Catalytic polyforming of gas oil with a hydrocarbon gas mixture
by Robert B Hamilton

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

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Houdry fixed-bed aluminum silicate catalyst was used for all runs and the carbon was burned from it at the conclusion of each run. The investigation was conducted at temperatures varying from 392° C, to 509° C.; and the liquid space velocities used were 0.6 to 0.8 and 4.0 to 6.0 volumes of charge per volume of catalyst per hour. During a typical run, approximately 450 grams of feed were passed over the 1000 ml. of catalyst.

Characteristics of mixed-gas catalytic polyforming are as follows: (1) yields of gasoline increase with each additional increase of pressure up to 2000 psig at which point the yields decrease, (2) gasoline yields surpass those obtained from conventional catalytic cracking using a space velocity of 0.6 -0.8 hr^-1 only at 1500 psig, and (3) carbon formation -exceeds that occurring in conventional catalytic cracking at comparable oil conversions^, It was found that the time of stream best suited for mixed-gas catalytic polyforming of gas oil at 900 psig was approximately 20 minutes.

CATALYTIC POLYFORMING OF GAS OIL WITH A HYDROCARBON GAS MIXTURE

by

Robert B. Hamilton

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ABSTRACT

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It was found that the time of stream best suited for mixed-gas catalytic polyforming of gas oil at 900 psig was approximately 20 minutes.

INTRODUCTION

During the last twelve years, the need for economy in motor fuel production has fostered the development of a number of new processes in petroleum technology. Two of these, the polyforming process and catalytic cracking, when applied to gas oil, are of interest to this investigation.

Catalytic cracking is a process for converting petroleum fractions in the fuel oil range into gasoline and other lower boiling fractions. This process produces a high octane gasoline in better yields per pass than can be produced by thermal cracking. It also gives greater yields of the lower molecular weight hydrocarbons which are needed for the manufacture of 100 octane aviation gasoline.

As cracking proceeds, a carbonaceous deposit sometimes called "coke" or "carbon" is formed upon the catalyst. The composition of this deposit ranges from $CH_{0.6}$ to $CH_{1.1}$. Since the carbon reduces the activity of the catalyst, the time on stream between regenerations is a factor vital to the successful economic development of any fixed-bed catalytic cracking process.

Frost (1) investigated catalyst deactivation as a result of "coking" by passing gas oil over a fixed-bed aluminum silicate catalyst. The operating conditions used were as follows: space velocity - 0.75 $hr.^{-1}$, temperature - 450° C., and pressure - 0 psig. With a time on stream of 30 minutes, the per cent conversion did not change from that observed at shorter times although the accumulation of "coke" upon the catalyst amounted to two per cent by weight. After two hours on stream,

the activity of the catalyst gradually decreased to 75 per cent of its original activity. In this case, the deposit of "coke" on the catalyst was five weight per cent. According to Frost, this continued activity can be explained by the fact that the gaseous hydrocarbons are soluble in the deposit and can contact the catalyst surface despite the interfering deposit.

Present fixed-bed catalytic cracking processes limit the carbon accumulation on the catalyst to about 1.1 weight per cent which corresponds approximately to 10 minutes on stream.

The polyform process employs the principle of cracking naphtha and heavier oils in admixture with varying amounts of normally gaseous cheap hydrocarbons, with resulting increases in the octane number, and at the same time allows a higher degree of conversion per pass than possible in the ordinary thermal cracking process without an uneconomical increase in the production of permanent gases.

Offutt et al (2) in a study of gas reactions of gas with products from naphtha cracking found that gas (C_3 and C_4 hydrocarbons) suppressed tar and coke formation by reacting with some of the products from the cracking reaction which ordinarily interact to form tar and coke. It was noted that lower tar yields were produced when the naphtha was reformed in a high gas dilution. Offutt et al (3) showed that the same type of reactions take place in gas oil polyforming. Gas oils which tend to form coke at moderate conversions with ordinary thermal cracking give increasing yields of gasoline when cracked in a one-pass operation with increasing gas dilutions. The increase in yield is attri-

buted to the products formed by thermal alkylation, thermal polymerization, and other addition type reactions between the gas and the reactive cracked products of the gas oil.

The superiority of catalytic over thermal cracking led Dev (4) to an investigation to evaluate the process of gas oil polyforming under catalytic conditions using propane as an outside gas. This process was called catalytic polyforming. The yields of gasoline from the catalytic cracking of virgin gas oil with and without propane at different pressures were compared. It was noted that at the higher pressures using propane as an outside gas an increased yield of gasoline was obtained at a temperature which was too low for thermal polyforming.

Mayfield (5) investigated gas oil polyforming under catalytic conditions using propane, iso-butylene, and n-butane as the outside gases. For all runs using an outside gas, the pressure, was held constant at 900 psig and the temperature and space velocity were the variables. Atmospheric catalytic cracking of gas oil gave a definite increase in gasoline yield on oil charge over that obtained from catalytic polyforming with propane. A large increase in gasoline yield over that obtained from straight, catalytic cracking was noted for the iso-butylene catalytic polyforming runs. It was further noted that the same runs made at a space velocity of 4-6 $hr.^{-1}$ gave an essentially constant yield of gasoline over the entire temperature range investigated. n-Butane catalytic polyforming gave a definite increase in gasoline yield over that obtainable from atmospheric catalytic cracking.

Polich (6) evaluated several catalysts, both natural and synthetic, for use in the catalytic polyforming process. Normal butane was used as outside gas and the runs were conducted at 900 psig using a liquid space velocity of 4-6 $hr.^{-1}$. Houdry aluminum silicate catalyst was found to be the catalyst best suited for catalytic polyforming as a result of the following considerations: (1) Houdry catalyst was less expensive than the other synthetic catalysts which yielded a like amount of gasoline, and (2) there was no detectable loss in catalyst activity on regeneration after the passage of 27 volumes of feed per volume of catalyst.

Ennenga (7) investigated the effect of 0, 500, 600 900 and 1200 pound pressures upon catalytic polyforming using iso-butane as the outside gas. Space velocity was held relatively constant at 4-6 $hr.^{-1}$. It was noted that the gasoline yields steadily increased through 900 psig and decreased when 1200 psig was applied.

The results of these previous investigations indicate that paraffinic gases inhibit carbon deposition and olefinic gases materially increase the yields of gasoline and the through-put of charge. These results suggested that the use of a gaseous mixture similar in composition to extraneous refinery gases would combine the advantages of each separate gas. The synthetic gas mixture employed in this investigation consisted of the following constituents expressed in weight per cents: 30

per cent n-butane, 10 per cent iso-butane, 20 per cent iso-butylene, 20 per cent propane, and 20 per cent propylene. The yields of gasoline from the catalytic cracking of gas oil with the outside gas at 0, 900, 1500, and 2000 pounds pressure and varying temperatures were compared with the results of catalytic cracking without a gas. Houdry fixed-bed synthetic catalyst was used and the space velocities were held relatively constant at 0.6 - 0.8 $hr.^{-1}$ for catalytic cracking and at 4-6 $hr.^{-1}$ for catalytic polyforming.

In addition, the need for a determination of the time of stream for catalytic polyforming led to the evaluation of this process variable at 900 psig using the gas mixture as the outside gas. The optimum temperature determined at 900 psig, 455° C., was used with a space velocity of 4-6 $hr.^{-1}$.

II EQUIPMENT, METHODS AND MATERIALS

A. Equipment

The equipment used in this investigation consisted of a 0-1000 psig reaction system, shown in Figure 1, and a 0-2500 psig reaction system, shown in Figure 2. Each reaction system was divided into four major parts according to their function: (1) feeding section, (2) reactor section, (3) condensing and receiving section, and (4) gas section.

Low Pressure Unit

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 length of three-inch, extra strong steel pipe. The pipe was threaded at both ends and fitted with extra strong steel caps which were welded on in the final assembly. Both caps were drilled and tapped for one-half inch pipe and the inside of the cap machined to facilitate draining. These caps were fitted with close nipples and high pressure stainless steel Kerotest globe valves. 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. This line served to equalize the pressure across the feed cylinder in order to obtain flow of 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. 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 which was used to regulate the feed rate. The bottom of the valve was connected to the top of the reactor with one-half inch extra strong steel pipe through a tee and a union, the male half of which 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 which was equipped with a 1255 psig Monel 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. A one-eighth inch mesh 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 steel 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 with a 0-2000 pound pressure gage, and the run to a one-half inch, 6000 pound Vogt valve for regulating pressure.

The top of the reactor was threaded and fitted with an extra strong steel cap, to which the previously mentioned male half of the union had been welded. An 11/16-inch hole was drilled through the cap, thus giving a smooth, continuous surface. This design feature facilitated the changing of the Houdry catalyst and the 500 ml. of assorted size steel balls which served as a preheater section on the top of the catalyst. In the final assembly, the steel cap was arc welded to the reactor body to prevent leakage.

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. Two pieces of 1/2-inch by one-inch flat bar stock were welded to the top of the cap and they, in turn, were fastened by 1/2-inch pins to the back of the barricade to keep the reactor from turning when the union was being tightened or broken apart.

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 symetrically at three-inch intervals along the length of the reactor. The wells were welded in place with the ends on the reactor axis. Into the wells were inserted iron-constantan thermocouples connected to a Leeds and Northrup indicating potentiometer, calibrated in degrees centigrade and indicating from 0-1100° C.

The reactor was wrapped with asbestos tape. The top one-half of the reactor was wound with 30 feet of Nichrome wire with a resistance of 1.71 ohms per foot, and threaded with porcelain flish-spine insulators. The lower one-half was similarly wound. Each of these windings

drew five amperes maximum from a 220-volt autotransformer. These windings were covered with a layer of asbestos tape and two additional 15-foot windings of Nichrome wire were placed around the reactor section, one on the top one-third of the section and one around the bottom one-third. Each of these windings was connected to a 110-volt autotransformer and drew five amperes maximum. The length of the reactor was then covered with one-inch asbestos blocks and the entire reactor covered with asbestos mud.

The autotransformers were Superior Electric Company Powerstats. The 110-volt powerstats had a voltage range of 0-135 volts and were fused at 7.5 amperes. The 220-volt powerstats had a range of 0-260 volts and were fused at three amperes.

A 1/4-inch steel plate 26 inches by 90 inches was mounted against the laboratory rack and the reactor was fastened to this plate. Then 1/8-inch steel plate rolled into a semi-circle 22 inches in diameter and 40 inches long was hinged to the barricade so that it would close around the reactor and could be fastened solidly with 1/2-inch pins. A frame work was built up from the hinged section in front of the Jerguson gage and two thicknesses of safety plate glass were fastened in the frame. This provided a safety window through which the gage could be observed during feed regulation.

Condensing and Receiving Section - The bottom of the pressure regulating 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 onto the bottom

of the 1000 ml. flask which was used as a receiver. The flask was immersed in an isopropanol-dry ice bath contained in a one-gallon thermo-flask. The outlet of the receiver was connected by rubber tubing to the gas condensing system shown in Figure 1.

Immediately following the cold traps was a tee, the off side of which was connected to a 200 ml. evacuated glass bottle so that a sample of the uncondensable gases could be taken during the run. The gas meter following the gas sample bottle, was a three-liter Precision Wet Test Meter. It, in turn, was connected to a blow-down line to the outside of the building.

The distillation equipment consisted of a 16-plate Oldershaw column, a head suitable for either high or low temperature fractionation, and two vapor traps. The head was filled with dry ice-isopropanol for low boiling constituents and with wet ice for those boiling above 20° C. The distillation flask was heated by a 110-volt, 550 watt heater controlled by another autotransformer.

High Pressure Unit

Feeding Section - The feeding section consisted of a pump, a feed cylinder, and a Jerguson gage. The feed cylinder used was constructed in a similar manner as the one for low pressure runs with the exception that it was 16 inches in length rather than 12. This added capacity was a means of allowing for the hold-up in the pump and the 20 feet of tubing leading to the reactor. A short length of 1/2-inch copper tubing connected the cylinder to the Jerguson gage. This large tubing, together with the pressure equalization line shown in Figure 2, insured the free flow of feed to the Jerguson. The bottom of the Jerguson was connected by 1/4-inch copper tubing to a stainless steel Kerotest globe valve, its only purpose being to aid in the control of the initial rate of feed. The valve was, in turn, connected by two lengths of tubing to each side of the double acting pump.

Feed to the reactor was accomplished by a Hills-McCanna, Type UM-2F, single unit, two feed, 1/4 horse-power pump. The pump was connected to the top of the reactor by 1/8-inch stainless steel tubing and Weatherhead Ermeto pressure couplings and fittings.

Reactor Section - The catalyst chamber was constructed from a three-footppiece of 18-8-C, Type 347, 2-1/2-inch extra strong I.P.S. pipe. A 2-1/2-inch welding cap, fitted with a short length of 1/2-inch extra strong pipe, was welded to the lower end of the stainless steel pipe. An extra heavy tee was fitted to the 1/2-inch pipe to hold the 4-foot long, 1/4-inch standard pipe thermowell which extended through the reactor along the ce ntral axis. The remaining opening of the tee was fitted for the

escape of cracked products. This was accomplished by inserting a 1/2-inch pipe into the off-side of the tee and allowing it to protrude horizontally through the reactor case. An extra strong ell was screwed onto the short length of pipe and was fitted with a six-inch nipple leading to an extra strong tee. The branch of the tee was connected to a 0-5000 pound pressure gage and the run to a 1/4-inch, 25,000 pound stainless steel Aminco superpressure valve. This type valve necessitated the use of superpressure couplings, bushings, and tubing made by the American Instrument Company.

A 2-1/2 inch extra strong welding neck flange was welded to the top of the reactor and a 2-1/2 inch extra strong blind flange bolted to the welding neck flange. Prevention of leaks was made possible by inserting a stainless steel gasket between the flanges in the final assembly. A short nipple was welded to the flange and was, in turn, fitted with an extra strong cross. The top opening of this cross was connected to a high pressure Hoke needle valve by means of a one-half to one-quarter inch bushing. An Ermeto tee was screwed into the valve and the run openings were connected to the feed lines from the pump. Another opening of the cross was similarly fitted with a Hoke valve to afford a means of purging the chamber with nitrogen. The remaining opening was connected by a short nipple to an extra strong tee. The off-stream side of the tee was fitted with a Black, Sivalls, and Bryson frangible safety disc which was equipped with a 3100 psig Monel diaphragm discharging to the exterior of the building by a blow-down pipe. The run of the tee was connected to another Hoke valve to permit passage of air into the reactor for the catalyst burn-off.

The reactor was originally designed to hold 3000 ml. of catalyst. At the time the design was made, it was believed that liquid space velocities of 0.5 - 1.0 hour^{-1} would be optimum. Subsequent research with the 900 pound unit showed that the process operated efficiently at liquid space velocities of 4-6 hour^{-1}. It was necessary, therefore, to reduce the catalyst volume from 3000 ml. to 1000 ml. This was done by fabricating a number of cylindrical mild steel inserts which would fit snugly inside the reactor but allow sufficient space for the flow of feed between the inserts and the thermowell. These blocks also effectively served as a preheat section.

The outside of the reactor was completely wrapped with asbestos tape and then wound with five 48-foot lengths of Nichrome wire with a resistance of 1.71 ohms per foot, and threaded with porcelain fish-spine insulators. Three of the coils furnished the heat for the preheat section and the remaining two covered the catalyst section. Each of the windings drew six amperes from a 110-volt autotransformer.

Four iron-constantan thermocouples were inserted into the thermowell; one junction was placed in the preheat section and the other three were equally spaced along the 15-inch catalyst bed. Four-hole porcelain insulators were obtained from the Stupakoff Company which were of small enough diameter so that two separate lengths of the insulators could be simultaneously inserted into the 1/4-inch thermowell. This arrangement made possible a permanent thermocouple rather than necessitating a probe. The thermocouples were connected to the potentiometer.

The reactor was housed in a steel case, the shape of which was an inverted frustrum of a pyramid. The dimensions of the sides were 1/4-inch by 17 inches by eight inches by 60 inches. Three sides were fastened together by fillet welding 1/8-inch by 1-1/2 inch angle irons in the corners of the case. The front plate was bolted to the remaining edges of the angle iron. The case was stabilized by three one-inch pipes which were welded to the tops of the sides and were extended to the floor to form a tripod. In addition, two short lengths of angle iron were welded to the top of the case and to the laboratory rack. A one-inch hole was drilled in a 20-inch piece of 1/4-inch flat bar stock and was then slipped over the one-inch pipe extending from the blind neck flange of the reactor. This piece was then pinned to the sides of the case so that the reactor would be rigidly held in place. After the reactor had been lowered into place, the space between the reactor and case was completely filled with diatomaceous earth to minimize the heat losses.

The remaining parts of the system were identical to those used for the 1000-pound unit.

B. Methods

900 psig runs

The feed cylinder was evacuated with a Cenco Megavac pump, charged with the desired amount of gas oil, weighed on a 20-kg. capacity triple beam balance, and 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 a balance and connected to the tank of mixed gas by means of Saran tubing. After the scale had been tared, the desired amount of mixed gas was admitted to the feed cylinder by opening both connecting valves. The actual amount of outside gas was determined by reweighing the cylinder on the balance without the attached tubing. The contents were then allowed to warm to room temperature.

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 regulating valves, the system was flushed with a short nitrogen purge and the valves then reclosed. To the Dewar flasks containing isopropanol, dry ice was added until carbon dioxide was no longer evolved. The gas sample bottle was evacuated, weighed, and connected to the system. The feed cylinder was then connected into the system as shown in Figure 1 and 300 pounds of nitrogen pressure was applied to the balanced pressure feed system. The Jerguson gage was filled with a portion of the charge by opening the valve at the bottom of the feed cylinder.

The thermocouple readings were noted at the start of the run and continued at one-minute intervals throughout the duration of the run.

Timing of the run began when the feed regulating valve was opened. Feed rate was determined by noting the time for any given drop in liquid level in the gage which had been previously calibrated. For a space velocity of 4-6 $hr.^{-1}$, the feed rate was maintained at 17 linear centimeters or 85 ml. per minute.

As a result of the closed pressure regulating valve, the hot expanding gases within the reactor caused the pressure gradually to rise. A differential back-pressure of 100 pounds was maintained during this pressure rise through the use of the nitrogen cylinder. When the pressure reached 900 psig, the pressure regulating valve was opened just enough to maintain this pressure. The system remained static until the end of the feeding period which was indicated by a sharp pressure rise in the reactor section as a result of the 100 pound back-pressure. The feed valve was immediately closed and the reactor reduced to atmospheric pressure at approximately the same rate it had been pressurized. During this depressurization, a gas sample was taken. The gas was allowed to come to room temperature, balance against atmospheric pressure, and weighed. From these data, the density of the noncondensable gases was determined.

Upon completion of the run, the feed cylinder was removed from the system and weighed, the amount of oil charged thus being determined by the difference. The receiving flask and vapor traps were removed from the system, wiped dry of isopropanol and immediately weighed to determine the weight of the condensable product. The liquids were poured into the receiving flask and the total weight recorded. The flask was then attached to the Oldershaw column and distilled for gasoline to 204° C. end point.

So that any traces of oil in the reactor might be recovered, the reactor was connected through a series of cold traps to the vacuum pump and evacuated. The reactor was simultaneously purged with nitrogen which aided materially in recovering the last traces of oil. The recovered material was weighed and added into the weight balance as residue since under these conditions the potential gasoline in it would be negligible.

Distillation Procedure

The receiving flask which contained the condensable gases in addition to cracked stock was attached to the Oldershaw column by means of a ground glass taper joint. The distilling head and -10-250° C. thermometer were also attached by means of ground glass joints using silicone grease as the sealing compound. The head was filled with isopropanol-dry ice. The product take-off was connected to two vapor traps placed in Dewar flasks which also contained isopropanol-dry ice. The vapors in the pot were allowed to reflux until a temperature of -15° C. was reached. The autotransformer was set at 34 volts and the distillation allowed to proceed to 7° C. At this point, after a period of total reflux, the vapor traps containing the lights were weighed and replaced by a weighed gasoline trap was placed into a thermoflask. When the temperature approached 20° C., the isopropanol was removed and wet ice inserted in its place. The distillation was then allowed to proceed to 204° C. for a final reflux. The gasoline so obtained was weighed and the residue was weighed when the column reached room temperature.

Catalyst Burn-off

During the run, a deposit of carbonaceous material was laid down upon

the catalyst reducing its activity and necessitating a burn-off after each run. In order that a weight balance might be established for the system, the weight of this carbon laydown had to be determined. This was accomplished by passing air at a constant rate through the gas meter and into the reactor while maintaining the reactor temperature at about 400° C. by means of the heating elements. The effluent gas was analyzed at regular intervals by means of an Orsat apparatus to determine the per cent of carbon dioxide, carbon monoxide, and oxygen. These per cents were plotted and the carbon lay-down was calculated as shown in the sample calculations. The temperature of the burn-off was maintained below the sintering temperature of the catalyst, about 600° C., by controlling the rate at which the air was admitted to the reactor.

Determination of Per Cent Outside Gas in Feed Cylinder at End of Run

Samples of the gases remaining in the feed cylinder were taken at 1000 psig and also after the cylinder pressure had been reduced to 300 psig. These samples were analyzed with the low-temperature gas-fractionation unit to determine the per cent mixed gas remaining in the feed cylinder and not charged. The data obtained were inconclusive; so the method used by Mayfield (3) was adopted. By this method, the valves of the feed cylinder were closed at the end of the run before the feed system was depressurized. The feed was then removed from the system and the residual gases, containing nitrogen and mixed gas, were bled into a 34-liter tank. This allowed all the mixed gas in the cylinder to vaporize and be accounted for in the analysis of the low-pressure gases in the tank. Analysis showed the residual mixed gas to be 10 grams. This value of 10 grams was used in the calculations of all runs involving an outside gas. Since the 10 grams was outside gas uncharged, it

was subtracted from the weight of gas charged to the feed cylinder prior to each run; and calculations were based on the corrected gas weight.

1500 and 2000 psig Runs

The procedure in these runs was essentially the same as described for the 900 psig runs with the exception of the difference in feed rate regulation.

The feed cylinder was filled with an additional 70 gm. of charge to compensate for the hold-up in the pump and feed lines. It was then connected to the top of the Jerguson gage in the usual manner. The gage was filled by gravity flow and the feed pump was started. The proper feed rate was obtained by a trial and error adjustment of the piston stroke so that a space velocity of 4-6 $hr.^{-1}$ would result. Timing of the run began when the first pressure rise in the reactor was noted. The rest of the procedure was identical to that described for 900 psig runs.

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 I.

The outside gas used was a mixture of 30% n-butane, 10% iso-butane, 20% iso-butylene, 20% propane, and 20% propylene prepared by the Matheson Company.

III SAMPLE CALCULATIONS

Calculations of space velocity, weight of permanent gases, carbon lay-down on the catalyst from burn-off analysis, over-all weight balance, yield of gasoline, per cent conversion, and per cent ultimate yield are presented for run Number 15 as typical of all the runs made.

A. Calculation of Liquid Space Velocity:

Data:

Volume of catalyst in the reactor	= 1000	ml.
Feeding time	= 6.58	min.
Weight of charge	= 444.0	gm.
Density of charge	= 0.8	gm./ml.
Volume of charge	= 555.03	ml.

$$\text{Space velocity} = \frac{555 \text{ ml.} \times 60 \text{ min./hr.}}{6.58 \text{ min.} \times 1000 \text{ ml.}} = 5.03 \text{ hr.}^{-1}$$

B. Calculation of Weight of Permanent Gas:

Data:

Volume of uncondensable gases	= 40.0	l.
Volume of gas sample bottle	= 208.2	ml.
Weight of bottle and gas	= 124.115	gm.
Weight of evacuated bottle	= 123.933	gm.
Weight of gas sample by difference	= 0.182	gm.

Weight of permanent gases =

$$\frac{40 \text{ l.} \times 0.182 \text{ gm.}}{0.2082} = 35.0 \text{ gm.}$$

C. Calculation of Burn-off

Data: (Plotted on Figure 3)

Time (min.)	Air (Liters)	By CO_2	Analysis CO	Analysis O_2	Ave. CO_2	From CO	Plot O_2	By Diff. N_2	Vol. Eff. Gas	Vol. % CO_2 + CO	Liters CO_2 + CO
5	13	9.0	2.2	0.6	4.5	1.1	9.3	85.1	12.1	5.6	.68
15	13	10.4	3.8	0	9.9	3.2	0.3	86.6	11.9	13.1	1.56
30	25	11.6	7.3	0	11.0	5.5	0	83.5	23.7	16.5	3.91
60	50	12.6	7.8	0	12.2	7.7	0	80.1	49.5	19.9	9.85
90	51	14.0	9.0	0	13.6	8.3	0	78.1	51.7	21.9	11.31
150	48	12.4	10.0	0	13.5	9.6	0	76.9	49.5	23.1	11.43
180	40	10.8	11.6	0	11.6	10.7	0	77.7	40.9	22.3	9.13
210	43	10.6	11.8	0	10.7	11.8	0	77.5	44.0	22.5	9.90
270	46	5.8	5.9	9.0	8.5	9.5	4.2	77.7	46.9	18.0	8.44
330	47	1.0	0	18.0	3.3	3.0	13.4	80.3	46.4	6.3	2.92
										Total	69.12

$$\text{Weight of Carbon} = \frac{69.12 \times 640 \times 273 \times 12}{22.4 \times 760 \times 303} = 28.1 \text{ gm.}$$

D. Calculation of an Over-all Weight Balance:

Data:

Weight of cylinder and charge	= 10850	gm.
Weight of cylinder after run (Atmospheric pressure)	= 10396	gm.
Weight of gas remaining in cylinder	= 10	gm.
Weight of material charged	= 444	gm.

Recovered material:

Hydrocarbon liquid product	= 164.9	gm.
Condensable gases	= 208.0	gm.
Permanent gases	= 35.0	gm.
Carbon from burn-off	= 28.1	gm.
Oil from catalyst bed	= 1.0	gm.
Total weight recovered	= 437.0	gm.
Weight of charge lost by difference	= 7.0	gm.

1 Per cent of charge lost = $\frac{7 \times 100}{444}$ = 1.58 %

E. Calculation of Per Cent Gasoline Yield:

Data:

Gasoline from distillation	= 81.8	gm.
Gas oil charged	= 263.0	gm.

Per Cent gasoline on oil charge = $\frac{81.8 \times 100}{263}$ = 30.75 %

F. Calculation of Per Cent Conversion:

Data:

Residue from distillation	= 115.0	gm.
Oil from catalyst bed	= 1.0	gm.
Total residue	= 116.0	gm.

Per Cent conversion on oil charge =

$$100 - \frac{116.0}{263.0} \times 100 = 55.9\ \%$$

C. Calculation of Per Cent Ultimate Yield:

Data:

Per cent gasoline on oil charge	=	30.75 %
Per cent conversion on oil charge	=	55.9 %

$$\text{Per cent ultimate yield} = \frac{30.75 \times 100}{55.9} = 55.0\ \%$$

Calculation of Apportionment of Carbon Per Pass for the Time on Stream Determination:

The procedure followed for this determination was to pass about 450 gm. of charge over the catalyst during a six-minute period. The hydrocarbon liquid product was collected and distilled. From this distillation, the per cent gasoline yield and per cent conversion per pass could be calculated. Six such passes were made and the carbon was burned off the catalyst at the end of the cumulative 40-minute period. Thus, a method by which the carbon could be apportioned per pass was needed.

According to Frost (1), gaseous hydrocarbons are soluble in the carbon regardless of the amount of deposit. In other words, after an extended time on stream, the formation of carbon is still due to catalytic action rather than to thermal cracking. Voorhies (8) in a study of carbon formation in fixed-bed cracking found that there is a good correlation between feed stock conversion and carbon yield based on feed for a given catalyst, feed stock, and temperature. It may be mentioned that there are numerous other data available which show that conversion is linear with the logarithm of carbon yield.

Since Figure 4 prepared from runs 13-18, presents the above relationship for mixed-gas polyforming at 900 psig, the carbon deposited per pass during the 40-minute residence time could be determined from the per cent conversions calculated from the distillation residues. The following data illustrate this procedure.

Total carbon from burn-off = 116.0 gm.

Run No.	Elapsed Time (Min.)	Per Cent Conversion	Per Cent Carbon on Feed (Figure 4)	Weight Carbon	Revised Carbon
25	6.53	59.5	7.35	32.0	33.3
26	13.33	46.7	4.70	20.5	21.7
27	19.91	45.5	4.50	19.5	20.8
28	26.23	34.0	3.10	13.3	14.6
29	33.53	31.2	2.85	12.5	13.6
30	40.08	28.4	2.55	10.18	12.0
			Total	108.6	116.0

Since the weight of carbon determined from Figure 4 did not quite total 116 gm., equal increments were added so that the revised carbon would meet this quantity.

IV RESULTS

Runs 1, 2, 3 and 4 in Table II present the catalytic cracking of gas oil with a Houdry synthetic aluminum silicate catalyst at low space velocities. Four atmospheric runs were made at temperatures varying from 413° to 509° C.; space velocity was held between 0.65 and 0.75 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 5. The highest yield of gasoline obtained from the catalytic cracking of gas oil was 33.6 per cent at 429° C. This point, however, does not occur at the peak of the curve. The trend of the curve indicates that the maximum yield of gasoline is approximately 34 per cent at a temperature near 460° C.

The theoretical figure, ultimate yield on oil charge, is calculated by assuming that all of the material boiling above the gasoline range would, upon recycling, effect the same conversion. This theoretical figure is plotted as a function of per cent conversion on oil charge in Figure 6. It is seen that a maximum ultimate yield of gasoline was not obtained.

Runs 5, 6, and 7 in Table II present the catalytic cracking of gas oil at high space velocities. Three atmospheric runs were made at temperatures varying from 380° C. to 444° C.; space velocity was held between 4.35 and 4.4 volumes of feed per volume of catalyst per hour.

At comparable conversion, approximately 25 per cent (relative) more gasoline was obtained at low than at high space velocities.

The sole purpose of investigating catalytic cracking was to establish a basis by which mixed-gas catalytic polyforming could be evaluated. It is well agreed that space velocities held between 0.5 and 1.0 volumes of feed per volume of catalyst per hour are best suited to catalytic cracking.

Mayfield (5) found that gasoline yields from iso-butylene polyforming were approximately the same whether obtained at space velocities of 4.0 to 6.0 $hr.^{-1}$ or 0.5 to 1.0 $hr.^{-1}$. On the basis of this observation, the higher space velocity was chosen for the investigation.

Thus, gasoline yields from mixed-gas polyforming at high space velocities will be compared with those obtained from catalytic cracking at low space velocities.

Table III presents the results of mixed-gas catalytic polyforming gas oil at atmospheric pressure. Five runs were made at temperatures varying from 405° to 475° C.; space velocity was held between 4.5 and 4.8 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 7. The curve shows the maximum yield of gasoline as 26.6 per cent at 46.4 per cent conversion. The gasoline yield, then, was 27.8 per cent less relative than for atmospheric catalytic cracking. The curve showing per cent ultimate yield of gasoline versus per cent conversion in Figure 8 is also lower than for the catalytic cracking curve.

The conversion products, carbonand permanent gas, tend to be more

pronounced when the gas oil is cracked in the presence of the mixed gas.

Runs 13 to 18 in Table IV present the catalytic cracking of gas oil at 900 psig in the presence of mixed gas. Six runs were made at temperatures from 392° to 498° C. and at space velocities held between 4.92 and 5.15 volumes of liquid feed per volume of catalyst per hour.

Figure 9 shows the plot of per cent gasoline yield as a function of per cent conversion. The maximum yield of 30.75 per cent occurred at 455° C. and at a conversion of 55.9 per cent. This yield represents a relative increase of 15.6 per cent over the atmospheric polyforming yields. The yields of gasoline from conventional cracking, however, still surpass those obtained by mixed-gas polyforming at 900 psig.

The relationship between ultimate yield on oil charge and per cent conversion on oil charge shown in Figure 10 indicates that the maximum yield is obtained at approximately 392° C.; this yield is less than for the atmospheric cracking curve.

Carbon deposition is greater and gas formation is less at 900 psig than for atmospheric polyforming.

Runs 19, 20, and 21 in Table V present the results of mixed-gas catalytic polyforming gas oil at 1500 pounds pressure. Three runs were made at temperatures from 439° to 480° C. and at space velocities held between 4.6 and 4.7 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 11. The yield of gasoline was 35.0 per cent for each of the three runs made. The conversion range was limited as a re-

sult of two operational difficulties: (1) a temperature lower than 430° C. would not develop the desired pressure with a 500 gm. charge, and (2) a temperature higher than 480° C. developed pressure so rapidly that violent surging accompanied pressure regulation. The 35 per cent yields represent a relative increase of three per cent over the yields of gasoline obtained by conventional catalytic cracking. The ultimate yield of gasoline at 1500 psig as shown in Figure 12 is also slightly greater than for atmospheric cracking.

Runs 22, 23 and 24 in Table V present the mixed-gas catalytic polyforming of gas oil at 2000 psig. Three runs were made at temperatures varying from 440° C. to 470° C.; space velocities were held between 4.3 and 4.9 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 13. The curve is very similar to the 1500 psig curve. The yields of gasoline are 30 per cent for the conversion range studied. The reason for the narrow conversion range has been previously discussed. It will be noticed from the curve that in order to obtain comparable conversions, a lower temperature is required at 1500 pounds than at 2000 psig. The curve showing per cent ultimate yield of gasoline versus per cent conversion in Figure 14 follows a trend similar to the 1500 pound curve, the exception being a 15.2 per cent relative decrease in yield at conversions of 56 per cent.

Table VI presents the results of the time of stream determination with gas oil and mixed gas at 900 psig. Six runs were made at temperatures held relatively constant near 455° C. (the temperature found to

be optimum in Figure 9); space velocity was held between 4.5 and 5.12 volumes of feed per volume of catalyst per hour.

A plot of cumulative weight per cent of conversion products as a function of cracking time or time on stream is shown in Figure 14. The yields of gasoline and permanent gas had decreased about three per cent at the end of 20 minutes. Upon continued cracking, the yields of these products rapidly decreased. It will be noticed that the weight of carbon on the catalyst is approximately a linear logarithmic function with time. The curves show that the catalyst retains most of its original activity after 40 minutes despite the considerable amount of carbon which was deposited.

V SUMMARY

The results found in this investigation may be summarized as follows:

(1) The increase of reaction pressure used for mixed-gas catalytic polyforming of gas oil results in a definite increase in gasoline yield until 2000 psig is reached at which point the yields decrease.

(2) Carbon deposition increases with each additional pressure increase.

(3) Gas formation in mixed-gas catalytic polyforming is at a minimum near 1500 pounds pressure.

(4) Carbon formation in mixed-gas catalytic polyforming is noticeably greater than in conventional catalytic cracking.

(5) Mixed-gas catalytic polyforming at 1500 pounds pressure gives a definite increase in gasoline yield over that obtainable from atmospheric catalytic cracking.

(6) A suitable time of stream for mixed-gas catalytic polyforming is 20 minutes.

(7) The results of the time of stream determination tend to indicate that mixed-gas catalytic polyforming could be operated at a cycle through-put considerably greater than that used in normal petroleum cracking.

VI ACKNOWLEDGEMENT

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VIII APPENDIX

page

TABLE I

Gas Oil Inspection Data

(Borger, Texas 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 II

Catalytic Cracking of Gas Oil at Atmospheric Pressure

Run No.	1	2	3	4	5	6	7
No. Runs on Catalyst	49	47	48	50	6	7	8
Avg. Reactor Temp. °C.	413	429	482	509	398	380	444
Space Velocity hr.$^{-1}$	0.75	0.65	0.70	0.67	4.35	4.4	4.4
Material Charged							
Outisde Gas	------	------	------	------	------	-----	-----
Charge Stock, gm.	264	250	267	261	254	269	263
Total Charge	264	250	267	261	254	269	263
Recovered Material							
H.C. Liqd. Prod.	233.7	222.4	215.7	192.4	216.8	232.7	206.1
Condensable Gases	4.6	9.6	23.8	31.9	13.2	8.3	26.6
Permanent Gases	3.5	4.13	14.3	17.7	5.5	2.3	5.8
Oil from Cat. Bed	5.0	1.9	1.6	0.8	12.0	9.2	11.0
Carbon by Burn-off	6.45	6.4	12.4	15.3	7.5	11.0	7.2
Total Recovery	253.25	244.4	267.3	258.1	255.0	263.5	256.7
Losses by Difference, gm.	10.75	5.6	-0.3	2.0	-1.0	5.5	6.3
% Losses on Charge	4.46	2.24	-0.11	1.1	-0.4	2.04	2.9
Distillation Data							
Wt. of (7-204)°C. Gasoline	86.3	84.0	88.8	83.0	58.6	59.1	62.3
Wt. of Residue	120.6	104.8	84.7	73.2	132.0	159.1	133.4
Wt. of Condensable Gases	26.5	31.7	48.6	52.1	8.4	6.3	21.9
% Carbon on Total Chg.	2.44	2.56	4.64	5.86	2.95	4.09	2.8
% Gasoline on Oil Chg.	32.7	33.6	33.2	31.8	23.1	22.0	23.7
% Conversion On Oil Chg.	52.4	57.3	67.7	71.6	43.4	37.5	45.0
% Ultimate Yield	62.4	58.6	49.0	44.4	53.2	58.7	52.7

TABLE III

Mixed-Gas Catalytic Polyforming of Gas Oil at Atmospheric Pressure

Run No.	8	9	10	11	12
No. Runs on Catalyst	44	45	46	51	52
Avg. Reactor Temp. $^{\circ}$ C.	405	412	443	458	475
Space Velocity hr.$^{-1}$	4.6	4.7	4.8	4.65	4.5
Material Charged					
Outside Gas		Synthetic Gas Mixture			
Outside Gas, gm.	156.4	149.4	165.4	158.4	148.4
Charge Stock, gm.	259	264	259	267	270
Total Charge	415.3	413.4	424.4	425.4	418.4
Recovered Material					
H. C. Liqd. Prod.	219.7	226.1	203.1	176.3	149.3
Condensable Gases	152.4	157.9	188.5	208.5	215.8
Permanent Gases	5.9	6.8	9.1	22.6	39.2
Oil from Cat. Bed	15.5	6.0	11.3	2.9	0.9
Carbon by Burn-off	10.3	11.2	11.3	11.5	11.6
Total Recovery	502.7	403.8	408.0	421.8	416.8
Losses by Difference, gm.	11.6	5.4	1.2	3.6	1.6
% Losses on Charge	2.7	1.3	0.3	0.85	0.38
Distillation Data					
Wt. of (7-204)$^{\circ}$ C. Gasoline	51.4	53.4	66.0	71.0	67.3
Wt. of Residue	153.3	164.4	146.7	140.1	118.4
Wt. of Condensable Gases	137.8	137.7	153.1	134.0	133.4
% Carbon on Total Chg.	2.5	2.7	2.7	2.7	2.78
% Gasoline on Oil Chg.	19.8	20.2	25.4	26.6	24.9
% Conversion on Oil Chg.	34.9	35.5	39.0	46.4	55.9
% Ultimate Yield	56.7	57.0	65.1	57.4	44.5

TABLE IV

Mixed-Gas Catalytic Polyforming of Gas Oil at 900 psig

Run No.	13	14	15	16	17	18
No. Runs on Catalyst	42	31	32	34	33	41
Avg. Reactor Temp. °C.	392	430	455	470	492	498
Space Velocity $hr.^{-1}$	4.95	4.92	5.03	5.15	5.09	5.0
Material Charged						
Outside Gas		Synthetic Gas Mixture				
Outside Gas, gm.	161	157	181	170	166	164
Charge Stock, gm.	268	270	263	269	262	271
Total Charge	429	427	444	439	428	435
Recovered Material						
H. C. Liqd. Prod.	224.7	202.6	164.9	168.2	125.6	178.4
Condensable Gases	153.0	170.0	208.0	210.6	186.5	192.4
Permanent Gases	18.9	25.2	35.0	21.0	60.0	64.6
Oil from Cat. Bed	12.6	0.5	1.0	0.6	0.6	1.6
Carbon by Burn-off	15.1	20.5	28.1	29.4	44.5	45.4
Total Recovery	424.3	418.8	437.0	429.8	417.2	422.4
Losses by Difference, Gm.	4.7	8.2	7.0	9.2	10.8	12.6
% Losses on Charge	1.1	1.9	1.58	2.1	2.52	2.9
Distillation Data						
Wt. of (7-204) °C. Gasoline	59.0	79.3	81.8	80.7	72.3	70.5
Wt. of Residue	162.6	134.2	115.0	106.3	81.1	74.9
Wt. of Condensable Gases	97.2	140.3	147.5	161.1	125.6	137.4
% Carbon on Total Chg.	3.5	4.8	6.2	6.7	10.4	10.4
% Gasoline on Oil Chg.	22.0	29.5	30.75	30.0	27.6	26.0
% Conversion on Oil Chg.	34.5	50.1	55.9	60.2	68.8	71.8
% Ultimate Yield	63.8	58.8	55.0	49.9	40.1	36.2

TABLE V

Mixed-Gas Catalytic Polyforming of Gas Oil at 1500 and 2000 psig

Run No.	19	20	21	22	23	24
No. Runs on Catalyst	4	6	5	7	8	9
Avg. Reactor Temp. °C.	439	449	480	440	460	470
Avg. Oper. Press. psig	1500	1500	1500	2000	2000	2000
Space Velocity $hr.^{-1}$	4.6	4.7	4.6	4.5	4.3	4.9
Material Charged						
Outside Gas		Synthetic Gas Mixture				
Outside Gas, gm.	165.5	152	180.3	195	202	200.5
Charge Stock, gm.	266.5	264	255.7	306	304	306.5
TotalCharge	432.0	416	436.0	501	506	507
Recovered Material						
H. C. Liqd. Prod.	249.7	216.0	183.2	265.4	263.4	256.2
Condensable Gases	137.5	127.4	164.2	181.7	170.7	161.9
Permanent Gases	12.9	23.5	29.0	17.8	24.2	34.6
Oil from Cat. Bed	3.9	8.5	4.8	5.1	8.3	11.5
Carbon by Burn-off	28.8	36.7	46.5	27.7	36.5	38.5
Total Recovery	432.8	412.1	427.7	497.7	503.1	502.7
Losses by Difference, gm.	-0.8	3.9	8.3	3.3	2.9	4.3
% Losses on Charge	-0.2	0.9	1.9	0.7	0.6	0.9
Distillation Data						
Wt. of (7-204)°C. Gasoline	93.1	92.5	89.5	91.0	91.8	91.8
Wt. of Residue	113.1	85.4	63.2	143.9	126.2	113.3
Wt. of Condensable Gases	137.8	144.4	152.9	161.0	167.3	155.9
% Carbon on Total Chg.	6.7	8.8	10.7	5.5	7.2	7.6
% Gasoline on Oil Chg.	34.9	35.0	35.0	29.7	30.2	30.0
% Conversion on Oil Chg.	56.1	64.4	73.4	51.4	55.9	59.3
% Ultimate Yield	62.2	54.4	47.7	57.9	54.0	50.7

TABLE VI

Time of Stream Determination - Gas Oil With Mixed Gas at 900 psig

Run No.	25	26	27	29	20	30
No. Runs on Catalyst	35	36	37	38	39	40
Avg. Reactor Temp. °C.	456	463	460	456	458	454
Cumulative Time on Stream, min.	6.53	13.33	19.91	26.23	33.53	40.08
Space Velocity $hr.^{-1}$	4.74	4.80	4.96	5.12	4.50	4.85
Material Charged						
Outside Gas		Synthetic Gas Mixture				
Outside Gas, gm.	164	173	167	166	165	162
Charge Stock, gm.	271	262	266	264	272	261
Total Charge	435	433	430	437	423	
Recovered Material						
H. C. Liqd. Prod.	166.5	196.1	208.0	225.8	220.3	234.8
Condensable Gases	201.0	188.1	155.9	156.7	166.9	154.1
Permanent Gases	31.5	27.3	33.2	26.8	27.6	21.0
Oil from Cat. Bed	0.4	0.5	0.3	1.1	0.3	1.0
Carbon by Calculation	33.3	21.7	20.8	14.6	13.6	12.0
Total Recovery	432.7	433.8	418.2	425.0	428.6	422.4
Losses by Difference, gm.	2.3	1.2	14.8	5.0	8.4	0.1
% Losses on Charge	0.53	0.28	3.42	1.16	1.92	0.00
Distillation Data						
Wt. of (7-204)° C. Gasoline	81.5	71.6	72.0	50.0	59.8	50.5
Wt. of Residue	108.9	138.9	144.9	173.1	187.0	186.0
Wt. of Condensable Gases	155.4	144.3	128.0	113.3	121.2	134.6
% Carbon on Total Chg.	7.65	5.00	4.80	3.39	3.11	2.84
% Gasoline on Oil Chg.	30.0	27.4	27.0	22.7	22.0	19.35
% Conversion on Oil Chg.	59.5	46.7	45.5	34.0	31.2	28.4
% Ultimate Yield	50.5	58.6	59.4	66.7	70.5	68.2

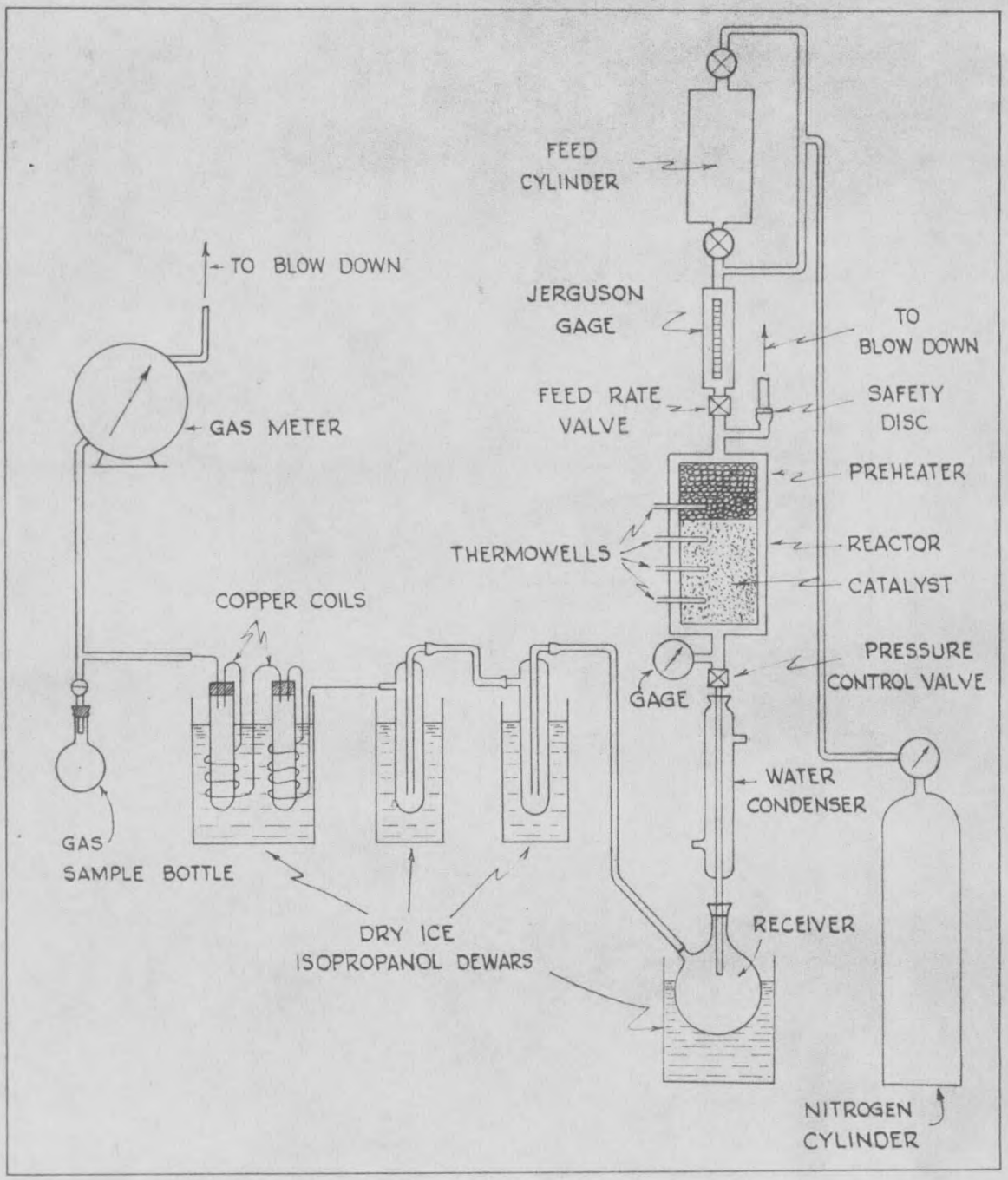

Figure 1

Schematic Diagram of Low Pressure Unit

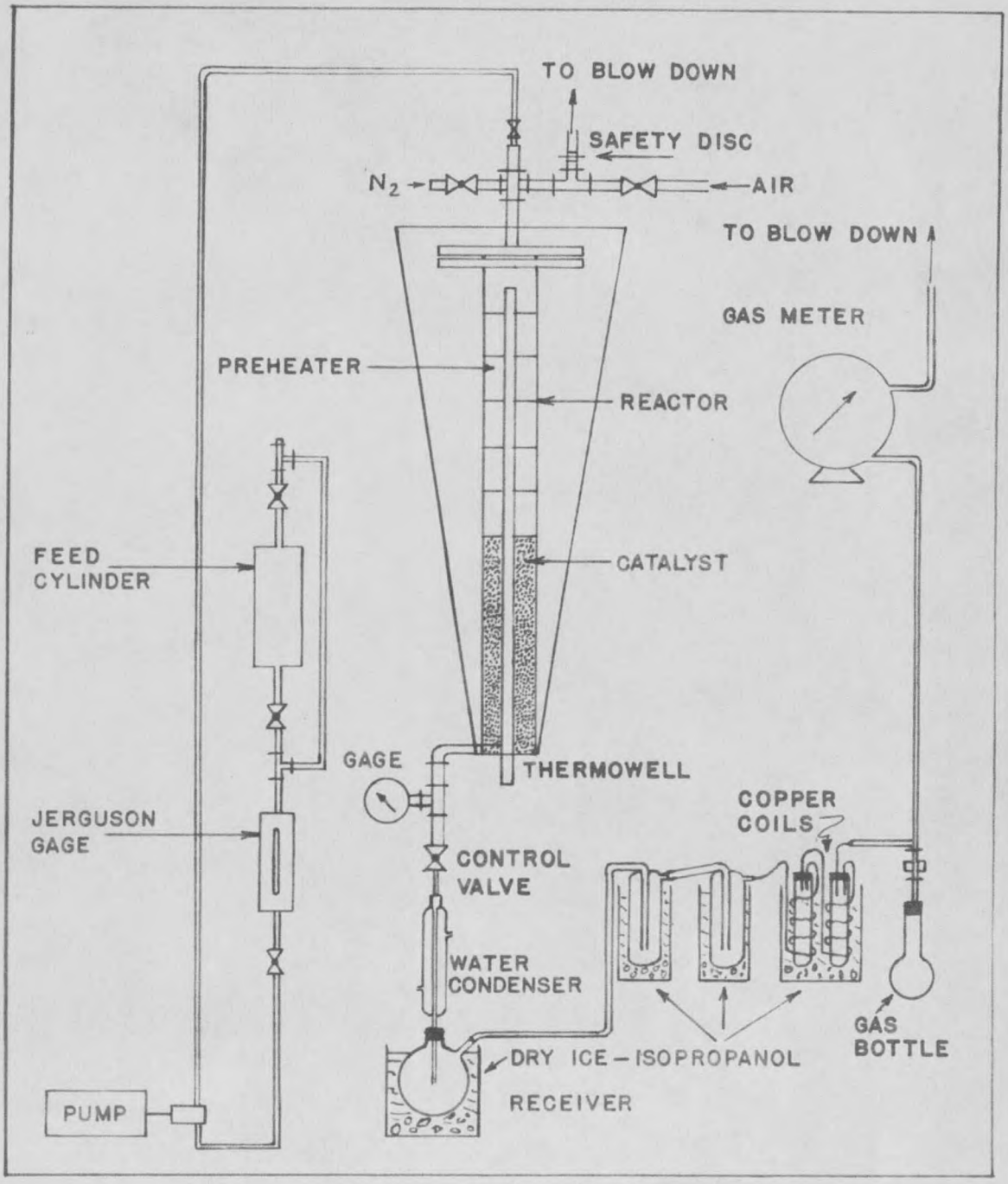

Figure 2

Schematic Diagram of High Pressure Unit

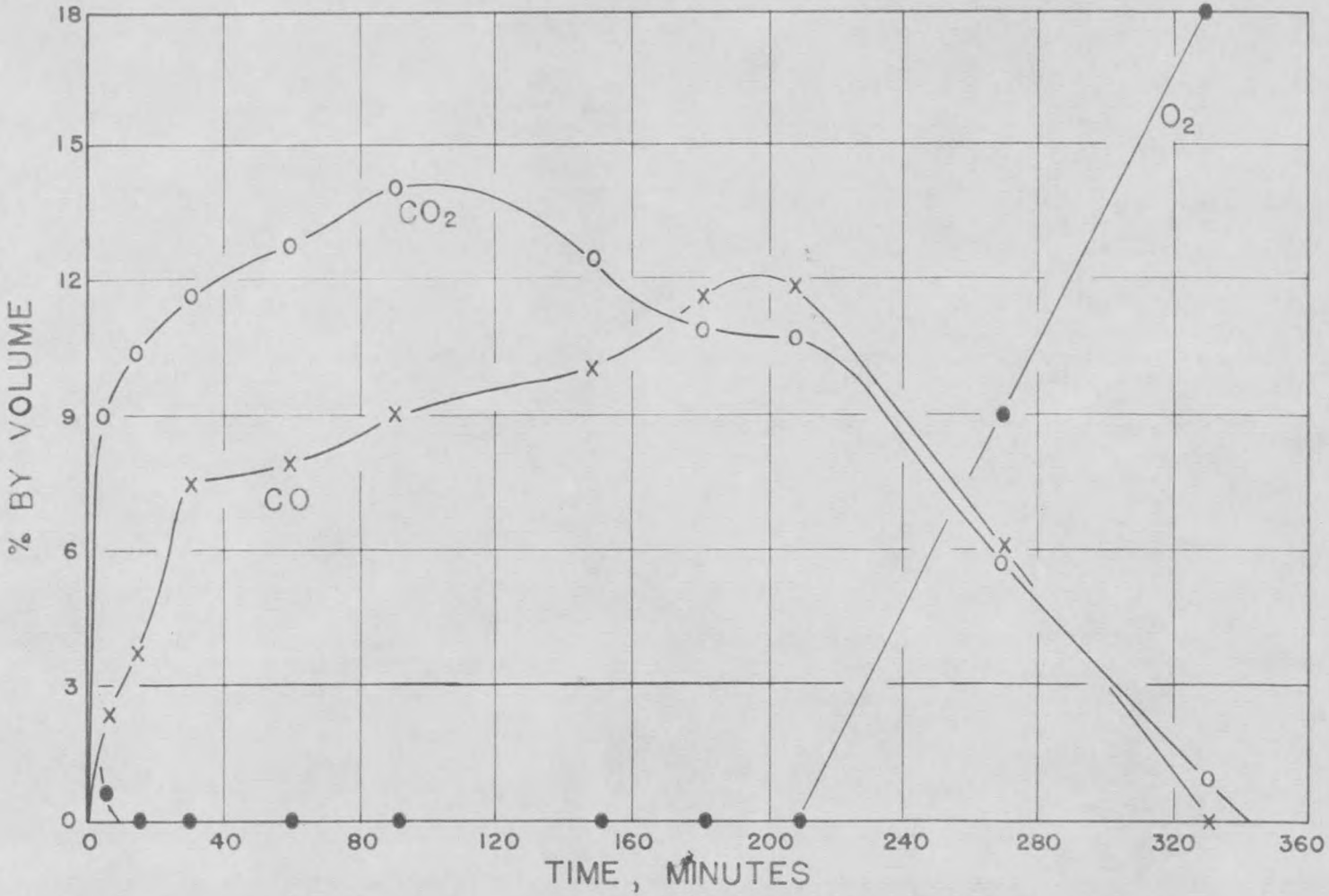

Figure 3

Composition of Effluent Gas During Catalyst Burn-off

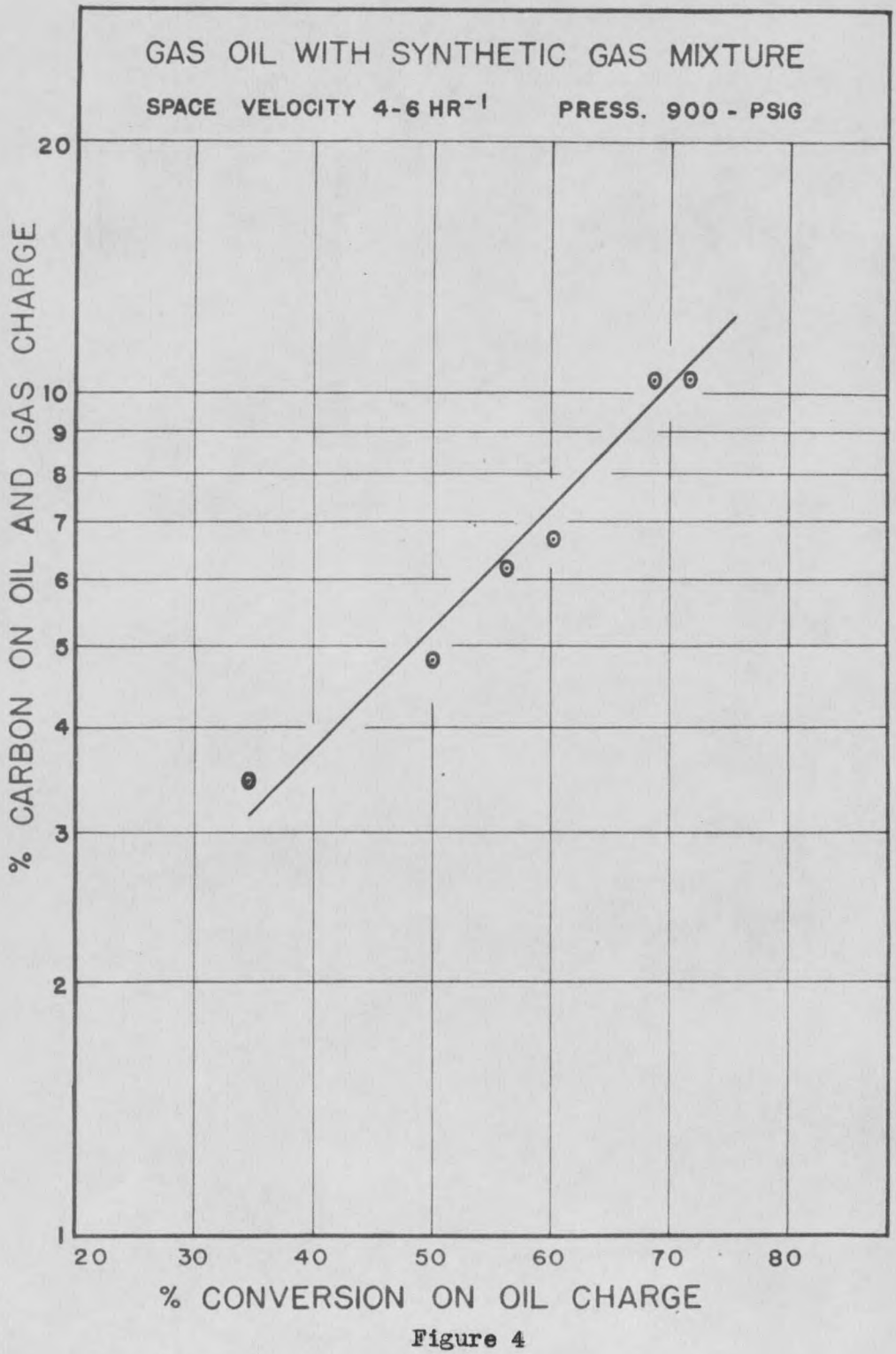

Figure 4

Effect of Conversion on Carbon Yield at 900 psig

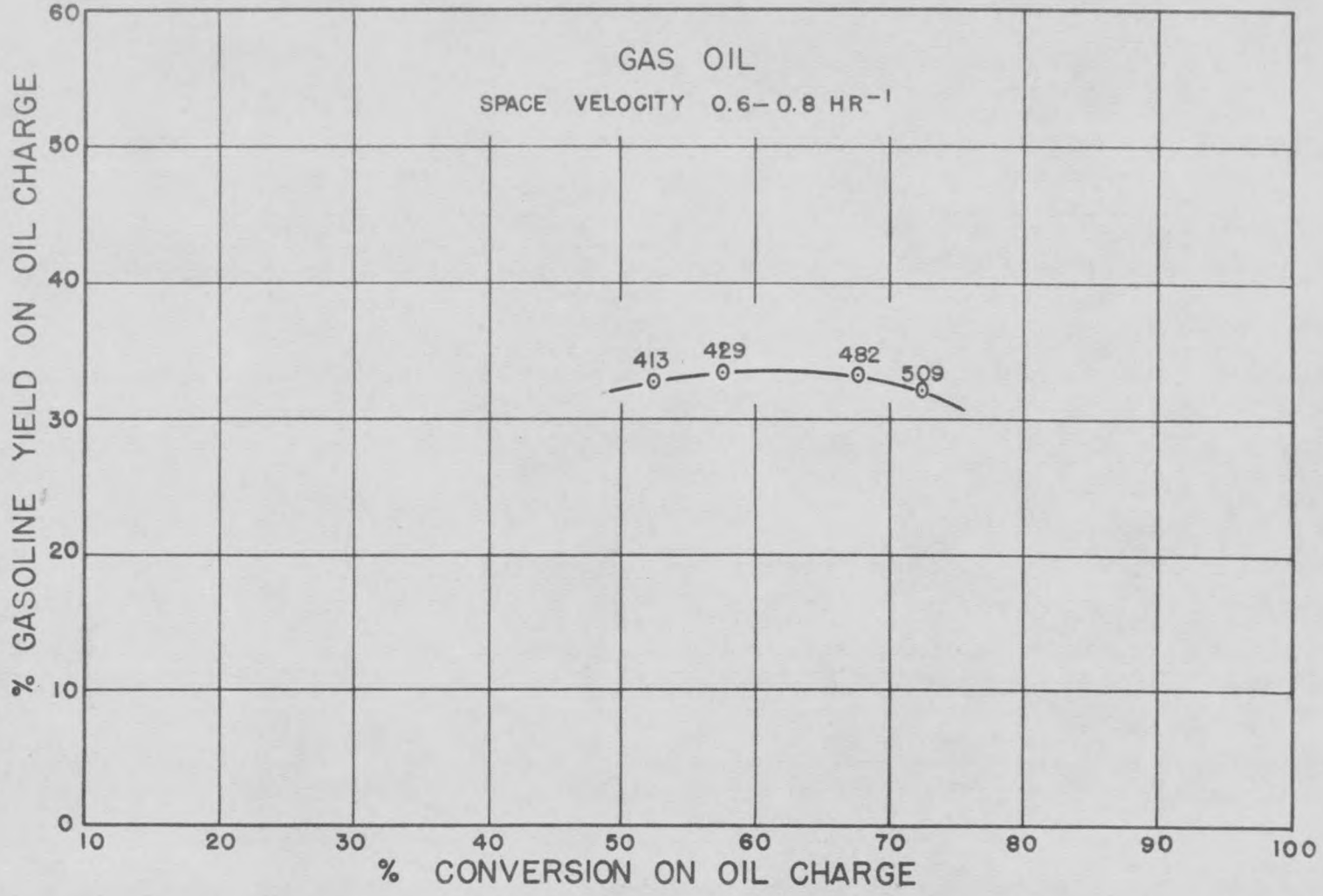

Figure 5

Effect of Conversion on Gasoline Yield at Atmospheric Pressure

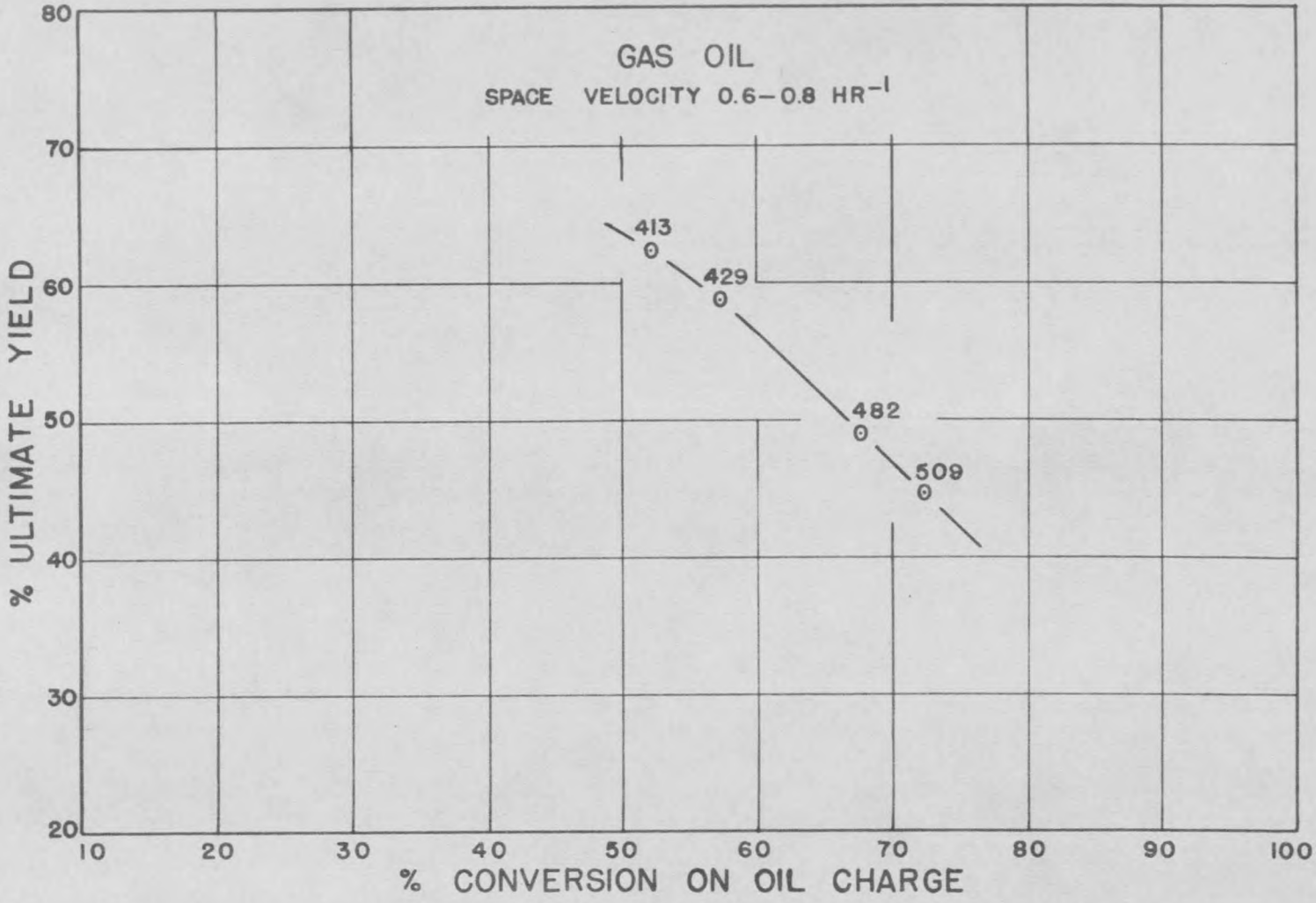

Figure 6

Effect of Conversion on Ultimate Yield of Gasoline at Atmospheric Pressure

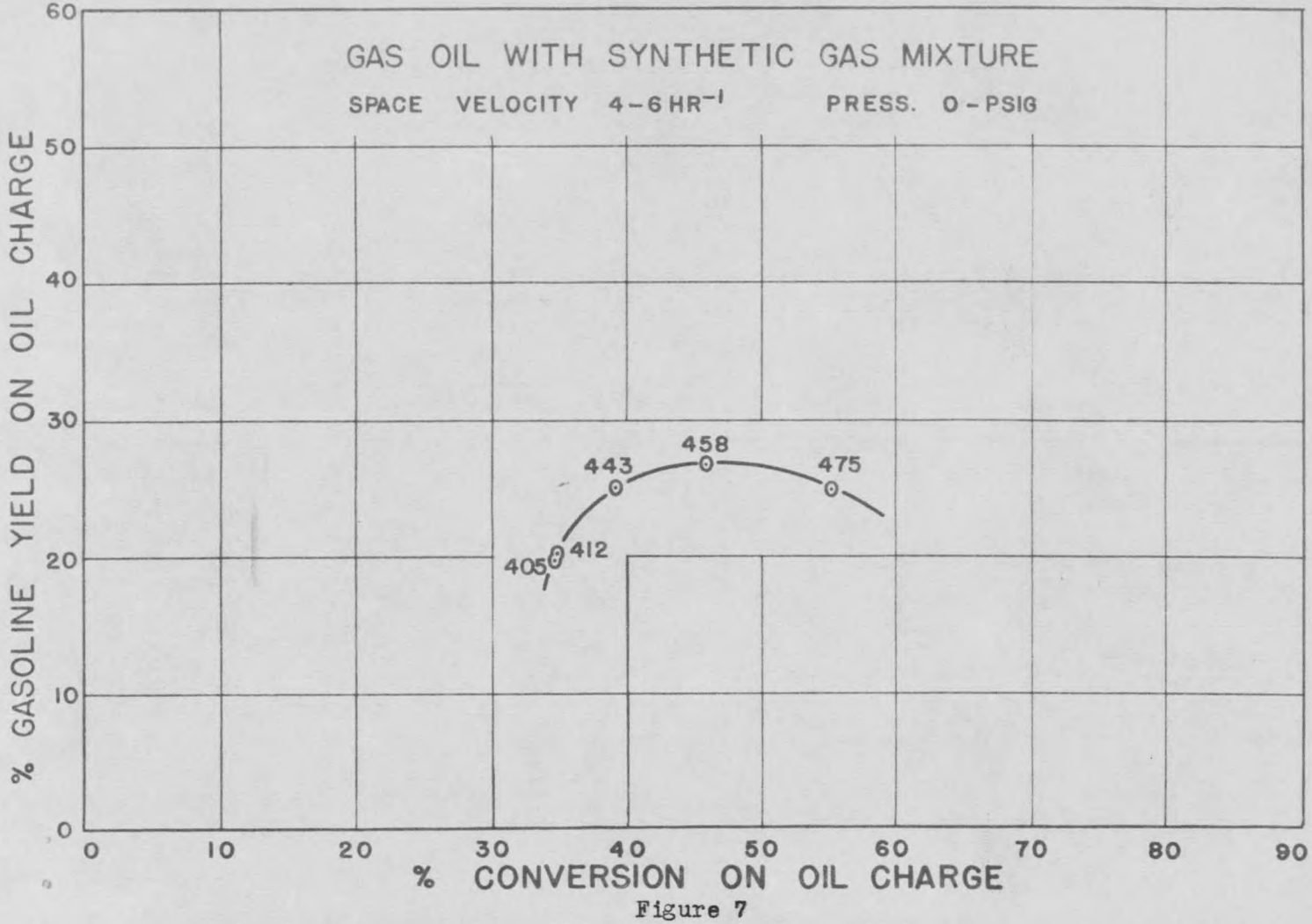

Figure 7

Effect of Conversion on Gasoline Yield at Atmospheric Pressure With Mixed Gas

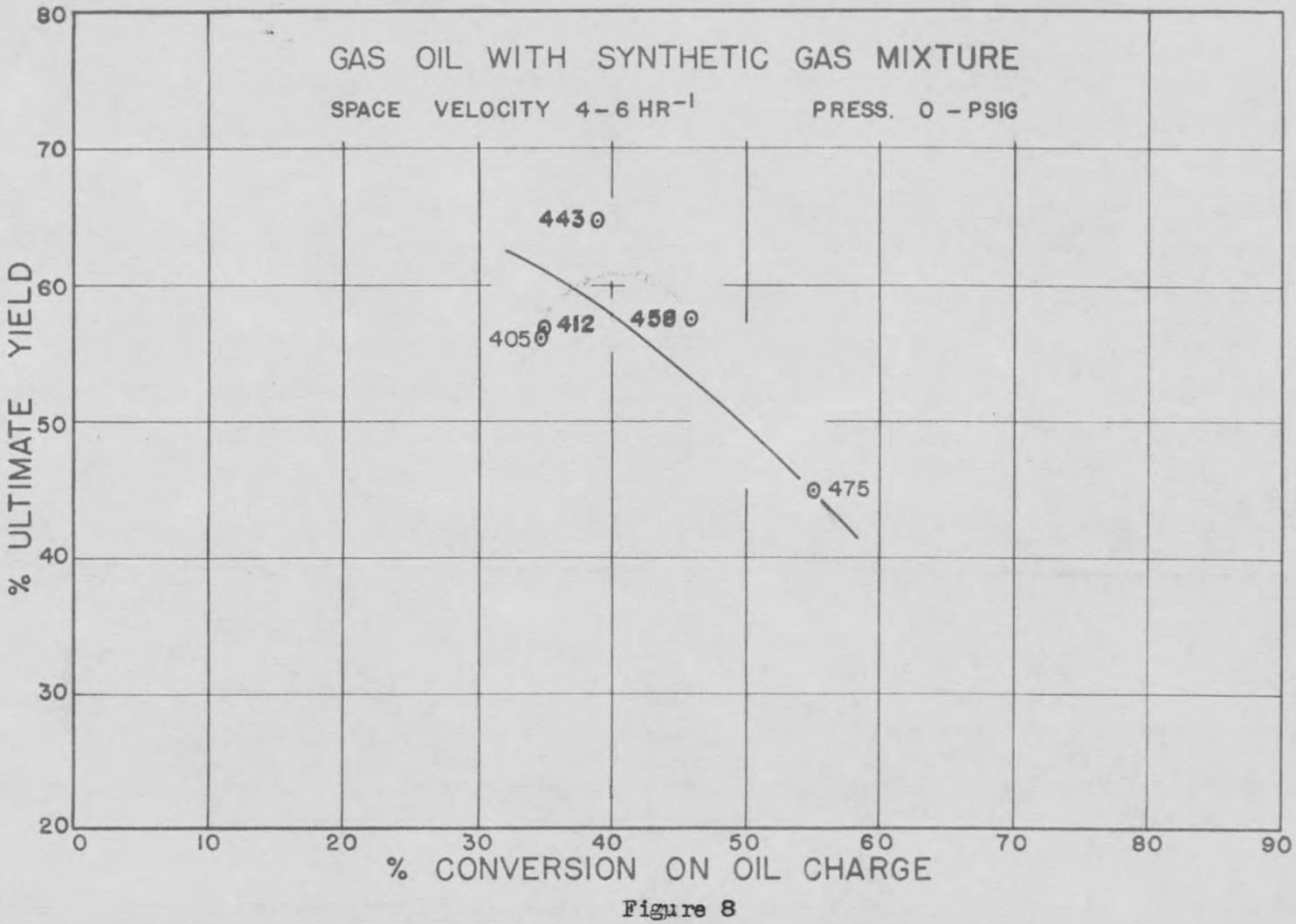

Figure 8

Effect of Conversion on Ultimate Yield of Gasoline at Atmospheric Pressure With Mixed Gas

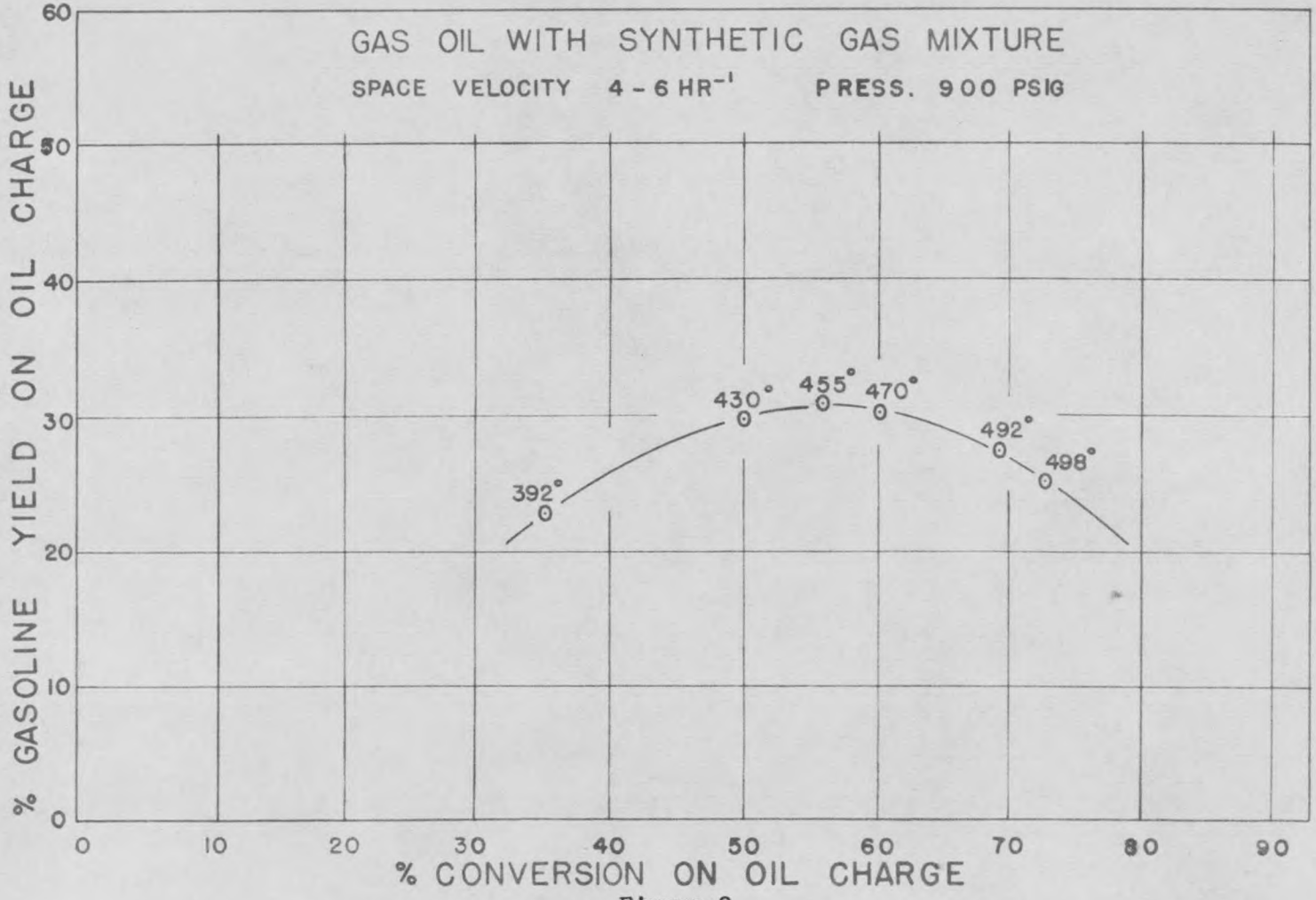

Figure 9

Effect of Conversion on Gasoline Yield at 900 psig With Mixed Gas

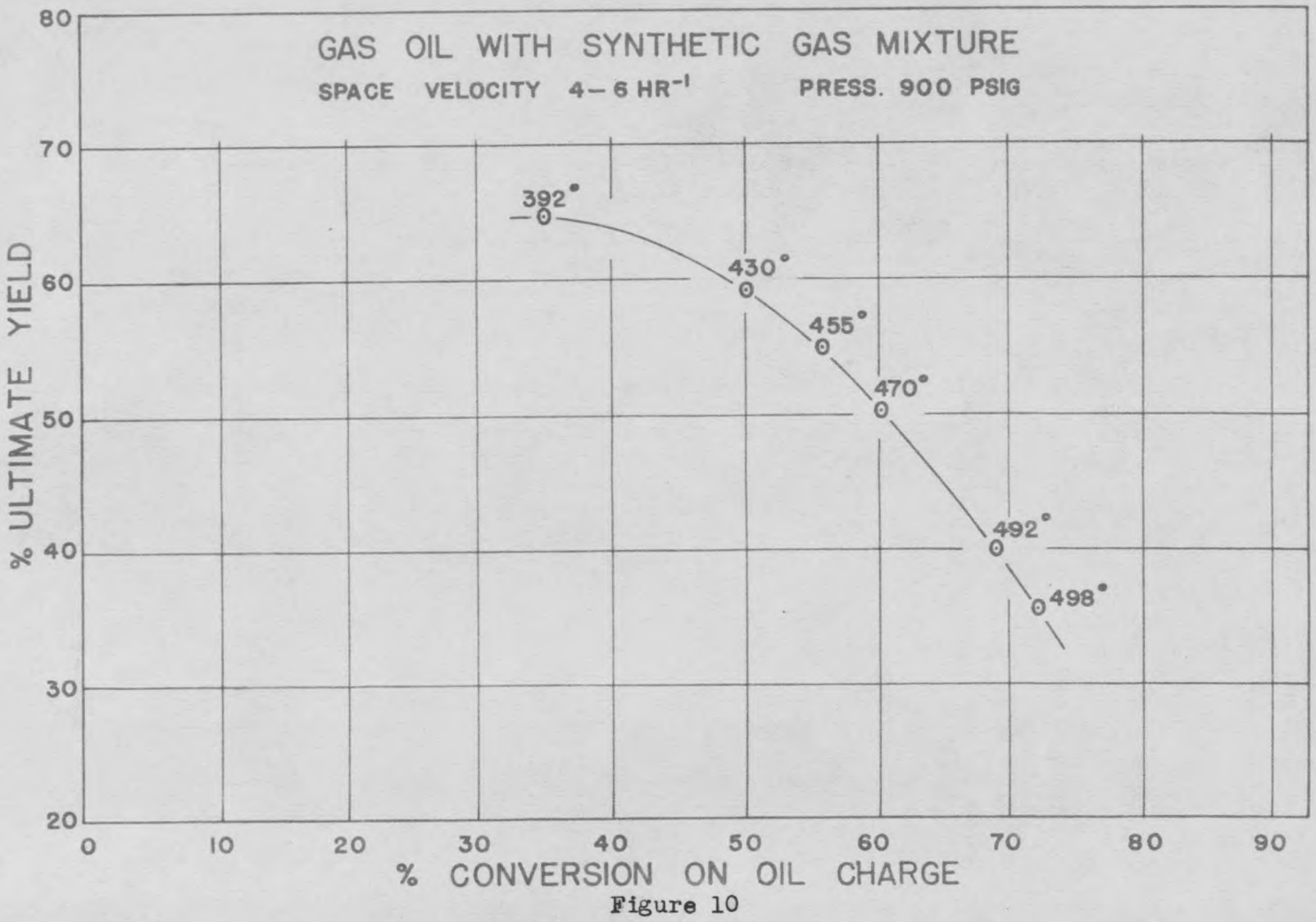

Figure 10

Effect of Conversion on Ultimate Yield of Gasoline at 900 psig With Mixed Gas

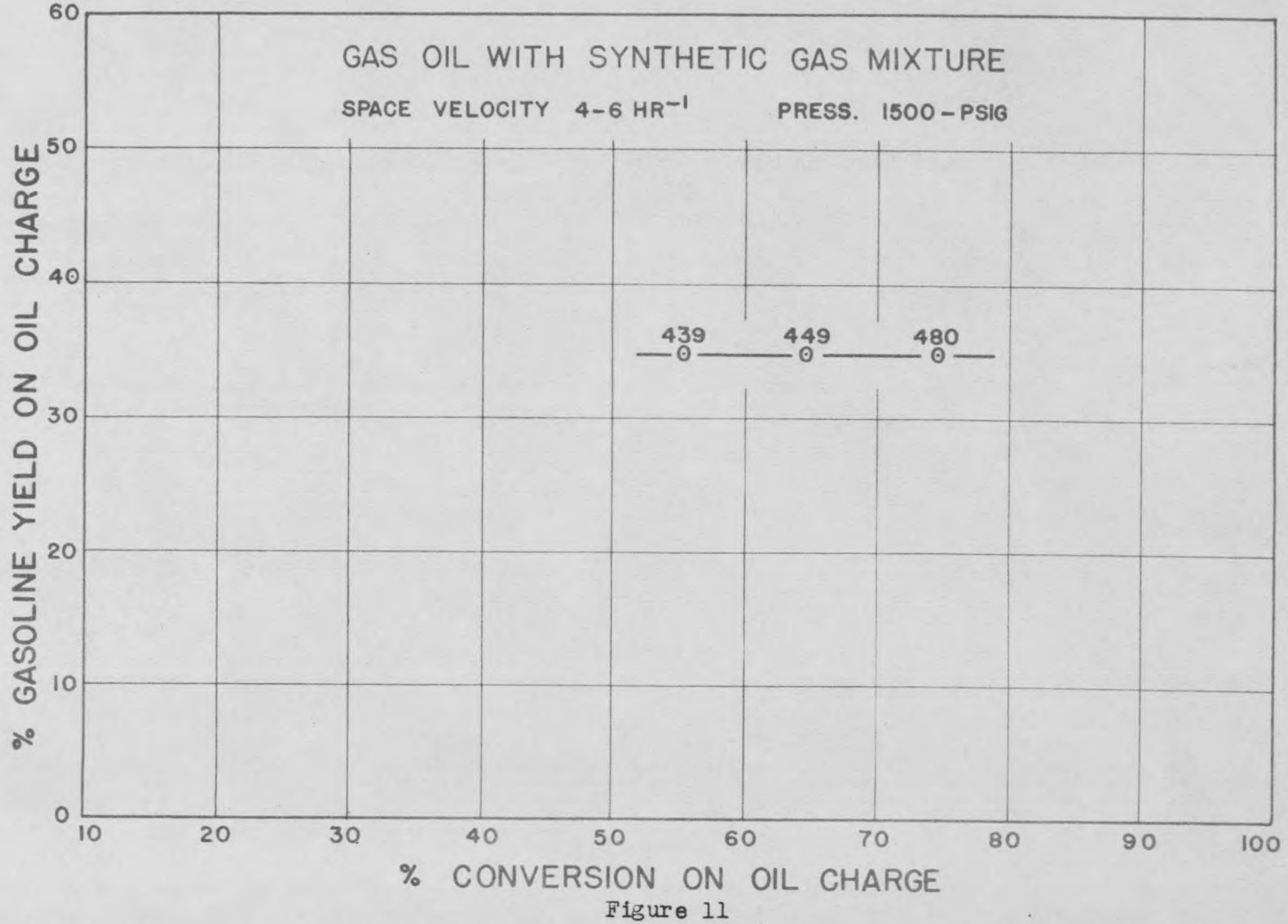

Figure 11

Effect of Conversion on Gasoline Yield at 1500 psig With Mixed Gas

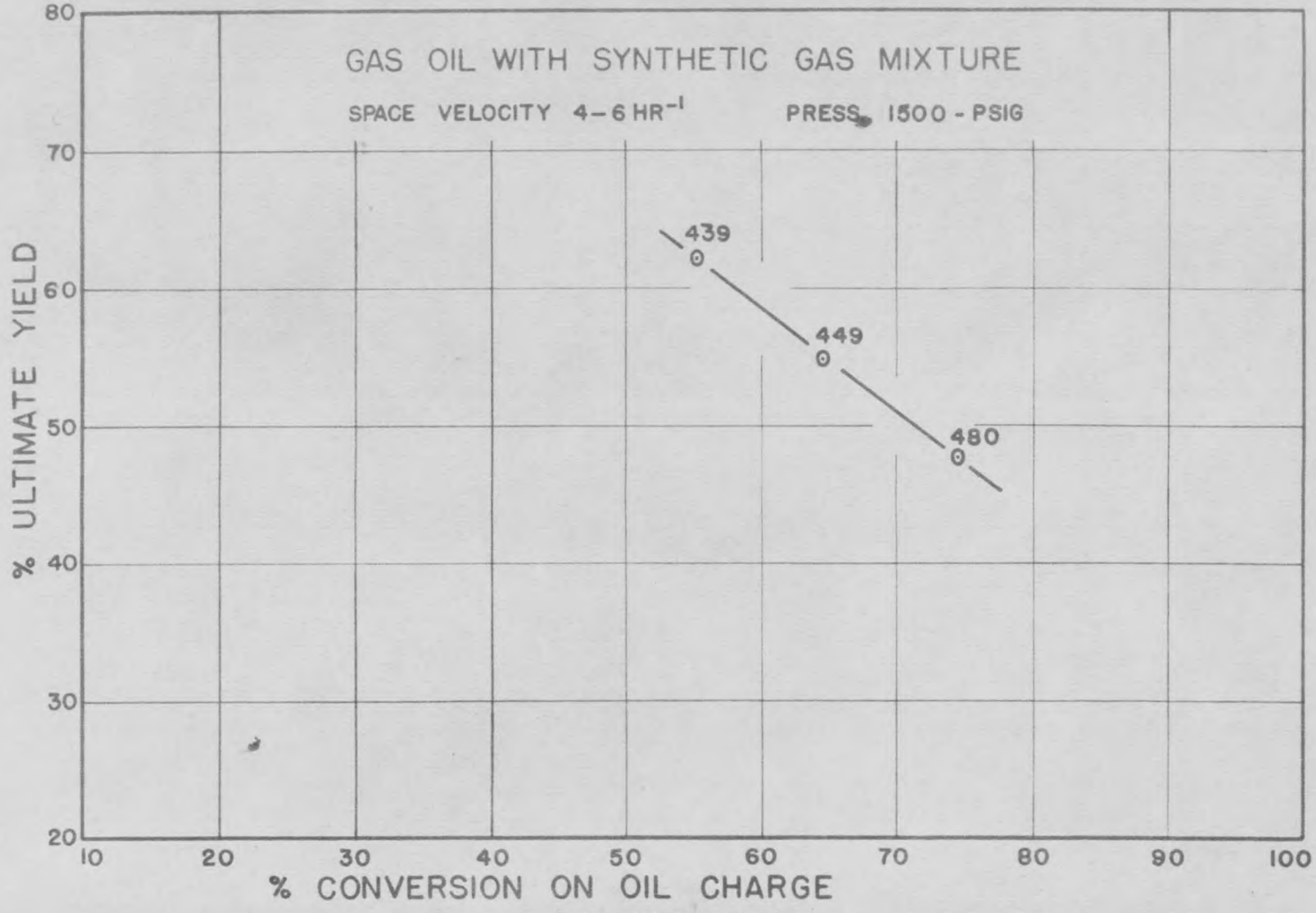

Figure 12

Effect of Conversion on Ultimate Yield of Gasoline at 1500 psig with Mixed Gas

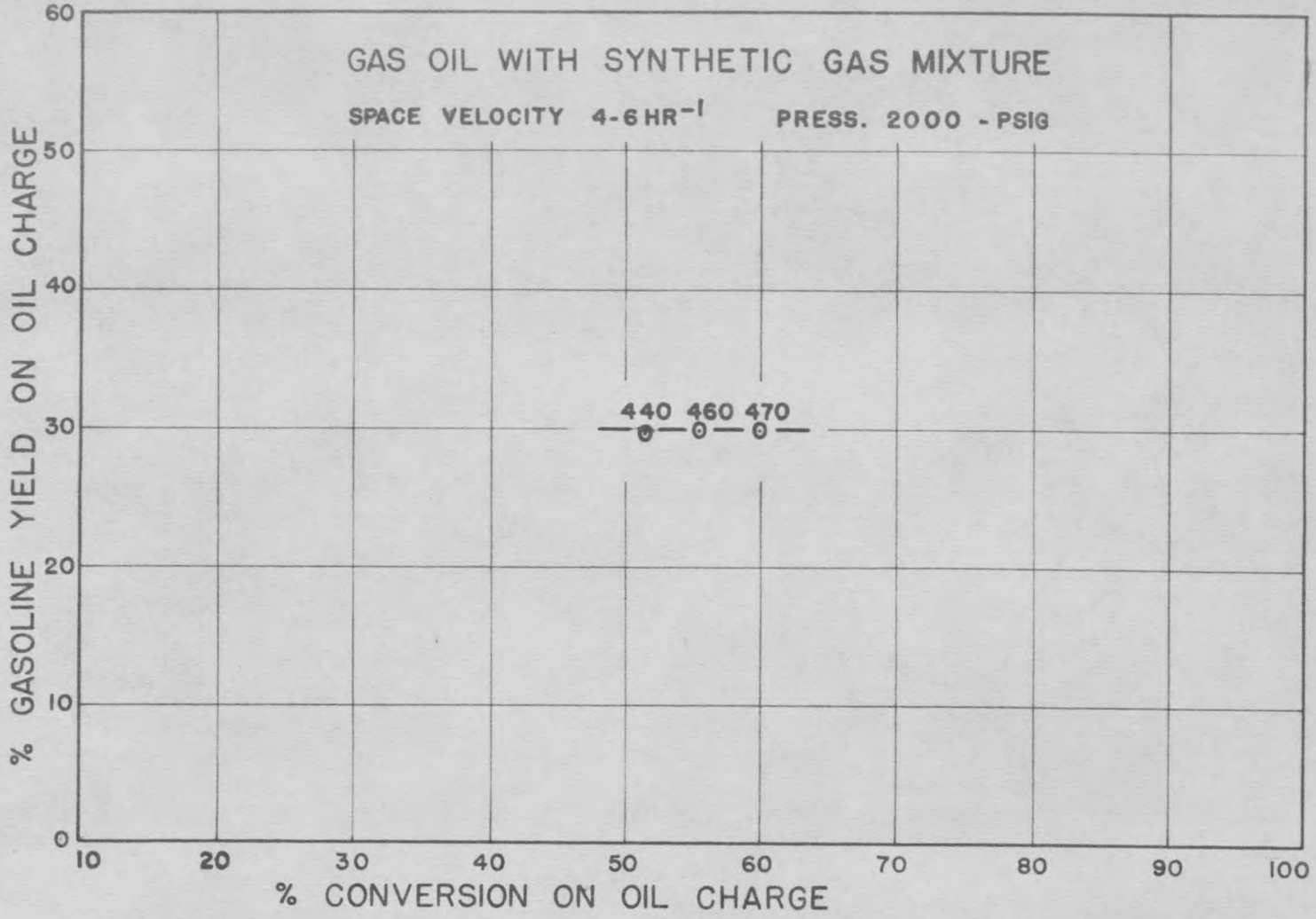

Figure 13
Effect of Conversion on Gasoline Yield at 2000 psig with Mixed Gas

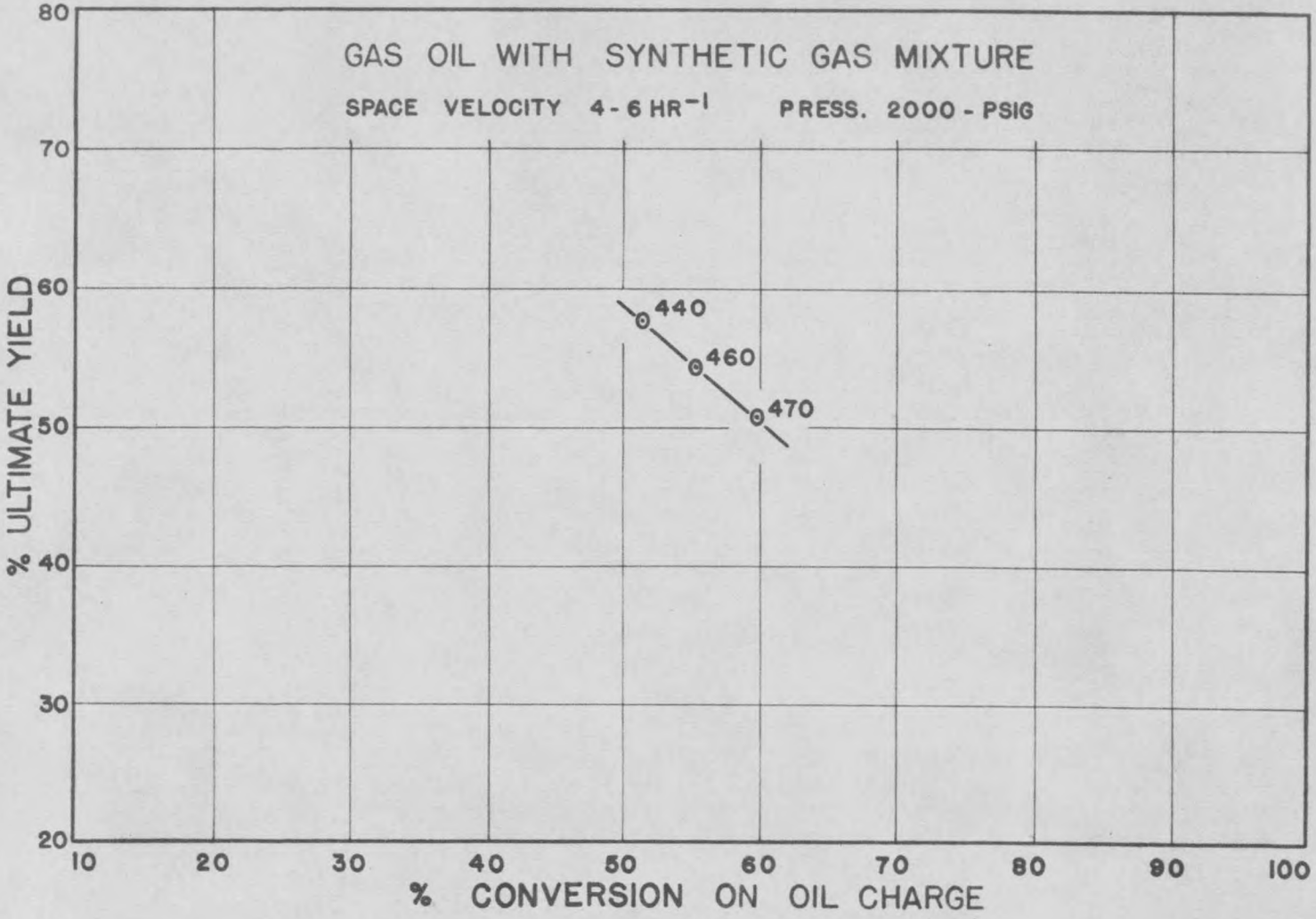

Figure 14

Effect of Conversion on Ultimate Yield of Gasoline at 2000 psig with Mixed Gas

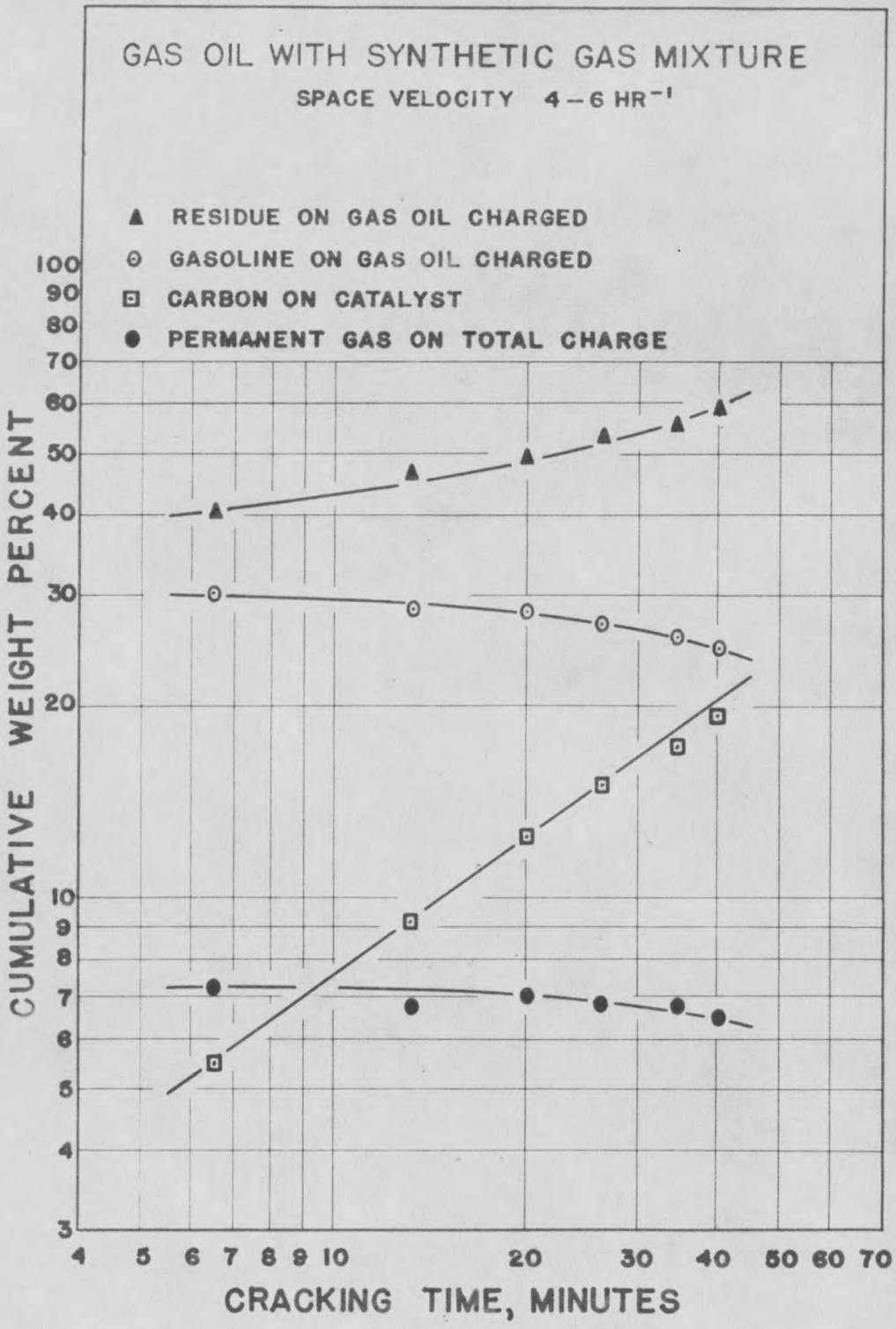

Figure 15

Effect of Stream Time on Yield of Conversion Products at 900 psig With Mixed Gas