



Catalytic hydrodesulfurization of fuel oil
by Albert J Westby

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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.

The Filtrol Corporation's molybdenum oxide catalysts did not yield an oil which met specifications. National Aluminate Corporation's molybdenum oxide catalyst did not give acceptable results.

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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ABSTRACT

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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.³/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° 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_3 . 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-O2O3-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 $\text{Al}_2\text{O}_3\text{-MoO}_3$ 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 $\text{Al}_2\text{O}_3\text{-MoO}_3$ catalyst is given in Table XXXVI. Table XXXVII compares its rate of degeneration with that of Harshaw's Mo-O2O3-T-1/8" catalyst and it is found that the rate of degeneration is significantly greater for pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$ than for Mo-O2O3-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 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 GeO_2 , gave results which compared with Filtrol's R-3414 catalyst, and specification oil was not produced. Hydrogenating the 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 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_3 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_3 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_3 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 CoO and 10.0 percent 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-H₂ 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

assumed to hold.

Run Cobalt Molybdate-H₂ used pure hydrogen as the recycle gas and was operated at a total pressure of 200 psig. Union Oil Company's Cobalt Molybdate catalyst was used for both runs.

The data for these two runs are plotted in Figure 9. These data indicate that better desulfurization is obtained using pure hydrogen at a total pressure of 200 psig than when using mixed gases containing 25 percent hydrogen under a total pressure of 800 psig (partial pressure of hydrogen equal to 200 psig). This conclusion is verified by the analysis of variance in Table XXXVII, which shows that the desulfurization obtained during Run Cobalt Molybdate-H₂ was significantly greater than that obtained during Run FUR-3. The regression lines for these two runs are given in Table XXXVI. The comparison of the slopes of these regression lines, given in Table XXXVII, shows that there is no significant difference in the rate of decrease of catalyst activity under the conditions used in these two runs.

Five runs were made using pure hydrogen as the recycle gas and varying the pressure on the system and using Filtrol's R-3414 catalyst. Pressures of 100, 200, 300, 400, and 500 psig were used. The results of these runs are given in Tables XXIII, XXIV, XXV, XXVI and XXVII. Three runs were made utilizing mixed gases and operating under a total pressure of 500 psig in each case. The gas mixtures used consisted mainly of hydrogen and methane with a small percentage of ethane and other hydrocarbon gases. These gases were 15.6 percent hydrogen in Run R-3414-1 P.P., 35.0 percent hydrogen in Run R-3414-2 P.P., and 59.8 percent hydrogen in Run R-3414-3

P.P. The run designation signifies that Filtrol's R-3414 was used as a catalyst and the figure after this indicates the supposed partial pressure of hydrogen in hundreds of pounds. Analysis of recycle gas after each run made possible a more accurate calculation of the partial pressure of hydrogen on the system. These gas analyses are given in Table II.

The pure hydrogen runs were made in order of increasing pressure without regenerating the catalyst between runs. The first pure hydrogen run lasted 46 hours and the others lasted for 48 hours each. The average of the sulfurs obtained for each run were utilized in the plot of percent sulfur in effluent oil versus operating partial pressure of hydrogen given in Figure 10.

The mixed gas runs were made in the order R-3414-2 P.P., R-3414-1 P.P., then R-3414-3 P.P. The data for these three runs is tabulated in Tables XXVIII, XXIX, and XXX. The averages of these three runs are also plotted in Figure 10. These runs were made in the order mentioned above without regenerating the catalyst between runs.

Loss of catalyst activity seems to be a major factor in these runs. Each of the pure hydrogen runs was on stream for 48 hours with the exception of the first which lasted 46 hours. Hence, the run utilizing 200 psig pressure was made using a catalyst which had already been on stream for 46 hours. However, the mixed gas run which corresponded to 200 psig partial pressure of hydrogen was made using fresh catalyst. This may have been the reason for the inconsistencies in Figure 10. It cannot be stated positively that the desulfurization obtainable at 200 psig partial pressure of hydrogen is greater using mixed gases than using pure hydrogen because

catalyst degeneration may have an effect.

Run R-3414-1 P.P. was made with catalyst that had been on stream for 48 hours so the degree of desulfurization obtained during this run could be expected to be less than that obtained from the first pure hydrogen run, which was started with fresh catalyst. This is the case, as Figure 10 shows. Therefore, it cannot be stated conclusively that the pure hydrogen gives better desulfurization at 100 psig pressure than do mixed gases at a partial pressure of 100 psig of hydrogen.

Run R-3414-3 P.P. utilized a catalyst which had been on stream for 68.5 hours and Run R-3414-3 (H_2) utilized a catalyst which had been on stream for 94 hours. The desulfurization obtained with the pure hydrogen was greater than for mixed gases, Run R-3414-3 P.P. giving an average percent sulfur of 1.32 while Run R-3414-3 (H_2) yielded an effluent oil which was 1.02 percent sulfur on the average.

The percent sulfur in the effluent oil is, therefore, less when using pure hydrogen at 300 psig total pressure than when using mixed gases at 500 psig total pressure with a partial hydrogen pressure of 300 psig, Filtrol's R-3414 catalyst being used in both cases.

ARABIAN AMERICAN OIL COMPANY LIGHT WAX
DISTILLATE STUDY

The light wax distillate received from the Arabian American Oil Company (ARAMCO) was to be tested to determine the optimum conditions for desulfurizing it to 0.1-0.2 percent sulfur. The properties of this light wax distillate are given in Table I. It contained 1.12 percent sulfur, had a gravity of 35.1° A.P.I., and had a boiling range of 348° F. to 728° F. A statistical approach was to be used on this problem and so a randomized order of runs under varying conditions of space velocity and temperature was set up. The recycle gas used consisted of 65 percent hydrogen and 35 percent methane and the recycle rate was set at 4,000 cu. ft. per barrel of charge oil. The original conditions to be tested were space velocities of 0.8, 1.0, and 1.2 $\frac{\text{gm oil}}{\text{gm cat. hr}}$ and temperatures of 775° F., 800° F., and 825° F. Harshaw's molybdenum oxide (Mo-O2O3-T-1/8") was used as the catalyst.

The two runs made for this study are designated Aramco Stock #1 Statistical Run and Aramco Stock #2 Statistical Run. Aramco Stock #1 Statistical Run (Aramco #1) was intended to determine general operating conditions which would yield an effluent oil of 0.1-0.2 percent sulfur. The data for this run are tabulated in Table XXXI. However, shortly after the run was started, changing the space velocity and temperature seemed to affect the percent sulfur in the effluent oil only slightly. Also, at a space velocity of 0.799 and a temperature of 825° F., the sulfur in the effluent oil was only reduced to 0.656 percent. These results led to the conclusion that either the catalyst had become carboned up or that the oil contained a high proportion of refractory sulfur compounds which could only

be removed by utilizing a higher temperature and a lower space velocity. Analysis by the Husky Oil Company revealed that the catalyst from Aramco #1 contained over 50 percent carbon so that the catalyst had lost its activity because of becoming coated with carbon.

After Aramco #1 was abandoned, Aramco Stock #2 Statistical Run (Aramco #2) was set up. The variables in this run were space velocities of 0.5, 0.8, and $1.2 \frac{\text{gm oil}}{\text{gm cat. hr.}}$ and temperatures of 775° F., 825° F., and 850° F. Tabulated data for this run appear in Table XXXII. Table XXXIV shows the randomized order of the runs and Table XXXV shows the average percent sulfur obtained under each operating condition. Figure 11 shows the effect of temperature on percent sulfur in effluent oil at constant space velocity and Figure 12 shows the effect of space velocity on percent sulfur in the effluent oil at constant temperature. Variations in space velocity and temperature from the prescribed levels were neglected in plotting Figures 11 and 12.

A study of Figures 11 and 12 shows that there is a definite interaction effect between temperature and space velocity, that is, the temperature effect varies in a different manner for each space velocity. Part of this interaction effect may be attributed to catalyst deterioration but this cannot be corrected for, since no data are available on the rate of degeneration of Harshaw's Mo-0203-T-1/8" at these temperatures and space velocities. Ostle (8) gives a very clear explanation of the interaction effect and its influence in analysis of variance. Without replication, this data cannot be analyzed by the analysis of variance technique, so the statistical approach to this problem had to be abandoned.

The rows and columns in Table XXXIV were each added individually to give the totals shown. These totals, at constant temperature, indicate that a temperature of 825° F. will give better desulfurization than either 775° F. or 850° F. under the randomized order shown in Table XXXIV. Similarly, the totals at constant space velocity indicate that a space velocity of $0.5 \frac{\text{gm oil}}{\text{gm cat. hr.}}$ gives the best desulfurization.

The amount of cracking which takes place is a definite factor which must be considered at the high temperatures which are necessary to desulfurize this oil. An A.S.T.M. distillation (1) was run on each of the product oils and the volume percent in the gasoline range was recorded as the amount distilled over at $\leq 400^\circ$ F. These results are tabulated in Table XXXVIII. The light wax distillate originally was less than 5 percent in the gasoline range as shown by the A.S.T.M. distillation given in Table I.

For a space velocity of 0.5 and a temperature of 825° F., the volume percent of effluent oil in the gasoline range was 26 percent. That is, nearly one-fourth of the charge oil was cracked to gasoline under these operating conditions. However, the percent sulfur in the effluent oil was also very low (0.236 percent). Run 9, which utilized a space velocity of 0.5 and a temperature of 850° F., contained 16 percent of the oil in the gasoline range and was 0.518 percent sulfur. This shows that the catalyst had definitely deteriorated during the run, much of the loss of activity being attributable to carbon laydown on the catalyst from the cracked products. Since there is likely to be much more cracking occurring at 850° F. than at 825° F. if fresh catalyst is used in both cases, 825° F. would be the best temperature to use to obtain low sulfur in the effluent

oil with a relatively small amount of cracking taking place.

A space velocity of 0.8 at 825° F. yielded 19 percent of the effluent oil in the gasoline range. The run specified by this temperature and space velocity was Number 2 in the randomized order of runs. Since it followed immediately after Run 1 and was made at the same temperature as Run 1, catalyst deterioration is not a large factor in the difference in results obtained. The effluent oil contained 0.397 percent sulfur.

The hydrogen concentration in the effluent gas at the end of each run is plotted versus the number of the run in Figure 13. For the last four runs of Aramco #2, the hydrogen concentration remained fairly constant at about 58 percent. This result indicates that little hydrogen was used during these runs. This result also verifies the conclusion reached earlier that the catalyst was relatively inactive at the end of the run.

Arabian American Oil Company's light wax distillate can successfully be desulfurized at a space velocity of $0.5 \frac{\text{gm oil}}{\text{gm cat. hr.}}$ and a temperature of 825° F. when using a makeup gas which is 65 percent hydrogen, a gas recycle rate of 4,000 cu. ft. per barrel of charge oil, and Harshaw's molybdena catalyst Mo-0203-T-1/8".

SUMMARY

1. Filtrol's molybdenum oxide catalyst, SV-5003, produced oil which was less than 0.5 percent sulfur for 17 hours on stream. When broken up into smaller particle sizes, this catalyst produced oil which was less than 0.5 percent sulfur for 55 hours on stream. Regeneration destroyed the catalyst activity.
2. National aluminate's molybdenum oxide catalyst, pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$, does not compare favorably with Harshaw's molybdenum oxide catalyst, Mo-0203-T-1/8", because it degenerates faster and doesn't give as good desulfurization. Pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$ loses some of its activity after regeneration.
3. Filtrol's molybdenum oxide catalyst, R-3411, produced no oil which was less than 0.5 percent sulfur. Catalyst activity was not affected by regeneration.
4. Adding germanium, in the form of GeO_2 , as a catalyst promoter did not enhance the activity of Filtrol's molybdenum oxide catalyst, R-3432. Converting the GeO_2 to germanium metal by hydrogenation did not enhance the catalyst activity.
5. Girdler's molybdenum oxide catalyst, Sample No. 1319-A, compared favorably with Harshaw's molybdenum oxide catalyst, Mo-0203-T-1/8", on the basis of 24 hour runs made on each catalyst.
6. Porocel's molybdenum oxide catalyst, Sample No. SB-73-54 and Sample No. SB-64-55, both gave the same degree of desulfurization. The oil produced contained an average of less than 0.4 percent sulfur. This catalyst degenerates faster than, and is not as active as Harshaw's

molybdenum oxide catalyst, Mo-0203-T-1/8".

7. Peter Spence and Sons' cobalt molybdate catalyst, No. R-D-2539, is superior to Harshaw's Mo-0203-T-1/8" catalyst but inferior to Harshaw's cobalt molybdate catalyst, CoMo-0201-T-3/16", in both rate of degeneration and catalyst activity. Using this catalyst, the effluent oil contained less than 0.1 percent sulfur after 112 hours on stream.
8. Pure hydrogen, under 200 psig pressure, gave better desulfurization than mixed gases containing 25 percent hydrogen under a total pressure of 800 psig (200 psig partial hydrogen pressure) when desulfurizing Husky No. 3 fuel oil at 775° F., a space velocity of $1 \frac{\text{gm oil}}{\text{gm cat. hr.}}$ and a gas recycle rate of 3,000 cu. ft. per barrel of charge oil using Union Oil Company's cobalt molybdate catalyst. Pure hydrogen under 300 psig pressure, gave better desulfurization than mixed gases containing 60 percent hydrogen under a total pressure of 500 psig (300 psig partial hydrogen pressure) when desulfurizing Husky No. 3 fuel oil at 775° F., space velocity of $1 \frac{\text{gm oil}}{\text{gm cat. hr.}}$ and gas recycle rate of 5,000 cu. ft. per barrel of charge oil using Filtrol's molybdenum oxide catalyst, R-3414.
9. Arabian American Oil Company's light wax distillate can be desulfurized using 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, Mo-0203-T-1/8" is used.

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TABLE I
CHARGE OIL INSPECTION DATA

Husky No. 3 Fuel Oil
% Sulfur = 2.04 or 2.18 as
noted on each run
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.	642
Recovery	99.0 Vol. %
Residue	0.8 Vol. %
Loss	0.2 Vol. %

Aramco Light Wax Distillate
% Sulfur = 1.12
Gravity °A.P.I. = 35.1

A.S.T.M. Distillation

Vol. %	Temp. °F
I.B.P.	348
5	422
10	458
20	496
30	524
40	546
50	570
60	592
70	616
80	642
90	676
95	698
E.P.	728
Recovery	99.0 Vol. %
Residue	1.0 Vol. %
Loss	0.0 Vol. %

TABLE II
RECYCLE GAS INSPECTION DATA

Run	Gas	% H ₂	% CH ₄	% C ₂ H ₆	% C ₃ H ₈	% C ₃ H ₆
Catalyst Study Runs	Catforming	89	3.5	1.5	2.5	3.5
Partial Pressure						
Runs	H ₂	91.2	3.9	4.9*		
R-3411-100 P.P.	Mixed Gas	15.6	75.3	9.1*		
R-3411-200 P.P.	Mixed Gas	35.0	47.3	17.7*		
R-3411-300 P.P.	Mixed Gas	59.8	35.0	5.2*		
Aramco No. 1 and No. 2	Mixed Gas (Makeup gas)	65.4	33.3	1.3*		
Aramco No. 1						
Run 2	Mixed Gas	66.0	28.6	6.0*		
Run 3	Mixed Gas	58.0	35.3	6.7*		
Aramco No. 2						
Run 1	Mixed Gas	52.8	34.1	13.1*		
Run 2	Mixed Gas	57.5	37.2	5.3*		
Run 3	Mixed Gas	61.2	35.4	3.4*		
Run 4	Mixed Gas	60.6	32.1	7.3*		
Run 5	Mixed Gas	51.7	40.6	7.7*		
Run 6	Mixed Gas	57.8	36.2	6.0*		
Run 7	Mixed Gas	58.1	37.8	4.1*		
Run 8	Mixed Gas	57.8	36.4	5.8*		
Run 9	Mixed Gas	57.8	35.8	6.4*		

*C₂ and higher hydrocarbons

TABLE III
COMPOSITION AND IDENTIFICATION OF CATALYST USED

Catalyst Name and Composition	Identification Code	Catalyst Manufacturer
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
Cobalt Molybdate 9.5% MoO ₃ 3.0% CoO 5.0% SiO ₂ 2.0% Graphite 80.5% Al ₂ O ₃	CoMo-0201-T-3/16"	Harshaw Chemical Company
Cobalt Molybdate 3.5% CoO 10.0% MoO ₃ Graphite Type Base	No. R-D-2539 5/32" Pellets	Peter Spence and Sons, Ltd.
Germanium Molybdate 5% GeO ₂ 16% MoO ₃ Alumina Base 3/16" Pellets	R-3431	Filtrol Corporation
Molybdenum Oxide 16% MoO ₃ Alumina Base 3/16" Pellets	R-3432	Filtrol Corporation
Molybdenum Oxide 16 $\frac{1}{4}$ % MoO ₃ Alumina Base	R-3414-1/8"	Filtrol Corporation
Molybdenum Oxide 10% MoO ₃ Alumina Base $\frac{1}{4}$ " Pellets	SV-5003	Filtrol Corporation
Molybdenum Oxide 12-13% MoO ₃ Alumina Base	Sample No. 1319-A $\frac{1}{4}$ " X $\frac{1}{4}$ " Tablets	Girdler

TABLE III (Cont'd.)

Molybdenum Oxide 16% MoO ₃ 79% Al ₂ O ₃ 5% SiO ₂	Mo-0203-T-1/8"	Harshaw Chemical Co.
Molybdenum Oxide 10.9% MoO ₃ Alumina Base 3/16" Pellets	Pelleted Al ₂ O ₃ -MoO ₃	National Aluminate Corporation
Molybdenum Oxide 5-10% Mo as MoO ₃ 3/5% SiO ₂ Porocel Base	Sample No. SB-73-54 4/8 Mesh	Porocel Corporation
Molybdenum Oxide 5-10% Mo as MoO ₃ 3.5% SiO ₂ Porocel Base	Sample No. SB-64-55	Porocel Corporation

TABLE IV
TABULATED DATA FROM RUN MO. FILTROL-1

Catalyst: 100 grams of Filtrol SV-5003, Moly. Impregnated Alumina
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catformer Gas (89% H₂)
Reactor Pressure: 500 psig
Yield: 97.5 Weight %

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	9	776	0.999	8000	101	778	34.4	0.397
2	17	777	1.017	7860	98	792	34.4	0.495
3*	25*	---	---	---	---	---	---	---
4	33	775	1.032	7710	98	806	34.2	0.556
5	41	775	1.035	7600	96	808	34.1	0.560
6	49	769	1.048	7600	94.5	816	33.8	0.594
7	57	775	1.030	7760	94.8	805	34.0	0.565
8	65	776	1.053	7510	93	821	34.1	0.594
9	73	774	1.053	7560	92.2	821	33.6	0.617
10	81	775	1.069	7460	92	834	34.0	0.554
11	89	775	1.048	7600	91	816	34.2	0.575

*Sample No. 3 - Power off 1 $\frac{1}{4}$ hours

TABLE V
TABULATED DATA FROM RUN MO. FILTROL-2

Catalyst: 100 gms of Filtrol SV-5003, Moly. Impregnated Alumina
(regenerated by air blowing)
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas; Catforming Gas
Reactor Pressure: 500 psig
Yield: 97.7 weight %

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	12	775	1.030	7750	147	804	33.4	.700
2	20	775	0.994	8000	157	776	33.5	.747
3	28	775	1.005	7950	167	787	33.4	.743
4	36	776	0.975	8200	171	762	33.4	.712
5	44	775	1.033	7700	169	808	33.3	.706
6	51	761	1.020	7300	164	700	32.5	.782

TABLE VI
TABULATED DATA FROM RUN MO. FILTROL-3

Catalyst: 100 grams of Filtrol SV-5003, Moly. Impregnated Alumina
(broken up to approximately 1/8")
Oil Charge: Husky #3 Fuel Oil 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming (89% H₂)
Reactor Pressure: 500 psig
Yield: 97.5 weight %

Samp No.	Total Hours	Cat Temp of 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
0	5½	778	0.970	8250	202	520	34.5	.372
1	15	774	0.985	8110	157	767	34.5	.366
2	23	774	0.980	8150	143	764	34.1	.445
3	31	775	1.052	7560	132	821	34.1	.466
4	39	777	1.000	7860	126	779	34.1	.461
5	47	768	0.992	8060	123	774	33.9	.543
6	55	779	1.001	7860	120	781	34.0	.482
7	63	775	0.995	8000	119	776	34.1	.518
8	71	776	1.010	7910	122	787	34.0	.538
9	79	776	1.001	7960	121	782	34.1	.530
10	87	775	1.010	7910	120	788	33.6	.505
11	95	774	1.170	6840	119	911	33.8	.545
12	103	783	1.010	7910	118	788	34.1	.511
13	111	778	1.008	7910	118	786	34.1	.563

TABLE VII
TABULATED DATA FROM RUN MOLY. NATIONAL-1

Catalyst: 100 gms of National Aluminate Pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming (89% H_2)
Reactor Pressure: 500 psig
Yield: 95.09 weight %

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	9	780	0.914	8700	---	781.6	34.4	0.461
2	17	772	1.013	7850	---	771.2	34.3	0.531
3	25	775	1.000	7950	---	761.5	34.5	0.551
4	33	775	1.007	7900	---	766.6	34.6	0.563
5	41	775	1.005	7930	---	764.0	34.4	0.530
6	49	773	1.025	7770	---	779.0	34.3	0.619

TABLE VIII
TABULATED DATA FROM RUN MOLY. NATIONAL-2

Catalyst: 100 gms of National Aluminate Pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$
(regenerated)
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming (89% H_2)
Reactor Pressure: 500 psig
Yield: 96.92 weight %

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	7	771	1.015	7850	147	688.8	33.8	0.83
2	15	778	0.990	8050	142	767.1	33.8	0.79
3	23	774	1.000	7950	139	775.6	33.3	0.87
4	31	778	0.987	8100	137	763.3	33.5	0.76
5	39	776	0.955	8350	137	739.4	33.2	0.79
6	47	779	0.978	8150	137	755.7	33.6	0.74
7	55	777	0.967	8250	135	749.0	33.6	0.81
8	63	776	0.955	8350	150	740.0	33.6	0.81
9	71	776	1.020	7810	158	792.8	33.2	0.71

TABLE IX
TABULATED DATA FROM RUN MOLY. FILTROL-R-3414-1

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming (89% H₂)
Reactor Pressure: 500 psig
Yield: 97.22 Weight %

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	5	776	1.027	7760	172	498.6	34.0	0.575
2	13	777	0.978	8150	176	760.6	34.0	0.554
3	21	775	0.981	8150	177	763.2	34.1	0.570
4	29	777	1.016	7850	177	790.6	34.2	0.616
5	37	776	0.997	8000	177	775.6	34.0	0.662
6	45	775	1.002	7950	177	780.0	34.0	0.630
7	53	774	1.016	7850	177	790.7	33.9	0.633

TABLE X
TABULATED DATA FROM RUN MOLY. FILTROL, R-3414-2

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ (Regenerated)
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming (89% H₂)
Reactor Pressure: 500 psig
Yield: 96.63 Weight %

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	776	0.960	8300	302	742.2	34.2	0.527
2	16	775	1.000	7980	294	772.0	34.0	0.625
3	24	776	1.030	7770	289	795.6	34.0	0.565
4	32	777	1.025	7790	288	791.9	34.0	0.535
5	40	776	1.069	7460	285	825.8	33.7	0.652

TABLE XI
TABULATED DATA FROM RUN MOLY. FILTROL R-3431

Catalyst: 100 gms of Filtrol, R-3431, 3/16" pellets (containing 5% Ge)
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming Gas
Reactor Pressure: 500 psig
Yield: 97.54% Weight

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	7.5	777	0.911	8770	518	666.5	34.7	0.615
2	15.5	774	0.994	8030	498	774.6	34.6	0.628
3	23.5	774	0.990	8050	493	771.8	34.4	0.694

TABLE XII
TABULATED DATA FROM RUN MOLY. FILTROL R-3431 (hydrogenated)

Catalyst: 85.6 gms of Filtrol, 3/16" pellets (containing 5% Ge, Hydrogenated)
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming Gas
Reactor Pressure: 500 psig
Yield: 97.15 Weight %

Samp No.	Total Hours	Cat Temp °F Av.	Space Vel gms/gm/hr	Recycle Ft ³ /bbl	Av Gas Consump	Yield Gms	Product A.P.I.	Product % S
1	8	779	0.956	9790	74.7	635.8	34.4	0.692
2	16	774	0.992	9400	71.9	662.5	34.3	0.705
3	24	774	0.968	9630	75.3	646.0	34.3	0.700

TABLE XIII
TABULATED DATA FROM RUN MOLY. FILTROL R-3432

Catalyst: 100 gms of Filtrol, R-3432, 3/16" pellets (containing no Ge)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Catforming Gas
 Reactor Pressure: 500 psig
 Yield: 97.47 Weight %

Samp No.	Total Hours	Gat 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	5	774	0.988	8190	764	480.7	35.3	0.393
2	13	779	0.958	8330	777	746.8	35.3	0.382
3	21	776	0.996	8000	772	775.5	35.2	0.495

TABLE XIV
TABULATED DATA FROM GIRDLER CATALYST RUN

Catalyst: 100 gms of Girdler Moly Alumina.
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming Gas
Reactor Pressure: 500 psig
Yield: 96.23 Weight %

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	777	1.028	7790	---	791	35.1	0.374
2	16	775	0.963	8200	---	740	34.6	0.392
3	24	769	1.031	7760	---	795	34.9	0.441

TABLE XV
TABULATED DATA FROM MOLYBDENUM OXIDE RUN

Catalyst: 100 gms Harshaw Mo-0203-T-1/8"
Pressure: 500 psig
Oil: Husky #3 Fuel Oil
Recycle Gas: Catforming (89% H₂)
Yield: 94.65 Weight %

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	774	0.950	8380	153	726.7	35.0	0.372
2	16	775	1.044	7660	142	790.6	35.2	0.435
3	24	775	1.071	7460	138	810.5	34.7	0.457

TABLE XVI
TABULATED DATA FROM RUN POROCEL-1

Catalyst: 100 gms of Porocel's Sample No. SB-73-54
Oil Charge: Husky #3 Fuel Oil - 2.12% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming Gas
Reactor Pressure: 500 psig
Yield: 96.2 Weight %

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	9	780	1.056	7570	82	819	34.6	0.319
2	17	775	1.051	7570	82	816	34.6	0.373
3	25	767	1.040	7680	80	809	34.4	0.426
4	33	783	1.048	7630	79	813	34.7	0.390
5*	41	---	0.576	7490	93	448	34.4	0.441
6*	49	---	1.000	7970	92	775	33.0	-----

*Sample 5 - Power failure 2:18 to 4:48 and 8:05 to 8:25 no oil flow.

*Sample 6 - Power failure 9:45 to 10:05 no oil flow.

TABLE XVII
TABULATED DATA FROM RUN POROCEL-2

Catalyst: 100 gms of Porocel Supported Molybdena
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Catforming Gas
Reactor Pressure: 500 psig
Yield: 95.15 Weight %

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	777	1.050	7650	---	799.0	35.0	0.244
2	16	775	1.015	7910	---	773.6	34.4	0.285
3	24	775	1.003	8000	---	763.4	34.2	0.284

TABLE XVIII

TABULATED DATA FROM RUN COBALT MOLYBDATE, GRAPHITE TYPE

Catalyst: 100 gms of calcined 5/32" graphite type - tablets No. R-D-2539
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Catforming Gas
 Reactor Pressure: 500 psig
 Yield: 93.54 Weight %

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	778	1.086	7370	---	812.3	35.2	0.034
2	16	774	1.058	7560	---	791.5	35.1	0.034
3	24	778	1.011	7900	---	755.0	35.1	0.036
4	32	778	1.068	7500	---	798.5	35.0	0.0355
5	40	779	1.073	7450	---	800.8	35.1	0.0447
6	48	779	0.921	8690	---	688.5	35.3	0.0590
7	56	776	0.893	8960	---	667.5	35.4	0.0433
8	64	774	0.888	9000	---	662.5	35.1	0.0547
9	72	777	0.873	9150	---	652.5	35.1	0.0640
10	80	775	0.878	9120	---	655.7	35.1	0.0581
11	88	776	0.891	8960	---	665.4	35.1	0.0667
12	96	776	1.016	7850	---	759.5	35.1	0.0610
13	104	777	1.035	7730	---	774.0	35.0	0.0570
14	112	776	1.039	7700	---	776.7	35.0	0.0730

TABLE XIX
TABULATED DATA FOR COBALT MOLYBDATE RUN (CMR-1)*
For Figure 7

Sample No.	Total Hours	% Sulfur in Effluent Oil	Grams Sulfur Removed Per Kilogram Charge Oil
1	8	0.156	20.20
2	16	0.127	20.49
3	24	0.102	20.74
4	32	0.087	20.89
5	40	0.075	21.01
6	48	0.075	21.01
7	56	0.076	21.00
8	64	0.076	21.00
9	72	0.076	21.00
10	80	0.078	20.98
11	88	0.079	20.97
12	96	0.079	20.97
13	104	0.078	20.98
14	112	0.077	20.99

*Research by F. C. Silvey (9)

TABLE XX
TABULATED DATA FROM RUN MOS-V*
For Figures 3, 6, and 8

Sample No.	Hours on Stream After Regeneration	% Sulfur in Effluent Oil	Grams S Removed Per Kilogram Charge Oil
76	8	0.199	20.24
77	16	0.255	19.68
78	24	0.298	19.25
79	32	0.297	19.26
80	40	0.312	19.11
81	48	0.317	19.06
82	56	0.326	18.97
83	64	0.337	18.86
84	72	0.346	18.77
85	80	0.341	18.82
86	88	0.343	18.80
87	96	0.347	18.76
88	104	0.380	18.43
89	112	0.371	18.52

*Research by F. C. Silvey (9).

TABLE XXI
TABULATED DATA FROM FARMERS UNION RUN FUR-3*
For Figure 9

Sample No.	Total Hours	% Sulfur in Effluent Oil	Grams Sulfur Removed Per Kilogram Charge Oil
1	8	0.945	12.31
2	16	1.180	9.96
3	24	1.210	9.66
4	32	1.275	9.01
5	40	1.260	9.16

*Research by H. C. Hooper (5)

Recycle Gas Analysis

25.3% H_2/N_2

62.1% CH_4

12.6% C_2

TABLE XXII
TABULATED DATA FROM RUN COBALT MOLYBDATE H_2

Catalyst: 100 gms Union Oil Co. Cobalt Molybdate 3/16" pellets
Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
Recycle Gas: Hydrogen (H_2)
Reactor Pressure: 200 psig
Yield: 96.2 Weight %

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	5.5	775	1.050	3040	185.0	557.0	33.3	0.757
2	13.5	775	1.055	3020	189.5	813.6	33.5	0.476
3	21.5	775	0.995	3210	195.0	767.2	33.6	0.512
4	29.5	774	1.015	3150	196.5	781.1	33.6	0.515
5	37.5	776	1.010	3160	197.6	778.5	33.3	0.547

TABLE XXIII

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-1 (H₂)

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂-1/8"
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Hydrogen (H₂)
 Reactor Pressure: 100 psig
 Yield: 98.19 Weight %

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	6	776	1.092	1460	-8.73	644.9	32.3	1.17
2	14	776	1.056	1515	-7.96	829.9	32.1	1.17
3	22	774	1.025	1560	-7.81	804.8	32.2	1.23
4	30	777	1.011	1580	-7.95	793.6	32.1	1.23
5	38	777	1.014	1575	-7.90	796.6	32.0	1.27
6	46	777	1.011	1580	-7.23	794.0	31.9	1.29

Avg. % S = 1.23

TABLE XXIV

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-2 (H₂)

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ - 1/8" (unregenerated)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Hydrogen (H₂)
 Reactor Pressure: 200 psig
 Yield: 98.48 Weight %

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	774	0.847	3830	31.0	657	32.2	1.250
2	16	775	1.008	3170	30.3	793	32.3	1.165
3	24	774	1.038	3080	28.8	819	32.3	1.152
4	32	774	1.020	3130	29.6	804	32.0	1.130
5	40	776	1.006	3180	30.4	792	32.1	1.150
6	48	776	0.974	3280	29.9	767.5	32.1	1.155

Avg. % S = 1.17

TABLE XXV

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-3 (H₂)

Catalyst: 100 gms of Filtrol, R-3414, 16½% MoO₂ - 1/8" (unregenerated)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Hydrogen (H₂)
 Reactor Pressure: 300 psig
 Yield: 97.56 Weight %

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	774	0.796	6010	102.0	620.5	32.4	0.992
2	16	778	1.031	4650	95.9	805.6	32.7	0.995
3	24	774	1.055	4540	91.9	822.3	32.4	1.030
4	32	776	0.998	4800	91.5	779.0	32.3	1.080
5	40	776	0.963	4970	91.5	750.1	32.5	0.998
6	48	777	1.013	4730	90.5	789.0	32.4	0.998

Avg. % S = 1.02

TABLE XXVI

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-4 (H₂)

Catalyst: 100 gms of Filtrol, R-3414, 16½% MoO₂ - 1/8" (unregenerated)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Hydrogen (H₂)
 Reactor Pressure: 400 psig
 Yield: 97.45 Weight %

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	778	0.973	6480	75.3	758.4	32.7	0.916
2	16	776	0.999	6390	80.4	777.7	32.8	0.865
3	24	770	0.988	6460	81.4	770.0	32.8	0.883
4	32	775	0.896	7120	81.9	697.9	32.8	0.850
5	40	777	0.945	6750	83.1	736.5	33.0	0.790
6	48	774	0.988	6460	80.8	769.4	33.0	0.876

Avg. % S = 0.863

TABLE XXVII

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-5 (H₂)

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ - 1/8" (unregenerated)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Hydrogen (H₂)
 Reactor Pressure: 500 psig
 Yield: 96.59 Weight %

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	774	0.948	8400	121.6	723.0	33.2	0.795
2	16	777	0.990	8050	111.2	765.4	33.4	0.753
3	24	774	0.996	8000	108.1	770.5	33.3	0.842
4	32	777	1.004	7950	106.3	776.1	33.3	0.785
5	40	777	1.003	7950	105.2	775.1	33.5	0.771
6	48	775	1.028	7750	104.3	794.1	33.5	0.783

Avg. % S = 0.788

TABLE XXVIII

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-1 P.P.

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ - 1/8" (unregenerated from 2 P.P.)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Mixed Gas - 20% (H₂)
 Reactor Pressure: 500 psig
 Yield: 98.81% Weight

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	4.5	776	0.966	8250	---	429.5	31.7	1.430
2	12.5	775	0.985	8110	---	777.0	31.9	1.460
3	20.5	774	0.979	8160	---	773.8	31.8	1.540

Avg. % S = 1.48

TABLE XXIX

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-2 P.P.

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ -1/8"
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Mixed Gas - 40% (H₂)
 Reactor Pressure: 500 psig
 Yield: 97.68 Weight %

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	780	0.777	10250	---	607.3	33.3	0.908
2	16	773	0.797	10020	---	623.0	33.0	0.956
3	24	773	0.977	8160	---	764.6	32.8	1.072
4	32	776	0.989	8070	---	772.4	32.7	1.112
5	40	775	1.000	7980	---	780.5	32.6	1.170
6	48	776	1.022	7810	---	798.6	32.6	1.220

Avg. % S = 1.07

TABLE XXX

TABULATED DATA FROM RUN MOLY. FILTROL R-3414-3 P.P.

Catalyst: 100 gms of Filtrol, R-3414, 16 $\frac{1}{2}$ % MoO₂ - 1/8" (unregenerated)
 Oil Charge: Husky #3 Fuel Oil - 2.04% Sulfur and 29.7 °A.P.I.
 Recycle Gas: Mixed Gas - 60% (H₂)
 Reactor Pressure: 500 psig
 Yield: 97.9 Weight %

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	5.3	776	1.028	7740	---	532.8	31.7	1.42
2	13.3	774	0.977	8160	---	765.0	31.9	1.31
3	21.3	777	0.990	8070	---	775.5	32.0	1.23

Avg. % S = 1.32

TABLE XXXI
TABULATED DATA FOR ARAMCO STOCK #1 STATISTICAL RUN

Catalyst: 100 gms of Harshaw Mo-0203-T-1/8"
Oil Charge: ARAMCO Stock* - 12.1% Sulfur and 35.1 °A.P.I.
Recycle Gas: 65.4% H₂, 33.3% CH₄, and 1.3% C₂
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 ³ /bbl	Product A.P.I.	% S	Av Gas Consumed Per Samp. Ft ³ /bbl	Av. Yield Wt. %
1	1	8	516.9	829	0.737	4410	40.0	0.635		
	2	16	527.0	823	0.750	4270	40.9	0.642	----	87.7
	Av. 1 & 2			826	0.744	4340	40.5	0.639		
2	3	24	576.3	825	0.780	4120	38.8	0.526		
	4	32	585.9	824	0.794	4050	39.3	0.648		
	5	40	593.5	827	0.803	4000	39.3	0.664	54.8	92.3
	Av. 4 & 5			826	0.799	4025	39.3	0.656		
3	6	49.5	1019.0	775	1.210	3950	36.9	0.789		
	7	57.5	824.0	775	1.165	4120	36.3	0.791		
	8	61.5	432.0	773	1.220	3930	35.6	0.795	40.6	88.5
	Av. 7 & 8			774	1.193	4025	36.0	0.793		

*Arabian American Oil Co. Light Wax Distillate.

Since the sulfurs were bad at this point a new run was started using lower space velocities and higher temperatures.

TABLE XXXII
TABULATED DATA FOR ARAMCO STOCK #2 STATISTICAL RUN

Catalyst: 100 gms of Harshaw Mo-0203-T-1/8"
Oil Charge: ARAMCO Stock* - 1.21% Sulfur and 35.1 °A.P.I.
Recycle Gas: 65% H₂, 35% CH₄ approximately
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 ³ /bbl	Product A.P.I.	% S	Av. Gas Consumed Per Samp. Ft ³ /bbl	Av. Yield Wt. %
1	1	8	345.6	824	0.475	5970	39.6	0.190		
	2	16	351.5	823	0.483	5870	39.5	0.260		
	3	24	363.7	827	0.500	5680	39.5	0.212	-73	90.9
	Av. 2 & 3			825	0.492	5775	39.5	0.236		
2	4	32	572.1	825	0.757	4250	37.2	0.286		
	5	40	583.5	824	0.772	4160	37.2	0.385		
	6	48	616.7	826	0.815	3940	37.1	0.408	26	94.4
	Av. 5 & 6			825	0.794	4050	37.2	0.397		
3	7	56	592.5	851	0.793	4050	37.6	0.425		
	8	65	639.8	850	0.761	4220	37.8	0.445		
	9	72	478.6	850	0.732	4400	39.5	0.352	120	93.4
	Av. 8 & 9			850	0.747	4310	38.7	0.399		
4	10	80	821.4	777	1.163	4120	37.4	0.742		
	11	88	827.0	776	1.172	4090	36.6	0.627		
	12	96	876.8	774	1.242	3860	36.4	0.715	50	88.1
	Av. 11 & 12			775	1.207	3975	36.5	0.671		
5	13	104	595.0	776	0.799	4020	36.3	0.765		
	14	112	596.0	775	0.800	4020	36.4	0.745		
	15	120	592.5	778	0.795	4040	36.3	0.745	-42	93.1
	Av. 14 & 15			777	0.798	4030	36.4	0.745		

TABLE XXXII (Continued)
TABULATED DATA FOR ARAMCO STOCK #2 STATISTICAL RUN

Run No.	Samp No.	Total Hrs on Stream	Sample Wt. Gms	Av. Cat. Temp °F	Space Vel lbs oil/ lb. cat. hr.	Recycle Ft ³ /bbl	Product A.P.I.	% S	Av. Gas Consumed Per Samp. Ft ³ /bbl	Av. Yield Wt. %
6	16	128	828.0	851	1.188	4030	38.0	0.615	130	87.1
	17	136	845.2	847	1.212	3960	38.3	0.648		
	18	144	873.5	850	1.255	3830	38.5	0.667		
	Av. 17 & 18			849	1.234	3895	38.4	0.658		
7	19	152	837.8	824	1.182	4050	37.7	0.720	-57	88.5
	20	160.17	827.0	823	1.143	4180	37.2	0.750		
	21	168	821.0	828	1.185	4030	37.4	0.747		
	Av. 20 & 21			826	1.164	4105	37.3	0.749		
8	22	176	388.7	774	0.502	6000	36.9	0.755	64	96.9
	23	184	365.5	774	0.471	6400	36.5	0.782		
	24	192.25	433.0	774	0.541	5570	36.4	0.762		
	Av. 23 & 24			774	0.506	5985	36.5	0.772		
9	25	200	371.1	835	0.512	5890	37.2	0.673	109	93.8
	26	208	388.0	850	0.517	5830	38.4	0.542		
	27	216	378.0	853	0.504	5970	39.3	0.494		
	Av. 26 & 27			852	0.511	5900	38.9	0.518		

*Arabian American Oil Co. Light Wax Distillate.

TABLE XXXIII
VOLUME PERCENT OF PRODUCT OIL IN THE GASOLINE RANGE
FOR ARAMCO RUN #2

<u>Conditions of Run</u>		Run No.	Vol. % in Gasoline range in Effluent Oil
<u>Sp. Vel.</u>	<u>Temp °F</u>		
0.5	775	8	7
	825	1	26
	850	9	16
0.8	775	5	10
	825	2	19
	850	3	20
1.2	775	4	6
	825	7	12
	850	6	16

TABLE XXXIV
ORDER OF RUNS, ARAMCO #2

Temperature	Space Velocity		
	0.5	0.8	1.2
775	8	5	4
825	1	2	7
850	9	3	6

TABLE XXXV
PERCENT SULFUR FOR ARAMCO #2
For Figures 11 and 12

Temperature	Space Velocity			Total
	0.5	0.8	1.2	
775	0.772	0.745	0.671	2.188
825	0.236	0.397	0.749	1.382
850	<u>0.518</u>	<u>0.399</u>	<u>0.658</u>	<u>1.575</u>
Total	1.526	1.541	2.078	5.145

TABLE XXXVI
LINEAR REGRESSION ANALYSES
(H = Hours On Stream)
(S = Grams S Removed Per Kilogram Charge Oil)

Run MOS-V (Harshaw Mo-0203-T-1/8")

$S = 19.438 - 0.00826 H$ (Range = 40-112 Hr)

$r^2 = 0.8683$

$r = 0.9318^{**}$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.3600	52.75 ^{**}
Deviations About Regression	8	0.00683	
<u>Total</u>	<u>9</u>		

Run CMR-1 (Harshaw CoMo-0201-T-3/16")

$S = 21.028 - 0.000492 H$ (Range = 40-112 Hr)

$r^2 = 0.6190$

$r = 0.7868^{**}$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.0013	13 ^{**}
Deviations About Regression	8	0.0001	
<u>Total</u>	<u>9</u>		

TABLE XXXVI (Continued)

RUN MOLY NATIONAL-1 (Pelleted $\text{Al}_2\text{O}_3\text{-MoO}_3$)

$$S = 16.564 - 0.0277 H \text{ (Range = 9-49 Hr)}$$

$$r^2 = 0.6528$$

$$r = 0.8080$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.8581	7.52
Deviation About Regression	4	0.1141	
<u>Total</u>	<u>5</u>		

RUN MOLY FILTROL R-34114-1

$$S = 15.684 - 0.01866 H \text{ (Range = 5-53 Hr)}$$

$$r^2 = 0.6568$$

$$r = 0.8104^*$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.6240	9.57*
Deviation About Regression	5	0.0652	
<u>Total</u>	<u>6</u>		

TABLE XXXVI (Continued)

RUN MOLY FILTROL R-3414-2

$$S = 15.072 - 0.020 H \text{ (Range = 8-40 Hr)}$$

$$r^2 = 0.2807$$

$$r = 0.4569$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	(F ¹)#
Regression	1	0.2560	1.26
Deviation About Regression	3	0.3235	
<u>Total</u>	<u>4</u>		

$$\#(F^1) = \frac{1}{F}$$

RUN POROCEL-1 (Sample No. SB-73-54)

$$S = 18.118 - 0.0326 H \text{ (Range = 9-41 Hr)}$$

$$r^2 = 0.7384$$

$$r = 0.8593$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.6813	8.47
Deviation About Regression	3	0.0805	
<u>Total</u>	<u>4</u>		

TABLE XXXVI (Continued)
 RUN COBALT MOLYBDATE-H₂ (Union Oil Co. CoMo)

$$S = 15.964 - 0.027 H \text{ (Range = 13.5-37.5 Hr)}$$

$$r^2 = 0.9225$$

$$r = 0.9605^*$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.2333	23.81*
Deviation About Regression	2	0.0098	
<u>Total</u>	<u>3</u>		

RUN FUR-3 (Union Oil Co. CoMo)

$$S = 10.515 - 0.0381 H \text{ (Range = 16-40 Hr)}$$

$$r^2 = 0.7995$$

$$r = 0.8941$$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.4652	7.97
Deviation About Regression	2	0.0584	
<u>Total</u>	<u>3</u>		

TABLE XXXVI (Continued)

RUN COBALT MOLYBDATE, GRAPHITE TYPE

$S = 20.024 - 0.00271 H$ (Range = 40-112 Hr)

$r^2 = 0.5132$

$r = 0.7164^*$

Analysis of Variance

Source of Variation	Degrees of Freedom	Mean Square	F
Regression	1	0.0388	8.43*
Deviation About Regression	8	0.0048	
<u>Total</u>	<u>9</u>		

*Significant at $P = 0.05$

**Significant at $P = 0.01$

TABLE XXXVII
TESTS OF HYPOTHESES ABOUT THE DECREASE OF CATALYST ACTIVITY WITH
TIME ON STREAM

$$H_0: B_1 = B_2^{\#}$$

Run 1	Run 2	Degrees of Freedom	$\frac{1}{t}$
Moly Filtrol R-3414-1	Moly Filtrol R-3414-2	8	0.091
Moly National-1	MOS-V	12	2.862*
Porocel-1	MOS-V	11	3.550**
Cobalt Molybdate-H ₂	FUR-3	4	0.763
Cobalt Molybdate Graphite Type	CMR-1	16	2.353*
Cobalt Molybdate Graphite Type	MOS-V	16	3.770**

[#]B is the slope of the population regression line and is estimated by b in the calculated equation - $S = a + bH$

$\frac{1}{t}$ is the value calculated for "Students" t test and equals $\frac{b_1 - b_2}{s_{b_1 - b_2}}$

*Significant at $P = 0.05$

**Significant at $P = 0.01$

TABLE XXXVIII
ANALYSES OF VARIANCE FOR TESTING THE HYPOTHESIS - $H_1: u_1 = u_2^{\#}$

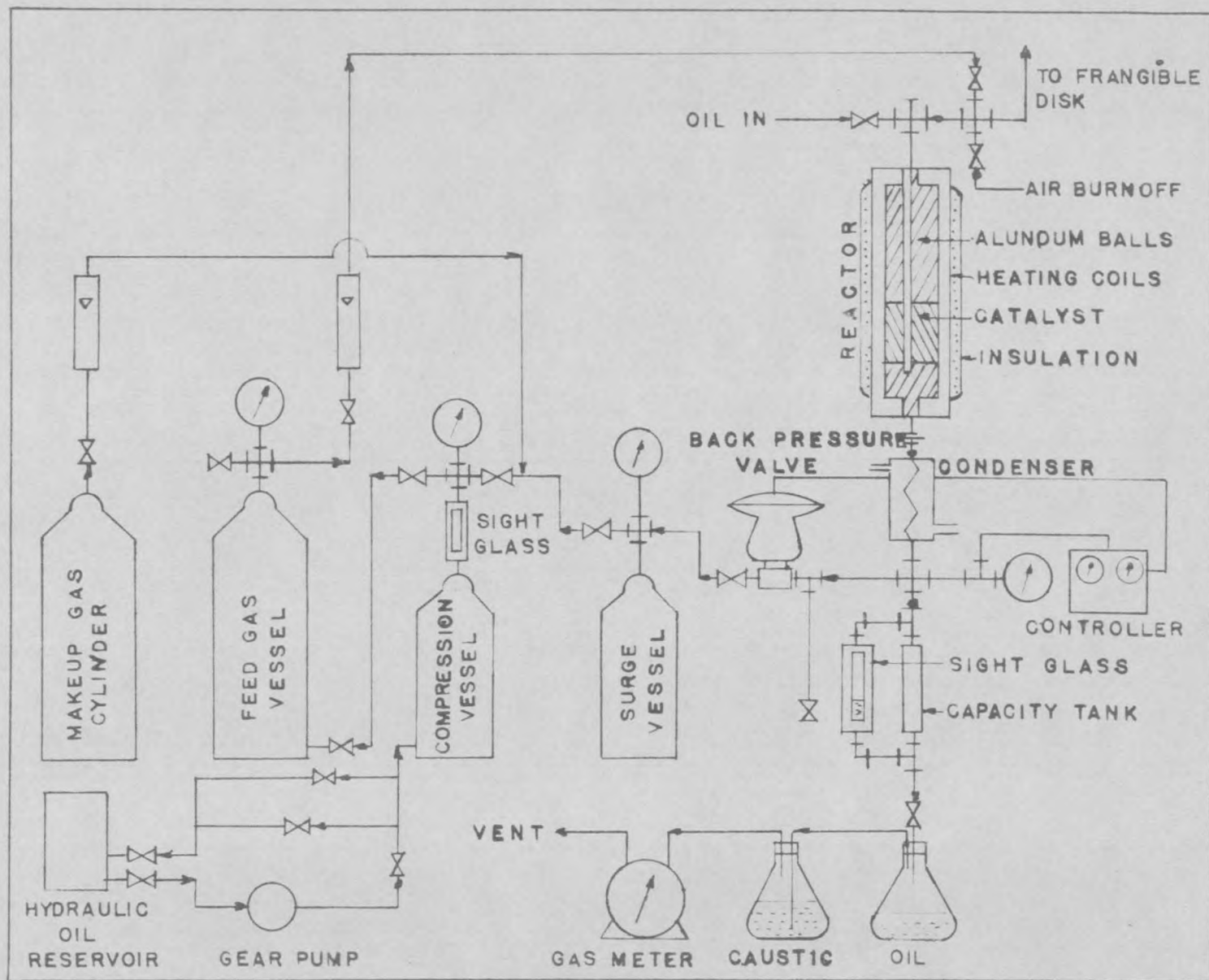
Run 1	Run 2	Source of Variation	Analysis of Variance Degrees of Freedom	Mean Square	F
Moly Filtrol-1	Moly Filtrol-3	Among Runs	1	0.8910	11.00*
		Within Runs	6	0.0810	.
		Total	7		
Moly Filtrol-3	MOS-V	Among Runs	1	18.3682	257.98**
		Within Runs	18	0.0712	
		Total	19		
Moly National-1	Moly Filtrol-3	Among Runs	1	0.2202	1.41
		Within Runs	14	0.1558	
		Total	15		
Moly Filtrol R-3414-1	Moly Filtrol R-3414-2	Among Runs	1	0.8851	4.07
		Within Runs	10	0.2177	
		Total	11		
Porocel-1	Porocel-2	Among Runs	1	0.2818	1.64
		Within Runs	6	0.1719	
		Total	7		
Porocel-1	MOS-V	Among Runs	1	7.5802	73.74**
		Within Runs	13	0.1028	
		Total	14		
Cobalt Molybdate-H ₂	FUR-3	Among Runs	1	67.9195	488.28**
		Within Runs	6	0.1391	
		Total	7		
Cobalt Molybdate Graphite Type	CMR-1	Among Runs	1	6.8797	1593.63**
		Within Runs	18	0.00432	
		Total	19		
Cobalt Molybdate Graphite Type	MOS-V	Among Runs	1	5.0803	186.98**
		Within Runs	18	0.02717	
		Total	19		

$^{\#}u$ is the population average of the grams of sulfur removed per kilogram of charge oil for a given catalyst and is estimated by $\bar{S}$, the average sulfur removed in a given run.

*Significant at $P = 0.05$

**Significant at $P = 0.01$

Figure 1. Schematic Flow Diagram of the Desulfurization Unit.



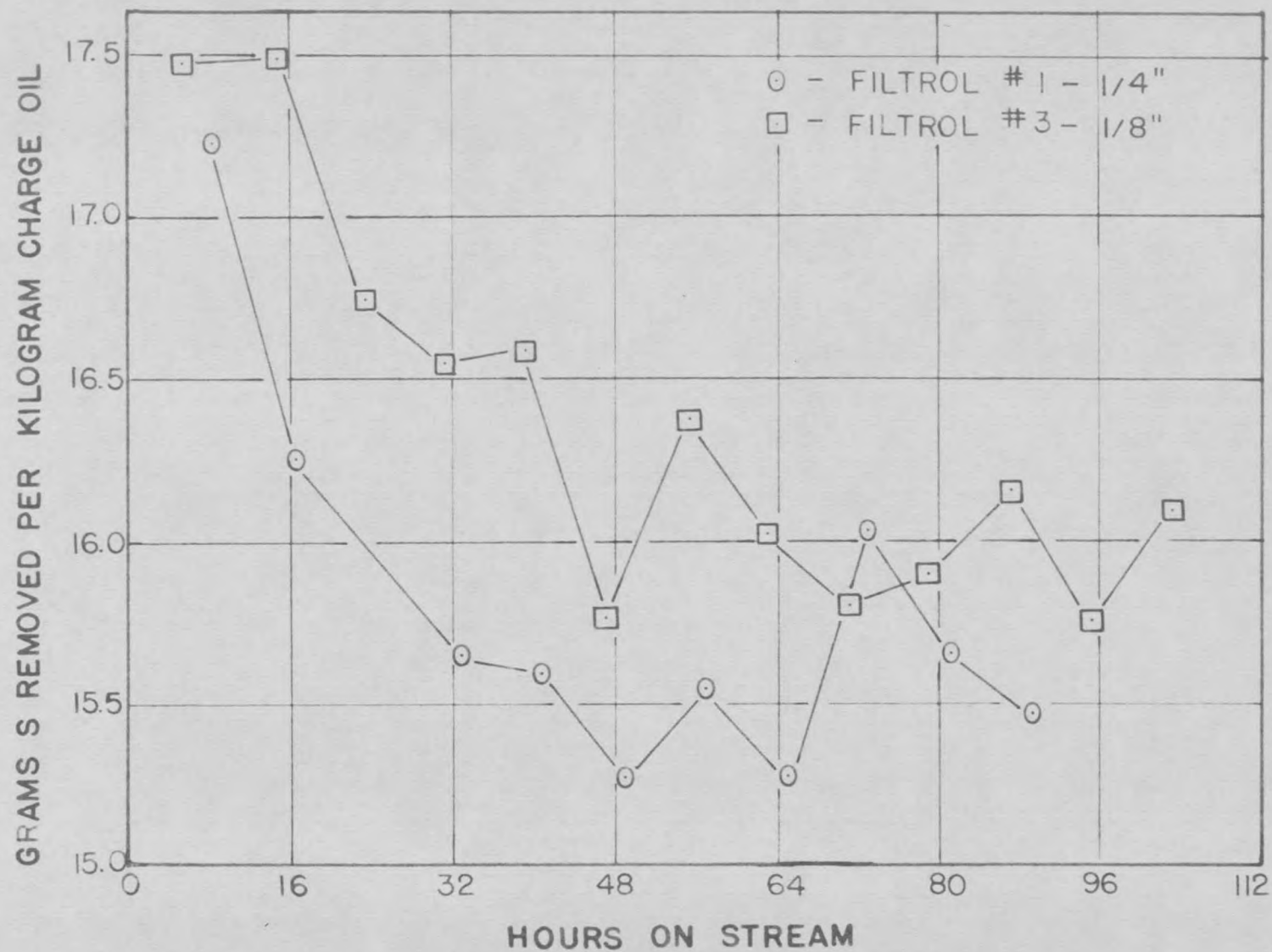


Figure 2. Effect of Particle Size of Catalyst on Desulfurization Attainable Using Filtrol's SV-5003 Catalyst.

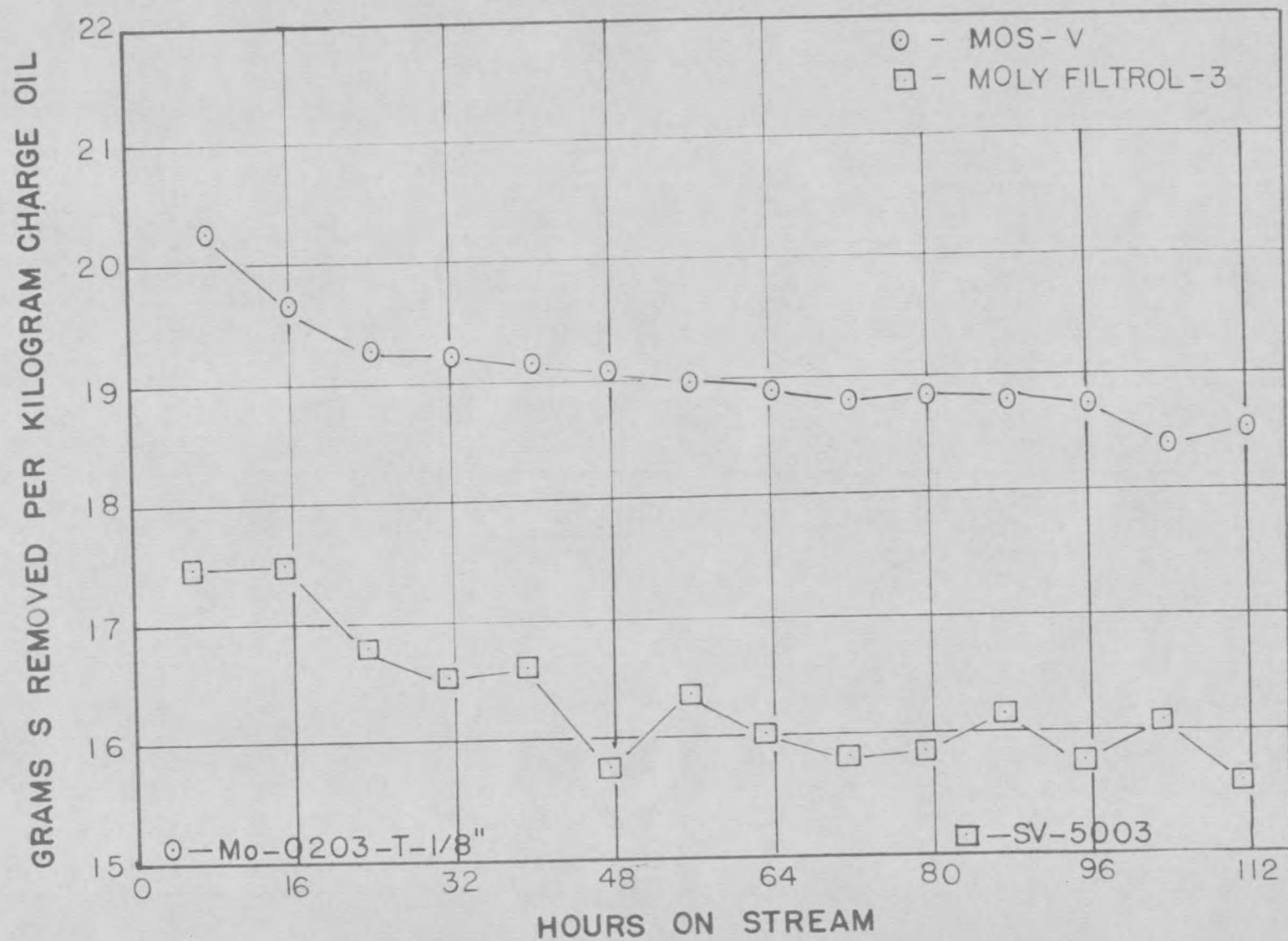


Figure 3. Desulfurization of Husky #3 Fuel Oil When Using Harshaw's Mo-Q203-T-1/8" and Filtrol's SV-5003 Catalysts.

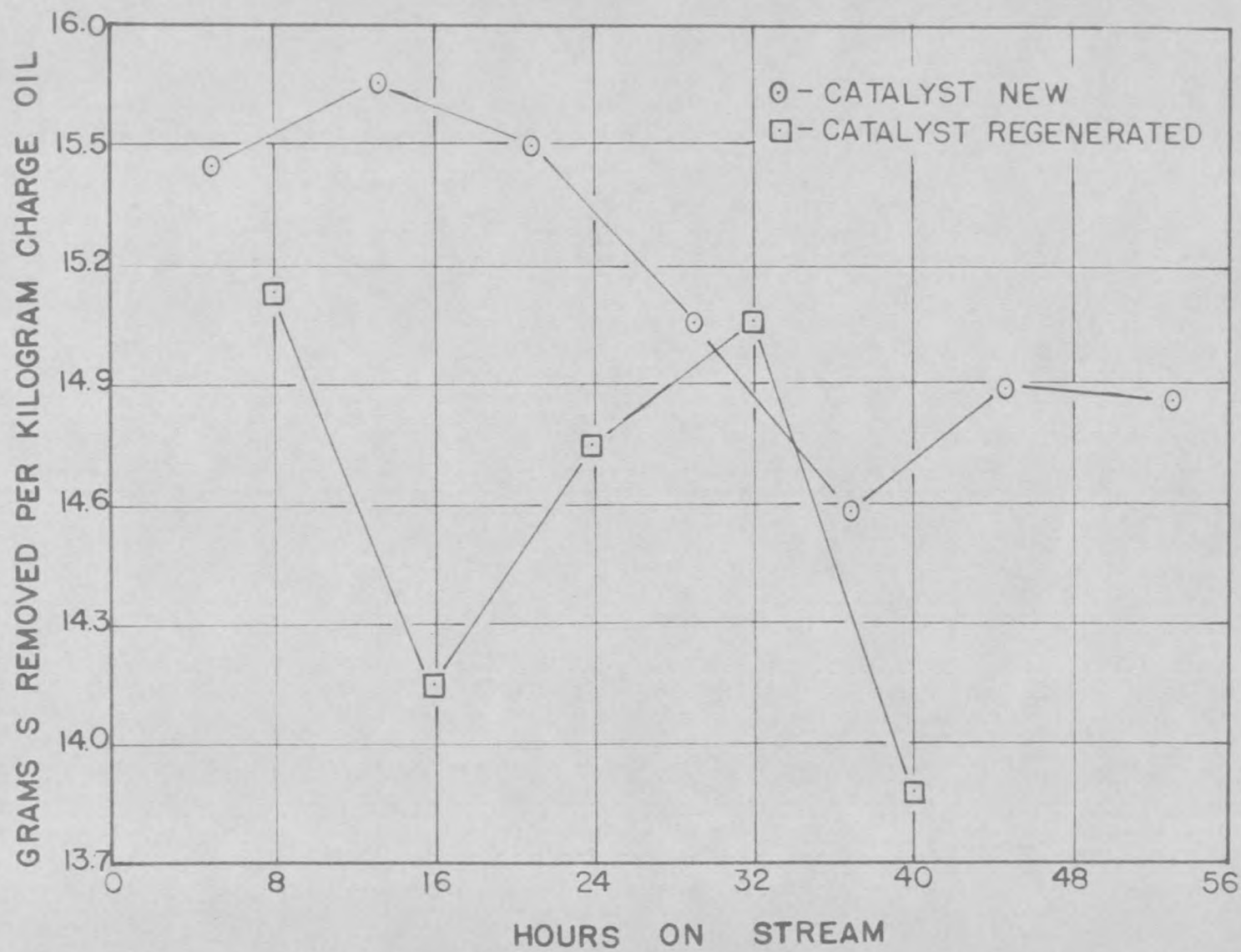


Figure 4. Effect of Regeneration on the Activity of Filtrol's R-3411 Catalyst.

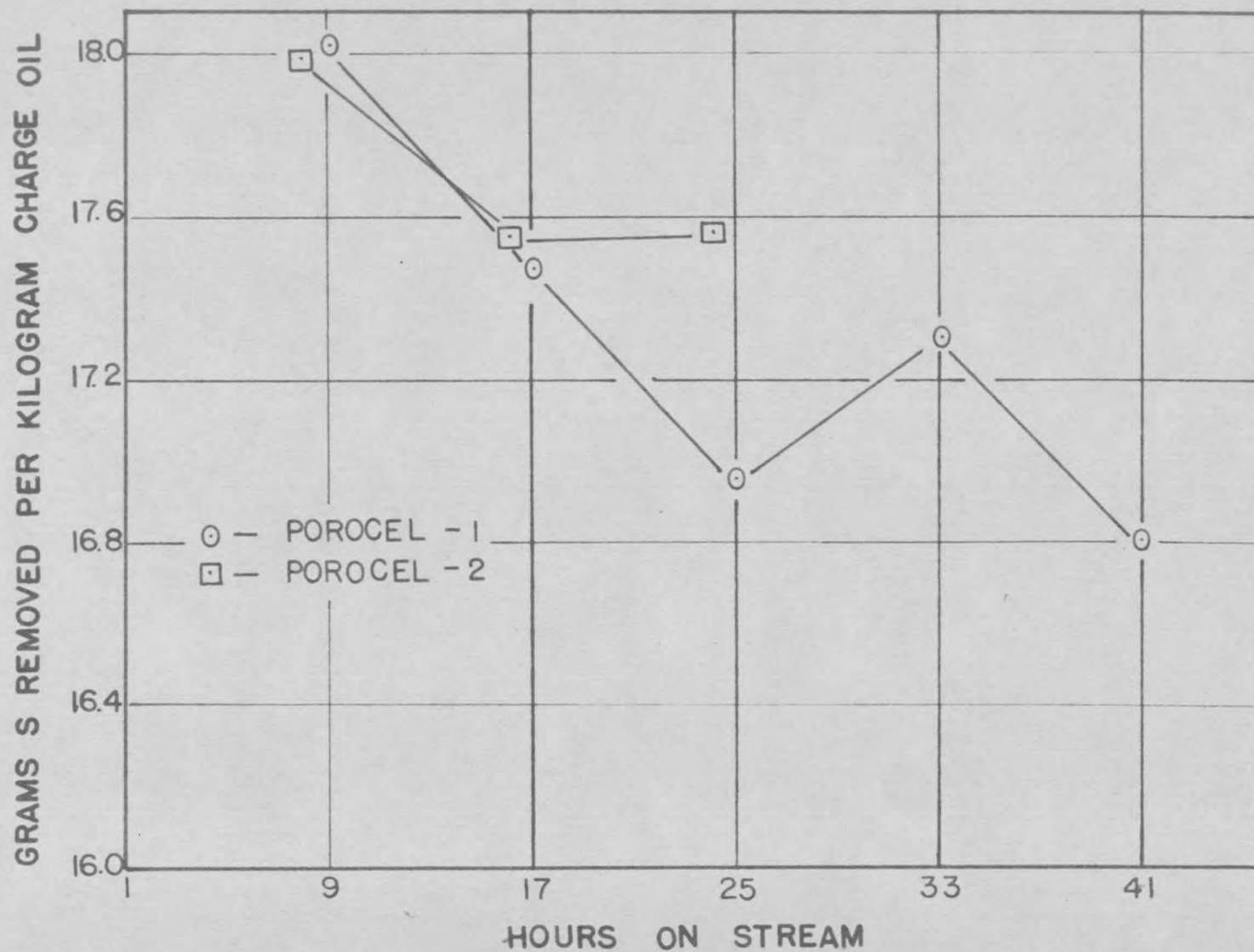


Figure 5. Comparison of Catalyst Activity Between Porocel-1 (Sample SB-73-54) and Porocel-2 (Sample SB-64-55).

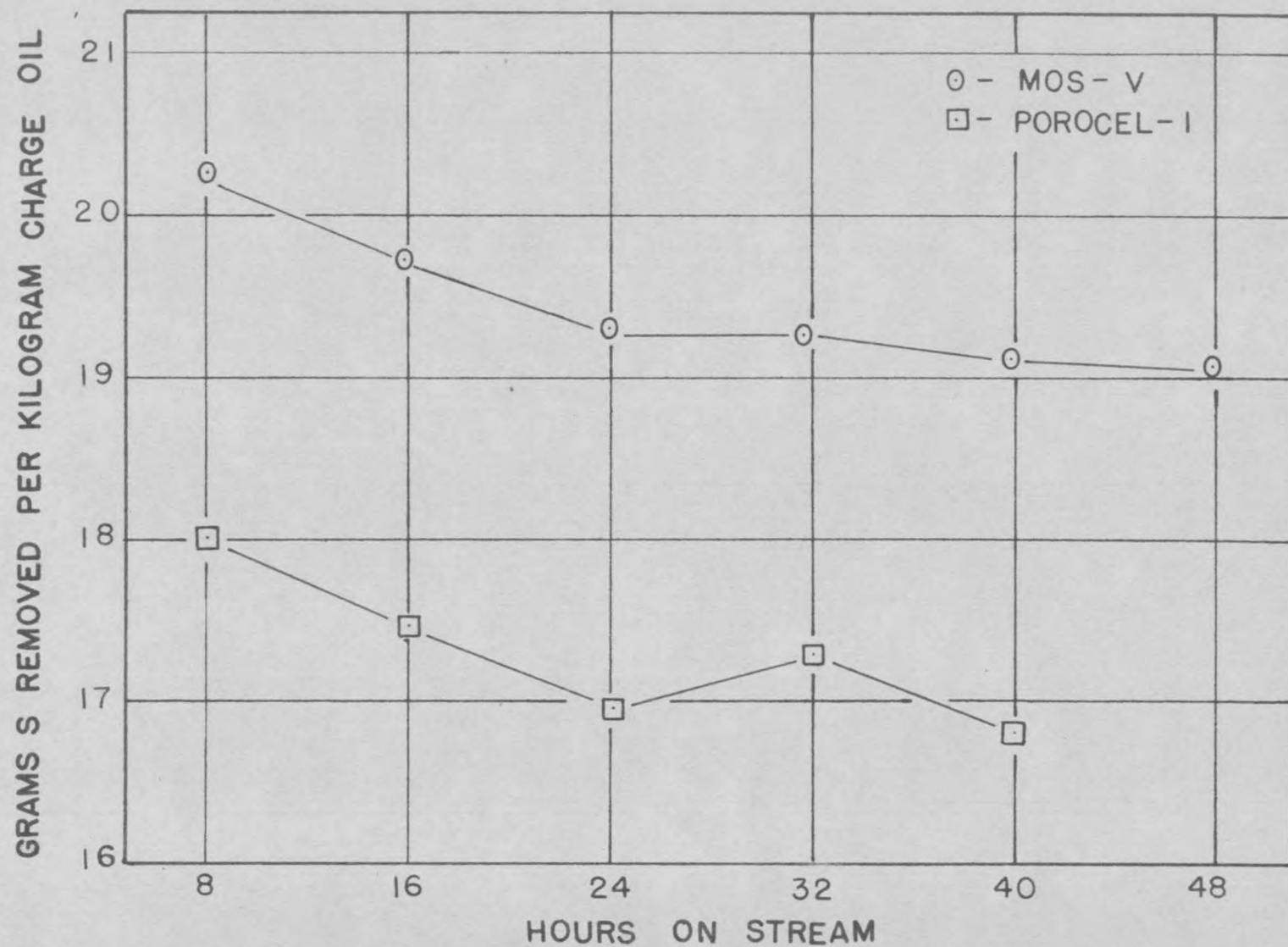


Figure 6. Effect of On-Stream Time on Sulfur Removal for Runs MOS-V, (Harshaw's Mo-0203-T-1/8" Catalyst) and Porocel-1.

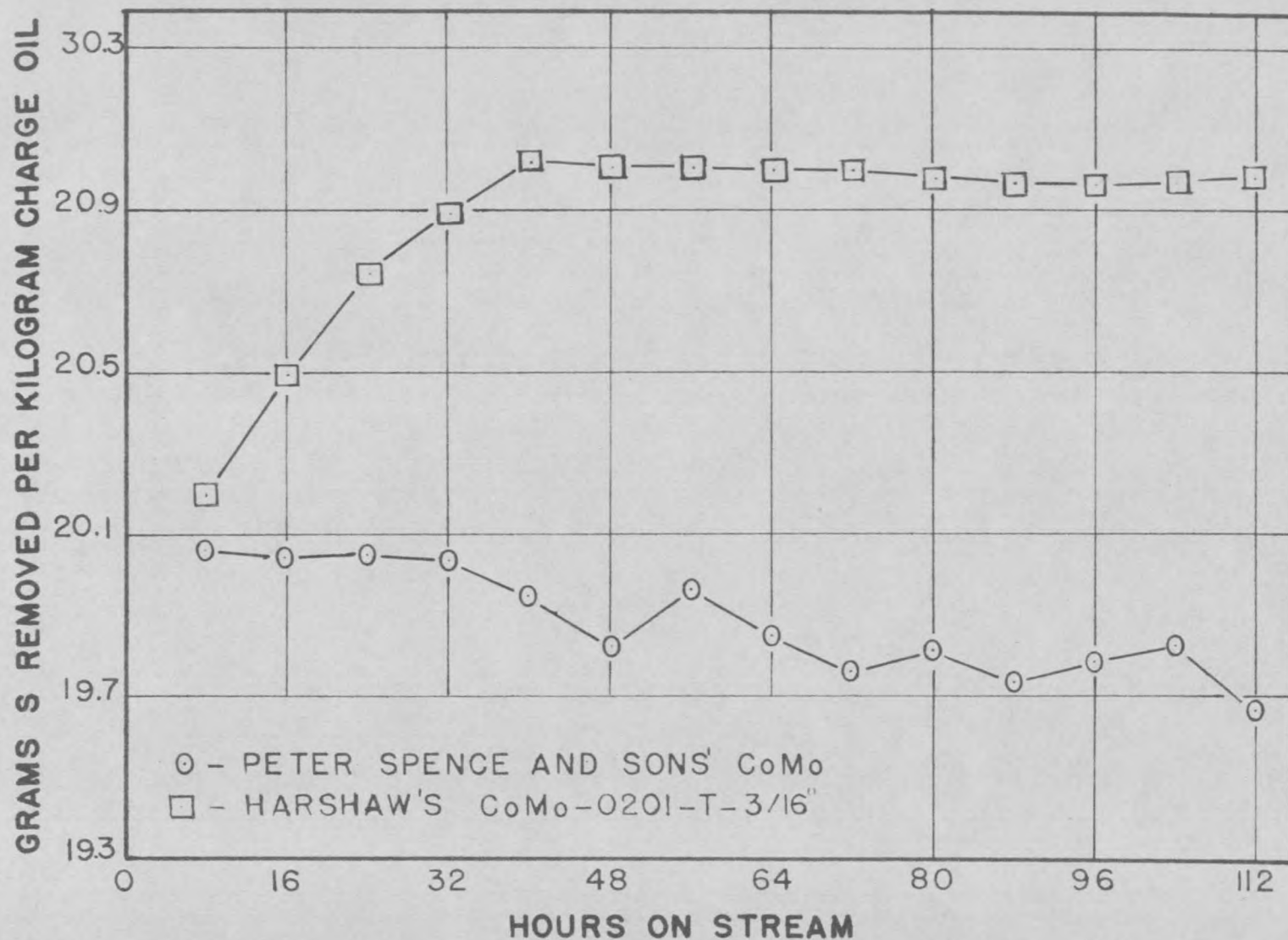


Figure 7. Desulfurization of Husky #3 Fuel Oil Using Peter Spence and Sons' CoMo and Harshaw's CoMo-0201-T-3/16" Catalysts.

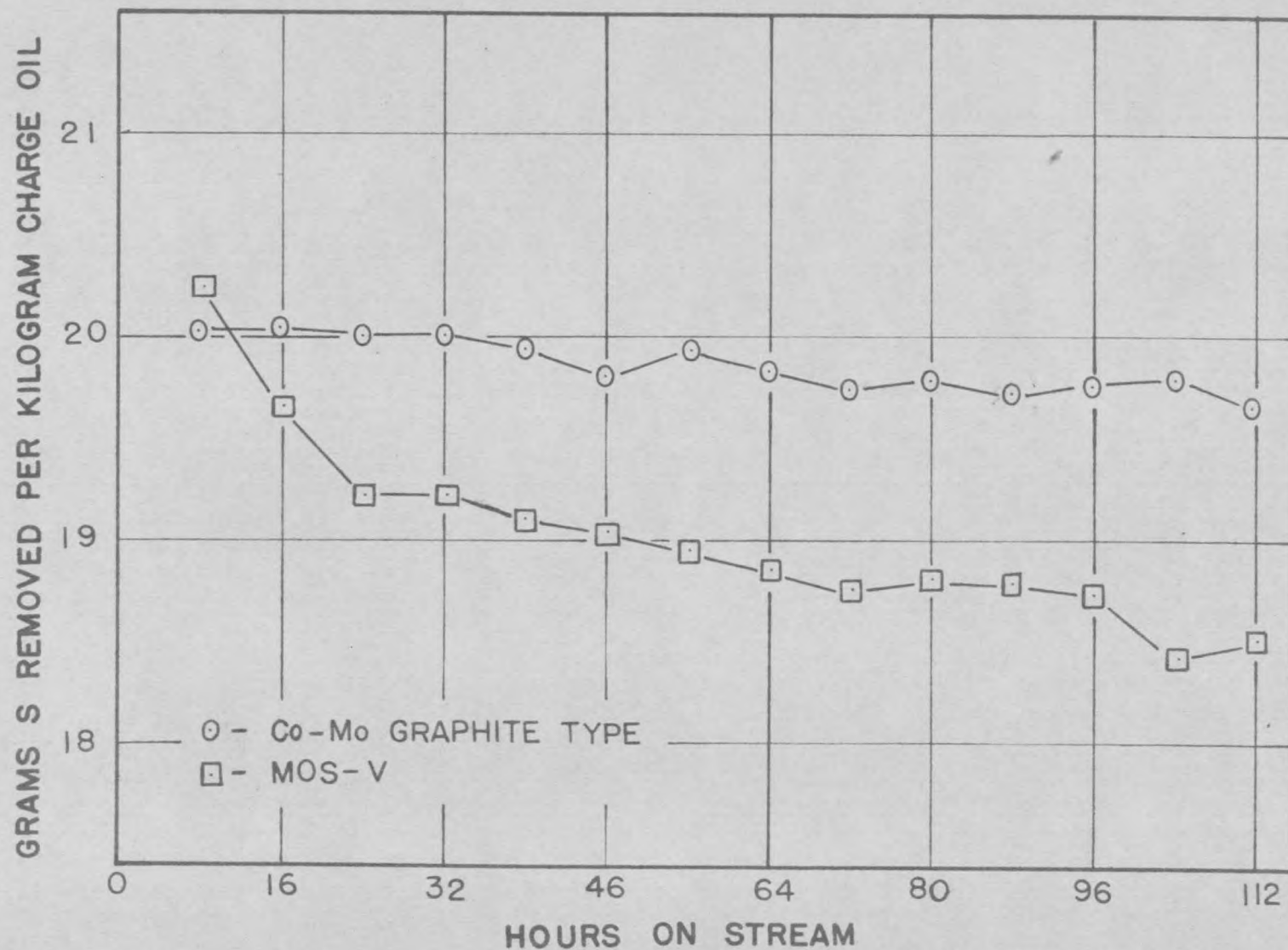


Figure 8. Effect of On-Stream Time on Sulfur Removal for Runs CoMo Graphite Type and MOS-V(Mo-0203-T-1/8" Catalyst).

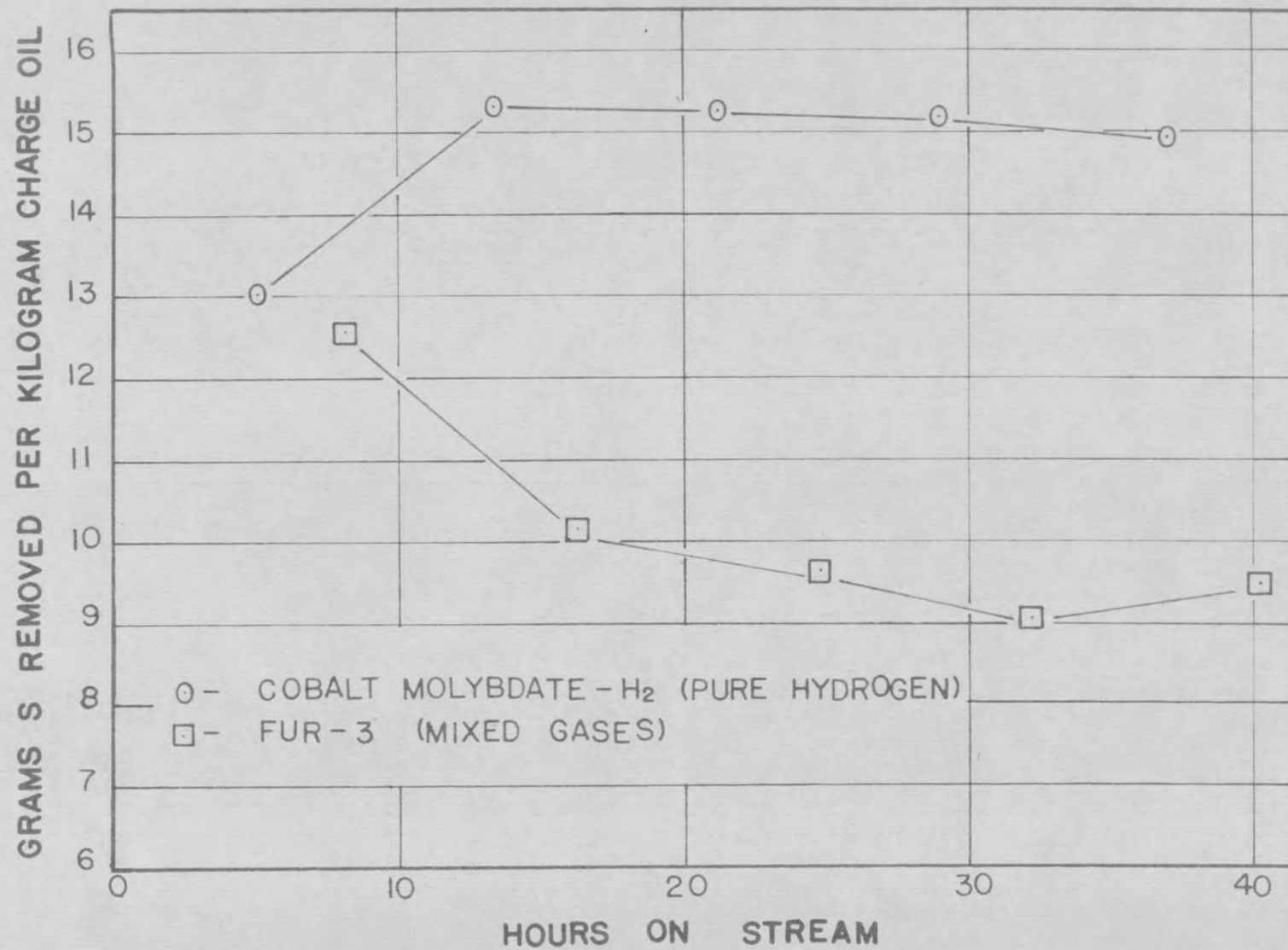


Figure 9. Desulfurization of Husky #3 Fuel Oil Using Pure Hydrogen and Mixed Gases.

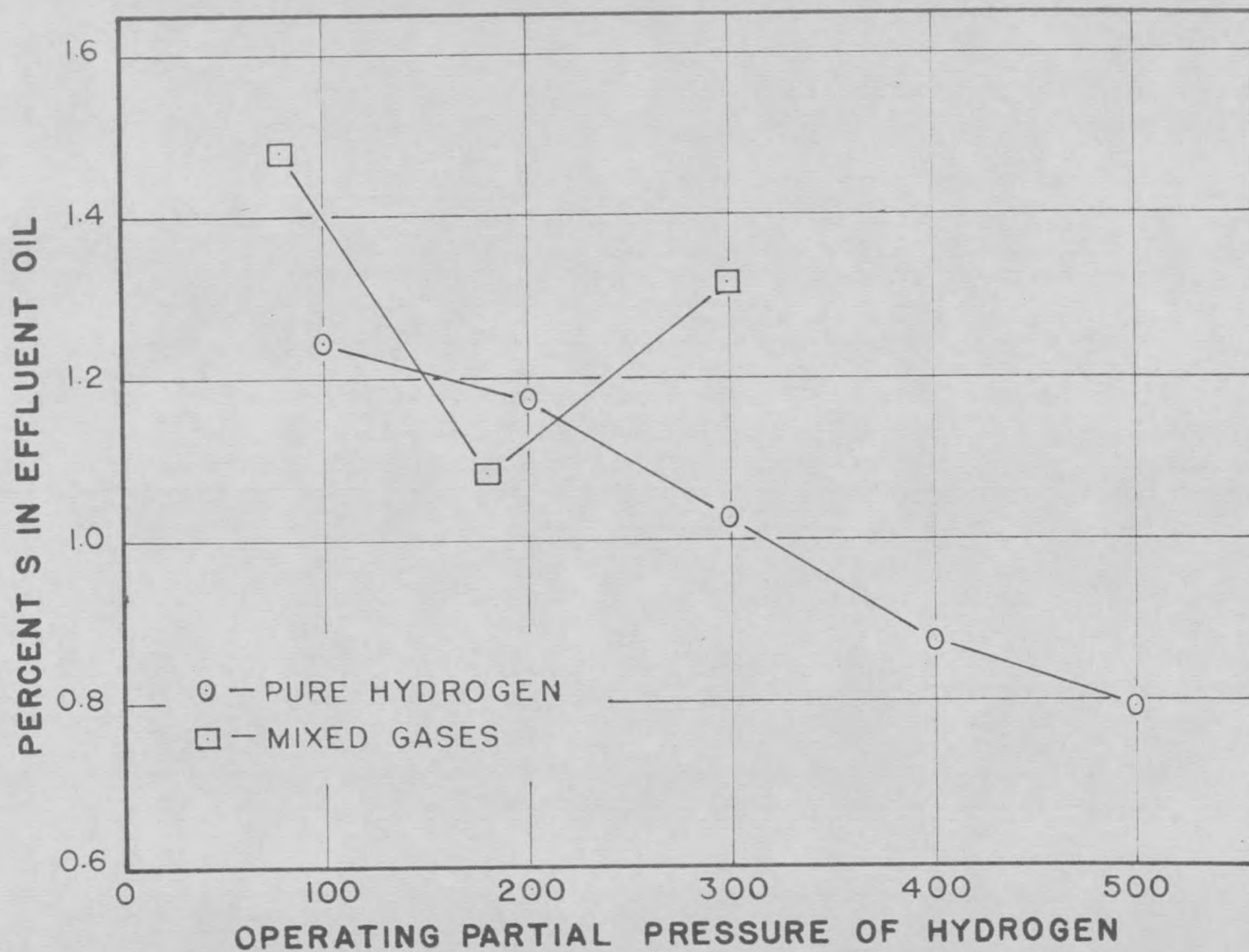
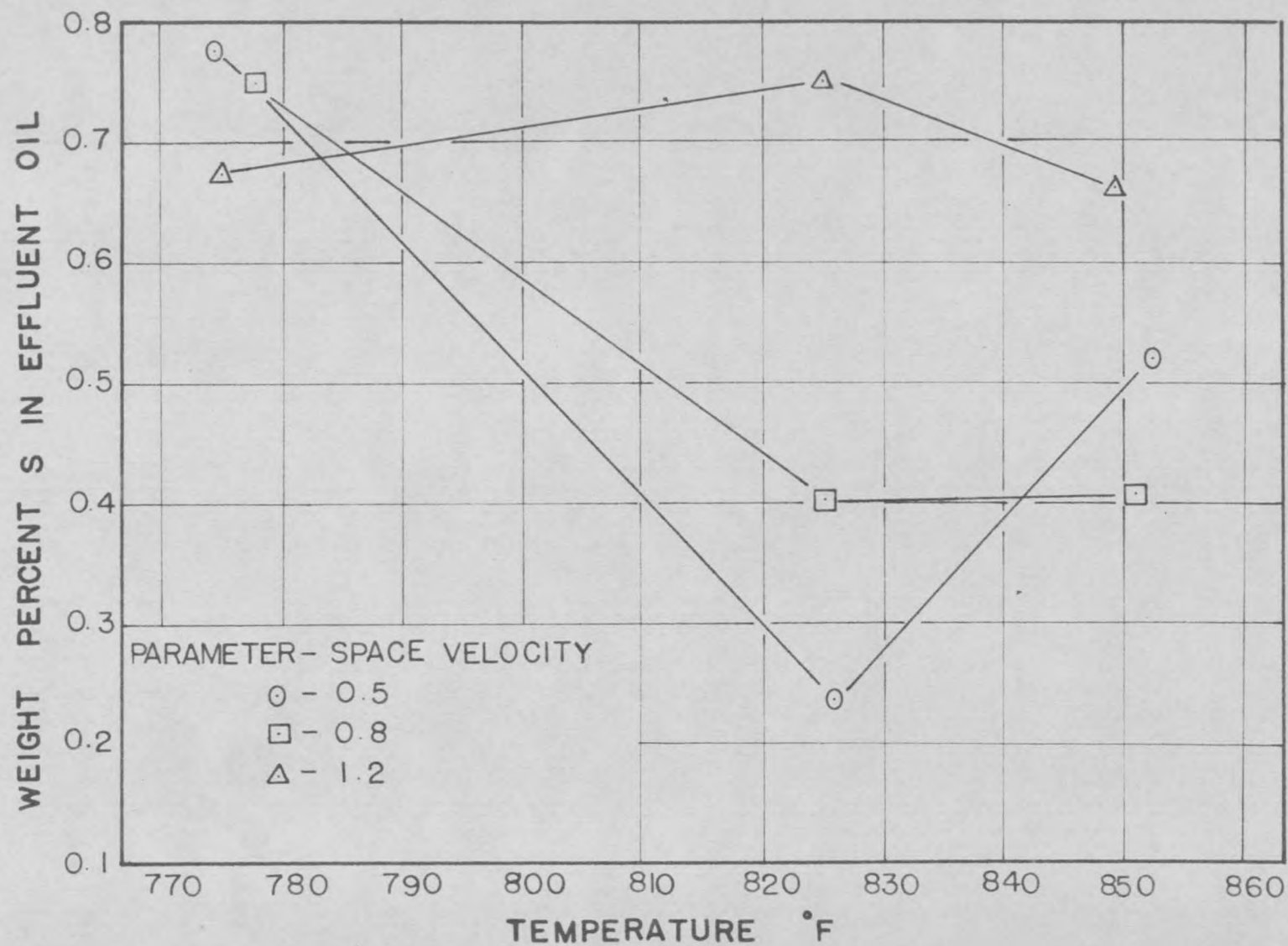


Figure 10. Effect of Partial Pressure of Hydrogen on Percent Sulfur in Effluent Oil When Desulfurizing Husky #3 Fuel Oil.



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Figure 11. Effect of Temperature on Percent Sulfur in Effluent Oil for Aramco #2.

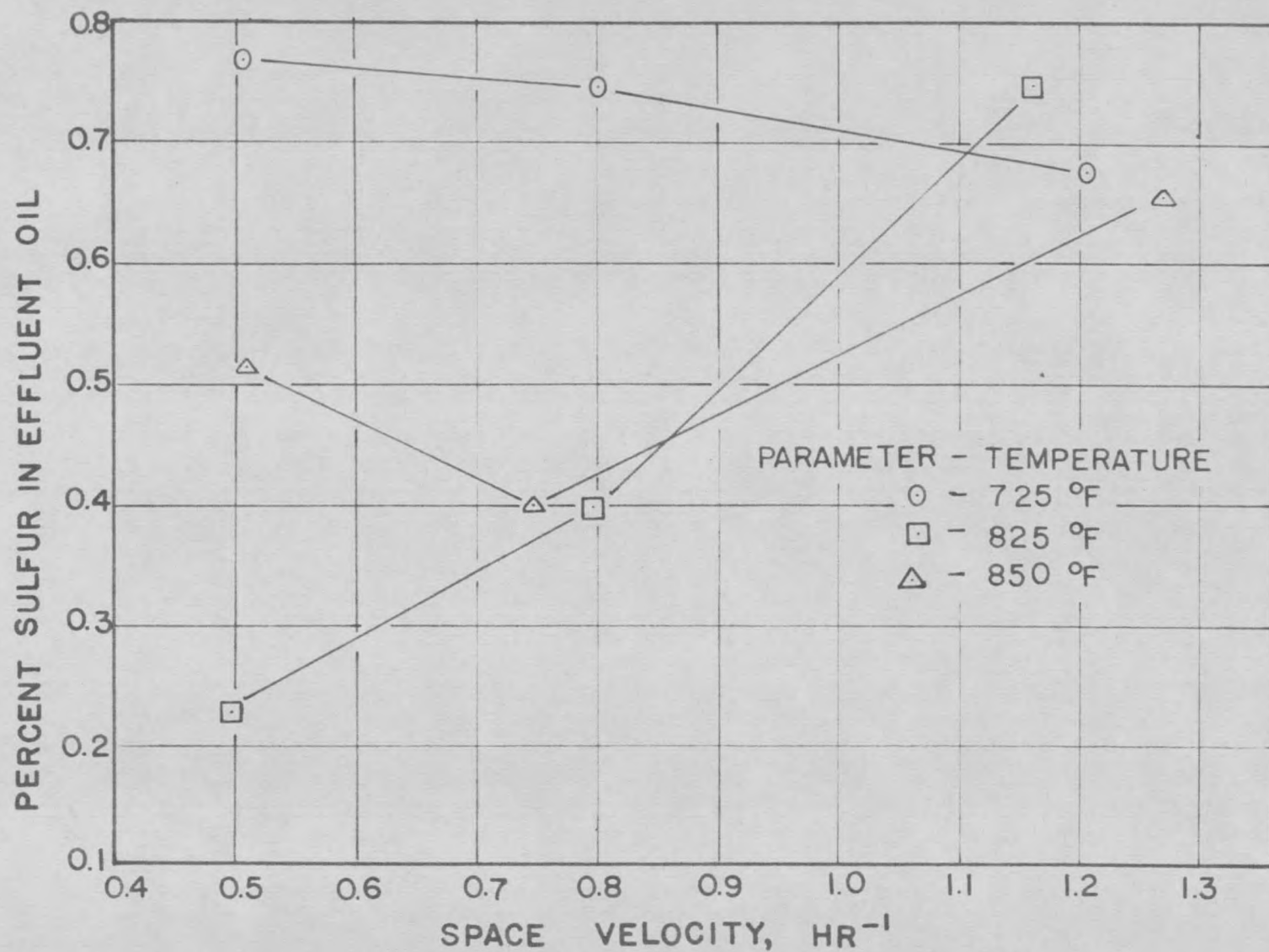


Figure 12. Effect of Space Velocity on Percent Sulfur in Effluent Oil for Aramco #2.

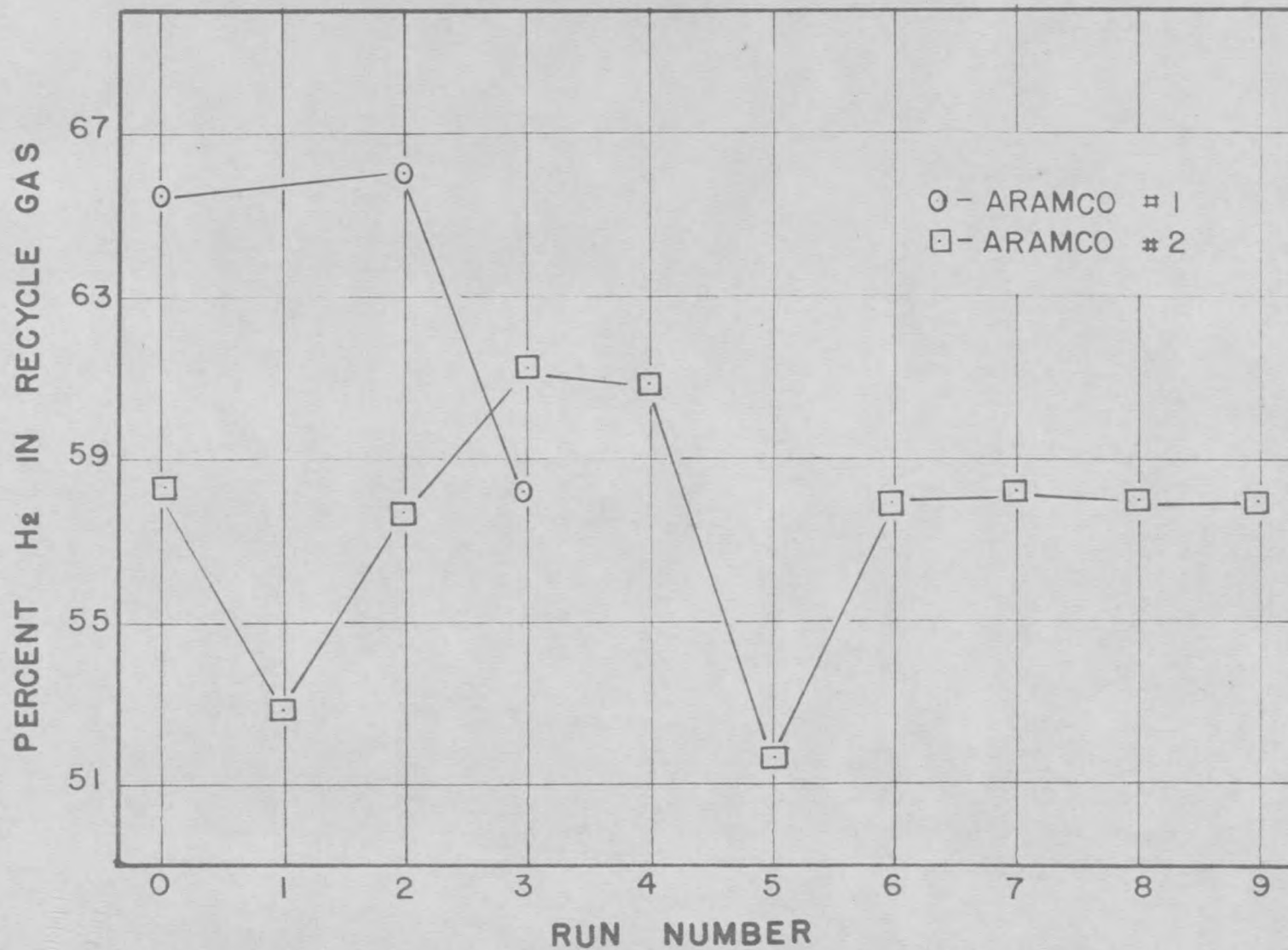


Figure 13. Variation of Hydrogen Concentration in Recycle Gas During Each Run for Aramco Statistical Runs #1 and #2.



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Westby, A. J.

Catalytic hydrodesulfuriza-
tion of fuel oil.

NAME AND ADDRESS

10-27-67	Jayant Sarain
	Ronald Lalonde
	106 LAWRENCE ST
11-29-67	Lam-yuk Kan 915
	651 19
1-14-68	A Doornbos
	QUAD D. C.
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