen rate, and oil recycling in a glass reactor.

The results of the study were summarized as follows:

1. Desulfurization was independent of temperature between 600-675°F.
2. The nickel oxide catalyst desulfurizes as a chemical reagent.
3. Inactive forms of nickel oxide existed.
4. Desulfurization depends directly on total contact time, seemingly independent of whether the time was from one or more passes.
5. Hydrogen rate did not seem to be a critical factor except that high rates reduced the contact time.
6. Oxidation of nickel sulfide with air produced nickel sulfate, which had no activity as a desulfurization agent.
7. Nickel oxide prepared by decomposition of nickel hydroxide and nickel carbonate precipitated from solutions could not be activated with air or hydrogen to produce active desulfurization catalysts.

Working concurrently with Haas were J. W. Coykendall (4) and O. J. Koski (5).

The investigation by Coykendall was concerned with the desulfurization activity of a regenerated nickel oxide catalyst. His results were the following:

1. Active nickel oxide catalysts may be prepared by dissolving spent catalyst in sulfuric acid, precipitating the carbonate,

and calcining the precipitate in an air stream in the neighborhood of 800°F.

2. Fresh Harshaw (Harshaw Chemical Company) catalyst containing 53.24 percent nickel, 4.47 percent carbon, 17.34 percent silica, and 24.95 percent oxygen and Gwynn catalyst containing 38.44 percent nickel, 2.22 percent carbon as graphite, 0.15 percent carbon as carbonate, 37 percent silica and 22.19 percent oxygen show a decrease in activity upon calcining at temperatures in excess of 1000°F.
3. Nickel oxide acts both as a catalyst and a chemical reagent in desulfurizing fuel oil.

Koski (5) made desulfurization studies at atmospheric pressure with the following catalyst in 500 gram samples:

1. Chrome alumina
2. Molybdena alumina
3. Cobalt molybdate
4. Acid activated alumina
5. Acid activated bauxites

The conditions were 418-422°C, space velocity of one, and hydrogen rate of 482 SCF/bbl of oil. Of these catalysts the acid activated bauxites gave the maximum desulfurization of 1.01 percent sulfur.

In a pressure reactor using 1000 grams of catalyst, both molybdena alumina and cobalt molybdate gave a product oil containing less than 0.5 percent sulfur.

Koski stated that with molybdena alumina the following factors all decreased the sulfur content of the effluent oil:

1. Pressure up to 500 psig
2. Temperature up to 430°C
3. Hydrogen to oil ratio up to 750 SCF/bbl of oil

The following year, 1951-1952, R. J. Fischbach (6), B. L. Munro (7), and K. J. Green (8) continued the work upon desulfurization.

R. J. Fischbach (6) carried on the desulfurization studies concerned with nickel oxide. The study was made of catalyst activity with respect to various procedures of syntheses of nickel oxide catalyst. A catalyst dried at room temperature showed more activity than one which is dried at 225°F or calcined at 850°F.

All nickel oxide catalyst studied required chemical methods of regeneration and disposal of the by-product sodium sulfate. The regeneration of such a catalyst is inherently uneconomical and impractical.

The work by Koski was continued by Munro (7) and Green (8). They investigated the following hydrodesulfurization catalysts:

1. Activated bauxite (cyclocel)
2. Molybdena alumina
3. Cobalt molybdate
4. Molybdenum sulfide
5. Tungstic sulfide

A nickel oxide catalyst was briefly studied at hydrodesulfurization conditions (300-500 psig hydrogen pressure, 375-430°C, and space velocities of 0.75 to 1.3 gram oil per gram catalyst per hour).

Cobalt molybdate, molybdenum sulfide, and molybdena alumina catalysts produced oil containing less than 0.5 percent sulfur.

At conditions of 500 psig and 410°C molybdenum sulfide catalyst produced oil containing less than 0.5 percent sulfur in excess of 2000 hours with space velocities in the neighborhood of 0.6.

Using a gas mixture of hydrogen and methane they found that oil containing less than 0.5 percent sulfur could be produced from a gas containing 45 percent methane and 55 percent hydrogen, with space velocities less than 0.45 while using the molybdenum sulfide catalyst. This catalyst was not adversely affected by regeneration with air, in fact, the activity after regeneration was twice the original activity. The activated bauxite catalyst successfully desulfurized a No. 1 fuel oil from 1.09 percent sulfur to less than 0.5 percent sulfur while desulfurization of No. 3 fuel oil was unsuccessful as the product oil had from 1.1 to 1.9 percent sulfur in 100 hours of operation.

With the knowledge that pure hydrogen was not necessary for successful desulfurization, J. R. Hartwig (9) and F. C. Silvey (10) directed their efforts toward the use of an effluent gas (89.1 percent hydrogen, 3.5 percent methane, 1.5 percent ethane, 2.5 percent propane, and 3.5 percent propylene) from a catforming unit for a desulfurization atmosphere. Hartwig (9) studied the effect of gas recycle on desulfurization with gas consumption being the main objective. The results with a molybdenum oxide catalyst were 140 SCF/bbl of oil and 250-300 SCF/bbl of oil for pure hydrogen gas and catforming gas respectively.

Silvey (10) reported that both cobalt molybdate and molybdenum oxide gave successful desulfurization results when used in conjunction with catforming gas for the desulfurization atmosphere.

The studies were carried out at 500 psig 415°C and a liquid space velocity of 1. The cobalt molybdate catalyst showed a considerably higher activity and longer catalyst life than the molybdenum oxide catalyst.

After 480 hours of catalyst on stream time, Silvey found that the critical hydrogen content (minimum amount of hydrogen necessary to produce an oil with a sulfur content less than 0.5 percent) was approximately 83 percent by volume.

The data obtained by Koski (5), Munro (7), and Green (8) permitted development of a process to desulfurize Husky's No. 3 fuel oil. Data by Hartwig (9) and Silvey (10) supplemented by previous data, were the basis for the design of a desulfurization plant constructed at Cody, Wyoming.

The prime purpose of this research was to continue to gather data so that a comparison may be made of Harshaw's (Harshaw Chemical Company) molybdenum oxide catalyst, Harshaw's cobalt molybdate, and Union Oil's cobalt molybdate with regards to critical hydrogen content, and catalyst activity after repeated regenerations.

In addition to this research, preliminary research was carried out on the desulfurization of oils from the Continental Oil Company refinery and the Farmers Union Central Exchange refinery at Billings, and Laurel, Montana, respectively. The desulfurization atmosphere was to be an effluent waste gas from each of the two refineries. Conoco's oil for desulfurization studies was their crude tower overhead having a gravity of 43.6° A.P.I. at 60°F, an I.B.P. (initial boiling point) of 138°F, an E. P. (end point) of 620°F, and containing 0.874 percent sulfur. The desulfurization was to be such that the overhead distillate of 350-375°F end point would contain not more 0.1 weight percent sulfur while that portion of the fraction remaining would contain not more than 0.25 percent sulfur. Conoco's gas for the desulfurization atmosphere was made up of

35.6 percent hydrogen, 9.2 percent nitrogen, 32.0 percent methane, 7.8 percent ethylene, 10.1 percent ethane, and 5.3 percent propane plus.

Farmers Union's oils were a No. 1 burner oil and a diesel fuel. The burner fuel had a gravity of 41.4° A.P.I. at 60°F, an I.B.P. of 334°F, an E.P. of 534°F, and a sulfur content of 0.600 weight percent. The diesel fuel had a gravity of 34.2° A.P.I. at 60°F, an I.B.P. of 406°F, an E.P. of 606°F, and a sulfur content of 1.28 weight percent. The gas for desulfurization was to be similar to waste gas stream off from Farmers Union's catalytic cracking unit. This gas was made up of 10.5 percent hydrogen, 13.9 percent nitrogen, 27.9 percent methane, 15.5 percent ethane, and the remaining gases being hydrogen sulfide, carbon dioxide, carbon monoxide, oxygen, ethylene, and some C₃'s and C₄'s.

EQUIPMENT

A schematic flow diagram of the desulfurization unit is illustrated in Figure 1. The unit may be divided into two parts, the gas recycle section and the reactor and condenser section. Figure 2 is a detailed working drawing of the reactor and condenser section.

The gas recycle section consisted of a surge vessel, a compression vessel, and a feed vessel. The surge and compression vessels were number two gas cylinders. The feed vessel was a number one gas cylinder.

The piping used in the unit was 1/8-inch stainless steel high pressure tubing except for the reactor section and the recompression oil lines of the gas recycle system. The piping for the reactor section is illustrated in Figure 2. The piping for the oil lines of the gas recycle system is of 1/8-inch schedule 40 black iron pipe.

During the first part of this research, a two cylinder Hills-McCanna high pressure proportioning pump was used as the compression pump. This pump had a capacity of four gallons per hour. The present pump is a Pesco gear pump capable of pumping 2.5 gallons per minute continuously at 1200 psig.

The reactor pressure was maintained at a relatively constant value by means of a Mason-Neilan small volume air-to-close back pressure valve. This pressure regulator was controlled by a Fisher-Wizard proportional controller.

Current was supplied to the three reactor heating coils by three 120-volt autotransformers. Alundum balls were used as a preheat media. The reactor temperature was measured with iron-constantan thermocouples in

conjunction with a Leeds-Northrup indicating potentiometer.

MATERIALS

Catalysts for this research were Harshaw's cobalt molybdate, Union Oil Company's cobalt molybdate and Harshaw's molybdenum oxide. The data for these catalysts are presented in Table I.

Oils from Husky Oil Company, Cody, Wyoming; Continental Oil Company, Billings, Montana; and Farmers Union Central Exchange, Laurel, Montana, were used in the research reported herein. Inspection data for these oils can be found in Table II.

Gases used in the recycle system were the following four:

1. Methane
2. Catforming gas
3. Continental Oil Company waste gas
4. Farmers Union Central Exchange waste gas

All gases were obtained from The Matheson Company, East Rutherford, New Jersey.

The composition of the catforming gas was 89.0 percent hydrogen, 3.5 percent methane, 1.5 percent ethane, 2.5 percent propane, and 3.5 percent propylene.

The composition of Conoco's waste gas was 35.6 percent hydrogen, 9.2 percent nitrogen, 32.0 percent methane, 7.8 percent ethylene, 10.1 percent ethane, and 5.3 percent propane plus.

The composition of Farmers Union's waste gas, with modification, was 18.3 percent hydrogen, 24.2 percent nitrogen, 48.6 percent methane, 4.2 percent carbon monoxide, and 4.7 percent carbon dioxide.

METHODS

The desulfurization unit was put into operation by applying electricity to the heating coils. During the heating-up period, gas flow was started and the reactor pressure was maintained at the desired operating pressure (500 psig or 800 psig). When the catalyst temperature reached 320-340°C the oil flow was started and the space velocity was adjusted to the proper rate. Data was taken as soon as the oil flow was started.

The product oil was collected in and allowed to drip slowly from the sight glass (see Figure 1) at the bottom of the condenser. The product oil was collected in a one-liter Erlenmeyer flask where any dissolved gases could flash off to pass on to a caustic scrubber (to remove hydrogen sulfide) and a gas meter. The oil sample was removed from the one-liter flask once every eight hours. Analyses of each collected oil sample were made of the gravity as °A.P.I. and sulfur content as weight percent. The gravity was checked by a hydrometer. The sulfur analysis of each sample was made by the lamp method (12).

In the operation of the unit the recycle gas was metered through the feed gas rotameter (see Figure 1) to the reactor. From the reactor the gas passed through the condenser and back pressure valve and was collected in the surge and compression vessels up to a pressure of 400 psig. At this pressure the compression vessel was isolated from the surge vessel and the compression pump started. The pump forced oil into the compression vessel and the oil forced the recycle gas over into the feed vessel. Compression was stopped when the gas pressure in the feed cylinder reached 600 psig or when the oil appeared in the sight glass at the top of the compression

cylinder. To complete the compression cycle the oil was drained back to the compression oil reservoir and makeup gas was added to the compression and surge vessels to bring the pressure up to an arbitrary value of 250 psig, while the feed cylinder was at a pressure of 600 psig.

Recycle gas samples were taken from a bleed-off valve located on the downstream side of the back pressure valve. The recycle gas was caustic scrubbed, metered, and collected in eight-liter glass sample bottles.

SAMPLE CALCULATIONS

Typical Data From a Short Duration Run

H. C. Hooper, A. Harris

FUR-3 January 27-28, 1954

Oil: Husky No. 3 fuel oil 29.7° A.P.I. and 2.176 % S.

Recycle Gas: Farmers Union ≈ 17% H₂

Catalyst: 100 grams (not regenerated from FUR-2)
Union Oil's Cobalt Molybdate 3/16"

Sample No.	Total Hours	Sample Weight Grams	Percent Sulfur	Average Catalyst Temp °C	Liters STP Makeup Gas	Liters STP Bleedoff Gas
1	8	749	0.945	416	83.5	18.4
2	16	751	1.180	411	91.8	14.6
3	24	746	1.210	414	55.6	15.3
4	32	791	1.275	416	55.6	18.9
5	40	740	1.260	416	60	14.6
		<u>3777</u>			<u>346.5</u>	<u>81.8</u>

Oil in 3831 grams

Calculation of Average Space Velocity

$$\frac{(3831 \text{ grams oil charged})}{(100 \text{ grams catalyst})(40 \text{ hr})} = 0.957 \text{ grams oil/gram catalyst/hr}$$

Calculation of Average Gas Consumption

Total liters STP makeup gas	346.5
Total liters STP bleedoff gas	81.8
Total liters STP consumed	<u>264.7</u>

$$\frac{(264.7 \text{ liters consumed})}{3831 \text{ grams oil in}} \cdot \frac{1000 \text{ grams}}{\text{kilogram}} = 69.1 \frac{\text{liters consumed}}{\text{kilogram oil}}$$

oil at 29.7° A.P.I. = 7.309 lb/gal

$$\frac{69.1 \text{ liters}}{\text{kgm}} \left(\frac{1 \text{ ft}^3}{28.316 \text{ liters}} \cdot \frac{7.309 \text{ lb}}{\text{gal}} \cdot \frac{42.0 \text{ gal}}{\text{bbl}} \cdot \frac{0.4536 \text{ kgm}}{\text{lb}} \right)$$

$$= \frac{69.1 \text{ liters}}{\text{kgm}} \left(\frac{4.91 \text{ ft}^3\text{-kgm}}{\text{liters-bbl}} \right) = 340 \text{ ft}^3/\text{bbl}$$

Calculation of Weight Percent Loss of Oil

Charge oil	3831 grams
Effluent oil	<u>3777 grams</u>
	54 grams

$$\frac{54}{3831} = 1.41\%$$

Calculation of Grams of Sulfur Removed per Kilogram of Charge Oil

(Sample No. 2)

$$\text{Charge oil} = \frac{751}{0.9859} = 761 \text{ grams}$$

$$\text{Original S content} = 2.176 \%$$

$$\text{Final S content} = 1.180 \%$$

$$\frac{(761)(0.02176) - (761)(0.01180)1000 \text{ gm}}{761 \text{ grams} \quad \text{kgm}} = (2.176 - 1.180)10$$

$$= 9.6 \text{ grams S/kgm charge oil}$$

DISCUSSION OF RESULTS

As stated before, the purpose of this research was to continue to gather data so that a comparison could be made of Harshaw's molybdenum oxide catalyst, Harshaw's cobalt molybdate, and Union Oil's cobalt molybdate with regard to critical hydrogen content and catalyst activity after repeated regenerations.

In addition to this work, some preliminary research was carried out on the desulfurization of fuel oils from the Continental Oil Company refinery at Billings, Montana, and the Farmers Union Central Exchange refinery at Laurel, Montana.

The experimental run to obtain data on the critical hydrogen content for Harshaw's cobalt molybdate catalyst, designated Co-Mo-0201-T-3/16" (see Table I for composition), was cobalt molybdate Run CMR-2. This run followed cobalt molybdate Run CMR-1 (10) without regeneration or shutdown; consequently the total hours of producing specification oil or of successful desulfurization (sulfur content less than 0.5 weight percent of effluent oil) are those total hours on stream for Run CMR-1, 864 hours, plus the hours of Run CMR-2, 704 hours, giving a total of 1568 hours. The conditions for this run are a temperature of 415°C, a space velocity of 1.0 and a gas recycle rate of 7500 ft³/bbl.

The data collected from CMR-2 are tabulated in Tables III and IV and illustrated in Figures 3 and 4.

Table V is a tabulation of data of every fifth oil sample from Run CMR-1 (10). This data is illustrated in Figure 5. Figure 5 illustrates that the catalyst was not rapidly losing its activity, indicating that the

catalyst was in a relatively stable state. With this knowledge then, the degree of desulfurization would depend to a greater extent on the amount of hydrogen present in the recycle gas than on the relative activity of the catalyst and a critical hydrogen gas determination would be more representative of the minimum amount of hydrogen necessary in a recycle gas to produce specification oil.

In order to determine the critical hydrogen content, methane was added to the recycle gas. Gas samples were taken periodically and analyses were made for the various constituents of the recycle gas. A tabulation of the data obtained from gas sample analyses is in Table IV.

Figures 3 and 4 indicate that the critical hydrogen content for Harshaw's cobalt molybdate catalyst desulfurizing Husky's No. 3 fuel oil (2.176 percent sulfur) after 1568 hours of operation at 415°C., 1.0 space velocity and a gas recycle rate of 7500 ft³/bbl is between 30 and 40 percent hydrogen. This is considerably less than 83 percent minimum for a 16 percent molybdenum oxide catalyst after 480 hours of operation and under the same conditions (10). From this comparison then, it may be concluded that Harshaw's cobalt molybdate is a superior catalyst in that it requires less hydrogen to facilitate successful desulfurization of Husky's No. 3 fuel oil.

The catalyst activity Runs CAR-1,2,3,4 were carried out to obtain data so that a comparison with regards to catalyst activity, after repeated regenerations of Harshaw's catalysts molybdenum oxide and cobalt molybdate, and Union Oil's catalyst cobalt molybdate could be made. The data for these four runs are tabulated in Tables VI, VII, VIII, and IX.

The catalyst activity Runs CAR-1 and 3 were started at a temperature of 415°C (779°F) for 24 hours. The temperature was then increased as follows:

Second 24-hour period	425°C (797°F)
Third 24-hour period	435°C (815°F)
Fourth 24-hour period	445°C (833°F)
Fifth 24-hour period	470°C (878°F)
Sixth 24-hour period	495°C (923°F)

After the sixth 24-hour period the catalyst was burned off. The oil charge to the reactor was Husky's vacuum heavy gas oil with a sulfur content of 3.18 weight percent. The space velocity and recycle rate was set at 1.0 gram of oil per gram catalyst per hour, and 7500 ft³/bbl of oil respectively.

Run CAR-1 was on Harshaw's molybdenum oxide catalyst, designated Mo-0203-T-1/8". The run was carried out as outline and after the 24-hour period at 495°C the catalyst was burned off (regenerated) and the study was continued as Run CAR-2 at a temperature of 495°C. The sulfur content of the effluent oil was greater than that from the end of CAR-1. It was then concluded that regeneration had been incomplete at best, and a second regeneration was started. During the second regeneration, the catalyst reached a temperature of over 900°C, consequently a portion of it was sintered.

Run CAR-3 is a catalyst activity study of Union Oil's catalyst cobalt molybdate 3/16". This study was run at the same conditions of CAR-1. After the sixth 24-hour period at 495°C, the catalyst was regenerated and Run CAR-4 was begun at 495°C.

Figures 6 and 7 illustrate the data taken from Runs CAR-1 and 3.

Figure 6 illustrates that Union Oil's cobalt molybdate is a more active desulfurization catalyst than is the molybdenum oxide. Figure 7 better illustrates that the cobalt molybdate catalyst is a superior desulfurization catalyst. Figure 7 shows that the cobalt catalyst removes more sulfur and remains active longer than does molybdenum oxide.

Studies would have been carried out on Harshaw's cobalt molybdate, but correspondence from the Harshaw Chemical Company stated that the two catalysts, Harshaw's cobalt molybdate and Union Oil's cobalt molybdate, had the same composition.

With the knowledge that desulfurization of Husky's No. 3 fuel oil from 2.176 weight percent sulfur to less than 0.5 percent sulfur is possible with Harshaw's cobalt molybdate catalyst and a recycle gas containing less than 40 percent hydrogen, preliminary research was carried out on oils from the Continental Oil Company and Farmers Union Central Exchange. The recycle gas was to be a waste gas containing hydrogen from each company's refinery.

The oil from Conoco's refinery at Billings, Montana, was a crude tower overhead sample identified as No. Bi 987. The gravity and sulfur content of this oil was 43.1 °A.P.I. and 0.874 percent sulfur (for ASTM distillation data see Table II).

The waste gas stream from Conoco's refinery was composed of 35.6 percent hydrogen, 9.2 percent nitrogen, 23.0 percent methane, 7.8 percent ethylene, 10.1 percent ethane, 2.8 percent propylene, 2.0 percent propane, and 0.5 percent butane plus.

The gas mixture used for the desulfurization atmosphere was essential-

ly the same as the above mixture except that the propylene, propane, and butanes plus were all lumped together as 5.3 percent C₃ plus.

The oil was to be desulfurized to a point such that an overhead distillate of 350-375°F end point would have a sulfur content of not over 0.1 percent and that of the remaining portion of the product contain not more than 0.25 percent sulfur.

The data collected from research on Conoco's oil is tabulated in Table X and XI. The data may be summarized as follows:

Average catalyst temperature = 778°F (varying from 775-782°F)

Average liquid space velocity = 0.955 gm oil/gm catalyst/hr
(varying from 0.862 to 1.04)

Reactor pressure = 500 psig

Average gas recycle rate = 8700 ft³/bbl oil (varying from 7880 to 9600 ft³/bbl)

Initial hydrogen content of recycle gas = 35.6 volume percent

Final hydrogen content of recycle gas = less than 30 percent

Total hours on stream = 128 hours

Average recycle gas consumption = 250-300 ft³/bbl oil

Oil yield = 95.4 weight percent

Oil yield = 96.2 volume percent

Charge oil properties:

°A.P.I. = 43.1 at 60°F

Percent sulfur = 0.874

Product properties:

Composite, °A.P.I. = 43.5 at 60°F

Composite, percent sulfur = 0.124

Composite, I.B.P. = 139°F

Fraction boiling < 365°F. 38.5 weight percent of product

" " < " 41.0 volume percent of product

" " < " 0.037 percent sulfur

Fraction boiling > 365°F. 61.5 weight percent of product

" " > " 59.0 volume percent of product

" " > " 0.19 percent sulfur

Figure 8 illustrates how desulfurization progressed during the Conoco run as catalyst on-stream time increased.

Table XII is a tabulation of analytical data of a composite sample of the desulfurized Conoco oil. The analytical work was done by Continental

Oil Company personnel at Ponca City, Oklahoma. This Table is included with this thesis for record purposes only.

Runs FUR-1 and 2 are research on the desulfurization of Farmers Union Central Exchange oil utilizing a waste gas stream from Farmers Union's refinery as the hydrogen source necessary for a desulfurization atmosphere. The catalyst used for desulfurization was Union oils cobalt molybdate 3/16".

The waste gas contained 10.5 percent hydrogen, 13.9 percent nitrogen, 27.9 percent methane, 15.5 percent ethane, and the remaining gases being hydrogen sulfide, carbon dioxide, carbon monoxide, oxygen, ethylene, and some C₃'s and C₄'s. This gas is too low in hydrogen to be of great value for use in desulfurization so it was thought that if this gas mixture were pressurized to 800 psig, and cooled to less than 80°F all hydrocarbons higher than and including ethane would be condensed and could be removed from the other gases. Removal of these hydrocarbons would bring the hydrogen content up to 18.3 percent and at a pressure of 800 psig the partial pressure of the hydrogen would be about 146 psig. This compares to the Gonoco gas at 500 psig and 35.6 percent hydrogen, the partial pressure of which is about 178 psig. From this, then, the recycle gas mixture used in desulfurizing Farmers Union's oils contained initially 18.3 percent hydrogen, 24.2 percent nitrogen, 48.6 percent methane, 4.2 percent carbon monoxide, and 4.7 percent carbon dioxide.

The Farmers Union oils that were to be desulfurized contained 0.600 percent sulfur and 1.28 percent sulfur. The desulfurization studies on these oils were listed as Farmers Union Run FUR-1 and 2, respectively. Run FUR-3 is a desulfurization of Husky's No. 3 fuel oil using Farmers

Union recycle gas. The data from FUR-1, 2, and 3 are tabulated in Tables XIII, XIV, XV, and XVI. These runs were made consecutively on the same catalyst without regeneration.

An analysis of the recycle gas for hydrogen content was not possible as the recycle gas contained nitrogen and gas analysis are made in a low temperature micro-still with the pot and head being cooled with liquid nitrogen at its boiling point at 640 mm Hg. Boiling liquid nitrogen at atmospheric pressure cannot condense gaseous hydrogen or nitrogen at atmospheric pressure and the gases come off as a mixture. The results of gas analyses pertaining to the Farmers Union studies are listed in Table XVI.

In Farmers Union Run FUR-1 the sulfur content was reduced from 0.600 percent sulfur to a varying percent of 0.062 to 0.109 percent sulfur with Union Oil's catalyst cobalt molybdate 3/16" during 93 hours of operation.

The conditions were as follows:

Temperature	415°C
Pressure	800 psig
Recycle rate	10,000 and 6000 ft ³ /bbl

It should be noted that when the recycle rate was changed from 10,000 ft³/bbl to 6000 ft³/bbl the sulfur content varied from a relatively constant value of 0.076 percent to a relatively constant value of 0.104 (see Table XIII), indicating that desulfurization for this run was more dependent on the number of hydrogen molecules present per unit of time than the contact time of the hydrogen molecule. This is understandable because the recycle gas is deficient in hydrogen and increasing the velocity of the gas over the catalyst bed would also increase the number of hydrogen

atoms available for reaction to hydrogen sulfide per unit of time. Figure 9 is an illustration of how desulfurization progressed during FUR-1 as on stream time increased.

The desulfurization study on Farmers Union oil containing 1.28 percent sulfur was designated FUR-2. The data tabulated for this run is in Table XIV. The total time of the run was 65 hours. Desulfurization was from 1.28 percent sulfur in the charge oil to a varying value from 0.421 to 0.534 percent sulfur in the effluent oil. The composite sulfur percent being about 0.477 percent sulfur. In order to achieve this desulfurization it was necessary to raise the recycle rate from about 6000 ft³/bbl for the first half of the run to about 9000 ft³/bbl for the last part of the run. This indicates that the hydrogen content of the gas was rapidly becoming leaner as an increase of recycle rate from 6000 to 9000 ft³/bbl did not even maintain the same degree of desulfurization as was encountered at the first part of the run. Other than recycle rate, FUR-2 was run at the same conditions as FUR-1.

The tabulated data in Table XV are from Farmers Union Run FUR-3. This run followed FUR-2, and was operated at the same conditions except that the charge oil was Husky's No. 3 fuel oil (2.176 percent sulfur). The effluent oil for this run contained from 0.945 to 1.275 percent sulfur. Concurrently with the preceding research, a study was made on desulfurizing a blend of Husky's kerosene distillate and light gas oil with an activated bauxite catalyst (Cyclocel Sb-2446-51). The blend oil contained about 0.8 percent sulfur. The product contained less than 0.5 percent sulfur. The data from this study are listed in Tables XVII and XVIII. The Run is designated

LMR-1 (from Husky at Lloydminster, Canada). The data on the blend oil are in Table XVIII. Table XIX contains data from an A.S.T.M. distillation of a composite sample of the desulfurized oil.

This desulfurization study was run at atmospheric pressure and with no recycle gas. The catalyst temperature and space velocity was 400°C and 1 gram oil/gram catalyst/hour respectively.

When the sulfur content of the effluent oil reached 0.5 percent sulfur, the unit was shut down and the catalyst was regenerated by air burnoff. The catalyst was regenerated twice. A plot of the sulfur removed versus the hours of operation is illustrated in Figure 12. Three curves are plotted, the first curve is desulfurization with new catalyst, the last two curves are desulfurization with regenerated catalyst. This graph illustrates that regeneration does effect catalyst life between regenerations. The initial activity of the catalyst increased after regeneration.

SUMMARY

The results of the research reported herein may be summarized as follows:

1. The critical hydrogen content for Harshaw's cobalt molybdate catalyst, Co-Mo-0201-T-3/16", desulfurizing Husky's No. 3 fuel oil (2.176 percent sulfur) after 1568 hours of operation at 415°C, Space velocity of 1.0 and a gas recycle rate of 7500 ft³/bbl is between 30 and 40 volume percent.
2. Harshaw's cobalt molybdate catalyst, Co-Mo-0201-T-3/16", is superior to Harshaw's molybdenum oxide catalyst, Mo-0203-T-1/8", in that it has a greater activity and longer catalyst life.
3. After 128 hours on-stream, an oil from Continental Oil Company having gravity and sulfur content of 43.1 °A.P.I. and 0.874 percent sulfur respectively, was desulfurized in an atmosphere of recycle gas containing less than 35 percent hydrogen to yield an effluent oil containing 0.142 percent sulfur. The conditions of desulfurization were as follows:

Reactor pressure = 500 psig
Average gas recycle rate = 8700 ft³/bbl oil (varying from
7880-9600 ft³/bbl)
Average catalyst temperature = 778 (varying from 775-782°F)
Average space velocity = 0.955 gm oil/gm catalyst/hr
(varying from 0.862 to 1.04)

4. Oils from Farmers Union Central Exchange containing 0.600 and 1.28 percent sulfur were desulfurized in a desulfurization atmosphere containing less than 18 percent hydrogen to less than 0.109 and 0.534 percent sulfur respectively. The total hours of

desulfurization for the oils containing 0.600 and 1.28 percent sulfur were 93 and 65 hours respectively.

5. Regeneration of activated bauxite catalyst (Cyclocel Sb-2446-51) decreased the catalyst life, but seemed to increase the initial catalyst activity.

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TABLE I
COMPOSITION AND IDENTIFICATION OF CATALYSTS USED

Run No.	Catalyst and Composition	Identification Code	Catalyst Manufacturer
LMR-1	Cyclocel 100% Bauxite	Sb-2446-51	Porocel Corp.
CMR-2	Cobalt Molybdate 9.5% MoO ₃ 3.0% CoO 5.0% SiO ₂ 2.0% Graphite 80.5% Al ₂ O ₃	Co-Mo-0201-T-3/16"	Harshaw Chemical Company
Genoco-1	Cobalt Molybdate 9.5% MoO ₃ 3.0% CoO 5.0% SiO ₂ 2.0% Graphite 80.5% Al ₂ O ₃	Co-Mo-0201-T-3/16"	Harshaw Chemical Company
FUR-1,2 & 3	Cobalt Molybdate 9.5% MoO ₃ 3.0% CoO 5.0% SiO ₂ 2.0% Graphite 80.5% Al ₂ O ₃	Union Oil Co. Cobalt Molybdate 3/16"	Harshaw Chemical Company
CAR-3 & 4	Cobalt Molybdate 9.5% MoO ₃ 3.0% CoO 5.0% SiO ₂ 2.0% Graphite 80.5% Al ₂ O ₃	Union Oil Co Cobalt Molybdate 3/16"	Harshaw Chemical Company
CAR-1 & 2	Molybdenum Oxide 16% MoO ₃ 79% Al ₂ O ₃ 5% SiO ₂	Mo-0203-T-1/8" 160-A-2-1	Harshaw Chemical Company

TABLE II
CHARGE OIL INSPECTION DATA

Designation:	Husky #3 Fuel Oil	Lt. Gas Oil Samp #598	Lt. Gas Oil Samp #601	Kerosene Dist. Samp #597	Kerosene Dist. Samp #600	Conoco Crude Tower Overhead Samp #Bi 987	Farmers Union Central Ex. Oil Samp #1526-53S	Farmers Union Central Ex. Oil Samp #1527-53S	Husky Vac. Heavy Gas Oil
Gravity, °A.P.I., 60°F:	30.6	33.0	32.6	38.2	36.8	43.6	41.0	33.8	22.66
ASTM Distillation °F, 640 mm Hg									
I.B.P.	425	294	294	252	300	138	334	406	
5 %	504	390	403	308	351	---	359	470	
10	520	415	427	330	372	236	372	490	
20	536	449	451	371	393	---	389	503	
30	548	471	469	394	410	---	402	515	
40	558	490	484	413	424	---	415	524	
50	567	508	500	427	436	422	427	532	
60	575	526	514	442	449	---	442	540	
70	584	543	530	459	460	---	457	550	
80	594	565	550	475	---	---	475	558	
90	611	594	581	497	492	573	500	566	
95	625	627	610	520	514	---	520	574	
E.P.	652	649	642	535	528	620	534	606	
Recovery, Vol %	99.0	99.0	99.0	99.0	99.0	---	99.0	99.0	
Residue, Vol %	0.8	0.5	0.5	0.5	0.5	---	1	1	
Loss, Vol %	0.2	0.5	0.5	0.5	0.5	---	0	0	
Wt. % S	2.176	0.961	0.975	0.551	0.623	0.874	0.600	1.280	3.18

TABLE III
TABULATED DATA FROM COBALT MOLYBDATE RUN-CMR-2

Catalyst: Co-Mo-0201-T-3/16"
100 grams (unregenerated from CMR-1*)
Pressure: 500 psig
Oil: Husky No. 3 fuel oil, 29.7° A.P.I. and 2.18% S
Recycle Gas: Catforming gas (See Table IV)
Yield: 97.46 Weight % 33.8 °A.P.I.
103 Volume % 0.309 % S

* Research by Silvey (10)

Samp No.	Total Hours	Cat Temp °F Av.	Space Vel gms/gm/hr	Recycle Ft ³ /bbl	Av Gas Consump Ft ³ /bbl	Yield Gms Oil	Product A.P.I.	Product % S
1	8	779	1.003	7150	0	779	35.4	0.154
2	16	779	1.032	7010	0	800	35.3	0.143
3	24	779	1.015	7060	80.9	787	35.1	0.144
4	32	779	1.003	7150	186.5	777	35.2	0.145
5	40	777	1.012	7080	318	786	35.0	0.165
6	48	780	1.002	7200	253	778	35.2	0.148
7	56	777	0.985	7270	329	765	35.1	0.160
8	64	779	1.010	7100	362	783	35.6	0.157
9	72	779	0.984	7300	319	762	35.6	0.208
10	80	779	0.970	7400	336.2	753	35.7	0.210
11	88	783	0.996	7200	345	773	35.6	0.220
12	96	780	0.967	7450	310	750	35.7	0.242
13	104	779	0.967	7360	352	750	35.7	0.238
14	112	780	0.984	7300	354	763	35.6	0.254
15	120	779	0.980	7350	332	760	35.2	0.312
16	128	778	0.955	7520	321	740	35.2	0.316
17	136	777	0.980	7330	298	760	35.2	0.348
18	144	770	1.070	6795	313	830	34.8	0.299
19	152	780	0.973	7320	310	755	34.8	0.302
20	160	779	0.990	7200	313	768	34.8	0.314
21	168	766	0.946	7660	294	734	34.3	0.314
22	176	780	0.972	7400	330	764	34.4	0.301
23	184	780	1.050	6990	313	814	34.5	0.286
24	192	781	0.975	7400	310	757	34.5	0.290
25	200	781	1.013	7130	294	787	34.5	0.288
26	208	779	1.004	7150	280	780	34.5	0.314
27	216	781	0.975	7360	286	756	34	0.310
28	224	781	0.975	7420	279	756	34.10	0.292
29	232	779	1.003	7150	273	779	34	0.319
30	240	781	0.980	7325	274	761	34.1	0.337
31	248	780	0.975	7375	264	757	34.2	0.342
32	256	779	1.016	7100	279	788	34.1	0.333

