



Catalytic hydrotreating of shale oil and shale oil coker distillates
by Dale Bulen Benson

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
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Abstract:

Because of the great interest expressed by several of the major oil companies throughout the United States in the development of liquid fuels from oil shales, a bench-scale, continuous-flow, fixed-bed catalytic processing unit was designed and constructed at Montana State College. This paper presents a study of the effects of several process variables on the denitrogenation and desulfurization of shale oil charge stocks, a study of two types of chemical treatments to denitrogenate a coker distillate, a study of the efficiency of several catalysts as denitrogenation catalysts, and a kinetic study.

By adjusting the process variables one at a time, it was found that the nitrogen content of the effluent oil decreased as the space velocity decreased or as the reactor pressure increased. Little difference in the efficiency of denitrogenation was noted by varying the hydrogen gas rate between 2000 SCF/bbl and 5000 SCF/bbl; only 5 percent better nitrogen conversion was noted at 7500 SCF/bbl. The optimum catalyst-bed temperature was between 825°F. and 875°F. As the mol percent hydrogen in the recycle gas decreased, both the weight percent nitrogen and the weight percent sulfur in the effluent oil increased. Yields were found to vary inversely with the operating temperature and directly with the space velocity.

Of the twelve different catalysts which were investigated as potential hydrodenitrogenation catalysts, four catalysts were found to be very effective. These are an HF-activated cobalt molybdate, a Peter Spence cobalt molybdate, a palladium promoted Harshaw molybdenum oxide, and a Harshaw cobalt molybdate.

A diffusion study performed prior to the kinetic study showed that film diffusion is definitely not a rate controlling step in the reaction mechanism, at least over the range of space velocities employed in this investigation. Plots which were drawn to show the effect of temperature, pressure, and hydrogen content of the hydrotreating gas indicate that the controlling reaction for the denitrogenation of shale oil coker distillates is primarily one of first order. The Arrhenius equation obtained was $k = 2.54 \times 10^4 e^{-14750/RT}$

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AND

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ABSTRACT

Because of the great interest expressed by several of the major oil companies throughout the United States in the development of liquid fuels from oil shales, a bench-scale, continuous-flow, fixed-bed catalytic processing unit was designed and constructed at Montana State College. This paper presents a study of the effects of several process variables on the denitrogenation and desulfurization of shale oil charge stocks, a study of two types of chemical treatments to denitrogenate a coker distillate, a study of the efficiency of several catalysts as denitrogenation catalysts, and a kinetic study.

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$$k = 2.54 \times 10^4 e^{-14,750/RT}$$

I INTRODUCTION

Since man began to use stored energy, he has been dependent for fuels upon products stored away by nature. Gradually, however, the easily obtained concentrated fuels are becoming exhausted so man will have to resort to those fuel sources which are more difficult to prepare in a concentrated form from their natural diffused form. With the realization that the world's supply of petroleum is rapidly being depleted, technologists have become vitally concerned with the opening up of new fields of petroleum and the processes whereby other oils can be used in place of petroleum products. Of all the possible products which might be used to supplement the supply of petroleum, oil from oil shale has the greatest promise since the products obtained from the upgrading of shale oil or shale-oil fractions are hardly distinguishable from the similar products produced from well petroleum, and since the quantity of oil shale is sufficiently abundant to supply the anticipated demand for oil.

The oil shale itself is a compact, laminated rock of sedimentary origin which contains a solid, organic matter called "kerogen". Kerogen is not a definite chemical compound but a complex mixture of complex compounds. Furthermore, the kerogen of different shales are dissimilar. Oil is obtained from this oil shale by destructive distillation and not by solvent treatments as is done with the tar sands which are saturated with oil or asphalt.

Oil shale deposits in the United States are located primarily in Colorado, Wyoming, and Utah in a 16,500 square mile area called the Green

River formation (48). A 500-foot-thick layer of this formation in Colorado assays 15 gallons of crude shale oil per ton (22) and, therefore, has a potential reserve of about 494 billion barrels of shale oil (51). The lower segment of this layer has been named the Mahogany ledge and assays an average of 30 gallons per ton (22). The United States Geological Survey has estimated that the oil shale deposits in the Utah portion can yield over 42 billion barrels of oil. Almost every country in the world possesses some oil shale deposits. Both France and Scotland have used oil made from oil shale for more than seventy years, but the severe competition from imported petroleum has prevented extensive development of the shale oil industry. There is little doubt that the development in the United States will be of great commercial importance to the country when the economic conditions involved become favorable.

More than 150 companies in the United States have been organized for the stated purpose of developing oil shale but as yet there is no shale oil industry. Realizing the increased consumption of petroleum and the need for a long-term supply of liquid fuels, the Congress of the United States passed the Synthetic Liquid Fuels Act of 1944. This act authorized research and development on new sources of oil among which was oil shale (31, 22). Immediately, the United States Bureau of Mines at Laramie, Wyoming (46) proceeded with plans to construct large retorts and set up a demonstration mine near Rifle, Colorado. Together with other research groups, they went ahead with the investigation of problems concerning the mining and retorting of oil shale and the development of

economical refining techniques.

A number of deposits of widely different character and origin have been referred to as oil shale. These might be grouped as indicated below (34):

1. Shale partially or completely saturated with oil from outside sources. A portion of this oil may have been converted into bituminous or carbonaceous residues.
2. Lignitic and coaly shales.
3. Torbanites.
4. True oil shales. Inspection of these shales seldom reveals the presence of oil itself.

The geological similarity between oil shales and coal suggests that both were formed in swamps, lagoons, deltas, and the like. Very rich oil shale possesses an extremely fine texture and has a dull silky or satiny luster. It also kindles readily and yields a fairly large amount of volatile matter. Microscopic examination reveals the presence of vegetable matter in various stages of disintegration. The resemblance of the rich shales to some of the coals of the bituminous group is indicated by the coking of the oil shales when they are subjected to heat. Inorganic matter present may consist of clay, fine sand, calcium carbonate, iron oxides, iron carbonate, and iron sulfide (as marcasite and pyrite)(48). Animal remains including insects, larvae, fish, and crustaceans can often be detected in some oil shales. It is the presence of this carbonaceous

matter derived from plant and animal remains which usually causes the black color of the oil shales (34).

The method of underground mining for oil shale employed by the United States Bureau of Mines at Rifle is a room-and-pillar type (22) whereby about 25 percent of the oil shale is allowed to remain to serve as a roof support. This method enabled the Bureau to supply processing plants at a direct cost of \$0.32 per ton of shale (16). The broken shale is conveyed to crushers and retorts like the continuous gas combustion type developed by the Bureau and the Union Oil Company (3, 22). In this type of retort the crushed shale rock is passed downward counter-current to a rising stream of hot combustion gases resulting from burning recycled product gas and carbonaceous residue in the spent shale. The rate of combustion is regulated so that the vapors are condensed within the retort; consequently, the crude shale oil is removed from the retort in a liquid state. No additional condensation is required. The design of really efficient oil-shale retorting plants and the evaluation of their thermal efficiency requires extensive data on the heat needed to retort the oil shale (45), but much work was done along this line by the Bureau of Mines Petroleum and Oil-Shale Experiment Station at Laramie.

The crude shale oil recovered from the continuous retort is a black, waxy liquid with an earthy odor. It has a specific gravity of 0.9301 at 60°/60°F. and a pour point of about 90°F. (22). The untreated shale oil contains considerable quantities of nitrogen, sulfur, and oxygen-containing compounds. The heavy gas-oil fraction may contain as much as 45 per-

cent of these compounds (51). Because of the large percentage of olefinic hydrocarbons present (3) which are affected adversely by severe chemical treatments, hydrogenation is recommended to remove the undesirable elements. Neither the large quantity of olefins nor the high percentage of nonhydrocarbons is found in petroleum (33, 50). The crude oil contains very little gasoline-boiling range material and because of the straight-chain nature of the paraffins and olefins in the shale oil naphtha, the gasoline produced from the crude oil does not have an exceptionally high octane rating (20). Tar acids in the crude include such compounds as phenol, cresols, and xylenols, and tar bases include substituted pyridines and quinolines (50). Destructive distillation of oil shale indicates that the basic nitrogen compounds are primarily heterocyclic derivatives of the pyrrole and pyridine series (46).

The tar bases in the crude shale oil from Colorado and Utah are mostly methylated pyridines and closely related compounds for the boiling range from 200°C. to 390°C. Below 200°C., the bases are almost entirely crude solvent pyridine (34). From a Scottish shale naphtha, Garrett and Smythe (17) isolated pyridine (C_5H_5N), a picoline ($C_5H_4(CH_3)N$), four lutidines ($C_5H_3(CH_3)_2N$), and a collidine ($C_5H_2(CH_3)_3N$). Back in 1905, Petrie (43) obtained an extract from a crude shale sample which contained what he identified as pyrrole (C_4H_5N). Very small amounts of the quinolines, the isoquinolines, the hydroquinolines, and the hydroisoquinolines may be present in some crudes (34). Janssen and his associates (23) isolated and identified both pyrrole and 2-methylpyrrole from a shale

oil from Colorado shale of the Green River formation. Thorne and his associates (48) identified pyridines, quinolines, pyrrole, 2,4,6-trimethylpyridine, 2-methylpyridine, and 2-methylquinoline from shale oil samples. The sulfur in the shale oil is present primarily as substituted thiophenes (48).

Both the untreated crude and the coker distillates have high sulfur and nitrogen contents, are highly unsaturated, and possess color instability when exposed to air. The sulfur content of a typical gas combustion crude shale oil (52) is 0.77 weight percent and the nitrogen content of the oil is about 2.07 weight percent. The sulfur compounds not only promote corrosion but also have objectionable odors and contribute to the poor color stability (14). Furthermore, a high sulfur content results in poor lead susceptibility (7, 14). The exact effect of each sulfur compound is not known, but sulfides are less harmful than disulfides (38). The most obnoxious odors are caused by low-boiling sulfur compounds like hydrogen sulfide and mercaptans (38). Information, which was confirmed by Byrnes and his associates (6), suggests that, at least in the case of gasolines to be blended with tetraethyllead, it is desirable to reduce the sulfur content to 0.01 percent or less; the additional cost of the refining is partially offset by the decreased amount of tetraethyllead required to obtain any given octane rating.

The nitrogen compounds are partially responsible for the extensive gum formation in that they accelerate the oxidation of the numerous unsaturated compounds present (50). Nitrogen compounds are also assuming

considerable importance because of their adverse effect on many of the cracking catalysts (2).

Such properties of the crude shale oil as the high carbon/hydrogen ratio, the high percentage of nitrogen compounds, and the large amount of unsaturates suggest a considerable number of methods for refining. Since direct removal of the unsaturated compounds would result in very high losses, some method of refining must be employed which will saturate these compounds. As much as possible of the crude must be converted into stable products. Catalytic cracking processes increase the gasoline yield but petroleum-cracking catalysts (31) are deactivated very readily by nitrogen-containing compounds of which the crude contains over 40 percent. When petroleum-refining catalysts are used in shale-oil cracking operations, there is a high formation of gas and the deposition of coke on the catalyst is large. Likewise, any refining process which might be utilized must remove the nitrogen as ammonia or similar compounds for direct removal of the nitrogen-containing compounds in the crude would obviously result in too low a yield.

Among the refining processes which have been studied are the use of successive distillations, visbreaking, polyforming, both catalytic and thermal cracking, solvent extraction and several chemical treatments, and hydrotreating. In the successive distillation process, the initial distillation, in which the crude is distilled to dryness without steam, yields a distillate with a larger portion of saturated compounds than was present in the original crude oil obtained directly from the retort.

A re-run distillation will give a distillate with a still higher percentage of saturated compounds. Additional distillations will eventually give a distillate which contains the minimum amount of compounds soluble in strong sulfuric acid (1.84 sp. gr. sulfuric acid). However, because of the high percentage of unsaturated compounds in the various cuts, there are high treating losses as well as excessive carbon deposits. A Scottish refining operation (34) resulted in a total loss of about 24 percent of the crude oil. This method of successive distillations was used by a commercial plant, the Catlin Shale Products Company of Elko, Nevada (34).

Some visbreaking operations were performed by the Bureau of Mines (31). Results of these operations indicated that the sulfur content of the visbroken crude naphtha was about the same as that of straight-run naphtha, but the nitrogen content was reduced by about 40 percent. Visbroken light gas oil which had been treated with cold sulfuric acid to produce Diesel fuel was actually used to power some of the equipment in the mines at Rifle. The performance of this Diesel fuel was comparable to commercial Diesel fuels.

In the polyforming process, naphtha and heavier oils are cracked in admixture with varying amounts of gaseous hydrocarbons like propane and butane. If catalytic conditions are used, the process is called catalytic polyforming. Crecelius (12), who used this technique for the refining of shale oil, discovered that this method utilizing iso-butylene as the outside gas gave higher yields of gasoline than were obtainable

by straight catalytic cracking. Catalytic polyforming lowers the temperature at which a maximum yield of gasoline can be obtained and enhances the color stability of the gasoline, but has little or no effect on the gum content or the octane number of the gasoline produced.

Catalytic cracking, a process which converts petroleum fractions in the fuel oil boiling range into gasoline and other lower boiling hydrocarbons, produces a high octane number gasoline in better yields than can be produced by thermal cracking. However, catalysts which have basic nitrogen compounds chemisorbed are poisoned for cracking (36), so most of the nitrogen in the charge stock must be removed prior to a catalytic cracking type of refining process.

Morris and Cameron (37) reported that thermal cracking followed by sulfuric acid treatment of the naphtha is a feasible means of producing gasoline and residual fuel oil from Colorado-shale oil.

Because catalytic hydrotreating, a process which would not only remove much of the nitrogen and sulfur in the shale oil but also reduce considerably the number of unsaturated compounds, appeared worthy of additional study, investigations employing this process were begun at Montana State College in 1954. Although several of the major oil companies have been interested in shale oil research, the initial investigations here were conducted under the sponsorship of the Esso Research and Engineering Company. They were interested in developing an economical process which would result in a low nitrogen and low sulfur effluent oil which could be used as a charge stock by a conventional petroleum refining

process. This research included studies of the effects of the operating variables such as temperature, pressure, space velocity, hydrotreating gas composition, and hydrotreating gas rate on the desulfurization and denitrogenation of shale oil coker distillates; studies of caustic and tetrahydronaphthalene batch treatments of a shale oil coker distillate in order to decrease the nitrogen content of the charge stock; studies of the efficiency of denitrogenation of twelve different catalysts in an effort to find one which would show significantly better denitrogenation of shale oil coker distillates than any of those presently being used; and a kinetic study in order to determine approximately the order of the controlling reaction for the catalytic denitrogenation of shale oil charge stocks.

II EQUIPMENT

A. Flow Diagram.

A schematic flow diagram of the catalytic hydrotreating unit is shown in Fig. 1. All seven of the reactors which are described in the specifications section of this paper were designed for a continuous-flow process and for the use of a fixed-bed catalyst. The arrangement of nichrome-wire heating coils connected to Powerstats made possible operation of the reactor over a wide temperature range, and the Mason-Neilan pressure regulator valve enabled operation at constant pressures ranging from 200 psig to 1200 psig. In conjunction with the reactor and condenser section, a gas recycle section was designed and constructed. Included in this gas recycle section was a storage tank into which the effluent gas from the reactor passed during a recycling process. From here the gas passed into a compression cylinder where oil from the compression oil reservoir displaced the gas and forced it into the feed cylinder for the reactor. The hydrotreating gas from the feed cylinder, pure hydrogen from a hydrogen bottle, or mixed gas from a bottle passed through a rotameter and into a cross at the top of the reactor where it mixed with the charge oil pumped from the oil feed reservoir. Together, the hydrotreating gas and the charge oil entered the stainless steel reactor. Treated oil was condensed in a water condenser and collected in a sample bottle. The effluent gas either passed through caustic scrubbers and was vented to the atmosphere or was fed to the storage cylinder to be recycled. When the charge stock used was the crude shale oil, a heated oil feed

reservoir, a heated storage system, and a heated filter were used because the pour point of the crude is above normal room temperature. The filter was used to trap any undesirable solids present in the crude oil.

B. Specifications for Unit for Continuous Flow.

Reactor H-K: This reactor, the first reactor to be used in the shale oil project at Montana State College, was made from an 18-in. length of 2-1/2-in., schedule 80, austenitic stainless steel pipe. The end blocks for the reactor were machined from 18-8 stainless steel. Maximum operating pressure was 3000 psig. The reactor was wound with three nichrome heating coils. The top and bottom coils were 33 feet long and the middle coil was 28 feet long. The nichrome wire for the coils was first strung with ceramic beads and wrapped over a layer of asbestos tape on the reactor wall; then, the coils were covered with a layer of asbestos tape and about one inch of 85 percent magnesia insulation. A 1/2-inch, schedule 80, 18-8 stainless steel pipe was used as a thermowell in the reactor. The bottom of the reactor was fitted with a screw-type union to allow removal and insertion of catalyst and catalyst supports. The catalyst supports were 1/4-in. Alundum balls. Two iron-constantan thermocouples were used to check reactor temperatures. One thermocouple was located in the middle of the preheat section and the other was located in the middle of the catalyst bed.

Reactor B-M: This reactor was made from a 30-in. length of nominal 1-in. OD, seamless, Type 18-8 stainless steel pipe. For easy access it

was equipped with a Vogt 6000 lb. flanged union at each end. The reactor was covered with a layer of asbestos tape and then wrapped with three 33-ft. nichrome heating coils. Over these coils was placed a pre-formed section of 85 percent magnesia insulation. A length of 5/32-in. OD stainless steel tubing was utilized as a pyod by brazing shut the end extending into the reactor and by placing an Ermeto tubing union at the top of the reactor. Three iron-constantan thermocouples were used to check the reactor temperature. One thermocouple was located at the top of the catalyst bed, one was located in the middle of the catalyst bed, and one was brazed to the outside of the reactor wall at a position which would correspond to the bottom of the catalyst bed. The catalyst was packed in the reactor so that the end of the pyod would extend only half-way through the catalyst bed. The catalyst supports used were 1/4-in. Alundum balls or 1/8-in. Alundum pellets, depending upon the size of the catalyst employed.

Reactor B=D=1: This reactor was similar to reactor B=M except for the positioning of the pyod and the thermocouples. The pyod was allowed to extend completely through the catalyst bed and an additional thermocouple was added. One thermocouple was placed at the top of the catalyst bed, one was placed one-third of the way down from the top of the catalyst bed, one was brazed to the outside of the reactor wall about two-thirds of the way down from the top of the catalyst bed, and one was located at the bottom of the catalyst bed.

Reactor B=D-2: This reactor is also similar to reactor B=M except for the heating coils and the location of the thermocouples. The top, middle, and bottom coils consisted of 27.0, 30.9, and 29.3 feet of 0.402 ohm electrically-insulated nichrome wire, respectively. Then, 14.0 feet of 0.402 ohm nichrome wire was wrapped over the upper half of the top or preheat coil. A 700-watt bulb was placed in series with the overlaid coil to enable more sensitive temperature control with the variac. The preheat coils were covered with a heavy layer of magnesia insulation, but the coils over the catalyst bed were covered with only a light layer of insulation. A removable insulation jacket was constructed for use over the catalyst-bed section if needed. Again, catalyst was packed in the reactor so that the pyrod would extend only to the bottom of the catalyst bed but the thermocouples were positioned in the pyrod so that there would be one in the middle of the preheat section, one at the top of the catalyst bed, and one at the bottom of the catalyst bed. A fourth thermocouple was brazed to the skin of the reactor at about the middle of the catalyst bed.

Reactor B=D-3: This reactor was identical to reactor B=D-2 except that within the preheat section was twisted a 3-ft. coil of 1/8-in. stainless steel tubing. A perforated stainless steel disc was used above the catalyst bed and the preheat section was packed with stainless steel Fenske rings.

Reactor B-D-4: This reactor was like reactor B-D-2, except a 6-ft. length of 1/8-in. stainless steel tubing was coiled and twisted into the preheat section. A perforated stainless steel disc was set at the top of the catalyst bed and the preheat section was packed with 1/4-in. Alundum balls.

Reactor B-D-5: This reactor was identical to reactor B-D-2 except the 5/32-in. OD pyod was replaced with a 3/16-in. OD pyod to allow the use of four thermocouples within the reactor. Thermocouples were positioned in the pyod so that there would be one in the middle of the preheat section and one at the top, one at the middle, and one at the bottom of the catalyst bed.

The other equipment used on the unit is described in detail in the appendix, see Table XI. In brief, some of the items of which it consisted are an oil-feed reservoir and a 5-gallon oil-storage reservoir, a Hills-McCanna high-pressure proportioning pump, a water condenser, Jerguson sight glasses, a Mason-Neilan pressure control valve and a Fisher-Wizard pressure controller, Brooks rotameters, Powerstats, a Pesco gear pump, pressure gauges, a Leeds and Northrup temperature indicator, a wet test meter, tubing, and valves.

III MATERIALS, METHODS, AND ANALYSES

A. Materials

Charge stocks: The charge stocks were supplied by the United States Bureau of Mines demonstration plant at Rifle, Colorado, and consisted of nominal 650°F. E.P. coker distillate, 750°F. E.P. coker distillate, 850°F. E.P. coker distillate, and full-range gas-combustion crude shale oil. The coker distillates were prepared from a gas-combustion crude by a recycle delayed coking operation. Table I is a tabulation of some of the laboratory data for these charge stocks.

Hydrotreating gas: The 100 percent hydrogen was supplied by the Whitmore Oxygen Company of Salt Lake City, Utah. The mixed gas and the commercial grade methane were supplied by the Matheson Company of Joliet, Illinois.

Catalysts: The catalysts were obtained from the Harshaw Chemical Company, Peter Spence and Sons, Ltd., and the Esso Research and Engineering Company, or were prepared in the laboratory at Montana State College. Table VII is a tabulation of the various catalysts used for the studies described in this paper.

Catalyst supports: The catalyst supports were 1/4-in. Alundum spheres or 1/8-in. Alundum pellets obtained from the Norton Abrasive Company.

B. Methods

Start-up: The reactor was charged by inverting the reactor tube and placing it in a wall support. Alundum balls or pellets for catalyst support were poured slowly into the tube and the reactor was tapped gently every little while with a hammer so that the catalyst support would pack evenly. After sufficient catalyst support had been added to allow room for the catalyst bed at its proper position in the reactor, the correct weight of catalyst was poured in slowly. The remaining space was filled with catalyst support, and a stainless steel screen was pressed in the union to hold the reactor contents in position. The reactor was then connected at its proper location in the unit. Powerstat cords, gas and oil feed lines, thermocouple leads, and the product receiver were connected. Finally, the unit was readied for a run by evacuation, pressurizing, and heating of the reactor to the desired operating temperature. Hydrotreating gas was allowed to flow through the reactor while it was warming up.

Operation: After the catalyst bed temperature had remained at operating temperature for approximately an hour, the feed pump was started. By adjusting the stroke of the piston in the feed pump, the space velocity was set at the desired value as measured by the volumetric oil feed rate. Temperatures were lined out as quickly as possible and the product was continuously being drained into the sample receiver. Temperature readings, pressure readings, and rotameter readings were checked every fifteen minutes during the initial portion of the run, and were recorded

every half hour for the remainder of the run. When the pressure in the gas-feed cylinder had dropped to within about 100 pounds of the operating pressure, storage-cylinder gas was recompressed in the feed cylinder or a new, full tank of feed gas was connected to the system. Holecek (20) reported the exact procedure used for gas make-up when the hydrotreating gas was recycled and sufficient hydrogen was introduced into the system to keep the composition of the in-going gas constant.

During a run, the weight of charge oil added and the weight of sample recovered were recorded so that approximate yields could be determined. Samples were taken at fifteen-minute intervals, half-hour intervals, hour intervals, or over longer intervals, depending upon the objective of the run. At all times, sufficient effluent oil was allowed to remain in the Jerguson to form a liquid seal and thus prevent loss of pressure in the reactor. All of the samples were stored in glass sample bottles for further analysis. The effluent gases passed through a caustic scrubbing train to remove the hydrogen sulfide. During some of the runs, a wet test meter was connected to the end of the scrubbing train to meter the effluent gases. When it was desirable to know the composition of the hydrotreating gas, a sample line was purged and gas was collected in an eight-liter glass bottle by the displacement of water.

Shut-down: To shut down the unit either because of some mechanical failure, because of coking and consequent plugging of the reactor, or because sufficient data had been collected at a given set of conditions, it was necessary to switch off the oil-feed pump and the Powerstats. Then

the sampling valve and the oil-feed line valve were closed. However, the hydrotreating gas was allowed to flow through the reactor until the reactor temperature dropped to at least 200°F. Before the reactor was torn down and dumped, it was necessary to vent the gas in the reactor. This was accomplished by shutting off the air supply to the pressure regulator valve and bleeding the lines leading to the back-pressure valve.

C. Analyses.

The gas samples in the eight-liter bottles were analysed in a low-temperature micro-still cooled with liquid nitrogen and connected to a Micromax automatic temperature recorder. By this method the composition, the volume of hydrogen, methane, ethane, and propane in the gas sample, could be accurately determined.

The API gravities were determined by using a Westphal balance to obtain the specific gravity of the oil sample and then by using the conversion equation, $^{\circ}\text{API} = (141.5/\text{sp. gr.}) - 131.5$.

The weight percent nitrogen in a sample was determined by the Boyd Guthrie modification (29) of the Kjeldahl method. This method, designed specifically for shale oil and its fractions, utilizes a mercury catalyst, a catalyst which has been found to be exceptionally effective (28). All samples were water-washed first to remove free nitrogen and then dried with calcium chloride.

The weight percent sulfur in a sample was determined by the lamp-gravimetric method, D90-50T, outlined in the ASTM manual (1). All samples

were caustic washed to remove free hydrogen sulfide and then water-washed and dried.

The few distillations run were carried out according to the ASTM distillation procedure, D86-54, (1).

IV THERMODYNAMIC STUDY

Some consideration was also given to the thermodynamics of possible reactions involved in the hydrotreating of shale oil. The following points were studied:

- (1) The determination of the equilibrium constants and activity coefficients for several reactions, assuming various nitrogen-containing compounds were present.
- (2) The comparison of the conversion of a sulfur-containing compound like thiophene with a nitrogen-containing compound like pyrrole at different pressures. (Two sets of conditions, one, atmosphere pressure and 25°C., and 70 atmospheres pressure and 440°C., were used.)
- (3) The thermodynamic calculations for the reaction of a cobalt molybdate catalyst with thiophene at the start of a run.

Since the thermodynamic data available for most of the compounds studied was very limited, several estimations had to be made. Table II gives the values of H_f_{298} and S°_{298} for the various compounds used in the calculations and Table III lists the critical constants. Several methods of estimation were used when possible in order to obtain checks on the values obtained; then, the value which was arrived at by the

seemingly most reliable method was used in the calculations. Because of the difficulty of estimation, only a limited number of nitrogen-containing cyclic compounds were considered.

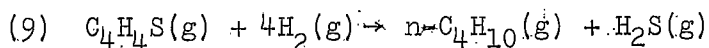
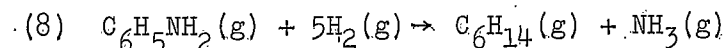
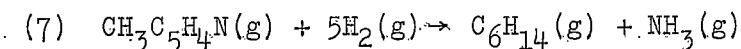
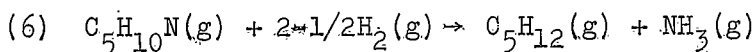
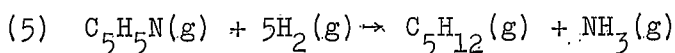
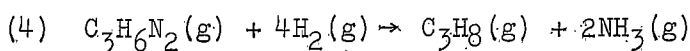
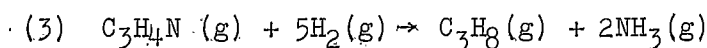
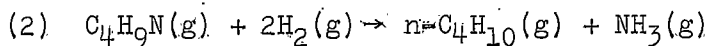
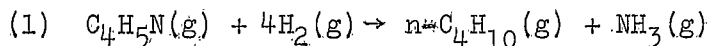
Below are listed the methods of estimation used, and in Table V are given examples of each of these methods:

- (1) Entropies and heats of formation calculated by assuming the addition of a methyl group will have the same effect on these thermodynamic properties of compounds of similar structure (4).
- (2) Entropy values calculated by using a given entropy value for the change of a single bond to a double bond (40).
- (3) Entropy values calculated by considering the changes in molal entropy accompanying the substitution of an NH_2 group for an N (39).
- (4) Liquid entropies converted to vapor entropies by a general equation relating the two entropies (15).
- (5) Heats of formation calculated with the aid of heats of combustion values (30).

The values of the critical constants which were not found in the literature were estimated by the Meissner and Redding method of parachors (35).

The following list of reactions are those reactions which were considered thermodynamically. The equilibrium constants calculated for

these reactions are tabulated in Table IV.

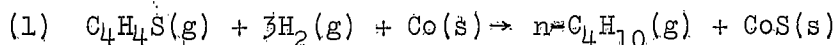


To summarize the results of this portion of the study, it may be said that all of the reactions for the hydrogenation of heterocyclics which were checked were favorable except for the reaction involving pyrrolidine. Although the equilibrium constant for the reaction of pyrrolidine with hydrogen to form ammonia as the nitrogen-containing product improves considerably with increased temperature, it is still 10^{-13} at 440°C .

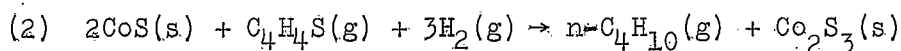
From the calculations of the K_N 's, see Table IV, it was shown that pressure favors the two reactions considered. For these reactions, when the K_N 's were greater than 10^8 , the conversion was greater than 99 percent.

even at 70 atmospheres pressure.

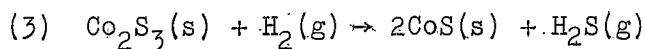
To check the possibility of the catalyst forming sulfides and then going back and forth between these sulfides as hydrogen sulfide is released, a series of reactions were tested thermodynamically. The catalyst studied was cobalt molybdate because this catalyst had been found to be the most efficient for both sulfur and nitrogen removal from shale oils and because considerable data are available on the oxides and sulfides of cobalt molybdate. The composition of the catalyst was assumed to be similar to that of a Peter Spence catalyst given in Table VII. Below is given a list of the reactions postulated and the values of the equilibrium constants for each reaction at two temperatures.



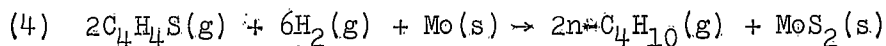
$$K_{eq298} = 7.94 \times 10^{39}; \quad K_{eq713} = 2.95 \times 10^6$$



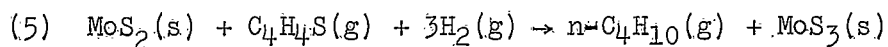
$$K_{eq298} = 3.16 \times 10^{24}; \quad K_{eq713} = 1.38 \times 10^{15}$$



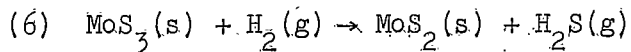
$$K_{eq298} = 0.724; \quad K_{eq713} = 135$$



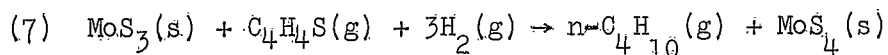
$$K_{eq298} = 6.31 \times 10^{88}; \quad K_{eq713} = 3.98 \times 10^{15}$$



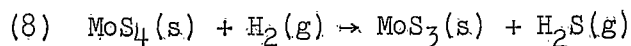
$$K_{\text{eq}298} = 1.78 \times 10^{27}; \quad K_{\text{eq}713} = 1.77$$



$$K_{\text{eq}298} = 2.82 \times 10^3; \quad K_{\text{eq}713} = 4.17 \times 10^3$$



$$K_{\text{eq}298} = 4.47 \times 10^{31}; \quad K_{\text{eq}713} = 1.12 \times 10^2$$



$$K_{\text{eq}298} = 0.106; \quad K_{\text{eq}713} = 63.1$$

These calculations indicate that it is possible for the higher sulfides to form for both cobalt and molybdenum. It also appears very possible for the higher sulfides to go to the lower sulfides accompanied by the release of hydrogen sulfide gas.

V DISCUSSION AND EXPERIMENTAL RESULTS

A. General Considerations

Following the completion of the construction of the shale oil hydro-treating unit, a few shake-down runs were made to check the system for gas and oil leaks, for faulty electrical connections, for pressure control, for control of feed rates, and for general smoothness of operation. Then a few runs of about 100 hours each were made to determine what approximately would be the optimum operating conditions.

The operating conditions used in this study varied over the following ranges: catalyst-bed temperature 385°C . to 496°C . (725°F . to 925°F .); reactor pressure 200 psig to 1200 psig; hydrotreating gas flow rate 2000 SCF/bbl to 7500 SCF/bbl; hydrotreating gas composition 30 percent hydrogen and 70 percent methane to 100 percent hydrogen; space velocity 0.1 g/g hr to 3.0 g/g hr; and grams of catalyst 50 grams to 300 grams. In Table IX are tabulated the specific operating conditions for most of the runs made with the unit. Also included in this table are the product data: yields based on weight of oil charged, results of gravimetric sulfur analyses, and results of Kjeldahl nitrogen analyses.

The four charge stocks used and the weight percent sulfur and nitrogen which they contained are as follows: 650°F . E.P. coker distillate (0.63 percent sulfur, 1.65 percent nitrogen), 750°F . E.P. coker distillate (0.61 percent sulfur, 1.90 percent nitrogen), 850°F . E.P. coker distillate (0.63 percent sulfur, 1.95 percent nitrogen), and gas.

combustion crude shale oil (0.77 percent sulfur, 2.07 percent nitrogen).

The first two run series were made using an 850°F. E.P. coker distillate, 100 grams of Union oil cobalt molybdate catalyst (see Table VII), a shallow catalyst bed (1-1/2 inches in depth), catalyst bed temperatures ranging from 725°F. to 925°F., reactor pressures of 500 and 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 65 percent hydrogen, 35 percent methane. This series demonstrated that 1000 psig reactor pressure was more conducive to both nitrogen and sulfur removal than 500 psig. Runs 3 and 8 show that by increasing the reactor pressure to 1000 psig, sulfur conversion at 825°F. was increased from 34.2 percent to 71.5 percent and nitrogen conversion was increased from 13.8 percent to 33.4 percent. These runs also indicated that the denitrogenation and desulfurization properties of the catalyst decrease as the deactivation increases. The activity level of the catalyst varied the most at 925°F. when a rapid deactivation did occur, perhaps due to increased carbon lay-down on the catalyst. Runs 9 and 10 show that at 925°F., nitrogen conversion was 15.8 percent after 16 hours on stream at that temperature, and was dropping, whereas at 875°F., nitrogen conversion was 48.7 percent after 16 hours on stream and was remaining fairly constant. Other runs also show this steady increase in nitrogen conversion at 925°F. but to a lesser degree. At this time in the study, 875°F. seemed to be the optimum operating temperature.

During the course of the runs to determine the effects of the operating variables like temperature, pressure, space velocity, gas feed rate, and recycle gas composition, several problems arose. One of these problems was the operation with a gas-combustion crude shale oil. Run 72 of 48 hours duration, and Run 74 of 300 hours duration were both made at 825°F. with a Harshaw cobalt molybdate catalyst, with 1000 psig reactor pressure, with a feed gas composition of 100 percent hydrogen, and with a space velocity varying from about 0.1 to 0.5 g/g hr. Run 72 was made with a recycle gas rate of 7500 SCF/bbl, whereas Run 74 was made with a recycle gas rate of 2500 SCF/bbl. Both runs indicated that after about 15,000 grams of charge oil had passed into the reactor, the preheat section of the reactor became plugged solid with coke. One might conclude from this that a coker distillate of indefinite characteristics was being formed in the preheat section. One method of preventing this coking in the preheat section might be to devise a preheater with a very low residence time for the crude oil. However, all the runs both prior to Run 72 and following Run 78 were made using coker distillate as the charge stock.

Several ASTM distillations were carried out on the effluent oils. Table VI gives the results of these distillations. Those ASTM distillations performed on product oil from a series of runs made with the only variable being the mol percent hydrogen in the recycle gas showed that there seems to be no correlation between the hydrogen content of the recycle gas and the boiling range of the product. Although the mol percent

hydrogen in the recycle gas varied from 40 to 100 percent, 45 to 50 volume percent of each of the products obtained was in the gasoline boiling range (below 400°F.). Furthermore, the distillation end points, around 630°F., were nearly the same for every product. The ASTM distillations performed on product oil from runs made with four different catalysts, palladium promoted molybdenum oxide, indium promoted molybdenum oxide, Peter Spence 5/32" cobalt molybdate pellets, and Harshaw 1/8" cobalt molybdate pellets, at 875°F. using 650°F. E.P. coker distillate, showed that the palladium catalyst and the Peter Spence catalyst gave higher percentages of material, 60 to 62 percent, in the gasoline range than the other two catalysts used. These two catalysts, the indium catalyst and the Harshaw catalyst, gave only 48 to 53 percent in the gasoline range.

One run, Run 107, was performed with regenerated 1/8" Peter Spence cobalt molybdate catalyst at 825°F., 1000 psig, and 7500 SCF/bbl, with a feed gas composition of 100 percent hydrogen and a space velocity of 1.0 g/g hr.. The value for the nitrogen content of the product oil after equilibrium had been reached was about the same as the value for a similar product from a run, Run 104, using fresh catalyst, namely, 0.57 weight percent nitrogen.

An attempt was made to determine the required line-out time, the time required for equilibrium to be reached. Equilibrium was considered to have been obtained when nitrogen conversion values for samples of effluent oil fluctuated about some constant value and showed no definite upward or downward trend. The nitrogen analyses tabulated in Table IX

for the effluent oil from Run 41 indicate that about 12 hours of operation are required to reach equilibrium. This time was about 12 hours either when starting up with fresh catalyst or when changing gas composition within a run. All variations following this time and up to at least 200 hours on stream were attributed to fluctuations in operating conditions and slight catalyst deactivation. In later runs, Runs 100 to 142, however, the nitrogen value used to compare the results of various operating conditions and catalysts was an average value for the period between 6 and 8 hours of operation. By this time, excessive cycling of the values for the nitrogen content of the effluent oil had ceased in nearly all instances.

As far as duplication of results is concerned, Figure 2 shows that with reactor B=M, reproducibility was good. Three successive runs were made, Runs 100, 101, and 102, all three of which gave a series of values for the percent nitrogen conversion which fell on the same line. These three runs were each carried out with a 750°F. E.P. coker distillate charge stock and with 100 grams of Peter Spence 5/32" cobalt molybdate catalyst pellets in the 1-in. OD reactor (reactor B=M) so the catalyst bed depth was about 10 inches. The operating conditions were 825°F., 1000 psig, 1.0 g/g hr. space velocity, 7500 SCF/bbl gas feed rate, and 100 percent hydrogen feed gas composition. The nitrogen conversion value after 6 hours on stream was about 0.42 percent.

Excessive channeling was believed to be the major cause of failure to get good reproducibility when a shallow catalyst bed, one less than 1 1/2

inches in depth, was used. The channeling was thought to be due partially to catalyst orientation (position acquired by the catalyst pellets in the catalyst bed as a result of pouring the catalyst into the reactor), partially to the catalyst pellet size, and partially to the extension of the thermowell all the way through the catalyst bed.

A fractionation was run on an effluent oil obtained from the hydrotreating of a 650°F. E.P. coker distillate in order to obtain cuts of 30, 30, 20, and 20 volume percent. Then nitrogen analyses were run on these cuts and a nitrogen profile was drawn, see Figure 3. The purpose of this fractionation was to determine wherein the majority of the nitrogen-bearing compounds lie, for it might be feasible to produce a low-nitrogen gasoline from a shale oil coker distillate by hydrotreating only a fraction of the coker distillate. Figure 3 shows that the 30, 30, 20, and 20 volume percent cuts contained respectively, 0.020, 0.105, 0.267, and 0.356 weight percent nitrogen. Therefore it is evident that the bulk of the nitrogen is in the high molecular weight portion of the oils.

B. Effects of Process Variables

Temperature: Optimum catalyst-bed operating temperature for the desulfurization and denitrogenation of shale oil coker distillates was the first variable studied. Sulfur analyses show that with two of the catalysts tested, Union Oil's cobalt molybdate and the indium promoted molybdenum oxide, the point of maximum sulfur conversion (77.8 percent)

was at about 875°F., see Figure 5. Two other catalysts, palladium promoted molybdenum oxide and 5/16" Peter Spence cobalt molybdate pellets, showed a continued excellent sulfur conversion (93.6 percent) up to at least 925°F.; however, the product yield at this high temperature was low, 69 to 76 percent, see Table IX. The charge stock for these runs was either 650 or 850°F. E.P. coker distillate and the other operating conditions were 500 or 1000 psig, 1.0 g/g hr. space velocity, 7500 SCF/bbl gas feed rate, and 65 percent hydrogen-35 percent methane feed gas composition.

In general, product yields vary inversely with the operating temperature and directly with the space velocity. For example, Runs 12-16 (made with 100 grams of indium promoted molybdenum oxide catalyst and 650°F. E.P. coker distillate charge stock at 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composed of 65 percent hydrogen and 35 percent methane) show that as the reactor temperature increases from 725 to 925°F., product yields drop from 99 to 71 weight percent. Runs 50 and 51 (made with 100 grams of Harshaw 1/16" cobalt molybdate pellets and 650°F. E.P. coker distillate charge stock at 825°F., 1000 psig, a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 100 percent hydrogen) show that when the space velocity is increased from 0.25 to 1.0 g/g hr., product yield increases from 82 to 91 weight percent. The nitrogen analyses for Runs 1-16 indicate that the efficiency of nitrogen removal increases with temperature up to at least 825°F. Run 12 at 725°F. gave a nitrogen conversion of 30.8

