



Catalytic polyforming of shale oil
by R L Crecelius

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

The purpose of this investigation was the evaluation of the polyforming process under catalytic conditions as a method for motor fuel production from a shale oil diesel fraction and the outside gases iso-butylene and n-butane.

The same Houdry fixed bed aluminum silicate catalyst was used for all runs and the carbon was burned off the catalyst at the conclusions of each run. The investigation was conducted at temperatures varying from 366°C to 573°C.; and the liquid space velocities used were 0.5 to 0.7 and 4.0 to 6.0 volumes of charge per volume of catalyst per hour. During an average run approximately 450 grams of feed were passed over 1000 ml. of catalyst using a pressure of 900 psig.

It was found that higher yields of gasoline were obtained when iso-butylene was used as an outside gas at both high and low space velocities than could be obtained from a straight catalytic crack of the shale oil. No such effect in increasing the yield was noted when n-butane was used as the outside gas. The increased yield of gasoline with iso-butylene catalytic polyforming over that from a catalytic cracking operation is quite interesting in that it can be obtained at a space, velocity ten times that normally used in catalytic cracking.

At the same time, the maximum gasoline yield for catalytic polyforming runs occurred at temperatures varying from 40 to 100°C. lower than for catalytic cracking.

It was indicated that pressures higher than 900 psig. may give even higher yields of gasoline. The gum content of the gasoline was essentially the same regardless of the process by which the sample was prepared.

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Approved:

Lloyd Berg

Head, Major Department

Lloyd Berg

Chairman, Examining Committee

J. A. Nelson

Dean, Graduate Division

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ABSTRACT

The purpose of this investigation was the evaluation of the polyforming process under catalytic conditions as a method for motor fuel production from a shale oil diesel fraction and the outside gases iso-butylene and n-butane.

The same Houdry fixed bed aluminum silicate catalyst was used for all runs and the carbon was burned off the catalyst at the conclusions of each run. The investigation was conducted at temperatures varying from 360°C. to 573°C.; and the liquid space velocities used were 0.5 to 0.7 and 4.0 to 6.0 volumes of charge per volume of catalyst per hour. During an average run approximately 450 grams of feed were passed over 1000 ml. of catalyst using a pressure of 900 psig.

It was found that higher yields of gasoline were obtained when iso-butylene was used as an outside gas at both high and low space velocities than could be obtained from a straight catalytic crack of the shale oil. No such effect in increasing the yield was noted when n-butane was used as the outside gas. The increased yield of gasoline with iso-butylene catalytic polyforming over that from a catalytic cracking operation is quite interesting in that it can be obtained at a space velocity ten times that normally used in catalytic cracking. At the same time, the maximum gasoline yield for catalytic polyforming runs occurred at temperatures varying from 40 to 100°C. lower than for catalytic cracking.

It was indicated that pressures higher than 900 psig. may give even higher yields of gasoline. The gum content of the gasoline was essentially the same regardless of the process by which the sample was prepared.

I INTRODUCTION

The investigation of oil shale has been carried on for a number of years by the Bureau of Mines of the U. S. Department of the Interior. In 1944 this program was given added impetus by the passage of the Synthetic Liquid Fuels Act when Congress became alarmed by reports that the United States' oil reserves were being rapidly depleted by the nation's ever increasing fuel consumption.

Oil shale is a stratified rock formed from mud and organic matter laid down on the floor of ancient seas and lakes. Later upheavals of the ocean bottom followed by water erosion have laid bare these tremendous seams of oil shale. The deposits, known as the Green river oil shale beds, are located in the states of Colorado, Utah and Wyoming. Estimates of the oil reserves in the Rifle-DeBeque area of Western Colorado alone vary from 200 to 300 billion barrels, which is more than ten times as much oil as has been produced from the time of the opening of the Drake well to date.

Development of oil shale resources has not been of commercial interest because it was felt that oil could not be produced as cheaply by mining oil shale as from the normal petroleum crude sources and that the production of acceptable end products was considerably more expensive. As a result of the gradual decline of petroleum resources, particularly in North America, and in view of the need, in case of national

emergency, of great quantities of fuels and lubricants from sources within the continental United States, Congress passed the Synthetic Liquid Fuels Act which enabled the U. S. Bureau of Mines to build large retorts and set up a demonstration mine close to the small mountain town of Rifle, Colorado (1). In general, the unit mining costs in surface workings are less than in underground mines. The aim of the demonstration mine, therefore, has been to take a quarry underground and adopt as many surface mining practices as practicable to underground conditions. The oil shale beds in Colorado, which vary in thickness from 70 to 500 feet, are well suited to large scale mechanized mining. It has been demonstrated at the Rifle mine that rooms 60 by 100 feet can be opened safely without supports for the stone overlying the oil shale to be mined. The beds are essentially flat, and multiple drills mounted on trucks are taken underground to drill the oil shale preparatory to blasting to advance the heading and bench. An electric shovel with a three yard bucket is used to load the shale from the blasting operation onto 15 cubic yard capacity diesel trucks for transportation to the crusher plant charge hopper. Disposal of waste rock from the mine or the retorts is no problem since it can easily be dumped off the cliff into the canyon. By applying the above mentioned efficient methods to the demonstration mine, a monthly average shale production of 100 tons per man shift has been attained. It is thought that addition-

al development of underground techniques will eventually bring the average production figure to 125 tons per man shift or 25 times the production of the average American coal miner.

In conjunction with the work being carried on at Rifle, Colorado and Laramie, Wyoming, additional research to find a commercial retorting process is being carried on by the Colorado Fuel and Iron Corporation, the Tennessee Valley Authority, the Union Oil Company of California and the Standard Oil Development Company. Most of the research has been directed toward making the retorting operation a continuous process since the N.T.U. retorts used at Rifle are operated as a batch process.

The oil is present in the shale as a brown to black solid organic material called Kerogen. The oil is extracted in the retorts by burning part of the Kerogen to furnish the heat necessary to crack the rest of the Kerogen and distill off the resulting oil vapors. The cracked vapors are condensed into a very viscous crude shale oil similar in some physical properties to heavy petroleum crude.

The crude has been fractionated and given some of the more common petroleum treatments which has resulted in the production of gasoline, diesel oil and other fuels. These fuels are characterized by a high gum content, high degree of unsaturation, high sulfur and nitrogen content, low color stability and a quite offensive odor suggestive of pyridine, picoline, or collidine. From these results it would seem that the usual

petroleum treatments are not suitable for the processing of shale oil fractions both from the standpoint of quality of product and cost of the finished product.

During the last ten years, economy in production both as to money and material has fostered the development of a number of new processes in petroleum technology. Two of these, the polyform process and catalytic cracking, when applied to shale oil, are of interest to this investigation.

The polyform process employs the principle of cracking naphtha and heavier oils in admixture with varying amounts of normally gaseous cheap hydrocarbons (propane and butanes). This charge mixture can be subjected to higher temperatures, with resulting increases in the octane number, and at the same time obtain 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 and 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 higher and higher yields of gasoline when cracked in a one-pass operation with increasing gas dilutions. The increase in yield is attributed 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.

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

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 stock 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 and the temperature and space velocity were the variables. 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.

The results of Dev and Mayfield led the author to an investigation to evaluate the process of shale oil polyforming under catalytic conditions using iso-butylene and n-butane as the outside gases. The yields of gasoline from the catalytic cracking of shale oil with outside gases at 900 psig and varying temperatures were compared with the results of catalytic cracking without a gas. Houdry fixed bed synthetic catalyst was used. Space velocities used were 0.5 - 0.7 hr.⁻¹ and 4 - 6 hr.⁻¹.

II EQUIPMENT, METHODS AND MATERIALS

A. Equipment

The equipment used in this investigation consisted of the 0-1000 psig reaction system which is shown in a schematic drawing, Figure 1. The feed cylinder was made from a piece of three-inch extra strong steel pipe, 8 inches long. 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 to take one-half inch pipe and the inside of the cap machined down to facilitate draining. Both caps were fitted with close hipples and high pressure stainless steel Kerotest globe valves.

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

A semi-transparent plastic cm. scale was fastened into the back of the Jerguson gage and a light placed behind it to facilitate the reading of the scale. The Jerguson gage was then calibrated so that the volume of liquid in the gage

would be known for any reading on the scale.

The bottom of the Jerguson gage was connected with extra strong steel pipe to a Henry Vogt 6000 pound, 1/2" valve which was used to control 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 with the male side of the union welded directly to the top of the reactor. The off-stream side of the tee was fitted with a Black, Sivalls & Bryson frangible disc safety valve. The atmospheric pressure side of the safety valve was connected to a blow-down line leading to the outside of the building. Since the maximum pressure to be used on this system was 1000 psig, the safety valve was fitted with a diaphragm that would blow out between 1190 and 1210 psig.

The reactor was made from a three-inch extra strong steel pipe, 15 inches in length. The bottom of this pipe was welded shut with a one-half inch steel plate into which a six inch piece of extra strong steel pipe had been welded flush with the top of the plate. This pipe was threaded at the lower end and screwed into a tee which in turn was connected by a short nipple to another 6000 pound Vogt 1/2" valve. The valve, which was used to regulate the pressure on the system, was turned around so that the pressure was under the stem, both for ease in cracking the valve to relieve pressure and to prevent leaks through the packing. The third side of the tee was fitted with

a pressure gage convenient to the pressure control valve for maintenance of the desired 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 using the hole in the union as a jig. The hole was purposely drilled large for ease in changing the Houdry catalyst and the 500 ml. of assorted size steel balls which were put in on top of the catalyst to act as a preheater section. Nine-sixteenths inch in diameter balls were the largest size used in the pre-heater. In the final assembly, the steel cap was arc welded onto the reactor body.

Two three-eighths inch low carbon steel rods were welded to the reactor on the opposite side from the thermowells to act as supports for the reactor chamber. Two pieces of 1/4" x 1" flat bar stock were welded to the top of the cap and they, in turn, were fastened by 1/2" pins to the back of the barricade to keep the reactor from turning when the union was being tightened or broken apart.

The reactor was fitted with four thermocouple wells approximately symmetrically spaced at 3 inch intervals. The iron constantan thermocouples were connected to a Leeds and Northrup indicating potentiometer. This potentiometer was calibrated in degrees centigrade and could be used to record temperatures up to 1100°C.

The reactor was wrapped with asbestos tape. Over this tape 48 feet of Nichrome wire with a resistance of 1.71 ohms per foot, were wound to furnish heat for the pre-heater section which was about the top one-third of the reactor. Another 48-foot section was wound around the reactor section, approximately the bottom two-thirds of the reactor. Each of these windings drew three amperes maximum from a 220-volt autotransformer. These windings were covered with a thin layer of asbestos mud and two additional 12-foot windings of Nichrome wire were placed around the reactor section, one on the top half of the section and one around the bottom. Each of these windings was connected to a 110-volt autotransformer and drew six amperes maximum. Another heavier coating of asbestos mud was placed over the entire length of the reactor, followed by a layer of inch thick magnesia blocks cut to fit around the reactor. These, in turn, were covered with another layer of asbestos mud. The ends of the reactor were also covered with a heavy layer of mud to reduce heat losses.

A 1/4" steel plate 26" x 90" was mounted against the laboratory rack and the reactor was fastened to this plate. Then a 1/8" steel plate rolled into a half circle 22" in diameter and 40 inches long was hinged to the backing plate so that it would close around the reactor and could be fastened solidly with 1/2" pins. A framework was built up from the hinged section in front of the Jerguson gage and two thicknesses of

automobile safety plate glass were fastened in the frame. This provided a safety window through which the gage could be observed during feed control operations.

The bottom of the pressure control valve was connected to the top of a Liebig Pyrex glass condenser. A piece of glass tubing was sealed onto the bottom of the condenser in order to carry the vapors down to the rounded bottom of the 500 ml. Claisen distillation flask which was used as a receiver. The Claisen flask was immersed in an acetone-dry ice bath contained in a one gallon thermoflask. The side arm 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 autotransformers were Superior Electric Company Powerstats. The 110-volt powerstats had a voltage range of 0 to 135 volts and were fused at 7.5 amperes. The 220-volt powerstats had a range of 0 to 260 volts and were fused at three amperes.

The distillation equipment consisted of a Claisen flask

with a -10 to 250°C. thermometer inserted in the side arm through a neoprene stopper, and a water cooled finger inserted in the main stem. The side arm of the flask was connected to a 100 ml. graduate and the graduate, in turn, to two more cold traps in an acetone-dry ice bath. The distillation flask was heated by a 110-volt 550-watt heater controlled by another autotransformer.

B. Methods

1. Atmospheric Pressure Runs:

The reactor was heated until the thermocouples showed that the temperature was high enough for the run to average the desired temperature. Dry ice was placed in the Dewar flasks containing acetone to give a better cooling medium. Air was swept from the system by using a ten minute nitrogen purge. The feed cylinder was weighed on the Harvard triple beam balance. After the charge had been run into the cylinder, the cylinder was weighed again and the weight recorded. The feed cylinder was then connected into the system as shown in Figure 1 and about a hundred pounds of nitrogen pressure was applied to the balanced pressure feed system. The Jerguson gage was filled with charge by opening the valve at the bottom of the feed cylinder after which the valve was shut off.

The readings of the thermocouples were noted at the start of the run and continued at five-minute intervals throughout the duration of the run. As soon as the control valve was opened and the charge started to enter the reactor, as shown by a drop in level of the liquid in the gage, the stop watches were started. Feed rate was determined by noting the time for any given drop in liquid level in the gage, which had been calibrated previously. For low space velocity runs, the feed rate was maintained at 2 linear centimeters or 10.6 ml. per minute. The rate was adjusted by manually opening or closing the 6000

pound Henry Vogt valve as required. The valve at the bottom of the feed cylinder was opened to refill the Jerguson gage whenever necessary during the course of the run.

A sample of uncondensable gas was collected in a previously evacuated and weighed glass bottle. The bottle thus filled with gas was allowed to come to room temperature, the pressure in the bottle balanced against atmospheric and then weighed, noting room temperature and barometric pressure. This data was required for the calculation of the weight of the uncondensable gases. The sample was taken approximately at the middle of the run to allow time for the nitrogen from the nitrogen purge to be swept from the system before the gas sample was taken.

Upon completion of the run, the feed cylinder was depressurized, disconnected from the Jerguson gage and reweighed. The weight of feed stock charged to the reactor was thus determined by difference. The receiver and cold traps were removed from the system and weighed to obtain the weight of product. The liquids from the cold traps were poured into the Claisen distilling flask receiver and reweighed. The mainstem and side arm were then packed with 12 grams of 1/8" glass helices, the flask reweighed, and immediately distilled for gasoline to 210°C. end point. During the time of distillation, dry ice traps were kept in series with the graduated receiver to condense any light hydrocarbon vapors passing

through the latter.

In order to recover any traces of liquid left in the reactor and thereby help in establishing a weight balance on the system, the reactor was connected through a series of cold traps to the vacuum pump and evacuated. At the same time that the reactor was being evacuated it was given several blasts of nitrogen gas which also aided materially in recovering the last traces of oil from the reactor. The recovered material was then weighed and added into the weight balance as residue since under these conditions the amount of gasoline it contained would be quite small.

2. Catalyst Burn-off

During the run, a deposit of carbonaceous material was laid down upon the catalyst surface 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 lay-down 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.

3. Super-Atmospheric Runs

The procedure in these runs was essentially the same as described for the atmospheric runs with the exception of the difference in charge and the pressure at which the system was operated.

The feed cylinder was weighed, charged with the desired amount of shale oil, reweighed and placed in a refrigerator maintained at -40°C. to chill the oil. After the oil had been thoroughly chilled, the cylinder was evacuated using a Cenco Megavac pump. The evacuated cylinder was placed on the Harvard triple beam balance and connected by means of saran tubing to a cylinder of the desired outside gas placed upside down on a metal tubing stand. After the balance had been tared, the desired amount of the outside gas was admitted to the feed cylinder by opening the valve on the gas cylinder and the valve on the feed cylinder. The feed cylinder was then allowed to warm to room temperature and the charge was mixed thoroughly by shaking the cylinder.

The feed cylinder was then connected to the top of the Jerguson gage in the usual manner. Nitrogen pressure was applied at 1000 psig. to the feed system and the Jerguson gage was filled. The charge was then forced into the reactor

system. The pressure control valve was kept closed until the pressure in the reactor reached 900 psig, at which time it was opened just enough to maintain this pressure. As in the atmospheric runs, space velocity was controlled by observing the liquid level in the Jerguson gage and adjusting the feed control valve accordingly. When the last of the charge had entered the reactor as shown by a sudden drop in pressure on the feed system, the feed cylinder valves were closed and the pressure noted. Then the pressure control valve was opened gradually until the pressure on the reactor system reached atmospheric which was taken as the end of the run. The handling of the liquid product from this point on was exactly the same as for the atmospheric runs.

The feed cylinder was then disconnected and bled off into an evacuated 34 liter metal tank. The pressure on the tank was then dropped to slightly more than atmospheric pressure. A sample was then withdrawn from the tank and analyzed by absorption in fuming sulfuric acid using the Orsat apparatus to determine the volume per cent absorbed. As shown in the sample calculations, it was thus possible to determine the amount of the outside gas left in the feed cylinder at the end of the run further helping to establish the weight balance.

4. Gum Determinations

In order to establish the gum content of the shale oil gasoline, 25 ml. of the gasoline to be tested was evaporated

to dryness in a previously weighed evaporating dish on a heated sand bath. The temperature of the sand was gradually raised from 150°C. to 210°C. during the evaporation. The evaporating dish was allowed to stand in a dessicator for four hours and then weighed to the closest one-half milligram. The difference in weight of the evaporating dish was multiplied by four to give the milligrams of gum per 100 ml. of gasoline.

5. Gum Removal

The shale oil gasoline samples were given a standard chemical treatment in preparation for the octane number determinations. This treatment consisted of shaking the gasoline sample with 10 per cent by volume of a 10 per cent sodium hydroxide solution for two minutes in a separatory funnel and separating, two minutes with 10 per cent by volume of 10 per cent sulfuric acid, two minutes with 10 per cent by volume of water, and finally six minutes with 2.3 ml. of 98 per cent sulfuric acid per 100 ml. of gasoline. No determination was made of gum content after the standard treatment. Samples on which octane number determinations were made were redistilled after the chemical treatment.

C. Materials

The shale oil was a diesel oil fraction from the shale oil crude produced in the retorting operation carried out by the Bureau of Mines Demonstration plant at Rifle, Colorado. Laboratory inspection data for this shale oil are given in Table V. The sample had been given Bureau of Mines identification number RRS-48-442.

The iso-butylene and n-butane used as outside gases were commercial grade obtained from Phillips Petroleum Company.

III SAMPLE CALCULATIONS

The calculations of space velocity, weight of permanent gases, carbon lay-down on catalyst from analysis of burn-off gases, weight of outside gas remaining in feed cylinder at end of run, overall weight balance, yields of gasoline, percentage conversion and per cent ultimate yield for run Number 7 are presented as typical of all the runs made.

A. Calculation of Liquid Space Velocity:

Data:

Volume of catalyst in the reactor = 1000 ml.

Feeding time = 19 minutes, 10 seconds.

Volume of charge = 36 cm. x 5.3 ml./cm. = 191 ml.

$$\text{Space Velocity} = \frac{191 \text{ ml.} \times 60 \text{ min.}}{19.17 \text{ min.} \times 1000 \text{ ml.}} = 0.6 \text{ hr}^{-1}$$

B. Calculation of the Weight of Uncondensable Gases:

Data:

Volume of uncondensable gases = 11.5 liters

Volume of gas sample bottle = 208.2 ml.

Pressure 639 mm. Hg. Temperature 21°C.

Weight of bottle and gas = 124.3515 gm.

Weight of bottle evacuated = 124.1430 gm.

Weight of gas sample by difference = .2085 gm.

Weight of 1 liter of gas at 21°C. and 639 mm. Hg.

$$\frac{.2085}{208.2} \times 1000 = 1.0 \text{ gm.}$$

Weight of permanent gases = 11.5 x 1.0 = 11.5 gm.

CALCULATION OF BURN-OFF

Data: (Plotted on Figure 1A)

Time (minutes)	6	30	60	120	190	205
Time increments (minutes)	6	24	30	60	70	15
Air increments (liters)	12	41	51	99	124	23
By analysis						
CO ₂	9.0	13.2	13.2	12.2	4.0	1.0
CO	3.8	5.0	4.8	5.8	1.0	0
O ₂	0.2	0	0	0	14.2	18.0
Av. from plot (see Fig- ure 1A)						
CO ₂	8.5	12.7	13.2	12.9	10.1	2.0
CO	3.5	4.6	4.9	5.5	4.4	0.3
O ₂	0.3	0.1	0	0	2.5	16.4
By Diff. N ₂	87.7	82.6	81.9	81.6	83.0	81.3
Volume of eff. gas (liters)	10.8	39.2	49.2	95.8	118	22.4
Volume per cent CO ₂ / CO	12.0	17.3	18.1	18.4	14.5	2.3
Volume (liters) CO ₂ / CO	1.30	6.20	8.90	17.60	17.10	0.5
Total Volume (liters) eff. CO ₂ / CO	----- 52.20 -----					
Temperature 21°C.	Pressure 639 mm. Hg.					
Weight Carbon Burned-off	$\frac{52.2 \times 639 \times 273 \times 12.0}{22.4 \times 760 \times 294} = 21.6 \text{ gm.}$					

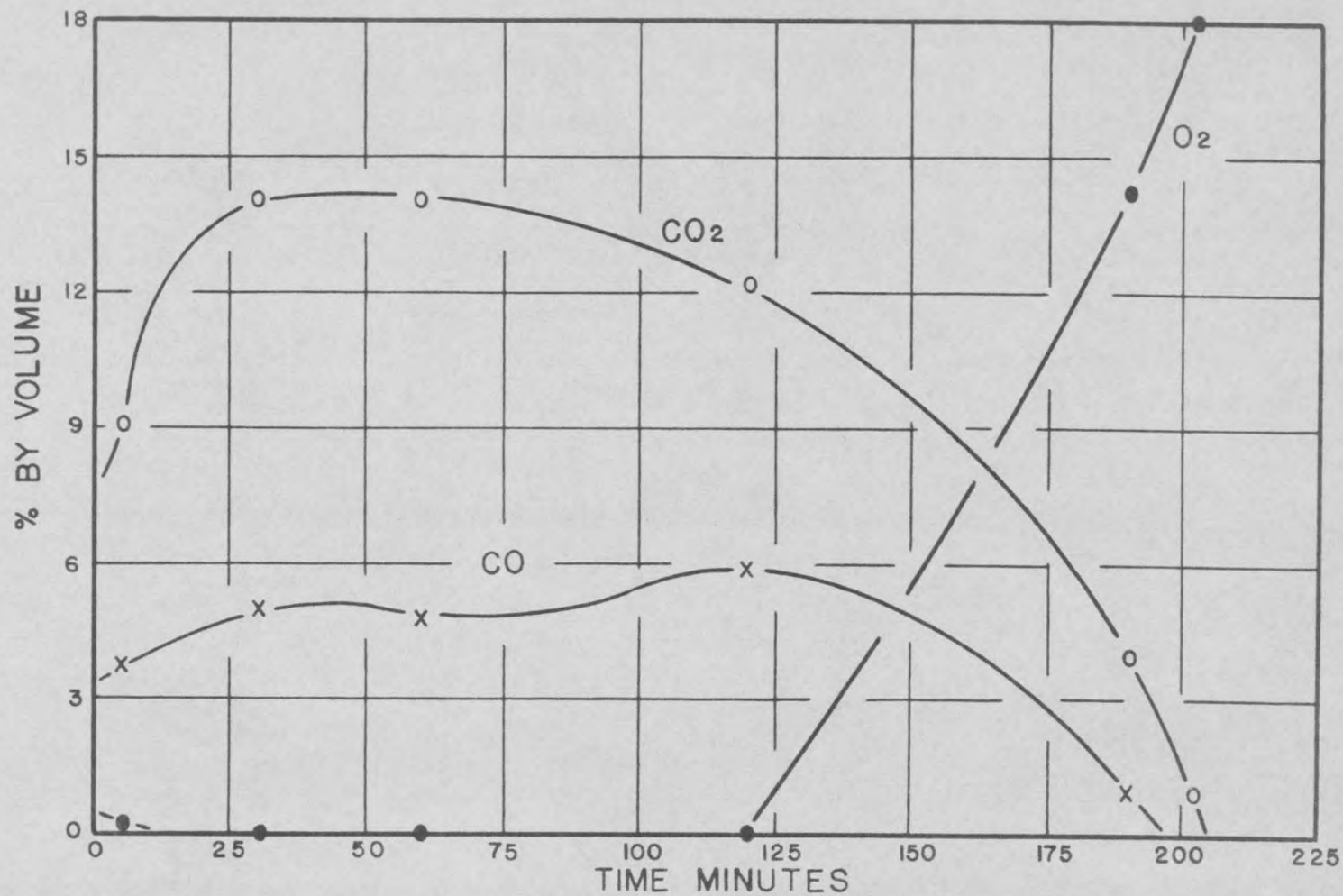


Figure 1a. Relationship between Time and Composition of Effluent Burn-off Gases

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

Data:

Volume of cylinder and Jerguson gage = 1390 ml.

Final Pressure = 1015 psia. Temperature 21°C.

Iso-butylene volume per cent of gas = 4.5%

$$\frac{1390}{1000} \times \frac{1015}{14.7} \times \frac{273}{294} \times \frac{.045}{22.4} \times 56 = 10 \text{ gm.}$$

E. Calculation of an Over All Weight Balance:

Data:

Initial Weight of Cylinder and charge = 10.892 Kg.

Final Weight of Cylinder = 10.416 Kg.

Weight of Gas in Cylinder from (D) = 10 gm.

Weight Charged to the Reactor = 466 gm.

Recovered Material

Hydrocarbon liquid product = 326.0 gm.

Condensable gases = 73.5 gm.

Permanent gases = 11.5 gm.

Oil from catalyst bed = 26.9 gm.

Carbon from burn-off = 21.6 gm.

Total weight recovered = 459.5 gm.

Weight of losses by difference = 466 - 459.5

= 6.5 gm.

Per cent losses on charge = $\frac{6.5}{466} \times 100 = 1.4\%$

F. Calculation of Per Cent Gasoline Yield:

Data:

Weight of oil charge = 281 gm.

Weight of gasoline from distillation = 69.3 gm.

Per cent gasoline on oil charge = $\frac{69.3}{281} \times 100 = 24.0\%$

G. Calculation of Percentage Conversion on Oil Charge:

Data:

Weight of oil charged = 281 gm.

Weight of residue from distillation = 197.5 gm.

Weight of oil recovered from catalyst bed
= 26.9 gm.Total weight of unconverted oil = 197.5 / 26.9
= 225.5 gm.

Per cent conversion on oil charge

= $100 - \frac{224.4}{281} \times 100 = 20.1\%$

H. Calculation of Per Cent Ultimate Yield:

Data:

Per cent gasoline on oil charge = 24.0%

Per cent conversion on oil charge = 20.1%

Per cent ultimate yield = $\frac{24.0}{20.1} \times 100 = 119.5\%$

IV RESULTS

1. Catalytic Cracking of Shale Oil

Table I presents the results of cracking shale oil with a Houdry synthetic aluminum silicate catalyst. Six runs were made at temperatures varying from 401°C. to 573°C.; space velocity was held between 0.66 and 0.71 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 2. The highest yield of gasoline obtained from the catalytic cracking of shale oil was 27.1 per cent at 573°C. It will be noted that gasoline yield does not go through a maximum as might be expected, since it is not possible with the Houdry catalyst (sintering point 600°C.) to go to a high enough temperature to obtain the higher conversions where the gasoline yield would fall off. The maximum single pass yield of gasoline from catalytic cracking of shale oil must occur at 570°C. or higher while Mayfield (5) found that maximum single pass yield for a Phillips Petroleum Company topped Virgin Gas Oil cracked under the same conditions occurred at a temperature between 380 and 400°C. From this it is apparent that the structure of the shale oil molecule must be such that it required a much higher average energy of activation for cracking than does a petroleum gas oil.

The theoretical figure, ultimate yield on oil charge, is

determined by assuming that all material boiling at a temperature higher than that of the gasoline fraction is unchanged shale oil and if it were recycled the same conversion could be effected again. Actually this is not true since each successive recycle makes the oil more refractory. This theoretical figure is plotted as a function of per cent conversion on oil charge in Figure 3 and as a function of temperature in Figure 4. From these plots it can be seen that there is a fairly wide range over which a maximum ultimate yield of approximately 50 per cent can be obtained.

The increase in per cent ultimate yield of carbon at lower temperatures would seem to indicate that the character of the shale oil is such that it polymerizes to coke and carbon at the lower temperatures as shown by an ultimate yield of carbon on oil charge of 23.3 per cent at 401°C. and 16 per cent at 549°C.

The gasoline produced from the high temperature catalytic cracking of shale oil had a more offensive odor than the low temperature cracked gasoline, but at the same time, was characterized by a much better color stability.

2. Iso-butylene Catalytic Polyforming

Table II presents the results of catalytic polyforming of shale oil at a pressure of 900 psig using iso-butylene as the outside gas. Four runs were made at temperatures varying from 364°C. to 479°C. using a space velocity of 0.6 to 0.68

hr.⁻¹, and four runs at temperatures varying from 365°C. to 501°C. using a space velocity of 4.0 to 5.0 hr.⁻¹.

A plot of per cent gasoline yield as a function of per cent conversion for the low space velocity iso-butylene catalytic polyforming runs is shown in Figure 5. A maximum yield of 34 per cent gasoline was obtained at a temperature of 443°C. in this series of runs. This is 6.9 per cent more gasoline on oil charge than the maximum obtained from a straight catalytic crack. The maximum yield was obtained at a temperature 130°C. lower than that required in catalytic cracking.

Ultimate yield on oil charge is plotted as a function of per cent conversion in Figure 6 and as a function of temperature in Figure 7. When these plots are compared with those for straight catalytic cracking (Figures 3 and 4), it can be readily seen that catalytic polyforming using iso-butylene as the outside gas gives an increased ultimate yield. This can be accounted for by polyforming of the shale oil, polymerization of iso-butylene to hydrocarbons in the gasoline boiling range and polymerization to material with a boiling point greater than that of the gasoline fraction. The latter would, in effect, make it appear that there were a larger percentage of the unchanged shale oil remaining and therefore increase the calculated ultimate yield.

A plot of per cent gasoline yield on oil charge as a function of per cent conversion on oil charge for the high

(4.0 to 5.0 hr.⁻¹) space velocity iso-butylene catalytic polyforming runs is shown in Figure 8. A maximum yield of 34 per cent gasoline on oil charge was obtained at a temperature of 464°C. which is quite comparable to that (38-39 per cent) obtained by Mayfield (5) from the catalytic polyforming of petroleum gas oil under the same conditions. It is quite remarkable that exactly the same yield was obtained as from the low (0.6-0.68 hr.⁻¹) space velocity runs with a slightly smaller conversion, a temperature only 21°C. higher, and a space velocity more than six times as great. The design of the equipment was not such that it would allow the employment of space velocities higher than 6.0 volumes of charge per volume of catalyst per hour. However, in view of the slight effect of space velocity on gasoline yield noted in this series of runs, it would seem to be indicated that much higher space velocities might be obtainable with no appreciable effect on gasoline yield.

The relationship between ultimate yield on oil charge and per cent conversion on oil charge and temperature as shown in Figures 9 and 10 indicate that the high space velocity had little effect upon the final yield of gasoline that could theoretically be obtained with recycling. The most noticeable change is found in the low temperature-low conversion runs where the drop in ultimate yield is quite appreciable. It is possible that at the lower temperatures the high space velocity

does not allow enough time for the same degree of polymerization to take place as it does at low space velocity and as a result either lowers the gasoline yield or raises the apparent conversion giving a lower ultimate yield.

3. n-Butane Catalytic Polyforming

The results of the catalytic polyforming of shale oil at a pressure of 900 psig using n-butane as the outside gas are presented in Table III. Five runs were made at temperatures varying from 385°C. to 509°C. using a space velocity of 0.54 to 0.68 hr.⁻¹ and six runs at temperatures from 392°C. to 511°C. using a space velocity of 4.2 to 5.2 hr.⁻¹.

Per cent yield of gasoline on oil charge is plotted in Figure 11 as a function of per cent conversion for the low space velocity n-butane catalytic polyforming runs. A maximum yield of 24.4 per cent gasoline was found at a temperature of 481°C. This is approximately three per cent less gasoline on oil charge than the maximum obtained from a straight catalytic crack; however, the temperature at which this yield occurred was 90°C. lower than that required in catalytic cracking.

Figure 12 is a plot of the relationship between ultimate yield and per cent conversion. Figure 13 shows the relationship of ultimate yield to temperature. It can be seen in comparing Figures 12 and 13 with Figures 3 and 4 that the maximum ultimate yield is essentially the same or possibly a little

higher with low space velocity n-butane catalytic polyforming than it is with a straight catalytic crack except that it is found at a temperature 30°C. lower in catalytic polyforming.

The yield of gasoline from high (4.2 to 5.2 hr.⁻¹) space velocity n-butane catalytic polyforming runs is plotted in Figure 14 as a function of the per cent conversion on oil charge for each run. A large decrease in gasoline yield was noted in this series of runs. The maximum yield of 19.2 per cent gasoline on oil charge is five per cent less than that obtained for the low space velocity n-butane catalytic polyforming runs and eight per cent less than that obtained from an atmospheric catalytic crack. This decrease in yield could be a result of the high space velocity not allowing enough time for the n-butane to crack to a hydrocarbon capable of entering into a polyforming reaction with the shale oil.

It is evident from Figures 15 and 16, showing the relationship of ultimate yield to per cent conversion and to temperature, that a sharp decrease in ultimate yield of gasoline is encountered in the high space velocity catalytic polyforming of shale oil using n-butane as the outside gas. The maximum ultimate yield is about ten per cent less than that from low space velocity n-butane catalytic polyforming or from a straight catalytic crack.

4. Ultimate Yield

It is of interest to note in Figures 3, 4, 9, 10, 12,

13, 15, and 16 that the ultimate yield of gasoline on shale oil charge passes through a maximum, this is contrary to what might be expected with petroleum gas oil where ultimate yield goes to infinity as the conversion approaches zero. This phenomenon can possibly be explained by the character of the shale oil which tends to give coke and carbon at the lower temperatures. The exception to this rule, as shown in Figures 6 and 7, might be explained by the greater tendency of the iso-butylene to react giving gasoline and hydrocarbon material which would appear as a greater amount of unchanged oil thereby raising the ultimate yield and masking the tendency of the shale oil to go to coke and carbon.

5. Catalyst

It was planned to change the catalyst whenever a run showed sufficient loss in catalyst activity; however, in 72 runs with both shale oil and petroleum gas oil at atmospheric and super atmospheric pressures, both with and without an outside gas, the catalyst showed no apparent loss in activity. Approximately 40 liters of various charges have been fed over the one liter of catalyst during the 72 runs. During the use of the catalyst for shale oil research alone, approximately 9500 ml. of shale oil and 6000 ml. of iso-butylene and n-butane were passed through the 1000 ml. of catalyst volume. The final run, No. 72 on the catalyst, showed no drop in activity from that found for run No. 2. Thus, no decline in activity was

noted over a period of use of the magnitude reported here.

6. Shale Oil Gasoline

Table IV presents the results of the gum tests which were made on the shale oil gasoline samples. Figure 17 shows the relationship between milligrams of gum per 100 ml. of gasoline sample and the per cent conversion obtained when the gasoline sample was made. It is clearly shown in Figure 17 that independently of the process by which the gasoline sample was made the minimum gum content will be essentially the same and will occur at approximately the same per cent conversion on oil charge. The gasoline samples from high space velocity runs will have a slightly higher minimum gum content and will require a higher degree of conversion to reach this minimum. The relationship between milligrams of gum per 100 ml. of gasoline sample and the temperature at which the gasoline sample was made is shown in Figure 18. It is quite apparent from this Figure that a much higher temperature is required to reach minimum gum content with catalytic cracking than is required with catalytic polyforming.

The results of the laboratory determinations on shale oil gasoline are presented in Table VI. The losses encountered when the shale oil gasoline samples are given the standardized chemical treatment run from a minimum of 8.4 per cent for low space velocity iso-butylene catalytic polyforming at 460°C. to a maximum of 13.0 per cent for both straight

catalytic cracking at 560°C. and high space velocity n-butane catalytic polyforming at 490°C. These losses would probably be smaller with larger amounts of sample because of a smaller percentage of handling losses. The losses compare very favorably with those found by the Bureau of Mines, who reported losses of 17-18 per cent. Catalytic polyforming gives a slight but definitely noticeably improvement in the color stability of the shale oil gasoline produced.

The octane numbers of the shale oil gasoline samples seem to fall fairly well in the same range regardless of the process by which the gasoline sample was made. The octane ratings were determined by the method of Alexander and Pfeiffer (6) using small samples, approximately 20 ml. for each determination. This short method will ordinarily check the standard method within ± 0.5 octane number. A definite increase in octane number is noted for the high space velocity iso-butylene catalytic polyforming gasoline over that from low space velocity runs. In catalytic polyforming using n-butane as the outside gas the octane number of the gasoline made at a high space velocity showed a slight decrease from that made at a low space velocity. This high research octane number of the straight catalytically cracked shale oil gasoline can probably be explained by the very high temperature (560°C.) at which the operation was carried out.

In general it can be stated that the octane numbers of

gasoline produced from shale oil fall in essentially the same range as the octane numbers of the gasoline produced from petroleum gas oil by the same process under similar conditions.

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 cracking catalyst for shale oil within the temperature limits of the catalyst.
2. There was no detectable loss in the activity of the catalyst in straight catalytic cracking or catalytic polyforming of shale oil at 900 psig using either iso-butylene or n-butane as the outside gas after the passage of 15 volumes of charge per volume of catalyst.
3. Iso-butylene catalytic polyforming gives a definite increase in gasoline yield on oil charge over that obtainable from a conventional catalytic crack and allows the attainment of a space velocity approximately ten times that used in normal petroleum catalytic cracking.
4. n-Butane catalytic polyforming gives no increase in gasoline yield on oil charge over that from a straight catalytic crack.
5. Catalytic polyforming appreciably lowers the temperature at which the maximum yield of gasoline can be obtained.
6. Catalytic polyforming using either iso-butylene or

n-butane as the outside gas has little or no effect on the minimum gum content of the shale oil gasoline produced.

7. Catalytic polyforming has little or no effect on the octane number of the gasoline produced even though it increases the gasoline yield considerably.

VI ACKNOWLEDGMENT

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TABLE I

Catalytic Cracking of Shale Oil

Run No.	1	2	3	4	5	6
No. Runs on Catalyst	2	51	53	54	55	56
Av. Reactor Temp. °C	502	401	466	517	549	573
Oper. Press. psig	Atmospheric					
Space Velocity hr ⁻¹	.67	.71	.70	.70	.66	.67
Material Charged	none					
Outside Gas,	none					
Outside Gas, gms	none					
Charge Stock, gms	309	269	295	303	298	311
Total Charge	309	269	295	303	298	311
Recovered Material						
H-C Liq. Prod.	217.7	218.4	252.2	221.4	179.9	144.1
Condensable Gases	13.0	1.3	5.9	20.7	31.8	51.1
Permanent Gases	21.0	3.2	12.0	25.6	46.5	63.0
Oil from Catalyst	0	19.4	7.2	6.2	2.3	4.5
Carbon by Burn-off	25.0	17.0	16.0	24.4	30.2	44.1
Total Recovered	276.7	259.3	293.3	298.3	290.7	306.8
Losses by Difference gms	32.0	9.7	1.7	4.7	7.3	4.2
% Losses on Charge	10.3	3.6	.57	1.5	2.4	1.35
Wt. of Gasoline	73.0	34.1	45.8	70.3	74.8	84.5
Wt. of Residue	141.0	196.7	205.0	153.8	109.9	82.3
% Gasoline on Oil Chg.	24.6	12.6	15.5	23.2	25.1	27.1
% Conversion on Oil Chg.	54.4	27.0	30.5	49.4	63.2	73.5
% Ultimate Yield	45.3	46.9	50.8	47.0	39.7	36.9

TABLE II

Catalytic Polyforming of Shale Oil with Iso-Butylene

Run No.	7	8	9	10	11	12	13	14
No. Runs on Catalyst	45	48	49	50	43	44	46	47
Av. Reactor Temp. °C.	364	443	388	479	365	424	464	501
Oper. Press. psig				900				
Space Velocity hr ⁻¹	.6	.65	.68	.60	4.9	5.0	4.0	5.0
Material Charged								
Outside Gas								
Outside Gas, gms	185	190	176	181	152	176	201	189
Charge Stock, gms	281	278	270	266	282	279	275	265
Total Charge	466	468	446	447	434	455	476	454
Recovered Material								
H-C Liq. Prod.	326.0	258.2	297.1	183.3	275.7	254.0	226.5	128.4
Condensable Gases	73.5	89.1	76.6	108.2	98.6	135.4	151.5	141.3
Permanent Gases	11.5	30.6	13.0	56.0	9.8	18.7	41.0	85.0
Oil from Catalyst	26.9	6.2	19.7	4.7	18.6	8.2	4.5	4.2
Carbon by Burn-off	21.6	54.3	30.7	76.5	17.9	29.8	49.0	64.0
Total Recovered	459.5	438.4	437.1	428.7	420.6	448.1	472.5	422.9
Losses by Difference, gms	6.5	29.6	8.9	18.3	13.4	6.9	3.5	31.1
% Losses on Charge	1.4	6.3	2.0	4.1	3.0	1.5	.73	6.8
Wt. of Gasoline	69.3	94.7	75.6	89.0	47.6	83.5	94.9	89.1
Wt. of Residue	224.5	112.8	190.8	64.9	211.1	158.6	97.9	77.3
% Gasoline on Oil Chg.	24.0	34.0	28.0	33.4	16.9	29.9	34.0	33.6
% Conversion on Oil Chg.	20.1	59.5	29.4	75.6	25.1	43.3	56.4	70.8
% Ultimate Yield	119.5	57.1	95.1	44.1	67.3	69.0	60.3	47.5

TABLE III

Catalytic Polyforming of Shale Oil With n-Butane

Run No.	17	18	19	20	21	22	23	24	25	26	27
No. Runs on Catalyst	56	57	58	59	60	61	62	63	64	65	66
Av. Reactor Temp. °C.	385	460	433	509	481	392	427	486	487	480	511
Oper. Press. psig						900					
Space Velocity hr ⁻¹	.6	.68	.65	.63	.54	4.4	4.2	4.8	5.0	5.0	5.2
Material Charged											
Outside Gas						n-butane					
Outside Gas, gms	168	182	184	174	178	164	197	162	192	179	168
Charge Stock, gms	276	272	284	271	266	274	270	269	271	269	266
Total Charge	444	454	468	445	444	438	467	431	463	448	434
Recovered Material											
H-C Liq. Prod.	317.2	313.3	336.1	185.1	250.5	277.9	318.9	207.8	228.2	221.4	169.0
Condensable Gases	72.7	69.7	73.4	105.3	90.9	117.3	108.0	167.7	167.5	164.0	160.2
Permanent Gases	10.0	28.8	16.0	80.0	58.5	7.5	12.7	23.0	31.9	35.2	71.6
Oil from Catalyst	19.7	6.5	11.0	3.2	5.0	17.6	9.3	6.1	4.8	5.6	2.3
Carbon by Burn-off	18.8	30.0	24.4	59.5	47.2	16.9	15.5	15.5	30.2	25.8	34.0
Total Recovered	438.4	448.3	460.9	433.1	452.1	437.2	465.4	420.1	462.6	452.0	437.1
Losses by Difference, gms	5.6	5.7	7.2	11.9	8.1	.8	1.6	10.9	.4	4.0	3.1
% Losses on Charge	1.26	1.25	1.54	2.67	1.82	.18	.34	2.52	.09	.89	.71
Wt. of Gasoline	22.4	62.0	57.7	64.9	65.1	19.4	27.9	41.6	52.2	40.6	47.9
Wt. of Residue	215.9	127.7	173.6	51.8	96.1	214.0	198.5	158.8	136.4	155.8	110.3
% Gasoline on Oil Chg.	8.14	22.8	20.4	23.9	24.4	7.1	10.4	15.5	19.2	15.1	18.0
% Conversion on Oil Chg.	21.8	53.3	39.0	80.8	63.9	22.0	26.2	41.0	49.7	42.1	58.5
% Ultimate Yield	37.5	42.6	52.4	29.6	38.1	31.8	39.7	37.8	38.6	35.9	30.8

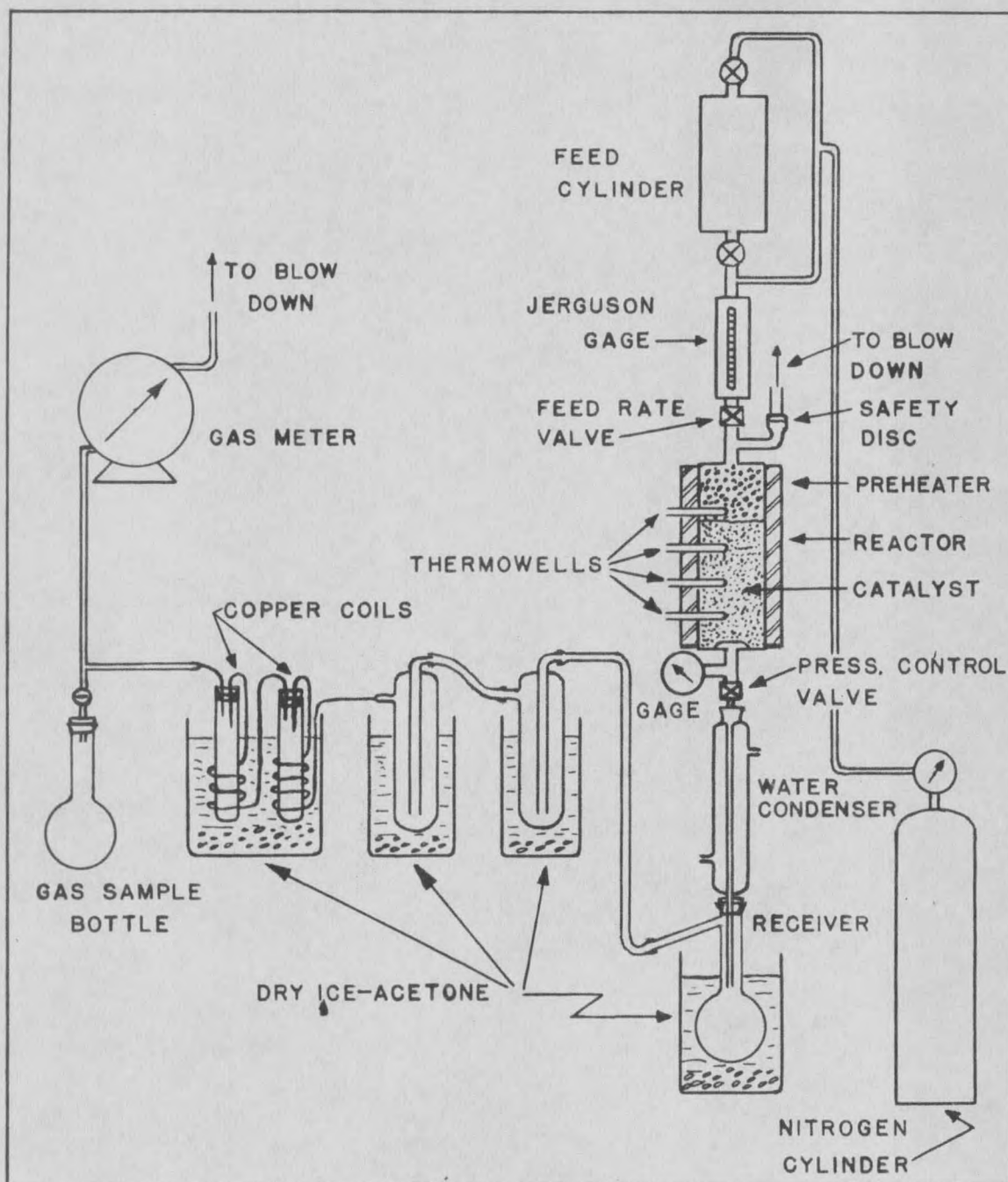


Figure 1. Diagram of Equipment

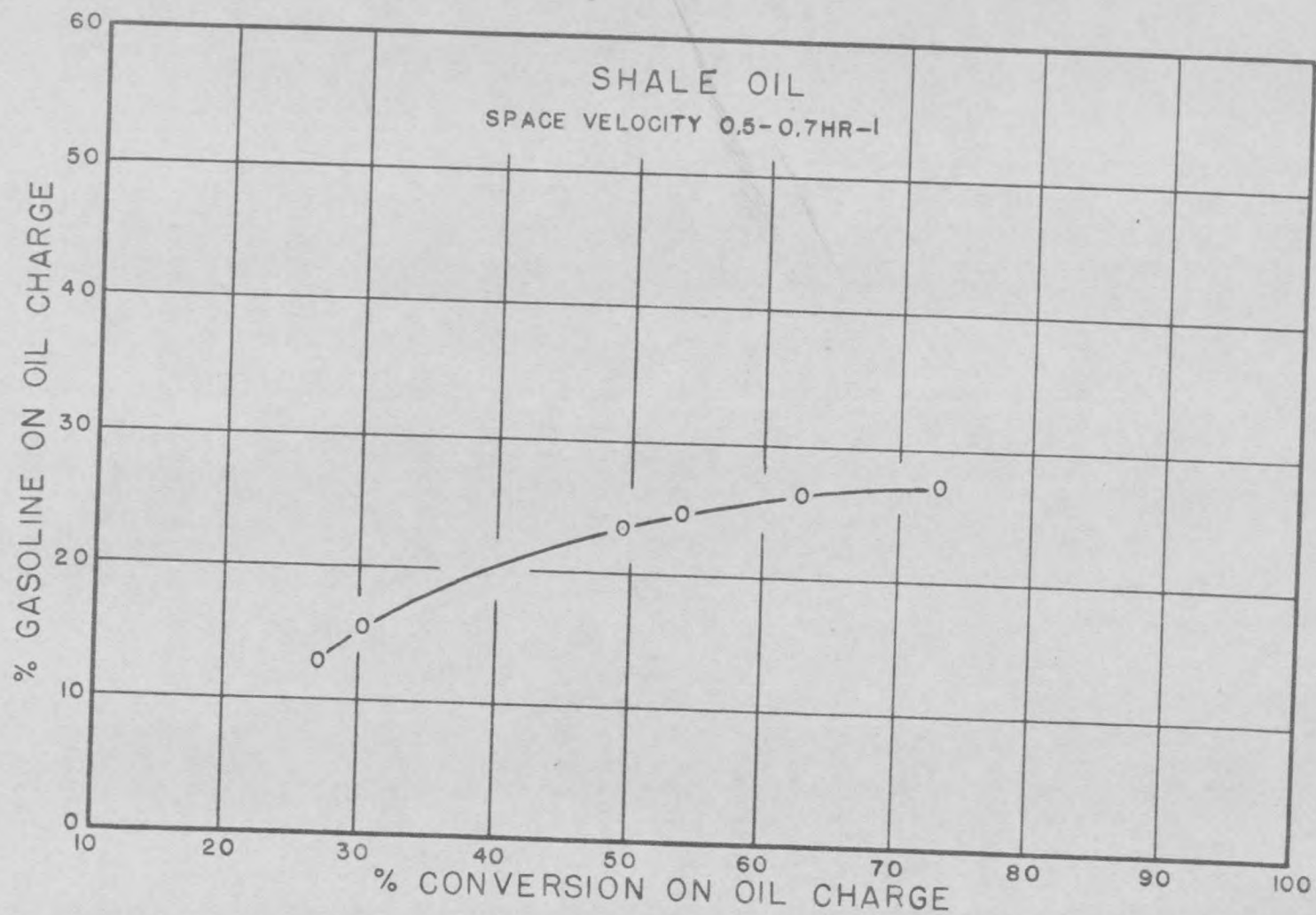


Figure 2. Relationship between Conversion and Yield of Gasoline

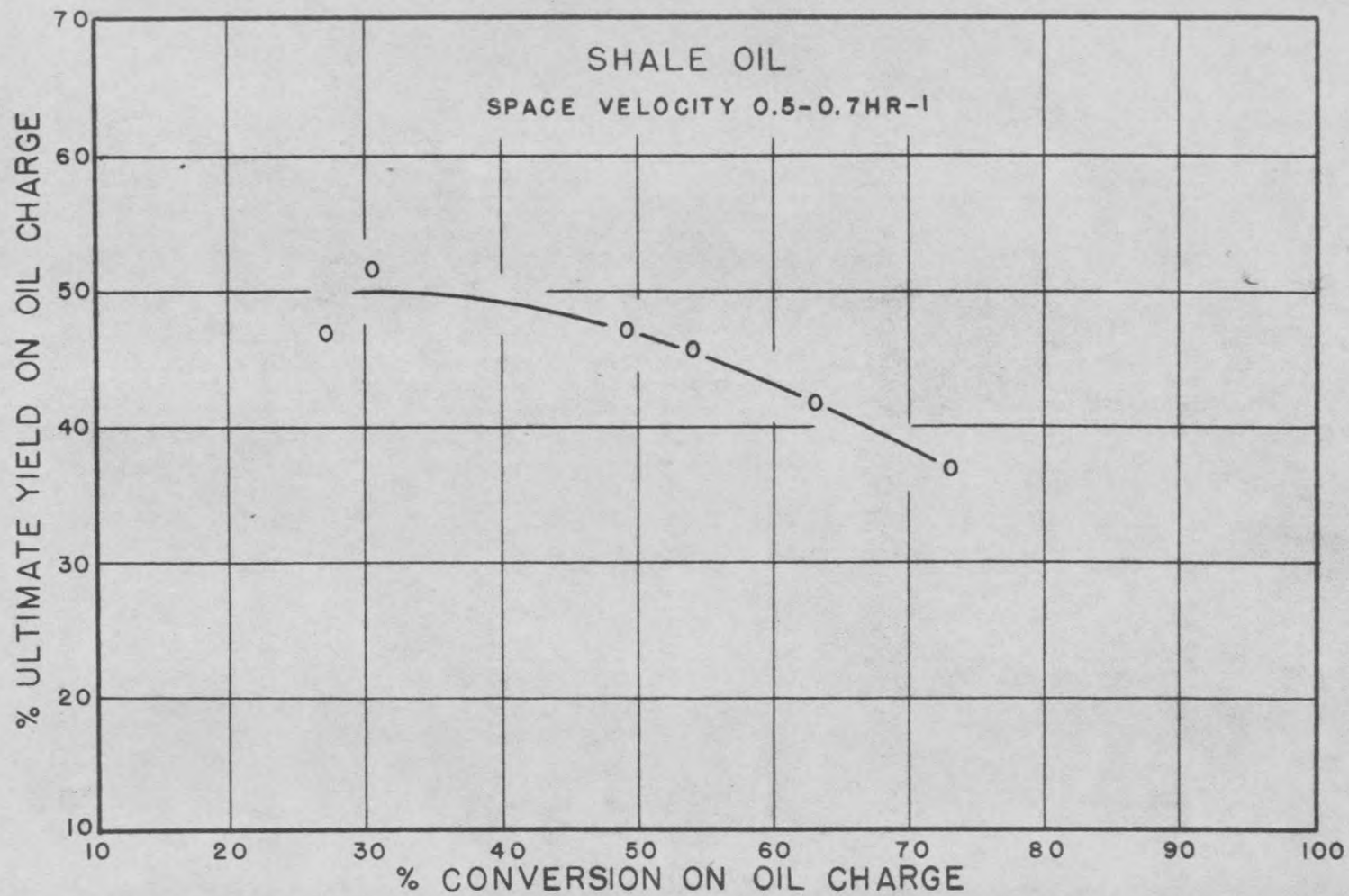
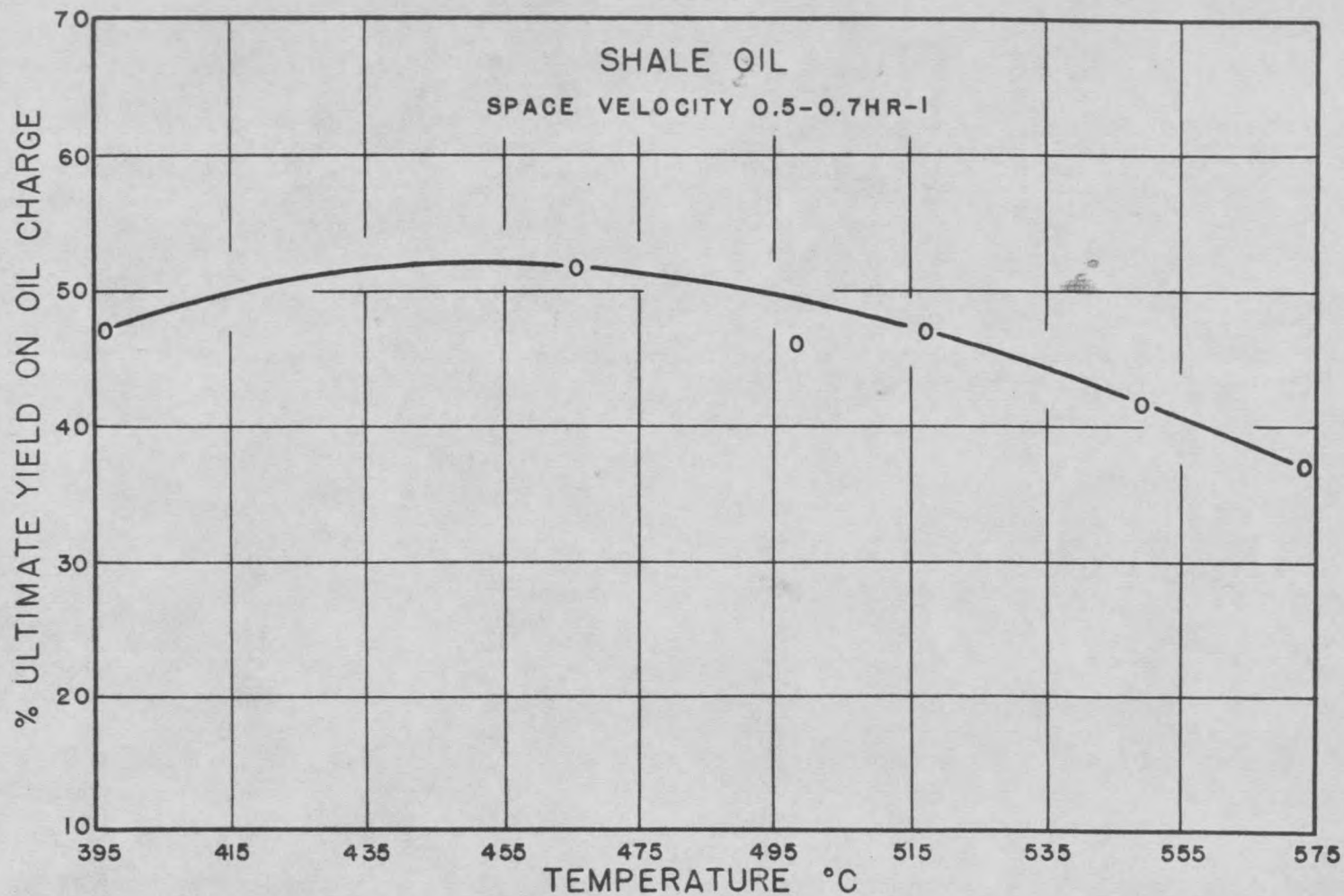
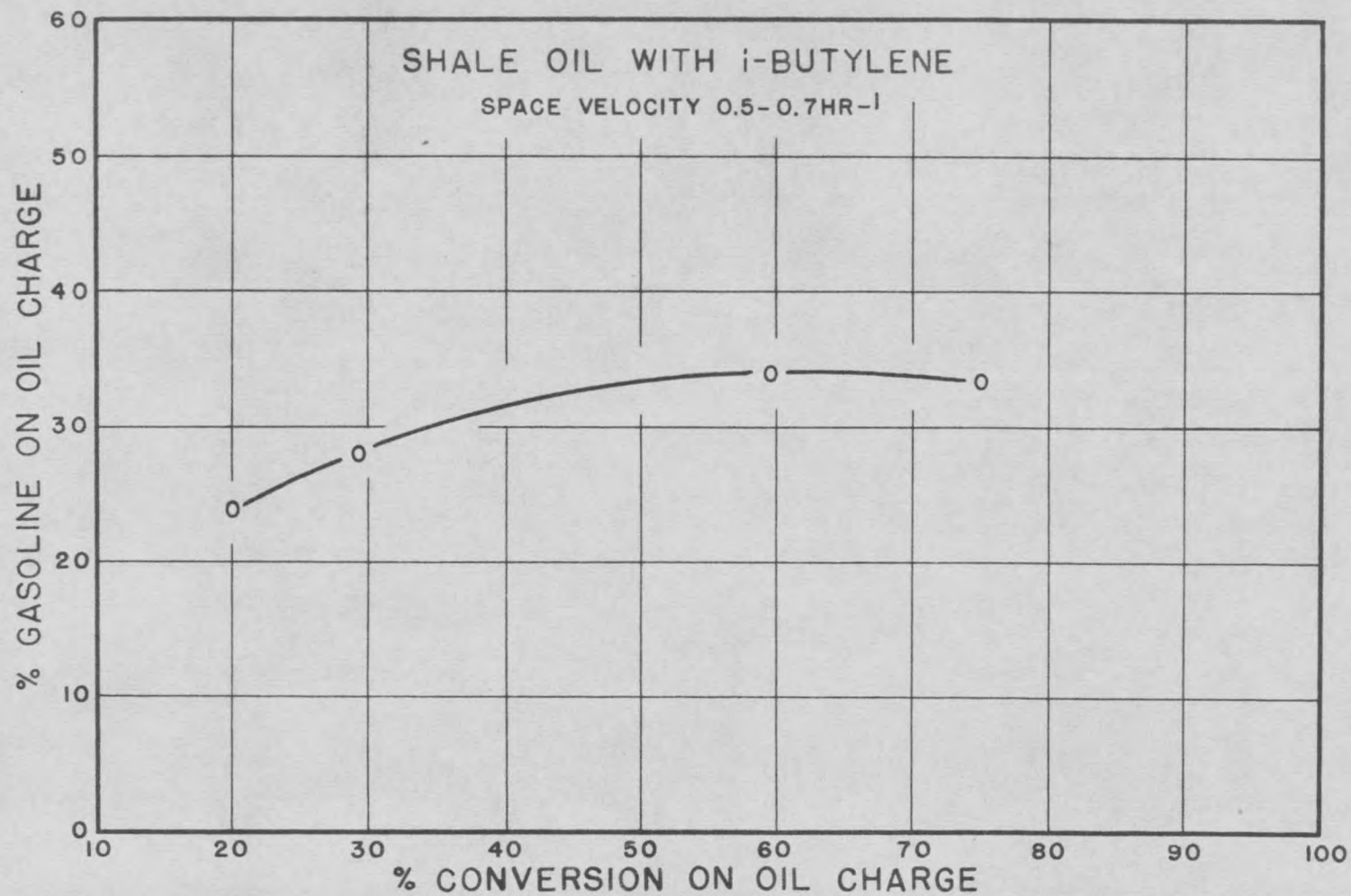


Figure 3. Relationship between Conversion and Ultimate Yield



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Figure 4. Relationship between Temperature and Ultimate Yield



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Figure 5. Relationship between Conversion and Yield of Gasoline

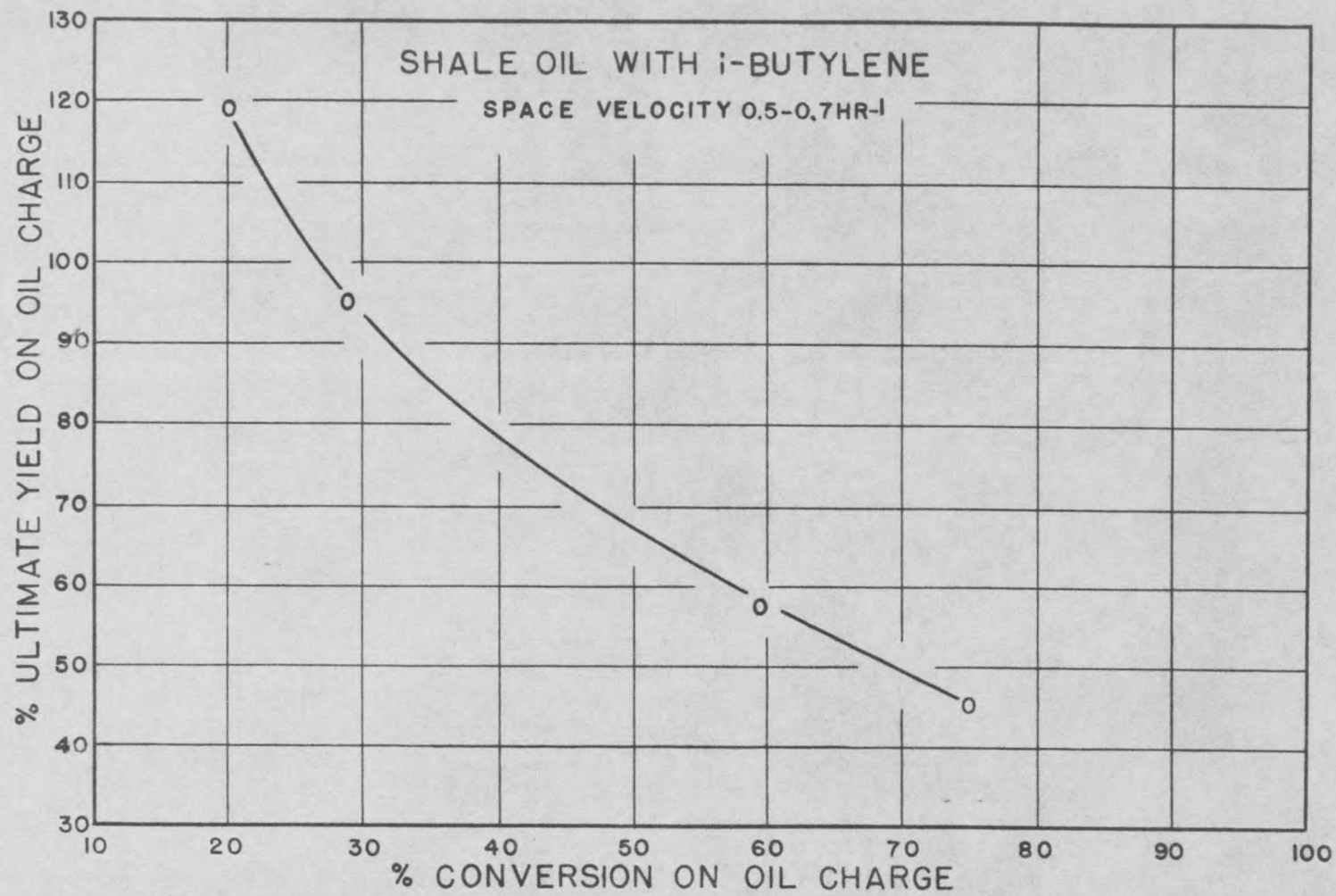


Figure 6. Relationship between Conversion and Ultimate Yield

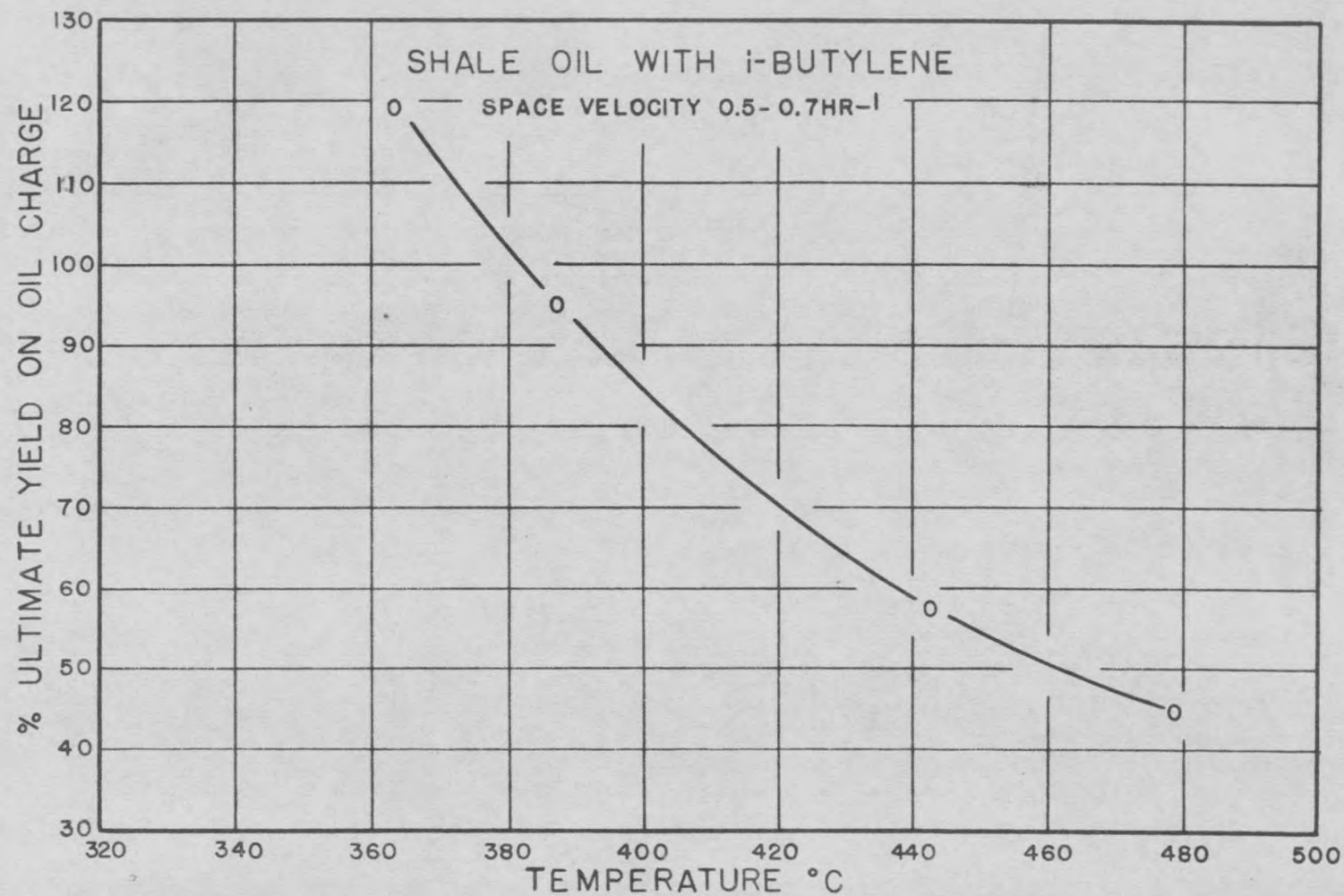


Figure 7. Relationship between Temperature and Ultimate Yield

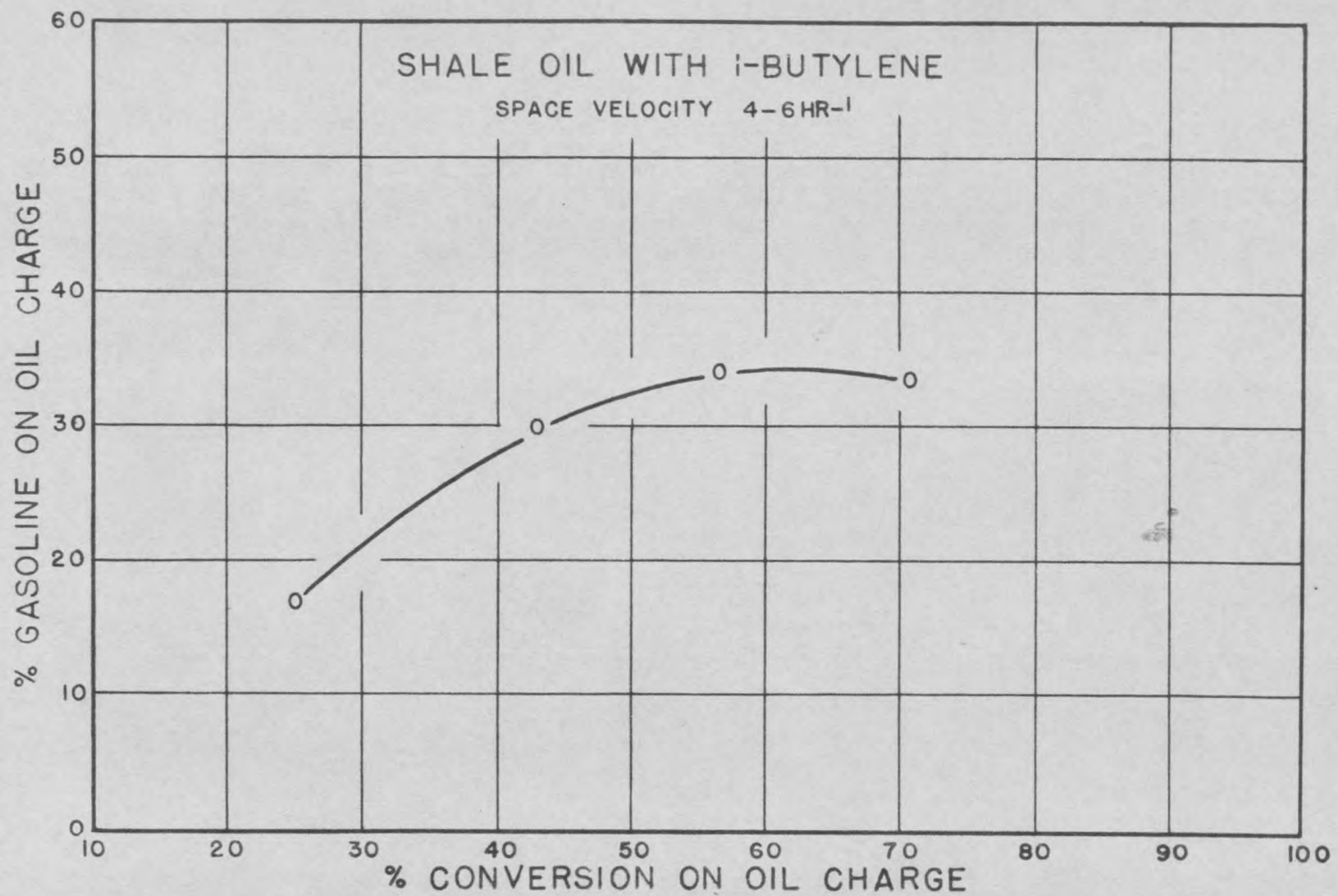


Figure 8. Relationship between Conversion and Yield of Gasoline

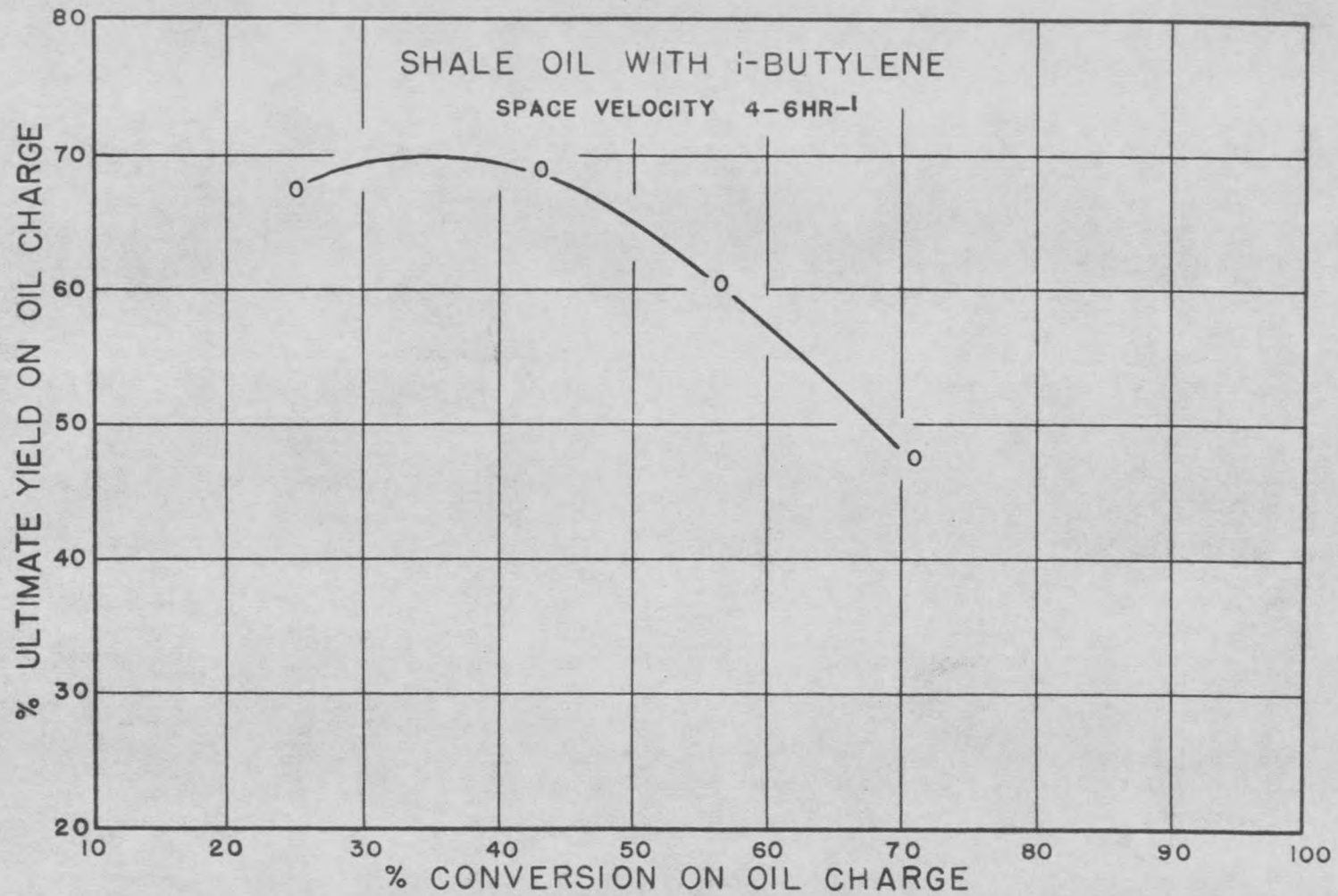
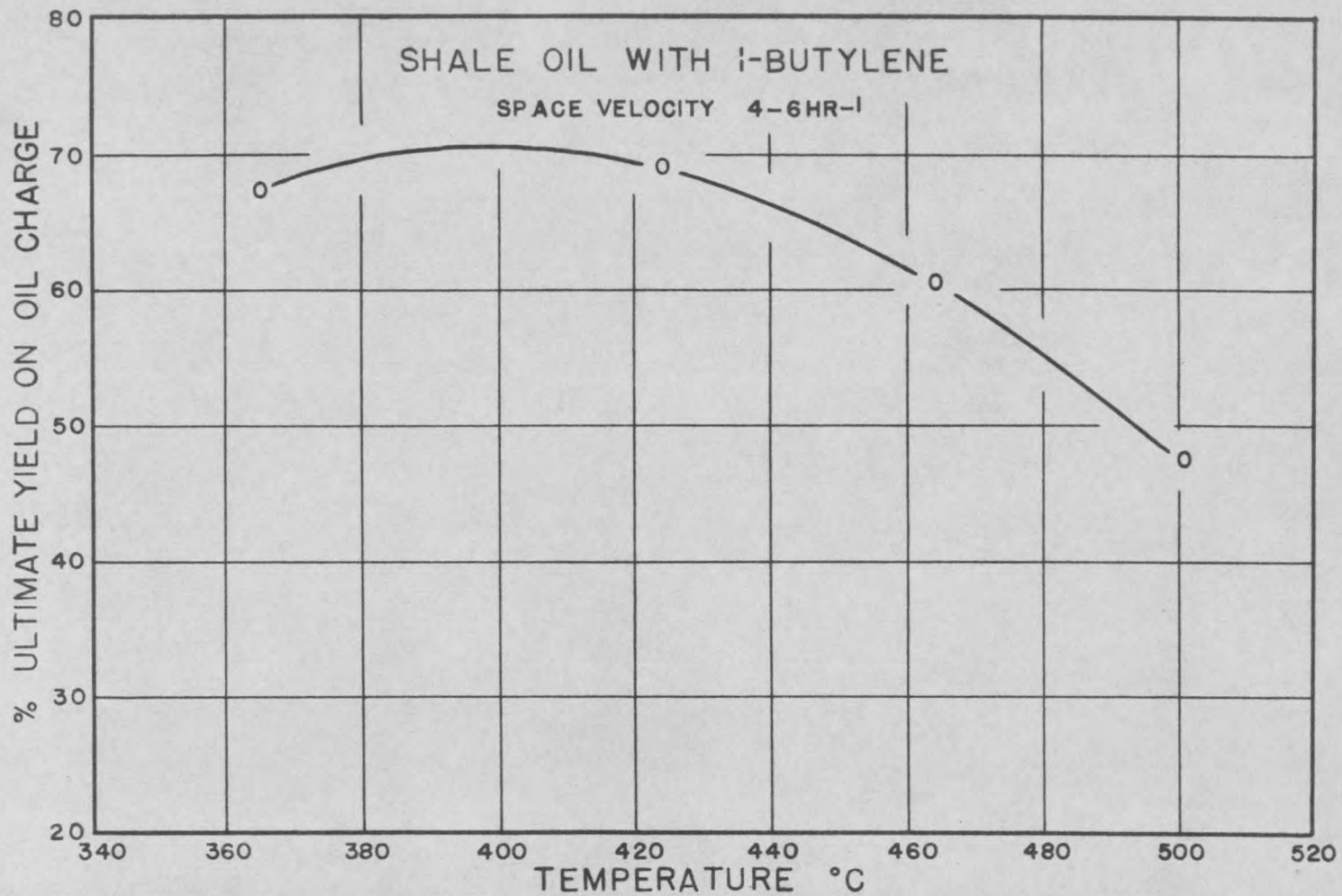


Figure 9. Relationship between Conversion and Ultimate Yield



55

Figure 10. Relationship between Temperature and Ultimate Yield

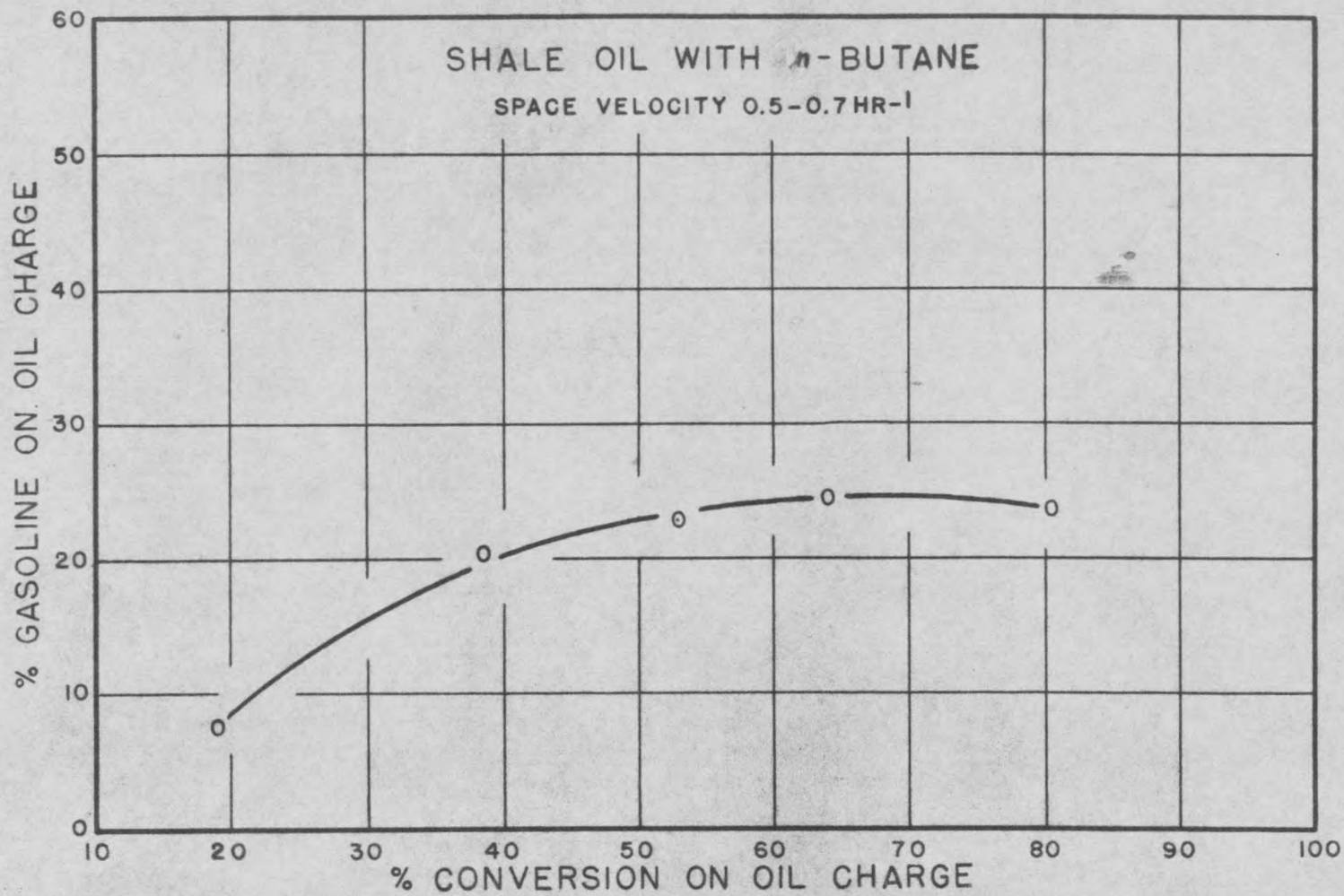


Figure 11. Relationship between Conversion and Yield of Gasoline

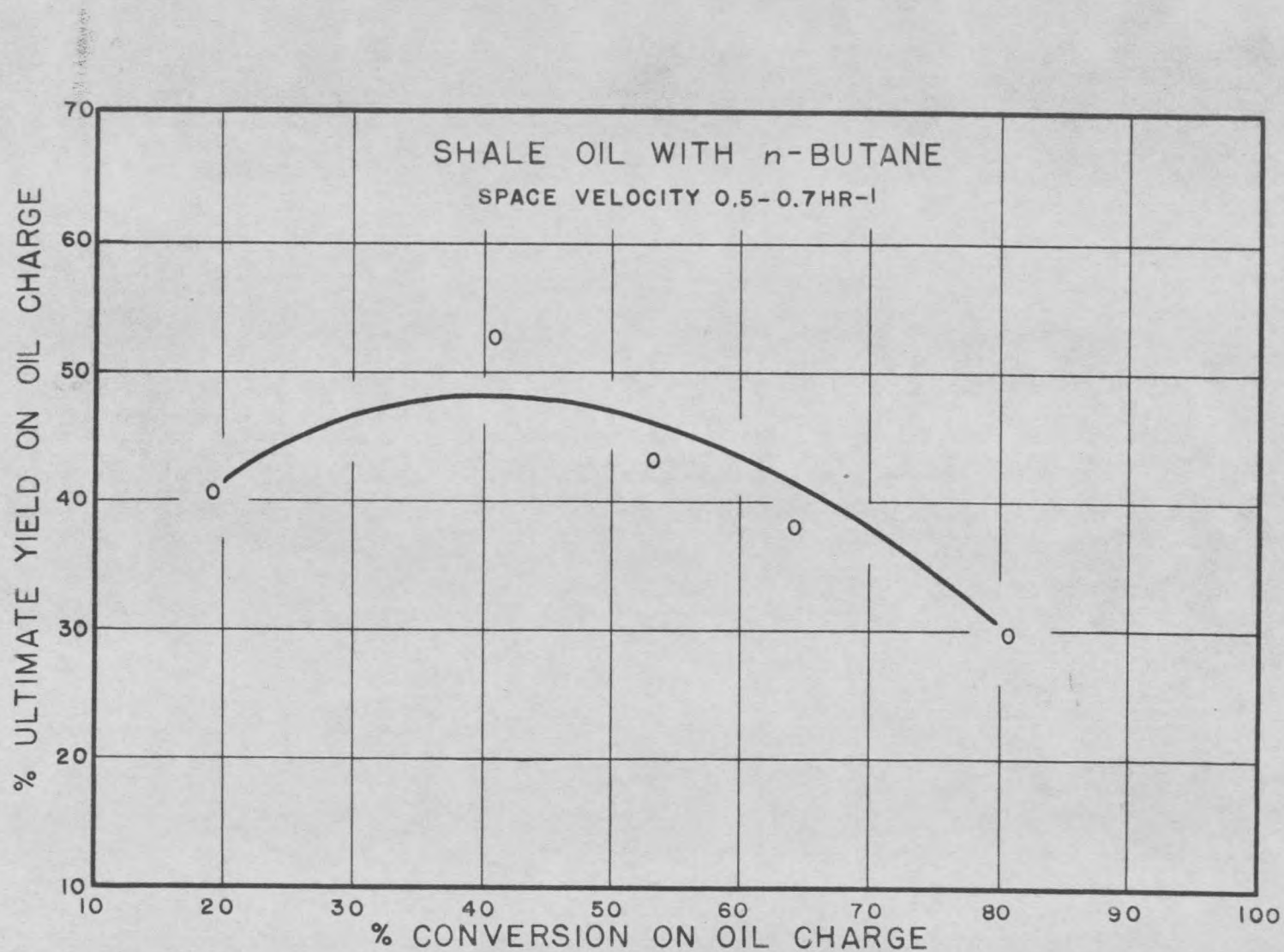
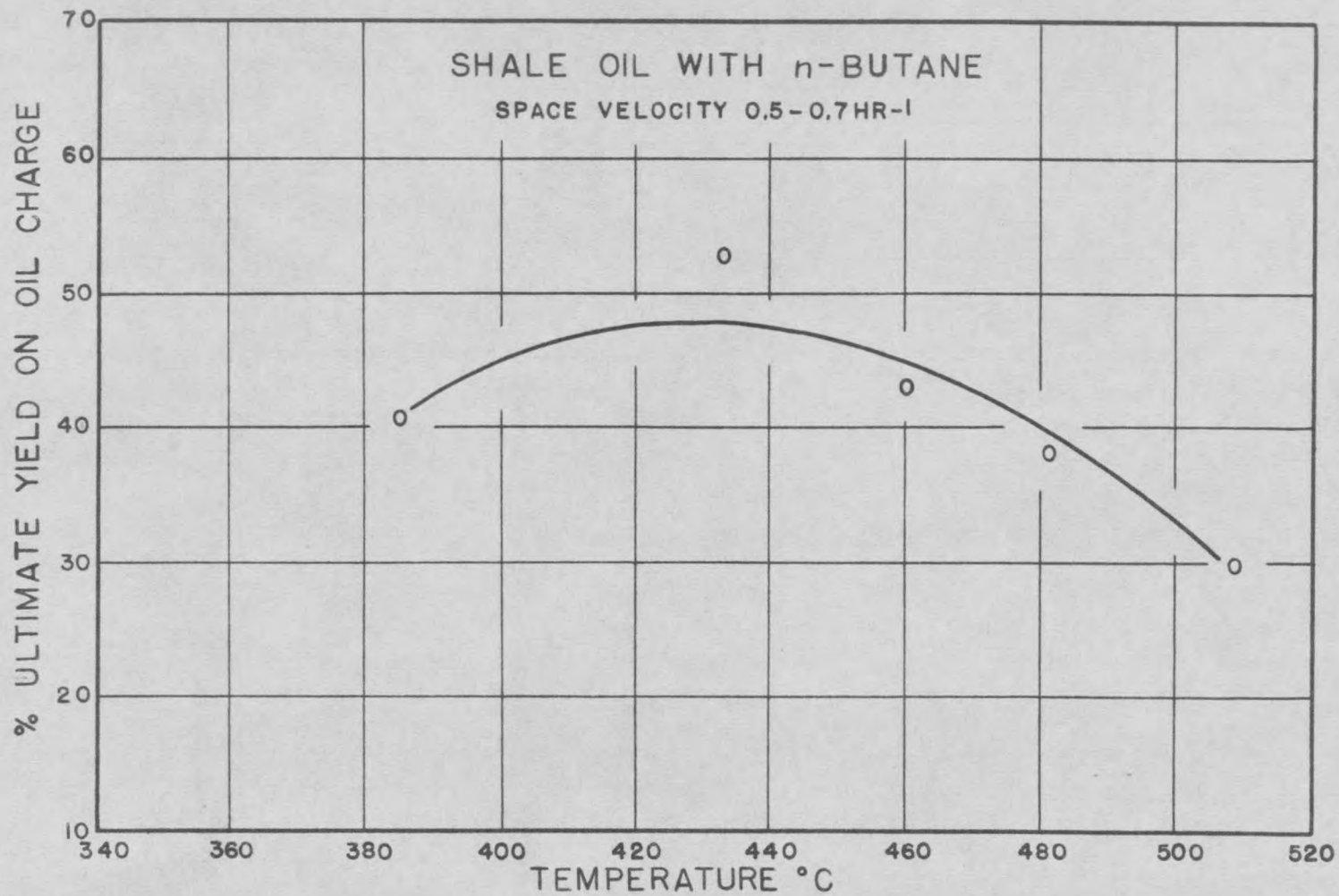
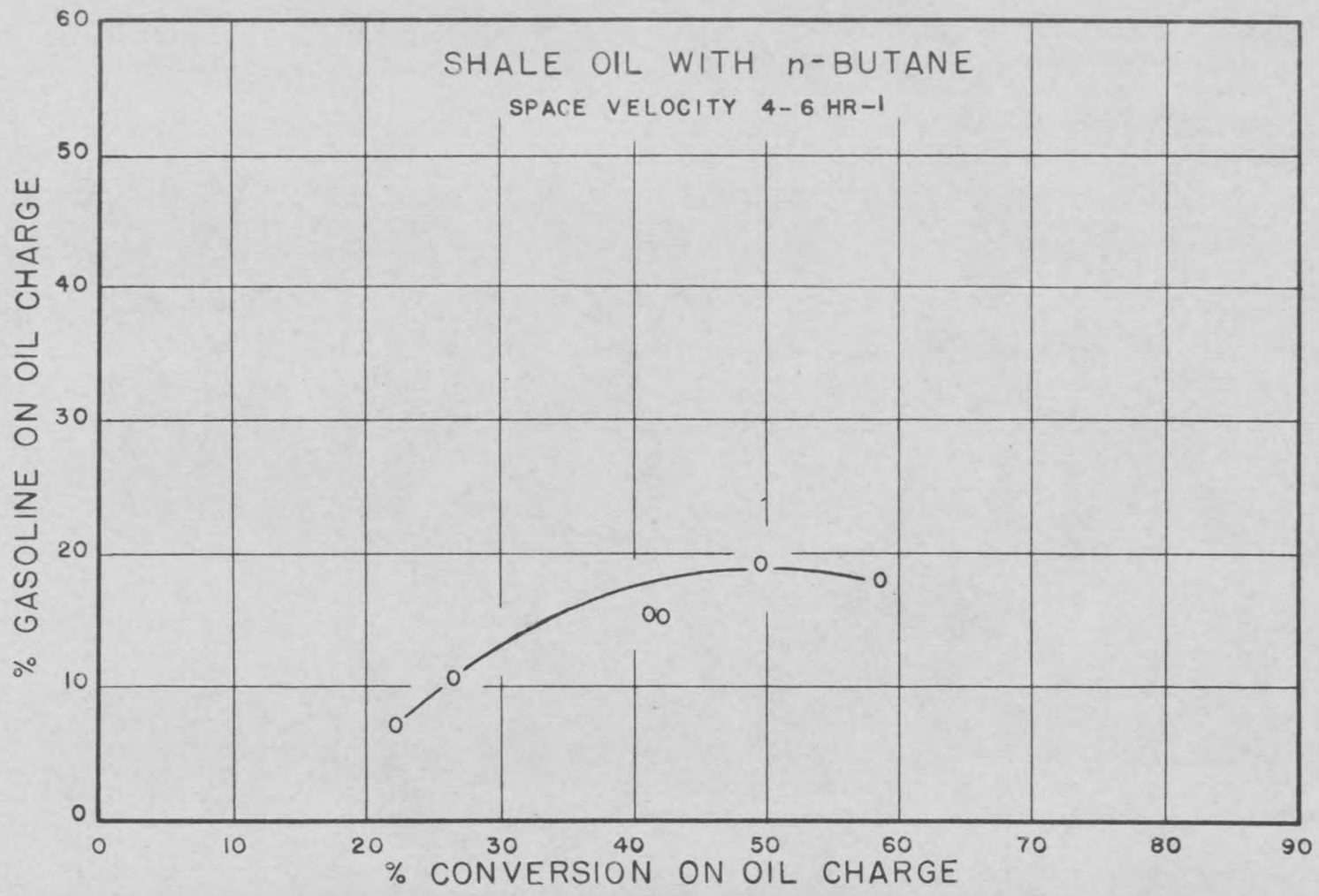


Figure 12. Relationship between Conversion and Ultimate Yield



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Figure 13. Relationship between Temperature and Ultimate Yield



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Figure 14. Relationship between Conversion and Yield of Gasoline

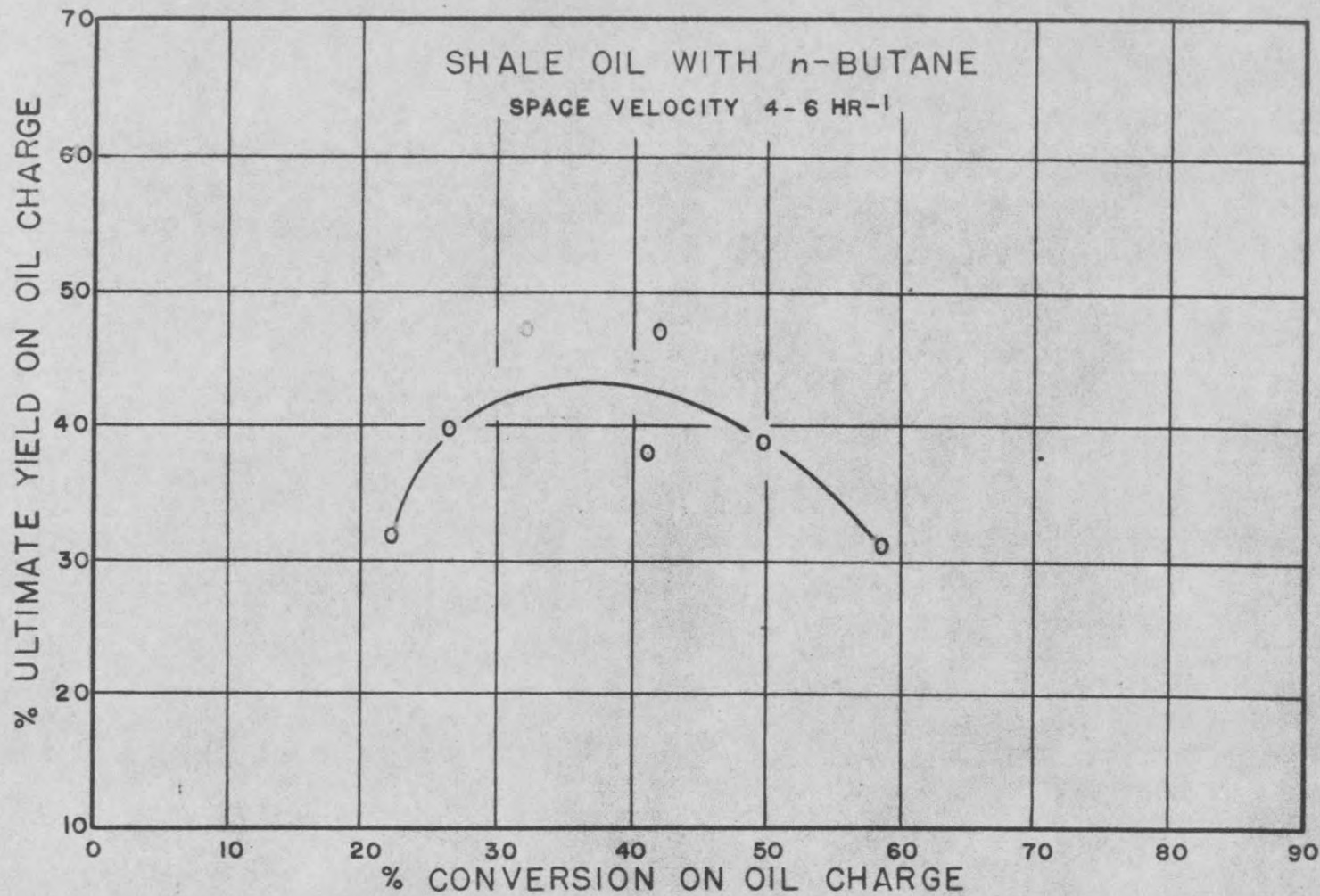
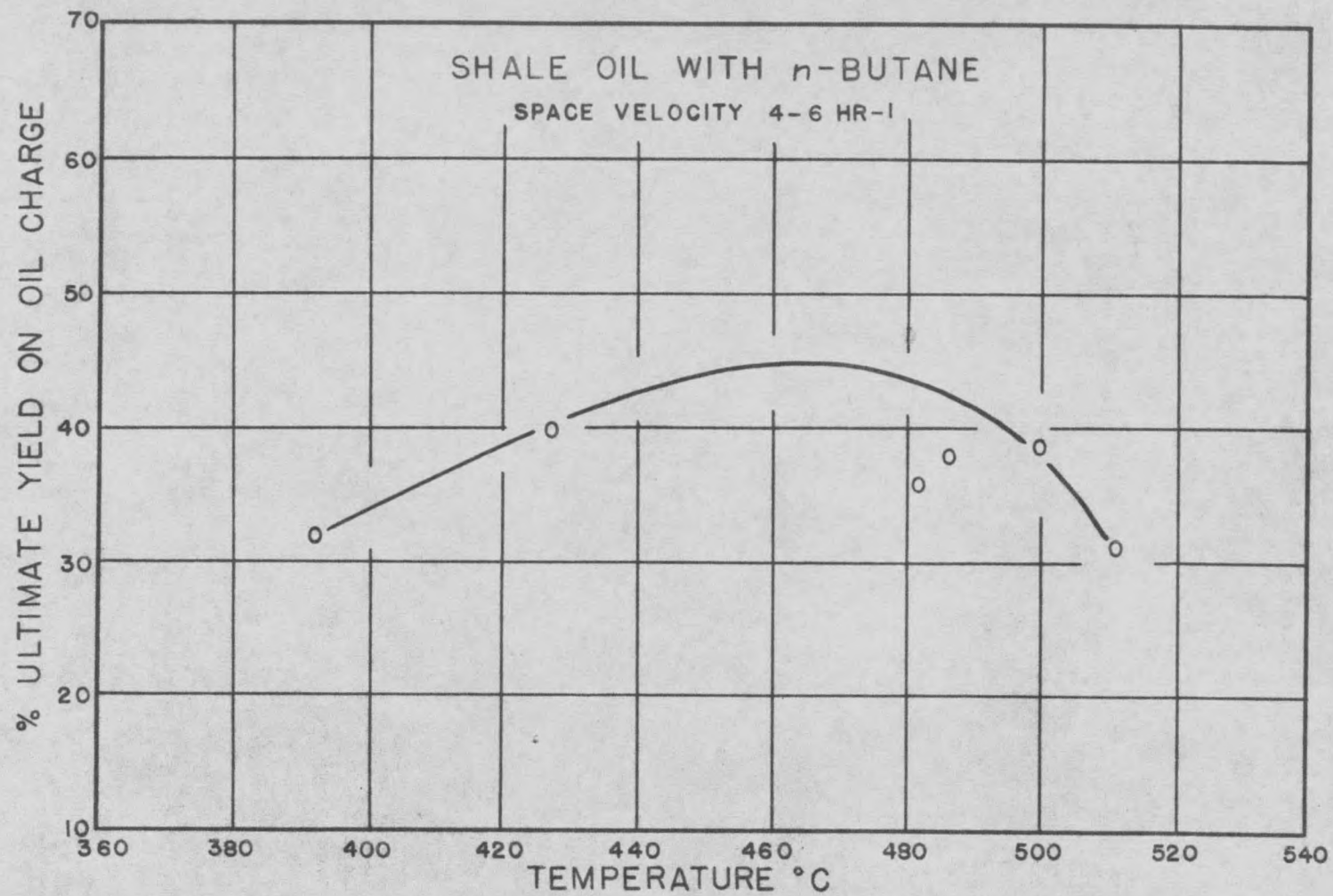


Figure 15. Relationship between Conversion and Ultimate Yield



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Figure 16. Relationship between Temperature and Ultimate Yield

TABLE IV

Results of Gum Tests on Shale Oil Gasoline*

Run No.	Outside Gas	Av. Temp. °C.	% Conversion	Space Velocity hr ⁻¹	mg. Gum per 100 cc.
3	None	466	30.5	.70	744
5	"	549	63.2	.66	120
6	"	573	73.5	.67	136
7, 9	i-C ₄ H ₈	376	56.5	.64	930
8	"	443	59.5	.65	190
10	"	479	75.6	.60	216
13, 14	"	394	34.0	5.0	1630
15	"	464	56.4	4.0	917
16	"	501	70.8	5.0	361
17, 19	n-C ₄ H ₁₀	409	29.0	.63	1402
18	"	460	53.3	.68	158
21	"	481	63.9	.54	380
22	"	392	22.0	4.4	2320
24	"	486	41.0	4.8	507
27	"	511	58.5	5.2	319

* Charge stock, shale oil plus indicated outside gas

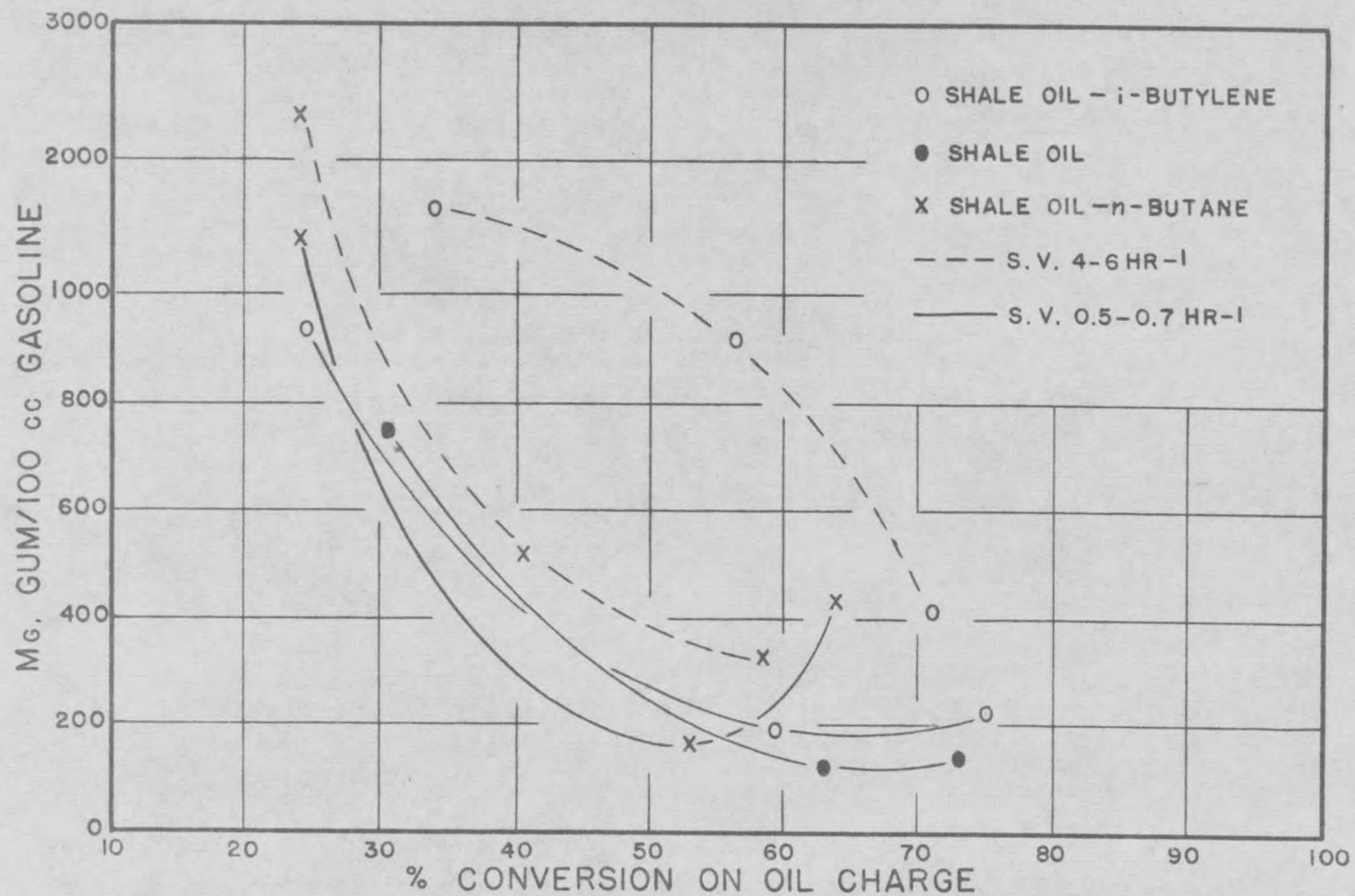


Figure 17. Relationship between Conversion and Gum Content

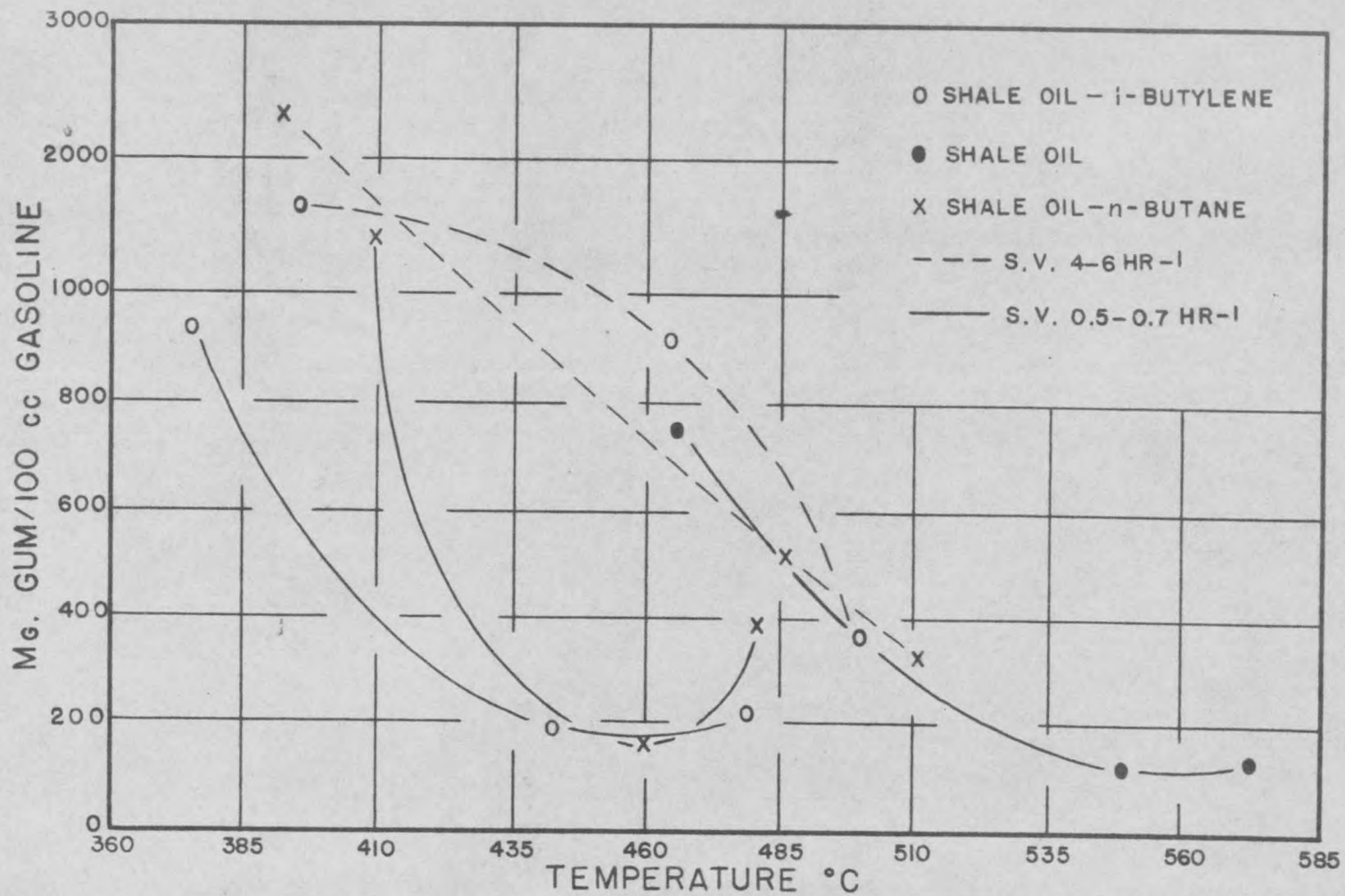


Figure 18. Relationship between Temperature and Gum Content

TABLE V

Shale Oil Inspection Data

A. S. T. M. Distillation of Diesel Fuel Cut RRS-48-442 from
Crude N-T-U Shale Oil RRS-48-395.

Temperatures in °F. corrected to 760 mm.

IBP	498
5%	524
10%	532
20%	540
30%	547
40%	552
50%	558
60%	565
70%	575
80%	586
90%	602
95%	617
E.P.	643
Recovery	99.0%
Residue	0.9%
Loss	0.1%
Specific Gravity @ 60°F.	0.8855

TABLE VI

Laboratory Determinations on Shale Oil Gasoline

Sample No.	1	2	3	4	5
Outside gas	Iso-butylene		None		n-Butane
Space Velocity (hr. ⁻¹)	0.65	4.5	0.68	0.65	5.0
Temperature (°C.)	460	480	560	480	490
Per cent losses with standard chemical treat.	8.4	12.5	13.0	11.1	13.0
Octane Number Motor Method					
Clear	80.6	82.5	82.3	80.4	80.1
1 ml. TEL	84.5	84.7	84.8	84.8	84.1
3 ml. TEL	86.8	87.3	86.7	86.5	86.2
Research Method					
Clear	85.7	88.6	92.3	88.1	86.9

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