Evaluation of catalysts for the catalytic polyforming process
by William F Polich

A THESIS Submitted to the Gradtuate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:
This investigation was conducted to evaluate the available commercial cracking catalysts as to their applicability for the catalytic polyform process with n-butane as the outside gas and to determine the most desirable of these catalysts for this process.

A small laboratory-scale fixed-bed catalytic polyforming unit was used in which 1000 ml. batches of catalysts were subjected to operating conditions chosen to duplicate those which would be used in a commercial unit. A standard charge of virgin gas oil and n-butane was used throughout the investigation. The average temperature was varied for each run, while the pressure and space velocity were held constant at 900 psig, and 4-6 hr.^-1, respectively, A total of eight commercial cracking catalysts were tested. These catalysts were: Cyclocel, Filtrol, Houdry, synthetic bead, HF activated alumina, silica-magnesia, chrome-alumina, and molybdenum-alumina.

The over-all results obtained in this investigation indicate that the Houdry catalyst is superior to the other catalysts investigated with respect to gasoline yields.

The maximum gasoline yield obtained with Houdry catalyst was 1.5 absolute per cent higher than that obtained with any other catalyst. Synthetic bead and silica-magnesia also produced relatively high gasoline yields. The Cyclocel, Filtrol, HF activated alumina, chrome-alumina, and molybdenum-alumina catalysts produced such low yields of gasoline per pass, that further consideration of these catalysts for this process was not warranted.

The ultimate yields, carbon deposition, and gas formation with the Houdry catalyst were similar to those obtained with silica-magnesia and synthetic bead.

In general, the use of Houdry catalyst seems warranted in any commercial application of the catalytic polyform process, especially where high gasoline yields are of primary importance.

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CATALYTIC POLYFORMING PROCESS

by

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I INTRODUCTION

Material and financial economics forced upon the petroleum industry within the last ten years have fostered the development of a number of new processes in petroleum refining. Two of these which are of interest to this investigation are catalytic cracking and the polyform process.

The catalytic cracking process is an efficient and satisfactory means of producing high quality aviation and motor gasolines from gas oils. Throughout the war period, the commercial catalytic cracking units were devoted to the production of aviation base stock together with large quantities of butanes and butylenes that were used to make alkylate as a high octane blending agent or as a raw material for synthetic rubber. Since the war this process has been devoted largely to the production of motor gasoline.

The generally higher yield and quality level of the cracked motor gasoline over that of thermal cracking is the principle advantage of catalytic cracking. The gradually rising standard for automotive gasoline has forced the replacement of thermal cracking, which produced 65-70 octane gasoline, with catalytic cracking making 80 octane or higher. It has been noted (2) that this higher quality of catalytically cracked gasoline is largely due to the presence of isoparaffins and the absence of normal paraffins as well as to its high aromatic content.

The polyform process, as described by Offutt et al (8), is an efficient means for producing high quality motor gasoline by the thermal conversion of naphthas or gas oils at high temperatures and high pressures in the presence of recirculated hydrocarbon gases. These light hydrocarbons in the furnace make possible a substantially greater degree of severity of cracking by lowering the average molecular weight of the charge than it is possible to achieve in conventional thermal process. These gases also minimize tar and coke formation by interaction with many of the olefins produced, some of which would otherwise undergo polymerization to form tar and coke. At the same time, the conditions of temperature and pressure are suitable for the conversion of C_3 and C_4 fractions into gasoline and increasing yields of gasoline are obtained at higher gas dilutions. The propane and butane fractions recycled within the process are in many cases supplemented with extraneous refinery gas streams for additional yields of gasolines.

The advantages of the polyform process can be readily seen in the attractive yields of motor gasoline, which are obtained in naphtha polyforming, having A.S.T.M. octane numbers of 75-80 and research octane numbers of 84-93 without the addition of tetraethyl lead (10). Furthermore, according to Offutt et al (9), gas oils are readily converted to gasoline by the polyform process. For example,

a light paraffinic gas oil can be converted to gasoline with a yield of 60-70 per cent and an octane number of 73-76 A.S.T.M. in a single pass, or a light catalytic cycle stock can be converted to 50-60 per cent gasoline of 76-82 octane number.

To incorporate the advantages of the thermal polyforming and catalytic cracking process, Dev (3) investigated the process of gas oil polyforming under catalytic conditions using propane as the outside gas. This process was called catalytic polyforming. The yields of gasoline from the catalytic cracking of virgin gas oil over Houdry catalyst with and without propane at different pressures were compared. This study showed that an increased yield of gasoline could be obtained at higher pressures in the catalytic polyform process using propane as the outside gas. The increased gasoline yield was obtained at temperatures lower than those for thermal polyforming.

Mayfield (7) investigated the catalytic polyforming of gas oil using propane, isobutylene, and n-butane as the outside gases. There seemed to be some indication of increased gasoline yield over that obtained in conventional catalytic cracking when isobutylene and n-butane were used as the outside gas. This increased yield of gasoline was also reported to be obtained at space velocities somewhat higher than those normally used in catalytic cracking.

In order to add to the available information on cata-
lytic polyforming, this investigation was undertaken to
evaluate the adaptability of the available commercial crack-
ing catalysts to this process and determine whether or not
the process could be improved by the choice of catalyst.

Catalytic cracking has been carried out principally by
means of two catalysts: (a) the synthetic silica-alumina
catalysts as typified by beads, pellets or powder, and (b)
the natural or clay catalysts such as Filtrol or Cyclocel.
Other catalysts such as silica-magnesia (1), chrome-alumina
(5), molybdenum-alumina (5), and HF activated alumina (8)
have been suggested.

The comparative merits of synthetic and natural cata-
lysts have been the subject of much study since the termin-
ation of all-out aviation gasoline manufacture. One of the
chief competitive factors is the large difference in cost
between synthetic and natural catalysts, the natural cata-
lysts being much cheaper. To offset the difference in price,
however, synthetic alumina catalysts are generally conceded
to make substantially less carbon and to give a higher octane
gasoline than the natural type catalysts under comparable
conditions. Simpson et al (12) stated that a substantial
yield and quality increase was obtained with synthetic bead
catalyst as compared to clay catalysts. Anderson and Sterba
(1) indicate comparative A.S.T.M. octane numbers of 80.3,

79.1 and 82.1 for natural, silica-magnesia, and silica-
alumina catalysts respectively. Richardson et al (11) found
that silica-magnesia was superior to silica-alumina and
natural clay catalysts with respect to gasoline yield. The
octane numbers, however, were lower for silica-magnesia than
for silica-alumina but approached those obtained with natural
clay catalyst. Clay catalysts were found by Evans (4) to be
readily poisoned by charge stocks high in sulfur and nitro-
gen compounds, sometimes to a prohibitive rate of decrease
in gasoline yield and increase in gas and coke formation,
whereas the synthetic bead catalyst is not affected in its
efficiency by such stocks. Natural catalysts are also
softer and are therefore destroyed more rapidly than most
synthetic catalysts. Thus, when all of these features are
weighed in an over-all refining analysis, it is generally
indicated that the low cost advantage of natural catalysts
is often a superficial one and that synthetic catalysts are
justifiable in many cases. Because of the lower cost of
natural catalysts, however, their use should always be con-
sidered in any catalyst study.

Various test methods for evaluating the activity of a
catalyst have been proposed and used by industry. These
procedures fall into two principal groups: One group of
methods is based on physical tests which use surface-area
reactions to determine the activity. Three common methods

of this type are the potassium hydroxide adsorption test,
the aromatic adsorption index, and the nitrogen adsorption
surface-area measurement. In contrast with these methods,
the second type of catalyst-activity measurement is based
on a standardized laboratory cracking operation. The cata-
lyst is placed in a small cracking unit and a series of
runs made under conditions which approximate plant condi-
tions to determine the gasoline producing ability of a cata-
lyst as well as its tendency to form carbon and gaseous
products. Although physical tests are of interest and
utility in evaluating new catalysts, this direct technique
is certainly the best way to arrive at the activity of a
catalyst, inasmuch as the conditions to which the catalyst
is subjected are essentially the same as are used in the com-
mercial unit and the amount of gasoline, carbon, and gaseous
products produced are actually measured.

In this investigation the standard procedure for acti-
vity determination of the catalysts used was of the second
type. The catalysts tested were: Cyclocel, Filtrol,
synthetic bead, HF activated alumina, silica-magnesia,
chrome-alumina, molybdenum-alumina, and Houdry.

II EQUIPMENT, METHODS, AND MATERIALS

A. EQUIPMENT

The equipment used in this investigation consisted of the 0 to 1200 psig. reaction system which is shown in a schematic drawing, Figure 1. A distillation unit and a gas analysis unit were used in conjunction with the reaction system. The reaction system was composed of four major sections: the feeding section, reactor section, condensing and receiving section, and the safety equipment.

FEEDING SECTION - The feeding section included a nitrogen cylinder, a feed cylinder, and a Jerguson gage. The feed cylinder was constructed from an eight inch section of three inch, extra strong steel pipe. The pipe was threaded at both ends and fitted with extra strong steel caps which were welded to the pipe. Both caps were drilled and tapped for one-half inch pipe and the inside of the cap machined down to facilitate draining. The caps were fitted with close nipples of extra-strong steel pipe and high pressure stainless steel Kerotest globe valves of 3000 psig capacity. Each valve was fitted with one-half to one-quarter inch steel bushings and brass one-quarter inch pipe to one-quarter inch copper tubing adapters.

The bottom of the feed cylinder was connected to the top of the Jerguson gage with copper tubing and a tee. The third side of the tee was connected with tubing to another

tee and in turn to the Kerotest valve at the top of the feed cylinder. Pressure equalization by this line was necessary in order to obtain flow of the feed into the Jerguson gage. The other side of the second tee was connected by tubing to a pressure gage and nitrogen cylinder. Nitrogen was used to furnish the pressure necessary to force the feed into the reactor.

A semitransparent plastic centimeter scale was fastened into the back of the Jerguson gage and a light placed behind it to facilitate the reading of the scale. The Jerguson gage was then calibrated so that the volume of liquid in the gage would be known for any reading on the scale.

The bottom of the Jerguson gage was connected with extra strong steel pipe to a one-half inch, 6000 pound, Vogt valve which was used to adjust the rate of feed. The bottom of the valve was connected directly to the reactor through one-half inch extra-strong, short nipples, a one-half inch tee, and a one-half inch union. The female half of the union was welded directly to the top of the reactor. The off-stream side of the tee was fitted with a Black, Sivalls and Bryson frangible-disc safety valve, equipped with a 1255 psig Monel diaphram. The atmospheric pressure side of the safety valve was connected to a blow-down line leading to the outside of the building.

REACTOR SECTION - The reactor was made from a fifteen-

inch section of three-inch extra strong steel pipe. The top
of the reactor was threaded and fitted with an extra strong
steel cap to which the previously mentioned female half of
the union had been welded. The steel cap was welded onto
the three inch pipe in the final assembly. An 11/16 inch
hole was drilled through the cap using the hole in the union
as a jig. The enlarged hole facilitated the changing of the
catalyst and the 500 ml. of assorted size steel balls which
were placed on top of the catalyst to act as a preheater
section. The catalyst filled the lower 11 inches of the
reactor body and the remaining four inches were filled with
the steel balls. Nine-sixteenths inch in diameter balls
were the largest size used in the pre-heater.

Welded into the bottom of the reactor was a one-half
inch steel plate, beveled on the top side and drilled at
the center for one-half inch pipe. A one-eighth inch stain-
less steel screen was inserted on top of the beveled end of
the plate to act as a catalyst support. A section of extra-
strong one-half inch steel pipe was inserted flush with the
bevel of the plate and welded on the bottom side. This pipe
was threaded at the lower end and screwed into a tee. A
one-half inch, 6000 pound Vogt valve was connected on the
run of the tee by means of a short nipple of extra strong
pipe. This valve was used to regulate the pressure in the
reactor. A 0-2000 psig pressure gage was connected to the

branch of the tee and was used to indicate the pressure in
the reactor. A one-half to one-fourth inch bushing in the
lower end of the valve was fitted with a brass fitting and
approximately three inches of copper tubing.

Four thermocouple wells, made from four inch lengths
of one-eight inch steel pipe sealed at one end by welding,
were inserted through holes drilled symetrically at three
inch intervals along the length of the reactor. These pipes
were welded into the reactor such that the sealed ends were
along the axis of the reactor. Iron-constantan thermo-
couples were inserted into the thermowells and connected
to a Leeds and Northrup indicating potentiometer, calibrated
to read from 0-1200° C.

A safety wall of one-fourth inch steel plate, 25 inches
wide and 72 inches long, was erected behind the position
in which the reactor was to stand. Two three-eighth inch
steel rods were welded to the reactor on the opposite side
from the thermowells to act as supports for the reactor
chamber. Two one-fourth by one inch flat steel bars were
welded to the top of the cap at approximately 90° to each
other and fastened by means of one-half inch pins to cleats
welded to the safety wall. These steel bars prevented the
reactor from turning when the union was being tightened or
broken apart.

The reactor was wrapped with one-inch asbestos tape.

The upper one-half of the reactor was then wound with 30 feet of nichrome wire (resistance 1.71 ohms per foot) which had been threaded with porcelain fish-spine insulators. The lower half of the reactor was then similarly wound. Each of these windings was connected to a 220-volt autotransformer. These windings were covered with another layer of one-inch asbestos tape and two additional fifteen-foot windings of nichrome wire were wound around the reactor section. One coil was placed on the lower one-third of the reactor and the other on the upper one-third. These windings were connected to 110-volt autotransformers. Fifteen feet of nichrome wire was wound about the neck of the reactor and on top of the upper cap to supply additional heat for the pre-heater section. This winding was also connected to a 110-volt autotransformer.

The nichrome windings were covered with a layer of one-inch asbestos tape and the entire length of the reactor was then covered with a layer of one-inch magnesia blocks cut to fit around the reactor. These blocks were secured by a few coils of asbestos tape, and a heavy layer of asbestos cement was used to cover the entire reactor.

CONDENSING AND RECEIVING SYSTEM. - The bottom of the pressure regulating valve was connected to the top of a 300 mm. Liebig Pyrex glass condenser by means of a short piece of copper tubing inserted through a neoprene stopper.

Water was used as the cooling medium in the Liebig conden-
ser. An extension of glass tubing was added to the lower
end of the Liebig condenser to carry the vapors well into
the 500 ml. side-arm flask used as the receiver.

The receiver flask was immersed in a dry ice-isopro-
panol bath contained in a one-gallon thermoflask. A series
of vapor traps were connected to the side arm of the receiv-
ing flask with rubber tubing. This series consisted of four
glass cold traps and two copper coil condensors. The cold
traps and copper coil condensors were immersed in dry ice-
isopropanol baths contained in thermoflasks. The outlet
of the second copper coil condensor was connected with
rubber tubing to a tee, the run of which was connected to
a three liter precision wet test gas meter. An evacuated
200 ml. round bottom, stopcock-equipped flask, which was
used to take a sample of the noncondensable gases during
the run, was connected to the branch of the tee. The out-
let of the gas meter was connected to a blow-down line lead-
ing to the outside of the building.

SAFETY SYSTEM - The previously mentioned steel safety
wall was mounted against the laboratory rack and the reactor
was fastened to this plate. A piece of one-eighth inch steel
plate, rolled in a semicircle 22 inches in diameter and 40
inches long, was hinged to the back plate so that it would
close around the reactor. A frame work of one-half inch

angle iron was built upward from the center of the hinged
section to support two thicknesses of automobile safety
glass. This provided a safety window through which the
gage could be observed during feed control operation.

AUXILIARY EQUIPMENT - An Oldershaw vacuum-jacketed
distillation column containing 16 actual plates was used to
fractionate the reactor products. This column was fitted
with a distilling head suitable for low temperature distil-
lations. The receiver flask, employed directly beneath the
reactor to condense a portion of the effluent gases from
the reactor, was also used as the distillation flask. The
distillation flask was heated by a 110-volt 550 watt heater
controlled by an autotransformer.

The take-off line from the distillation head was con-
nected to a series of two cold traps by means of rubber
tubing. The cold traps were immersed in dry ice-isopropanol
baths contained in one-quart thermoflasks. The light over-
head products vaporizing after leaving the distillation head
were condensed by the low-temperature baths and the arrange-
ment afforded a close weight balance across the column.

An Orsat gas analyzer was employed to analyze the gases
from the reactor during the carbon burn-off. The gases were
analyzed for CO_2, O_2, and CO using, respectively, a strong
KOH solution, an alkaline pyrogallol solution, and a solu-
tion of Cu_2Cl_2.

A low temperature fractionating column was used to analyze the gases remaining in the feed cylinder at the end of the run. This analysis was used in determining the amount of outside gas retained in the feed system and not charged to the reactor.

B. METHODS

A small laboratory scale fixed-bed catalytic polyforming unit was used in which 1000 ml. batches of catalyst were subject in so far as possible to operating conditions chosen to duplicate those which would be used in a commercial unit. A standard virgin gas oil with n-butane as the outside gas was used as the charge stock, and a series of runs were made on each catalyst covering a wide conversion range.

A different average temperature was used on each run to vary the conversion level, while the pressure and space velocity were held constant at 900 psig. and 4-6 hr.$^{-1}$, respectively. A total of eight commercial cracking catalysts were tested by this method and the amount of gasoline, carbon and gaseous products produced by the various catalysts were compared to determine the most desirable catalyst for the process.

CONDITIONING OF THE CATALYST - The fresh catalyst was placed in the reactor and, prior to making the actual test runs, a charge of gas oil was passed over the catalyst at atmospheric pressure and cracking temperature as a break-in run on the catalyst. The object of this run was to reduce the moisture content and to stabilize the activity of the catalyst. Catalysts are exceedingly active initially and the first run over a cracking catalyst is not a true indication of its activity and the results are usually

nonreproducible. Upon completion of the run, the carbon was burned off according to the procedure described later.

This standard catalyst conditioning procedure was carried out on each new catalyst.

RUN PROCEDURE - The feed cylinder was evacuated by means of a Cenco Megovac vacuum pump, charged with approximately 260 grams of gas oil, and weighed on a Harvard triple beam balance. The feed cylinder was then placed in a refrigerator maintained at -40° C. to chill the oil. After the oil had been thoroughly chilled, the cylinder was placed on the Harvard triple beam balance and connected by means of Saran tubing to an n-butane cylinder. After the balance had been tared, the connecting valves were opened and the outside gas was admitted to the feed cylinder. When the desired amount of gas had been delivered, the valves were closed and the tubing disconnected. The feed cylinder was then allowed to warm to room temperature and reweighed.

The reactor was heated until the temperature, as indicated by the thermocouples, was sufficient for the run to average the desired temperature. Dry ice was added to the thermoflasks containing isopropanol until carbon dioxide evolution was slight. The cold traps and copper coil condensors were weighed and immersed in the thermoflasks. The gas sample bottle was evacuated, weighed and attached to the system.

The feed cylinder was then connected into the system as shown in Figure 1 and the feed regulating valve at the top of the reactor and the pressure regulating valve at the base of the reactor were securely closed. Nitrogen pressure of about 200 psig. was applied to the balanced pressure feed system and the Jerguson was filled with charge by opening the valve at the bottom of the feed cylinder.

The readings of the thermocouples were noted at the start of the run and continued at one-minute intervals throughout the duration of the run. As soon as the feed regulating valve was opened and the charge started to enter the reactor, a stop watch was started to determine the feed time. The desired feed rate was maintained by observing the liquid level in the Jerguson and adjusting the feed regulating valve accordingly. Nitrogen pressure was maintained at 100 psig. above the pressure in the reactor. When the pressure in the reactor had built up to 900 psig. the reactor pressure regulating valve was opened and the pressure maintained at this level during the remaining feeding time.

When the last of the charge had entered the reactor as shown by a sudden rise of pressure in the reactor, the feed regulating and reed cylinder valves were immediately closed. Then the reactor pressure regulating valve was opened gradually, the feed system line broken, and the

reactor and the feed system bled to atmospheric pressure simultaneously.

The feed cylinder was removed from the system and the residual gas remaining in the cylinder was bled into a 34 liter tank. A sample of the gas was then taken from the tank by means of water displacement from a five liter glass bottle. This gas sample was later analyzed in the low temperature gas fractionation unit and the per cent of n-butane contained was used to calculate the amount of gas remaining in the feed cylinder.

A sample of the noncondensable gases was collected near the middle of the run in the gas sample bottle. The bottle thus filled with gas was allowed to come to room temperature, the pressure in the bottle balanced against atmospheric and then weighed, noting the room temperature and barometric pressure. The difference in weights of the gas sample bottle gave the weight of the known volume of noncondensable gas. These data were required for the estimation of the weight of the noncondensable gases. The number of liters of noncondensable gases passing through the gas meter was read and recorded.

In order to recover any traces of oil left in the reactor after completion of the run, the reactor was evacuated through a series of cold traps. Nitrogen was used to purge the reactor after the evacuation was completed. The

recovered material was weighed and added to the residue since the amount of gasoline it would contain under these conditions would be negligible.

Upon completion of the run, the cold traps, receiver flask, and copper coil condensors were removed from the system and weighed immediately to determine the amount of condensable product. The condensed product in the cold traps and copper coil condensors was transferred to the receiver flask and reweighed to determine transfer losses. The receiver flask was then attached to the bottom of the Oldershaw column.

DISTILLATION - The cold finger of the distillation head was filled with a dry ice-isopropanol mixture and the delivery stopcock of the distillation head connected by means of rubber tubing to a series of two cold traps in dry ice-isopropanol baths. An electric heater was placed beneath the distillation flask and the current adjusted to a predetermined value of approximately 40 volts.

After the column had refluxed for 45 minutes, the delivery stopcock was opened, and distillate removed until the lower cut point of 7° C. was reached. The column was then allowed to reflux and if the temperature dropped, further removal was made until the temperature would remain constant at 7° C. Upon removal of the lower fraction, the cold traps were removed, weighed and replaced by another

set of cold traps to collect the gasoline. More heat was
then applied to the system and the 7° to 203° C. gasoline
cut made. These cut points were made at a barometric pres-
sure of 640 mm. and correspond to a 12°-210° C. cut at
atmospheric pressure. During the distillation of the gaso-
line fraction, the dry ice-isopropanol mixture was removed
from the distillation head and replaced with wet ice.

Upon completion of the distillation, the cold traps
were removed and weighed, and the column allowed to cool.
When the column had drained, the distillation flask was re-
moved and weighed to determine the amount of residue.

CATALYST BURN-OFF - During the run, a deposit of carbon-
aceous material was laid down upon the catalyst surface re-
ducing its activity and necessitating a burn-off after each
run. A continuous burn-off was accomplished by holding the
unburned portion of the catalyst at approximately 425° C.
and passing air through the reactor at a definite rate.
Since the catalyst sinters and loses activity at temperatures
above 600° C., care was taken to control the air rate and
hence the temperature of the burning zone. The effluent
gas was analyzed at regular intervals by means of an Orsat
gas analyzer to determine the per cent of carbon dioxide,
carbon and oxygen. These per cents were plotted as a
function of time and the amount of carbon deposited on the
catalyst was determined as shown in the sample calculations.

C. MATERIALS

The gas oil used in this investigation was a Borger, Texas, virgin gas oil obtained from Phillips Petroleum Company. Laboratory inspection data for the virgin gas oil are given in Table IX.

The n-butane used as the outside gas was of a commercial grade obtained from Phillips Petroleum Company.

Cyclocel, synthetic bead, and silica-magnesia catalysts were obtained from the Phillips Petroleum Company.

The molybdenum-alumina and chrome-alumina catalyst were obtained from the Harshaw Chemical Company, Cleveland, Ohio.

The HF activated alumina catalyst was prepared from alumina pellets obtained from the Harshaw Chemical Company and activated with anhydrous HF according to the procedure outlined by Herzel (6).

The Filtrol catalyst was obtained from the Filtrol Corporation, Los Angeles, California.

Houdry catalyst was obtained from the Houdry Process Corporation, Philadelphia, Pennsylvania.

The nitrogen and anhydrous hydrogen fluoride used in this investigation were obtained from the Matheson Company, Joliet, Illinois.

III   SAMPLE CALCULATIONS

Calculations of space velocity, weight of permanent gases, carbon laydown on catalyst from analysis of burn-off gases, weight of outside gas remaining in the feed cylinder at the end of the run, over-all weight balance, yield of gasoline, percentage conversions and per cent ultimate yield are presented for run Number 33 as typical of all the runs made.

A. Calculation of Liquid Space Velocity:

Data:

Volume of catalyst in the reactor	=	1000 ml.
Feeding time	=	6.92 min.
Weight of charge	=	440 gm.
Density of charge	=	0.80 gm/ml.
Volume of charge = $\frac{440}{0.8}$	=	550 ml.
Space Velocity = $\frac{550 \text{ ml. x } 60 \text{ min/hr.}}{6.92 \text{ min. x } 100 \text{ ml.}}$	=	4.73 hr.$^{-1}$

B. Calculation of Weight of Outside Gas remaining in Feed Cylinder at End of Run:

Data:

Volume of cylinder and Jerguson gage	=	1390 ml.
Final pressure	=	1015 psia
Temperature	=	22°C.
Volume per cent n-butane	=	4.5%
$\frac{1390}{1000} \times \frac{1015}{14.7} \times \frac{273}{295} \times \frac{0.045}{22.4} \times 58$	=	10 gm.

C. Calculation of Burn-off

Data

Time (min.)	Air (Liters)	By Analysis			Ave. from Plot			By Diff.	Vol.Eff.	Vol.%	Liters
		CO_2	CO	O_2	CO_2	CO	O_2	N_2	Gas	$CO_2 \neq CO$	$CO_2 \neq CO$
5	8	7.4	0.4	0.6	6.3	1.7	0.7	91.3	6.8	8.0	0.54
15	14	10.4	4.6	0.4	8.8	3.5	0.5	87.2	13.6	12.3	1.67
30	30	12.6	6.6	0.0	11.7	6.1	0.2	82.0	28.9	17.8	5.15
60	44	13.0	6.2	0.0	13.0	6.4	0.0	80.6	43.2	19.4	8.36
90	44	13.0	6.2	0.0	13.0	6.1	0.0	80.9	43.0	19.1	8.21
120	43	14.0	5.4	0.4	13.7	5.9	0.0	80.4	42.3	19.6	8.28
150	49	13.0	5.2	1.8	13.5	5.4	0.9	80.2	48.2	18.9	9.12
180	38	11.0	3.8	4.8	12.4	4.7	2.6	80.3	37.4	17.1	6.38
195	30	6.0	1.0	12.0	8.6	3.0	8.4	80.0	29.7	11.6	3.45
210	30	1.0	0.2	18.6	3.3	1.3	15.3	80.1	29.6	4.6	1.31

Total   52.47

Temperature: 22° C.   Pressure: 640 mm.

$$\text{Weight of Carbon} = \frac{52.47 \times 640 \times 273 \times 12.0}{22.4 \times 760 \times 295} = 21.7 \text{ gm.}$$

D. Calculation of the Weight of Noncondensable Gases:

Data:

$$\text{Volume of noncondensable gases} = 26.0 \text{ l.}$$

$$\text{Volume of gas sample bottle} = 208.2 \text{ ml.}$$

$$\text{Weight of bottle and gas} = 124.156 \text{ gm.}$$

$$\text{Weight of bottle evacuated} = 124.006 \text{ gm.}$$

$$\text{Weight of sample by difference} = 0.150 \text{ gm.}$$

$$\text{Density of gas} = \frac{0.150 \times 1000}{208.2} = 0.721 \text{ gm./l.}$$

$$\text{Weight of noncondensable gases} = 26.0 \times .721 = 18.8 \text{ gm.}$$

E. Calculation of an Over-all Material Balance:

Data:

$$\text{Initial weight of cylinder and charge} = 1727 \text{ gm.}$$

$$\text{Final weight of cylinder} = 1277 \text{ gm.}$$

$$\text{Weight of n-butane remaining in the cylinder} = 10 \text{ gm.}$$

$$\text{Weight of material charged} = 440 \text{ gm.}$$

Recovered material

$$\text{Hydrocarbon Liquid Product} = 197.4 \text{ gm.}$$

$$\text{Condensable gases} = 204.7 \text{ gm.}$$

$$\text{Noncondensable gases} = 18.8 \text{ gm.}$$

$$\text{Carbon from burn-off} = 21.7 \text{ gm.}$$

$$\text{Oil from catalyst bed} = 3.7 \text{ gm.}$$

$$\text{Total weight recovered} = 446.3 \text{ gm.}$$

$$\text{Difference} = 6.3 \text{ gm.}$$

$$\text{Per Cent Gain on charge} = \frac{6.3}{440} \times 100 \qquad = \qquad 1.43\ \%$$

F. Calculation of Per Cent Gasoline Yield:
   Data:

Weight of oil charge	=	253 gm.
Weight of Gasoline from distillation	=	79.9 gm.

$$\text{Per cent gasoline on oil charge} = \frac{79.9}{253} \times 100 = 30.8\ \%$$

G. Calculation of Per Cent Conversion on Oil Charge:
   Data:

Weight of oil charged	=	253 gm.
Weight of residue from distillation	=	105.7 gm.
Weight of oil recovered from catalyst bed	=	3.7 gm.
Total weight of unconverted oil	=	109.4 gm.

Per Cent conversion on oil charge=

$$100 - \frac{109.4}{253} \qquad = \qquad 56.7\ \%$$

H. Calculation of Per Cent Ultimate Yield:
   Data:

Per cent gasoline on oil charge	=	30.8 %
Per cent conversion on oil charge	=	56.7 %

$$\text{Per cent ultimate yield} = \frac{30.8}{56.7} \times 100 \qquad = \qquad 54.3\ \%$$

I. Calculation of Per Cent Carbon Lay-Down:
   Data:

Weight of material charged	=	440 gm.
Weight of Carbon by burn-off	=	21.7 gm.

Per cent carbon lay-down on total

$$\text{charge} = \frac{21.7}{440} \times 100 \qquad = \qquad 4.93\ \%$$

IV RESULTS

The results obtained from catalytic polyforming of gas oil with n-butane using various catalysts are presented in tabular and graphic form in Table I-VIII and Figures 3-14. These results were correlated and compared with respect to gasoline production, carbon deposition, and gas formation. The quantity and quality of the gasoline produced are of primary importance in any catalyst study. Carbon and gas are generally considered undesirable products and rating catalysts in terms of carbon and gas producing tendency is also important. Consequently, in evaluating the catalysts, the undesirable factors of carbon and gas formation were weighed against the desirable factors of increased quality and quantity of the gasoline to determine the better catalysts for the process.

The per cent gasoline yield from each run was determined with respect to the quantity of gas oil charged. To determine a curve for optimum conditions for gasoline production, this figure was plotted versus conversion per pass.

The theoretical figure, ultimate yield of gasoline on oil charge, is determined by assuming that all material boiling above the gasoline fraction would on recycling, give the same yield of gasoline as the original gas oil. Actually this is not true since each successive recycle makes the oil more refractory. A plot of this theoretical

figure versus the per cent conversion on oil charge shows

the maximum yield that would be obtained with recycle. These

plots of the yield per pass and ultimate yield of gasoline

as a function of conversion for the various catalysts are

shown in Figures 3-12.

The per cent carbon and noncondensable gas produced were

determined with respect to the total charge of gas oil and

n-butane. The percentages were plotted in Figures 13 and

14 as a function of the conversion so that the amount of

carbon and gas production could be determined at any desired

conversion.

Table I presents the results of n-butane catalytic poly-

forming of gas oil with Cyclocel as the catalyst. Four runs

were made with this catalyst at temperatures varying from

457° C. to 550° C.

A plot of per cent gasoline yield as a function of con-

version is shown in Figure 3. This plot shows that the gaso-

line yield per pass reached a maximum value of 18 per cent

at 48 per cent conversion. This curve is seen to be rel-

atively flat indicating that the gasoline yield per pass

would remain essentially constant over a wide range of con-

versions.

The curve of ultimate yield rises to a maximum of 42

per cent at 39 per cent conversion and drops off quite

rapidly after reaching this maximum, approaching the curve

of yield per pass at higher conversion levels. In view of the fact that the yield per pass remains essentially constant over a wide range of conversions, a process using this catalyst could be operated under conditions such that both the maximum ultimate yield and the maximum yield per pass could be obtained.

The amount of carbon produced with Cyclocel catalyst was lower than average for the catalysts tested, being 3.2 per cent at maximum gasoline production per pass. Gas formation, however, was exceedingly large at higher conversions, and amounted to 40.2 per cent of the total charge at a conversion of 78 per cent. The amount of gas produced at maximum gasoline production per pass was 9.2 per cent.

A total of five runs at temperatures varying from 443°C. to 518°C. were made using the Filtrol catalyst. The results of these runs are presented in Table II.

A plot of the gasoline yield as a function of conversion for the Filtrol catalyst is shown in Figure 4. The production of gasoline from this catalyst was considerably greater than that formed with Cyclocel catalyst, the maximum being 24.5 per cent at 52.5 per cent conversion. The curve of ultimate yield, as shown in Figure 4, attains its maximum of 52.5 per cent at a conversion of 42.5 per cent. An ultimate gasoline yield of 46 per cent could be obtained at maximum gasoline yield per pass with this catalyst.

The carbon deposition with Filtrol catalyst, 5.2 per cent at maximum gasoline production per pass, was average for the catalysts investigated. The amount of gas formed at this point, 5 per cent, was relatively low. As in the case of Cyclocel, however, the amount of gas produced became excessive at higher conversions.

The third catalyst investigated was alumina activated with anhydrous hydrogen fluoride. A series of four runs was made with this catalyst at temperatures varying from 450°C. to 506°C. The results of the runs made with this catalyst are presented in Table III.

A plot of gasoline yield as a function of conversion, Figure 5, shows that the maximum gasoline production per pass of 25 per cent occurs at a conversion of 38.5 per cent. The ultimate yield attained from this catalyst was the highest of the catalysts tested. The maximum achieved was 62.5 per cent at a conversion of 35 per cent. The ultimate yield corresponding to maximum yield per pass was 62 per cent.

This catalyst was unique in the small amount of carbon deposited on the catalyst within its active temperature range. The carbon deposited was only 1.6 per cent of the total charge at the point of maximum gasoline production. Gas formation at this point was also low, being only 4 per cent of the total charge.

The results of catalytic polyforming with the synthetic

bead catalyst are shown in Table IV. Five runs were made on this catalyst at temperatures from 417°C. to 558°C. A plot of the gasoline yield as a function of conversion is shown in Figure 6.

The synthetic bead catalyst exhibited very good properties with respect to the production of gasoline. The gasoline yield per pass was higher than that given by any other than the Houdry catalyst. A maximum yield of gasoline per pass of 33 per cent was obtained at a conversion of 62.5 per cent. The curve of ultimate yield reached a maximum of 59 per cent at a 56 per cent conversion. It is seen from Figure 6, that an ultimate yield of 54.5 per cent can be obtained at maximum gasoline yield per pass.

The amount of carbon and gas produced were 4.5 and 7.1 per cent respectively, at the point of maximum gasoline production.

Table V presents the results of catalytic polyforming with chrome-alumina as the catalyst. Four runs were made at temperatures from 390°C. to 500°C. The temperature in Run 19 and in Runs 23 to 25 are only approximate because of an error in the recording instrument. These temperatures were estimated by extrapolating a curve of temperature versus conversion for each catalyst.

A plot of the gasoline yield as a function of conversion for the chrome-alumina catalyst is shown in Figure 7. The

gasoline yields obtained from this catalyst were relatively
poor, exceeding only those obtained from Cyclocel catalyst.
Figure 7 shows that the maximum gasoline yield per pass of
22 per cent was obtained at 42 per cent conversion. A maxi-
mum ultimate yield of 60 per cent can be obtained at a con-
version of 32 per cent. The ultimate yield corresponding to
maximum gasoline production per pass is 52.5 per cent.

Carbon deposition with chrome-alumina catalyst at the
point of maximum gasoline yield was 4 per cent. Gas form-
ation at this point was 7.3 per cent which is slightly high-
er than average for the catalysts studied.

A series of eight runs at temperatures varying from
380°C. to 543°C, was made with molybdenum-alumina catalyst.
The results of these runs are presented in Table VI.

The yield of gasoline obtained from molybdenum-alumina
catalyst was comparatively low. The plot of the gasoline
yield as a function of conversion, Figure 8, indicates
that a maximum gasoline yield of 24 per cent would be ob-
tained with this catalyst at a conversion of 60 per cent.
The ultimate yield curve is seen to reach a maximum of 47
per cent at 46.5 per cent conversion. An ultimate yield
of 41 per cent can be obtained with this catalyst at maxi-
mum gasoline production.

This catalyst produced the highest percentage of carbon
deposited of any catalyst tested, reaching 18.6 per cent of

the total charge at 79 per cent conversion. The amount of
carbon produced at maximum gasoline production was 12 per
cent. The amount of gas formation was also very large,
11.2 per cent at the point of maximum gasoline production,
exceeding that produced by any other catalyst.

The results of catalytic polyforming with silica-mag-
nesia catalyst are presented in Table VII. Five runs were
made at temperatures from 403°C. to 528°C.

Silica-magnesia exhibited very good properties with
respect to gasoline yield. The quantity of gasoline pro-
duced was exceeded only by that produced by the Houdry
and synthetic bead catalysts. A plot of the gasoline yield
as a function of conversion for the silica-magnesia catalyst
is shown in Figure 9. This figure indicates that a maximum
yield per pass of 31 per cent was obtained at 59 per cent
conversion. The curve of ultimate yield as a function of
conversion shows that a maximum ultimate yield of gasoline
was not obtained. Thus, at lower conversions, the maximum
ultimate yield would be higher than any value of ultimate
yield obtained in this study. The ultimate yield at maxi-
mum yield per pass is 52 per cent.

The carbon and gas production for the silica-magnesia
catalyst were relatively low, being 4.2 per cent and 5 per
cent respectively at the points of maximum gasoline yield
per pass.

Table VIII presents the results of catalytic polyforming with the Houdry catalyst. A series of four runs was made on this catalyst at temperatures varying from 421°C. to 503°C.

The Houdry catalyst was found to have excellent properties with respect to the production of gasoline. The gasoline yield per pass was higher than that given by any other catalyst tested. A plot of the gasoline yield as a function of conversion is shown in Figure 10. This curve shows that a maximum of 34.5 per cent gasoline was obtained at 67 per cent conversion. The maximum ultimate yield of gasoline with this catalyst was not obtained.

The amount of carbon produced by the Houdry catalyst was 5.8 per cent at the point of maximum gasoline production while the amount of gas formed was 7.2 per cent.

Because of the fact that gasoline yields for catalytic cracking as published in the literature vary so widely depending on end points and methods of calculation selected, a series of conventional catalytic cracking runs was made with Houdry catalyst to allow comparison of catalytic polyforming yields with the gasoline yield obtained in conventional catalytic cracking using the equipment and procedure of this investigation. The virgin gas oil was used as the charge stock, and a series of four catalytic cracking runs was made at atmospheric pressure and a space velocity of

$0.6-0.8$ hr^{-1}.

The results of these catalytic cracking runs are presented in tabular form in Table IX and graphically in Figures 15 and 16.

Figure 15 shows that the gasoline yield per pass reached a maximum value of 34 per cent at 62.5 per cent conversion. From the curve of ultimate yield, as shown in Figure 16, it is seen that the maximum ultimate yield of gasoline was not obtained.

On the basis of quantity of gasoline produced per pass, Houdry was found to be the best catalyst. The Houdry catalyst produced a maximum of 34.5 per cent gasoline per pass at a conversion of 67 per cent. The synthetic bead catalyst produced the second highest yield of gasoline per pass, this yield being 33 per cent at 62.5 per cent conversion. No other catalyst, except silica-magnesia, approached the Houdry and synthetic bead in relation to gasoline produced per pass. The silica-magnesia catalyst produced a maximum of 31 per cent at a conversion of 59 per cent.

Relative to the ultimate yield of gasoline obtainable with recycle, the HF activated alumina catalyst gave the highest ultimate yield obtained in this investigation. The yields per pass with this catalyst, however, were inferior. Of the catalyst producing a relatively high yield per pass, namely silica-magnesia, synthetic bead, and Houdry, synthetic

bead is slightly superior at the conversions which give each its maximum yield per pass. At a conversion of 62.5 per cent, which gives maximum yield per pass for synthetic bead, this catalyst gives an ultimate yield of 55 per cent. Silica-magnesia, which gives its maximum yield per pass at 59 per cent conversion, has an ultimate yield of 52 per cent at this conversion. An ultimate yield of 50 per cent is obtained with Houdry catalyst at its point of maximum yield per pass. Although some of the other catalysts investigated gave relatively high ultimate yields, the yields per pass obtainable with these catalysts were very inferior.

In relation to carbon formation, the HF activated alumina catalyst was superior to all others tested, producing only 1.6 per cent carbon at the conditions of maximum gasoline yield. The three catalysts which gave acceptable yields of gasoline per pass had essentially the same carbon production at the point of maximum gasoline yield. Consequently, no distinction can be made between them on this basis.

The silica-magnesia catalyst produced slightly less noncondensable gas than was produced by Houdry or the synthetic bead catalyst at maximum gasoline yield. HF activated alumina produced less gas than silica-magnesia but this catalyst was not suitable for gasoline production.

V SUMMARY

The over-all results obtained in this investigation indicate that the Houdry catalyst is superior to the other catalysts investigated with respect to gasoline yields when charging gas oil with n-butane. The maximum gasoline yield of 34.5 per cent obtained with Houdry catalyst was 1.5 absolute per cent higher than that obtained with the next best catalyst. Synthetic bead and silica-magnesia also produced relatively high gasoline yields, the maximum being 33 and 31 per cent, respectively. Cyclocel, Filtrol, HF activated alumina, chrome-alumina, and molybdenum-alumina produced considerably lower yields of gasoline per pass.

The ultimate yields obtained from Houdry catalysts were similar to those obtained with silica-magnesia and synthetic bead; synthetic bead having a slightly higher ultimate yield at maximum gasoline production.

Carbon deposition and gas formation with the Houdry catalyst were equivalent to those obtained with synthetic bead. The silica-magnesia catalyst produced an equivalent amount of carbon and slightly less gas than that produced by Houdry at the point of maximum gasoline yield.

In general, the use of Houdry catalyst seems warranted in any commercial application of the catalytic polyforming process with n-butane as the outside gas, especially where high gasoline yields per pass are of primary importance.

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VIII APPENDIX

TABLE I

Catalytic Polyforming of Gas Oil with n-Butane Using Cyclocel Catalyst

Run No.	1	2	3	4
No. of Runs on Catalyst	3	6	7	8
Avg. Reactor Temp. °C.	488	457	550	497
Space Velocity hr.$^{-1}$	4.55	5.82	5.1	4.84
Material Charged, gm.				
Outside Gas	189	140	173	165
Charge Stock	255	247	260	255
Total Charge	444	387	433	420
Recovered Material, gm.				
H-C Liq. Prod.	198.8	186.5	67.0	197.8
Condensable Gases	193.6	148.8	125.1	169.3
Permanent Gases	14.5	32.4	174.0	33.2
Oil from Catalyst	5.5	3.1	0.9	3.1
Carbon by Burn-off	13.9	11.3	57.8	16.5
Total recovered	436.3	382.1	424.8	419.9
Difference, gm.	7.7	4.9	8.2	0.1
% Loss or Gain on Charge	1.73	1.27	1.89	0.02
Distillation Data, gm.				
Gasoline	44.4	33.8	41.2	44.5
Residue	141.2	156.9	54.7	123.5
Distillation Lights	177.6	73.6	54.5	132.2
% Gasoline on Oil Charge	17.55	13.8	15.85	17.45
% Conversion on Oil Charge	42.0	35.1	78.6	46.9
% Ultimate Yield	41.8	39.3	20.2	37.2
% Carbon on Total Charge	3.13	2.92	13.30	3.17
% Gas on Total Charge	3.27	8.38	40.20	7.91

TABLE II

Catalytic Polyforming of Gas Oil with n-Butane
Using Filtrol Catalyst

Run No.	5	6	7	8	9
No. Runs on Catalyst	2	3	4	5	7
Avg. Reactor Temp. °C.	443	472	513	530	581
Space Velocity hr.$^{-1}$	4.59	5.16	4.62	5.21	5.53
Material Charged, gm.					
Outside Gas	144	158	188	159	178
Charge Stock	259	257	263	258	264
Total Charge	403	415	451	417	442
Recovered Material, gm.					
H-C Liq. Prod.	220.4	210.1	190.8	151.4	131.3
Condensable Gases	117.7	179.1	204.3	189.3	121.6
Permanent Gases	12.7	13.1	42.2	48.0	153.0
Oil from Catalyst	39.5	5.7	2.1	1.2	1.1
Carbon by Burn-off	14.7	12.3	24.2	17.1	28.0
Total Recovered	405.0	420.3	463.6	407.0	435.0
Difference, gm.	2	5.3	12.6	10.0	7.0
% Loss or Gain on Charge	0.5	1.28	2.79	2.39	1.58
Distillation Data, gm.					
Gasoline	35.5	58.7	62.2	62.0	58.8
Residue	137.6	141.5	125.2	109.5	101.4
Distillation Lights	130.7	143.8	174.8	134.9	70.8
% Gasoline on Oil Charge	13.7	22.85	23.65	24.0	22.3
% Conversion on Oil Charge	31.6	42.7	51.6	57.1	61.2
% Ultimate Yield	43.4	53.5	45.9	42.0	36.4
% Carbon on Total Charge	3.64	2.96	5.37	4.11	6.33
% Gas on Total Charge	3.15	3.16	9.37	11.51	34.70

TABLE III

Catalytic Polyforming of Gas Oil with n-Butane
Using HF Activated Alumina Catalyst

Run No.	10	11	12	13
No. Runs on Catalyst	2	3	4	5
Avg. Reactor Temp. °C.	450	462	495	506
Space Velocity hr.-1	5.18	5.14	4.98	5.26
Material Charged, gm.				
Outside Gas	175	186	157	169
Charge Stock	264	259	259	258
Total Charge	439	445	416	427
Recovered Material, gm.				
H-C Liq. Prod.	229.2	244.3	208.4	207.7
Condensable Gases	182.3	175.6	176.3	185.2
Permanent Gases	12.0	10.9	22.3	22.0
Oil from Catalyst	5.7	2.8	2.3	1.6
Carbon by Burn-off	3.4	4.2	10.3	12.0
Total Recovered	432.9	437.8	419.6	428.5
Difference, gm.	6.1	7.2	3.6	1.5
% Loss or Gain on Charge	1.39	1.62	0.87	0.35
Distillation Data, gm.				
Gasoline	57.7	59.1	63.1	59.9
Residue	168.2	165.5	150.1	147.2
Distillation Lights	160.2	176.8	151.0	159.1
% Gasoline on Oil Charge	21.85	22.8	24.36	23.2
% Conversion on Oil Charge	34.0	35.0	41.2	42.4
% Ultimate Yield	64.4	65.2	59.1	54.7
% Carbon on Total Charge	0.774	0.943	2.48	2.81
% Gas on Total Charge	2.73	2.45	5.36	5.16

TABLE IV

Catalytic Polyforming of Gas Oil with n-Butane
Using Synthetic Bead Catalyst

Run No.	14	15	16	17	18
No. Runs on Catalyst	2	3	4	5	6
Avg. Reactor Temp. °C.	417	454	506	558	499
Space Velocity hr.$^{-1}$	5.4	5.06	4.52	4.6	5.5
Material Charged, gm.					
Outside Gas	162	159	154	172	176
Charge Stock	270	257	256	261	255
Total Charge	432	416	410	433	431
Recovered Material, gm.					
H-C Liq. Prod.	204.7	185.2	179.2	114.0	173.4
Condensable Gases	166.0	174.2	158.9	238.5	193.4
Permanent Gases	13.3	26.8	33.4	51.6	40.8
Oil from Catalyst	24.3	4.6	2.0	0.5	1.5
Carbon by Burn-off	7.9	16.7	22.2	31.0	20.2
Total Recovered	416.2	406.5	395.7	435.6	429.3
Difference, gm.	15.8	9.5	14.3	2.6	1.7
% Loss or Gain on Charge	3.66	2.24	3.49	0.60	0.39
Distillation Data, gm.					
Gasoline	59.8	83.8	85.8	77.8	80.1
Residue	135.4	108.7	79.9	60.3	80.4
Distillation Lights	159.4	140.1	150.7	182.4	167.3
% Gasoline on Oil Charge	22.15	32.6	33.53	29.8	31.4
% Conversion on Oil Charge	42.0	55.9	68.0	76.7	67.9
% Ultimate Yield	52.75	58.35	49.3	38.8	46.3
% Carbon on Total Charge	1.83	4.01	5.42	7.15	4.68
% Gas on Total Charge	3.08	6.44	8.15	11.9	9.48

TABLE V

Catalytic Polyforming of Gas oil with n-Butane
Using Chrome-Alumina Catalyst

Run No.	19	20	21	22
No. Runs on Catalyst	2	3	4	6
Avg. Reactor Temp. °C.	390*	458	500	477
Space Velocity hr.$^{-1}$	4.84	6.3	5.95	5.93
Material Charged, gm.				
Outside Gas	168	196	158	174
Charge Stock	272	251	264	260
Total Charge	440	447	422	434
Recovered Material, gm.				
H-C Liq. Prod.	259.8	204.5	184.2	184.2
Condensable Gases	144.2	207.6	142.6	194.8
Permanent Gases	14.2	23.2	44.4	51.5
Oil from Catalyst	7.9	1.7	2.5	1.0
Carbon by Burn-off	8.0	13.4	33.2	17.0
Total Recovered	434.1	450.4	406.9	448.5
Difference, gm.	5.9	3.4	15.1	14.5
% Loss or Gain on Charge	1.34	0.76	3.58	3.34
Distillation Data, gm.				
Gasoline	19.5	54.3	55.0	56.6
Residue	225.6	154.2	126.0	135.8
Distillation Lights	137.3	169.4	113.2	151.6
% Gasoline on Oil Charge	7.16	21.6	20.8	21.8
% Conversion on Oil Charge	14.2	36.6	51.3	47.4
% Ultimate Yield	50.5	59.0	40.5	46.0
% Carbon on Total Charge	1.82	3.01	7.87	3.92
% Gas on Total Charge	3.23	5.19	10.51	11.86

* Approximate value

Catalytic Polyforming of Gas Oil with n-Butane
Using Molybdenum-Alumina Catalyst

Run No.	23	24	25	26	27	28	29
No. Runs on Cat.	2	3	4	5	6	7	8
Avg. Reactor Temp. ^{o}C	420*	380*	406*	487	543	529	452
Space Vel. hr.$^{-1}$	4.65	4.93	4.63	5.07	5.25	5.51	5.5

Material Charged, gm.

Outside Gas	164	165	164	158	165	165	172
Charge Stock	254	259	261	248	255	262	257
Total Charge	418	424	425	406	420	427	429

Recovered Material, gm.

H-C Liq. Prod.	204.6	251.7	233.1	141.6	73.1	84.2	191.2
Condensable Gases	137.1	126.2	117.7	149.9	109.6	141.4	168.2
Permanent Gases	37.5	22.3	30.3	49.2	138.0	111.5	22.3
Oil from Catalyst	6.3	11.0	3.3	2.4	0.8	0.8	2.0
Carbon by Burn-off	32.0	26.2	37.5	54.0	78.0	75.2	36.4
Total Recovered	417.5	437.4	421.9	407.1	399.5	413.1	420.1

Difference, gm.	0.5	13.4	3.1	1.1	20.5	13.9	8.9
% Loss or Gain on Charge	0.12	3.16	0.73	0.27	4.87	3.25	2.08

Distillation Data, gm.

Gasoline	50.4	25.4	37.2	60.5	41.4	56.5	54.0
Residue	143.6	181.2	165.7	85.0	51.8	55.8	117.4
Distilliation Lights	123.9	137.7	117.9	119.0	59.6	81.1	139.0

% Gasoline on Oil Charge	19.8	9.3	14.3	24.4	16.2	21.6	21.0
% Conversion on Oil Charge	41.0	27.2	35.2	64.8	79.4	78.4	53.5
% Ultimate Yield	48.4	34.1	40.5	38.3	20.4	27.4	39.3
% Carbon on Total Charge	7.65	6.18	8.82	13.3	18.6	17.6	8.5
% Gas on Total Charge	8.97	5.26	7.13	12.1	32.40	26.1	5.21

* Approximate value

Catalytic Polyforming of Gas Oil with n-Butane
Using Silica-Magnesia Catalyst

Run No.	30	31	32	33	34
No. Runs on Catalyst	2	3	4	5	6
Avg. Reactor Temp. °C.	463	479	528	444	403
Space Velocity hr.⁻¹	5.07	4.71	4.90	4.73	5.5
Material Charged, gm.					
Outside Gas	168	175	153	187	162
Charge Stock	257	266	254	253	259
Total Charge	425	441	407	440	421
Recovered Material, gm.					
H-C Liq. Prod.	154.5	145.0	77.7	197.4	210.4
Condensable Gases	215.1	193.4	156.3	204.7	169.3
Permanent Gases	12.7	58.0	111.0	18.8	8.5
Oil from Catalyst	1.1	0.8	0.8	3.7	21.8
Carbon by Burn-off	24.6	36.8	53.0	21.7	18.5
Total Recovered	408.0	434.4	398.8	446.3	428.5
Difference, gm.	17.0	6.6	8.2	6.3	7.5
% Loss or Gain on Charge	4.00	1.50	2.02	1.43	1.78
Distillation Data, gm.					
Gasoline	77.3	77.6	46.8	79.9	69.4
Residue	92.3	77.7	49.2	105.7	129.3
Distillation Lights	163.4	140.8	115.9	181.0	154.3
% Gasoline on Oil Charge	30.0	29.2	18.0	30.8	26.8
% Conversion on Oil Charge	63.7	70.5	80.3	56.7	41.7
% Ultimate Yield	47.2	41.5	22.4	54.3	64.1
% Carbon on Total Charge	6.02	8.35	13.0	4.93	4.40
% Gas on Total Charge	2.99	13.12	27.3	4.28	2.02

TABLE VIII

Catalytic Polyforming of Gas Oil with n-Butane
Using Houdry Catalyst

Run No.	35	36	37	38
No. Runs on Catalyst	- 2	3	4	43
Avg. Reactor Temp. °C.	445	503	478	421
Space Velocity hr.$^{-1}$	4.71	4.69	4.67	4.98
Material charged, gm.				
Outside Gas	168	176	167	177
Charge Stock	255	254	269	268
Total Charge	423	430	436	445
Recovered Material, gm.				
H-C Liq. Prod.	211.1	141.1	156.5	248.0
Condensable Gases	180.6	203.5	209.5	170.5
Permanent Gases	18.1	49.3	35.0	21.8
Oil from Catalyst	1.4	0.3	0.2	4.7
Carbon by Burn-off	15.8	35.6	21.7	10.3
Total recovered	427.0	429.8	422.9	455.3
Difference, gm.	4.0	0.2	13.1	10.3
% Loss or Gain on Charge	0.95	0.05	2.92	2.32
Distillation Data, gm.				
Gasoline	82.7	83.1	92.3	77.6
Residue	104.0	65.7	80.2	140.6
Distillation Lights	181.4	164.8	163.7	176.4
% Gasoline on Oil Charge	32.45	32.7	34.3	29.0
% Conversion on Oil Charge	58.6	74.0	70.2	45.7
% Ultimate Yield	55.5	44.2	48.9	63.5
% Carbon on Total Charge	3.74	8.28	4.97	2.37
% Gas on Total Charge	4.28	11.45	8.03	4.90

TABLE IX

Catalytic Cracking of Gas Oil Using Houdry Catalyst
at a Space Velocity of 0.6-0.8 hr.$^{-1}$

	39	40	41	42
Run No.	39	40	41	42
No. Runs on Catalyst	47	48	49	50
Avg. Reactor Temp. °C.	429	482	413	509
Space Velocity hr.$^{-1}$	0.65	0.70	0.75	0.67
Material Charged, gm.				
Gas Oil	250	267	264	261
Recovered Material, gm.				
H-C Liq. Prod.	222.4	215.7	233.7	192.4
Condensable Gases	9.6	23.8	4.6	31.9
Permanent Gases	4.1	14.3	3.5	17.7
Oil from Catalyst	1.9	1.6	5.0	0.8
Carbon by Burn-off	6.4	12.4	6.45	15.3
Total Recovered	244.4	267.3	253.2	258.1
Difference, gm.	5.6	0.3	17.8	2.9
% Loss or Gain on Charge	2.24	0.11	4.46	1.10
Distillation Data, gm.				
Gasoline	84.0	88.8	86.3	83.0
Residue	104.8	84.7	120.6	73.2
Distillation Lights	31.7	48.6	26.5	52.1
% Gasoline on Oil Charge	33.6	33.2	32.7	31.8
% Conversion on Oil Charge	57.3	67.7	52.4	71.6
% Ultimate Yield	58.6	49.0	62.4	44.4
% Carbon on Total Charge	2.56	4.65	2.44	5.86
% Gas on Total Charge	1.6	5.36	1.33	6.78

TABLE X

GAS OIL INSPECTION DATA

Borger (Panhandle) Virgin Gas Oil

A.S.T.M. Dist. °F.

First drop	527
5% cond. 760 mm.	555
10%	565
20%	577
30%	591
40%	605
50%	622
60%	639
70%	662
80%	692
90%	725
95%	740
End Point	742
Recovery	98%
Residue and loss	2.0%
Gravity °API	36.0
Viscosity, SSU/100°F.	53.6
Weight per cent sulphur	0.31

54
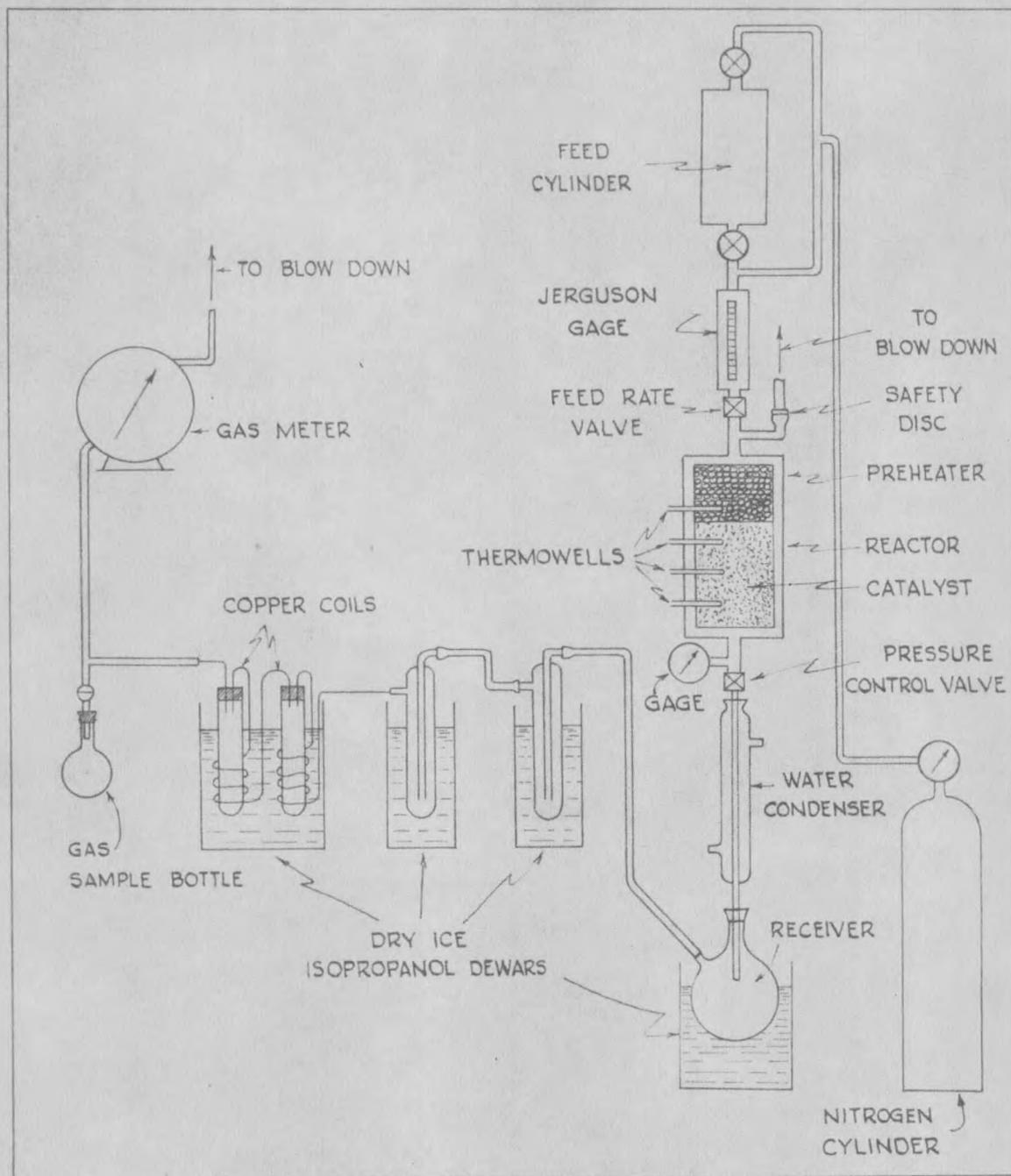
Figure 1. Schematic Diagram of Equipment
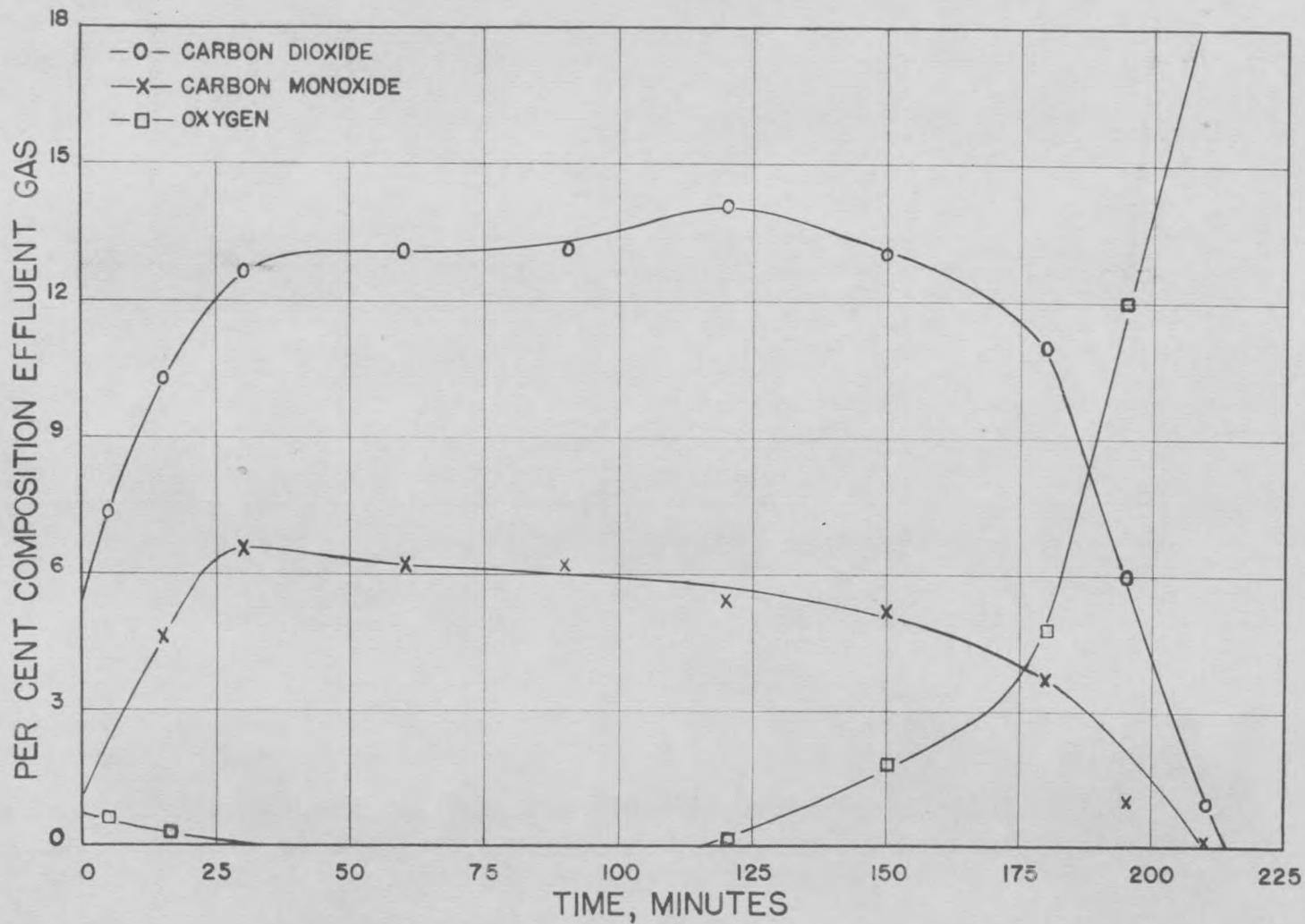
Figure 2. Composition of Effluent Gas During
Catalyst Burn-off
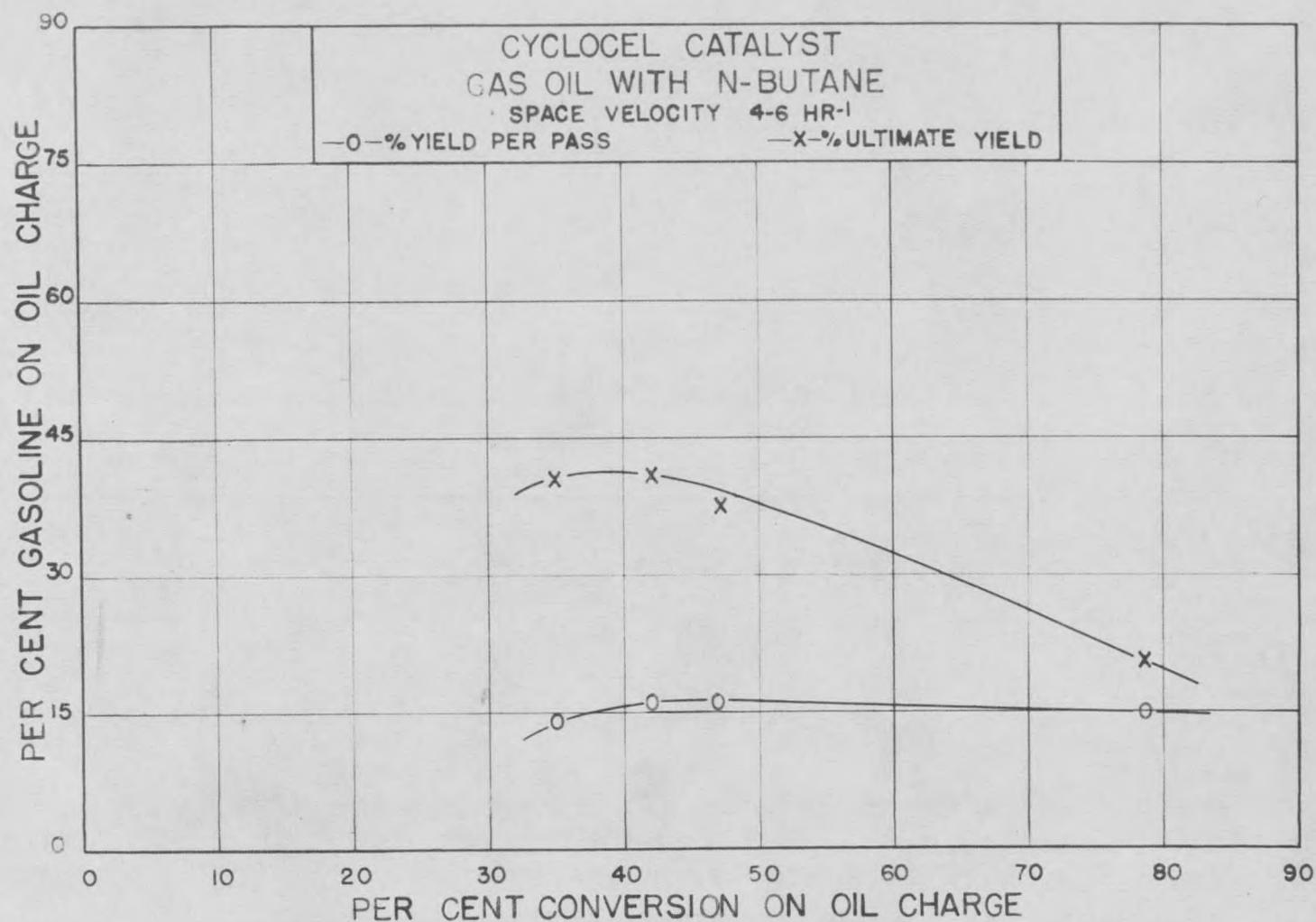
Figure 3. Effect of Conversion on Gasoline Yield
for Cyclocel Catalyst
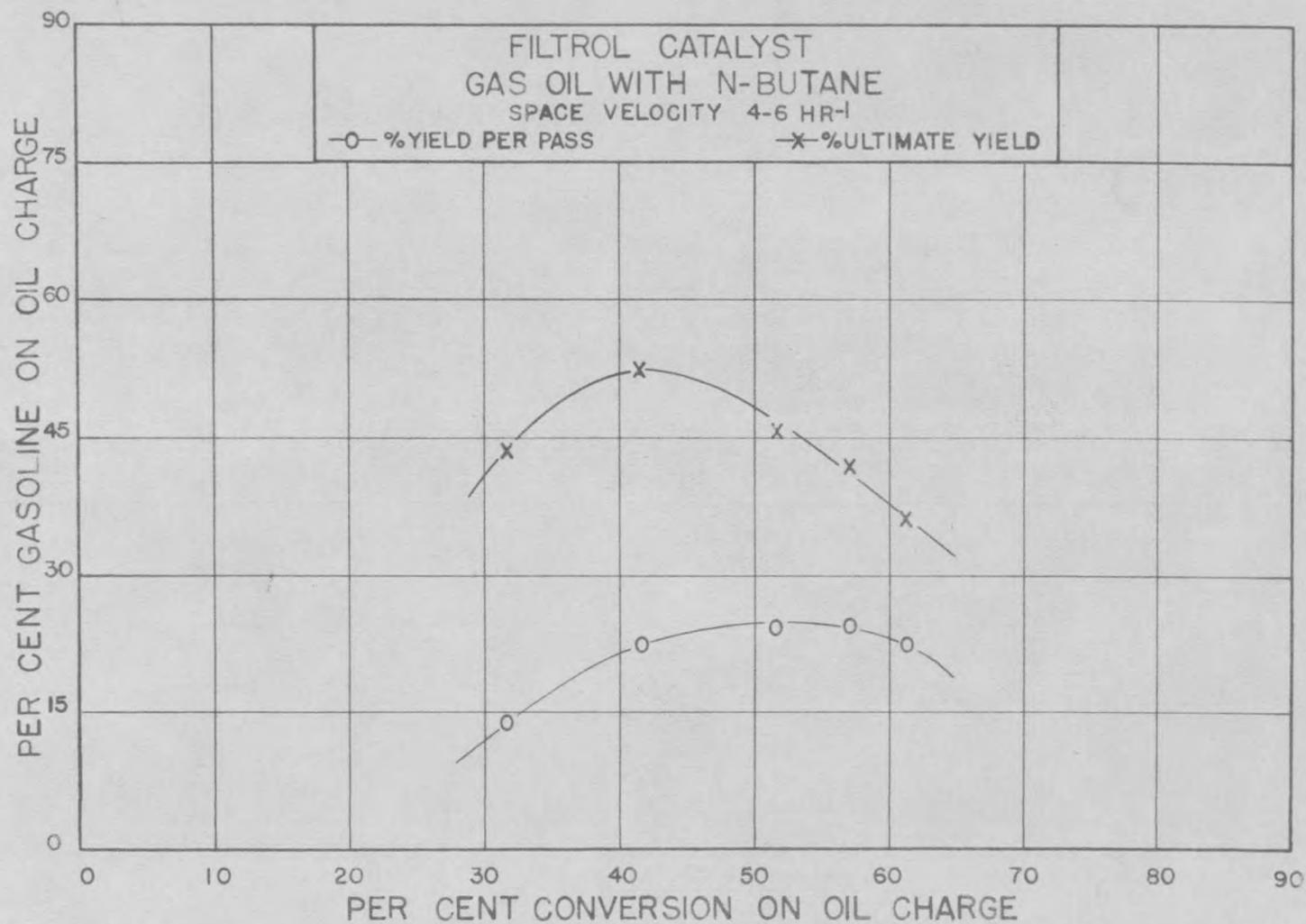
Figure 4. Effect of Conversion on Gasoline Yield
for Filtrol Catalyst
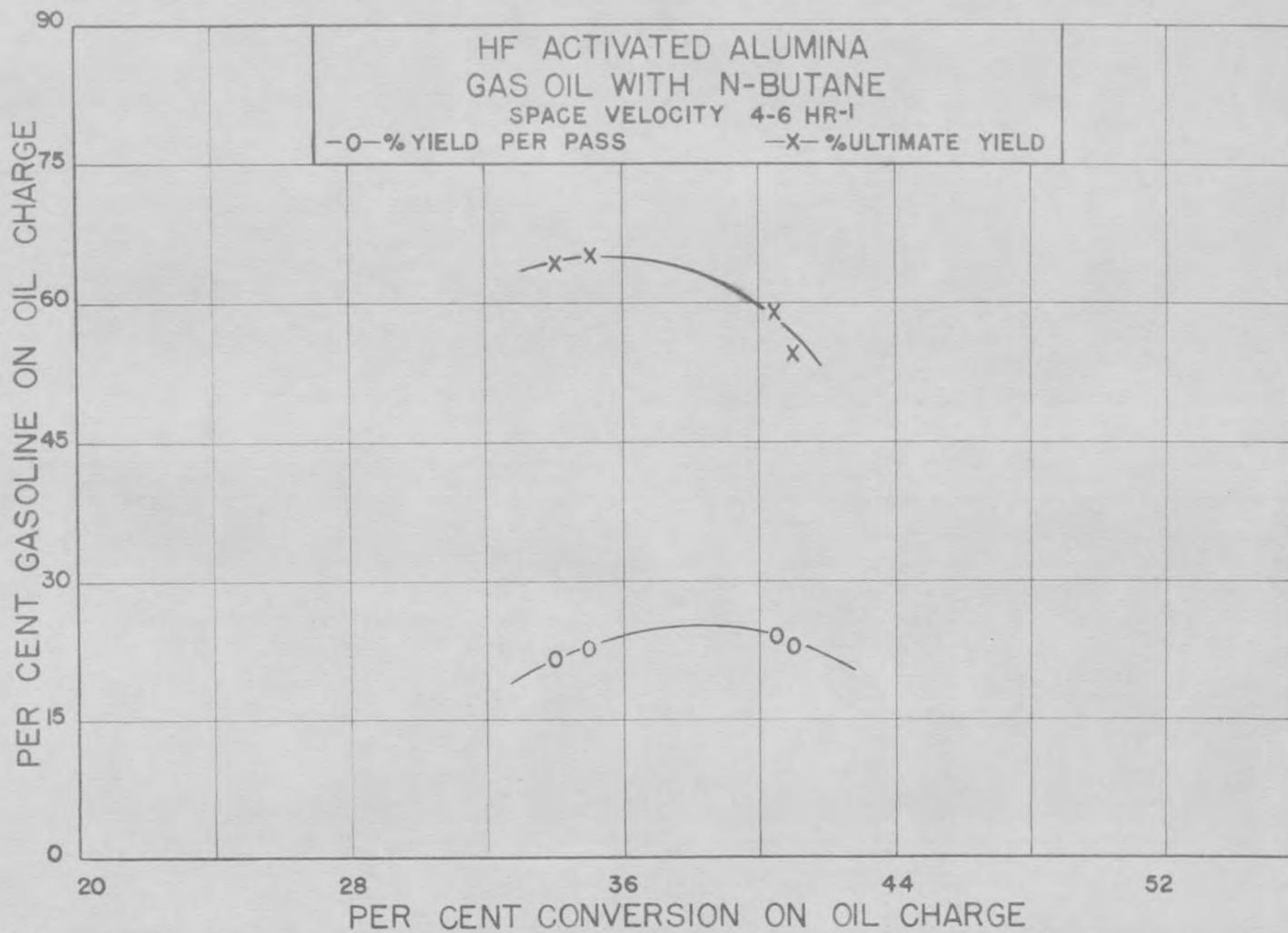
Figure 5. Effect of Conversion on Gasoline Yield
for HF Activated Alumina Catalyst
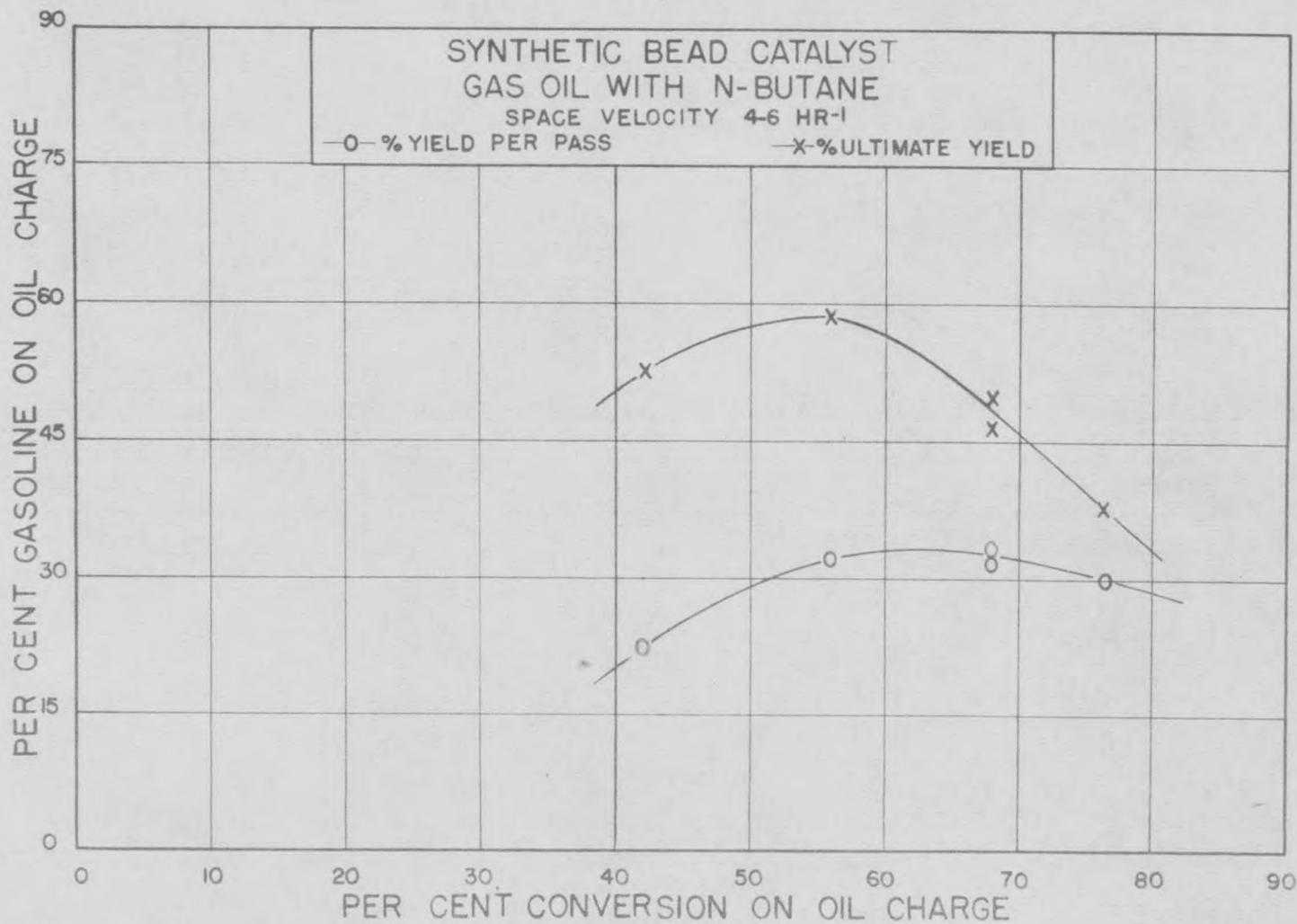
Figure 6. Effect of Conversion on Gasoline Yield
for Synthetic Bead Catalyst
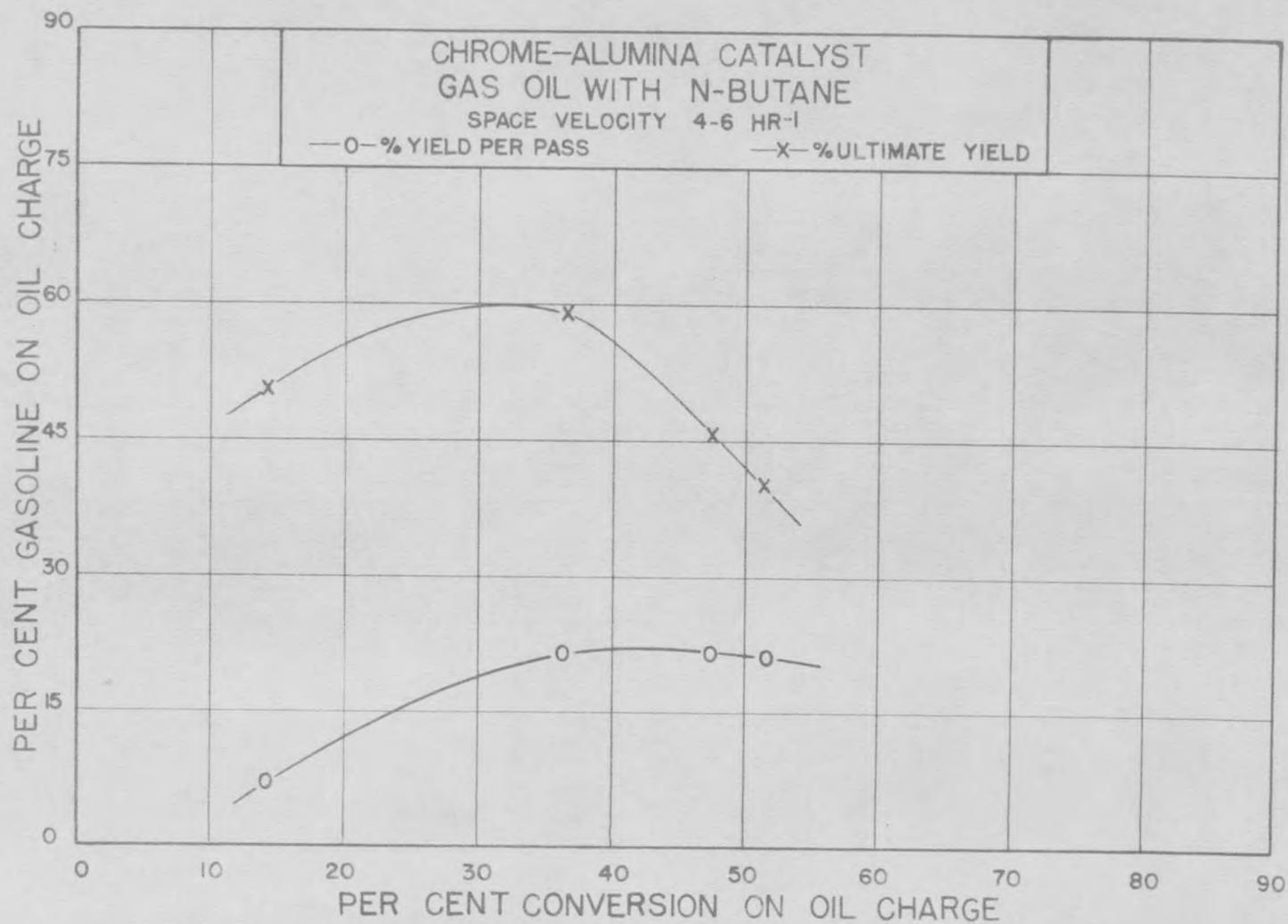
Figure 7. Effect of Conversion on Gasoline Yield
for Chrome-Alumina Catalyst
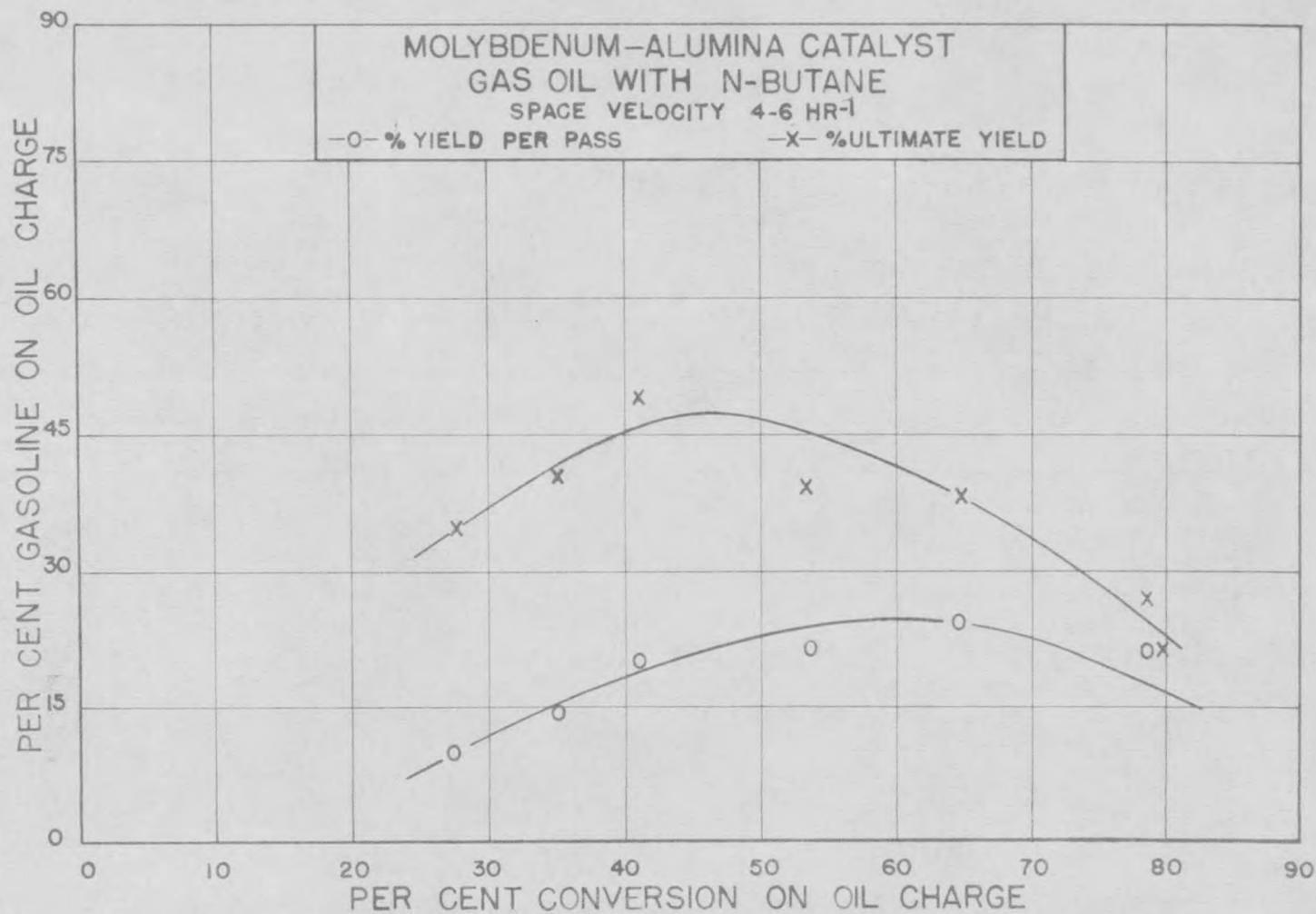
Figure 8. Effect of Conversion on Gasoline Yield
for Molybdenum-Alumina Catalyst
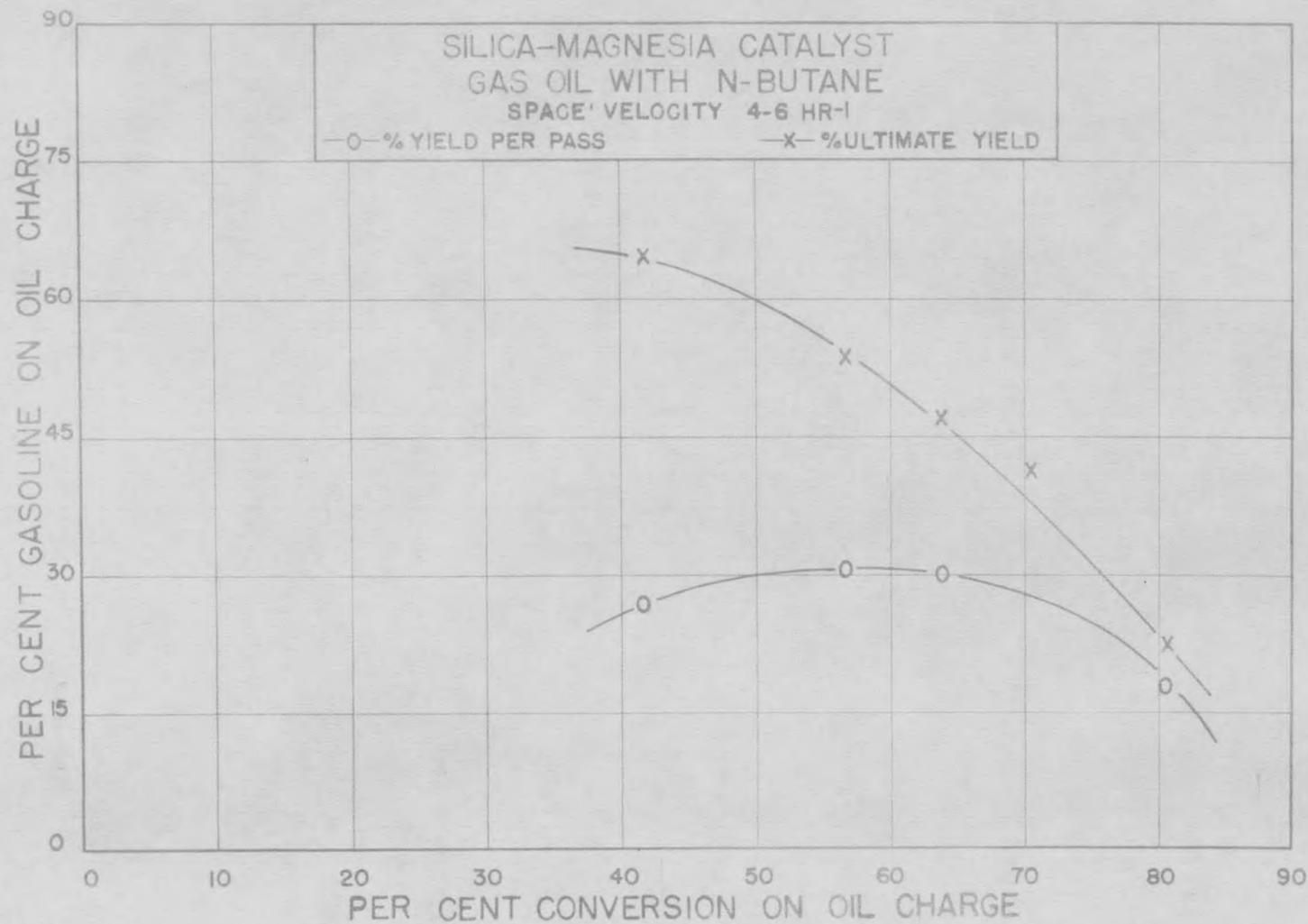
Figure 9. Effect of Conversion on Gasoline Yield
for Silica-Magnesia Catalyst
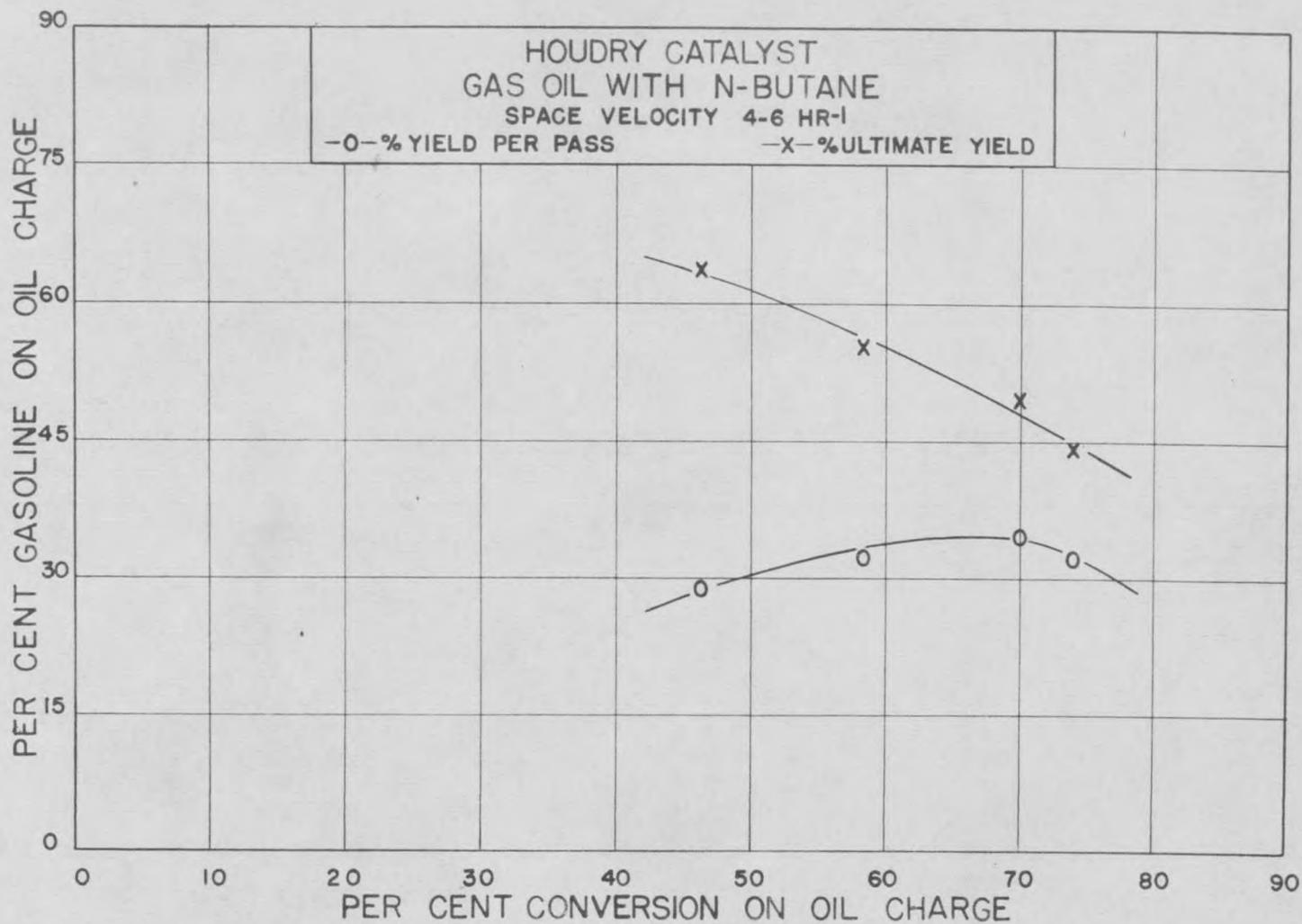
Figure 10. Effect of Conversion on Gasoline Yield
for Houdry Catalyst
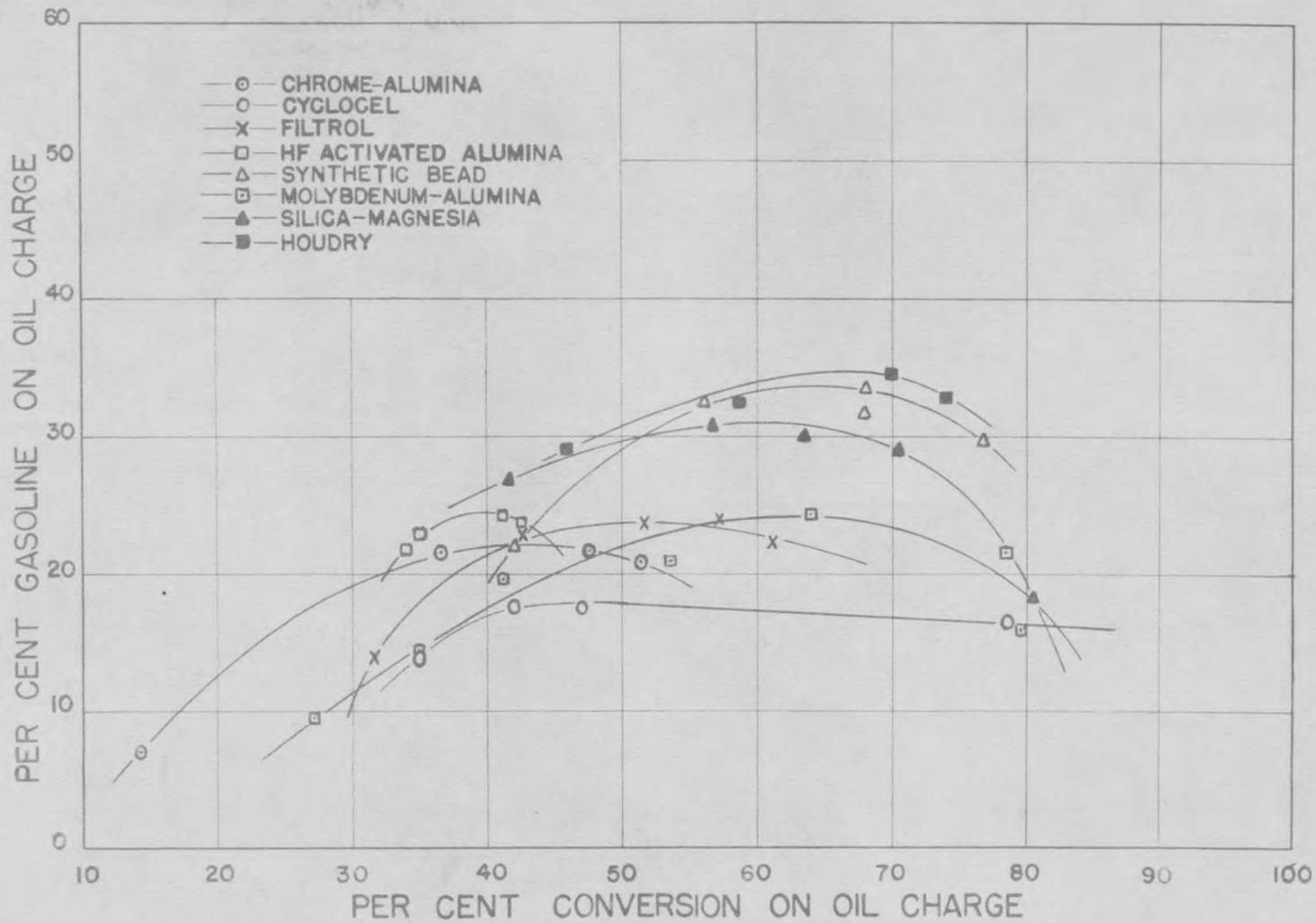
Figure 11. Effect of Conversion on the Gasoline
Yield Per Pass for the Catalysts
Tested
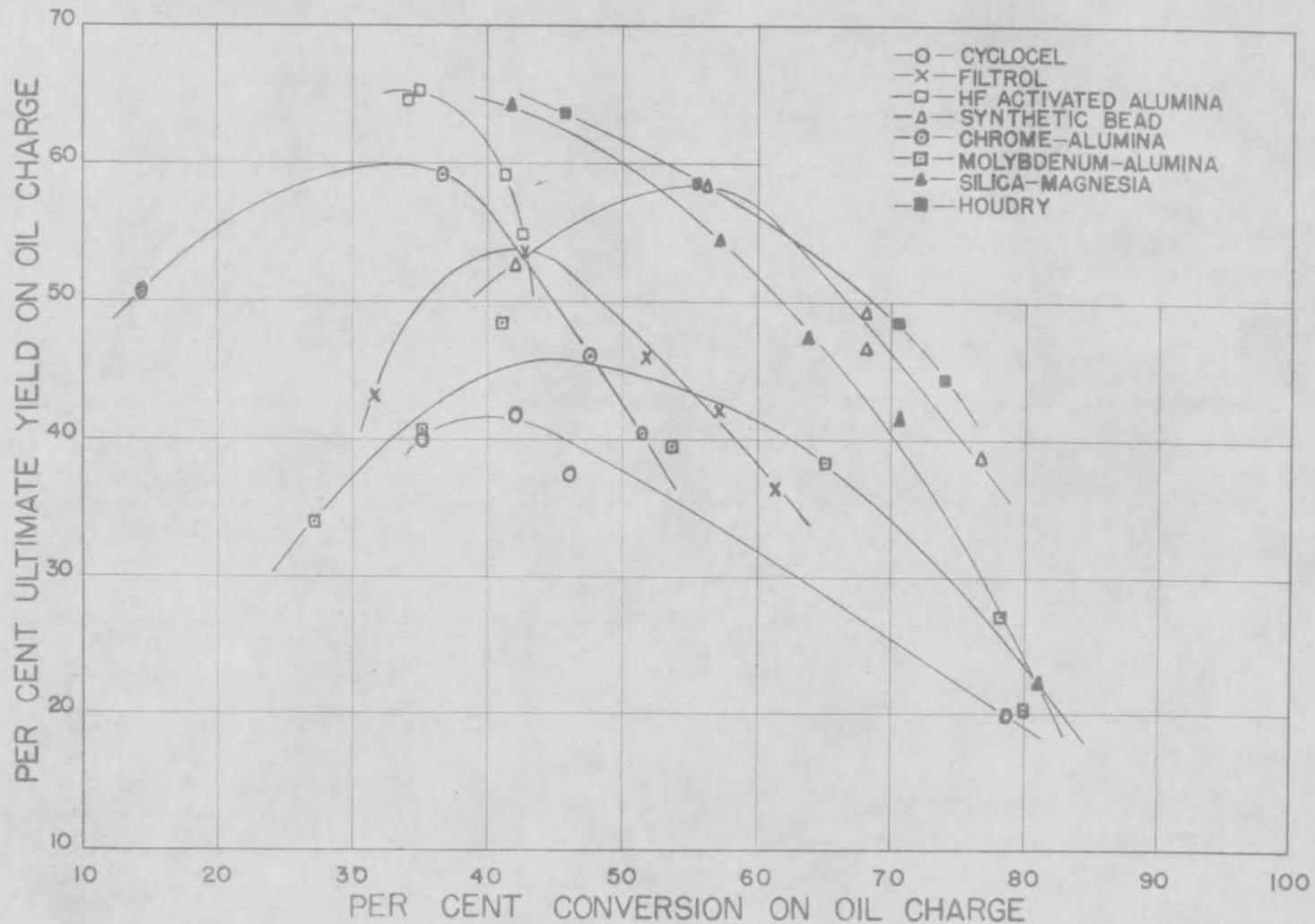
Figure 12. Effect of Conversion on the Ultimate
Yield for the Catalysts Tested
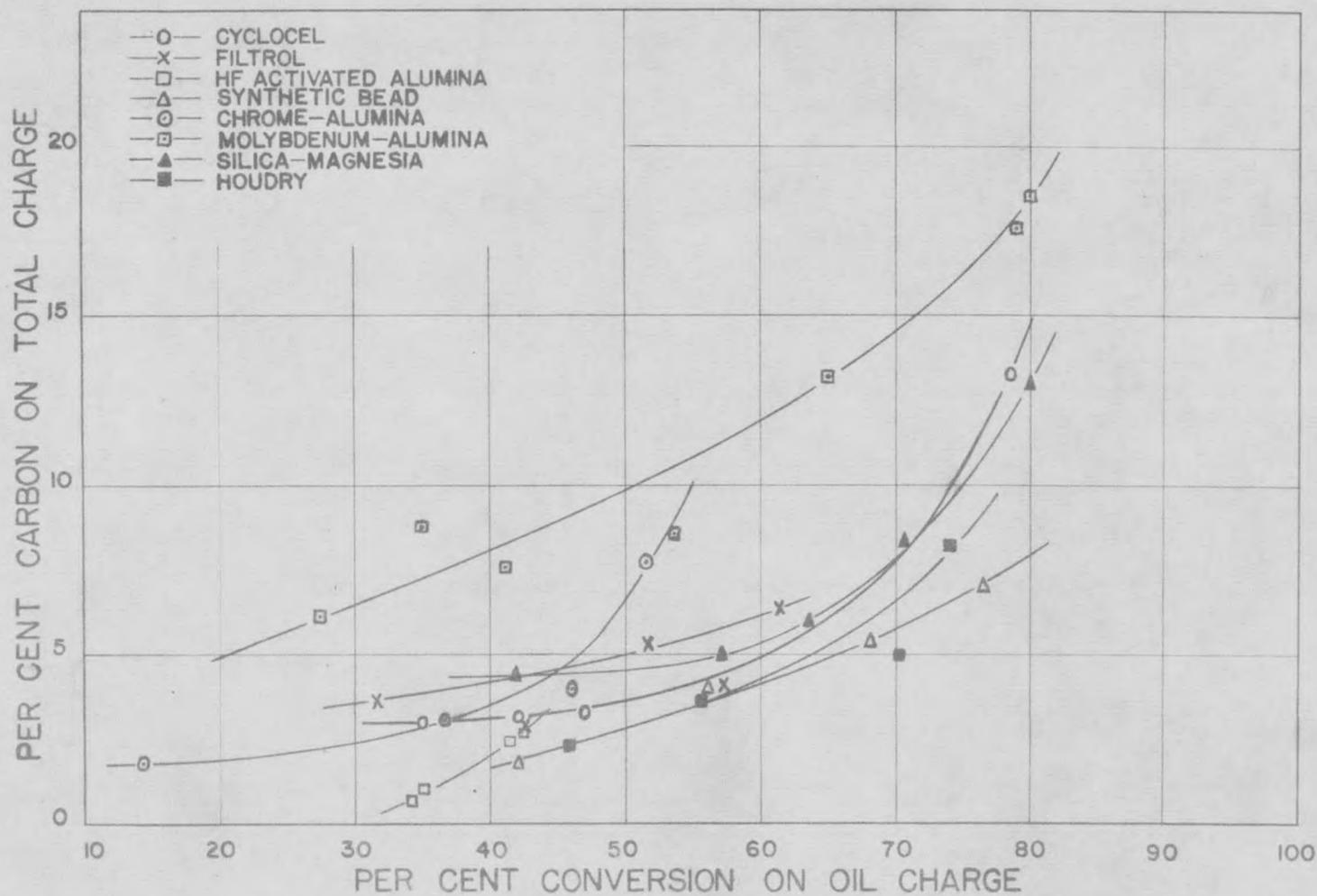
Figure 13. Effect of Conversion on Carbon Deposition
for the Catalysts Tested
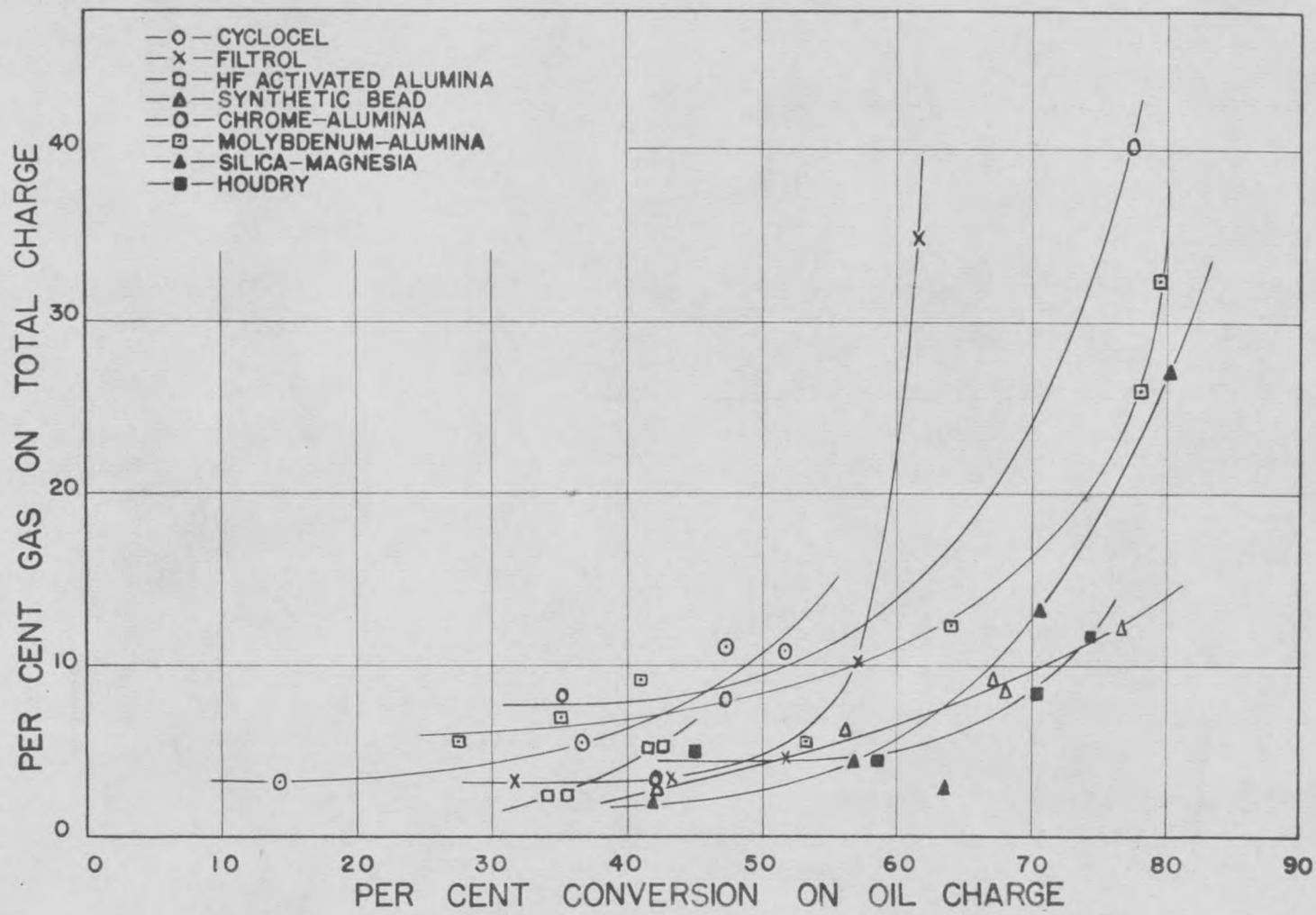
Figure 14.   Effect of Conversion on Gas Production
for the Catalysts Tested
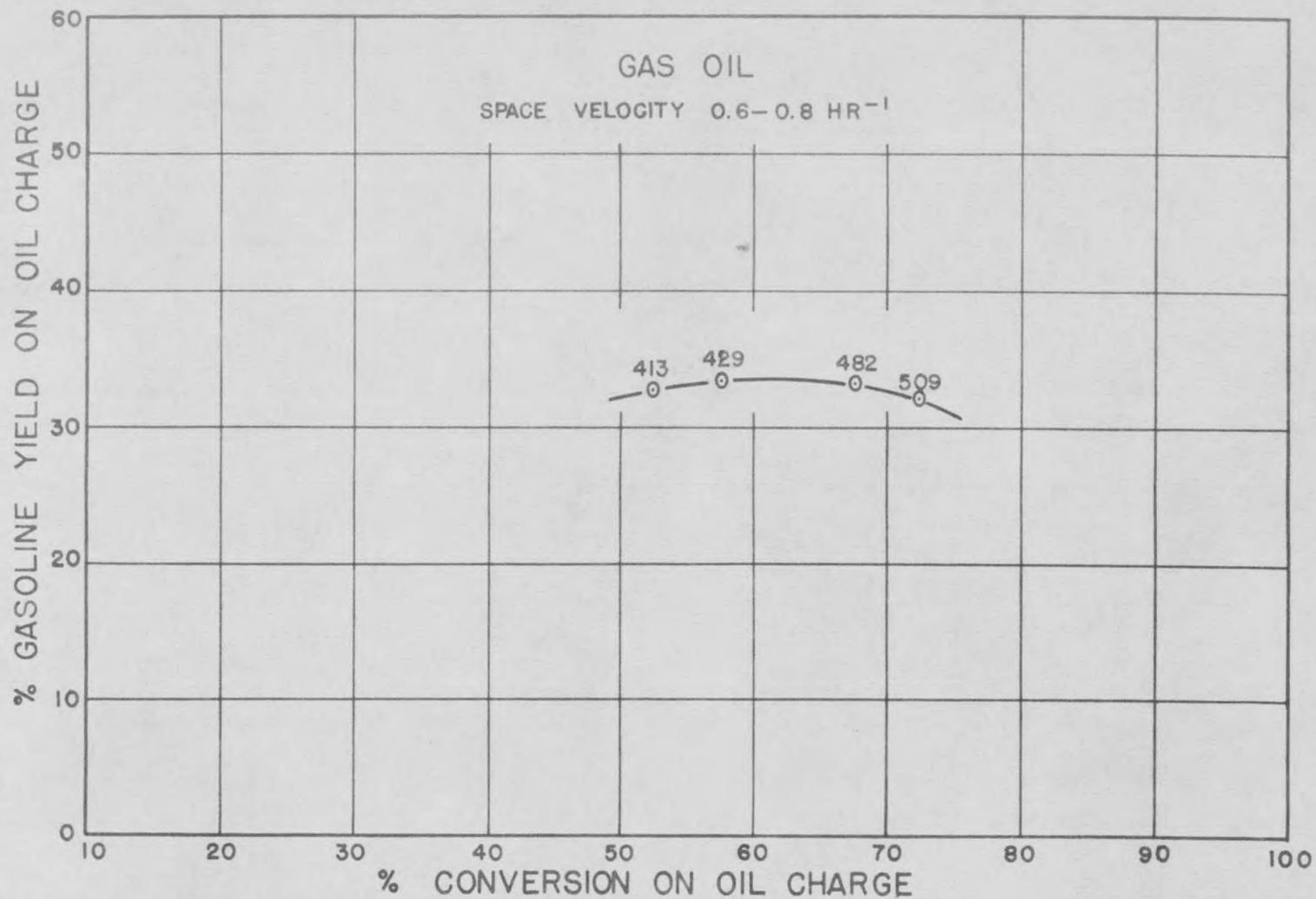
Figure 15. Effect of Conversion on the Gasoline Yield
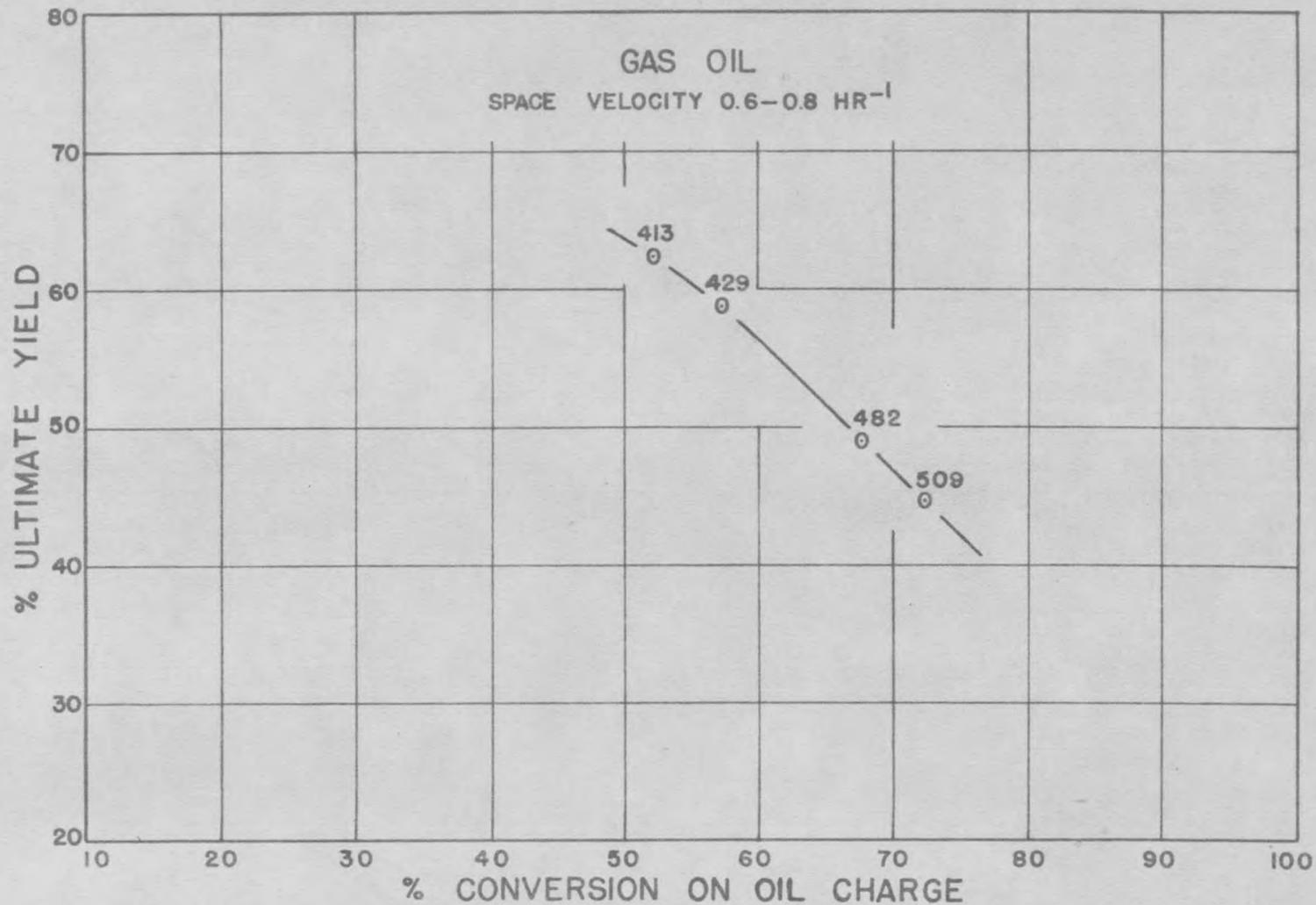for Catalytic Cracking with Houdry Catalyst

Figure 16. Effect of Conversion on the Ultimate Yield
for Catalytic Cracking with Houdry Catalyst