



Catalytic gas oil polyforming with propane, iso-butylene and butane
by Lewis G Mayfield

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering
Montana State University
© Copyright by Lewis G Mayfield (1949)

Abstract:

This investigation was conducted to evaluate the polyforming process under catalytic conditions as a method for producing motor fuel from a gas oil using propane, isobutylene and n-butane, respectively, as outside gases under 900 psig reaction pressure.

Houdry fixed-bed aluminum-silicate catalyst was used and the carbon burned from it at the conclusion of each run. Temperatures varied from 312° to 490°C.; liquid space velocities ranged from 0.54 to 0.94 and 3.7 to 5.7 hr⁻¹. During an average run 460 gm. of material were passed over the 1000 ml. of catalyst.

It was found that at low space velocities higher yields of gasoline were obtained from catalytic polyforming using isobutylene than from conventional catalytic cracking of gas oil. The increased yield of gasoline from isobutylene catalytic polyforming can be obtained at space velocities approximately ten times those of normal catalytic cracking. Carbon lay-down, however, exceeds that occurring in conventional, catalytic cracking at comparable oil conversions. No such effect in increasing gasoline yield was noted for propane catalytic polyforming.

Characteristics of n-butane catalytic polyforming are a reduction in amounts of carbon formed and increased yields of gasoline at approximately ten times the space velocities normally used for conventional catalytic-cracking.

CATALYTIC GAS OIL POLYFORMING WITH
PROPANE, ISO-BUTYLENE AND BUTANE

by

LEWIS G. MAYFIELD

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

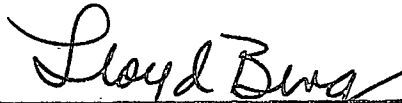
for the degree of

Master of Science in Chemical Engineering

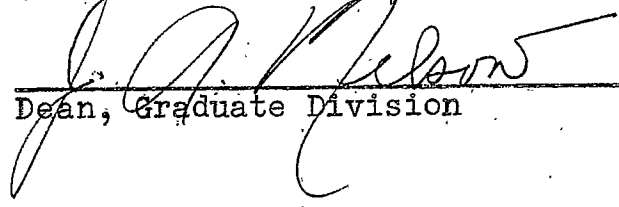
at

Montana State College

Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

Bozeman, Montana
September, 1949

RECEIVED
SEP 20 1949

N378

M 453c

Cap. 2

2

TABLE OF CONTENTS

	page
Abstract.	3
I Introduction	4
II Equipment, Methods and Materials	8
A. Equipment	8
B. Methods	14
C. Materials	18
III Sample Calculations.	19
IV Results.	23
V Conclusions.	29
VI Acknowledgment	31
VII Literature Cited	32
VIII Appendix	33

100898

ABSTRACT

This investigation was conducted to evaluate the polyforming process under catalytic conditions as a method for producing motor fuel from a gas oil using propane, isobutylene and n-butane, respectively, as outside gases under 900 psig reaction pressure.

Houdry fixed-bed aluminum-silicate catalyst was used and the carbon burned from it at the conclusion of each run. Temperatures varied from 312° to 490°C.; liquid space velocities ranged from 0.54 to 0.94 and 3.7 to 5.7 hr⁻¹. During an average run 460 gm. of material were passed over the 1000 ml. of catalyst.

It was found that at low space velocities higher yields of gasoline were obtained from catalytic polyforming using isobutylene than from conventional catalytic cracking of gas oil. The increased yield of gasoline from isobutylene catalytic polyforming can be obtained at space velocities approximately ten times those of normal catalytic cracking. Carbon lay-down, however, exceeds that occurring in conventional catalytic cracking at comparable oil conversions. No such effect in increasing gasoline yield was noted for propane catalytic polyforming.

Characteristics of n-butane catalytic polyforming are a reduction in amounts of carbon formed and increased yields of gasoline at approximately ten times the space velocities normally used for conventional catalytic cracking.

I. INTRODUCTION

The polyform process, according to Offutt et al (1), is an efficient means for producing high quality motor gasoline by 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 charge make possible a substantially greater degree of severity of cracking and a higher octane level of the gasoline product than it is possible to achieve in most other thermal cracking processes. At the same time the conditions of temperature and pressure are suitable for conversion of C_3 and C_4 hydrocarbons to gasoline. The propane and butane fractions recycled within the process are in many cases supplemented with extraneous refinery gas streams for additional yields of gasoline.

Conventional processes for thermal cracking of residual stocks and gas oils are usually carried out to give a maximum recycle yield of gasoline having a relatively low octane number; oil recycle ratios are high and a substantial amount of tar is produced. Gasoline obtained from thermally cracking a paraffin stock will have an octane number from 65 to 70 (A.S.T.M. Method) which is considerably lower than that desired for the blending of motor fuels for the competitive market of today.

Since the advent of commercial catalytic cracking of

petroleum to produce gasoline there has been much speculation concerning the reason for the high octane number of this material as a motor fuel in comparison with fuels produced by thermal cracking and those produced from the virgin crude by simple distillation. Bates et al (2) showed that this higher octane is due to the presence of a large excess of iso-paraffins over normal paraffins in the lower boiling fractions of the gasoline and to a high content of aromatic compounds in the higher boiling fractions. Olefin content of the catalytically cracked gasoline may vary over a wide range with varying conditions of cracking. It is known that optimum gasoline yields are obtained from Houdry fixed bed catalytic cracking at liquid space velocity of 0.5 volume of feed per volume of catalyst per hour.

Material and financial economies forced upon the gasoline industry during the war led oil refining companies to investigate and introduce new polyforming and gas reversion processes based upon utilization of propane and butanes available from the natural gasoline industries. These new methods aided materially in meeting the war-time demand for a cheaper, higher octane gasoline.

Offutt et al (1) reported that with increasing cracking severity the aromatic content of a polyform distillate from an East Texas naphtha increases with the octane number. It was also shown that a polyform gasoline had essentially the same

octane number at 300°F. (A.S.T.M. end point) as at 400°F. end point.

Advantages of the polyform process may easily be seen in the attractive yields of motor gasoline having A.S.T.M. octane numbers of 75 to 80 and research octane numbers of 84 to 93 (without the addition of tetraethyl lead) which are obtainable by this flexible process for the upgrading of naphthas and straight run gasoline (3). Furthermore, according to Offutt et al (4), refractory catalytic gas oils are readily converted to gasoline by the polyform process owing to the severity of cracking attainable, which, in turn, is made possible by a moderately high gas dilution. Those crude oil fractions which are least desirable as normal catalytic charging stocks are handled to advantage in the polyform process.

Ram Dev (5) showed that when catalytically cracking a gas oil in the presence of propane there was no effect upon gasoline yield below 300 pounds pressure but that at 600 pounds pressure a higher gasoline yield was indicated and at 900 psig a still higher gasoline yield was obtained. It was also pointed out that a higher yield of gasoline could be obtained in catalytic polyforming of gas oil conducted at 900 psig and 428°C., a temperature too low for thermal polyforming at the usual space velocities.

This greater yield of high octane gasoline obtained in catalytically polyforming a gas oil with propane (5) led the

author to investigate and evaluate the separate use of propane, isobutylene and n-butane in the process of catalytic polyforming. This was done in order that the catalytic polyform process, using these gases, might be better understood. The yields of gasoline and the octane numbers from the atmospheric catalytic cracking of the virgin gas oil were compared with those obtained at 900 pounds pressure with the admixed outside gas. An attempt was made to find maximum gasoline yield obtainable at 900 psig using temperature as the variable for each system. Four catalytic polyforming systems were compared with atmospheric catalytic cracking of gas oil at the following liquid space velocities (volume of feed per volume of catalyst per hour): Propane - 0.54 to 0.84; isobutylene - 0.43 to 0.94 and 3.7 to 5.7 and n-butane - 4.7 to 5.7.

II EQUIPMENT, METHODS AND MATERIALS

A. Equipment

The equipment used in this investigation consisted of a 0 to 1000 psig reaction system, shown in Figure 1, and a distillation system. The reaction system was divided into five major parts according to their function: (1) Feeding section, (2) reactor section, (3) condensing and receiving section, (4) gas section and (5) safety equipment.

FEEDING SECTION - The feeding section included a nitrogen cylinder, a feed cylinder and a Jerguson gauge. The feed cylinder consisted of an eight inch length of three-inch, extra strong steel pipe at each end of which were welded extra strong steel caps, drilled and tapped at both ends for one-half inch pipe. Short, one-half inch nipples and Kerotest globe valves were screwed into each cap. 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 two Kerotest globe valves, the top of the Jerguson and the pressure gauge on a nitrogen cylinder were interconnected by means of copper tubing and two tees. The glass at the back of the Jerguson was equipped with a semi-transparent rule behind which was placed a light to facilitate the reading of the scale.

The bottom of the Jerguson was connected with extra strong steel pipe to a one-half inch 6000 pound Vogt valve

for controlling the feed rate. The valve was connected to the top of the reactor through a tee and a 1000 pound union, the male half of which was welded directly to the reactor. The branch of the tee was fitted with a Black, Sivalls and Bryson frangible disc safety valve, equipped with an 1190 to 1210 psig diaphragm discharging to the outside of the building through a one-half inch pipe.

REACTOR SECTION - The reactor was made from a 15-inch length of three-inch extra strong steel pipe. 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. An one-eighth inch stainless steel screen to act as a catalyst support was inserted on top of the beveled end of the plate. A six-inch piece of extra strong pipe was inserted flush with the bevel of the plate and welded on the bottom side. The threaded lower end of this pipe was screwed into a tee, the branch being fitted to a 0 to 2000 pound pressure gauge and the run to an one-half inch 6000-pound Vogt valve for controlling pressure.

The top of the reactor was fabricated by welding the male half of an one-half inch union at the top center of an extra strong steel cap and by drilling an 11/16-inch hole through the cap, thus giving a smooth, continuous surface. This characteristic facilitated the charging of the Houdry catalyst and its preheater section consisting of 500 cc. of

assorted steel balls placed on the top of the catalyst. The cap was screwed and then arc welded to the reactor body in final assembly to prevent leakage.

Four thermocouple wells, made from four-inch lengths of 1/8-inch iron pipe sealed at one end by welding, were inserted through holes drilled at equidistant points along the length of the reactor and welded so that the sealed end of the well was located approximately at the center of the reactor. Into the wells were inserted iron-constantan wire thermocouples connected to a Leeds and Northrup indicating potentiometer, calibrated in degrees centigrade and indicating from 0° to 1100°C.

Supports for the reactor were made by welding two 1/2-inch low carbon steel rods to the reactor on the side opposite the thermowells. A brace to keep the reactor from turning was made by welding to the top of the cap, at approximately 90° to each other, two pieces of one-half by one-inch flat bar stock of sufficient length to enable fastening to the safety barricade by means of pins and brackets.

The reactor was wrapped carefully throughout its entire length with one-inch asbestos tape. The upper third was then wound with 50 feet of nichrome wire (resistance 1.70 ohms/ft.), threaded with porcelain fish-spine insulators. The lower two-thirds was wound similarly. These windings were covered with a thin layer of asbestos mud. Each of these windings was

connected to a 220-volt autotransformer, drawing 3 amperes. The lower and middle thirds of the reactor were then wound with two twelve-foot eight-inch nichrome windings, and covered with asbestos mud. These were connected to 110-volt autotransformers drawing a maximum of six volts. All of the nichrome wires were secured at both ends to a loop in a beaded wire which was fastened around the reactor. The length of the reactor was then covered with one-inch asbestos blocks cut to fit and the entire reactor covered with asbestos mud.

CONDENSING AND RECEIVING SYSTEM. - The bottom of the pressure control valve was connected to the top of a 300 mm. Pyrex glass Liebig condenser by means of a short piece of copper tubing inserted through a neoprene stopper. A piece of glass tubing was sealed to the bottom of the condenser in order to carry the vapors well into the rounded portion of a 500 ml. Hempel distillation flask which was used as a receiver. The rounded portion of the distillation flask was immersed in a dry ice-acetone bath contained in a one-gallon thermoflask. The side arm of the distillation flask was connected by rubber tubing to two vapor traps in series and in turn with two copper coil condensers in series. The vapor traps and copper coil condensers were immersed in dry ice-acetone baths contained in thermal flasks. The outlet of the second condenser was connected to a tee followed by a three-liter precision wet test meter. The other end of the tee was connected to a

200 cc. round bottom, stopcock-equipped, evacuated flask which was used to take a gas sample during the run. The outlet of the gas meter was connected to a blow-down line leading to the outside of the building.

The distillation equipment consisted of the Hempel distilling flask, a 300 mm. Liebig Pyrex glass condenser, an 100 cc. graduate and two vapor traps. The mouth of the distilling flask was fitted with a -10° to $250^{\circ}\text{C}.$ thermometer and neoprene stopper. The side arm of the flask was connected with a neoprene stopper to the Liebig condenser. A piece of glass tubing was sealed on the bottom of the condenser and bent in such a manner that the graduated cylinder, equipped with a two-hole stopper and used as a receiver, could be installed in a vertical position. The graduate was then connected to two vapor traps in series contained in a dry ice-acetone bath. The distillation flask was heated by a 110-volt 550-watt heater controlled by another autotransformer.

SAFETY EQUIPMENT - Safety equipment consisted of the afore-mentioned Black, Sivalls and Bryson frangible disc safety valve, a steel barricade and a carbon dioxide fire extinguisher. The barricade was made by mounting a piece of 1/4-inch steel plate 24 x 90 inches against the laboratory rack. A slit was cut in the plate so the reactor supports could be clamped to the laboratory rack. A piece of 1/8-inch steel plate, rolled in a semi-circle 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 1/2-inch angle iron was built upward from the center of the hinged section to support two thicknesses of automobile safety glass which would allow the operator of the feed control valve to view the Jerguson gauge with safety.

B. Methods

ATMOSPHERIC PRESSURE RUN - The feed cylinder was weighed on a 20 kg. capacity triple beam balance, charged with gas oil and reweighed. The reactor was heated until the thermocouples indicated that the temperature was sufficiently high for the reactor to average the desired temperature for the run. After opening the feed rate and pressure control valves, the system was flushed for a 10-minute period with nitrogen and the feed rate valve then closed. To the thermoflasks containing the acetone, dry ice was added until carbon dioxide was no longer evolved. The gas sample bottle was evacuated and attached to the system and the feed cylinder was placed in the system as shown in Figure 1, the top valve of the cylinder being opened to allow equalization of pressure in the feed section. The Jerguson gauge was filled with a portion of the charge by opening the bottom valve of the feed cylinder. A nitrogen pressure of about 100 pounds was then applied to the feed system. Timing of the run was begun when the operator opened the feed control valve. Feed rate was gauged by noting the time required for a given drop of the liquid level in the Jerguson and the necessary adjustment in the valve opening was made to obtain the desired rate. For low space velocity runs the rate was maintained as closely as possible to 2 linear centimeters or 10.6 cubic centimeters per minute. The Jerguson was refilled when necessary by opening the bottom valve of the

feed cylinder. The gas sample was taken toward the middle of the run by opening the stopcock of the evacuated gas sample bottle when the quantity of non-condensable gas produced was deemed sufficient to have purged the system of nitrogen. The stopcock was closed and the gas allowed to come to room temperature, balanced against atmospheric pressure and weighed. Room temperature and barometric pressure were noted. The density of the gas was calculated from this data.

Upon completion of the run the feed cylinder was removed from the system and weighed, the amount of oil charged thus being determined by difference. The receiving flask and vapor traps were taken out of the system, wiped dry of acetone and immediately weighed to determine the weight of the condensable product. The material in the vapor traps was then added to the distillation flask and the condensable product distilled to 210°C. end point. Volatile products not condensable by the Liebig condenser were collected in vapor traps in series with the graduated receiver. Weight of gasoline thus obtained was recorded.

Small amounts of oil remaining in the reactor after completion of the run were secured by evacuating the reactor through a series of vapor traps. Simultaneous blasting of the reactor with small amounts of nitrogen gas aided in driving the last traces of oil from the catalyst. The weight of this material was added to the weight of the residue obtained from

distillation since the amount was usually small and under these conditions was essentially free of gasoline.

CATALYST BURN-OFF - Continuous burn-off of the catalyst was accomplished by holding the unburned portion at approximately 400°C . and by passing metered air at a definite rate through the reactor. 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. At approximately fifteen minute intervals, per cents carbon dioxide, carbon monoxide and oxygen were determined by Orsat analysis in the effluent gas. The amount of air passed through the reactor and the time were also recorded. The amount of carbon lay-down was determined by plotting percentage compositions of the effluent gas versus time, as shown in the sample calculations.

SUPER ATMOSPHERIC RUNS - With the exception of the charge and the pressure at which the system was operated, these runs were conducted in a manner similar to the atmospheric runs.

The gas oil was charged to a cylinder of known weight and the cylinder reweighed to determine the amount of oil charge. A Cenco Megavac pump was then used to evacuate the air from the cylinder. A tank containing the liquified outside gas was connected by means of Saran tubing to the feed cylinder and tared on a scale. Both connecting valves were then opened and when the proper amount of gas had flowed into the cylinder, as

determined by the scale, the valves were closed. The actual amount of outside gas was determined by reweighing the cylinder on the scale without the attached tubing. The contents were mixed by shaking the feed cylinder for several minutes.

After flushing the system with nitrogen the feed cylinder was connected into the reaction system as previously described and nitrogen pressure applied to the feed section. The Jer-guson was then filled with the charge stock and the run started. The pressure control valve remained closed until the pressure gauge registered 900 pounds. The pressure control valve was then adjusted manually to maintain pressure in the system.

Control of the feed rate and handling of the products were the same as for the atmospheric runs. The end of the feeding period was indicated by a sharp pressure rise in the reactor section. The feed valve was immediately closed and the reactor bled to atmospheric pressure at approximately the same rate it had been pressurized.

Valves on the feed cylinder were closed and the pressure noted. The cylinder was removed from the system and the residual gas, containing nitrogen and the outside gas, was bled with a 34 liter tank. When using isobutylene as the outside gas, per cent composition of the gas was determined by adsorption in fuming sulphuric acid and the weight of the outside gas remaining in the cylinder determined, as shown in the sample calculations.

C. Materials

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

The propane, isobutylene and n-butane used as outside gases were of a commercial grade obtained from Phillips Petroleum Company.

III SAMPLE CALCULATIONS

Calculations of space velocity, weight of outside gas remaining in the cylinder at the end of the run, weight of permanent gases, carbon lay-down on the catalyst from burn-off analysis, over-all weight balance, yields of gasoline and conversion are presented for run Number 24 as typical of all runs made.

A. Calculation of Liquid Space Velocity:

Data:

Volume of catalyst in the reactor = 1000 ml.

Feeding time = 7.25 minutes

Weight of charge = 493 gm.

Density of charge = 0.80 gm/ml.

Volume of charge = $\frac{493}{.80} = 616$ ml.
$$\text{Space velocity} = \frac{616 \text{ ml.} \times 60 \text{ min.}}{7.25 \text{ min.} \times 1000 \text{ ml.}} = 5.1 \text{ hr}^{-1}$$

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

Data:

Volume of cylinder and Jerguson gauge = 1390 ml.

Final pressure = 1000 psia

Temperature = 20°C.

Volume per cent isobutylene (Orsat anal.) = 4.9%

$$\frac{1390}{1000} \times \frac{1000}{14.7} \times \frac{273}{293} \times \frac{.049}{22.4} \times 56 = 11 \text{ gm.}$$

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 / CO	CO ₂ / CO
5	10	8.4	1.2	0	8.0	1.0	0	91.0	8.7	19.0	0.78
15	22	11.6	6.6	0	10.5	5.0	0	84.0	20.6	15.5	3.20
45	53	12.0	8.0	0	11.8	7.4	0	80.8	52.0	19.2	10.00
80	60	12.0	8.2	0	12.0	8.1	0	79.9	59.5	20.1	12.00
110	50	11.8	8.4	0	11.9	8.4	0	79.7	49.6	20.3	10.05
157	79	11.8	8.4	0	11.8	8.5	0	79.7	78.4	20.3	15.90
180	38	11.2	9.2	0	11.6	8.7	0	79.7	37.7	20.3	7.66
225	80	10.0	8.8	0	11.3	8.7	0	80.0	79.2	20.0	14.84
245	23	10.6	8.8	0.6	10.6	8.8	0	80.6	22.6	19.4	4.39
260	28	8.4	6.6	4.0	9.7	8.1	3.3	78.9	28.1	17.8	4.99
275	25	6.4	3.0	10.4	8.4	5.1	7.8	78.7	25.2	13.5	3.40
290	22	1.8	0	17.0	4.2	1.6	13.0	81.2	21.5	5.8	1.25
										Total	88.46

20

$$\text{Weight of carbon} = \frac{88.46 \times 636 \times 273 \times 12}{22.4 \times 760 \times 295} = 36.9$$

D. Calculation of Weight of Permanent Gases:

Data:

Volume of uncondensable gases = 16.0 liters

Volume of gas sample bottle = 208.2 ml.

Barometric pressure = 631 mm. Hg.

Room Temperature = 21°C.

Temperature at which gas was measured = 21°C.

Weight of bottle and gas = 124.3806 gm.

Weight of bottle evacuated = 124.1727 gm.

Weight of gas sample by difference = .2079 gm.

Weight of 1 liter of gas at 21°C. and 631 mm.Hg.

$$\frac{.2079 \times 1000}{208.2} = .999 \text{ gm/liter}$$

Weight of permanent gases = 16.0 x .999 = 16 gm.

E. Calculation of an Over-all Weight Balance:

Data:

Weight of cylinder and charge stock = 11.017 Kg.

Weight of cylinder after run
(atmospheric pressure = 10.513 Kg.

Weight of isobutylene remaining
in cylinder = 11 gm.

Weight of material charged = 493 gm.

Recovered material:

Hydrocarbon liquid product
from first condenser = 275.3 gm.

Hydrocarbon liquid product
from vapor traps = 158.8 gm.

Permanent gases = 16.0 gm.
 Oil from catalyst bed = 9.0 gm.
 Carbon from burn-off = 36.9 gm.
 Total weight recovered = 496.0 gm.

Weight of charge lost by difference = + 3.0 gm.

Per cent of charge lost = $\frac{3}{493} \times 100 = +.61\%$

F. Calculation of Per Cent Gasoline Yield:

Data:

Gasoline from distillation = 107.6 gm.

Gas oil charged = 286 gm.

Per cent gasoline on oil charge = $\frac{107.6}{286} \times 100 = 37.6\%$

G. Calculation of Per Cent Conversion:

Data:

Residue from distillation = 169.5 gm.

Oil from catalyst bed = 9.0 gm.

Total residue = 178.5 gm.

Per cent conversion on oil charge =

$$100 - \frac{178.5}{286} \times 100 = 41.1\%$$

H. Calculation of Per Cent Ultimate Yield:

Data:

Per cent gasoline on oil charge = 37.6%

Per cent conversion on oil charge = 41.1%

Per cent ultimate yield = $\frac{37.6}{41.1} \times 100 = 91.5\%$

IV RESULTS

Runs 1, 2, 3 and 4 in Table I present the catalytic cracking of gas oil with a Houdry synthetic aluminum-silicate catalyst. Four atmospheric runs were made at temperatures varying from 358° to $466^{\circ}\text{C}.$; space velocity was held between 0.63 and 0.70 volumes of feed per volume of catalyst per hour.

A plot of per cent gasoline yield as a function of per cent conversion is shown in Figure 3. The curve shows the maximum yield of gasoline as 36.5 per cent while the conversion is 52 per cent at temperatures between 375° and $400^{\circ}\text{C}.$ A plot of the theoretical figure, per cent ultimate yield as a function of per cent conversion, shows that a maximum ultimate yield of gasoline was not obtained. Per cent ultimate yield is calculated by assuming that all of the material boiling above the gasoline range would, upon recycling, yield the same conversion. However, this is not strictly the case since the material becomes more refractory with each successive pass. It is seen, then, that with very small conversion the theoretical ultimate yield of gasoline approaches 100 per cent. These yields compare very favorably with general knowledge concerning catalytic cracking.

Runs 5 to 12 in Table I present the catalytic cracking of gas oil at 900 pounds pressure in the presence of propane. Eight runs were made at liquid space velocities between 0.54 and 0.84 volumes of feed per volume of catalyst and at

temperatures ranging from 312° to 457°C . A plot of per cent gasoline as a function of per cent conversion is shown in Figure 4. The curve shows the maximum yield of gasoline as 32.6 per cent at 55 per cent conversion. The gasoline yield, then, was slightly less than for atmospheric cracking but a greater conversion was obtained at lower temperatures. It is generally accepted that with small scale equipment higher temperatures are very hard to control and may fluctuate quite rapidly. As a result, temperatures taken at intervals may not always indicate true average temperatures. For that reason the same conversions are shown at 380° and 410°C . The curve showing per cent ultimate yield of gasoline versus per cent conversion is also slightly lower than for the atmospheric curve.

Runs 13 to 20 in Table II present the catalytic cracking of gas oil at 900 pounds pressure in the presence of isobutylene. Nine runs were made at temperatures from 345° to 472°C . and at space velocities held between 0.43 and 0.94 volumes of liquid feed per volume of catalyst. Curves presented in Figure 5 show a maximum yield of gasoline of 44.1 per cent at a conversion of 72 per cent. The high ultimate yield of gasoline obtained at the lower conversions is undoubtedly due to polymerization of the isobutylene at those temperatures. While an average temperature of 358°C . produced a conversion of 40 per cent in the atmospheric runs, isobutylene, as the

outside gas at approximately the same space velocities and temperature, gave only a 27 per cent conversion of the gas oil, thereby indicating that polymerization of the isobutylene to a material boiling higher than gasoline was also taking place and suppressing the conversion based on the gas oil charged. Thomas (6) found that a normally gaseous mixture of isobutylene, butene and butane would polymerize at 175°C. and 645 pounds pressure when passed over an aluminum-silicate catalyst. Comparison of gasoline yields from Figure 3 and Figure 5 at 65 per cent conversion shows that catalytically polyformed gasoline yields are 16 per cent higher and that the ultimate yield is 19 per cent higher than those at atmospheric conditions.

Runs 21 to 27 in Table III present the catalytic cracking of gas oil at 900 pounds pressure in the presence of isobutylene and with space velocities between 3.7 and 5.7 volumes of liquid feed per volume of catalyst. Seven runs were made at temperatures from 328° to 472°C. Curves presented in Figure 6 show that at these space velocities the gasoline yields obtained between 13.6 and 75.3 per cents conversion are 38 per cent. Ultimate yield of gasoline at 13.6 per cent conversion was 278 per cent. Apparently at these space velocities and at the low conversions, polymerization was taking place at a much faster rate than cracking of the same polymerized molecules. As the temperature was increased the

amount of gasoline produced by cracking of the gas oil increased, but the amount formed by polymerization decreased by the same amount. Further elevation of the temperature to 481°C. did not change the per cent gasoline formed.

Runs 28 and 29 in Table III were made under conditions similar to those of the isobutylene catalytic polyforming runs made at high space velocities. In Run 28 n-butane was used in place of gas oil; in Run 29 isobutylene alone was charged. These runs show conclusively that polymerization to a material boiling in the gasoline range and higher will occur under the catalytic polyforming conditions used in this investigation.

Runs 30 to 36 in Table IV present the catalytic cracking of gas oil at 900 pounds pressure in the presence of n-butane and at space velocities from 4.7 to 5.6 volumes of feed per volume of catalyst per hour. Seven runs were made at temperatures from 366° to 480°C. Curves presented in Figure 7 indicate a 35 per cent yield of gasoline and an 80 per cent ultimate yield of gasoline at 40 per cent conversion. Although the curve levels off at 52 per cent yield and 72 per cent conversion, a maximum yield of gasoline was not obtained. Difficulties were encountered in the separation of the butane from the gasoline because of the presence of larger amounts of material boiling at the lower gasoline range. However the separation was made by allowing the distillation flask

to attain room temperature and by condensing the vapors produced in cold traps which were then placed in a wet ice bath and the material allowed to evaporate until no further evolution of gas was perceived. The remaining material was then said to be gasoline.

The large percentage of carbon lay-down in the catalytic polyforming runs using isobutylene as the outside gas was not affected materially by space velocity, as shown in Figure 6. Per cent carbon lay-down was considerably higher at a given conversion than in atmospheric catalytic cracking. When using propane as the outside gas carbon formation was slightly less than in atmospheric cracking runs at conversions below 47 per cent. Comparison of the two curves at higher conversion indicates that the percentage of carbon lay-down was greater when propane was the outside gas used. Figure 8 also indicates that, at given conversions, carbon lay-down is less when the gas oil is cracked in the presence of n-butane than in atmospheric catalytic cracking runs.

Octane numbers are presented in Table VII together with the average temperatures and space velocities of the runs from which the samples were obtained. Polymerization of isobutylene at low temperatures is again indicated by the high octane number of that sample. Further study of Table VII and Table VI Inspection Data, indicates that catalytic polyforming of the gas oil does materially affect the octane

number of the polyform distillate.

Plans were made to replace the catalyst when a positive lessening of its activity was detected; however, over a period of 42 runs, 12.7 liters of gas oil and 11.9 liters of propane, isobutylene and n-butane were passed over the 1000 ml. of catalyst in both atmospheric and high pressure runs and no loss of activity was observed. The condition of the catalyst was considered such that its use was continued exclusively in shale oil catalytic polyforming work. Rapid loss of catalyst activity is not to be expected in the catalytic polyforming of gas oil if care is taken during burn-off periods to maintain a catalyst temperature not exceeding 600°C.

V CONCLUSIONS

The following conclusions may be drawn from the results found in this investigation:

1. Houdry synthetic aluminum-silicate fixed bed catalyst is a satisfactory agent for petroleum gas oil catalytic polyforming.
2. There was no detectable loss in catalyst activity after the passage of 34.6 volumes of feed per volume of catalyst at atmospheric and at 900 pounds pressure.
3. Atmospheric catalytic cracking of gas oil gives a definite increase in gasoline yield on oil charge over that obtainable from catalytic polyforming with propane at 900 pounds pressure.
4. Isobutylene catalytic polyforming gives a positive increase in the gasoline yield over conventional catalytic cracking at the same space velocities and at space velocities approximately ten times those used in normal petroleum cracking.
5. Carbon formation in isobutylene catalytic polyforming is noticeably greater than in conventional catalytic cracking.
6. n-Butane catalytic polyforming at 900 pounds pressure gives a definite increase in gasoline yield over that obtainable from atmospheric catalytic cracking.

7. Carbon formation based on total charge is markedly less in n-butane catalytic polyforming at 900 pounds pressure than in atmospheric catalytic cracking.

VI. ACKNOWLEDGMENT

The author acknowledges with thanks the courtesy of Phillips Petroleum Company who furnished the virgin gas oil and the outside gases used in this investigation.

He further acknowledges the courtesy of Phillips Petroleum Company who made the octane-number and other laboratory determinations on the gasoline samples and sponsored the fellowship under which the work was carried out.

VII LITERATURE CITED

- (1) Offutt, W. C., Fogle, M. C. and Beuther, H., Polyform Distillate, IND. ENG. CHEM., 41, 417-23 (1949)
- (2) Bates, J. R., Rose, F. W., Jr., Kurtz, S. S., Jr. and Mills, I. W., Composition of Catalytically Cracked Gasoline, IND. ENG. CHEM., 34, 147-52 (1942).
- (3) Offutt, W. C., Ostergaard, P., Fogle, M. C. and Beuther, H., Naphtha Polyforming, Oil Gas J., 45, No. 27, 180-8 (1946). (C.A., 41, 851)
- (4) Offutt, W. C., Ostergaard, P., Fogle M. C. and Beuther, H. Gas Oil Polyforming, Oil Gas J., 46, No. 21, 80-9 (1947). (C.A., 41, 7714).
- (5) Dev, Ram. M. S. Thesis, Montana State College. (1948).
- (6) Thomas, C. L., Reactions of Hydrocarbons in the Presence of Cracking Catalysts, IND. ENG. CHEM., 37, 543-5 (1945).

VIII APPENDIX

	page
Table I - Catalytic Cracking and Propane Catalytic Polyforming of Gas Oil	34
Table II - Isobutylene Catalytic Polyforming at Low Space Velocities.	35
Table III - Isobutylene Catalytic Polyforming at High Space Velocities.	36
Table IV - n-Butane Catalytic Polyforming at High Space Velocities.	37
Table V - Gas Oil Inspection Data	38
Table VI - Gasoline Inspection Data.	39
Table VII - Effect of Catalytic Polyforming upon Octane Numbers	40
Figure 1 - Schematic Diagram of Equipment	41
Figure 2 - Composition of Effluent Gas During Catalyst Burn-off.	42
Figure 3 - Effect of Conversion on Gasoline Yield at Atmospheric Pressure.	43
Figure 4 - Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas Propane	44
Figure 5 - Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas Isobutylene, Low Space Velocities.	45
Figure 6 - Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas Isobutylene, High Space Velocities.	46
Figure 7 - Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas n-Butane, High Space Velocities.	47
Figure 8 - Effect of Conversion on Carbon Lay-down at Indicated Outside Gases and Space Velocities.	48

TABLE I

CATALYTIC CRACKING AND PROPANE CATALYTIC POLYFORMING OF GAS OIL

Run No.	1	2	3	4	5	6	7	8	9	10	11	12
No. Runs on Catalyst	1	9	10	11	3	4	2	3	4	6	7	8
Ave. Reactor Temp. °C.	466	395	375	358	457	451	410	380	368	367	344	312
Oper. Press. psig	0	0	0	0	900							
Space Velocity hr ⁻¹	0.64	0.70	0.68	0.63	0.67	0.60	0.84	0.54	0.74	0.68	0.67	0.67
Material Charged												
Outside Gas		None				Propane						
Outside Gas, gm.						124	143	142	120	165	164	156
Charge Stock, gm.	287	282	297	289		257	249	261	255	284	285	279
Total Charge	287	282	297	289		381	392	403	375	449	449	435
Recovered Material												
H. C. Liqd. Prod.	191.5	242.4	243.7	216.1	229.9	192.7	253.5	251.6	301.7	280.5	273.0	215.9
Condensable Gases	33.0	5.0	3.8	1.6	28.0	107.4	76.0	56.7	50.7	102.1	76.0	120.5
Permanent Gases	23.4	3.5	1.0	1.6	101.5	54.7	50.0	6.0	7.0	10.8	8.0	9.0
Oil from Cat. Bed	3.0	8.7	36.4	59.5	4.3	5.0	8.0	8.7	7.4	20.0	54.1	92.7
Carbon by Burn-off		12.8	6.4	11.5	6.4	29.2	6.5	26.5	24.2	17.2	9.9	6.0
Total Recovered	250.9	272.4	291.3	290.3	370.1	389.0	394.0	349.5	391.0	430.6	421.0	444.1
Losses by Difference, gm.		9.6	5.7	1.3	9.9	4.0	9.0	25.5	58.0	19.6	14.0	7.9
% Losses on Charge		3.4	1.92	0.45	2.52	1.02	2.23	6.8	12.9	4.37	3.22	1.75
Wt. of Gasoline	76.0	97.3	115.1	85.7	49.0	47.3	74.2	98.8	92.7	80.1	82.9	53.5
Wt. of Residue	94.5	124.1	140.9	173.8	60.0	78.5	107.3	101.5	118.8	132.6	151.1	205.3
% Carbon on Total Chg.		4.54	2.15	3.98	1.68	7.45	1.62	7.06	5.40	3.84	2.28	1.33
% Gasoline on Oil Chg.	26.4	34.5	38.4	29.7	19.0	19.0	28.5	38.7	32.6	28.1	29.7	18.7
% Conversion on Oil Chg.	67.2	56.0	52.4	40.0	76.7	68.6	58.8	60.1	58.3	53.5	45.6	28.5
% Ultimate Yield	39.3	61.7	73.4	74.5	24.8	27.7	48.5	64.0	56.0	52.5	65.0	65.5

TABLE II

ISOBUTYLENE CATALYTIC POLYFORMING AT LOW SPACE VELOCITIES

Run No.	13	14	15	16	17	18	19	20
No. Runs on Catalyst	12	13	15	16	17	18	19	20
Ave. Reactor Temp. °C.	382	361	345	404	427	449	472	411
Oper. Press. psig	900							
Space Velocity hr ⁻¹	0.43	0.63	0.64	0.63	0.68	0.64	0.57	0.94
Material Charged								
Outside Gas	Isobutylene							
Outside Gas, gm.	199	214	161	203	197	177	206	199
Charge Stock, gm.	290	289	292	291	293	287	288	292
Total Charge, gm.	489	503	453	494	490	464	494	491
Recovered Material, gm.								
H. C. Liqd. Prod.	294.2	349.5	289.1	310.2	275.6	216.7	210.6	305.6
Condensable Gases	76.5	64.0	41.8	85.4	114.5	135.5	137.8	100.8
Permanent Gases	13.6	10.6	6.9	18.1	28.1	29.4	40.5	19.1
Oil from Cat. Bed	46.0	34.2	73.6	17.0	9.5	6.3	5.8	11.3
Carbon by Burn-off	46.6	32.4	23.5	48.5	65.8	65.0	93.5	51.8
Total Recovered	476.9	490.7	434.9	479.2	493.5	452.9	488.2	488.6
Losses by Difference, gm.	12.1	12.3	18.1	14.8	+3.5	11.1	5.8	2.4
% Losses on Charge	2.48	2.43	4.0	3.0	0.71	2.4	1.17	0.49
Wt. of Gasoline, gm.	107.5	86.6	80.5	127.1	130.0	129.6	117.6	128.3
Wt. of Residue, gm.	149.7	211.0	220.7	107.3	75.0	36.3	35.0	101.8
% Carbon on Total Chg.	9.54	6.45	5.19	9.85	13.4	14.0	18.9	10.5
% Gasoline on Oil Chg.	37.0	30.0	27.6	43.7	44.3	45.1	40.7	44.0
% Conversion on Oil Chg.	48.5	27.0	24.5	63.0	74.4	87.3	87.8	65.2
% Ultimate Yield	75.3	111.0	112.0	69.5	59.7	51.6	46.4	67.5

TABLE III

ISOBUTYLENE CATALYTIC POLYFORMING AT HIGH SPACE VELOCITIES

Run No.	21	22	23	24	25	26	27	28	29
No. Runs on Catalyst	22	23	24	27	29	30	31	32	33
Ave. Reactor Temp. °C.	464	481	458	396	370	351	328	325	387
Oper. Press. psig	900								
Space Velocity hr ⁻¹	3.82	5.0	3.70	5.1	5.35	4.7	5.7	7.6	6.2
Material Charged									
Outside Gas	Isobutylene								
Outside Gas, gm.	190	195	173	207	219	201	227	203	426
Charge Stock, gm.	293.0	289	294	286	290	287	300	(303)*	---
Total Charge, gm.	483	484	467	493	509	488	527	506	426
Recovered Material, gm.									
H. C. Liqd. Prod.	205.3	156.2	209.0	275.3	294.9	301.2	324.9	196.3	167.2
Condensable Gases	182.1	202.7	182.0	158.8	156.9	122.6	132.3	275.2	187.9
Permanent Gases	32.0	45.1	20.8	16.0	14.0	10.5	10.5	20.0	33.0
Oil from Cat. Bed	3.0	2.6	1.1	90.0	15.5	40.0	42.0	5.1	1.9
Carbon by Burn-off	59.0	74.5	56.5	36.9	30.7	23.0	16.3	15.5	45.4
Total Recovered	481.4	481.1	469.4	496.0	512.0	507.3	526.0	512.1	435.4
Losses by Difference, gm.	1.6	2.9	+2.4	+3.0	+3.0	+19.0	1.0	+6.1	+9.4
% Losses on Charge	0.35	0.60	0.51	0.61	0.61	3.9	.20	1.2	2.2
Wt. of Gasoline, gm.	110.8	111.0	111.8	107.6	114.4	105.1	113.5	68.5	108.5
Wt. of Residue, gm.	82.9	71.6	100.3	169.5	203.2	227.8	259.1	19.0	12.1
% Carbon on Total Chg.	12.2	15.4	12.1	7.5	6.0	4.7	3.1	3.1	10.5
% Gasoline on Oil Chg.	37.7	38.4	38.0	37.6	39.4	36.7	37.8	33.7	25.4
% Conversion on Oil Chg.	71.8	75.3	64.7	41.1	30.0	20.6	13.6		
% Ultimate Yield	52.5	51.0	58.7	91.5	131	178	278		

* n-Butane

TABLE IV

n-BUTANE CATALYTIC POLYFORMING AT HIGH SPACE VELOCITIES

Run No.	30	31	32	33	34	35	36
No. Runs on Catalyst	34	35	37	39	40	41	42
Ave. Reactor Temp. °C.	429	375	455	480	480	411	366
Oper. Press. psig	900						
Space Velocity hr ⁻¹	5.0	5.0	4.7	4.75	5.65	5.0	4.8
Material Charged							
Outside Gas	n-Butane						
Outside Gas, gm.	196	194	165	169	174	160	167
Charge Stock, gm.	279	287	270	265	272	277	267
Total Charge, gm.	475	481	435	434	446	437	434
Recovered Material, gm.							
H. C. Liqd. Prod.	245.7	298.4	218.1	177.7	179.3	262.6	280.7
Condensable Gases	206.3	160.5	185.6	204.1	210.1	148.5	130.6
Permanent Gases	16.0	9.8	16.0	31.4	25.2	8.1	7.5
Oil from Cat. Bed	2.6	10.7	2.9	2.3	1.4	6.0	5.7
Carbon by Burn-off	13.5	9.1	16.0	18.0	32.6	6.9	11.4
Total Recovered	484.1	488.5	433.6	433.5	448.6	432.1	435.9
Losses by Difference, gm.	-9.1	-7.5	1.4	0.5	-2.6	4.9	1.9
% Losses on Charge	1.9	1.6	0.32	0.11	0.58	1.12	0.44
Wt. of Gasoline, gm.	136.3	100.6	135.5	140.8	141.7	123.8	91.4
Wt. of Residue, gm.	122.3	175.0	101.1	74.3	75.1	133.3	158.6
% Carbon on Total Chg.	2.85	1.89	3.68	4.15	7.30	1.58	2.63
% Gasoline on Oil Chg.	48.5	35.0	51.0	53.0	52.0	44.6	34.2
% Conversion on Oil Chg.	56.1	39.0	62.5	72.0	72.4	51.8	40.5
% Ultimate Yield	86.5	89.7	81.6	73.6	71.8	86.1	84.3

TABLE V

GAS OIL INSPECTION DATA

(Topped 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

TABLE VI

GASOLINE INSPECTION DATA

A.S.T.M. Distillation, °F.

Runs	1-4	5-6	18-19	23-25	27-29	30-31	33-34
First Drop	94	94	96	126	129	108	99
5% cond. 760 mm.	122	117	112	163	158	135	117
10%	138	132	121	174	174	151	126
20%	168	153	135	202	195	174	137
30%	196	175	149	214	217	196	152
40%	229	200	168	228	237	222	171
50%	260	229	195	238	257	246	198
60%	294	260	230	248	276	271	232
70%	329	290	263	262	298	295	266
80%	366	326	295	290	321	322	299
90%	412	373	330	333	349	351	337
95%	449	415	355	361	368	370	363
End Point	545	463	398	394	398	401	393
Recovery, %	98	97.8	98.3	98.0	98.7	98.6	98.7
Residue, %	1.3	1.2	0.5	0.9	0.7	0.6	0.5
Gravity, A.P.I.	57.1	56.6	62.3	60.6	56.6	56.6	62.0

TABLE VII

Effect of Catalytic Polyforming upon Octane Number

Outside Gas	Runs	Cracking Temp. (Ave.)	Space Velocity (ave.)	A.S.T.M. Octane No.	Research Octane No.
None	1-4	376	.67	---	66.7
Propane	5-6	454	.65	71.5	77.7
Isobutylene	18-19	459	.60	79.6	86.4
Isobutylene	23-25	473	3.73	79.3	89.2
Isobutylene	27-29	349	5.3	81.4	92.7
Butane	30-31	401	5.0	74.5	80.3
Butane	33-34	480	5.20	79.0	86.6

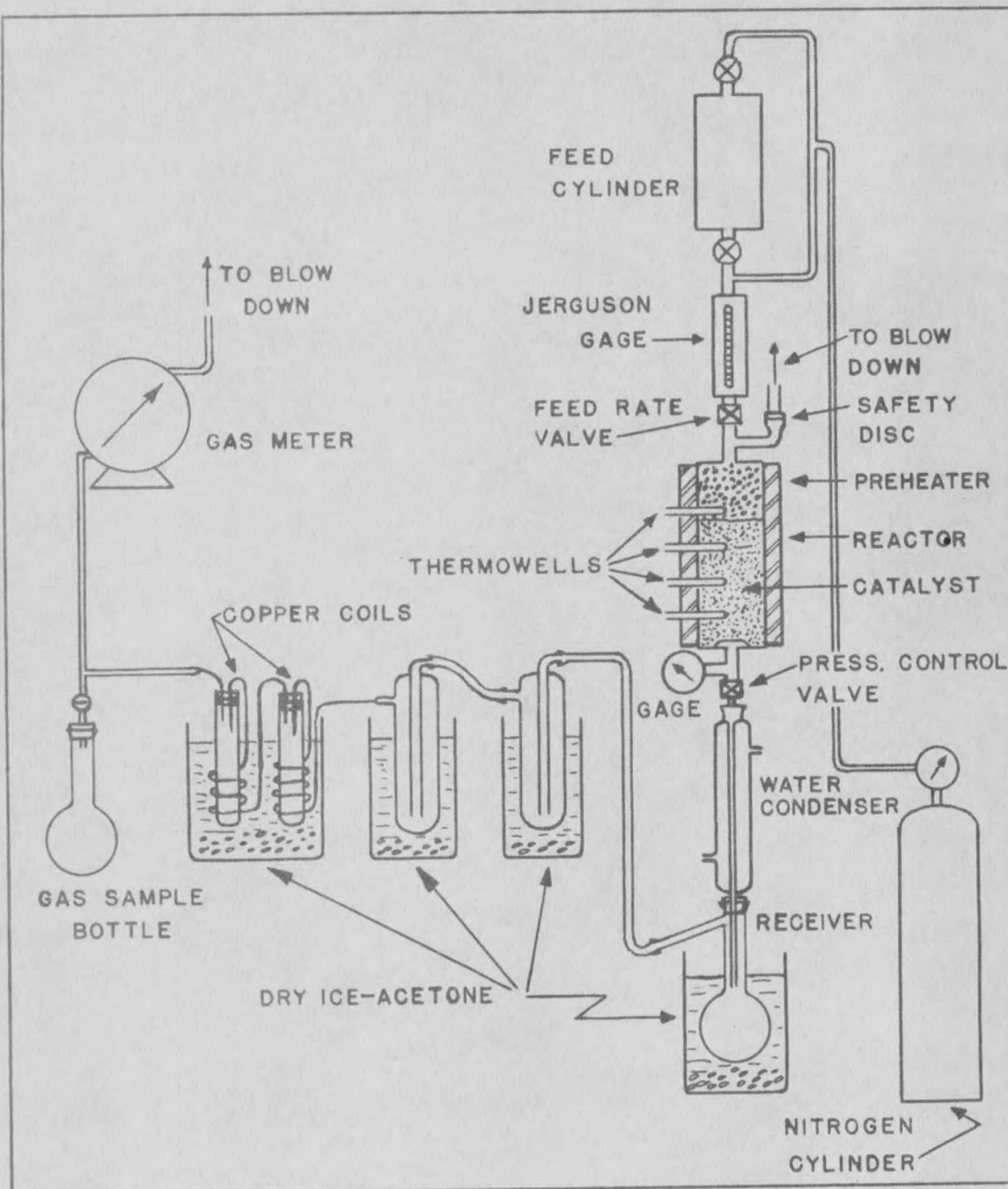


Figure 1
Schematic Diagram of Equipment

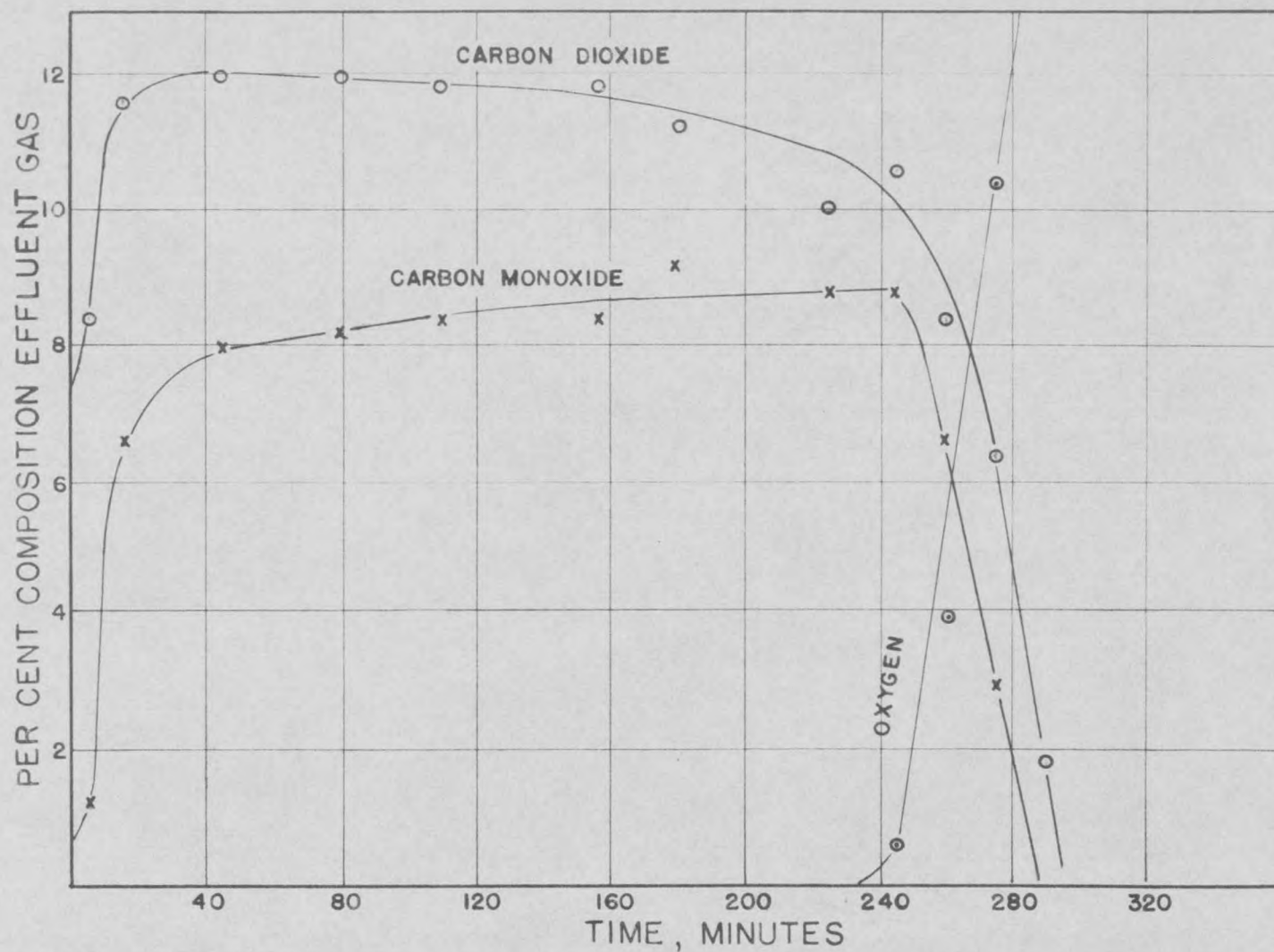


Figure 2. Composition of Effluent Gas During Catalyst Burn-off

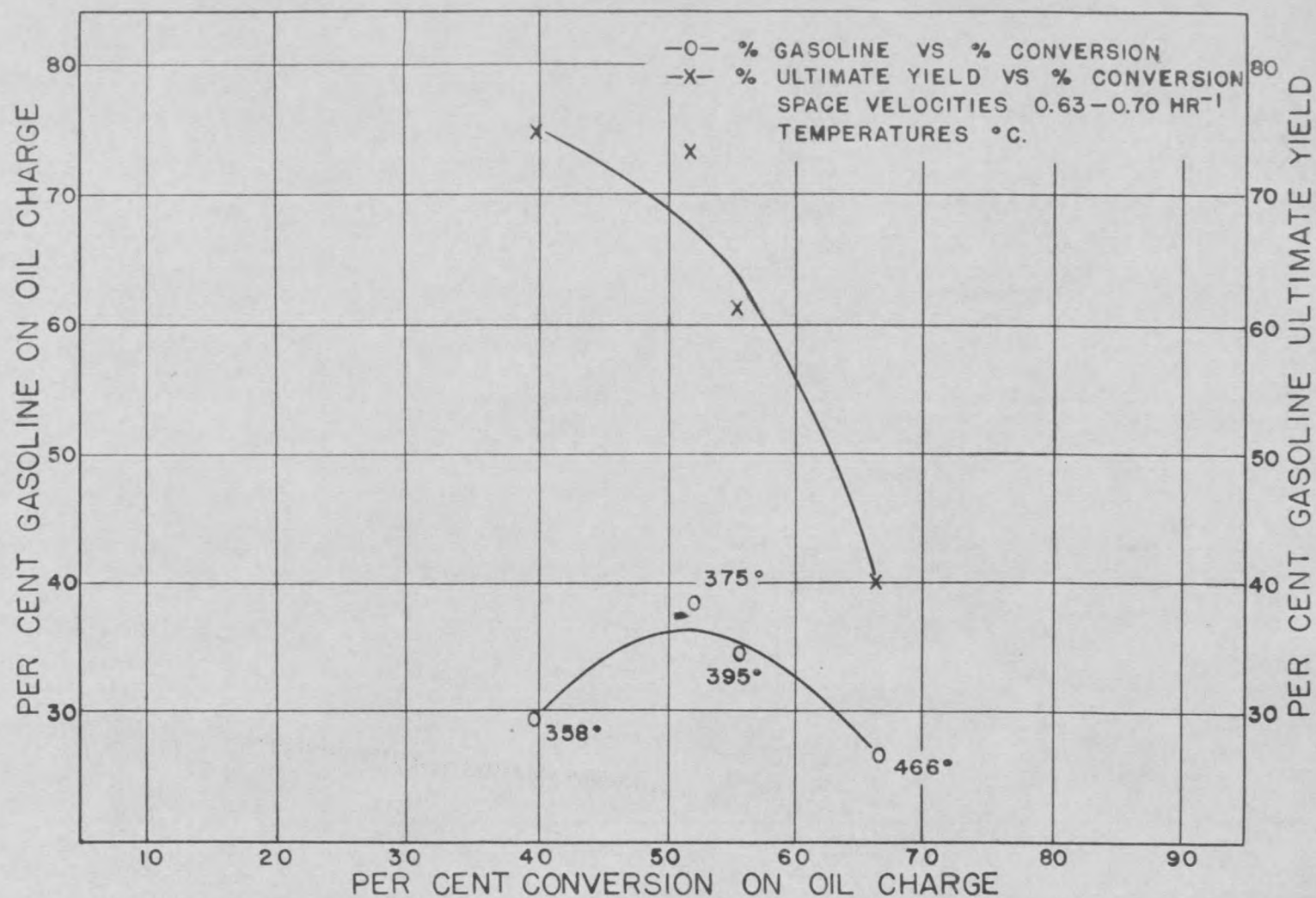


Figure 3. Effect of Conversion on Gasoline Yield at Atmospheric Pressure

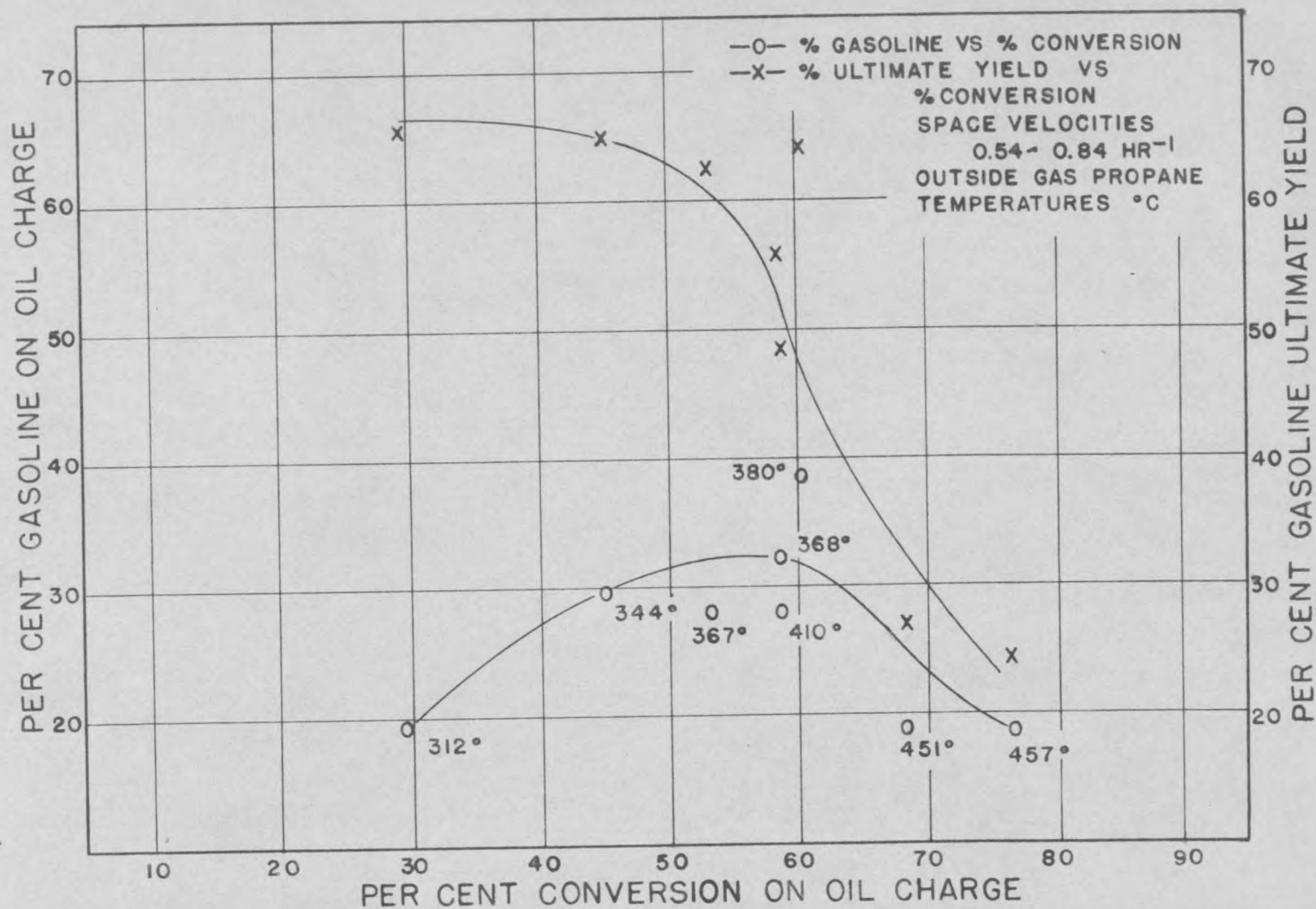


Figure 4. Effect of Conversion on Gasoline Yield
 at 900 psig, Outside Gas Propane

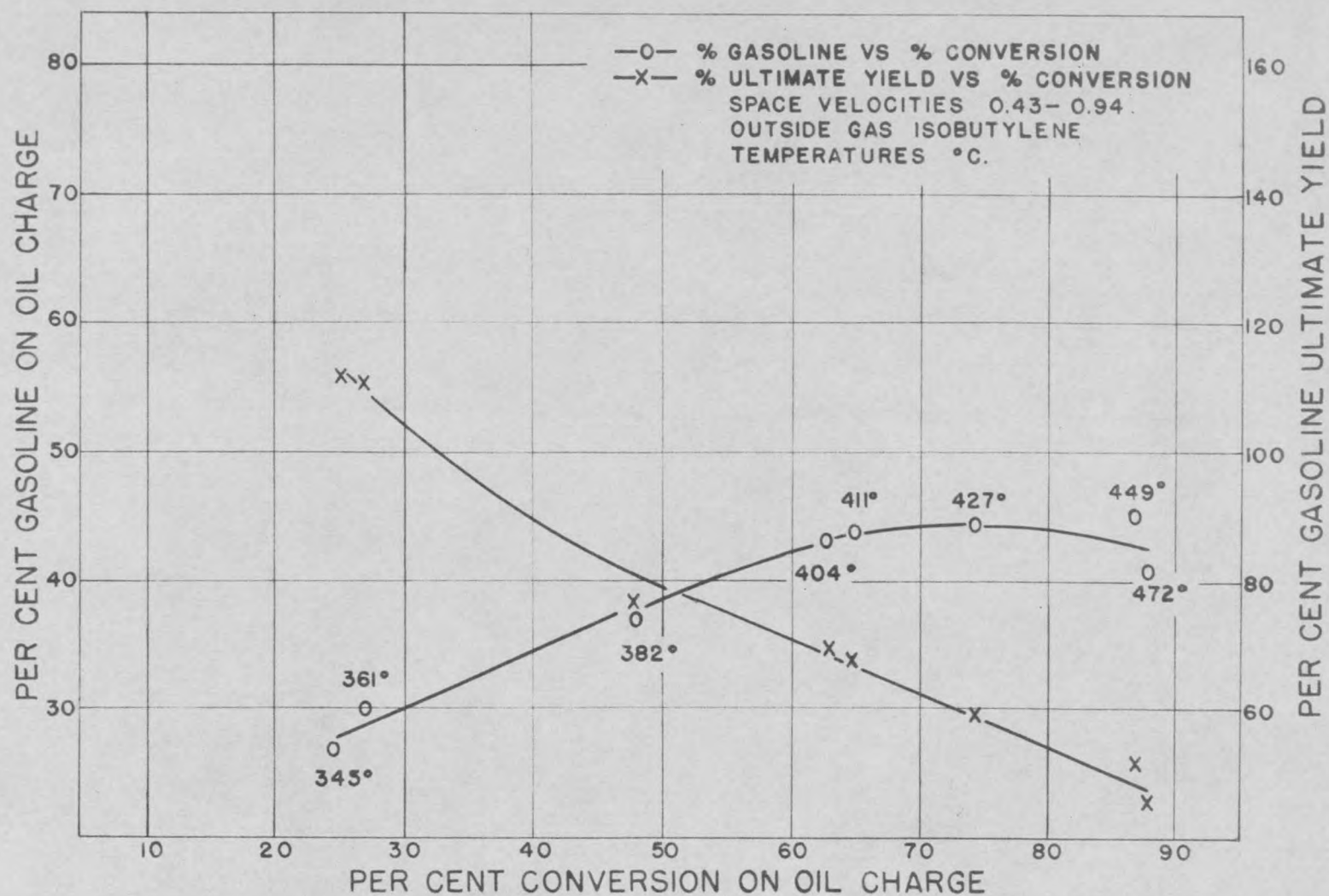


Figure 5. Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas Isobutylene, Low Space Velocities

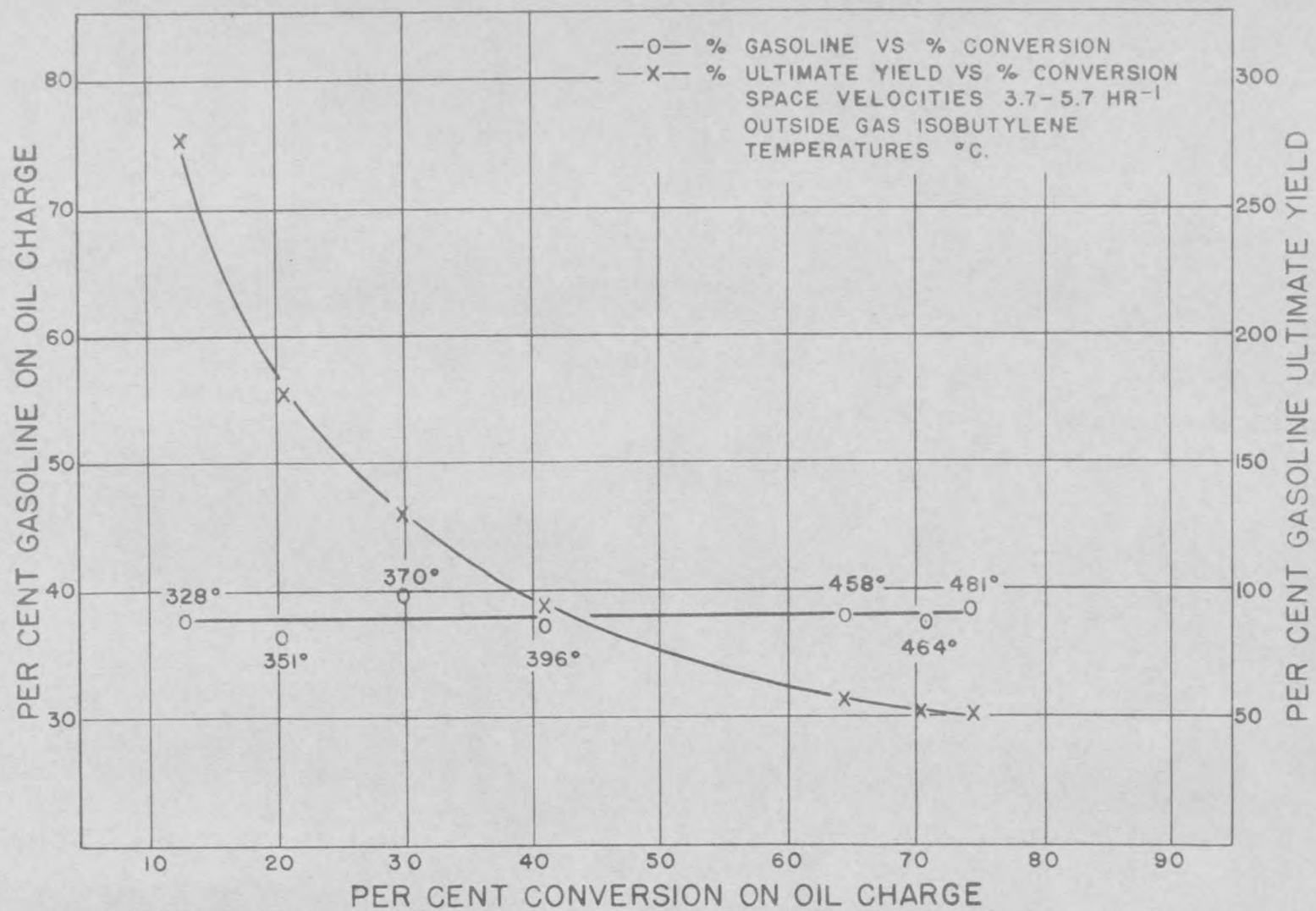


Figure 6. Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas Isobutylene, High Space Velocities

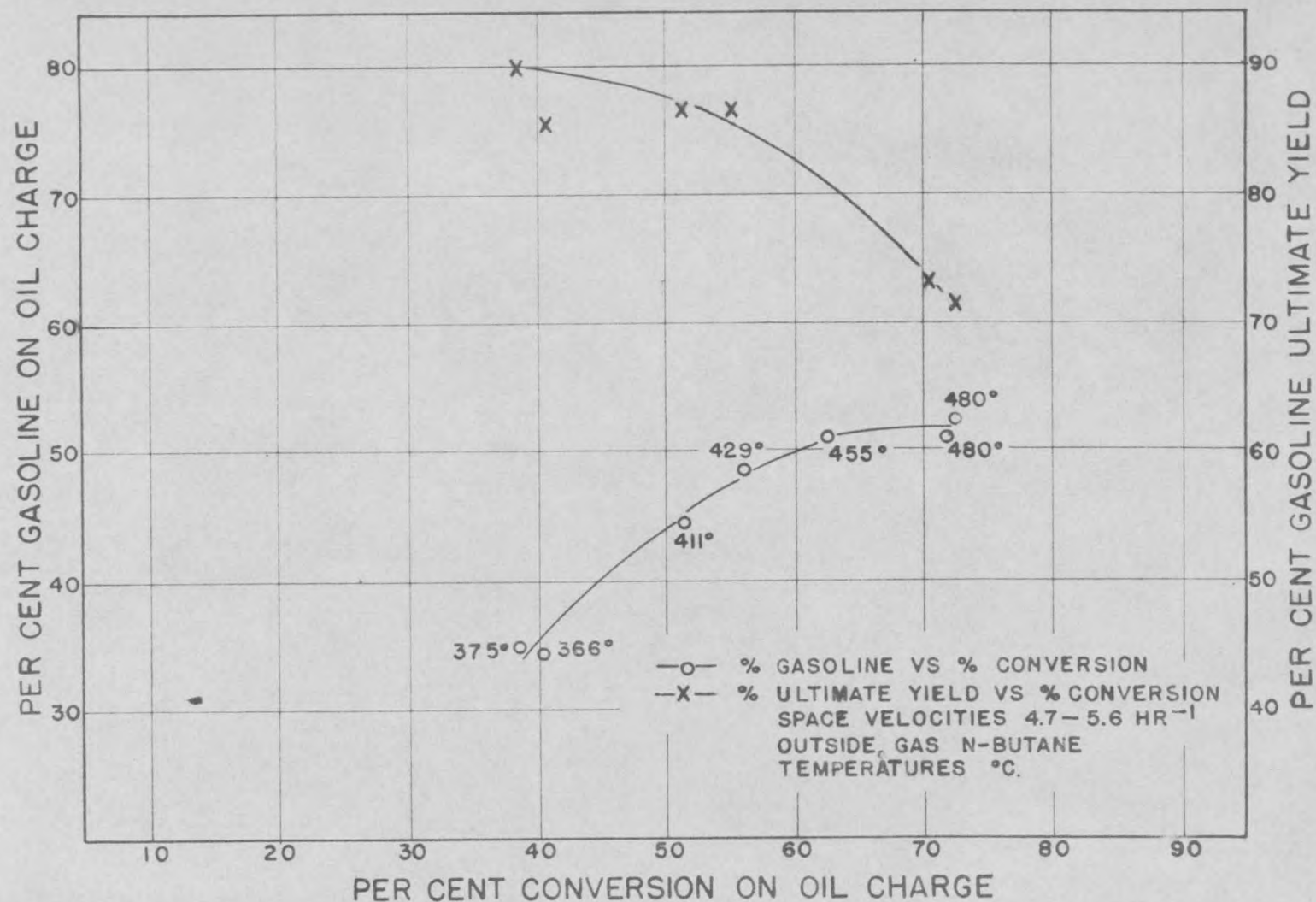


Figure 7. Effect of Conversion on Gasoline Yield at 900 psig, Outside Gas n-Butane, High Space Velocities

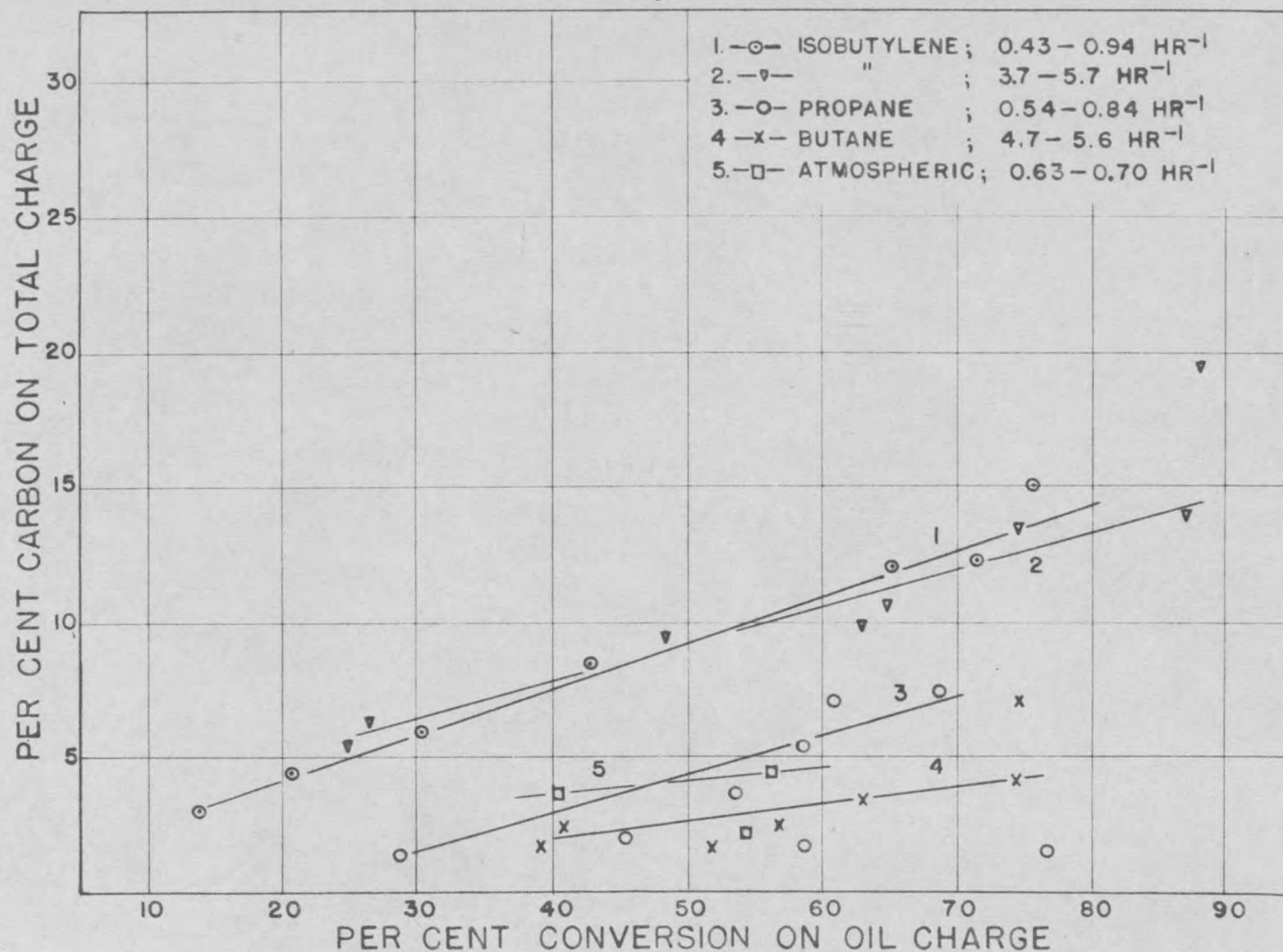


Figure 8. Effect of Conversion on Carbon Lay-down
at indicated Outside Gases and Space Velocities

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10014947 3

N378 cop.2 100898

M453c

Mayfield, L. G.

Catalytic gas oil polyforming
with propane, iso-butylene &...

DATE

ISSUED TO

INDEFINITE LOAN

SEP 17 '82

2/19/61

#9. Mayfield cont.
Gordon R. Julian
Chem. Dept.N378
M453c
cop.2

100898