



A study of catalysts in hydrodesulfurization of fuel oil  
by Arlen N Harris

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree  
of Master of Science in Chemical Engineering  
Montana State University  
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The purpose of this investigation was to determine the effectiveness of several hydrodesulfurization catalysts. The three catalysts studied were Harshaw Chemical Company's molybdenum oxide and cobalt molybdate catalysts, and Union Oil Company's cobalt molybdate catalyst. The Atlantic Catformer catalyst and a chrome alumina catalyst were also studied very briefly.

A small pilot plant hydrodesulfurization unit capable of holding 100 grams of catalyst was used. Catforming gas containing 89 percent hydrogen, and Husky Oil Company's No. 3 fuel oil containing 2.18 percent sulfur, were used throughout this investigation.

Cobalt molybdate was found to be the most effective desulfurizing catalyst. Union Oil Company's cobalt molybdate was found to be more active than the Harshaw Chemical Company's cobalt molybdate catalyst. Under the conditions studied the Atlantic Catformer catalyst and the chrome alumina catalyst did not compare favorably with either cobalt molybdate or molybdenum oxide as hydrodesulfurization catalysts.

A STUDY OF CATALYSTS IN HYDRODESULFURIZATION  
OF FUEL OIL

by

ARLEN N. HARRIS

A THESIS

Submitted to the Graduate Faculty  
in  
partial fulfillment of the requirements  
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at  
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ABSTRACT

The purpose of this investigation was to determine the effectiveness of several hydrodesulfurization catalysts. The three catalysts studied were Harshaw Chemical Company's molybdenum oxide and cobalt molybdate catalysts, and Union Oil Company's cobalt molybdate catalyst. The Atlantic Catformer catalyst and a chrome alumina catalyst were also studied very briefly.

A small pilot plant hydrodesulfurization unit capable of holding 100 grams of catalyst was used. Catforming gas containing 89 percent hydrogen, and Husky Oil Company's No. 3 fuel oil containing 2.18 percent sulfur, were used throughout this investigation.

Cobalt molybdate was found to be the most effective desulfurizing catalyst. Union Oil Company's cobalt molybdate was found to be more active than the Harshaw Chemical Company's cobalt molybdate catalyst. Under the conditions studied the Atlantic Catformer catalyst and the chrome alumina catalyst did not compare favorably with either cobalt molybdate or molybdenum oxide as hydrodesulfurization catalysts.

## INTRODUCTION

The increasing demand for petroleum products has forced refiners to utilize the lower quality high sulfur crude oils such as those found in certain sections of California, Texas, and Wyoming. The vast reserves of the Arabian Middle East oil and the large reserves of oil which can be derived from shale and tar sands are very high in sulfur content. In using these high sulfur crudes, refiners have to use various methods for desulfurizing, depending upon the individual economic situation and the relative amounts and types of sulfur compounds present.

Sulfur in petroleum products causes objectionable odor, corrosion to metal, poor color stability, and poor tetra ethyl lead susceptibility in gasoline, as well as producing acrid fumes on burning. Sulfur in petroleum is present in a number of forms among which are: elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and thiophenes. The cyclic or thiophenic sulfur compounds are very stable and can not be affected by the common desulfurization methods. The higher boiling petroleum fractions tend to have a higher concentration of sulfur and a greater proportion of cyclic sulfur compounds.

There has been an increased demand for heavier distillates for use in diesel engines, jet aircraft motors, and gas turbines. To prevent excessive engine wear, it is desirable to have the sulfur content less than 0.5 percent. There are a great number of highly specialized methods for removing or rearranging the objectionable non-cyclic sulfur compounds in gasoline and light distillates. The relatively high concentration of cyclic sulfur compounds in some diesel fuels and gas oils are not affected

by these methods but may be partially removed by such processes as destructive hydrogenation and catalytic cracking or almost completely removed by hydroforming. Using these processes, however, the product oil is materially altered in basic characteristics by dehydrogenation, cracking or other reactions. All sulfur compounds may be removed by use of a selective solvent, however, losses of hydrocarbon usually make this method prohibitive.

The most efficient method for removing the so-called refractory or cyclic type of sulfur compounds is by the well known process of catalytic hydrodesulfurization. Cobalt-molybdate, molybdenum oxide, and tungsten-nickel catalysts are the most commonly used contact agents in this type of process. Besides removing sulfur, nitrogen, oxygen, and diolefins or gum forming constituents are also largely removed from the oil.

In catalytic hydrodesulfurization the oil is treated with a large amount of hydrogen in the presence of a sulfur resistant hydrogenation catalyst under suitable conditions of temperature and pressure. For this type of process to be economically feasible a relatively cheap source of hydrogen rich gas is required. A cheap source of hydrogen is now produced in the process of catalytic reforming. In the typical catalytic reforming process used for upgrading low octane gasoline there is a net production of a gas mixture which is usually greater than 85% hydrogen, the remainder being mostly hydrocarbon gases which do not affect hydrodesulfurization appreciably.

The minimum hydrogen concentration or critical hydrogen content required to produce a desired degree of desulfurization under constant

operating conditions increases with the on stream time for a particular catalyst. Silvey (7) has shown the critical hydrogen concentrations using a molybdenum oxide catalyst.

The hydrogen rich gas used in catalytic hydrodesulfurization is recycled through the system and as it is continually used over again it picks up small amounts of hydrogen sulfide and hydrocarbon gases which are not totally condensed in the effluent oil. Hartwig (3) investigated the rate of hydrocarbon buildup for the particular conditions under which he was operating and claims that this rate of buildup is relatively slow. Hydrogen sulfide in the recycle gas is not particularly harmful, however, to prevent dilution of the recycle gas, it may be removed by caustic scrubbing. When the concentration of the hydrocarbon gases gets too high, these gases can be removed by conventional means, however, this low hydrogen concentration recycle gas is usually removed from the system and new recycle gas of high hydrogen concentration added.

Hydrogen is used up in this process, the amount depending upon the charge oil requirements, conditions employed, or degree of desulfurization required. This requires that a makeup gas be added to the system; Hartwig (3) has determined the consumption of catforming gas, containing approximately 89% hydrogen, which is required for a number 3 fuel oil while using a molybdenum sulfide catalyst.

The ratio of hydrogen to oil that is passed over the catalyst affects both the catalyst life and the degree of desulfurization. Variations in the mole ratio of hydrogen to liquid feed above 2 to 1 have very little effect on the sulfur content of the effluent oil (2). This ratio is in the

range of 2000 cubic feet per barrel of oil. To maintain catalyst activity, however, it has been found desirable to recycle about 6000 cubic feet of gas per barrel of charge oil.(2).

The catalyst life or activity is affected by tarry deposits and carbon laydown. These deposits also cause an increased pressure drop across the catalyst bed. When the sulfur concentration in the product oil gets too high or the pressure drop becomes so large as to hinder passage of the recycle gas, the catalyst must be regenerated by burning off the tarry substances with air or gases diluted with oxygen.

When heavy gas oils are desulfurized, it is desirable to increase the pressure in order to decrease the rate of carbon and tar laydown on the catalyst. Increasing the pressure also promotes a higher degree of desulfurization and Koski (6) has shown the effect of pressure up to 600 psig.

It is desirable to keep the temperature low enough to prevent excessive thermal cracking. The bond energy for a carbon to carbon bond ( $58.6 \frac{\text{K cal}}{\text{mol}}$ ) is only slightly higher than that for a carbon to sulfur bond ( $54.5 \frac{\text{K cal}}{\text{mol}}$ ) and so a temperature required for cracking of a carbon to sulfur bond would also promote some carbon to carbon cracking. The temperature required for a certain degree of desulfurization is dependent upon a number of things, the most important being the amount of refractory sulfur compounds present in the charge oil and the type of catalyst employed.

For most operating ranges, small decreases in space velocity promote a higher degree of desulfurization. Space velocity in weight or volume



ratios of charge oil to catalyst per unit of time is an expression for the extent of contact between oil and catalyst. High space velocities designate less contact time of the oil with the catalyst and hence a lower degree of desulfurization.

The object of this research was to compare three catalysts, a molybdenum oxide catalyst and two cobalt molybdate catalysts by showing the relative effects of temperature, space velocity, and recycle rate on desulfurization, while using these catalysts. A statistical approach was used for this study. Both chrome-alumina and platinum catalysts were also tested briefly in order to determine whether they would make effective catalysts or contact agents for catalytic hydrodesulfurization.

#### EQUIPMENT

A schematic 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 recycle gas inlet, oil inlet, an air inlet for catalyst regenerations, and a 1200 lb frangible disk safety blowout. A  $1/4$ -inch extra strong black iron pipe was extended downward from the cross attached to the top of the reactor to within 1 inch of the bottom of the  $1\frac{1}{2}$ -inch reactor pipe. This tube was welded shut at the bottom and served as a thermowell tube for three iron-constantan thermocouples inserted from the top. This type of thermowell allows for adjusting the thermocouples to any desired height in the center of the reactor.

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

The effluent oil and condensed vapors flowing from the Jerguson receiver were collected in a one-liter Erlenmyer flask. The condensed gases in the oil, which flash off at atmospheric pressure, 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 hydraulic gear pump, made by the Pesco Company, and the other side was fitted with a valve for returning the

compression oil to a 5-gallon tank oil storage reservoir. Between the gear pump and the oil storage tank was connected an unloading relief valve for returning the oil to the storage tank in case the pressure in the compression tank exceeded 1000 psig. A pressure gage was fitted between this relief valve and the gear pump. The feed tank was a number one gas cylinder fitted at the top with a cross and pressure gage and at the bottom with a valve.

Gas flow from the feed tank to the reactor was metered by a Fisher flowrator and regulated by an American Instrument Company needle valve located between the feed tank and the flowrator.

A Brook's Rotameter was used to measure the amount of makeup gas from the makeup tank to the surge and compression tanks.

Extra strong black iron pipe and high pressure fittings were used throughout the unit where piping is indicated by double lines on Figure 1. Single lines on this drawing indicate 1/8-inch stainless steel high pressure tubing.

Three 33-foot lengths of beaded Nichrome wire, supplied with current from three 110-volt Powerstat variacs, provided heat for the reactor. Two of these heating coils were located near the bottom of the reactor to heat the catalyst section and one was wound higher up on the reactor to provide heat for the preheat section. The coils were wound around the reactor over a layer of asbestos tape and insulated with an additional covering of asbestos tape and a two-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 an adjustable stroke piston pump and an oil reservoir.

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 Microstill with a Micromax automatic temperature recording device made by the Leeds and Northrup Company.

#### MATERIALS

The oil used for desulfurization studies was Husky Oil Company's number three fuel oil. The sulfur content of this oil varied from 2.12 to 2.18 percent by weight. Additional data for this oil can be found in Table I of the Appendix.

Table II presents data for all the catalysts used in this research.

The composition of the recycle gas or catforming gas used is shown in Table I.

#### METHODS

The desulfurization unit was put into operation by first applying electric current to the heating coils of the reactor by means of three Powerstat variacs. When the temperature in the catalyst bed reached 300°C, the reactor was pressurized with catforming gas containing approximately 89% hydrogen. The flow rate of this gas was adjusted by means of a needle valve and measured by a Fisher flowrator. The pressure in the reactor was adjusted to the desired level by setting the Fisher-Wizard proportional

controller connected to the Mason-Neilan back pressure valve. When the catalyst bed temperature reached approximately  $380^{\circ}\text{C}$ , the oil to be desulfurized was charged to the reactor by starting the piston pump. The oil flow rate was then adjusted by a proper setting of the piston stroke. Temperature, pressure, and flowrator readings were taken every half hour and averaged for the total time of each oil sample taken.

As the product oil collected in the Jerguson pressure receiver it was allowed to drip slowly into the receiving flask. Dissolved gases, which floated from the oil in the receiving flask at atmospheric pressure, passed through a caustic scrubbing train to remove the hydrogen sulfide, and then were metered through a wet test meter. Effluent oil samples were taken every eight hours, at which time the wet test meter readings were taken.

The oil was maintained at a certain level in the Jerguson pressure receiver. This acted as a liquid seal preventing the recycle gas from escaping. The recycle gas flowed through the Mason-Neilan back pressure valve into the surge tank and compression tank. When the pressure in these two tanks reached approximately 200 psig below the reactor pressure, the compression tank was isolated from the surge tank. The recycle gas collected in the compression tank was then forced back into the feed tank by means of the hydraulic gear pump and compression oil. The length of time required between these compressions varied with the flow rate of catforming gas through the reactor. Makeup gas had to be added periodically to the surge and compression tanks. Gas flow from the makeup tank was metered through a Brooks rotameter and this flow was timed with a stopwatch.

Gas samples of the recycle gas were taken periodically by displacement of water in eight-liter bottles. These gas samples were analyzed in a low temperature micro-still with a Micromax automatic temperature recorder. Liquid nitrogen was used for cooling the micro-still.

The weight and gravity in °A.P.I. were recorded for each sample taken. A portion of each sample was washed in an eight percent sodium hydroxide solution before determining the sulfur content by the lamp method (1).

#### SAMPLE CALCULATIONS

Tables III, IV, V, VI, VII, VIII, IX, and X contain the tabulated data for all the runs made in this investigation.

The space velocity recorded was based on the weight of the oil charged to the reactor.

For example: Percent loss, wt. basis = 2.5%. Then, for an individual effluent oil sample weighing 780 gms., the charge oil weight would be  $\frac{780}{0.975} = 800$  gms.

Then, for an 8-hour sample period and using 100 gms of catalyst, the space velocity would equal:

$$\frac{800 \text{ gms oil}}{(100 \text{ gms cat})(8 \text{ hrs})} = 1.000 \frac{\text{gms oil}}{\text{gm cat hr}}$$

The recycle gas flow in standard cubic feet per barrel of oil charged (SCF/bbl) was calculated by dividing the gas flow per sample period by the charge oil weight per sample period. For example:

With an effluent oil sample weighing 780 gms (800 gms. of charge oil) and a gas recycle rate (as indicated by the Fisher flowrator) of 950 liters (S.T.P.) per 8 hours then;

$$\frac{950 \text{ liters gas}}{800 \text{ gms oil}} \times \frac{0.875 \text{ gms oil}}{\text{c.c. oil}} \times \frac{1000 \text{ c.c.}}{\text{liter}} \times \frac{28.32 \text{ liters}}{7.48 \text{ gal}}$$
$$\times \frac{42 \text{ gal}}{\text{bbl}} \times \frac{1 \text{ ft}^3}{28.32 \text{ liter}} = 5840 \text{ S.C.F./bbl}$$

Hydrogen consumption was calculated from the makeup and bleedoff gas figures recorded for each sample period. Bleedoff figures were the wet test meter readings. Makeup figures were from the Brooks rotameter readings. For example:

For an effluent oil sample weighing 780 gms (800 gms charge oil) and a gas makeup equal to 38 liters (STP) and a bleedoff equal to 10 liters (STP), the gas consumed by difference would be 28 liters (STP).

Then  $\frac{28}{800} \times 1000 = 35$  liters consumed per Kgm oil and

$$\frac{35 \text{ liters}}{\text{Kgm}} \times \frac{4.91 \text{ Kgm ft}^3}{\text{liters bbl}} = 172 \text{ ft}^3 \text{ consumed per bbl of oil.}$$

Gas consumption figures varied widely so the figures presented in the statistical runs were cumulative averages from the three samples for each run.

Standard statistical procedures were used in analyzing the data shown in Tables XII and XIII for the analyses of variance Table XIV. These calculations were made and checked by the Montana State College Statistical Department headed by Dr. B. Ostle.

DISCUSSION

Method Used for Comparing Catalysts

A comparison of three hydrodesulfurization catalysts was made by showing the relative effects, while using each catalyst, of recycle rate, space velocity, and temperature on the percent sulfur and gravity of the effluent oil. The three catalysts used were Harshaw's molybdenum oxide, Harshaw's cobalt molybdate and Union Oil Company's cobalt molybdate. Table II shows the chemical composition, manufacturer, and identification code of each catalyst used.

The following levels were used for the independent variables, while using each catalyst:

1. Two temperatures -- 725 and 775°F.
2. Three space velocities -- 0.6, 1.0, and 1.4 pounds of oil per pound of catalyst per hour.
3. Three recycle rates -- 6000, 7500, and 9000 cubic feet of recycle gas per barrel of charge oil.

The eight levels of the three factors described above provide a total of 18 different operating conditions. These 18 different operating conditions, for each of the Statistical Runs, Sets 1, 2, 3, and 4, are called runs as shown in Tables VII, VIII, IX, and X. Molybdenum oxide was used for Statistical Run, Set 1 shown in Table VII, and this same catalyst was regenerated by blowing with air at 600°C and used for Statistical Run, Set 2 shown in Table VIII to provide a replicate set of data. Harshaw's cobalt molybdate catalyst was used in Statistical Run, Set 3 shown in Table IX and Union Oil Company's cobalt molybdate catalyst was used for



Statistical Run, Set 4 shown in Table X.

The experiments were conducted at a reactor pressure of 500 psig. Husky Oil Company's No. 3 fuel oil containing 2.18 percent sulfur and having a gravity of 29.7° A.P.I. was used. Catforming gas having the composition shown in Table I was used as the recycle gas. The same recycle gas was used for Statistical Runs, Sets 1, 2, and 3. The hydrogen concentration was 86.7 percent at the end of Statistical Run, Set 2, and 79.2 percent at the end of Statistical Run, Set 3. This drop in hydrogen content can be explained by the higher degree of desulfurization and greater production of light ends in the effluent oil accomplished by the cobalt molybdate catalyst, than was accomplished by the molybdenum oxide catalyst for Statistical Runs, Sets 1 and 2.

To help prevent prejudice in analyzing the effluent oil from each of the statistical runs, a random changing of the conditions was employed as shown in Table XI. Each of the four statistical runs shown in Tables VII, VIII, IX, and X contain eighteen individual runs representing the eighteen different operating conditions employed. Each of these individual runs was allotted 24 hours of operating time allowing for three 8-hour samples. The sample from the first 8 hours of each run was not considered in the analyses, and was regarded only as a flushing sample to remove oil from the previous run and allow a line out period for the change in conditions. The properties of the last two 8-hour samples for each run were averaged and only these average values were used to represent the conditions of each particular run.

Figures 2 and 3 are plots of these average values from the Molybdenum

Oxide Statistical Run, Set 2. The percent sulfur in the effluent oil is plotted against space velocity in Figure 2 and against recycle rate in Figure 3. Both figures show the relative effects on the percent sulfur in the effluent oil due to space velocity and temperature, but no definite effect can be attributed to recycle rate. Similar plots of the data for the Statistical Runs, Sets 1, 3, and 4 were not included since no further information could be obtained from them.

#### Statistical Analysis of the Variables

For further proof that the gas recycle rate produced no significant effect on the dependent variables of percent sulfur and gravity of the effluent oil a statistical approach was used. Tables XII and XIII show the data taken from the appropriate runs which were used for the Analyses of Variance Table listed as Table XIV in the Appendix. In order to use this statistical approach the deviations of the independent variables of temperature, space velocity, and recycle rate from the prescribed levels as listed above have been neglected. The decrease in the activity of the various catalysts with on-stream time could not be taken into account either. For the case of molybdenum oxide this decrease in activity which was studied by Silvey (7) produces a great deal of uncertainty for any type of analyses of these data. The changing of conditions at random was desirable to offset this effect as much as possible.

An analysis of variance table for each of the three catalysts is shown in Table XIV. The gravity of the effluent oil in °A.P.I. was used as a second dependent variable since its measurement is very accurate, and also because a change in the percent sulfur of the effluent oil can always be

predicted if there is a change in the gravity of the effluent oil.

The single and double asterisks beside the values in the mean square column of Table XIV denote that the corresponding independent variable listed under the source of variation column produce an effect on the dependent variables. The single and double asterisks denote that these factors produce an effect which is significant at the 5 and 1 percent significance levels, respectively. This means that there is a 5 and 1 percent chance of falsely concluding that these variables actually do produce any real effect.

In Table XIV both space velocity and temperature were shown to produce an effect on the dependent variables at the one percent level of significance for all three catalysts. A linear regression was noted for both space velocity and temperature at the 1 percent level of significance. The equations of the regression lines were not included with this table, but they showed that as temperature increases and as space velocity decreases a higher degree of desulfurization results. It was also shown in Table XIV that when the molybdenum oxide catalyst from Statistical Run, Set 1 was regenerated and used for Statistical Run, Set 2 to give a replicate set of data, that a significant difference between replications resulted. This fact is also shown very plainly in Table XIII by the mean values of the dependent variables which are listed under each set of data. The mean of Set 2 is 0.630 and the mean of Set 1 is 0.580 percent sulfur in the effluent oil showing that the molybdenum oxide catalyst was not nearly as effective in desulfurizing after regeneration as before.

The Analysis of Variance Table showed no effect due to gas recycle

rate for any of the catalysts used. A linear regression effect at the 5 percent level of significance was noted for recycle rate with the molybdenum oxide catalyst on the percent sulfur in the effluent oil, however, no similar effect was noted due to gravity.

An interaction was shown to exist at the 5 percent level of significance between temperature and space velocity for both of the cobalt molybdate catalysts. This means that the effect of space velocity varies with the temperature level as pictured in Figure 5. No similar effect was noticed for the molybdenum oxide catalyst by either Figure 4 or the Analyses of Variance Table.

#### Comparison of The Catalysts by Means of Graphs

It was assumed that varying the recycle rate in the range of 6000 to 9000 cubic feet of gas per barrel of oil produces no noticeable effect on the dependent variables. If this is true there are really only six different sets of conditions for each statistical run and not eighteen as formerly thought. This allowed for all the runs with space velocities at the same prescribed level to be averaged giving a total of only three points for each temperature level. These average data which are listed in Table XV were used to plot Figures 4, 5, 6, 7, 8, and 9.

Figures 4 and 5 are plots of percent sulfur versus space velocity at the two temperature levels of 725 and 775°F. These figures show that Union Oil Company's cobalt molybdate catalyst is a better desulfurization catalyst than Harshaw's cobalt molybdate catalyst, and furthermore that both cobalt molybdate catalysts produce a higher degree of desulfurization at the low temperature level of 725°F than does the molybdenum oxide

catalyst at the higher temperature level of 775°F.

An interaction was shown to exist in Figure 5 whereby the space velocity is shown to have less effect on the percent sulfur in the effluent oil as the temperature is raised. This suggested the hypothesis that at some temperature level, higher than 775°F, a change in the space velocity would produce very little effect on the degree of desulfurization and could be altered merely to control the gravity of the effluent oil. This was the purpose for performing the Oil Cracking Run I (O.C.R.I.) shown in Table III whereby a temperature of approximately 810°F was used and the space velocity raised to approximately 5 in order to prevent excessive cracking of the oil at the higher temperature. Sample No. 4 produced at a temperature of 808°F and a space velocity of 4.9 showed the gravity to be 34.3 °A.P.I. This gravity was in the desired range for good desulfurization as shown by Figure 7, however, the sulfur content of 0.406 percent was much higher than was predicted. The space velocity was then lowered to approximately 3 which raised the gravity to 34.7 °A.P.I. and gave a sulfur content of 0.274 percent for sample No. 13. The data from this Oil Cracking Run I has disproved the fallacy that at the relatively high temperature level of 810°F the space velocity produces an effect in the gravity but no effect in the degree of desulfurization.

Figures 6 and 7 are plots of gravity versus space velocity at the two temperature levels of 725 and 775°F. These plots show that the Union Oil Company's cobalt molybdate catalyst is a more effective cracking catalyst or produces more low boiling hydrocarbons as shown by the higher values of °A.P.I. gravity. The molybdenum oxide catalyst produces effluent oil at

775°F with gravities that are in the same range as those produced by the cobalt molybdate catalysts at 725°F.

Figure 8 is a plot of percent sulfur in the effluent oil versus gravity in °A.P.I. of the effluent oil. This plot shows a linear relationship between these two dependent variables for a particular catalyst and temperature level. The two cobalt molybdate catalysts are satisfied by the same curves. This relationship should prove valuable in routine quality control work where the percent sulfur in the effluent oil could be approximated by merely checking the gravity.

Figure 9 shows the effect of the two temperature levels on the gravity of the effluent oil for each of the three catalysts. This plot shows the relative ability of each catalyst to crack the oil, and furthermore emphasizes that the molybdenum oxide catalyst is only as effective in this respect at 775°F as the cobalt molybdate catalysts are at the lower temperature level of 725°F. Figures 5, 7, and 9 show that Union Oil Company's cobalt molybdate catalyst is better than Harshaw's cobalt molybdate catalyst for the dual purpose of cracking and desulfurizing. Table II shows that these catalysts have the same chemical composition and if this fact is not in error then the difference in the two catalysts' ability must be attributed to some physical quality.

#### Brief Study of Other Contact Agents for Hydrodesulfurization

An Atlantic catformer catalyst which had been previously used in a reforming process for upgrading straight run gasoline and which had been regenerated four times was briefly tested as a hydrodesulfurization catalyst. Husky Oil Company's No. 3 fuel oil was used and a catformer gas

containing approximately 87 percent hydrogen was used as the recycle gas. The conditions for the Platinum Run I shown in Table IV were a pressure of 400 psig, a temperature of 750°F, and a space velocity of approximately 10.0. These conditions were used since it was originally thought that this catalyst would promote a high degree of cracking, however, as shown by Sample No. 2, the gravity of the effluent oil was increased by only 0.7 °A.P.I. and the sulfur removal amounted to only 6 percent. When this catalyst was used at a temperature of 779°F, a pressure of 500 psig and a space velocity of 0.945 as shown in Table V, the gravity of the effluent oil was increased to 33.4 °A.P.I. and a 57 percent sulfur removal resulted. This catalyst does not compare favorably with either cobalt molybdate or molybdenum oxide catalysts under these conditions, however, since no specification oil containing less than 0.5 percent sulfur was produced.

The chrome alumina catalyst listed in Table II was tested by Koski (6) under atmospheric pressure and using pure hydrogen. He found that at a temperature of 775°F and a space velocity of 1.083 that only 42 percent of the sulfur was removed from the oil. It was thought that under relatively the same conditions of temperature and space velocity but under a pressure of 500 psig, a much higher degree of desulfurization would result. This was the purpose of the Chrome Alumina Run I shown in Table VI. The use of pressure increased the degree of desulfurization to 60.5 percent. When the space velocity was reduced to 0.485 as shown by Sample 6, the degree of desulfurization was raised to 71 percent. It may be concluded that pressure produced a very definite effect on the degree of desulfurization, however, the chrome alumina catalyst does not compare favorably

under these conditions with either the cobalt molybdate or molybdenum oxide catalysts.

#### CONCLUSIONS

1. Cobalt molybdate is the most effective catalyst studied from the dual point of view of desulfurization and production of light ends.
2. Lower temperatures can be used for cobalt molybdate than for molybdenum oxide.
3. Union Oil Company's cobalt molybdate is more active than Harshaw's cobalt molybdate catalyst.
4. Temperature and space velocity are the important independent variables. Recycle rates in the range of 6000 to 9000 cubic feet of gas per barrel of oil produced no noticeable effect on the degree of desulfurization and gravity of the effluent oil.
5. Under the conditions studied, the chrome alumina and Atlantic Catformer catalyst do not compare favorably with either cobalt molybdate or molybdenum oxide as hydrodesulfurization catalysts.



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TABLE I  
CHARGE OIL & RECYCLE GAS INSPECTION DATA

Charge Oil - Husky No. 3 Fuel Oil  
% Sulfur - 2.176  
Gravity °A.P.I. 29.7

A.S.T.M. Distillation

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

Recycle Gas - Catforming Gas

Composition Vol %

H <sub>2</sub>	89 %
CH <sub>4</sub>	3.5 %
C <sub>2</sub> H <sub>6</sub>	1.5 %
C <sub>3</sub> H <sub>8</sub>	2.5 %
C <sub>3</sub> H <sub>6</sub>	3.5 %

TABLE II

COMPOSITION & IDENTIFICATION OF CATALYSTS USED

Catalyst Name and Composition	Identification Code	Catalyst Manufacturer
Cobalt Molybdate 9.5% MoO <sub>3</sub> 3.0% CoO 5.0% SiO <sub>2</sub> 2.0% Graphite 80.5% Al <sub>2</sub> O <sub>3</sub>	Co-Mo-0201-T-3/16"	Harshaw Chemical Co.
Cobalt Molybdate 9.5% MoO <sub>3</sub> 3.0% CoO 5.0% SiO <sub>2</sub> 2.0% Graphite 80.5% Al <sub>2</sub> O <sub>3</sub>	Union Oil Co. Cobalt Molybdate 3/16"	Harshaw Chemical Co.
Molybdenum Oxide 16% MoO <sub>3</sub> 79% Al <sub>2</sub> O <sub>3</sub> 5% SiO <sub>2</sub>	Mo-0203-T-1/8" 160-A-2-1	Harshaw Chemical Co.
Chrome-alumina	Cr-0202-T-1/8"	Harshaw Chemical Co.
Atlantic Catformer 0.4% Platinum	Atlantic Catformer 1/8" pellets	Atlantic Refining Co.

TABLE III

TABULATED DATA FOR OIL CRACKING RUN (O.C.R. I)

Catalyst: 100 gms of Union Oil Co. Cobalt Molybdate 3/16"

Oil Charge: Husky #3 Fuel Oil -°A.P.I. 29.7 and containing 2.176% Sulfur.

Recycle Gas: Catforming (89% H<sub>2</sub>)

Reactor Pressure: 500 psig

Samp. No.	Total Hrs on Stream	Sample Wt Gms	Av. Cat. Temp °F	Space Vel. lbs oil/ lb cat hr	Recycle Ft <sup>3</sup> /bbl	Product A.P.I., % S.	Av. Gas Consumed per samp Ft <sup>3</sup> /bbl oil
1	5	2127	758	4.00	6790	34.2 0.450	0
2	13	3636	817	4.65	6300	34.5 0.386	58
3	21	3772	737	4.82	6070	33.3 0.773	39
4	29	3817	808	4.90	6000	34.3 0.406	89
5	37	3638	816	4.67	6250	34.3 0.425	101
6	45	3790	810	4.87	5960	34.1 0.445	92
7	53	3772	815	4.82	7160	34.0 0.470	107
8	61	3858	805	4.94	7000	33.7 0.510	96
9	69	3829	792	4.90	7020	33.7 0.535	90
10	77	3106	796	3.98	7580	33.9 0.450	83
11	85	2336	807	3.00	8100	34.4 0.300	147
12	93	2324	808	2.98	8150	34.5 0.311	102
13	101	2325	810	2.98	8150	34.7 0.274	88

Maximum oil charge loss 2.69% by weight.

TABLE IV  
TABULATED DATA FOR PLATINUM RUN I

Catalyst: 30 gms of Atlantic Catformer Catalyst regenerated 4 times and not used after last regeneration.  
 Recycle Gas: Catforming (89% H<sub>2</sub>)  
 Oil Charge: Husky #3 Fuel Oil - 2.176% Sulfur and 29.7°A.P.I.  
 Reactor Pressure: 400 psig

Samp No.	Total Hrs on Stream	Sample Wt Gms	Av. Cat. Temp °F	Space Vel. lbs oil/ lb cat hr	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I.	% S.
0	4.5	388	755	10.0	8000	31.0	1.972
1	10.0	1666	756	10.1	7920	30.5	1.987
2	18.0	2452	749	10.2	7800	30.4	2.047

Remarks: Catalyst bed 2.5 inches deep.  
 No oil loss detectable.

TABLE V  
TABULATED DATA FOR PLATINUM RUN II

Catalyst: 100 gms of Atlantic Catformer Catalyst regenerated 4 times and not used after last regeneration.  
 Oil Charge: Husky #3 Fuel Oil - 2.176% Sulfur and 29.7°A.P.I.  
 Recycle Gas: Catforming (89% H<sub>2</sub>).  
 Reactor Pressure: 500 psig

Samp No.	Total Hrs on Stream	Sample Wt Gms	Av. Cat. Temp °F	Space Vel. lbs oil/ lb cat hr	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I.	% S.
1	10	734	769	0.941	8500	33.3	0.904
2	18	737	779	0.945	8450	33.4	0.931

Remarks: Oil lost in reaction 2.5% by weight.  
 Catalyst bed 8.3 inches deep.  
 At the end of the run a portion of the catalyst at the bottom of the bed looked untouched while the remainder was black.

TABLE VI  
TABULATED DATA FOR CHROME ALUMINA RUN I

Catalyst: 100 gms of Harshaw Cr-0202 T 1/8"  
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7° A.P.I.  
Recycle Gas: Catforming (89% H<sub>2</sub>)  
Reactor Pressure: 500 psig

Samp No.	Total Hrs on Stream	Sample Wt Gms	Av. Cat. Temp °F	Space Vel. lbs oil/ lb cat hr	Recycle Ft <sup>3</sup> /bbbl	Product °A.P.I	% S.
0	5.5	408	779	1.000	8000	33.2	0.872
1	13.5	794	774	1.017	8060	33.0	0.814
2	21.5	782	775	1.000	8000	33.0	0.836
3	29.5	802	764	1.024	7800	32.5	---
4	37.5	359	779	0.460	9350	33.5	0.668
5	45.5	390	786	0.499	8600	33.8	0.569
6	53.5	379	775	0.485	8850	33.4	0.613

Remarks: Oil lost in reaction 2.4% by weight.  
Catalyst removed from reactor had same appearance as when charged.



TABLE VII  
TABULATED DATA FOR MOLYBDENUM OXIDE STATISTICAL RUN (SET 1)

Catalyst: 100 gms of Harshaw Mo-0203-T 1/8" 160 A-2-1  
 Oil Charge: Husky #3 Fuel Oil -°A.P.I. 29.7 and containing 2.176% sulfur  
 Recycle Gas: Catforming Gas (89% H<sub>2</sub>)  
 Reactor Pressure: 500 psig

Run No.	Samp. No.	Total Hrs on Stream	Sample Wt. Gms.	Av. Cat. Temp °F	Space Vel. lbs oil/lb cat. hr.	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I.	% S.	Av. Gas Consumed per Samp. Ft <sup>3</sup> /bbl oil
0	0	8	---	---	---	---	---	---	
	1	16	1096	780	1.400	8580	35.2	0.321	
	2	24	1062	774	1.362	9350	35.1	0.342	192
1	3	32	1047	777	1.340	9400	34.9	0.313	
	4	40	1101	775	1.410	8930	35.0	0.354	
	5	48	1094	775	1.400	9010	34.7	0.348	188
	Av. 4 & 5			775	1.405	8970	34.8	0.351	
2	6	56	490	779	0.620	5790	35.0	0.260	
	7	64	439	775	0.556	6620	35.2	0.190	
	8	72	472	777	0.599	6000	35.2	0.208	63
	Av. 7 & 8			776	0.578	6310	35.2	0.199	
3	9	80	766	776	0.998	7610	34.9	0.298	
	10	88	780	775	1.000	7580	34.5	0.344	
	11	96	778	775	1.000	7600	34.6	0.358	62
	Av. 10 & 11			775	1.000	7590	34.6	0.351	
4	12	104	472	774	0.605	7460	34.8	0.282	
	13	112	464	776	0.595	7520	35.0	0.251	
	14	120	455	774	0.585	7640	35.0	0.255	57
	Av. 13 & 14			775	0.590	7580	35.0	0.253	

TABLE VII (cont'd)  
 TABULATED DATA FOR MOLYBDENUM OXIDE STATISTICAL RUN (SET 1)

Run No.	Samp. No.	Total Hrs on Stream	Sample Wt. Gms	Av. Cat. Temp °F	Space Vel. lbs oil/lb cat hr	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I. % S.	Av. Gas Consumed per samp. Ft <sup>3</sup> /bbl oil
5	15	128	764	728	0.978	7760	33.8 0.574	241
	16	136	800	725	1.021	7410	33.6 0.712	
	17	144	816	724	1.046	7270	33.6 0.722	
	Av. 16 & 17			724	1.033	7340	33.6 0.717	
6	18	152	506	775	0.648	8230	35.3 0.401	97
	19	160	487	775	0.622	8700	34.8 0.267	
	20	168	472	775	0.604	8850	34.9 0.272	
	Av. 19 & 20			775	0.613	8775	34.8 0.270	
7	21	176	1058	779	1.355	7740	34.3 0.459	95
	22	184	1121	775	1.436	7300	34.1 0.527	
	23	192	1099	775	1.406	7440	34.1 0.540	
	Av. 22 & 23			775	1.421	7370	34.1 0.534	
8	24	200	1102	778	1.419	5920	33.8 0.504	50
	25	208	1102	779	1.419	5920	33.7 0.541	
	26	216	1090	775	1.400	5950	33.7 0.555	
	Av. 25 & 26			777	1.410	5935	33.7 0.548	
9	27	224	462	730	0.594	7690	33.6 0.566	120
	28	232	481	725	0.616	7250	33.6 0.568	
	29	240	479	726	0.615	7370	33.6 0.574	
	Av. 28 & 29			726	0.616	7310	33.6 0.571	
10	30	248	779	772	1.025	6050	34.0 0.519	74
	31	256	801	776	1.028	5920	34.1 0.478	
	32	264	807	775	1.035	5875	34.1 0.486	
	Av. 31 & 32			776	1.032	5902	34.1 0.482	

TABLE VII(cont'd)  
 TABULATED DATA FOR MOLYBDENUM OXIDE STATISTICAL RUN (SET 1)

Run No.	Samp. No.	Total Hrs on Stream	Sample Wt. Gms.	Av. Cat. Temp °F	Space Vel. lbs oil/lb cat hr	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I.	% S.	Av. Gas Consumed per samp. Ft <sup>3</sup> /bbl oil
17	33	272	754	777	0.970	9190	34.2	0.446	138
	34	280	747	777	0.961	9350	34.2	0.444	
	35	288	769	775	0.988	9090	34.0	0.450	
	Av. 34 & 35			776	0.974	9220	34.1	0.447	
11	36	296	756	719	0.974	9250	33.2	0.810	54
	37	304	737	725	0.948	9500	33.1	0.805	
	38	312	660	724	0.850	10600	33.3	0.752	
	Av. 37 & 38			724	0.899	10050	33.2	0.778	
12	39	320	1022	724	1.312	6390	32.7	0.933	66
	40	328	1116	722	1.431	5850	32.6	1.020	
	41	336	1155	724	1.485	5650	32.6	1.025	
	Av. 40 & 41			723	1.458	5750	32.6	1.022	
13	42	344	1126	728	1.445	7220	32.7	0.945	39
	43	352	1078	726	1.382	7560	32.6	0.947	
	44	360	1124	725	1.445	7250	32.5	0.976	
	Av. 43 & 44			726	1.413	7405	32.6	0.961	
14	45	368	786	729	1.010	6040	32.6	0.876	100
	46	376	783	724	1.004	6060	32.8	0.845	
	47	384	792	725	1.018	5960	32.8	0.872	
	Av. 46 & 47			724	1.011	6010	32.8	0.858	
15	48	392	432	727	0.554	6600	33	0.677	111
	49	400	349	727	0.446	8150	33.3	0.612	
	50	408	511	725	0.653	5590	33.4	0.595	
	Av. 49 & 50			726	0.549	6870	33.4	0.604	

TABLE VII (cont'd)  
 TABULATED DATA FOR MOLYBDENUM OXIDE STATISTICAL RUN (SET 1)

Run No.	Samp. No.	Total Hrs on Stream	Sample Wt. Gms.	Av. Cat Temp °F	Space Vel. lbs oil/lb cat.hr	Recycle Ft <sup>3</sup> /bbl	Product °A.P.I.	% S	Av. Gas Consumed per samp. Ft <sup>3</sup> /bbl oil
16	51	416	1008	722	1.275	9900	32.9	0.996	283
	52	424	1116	725	1.413	8840	32.6	0.913	
	53	432	1123	725	1.425	8810	32.6	0.940	
	Av. 52 & 53			725	1.419	8825	32.6	0.927	
18	54	440	483	726	0.611	8880	33.0	0.730	199
	55	448	443	723	0.560	9560	33.6	0.565	
	56	456	457	725	0.580	9300	33.6	0.578	
	Av. 55 & 56			724	0.570	9430	33.6	0.572	





























































