



Catalytic hydrogenation of shale oil coker distillate  
by Glenn A King

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:

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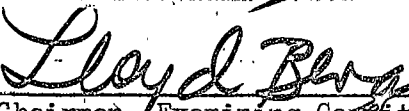
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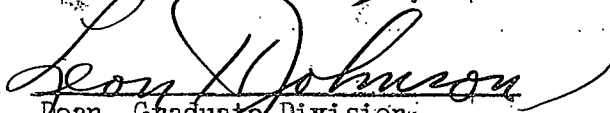
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ABSTRACT

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The investigations were conducted in a bench-scale pilot plant unit. The preliminary runs showed that an operating pressure of 1000 psig. was more conducive to a successful hydrogenation process for shale oil coker distillate than was a pressure of 500 psig. Conditions used in the catalyst studies were a reactor pressure of 1000 psig., a space velocity of 1.0 gms. of oil per gm. of catalyst per hour, and the recycle gas rate was 7500 cu. ft. of 65 percent hydrogen, 35 percent methane, per bbl. of oil charged. The temperature was raised from 725° F. to 925° F. in increments of 50° F. every 24 hours during each catalyst study. The average run length for each catalyst was 120 hours of on-stream operation plus a 24-hour lineout period at the beginning of a series of runs and an eight-hour lineout period between temperature increments.

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## I INTRODUCTION

The investigation of oil shale as a possible source of commercial fuels has been carried on by the Bureau of Mines of the United States Department of the Interior since about 1925. From 1929 until 1944 however, very little investigation was conducted because of the ever increasing supply of petroleum. In April of 1944, the Synthetic Liquid Fuels Act was passed by the 78th Congress for the purpose of investigating possible sources of liquid fuels with which to supplement those derived from petroleum. The passage of this act was prompted by the heavy wartime consumption of fuels which seemingly threatened to deplete the nation's oil reserves. It was extended when peace time demands for oil and oil products surpassed peak requirements of World War II. In 1943 the consumption of liquid fuels was 1.7 billion barrels while in 1953 it had increased to 3 billion barrels per year.

It is true that supply has managed to keep pace with this demand, but only through imports of more and more oil. These imports approached one-half billion barrels of oil in 1953. This fact alone justifies the governmental appropriations to the Bureau of Mines so that new sources of fuels may be opened up to lessen the nation's dependence on other countries for its fuels.

Oil shale can be defined as a compact laminated rock of sedimentary origin which contains solid organic matter called "kerogen," that will yield oil upon distillation. It is interesting to note that the word petroleum is derived from two Latin words, petra and oleum, which mean rock and oil, respectively. Thus petroleum means "rock oil." The derivation of this

word plus the fact that oil shale was known to exist and was used as early as 1694 in England and Scotland gives an indication of how long the knowledge of oil shale preceded the discovery of what is now known as petroleum.

The origin of oil shale is believed to be quite similar to that of coal. Beds of organic matter, vegetable spores, pollen, algae, shells of minute crustaceans, etc., were deposited at the bottom of lakes. Upheaval of the lake bottom followed by erosion have laid bare the vast stratified seams of oil shale.

The fields of oil shale that appear to be the most promising for commercial exploitation in the United States are those located in Colorado, Wyoming, and Utah. This is the Green River formation. This formation is approximately 17,000 sq. mi. in area of which 9200 sq. mi. are in Wyoming, 5200 sq. mi. are in Utah, and the remainder is in Colorado. The Colorado portion of the formation has been the most thoroughly investigated. Estimates of partly blocked and inferred shale for this area indicate that a 500-foot-thick measure, assaying 15 gal. per ton, contains a potential reserve of 494 billion barrels of shale oil. The lower segment of this measure, called the Mahogany ledge, is up to 90 feet thick and averages 30 gal. per ton. This represents an estimated reserve, in place, of 126 billion barrels of shale oil. In this zone alone, the potential shale oil reserve is about four times the known petroleum reserve of this country. Despite this large reserve, development of oil shale resources has not been of commercial interest because it was felt that oil could not be produced as cheaply by mining oil shale as from the normal petroleum crude sources

and that the petroleum reserves were quite adequate.

As a result of the Synthetic Liquid Fuels Act, the Bureau of Mines was enabled to set up a demonstration mine along with retorting and refining facilities near the small mountain town of Rifle, Colorado. Although this venture cannot be classified as a commercial one, many companies, among which are some of the larger oil companies, have begun to express an interest in the possibilities of utilizing oil shale. Union Oil Company, in particular, is said to have made considerable progress towards commercializing oil shale as a fuel source (3). The Bureau of Mines also has many cooperative agreements with firms other than oil companies and with various colleges and universities, among which is Montana State College. Although industry has been slow to see the possibilities of oil from shale, the engineering and cost data which the Bureau of Mines has obtained from their research during the past several years, both at Rifle and at the shale oil laboratory in Laramie, Wyoming, is available for its use.

One of the biggest problems of the Bureau of Mines has been to develop a safe, economical method of mining oil shale. In order to produce oil from shale economically, the mining step has to be extremely efficient. It has been known for years that the mining costs in surface workings are less than in underground mines. The aim of the demonstration mine, therefore, has been to literally take a quarry underground and adopt as many surface mining techniques as practicable to underground conditions. The Bureau of Mines has developed such a method of underground mining, called the room and pillar method, and have found that 75 percent of the oil shale could be safely removed leaving the other 25 percent to serve

as pillar-type roof supports. Using the room and pillar type mining method, a monthly average shale production up to 165 tons per man-shift at an approximate cost of \$0.50 per ton has been attained (9). This represents about 25 times the production of the average American coal miner.

Much of the research that has been conducted on the retorting operation has been to develop a continuous type retort. When the operation was first begun, a batch-type retort was used. A continuous retorting process, called the gas-combustion process, has been developed and has taken the place of the old NTU retort at the demonstration mine. In this process, the oil shale is retorted as a downward moving bed heated by an ascending stream of hot combustion gases. The combustion gases are generated by burning recycled product gas and carbonaceous residue from the retorted shale directly in the shale bed. By controlling the rate of cooling, the shale oil vapors are condensed within the retort as a fog or mist in the gas stream. Thus, shale oil is removed from the shale bed in a liquid state and can be recovered without further cooling or condensation. This fact brings out a distinct advantage for the gas combustion retort over other retorts; eg., it requires no water in an area where water is extremely scarce.

The crude from the retort has been given some of the more common petroleum treatments such as coking, visbreaking, fractionation, thermal cracking, catalytic cracking, hydrogenation, and acid treating. The fuels obtained from these processes are characterized by a high gum content, high degree of unsaturation, high sulfur and nitrogen content, poor color



stability, and an offensive odor suggestive of pyridine. A gasoline and diesel fuel, which were actually used in a truck and a train, have been obtained by thermal cracking and sulfuric acid treating, but the yield was too poor to suggest utilizing that procedure for a commercial process.

In recent years, several processes in petroleum technology have been developed that are of interest in their application to shale oil. The polyform process, catalytic cracking, and catalytic hydrogenation are three of the processes that appear to be promising. The polyform process employs the principle of cracking naphtha and heavier oils in admixture with varying amounts of cheap, gaseous hydrocarbons such as the propanes and butanes. Catalytic cracking is a process for converting petroleum fractions in the gas oil boiling range into gasoline and other lower boiling hydrocarbons. The two processes may be combined to form a process called catalytic polyforming. The effects of this process on shale oil were investigated by Crecelius (6). He determined that higher yields of gasoline were obtainable through this process than from thermal cracking, chemical treatment, etc., but that the quality of the products was not materially improved over other methods of refining shale oil. The minimum gum content, in particular, was still too great.

It has been suggested by various researchers on shale oil and the products obtained thereof, that the key to their instability might be the presence of nitrogen. They feel that nitrogen either takes part in or possibly catalyzes the gum forming reactions. The obvious answer to solving such a problem is removal of the nitrogen. The Bureau of Mines and others have demonstrated that by the use of destructive catalytic

hydrogenation, eg., temperatures above 850° F. and pressures of 1000 psig. or greater in the presence of hydrogen, both nitrogen and sulfur can be essentially removed from the product.

The fact that the usual methods of treating petroleum do not appear economically applicable to the refining of shale oil, led the author to investigate the possibilities of a mild type catalytic hydrogenation process. The investigation was initiated by determining the optimum operating conditions. Once these conditions were established, a study of the effects of several different catalysts on the mild hydrogenation of a 650° F.E.P. coker distillate was made. The catalysts used and their preparations are described on page 17.

## II EQUIPMENT, METHODS, AND MATERIALS

### A EQUIPMENT

A schematic diagram of the unit is shown in Figure 1. The unit can be divided into two main parts: (1) the reactor section and (2) the recycle gas section.

The reactor section consisted of a feed system, the reactor, and the sampling facilities. The feed was pumped from a reservoir through 1/8 in. ID high pressure stainless steel tubing into the top of the reactor by a Hills-McCanna Chemical Proportioning Pump. The flow rate of the pump was adjustable to any desired rate up to 1.02 gal./min. at 2900 psi.

The reactor was made from an 18 in. length of  $2\frac{1}{2}$  in. schedule 80, austenitic, stainless steel pipe and was designed to operate at a maximum pressure of 3000 psi. with a safety factor of 10. It was closed at each end by a specially designed screw-type fitting which was machined here at Montana State College; however, because of difficulty in obtaining a satisfactory seal, both ends were eventually welded permanently in place. Three nichrome heating coils, each approximately 33 feet long, were beaded and wrapped around the reactor which had first been wrapped with asbestos tape. Another layer of asbestos tape covered the coils to protect them against the magnesia mud layer which provided the necessary insulation. The top of the reactor was fitted with the necessary fittings, valves, etc. to provide for feed gas inlet, oil inlet, oil feed-line bleed, vacuum line connection, blowout-disk exhaust system, and thermowell. The thermowell was made from a length of  $\frac{1}{4}$  in. seamless,

schedule 80, stainless steel pipe. It fitted into the top of the reactor and allowed for the locating of three thermocouples at any desired point along the vertical axis of the reactor.

At the bottom of the reactor, a condenser was connected by means of a 3/4 in. schedule 80 union. Below the condenser was fitted a sample reservoir which was a short length of 2 in. schedule 80 pipe closed at both ends by caps welded in place. The caps were tapped for 1/2 in. pipe. Connected to the reservoir as shown in Figure 1, was a Jerguson sight glass for liquid level control. From this Jerguson through a valve, the sample was drawn off as desired in an 800 ml. Erlenmeyer flask. The non-condensable gases contained in the sample were passed through a series of three caustic wash bottles and metered through the wet test meter before being vented.

Pressure in the reactor was maintained by use of a Mason-Neilan air-to-close valve which was controlled by a Fisher-Wizard proportional controller. The power for heating the reactor was furnished by two 260 volt, 3 amp Powerstats and one 130 volt, 7.5 amp Powerstat. Temperatures were read directly from a Leeds-Northrup indicating potentiometer connected to the thermocouples, and adjustments of the Powerstats were made accordingly.

The recycle gas section consisted of a storage cylinder, compression cylinder, feed gas cylinder, makeup gas cylinder with regulator, rotameters, a recompression system, and the necessary valves, fittings, and tubing. The surge or storage cylinder collected the gases which had passed through the reactor and stored them until time to recompress them back to the feed cylinder. Recompression was accomplished by pumping oil

from the oil reservoir indicated in Figure 1, through a Pesco high pressure, gear-type pump into the bottom of the compression cylinder. The piping in the recompression system was done with 1/8 in. schedule 80 pipe and fittings. The Pesco pump was capable of delivering 4.5 gpm. at 2800 RPM and 1200 psi. The pump was directly coupled at a 3.2:1 pulley ratio to a Powr-Kraft 1 hp. repulsion-induction-type electric motor. High pressure stainless steel tubing, fittings, and valves were used in the recycle gas system.

The valves were Hoke #321 needle valves with blunt spindles. The rotameters were Brooks High Pressure Indicating Rotameters and were equipped with a number of different weight floats which afforded a fairly wide range of flow rates. Flow through the rotameters was controlled by two Hoke metering valves.

The reactor heat control Powerstats, pressure controller, pressure gages, rotameters, pump switches, and principal operating valves were mounted on a panel board to afford quick and efficient operation of the unit.

B METHODS

1. Catalyst Changeover

In order to charge fresh catalyst to the reactor, it was taken down from its operational position within the unit, inverted, and the used catalyst and the alundum balls were removed. The used catalyst was screened to separate it from the alundum balls, part of which were then replaced in the reactor to serve as preheat media. One-hundred grams of new catalyst was placed in the reactor and enough additional alundum balls were added to completely fill it. A circular wire screen, the size of the opening through which the catalyst and alundum balls were added, was used to support the contents of the reactor. The reactor, charged with fresh catalyst, contained a preheat section of about ten inches, a catalyst bed approximately 1.5 inches in depth, and about 3 inches of bottom support for the catalyst bed. After the catalyst changeover was completed, the reactor was replaced within the unit.

2. Start-up

The unit was placed into operation by applying current to the heating coils. When the temperature of the catalyst bed reached about 600° F., the reactor was evacuated and the recycle gas flow was started. The reactor was then pressurized by adjusting the back-pressure valve and the flow of oil was started. The desired liquid-hourly-space velocity was set on the Hills-McGanna pump by timing the flow of oil from a graduated reservoir with a stop watch. After the space velocity was adjusted the reactor was allowed to lineout for 24 hours before the taking of data was begun.

The oil in the reservoir was drained down to the indicated mark on the sample Jerguson; the feed reservoir was filled, and the feed bottle was weighed in order that a weight balance might be taken at the end of the run.

### 3. Recycle Gas Procedures

Makeup gas was prepared here at the laboratory by metering the desired quantities of hydrogen and methane through the makeup rotameter into the compression cylinder. The rotameter had been calibrated with both gases for this purpose. The makeup gas ranged from 65 percent hydrogen, 35 percent methane to 100 percent hydrogen. The desired result was to maintain the composition of the gas passing over the catalyst bed as near 65 percent hydrogen as possible.

A periodic check on the composition of the recycle gas was made at the beginning of the series of runs and at the end of each run. A sample of the recycle gas was taken by displacing water in a two-gallon, inverted, glass bottle with gas from the feed gas cylinder. This gas was analyzed in the low-temperature fractionation unit in the laboratory. This analysis is described later in this section.

The feed gas which had passed through the reactor was collected in the surge and compression cylinders. When the pressure in the feed cylinder had dropped to approximately 100 psig. above the reactor operating pressure, the collected gas was returned to the feed cylinder by recompressing it. To accomplish this, the compression tank was isolated from the system and the recompression pump was started. When equal pressures were reached, the valve between the compression and feed

tanks was opened and the compression continued. When the compression cylinder was completely filled with oil, the pump was stopped, and the valve between it and the feed cylinder was closed. The valve between the compression tank and the oil reservoir was opened, and when the pressures in the surge or storage tank and compression tank were equalized, the valve connecting the two was opened. The pressure in the two cylinders was used to drive the oil back into its reservoir, thus completing the recompression cycle.

#### 4. Sampling the Product

A sample of the product was taken every eight hours, three samples making up a run. The eight-hour sample was a composite of the four two-hour samples on which the API gravities were taken. At the time of sample taking, the sample was drained down to the indicated mark on the sample Jerguson and weighed. The feed reservoir was filled, and the charge bottle was weighed also. The sample weight and the charge weight were recorded on the data sheet providing a weight balance for the run.

#### 5. Shut-down

The unit was shut down by stopping the oil feed pump and shutting off the Powerstats to the reactor. Recycle gas flow was continued until the reactor was cooled to about 250° F. All interconnecting valves to the reactor and between the cylinders were closed after the gas flow ceased. The air supply to the controller was shut off, and the pressure was bled from the lines leading to the back-pressure valve. Once the control valve was inoperative, the reactor pressure was vented, thus completing that series of runs.



## 6. Analyses

The analyses performed in the studies were nitrogen and sulfur determinations, ASTM distillations, and API gravities on the product; and low-temperature distillations to determine the composition of the recycle gas samples.

The nitrogen content of each sample was determined by use of the standard Kjeldahl analysis for nitrogen as set up by Boyd Guthrie et al. (1) for shale oil and its fractions. Determination of the sulfur content of each sample was made by use of the Lamp-Gravimetric method, D 90-50T, established by the American Society for Testing Materials (2). The ASTM distillation procedure, D 86-54, was also taken from that source. Determination of the specific gravity of the product was done with a Westfall Balance. Conversion of specific gravity to °API was accomplished with the equation,

$$^{\circ}\text{API} = 141.5/\text{s.g.} - 131.5.$$

The gas analysis equipment consisted of a well-insulated fractionating column in which condensation of the low boiling constituents of the gas was accomplished by the use of liquid nitrogen. The overhead distillate was collected and measured in the vapor state under reduced pressure. Using this method, the amounts of hydrogen, methane, ethane, and propane, if any, present in the sample were determined.

C MATERIALS

The materials used for the hydrogenation studies were a 650° F. and an 850° F. E.P. shale oil coker distillate, hydrogen, methane, and various catalysts.

The Bureau of Mines supplied the coker distillates, the properties of which are found in Table I.

The hydrogen used for these studies was obtained from the Whitmore Oxygen Company in Salt Lake City, Utah. The methane was supplied by the Matheson Company of Joliet, Illinois. The gas with the desired composition of hydrogen and methane was made up here at the laboratory.

The catalysts investigated were a cobalt-molybdate manufactured by the Harshaw Chemical Company, a cobalt-molybdate made by Peter Spence & Sons, Ltd., and two catalysts made up here at the laboratory; Harshaw's molybdenum oxide catalyst promoted with (1) indium and (2) palladium. The code letters and compositions of the catalysts may be found in Table II.

The two catalysts prepared here were made as follows:

Nine grams of metallic indium was dissolved in 50 cc. of concentrated nitric acid. The resulting solution was evaporated to about 10 cc., and enough water was added to make the volume up to 60 cc. This solution was added to 100 grams of Harshaw Mo-0203-T-1/8" pelletized molybdenum oxide catalyst. Thirty-three cc. of the nitrate was taken up in the first impregnation. The catalyst was dried and given a second impregnation of 17 cc. It was again dried and then reduced for eight hours at 400-450° C. in an atmosphere of hydrogen. It was estimated that 7.5 grams of elemental

indium was added to 100 grams of the catalyst support.

An acid solution (12.5 cc. of concentrated nitric acid and 17.5 cc. of water) of palladium nitrate (3.5 grams) was impregnated in 100 grams of Harshaw Mo-0203-T-1/8" molybdenum oxide catalyst. The promoted catalyst was dried slowly at about 60° C. in air, and then reduced in a hydrogen atmosphere at 350° C. for eight hours. It was estimated that 1.6 grams of palladium was added to 100 grams of the catalyst support.

### III DISCUSSION OF RESULTS

After the design and construction work on the unit was finished, a series of shakedown runs were made to test it. Only a few minor corrections were needed to ready the unit for the start of the hydrogenation studies.

#### A. Determination of the Optimum Operating Conditions

The first studies, runs 1 through 10, were aimed at determining the effect of temperature and pressure on the hydrogenation of an 850° F.E.P. coker distillate. Runs were made at both 500 psig. and 1000 psig. to determine the effects of pressure on the hydrogenation process. The results of those runs are shown in Tables III and IV and Figures 2 and 3. The compositions of the recycle gas are shown in Figures 8 and 9. The initial temperature was 725° F. at which four two-hour samples were collected and composited after API gravities were run on each one. The gravities were used as a quick check on the activity of the catalyst. They were plotted versus on-stream time, and the slope of the line gave an indication of the catalyst activity. Three of the eight-hour composite samples made up a run, and nitrogen and sulfur analyses were performed on each sample. At the end of each 24 hours, the temperature was increased 50° F. and another run was made. The last run was made at 925° F., thus completing that study. The catalyst used was Harshaw's cobalt molybdate, Co-Mo-0201-T-3/16". The space velocity was 1.0, and the recycle gas rate was 7500 cu. ft./bbl. (65 volume percent hydrogen).

It was found that the 1000 psig. pressure was more conducive to nitro-

gen and sulfur removal than the lower pressure. At 1000 psig. the sulfur content of the 850° F.E.P. coker distillate was reduced to a minimum value of 0.087 weight percent. This compared to a minimum sulfur content of 0.39 weight percent when the charge stock was treated at 500 psig. The minimum value in each case was obtained at 875° F. The minimum nitrogen content for the 1000 psig. run was 0.85 weight percent and occurred at 875° F., while the minimum for the 500 psig. run was 1.683 weight percent occurring at 825° F. Over the entire range of temperatures investigated the 1000 psig. study gave better results than did the study at 500 psig.

Figures 2 and 3 illustrate the correlation between catalyst activity and sulfur and nitrogen content for the 500 psig. and the 1000 psig. studies, respectively. They showed definitely that the denitrogenation and desulfurization properties of the catalyst dropped off as it was deactivated. For both studies it was noticed that the activity level of the catalyst remained fairly constant within a run at a given temperature, and that it increased with a rise in temperature up to 925° F. At that time a rapid deactivation occurred. Figures 8 and 9 show that during the 925° F. run the hydrogen content of the recycle gas dropped off rapidly. It was suspected that this effect was caused by a greatly increased hydrogen consumption at that high temperature. The decrease in hydrogen content could possibly have had a bearing on the rapid deactivation of the catalyst, but it was believed that most of the deactivation occurred as a result of the increased carbon lay-down on the catalyst due to increased cracking at 925° F.

On the basis of the data obtained from the above studies, it was

concluded that a 1000 psig. operating pressure was more conducive to the successful hydrogenation of a shale oil coker distillate than was a pressure of 500 psig., and that the optimum temperature appeared to be 875° F.

The effects that four different catalysts had on the hydrogenation of a 650° F.E.P. shale oil coker distillate were investigated in an effort to uncover a suitable catalyst with which to treat shale oil and its fractions. The catalysts used were: (1) Harshaw's molybdenum oxide catalyst promoted with indium, (2) Harshaw's molybdenum oxide catalyst promoted with palladium, (3) a graphite base cobalt molybdate catalyst obtained from Peter Spence & Sons, Ltd., and (4) Harshaw's cobalt molybdate catalyst.

#### B. Harshaw's Molybdenum Oxide Catalyst Promoted with Indium

The series of runs from 12 through 16 were made using the indium molybdate catalyst. The runs were made on the 650° F.E.P. coker distillate using a pressure of 1000 psig., space velocity of 1.0, recycle gas rate of 7500 cu. ft./bbl., and temperatures beginning at 725° F. and going to 925° F. by 50° F. increases every 24 hours. The properties of the charge stock are shown in Table I. Results of the runs are shown in Table V and Figure 4. The composition of the recycle gas during the runs is shown in Figure 10.

In Figure 4 it can be noticed that the activity of the catalyst increased with each temperature increase up to the start of the run at 925° F. At that time a rapid deactivation occurred and was due in part to the high temperature effect on the catalyst; however, in Figure 10, the recycle gas composition for that run, run 16, is shown to have dropped from about 65 percent hydrogen to 40 percent hydrogen. This was probably

caused by an increase in the hydrogen consumption rate. The makeup gas at the time was only approximately 65 percent hydrogen, since it was not known that the rate at which hydrogen was consumed would increase that drastically at 925° F.

The nitrogen and sulfur contents of each sample are also shown in Figure 4. The low value in each case occurred within the 875° F. run. This corresponds to the point where the catalyst activity was the highest. The best nitrogen and sulfur values were 0.87 and 0.172 weight percent, respectively. These compare to 1.65 weight percent nitrogen and 0.63 weight percent sulfur in the charge stock. The indication, therefore, would seem to be that this catalyst was better for removing sulfur than nitrogen. The nitrogen content should be reduced still further, but the sulfur content is well within the 0.25 weight percent limit which is set as a standard for petroleum gasolines on the market.

C. Harshaw's Molybdenum Oxide Catalyst Promoted with Palladium

The series of runs from 17 through 21 were made using the palladium molybdate catalyst. The study was made using the 650° F.E.P. coker distillate as the charge stock, a reactor pressure of 1000 psig., space velocity of 1.0, a recycle gas rate of 7500 cu. ft./bbl., and temperatures beginning at 725° F. and going to 925° F. by 50° F. increases every 24 hours. Results of the study are shown in Table VI and Figure 5.

Figure 11 contains the recycle gas composition data.

The activity of the catalyst appears to have increased with each increase in temperature, but a decline was again noticeable during the 925° F. run. Although a makeup gas of 80 percent hydrogen was used during that

period, the recycle gas composition dropped to about 58 percent hydrogen. This indicated that the hydrogen was again being consumed at a faster rate than it was being added.

With this catalyst the low values for nitrogen content, 0.409 weight percent, and sulfur content, 0.022 weight percent, were obtained at 925° F. The effect that the decline in catalyst activity had on nitrogen and sulfur was not as noticeable as with the indium catalyst. However, at that high temperature, the product yield had dropped from 90 to 70 weight percent of the charge. At lower temperatures, 825° F. and 875° F., satisfactory sulfur elimination was accompanied by yields of greater than 90 percent. This would indicate that 975° F. was a satisfactory temperature at which to operate.

Both the nitrogen and the sulfur determinations indicate that the palladium catalyst is definitely superior to the indium catalyst. Even at the lower temperatures, 725° F. and 775° F., the palladium catalyst yielded a product with a higher API gravity and a considerably lower sulfur content.

#### D. Peter Spence & Sons, Ltd., Cobalt Molybdate Catalyst

The study of the Spence cobalt molybdate catalyst was made in runs 22 through 26. This catalyst was supported on a graphite-type base instead of alumina as was Harshaw's cobalt molybdate. The data collected is shown in Table VII and the results are plotted in Figure 6. The recycle gas composition data is contained in Figure 12. The charge stock used was the 650° F.E.P. coker distillate. The reactor pressure was



100 psig., the space velocity was 1.0, the recycle gas rate was 7500 cu. ft./bbl., and the temperature was started at 725° F. and raised to 925° F. by 50° F. increases every 24 hours. The catalyst pellet diameter was 5/32 in. as compared to 1/8 in. for the other catalysts.

The API gravities of the samples from these runs were on the average about 4° API higher than the gravities on the samples from the indium investigation and were somewhat higher than those from the palladium study. This fact was probably due to the higher hydrogen content of the recycle gas. By comparing Figures 10, 11, and 12 it was found that the average hydrogen content of the recycle gas during the Spence catalyst study was 75 percent as compared to about 65 and 70 percent for the indium and palladium studies, respectively.

The best product from this study had a nitrogen content of 0.371 weight percent and a sulfur content of 0.018 weight percent. Both lows occurred during the 875° F. run, as did the best values for the indium and palladium catalyst investigations. Above 875° F. the product yield dropped off to 65 weight percent of the charge. At 875° F. the yield was about 83 percent, and although the yield of the indium catalyst was better, 92.5 percent, the ability of the Spence catalyst to denitrogenize and desulfurize seemed to be better. The palladium catalyst also gave better yields than did the Spence catalyst, but was not as efficient for removing nitrogen and sulfur. Perhaps the difference in hydrogen content of the recycle gas could have had a bearing in the performances of the catalyst.

E. Harshaw's Cobalt Molybdate Catalyst

The results of the Harshaw cobalt molybdate study are given in Table VIII and Figure 7. The recycle compositions for these runs, 27 through 31, are shown in Figure 13. The charge stock and the conditions were the same used in the other studies; eg., 650° F.E.P. coker distillate, 1000 psig., space velocity of 1.0, recycle gas rate of 7500 cu. ft./bbl., and temperatures from 725° F. to 925° F.

As was the case with the Spence cobalt molybdate, the recycle gas composition was considerably higher for this investigation than the desired 65 percent hydrogen, 35 percent methane. The Bureau of Mines reported that recycle gas rates of pure hydrogen above 3500 cu. ft./bbl. had very little noticeable effect on increasing the quality of the product, but that below about 2000 cu. ft./bbl. the product quality decreased rapidly. It is quite possible that a similar correlation might exist for the hydrogen content of the recycle gas; eg., increasing the percent hydrogen in the gas to above 65 percent may have very few beneficial effects, but below that standard the product quality might become increasingly poor.

Once again the best nitrogen and sulfur removal occurred at 875° F. The low values were 0.057 weight percent sulfur and 0.642 weight percent nitrogen. Considerable catalyst deactivation occurred at 925° F., and the product yield dropped to as low as 49 weight percent of the charge. The yield was only 78 weight percent at 875° F. The Bureau of Mines at a temperature of 850° F. using cobalt molybdate and a pressure of 1000 psig. obtained yields of about 92 weight percent. The reason for the lower

yields is not known.

Table IX gives a tabulated comparison between the 875° F. runs for each catalyst studied.

F. ASTM Distillation Data for the 875° F. Run for Each Catalyst

Table IX and Figure 14 present the data and results of the ASTM distillations of the 875° F. run for each catalyst. This run was chosen because in each case 875° F. appeared to be the temperature at which each catalyst performed best. The distillations were done on a composite sample for the run; eg., the three eight-hour samples were composited to give a uniform sample for the 24 hour run. The ASTM distillation curve for the 650° F.E.F. coker distillate charge stock is also included in Figure 14. All curves were corrected to 760 mm. of mercury.

The palladium catalyst and the Spence cobalt molybdate gave the highest percentages of material boiling in the gasoline range (considering the gasoline boiling range to be below 400° F.). They yielded 62 and 60 volume percent, respectively. Forty-seven volume percent of the 875° F. sample from the indium study was in the gasoline range, while 52 volume percent of the same sample from the Harshaw cobalt molybdate investigation boiled below 400° F. The remainder of the material in each case boiled within the boiling range of diesel fuel.

#### IV SUMMARY

A comparison of the 875° F. runs for each catalyst is shown in Table IX. The data from those runs was well suited as a basis on which to make a comparison. The catalyst bed temperature which was supposed to be 875° F. or 468° C. varied no more than 5° C. for any catalyst. The hydrogen content of the recycle gas was fairly constant for all four runs, not varying more than a maximum of 7 percent. The pressure was constant at 1000 psig., and the space velocity was essentially 1.0 at all times.

On the basis of the data obtained in the investigations, the Spence cobalt molybdate appeared to be the best. It gave better nitrogen and sulfur removal and yielded a product which contained about 60 volume percent of material boiling in the gasoline range. The charge stock contained 30 volume percent gasoline boiling range material. The product yield from the Spence catalyst was 83.3 weight percent of the charge which was better than the yield from the Harshaw cobalt molybdate, but not as good as that obtained from the indium or palladium promoted catalysts.

The palladium catalyst at 925° F. gave results which were almost as good as those obtained from the Spence cobalt molybdate at 875° F., but the product yield was poor, about 75 weight percent. This was the only catalyst investigated which did not show a decline in sulfur and nitrogen removing properties, when the temperature was raised from 875° F. to 925° F. It is possible that this catalyst could be used at higher temperatures if the yield could be enhanced.

The other two catalysts, Harshaw's cobalt molybdate and the indium molybdate, were less effective than the Spence cobalt molybdate and the

palladium molybdate. The Harshaw catalyst had poor denitrogenizing properties and gave low product yields above 825° F. A more thorough investigation should be conducted to determine the reasons for the differences in results obtained in these studies and those obtained by the Bureau of Mines. They found Harshaw's cobalt molybdate catalyst to be very effective. The indium catalyst gave good product yields, but it had poor nitrogen and sulfur removing properties.

The critical hydrogen content of the recycle gas is believed to increase with increases in temperature. The effect was particularly noticeable at 925° F. This was probably due to increased hydrogen consumption at the higher temperatures. The only corrective measure found to be of value was to use a makeup gas during that period of increased hydrogen consumption which had an 80 percent or better hydrogen content. A more thorough study of the effects of recycle gas composition should be made in order to determine their bearing on the shale oil hydrogenation process.

A study of physical effects should be made to determine the extent of their bearing on the process. It is known that the Bureau of Mines received consistently better nitrogen and sulfur removal using the same conditions at which these investigations were made. Reactor shape factor appears to have resulted in that difference; eg., the Bureau's catalyst bed was 35 in. long, and the reactor was 1.5 in. in diameter. The reactor used in these studies was 2.5 in. in diameter, and the catalyst bed was 1.5 in. thick.

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TABLE I

PROPERTIES OF THE CHARGE STOCKS

| Charge Stock.....coker distillate.....          | <u>650° F. E.P.</u> | <u>850° F. E.P.</u> |
|---|---------------------|---------------------|
| Gravity.....°API at 60° F.....                  | 35.4                | 25.4                |
| Viscosity, S.U. at 130° F.....seconds.....      | 31                  | 43                  |
| Sulfur.....wt. %.....                           | 0.63                | 0.63                |
| Nitrogen.....".....                             | 1.65                | 1.95                |
| ASTM Distillation (corrected to 760 mm. of Hg): |                     |                     |
| IBP.....°F. ....                                | 161                 | 113                 |
| 10 %.....".....                                 | 297                 | 385                 |
| 20 ".....".....                                 | 354                 | 475                 |
| 30 ".....".....                                 | 396                 | 525                 |
| 40 ".....".....                                 | 432                 | 570                 |
| 50 ".....".....                                 | 464                 | 620                 |
| 60 ".....".....                                 | 492                 | 665                 |
| 70 ".....".....                                 | 522                 | 710                 |
| 80 ".....".....                                 | 554                 | 760                 |
| 90 ".....".....                                 | 591                 | 805                 |
| EP.....".....                                   | 672                 | Cut Point           |
| Recovery.....vol. %.....                        | 98.0                | 89.0                |

TABLE II

IDENTIFICATION CODE AND COMPOSITION OF CATALYSTS USED

| Catalyst and Composition   | Identification Code                     | Manufacturer                 |
|--|---|------------------------------|
| Cobalt Molybdate<br>9.5 % MoO <sub>3</sub><br>3.0 % CoO<br>5.0 % SiO <sub>2</sub><br>2.0 % Graphite<br>80.5 % Al <sub>2</sub> O <sub>3</sub> | Co-Mo-0201-T-1/8"                       | Harshaw Chemical Co.         |
| Cobalt Molybdate<br>2.5 % CoO<br>14.0 % MoO <sub>3</sub><br>Graphite Base  | Graphite-type Pel-<br>lets, 5/32" diam. | Peter Spence & Sons,<br>Ltd. |
| Molybdenum Oxide *<br>16 % MoO <sub>3</sub><br>79 % Al <sub>2</sub> O <sub>3</sub><br>5 % SiO <sub>2</sub>                                   | Mo-0203-T-1/8"                          | Harshaw Chemical Co.         |

\* The indium and palladium catalysts were prepared by impregnating Harshaw's Mo-0203-T-1/8", Molybdenum Oxide catalyst.

TABLE III

OPERATION AND PRODUCT DATA FOR 500 PSIG RUN TO  
DETERMINE OPTIMUM OPERATING CONDITIONS

| Run No. | Temperature °C |          | Yield<br>Wt. % of Charge | °API | Product |         |
|---------|----------------|----------|--------------------------|------|---------|---------|
|         | Preheat        | Catalyst |                          |      | Wt. % S | Wt. % N |
| 1 A     | 385.1          | 385.8    |                          | 28.1 |         | 1.788   |
| 1 B     | 384.5          | 386.0    | 97.8                     | 28.2 | 0.497   | 1.810   |
| 1 C     | 381.2          | 384.5    |                          | 28.4 |         | 1.820   |
| 2 A     | 417.3          | 413.1    |                          | 29.5 |         |         |
| 2 B     | 415.7          | 413.2    | 98.5                     | 29.7 | 0.435   | 1.735   |
| 2 C     | 412.5          | 412.9    |                          | 29.7 |         |         |
| 3 A     | 439.4          | 440.7    |                          | 31.4 |         |         |
| 3 B     | 441.2          | 441.2    | 94.5                     | 31.4 | 0.417   | 1.683   |
| 3 C     | 440.0          | 441.3    |                          | 31.3 |         |         |
| 4 A     | 468.2          | 466.5    |                          | 32.2 | 0.390   | 1.772   |
| 4 B     | 466.0          | 468.1    | 92.0                     | 30.9 | 0.402   | 1.800   |
| 4 C     | 460.2          | 466.5    |                          | 30.6 | 0.505   | 1.897   |
| 5 A     | 496.1          | 496.3    |                          | 29.3 | 0.604   | 2.185   |
| 5 B     | 493.5          | 494.5    | 86.8                     | 29.0 | 0.852   | 2.225   |
| 5 C     | 495.6          | 498.2    |                          | 29.0 | 0.796   | 2.245   |

Catalyst.....Union Oil Co. Cobalt Molybdate, 3/16"  
 Reactor Pressure....500 psig.  
 Space Velocity.....1.0 gms./gm./hr.  
 Recycle Gas Rate....7500 cu. ft./bbl. (65 percent hydrogen)  
 Charge Stock.....850° F. E.P. Coker Distillate















































