



The catalytic hydrodesulfurization of Wyoming fuel oil  
by John R Hartwig

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:

This investigation was primarily concerned with the effect of gas recycle on the catalytic hydrodesulfurization of a number-three-fuel oil from a sulfur content of 2.2 percent to 0.5 percent or below. Initial gas compositions were either pure hydrogen or a gas mixture that was approximately 84 percent hydrogen. In the runs with an initial gas composition of pure hydrogen the make-up gas added was also pure hydrogen. Make-up gas for runs where gas mixtures were used was the same composition as the initial gas composition (i. e. approximately 84 percent hydrogen).

Nickel oxide and nickel hydroxide catalysts were studied briefly, but the major emphasis was on molybdenum sulfide catalysts.

Optimum desulfurization conditions were not evaluated. The emphasis was on the determination of gas consumption during continuous gas recycle operation.

Conditions for the nickel study runs were: space velocity 0.1 to 3.0 gm. oil/gm. cat-hr., temperature 385 to 390°C, pressure 60 to 100 psig, and gas recycle rate from 0.4 to 2.0 liters gas/gm oil. Process variables for the molybdenum runs were: space velocity 0.7 to 1.3 gm oil/gm cat-hr, temperature 410 to 415°C pressure 500 psig, and gas recycle rate 0.9 to 1.8 liters gas/gm oil.

The gas consumption when pure hydrogen was used as the recycle gas was approximately 140 SCF/bbl and the gas consumption with a gas mixture on recycle was between 250 to 300 SCF/bbl. These consumption figures were obtained with molybdenum catalysts.

The effectiveness of the desulfurization process when a gas recycle system was used was noticeably different than that when the process was carried out with the gas on a one pass system. Specification oil was produced with molybdenum catalysts and a recycle gas with a hydrogen content as low as 80 percent by volume.

The molybdenum catalysts were far superior to the nickel catalysts as far as catalyst life and the degree of desulfurization were concerned.

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OF WYOMING FUEL OIL

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Approved:

*Lloyd Berg*

Head, Major Department

*Lloyd Berg*

Chairman, Examining Committee

*J. A. Nelson*

Dean, Graduate Division

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ABSTRACT

This investigation was primarily concerned with the effect of gas recycle on the catalytic hydrodesulfurization of a number three fuel oil from a sulfur content of 2.2 percent to 0.5 percent or below. Initial gas compositions were either pure hydrogen or a gas mixture that was approximately 84 percent hydrogen. In the runs with an initial gas composition of pure hydrogen the make-up gas added was also pure hydrogen. Make-up gas for runs where gas mixtures were used was the same composition as the initial gas composition (i. e. approximately 84 percent hydrogen).

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The gas consumption when pure hydrogen was used as the recycle gas was approximately 140 SCF/bbl and the gas consumption with a gas mixture on recycle was between 250 to 300 SCF/bbl. These consumption figures were obtained with molybdenum catalysts.

The effectiveness of the desulfurization process when a gas recycle system was used was not noticeably different than that when the process was carried out with the gas on a one pass system. Specification oil was produced with molybdenum catalysts and a recycle gas with a hydrogen content as low as 80 percent by volume.

The molybdenum catalysts were far superior to the nickel catalysts as far as catalyst life and the degree of desulfurization were concerned.

## INTRODUCTION

The depletion of low sulfur content crudes in the United States is forcing refiners to employ increasing amounts of high sulfur crudes. Utilization of these crudes has forced refiners to develop economical processes for removal or conversion of sulfur compounds in the various products refined from them. Methods commonly used for desulfurization of gasoline are not satisfactory for the treatment of higher boiling petroleum fractions such as diesel and fuel oils. Such commercial processes as the Unisol process, the Solutizer and Tannin Solutizer processes, hypochlorite treatment, Gray desulfurization, treatment with bauxite catalysts, as well as caustic and acid washes, either do not reduce the sulfur content in the heavier distillates to the desired percentages or hydrocarbon losses are excessive. Although the identification of specific sulfur compounds in any particular petroleum fraction is a difficult task, and research in this direction has not been extensive until fairly recently (8) (9), it has been fairly well established (9) that the sulfur compounds in kerosine and fuel oil distillates are predominantly thiophenic in nature. These compounds are not receptive to any of the desulfurization treatments mentioned above.

Successful desulfurization of fuel oil distillates to very low limits has been accomplished by catalytic hydrodesulfurization. Work by Green (6) and Munro (3) with a molybdenum sulfide catalyst in a hydrogen atmosphere reduced the sulfur content in a number of fuel oils from approximately 2.2 percent to less than 0.5 percent. Several commercially adaptable

catalytic desulfurization processes have been patented by the Anglo-Iranian and Union Oil Companies (10) (11). These processes utilize cobalt and molybdena catalysts and hydrogen gas atmospheres at various pressures (200-700 psig).

The inherent economic disadvantage of these catalytic hydrodesulfurization processes is the need for a relatively rich (greater than 90%) hydrogen gas supply. This difficulty can be overcome, however, by using the desulfurization process in conjunction with a "catforming" unit for upgrading low octane gasoline. In a typical catalytic reforming process (12) there is a net make of a gas mixture which is predominantly hydrogen (approximately 90%), with small quantities of methane, ethane, and propane present.

The capacity of such a desulfurization unit would naturally be regulated by the quantity of make gas from the catformer and the amount of gas consumed in the desulfurization process. The primary objective of this research was the determination of gas consumption (as SCF/bbl.) for the catalytic hydrodesulfurization process developed here in the past few years by Koski (2), Munro (3), and Green (6). This process was developed for the desulfurization of Husky Oil Company's number three fuel oil. The sulfur content in this fuel oil was to be reduced from 2.2 percent to 0.5 percent or below. As mentioned previously, the catalyst used was molybdenum sulfide (approximately 15% Mo) impregnated on an alumina carrier. The process variables for this catalyst were fairly well established in the preceding work. The optimum conditions found were: pressure, 500

psig; temperature 400-410°C (752-770°F); gas to oil ratio, 1.3 to 1.5 liters gas/gm oil; and a variable space velocity, (this varied between approximately 0.4 and 1.0 gm oil/gm cat.-hr., depending upon the activity of the catalyst).

Aside from the stated objective of the determination of gas consumption data, three runs were made using nickel catalysts. The purpose of these runs was a final attempt (see work by Coykendall (7) and Haas (5)) to determine if there was any true catalytic effect with nickel catalysts, and to prove whether the process with nickel catalysts would work in the recycle apparatus used for the molybdenum catalyst studies.

The gas recycle study (GRS) and the molybdenum comparison run (MCR) were made using pure hydrogen gas. The catforming gas study run (CGR) used a gas mixture typical of the make gas from a "catforming" unit.

In all the runs with molybdenum catalysts (i.e., GRS, MCR & CGR), the effect of gas recycle on catalyst activity was also observed. The molybdenum comparison run (MCR), as the name indicates, was primarily a comparison test on a different batch of molybdenum catalyst delivered from the Harshaw Chemical Company.

EQUIPMENT, MATERIALS, AND METHODS

EQUIPMENT

A schematic diagram of the recycle unit is shown in Figure 1. The reactor itself is the same as that used by both Munro (3) and Green (6). Essentially it consists of a 16 inch length of  $1\frac{1}{2}$  inch extra strong black iron pipe fitted with a  $1\frac{1}{2}$  to  $3/4$  inch reducer at the top and a  $1\frac{1}{2}$  to  $\frac{1}{2}$  inch reducer at the bottom. Both the top and bottom of the reactor were fitted with unions to allow for easy takedown of the reactor for loading and unloading. Fitted on the top of the reactor were two crosses and an assembly of valves for gas, oil, and regeneration air inlet. A blow-out line and thermowell tube were also fitted to this assembly. The thermowell tube was a  $\frac{1}{4}$  inch black iron pipe which extended from the cross at the top of the reactor down through the vertical axis of the reactor to within one inch of the bottom. It was possible to position three thermocouples at any point within the reactor with this system. The thermocouples were iron-constantan and were used in conjunction with a Leeds and Northrup indicating potentiometer for temperature measurement.

Fitted at the bottom of the reactor was a water cooled condenser. At the bottom of the condenser, connected from a cross, was the reactor pressure gage, high pressure product receiver (a 12 inch Jerguson sight gage), a standpipe, and the reactor back pressure valve.

At the bottom of the Jerguson product receiver was the receiving flask, caustic scrubbing train, and a wet test meter manufactured by the Precision Scientific Company. A constant oil level was maintained in the

Jerguson receiver by hand adjustment of a needle valve at the bottom of the receiver.

The reactor pressure was maintained by a Mason-Neilan small-volume air-to-close regulator valve. This pressure regulator was controlled by a Fisher Wizard proportional controller.

A two cylinder, adjustable stroke, high pressure piston pump and an oil reservoir comprised the oil feed system.

Three 33-foot lengths of beaded Nichrome wire, supplied with current from three 110-volt Powerstat autotransformers, provided variable heat input for the reactor. Two of these heating coils were located near the bottom of the reactor to heat the catalyst section and one was located higher up on the reactor to heat the preheat section. Alundum balls were used as preheat media.

Gas flow to the reactor was metered by a Fisher flowrater and regulated by a needle valve manufactured by the American Instrument Company. This needle valve was located ahead of the flowrater.

The remaining equipment of the unit made up the gas recycle system. The compression pump was a two cylinder Hills-McCanna high pressure proportioning pump. The feed tank was made from a number one gas cylinder and the surge and compression tanks were made from number two gas cylinders. A Brook's Rotameter metered the flow from the make-up tank.

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

tubing.

Before the recycle unit as shown in Figure 1 was constructed, a different unit was used. This unit was essentially the same as the later unit with the exception of the gas recycle system. Instead of using an oil displacement method for gas compression, a small refrigerator compressor was used to move the gas from the surge tank to the feed tank. This system worked quite well until the middle of the "catforming" gas study run. At that time repeated compressor breakdowns caused so much trouble and unit shutdown time that the recycle unit as shown on Figure 1 was constructed. This unit did not cause any operational troubles and proved to be a great improvement over the old system.

#### MATERIALS

The oil used throughout this work was Husky Oil Company's number three fuel oil. The sulfur content of this oil varied between 2.09 and 2.19 percent. Additional data for this oil can be found on Table I in the appendix.

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

Recycle gas used was either pure hydrogen or a gas mixture. The hydrogen was obtained from the Whitmore Oxygen Company of Salt Lake City, Utah. The gas mixture was obtained from the Matheson Chemical Company in East Rutherford, New Jersey. The composition of this gas mixture (as ordered) was: hydrogen, 89 percent; methane, 3.5 percent; ethane, 1.5 percent; propane, 2.5 percent; and propylene, 3.5 percent. To obtain this gas composition a Husky gasoline stock was sent to the Atlantic Refining

Company and run through their catalytic reforming unit. Analysis of the make gas from the run with the Husky stock gave the above composition.

#### METHODS

The unit was started by applying heat to the heating coils with the gas flowing through the reactor. The reactor was set at the desired pressure during this period or when the catalyst temperature reached 300°C. Oil flow was started and the space velocity adjusted when the catalyst temperature reached 380°C. Readings were recorded after the desired catalyst temperature was reached, with the gas flow, reactor pressure, and space velocity properly adjusted and maintained.

As the product oil collected in the Jerguson pressure receiver it was allowed to drip slowly to the receiving flask. The receiving flask was removed and replaced at the desired sampling periods. Dissolved gases (predominately H<sub>2</sub>S), which flashed from the oil when the oil left the pressure receiver, went to the caustic scrubbing train and then to the wet test meter where the gases were metered and passed to the exhaust line.

In the operation of the unit, the recycle gas flowed from the feed tank through the flowrator and to the reactor. After the gas passed through the reactor and the reactor back-pressure regulator, it flowed to the surge and compression tanks. When the pressure in these two tanks reached 300 psig the surge tank was isolated from the compression tank and the compression pump was started. Compression oil (Husky's number three fuel oil) was pumped from the compression oil reservoir to the compression tank, compressing the gas in the compression tank. When the pressure in

the compression tank became equal to that in the feed tank (usually between 550 and 560 psig) the valve between these two tanks was opened and the gas in the compression tank was pushed over to the feed tank. When all the gas in the compression tank had been pushed to the feed tank (as indicated by the appearance of oil in the sight glass on the compression tank) or when the pressure in the feed tank reached 600 psig, the compression pump was stopped and the valve between the feed and compression tank was closed. The valve between the surge and compression tank was then opened. The oil in the compression tank was forced back to the compression oil reservoir by the pressure from the surge tank when the valve between the oil reservoir and the compression tank was opened. The compression cycle was started again when the pressures in the compression and surge tanks again reached 300 psig. The compression cycle usually took about 1.5 hours for completion with 45 minutes to an hour between cycles.)

Arbitrary, standard pressures were set for the feed tank and the compression and surge tanks; that for the feed tank was 600 psig, and for the compression and surge tanks it was 250 psig. When the pressure in the surge and compression tanks fell below 250 psig (with the pressure in the feed tank up to 600 psig) at the end of a compression cycle, make-up gas was added to bring the pressure in these two tanks back to 250 psig. Gas flow from the make-up tank was metered through the Brooks rotameter and this flow was timed with a stopwatch.

When desired, recycle gas samples were taken from a bleed-off valve located on the downstream side of the reactor back pressure regulator.

The gas sample was passed through the caustic scrubbing train and the wet test meter before it was collected over water in eight liter glass sample bottles. Analysis of the gas samples was made in a low temperature fractionation column.

Sulfur analysis of each oil sample was made by the lamp method (1).

#### CALCULATIONS

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

The space velocity recorded was based on input oil. Each individual sample weight was corrected by the percent loss over a longtime period of the run as calculated from oil weight balances.

For example:

Percent loss, wt. basis = 2%. Then, for an individual sample weighing 800 gms., input weight =  $\frac{800}{.98} = 816$  gms. Then, for an 8 hr. sample period with a 100 gm. catalyst charge, space velocity =

$$\frac{816 \text{ gms. oil}}{(100 \text{ gms. cat.})(8 \text{ hrs.})} = 1.020.$$

The gas flow (as recycle gas, SCF/bbl.) was calculated by dividing the gas flow per sample period by the oil weight per sample period.

For example:

With an 800 gm. oil sample (816 corrected wt.) and a gas recycle rate (as indicated by the Fisher flowrater) of 1070 liters (STP) per 8

hours;  $\frac{1070}{816} = 1.3$  liters gas/gm oil. Then 1.31 liters gas/gm. oil

x .875 gm. oil/cc. oil x 1000 cc/liters x  $\frac{28.32}{7.48}$  liters/gal x

42 gal/bbl x  $\frac{1}{28.32}$  Ft<sup>3</sup>/ liters = 6430 Ft<sup>3</sup>/bbl. (STP).

Hydrogen consumption was calculated from the make-up and bleed-off gas figures recorded for each sample period. Bleed-off figures were the wet test meter readings. Make-up figures were from the Brook's rotameter readings.

For example:

For an 800 gm-oil sample (816 corrected) and gas make-up equal to 40 liters (STP) and bleed-off equal to 8 liters (STP), the gas consumed would be 32 liters (STP).

Then  $\frac{32}{816} \times \frac{1000}{1} = 39.2$  liters consumed/kilogram oil.

$39.2 \times 4.91$  (conversion factor) = 193 Ft<sup>3</sup> consumed/bbl oil.

Gas consumption for any individual sample period varied widely so the figures presented in the data were cumulative averages.

For example:

After ten samples, total gas consumption equalled 3100 Ft<sup>3</sup>. Then

for the tenth sample,  $\frac{3100}{10} = 310$  Ft<sup>3</sup>/bbl.

The catalyst temperatures presented in the data are averaged temperatures for each sample period indicated. The thermocouples for the catalyst bed were located at the top and bottom of the catalyst bed. The top and bottom catalyst temperatures were averaged and these average temperatures were averaged over the sample period.

A thermodynamic study of probable reaction mechanisms for the catalysts used and reported in this paper was not made since this was done previously by Munro (3) and Green (6) for the molybdenum sulfide catalysts, and by Haas (5) for the nickel catalysts.

## RESULTS AND DISCUSSION

With the exception of three relatively short runs using nickel catalysts, only one type of catalyst ( $\text{MoS}_2$ ) was used. The primary concern of this research was the study of the effect of gas recycle on the desulfurization process, with determination of gas consumption especially emphasized. Tabulated data for all runs made in this study are presented in the appendix.

All of the studies made on nickel catalysts were made primarily to observe the effectiveness of these nickel catalysts in the recycle unit and to determine whether the nickel catalysts' desulfurization action was a chemical or catalytic reaction. In respect to the type of reaction of the nickel catalysts, Haas (5) has already stated that the desulfurization by nickel catalysts was strictly a chemical reaction.

If desulfurization was accomplished through a catalytic mechanism when nickel catalysts were used, a certain amount of hydrogen would necessarily have to be consumed. The hydrogen is consumed by the combination with the sulfur in the oil (to form  $\text{H}_2\text{S}$ ) and the combination with the hydrocarbon from which the sulfur was removed. However, for NSR-I and NSR-II (Tables III and IV) gas was produced and it was not necessary to add any make-up gas. For the third nickel study run (NSR-III, Table V) a total of 21.8 SCF/bbl was consumed. When compared to gas consumption with molybdenum catalysts (140 to 300 SCF/bbl) the consumption of 21.8 SCF/bbl is not large.

A possible conclusion to be drawn from the above discussion would be

that the sulfur was removed by some other means (e.g. by chemical combination with the nickel) and not by carbon to sulfur bond fissure with subsequent formation of  $H_2S$ , and resultant hydrogen consumption.

For all the nickel study runs, gas analysis of the recycle gas revealed a high hydrocarbon gas buildup (predominately methane). The hydrocarbon buildup in the recycle gas that occurred when nickel catalysts were used indicates to some extent the non-selectivity of these catalysts when they are used as desulfurization agents. Instead of breaking the carbon to sulfur bonds the nickel catalysts evidently induced a predominate carbon to carbon cracking with the production of large amounts of methane.

Haas (5) also states that the desulfurization depends in a large part on space velocity. This is amply demonstrated by comparison of NSR-I and NSR-II with NSR-III. The average space velocity for the first two runs was approximately 3.0 gm oil/gm cat.-hr, whereas that for the last run (NSR-III) was 0.1 gm oil/gm cat.-hr. In the first two runs no specification of oil was produced at all, whereas approximately 12 throughputs (i.e. 2400 gms oil) were achieved by blending samples 1 through 27 in the third 200 gms. cat. nickel study run.

The different pressures used (i.e. 60 psig for NSR-I and NSR-II, and 100 psig for NSR-III) in the nickel runs did not have any apparent effect on the degree of desulfurization.

Results from the three nickel runs show that the nickel catalysts do not have a long catalyst life and that their desulfurization action is quickly lost after only a few oil throughputs.

Operating conditions for the NSR runs were established by the research laboratory of Husky Oil Company in Cody, Wyoming.

The Gas Recycle Study (GRS, Table VI) was the first run made with gas recycle operation with an  $\text{MoS}_2$  catalyst. The molybdenum catalyst used for this run had been used previously by Green (6) in his mixture study run for a total of 607 hours. Successful desulfurization was accomplished for an additional 526 hours with this catalyst. During the GRS run the space velocity varied between 0.5 and 0.8 gm oil/gm cat.-hr. Gas recycle varied between 6000 and 11,000 SCF/bbl. Pure hydrogen was used as make-up during this run.

At the start of the run the recycle gas was approximately 100 percent hydrogen. At the end of the run the hydrocarbon buildup in the recycle gas did not exceed five percent.

Gas consumption calculations were not made during the first 26 samples of this run. During this period, considerable difficulty was encountered in establishing operating procedures with the gas recycle system, and in establishing standard tank pressures to assure continuous gas flow and an accurate gas balance.

Calculation of gas consumption was started after sample 26. From sample 26 through 36 there was a gas leak in one of the valve stems on the unit. Rather than shut down the unit and repair this leak, the gas escaping from the valve stem was metered and the run was continued. The amount of gas leaking from the valve stem was approximately one-tenth of the gas recycle rate. Gas consumption during this period of gas bleed-off and

including the gas bleed-off was between 220 to 275 SCF/bbl oil.

From sample 37 to the end of the run the gas leak was repaired and with no gas bleed-off the gas consumption leveled off at about 140 SCF/bbl.

Gas samples were taken from the recycle unit at various times during the GRS run. Analysis of these gas samples revealed a buildup of hydrocarbon gases. In order to ascertain the trend of this hydrocarbon gas buildup a method had to be developed to correlate the hydrocarbon buildup with some factor which would be independent of the size of the recycle unit and the total amount of gas being recycled.

When the space velocity and gas flow are kept constant, the rate of hydrocarbon gas buildup should also remain constant. However, the time it would take to obtain a specified hydrocarbon buildup would vary with the size of the reactor system and the total amount of gas in the system. Correlation between hydrocarbon gas buildup and hours on stream would be meaningless if applied to other reactors. To overcome this, the number of gas recycles was calculated at each gas sample period and in this way it was possible to compare the hydrocarbon content of the recycle gas with the number of times the total volume of gas in the reactor system had been passed through the reactor proper.

The following calculation was applied to the GRS run to determine the number of recycles at each gas sample period. The calculation cited is for a ten day period of the run.

109 = average cubic feet recycled per day.

10 = number of days for which the calculation was made.

70 = cubic feet of gas in the reactor system at the arbitrary standard pressures.

12 = average cubic feet of make-up gas added per day during the period of calculation.

$$\frac{(109)(10)}{70 + 12} = 13 \text{ recycles.}$$

When the above method of calculation was applied to the GRS run the hydrocarbon buildup after 8 recycles was 4.4 percent (volume percent), after 9 recycles it was 5.0 percent, after 11 recycles it was 6.0 percent, and after 13 recycles the hydrocarbon content in the recycle gas was 4.6 percent. These calculations indicate that the amount of hydrocarbon gas buildup in the recycle gas was not excessive and that the percentage increase in hydrocarbon content per recycle was relatively small (i.e. after 8 recycles it was .55 percent per recycle and after 13 recycles it was .35 percent per recycle).

Oil losses for the gas recycle study on a weight basis were 3.1 percent. In the work by Munro (3) and Green (6), oil losses averaged around 6.0 percent. In their studies the oil samples were collected at atmospheric pressure and some oil was carried off as a mist. With the recycle unit the oil samples were collected under pressure and no oil loss as a mist occurred.

The  $\text{MoS}_2$  catalyst used in the GRS (Table VI) run was used previously by Green (6) in his mixture study run. The same operating conditions were used for the first 34 samples of Green's mixture study run as were used in the gas recycle study. The only difference in that part of the mixture

study run being cited and the GRS run was the recycle of gas during the GRS run. With this in mind a comparison of the relative catalyst activity during the GRS run can be made with the activity of the same catalyst when no gas recycle was being used. Green's mixture study run had an average space velocity (samples 1 through 34) of approximately 0.7 gm oil/gm cat.-hr. With this space velocity the average sulfur content of the effluent oil was approximately 0.3 percent. In the gas recycle study the average space velocity was also approximately 0.7. The average sulfur content in the product oil was about 0.4 percent. From these figures it would seem that the catalyst was not as active under gas recycle conditions. However, when the deactivation of catalyst with use is considered (the mixture study run by Green added 333 hours on stream time to the catalyst before it was used in the gas recycle study) the activity of the catalyst with gas recycle would seem to be the same as that without gas recycle.

The molybdenum comparison run (MOR, Table VII) was started with approximately the same operating conditions as were used for the gas recycle study. This run was made to compare the activity of MoS<sub>2</sub> catalysts used in the past with a MoS<sub>2</sub> catalyst prepared on a larger scale by the Harshaw Chemical Company. With an initial space velocity of 0.7 gm oil/gm cat.-hr the sulfur content of the effluent oil was only 0.1 percent.

When the space velocity was nearly doubled, the percent sulfur in the product oil also increased, but it did not exceed 0.5 percent until the space velocity was raised above 1.35 gm oil/gm cat.-hr. The percent sulfur dropped from .519 to .304 when the space velocity was lowered from 1.331 to

.869 gm oil/gm cat.-hr.

Although this run (MCR) was comparatively short (160 hours), the above results demonstrate readily the higher activity of the  $\text{MoS}_2$  catalyst used as compared to any of the molybdenum sulfide catalyst used previously, either in this research or in the work by Munro (3) and Green (6). In these studies specification oil was rarely produced if the space velocity exceeded 1.0. The average gas consumption was 140 SCF/bbl which was the same as the gas consumption for the gas recycle study. The buildup of hydrocarbons in the recycle gas was 4.2 percent after 10 recycles. This is also comparable to the gas recycle study.

There is no apparent reason for the greater activity shown by the catalyst used in the MCR run (Table VII). The composition of this catalyst was nearly the same as the composition of  $\text{MoS}_2$  catalysts used previously (see Table II). The catalyst used for this run was a part of a somewhat larger batch than was usually ordered from the Harshaw Chemical Company for desulfurization studies. Usually, small (5 to 10 pounds) samples of catalyst were ordered, but in this case about 40 pounds of the catalyst was made. A possible reason then, for the higher catalyst activity could be the method of manufacture of the catalyst.

The same catalyst that was used for the MCR run was used for the "catforming" gas study run (CGR), Table VIII. The catalyst had been used for 160 hours during the MCR run. It was not regenerated or treated in any other way prior to its use in the CGR run. This catalyst exhibited a somewhat higher activity than those used in the past, but as the CGR run

progressed the activity of the catalyst did decline.

During the CGR run two air regenerations of the catalyst were made. The regenerations were made with the catalyst in the reactor. The first air regeneration was made after sample 61. In a total time of  $2\frac{1}{4}$  hours 938 liters (STP) of air was passed over the catalyst. The average temperature during this time was  $450^{\circ}\text{C}$  and the maximum temperature attained in the catalyst bed was  $600^{\circ}\text{C}$ . In the second catalyst regeneration (after sample 168) a total of 700 liters (STP) of air was passed over the catalyst for a period of 2 hours. The maximum temperature of the catalyst during this regeneration was  $620^{\circ}\text{C}$ . The level of the catalyst activity was increased after each air regeneration. Sample 61 had a sulfur content of .533 percent. Sample 62 (the first sample after the first catalyst regeneration) had a sulfur content of .279 percent. The sulfur content of the product oil before the second regeneration was .589 percent. After this regeneration the sulfur content dropped to .264 percent.

The gas used for the CGR run was a gas mixture considered typical of the make gas from a "catforming" unit. The analysis of this gas (as volume percent) was presented in the materials section. An analysis of the gas delivered was made as a check on its composition. Presented below is this analysis along with the composition specified when the gas mixtures were ordered.

	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
Specified composition (percent by volume)	89	3.5	1.5	3.5	2.5
Delivered composition	84	6.0	3.7	3.9	2.4

This check analysis indicated a somewhat leaner hydrogen composition than was anticipated.

The initial hydrogen content of the recycle gas was 84 percent. The hydrogen content of the recycle gas after 1341 hours of operation had dropped to 81.1 percent. This small decrease in hydrogen content did not noticeably affect the effective desulfurization during the run. Green (6) investigated the effect of gas composition on effective desulfurization and Silvey (4) has made a more thorough search in this direction.

The average gas consumption for the CGR run was approximately twice that found for previous runs (GRS and MGR) where pure hydrogen was used for recycle and make-up. Average consumption data for the CGR run varied between 280 to 290 SCF/bbl.

The temperature readings shown on the data for samples 30, 35, and 36 (Table VIII) are not the actual temperatures for these samples. The dry cell in the temperature indicating potentiometer was nearly dead for the period between samples 30 to 36. For the three samples cited, a close check on the standardization of the potentiometer was not made and the temperatures for samples 30, 35, and 36 were lower than the actual readings taken. The fact that temperature is a critical factor in effective desulfurization is readily shown by these three sample periods. They show that when the temperature is below a certain critical level (Munro (3) thought this was below 400°C) the sulfur content is correspondingly higher. For samples 30, 35, and 36 respectively the sulfur content of the effluent oil was .646, .552, and .568 percent. The other samples taken during this

period were all below 0.5 percent sulfur.

From sample 99 to sample 106 gas consumption calculations were not made. At this time the method of gas compression was changed (see Equipment section), and establishment of new operating procedure precluded any gas balance or gas consumption calculations.

The period of the run from sample 130 to sample 145 also did not have any gas consumption data. At this time the pressure in the gas make-up cylinder fell below the pressure for which the Brooks rotameter was calibrated and it was not possible to measure the quantity of make-up gas added to the reactor system. When new cylinders of the make-up gas were delivered the gas consumption calculations were resumed with sample 146.

The primary purpose of the CGR run (Table VIII) up to sample 61 was the determination of gas consumption and catalyst life using the "cat-forming" gas on recycle. After sample 61 it was decided to run at a space velocity of 1.0 until the sulfur content in the product oil exceeded 0.5 percent. When this occurred the catalyst was to be regenerated and the process repeated until the time between regeneration periods became excessively short. As the run progressed from sample 61, the decision was then made to run until the composite blend of the product oil samples reached 0.5 percent sulfur. The catalyst would then be regenerated, and a composite blend equal to 0.5 percent sulfur would again be the point at which catalyst regeneration would take place.

The run was ended, however, when it became obvious that the time interval between catalyst regeneration was prohibitively long if the

ultimate deterioration of the catalyst was to be determined.

### CONCLUSIONS

The brief studies made with nickel catalysts indicate that these catalysts are inferior to molybdenum catalysts as far as catalyst life and the degree of desulfurization are concerned. Data from these studies also substantiate in some measure the contention that the nickel catalysts desulfurize for the most part through a chemical reaction mechanism and that they do not act as true catalytic desulfurization agents.

Gas consumption data found with  $\text{MoS}_2$  catalysts indicate a higher consumption figure with a "catforming" gas mixture than with pure hydrogen when these gases are recycled.

When either hydrogen or a gas mixture was used as the recycle gas, the hydrocarbon gas buildup per recycle was not excessive and the buildup of hydrocarbon gases that did occur did not noticeably affect the desulfurization process.

Use of a gas mixture in the desulfurization process, as well as the continuous recycle of the effluent gases, did not noticeably affect the degree of desulfurization obtained with  $\text{MoS}_2$  catalysts.

Deactivation of the molybdenum catalysts with prolonged use was indicated by the studies made, but air regeneration restored the activity of these catalysts to a higher level than that of the fresh catalyst.

Although the molybdenum catalysts did exhibit some deterioration with use, specification oil was produced for 526 hours without catalyst regeneration when pure hydrogen was used as make-up and for 493 hours

before regeneration was necessary when "catforming" gas was used as make-up. -

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LITERATURE CITED

- (1) A. S. T. M. STANDARDS ON PETROLEUM AND LUBRICANTS, American Society for Testing Materials, Philadelphia, (1941).
- (2) Koski, O. H., M.S. Thesis, Montana State College (1951).
- (3) Munro, B. L., M.S. Thesis, Montana State College (1952).
- (4) Silvey, F. C., M.S. Thesis, Montana State College (1953).
- (5) Haas, P. A., M.S. Thesis, Montana State College (1951).
- (6) Green, K. J., M.S. Thesis, Montana State College (1952).
- (7) Coykendall, J. W., M.S. Thesis, Montana State College (1952).
- (8) Brown, H. R., and Meyerson, S., Ind. Eng. Chem., 44, No. 11, 2620-2631, (1952).
- (9) Hatch, L. F., Petroleum Refiner, 32, No. 6, 105-107 (1953).
- (10) Anon, Petroleum Refiner, 31, No. 6, 108 (1952).
- (11) Anon, Petroleum Refiner, 31, No. 9, 226 (1952).
- (12) Anon, Petroleum Refiner, 31, No. 9, 114 (1952).

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TABLE I  
FUEL OIL INSPECTION DATA

Sample Designation	Charge Stock No. 3 Oil	C G R Comp. 103-107	C G R Comp. 60-168
A.P.I	30.6	34.6	34.2
A.S.T.M. Distillation	<u>OF</u>	<u>OF</u>	<u>OF</u>
I.B.P.	425	160	146
5%	504	418	411
10%	520	462	461
20%	536	497	494
30%	548	513	512
40%	558	526	524
50%	567	538	536
60%	575	550	548
70%	584	562	560
80%	594	572	575
90%	611	603	599
95%	625	630	627
E. P.	652	649	645
Recovery	99.0%	97.0%	97.5%
Residue	0.8%	1.25%	1.5%
Loss	0.2%	1.75%	1.0%
Wt. % Sulfur	2.19%	.460%	.539%

TABLE II  
CATALYSTS

Run Number	Catalyst and Composition	Identification Code
NSR-I and NSR-III	Nickel Oxide NiO 10% Al <sub>2</sub> O <sub>3</sub> Balance	Harshaw Number 3 Calcined Ni-0301 T 1/8"
NSR-II	Nickel Hydroxide Ni(OH) <sub>2</sub>	Harshaw Number 3
GRS	Molybdenum Sulfide MoS <sub>2</sub> 15% Al <sub>2</sub> O <sub>3</sub> Balance	Harshaw Mo-X-1321 -42 T 1/8"
MCR and CGR	Molybdenum Sulfide Mo 9.66% S 7.97% Al <sub>2</sub> O <sub>3</sub> Balance	Harshaw Mo-0801-T 1/8" RI 34-1 Lot 191 A-1-1

TABLE III  
 TABULATED DATA FOR NICKEL STUDY RUN ONE (NSR-I)

Run Number: NSR-I  
 Grams Catalyst: 100  
 Catalyst Reference: NiO Harshaw #3 Calcined, Ni-0301 T 1/8"  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19

Samp. No.	Total Hours	Avg. Temp. °F	Cat. Reactor Space Vel. psig	Space Vel. Gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
1	1	734	59	1.94	3530		190	.68	96.9	3.1
2	3	673	60	3.12	2100		612	1.22		
3	5	711	61	3.07	2070		600	1.24		
4	7	732	63	3.24	2010		634	1.43		
5	9	714	60	2.66	2260		520	1.68		
6	11	723	64	2.67	2260		522	1.71		
7	13	730	64	3.21	1920		629	1.69		
8	15	729	61	3.03	2040		594	1.61		
9	17	729	62	3.41	2010	-7.13	658	1.76	83.4	16.6

Yield: Wt.% 97.7

TABLE IV  
 TABULATED DATA FOR NICKEL STUDY RUN TWO (NSR-II)

Run Number: NSR-II  
 Grams Catalyst: 100  
 Catalyst Reference: Ni(OH)<sub>2</sub>, Harshaw #3  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Reactor psig	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
1	1	757	59	2.09	3120		206	.83	~100	-
2	2	729	61	3.07	1970		304	1.18		
3	4	725	58	2.99	2130		590	1.44		
4	6	721	60	3.37	1890		665	1.58		
5	8	725	57	3.12	2040		615	1.70		
6	10	725	58	3.05	2030		601	1.70		
7	12	725	61	3.22	1870		635	1.71		
8	14	725	61	2.89	2210		572	1.76		
9	16	725	61	3.12	1980		616	1.82		
10	18	725	62	3.08	2060		608	1.82		
11	20	725	60	3.14	2030		620	1.87		
12	21	725	61	3.47	1880	-9.65	342	1.89	86.7	13.3

Yield: Wt. % 98.6

TABLE V  
TABULATED DATA FOR NICKEL STUDY RUN THREE (NSR-III)

Run Number: NSR-III  
 Grams Catalyst: 200  
 Catalyst Reference: NiO Harshaw #3 Calcined  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Reactor psig	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
1	3	579	102	.0588	18,400		31	1.18	~100	-
2	11	741	100	.0264	40,300		37	.27		
3	15	720	98	.0869	11,300		61	.09		
4	19	723	99	.1081	9,080		76	.17		
5	23	723	99	.1243	8,500		88	.14		
6	27	725	97	.1238	9,230		87	.13		
7	31	725	101	.1211	9,430		85	.19		
8	35	723	97	.1205	8,800		84	.22		
9	39	725	98	.1175	9,710		82	.25		
10	43	725	98	.1191	8,250		84	.24		
11	47	723	100	.1300	8,150		92	.26		
12	51	725	100	.1175	9,720		82	.31	34.4	65.6
13	55	723	102	.1125	9,420		80	.38		
14	59	725	103	.1250	8,500		88	.36		
15	63	725	105	.1053	10,100		74	.41		
16	67	725	102	.1204	8,800		84	.43		
17	71	723	103	.1225	8,660		86	.47		
18	75	725	105	.1125	9,440		79	.56		
19	79	725	104	.1175	9,700		82	.65		
20	83	725	101	.1132	8,660		81	.68		
21	87	725	102	.1090	9,010		76	.77		
22	91	725	99	.1211	8,750		85	.84		
23	95	725	99	.1225	8,660		86	.90		
24	99	725	101	.1131	8,690		80	.92		
25	103	725	101	.1190	8,910		84	.97		

TABLE V (continued)  
 TABULATED DATA FOR NICKEL STUDY RUN THREE (NSR-III)

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Reactor psig	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S		Recycle Gas	
								H <sub>2</sub>	Hc	H <sub>2</sub>	Hc
26	107	725	97	.1190	8,910		84	1.04			
27	111	725	99	.1131	9,370		80	1.08			
28	115	725	98	.1219	8,710		86	1.10			
29	119	723	98	.1225	8,660		86	1.10			
30	123	725	96	.1769	6,040		124	1.20	37.7	62.3	

Yield:           Wt. % 87.8  
                   Vol. % 90.4

Composite Samples #1-27: .514% S.  
 Composite Samples #1-27 consumed 21.8 Ft<sup>3</sup> H<sub>2</sub>/bbl oil.

TABLE VI  
TABULATED DATA FOR GAS RECYCLE STUDY

Run Number: GRS  
 Grams Catalyst: 100  
 Catalyst Reference: Harshaw MoX-L321-42  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19

Samp. No.	Total Hours	Avg. Cat. Temp °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle H <sub>2</sub>	Gas Hc
1	6	770	.900	5,350	---	500	.681	100	---
2	14	770	.664	8,740	---	493	.566		
3	22	770	.637	10,000	---	474	.511		
4	30	772	.670	9,340	---	497	.471		
5	38	770	.540	12,020	---	401	.453		
6	46	770	.575	11,100	---	426	.415		
7	54	770	.572	11,150	---	425	.400		
8	62	770	.550	11,250	---	408	.396		
9	70	770	.535	11,200	---	397	.397		
10	78	770	.554	11,100	---	410	.375		
11	86	770	.565	11,100	---	418	.403		
12	94	774	.561	11,600	---	416	.403	96.5	3.5
13	102	772	.566	10,900	---	418	.375		
14	110	774	.527	11,450	---	391	.388		
15	118	770	.530	11,300	---	394	.356		
16	126	770	.604	10,200	---	464	.397		
17	134	768	.655	9,620	---	504	.452		
18	142	770	.636	9,660	---	488	.437		
19	150	770	.626	10,000	---	481	.402		
20	158	768	.631	9,430	---	484	.397		
21	166	770	.632	9,720	---	476	.423		
22	174	770	.655	9,230	---	502	.458		
23	182	770	.655	9,360	---	502	.417	95.7	4.3
24	190	768	.619	9,610	---	474	.403		

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TABLE VI (continued)  
TABULATED DATA FOR GAS RECYCLE STUDY

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
25	198	768	.648	9,520	---	498	.438		
26	206	770	.681	9,230	174	521	.408		
27	214	770	.650	9,660	217	499	.413		
28	222	770	.664	9,030	277	504	.431		
29	230	772	.641	9,520	286	490	.393	95.2	4.8
30	238	768	.652	9,030	275	499	.417		
31	246	768	.633	9,370	242	484	.428		
32	254	770	.622	9,660	269	476	.395		
33	262	772	.633	9,910	246	485	.382		
34	270	770	.672	9,180	258	514	.397		
35	278	770	.718	8,840	257	552	.412		
36	286	770	.682	9,080	249	523	.414		
37	294	774	.967	6,480	55	750	.528		
38	302	772	.854	7,410	68	660	.504	96.3	3.7
39	310	772	.606	10,450	89	464	.425		
40	318	770	.567	11,100	94	434	.358		
41	326	770	.531	11,440	96	425	.381		
42	334	772	.672	9,420	82	518	.422		
43	342	772	.688	9,130	82	532	.456		
44	350	770	.678	8,980	82	523	.454		
45	358	772	.688	9,270	73	532	.455		
46	366	770	.685	9,130	69	530	.447		
47	374	768	.713	8,740	89	552	.467		
48	382	770	.690	8,940	103	532	.447		
49	390	770	.690	9,040	123	532	.452		
50	398	770	.697	9,220	131	535	.454		
51	406	772	.705	8,880	133	550	.460		
52	414	770	.715	8,740	134	558	.467		
53	422	770	.707	8,740	141	551	.481		
54	430	770	.722	8,780	134	560	.474	95.6	4.4
55	438	772	.712	8,840	132	553	.464		

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TABLE VI (continued)  
TABULATED DATA FOR GAS RECYCLE STUDY

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
56	446	768	.713	8,780	142	560	.464		
57	454	770	.699	9,080	137	543	.472	95.0	5.0
58	462	770	.718	8,740	135	558	.471		
59	470	770	.725	8,740	134	564	.481		
60	478	770	.720	8,840	132	560	.476		
61	486	772	.675	9,340	131	525	.443		
62	494	770	.703	9,080	130	546	.480		
63	502	770	.691	9,230	134	536	.471	94.0	6.0
64	510	772	.692	9,520	137	537	.478		
65	518	768	.680	9,230	141	528	.455		
66	526	770	.769	8,590	140	596	.478	95.4	4.6

Yield: Wt. % 96.9

TABLE VII  
TABULATED DATA FOR MOLYBDENUM COMPARISON RUN

Run Number: MCR  
 Grams Catalyst: 100  
 Catalyst Reference: Harshaw Mo-0801 T 1/8" RI 34-1 Lot 191A-1-1  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19  
 Reactor Pressure: 500 psig

Samp. No.	Total Hours	Avg. Temp. °F	Cat. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle H <sub>2</sub>	Gas Hc
1	1	761		.743	8,550	128	574	.101	~100	—
2	16	768		.697	9,000	126	538	.086		
3	24	770		.694	8,820	74	536	.109		
4	32	770		.961	6,260	100	743	.211		
5	40	770		1.012	6,180	110	783	.255		
6	48	770		1.021	6,060	107	790	.224		
7	56	768		1.289	4,800	127	997	.421		
8	64	770		1.301	4,540	138	1017	.413	95.6	4.4
9	72	772		1.298	4,920	123	1002	.419		
10	80	768		1.296	4,780	130	1001	.420		
11	88	770		1.300	4,650	133	1016	.423		
12	96	772		1.300	4,750	123	1011	.442		
13	104	770		1.310	4,860	140	1015	.457		
14	112	768		1.300	4,710	141	1011	.491	95.5	4.5
15	120	770		1.365	4,600	132	1065	.496		
16	128	772		1.350	4,600	138	1052	.515		
17	136	768		1.369	4,550	141	1067	.532		
18	144	770		1.331	4,810	134	1039	.519		
19	152	772		.869	5,140	139	678	.304		
20	160	770		.868	5,150	143	677	.317	95.8	4.2

Composite Yield: Wt. % 97.5

TABLE VIII  
TABULATED DATA FOR CATFORMING GAS STUDY RUN

Run Number: CGR  
 Grams Catalyst 100  
 Catalyst Reference: Harshaw Mo-0801 T 1/8" RI 34-1, Lot 191A-1-1,  
 Previously on MCR 160 Hrs.  
 Oil Charge °API: ~30  
 Percent Sulfur: 2.19  
 Reactor Pressure: 500 psig

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Hc
1	3	766	1.140	5,610	-83	333	.515	84.0	16.0
2	11	770	.936	5,600	-82	730	.441		
3	19	768	.662	9,550	216	515	.304		
4	27	768	1.031	6,040	234	825	.427		
5	35	770	.849	7,280	279	660	.377		
6	43	772	1.000	6,250	245	779	.457		
7	51	768	.901	7,120	247	701	.421		
8	59	766	.740	8,640	296	576	.379		
9	67	766	1.005	6,400	284	783	.459		
10	75	765	1.008	6,350	288	785	.498		
11	83	768	1.045	6,130	288	814	.491		
12	91	768	1.012	6,230	286	786	.481		
13	99	772	1.004	6,070	284	781	.450		
14	107	770	.990	6,380	293	779	.495		
15	115	770	1.078	5,940	301	838	.518		
16	123	768	1.012	6,190	298	787	.474		
17	131	768	.895	7,240	306	696	.472		
18	139	770	.874	7,500	311	670	.473		
19	147	770	.917	7,350	318	716	.478		
20	155	765	.944	7,050	314	734	.496		
21	163	772	.946	6,730	308	736	.479		
22	171	770	.926	7,000	306	720	.448		
23	179	775	.940	6,860	292	732	.453		

TABLE VIII (continued)  
 TABULATED DATA FOR CATFORMING GAS STUDY RUN.

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
24	187	768	.906	7,250	291	705	.483	82.6	17.4
25	195	772	.964	6,760	275	751	.483		
26	203	759	.860	7,460	261	669	.494		
27	211	770	.934	6,840	276	727	.438		
28	219	770	.943	6,960	263	734	.481		
29	227	770	.934	6,900	255	726	.576		
30	235	763*	.918	7,000	264	714	.646		
31	243	772	.869	7,400	268	675	.482		
32	251	770	.765	8,410	264	594	.439		
33	259	774	.732	8,910	262	569	.448		
34	267	770	.784	8,260	264	610	.467		
35	275	770*	.793	8,060	265	624	.552		
36	283	770*	.789	8,220	267	613	.568		
37	291	772	.773	8,320	258	600	.456		
38	299	772	.808	8,290	265	628	.425		
39	307	770	.782	8,320	266	608	.468		
40	315	768	.797	8,020	263	628	.450		
41	323	772	.865	7,660	262	673	.436	82.3	17.7
42	341	768	.842	7,770	261	655	.465		
43	349	770	.921	6,980	260	718	.447		
44	357	768	1.048	6,070	258	816	.496		
45	365	770	.888	7,150	258	692	.514		
46	373	770	.864	7,550	258	673	.483		
47	381	774	.957	6,810	257	747	.482		
48	389	770	.854	7,610	254	666	.496		
49	397	770	.743	8,650	256	578	.455		
50	405	772	.692	9,210	257	541	.393		
51	413	770	.695	9,300	259	542	.417		
52	421	772	.698	9,260	260	543	.368		
53	429	772	.706	9,110	261	550	.415		

TABLE VIII (continued)  
 TABULATED DATA FOR CATFORMING GAS STUDY RUN

Samp. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
54	437	770	.686	9,450	262	535	.424		
55	445	768	.737	8,820	263	574	.477		
56	453	770	.709	9,460	264	552	.466		
57	461	768	.694	9,310	265	542	.482		
58	469	770	.804	7,760	265	627	.472		
59	477	781	1.139	5,800	264	887	.579		
60	485	777	1.148	5,640	261	895	.592		
61	493	779	.926	6,910	263	743	.533	81.0	19.0
62	501	775	.915	7,150	256	711	.279		
63	509	768	.932	7,190	255	725	.353		
64	517	775	1.075	5,980	253	835	.359		
65	525	775	1.103	5,590	255	893	.387		
66	533	775	1.095	5,540	254	875	.384		
67	541	779	1.059	5,910	251	846	.399		
68	549	774	1.080	5,940	251	863	.455		
69	557	770	1.080	5,860	252	863	.450		
70	565	775	.990	6,580	254	759	.416		
71	573	781	.976	6,600	253	758	.400		
72	581	779	.998	6,450	254	776	.393		
73	589	777	1.006	6,380	252	783	.413		
74	597	775	1.032	6,370	252	803	.458		
75	605	775	.979	6,380	252	761	.419		
76	613	779	1.006	6,550	248	783	.423		
77	621	781	.989	6,530	249	768	.436		
78	629	781	.940	6,830	247	730	.414		
79	637	775	.968	6,640	246	746	.441		
80	645	779	.975	6,650	246	752	.438		
81	653	779	.961	6,750	245	741	.437		
82	661	779	.963	6,320	243	743	.443		
83	669	772	1.081	5,930	245	835	.460		
84	677	775	1.062	6,140	241	822	.491		

TABLE VIII (Continued)  
TABULATED DATA FOR CATFORMING GAS STUDY RUN

Sampl. No.	Total Hours	Avg. Cat. Temp. °F	Space Vel. gms/gm/hr	Recycle Ft <sup>3</sup> /bbl	H <sub>2</sub> Consump. Ft <sup>3</sup> /bbl	Yield gms oil	Product % S	Recycle Gas H <sub>2</sub>	Gas Hc
85	685	777	1.068	6,140	239	824	.503		
86	693	777	1.091	6,170	239	842	.514		
87	701	779	1.098	5,960	237	847	.516		
88	709	775	1.098	5,800	235	842	.545		
89	717	779	1.062	6,000	233	821	.500		
90	725	781	1.058	6,010	231	817	.506		
91	733	775	.981	6,600	230	757	.468		
92	741	777	.981	6,830	231	757	.470	81.5	18.5
93	749	779	.972	6,730	231	749	.468		
94	757	779	1.175	5,540	234	923	.557		
95	765	779	1.114	5,670	233	892	.558		
96	773	779	1.061	5,950	237	850	.507		
97	781	779	1.031	6,240	232	809	.487		
98	789	779	.956	6,220	232	750	.536		
99	797	781	.947	6,700	---	736	.425		
100	805	779	.974	6,780	---	758	.448		
101	813	779	.968	6,810	---	753	.461		
102	821	779	.990	6,520	---	771	.475		
103	829	777	.976	6,460	---	759	.477		
104	837	779	.973	6,710	---	757	.453		
105	845	779	.923	6,980	---	718	.424		
106	853	779	.963	6,650	---	749	.436		
107	861	779	.963	6,780	560	749	.460		
108	869	779	1.021	6,340	364	795	.431		
109	877	779	1.036	6,250	299	807	.473		
110	885	779	1.041	6,230	309	810	.489		
111	893	777	1.034	6,250	308	806	.510		
112	901	777	1.048	6,070	269	814	.543		
113	909	781	1.062	6,080	290	829	.514		
114	917	779	1.043	6,190	357	813	.534		
115	925	777	1.034	6,100	310	806	.517		









