MONTANA STATE UNIVERSITY

Effect of pressure on catalytic polyforming of gas oil
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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, 000, 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 wore made at a space velocity of 0*0 to 0.8 hr,-3 in which no outside gas was employed, Three additional conventional catalytic cracking runs wore made at the higher space velocity of 4 to 6 hr-3 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 polyforsing 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,-l The conventional catalytic cracking process at this apace velocity produced a maximum of approxi-mately 24 per cent gasoline, If both processes were operated at their respective conditions of maximum, gasoline production per pass, a higher space velocity can he 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 O to 900 psig causes an increase in yield of approximately 1.8 absolute per cent or 6.2 relative per cost.

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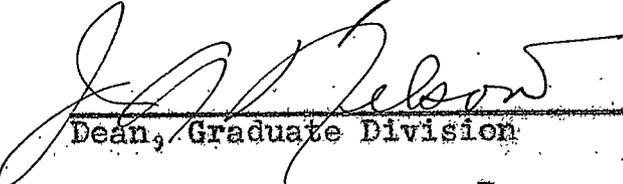for the degree of

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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, 600, 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.

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 C_3 and C_4 hydrocarbons to gasoline. The propane and butane fractions recycled within the process are in many cases supplemented with extraneous refinery gas streams for additional 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 C_3 and C_4 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 Nemtzov 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 if 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 diaphram during runs below 1000 psig and a 1445 psig Monel diaphram 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 bushing 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 con- denser 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-isopro- panol bath. Noncondensable vapors leaving the coils passed through rubber tubing to a tee, the run of which was connect- ed 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