



Catalytic hydrodesulfurization of fuel oil  
by Albert J Westby

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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Abstract:

The purpose of the first part of this research was to determine which of several catalysts could be used to desulfurize Husky No. 3 fuel oil (2.04 percent sulfur) using catforming gas (89 percent hydrogen).

Suitable catalysts were compared with Harshaw Chemical Company's cobalt molybdate and molybdenum oxide catalysts as to activity and rate of degeneration. The effluent oil was to be less than 0.5 percent sulfur before the catalyst would be accepted.

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Girdler's molybdenum oxide catalyst gave results which compared favorably with Harshaw's molybdenum oxide on the basis of a 24-hour run for each catalyst.

Porocel's molybdenum oxide catalyst yielded an oil which contained less than 0.4 percent sulfur. This catalyst did not compare favorably with Harshaw's molybdenum oxide in either rate of degeneration or activity.

Peter Spence and Sons' cobalt molybdate catalyst yielded an effluent oil which contained less than 0.1 percent sulfur after 112 hours on stream. This catalyst was superior to Harshaw's molybdenum oxide but inferior to Harshaw's cobalt molybdate in rate of degeneration and in activity.

A study was made of the effect of using mixed gases containing hydrogen and hydrocarbon gases versus the effect of using pure hydrogen at a total pressure equivalent to the partial pressure of hydrogen in the mixed gas system. Husky No. 3 fuel oil was desulfurized in both of these atmospheres using identical conditions of space velocity and temperature. When using Union Oil Company's cobalt molybdate catalyst at 200 psig pressure of hydrogen, pure hydrogen gave better results than mixed gases. When using Filtrol's molybdenum oxide catalyst at 300 psig pressure of hydrogen, pure hydrogen gave better results than mixed gases.

A preliminary study was made to determine optimum conditions of operation to desulfurize a light wax distillate received from Arabian American Oil Company. Optimum conditions appeared to be a space velocity of 0.3 (Formula not captured by OCR) and a temperature of 823° F when using a recycle gas containing 65 percent hydrogen at a gas recycle rate of 4000 cu. ft. per barrel of charge oil under a total pressure of 500 psig. Harshaw's molybdenum oxide catalyst was used.

All research was carried out in bench scale equipment.

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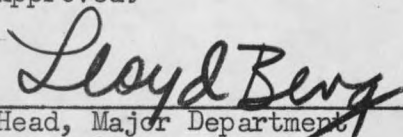
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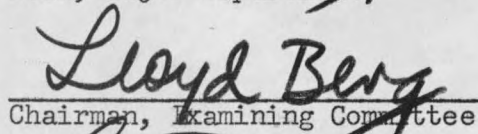
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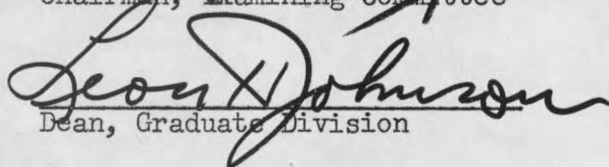
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ABSTRACT

The purpose of the first part of this research was to determine which of several catalysts could be used to desulfurize Husky No. 3 fuel oil (2.04 percent sulfur) using catforming gas (89 percent hydrogen). Suitable catalysts were compared with Harshaw Chemical Company's cobalt molybdate and molybdenum oxide catalysts as to activity and rate of degeneration. The effluent oil was to be less than 0.5 percent sulfur before the catalyst would be accepted.

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A preliminary study was made to determine optimum conditions of operation to desulfurize a light wax distillate received from Arabian American Oil Company. Optimum conditions appeared to be a space velocity of  $0.5 \frac{\text{gm oil}}{\text{gm cat. hr}}$  and a temperature of 825° F when using a recycle gas containing 65 percent hydrogen at a gas recycle rate of 4,000 cu. ft. per barrel of charge oil under a total pressure of 500 psig. Harshaw's molybdenum oxide catalyst was used.

All research was carried out in bench scale equipment.

## INTRODUCTION

Many low quality high sulfur crude oils are being used to meet the increased demand for petroleum products. Many crude oils, such as those found in certain sections of California, Texas, Wyoming, and the Arabian Middle East, are very high in sulfur content. The large reserves of oil which can be derived from shale and tar sands are also high in sulfur content. If these various sources of crude oil are to be utilized, refiners have to use various methods for desulfurizing the products, depending upon the economic situation and the relative amounts and types of sulfur compounds present.

Elemental sulfur or its compounds in petroleum products are undesirable for several reasons. They have undesirable odor and give off acrid fumes when burned. They cause corrosion to metal, poor color stability, and poor tetra ethyl lead susceptibility in gasoline. The more common forms of sulfur present in petroleum are: elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and thiophenes. The cyclic or thiophenic sulfur compounds are so stable that they are not affected by the common desulfurization methods.

In recent years, there has been a steadily increasing demand for heavy distillates for use in diesel engines, jet aircraft engines and gas turbines. The sulfur content of these heavy distillates must be less than 0.5 percent in order to prevent excessive engine wear. Higher boiling petroleum fractions tend to have a higher concentration of sulfur and a greater proportion of cyclic sulfur compounds. Many methods are available for removing or rearranging the objectionable non-cyclic sulfur compounds

but the relatively high concentrations of cyclic sulfur compounds found in some heavy distillates remain unaffected by these methods. The cyclic sulfur compounds may be partially removed by such processes as destructive hydrogenation and catalytic cracking or almost completely removed by hydroforming. However, the product oil is materially altered in basic characteristics by dehydrogenation, cracking, or other reactions if these processes are used. All sulfur compounds may be removed by selective solvent extraction but the loss of product is usually large if this method is used.

Catalytic hydrodesulfurization is the most efficient method so far found for removing the cyclic sulfur compounds. Several catalysts of varying efficiency are used as contact agents in this process. Among the most commonly used catalysts are cobalt-molybdate, molybdenum oxide, and tungsten-nickel. Besides removing sulfur, this process will remove much of the nitrogen, oxygen, and diolefins or gum forming constituents which may be present in the oil.

The process of catalytic hydrodesulfurization involves treating the oil with a large amount of hydrogen in the presence of a sulfur resistant hydrogenation catalyst under suitable conditions of temperature and pressure. Since a large amount of hydrogen is required, a cheap source of hydrogen must be available in order for this process to be economically feasible.

Munro (7) and Green (2) showed that pure hydrogen is not necessary in this process. Mixed gases, which are usually in excess of 85% hydrogen, are produced in the process of catalytic reforming and these gases may be used in catalytic hydrodesulfurization. Thus, the catalytic hydrodesulfur-

ization unit is usually operated in conjunction with the catalytic reforming unit, which is a relatively cheap source of hydrogen rich gas.

The 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 (9) has shown the critical hydrogen concentrations using a molybdenum oxide catalyst and Hooper (5) has shown them using a cobalt-molybdate catalyst.

The hydrogen rich gas used in this process is continually recycled through the system in order that the gas requirement will not be excessively high. As it is used over and over again, it picks up small amounts of hydrogen sulfide and hydrocarbon gases which are not totally condensed in the effluent oil. The rate of hydrocarbon buildup was investigated by Hartwig (4) and he claims that this rate of buildup is relatively slow. Hydrogen sulfide may be removed from the recycle gas by caustic scrubbing if desired. When the concentration of hydrogen got too low, make up gas of high hydrogen concentration was added to the system.

The hydrogen requirements for this process depend upon the nature of the charge stock, conditions employed, and the degree of desulfurization required. This hydrogen requirement is met by adding a gas to the system which is rich in hydrogen. Hartwig (4) has determined the consumption of catforming gas containing 89% hydrogen which occurs when desulfurizing a number 3 fuel oil using a molybdenum sulfide catalyst.

Hooper (5) has shown that Harshaw's cobalt molybdate catalyst gave successful desulfurization of a number 3 fuel oil for 1568 hours of on-stream time without regenerating the catalyst. This long catalyst life is

desirable because it minimizes replacement and regeneration costs. The life or activity of the catalyst is affected by tarry deposits and carbon laydown. When these deposits become excessive, as indicated by a high sulfur concentration in the effluent oil, the catalyst is regenerated by burning off the deposits with a stream of air.

Increasing the pressure promotes a higher degree of desulfurization. Koski (6) has shown the effect of pressure up to 500 psig.

Increasing the temperature also promotes a higher degree of desulfurization, but it is desirable to keep the temperature low enough to prevent excessive thermal cracking. Since the bond energy for 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), a temperature required for cracking a carbon to sulfur bond would also promote some thermal cracking.

Another factor which affects the degree of desulfurization is the space velocity. 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. A low space velocity designates greater contact time between the oil and catalyst and hence a greater degree of desulfurization than if a high space velocity were used.

The data obtained by Koski (6), Munro (7), and Green (2) permitted development of a process to desulfurize Husky's No. 3 fuel oil. Data by Hartwig (4) and Silvey (9) supplemented by previous data, were the basis for the design of a desulfurization plant constructed at Cody, Wyoming.

The purpose of this research was to continue to gather data on various catalysts in order to determine whether or not they would give successful

desulfurization of Husky No. 3 fuel oil under operating conditions of 775° F., five hundred psig pressure, and a recycle rate of 7500 to 8500 ft.<sup>3</sup> /bbl. These catalysts were also to be compared with Harshaw's molybdenum oxide and cobalt molybdate catalysts to determine which was more active. Harris (3) has shown the degree of desulfurization attainable with Harshaw's molybdenum oxide and cobalt molybdate catalysts and also with Union Oil Company's cobalt molybdate catalyst under various operating conditions.

The catalysts tested were Porocel's supported molybdena catalyst, Filtrol's molybdena impregnated alumina, National Aluminate Corporation's pelleted  $\text{Al}_2\text{O}_3\text{-MoO}_3$ , a germanium supported Filtrol catalyst, Girdler's molybdena alumina, and a cobalt molybdate catalyst manufactured by Peter Spence & Sons, Ltd. Data for these catalysts, including the approximate composition, catalyst reference, and catalyst maker, are given in Table III of the appendix.

A partial pressure study was undertaken to determine whether there was any point at which mixed gases containing hydrogen would give as good or better desulfurization than pure hydrogen at equivalent partial pressures of hydrogen.

Some preliminary research was carried out on a light wax distillate received from the Arabian-American Oil Company (Aramco) to determine the optimum operating conditions for successful desulfurization of this oil.

## EQUIPMENT

A schematic flow diagram of the desulfurization unit is shown in Figure 1. The unit may be divided into two sections, the reactor and condenser section and the gas recycle section. These two sections will be described separately.

### Reactor and Condenser Section

The reactor was a 16-inch length of  $1\frac{1}{2}$  inch extra strong black iron pipe. The top of the reactor was fitted with a  $1\frac{1}{2}$  to  $3/4$ -inch reducer to which was attached a union, two crosses, and an assembly of valves for oil inlet, recycle gas inlet, and air inlet for catalyst regeneration, and a 1200 pound frangible disk safety blowout. The thermowell was a length of  $\frac{1}{4}$  inch extra strong black iron pipe welded shut at one end. This thermowell was extended downward through the cross attached to the top of the reactor and was of such a length that it extended to within 1 inch of the bottom of the  $1\frac{1}{2}$  inch reactor pipe. Three iron-constantan thermocouples inserted into the top of the thermowell could be adjusted to any desired height within the center of the reactor.

At the bottom of the reactor was a  $1\frac{1}{2}$  to  $\frac{1}{2}$ -inch reducer. A  $\frac{1}{2}$ -inch union was attached to the reducer and the condenser was attached to this union. The condenser consisted of a 21-inch length of  $\frac{1}{2}$ -inch pipe with a 3-inch pipe as a water jacket. An assembly which was connected to the bottom of the condenser consisted of a cross, two tees, a pressure gauge, a 12-inch length of two-inch pipe which acted as a capacity tank for holding the product oil, 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. Extra capacity was added to the Jerguson receiver because it often happened that the product oil was allowed to overflow the receiver with its small capacity. This loss of oil was prevented upon addition of the capacity tank to the system. A Fisher-Wizard proportional controller was used in conjunction with the Mason-Neilan valve to maintain the correct pressure in the reactor and condenser.

The product oil was allowed to flow from the Jerguson receiver into a one-liter Erlenmeyer flask. Dissolved gases in the oil flashed off and were passed through caustic scrubbers to remove the hydrogen sulfide. The sweet gases were then metered in a wet test meter manufactured by the Precision Scientific Company.

The reactor was wound with asbestos tape over which was wound three 33-foot lengths of beaded nichrome wire which served as heating coils. The coils were insulated with an additional layer of asbestos tape and a two-inch layer of magnesia mud. Each of the heating coils was connected through a 0-5 amp ammeter to a Powerstat Variac which provided the means of temperature adjustment.

The preheat section of the reactor was filled with 1/8-inch alundum balls which acted 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 feed oil was kept in a 2 inch pipe 20 inches long which acted as a reservoir. A burette was attached to this pipe to facilitate the measurement of space velocities. An adjustable stroke piston pump was used to pump the feed oil from the reservoir to the reactor.

The iron-constantan thermocouples were used in conjunction with a Leeds and Northrup indicating potentiometer for temperature measurement.

#### Gas Recycle Section

Three tanks were used in the gas recycle section: A surge tank, a compression tank, and a feed tank. The surge and compression tanks were number two gas cylinders and the feed tank was a number one gas cylinder. These tanks could all be isolated from each other or from the system by means of a system of valves on top of each tank. On top of each tank was a cross and a pressure gauge. The surge tank was connected to the reactor section through the Mason-Nielan valve and the feed tank was connected to the top of the reactor through an American Instrument Company needle valve which regulated gas flow through a Fisher flowrater which metered the gas. One side of the compression tank was connected to the feed tank and the other side to the surge tank. All connections in the gas recycle section, with the exception of the recompression oil lines, were made with 1/8 inch stainless steel high pressure tubing.

The compression oil was kept in a 5 gallon tank which served as a reservoir for oil storage. This tank was connected to the inlet of a Pesco gear pump. The outlet of the pump was connected to the compression tank through a 1200 pound unloading relief valve. In case the pressure exceeded 1200 pounds in the compression tank, the oil would be returned to the oil reservoir through the unloading relief valve. When compression was complete, the oil was returned to the oil reservoir through a line which bypassed the pump. This line was fitted with a valve so it could be closed or opened, as desired. These recompression oil lines were all of 1/8 inch

Schedule 40 black iron pipe.

A tank containing makeup gas was connected to the gas recycle section through a tee located between the surge and compression tanks. Makeup gas was metered through a Brooks rotameter. There was a line which bypassed the Brooks rotameter so that the gas could be added directly and more rapidly if desired.

Recycle gas samples were taken from the feed cylinder at periodic intervals and collected in 8-liter glass sample bottles. The analysis of these samples was made in a low temperature micro-still with a Micromax automatic temperature recording device made by the Leeds and Northrup Company. Liquid nitrogen was used for the cooling medium when making a gas analysis.

#### MATERIALS

Husky Oil Company's No. 3 fuel oil was used as the feed during the greater part of this research. This oil varied between 2.04 and 2.12 percent sulfur and had an A.P.I. gravity of 29.7. Further information on this oil is found in Table I in the appendix.

A light wax distillate obtained from the Arabian American Oil Company was studied briefly to determine the optimum operating conditions necessary to obtain the best desulfurization. Some information concerning the properties of this oil can be found in the appendix in Table I.

Data for all the catalysts used in this research may be found in Table III. A description of all the gases used in this research is given in Table II.

METHODS

The reactor was filled with catalyst and connected in its proper place in the system. Heating was started by applying current to the heating coils by means of the Variacs. The system was purged of air by running catforming gas through the reactor and out through the bleed off line for a short period of time. The reactor was then pressurized with catforming gas and the proportional controller was set so that the desired pressure was maintained. The gas flow was maintained at the desired flow rate at all times. Excess oil from the previous run was bled out of the Jerguson receiver into the Erlenmeyer flask and was discarded. The flask was then cleaned and replaced in its position.

When the temperature was up to within several degrees of the desired operating temperature, the feed pump was started. The space velocity was set by adjusting the stroke of the piston in the feed pump. The temperatures were lined out during the interval of time it took the product oil to reach a specified height in the Jerguson receiver. The usual operating conditions were: a temperature of  $413^{\circ}$  Centigrade, a pressure of 500 psig, and a gas recycle rate of 8000 cu. ft. per barrel of feed oil.

Data was taken as soon as the product oil reached the specified point on the Jerguson receiver. Readings of temperature, pressure, and flowrator reading were taken at half hour intervals and recorded on the data sheet. A sample of product oil was taken every eight hours. This sample was weighed and stored in glass sample bottles to be kept for further analysis. The feed reservoir was filled at the beginning and at the end of each 8-hour sample period from a glass bottle containing the feed oil. The dif-

ference in weight of the feed bottle between the beginning and end of the sample period was equivalent to the weight of feed pumped to the reactor.

The oil in the Jerguson receiver contained some dissolved gases which flashed off when the oil was drained into the receiving flask. These gases were passed through the caustic scrubbing train to remove hydrogen sulfide and then were metered through the wet test meter. Wet test meter readings were taken every eight hours, at the same time that the oil samples were taken.

The oil was never allowed to drain completely from the Jerguson Pressure receiver during a run thus forming a liquid seal which prevented the recycle gas from escaping. The recycle gas flowed through the Mason-Nielan valve into the surge and compression tanks. When the pressure in either the feed tank or the surge tank approached within 50 psig of the reactor pressure, recompression was started. The compression tank was isolated from the surge tank and the gas contained in the compression tank was forced back into the feed tank by means of the hydraulic gear pump and compression oil. The length of time between compressions varied with the flow rate of the gas through the reactor. Arbitrary "standard" conditions for pressures in the three tanks were 650 psig in the feed tank and 300 psig in the surge and compression tanks. Makeup gas was added periodically so that the "standard" conditions in the three tanks could be maintained as closely as possible at all times. Gas flow from the makeup tank was metered through a Brooks rotameter and this flow was timed with a stopwatch. Time of flow and rotameter reading were recorded each time gas was added.

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 small portion of each sample was washed once in an eight percent sodium hydroxide solution and then three times with distilled water. Sulfur determinations were then run on these washed samples using the lamp method (1).

#### SAMPLE CALCULATIONS

The tabulation of data for all runs made in this series appears in Table IV through XXXII. The calculated values are space velocity, recycle rate, and gas consumption. All other values were obtained by direct observation or chemical analysis.

Space velocity was based on the weight of feed oil per sample period which is obtained by dividing the sample weight by the percent yield. An average percent yield over the entire run was used to minimize errors in weighing the product and the feed and to minimize drainage errors which occur when the sample is drained from the reactor. For a sample weighing 780 grams and a yield of 0.975, the weight of feed oil would be:

$$\frac{780 \text{ gm product}}{0.975 \text{ gm product/gm. feed}} = 800 \text{ gm. feed}$$

The sample period is 8 hours and 100 gms. of catalyst are used. Therefore, the space velocity for this case would be:

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

Recycle rate was expressed as standard cubic feet per barrel of feed oil (SCF/bbl) and was calculated by dividing the gas flow per sample period

by the feed oil weight per sample period. The feed oil in most cases was Husky #3 fuel oil which had an A.P.I. gravity of 29.7°. This corresponds to a density of 0.875 gm/c.c.

For the case where there are 800 gms. of feed oil per sample period and the recycle rate, measured by the Fisher flowrater and corrected to STP is 1300 liters per 8 hour sample period, the recycle rate is:

$$\frac{1300 \text{ liters}}{800 \text{ gms}} \times \frac{1000 \text{ gms}}{\text{Kgm}} = 1628 \frac{\text{liters}}{\text{Kgm}}$$

The conversion factor for converting  $\frac{\text{liters}}{\text{Kgm}}$  to SCF/bbl is calculated as follows:

$$\begin{aligned} \frac{0.875 \text{ gms oil}}{\text{c.c. oil}} \times \frac{1000 \text{ c.c.}}{\text{liter}} \times \frac{28.32 \text{ liters}}{7.48 \text{ gal.}} \times \frac{42 \text{ gal}}{\text{bbl.}} \times \frac{1 \text{ kgm}}{1000 \text{ gm}} \\ \times \frac{1 \text{ ft.}^3}{28.32 \text{ liters}} = \frac{4.91 \text{ kgm ft.}^3}{\text{liters bbl.}} \end{aligned}$$

The recycle rate in SCF/bbl is:

$$1628 \frac{\text{liters}}{\text{kgm}} \times \frac{4.91 \text{ kgm ft.}^3}{\text{liters bbl.}} = 8000 \frac{\text{SCF}}{\text{bbl}}$$

Gas 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 a period during which the feed oil weight was 800 gm, 40 liters (STP) of makeup gas were added, and 8 liters (STP) of bleedoff gas were recorded, the gas consumption would be:

$$\frac{(40-8) \text{ liters}}{0.8 \text{ kgm}} \times \frac{4.91 \text{ kgm ft.}^3}{\text{liters bbl}} = 196.4 \frac{\text{ft.}^3}{\text{bbl}}$$

Gas consumption varied greatly between samples of the same run so the values recorded represent cumulative averages. For the Aramco runs (Tables

XXXI and XXXII) the gas consumption represents the average of the cumulative averages for the three samples in each run.

#### DISCUSSION

The oil used throughout the catalyst investigation was Husky No. 3 fuel oil. The same operating conditions were used on each run so that results which could be compared would be obtained. These operating conditions were a temperature of 775° F, pressure of 500 psig, and gas recycle rate of 7500-8500 cu. ft. per barrel of charge oil. The percent sulfur in the charge oil varied from 2.18 for the first sample to 2.04 for the second and third samples during the period of time that the catalyst study runs lasted so it was necessary to use the grams of sulfur removed per kilogram of charge oil for the dependent variable rather than using the percent sulfur obtained in the effluent oil.

A statistical approach was used in comparing most of the catalysts tested. Linear regressions were calculated for the runs which showed a linear trend, as indicated by plots of grams of sulfur removed per kilogram charge oil versus hours on stream. The slopes of these lines were compared to gain some information as to which catalysts deteriorated most rapidly. Finally, analyses of variance were made to determine which catalysts, if any, gave desulfurization which was equivalent to, or better than, that obtained with Harshaw's molybdenum oxide, Mo-0203-T-1/8" or with Harshaw's cobalt molybdate, CoMo-0201-T-3/16".

A graphical comparison was made for the partial pressure studies. Statistical procedures were used for part of these studies but could not be used for all of them because some of the results obtained seemed to be

inconsistent.

A statistical approach was planned in evaluating the data from the Arabian-American Oil Company's light wax distillate but could not be carried out for reasons which will be explained later.

#### COMPARISON OF CATALYSTS

Charge oil and recycle gas inspection data are given in Table I and II respectively. Table III shows the catalysts used, their designation, and the manufacturer.

Results of reference catalyst runs CMR-1 and MOS-V, using Harshaw's CoMo-0201-T-3/16" and Harshaw's Mo-0203-T-1/8" respectively as catalysts are tabulated in Tables XIX and XX.

The data from runs Moly Filtrol-1, -2, and -3 are recorded in Tables IV, V, and VI respectively. The catalyst used was Filtrol's molybdena catalyst, designated SV-5003, and containing 10 percent MoO<sub>3</sub>. The data for Moly Filtrol 1 and 3 are plotted in Figures 2 and 3.

A comparison of Tables IV and V shows that the catalyst lost its activity after regeneration. For the first 17 hours on stream the fresh catalyst produced oil which was less than 0.5 percent sulfur. Since the desulfurization attainable may have been dependent on pellet size this indicated that it might be desirable to test a smaller pellet size so the 1/4" pellets were broken up to approximately 1/8" particles and run Moly Filtrol-3 was made. This run produced specification oil (less than 0.5 percent sulfur) for the first 55 hours on stream.

Reference to Figure 2 shows that no linear trend is obtained for either Moly Filtrol-1 or Moly Filtrol-3. Table XXXVIII shows a significant differ-

ence in the desulfurization obtained during these two runs, so the smaller pellet size seems to merit further investigation. Table XXXVIII also shows that the results obtained from run Moly Filtrol-3 are significantly different from those obtained during run MOS-V. Figure 3 verifies this conclusion. Run MOS-V employed Harshaw's Mo-0203-T-1/8" catalyst. Therefore, Filtrol's molybdena catalyst is inferior to Harshaw's.

Data from Runs Moly-National-1 and -2 are tabulated in Tables VII and VIII respectively. The National Aluminate Corporation's pelleted  $Al_2O_3-MoO_3$  catalyst containing 10.9%  $MoO_3$  was used fresh for the first run and then regenerated for the second run. Comparisons between Tables VII and VIII show that this catalyst loses its activity after regeneration.

The linear regression for pelleted  $Al_2O_3-MoO_3$  catalyst is given in Table XXXVI. Table XXXVII compares its rate of degeneration with that of Harshaw's Mo-0203-T-1/8" catalyst and it is found that the rate of degeneration is significantly greater for pelleted  $Al_2O_3-MoO_3$  than for Mo-0203-T-1/8". The desulfurization did not differ significantly between runs Moly-National-1 and Moly Filtrol-3. Therefore, National Aluminate Corporation molybdena catalyst is inferior to Harshaw's in two respects. It gives less desulfurization and it loses its activity faster.

After the results obtained from Filtrol's SV-5003 catalyst were noted, a new catalyst in smaller pellet size was ordered from the Filtrol Corporation. Filtrol's SV-5003 was supplied as 1/4" pellets and the new catalyst, designated R-34114 and containing  $16\frac{1}{2}$  percent  $MoO_3$ , was supplied as 1/8" pellets. Runs Moly Filtrol R-34114-1 and -2, the first made with fresh catalyst and the second made with regenerated catalyst, gave results which

are tabulated in Table IX and X respectively. These results are plotted in Figure 4 and the linear regressions, comparison of rates of degeneration, and comparison of desulfurization obtained are given in Tables XXXVI, XXXVII, and XXXVIII respectively. These comparisons show that neither the rate of loss of activity nor the desulfurization obtainable is affected significantly by regeneration of the catalyst. Filtrol's R-3414 catalyst was not active enough to yield an oil which met specifications under the standard operating conditions.

Since Filtrol's R-3414 catalyst was not sufficiently active to provide specification oil, two new catalysts were ordered from the Filtrol Corporation, one containing 5 percent germanium as  $\text{GeO}_2$  and the other to be used for comparison with the germanium promoted catalyst. These two catalysts were designated as R-3431 and R-3432 respectively and were both in the form of 3/16" pellets. Tabulated data for runs Moly Filtrol R-3431, R-3431 (hydrogenated) and R-3432 appear in Tables XI, XII, and XIII respectively.

Filtrol's R-3431 catalyst, containing 5 percent germanium as  $\text{GeO}_2$ , gave results which compared with Filtrol's R-3414 catalyst, and specification oil was not produced. Hydrogenating the  $\text{GeO}_2$  to produce germanium metal seemed to have no effect on the desulfurization attained.

The oil produced during the 21 hours of on stream time with Filtrol's R-3432 catalyst was all less than 0.5 percent sulfur. This led to the conclusion that there might have been a mixup in catalyst designations so a check was made with the Filtrol Corporation. This check revealed that, according to Filtrol's records, the designations were correct, so the only conclusion to be drawn is that  $\text{GeO}_2$  does not enhance the activity of

Filtrol's catalyst.

The results obtained with Girdler's catalyst, designated Sample No. 1319-A, are tabulated in Table XIV. A short run of 24 hours duration was made using Harshaw's Mo-0203-T-1/8" catalyst for comparison with the Girdler catalyst run. The results of this short run are tabulated in Table XV.

Effluent oil from the Girdler catalyst run averaged 0.402 percent sulfur while that from the short run on Harshaw's Mo-0203-T-1/8" catalyst averaged 0.421 percent sulfur. On the basis of a short run of 24 hours duration, Girdler's catalyst, containing 12-13 percent MoO<sub>3</sub> in the form of 1/4" pellets, seems to compare favorably with Harshaw's Mo-0203-T-1/8" catalyst.

Tabulated data from runs Porocel-1, and Porocel-2 are given in Tables XVI and XVII respectively. These data are plotted in Figures 4 and 5. The two runs specified were made with two different samples of the same catalyst. Run Porocel-1 was made with a catalyst containing 5-10 percent Mo as MoO<sub>3</sub> in 4/8 mesh particle sizes and designated as Sample No. SB-73-54. Run Porocel-2 utilized a catalyst which contained 5-10 percent Mo as MoO<sub>3</sub> in 4/8 mesh particle sizes and designated as Sample No. SB-64-55.

Figure 5 reveals that the two samples yielded equivalent desulfurization of Husky No. 3 fuel oil under the standard operating conditions. Figure 6 shows the sulfur removal obtained during run Porocel-1 as compared with that obtained during run MOS-V.

The linear regression, comparison of rate of degeneration, and comparison of desulfurization attainable for run Porocel-1 appear in Table XXXVI, XXXVII, and XXXVIII respectively.

Porocel Sample No. SB-73-54 loses its activity at a rate which is significantly greater than the rate at which Harshaw Mo-0203-T-1/8" loses its activity. The desulfurization obtainable with the Porocel catalyst is significantly less than that obtained using Harshaw's catalyst. The analysis of variance comparing the results of run Porocel-1 with those of run Porocel-2 shows that there is no significant difference between the two runs. This result verifies the conclusion drawn from Figure 5.

Run Porocel-1 was made using a charge oil which was 2.12 percent sulfur. The sulfur content of the charge oil for run Porocel-2 was 2.04 percent. These two runs yielded effluent oils containing an average of 0.390 percent sulfur during 41 hours on stream for Porocel-1 and 0.271 percent sulfur during 24 hours on stream for Porocel-2. All effluent oil from both runs was less than 0.5 percent sulfur. These sulfurs correspond to 18.30 and 17.69 grams of sulfur removed per kilogram of charge oil for runs Porocel-1 and Porocel-2 respectively. Analysis of variance showed that these two values were not significantly different.

A catalyst was received from Peter Spence and Sons, Ltd. which employed a graphite base rather than an alumina base, which was employed in most other catalysts. This was a cobalt molybdate catalyst containing 3.5 percent  $\text{CoO}$  and 10.0 percent  $\text{MoO}_3$ . The results obtained upon testing this catalyst are tabulated under the name of Run Cobalt Molybdate, Graphite Type, in Table XVIII.

Run Cobalt Molybdate, Graphite type, was compared with Run CMR-1 and Run MOS-V. Run CMR-1 employed Harshaw's Cobalt Molybdate, designated CoMo-0201-T-3/16", as a catalyst. Run MOS-V was carried out using Harshaw's

Mo-0203-T-1/8" catalyst. The data from Cobalt Molybdate, graphite type is compared with Run CMR-1 in Figure 7 and with Run MOS-V in Figure 8. The linear regression, comparisons of rates of degeneration, and comparison of the degree of desulfurization attainable for these three runs appear in Tables XXXVI, XXXVII, and XXXVIII, respectively.

The rate of catalyst degeneration for Run Cobalt Molybdate, Graphite type was found to be significantly greater than that for Run CMR-1 but significantly less than that for Run MOS-V. The desulfurization obtained was significantly less than for Run CMR-1 but significantly greater than for Run MOS-V.

Effluent oil from Run Cobalt Molybdate, Graphite type, contained less than 0.1 percent sulfur after 112 hours on stream. This indicates that it is a suitable catalyst for use in desulfurizing Husky No. 3 fuel oil at the standard operating conditions of 775° F., 500 psig pressure, and a gas recycle rate of 7500-8500 cu. ft. per barrel of charge oil.

#### PARTIAL PRESSURE STUDIES

Data from Run FUR-3 are tabulated in Table XXI and from Run Cobalt Molybdate-H<sub>2</sub> in Table XXII. Union Oil Company's Cobalt Molybdate catalyst was used during both of these runs.

Run FUR-1 was made using a recycle gas which was 25.3 percent hydrogen plus nitrogen at a total pressure of 800 psig. From the original data (5) it is logical to assume that the nitrogen content of this gas was negligible compared to the hydrogen content and therefore the gas contained about 25 percent hydrogen. Calculations on this basis show that the partial pressure of hydrogen on the system is 200 psig if the perfect gas law is





















































































































