



Catalytic hydrotreating of shale-oil coker distillate
by Russell J Holecek

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:

An investigation was conducted to determine what effect the concentration of hydrogen in the treating gas would have when hydrotreating a Colorado shale-oil coker distillate using a bench-scale, continuous-flow, fixed-bed, catalytic process unit. A nominal 650°F E.P. coker distillate from gas-combustion crude shale oil was treated with hydrogen-methane mixtures varying from 100 percent to 30 percent hydrogen under the following conditions: space velocity - 1.0 grams of oil per gram of catalyst per hour, temperature - 440°C, pressure - 1000 psig, gas flow rate - 7500 SCF/bbl, catalyst - 100 grams of 1/8-in. Harshaw cobalt molybdate pellets. When changing recycle gas (hydrotreating gas) from one composition to another, twelve hours -lineout time were found necessary to reach equilibrium conditions. Catalyst activity did not change appreciably during on-stream times of 200 hours or less." It did, however, decline slightly as the hydrogen content of the recycle gas decreased.

In the range 30-100 mol percent hydrogen, sulfur removal from the charge stock varied linearly in direct proportion to the hydrogen content, of the recycle gas. The regression equation for this relationship is $S = 0.305 H + k$ where S is the percent sulfur removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k is an intercept dependent upon physical characteristics of the reaction system. In the same range of gas concentration, nitrogen removal from the charge stock obeys the same type relation and follows the equation: $N = 0.523 H + k'$ where N is the percent nitrogen removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k' is an intercept dependent upon the physical characteristics of the reaction system.

No correlation was found between product boiling range and recycle gas hydrogen content.

At 1000 psig and 440°C with a space velocity of 1.0 gm/gm hr, a gas flow rate of 7300 SCF/bbl, cobalt molybdate catalyst, and pure-hydrogen recycle gas, sulfur in the coker distillate charge stock was reduced from 0.63 percent to 0.049 percent and nitrogen was reduced from 1.65 percent to 0.410 percent. Color stability of the oil was improved, but the sample still discolored on standing.

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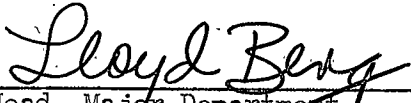
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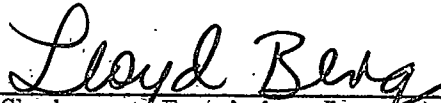
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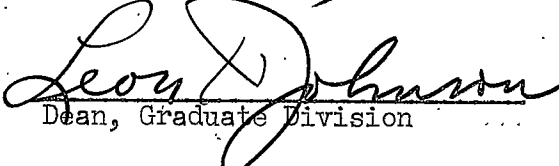
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ABSTRACT

An investigation was conducted to determine what effect the concentration of hydrogen in the treating gas would have when hydrotreating a Colorado shale-oil coker distillate using a bench-scale, continuous-flow, fixed-bed, catalytic process unit.

A nominal 650°F E.P. coker distillate from gas-combustion crude shale oil was treated with hydrogen-methane mixtures varying from 100 percent to 50 percent hydrogen under the following conditions: space velocity - 1.0 grams of oil per gram of catalyst per hour, temperature - 440°C, pressure - 1000 psig, gas flow rate - 7500 SCF/bbl, catalyst - 100 grams of 1/8-in. Harshaw cobalt molybdate pellets. When changing recycle gas (hydrotreating gas) from one composition to another, twelve hours lineout time were found necessary to reach equilibrium conditions. Catalyst activity did not change appreciably during on-stream times of 200 hours or less. It did, however, decline slightly as the hydrogen content of the recycle gas decreased.

In the range 50-100 mol percent hydrogen, sulfur removal from the charge stock varied linearly in direct proportion to the hydrogen content of the recycle gas. The regression equation for this relationship is:

$$S = 0.305 H + k$$

where S is the percent sulfur removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k is an intercept dependent upon physical characteristics of the reaction system. In the same range of gas concentration, nitrogen removal from the charge stock obeys the same type relation and follows the equation:

$$N = 0.523 H + k'$$

where N is the percent nitrogen removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k' is an intercept dependent upon the physical characteristics of the reaction system.

No correlation was found between product boiling range and recycle gas hydrogen content.

At 1000 psig and 440°C with a space velocity of 1.0 gm/gm hr, a gas flow rate of 7500 SCF/bbl, cobalt molybdate catalyst, and pure hydrogen recycle gas, sulfur in the coker distillate charge stock was reduced from 0.63 percent to 0.049 percent and nitrogen was reduced from 1.65 percent to 0.410 percent. Color stability of the oil was improved, but the sample still discolored on standing.

I INTRODUCTION

"In 1948 the United States became a net importer of oil."¹ These words, sounded by an official of the United States Bureau of Mines, are a warning for all to hear that a time will come when the nation's petroleum reserves will be exhausted. That time is not the present - our nation's known reserves are greater than ever before and have been increased every year for several decades at a rate greater than the nation's consumption rate. In spite of seventy years warnings that our petroleum resources will soon be exhausted, the time must come when the nation's petroleum consumption will exceed that available. Then we will be faced with the prospect of importing oil or developing other sources of hydrocarbon fuels. Although atomic power commercialization will undoubtedly relieve some of the demand for hydrocarbon fuels, the increased application of petroleum to uses other than fuels, e.g., petrochemicals, negates any possibility of a lessening in the demand for petroleum.

The Congress of the United States, contemplating the importance of a long-term supply of liquid fuels, passed the Synthetic Liquid Fuels Act of 1944 which authorized research and development work on new sources of oil - coal, oil shale, and agricultural and forestry products.

The development of liquid fuels from oil shale would seem to have great potential, for beneath the Green River plateau of Colorado, Utah, Wyoming and Idaho lies an oil shale bed containing an estimated 500 billion barrels of oil - more than our nation's total proven petroleum reserves. The principal part of this bed, the Piceance Creek Basin of

¹Reference 8, p. 1.

northwestern Colorado, extends over 1000 square miles, is 500 feet thick, and has an estimated reserve of 350 billion barrels. The lower 80 to 100 feet of this deposit is known as the Mahogany ledge and assays 30 gallons of oil per ton, or about twice that of the rest of the deposit. The estimated reserve of the Mahogany ledge is 100 billion barrels.

Although oil production from oil shale antedates the production of oil from wells by about twenty years, the shale oil industry was unable to survive competition from conventional petroleum. Those few plants that survived prior to World War II were located in Scotland, Estonia, and Manchuria (1).

With the passage of the Synthetic Liquid Fuels Act of 1944, the United States Bureau of Mines, together with cooperative research groups, set out to develop an economical method for mining and retorting Colorado shale, to investigate the properties of shale oil, and to develop suitable and economical refining techniques for shale oil.

Mining At Rifle, Colorado, a room-and-pillar method of mining using large mechanized equipment has been developed and can now produce oil shale for 32 cents/ton direct cost (2). In this method, rooms 70-ft high and 60-ft square are quarried in the shale bed leaving twenty-five percent of the original shale as supporting pillars. Broken shale is hauled to the mine entrance where it may be conveyed to crushing and retorting facilities.

Retorting Recent retort designs have progressed from the Bureau's NTU retort, a batch-type unit, to continuous gas combustion systems of the Bureau and Union Oil Company. Standard Oil Development Company (now Esso Research and Engineering Co.) worked on a fluidized retort design. The gas

combustion retort seems to be quite successful and both Union Oil Company and the Bureau have commercial designs.

Properties In general, crude shale oil is a black, waxy liquid having a gravity of about 21° API and, because of its high wax content, a pour point of 90°F. "Shale oil is composed of hydrocarbons, as well as lesser amounts of sulfur, nitrogen, and oxygen compounds. It differs from petroleum in that a large proportion of the hydrocarbons are olefinic and that the nonhydrocarbon constituents are present in larger amounts."¹ Paraffins and olefins in shale oil naphtha were found to be preponderantly of the straight chain type, thus accounting for the low octane rating of shale oil gasoline. Aromaticity of shale oil increases with increase in boiling point. "Tar acids present in shale oil were shown to contain phenol, the cresols, and some xylenols while the tar bases present contain substituted pyridenes and quinolines. Most of the sulfur in shale oil is present in the form of substituted thiophenes."² In addition, the Bureau of Mines has found that the NTU crude has an approximate molecular weight of 320 and that nitrogen compounds comprise 43 percent of NTU gas oil (625 - 1100°F.).

Untreated shale oil and its distillates do not make satisfactory liquid fuels because of their high sulfur content, high nitrogen content, unsaturation, low octane (for gasoline), color instability, and high gum content. Sulfur is objectionable because its compounds have objectionable odors, are corrosive or potentially corrosive, have poor color stability,

¹Reference 8, p. 47

²Reference 8, p. 48

and give off acrid fumes when burned. Unsaturated compounds, while improving octane rating of gasoline, are very prone to oxidation and are potent gum formers. Nitrogen is undesirable in that it is at least partially responsible for gum formation (8). Since color degradation accompanies gum formation it is undesirable not so much for itself as for the gum that occurs with it. Very dark colors are bad, however, because they cannot be masked and the buying public wants a product that resembles that to which they are accustomed.

Refining In their investigation of suitable refining processes for shale oil, the Bureau of Mines tried most petroleum refining processes, including vis-breaking, coking, distillation, thermal cracking, recycle cracking, catalytic cracking, chemical treating, solvent extraction, and hydrotreating. Since preliminary studies revealed that nitrogen compounds accounted for 43 percent of NTU gas oil and since a similar situation probably exists for sulfur compounds, it becomes necessary to remove only the nitrogen and sulfur, and not their compounds, if reasonable fuel yields are to be obtained. In addition, since nitrogen inhibits the activity of cracking catalysts and since cracking processes appear necessary to increase gasoline yields, nitrogen would have to be removed prior to a catalytic cracking operation. Further, since oxidation of unsaturates in the oil probably accounts for some of the color degradation, saturation of these compounds would be desirable.

Hydrotreating or hydrogenation is a process which meets most of the requirements set forth in the preceding paragraph for a successful refining process. In view of this, the Bureau of Mines directed many of their

efforts toward investigating this process and its application. Most of their work was done on naphthas and gas oils from NTU and entrained solids retorting (9). The NTU crude contained very little gasoline and about 50 percent nondistillable residuum. Initial hydrotreating studies were made in the range 500-1500 psig. Later studies were made from 1000 to 3000 psig. At the lower pressures nitrogen was reduced from around 1.6 percent to 0.48-0.35 percent and high pressure runs were successful in reducing nitrogen to less than 0.1 percent in the gasoline fraction. Although the latter gasoline was quite stable, its octane rating was about 46.

Inasmuch as shale oil is of interest to all major oil companies as a future source of hydrocarbon fuels, the Esso Research and Engineering Company agreed to sponsor a research project at Montana State College to develop an economical process for making gasoline or diesel fuel, or both, from shale oil. The plan for the initial part of the research has been to investigate low-pressure hydrotreating of shale-oil coker distillate using hydrogen diluted with methane as a treating gas. Pressures under consideration were 500 psig and 1000 psig. King (3) reported on the performance of four catalysts used for hydrotreating coker distillate charge stocks using a 65 percent hydrogen - 35 percent methane mixture as recycle gas.

This paper discusses an investigation of the effect of recycle gas composition on hydrotreating shale-oil coker distillate at 1000 psig and 440°C with a cobalt molybdate catalyst.

II EQUIPMENT

A. Flow Sheet. In anticipation of research investigations involving hydrogenation and other processes at various pressures and temperatures, a continuous-flow, fixed-bed, catalytic process unit with a gas recycle provision was designed and built. A block flow diagram of the process unit is shown in Fig. 1 and a detailed flow sheet of the unit is shown in Fig. 2. In this unit oil from the oil feed reservoir is pumped to the top of the reactor whence it flows downward through a preheat section containing alundum balls and thence over a catalyst bed. It then flows through a condenser to a capacity tank and sight glass and finally to a receiver at atmospheric pressure. The hydrotreating gas flows from a feed cylinder through a needle valve and rotameter to the top of the reactor and thence down through the preheat and catalyst sections to the condenser and out through the diaphragm pressure-control valve to a storage tank. If the hydrotreating gas is recycled it flows from the storage tank to a compression tank and is then displaced with oil to force it into the feed tank.

B. Specifications

Reactor: The reactor was made from an 18-in. length of $2\frac{1}{2}$ -in., schedule 80, austenitic stainless steel. End blocks were machined from 18-8 stainless steel. Maximum operating pressure for the reactor is 3000 psi. See Figures 3 and 4 for details on reactor construction. Three nichrome heating coils were wound on the reactor. The top and bottom coils were 33-ft long and the middle coil was 28-ft long. These ceramic-bead strung coils were first wrapped over a layer of asbestos tape, then

covered with a second layer of asbestos tape and finally insulated with about one inch of 85 percent magnesia. A $\frac{3}{4}$ -in., schedule 80, 18-8 stainless steel pipe was used as a thermowell in the reactor.

Oil feed reservoir: The oil feed reservoir was made from a 2-in., schedule 40, black-iron pipe 21-in. long. It was wound with a 10-ft nichrome heating coil and lagged with $\frac{1}{4}$ -in. of 85 percent magnesia. A 50-cc burette was attached through a side arm to indicate oil level in the reservoir.

Sediment bowl: A standard automobile-type sediment bowl.

Oil feed pump: A Hills-McCanna high-pressure proportioning pump with a $\frac{1}{4}$ -in. piston.

Condenser: A 16-in. length of $\frac{1}{2}$ -in., schedule 80, black-iron pipe surrounded by a 2-in., schedule 40, black-iron pipe acting as a water jacket.

Sight glasses: Eight-inch Jerguson sight glasses with $\frac{1}{2}$ -in. standard pipe taps.

Capacity tank: A 2-in., schedule 160, black-iron pipe, $9\frac{1}{2}$ -in. long.

Pressure control valve: An air-to-close, $\frac{1}{2}$ -in., Mason-Nielan diaphragm valve.

Pressure controller: A reverse-acting Fisher Wizard pressure controller with a 5000 psi Bourdon tube.

Rotameters: Brooks armored rotameters with $\frac{3}{32}$ -in. balls.

Autotransformers: Two 220 v. Powerstats for the 33-ft reactor coils and one 110 v. Powerstat for the 28-ft reactor coil.

Oil pump for the gas recompression system: A Pesco #051012-020 gear

pump rated at 4.5 gal/min at 2800 rpm and 1200 psi. Pressure limit for continuous operation is 1200 psi.

Gas cylinders: Harrisburg Steel Corp. cylinders, two 1320-cu in., and one 2640-cu in. capacity.

Compression oil reservoir: Two 5-gal oil cans.

High pressure piping: Schedule 80 black-iron.

High pressure pipe fittings: Henry Vogt 3000 psi forged steel.

Low pressure piping: Schedule 40 black- and galvanized-iron.

High pressure tubing: Type 304 SS, 1/8-in. OD, 0.020-in. wall.

Low pressure tubing: Copper, 1/4-in. OD.

High pressure valves: Hoke SS blunt-spindle needle valves.

Metering valves: Hoke brass-body, 20 turn-to-open needle valves.

Gas meter: Precision Scientific 20-cu ft Wet Test Meter.

Gages: Marshall 2000 psi.

Thermocouples: Three iron-constantan.

Temperature indicator: A Leeds and Northrup 18-point indicating potentiometer.

Rupture disk: A Black, Sivalls, and Bryson 4200 psi disk.

Scrubbers: One liter Erlenmeyer flasks.

III TESTS, PROCEDURES, AND MATERIALS

A. Tests

Sulfur analyses: These analyses were performed according to ASTM D90-50T with the air supply modified so that air was drawn from atmosphere outside the laboratory. Oil samples were washed once with an equal volume of 7.5 percent NaOH, three times with an equal volume of distilled water, and then dried $\frac{1}{2}$ -hour with CaCl_2 prior to burning.

Nitrogen analyses: Nitrogens were determined by a modified Kjeldahl method described in Analytical Chemistry (4). Oil samples were washed once with an equal volume of distilled water and dried with CaCl_2 before being analyzed.

Product distillation: Performed according to ASTM D86-54.

API gravity: Specific gravity was determined with a Westphal balance and then converted to $^{\circ}\text{API}$ by formula.

Gas analyses: Determined by low-temperature rectification.

B. Procedures

Reactor assembly: With the reactor supported in an inverted position, 1/4-in. alundum balls were poured into the reactor until it was about two-thirds full. Next 100 grams of catalyst were poured in and then the remaining space was filled with alundum balls. This scheme placed the catalyst bed in the middle of the lowest reactor heating coil. The reactor was tapped with a hammer during the filling operation to minimize void space. A stainless steel screen was placed in the union at the bottom of the reactor to keep the balls from falling out when the reactor was righted. The reactor was then set in place and the necessary lines

were connected to it. Thermocouples were inserted in the thermowell to read temperatures in the middle of the first preheat section, the second preheat section, and the catalyst section.

Start-up: With the reactor in place the reactor, condenser, and sight-glass sections of the unit were evacuated and then pressurized with hydrogen. The reactor was then heated to operating temperature over a two-hour period. When the catalyst temperature reached 400°C , gas flow was started through the system and oil flow was started when the catalyst temperature reached 440°C .

Operation: Temperatures were controlled by adjusting power input to the reactor heating coils with autotransformers. The first preheat section was held at $320\text{--}340^{\circ}\text{C}$; the second preheat section was held at 438°C ; and the catalyst section was held at 440°C . Space velocity was controlled by measuring the volumetric oil feed rate and then adjusting the stroke of the feed pump until the desired rate was attained. At the beginning and end of a sample period the oil level in the sight-glass above the product receiver was drained down to a line and the oil feed reservoir was filled to the zero on the burette. The charge bottle was weighed after each addition and the weight of oil added was obtained by the difference. The oil sample taken from the receiver was weighed and bottled. When pressure in the gas feed cylinder became too low to force gas through the reactor, gas in the storage cylinder was recompressed to the feed cylinder. Since the reaction under study consumed hydrogen and liberated methane, enough recycle gas was purged to remove all methane liberated and enough hydrogen was added to make up for that consumed plus that lost by purging. These

purges and additions were made before each recompression of the recycle gas. Purged gas was drawn off the storage cylinder, scrubbed, and metered before venting. Hydrogen was added to the compression cylinder via the makeup rotameter.

Shut-down: To shut the unit down, the oil feed pump was turned off, the reactor heaters were turned off, and gas flow was continued for an additional hour, then shut off.

Gas sampling: After purging the line through which the sample was to be drawn, the sample was collected over water in 8-liter glass bottles.

Gas makeup: Since various recycle gas mixtures were to be used in this research, it was decided to make them up as needed from stock hydrogen and methane. When making up a new cylinder of a particular gas mixture, the cylinder was first evacuated and then filled by metering via a rotameter sufficient quantities of hydrogen and methane to make a mixture of the desired composition. When a gas mixture was to be made up to a pressure greater than that deliverable by the diaphragm regulator used on the hydrogen and methane tanks, the gas was first metered to the compression cylinder and then pumped to the feed cylinder. Mixing of the gases was accomplished by allowing them to expand into the compression cylinder and then pumping them back to the feed cylinder. When the feed cylinder already contained a gas of given composition and a different composition was desired, the standard cubic feet of each gas present were computed assuming ideal gas behavior. Then the amount of hydrogen or methane necessary to adjust the composition to the desired value was metered into the compression cylinder and pumped to the feed cylinder. If the gas was

being made up in the storage cylinder, a similar procedure was followed.

C. Materials

The shale oil used in this research was a nominal 650°F E.P. coker distillate produced by recycle delayed coking of gas combustion crude shale oil. This coker distillate was supplied by the U. S. Bureau of Mines demonstration plant at Rifle, Colorado. Laboratory inspection data for this charge stock are given in Table I.

Hydrogen used for making up gas mixtures was supplied by the Whitmore Oxygen Company of Salt Lake City, Utah. Methane, commercial grade, was supplied by the Matheson Company.

Pelletized cobalt molybdate catalyst made by the Harshaw Chemical Company, designation Co-Mo 0201-T-1/8", was used for this study. One-eighth inch pellets were used.

The alundum balls used for preheat and catalyst support were $\frac{1}{4}$ -in. spheres supplied by the Norton Abrasive Company.

IV SAMPLE CALCULATIONS

Yield: (ESO 4LTA)

Grams oil charged	410.0
Grams oil product	<u>396.7</u>
Loss, grams	13.3

Yield: $396.7/410.0 = 96.7\%$

Space velocity: (ESO 4LTA)

Grams oil charged	410.0
Charge period, hours	4.0
Grams catalyst	100.0

Space velocity: $410.0/100.0 \times 4.0 = 1.025$

Recycle gas preparation: (ESO 44)

Unit Status

A cylinder (storage)	750 psig 40% H ₂
B cylinder (compression)	750 psig 40% H ₂
C cylinder (feed)	1080 psig 50% H ₂

Desired Status

A cylinder	400 psig 30% H ₂
B cylinder	400 psig 30% H ₂
C cylinder	1400 psig 40% H ₂

If C cylinder is vented to 800 psig, its contents are:

$$2640 \text{ in}^3 \times \frac{1 \text{ ft}^3}{1728 \text{ in}^3} \times \frac{815 \text{ psia}}{14.7 \text{ psia}} \times \frac{492^\circ\text{R}}{530^\circ\text{R}} = 78.5 \text{ SCF}$$

Hydrogen in C cylinder is:

$$0.5 \text{ mol fraction H}_2 \times 78.5 \text{ SCF} = 39.2 \text{ SCF H}_2$$

Volume of gas to be made is:

$$\frac{39.2 \text{ SCF H}_2}{0.40 \text{ mol fraction H}_2} = 98 \text{ SCF}$$

Volume of CH₄ to add is:

$$98 \text{ SCF} - 78.5 \text{ SCF} = 19.5 \text{ SCF}$$

Since B cylinder also contains 40% H₂, its contents are pumped to C cylinder.

Then the contents of A cylinder are:

$$1320 \text{ in}^3 \times \frac{1 \text{ ft}^3}{1728 \text{ in}^3} \times \frac{765 \text{ psia}}{14.7 \text{ psia}} \times \frac{492^\circ\text{R}}{530^\circ\text{R}} = 36.9 \text{ SCF}$$

Hydrogen in A cylinder is:

$$0.40 \text{ mol fraction H}_2 \times 36.9 \text{ SCF} = 14.8 \text{ SCF}$$

Volume of gas to be made in A cylinder is:

$$\frac{14.8 \text{ SCF H}_2}{0.30 \text{ mol fraction H}_2} = 48.2 \text{ SCF}$$

Volume of CH₄ to be added to A cylinder is:

$$48.2 \text{ SCF} - 36.9 \text{ SCF} = 8.6 \text{ SCF}$$

A cylinder and B cylinder are then equalized.

Purge and Addition: (ESO 40)

With one pass through the reactor, pure H₂ recycle gas was diluted with sufficient CH₄, et al. to have the analysis:

H ₂	91.6%
CH ₄ , et al	8.4%
	<u>100.0%</u>

Recycle gas flow rate - 7500 SCF/bbl, or 5.52 SCF/hr

Estimated hydrogen consumption - 800 SCF/bbl or 0.589 SCF/hr

When using pure hydrogen, hydrogen effluent from reactor is

$$5.52 \text{ SCF/hr} - 0.589 \text{ SCF/hr} = 4.93 \text{ SCF/hr}$$

When using pure hydrogen, volume of effluent gas is

$$\frac{4.93 \text{ SCF/hr H}_2}{0.916 \text{ mol fraction H}_2} = 5.38 \text{ SCF/hr}$$

Volume of CH₄, et al produced is

$$5.38 \text{ SCF/hr} - 4.93 \text{ SCF/hr H}_2 = 0.45 \text{ SCF/hr}$$

Flow rates for 80% H₂ - 20% CH₄ mixture

$$5.52 \text{ SCF/hr} \times 0.80 \text{ mol fraction H}_2 = 4.42 \text{ SCF/hr H}_2$$
$$5.52 \text{ SCF/hr} \times 0.20 \text{ mol fraction CH}_4 = 1.10 \text{ SCF/hr CH}_4$$

Effluent flow rates when using the above recycle mixture

$$4.42 \text{ SCF/hr} - 0.589 \text{ SCF/hr H}_2 = 3.83 \text{ SCF/hr H}_2$$
$$1.10 \text{ SCF/hr CH}_4 + 0.45 \text{ SCF/hr CH}_4 = 1.55 \text{ SCF/hr CH}_4$$

Composition of effluent gas is

$$\frac{1.55 \text{ SCF/hr CH}_4}{3.83 \text{ SCF/hr H}_2 + 1.55 \text{ SCF/hr CH}_4} = 0.29 \text{ mol fraction CH}_4$$

Gas to be purged from A cylinder is then

$$\frac{0.45 \text{ SCF/hr CH}_4}{0.29 \text{ mol fraction CH}_4} = 1.55 \text{ SCF/hr}$$

Hydrogen to be added is

$$0.589 \text{ SCF/hr} + (1.55 \text{ SCF/hr} - 0.45 \text{ SCF/hr CH}_4) = 1.689 \text{ SCF/hr}$$

V EXPERIMENT DESIGN

To obtain data regarding the effect of recycle gas hydrogen content on hydrotreating shale coker distillate the following sequence of runs was executed. Starting with fresh catalyst each time, runs ESO 32, 33, 34, 35, and 40 were made with nominal recycle gas compositions of 100, 80, 60, 40, and 80 percent hydrogen, respectively. For duplication purposes, runs ESO 36R, 37, 38, and 39 were made with nominal recycle gas compositions of 60, 80, 100, and 40 percent hydrogen, respectively. These runs were made consecutively following ESO 35 without shutting down the unit or changing the catalyst. With the exception of run ESO 33 the sequence for each of these runs was: lineout with pure hydrogen as recycle gas, run with pure hydrogen and take an effluent oil sample (T) for tie-in or comparative purposes, lineout with a recycle gas mixture, run with the mixture and take three samples, A, B, and C, for analysis. Run ESO 33 was not preceded by a tie period with pure hydrogen. The length of lineout period and sample period were changed during the course of the study. When starting up with fresh catalyst a 24-hour lineout period was used. When changing recycle gas composition a 4-hour lineout period was used in runs prior to ESO 36R and 8-hours was used thereafter. Before ESO 36R tie sample periods were 4-hours long and regular sample periods were 8-hours long; thereafter the regular sample periods were shortened to 4-hours.

Preliminary analysis of the data obtained from the foregoing runs indicated that further duplication was necessary and that a more accurate knowledge of required lineout time was needed. Hence runs ESO 41, 42, 43, and 44 were made with nominal recycle gas compositions of 70, 60, 50, and

40 percent hydrogen, respectively. Fresh catalyst was placed in the reactor at the start of the series and then used throughout the remaining runs. The scheme for these runs was the same used in the previous series - that is, a tie-in run with hydrogen followed by a run with the recycle gas mixture. Lineout times were estimated from nitrogen analyses of 4-hour samples taken during the initial tie run and the following run with 70 percent hydrogen. Using this information, each subsequent change in gas composition was followed by a 12-hour lineout period before starting a sample.

The following conditions were used for all of the runs in the study: space velocity - 1.0 grams of oil per gram of catalyst per hour, gas flow - 7500 SCF/bbl, catalyst temperature - 440°C, preheat temperature - 438°C, pressure - 1000 psig, catalyst charge - 100 grams.

Since preliminary studies indicated that the reaction under study produced methane and consumed hydrogen, a systematic purge and addition scheme was used to hold recycle gas composition constant. When running with pure hydrogen, the effluent gas from the reactor was not recycled, but was vented.

VI DISCUSSION OF RESULTS

A. Lineout time

Nitrogen analyses for samples ESO 4LTA-4LTG indicate that when starting up with 100 grams of fresh catalyst under the conditions set forth in the preceding section of this paper equilibrium was attained in 12 to 16 hours of operation. Although subsequent samples, i.e., ESO 4LTE, had higher nitrogen contents, these were attributed to fluctuation in operating

conditions, particularly temperature, and not to a delay in reaching equilibrium. The second lineout period study, runs 41A-41I, revealed that when recycle gas composition was changed, new equilibrium was reached in about 12 hours. Following the change in gas composition, the nitrogen content of the effluent oil samples changed steadily for about 12 hours, after which it merely fluctuated with temperature variations.

B. Catalyst orientation

The tie samples for runs ESO 32, 34, 35, 40, and 41 were all made under essentially the same conditions, that is, new catalyst, same lineout period, same length of sample period, same operating conditions, and pure hydrogen recycle gas. The only difference between the runs was that different people placed the catalyst in the reactor. Under these circumstances, one would expect that the nitrogen content of the tie samples would be about the same for all the runs. However, examination of the data in Table II shows that this definitely was not the case. This difference in nitrogen contents suggests that catalyst orientation within the reactor affects the performance of the catalyst. Since different people placed the catalyst, and since the catalyst bed was quite thin, about one-inch, it seems possible that the variations in placement could affect the contacting efficiency of the catalyst and hence could vary its performance. Without further investigation of contacting efficiency, no definite conclusion can be drawn regarding catalyst orientation and catalyst performance.

C. Catalyst activity

In Fig. 4 two curves are shown, both representing catalyst activity

as a function of on-stream time. All the points on these curves were obtained when using pure hydrogen as a recycle gas. Hence they represent checks of catalyst activity as the recycle gas composition was varied from one value to another. The difference in the original activity of the catalyst for the two curves is apparently due to some physical characteristic of the reaction system, perhaps catalyst orientation. The upper curve, for runs ESO 41T - 45T, indicates that catalyst activity declined as the run series progressed. This decline might be due to decreasing hydrogen content of the recycle gas or to a decrease in activity with time, or both. Inasmuch as the lower curve, for runs ESO 35T and 38C, shows no particular decrease in catalyst activity when the runs were made in order of increasing recycle gas hydrogen content, the major decline in activity must not be attributed to a time function, but rather to a hydrogen concentration function. This conclusion is further supported by Bureau of Mines investigations on the life of cobalt molybdate when used for a shale oil hydrogenation catalyst. Their investigation, made with pure hydrogen, revealed a catalyst life in excess of 500 hours (5). Since the studies under consideration here were 200 hours or less in length, it would seem that decline in catalyst activity with time would be quite small.

D. Sulfur and nitrogen removal

Upon applying linear regression, Table V, to the sulfur removal data from the two run series, ESO 35-38 and ESO 41-44, the following equations for sulfur removal in terms of recycle gas hydrogen content were obtained for the range 50-100 mol percent hydrogen:

$$S = 0.357H + 44.9 \quad (1)$$

$$S = 0.223H + 73.7 \quad (2)$$

where S is the percent sulfur removed and H is the mol percent hydrogen in the recycle gas. A "Student's" t test was applied to the hypothesis $H: B_1 = B_2$, where B is the true slope of the regression line. The hypothesis could not be rejected, so a pooled estimate of the regression line slope was made and found to be 0.305. Since the difference in intercepts of the above equations stems from non-reproducibility of catalyst performance, the relation between sulfur removal and recycle gas hydrogen content for the interval 50 - 100 mol percent hydrogen may be expressed by the equation

$$S = 0.305H + k \quad (3)$$

where k is an intercept. Figure 6 presents graphically the relation between sulfur removal and recycle gas hydrogen content.

When linear regression was applied to the nitrogen removal data, results similar to those for sulfur removal were obtained. The regression equations are

$$N = 0.473H - 11.3 \quad (4)$$

$$N = 0.601H - 2.46 \quad (5)$$

where N is the percent nitrogen removed from the charge stock and H is the mol percent hydrogen in the recycle gas.

A "Student's" t test was applied to the hypothesis $H: B_4 = B_5$ and, since the hypothesis could not be rejected, a pooled estimate of the regression line slope was made. Using this pooled estimate, the relation between nitrogen removal and recycle gas hydrogen content may be expressed by the

equation

$$N = 0.523H + k' \quad (6)$$

where k' is an intercept.

Graphically this relation is shown in Figure 7.

E. Boiling range of product

No correlation was seen between hydrogen content of recycle gas and the boiling range of the effluent oil samples given in Table IV.

VII SUMMARY

Twelve hours lineout time were found necessary when changing recycle gas composition from one value to another under these operating conditions: 100 grams catalyst, 1.0 gm/gm hr space velocity, 7500 SCF/bbl gas flow rate.

Since results from runs made with new catalyst and similar operating conditions were not the same, catalyst orientation within the reactor was thought to affect catalyst performance and data reproducibility.

Catalyst activity did not change appreciably during on-stream times of 200 hours or less. It did, however, decline slightly as the hydrogen content of the recycle gas decreased.

In the range 50-100 mol percent hydrogen, sulfur removal from the charge stock varied linearly in direct proportion to the hydrogen content of the recycle gas. The regression equation for this relationship is

$$S = 0.305 H + k$$

where S is the percent sulfur removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k is an intercept dependent upon physical characteristics of the reaction system. In the same range of gas concentration, nitrogen removal from the charge stock obeys the same type

relation and follows the equation

$$N = 0.523 H + k'$$

where N is the percent nitrogen removed from the charge stock, H is the mol percent hydrogen in the recycle gas, and k' is an intercept dependent upon the physical characteristics of the reaction system.

No correlation was found between product boiling range and hydrogen content of the recycle gas.

At 1000 psig and 440°C with a space velocity of 1.0 gm/gm hr, a gas flow rate of 7500 SCF/bbl, and cobalt molybdate catalyst, sulfur in the coker distillate charge stock was reduced from 0.63 percent to 0.049 percent and nitrogen was reduced from 1.65 percent to 0.410 percent. Color stability of the oil was improved, but the sample still discolored on standing.

VIII ACKNOWLEDGMENT

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TABLE I
CHARGE STOCK PROPERTIES (7)

Gravity	°API @ 60°F	35.4
Viscosity, S.U. @ 130°F	sec.	31
Carbon residue, Ramsbottom	wt. percent	0.62
Sulfur	" "	0.63
Nitrogen	" "	1.65
ASTM distillation, D-158 (corrected to 760 mm Hg)		
I.B.P.	°F	161
5% at	"	253
10	"	297
20	"	354
30	"	396
40	"	432
50	"	464
60	"	492
70	"	522
80	"	554
90	"	591
95	"	616
End Point	"	672
Recovery	vol. percent	98

TABLE II
OPERATING CONDITIONS AND PRODUCT DATA

Sample No.	Sample Interval Hr From Startup	Temperature °C		Space Velocity	Mol % H ₂ in Recycle Gas	Yield	Product Data		
		Preheat	Catalyst				°API	Wt. % S	Wt. % N
32	A 24 - 32	442	445	0.972	100.0	91.5)	0.803	0.089	0.635
	B 32 - 40	445	438	1.000	100.0	92.1)		0.084	0.670
	C 40 - 48	437	439	0.990	100.0	93.9)		0.084	0.684
33	A 24 - 32	439	443	0.998	76.8	93.7)	0.807	0.086	0.807
	B 32 - 40	438	441	1.006	81.8	95.6)		0.090	0.771
	C 40 - 48	445	442	0.992	82.2	94.2)		0.095	0.792
34	T 24 - 28	438	439	1.112	100.0	86.3)	0.807	0.049	0.410
	A 32 - 40	436	443	0.989	60.2	88.0)		0.075	0.727
	B 40 - 48	440	435	0.961	55.0	90.5)		0.064	0.739
	C 48 - 56	443	441	0.987	60.2	87.7)		0.053	0.687
35	T 24 - 28	441	439	1.055	100.0	88.3)	0.828	0.163	1.072
	A 32 - 40	437	443	0.994	41.2	88.2)		0.296	1.386
	B 40 - 48	441	442	1.000	46.3	87.2)		0.266	1.472
	C 48 - 56	440	440	1.008	47.2	87.8)		0.277	1.489
36	TR 88 - 92	434	434	1.020	100.0	93.2)	0.819	0.096	0.914
	AR 100 - 104	435	437	1.031	66.4	94.3)		0.207	1.305
	BR 104 - 108	441	444	1.000	67.2	90.6)		0.136	1.257
	CR 108 - 112	444	440	0.980	64.9	89.5)		0.151	1.306
37	T 120 - 124	446	443	1.028	100.0	92.7)	0.813	0.147	1.104
	A 132 - 136	436	435	0.987	83.4	94.0)		0.146	1.285
	B 136 - 140	436	440	1.040	82.1	89.8)		0.153	1.142
	C 140 - 144	437	440	1.025	84.6	92.8)		0.105	1.117

TABLE II (continued)
OPERATING CONDITIONS AND PRODUCT DATA

Sample No.	Sample Interval Hr From Startup	Temperature °C		Space Velocity	Mol % H ₂ in Recycle Gas	Yield	Product Data		
		Preheat	Catalyst				°API	Wt. % S	Wt. % N
38	A 152 - 156	437	442	0.965	100.0	95.7	0.813	0.112	1.015
	B 156 - 160	442	441	0.973	100.0	93.5		0.074	1.009
	C 160 - 164	441	437	1.012	100.0	89.7		0.124	1.032
39	A 172 - 176	435	439	0.987	38.5	91.4	0.826	0.184	1.357
	B 176 - 180	438	444	0.942	39.5	91.9		0.155	1.362
	C 180 - 184	440	441	0.950	40.8	88.8		0.170	1.430
40	T 24 - 28	444	441	0.950	100.0	93.6	0.815	0.087	0.902
	A 38 - 46	442	440	0.978	81.0	96.1		0.075	0.944
	B 46 - 54	443	441	0.959	81.1	95.5		0.076	0.971
	C 54 - 62	439	437	0.973	81.8	94.5		0.062	0.977
41	TA 12 - 16	440	440	1.025	100.0	96.7	-	-	0.727
	TB 16 - 20	438	438	1.054	100.0	95.5	-	-	0.796
	TC 20 - 24	441	444	1.030	100.0	96.1	-	-	0.741
	TD 24 - 28	441	440	1.015	100.0	96.8	-	-	0.803
	TE 28 - 32	449	434	1.038	100.0	96.8	-	-	0.839
	TF 32 - 36	443	437	1.079	100.0	93.1	-	-	0.718
	TG 36 - 40	441	441	1.051	100.0	96.7	-	0.0272	0.686
41	A 40 - 44	438	446	-	-	-	-	-	0.769
	B 44 - 48	441	446	-	-	-	-	-	0.907
	C 48 - 52	442	440	0.980	-	93.7	-	-	1.060
	D 52 - 56	444	446	0.985	-	93.1	-	-	1.034
	E 56 - 60	441	439	1.018	-	96.7	-	-	1.083
	F 60 - 64	445	442	0.996	-	94.6	-	-	1.030
	G 64 - 68	444	438	0.996	-	96.3	-	-	1.065
	H 68 - 72	436	435	1.015	-	96.3	-	-	1.028
	I 72 - 76	442	438	1.030	70.2	93.3	-	0.0518	0.997

TABLE II (continued)
OPERATING CONDITIONS AND PRODUCT DATA

Sample No.	Sample Interval Hr From Startup	Temperature °C		Space Velocity	Mol % H ₂ in Recycle	Yield	Product Data		
		Preheat	Catalyst				°API	Wt. % S	Wt % N
42 T	84 - 88	441	440	1.013	100.0	98.2	-	0.0318	0.722
	104 - 112	432	436	0.992	62.5	96.2	-	0.0973	1.100
43 T	124 - 132	442	442	0.983	100.0	97.1	-	0.0230	0.71
	144 - 152	438	439	1.018	57.6	95.9	-	0.0801	1.14
44 T	164 - 172	440	437	0.960	100.0	99.9	-	0.0467	0.80
	184 - 192	435	441	0.961	50.2	95.3	-	0.0944	1.15
45 T	192 - 204	440	440	0.961	100.0	94.4	-	-	0.76

TABLE III
CORRELATION DATA

Sample No.	Sample Interval Hr. From Startup	Mol % H ₂ in Recycle Gas	Sample Data		Percent S Removed	Percent N Removed
			Wt % S	Wt % N		
35 T	24 - 28	100.0	0.163	1.072	74.2	35.0
35 C	48 - 56	47.2	0.277	1.489	56.0	10.1
36 CR	108 - 112	64.9	0.151	1.306	76.1	20.8
37 C	140 - 144	84.6	0.105	1.117	83.3	32.3
38 C	160 - 164	100.0	0.124	1.032	80.3	37.4
39 C	180 - 184	40.8	0.170	1.430	73.0	13.3
41 TG	36 - 40	100.0	0.0272	0.686	95.7	58.4
41 T	72 - 76	70.2	0.0518	0.997	91.7	39.6
42 T	84 - 88	100.0	0.0318	0.722	94.9	56.2
42 A	104 - 112	62.5	0.0973	1.100	84.6	33.3
43 T	124 - 132	100.0	0.0230	0.710	96.3	57.0
43 A	144 - 152	57.6	0.0801	1.14	87.3	30.9
44 T	164 - 172	100.0	0.0467	0.80	92.6	51.5
44 A	184 - 192	50.2	0.0944	1.15	85.1	30.3
45 T	192 - 204	100.0	-	0.76	-	53.9

TABLE IV
ASTM DISTILLATIONS OF EFFLUENT OIL

Composite Sample Nos.	32A,B,C	34A,B,C	35A,B,C	36AR,BR,CR	37A,B,C	39A,B,C	40A,B,C
Mol % H ₂ in Recycle Gas	100.0	60.2	46.8	66.2	83.4	39.6	81.3
Barometric Pressure	635.6	635.6	642.1	642.1	642.1	642.1	642.1
IBP	150°F	144°F	138°F	138°F	132°F	148°F	142°F
10 cc	228	224	220	218	228	236	250
20 cc	280	271	276	278	293	284	302
30 cc	327	315	328	331	340	334	348
40 cc	365	350	374	376	380	376	388
50 cc	400	391	416	414	416	412	431
60 cc	442	434	456	446	452	448	467
70 cc	479	471	490	492	496	498	500
80 cc	515	508	531	534	535	534	532
90 cc	564	562	582	580	580	584	576
End Point	630	634	646	624	606	618	638
Recovery	97.2 cc	97.5 cc	97.4 cc	97.4 cc	95.7 cc	97.2 cc	97.1 cc

TABLE V
REGRESSION ANALYSES (6)

Regression equation: $Y = A + BX$

estimated by: $Y = a + bX$

where

$$b = \frac{n \sum XY - \sum X \sum Y}{n \sum X^2 - (\sum X)^2}$$

and

$$a = \frac{\sum Y - b \sum X}{n}$$

Equations representing sulfur removal data:

$$S = 0.357 H + 44.9$$

$$S = 0.233 H + 73.7$$

Equations representing nitrogen removal data:

$$N = 0.473 H - 11.3$$

$$N = 0.601 H - 2.46$$

Test of hypothesis $H: B_1 = B_2$ Reject at 95% level

$$t = \frac{b_1 - b_2}{s_{b_1 - b_2}} \text{ with } (n_1 + n_2 - 4) \text{ degrees of freedom}$$

where

$$s_{b_1 - b_2}^2 = s_E^2 \left[\frac{1}{\sum X_1^2 - \frac{(\sum X_1)^2}{n_1}} + \frac{1}{\sum X_2^2 - \frac{(\sum X_2)^2}{n_2}} \right]$$

and

$$s_E^2 = \frac{(\sum y_1^2 - b_1 \sum x_1 y_1) + (\sum y_2^2 - b_2 \sum x_2 y_2)}{n_1 + n_2 - 4}$$

TABEL V (continued)
REGRESSION ANALYSES (6)

$t_{\text{sulfur}} = 0.744$ with 6 degrees of freedom

$t_{\text{nitrogen}} = 2.1087^*$ with 6 degrees of freedom

Neither test is significant at the 95 percent level.

Pooled estimate of regression line slope:

$$\bar{b} = \frac{\sum x_1 y_1 + \sum x_2 y_2}{\sum x_1^2 + \sum x_2^2}$$

$$\bar{b}_S = 0.29476$$

$$\bar{b}_N = 0.53617$$

Note: While this pooling procedure may not be exact, it is sufficiently accurate to be used with the data presented herein.

*Significant at 90% level

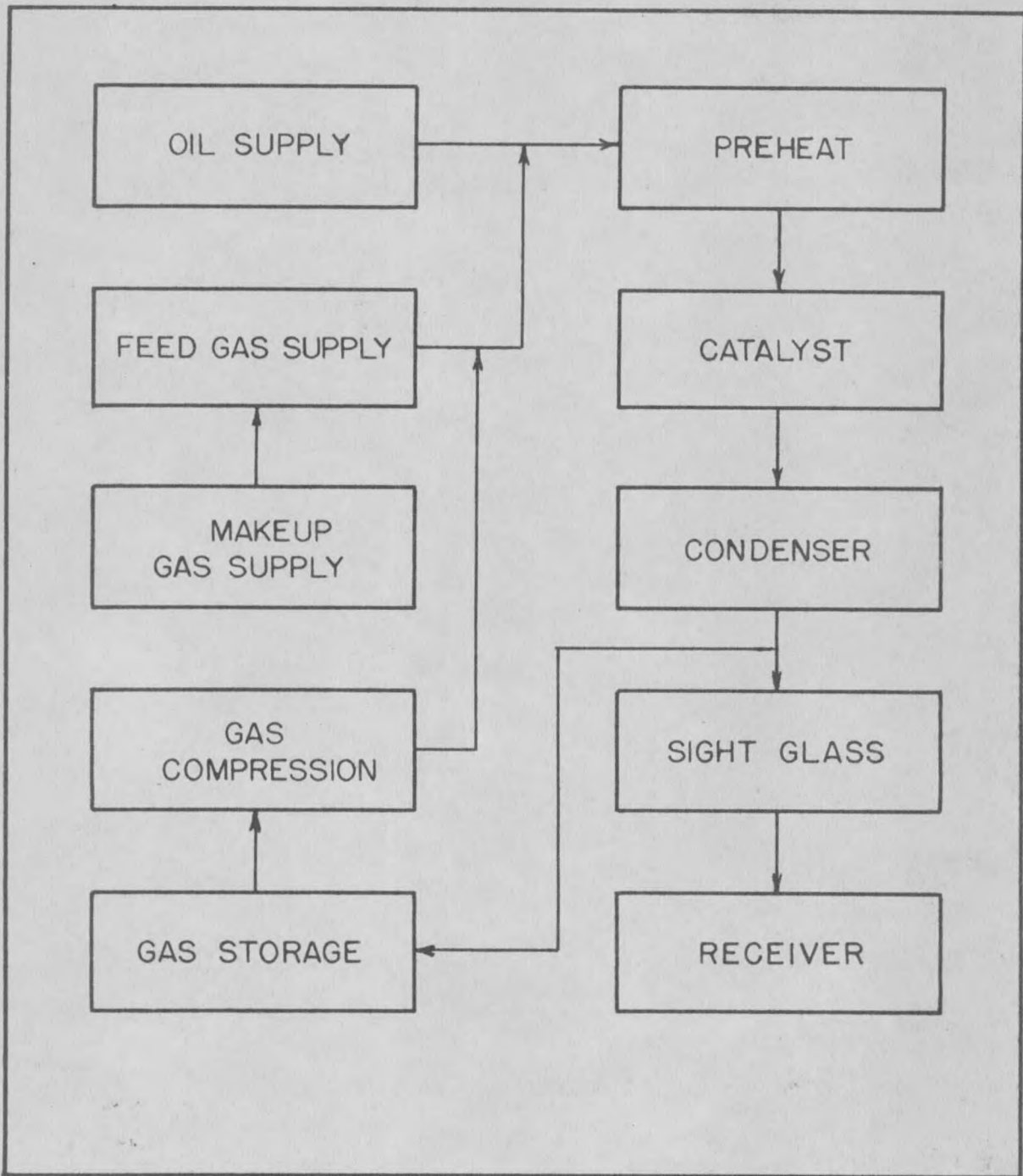


Figure 1. Block Flowsheet of Hydrotreating Unit

