



Effect of pressure on catalytic polyforming of gas oil
by Benard A Ennenga

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:

This investigation was made to determine the effect of an increase in pressure on gasoline yield in the catalytic poly-forming process* The investigation was made using a Houdry synthetic aluminum silicate fixed-bed catalyst as the catalytic agent, virgin gas oil as the charging stock, and isobutane as the outside gas. The pressures used were 0, 300, 500, 900, and 1200 psig. At each pressure the temperatures were varied from approximately 390° to 520°C, and the space velocities were held relatively constant at 4 to 6 hr⁻¹ Four preliminary conventional catalytic cracking runs were made at a space velocity of 0.6 to 0.8 hr⁻¹ in which no outside gas was employed, Three additional conventional catalytic cracking runs were made at the higher space velocity of 4 to 6 hr⁻¹ At the conclusion of each run, the carbon was burned from the catalyst and the liquid products were distilled.

It was found that conventional catalytic cracking at a space velocity of 0.6 to 0.8 hr⁻¹ produces a substantially greater quantity of gasoline per pass per unit of charging stock than is produced by the catalytic polyforming process using Isobutane as the outside gas. The yield from conventional catalytic cracking at this space velocity reached a maximum of 34 per cent at a conversion of 62.5 per cent based on oil charged, The maximum yield from catalytic polyforming at a space velocity of 4 to 6 hr⁻¹ was 30.7 per cent at 900 psig and at a conversion varying from 48 to 70 per cent, It was found that catalytic polyforming with isobutane produced a greater quantity of gasoline per pass per unit of charging stock than was produced by conventional catalytic cracking when both processes were operated at the same space velocity of 4 to 6 hr⁻¹ The conventional catalytic cracking process at this space velocity produced a maximum of approximately 24 per cent gasoline, If both processes were operated at their respective conditions of maximum, gasoline production per pass, a higher space velocity can be used with the catalytic polyforming process and a greater through-put can be obtained.

It was also found that the effect of pressure in increasing gasoline yield is greatest between 0 and 300 psig. The yield increases up to approximately 900 psig and decreases at pressures beyond 900 psig. Increasing the pressure from 0 to 900 psig causes an increase in yield of approximately 1.8 absolute per cent or 6.2 relative per cent.

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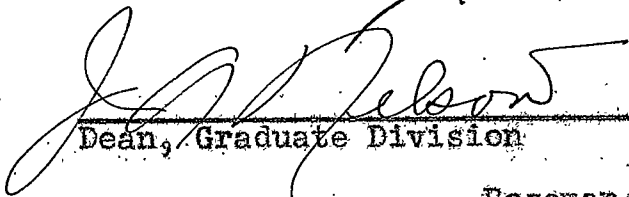
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Montana State College

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Bozeman, Montana
June, 1950

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ABSTRACT

This investigation was made to determine the effect of an increase in pressure on gasoline yield in the catalytic polyforming process.

The investigation was made using a Houdry synthetic aluminum silicate fixed-bed catalyst as the catalytic agent, virgin gas oil as the charging stock, and isobutane as the outside gas. The pressures used were 0, 300, 500, 900, and 1200 psig. At each pressure the temperatures were varied from approximately 300° to 520° C., and the space velocities were held relatively constant at 4 to 6 hr.⁻¹ Four preliminary conventional catalytic cracking runs were made at a space velocity of 0.6 to 0.8 hr.⁻¹ in which no outside gas was employed. Three additional conventional catalytic cracking runs were made at the higher space velocity of 4 to 6 hr.⁻¹ At the conclusion of each run, the carbon was burned from the catalyst and the liquid products were distilled.

It was found that conventional catalytic cracking at a space velocity of 0.6 to 0.8 hr.⁻¹ produces a substantially greater quantity of gasoline per pass per unit of charging stock than is produced by the catalytic polyforming process using isobutane as the outside gas. The yield from conventional catalytic cracking at this space velocity reached a maximum of 34 per cent at a conversion of 62.5 per cent based on oil charged. The maximum yield from catalytic polyforming at a space velocity of 4 to 6 hr.⁻¹ was 30.7 per cent at 900 psig and at a conversion varying from 48 to 70 per cent.

It was found that catalytic polyforming with isobutane produced a greater quantity of gasoline per pass per unit of charging stock than was produced by conventional catalytic cracking when both processes were operated at the same space velocity of 4 to 6 hr.⁻¹ The conventional catalytic cracking process at this space velocity produced a maximum of approximately 24 per cent gasoline. If both processes were operated at their respective conditions of maximum gasoline production per pass, a higher space velocity can be used with the catalytic polyforming process and a greater through-put can be obtained.

It was also found that the effect of pressure in increasing gasoline yield is greatest between 0 and 300 psig. The yield increases up to approximately 900 psig and decreases at pressures beyond 900 psig. Increasing the pressure from 0 to 900 psig causes an increase in yield of approximately 1.8 absolute per cent or 6.2 relative per cent.

I INTRODUCTION

According to Offut et al (1), the Polyform process is an efficient means for producing high quality motor gasoline by the thermal conversion of naphthas or gas oils at high temperatures and high pressures in the presence of recirculated hydrocarbon gases. The light hydrocarbons in the charge make possible a substantially greater degree of cracking severity and a higher gasoline octane level than is possible in most thermal cracking processes. The conditions of temperature and pressure are also suitable for the conversion of the C₃ and C₄ hydrocarbons to gasoline. The propane and butane fractions recycled within the process are in many cases supplemented with extraneous refinery gas streams for additional yield of gasoline.

Gasolines formed by the Polyform process have a high over-all volatility and contain more low-boiling and less high-boiling material than most gasolines from other refining processes using the same charging stock. An increase in severity of cracking as a result of the light hydrocarbons included in the charge results in an increase of both the volatility of the gasoline and the octane number. The volatility of the gasoline is also affected by the conversion of the C₃ and C₄ hydrocarbons to gasoline.

The gases used in the Polyform process may be those made by cracking the oil itself or may be those obtained from

outside sources (2). The use of greater amounts of gases is said to permit more severe cracking so that improved yields of gasoline of high anti-knock quality and high sensitivity are obtained. By using extraneous gases in conjunction with the charging stock, addition reactions apparently take place between the gas and the products made by cracking the oil; and there is a reduced formation of coke.

Polyforming distillates have high octane numbers which remain essentially constant throughout the boiling ranges. The gasoline production is of the same order as that obtained in catalytic cracking, the gasoline having octane numbers from 74 to 76 by the motor method. The gasoline has excellent blending value and road performance.

From a study of catalytic polyforming of gas oil using propane, isobutylene, and n-butane as outside gases and Houdry synthetic aluminum silicate fixed-bed catalyst as the catalytic agent, Mayfield (3) found both isobutylene and n-butane to give a definite increase in gasoline yield over that obtainable from conventional atmospheric catalytic cracking. He also found that there was no detectable loss in catalyst activity after the passage of 34.6 volumes of feed per volume of catalyst at atmospheric and at 900 pounds pressure. Carbon formation based on total charge is markedly lower in n-butane catalytic polyforming at 900 pounds pressure

than in conventional atmospheric catalytic cracking.

Mayfield also found catalytic polyforming to have a distinct advantage over other methods of cracking heavy petroleum fractions in respect to space velocity. He found catalytic polyforming to give essentially the same yields at the same space velocities and at space velocities approximately ten times those used in normal petroleum cracking.

Ellis (4) compiled controversial data of several investigators. In this compilation, Trusty summarized the advantages of the use of pressure as being a better condition for heat transfer, for absence of local overheating, and for increased yield of gasoline products. Sydnor, however, observed that, for operations carried out at the same temperature, distinctly higher yields of gasoline were obtained at low rather than at high pressure. The data by Sydnor were obtained using a Mid-Continent gas oil of 33.7° A.P.I. gravity, using a Tube and Tank unit. One direct effect of pressure, according to Nentzov as stated in the compilation, is the increased yields of gasoline in place of gases.

In view of the favorable possibilities of catalytic polyforming and the uncertainty of the effect of pressure, this investigation of the effect of pressure on catalytic polyforming was undertaken.

The yields of gasoline from catalytic polyforming at 0, 300, 600, 900, and 1200 psig were compared. The ultimate

yields and carbon formation at the various pressures were also compared. At each pressure, the maximum gasoline yield obtainable was found by varying the temperature at which the polyforming took place. This variation gave a curve of yield versus conversion for each pressure and thus determined the maximum gasoline yield obtainable at the given pressure.

Houdry synthetic aluminum silicate fixed-bed catalyst was used in this investigation since it was found to be well suited to the process.

II. EQUIPMENT, METHODS, AND MATERIALS

A. Equipment

The equipment used in this investigation consisted of a reaction system which could be operated from 0-1200 psig and was capable of being heated to somewhat above 600°C. A distillation unit and a gas-analysis unit were used in conjunction with the reaction system. The reaction system, shown in Figure 1, was composed of four major sections, the feeding section, the reactor section, the condensing and receiving section, and the safety equipment.

FEEDING SECTION - The feeding section included a nitrogen cylinder, a feed cylinder, and a Jerguson gage. The body of the feed cylinder was constructed from an eight-inch section of three-inch, extra-strong steel pipe and two extra-strong steel caps. The pipe was threaded at both ends and fitted with the caps which were securely welded to the pipe. Both caps were drilled and tapped for half-inch pipe, and close nipples of extra-strong steel pipe were fitted into the caps. Half-inch Kerotest valves of 3000 psig rating were fitted on each end of the feed cylinder, and each valve was fitted with one-half to one-fourth inch steel bushings, to which brass fittings for connection to one-fourth inch copper tubing were fitted.

The Jerguson visible-liquid-level gage, which was situated below the feed cylinder during operation and received

the charge from the feed cylinder, was fitted at either end with close nipples of one-half inch extra-strong steel pipe. The upper end of the gage was fitted with a one-half inch cross. One side arm of the cross was equipped with a bushing and a brass one-fourth inch valve. The other two arms were equipped with brass fittings for connection to one-fourth inch copper tubing. To the nipple at the lower end of the Jerguson was attached a one-half inch, 6000-pound Vogt valve for adjustment of the rate of feed. The bottom of the valve was connected directly to the reactor through one-half inch extra-strong short nipples, a one-half inch tee, and a one-half inch union. The male half of the union was secured to the feed section, while the female section was welded directly to the top of the reactor.

From the side of the tee, a one-half inch extra-strong pipe led to a safety valve. The valve was a Black, Sivalls, and Bryson frangible disk safety valve equipped with a 1255 psig Monel diaphragm during runs below 1000 psig and a 1445 psig Monel diaphragm during 1200 psig runs. The safety valve discharged outside of the building through a one-half inch pipe.

A nitrogen cylinder for pressurizing the system completed the major elements of the feeding system. The nitrogen cylinder was connected through one-fourth inch copper tubing to a 0-2000 psig pressure gage and a brass tee near the feed

cylinder, copper tubing connected to the upper valve of the feed cylinder and to the valve in one arm of the aforesaid cross. This arrangement allowed gases in the Jerguson to flow into the top of the feed cylinder as they were displaced by the liquid feed during the intermittent filling of the Jerguson.

REACTOR SECTION - The reactor was made from a 15-inch section of three-inch extra-strong steel pipe. An extra-strong steel cap was welded to the top end of the reactor body, and the female section of the previously mentioned union was welded at the center of the steel cap. The hole in the female section of the union was enlarged from one-half inch to $11/16$ -inch, and an $11/16$ -inch hole was drilled through the cap using the hole in the union as a jig. The enlarged hole facilitated the changing of the catalyst and preheater packing. The catalyst filled the lower 11 inches of the reactor body; and the remaining 4 inches were filled with approximately 500 ml. of assorted steel balls, the largest of which were $9/16$ -inch in diameter.

A one-eighth inch mesh stainless steel screen was inserted in the bottom end of the pipe to act as a catalyst support. This end was closed by welding on a plate of steel one-half inch thick. The plate was drilled and tapped at the center. A section of extra-strong one-half inch steel pipe led from the lower end of the reactor to a tee. A 6000-pound,

one-half inch Vogt valve was connected on the run of the tee by means of a short nipple of extra-strong pipe. This valve was employed to regulate the pressure in the reactor. A 0-2000 psig pressure gage was connected to the branch of the tee and was used to indicate the pressure in the reactor. A one-half to one-fourth inch pushing in the lower end of the valve was fitted with a brass fitting and approximately three inches of copper tubing.

Four holes were drilled approximately three inches apart along the length of the reactor body. Four-inch lengths of one-eighth inch steel pipe were sealed at one end by welding and inserted into the holes such that the sealed ends were inside the reactor. These pipes were welded into the reactor as thermowells in such a position that the sealed ends were along the axis of the reactor. Iron-constantan thermocouples were inserted into the thermowells and connected to a Leeds and Northrup indicating potentiometer, calibrated to read from 0-1200° C.

A safety wall of one-fourth inch steel plate 25 inches wide and 72 inches long was erected in the position in which the reactor was to stand. To give the reactor a firm and rigid support, two one-fourth by one inch flat steel bars were welded to the top of the cap at approximately 90° to each other. These bars fastened by means of one-half inch pins to cleats welded to the safety wall. Two one-half inch

round steel rods were welded to the reactor approximately eight inches apart and opposite to the thermowells. These rods passed through the safety wall and were secured to the network of rods which were used to support the entire unit.

The reactor was entirely wrapped with one-inch wide asbestos tape. The upper one-half of the reactor was wound with 30 feet of nichrome wire (resistance of 1.71 ohms per foot) which had been threaded with porcelain fish-spine insulators. The lower one-half was similarly wound. These windings were covered with another layer of one-inch asbestos tape. Each of these windings was connected to a 220-volt autotransformer and was designed to carry a maximum load of five amperes. A fifteen-foot coil of insulated nichrome wire was wound over the lower one-third of the reactor, and another similar coil was wound over the upper one-third. These coils were connected to 110-volt autotransformers. A fifteen-foot coil was wound about the neck of the reactor and on the top of the cap to supply additional heat to the preheat section. This coil was also connected to a 110-volt autotransformer.

A layer of asbestos tape was employed to cover the windings on the reactor. Over the asbestos tape was fitted a layer of one-inch magnesia blocks cut to fit around the reactor. These blocks were secured by a few coils of asbestos tape, and a heavy layer of asbestos cement was used to cover the entire reactor. The cap, the bottom, and approximately

three inches of pipe beneath the reactor were also covered with asbestos cement to reduce heat losses.

CONDENSING AND RECEIVING SECTION - A short section of copper tubing extended below the valve at the lower end of the reactor, as previously stated. A neoprene stopper was fitted around this copper tubing and a 300-mm. Pyrex-glass Liebig condenser was secured to the stopper. Water was used as the cooling medium in the Liebig condenser. An extension of glass tubing was added to the lower end of the Liebig condenser to carry vapors and liquids well into the receiving flask. A neoprene stopper was fitted over the lower end of the condenser, and a 500 ml. side-arm flask was fitted to the stopper.

The side-arm flask was three-fourths immersed in a dry ice-isopropanol bath contained in a one-gallon thermoflask. Vapors not condensed in the flask flowed out the side arm, through rubber tubing, and into a series of vapor traps. The series consisted of four glass traps immersed in a dry ice-isopropanol bath contained in one-quart thermoflasks. From the fourth trap, the vapors flowed through a series of two copper-coil condensers also immersed in a dry ice-isopropanol bath. Noncondensable vapors leaving the coils passed through rubber tubing to a tee, the run of which was connected to a three-liter precision wet test gas meter. The branch of the tee connected to an evacuated, 200-ml., round-bottom,

stopcock-equipped flask which was used to take a gas sample during the run. From the gas meter, the noncondensable gases passed to a blow-down line leading outside the building.

SAFETY SYSTEM - In addition to the frangible-disk safety valve and the safety wall behind the unit, both of which have been mentioned previously, there was a steel cover over the reactor. A piece of one-eighth inch steel plate, rolled in a semicircle 22 inches in diameter and 40 inches in length, was hinged to the safety wall so that it would close around the reactor. A framework of one-half inch angle iron was erected upward from the center of the hinged cover to support two thicknesses of automobile safety glass which would allow the operator of the feed-control valve to view the Jerguson gage in safety.

Fire fighting equipment was located within easy reach at all times.

AUXILIARY EQUIPMENT - An Oldershaw vacuum-jacketed distilling column containing 15 plates was used to distill the products of reaction. This column was fitted with a distilling head suitable for making a distillation over the range from -30° to 250° C. The collection flask employed directly beneath the reactor to condense a portion of the effluent products served also as a distilling flask. The ground glass joint at the bottom of the column fit directly into the joint at the mouth of the flask. The flask was heated by a 110-volt

550-watt heater controlled by an autotransformer.

The distilling head delivered the liquid condensates from the top of the column to a rubber tube connected to a series of two cold traps immersed in two dry ice-isopropanol baths. Overhead products vaporizing after leaving the head were condensed by the low-temperature baths and afforded a close weight balance across the column.

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

Analyses of gases from the feed cylinder after the run and of noncondensable gases issuing from the reactor during the run were made with a low-temperature gas-fractionation apparatus. This unit was also used to make analyses on outside gases used in conjunction with the gas oil charge.

B. Methods

ATMOSPHERIC PRESSURE RUN WITHOUT OUTSIDE GAS - The reactor was heated until the temperature of the reactor, as indicated by the thermocouples, was of sufficient magnitude to give the over-all average temperature desired for the particular run to be made. The feed cylinder was evacuated by means of a Cenco Megavac vacuum pump, charged with approximately 260 grams of gas oil, and weighed on a 20 kilogram-capacity triple-beam balance. The feed cylinder was then mounted on its supporting framework above the Jerguson gage and connected to the gage by a short length of copper tubing. The upper nitrogen line leading from the tee in the main nitrogen line was connected to the upper valve of the feed cylinder. The lower nitrogen line from this tee connected to the cross which was situated between the feed cylinder and the Jerguson.

The feed-regulating valve was closed, and the pressure-regulating valve below the reactor was opened to maintain essentially atmospheric pressure in the reactor.

Dry ice was added to the necessary number of thermoflasks containing isopropanol until carbon dioxide evolution was slight. A distillation flask was weighed and fitted to the lower end of the Liebig condenser below the reactor, and the flask was immersed in a one-gallon thermoflask. A rubber tube connected to the side arm of the flask and led to a

series of cold traps which had been weighed and immersed in the one-quart thermoflasks. Rubber tubing led from the cold traps to two copper-coil condensers which discharged condensate into glass receivers. The coils and receivers had been previously weighed and were immersed in a dry ice-isopropanol bath in a one-gallon thermoflask.

The gas-sample bottle was evacuated, weighed, and attached to the system; and the gas meter was set at zero.

A nitrogen pressure of about 100 pounds was applied to the feed system and the upper valve on the feed cylinder was opened to equalize pressure in the feed cylinder and in the Jerguson gage. By opening the lower feed-cylinder valve, a portion of the charge in the feed cylinder was allowed to run into the Jerguson, filling the gage. At this point the Lower feed-cylinder valve was closed, the feed-regulating valve was opened, and a stop watch was started. Feed rate was controlled by noting the time required for a given drop in the liquid level in the Jerguson gage. Any necessary adjustment in the feed-regulating valve was made to obtain the desired rate. The Jerguson was refilled when necessary by opening the lower feed-cylinder valve. Pressure was maintained on the feed system to force the charge through the Jerguson and into the reactor.

A sample of noncondensable gas was collected in the gas-sample bottle near the middle of the run. After completion

of the run, the bottle was allowed to come to atmospheric pressure and weighed, noting room temperature and barometric pressure. The difference in weight of the gas-sample bottle gave the weight of the known volume of noncondensable gas. These data were necessary for the determination of the weight of the noncondensable gases. The number of liters of noncondensable gases passing through the gas meter was read and recorded.

Upon completion of the run, the cold traps, distilling flask, and copper coils and receivers were removed from their cold baths, wiped dry, and weighed immediately to determine the weight of condensable product. Condensed product in the cold traps and receivers was transferred to the distillation flask which was immediately reweighed and attached to the bottom of the previously prepared distilling column. The second weighing of the distilling flask was to allow for determination of losses from transfer. Distillation was carried out as described later. The feed cylinder was removed and reweighed, the weight of charge being found by difference.

Small amounts of oil remaining in the reactor after completion of the run were removed by evacuating the reactor through a series of two cold traps. Nitrogen was used to purge the reactor after evacuation was completed. Oil recovered in this way helped in establishing a weight balance

on the system. The recovered material was weighed and added to the residue since the amount of gasoline contained under these conditions was negligible.

Following the completion of each run, and while the distillation was being made, the carbon laid down on the catalyst was burned off as described later in this section.

ATMOSPHERIC RUNS WITH OUTSIDE GAS - Prior to making a run, the feed cylinder was evacuated and filled with a charge of gas oil. The feed cylinder was then placed in a refrigerator maintained at -40°C , where the cylinder and charge were cooled for a minimum of two hours but preferably overnight. When thoroughly chilled, the feed cylinder was placed on a 20 kilogram-capacity balance and connected by means of Saran tubing to a cylinder of the desired outside gas. The cylinder of outside gas was situated in such a position that its valve was lower than the body of the cylinder and the liquid contents would be delivered through the tubing to the feed-cylinder. After the feed cylinder, connections, and tubing had been tared on the balance, the feed-cylinder valve attached to the tubing was opened. Next, the outside-gas-cylinder valve was opened and the outside gas flowed from the warm gas cylinder to the cold feed cylinder. When sufficient gas had been delivered, valves were closed and the tubing disconnected.

After filling, the feed cylinder was allowed to come to

room temperature and reweighed. The cylinder was then placed in position for the run, and the procedure previously described was followed.

SUPER-ATMOSPHERIC RUNS WITH OUTSIDE GAS - The procedure in the super-atmospheric runs was essentially the same as previously described with the exceptions of the pressure at which the system operated and the handling of the feed-regulating and reactor-pressure-regulating valves.

The feed cylinder was prepared as described in the section concerned with atmospheric runs with an outside gas. Cold traps, thermoflasks, receivers, and other equipment were prepared as described.

After placing the feed cylinder above the Jerguson and making the proper connections, both the feed-regulating valve at the top of the reactor and the reactor-pressure-regulating valve at the bottom of the reactor were securely closed. Nitrogen pressure of approximately 200 psig was supplied to the feed system, the upper feed-cylinder valve was opened to equalize pressure in the feed cylinder and in the Jerguson, and the Jerguson was filled.

When feeding began, a stop watch used to determine feed time was started, and close watch was maintained on the pressure gage indicating reactor pressure. Space velocity was controlled by observing the liquid level in the Jerguson gage and adjusting the feed-regulating valve accordingly.

Nitrogen pressure was maintained at approximately 100 psig above the pressure in the reactor. When hot gases and reaction products in the reactor had built up the pressure desired for the run in progress, the reactor-pressure-regulating valve was opened slightly. By observing the pressure gage, it was possible to adjust the pressure-regulating valve so as to maintain the desired pressure in the reactor.

A sudden drop in pressure on the feed system or rise in pressure in the reactor indicated that the last drop of charge had been delivered to the reactor. The feed-regulating valve was immediately closed. The reactor-pressure-regulating valve was opened gradually, and the reactor was bled to atmospheric pressure. At the same time the feed system was reduced to atmospheric pressure. The time of feeding was taken as the time elapsed between the beginning of the feed and the time at which the feed-regulating valve was closed.

The reactor was evacuated and purged and the other equipment was handled as previously described.

Samples of the gases remaining in the feed cylinder were taken at 1000 psig and also after the cylinder pressure had been reduced to 300 psig. These samples were analyzed on the low-temperature gas-fractionation unit to determine the per cent isobutane remaining in the feed cylinder and not charged. The data obtained were inconclusive; so the method used by Mayfield (3) was adopted. By this method, the valves

of the feed cylinder were closed at the end of the run before the feed system was depressurized. The feed cylinder was then removed from the system and the residual gases, containing nitrogen and isobutane, were bled into a 34 liter tank. This allowed all isobutane in the cylinder to vaporize and be accounted for in the analysis of the low-pressure gases in the tank. Analysis showed the residual isobutane to be 10 grams. This value of 10 grams was used in the calculations of all runs involving an outside gas. Since the 10 grams was outside gas uncharged, it was subtracted from the weight of gas charged to the feed cylinder prior to each run; and calculations were based on the corrected gas weight.

DISTILLATION - Prior to making a run on the reactor unit, the low-temperature distilling head was cooled with a dry ice-isopropanol mixture to provide for condensing vapors leaving the column.

As soon as the condensed products collected in cold traps and receivers had been transferred to the distillation flask and the flask reweighed as previously described, the flask was fitted to the bottom of the column by means of a greased ground-glass joint. A stopper was employed to plug the flask side arm. The delivery stopcock was closed to give total reflux. Approximately 30 volts were applied to the flask heater by the autotransformer.

Vapors leaving the column were condensed and refluxed

until the head temperature reached approximately $+15^{\circ}\text{C}$. At this point, the delivery stopcock was opened and part of the condensing gases were removed to the cold traps until the lower cut point of 7°C . was reached. If, upon returning to total reflux, the temperature dropped, further removal was made. When the condensing gases maintained 7°C ., the cold traps used to collect light fractions were removed, weighed, and replaced by another set of weighed cold traps to collect gasoline. The autotransformer was advanced, and a gasoline cut was made up to 204°C . During the distillation of the gasoline fraction, the dry ice-isopropanol mixture was removed from the distilling head and replaced with wet ice. The cut-point temperatures used were those for the local pressure of approximately 640 mm.

Upon completion of the distillation, the gasoline weight was determined, and the column was allowed to cool. When the column had drained, the distillation flask was reweighed to determine the weight of the major portion of the residue. The high-boiling liquids in the flask plus the oil from the catalyst constituted the residue.

CATALYST BURN OFF - Since a carbonaceous deposit was laid down on the catalyst surface during operation, a burn-off was necessary after each run. The weight of this carbon deposit was required in order that a weight balance might be established for the system.

When a run had been completed and the reactor had been evacuated and purged, a line was connected from the air supply to the top of the reactor. A three-liter gas meter was connected in the air line to measure the amount and rate of air supplied.

Continuous burn-off of the catalyst was accomplished by holding the unburned portion at approximately 425°C . and passing air at a definite rate through the reactor. The air rate was adjusted to maintain the temperature of the burning section at less than 600°C . By keeping the maximum temperature below 600°C ., the catalyst was in no danger of being sintered and did not lose its activity. At regular intervals, per cents of CO_2 , CO and O_2 in the effluent gas were determined by means of an Orsat gas analyzer. These per cents were plotted against time, and the weight of carbon deposited was determined as shown in the sample calculation.

C. Materials

Borger, Texas, virgin gas oil obtained from Phillips Petroleum Company was used as the charging stock in this investigation. Laboratory inspection data for the virgin gas oil is given in Table I.

The outside gas used in the investigation was a commercial isobutane obtained from the Matheson Company, Inc.

The catalytic agent used was Houdry synthetic aluminum silicate fixed-bed catalyst.

III. SAMPLE CALCULATIONS

The calculations of the liquid space velocity, weight of permanent gases, average temperature of the run, weight of carbon deposited on the catalyst, over-all weight balance, yield of gasoline, conversion, and ultimate yield for run Number 27 are presented as typical of all runs made.

A. Calculation of Liquid Space Velocity:

Data:

Volume of catalyst in the reactor	=	1000 ml.
Feeding time	=	6.77 min.
Weight of charge	=	419 gm.
Density of charge	=	0.80 gm./ml.
Volume of charge = $\frac{419}{.8}$	=	524 ml.

$$\text{Space velocity} = \frac{524 \text{ ml.} \times 60 \text{ min./hr.}}{6.77 \text{ min.} \times 1000 \text{ ml.}} = 4.65 \text{ hr.}^{-1}$$

B. Calculation of Carbon from Burn-off:

Data:

Time (min.)	Air (liters)	Analysis		
		CO ₂	CO	
5	9	8.2	0.2	
15	25	12.0	4.0	
30	48	12.2	5.2	
60	87	12.2	6.8	
120	166	12.0	6.8	
180	240	12.0	6.8	
240	318	12.4	6.2	
270	354	11.6	7.1	
300	390	3.0	0	
315	413	2.0	0	
				O ₂
				0.2
				0
				0
				0
				0
				0
				0
				0.9
				16
				17

Average from Plot (Fig. 2)

By Difference

CO ₂	CO	O ₂	N ₂
6	0	1.5	92.5
11	3	0	86
12.1	4.7	0	83.2
12.2	6.2	0	81.6
12.1	6.8	0	81.1
12.0	6.8	0	81.2
12.2	6.5	0	81.3
12.0	6.7	0.4	81.3
11	5	4	80
2.5	0	16.6	80.9

Vol. Effluent Gas (liters)

Vol. % CO₂ and COLiters CO₂ and CO

7.7	6	0.46
14.7	14	2.06
21.9	16.8	3.68
37.8	18.4	3.95
77	18.9	14.55
72	18.8	13.53
75.9	18.7	14.2
35	18.7	6.54
35.6	16	5.7
22.5	2.5	0.56
		<u>68.23</u>

$$\text{Weight of carbon} = \frac{68.23 \times 640 \times 273 \times 12}{22.4 \times 760 \times 298} = 28.2 \text{ gm.}$$

C. Weight of Permanent Gases:

Data:

Volume of noncondensable gases	=	35 l.
Volume of gas sample bottle	=	208.2 ml.
Barometric pressure	=	640 mm. Hg
Room temperature	=	25° C.
Weight of bottle and gas	=	124.169 gm.

Weight of bottle evacuated = 123.986 gm.
 Weight of gas sample by difference = 0.183 gm.*
 Weight of 1 liter of gas at 25° C. and
 640 mm. Hg = $\frac{0.183 \times 1000}{208.2}$ = 0.879 gm.*
 Weight of permanent gases = 30.8 gm.

D. Calculation of Average Temperature:

Data:

Time (min.)	Thermocouple Number			
	15	16	17	18
0	499	489	494	474
1	473	488	498	489
2	456	486	503	502
3	412	458	488	505
4	405	425	459	483
5	399	412	438	458
6	402	415	437	451
7	395	410	434	446
	<u>3441</u>	<u>3583</u>	<u>3751</u>	<u>3808</u>

$$\frac{3441 + 3583 + 3751 + 3808}{4 \times 8} = 455^{\circ} \text{ C.}$$

E. Calculation of Over-all Weight Balance:

Data:

Initial weight of cylinder and charge = 10699 gm.
 Weight of cylinder after run = 10270 gm.
 Weight of isobutane remaining in feed system = 10 gm.
 Weight of material charged = 419 gm.

Recovered material:

Hydrocarbon liquid product from first condenser	=	169.6 gm.
Hydrocarbon liquid product from vapor traps	=	180.4 gm.
Permanent gases	=	30.8 gm.
Oil from catalyst bed	=	0.5 gm.
Carbon deposited	=	28.2 gm.
Total weight recovered	=	409.5 gm.
Weight of losses by difference = 419 - 409.5	=	9.5 gm.
Per cent losses on charge = $\frac{9.5}{419} \times 100$	=	2.27 %

F. Calculation of Per cent Gasoline Yield:

Data:

Weight of oil charged	=	255 gm.
Weight of gasoline from distillation	=	78.3 gm.
Per cent gasoline on oil charged = $\frac{78.3}{255} \times 100$	=	30.7 %

G. Calculation of Per cent Conversion:

Data:

Weight of oil charged	=	255 gm.
Weight of residue from distillation	=	98.8 gm.
Weight of oil recovered from catalyst bed	=	0.5 gm.

Total weight of unconverted oil = 99.3 gm.

Per cent conversion on oil charged

$$= 100 - \frac{99.3}{255} \times 100 = 61.1 \%$$

H. Calculation of Per cent Ultimate Yield:

Data:

Per cent gasoline on oil charged = 30.7 %

Per cent conversion on oil charged = 61.1 %

Per cent ultimate yield = $\frac{30.7}{61.1} \times 100 = 50.2 \%$

IV RESULTS

Several series of catalytic polyforming runs were made at pressures of 0, 300, 600, 900, and 1200 psig, to determine the optimum temperature conditions for gasoline production at each pressure. The runs were made with the materials previously described. The temperature was varied at each pressure while the space velocity was held relatively constant at 4 to 6 hr.⁻¹ The purpose of varying the temperatures was to obtain yields of gasoline at various conversions. The curves of yield versus conversion were used to determine the conditions best suited to the production of the highest gasoline yield obtainable at each pressure.

Four preliminary runs were made at atmospheric pressure with no outside gas present. These were essentially conventional atmospheric catalytic cracking runs. These catalytic cracking runs were made in a manner similar to that used in the polyforming runs with the exception of the fact that space velocities of 0.6 - 0.8 hr.⁻¹ were used. This exception was to allow a comparison to be made between catalytic polyforming at a space velocity of 4 to 6 hr.⁻¹ and catalytic cracking at a space velocity commonly used. The results of the four runs are presented in Table II and Figures 3 and 4.

The yields of gasoline from the atmospheric catalytic cracking runs at space velocities of 0.6 - 0.8 hr.⁻¹ were.

in the range of 30 to 35 per cent. At the lowest conversion obtained, 52.4 per cent, the gasoline yield was 32.7 per cent. The yield increased to a maximum of 34 per cent at 62.5 per cent conversion and decreased at higher conversions. The ultimate yield obtainable with recycle is shown in Figure 4. The highest ultimate yield achieved was 62.5 per cent at the lowest conversion investigated, 52.4 per cent. Carbon production varied from 2.44 per cent at low conversion to 5.86 per cent at the high conversion of 71.6 per cent. Permanent gas formation varied from 3.5 to 17.7 grams on a charge of approximately 260 grams.

Three additional conventional catalytic cracking runs were made at atmospheric pressure but at a space velocity of 4 to 6 hr.⁻¹ This space velocity is the same as that used in the catalytic polyforming runs. The quantity of gasoline produced per pass by these three runs at the higher space velocity was in the range of 22 to 24 per cent based on gas oil charged. The ultimate yield varied from 52.7 per cent at 45 per cent conversion to 58.7 per cent at 37.5 per cent conversion. These data are presented in Table III and Figures 3 and 4.

Five runs were made at atmospheric pressure with the outside gas and with the temperature varying from 424° to 510° C. The permanent gas formation at this pressure and 4.3 to 5.2 hr.⁻¹ space velocity was very small, being from 7.0

to 29.5 grams on a charge of approximately 265 grams of gas oil. The greatest production of permanent gases occurred at the highest temperature employed as was true at all other pressures. Carbon laydown ranged from 2.12 to 2.75 per cent based on total charge. Per cent gasoline varied from 25.4 at 43.1 per cent conversion to 28.9 at 55.9 per cent conversion. The highest yield of gasoline, 28.9 per cent, occurred at an average temperature of 510° C. The curve of gasoline yield versus conversion was still rising as shown by the plot in Figure 3; but, since the catalyst tends to sinter at temperatures above 600°C., it was impractical to attempt to achieve a higher conversion. Consequently, the curve was not fully determined at atmospheric pressure. The trend as shown by the plot, however, indicates that the yield would not increase materially and would definitely not increase to the yield achieved at some higher pressures.

At 300 psig with temperatures varying from 434° to 535° C., five runs were made to determine a curve. Permanent gas formation and carbon laydown at 300 psig were considerably greater than at atmospheric pressure. Permanent gases formed varied from 12.4 to 132 grams, being 31.2 grams at the point of maximum gasoline formation. Carbon laydown increased from 4.4 to 11 per cent, based on total charge, being 6.01 at maximum gasoline formation. The gasoline production was also noticeably higher. The gasoline yield rose from 28.9

per cent maximum attained at 0 psig and 510° C. to 30.4 per cent maximum at 300 psig and 456° C., based on oil charged. An increase in pressure appears to have had the effect of requiring a lower temperature to realize a given conversion and gasoline yield. The temperature needed to achieve a maximum gasoline yield under 300 psig was at least 60° C. under that required at 0 psig, and it is possible that the difference is even greater since the maximum at atmospheric pressure was not attained.

Gasoline yield at 600 psig reached a maximum very close to that obtained at 300 psig, although at a slightly higher temperature, 471° C., and a slightly lower conversion. As can be seen from Figure 3, the curve at 600 psig broke much more rapidly than that at either 0 or 300 psig. Gasoline yield was slightly less than that at 300 psig, the difference being approximately 0.2 per cent; but the ultimate yield was a small amount greater. Permanent gas formation was close to that at 300 psig, while carbon formation continued to increase with increasing pressure.

Eight runs were made at 900 psig with the temperature varying from 389° to 512° C. The gasoline yield increased from 22.2 per cent to 30.7 per cent and tended to hold relatively static over a wide range of conversion. From a conversion of 48.1 per cent to a conversion of 70.8 per cent, the gasoline yields obtained in the investigation varied

from 29 to 30.7 per cent. Under conditions of relatively low conversion, an ultimate yield of approximately 60 per cent could be attained without sacrificing the yield per pass. Permanent gas formation and carbon laydown were relatively small at the conditions for maximum gasoline yield. The permanent gas formation appeared to have become static with respect to changes in pressure, but carbon formation continued to increase slightly.

Four runs were made at 1200 psig to determine a curve of yield per pass versus conversion and one of ultimate yield versus conversion. Carbon laydown at 1200 psig is quite similar to that at 900 psig, but somewhat greater, in general, than that at 600 psig. Curves of carbon versus conversion are shown in Figure 5. Permanent gas formation is similar to that at 300, 600, and 900 psig. The gasoline yield, however, decreased from that at 900 psig and compares very closely with the yields obtained at atmospheric pressure. The curves coincide so closely that one curve could be drawn through all points.

The effect of pressure on yield of gasoline from catalytic polyforming with isobutane appears to be greatest in the interval from 0 to 300 psig and to be less in the corresponding intervals at higher pressure. The maximum yield rose 1.5 per cent in the interval from 0 to 300 psig. The double interval from 300 to 900 psig resulted in a rise of

only 0.3 per cent. Beyond 900 psig, in the interval from 900 to 1200 psig, the gasoline yield decreased 1.5 per cent.

The tendency toward formation of permanent gases appears to be favored by pressure up to 300 psig but to become essentially static between 300 and 600 psig. Beyond 600 psig there was no rise in permanent gas formation.

As shown by the curve of carbon laydown versus conversion, there is a noticeable tendency for carbon laydown to increase with increasing pressure at the lower conversions. At higher conversions, the results are not so conclusive, the tendency appearing to be increased formation up to 600 psig with a gradual decrease beyond that point.

The curve of ultimate yields versus conversions for catalytic polyforming with isobutane shows a tendency for all points at all pressures to lie on one line across the chart. The main variation from pressure to pressure is merely a shift of position along the line. Atmospheric pressure tends to give a high ultimate yield at a low conversion. The ultimate yield decreases and the conversion increases for 300 and 600 psig. The ultimate yields at 900 and 1200 psig lie, in general, near the center of the curve. The curves of Figure 3 and Figure 4 indicate that 900 psig and a conversion of about 50 per cent would give a maximum yield of gasoline and a reasonably high ultimate yield of about 58 per cent.

As can be seen from Figure 3, the gasoline yield obtained from conventional atmospheric catalytic cracking at space velocities from 0.6 to 0.8 hr.⁻¹ was considerably greater than the maximum obtained from catalytic polyforming with isobutane. The highest yield obtained from catalytic polyforming was 30.7 per cent. This yield was obtained at 900 psig and over a general range of conversion from 48 to 70 per cent. Conventional catalytic cracking at the low space velocity gave a yield of 34 per cent at 62.5 per cent conversion, or a yield 3.3 absolute per cent greater.

The gasoline yield obtained from conventional atmospheric catalytic cracking at the higher space velocity of 4 to 6 hr.⁻¹, however, was considerably less than that obtained from catalytic polyforming with isobutane at the same space velocity. Conventional catalytic cracking at this space velocity gave a yield of approximately 24 per cent, or 6.7 absolute per cent less than was obtainable with catalytic polyforming at 900 psig and the same space velocity.

When operated at a low conversion of 50 per cent and without sacrificing gasoline yield per pass, the catalytic polyforming process operated at 900 psig will give a slightly greater ultimate yield with recycle than can be obtained from conventional atmospheric catalytic cracking at its conditions of maximum yield per pass. The difference in

ultimate yields obtainable under these conditions is the difference between 58 per cent for the polyforming process and 54 per cent for the cracking process, or 4 absolute per cent.

The major advantage of the catalytic polyforming process with isobutane over the conventional catalytic cracking process lies not in yield per pass or in ultimate yield but in space velocity. The polyforming process produces 30.7 per cent gasoline at space velocities of 4 to 6 hr.⁻¹, while the conventional catalytic cracking process is operated at space velocities of approximately 0.6 hr.⁻¹ to produce a maximum of gasoline. The polyforming process, therefore, allows for a greater through-put.

Detailed data for all runs made are tabulated in Tables II through VIII. The tables are arranged in order of increasing pressures while the runs within each table are arranged in the order of increasing temperatures.

V SUMMARY

The results of this investigation, which are presented in the preceding section, may be summarized as follows:

Conventional catalytic cracking at a space velocity of 0.6 to 0.8 hr.⁻¹ produces a substantially greater quantity of gasoline per pass per unit of charging stock than is produced by catalytic polyforming with isobutane at a space velocity of 4 to 6 hr.⁻¹. When the conventional catalytic cracking process and the catalytic polyforming process with isobutane are operated at the same space velocity of 4 to 6 hr.⁻¹, the catalytic polyforming process produces a substantially greater quantity of gasoline than the conventional catalytic cracking process.

The advantage of the catalytic polyforming process lies in the fact that, if both processes are operated at conditions approaching maximum gasoline production per pass, a higher space velocity can be used with the catalytic polyforming process, and therefore, a greater through-put can be obtained.

In the catalytic polyforming process using isobutane, an increase in pressure from 0 psig to 900 psig does not substantially increase the production of gasoline, the increase being approximately 2 absolute per cent based on oil charged. The effect of pressure in increasing the gasoline yield is greatest between 0 psig and 300 psig. The maximum

yield of gasoline is achieved at approximately 900 psig. Additional pressure decreases the per cent gasoline produced.

Permanent gas formation is favored up to 300 psig for the catalytic polyforming process but becomes relatively static between 300 and 600 psig. Carbon deposited increases with increasing pressure at low conversions, while at high conversions the carbon laydown increases up to 600 psig with a gradual decrease beyond 600 psig when plotted against conversion.

VI ACKNOWLEDGMENT

The author acknowledges the courtesy of Phillips Petroleum Company who sponsored the fellowship under which the investigation was carried out. This company also furnished the virgin gas oil used in the investigation and made necessary determinations on the gasoline samples produced.

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APPENDIX

TABLE I

GAS OIL INSPECTION DATA
(Borger, Texas, Virgin Gas Oil)

A.S.T.M. Dist. ° F.

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

TABLE II

CATALYTIC CRACKING AT ATMOSPHERIC PRESSURE
(Low Space Velocity)

Run No.	1	2	3	4
Charge Stock	Gas Oil			
Type of Catalyst	Houdry			
No. of Runs on Catalyst	49	47	48	50
Volume of Catalyst	1000 ml.			
Ave. Reactor Temp., °C.	413	429	482	509
Ave. Operating Pressure	Atm.			
Space Velocity, Hr. ⁻¹	0.745	0.65	0.696	0.666
Material Charged, gm.				
Outside Gas	None			
Charge Stock	264	250	267	261
Total Charge	264	250	267	261
Hydrocarbon Liquid Product	233.7	222.4	215.7	192.4
Condensable Gases	4.6	9.6	23.8	31.9
Permanent Gases	3.5	4.13	14.3	17.7
Oil from Catalyst	5.0	1.9	1.6	.8
Carbon by Burn-off	6.45	6.4	12.4	15.3
Losses by Difference, gm.	10.75	5.6	0.3	2.9
% Losses on Charge	4.46	2.24	0.11	1.1
Distillation Data, gm.				
(7-204) ^o C. Gasoline	86.3	84.0	88.8	83.0
Residue	120.6	104.8	84.7	73.2
Condensable Gases	26.5	31.7	48.6	52.1
% (7-204) Gasoline	32.7	33.6	33.2	31.8
% Conversion	52.4	57.3	67.7	71.6
% Ultimate Yield	62.4	58.6	49	44.4
% Carbon Laydown	2.44	2.56	4.64	5.86

TABLE III

CATALYTIC CRACKING AT ATMOSPHERIC PRESSURE
(High Space Velocity)

Run No.	5	6	7
Charge Stock	Gas Oil		
Type of Catalyst	Houdry		
No. of Runs on Catalyst	6	7	8
Volume of Catalyst	1000 ml.		
Ave. Reactor Temp., °C.	398	380	444
Ave. Operating Pressure	Atm.		
Space Velocity, Hr. ⁻¹	4.35	4.40	4.40
Material Charged, gm.			
Outside Gas	None		
Charge stock	254.	269	263
Total Charge	254	269	263
Hydrocarbon Liquid Product	216.8	232.7	206.1
Condensable Gases	13.2	8.3	26.2
Permanent Gases	5.5	2.3	5.8
Oil from Catalyst	12.0	9.2	11.0
Carbon by Burn-off	7.5	11.0	7.2
Losses by difference, gm.	1.0	5.6	6.3
% Losses on Charge	0.4	2.08	2.9
Distillation Data, gm.			
(7-204)° C. Gasoline	58.6	59.1	62.3
Residue	132.0	159.1	113.4
Condensable Gases	8.4	6.3	21.9
% (7-204) Gasoline	23.1	22.0	23.7
% Conversion	43.4	37.5	45.0
% Ultimate Yield	53.2	58.7	52.7
% Carbon Laydown	2.95	4.09	2.8

TABLE IV

CATALYTIC POLYFORMING AT ATMOSPHERIC PRESSURE

Run No.	8	9	10	11	12
Charge Stock	Gas Oil				
Type of Catalyst	Houdry				
No. of Runs on Catalyst	10	11	12	13	14
Volume of Catalyst	1000 cc				
Ave. Reactor Temp. °C.	424	435	449	503	510
Ave. Operating Pressure	Atm.				
Space Velocity Hr.	4.3	5.2	4.95	4.9	4.9
Material Charged, gm.					
Outside Gas	Isobutane				
Outside Gas	163.4	159.4	159.4	159.4	171.4
Charge Stock	258	264	258	267	265
Total Charge	421.4	423.4	417.4	426.4	436.4
Hydrocarbon Liquid Product	215.3	217.0	193.7	164.1	141.6
Condensable Gases	186.9	183.0	201.0	228.4	252.3
Permanent Gases	7.9	7.0	11.2	23.8	29.5
Oil from Catalyst	3.0	1.7	2.2	0.5	1.7
Carbon by Burn-off	9.3	9.0	10.2	11.7	12.0
Losses by Difference, gm.	1.0	5.7	0.9	2.4	0.5
% Losses on Charge	0.24	1.31	0.22	0.56	0.16
Distillation Data, gm.					
(7-204)° C. Gasoline	68.8	67.3	71.5	76.7	76.6
Residue	146.6	148.3	139.0	121.0	115.2
Condensable Gases	137.8	147.0	157.9	137.0	169.4
% (7-204) Gasoline	26.6	25.4	27.7	28.7	28.9
% Conversion	42.0	43.1	45.2	54.5	55.9
% Ultimate Yield (7-204)	63.4	59.0	61.4	52.6	51.6
% Carbon Laydown	2.21	2.13	2.44	2.74	2.75

TABLE V

CATALYTIC POLYFORMING AT 300 POUNDS PRESSURE

Run No.	13	14	15	16	17
Charge Stock	Gas Oil				
Type of Catalyst	Houdry				
No. of Runs on Catalyst	18	22	17	15	16
Volume of Catalyst	1000 cc				
Ave. Reactor Temp. °C.	434	453	456	490	535
Ave. Operating Pressure	300 psig				
Space Velocity Hr. ⁻¹	5.0	5.15	4.75	5.0	4.55
Material Charged, gm.					
Outside Gas	Isobutane				
Outside Gas	165	168	174.7	164	165
Charge Stock	269	267	266	269	271
Total Charge	434	435	440.7	433	436
Hydrocarbon Liquid					
Product	219.4	177.9	180.3	144.8	71.2
Condensable Gases	171.5	201.5	195.9	198.3	161.5
Permanent Gases	12.4	25.6	31.2	46.8	132.0
Oil from Catalyst	4.2	0.6	0.3	0.4	0.8
Carbon by Burn-off	20.3	19.1	26.5	30.4	47.8
Losses by Difference, gm.	6.2	10.3	6.5	2.3	22.7
% Losses on Charge	1.43	2.36	1.47	0.53	5.2
Distillation Data, gm.					
(7-204) ^o C. Gasoline	72.1	79.9	80.9	78.6	53.8
Residue	127.2	105.2	102.6	99.0	36.6
Condensable Gases	135.7	149.7	157.3	144	83.7
% (7-204) Gasoline	26.8	29.9	30.4	29.2	19.85
% Conversion	51.1	60.4	61.3	70.5	86.6
% Ultimate Yield (7-204)	52.5	49.5	49.6	41.4	22.9
% Carbon Laydown	4.68	4.4	6.01	7.02	11.0

TABLE VI

CATALYTIC POLYFORMING AT 600 POUNDS PRESSURE

Run No.	18	19	20	21
Charge Stock	Gas Oil			
Type of Catalyst	Houdry			
No. of Runs on Catalyst	20	19	26	21
Volume of Catalyst	1000 cc			
Ave. Reactor Temp. °C.	443	471	506	528
Ave. Operating Pressure	600 psig			
Space Velocity Hr. ⁻¹	5.5	5.1	4.63	5.15
Material Charged, gm.				
Outside Gas	Isobutane			
Outside Gas	175	180	178	178
Charge Stock	272	261	262	268
Total Charge	447	441	440	446
Hydrocarbon Liquid				
Product	201.9	165.6	117.6	90.8
Condensable Gases	191.5	193.2	173.5	160.9
Permanent Gases	22.5	46.5	92.5	118.3
Oil from Catalyst	0.9	0.2	0.9	0.2
Carbon by Burn-off	22.7	25.1	42.8	52.6
Losses by Difference gm.	7.5	10.4	12.7	23.5
% Losses on Charge	1.67	2.36	2.9	5.28
Distillation Data, gm.				
(7-204)° C. Gasoline	74.0	78.8	73.4	61.9
Residue	135.3	105.5	80.3	69.2
Condensable Gases	155.7	115.9	103.4	97.7
% (7-204) Gasoline	27.2	30.2	28.0	23.1
% Conversion	50.0	59.5	69.0	74.2
% Ultimate Yield (7-204)	54.4	50.8	40.5	31.2
% Carbon Laydown	5.08	5.7	9.74	11.8

TABLE VII

CATALYTIC POLYFORMING AT 900 POUNDS PRESSURE

Run No.	22	23	24	25	26	27	28	29
Charge Stock	Gas Oil							
Type of Catalyst	Houdry							
No. of Runs on Catalyst	8	7	25	23	24	6	5	9
Volume of Catalyst	1000 cc							
Ave. Reactor Temp. °C.	389	425	429	450	454	455	487	512
Ave. Operating Pressure	900 psig							
Space Velocity Hr. ⁻¹	4.92	4.89	4.8	5.38	4.8	4.65	4.74	4.89
Material Charged, gm.								
Outside Gas	Isobutane							
Outside Gas	162	165	167	168	174	164	161	167
Charge Stock	265	265	259	268	268	255	239	271
Total Charge	427	430	426	436	442	419	400	438
Hydrocarbon Liquid								
Product	237.4	216.8	209.8	177.3	177.2	169.6	126.9	101.8
Condensable Gases	149.9	177.3	164.7	193.9	195.7	180.4	178.0	172.8
Permanent Gases	14.8	16.1	21.8	30.2	31.5	30.8	50.1	105.3
Oil from Catalyst	7.4	0.5	2.1	0.4	0.6	0.5	0.5	0.4
Carbon by Burn-off	15.5	18.0	18.4	24.1	26.5	28.2	42.0	52.7
Losses by Difference, gm.	2.0	1.3	9.2	10.1	10.5	10.6	2.5	5.0
% Losses on Charge	0.47	0.3	2.16	2.3	2.38	2.27	0.62	1.17
Distillation Data, gm.								
(7-204)° C. Gasoline	58.9	81.5	76.5	77.8	80.4	78.3	72.2	64.3
Residue	162.6	137.1	124.9	116.7	106.9	98.8	69.4	64.8
Condensable Gases	132.1	136.8	127.0	143.0	140.4	142.8	136.8	113.3
% (7-204) Gasoline	22.2	30.7	29.5	29.0	30.0	30.7	30.2	23.7
% Conversion	35.7	48.1	51.0	56.2	60.0	61.1	70.8	75.9
% Ultimate Yield (7-204)	62.2	63.8	57.8	51.6	50.0	50.2	42.7	31.3
% Carbon Laydown	3.63	4.19	4.32	5.52	6.0	6.72	10.5	12

TABLE VIII

CATALYTIC POLYFORMING AT 1200 POUNDS PRESSURE

Run No.	30	31	32	33
Charge Stock	Gas Oil			
Type of Catalyst	Houdry			
No. of Runs on Catalyst	29	27	30	28
Volume of Catalyst	1000 cc			
Ave. Reactor Temp. °C.	423	452	460	491
Ave. Operating Pressure	1200 psig			
Space Velocity Hr. ⁻¹	5.0	4.97	5.05	4.58
Material Charged, gm.				
Outside Gas	Isobutane			
Outside Gas	163	161	164	158
Charge Stock	269	269	267	268
Total Charge	432	430	431	426
Hydrocarbon Liquid Product	210.1	171.2	165.3	127.1
Condensable Gases	174.8	191.7	198.2	177.7
Fermanent Gases	22.4	28.1	29.4	68.1
Oil from Catalyst	0.6	0.6	0.9	0.7
Carbon by Burn-off	22.5	25.5	28.0	40.0
Losses by Difference, gm.	1.6	12.9	9.2	12.4
% Losses on Charge	0.37	3.0	2.14	2.9
Distillation Data, gm.				
(7-204) ^o C. Gasoline	76.0	77.3	77.7	73.1
Residue	138.5	109.1	103.0	73.1
Condensable Gases	140.5	141.9	163.2	127.2
% (7-204) Gasoline	28.2	28.7	29.2	27.3
% Conversion	48.0	59.1	61.0	72.4
% Ultimate Yield	58.7	48.5	48.9	37.8
% Carbon Laydown	5.2	5.94	6.5	9.4

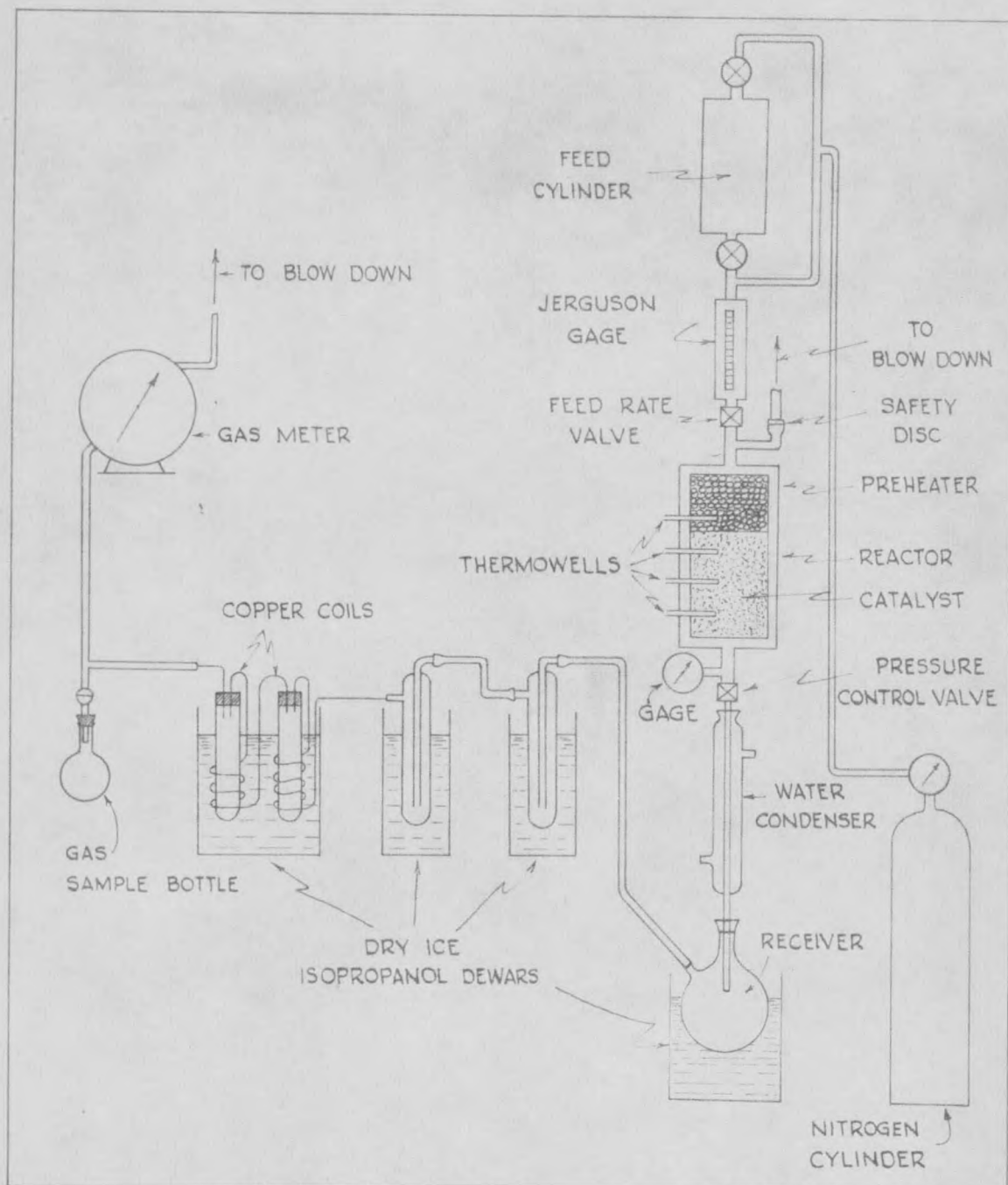


Figure 1. Schematic Diagram of Equipment

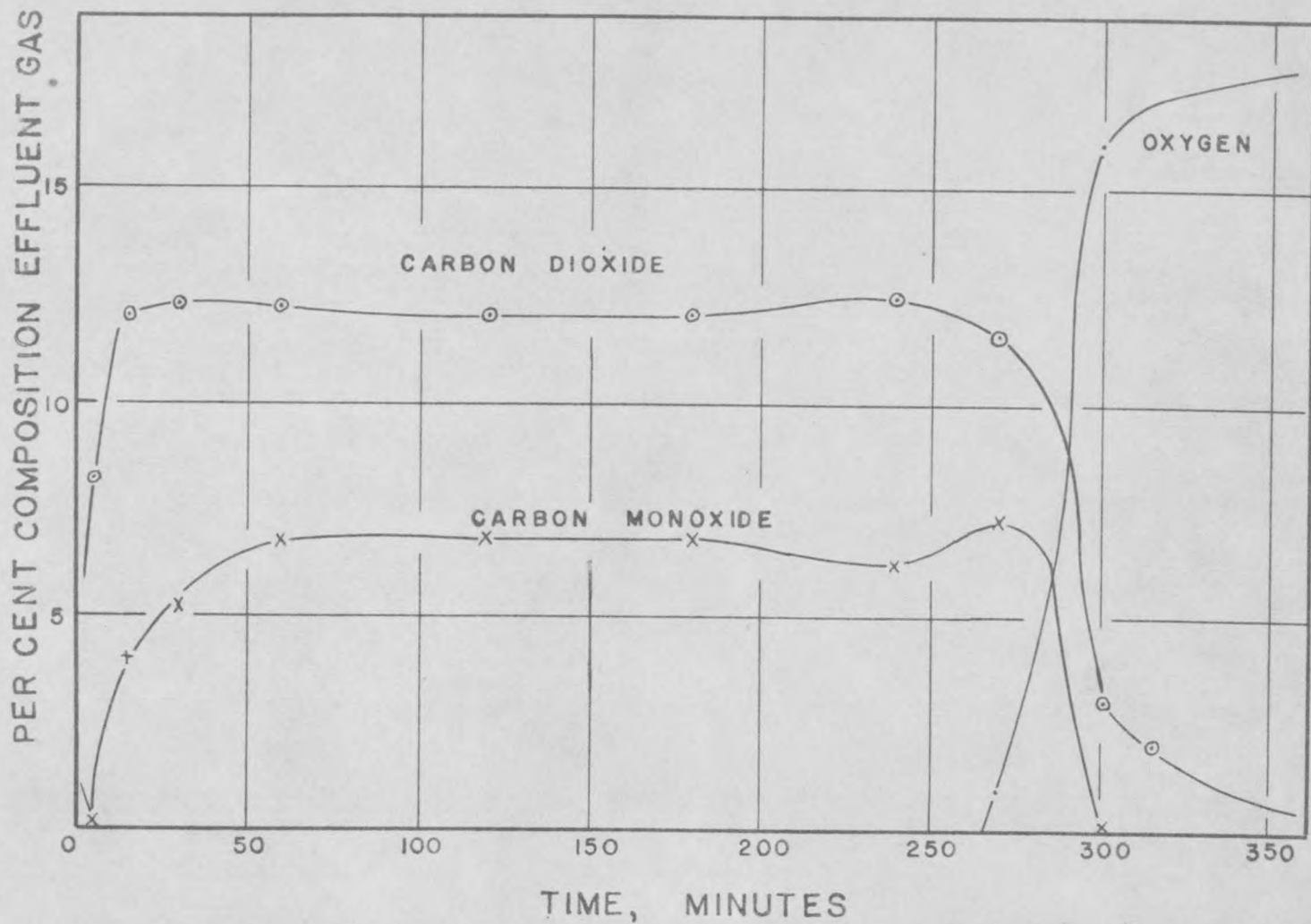


Figure 2. Composition of Effluent Gas During Catalyst Burn-off

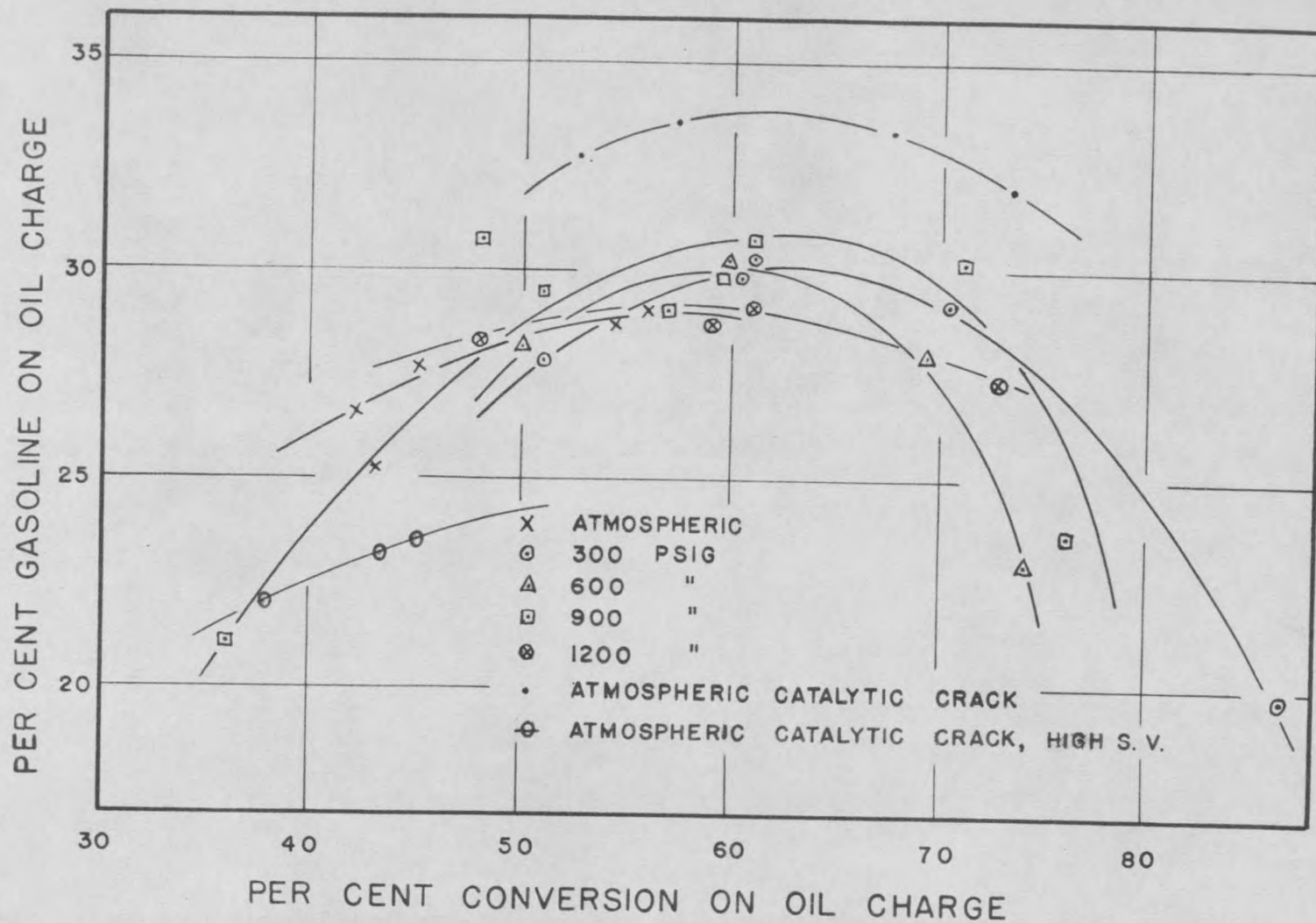


Figure 3. Relationship Between Conversion and Gasoline Yield in Catalytic Polyforming with Isobutane

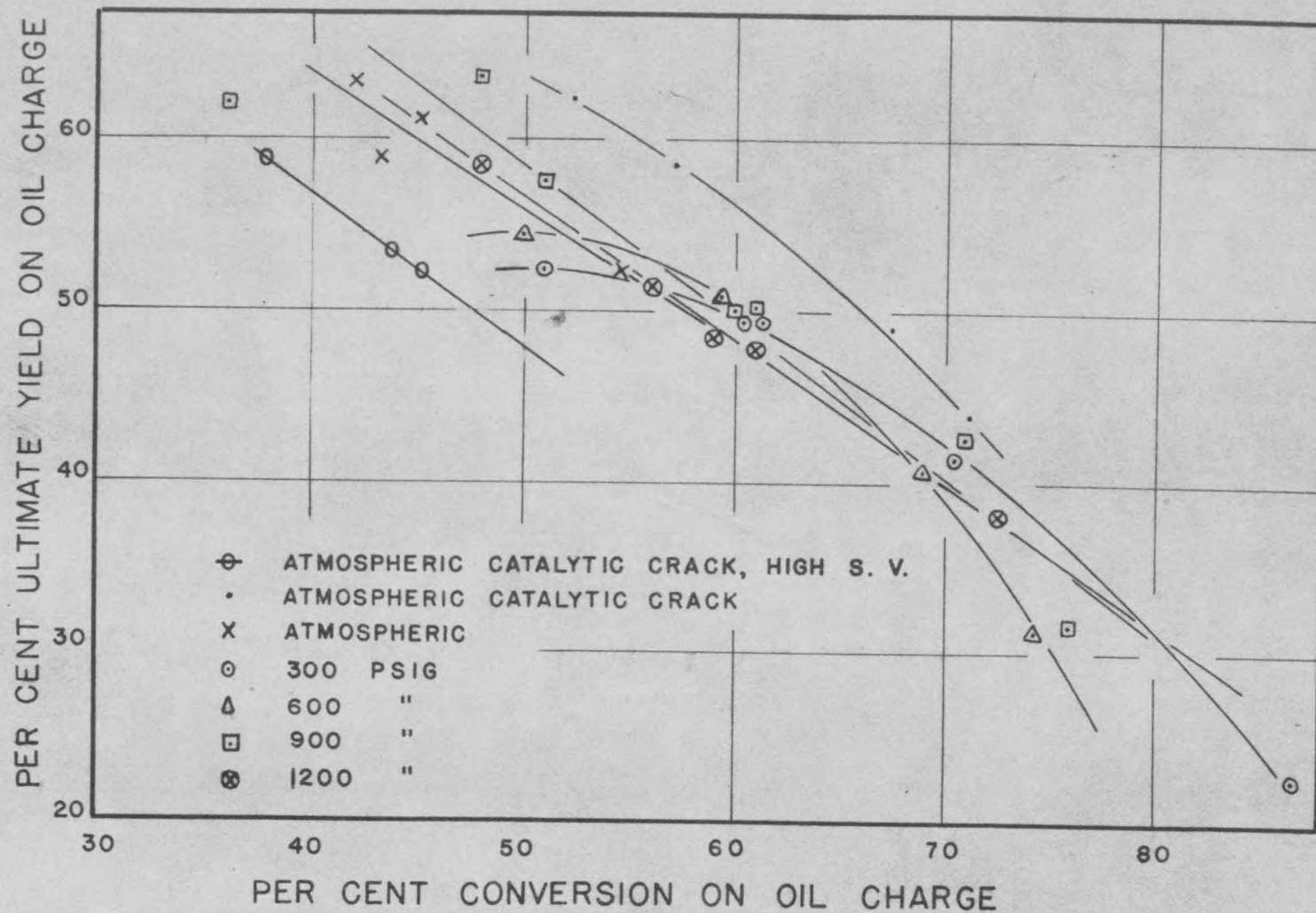


Figure 4. Relationship Between Conversion and Ultimate Yield in Catalytic Polyforming with Isobutane

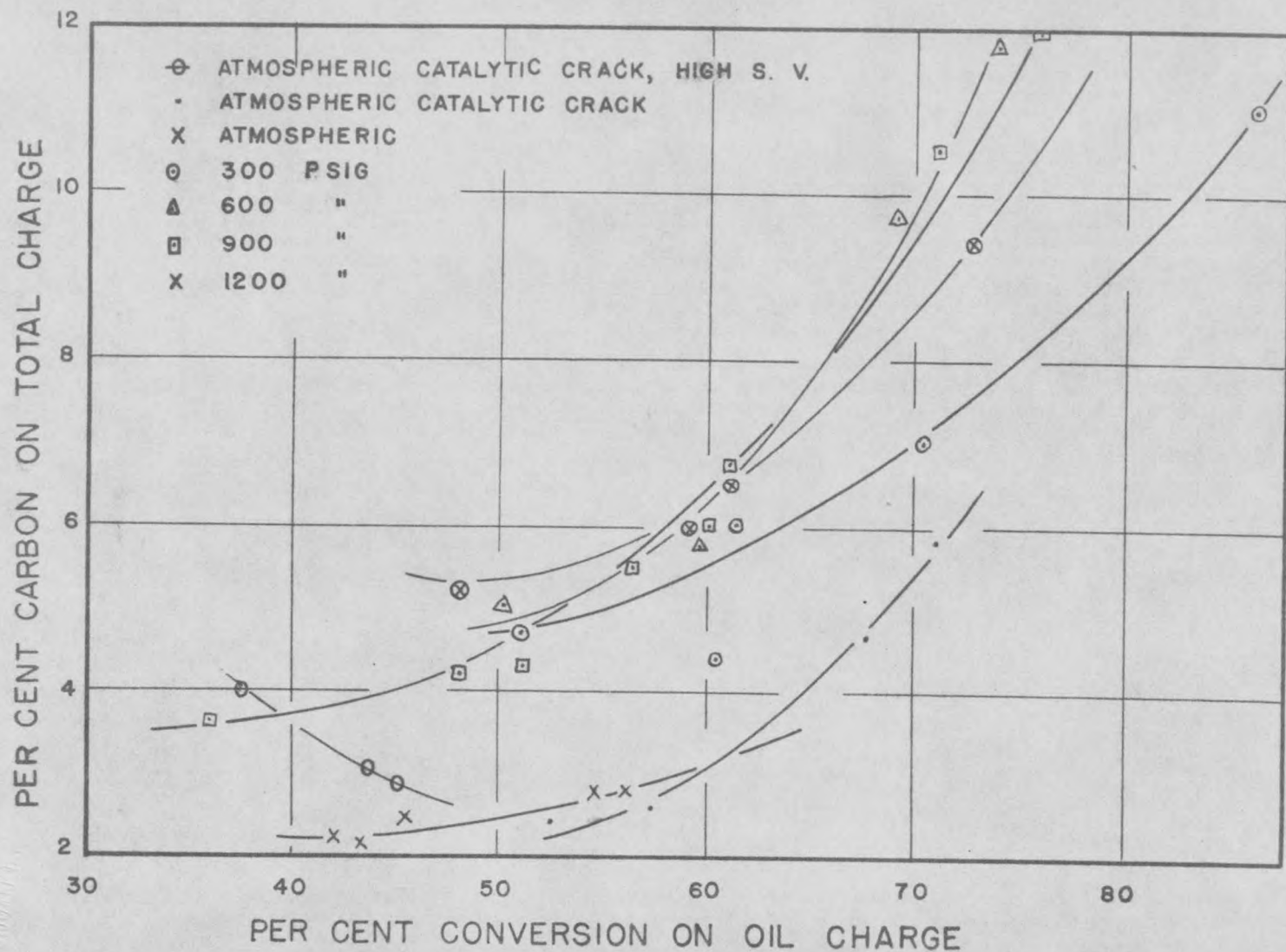


Figure 5. Relationship Between Carbon Formation and Conversion in Catalytic Polyforming with Isobutane

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