Catalytic hydrotreating of shale oil and shale oil coker distillates
by Alan F McKee

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of Master of Science in Chemical Engineering
Montana State University
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was found that, under the conditions used, coking preceded hydrogenation, and therefore, the material
being hydrotreated was actually a crude form of coker distillate having indeterminate characteristics.
Changes in preheater design might remedy this situation and enable the treating of true crude shale oil.

Seven new catalysts were evaluated as hydrodenitrogenation catalysts at both mild and severe
conditions by processing a nominal 750°F E.P. shale oil coker distillate at two sets of conditions. The
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An investigation was made of data from various denitrogenation studies to determine the order of the
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The results indicate that the controlling reaction involved is of the first order.

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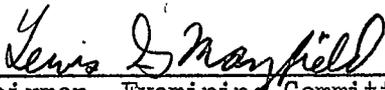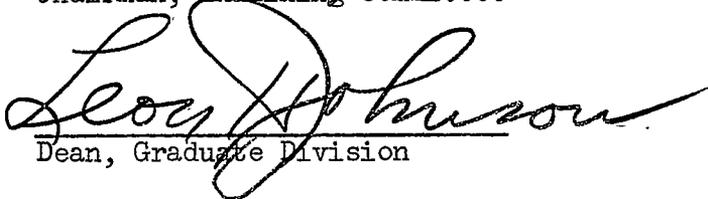Master of Science in Chemical Engineering

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TABLE OF CONTENTS

ABSTRACT

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Seven new catalysts were evaluated as hydrodenitrogenation catalysts at both mild and severe conditions by processing a nominal 750°F E.P. shale oil coker distillate at two sets of conditions. The first, or mild, treatment involved the following conditions: temperature -- 825°F; space velocity -- 1.0 g/g/hr; pressure -- 1000 psi; gas flow rate -- 2500 SCF/bbl. In the second, or more severe, set of conditions, the temperature was raised to 950°F and the gas flow rate to 4000 SCF/bbl. It was found that an HF-activated cobalt molybdate supplied by Esso Research and Engineering Company was the most efficient denitrogenation catalyst.

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I INTRODUCTION

"The United States is running short of petroleum." These words have echoed through the country for twenty years or more, and have caused concern, not only in the petroleum industry, but within the general populace as well. These concerns have been countered by the fact that new petroleum reserves have been discovered as rapidly as the old ones have been used up, and at the present time the known petroleum reserves in this country should suffice for twenty or twenty-five years at present rates of consumption. Nevertheless, the time is approaching when the rate of consumption will exceed that of discovery, and we will then be faced with the prospect of turning to foreign sources of petroleum or of developing other sources of hydrocarbon fuels. Our present rate of discovery is being maintained only by drilling to great depths, and by drilling in difficultly accessible areas such as the tidewater areas, and the time will come when drills can go no deeper, and rigs can be located no further from land. We are, at present, net importers of petroleum, and in the future we shall come to import more and more crude petroleum to satisfy our demands. Refiners, therefore, are searching for new materials from which to produce liquid hydrocarbon materials. It is true that the commercialization of atomic power will relieve some of the demand for fuel, but the increased use of petroleum for other purposes, e.g., petrochemicals, negates the possibility that our petroleum demands will decrease in the future.

The Congress of the United States has recognized the importance of

developing new sources of hydrocarbon materials, and in 1944 enacted into law the Synthetic Liquid Fuels Act, which provides for research into and development of new sources of liquid hydrocarbons, such as coal, oil shale, and agricultural products. The Bureau of Mines, under the auspices of this act, has accomplished a large amount of investigation dealing with the mining of shale, and the recovery and processing of the organic material present to yield liquid fuels.

The reserves of hydrocarbon material contained in oil shale are tremendous, and the actual production of liquid fuels from shale antedates the production from ordinary petroleum by about twenty years. However, the shale oil industry could not survive the competition following the discovery of petroleum, and only a small number of shale recovery operations in foreign countries were in existence at the beginning of World War II. (1).

The largest known reserve of oil shale in the United States lies under the Green River plateau in Colorado, Wyoming and Utah, and contains an estimated 500 billion barrels of crude shale oil, an amount greater than the known and proven petroleum reserves of the country. The bulk of this deposit is located under the Picance Creek basin, in northern Colorado. This section of the deposit covers an area of 1000 square miles, averages 500 feet in thickness, and contains reserves estimated at 350 billion barrels of material. The lower 80 to 100 feet of this deposit is known as the Mahogany Ledge, and the shale in this formation assays 30 gallons of hydrocarbon material per ton, more than twice that of the rest

of the deposit. The reserves in the Mahogany Ledge alone are estimated at 100 billion barrels.

The production of liquid fuel from oil shale involves some problems unique in the petroleum industry. Since the Mahogany Ledge lies deep under the earth's surface, the shale must be mined using hardrock techniques. Also, the hydrocarbons present in the rock are found in the form of a semisolid material known as kerogen, and at present the only satisfactory method of extracting this material involves retorting of the shale. The Bureau of Mines and other independent organizations have investigated problems involved in the mining of shale, recovery of the oil, and development of economical refining techniques applicable to the oil.

Mining. The Bureau, using a new mining technique known as the room-and-pillar method, has been able to mine the shale and deliver it to processing plants for a direct cost of 32 cents per ton of shale (13). In this method of mining, rooms 60 feet square and 70 feet high are cut out of the shale, leaving 25 percent of the original material as support for the roof. The broken shale is then hauled out of the mine and sent to crushing and recovery facilities.

Recovery. The hydrocarbon material is recovered from the rock by heating in a retort. The Bureau's first retort, known as the NTU retort, was a batch-type operation. Present retorts, as developed by the Bureau and by the Union Oil Company, are continuous. In these retorts the shale is passed downward countercurrent to a rising stream of hot combustion gases formed by burning recycled off-gases and carbonaceous material contained

in the spent shale. The organic material is driven off by the heat thus
supplied, and the rate of combustion is so regulated that the vapors are
condensed within the retort, thereby negating the need for condensing
water.

Properties. The crude shale oil recovered from the retorts is a heavy,
black material having a gravity of 21° API and a pour point of about 90°F.
It is dissimilar to normal petroleum in that it contains many olefins and
a high percentage of non-hydrocarbon material. The paraffins and olefins
are of a straight-chain nature, and therefore the gasoline produced from
the crude shale oil has a low octane rating. The crude contains tar acids
such as phenol, the cresols, and xylenols, and tar bases in the form of
substituted pyridines and quinolines. Sulfur is present in the form of
substituted thiophenes. Nitrogen compounds comprise approximately 43
percent by weight of the crude.

Untreated crude shale oil and the distillates produced therefrom are
rather unsatisfactory fuels. As mentioned, they have high sulfur and
nitrogen contents and a high percentage of unsaturated material. They
are odoriferous, corrosive, and unstable in regard to color in contact
with air. The sulfur compounds present cause corrosion, add to the gum-
forming tendency of the material, and produce an obnoxious exhaust upon
combustion. The unsaturated materials are easily oxidized to form gums,
and this oxidation is accelerated by the nitrogen compounds present (9).
Also, sulfur and nitrogen are detrimental to various catalysts now used
in refining processes, and it is now generally accepted that catalytic
proccesses are necessary to produce economically high-quality fuels,

especially gasoline. For these reasons, it becomes obvious that some treatment or treatments must be evolved to produce a material valuable to refiners as raw fuel material.

Refining. Many known petroleum refining processes have been investigated for applicability in the production of fuels from shale oil. Among these are vis-breaking, distillation, thermal cracking, catalytic cracking, various chemical treatments, solvent extraction, and hydrotreating. Also, since the crude shale oil has a rather high carbon-hydrogen ratio as compared to normal petroleum, the possibility of subjecting the crude to a delayed recycle coking to lower this ratio, followed by distillation of the vapors thus produced prior to refining, has been investigated.

Since nitrogen compounds comprise 43 percent of the crude material, and since a comparable situation probably exists for sulfur, it becomes obvious that only sulfur and nitrogen, and not their compounds, may be removed from the crude if it is to be utilized in fuel production. Further, since the unsaturates present cause gum formation, it would be desirable to stabilize the material before processing to produce fuels.

It would seem, from the reasons stated above, that hydrotreatment would accomplish most of the desired results. The Bureau of Mines has investigated catalytic hydrotreatment of naphthas and gas oils produced from NTU crudes, and has succeeded in producing a gasoline containing about 0.1 percent nitrogen. This gasoline was stable, but had a very low octane rating.

Since the production of fuels from shale oil is of interest to many large oil companies, the Esso Research and Engineering Company has spon-

sored a project at Montana State College to develop an economical hydro-
treating process which will produce a stable material having a low
nitrogen and sulfur content, suitable for refining by conventional methods
to produce liquid fuels such as gasoline and diesels. King (2) reported
an investigation of the action of four catalysts on coker distillate, and
Holecek (3) reported on the effect of varying recycle gas composition
upon hydrotreatment of coker distillate. This paper is intended to report
further investigations of the effect of process variables, including
temperature and space velocity, a study of seven new catalysts, and an
investigation of several batch-type treatments of shale oil coker
distillate.

II   EQUIPMENT

A. Flow Sheet. In the continuation of investigation of hydro-
genation processes, a continuous-flow, fixed-bed, catalytic process unit,
as previously built and installed, (3), was utilized. In addition,
another reactor, differing in configuration from the first in that it had
a long, narrow catalyst bed, was built and utilized in conjunction with
the remainder of the original unit. The catalyst bed of the original
reactor had a ratio of length to diameter of less than unity, while in
the second reactor this ratio was increased to approximately 7:1.

A block flow diagram of the process unit is shown in Fig. 1, and a
detailed flow sheet of the original unit is shown in Fig. 2. In the
original unit, oil from the oil feed reservoir was pumped to the top of
the reactor, whence it flowed downward over a pre-heat section containing

alundum balls and thence through a catalyst bed. It then flowed through
a condenser to a capacity tank and sight glass and finally to a receiver
at atmospheric pressure. The treating gas flowed from a feed tank through
a needle valve and rotameter to the top of the reactor, thence down
through the reactor and out through the pressure control valve to a
storage tank. If recycle of the feed gas was not desired, it was vented
to the atmosphere from the pressure control valve. If recycle was desired,
the gas was allowed to flow from the storage tank to a compression tank,
from which it was displaced with oil and forced into the feed tank. Upon
installation of the new reactor, the sight glass was eliminated from the
unit and the condenser was shortened in an effort to reduce holdup of
processed oil within the unit.

During the course of the experimentation, it became desirable to use
crude shale oil as the charge stock to the unit, rather than coker
distillate. Since crude shale oil has a high pour point, (+ 90°F), and
contains some solids, a heated storage reservoir was installed in the
unit in conjunction with a filter. The crude was placed in the reservoir,
and from there was pumped through heated piping to the filter, from whence
it flowed to the feed reservoir previously described.

Several batch-type treatments of shale oil coker distillate were
carried out as part of this project. In the study of these treatments,
a bomb apparatus built by the Parr Instrument Company was utilized in
order that the reactions might be carried out at elevated temperatures
and pressures. This bomb was of the rocking type, and possessed provi-
sions for pressurizing with process gas before or during the course of

the treatment.

B. Specifications.

Original Reactor: The reactor was made from an 18-in. length of $2\frac{1}{2}$-in., schedule 80, austenitic stainless steel pipe. End blocks were machined from 18-8 stainless steel. Maximum operating pressure for the reactor was 3000 psig. 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 $\frac{1}{4}$-in., schedule 80, 18-8 stainless steel pipe was used as a thermowell in the reactor.

New Reactor: The reactor was made from a 30-in. length of nominal 1-in. OD, seamless, Type 18-8 stainless steel pipe. Closure was obtained with two Vogt 6000-lb flanged unions. The reactor was wrapped with three 33-ft long nichrome heating coils in the manner previously described, and final insulation was accomplished by enclosing the reactor and heaters in a section of formed magnesia pipe insulation. A 3/16-in. length of stainless steel tubing was utilized as a thermowell by placing an Ermeto tubing union at the top of 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.

Oil Storage Reservoir: The storage reservoir was made from a 5-gallon oil can. It was wound with a 33-ft long nichrome heating coil and lagged with $\frac{1}{4}$-in. of 85 percent magnesia. When crude shale oil was used as charge stock, it was stored in this reservoir and kept at flowing temperature by means of the heater. The oil was transferred from the reservoir by means of a small gear pump to a filter and thence to the feed reservoir.

Sediment Bowl: A standard automobile-type sediment bowl.

Crude Filter: A standard automobile-type oil filter.

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 3/32-in. balls.

Autotransformers: Two-hundred-twenty v. Powerstats.

Recompression Pump: 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 Corporation   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-iron.

High Pressure Tubing: Type 304 SS, 1/8-in. OD, 0.020-in. wall.

Low Pressure Tubing: Copper, $\frac{1}{4}$-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 2250 psi disk.

Scrubbers: One-liter Erlenmeyer flasks.

III   TESTS, PROCEDURES, AND MATERIALS

A. Tests

Nitrogen analyses: All necessary nitrogen analyses were performed by a modified Kjeldahl method as described in Analytical Chemistry (4). Oil samples were washed twice with an equal volume of distilled water and dried with $CaCl_2$ before being analyzed.

B. Procedures

Reactor assembly: The reactor was placed in an inverted position and $\frac{1}{4}$-in. alundum balls were inserted until they attained a pre-determined level. At this point the desired charge of catalyst was inserted, and the reactor was then completely filled with more alundum balls. A circlet of stainless steel screen was then wedged into the union at the bottom of the reactor to keep the charge in place when the reactor was righted, the reactor was placed in position within the unit, and all necessary connections were made. Using the original reactor, thermocouples were then inserted to read temperatures in the centers of the first and second preheat sections and the catalyst bed. In the new reactor, thermocouples were permanently placed to indicate the temperature at the middle of the preheat section and the surface of the catalyst bed. A third thermocouple was welded to the outside of the reactor in such manner as to indicate the temperature at the bottom of the catalyst bed.

Start-up: With the reactor in place, the unit was first evacuated back to the feed rotameter and then pressurized with hydrogen and tested for leaks. The heating coils were then energized, and the reactor was

heated to operating temperature over an approximate two-hour period.
Gas flow was begun when internal temperatures reached about $400^{\circ}C$, and
oil flow was begun when the temperatures reached $440^{\circ}C$.

Operation: All internal temperatures were maintained at $440^{\circ}C$ by
means of the autotransformers supplying power to the various heater
coils. Space velocity was maintained by measuring the volumetric oil
flow rate and adjusting the oil feed pump stroke accordingly. Samples
were drawn as desired from the receiver at the bottom of the capacity
tank, weighed and bottled. At this time, when using coker distillate
feed stock, the feed reservoir was filled and the charge bottle weighed,
the amount of oil charged during a sample period being determined by
differences in weight of the charge bottle. When crude shale oil was
used as feed, the reservoir was filled, after sampling, by pumping the
material from the storage reservoir to the feed reservoir, the amount
charged being determined by the difference in reservoir levels before
and after filling. Gas feed was maintained at a predetermined rate by
means of the feed rotameter. Gas was generally fed from both the feed
cylinder and from a commercial cylinder connected in series with it.
Pure hydrogen was used as process gas without recycling. The recompres-
sion system was used to effect more complete exhaustion of commercial
hydrogen cylinders, since operating conditions made their direct use
impossible below 1000-psi. In practice, commercial cylinders were used
directly until their internal pressure fell to approximately 1100-psi.
They were then connected to the recompression system and exhausted to
approximately 500-psi.

Shut-down: When shut-down was desired, the oil flow to the reactor was stopped, the heaters were turned off, and gas flow was continued for an hour or more, then shut off.

C. Materials

The charge stocks used in this research were a nominal 650°F E.P. and a nominal 750°F E.P. coker distillate produced by recycle delayed coking of gas-combustion crude shale oil, and full-range gas-combustion crude shale oil. These stocks were supplied by the U. S. Bureau of Mines demonstration plant at Rifle, Colorado. Laboratory specifications for these stocks are given in Table I.

Hydrogen gas was supplied by the Whitmore Oxygen Company of Salt Lake City, Utah.

Catalysts were supplied by the Harshaw Chemical Company, the Peter Spence Company, and the Esso Research and Engineering Company. Specifications of the various catalysts used are given in Table III.

The alundum balls used for preheat and catalyst support were $\frac{1}{4}$-in. spheres and 1/8-in. rod sections supplied by the Norton Company.

IV   SAMPLE CALCULATIONS

Yield: (ESO 84-B)

Grams oil charged	848.0
Grams oil product	810.3
Grams loss	37.7

Yield: 810.3/848.0 = 95.6%

Space velocity: (ESO 84-B)

Grams oil charged	848.0
Charge period, hours	8.0
Grams catalyst	100.0

Space velocity: 848.0/100.0 x 8.0 = 1.061 g/g/hr.

V   EXPERIMENTAL DESIGN

A.   Effect of various operating variables on nitrogen content of effluent oil:

Lineout: Following unit startup or changes in operating conditions during operations, a certain amount of time was necessary to allow the unit to establish uniform rates of nitrogen removal. For the purposes of this paper, this time lag will be referred to as 'lineout time'. Previous data has indicated that this time lag should be approximately 24 hours following startup and 12 hours following changes in operating conditions during operations.

Temperature: To evaluate the effect of reaction temperature on nitrogen content of the effluent oil, runs ESO 55-65 were executed in the following manner: The reactor was charged and lined out at a temperature of 775°F and a space velocity of 1.0. Following lineout, a sample was taken, and the space velocity was altered to 0.5. Following lineout at

this space velocity, another sample was taken, and space velocity was again altered, this time to 0.25. Lineout time was again allowed, and a sample taken. Following this sequence of operations at 775°F, operating conditions were changed to 825°F and a space velocity of 1.0. The unit was allowed to line out and samples were taken as noted above at space velocities of 1.0, 0.50, and 0.25. The reactor temperature was raised to 875°F and another series of three samples were taken at the desired space velocities. The catalyst used during these runs was 100-grams of Harshaw 0201-T-1/16-in. cobalt molybdate, the charge stock was 750°F E.P. coker distillate, and the gas rate was 7500 SCF/bbl.

Space velocity: The effect of space velocity on nitrogen removal efficiency was evaluated in terms of all three standard charge stocks by executing runs ESO 50-52, 58-60, and 72-73. The method of evaluation used in runs 58-60 has been described. Runs ESO 50-52 were made using 650°F E.P. coker distillate as charge stock, and the reactor was operated at substantially constant space velocity for the duration of each run. Space velocities of 1.0 and 0.25 were investigated. Runs ESO 72-73 were executed using approximately the same scheme of operation, the charge stock being crude shale oil. During all of these runs, the catalyst used was 100 grams of Harshaw 0201-T-1/16-in. cobalt molybdate, the temperature was 825°F, and the gas rate was 7500 SCF/bbl.

To evaluate the efficiency of reprocessing effluent oil to effect further nitrogen removal, runs ESO 66-68 were made under the same conditions as those prevailing for runs ESO 52-52. The only difference was in charge stocks. Runs 66-68 were made using hydrogenated 650°F E.P. coker

distillate from the process unit. This material had originally been pro-
cessed at a space velocity of approximately 1.0.

Processing of crude: During the course of this experimentation, it
became desirable to evaluate the processing characteristics of gas-com-
bustion crude shale oil. Runs ESO 72-78 were executed for this purpose.
Attempts were made to investigate the effects of temperature and space
velocity upon efficiency of nitrogen removal, and two long runs were
executed in an effort to ascertain the effect of running time upon
catalyst activity. In the main, these runs were disappointing because of
difficulties involved in maintaining operating variables at specified
levels during the course of a run.

Duplication of results: During the course of this research, the
question arose as to whether or not adequate duplication of results be-
tween identical runs was being attained. Figure 10 shows the results
obtained in two identical runs, ESO 49 and 50, and another run, ESO 41,
which differed from these only in the size of catalyst pellets used.
Since visual examination of data suggested that correlation between
identical runs was only fair, it was decided to build a new reactor in an
attempt to obtain better duplication of results. The original reactor
involved use of a catalyst bed approximately $1\frac{1}{2}$-in. thick and $2\frac{1}{2}$-in. in
diameter, neglecting the space occupied by the thermowell, thus giving the
catalyst bed a ratio of length to diameter of less than unity. Since
there is an inverse relationship between the magnitude of this ratio and
the amount of channeling which may occur through the bed, and since chan-
neling can radically alter the effect of this type of catalytic process,

a new reactor was built having a catalyst bed approximately seven inches

long and one inch in diameter in an attempt to minimize the effect of

channeling through the catalyst bed. Also, the thermowell of the new

reactor was extended only through the upper surface of the catalyst bed

in the hope that channeling would be further minimized. Following in-

stallation of the new reactor, runs ESO 86 and 87 were executed under

identical conditions to determine whether or not the new reactor enabled

better duplication of results than did the old one. Visual examination

of data from these runs suggested that duplication was satisfactory. It

was also found by examining data from runs ESO 85 and 86 that the most

efficient nitrogen removal was accomplished when the temperature of the

catalyst bed was brought to $825^\circ F$ before the oil was started through the

unit. In run ESO 85, oil was started through at about $795^\circ F$, while in

run ESO 86 it was started through at $825^\circ F$.

Catalysts: Following installation and testing of the long-catalyst-

bed reactor, eight catalysts were tested for efficiency as compared to

the Harshaw cobalt molybdate catalyst which had been utilized up to that

point. This was done in an attempt to isolate a catalyst which would

effect relatively complete denitrogenation at reasonable space velocities.

The specifications of the catalysts tested are given in Table III. A

cobalt molybdate catalyst produced by the Peter Spence Company was

selected as a standard of comparison on the basis of previous experiment-

ation (3), and all other catalysts were compared to it for efficiency of

nitrogen removal under two sets of operating conditions. These condi-

tions are summarized in Table III. To evaluate these catalysts, runs

ESO 89-97 were executed in the following manner: The reactor was charged with the desired catalyst and started up under the first set of conditions. Samples were taken at intervals of 2, 4, 6, 8, 12, 20, and 28 hours. The unit was then changed to the second set of operating conditions and samples were taken at like intervals. The charge stock during all runs was 750°F E.P. coker distillate.

B. Effect of various chemical treatments on nitrogen content of shale oil coker distillate.

Caustic: To evaluate the effect of hot caustic bath treatment on coker distillate, runs ESO 80-81 were executed in the following manner: The Parr bomb reaction apparatus was charged with 100 grams of oil and 100 grams of anhydrous caustic. The apparatus was then heated to 825°F, and operated for periods of $2\frac{1}{2}$- and 9 hours, respectively, in an attempt to effect denitrogenation. The apparatus was then cooled, the charge removed and decanted, and proper analyses performed.

Tetralin: To evaluate the effect of tetralin treatment on coker distillate, run ESO 98 was executed in the following manner: The Parr bomb reaction apparatus was charged with 100 cc of 750°F E.P. coker distillate and 100 cc of tetralin, or tetrahydronaphthalene. The apparatus was then sealed, pressurized with hydrogen gas to 500 psi, and operated for a period of four hours at a temperature of 870°F in an attempt to effect denitrogenation. The apparatus was then cooled and the charge removed and analyzed. The maximum pressure attained during the operation was 1500 psi.

VI   DISCUSSION OF RESULTS

A. Temperature and Space Velocity

Nitrogen analyses for runs ESO 55-65 indicate that the efficiency of nitrogen removal increases with temperature at all of the space velocities under consideration. These results are indicated graphically in Fig. 3. Fig. 5, based on data obtained from runs ESO 50-52, 55-65, and 72-73, indicates that this situation is true for both crude shale oil and shale oil coker distillates. Since only a small amount of data were available, the relationship between temperature and nitrogen content of the effluent oil was assumed to be linear over the range considered, and, where necessary, the regression lines were obtained by the method of least squares. Variations from the lines are assumed to be due to fluctuations in operating conditions, e.g., space velocity. It may be noted that yields vary inversely with operating temperatures and directly with space velocity, (Fig. 4 and Table II). Hence, at an operating temperature of 875°F and a space velocity of 0.25, yields may be only about 65 percent of charge, while at lower operating temperatures and a space velocity of 1.0 yields tend to approach 100 percent of charge. Changes in space velocity seem to exert only a small effect when 650°F E.P. coker distillate is processed, while a larger effect is exerted when 750°F E.P. coker distillate or crude shale oil are processed.

B. Recycling of effluent

Runs ESO 50-52 and 66-68 were made under identical operating conditions in an effort to determine the effect of recycling effluent oil to

the process unit to effect further nitrogen removal. The charge stock

used in runs ESO 50-52 was a nominal 650°F E.P. coker distillate, while

that used in runs ESO 66-68 was nominal 650°F E.P. coker distillate which

had been hydrogenated once at a space velocity of 1.0. If materials were

to be processed twice, both times at space velocities of 1.0, and if the

effects of reprocessing and single-passing were equivalent, the effluent

material from the second pass should have a nitrogen content equivalent

to that of material which had been processed once at a space velocity of

0.5, all other operating conditions being the same. The results of these

runs indicate that this is not true. As shown in Fig. 6, a single treat-

ment at a space velocity of 0.5 will leave less nitrogen in the effluent

(0.19 percent) than will two treatments at a space velocity of 1.0 (0.22

percent). However, one treatment at a space velocity of 0.33 will leave

more nitrogen in the effluent (0.16 percent) than will two treatments at

space velocities of 1.0 and 0.50, respectively, (0.06 percent), and in

both schemes of processing the oil has equivalent residence times in

contact with the catalyst. Since this is contrary to reasoning, further

study of this problem would be most desirable.

C. Processing of crude shale oil

Two long runs (ESO 72 and 74) were made to determine the operating

characteristics of gas-combustion crude shale oil. Both runs were made

at the same temperature (825°F) but at different space velocities. It

was found that, in both cases, the reactor became solidly plugged with

coke after approximately 15,000 grams of material had been processed, and

in both cases coking occurred in the preheat section of the reactor and

not in the catalyst bed. Since coking of the crude shale oil occurred
prior to its passage through the catalyst bed, the material actually
passed over the catalyst was, in effect, a crude form of coker distillate
with indefinite characteristics. It would, therefore, seem desirable
either to coke the crude shale oil under controlled conditions prior to
hydrotreating or to devise some method whereby the crude could be heated
to reaction temperature without resultant coking. The first has been
accomplished by the Bureau of Mines in the production of coker distil-
lates. The last might possibly be accomplished by changes in preheater
design.

D. Catalysts

The study of seven new catalysts offered as denitrogenation catalysts
produced only one which was a more efficient nitrogen remover than was
the standard Spence cobalt molybdate catalyst. This one was an HF-
activated cobalt molybdate, and at the second set of operating conditions
(temperature - 950°F, gas rate - 4000 SCF/bbl) it produced an effluent
containing about 0.20 percent nitrogen, whereas the standard catalyst
produced an effluent having a nitrogen content of about 0.54 percent.
The performances of all catalysts studied are tabulated in Fig. 7.

The definition of catalyst activity is something of a problem. For
the purposes of this paper, it shall be defined as the ratio of the
nitrogen contained in the effluent oil from the standard catalyst to the
nitrogen content of the effluent oil from the catalyst under consider-
ation. Thus, the activity of the standard catalyst is 100 percent, while
the activity of the HF-activated cobalt molybdate is 270 percent at the

second set of operating conditions. Approximate activities for all

catalysts studied are listed in Table III.

E. Nitrogen profile of hydrotreated material

A sample of hydrogenated 650°F E.P. coker distillate was fraction-

ated to produce cuts of 30, 30, 20, and 20 volume percent of the material.

Nitrogen analyses were then performed on each of the cuts to determine

whether the low-boiling or high-boiling materials present contained the

residual nitrogen. Fig. 8 presents the results of this investigation.

It may be noted that the low-boiling materials contain almost no nitrogen,

(0.02 percent), while the high-boilers contain a high percentage of

nitrogen (0.33 percent). Thus, it might be possible to produce a low-

nitrogen gasoline from shale oil coker distillate without nearly complete

denitrogenation of all the material.

F. Reaction order

A first-order reaction is one in which the rate of reaction is found

to be directly proportional to the concentration of the reacting substance.

Thus, the situation is described mathematically as follows:

$$- \frac{dA}{dt} = kA$$

where:

A = concentration of reactant at time t

k = reaction proportionality constant

t = time

The integrated form of this equation is:

$$\ln \frac{A_o}{A} = \ln \frac{A_o}{A_o - x} = kt .$$

where:

$$A_o = \text{concentration of } N_2 \text{ at time } t = o$$

$$x = A_o - A = \text{amount of } N_2 \text{ (percent) removed up to time } t.$$

It therefore becomes obvious that, for a first-order reaction, a straight line is produced when the logarithm of the concentration is plotted against time. Data from runs ESO 55-65 were evaluated in an attempt to discover the order of the denitrogenation reaction involved in this research. A graph was made in which time was plotted versus the logarithm of concentration, as expressed by the relationship $\ln \frac{A_o}{A_o - x} = kt$. Time was defined as the reciprocal of space velocity. Fig. 9 shows the results of this evaluation at each of three operating temperatures, and these plots indicate that the overall denitrogenation reaction is of the first order over the temperature range considered in this experimentation. It is probable that more than one reaction is involved in the denitrogenation of shale oil, but the one which determines the rate of reaction, that is, the slowest one, is probably of the first order.

G. Batch reactions

The caustic and tetralin treatments of shale oil coker distillate at elevated temperatures and pressures produced little denitrogenation. The results of these treatments are indicated in Table IV, and show that the nitrogen content of the coker distillate was only reduced from 1.90 percent before treatment to 1.60 percent after treatment in both cases.

VII SUMMARY

The minimum reaction temperature used in this research to attempt the denitrogenation of shale oil and shale oil coker distillates was $775^{\circ}F$, and any increases above that figure tend to decrease the nitrogen content of the effluent oil, regardless of the charge stock used. Increases in temperature will also tend to decrease yields.

The nitrogen content of the effluent oil tends to decrease with decreases in space velocity, regardless of the charge stock used. Nitrogen may be almost totally removed at very low space velocities, but the yield tends to decrease as the space velocity is lowered.

Processing of crude shale oil under the preheat conditions set forth in this paper is not recommended, since coking occurs in the reactor preheat section. The result was that a crude form of coker distillate with indeterminate properties was actually passed over the catalyst bed.

Of the group of catalysts studied, the HF-activated cobalt molybdate appears to be the most efficient for hydrodenitrogenation of shale oil coker distillates. This catalyst is not available commercially. The Spence cobalt molybdate was the next-best catalyst.

Although several reactions are probably involved in the catalytic hydrodenitrogenation of shale oil, the controlling reaction appears to be first-order in nature.

Treatment of shale oil coker distillate with caustic or tetralin at elevated temperatures and pressures in an attempt to effect denitrogenation was not effective.

VIII ACKNOWLEDGMENT

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X   APPENDIX

TABLE I

CHARGE STOCK PROPERTIES ($\mathcal{8}$)

Property		Crude Shale Oil	Charge Stock 750°F. E.P. Coker Distillate	650°F. E.P. Coker Distillate
Gravity	°API at 60°F.	21.0	25.6	35.4
Viscosity, S.U. at 130°F.	sec.	90. +	46	31
Carbon Residue, Ramsbottom	Wt. percent	1.3	0.98	0.62
Sulfur	Wt. percent	0.77	0.61	0.63
Nitrogen	Wt. percent	2.07	1.90	1.65
ASTM Distillation, D-158				
IBP	°F.	370	257	161
5% at			362	253
10		517	425	297
20		577	484	354
30			529	396
40			571	432
50		699	612	464
60			647	492
70			682	522
80			716	554
90			742	591
95			754	616
E.P.			754	672
Recovery	Vol. percent		‑97	98

TABLE II

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
41-A	12-16	440	440	1.025			96.7	0.727
B	16-20	438	438	1.054			95.5	0.796
C	20-24	441	444	1.030			96.1	0.741
D	24-28	441	440	1.015	7500	650	96.8	0.803
E	28-32	449	434	1.038		Coker	96.8	0.839
F	32-36	443	437	1.079		Distillate	93.1	0.718
G	36-40	441	441	1.051			96.7	0.686
46-A	5- 9	447	438	0.260			82.0	0.180
B	9-13	441	440	0.270			91.0	0.154
C	13-17	439	437	0.232			82.0	0.152
D	17-21	439	440	0.217			86.0	0.110
E	21-25	444	439	0.175	7500	650	94.0	0.112
F	25-29	442	438	0.245		Coker	84.0	0.102
G	29-33	443	441	0.242		Distillate	81.0	0.094
H	33-37	441	438	0.245			86.0	0.100
I	37-41	436	443	0.237			87.0	0.111
J	41-45	438	441	0.227			86.0	0.090
K	45-49	439	440	0.217			80.0	0.100
L	49-53	435	439	----			----	0.096
47-A	0- 4	431	460	----		650	----	0.338
B	4- 6	443	454	1.072	7500	Coker	97.0	0.210
C	6- 8	444	441	1.362		Distillate	81.0	0.280
D	8-10	437	426	1.424			71.0	0.363

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time—Hours from Startup	Temperature Prht. °C.	Temperature Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
48-A	2- 6	430	476	0.995			89.6	0.538
B	6-10	420	446	1.000			88.8	0.757
C	10-14	417	440	0.968			92.6	0.811
D	14-18	410	438	0.986			93.2	0.859
E	18-22	410	443	1.002	7500	650	94.3	0.842
F	22-26	420	441	0.974		Coker	89.7	0.828
G	26-30	413	444	0.986		Distillate	94.2	0.811
H	30-34	415	435	0.985			94.3	0.818
I	34-38	414	439	1.005			93.1	0.882
J	34-42	424	448	1.028			91.8	0.785
K	42-46	422	442	0.918			96.6	0.869
L	46-50	421	441	----			----	0.895
49-A	4- 8	442	441	0.990			----	0.187
B	8-12	441	439	0.980			78.2	0.206
C	12-16	439	440	0.986			77.3	0.206
D	16-20	441	441	----			78.1	0.194
E	20-24	438	440	0.991	7500	650	78.4	0.215
F	24-28	439	438	0.920		Coker	84.8	0.224
G	28-32	445	443	0.887		Distillate	83.0	0.234
H	32-36	442	439	0.899			85.5	0.238
I	36-40	440	439	0.849			83.9	0.257
J	40-44	437	439	1.000			85.7	0.227
50-A	2- 6	446	442	0.960			93.2	0.257
B	6-10	444	440	0.980			91.6	0.233
C	10-14	443	441	0.960			93.4	0.249
D	14-18	441	437	0.948			94.0	0.240

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N$_2$ in Effluent
50-E	18-22	437	442	1.028	7500	650	88.6	0.234
F	22-26	440	440	0.995		Coker	94.2	0.279
G	26-30	442	440	1.041		Distillate	88.1	0.269
H	30-34	447	439	0.976			92.0	0.292
I	34-38	443	441	0.970			95.2	0.299
J	38-42	440	441	----			94.4	0.330
K	42-46	436	440	1.029			94.2	0.313
L	46-50	437	439	1.006			86.9	0.326
51-A	3-11	452	442	0.292			65.7	0.516
B	11-19	453	439	0.263			81.9	0.151
C	19-27	438	441	0.275			70.4	0.136
D	27-35	448	441	0.251			80.6	0.182
E	35-43	441	440	0.232			83.3	0.097
F	43-51	437	441	0.161			82.4	0.069
G	51-59	440	440	0.236			88.3	0.120
H	59-67	440	441	0.310			73.6	0.219
I	67-75	440	441	0.314	7500	650	89.8	0.221
J	75-83	440	440	0.277		Coker	85.1	0.165
K	83-91	441	441	0.312		Distillate	83.2	0.153
L	91-99	438	440	0.319			81.8	0.148
M	99-108	440	441	0.300			85.1	0.163
N	108-115	440	440	0.359			85.3	0.154
O	115-123	438	442	0.298			89.1	0.188
P	123-131	442	442	0.319			77.6	0.173
Q	131-139	441	440	0.321			----	----
R	139-147	438	441	0.322			79.0	0.151

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
55	31	409	412	1.148			----	1.129
56	31-46	408	413	0.496			----	0.786
57	46-63	413	413	0.271			----	0.535
58	63-83	441	438	0.956			----	0.674
59	83-96	432	440	0.700	7500	750	90.0	0.690
60	96-115	441	440	0.241		Coker	83.9	0.279
61	115-130	465	466	1.060		Distillate	78.6	0.960
62	130-143	467	467	0.509			75.9	0.657
63	143-164	460	470	0.244			64.3	0.446
64	164-174	470	470	0.201			65.1	0.252
65	174-190	440	440	0.284			88.9	0.412
66	222-254	442	442	0.982			90.2	0.222
67	254-254	444	440	0.438	7500	650	88.5	0.041
68	278-278	444	439	0.316		Coker Distillate Hydrogen- ated	92.5	0.041
72-A	36	440	440	0.513			78.8	0.874
B	44	440	440	0.616			73.1	0.816
C	70	440	440	0.129			90.0	0.663
D	79	440	440	0.237			90.0	0.563
E	92	440	440	0.084			78.5	0.510
F	100	440	440	0.591			----	0.868
G	108	440	440	0.195			----	0.727
H	116	440	440	0.198			69.5	0.680
I	124	440	440	0.349			83.0	0.850
J	132	440	440	0.240			79.4	1.031
K	140	440	440	0.120			69.6	0.689
L	148	440	440	0.090			----	0.465

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
72-M	164	440	440	0.105	7500	Crude	66.7	----
N	172	440	440	0.096		Shale	65.6	0.465
O	180	440	440	0.105		Oil	64.0	0.455
P	188	440	440	0.126			63.3	0.470
Q	196	440	440	0.091			---	0.470
R	204	440	440	0.087			---	0.470
S	220	440	440	0.108			66.3	0.477
T	236	440	440	0.119			64.4	0.467
U	252	440	440	0.096			68.5	0.467
V	268	440	440	0.170			67.8	0.534
W	284	440	440	0.086			---	0.519
X	300	440	440	---			67.6	---
Y	316	440	440	0.091			---	0.401
Z	332	440	440	---			68.8	0.713
AA	348	440	440	0.231			---	0.830
BB	364	440	440	0.103			---	0.859
CC	380	440	440	0.067	7500	Crude	---	0.425
DD	396	440	440	0.079		Shale	---	0.425
EE	412	440	440	0.130		Oil	---	0.737
FF	492	440	440	0.114			---	0.191
GG	503	440	440	0.337			---	0.437
74-A	246	440	440	0.211			80.0	----
B	254	440	440	0.173			80.0	----
C	260	440	440	0.186			80.0	----
D	267	440	440	0.203			80.0	0.650
E	273	440	440	0.206			80.0	0.698
F	279	440	440	0.232			80.0	----
G	282	440	440	0.189			80.0	----

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
74-H	288	440	440	0.242			85.0	0.800
I	294	440	440	0.249	2500	Crude	85.0	0.958
J	300	440	440	0.314		Shale	84.0	----
K	312	440	440	0.184		Oil	84.0	----
L	326	440	440	0.205			84.0	0.651
M	326	440	440	0.205			82.0	0.651
N	342	440	440	0.202			82.0	----
O	352	440	440	0.215			82.0	----
P	358	440	440	0.198			82.0	----
Q	375	440	440	0.102			87.0	----
R	383	440	440	0.130			87.0	----
S	391	440	440	0.213			87.0	----
T	349	440	440	0.186			87.0	----
U	407	440	440	0.174			87.0	----
V	415	440	440	0.171			87.0	----
W	423	440	440	0.218			87.0	----
X	431	440	440	0.191			87.0	----
Y	439	440	440	0.156			87.0	----
Z	447	440	440	0.179			87.0	----
85-A	17	440	440	1.017		750	87.5	0.802
B	25	440	440	1.017		Coker	87.5	0.945
C	34	440	440	1.017	7500	Distillate	87.5	0.960
D	42	440	440	1.017			87.5	0.980
E	49	440	440	1.017			87.5	----
86-A	2	440	440	1.045			95.0	0.749
B	4	440	440	1.045			95.0	0.807
C	6	440	440	1.045			95.0	0.678
D	8	440	440	1.045		750	95.0	0.807
E	12	440	440	1.045	7500	Coker	95.0	0.707
F	20	440	440	1.045		Distillate	95.0	0.826

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time—Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
86-G	28	440	440	1.045			95.0	0.870
H	36	440	440	1.045			95.0	0.922
I	44	440	440	1.045			95.0	0.928
J	52	440	440	1.045			95.0	0.941
87-A	2	440	440	0.987			96.7	0.598
B	4	440	440	0.987		750	96.7	0.617
C	6	440	440	0.987	7500	Coker	96.7	0.618
D	8	440	440	0.987		Distillate	96.7	0.689
E	12	440	440	0.987			96.7	0.702
F	19	440	440	0.987			96.7	0.713
G	24	440	440	0.987			96.7	0.819
88-A	2	440	440	1.010			---	0.798
B	4	440	440	1.010			---	0.843
C	6	440	440	1.010			---	0.785
D	8	440	440	1.010	2500	750	---	0.809
E	12	440	440	1.010		Coker	---	0.863
F	20	440	440	1.010		Distillate	---	0.871
G	28	440	440	1.010			---	0.885
89-I-A	2	440	440	1.030	2500		98.4	1.008
B	4	440	440	1.030	2500		98.4	0.856
C	6	440	440	1.030	2500		98.4	0.762
D	8	440	440	1.030	2500		98.4	0.742
E	12	440	440	1.030	2500		98.4	0.748
F	20	440	440	1.030	2500	750	98.4	0.791
G	24	440	440	1.030	2500	Coker	98.4	0.825
						Distillate		

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
89-II-A	29	510	510	1.017	4000		81.3	0.325
B	31	510	510	1.017	4000		81.3	0.501
C	33	510	510	1.017	4000		81.3	0.656
D	35	510	510	1.017	4000		81.3	0.523
E	39	510	510	1.017	4000		81.3	0.536
F	47	510	510	1.017	4000		81.3	----
91-I-A	2	440	440	1.040	2500		96.7	1.100
B	4	440	440	1.040	2500		96.7	1.019
C	6	440	440	1.040	2500		96.7	1.020
D	8	440	440	1.040	2500	750	96.7	1.118
E	12	440	440	1.040	2500	Coker	96.7	1.080
F	20	440	440	1.040	2500	Distillate	96.7	1.170
G	26	440	440	1.040	2500		96.7	----
II-A	32	510	510	1.050	4000		90.0	1.074
B	34	510	510	1.050	4000	750	90.0	0.864
C	36	510	510	1.050	4000	Coker	90.0	1.123
D	38	510	510	1.050	4000	Distillate	90.0	0.698
E	42	510	510	1.050	4000		90.0	0.673
F	50	510	510	1.050	4000		90.0	0.670
92-I-A	2	440	440	0.960	2500		96.1	0.551
B	4	440	440	0.960	2500		96.1	0.578
C	6	440	440	0.960	2500		96.1	0.500
D	8	440	440	0.960	2500		96.1	0.536
E	12	440	440	0.960	2500		96.1	0.578
F	20	440	440	0.960	2500		96.1	0.583
G	28	440	440	0.960	2500	750 Coker Dist.	96.1	0.670

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
92-II-A	33	510	510	0.975	4000	750	80.0	0.104
B	35	510	510	0.975	4000	Coker	80.0	0.147
C	37	510	510	0.975	4000	Distillate	80.0	0.203
D	39	510	510	0.975	4000		80.0	0.181
E	43	510	510	0.975	4000		80.0	0.206
F	51	510	510	0.975	4000		80.0	0.210
G	59	510	510	0.975	4000		80.0	0.198
93-I-A	2	440	440	1.000	2500		95.0	0.576
B	4	440	440	1.000	2500		95.0	0.863
C	6	440	440	1.000	2500		95.0	0.994
D	8	440	440	1.000	2500		95.0	1.038
E	12	440	440	1.000	2500	750	95.0	1.238
F	20	440	440	1.000	2500	Coker	95.0	1.413
G	25	440	440	1.000	2500	Distillate	95.0	1.528
II-A	33	510	510	1.020	4000		85.0	1.538
B	35	510	510	1.020	4000		85.0	1.747
94-I-A	2	440	440	1.010	2500		92.0	1.629
B	4	440	440	1.010	2500		92.0	----
C	6	440	440	1.010	2500		92.0	1.723
D	8	440	440	1.010	2500		92.0	----
E	12	440	440	1.010	2500		92.0	----
F	20	440	440	1.010	2500	650	92.0	1.645
II-A	24	510	510	0.980	4000	Coker	87.0	1.128
B	26	510	510	0.980	4000	Distillate	87.0	----
C	28	510	510	0.980	4000		87.0	1.297
D	30	510	510	0.980	4000		87.0	----
E	34	510	510	0.980	4000		87.0	1.441

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht.- °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
95-I-A	2	440	440	0.990	2500		99.0	1.136
B	4	440	440	0.990	2500		99.0	----
C	6	440	440	0.990	2500		99.0	1.212
D	8	440	440	0.990	2500		99.0	----
E	12	440	440	0.990	2500		99.0	1.350
F	20	440	440	0.990	2500		99.0	1.380
G	28	440	440	0.990	2500	650	99.0	1.474
II-A	39	510	510	1.010	4000	Coker	85.0	1.058
B	41	510	510	1.010	4000	Distillate	85.0	1.039
C	43	510	510	1.010	4000		85.0	1.419
D	45	510	510	1.010	4000		85.0	----
E	49	510	510	1.010	4000		85.0	1.011
F	57	510	510	1.010	4000		85.0	1.071
96-I-A	2	440	440	1.000	2500		96.0	1.155
B	4	440	440	1.000	2500		96.0	----
C	6	440	440	1.000	2500		96.0	1.376
D	8	440	440	1.000	2500		96.0	----
E	12	440	440	1.000	2500		96.0	1.510
F	20	440	440	1.000	2500		96.0	----
II-A	27	510	510	1.000	4000	650	85.0	1.090
B	29	510	510	1.000	4000	Coker	85.0	----
C	31	510	510	1.000	4000	Distillate	85.0	1.322
D	33	510	510	1.000	4000		85.0	----
E	37	510	510	1.000	4000		85.0	1.420
F	45	510	510	1.000	4000		85.0	1.483

TABLE II (continued)

OPERATING CONDITIONS AND PRODUCT DATA ON SHALE OIL TREATING

Sample No.	Time--Hours from Startup	Temperature Prht. °C.	Catalyst °C.	Space Velocity g/g/hr.	Gas Flow Rate SCF/bbl.	Charge Stock	Yield Percent	Percent N_2 in Effluent
97-I-A	2	440	440	0.990	2500		95.0	1.120
B	4	440	440	0.990	2500		95.0	----
C	6	440	440	0.990	2500		95.0	1.108
D	8	440	440	0.990	2500		95.0	----
E	12	440	440	0.990	2500		95.0	1.196
F	20	440	440	0.990	2500	650	86.0	1.230
II-A	23	510	510	1.000	4000	Coker	86.0	0.547
B	25	510	510	1.000	4000	Distillate	86.0	----
C	27	510	510	1.000	4000		86.0	0.579
D	29	510	510	1.000	4000		86.0	----
E	33	510	510	1.000	4000		86.0	0.652
F	41	510	510	1.000	4000		86.0	0.752

TABLE III

CATALYST ACTIVITY

Run No.	Catalyst	#1 Op. Condition %	#2 Op. Condition %
		Activity at	Activity at
ESO 89	Spence cobalt molybdate, 5/32-in. pellets	100	100
ESO 91	Large-pore cobalt molybdate	71	82
ESO 92	HF-activated cobalt molybdate	130	270
ESO 93	Molybdenum sulfide	59	
ESO 95	Platinum (Type 1000)	59	51
ESO 96	MoO_3 deposited on DA-1 cracking catalyst. 13.5% - 86.5%.	50	37
ESO 97	Oronite hydroforming catalyst	66	75

Operating Variable		Condition #1	Condition #2
Temperature	°F.	825	950
Space velocity	g/g/hr.	1.0	1.0
Gas recycle	SCF/bbl.	2500	4000
Charge stock	coker distillate	750 E.P.	750 E.P.

TABLE IV

RESULTS OF BATCH TREATMENTS OF SHALE OIL

Property	Treatment Caustic	Tetralin
N_2 in effluent, %	1.66	1.80
Charge stock, coker distillate	750 E.P.	750 E.P.
N_2 in charge stock, %	1.90	1.90
Temperature, °C.	450	450
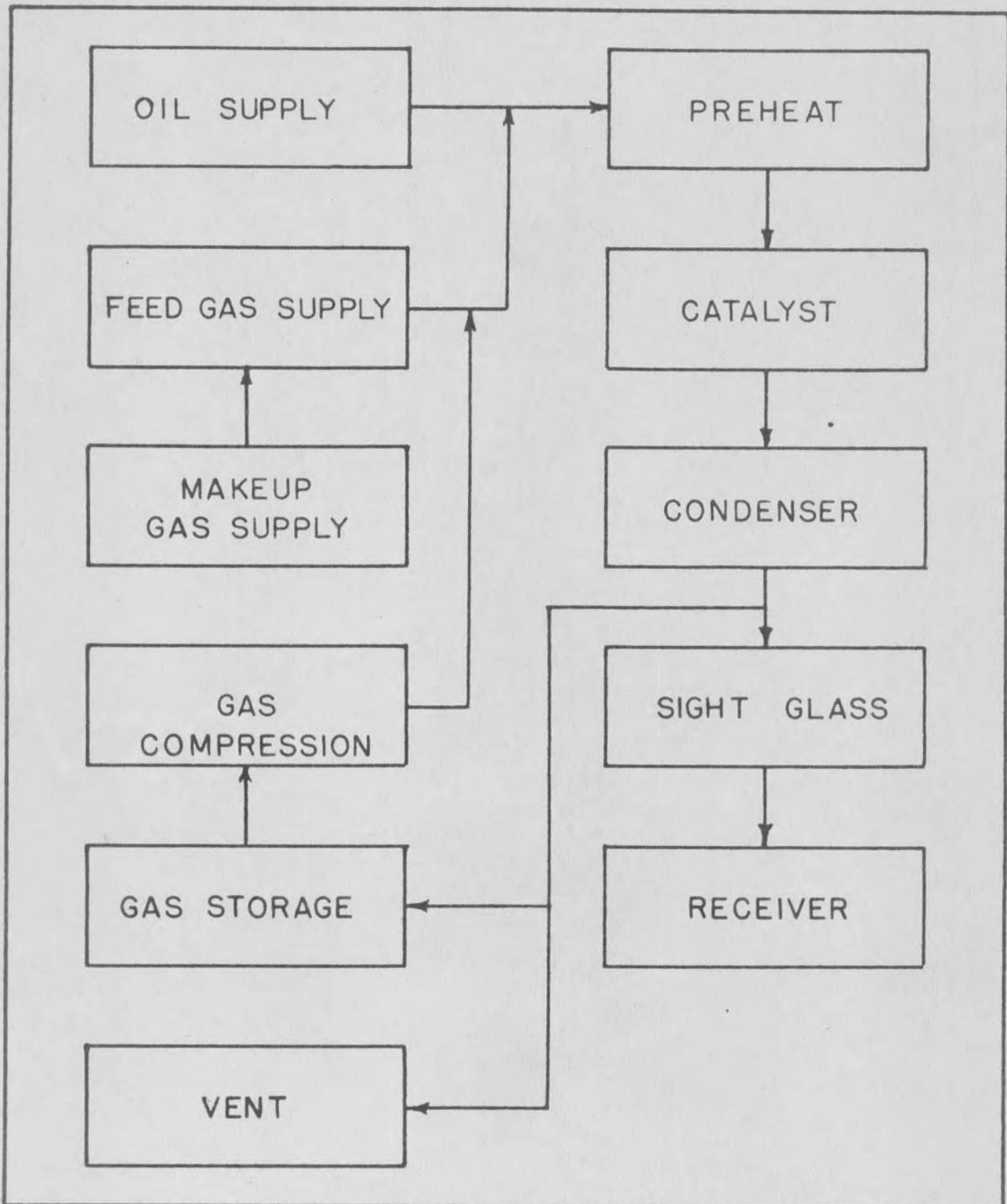
Figure 1. Block Flowsheet of Hydrotreating Unit.
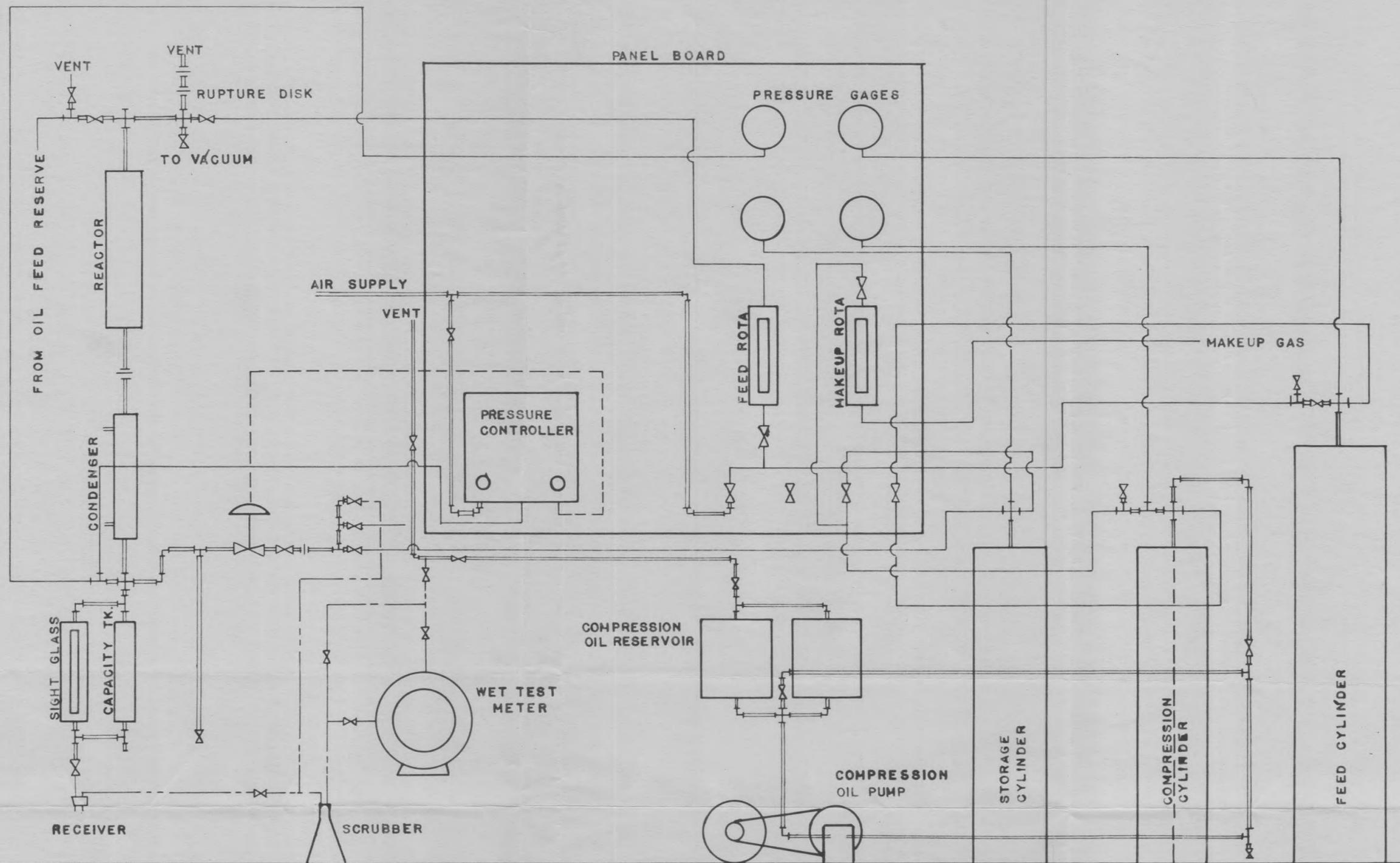
FIG. 2. DETAILED FLOWSHEET
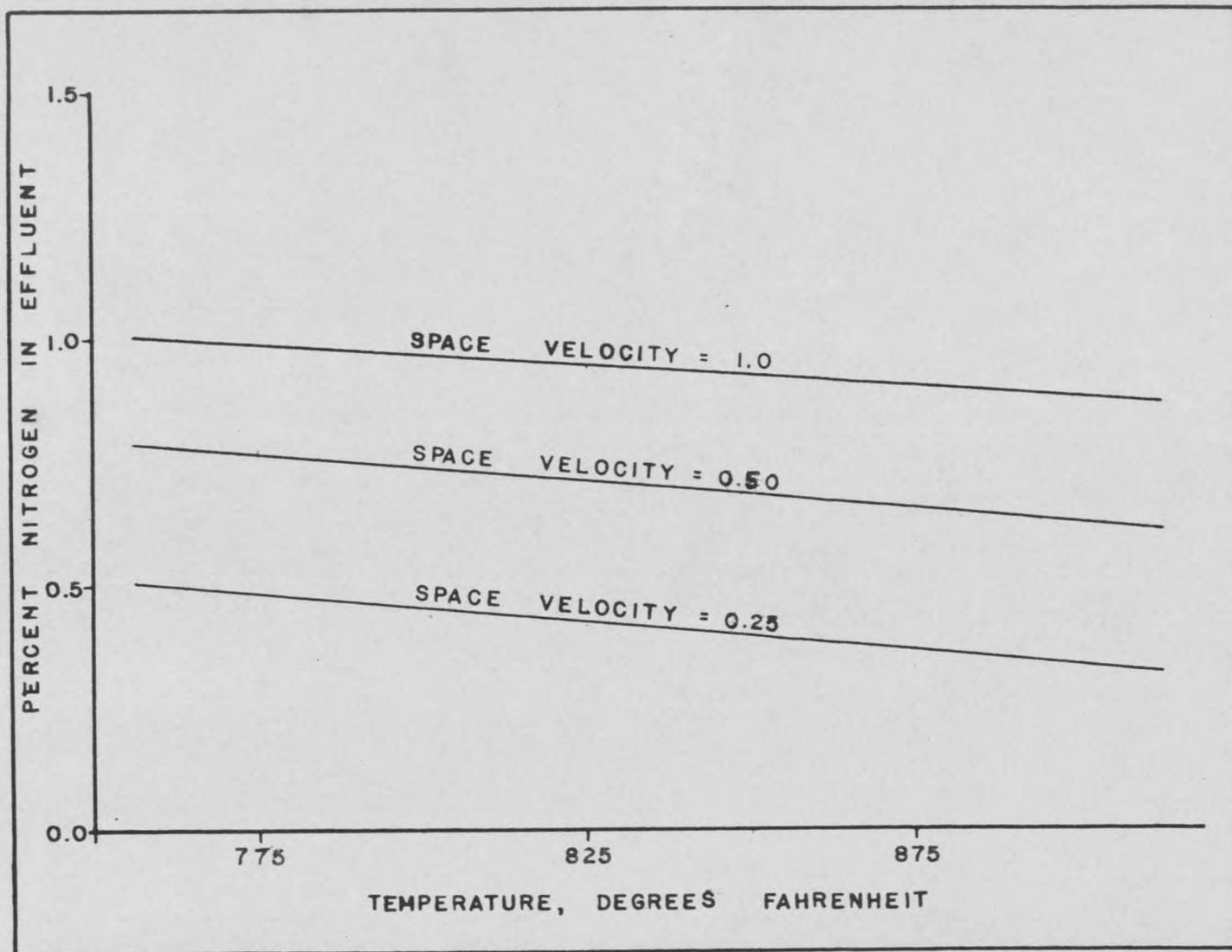
Figure 3. Nitrogen Removal as a Function of Temperature and Space Velocity.
Charge, 750°F E.P. coker distillate.
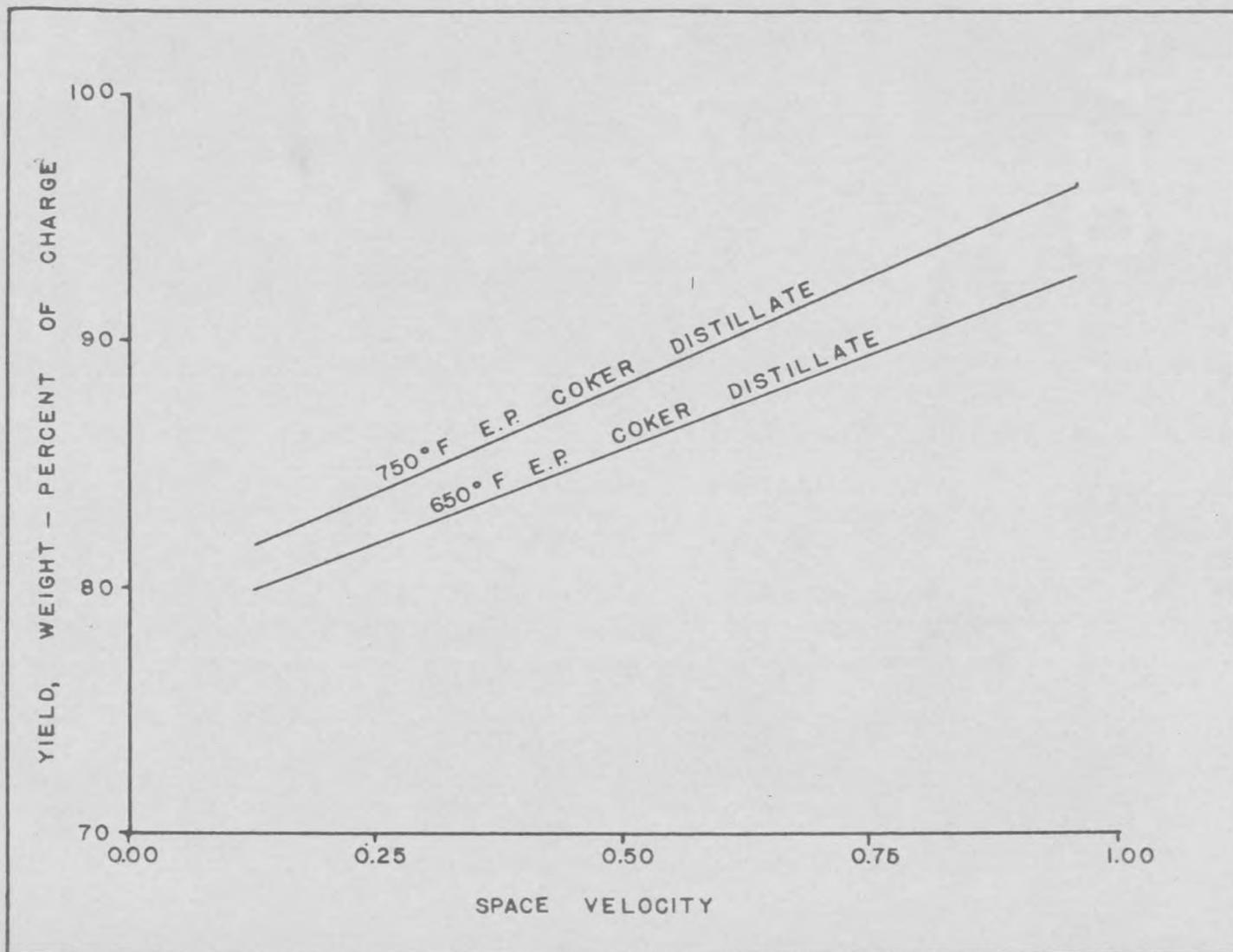
Figure 4. Yield as a Function of Space Velocity and Charge Stock. Temperature, 825°F.
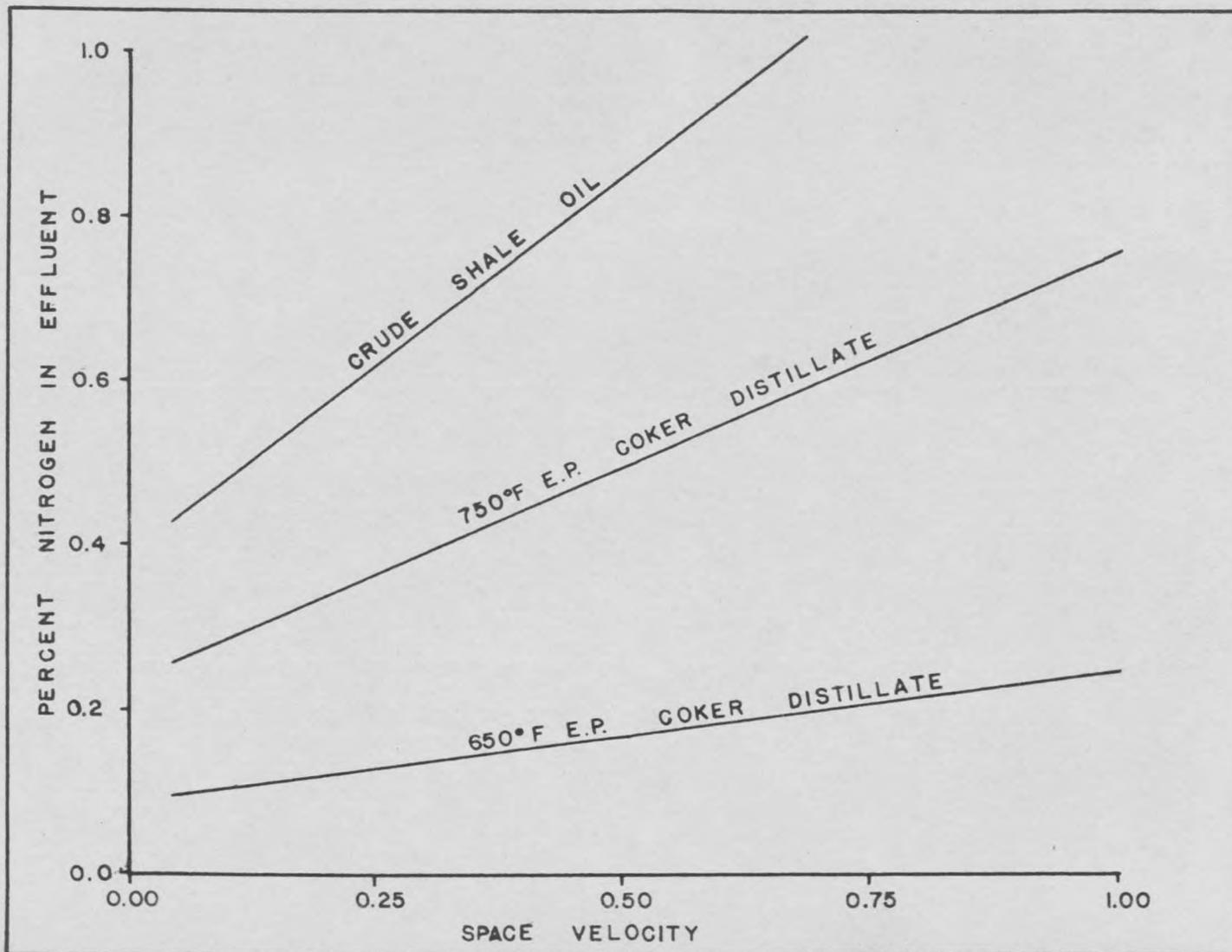
Figure 5. Nitrogen Removal as a Function of Space Velocity and Charge Stock. Temperature, 825°F.
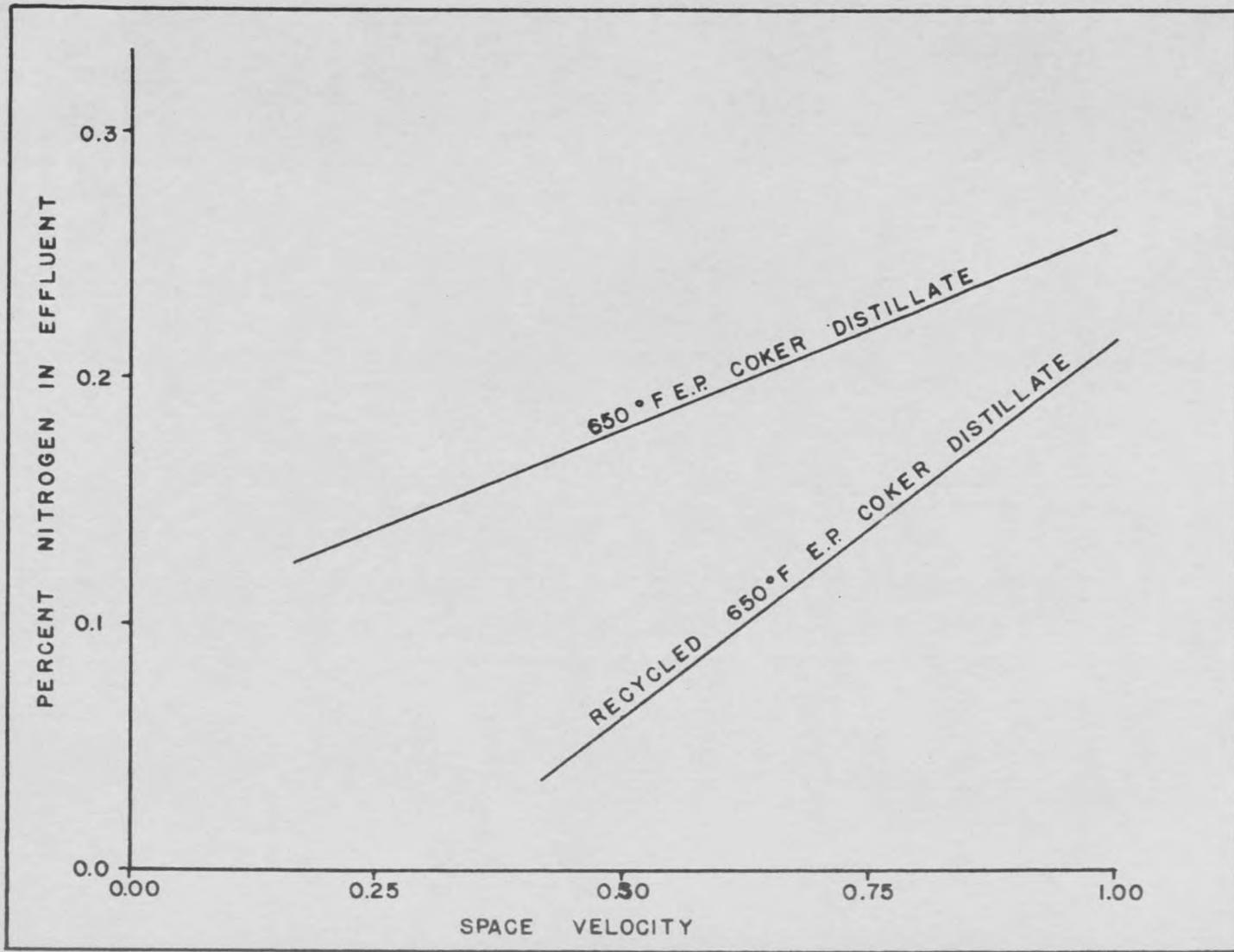
Figure 6.   Nitrogen Removal as a Function of Space Velocity and Effluent Recycle. Temperature, 825°F.
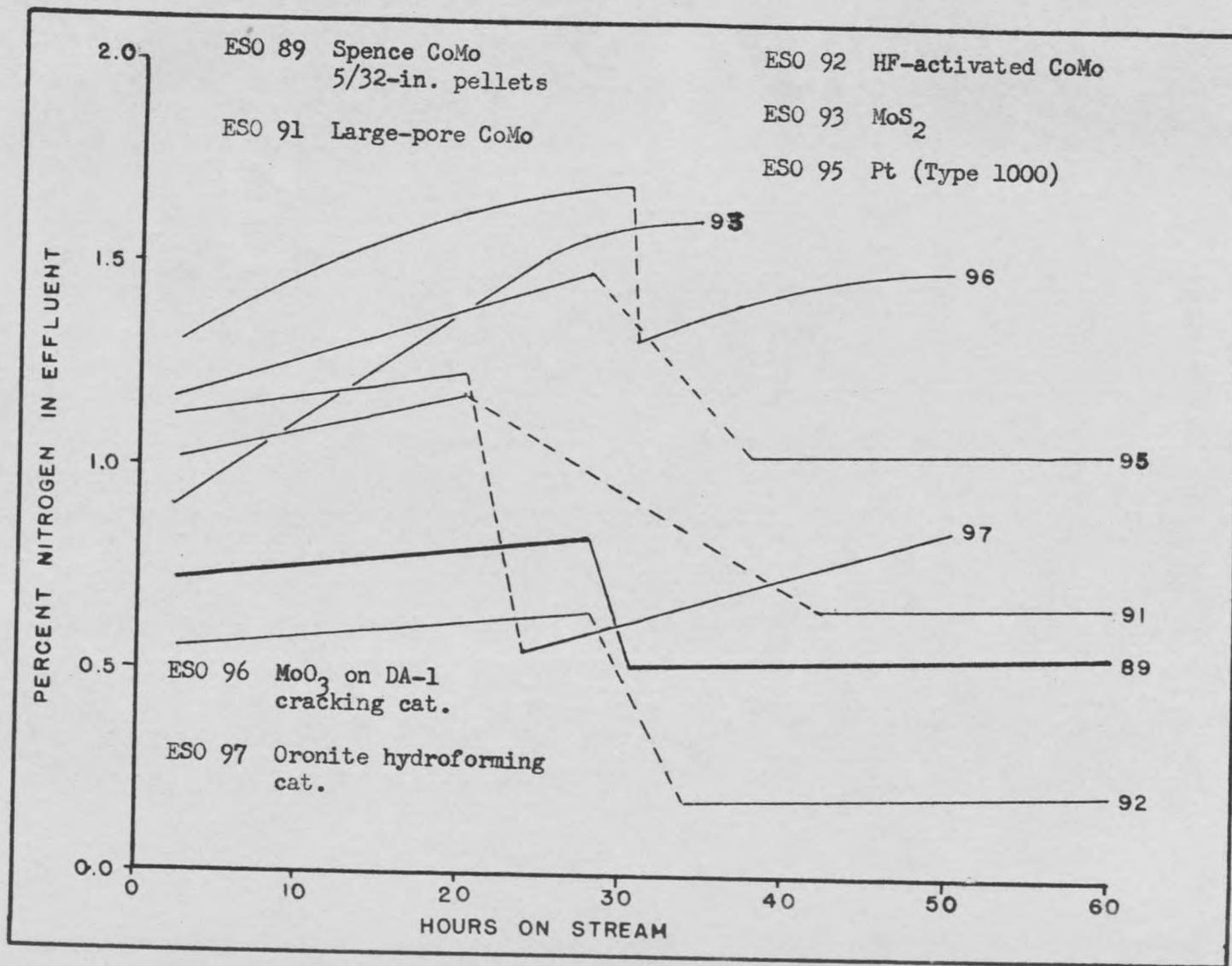
Figure 7. Nitrogen Removal as a Function of On-Stream Hours and Catalysts.
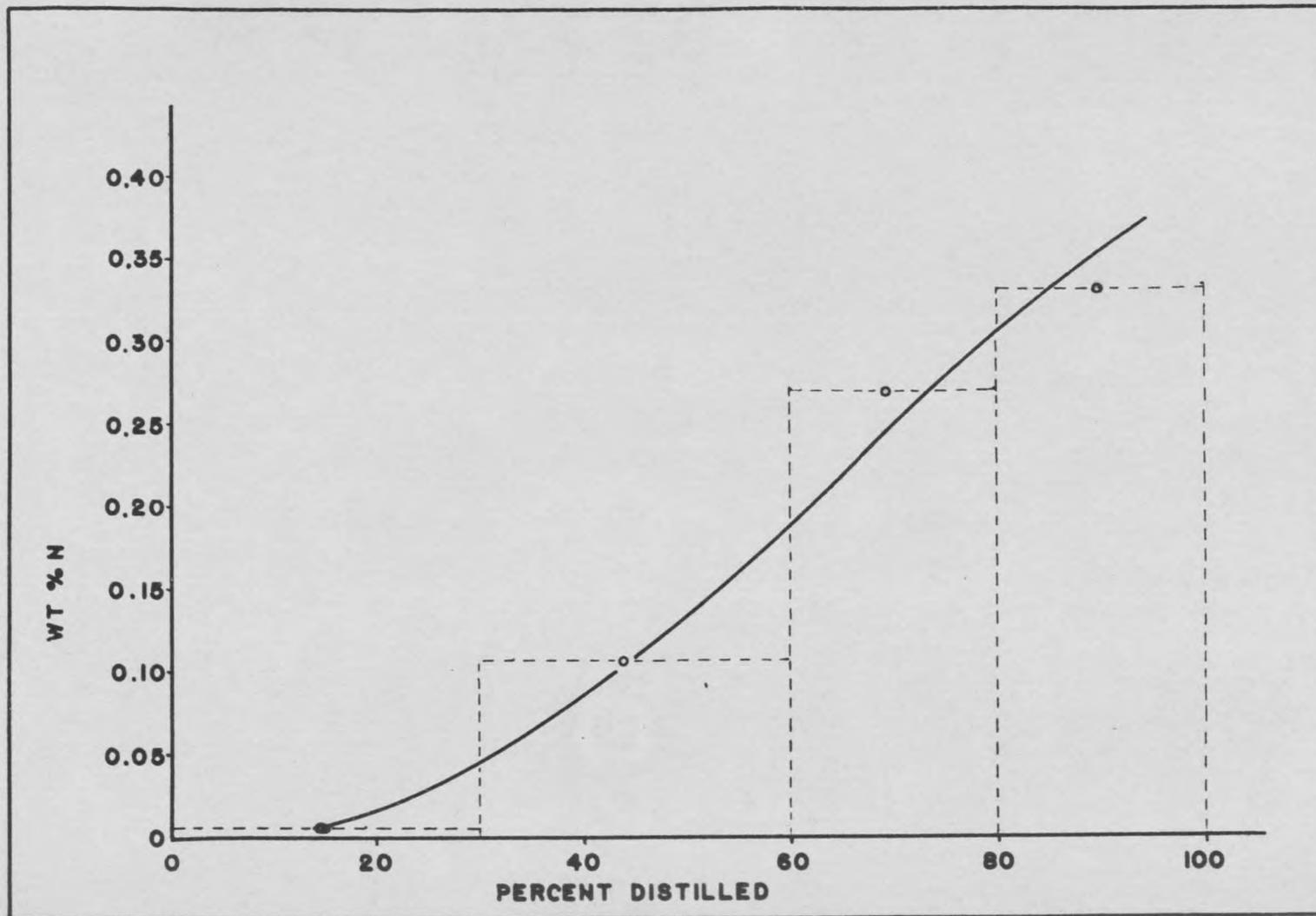
Figure 8. Nitrogen Profile as a Function of Percent of Material Distilled.
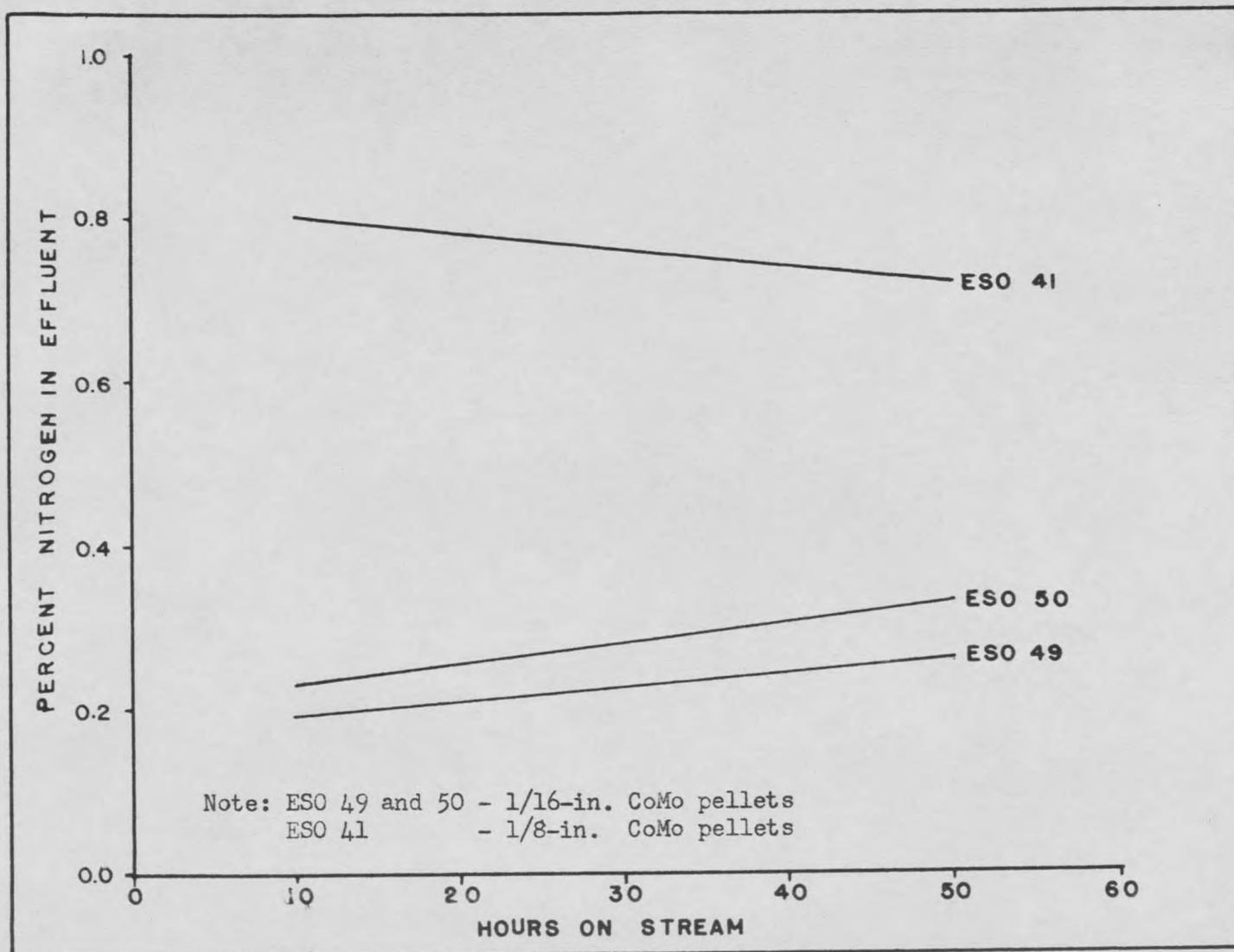Stock, hydrogenated 650°F E.P. coker distillate.
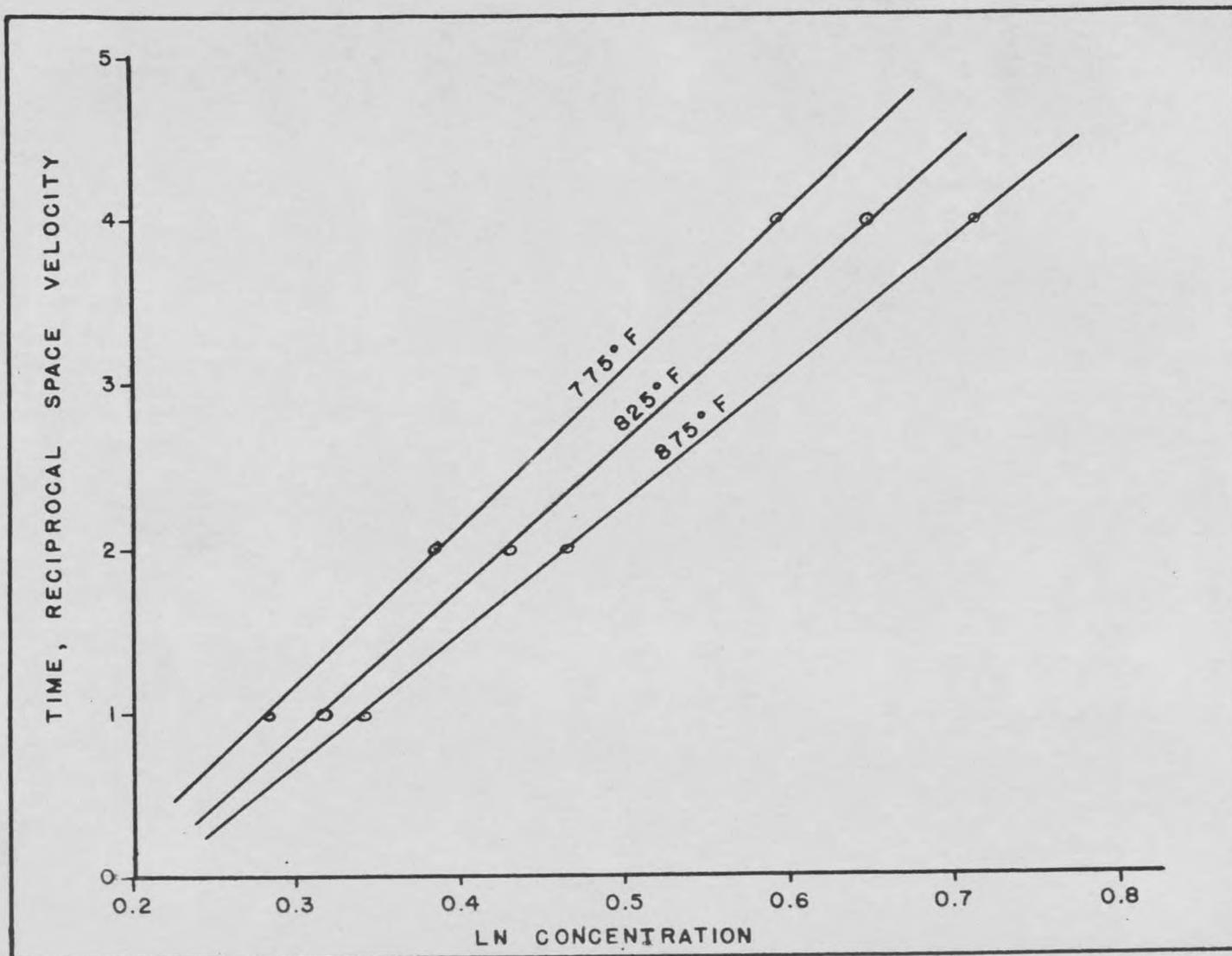
Figure 9. Reaction Time as a Function of the Logarithm of the
Concentration of Nitrogen in the Effluent.

Figure 10.   Nitrogen Removal as a Function of Time for Runs
Made Under Identical Conditions.