Catalytic gas oil polyforming using propane as outside gas
by Ram Dev

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at Montana State College
Montana State University
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It was found that higher yields of gasoline were obtained when propane was used as an,outside gas at 600 and 900 psig but no such effect of propane in increasing the yield was noted at 300 psig or below. It was indicated that pressures higher than 900 psig may give even higher yields of gasoline if a suitable catalyst is used which doe's not lose activity permanently at those pressures. '

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TABLE OF CONTENTS

Page

Abstract. . . . . 3

I Introduction . . . . . 4

II Equipment, Methods and Materials . . . . . 7
A. Equipment. . . . . 7
B. Methods. . . . . 14
C. Materials. . . . . 19

III Sample Calculations. . . . . 20

IV Results. . . . . 24

V Conclusions. . . . . 30

VI Acknowledgment . . . . . 31

VII Literature Cited . . . . . 32

VIII Appendix . . . . . 33

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## ABSTRACT

The purpose of this investigation was to evaluate the process of gas oil polyforming under catalytic conditions using propane as an outside gas. Various pressures were applied to determine the effect of propane on the yield of gasoline.

Houdry fixed bed catalyst was used for all the runs. The runs were conducted at temperatures varying from 426.7°C. to 527.7°C., and the liquid space velocity was held at about 0.7 vol. per vol. of catalyst per hour. The average run charged approximately 450 gms of feed over 1400 cc. of catalyst. The pressures investigated were atmospheric, 300, 600 and 900 psig.

It was found that higher yields of gasoline were obtained when propane was used as an outside gas at 600 and 900 psig but no such effect of propane in increasing the yield was noted at 300 psig or below. It was indicated that pressures higher than 900 psig may give even higher yields of gasoline if a suitable catalyst is used which does not lose activity permanently at those pressures.

# I. INTRODUCTION

The polyform process employs the principle of cracking an oil in admixture with various amount of normally gaseous hydrocarbons (propane and butanes). The oil in this mixture can be subjected to higher temperature and higher degree of conversion per pass than possible in the ordinary thermal cracking process without uneconomically large production of residual gases.

Conventional thermal cracking of residual stocks and virgin gas oils is characterized by (1) high oil recycle ratios for maximum gasoline yield, (2) relatively low octane numbers of cracked gasoline, and (3) relatively high yields of tar. The octane level of gasoline obtained by thermal cracking of paraffinic stocks is generally in the range 65-70 by the A.S.T.M. method which is substantially lower than desired for blending to produce a satisfactory motor fuel for the highly competetive market.

During the last war, economy in production both as to money and material was vitally important. The utilization of propane and butane from the natural gasoline industry adhered to this program as did the production of butylenes for the manufacture of valuable aviation alkylates. Large United States Government orders and demands for high octane gasoline caused many oil refining companies to investigate and install the new polyforming and gas reversion processes because these

processes make both cheaper and better gasoline of higher octane number.

Work has been done on naphtha polyforming. Offutt et al (2) in a study of gas reactions and reactions of gas with products from naphtha cracking showed that gas ($C_3$ and $C_4$ hydrocarbons) suppressed tar and coke formation by reacting with some of the products from naphtha cracking which ordinarily are subject to interaction to form tar and coke. It was found that lower tar yields were produced from naphtha when it was reformed in a high dilution of gas. 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 without the benefit of gas dilution yield higher and higher percentages of gasoline in one-pass operations when cracked in increasing gas dilutions. Products from the cracking of the oil are formed in an atmosphere of reactable gas and there is a tendency to promote thermal alkylation, thermal polymerization and other addition type reactions between the gas and the reactive products made from cracking of the gas oil.

Catalytic cracking is a process, developed about ten years ago, for converting petroleum fractions in the fuel oil boiling range into gasoline and other lower boiling hydrocarbons. It gives a higher yield of gasoline of better quality than can be produced by thermal cracking, and greater yields

of propylene, isobutane and butylenes which are important for synthetic rubber and 100-octane aviation gasoline. A considerable amount of work has been done on the catalytic cracking of gas oil, naphtha and petroleum hydrocarbons which has resulted in the improvement of the technique and the discovery of more active catalysts (4), (6), (7), (10), (11).

The superiority of catalytic over thermal cracking led the author to an investigation to evaluate the process of gas oil polyforming under catalytic conditions using propane as an outside gas. The yields of gasoline from the catalytic cracking of virgin gas oil stock with and without propane at different pressures were compared. No attempt was made to determine the operating variables which permit maximum yield of gasoline. Houdry fixed bed catalyst was used. All runs were conducted at a temperature around 450°C. and the liquid space velocity was held in the neighborhood of 0.7 vol. per vol. of catalyst per hour. The pressures chosen were atmospheric, 300 psig, 600 psig and 900 psig. The average barometric pressure during this study was approximately 635 mm. Hg. It was intended in this study to compare catalytic cracking with catalytic polyforming of gas oil under similar conditions of temperature, pressure and space velocity, so far as the yields of gasoline and their octane numbers were concerned.

# II. EQUIPMENT, METHODS AND MATERIALS

## A. Equipment

The equipment used in this investigation consisted of the reaction system shown in Figure 1, iron-constantan thermocouples, a potentiometer, a rectification column, two glass stem mercury thermometers, a Glas-Col heater, a one liter distillation flask, a Harvard type triple beam balance, four autotransformers, two thermoflasks and two pressure gauges reading up to 3000 psig.

The feed tank was made from a piece of six inch standard mild steel pipe, thirteen inches long. The pipe was threaded at both ends and fitted with mild steel caps. The upper cap was drilled at three places and tapped to take one-half inch standard pipe. Pieces of one-half inch standard mild steel pipes threaded at both ends were fitted in these holes. One of these pipes was fitted with a one-half inch tee. The side opening of the tee was reduced to one-fourth inch to take a pressure gauge reading up to 3000 psig, the smallest division being 40 psig. The top opening, fitted with a plug, served as an entrance for the feed. For every batch the plug was removed and the feed poured in. The second pipe was connected to the upper end of the Jerguson gauge by using two one-half inch elbows. In this line a one-half inch union was fitted for easy dismantling if needed. The third pipe was fitted with a globe valve.

The bottom of the cap was drilled at one place and tapped to take one-half inch standard pipe. A one-half inch long nipple fitted at one end with a one-half inch globe valve was screwed in this hole. A one-half inch tee was attached to the other end through a one-half inch close nipple. The side opening of the tee was fitted with a one-half inch standard pipe which connected the lower end of the Jerguson gauge by using an elbow and another piece of one-half inch pipe. The bottom hole of the tee was connected to a Zenith pump by means of proper fittings. Three pieces of angle iron were welded to the bottom cap to serve as legs. Two three-eighths inch low carbon steel rods were welded onto the feed tank to serve as supports.

The pump used was a Zenith one-half inch size type QE gear pump pumping 0.297 cc. per revolution. This was connected to a one-fourth H.P., 1752 R.P.M. motor, through a 20:1 reduction gear box and a Reeve's drive. The speed of the pump could be altered by changing the size of the pulleys as well as adjusting the Reeve's pulley.

The delivery end of the pump was connected to the pre-heater by means of one-half inch extra strong black steel pipe, twelve feet long and proper high pressure fittings as shown in Figure 1. A high pressure globe valve made of extra strong steel was inserted in this line at the top of the vertical pipe.

The pre-heater was made from a piece of two inch extra

strong steel pipe 24 inches long. The pipe was threaded at both ends and fitted with extra strong steel caps. The caps were drilled and tapped to take one-half inch extra strong pipe. The pre-heater was wrapped with asbestos tape. Over this tape 16 feet of Nichrome wire with a resistance of 1.03 ohms per foot was wound. The winding drew 7.5 amperes from a 120 volt autotransformer. The winding was covered with asbestos tape and then a one inch layer of magnesia was placed over it.

Two three-eighths inch low carbon steel rods were welded onto the pre-heater to act as supports. The pre-heater was packed with Berl saddles.

The reactor was made from a three inch extra strong steel pipe, 15 inches in length. The bottom of this pipe was welded with a strong steel plate through the center of which a one-half inch extra strong steel pipe jutted out. This pipe was threaded at the end and connected to the condenser through an extra strong steel union. The top of the reactor was threaded and fitted with an extra strong steel cap. A hole was drilled into this cap and tapped to take a one-half inch extra strong steel pipe three inches long. This pipe was braised to the cap on one end and connected to the pre-heater at the other.

Two three-eighths inch low carbon steel rods were welded onto the reactor on the opposite side from the thermowells to act as supports for the reactor chamber.

The iron constantan thermocouples were connected to a Brown potentiometer. This potentiometer was calibrated in millivolts and could be used to record temperatures up to 1200°C. The millivolt readings were converted into degrees centigrade using a standard conversion table for iron constantan thermocouples with the reference junction at 0°C.

The reactor was wrapped with asbestos tape. Over this tape 75 feet of Nichrome wire, with a resistance of 1.04 ohms per foot, was wound. This winding drew three amperes from a 220 volt autotransformer. The winding was covered with asbestos tape and two other resistance windings, each 16 feet long, were placed over it, one covering the upper half and the other the lower half of the reactor. Each of these windings was connected to a 120 volt autotransformer and drew 7.5 amperes. An asbestos covering was placed over these windings and then a one inch layer of magnesia put over all the windings and tape.

The condenser was made from a three inch standard mild steel pipe, 16 inches long. The pipe was threaded at both ends and fitted with caps. Two three-fourth inch holes, one on each cap, were drilled and a one-half inch extra strong steel pipe 20 inches long and threaded at both ends was slid through the holes. The one-half inch pipe was then braised at the holes extending two inches beyond the larger pipe on either end. The three inch pipe was drilled at two places, one about three

inches from the top and the other about three inches from the bottom. These holes were tapped to take pieces of one-half inch standard pipe, four inches in length. These pieces of pipe served as outlet and inlet for the cooling water.

Steel rods similar to those used in the pre-heater and reactor chamber were welded to serve as supports for the condenser.

The bottom of the condenser was connected to the receiver. The receiver was made of three inch extra strong steel pipe 16 inches long, threaded at both ends and fitted with extra strong steel caps. Two holes were drilled through the upper cap and tapped to take one-half inch extra strong steel pipe. One of these holes was fitted with a one-half inch extra strong steel pipe threaded at both ends. This pipe connected the condenser to the receiver through a one-half inch extra strong steel union. Through the other hole ran another piece of one-half inch extra strong steel pipe which joined the receiver to a Grove regulator controlling back pressure. This regulator could be set for any pressure reading up to 950 psig. A one-half inch tee was inserted in this line, the side hole of which was reduced to one-half inch to take a pressure gauge reading up to 3000 psig.

A one-half inch long nipple was fitted in the bottom hole of the receiver to the other end of which was screwed a one-half inch high pressure globe valve made of extra strong steel. Proper connections were made with one-half inch copper tubing

to receive the liquid from the receiver directly into a glass flask surrounded with dry ice as shown in Figure 1.

The free end of the Grove regulator was attached to the two dry ice traps. The first trap was cooled by acetone-dry ice mixture, and the second was surrounded by solid dry ice.

The gas meter following the dry ice traps was a three liter Precision Wet Test Meter.

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 voltage range of 0 to 260 volts and were fused at three amperes.

The heater used for the distillation flask was a Glas-Col heater.

The rectification column was constructed of three concentric glass tubes. The inner most tube was 33 mm. inside diameter and packed with one-eighth inch glass helices. A thermometer was fastened to the outside surface of the inner tube about half way between top and bottom. The second or middle tube was wrapped with Nichrome resistance wire which was connected to a 110 volt autotransformer to provide heat to the column. The third or outer tube served as a protector and insulator. The column was 26 inches high. The top of the column was fitted with an adjustable reflux head with a cold finger condenser and a thermometer to record temperatures. A receiver

was attached to the outlet from the distilling head which in turn was connected to a dry ice trap.

## B. Methods

1. Atmospheric Pressure Runs:

The reactor was heated until the two middle thermocouples gave a reading about 500°C. Dry ice was placed in the dry ice traps, using, in one case, a liquid such as acetone to give a better cooling medium. The density of gas oil was measured by weighing 1000 cc. on the Harvard triple beam balance. Air was swept from the system by using a ten minute nitrogen purge. After the reactor was completely purged of air, the nitrogen line was disconnected. The charge was placed in the feed tank and the pump started to fill completely all the connecting pipes to the preheater. A sudden increase in the rate of gas formation as seen in the gas meter showed that the oil vapors had reached the catalyst bed.

Readings from all four thermocouples and the gas meter were noted before the run was started and continued at five minute intervals throughout the duration of the run which was 30 minutes in all cases. The valve at the bottom of the feed tank was shut so that the charge was drawn from the Jerguson gauge which had been calibrated before hand. Time taken to withdraw 30 cc. of charge was noted in order to obtain the feed rate. This was repeated four or five times after five minute intervals throughout the run. The valve at the bottom of the feed tank was opened every time after the reading was taken. A sample of uncondensable gas was collected by displacement of

water in a five gallon glass bottle. The bottle thus filled with gas was weighed. The gas was then removed by filling the bottle with water. Water was then removed and the bottle weighed again filled with air. In pressure runs, it took some time before the reaction gases came out through the blow down line because nitrogen used for pressurization had to be displaced. This data was required for the calculation of the density of the uncondensed gas. Upon completion of the run, the reactor was purged of all hydrocarbon vapors by passing nitrogen through for ten minutes. During this purge the gas meter and the dry ice traps were taken out of the system and all condensable hydrocarbons were retained in the receiver. The condensed liquid from the metallic receiver was directly transferred to a cooled distillation flask and the liquid from the dry ice traps added to it. The liquid was then immediately distilled for gasoline to 210°C. end point. The reflux ratio was kept at about 5:1. During the time of distillation a dry ice trap was kept in series with the receiver to catch any light hydrocarbon vapors passing through the latter.

2. Catalyst Burn-off:

During the run, a deposit of carbonaceous material was laid down upon the catalyst surface reducing its activity and necessitating periodic burn offs. The catalyst was burned off after every run. Burning off was accomplished by passing air through the reactor while maintaining the burn off temperature

below the sintering point of the catalyst, about 600°C. The burn off was done immediately after the completion of the run before the catalyst bed had time to cool.

The catalyst was changed whenever a run showed sufficient loss in catalyst activity. For the runs made at atmospheric pressure and 300 psig the change was necessary after every fourth run, while for the runs made at 900 psig, the catalyst lost considerable activity in one run and had to be changed after every second run.

3. Gas Oil Propane Mixture at Atmospheric Pressure:

The procedure in these runs was exactly the same as described above. The only difference was in the charge composition.

A weighed amount of gas oil was cooled in a refrigerator maintained at -40°C. Required amounts of liquid propane were withdrawn from a tank, placed upside down on a wooden structure, into a wide mouth cooled Demar flask. The gas oil was then added slowly with vigorous stirring. Any loss of propane during this mixing was made up by adding more liquid propane to this charge from another thermos flask and stirring the whole mass vigorously. The charge was then finally weighed to find out the amount of propane contained in it. The charge, which was now quite volatile, was immediately transferred to the feed tank. The valve on it was then closed and the plug put in position, so that there was no way for any gas to escape

from the feed chamber. The level of the charge in the thermos flask was marked. After the charge had been transferred to the feed tank, the thermos flask was filled with water to the mark and weighed. This gave data for the determination of the density of the charge.

4. Gas Oil Propane at Superatmospheric Pressure:

The procedure in these cases was similar to that described above.

The difference is that in this case the system from the end of the Zenith pump to the Grove regulator was pressurized with nitrogen. The Grove regulator was set for the pressure desired in the system by rotating the head clockwise and nitrogen was passed from the cylinder to the system through valve A (Figure 1). When the proper pressure was indicated by the pressure gauge, Valve A was shut off, the nitrogen line was disconnected, and the pump started.

For 600 and 900 psig runs, a similar nitrogen pressure of about 450 psig had to be applied to the feed tank for a smooth running of the pump. After the run, the Valve B at the top of the long vertical pipe was closed; after fifteen minutes the pressure in the system was released through the Grove regulator. When there was still a pressure of about 50 psig on the system, the liquid in the receiver was forced to the glass distillation flask cooled in dry ice, by opening the valve at the bottom of the receiver. The liquid was then

immediately distilled for gasoline.

## C. Materials

The gas oil was a virgin atmospheric gas oil from Elk Basin and Frannie crude oils in approximately a 70:30 ratio. Laboratory inspection data for this gas oil is given in Table I in the appendix.

The propane used was commercial grade.

## III. SAMPLE CALCULATIONS

The calculations of space velocity, yields of gasoline and percentage conversions for run Number 15 are presented as typical of all the runs made.

A. Calculation of liquid space velocity.

Data.

Volume of catalyst in the reactor = 1350 cc.

Rate of charging the feed = 18.46 cc/min.

$$\text{Space velocity} = \frac{18.46 \text{ cc/min} \times 60 \text{ min/hr}}{1350 \text{ cc.}} = 0.82 \text{ hr}^{-1}$$

B. Calculation of percent yield of gasoline based on liquid product.

Data.

Weight of liquid product obtained on cracking = 247.6 gms.

Weight of gasoline recovered = 108.7 gms.

Percent yield of gasoline based on liquid product $= \frac{108.7 \times 100}{247.6} = 43.9$

C. Calculation of percent yield of gasoline based on total product.

Data.

Weight of liquid product obtained on cracking = 247.6 gms

Volume of uncondensable gas formed = 105.6 liters

Density of gas = 0.7 gm per liter

Weight of gasoline recovered = 108.7 gms.

Therefore, weight of uncondensable gas formed =

105.6 x 0.7 = 73.92 gms.

Total product (liquid product + gas) = 247.6 + 73.92

= 321.52 gms.

Percent yield of gasoline based on total product

$= \frac{108.7 \times 100}{321.52} = 33.8$

D. Calculation of percent yield of gasoline based on gas oil charged.

Data.

Rate of charging the feed = 18.46 cc. per min.

Duration of run = 30 minutes

Density of charge = 0.84 gm. per cc.

Percent gas oil in charge = 84.1

Weight of gasoline recovered = 108.7 gms.

Total input = 18.46 x 30 = 553.8 cc.

= 553.8 x 0.84 = 465.1 gms.

Weight of gas oil in this feed = 465.1 x 0.841

= 391.1 gms.

Percent yield of gasoline based on gas oil

charged $= \frac{108.7 \times 100}{391.1} = 27.8$

E. Calculation of percent conversion based on charge:

Data.

Total input = 465.1 gms.

Weight of the liquid product obtained = 247.6 gms.

Weight of gasoline recovered = 108.7 gms.

Weight of the charge unconverted = 247.6 - 108.7

= 138.9 gms.

Weight of the charge converted to gasoline, gas and coke & losses = 465.1 - 138.9 = 326.1 gms.

Percent conversion based on charge = $\frac{326.1 \times 100}{465.1}$

= 70.1

F. Calculation of the density of uncondensable gases.

Data.

Volume of the glass bottle = 19100 ml

Weight of the bottle & air = 6248 gms.

Weight of the bottle & gas = 6243 gms.

Pressure = 640 mm. Hg. Temperature = 25°C.

Weight of air - gas = 5 gms.

Weight of 1 liter of air at 0°C. and 760 mm. Hg.

= 1.2928 gms. or

$\frac{298 \times 760 \times 1000}{273 \times 640}$ = 1296.2 cc. of air at 25°C. and 640 mm. Hg. weigh 1.2928 gms.

19100 cc. of air under these conditions will weigh

$\frac{1.2928 \times 19100}{1296.2}$ = 19.05 gms.

Weight of same volume of gas = 19.05 - 5

= 14.05 gms.

Density of gas = $\frac{14.05}{19.10}$ = 0.73 gms. per liter.

## IV. RESULTS

Table II in the appendix tabulates the conditions and results of the runs made. Runs 1 - 6 were made using gas oil as the charge and carried out at atmospheric pressure. The liquid products from runs 1 - 3 were combined and then distilled for 210°C. E.P. gasoline. The temperature for these three runs varied from 457.8°C. to 527.7°C. Percent gasoline based on liquid product was 28.7. This basis seems to be better for comparison than the charge basis since there were losses amounting to 24 - 25 percent of the charge. The liquid products obtained from runs 4 - 6 were similarly combined and distilled for gasoline. The results were similar to those described above for runs 1 - 3. The temperature varied from 460.6°C. to 478.2°C. and the percent gasoline based on liquid product was 33.0. However, gasoline based on charge was 26.3 as against 25.4 obtained from runs 1 - 3. The space velocity in the first three runs was $0.58Hr^{-1}$ and in the last three $0.65Hr^{-1}$.

Runs 7 - 8 were made at atmospheric pressure and at temperatures 467.3°C. and 489.2°C. respectively.

The charge in these cases was a mixture of gas oil and liquid propane with 89.2 and 88,58 weight percent gas oil respectively. The yields of gasoline based on liquid product were 34.9 and 38.8 in the two runs and those based on gas oil charged were 23.01 and 23.3 respectively. The losses were high

in these cases amounting to 31.65% in the charge. When these results are compared with those obtained under similar conditions without using propane it seems that propane did not help in increasing the yield of gasoline. A comparison of the octane numbers and distillation data shows that propane had no effect on the quality of the gasoline produced. Octane number by motor method was 82.1 in both the cases. By Research method the octane numbers were 94.8 and 94.7 respectively.

Runs 9 and 10 used gas oil as charge and were conducted at around 300 psig. The temperatures were maintained at 426.7°C. and 474°C. for the two runs. The yields of gasoline based on liquid product were practically the same as that from runs 4 - 6.

A fall in the yield of gasoline based on gas oil charged as compared to that from runs under atmospheric pressure is evident. An increase in the percent gas formed and the presence of more light fraction in the gasoline as seen in the gasoline inspection data, clearly indicate a more severe cracking in these runs than in runs 1 - 6. The space velocity in runs 9 - 10 were 0.64 and 0.73 comparable to those for runs 1 - 6. It may therefore be concluded from these results that conditions for higher yield of gasoline from gas oil are better at atmospheric pressure than at 300 psig, other factors remaining the same.

Runs 11 and 12 were conducted with a charge consisting of

a mixture of gas oil and propane. Percent gas oil in the charge for run 11 was 81.7 and for run 12 was 83.4. The temperature and pressure in the two runs were about 448°C and 300 psig respectively. When the yields of gasoline are compared with those obtained from runs 9 - 10 which were conducted under similar conditions but without propane it seems that the gasoline yield based on liquid product is improved giving 41.6 percent for run 11 as against 33.8 percent for run 10. The yields based on gas oil charged do not show any marked change however. At this stage, therefore, nothing conclusive can be said about the effect of propane on gasoline yield. The octane numbers are slightly improved.

The charge for runs 13 - 14 was gas oil. The temperatures were 446.5°C. and 442.1°C. for the two runs and the pressure was kept at 600 psig. Runs 15 - 16 used a mixture of gas oil and propane for charge. The temperatures were 447.4°C. and 457.4°C. while the pressure was 600 psig in both cases. Runs 13 and 15 were conducted under practically identical conditions of temperature, pressure and space velocity. The amount of charges and percent losses were also practically equal. A 43.9% yield of gasoline based on liquid product for run 15 as against 38.9% for run 13 clearly shows the effect of propane in increasing the yield of gasoline. Also a 27.8% yield of gasoline based on gas oil charged for run 15 as against 20.3% for run 13, confirms this fact. The effect of propane on the

yield of gasoline is therefore apparent at 600 psig but not at 300 psig. No marked change was noticed in the octane numbers.

Runs 17 and 18 were made with gas oil as charge and at about 900 psig reaction pressure. The temperatures of reaction were 475.6°C. and 435.2°C. in the two cases. Runs 19 and 20 were conducted with a mixture of gas oil and propane as charge. The pressure in the two cases was around 900 psig and the temperatures were 428°C. and 452.5°C. It can be seen that runs 18 and 19 were made under similar conditions of temperature, pressure and space velocity. The amounts of the charge were also nearly equal -- 414.4 gms in the first case and 400.8 gms in the second case. The losses, however, were considerably higher in run 19. Percent gasoline yield on the basis of gas oil charged for run 19 was 32.3 as against 24.1 for run 18. These results are comparable irrespective of the losses since any compensation for the heavier losses in run 19 would only increase the yield of gasoline based on gas oil. This high yield of gasoline from run 19 is the highest ever obtained from any of the runs made in this investigation. The effect of propane in increasing the yield of gasoline at 900 psig is clearly seen. Similar yields obtained from run 20 confirm this fact. The yields of gasoline based on liquid product was 58.2 for run 19 as against 37.0 for run 18. This is also in accordance with the observation made.

Figures 2 - 4 are plots of percent conversion based on

charge against percent gasoline yield based on liquid product, total product and gas oil respectively. Each graph shows two plots, one for runs made with propane and the other for those made without it. The general trends of the curves are similar in all three cases. For runs made with propane, the percent yield of gasoline increases with percent conversions, the slope of the curve being greatest in Figure 2 and smallest in Figure 4. The slope of the curve in Figure 3 is intermediate between the two. For runs made without propane the increase in percent yield of gasoline with percent conversion in all three cases is very little. The lines are more nearly horizontal. From these graphs the achievement of propane in giving greater yield of gasoline is clearly seen.

Figures 5 - 7 show the effect of reaction pressure on percent gasoline yield based on liquid product, total product and gas oil charge, respectively. Here again the forms of the curves are the same in all cases. Percent yield of gasoline calculated on three different bases seems to be little affected by increase in pressure for the runs conducted without propane. The lines in the three figures are more or less horizontal. For the runs made with propane, it can be seen from these graphs that the percent yield of gasoline is markedly increased with increasing pressure. Here again the slope of the line is greatest when based on liquid product and least when based on gas oil charged. The slope of the line based on total

product is intermediate between the two. This indicates that under polyforming conditions a higher pressure is more suitable so far as the yield of gasoline is concerned.

Figure 8 is a plot of A.S.T.M. octane number - motor method against pressure of reaction. The figure indicated a fall in octane number with increasing pressure in both the cases, whether the runs are made with or without propane. The decrease, however, is slightly greater when no propane is used.

Figure 9 shows the effect of pressure on the A.S.T.M. octane number determined by research method. Here again is a decrease in octane number with increasing pressure, being greater in the case where no propane is used. The slope of the curves in this case, however, is much greater than that of the curves in Figure 8, showing that the fall in octane number determined by research method with increasing pressure of reaction is greater than that of octane number determined by motor method.

# V. CONCLUSIONS

The following conclusions may be drawn from the experiments made in this investigation.

1. Houdry fixed bed catalyst is a good cracking catalyst to give fairly high octane gasoline.
2. There is a considerable loss in the activity of the catalyst at 900 psig especially when propane is used as an outside gas, so that it becomes necessary to change the catalyst after every second run.
3. Propane does not seem to have any effect on gasoline yield at 300 psig or below. Its effect in increasing the gasoline yield is indicated at 600 psig while at 900 psig an even higher yield of gasoline is obtained.
4. A high yield of gasoline can be obtained in catalytic polyforming of gas oil conducted at 900 psig and 428°C, a temperature which is too low for thermal polyforming at the usual space velocities.

## VI. ACKNOWLEDGMENT

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# VIII. APPENDIX

Page

TABLE I - Gas Oil Inspection Data . . . . . 34

TABLE II - Catalytic Polyforming of Gas Oil . . . . . 35

TABLE III - Gasoline Inspection Data. . . . . 36

Figure 1 - Diagram of Equipment . . . . . 37

Figure 2 - Effect of Pressure on Gasoline Yield . . . . 38

Figure 3 - Effect of Pressure on Gasoline Yield . . . . 39

Figure 4 - Effect of Pressure on Gasoline Yield . . . . 40

Figure 5 - Relationship between Conversion and Yield of Gasoline. . . . . 41

Figure 6 - Relationship between Conversion and Yield of Gasoline. . . . . 42

Figure 7 - Relationship between Conversion and Yield of Gasoline. . . . . 43

Figure 8 - Effect of Pressure on Octane Number. . . . . 44

Figure 9 - Effect of Pressure on Octane Number. . . . . 45

TABLE I

Gas Oil Inspection Data

| | | |
|---|---|---|
| Gravity °API | 26.2 | |
| Distillation | I.B.P. | 524°F. |
| | 5% | 558°F. |
| | 10% | 570°F. |
| | 20% | 580°F. |
| | 30% | 588°F. |
| | 40% | 601°F. |
| | 50% | 614°F. |
| | 60% | 628°F. |
| | 70% | 648°F. |
| | 80% | 676°F. |
| | 90% | 714°F. |
| % Recovery | 95% @ | 730°F. |
| Viscosity | 52.6 sec. @ | 100°F.S.V. |

TABLE II

CATALYTIC POLYFORMING OF GAS OIL

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 | 7-3rd run on changed catalyst | 8-New Reactor | 9-Fresh Catalyst | 10 | 11-Fresh Catalyst | 12 | 13-Fresh Catalyst | 14 | 15 | 16-Fresh Catalyst | 17 | 18 | 19-Fresh Catalyst | 20-Fresh Catalyst |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Vol. of Cat. | 1350 cc. | 1350 cc. | 1350 cc. | 1350 cc. | 1350 cc. | 1350 cc. | 1400 cc. | 800 cc. | 1400 cc. | 1400 cc. | 1400 cc. | 1400 cc. | 1350 cc. | 1350 cc. | 1350 cc. | 1350 cc | 1350 cc. | 1350 cc. | 1350 cc. | 1350 cc. |
| Reactor Temp. | | | | | | | | | | | | | | | | | | | | |
| 1st | 340°C | 494°C | 465°C | 465°C | 462°C | 469°C | -- | 503°C | -- | -- | -- | -- | 479.6°C | 442.5°C | -- | -- | 481°C | -- | -- | 434.4°C |
| 2nd | 521.4°C | 559°C | 512°C | 482°C | 485°C | 487°C | 494.6°C | 515.4°C | 414.5°C | 476.4°C | 410.4°C | 448.6°C | 455.6°C | 439.5°C | 448°C | 453.2°C | 480.25°C | 437°C | 434.4°C | 459°C |
| 3rd | 513.5°C | 551°C | 517.5°C | 474.5°C | 489°C | 478.6°C | 440°C | 450.8°C | 439°C | 471.6°C | 486.0°C | 447.4°C | 446.8°C | 441°C | 446.8°C | 461.5°C | 479.25°C | 435.5°C | 421.6°C | 457.2°C |
| 4th | 456.5°C | 507°C | 484°C | 420°C | 440.5°C | -- | -- | -- | -- | -- | -- | -- | 453.6°C | 445°C | -- | -- | 462°C | -- | -- | 459.4°C |
| Average Temp. | 457.8°C | 527.7°C | 494.6°C | 460.6°C | 469.37°C | 478.2°C | 467.3°C | 489.2°C | 426.7°C | 474°C | 448.2°C | 448.0°C | 446.5°C | 442.1°C | 447.4°C | 457.4°C | 475.6°C | 435.2°C | 428°C | 452.5°C |
| Pressure | Atmosph. | Atmosph. | Atmosph. | Atmosph. | Atmosph. | Atmosph. | Atmosph. | Atmosph. | 325#/in$^2$ | 300#/in$^2$ | 325#/in$^2$ | 300#/in$^2$ | 600#/in$^2$ | 500#/in$^2$ | 600#/in$^2$ | 600#/in$^2$ | 950#/in$^2$ | 900#/in$^2$ | 950#/in$^2$ | 900#/in$^2$ |
| % Gas oil in charge | 100 | 100 | 100 | 100 | 100 | 100 | 89.2 | 88.58 | 100 | 100 | 81.7 | 83.4 | 100 | 100 | 84.1 | 83.4 | 100 | 100 | 83.3 | 79.8 |
| Mol ratio $C_3H_8$:G.O. | -- | -- | -- | -- | -- | -- | 0.75:1 | 0.8:1 | -- | -- | 1.2:1 | 1.12:1 | -- | -- | 1.07:1 | 1.13:1 | -- | -- | 1.13:1 | 1.44:1 |
| Density of charge gms/cc | .8973 | .8973 | .8973 | .8973 | .8973 | .8973 | 0.840 | -- | .8973 | .8973 | 0.878 | 0.833 | .8973 | .8973 | 0.840 | 0.814 | 0.8973 | 0.8973 | 0.835 | 0.814 |
| Charge rate | 12.9cc/min | 13.04cc/min | 13.04cc/min | 14.63cc/min | 14.63cc/min | 14.63cc/min | 17.6cc/min | -- | 15.0cc/min | 17.14cc/min | 15cc/min | 15.7cc/min | 17.6cc/min | 21.8cc/min | 18.46cc/min | 23.07cc/min | 21.8cc/min | 15.4cc/min | 16cc/min | 15.4cc/min |
| Total charge(gms) | ( 1048.94 ) | | | ( 1181.10 ) | | | 444.69 | 600.0 | 403.65 | 461.2 | 395.1 | 375.0 | 461.3 | 567.1 | 465.1 | 560.0 | 586.6 | 414.4 | 400.8 | 375.66 |
| Total $C_3H_8$ charged (gm) | -- | -- | -- | -- | -- | -- | 48.91 | 68.5 | -- | -- | 72.3 | 69 | -- | -- | 74 | 93 | -- | -- | 66.9 | 75.86 |
| Total G.O. charged (cc) | 387.0 | 391.2 | 391.2 | 438.9 | 438.9 | 438.9 | -- | -- | 450.0 | 514.2 | -- | -- | 514.3 | 654.5 | -- | -- | 354 | 462 | -- | -- |
| Total G.O. charged (gms) | 347.14 | 350.9 | 350.9 | 393.7 | 393.7 | 393.7 | 395.78 | 531.5 | 403.65 | 461.2 | 322.8 | 306 | 461.3 | 567.1 | 391.1 | 467 | 586.6 | 414.4 | 333.9 | 299.8 |
| H.C. Liqd.recovered | 234.8 gm | 234.7 gm | 230.9 gm | 293.40 gm | 312.30 gm | 335.4 gm | 260.7 gm | 361.5 gm | 298.9 gm | 288.5 gm | 169 gm | 191.4 gm | 241.3 gm | 402.4 gm | 247.6 gm | 310.5 gm | 401.9 | 269.45 | 185.3 | 143.3 |
| Gas formed - liters | 29.25 | 32.50 | 32.30 | 18.45 | 19.90 | 14.30 | 43.8 | 48.35 | 50.5 | 100.3 | 178.5 | leakage | 130.1 | 84.5 | 105.6 | 98.3 | 90 | 86.2 | 85 | 87.5 |
| Density of gas | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 1gm/liter | 0.7gm/liter | .996gm/liter | leakage | 0.7gm/liter | 0.7gm/liter | 0.7gm/liter | .69gm/liter | .69gm/liter | .69gm/liter | .78gm/liter | 1 gm/liter |
| Gas formed in grams | 29.25 gm | 32.5 gm | 32.3 gm | 18.45 gm | 19.9 gm | 14.3 gm | 43.8 gm | 48.35 gm | 50.5 gm | 70.2gm | 127.98 | -- | 91.07 | 59.15 | 73.92 | 68.81 | 63.0 | 60.34 | 66.3 | 87.5 |
| Wt.% liqd. prod. on charge | 67.64 | 66.88 | 65.80 | 74.50 | 79.30 | 85.18 | 58.6 | 60.25 | 74.04 | 62.5 | 42.8 | 62.5 | 58.3 | 58.5 | 53.2 | 55.4 | 68.5 | 65.02 | 46.2 | 38.1 |
| Wt.% gas on charge | 8.44 | 9.26 | 9.20 | 4.7 | 5.0 | 3.63 | 9.8 | 8.06 | 12.50 | 15.2 | 32.4 | -- | 19.7 | 10.07 | 15.89 | 12.2 | 10.74 | 14.56 | 16.5 | 23.3 |
| % losses on charge | 23.92 | 23.86 | 25.00 | 20.8 | 15.7 | 11.19 | 31.6 | 31.69 | 13.46 | 22.3 | 24.8 | -- | 28.0 | 21.43 | 30.91 | 32.4 | 20.76 | 14.42 | 37.3 | 38.6 |
| Gasoline rec. | ( 266.7 gm ) | | | ( 310.7 ) | | | 91.1 gms | 139.3 gms | 100.0 gms | 97.5 gm | 70.2 gm | 75.0 gm | 93.9 gm | 146.6 gm | 108.7 gm | 129.5 gm | 140 gm | 99.8 gm | 108 gm | 87.8 gm |
| Gasoline % on liquid prod. | ( 38.7 ) | | | ( 33.0 ) | | | 34.9 | 38.8 | 33.45 | 33.8 | 41.6 | 39.2 | 38.9 | 36.4 | 43.9 | 41.7 | 34.8 | 37.0 | 58.2 | 61.27 |
| % gasoline on total product | ( 33.5 ) | | | ( 31.2 ) | | | 29.9 | 26.2 | 27.8 | 27.1 | 23.6 | leakage | 28.2 | 31.7 | 33.8 | 34.1 | 30.1 | 30.2 | 42.9 | 38.04 |
| % gasoline on gas oil | ( 25.4 ) | | | ( 26.3 ) | | | 23.01 | 23.3 | 24.7 | 21.1 | 23.0 | 22.7 | 20.3 | 24.9 | 27.8 | 27.8 | 23.8 | 24.1 | 32.3 | 29.3 |
| Octane No. Motor Method | 82.1 | | | | | | ( 82.1 ) | ( 80.8 ) | ( 82.0 ) | ( 80.6 ) | ( 79.0 ) | ( 78.8 ) | ( 80.2 ) | | | | | | | |
| Research Method | 94.8 | | | | | | ( 94.7 ) | ( 89.4 ) | ( 93.4 ) | ( 90.2 ) | ( 87.0 ) | ( 86.4 ) | ( 88.1 ) | | | | | | | |
| Space Velocity $hr^{-1}$ | 0.61 | 0.58 | 0.58 | 0.65 | 0.65 | 0.65 | 0.75 | -- | 0.64 | 0.73 | 0.64 | 0.67 | 0.75 | 0.96 | 0.82 | 1.02 | 0.96 | 0.68 | 0.71 | 0.68 |
| Unconverted Charge (gms) | ( 434.7 ) | | | ( 630.4 ) | | | 169.6 | 222.2 | 196.9 | 191.0 | 98.8 | 116.4 | 147.4 | 255.8 | 138.9 | 181.0 | 261.9 | 169.65 | 77.3 | 55.5 |
| Converted charge (gms) | ( 614.24 ) | | | ( 550.7 ) | | | 275.09 | 277.8 | 204.75 | 270.2 | 296.8 | 258.5 | 313.9 | 331.3 | 326.1 | 379.0 | 324.7 | 244.75 | 323.5 | 320.16 |
| % Conversion | ( 58.5 ) | | | ( 47.1 ) | | | 61.9 | 63.0 | 50.9 | 58.5 | 75.0 | 69.1 | 68.0 | 56.3 | 70.1 | 67.6 | 55.5 | 59.1 | 79.3 | 85.0 |

TABLE III

Gasoline Inspection Data

| Runs | 1-6 | 7-8 | 9-10 | 11-12 | 13-14 | 15-16 | 17-18 | 19-20 |
|---|---|---|---|---|---|---|---|---|
| ASTM Distillation | | | | | | | | |
| IBP | -- | -- | -- | -- | -- | -- | -- | -- |
| 5% evaporated | -- | -- | -- | -- | -- | -- | -- | -- |
| 10 | 89 | 93 | 83 | 90 | 83 | 92 | 85 | 88 |
| 20 | 112 | 123 | 116 | 117 | 113 | 126 | 115 | 116 |
| 30 | 140 | 154 | 145 | 153 | 139 | 161 | 149 | 148 |
| 40 | 173 | 189 | 185 | 194 | 173 | 197 | 190 | 185 |
| 50 | 214 | 224 | 225 | 229 | 211 | 235 | 231 | 225 |
| 60 | 255 | 256 | 261 | 260 | 250 | 269 | 268 | 258 |
| 70 | 290 | 289 | 293 | 286 | 279 | 295 | 296 | 287 |
| 80 | 326 | 321 | 321 | 307 | 312 | 325 | 328 | 319 |
| 90 | 367 | 360 | 368 | 343 | 351 | 360 | 366 | 357 |
| 95 | 403 | 388 | 397 | 377 | 378 | 388 | 390 | 387 |
| End Point | 456 | 414 | 428 | 406 | 423 | 417 | 419 | 421 |
| Recovery % | 93.0 | 93.0 | 91.0 | 94.0 | 90.2 | 91.2 | 91.0 | 93.0 |
| Residue % | 0.9 | 0.9 | 0.6 | 0.5 | 0.6 | 0.7 | 0.5 | 0.8 |
| Gravity, API | 55.4 | 57.1 | 58.9 | 53.6 | 58.8 | 57.2 | 59.8 | 58.8 |

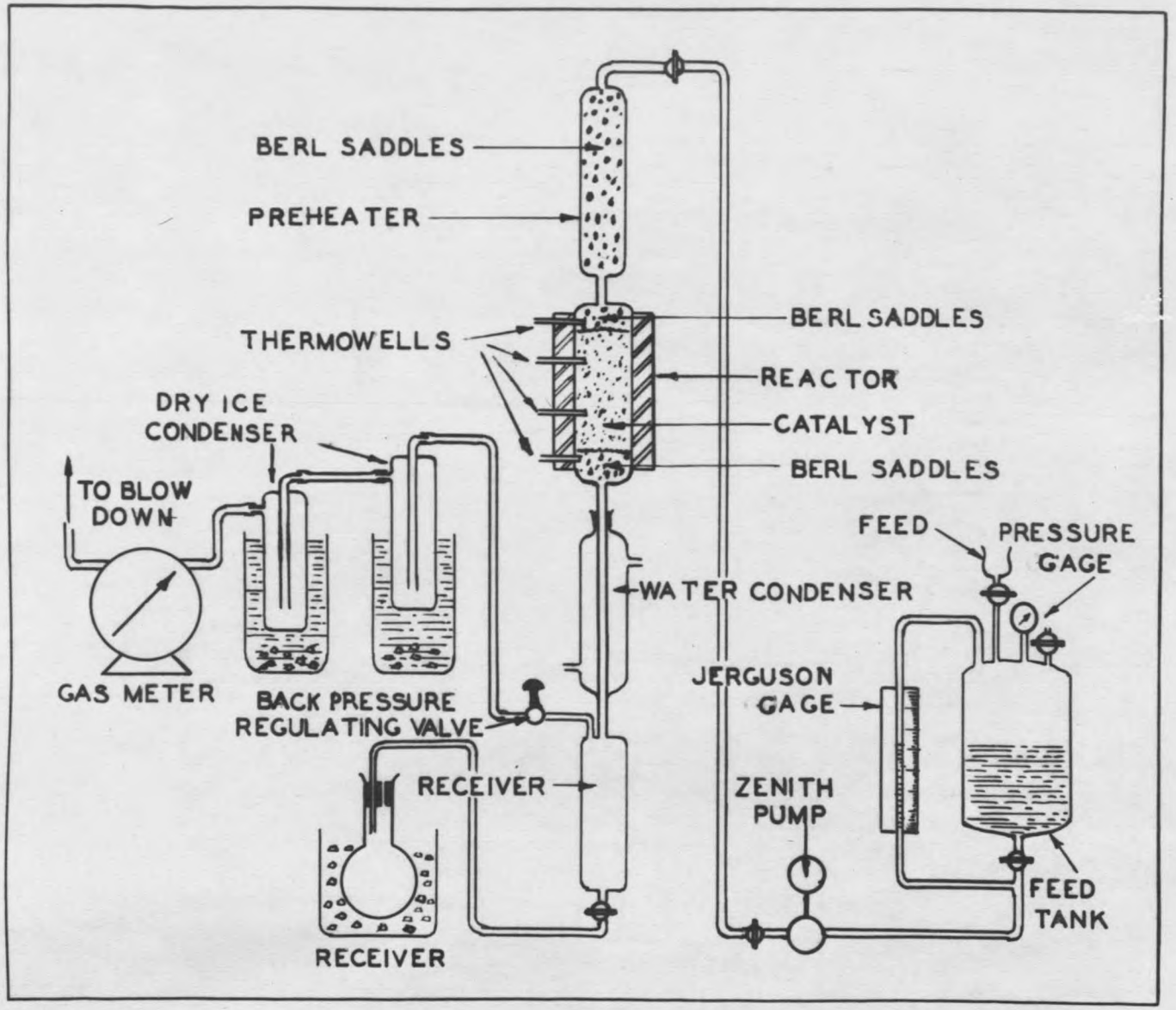



Figure 1

Diagram of Equipment

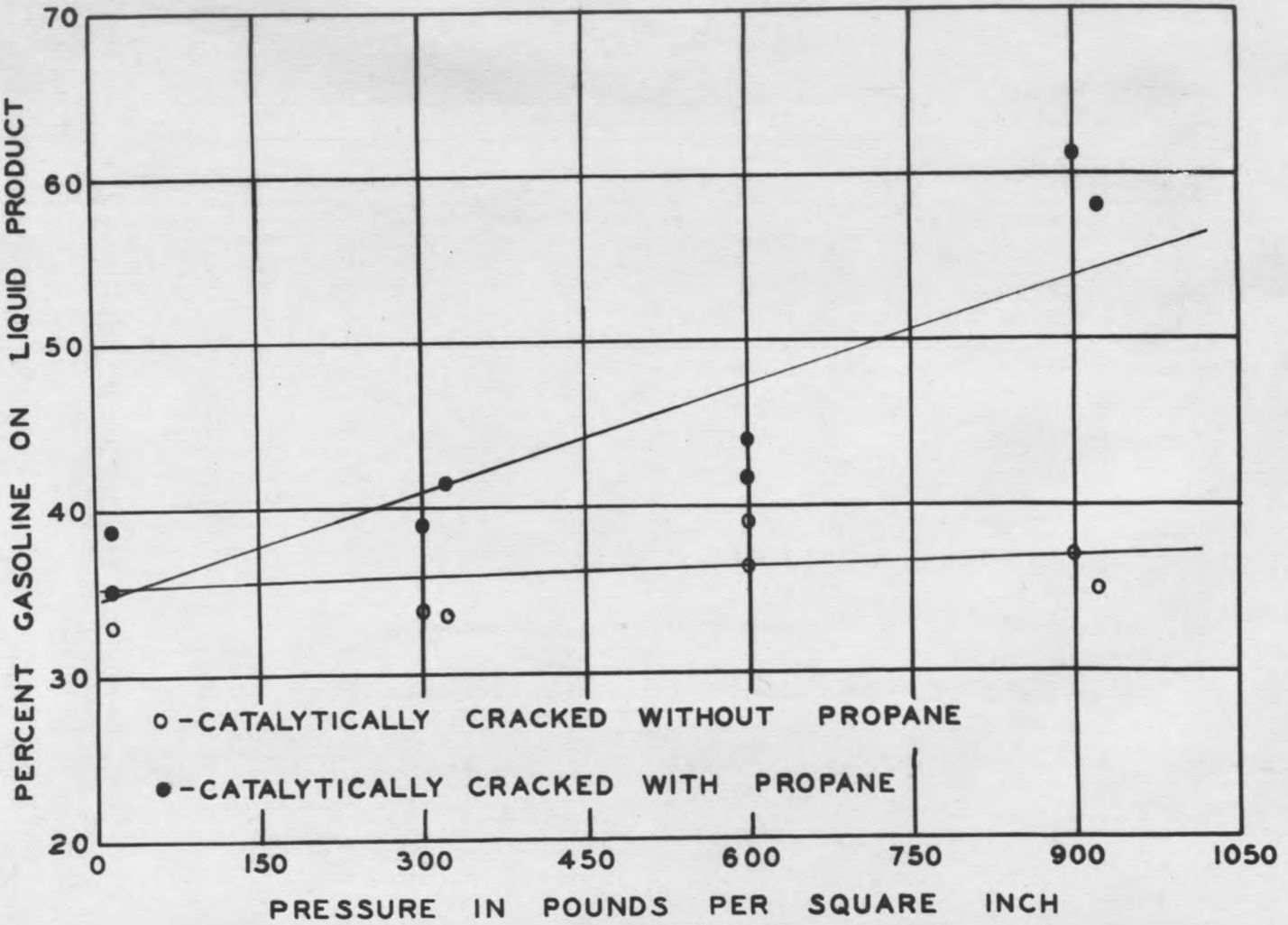



Figure 2

Effect of Pressure on Gasoline Yield

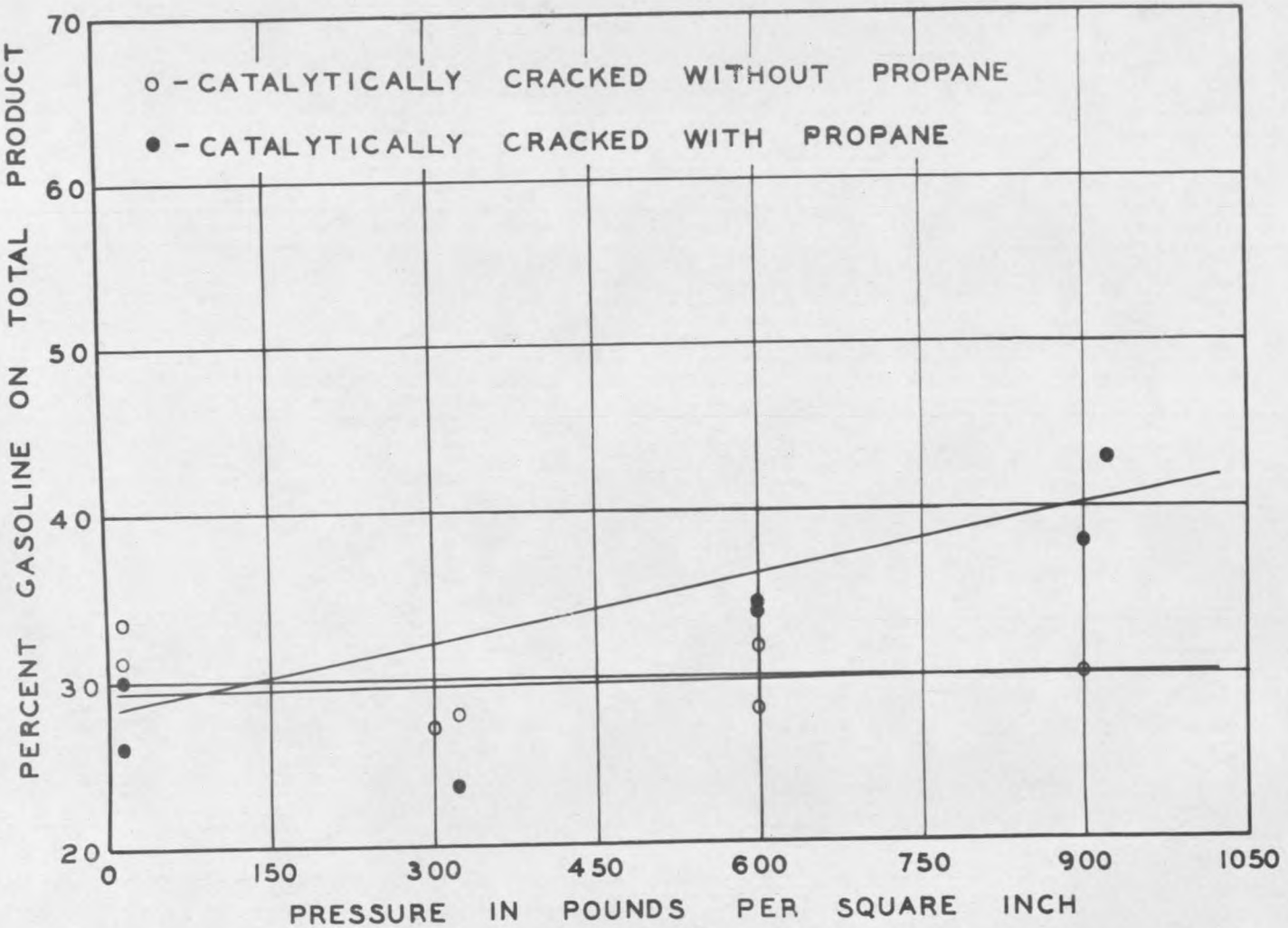



Figure 3

Effect of Pressure on Gasoline Yield

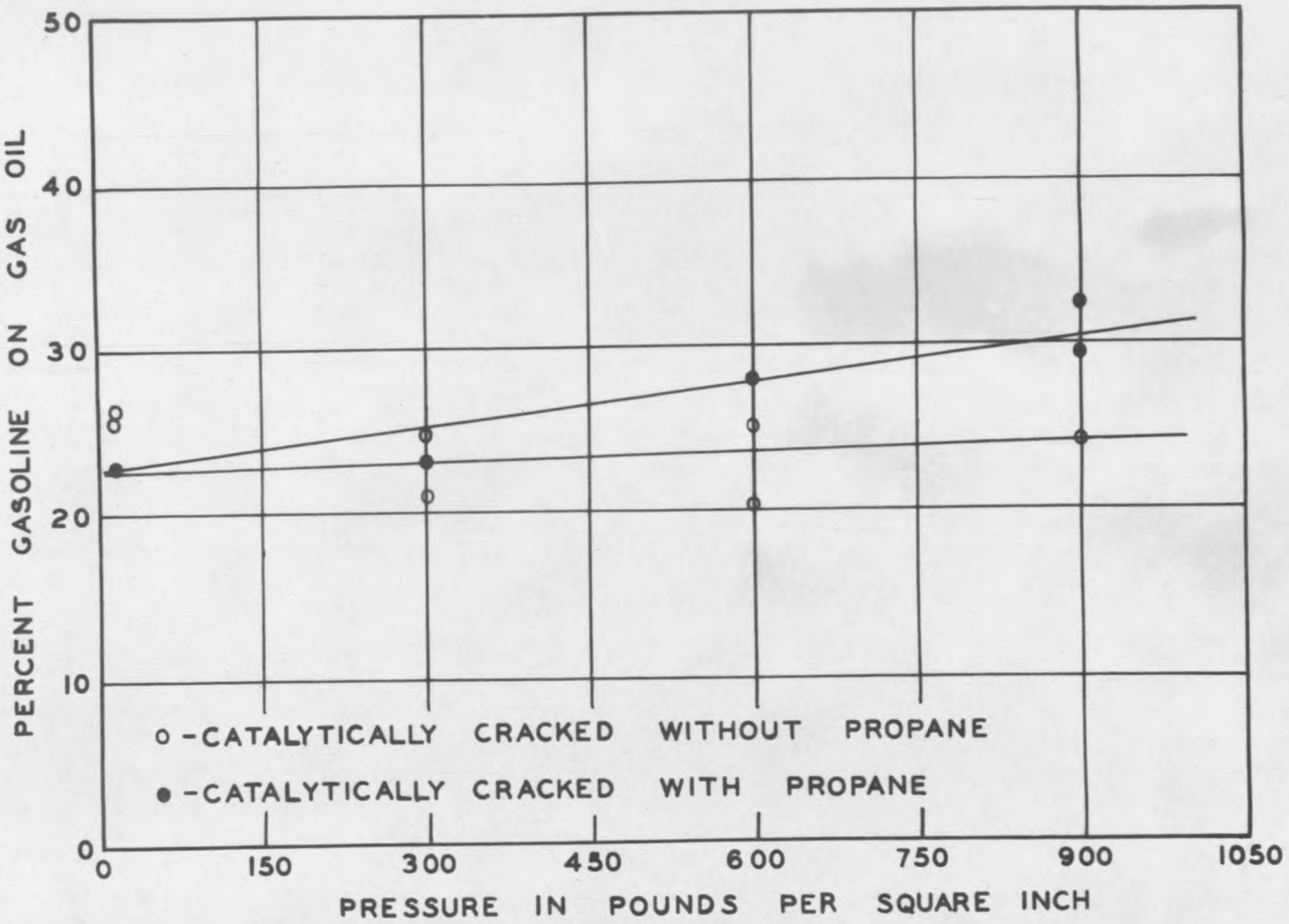



Figure 4

Effect of Pressure on Gasoline Yield

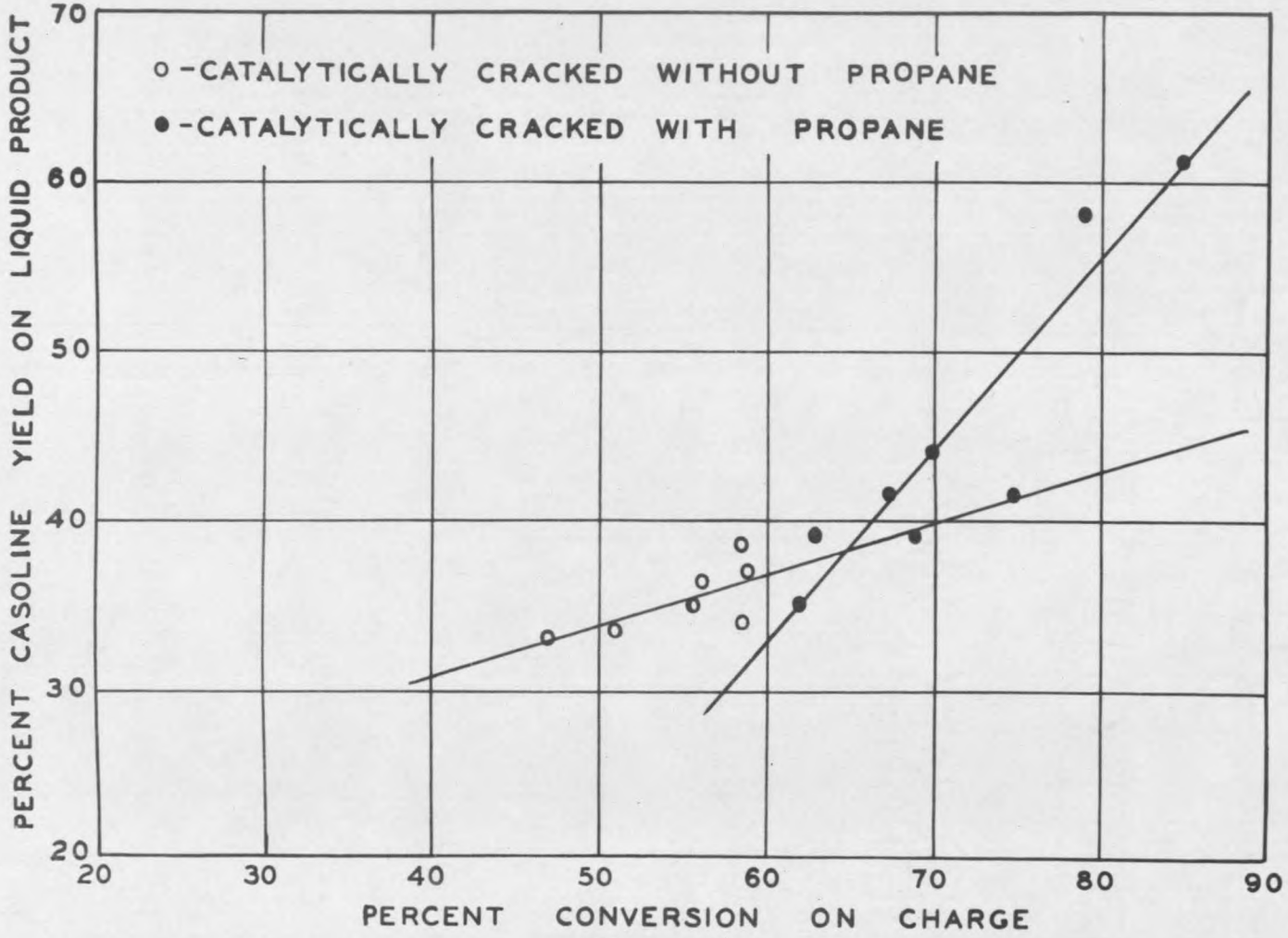



Figure 5

Relationship between Conversion and Yield of Gasoline

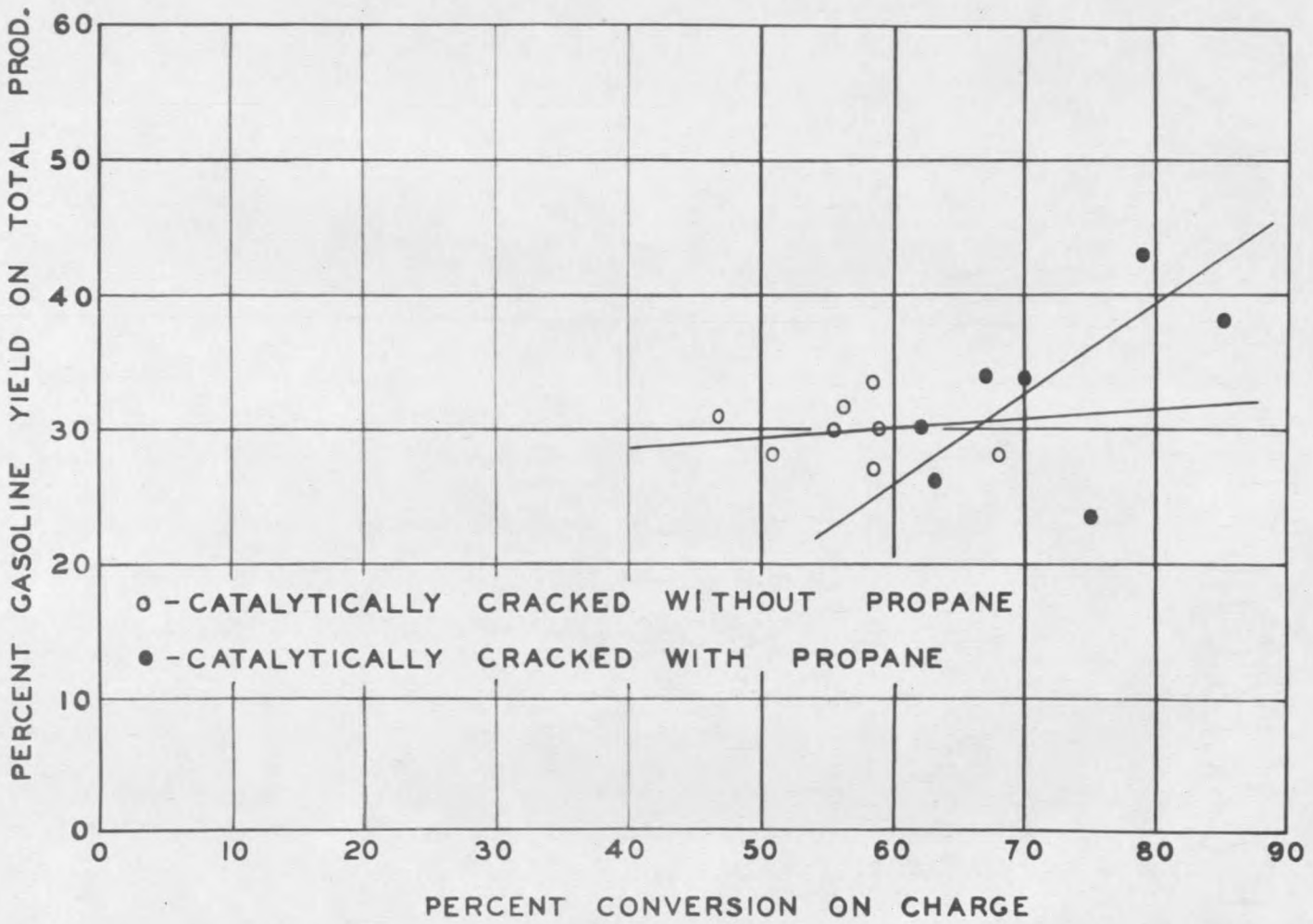



Figure 6

Relationship between Conversion and Yield of Gasoline

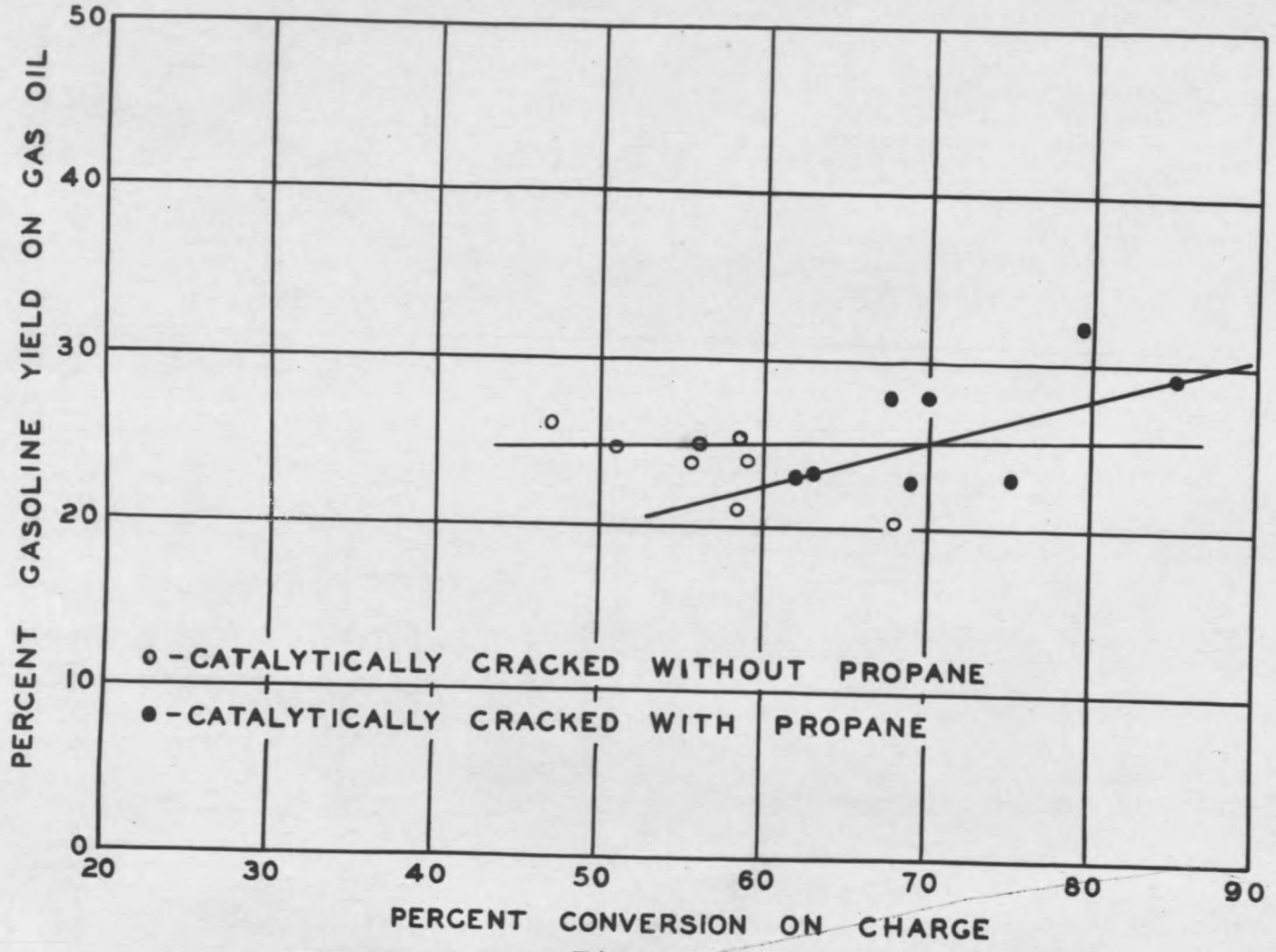



Figure 7

Relationship between Conversion and Yield of Gasoline

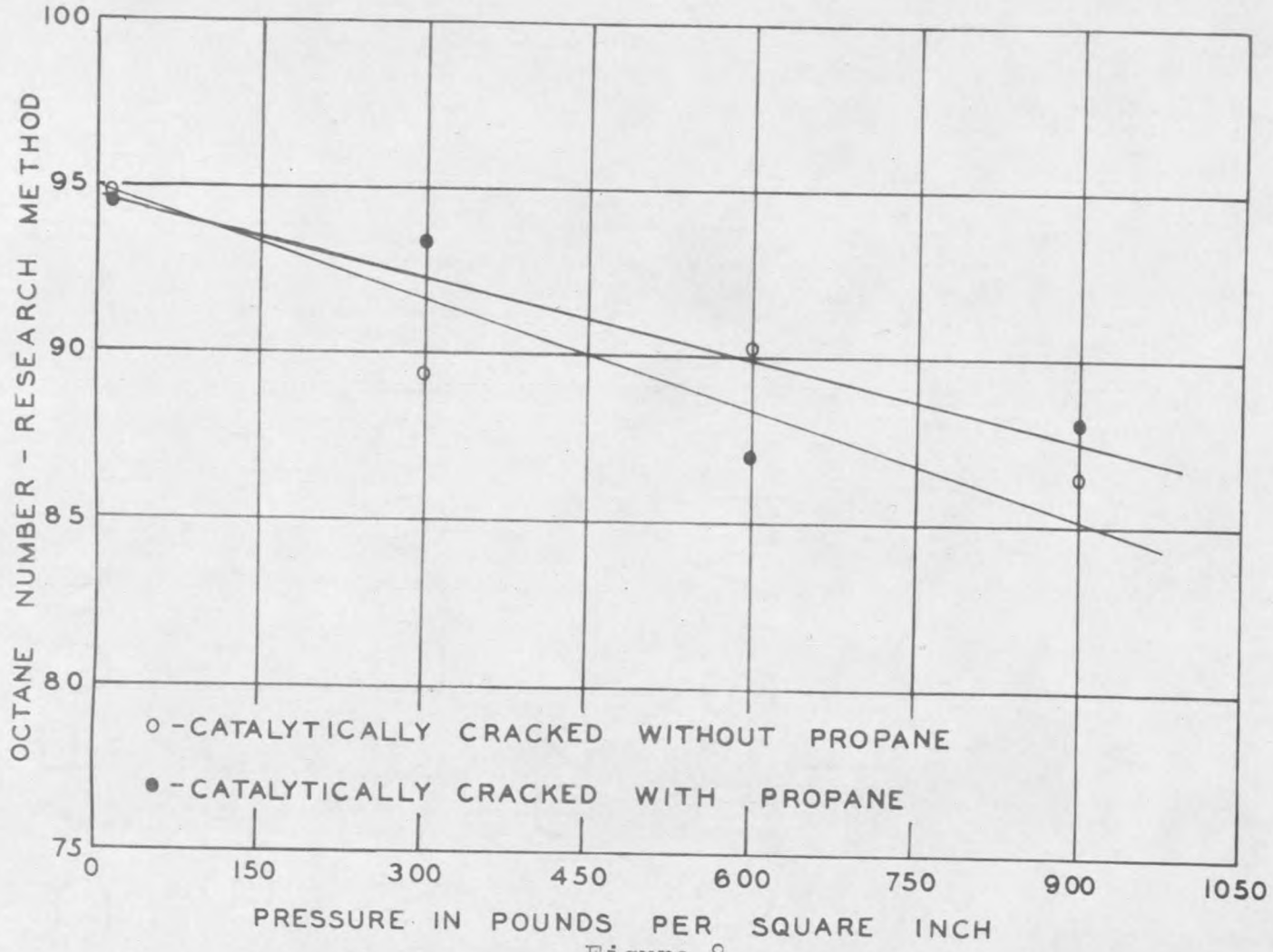



Figure 8

Effect of Pressure on Octane Number

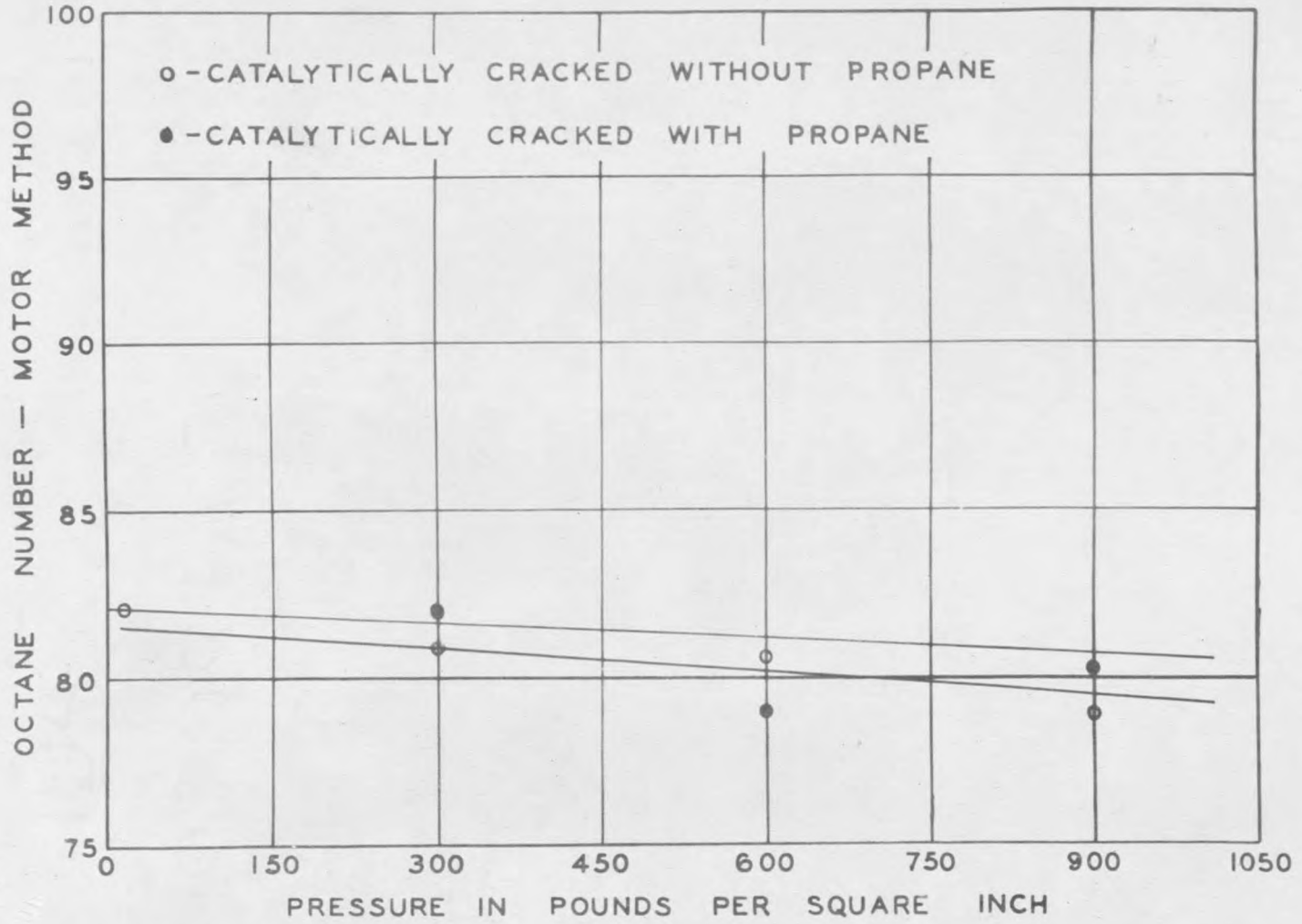



Figure 9

Effect of Pressure on Octane Number

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