Catalytic hydrotreating of shale oil and shale oil coker distillates
by Dale Bulen Benson

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

Abstract:
Because of the great interest expressed by several of the major oil companies throughout the United States in the development of liquid fuels from oil shales, a bench-scale, continuous-flow, fixed-bed catalytic processing unit was designed and constructed at Montana State College, This paper presents a study of the effects of several process variables on the denitrogenation and desulfurization of shale oil charge stocks, a study of two types of chemical treatments to denitrogenate a coker distillate, a study of the efficiency of several catalysts as denitrogenation catalysts, and a kinetic study.

By adjusting the process variables one at a time, it was found that the nitrogen content of the effluent oil decreased as the space velocity decreased or as the reactor pressure increased. Little difference in the efficiency of denitrogenation was noted by varying the hydrogen gas rate between 2000 SCF/bbl and 5000 SCF/bbl; only 5 percent better nitrogen conversion was noted at 7500 SCF/bbl. The optimum catalyst-bed temperature was between 825°F. and 875°F. As the mol percent hydrogen in the recycle gas decreased, both the weight percent nitrogen and the weight percent sulfur in the effluent oil increased. Yields were found to vary inversely with the operating temperature and directly with the space velocity.

Of the twelve different catalysts which were investigated as potential hydrodenitrogenation catalysts, four catalysts were found to be very effective. These are an HF-activated cobalt molybdate, a Peter Spence cobalt molybdate, a palladium promoted Harshaw molybdenum oxide, and a Harshaw cobalt molybdate.

A diffusion study performed prior to the kinetic study showed that film diffusion is definitely not a rate controlling step in the reaction mechanism, at least over the range of space velocities employed in this investigation. Plots which were drawn to show the effect of temperature, pressure, and hydrogen content of the hydrotreating gas indicate that the controlling reaction for the denitrogenation of shale oil coker distillates is primarily one of first order. The Arrhenius equation obtained was $k = 2.54 \times 10^4 e^{-14750/RT}$

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I, Dale Bulen Benson, was born on August 21, 1930, at Missoula, Montana. I attended grade and high schools in Missoula and matriculated at Montana State University in September, 1948. In June, 1952, I was graduated with a B.A. degree. In September, 1952, I came to Montana State College to take Chemical Engineering and was graduated with a B.S. degree in that field in June, 1955. I proceeded immediately with graduate study and completed all the requirements for the Ph.D. degree in Chemical Engineering at Montana State College in October, 1958.

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ABSTRACT

Because of the great interest expressed by several of the major oil companies throughout the United States in the development of liquid fuels from oil shales, a bench-scale, continuous-flow, fixed-bed catalytic processing unit was designed and constructed at Montana State College. This paper presents a study of the effects of several process variables on the denitrogenation and desulfurization of shale oil charge stocks, a study of two types of chemical treatments to denitrogenate a coker distillate, a study of the efficiency of several catalysts as denitrogenation catalysts, and a kinetic study.

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$$k = 2.54 \times 10^{4} e^{-14,750/RT}.$$

I INTRODUCTION

Since man began to use stored energy, he has been dependent for fuels upon products stored away by nature. Gradually, however, the easily obtained concentrated fuels are becoming exhausted so man will have to resort to those fuel sources which are more difficult to prepare in a concentrated form from their natural diffused form. With the realization that the world's supply of petroleum is rapidly being depleted, technologists have become vitally concerned with the opening up of new fields of petroleum and the processes whereby other oils can be used in place of petroleum products. Of all the possible products which might be used to supplement the supply of petroleum, oil from oil shale has the greatest promise since the products obtained from the upgrading of shale oil or shale-oil fractions are hardly distinguishable from the similar products produced from well petroleum, and since the quantity of oil shale is sufficiently abundant to supply the anticipated demand for oil.

The oil shale itself is a compact, laminated rock of sedimentary origin which contains a solid, organic matter called "kerogen". Kerogen is not a definite chemical compound but a complex mixture of complex compounds. Furthermore, the kerogen of different shales are dissimilar. Oil is obtained from this oil shale by destructive distillation and not by solvent treatments as is done with the tar sands which are saturated with oil or asphalt.

Oil shale deposits in the United States are located primarily in Colorado, Wyoming, and Utah in a 16,500 square mile area called the Green

River formation (48). A 500-foot-thick layer of this formation in Colorado assays 15 gallons of crude shale oil per ton (22) and, therefore, has a potential reserve of about 494 billion barrels of shale oil (51). The lower segment of this layer has been named the Mahogany ledge and assays an average of 30 gallons per ton (22). The United States Geological Survey has estimated that the oil shale deposits in the Utah portion can yield over 42 billion barrels of oil. Almost every country in the world possesses some oil shale deposits. Both France and Scotland have used oil made from oil shale for more than seventy years, but the severe competition from imported petroleum has prevented extensive development of the shale oil industry. There is little doubt that the development in the United States will be of great commercial importance to the country when the economic conditions involved become favorable.

More than 150 companies in the United States have been organized for the stated purpose of developing oil shale but as yet there is no shale oil industry. Realizing the increased consumption of petroleum and the need for a long-term supply of liquid fuels, the Congress of the United States passed the Synthetic Liquid Fuels Act of 1944. This act authorized research and development on new sources of oil among which was oil shale (31, 22). Immediately, the United States Bureau of Mines at Laramie, Wyoming (46) proceeded with plans to construct large retorts and set up a demonstration mine near Rifle, Colorado. Together with other research groups, they went ahead with the investigation of problems concerning the mining and retorting of oil shale and the development of economical refining techniques.

A number of deposits of widely different character and origin have been referred to as oil shale. These might be grouped as indicated below (34):

1. Shale partially or completely saturated with oil from outside sources. A portion of this oil may have been converted into bituminous or carbonaceous residues.
2. Lignitic and coaly shales.
3. Torbanites.
4. True oil shales. Inspection of these shales seldom reveals the presence of oil itself.

The geological similarity between oil shales and coal suggests that both were formed in swamps, lagoons, deltas, and the like. Very rich oil shale possesses an extremely fine texture and has a dull silky or satiny luster. It also kindles readily and yields a fairly large amount of volatile matter. Microscopic examination reveals the presence of vegetable matter in various stages of disintegration. The resemblance of the rich shales to some of the coals of the bituminous group is indicated by the coking of the oil shales when they are subjected to heat. Inorganic matter present may consist of clay, fine sand, calcium carbonate, iron oxides, iron carbonate, and iron sulfide (as marcasite and pyrite)(48). Animal remains including insects, larvae, fish, and crustaceans can often be detected in some oil shales. It is the presence of this carbonaceous matter derived from plant and animal remains which usually causes the black color of the oil shales (34).

The method of underground mining for oil shale employed by the United States Bureau of Mines at Rifle is a room-and-pillar type (22) whereby about 25 percent of the oil shale is allowed to remain to serve as a roof support. This method enabled the Bureau to supply processing plants at a direct cost of $0.32 per ton of shale (16). The broken shale is conveyed to crushers and retorts like the continuous gas combustion type developed by the Bureau and the Union Oil Company (3, 22). In this type of retort the crushed shale rock is passed downward counter-current to a rising stream of hot combustion gases resulting from burning recycled product gas and carbonaceous residue in the spent shale. The rate of combustion is regulated so that the vapors are condensed within the retort; consequently, the crude shale oil is removed from the retort in a liquid state. No additional condensation is required. The design of really efficient oil-shale retorting plants and the evaluation of their thermal efficiency requires extensive data on the heat needed to retort the oil shale (45), but much work was done along this line by the Bureau of Mines Petroleum and Oil-Shale Experiment Station at Laramie.

The crude shale oil recovered from the continuous retort is a black, waxy liquid with an earthy odor. It has a specific gravity of 0.9301 at 60°/60°F. and a pour point of about 90°F. (22). The untreated shale oil contains considerable quantities of nitrogen-, sulfur-, and oxygen-containing compounds. The heavy gas-oil fraction may contain as much as 45 percent of these compounds (51). Because of the large percentage of olefinic hydrocarbons present (3) which are affected adversely by severe chemical treatments, hydrogenation is recommended to remove the undesirable elements. Neither the large quantity of olefins nor the high percentage of non-hydrocarbons is found in petroleum (33, 50). The crude oil contains very little gasoline-boiling range material and because of the straight-chain nature of the paraffins and olefins in the shale oil naphtha, the gasoline produced from the crude oil does not have an exceptionally high octane rating (20). Tar acids in the crude include such compounds as phenol, cresols, and xylenols, and tar bases include substituted pyridines and quinolines (50). Destructive distillation of oil shale indicates that the basic nitrogen compounds are primarily heterocyclic derivatives of the pyrrole and pyridine series (46).

The tar bases in the crude shale oil from Colorado and Utah are mostly methylated pyridines and closely related compounds for the boiling range from 200°C. to 390°C. Below 200°C., the bases are almost entirely crude solvent pyridine (34). From a Scottish shale naphtha, Garrett and Smythe (17) isolated pyridine (C_5H_5N), a picoline ($C_5H_4(CH_3)N$), four lutidines ($C_5H_3(CH_3)_2N$), and a collidine ($C_5H_2(CH_3)_3N$). Back in 1905, Petrie (43) obtained an extract from a crude shale sample which contained what he identified as pyrrole (C_4H_5N). Very small amounts of the quinolines, the isoquinolines, the hydroquinolines, and the hydroisoquinolines may be present in some crudes (34). Janssen and his associates (23) isolated and identified both pyrrole and 2-methyl-pyrrole from a shale oil from Colorado shale of the Green River formation. Thorne and his associates (48) identified pyridines, quinolines, pyrrole, 2,4,6-trimethylpyridine, 2-methylpyridine, and 2-methylquinoline from shale oil samples. The sulfur in the shale oil is present primarily as substituted thiophenes (48).

Both the untreated crude and the coker distillates have high sulfur and nitrogen contents, are highly unsaturated, and possess color instability when exposed to air. The sulfur content of a typical gas-combustion crude shale oil (52) is 0.77 weight percent and the nitrogen content of the oil is about 2.07 weight percent. The sulfur compounds not only promote corrosion but also have objectionable odors and contribute to the poor color stability (14). Furthermore, a high sulfur content results in poor lead susceptibility (7, 14). The exact effect of each sulfur compound is not known, but sulfides are less harmful than disulfides (38). The most obnoxious odors are caused by low-boiling sulfur compounds like hydrogen sulfide and mercaptans (38). Information, which was confirmed by Byrnes and his associates (6), suggests that, at least in the case of gasolines to be blended with tetraethyllead, it is desirable to reduce the sulfur content to 0.01 percent or less; the additional cost of the refining is partially offset by the decreased amount of tetraethyllead required to obtain any given octane rating.

The nitrogen compounds are partially responsible for the extensive gum formation in that they accelerate the oxidation of the numerous unsaturated compounds present (50). Nitrogen compounds are also assuming considerable importance because of their adverse effect on many of the cracking catalysts (2).

Such properties of the crude shale oil as the high carbon/hydrogen ratio, the high percentage of nitrogen compounds, and the large amount of unsaturates suggest a considerable number of methods for refining. Since direct removal of the unsaturated compounds would result in very high losses, some method of refining must be employed which will saturate these compounds. As much as possible of the crude must be converted into stable products. Catalytic cracking processes increase the gasoline yield but petroleum-cracking catalysts (31) are deactivated very readily by nitrogen-containing compounds of which the crude contains over 40 percent. When petroleum-refining catalysts are used in shale-oil cracking operations, there is a high formation of gas and the deposition of coke on the catalyst is large. Likewise, any refining process which might be utilized must remove the nitrogen as ammonia or similar compounds for direct removal of the nitrogen-containing compounds in the crude would obviously result in too low a yield.

Among the refining processes which have been studied are the use of successive distillations, visbreaking, polyforming, both catalytic and thermal cracking, solvent extraction and several chemical treatments, and hydrotreating. In the successive distillation process, the initial distillation, in which the crude is distilled to dryness without steam, yields a distillate with a larger portion of saturated compounds than was present in the original crude oil obtained directly from the retort.

A re-run distillation will give a distillate with a still higher percentage of saturated compounds. Additional distillations will eventually give a distillate which contains the minimum amount of compounds soluble in strong sulfuric acid (1.84 sp.gr. sulfuric acid). However, because of the high percentage of unsaturated compounds in the various cuts, there are high treating losses as well as excessive carbon deposits. A Scottish refining operation (34) resulted in a total loss of about 24 percent of the crude oil. This method of successive distillations was used by a commercial plant, the Catlin Shale Products Company of Elko, Nevada (34).

Some visbreaking operations were performed by the Bureau of Mines (31). Results of these operations indicated that the sulfur content of the visbroken crude naphtha was about the same as that of straight-run naphtha, but the nitrogen content was reduced by about 40 percent. Visbroken light gas oil which had been treated with cold sulfuric acid to produce Diesel fuel was actually used to power some of the equipment in the mines at Rifle. The performance of this Diesel fuel was comparable to commercial Diesel fuels.

In the polyforming process, naphtha and heavier oils are cracked in admixture with varying amounts of gaseous hydrocarbons like propane and butane. If catalytic conditions are used, the process is called catalytic polyforming. Crecelius (12), who used this technique for the refining of shale oil, discovered that this method utilizing iso-butylene as the outside gas gave higher yields of gasoline than were obtainable by straight catalytic cracking. Catalytic polyforming lowers the temperature at which a maximum yield of gasoline can be obtained and enhances the color stability of the gasoline, but has little or no effect on the gum content or the octane number of the gasoline produced.

Catalytic cracking, a process which converts petroleum fractions in the fuel oil boiling range into gasoline and other lower boiling hydrocarbons, produces a high octane number gasoline in better yields than can be produced by thermal cracking. However, catalysts which have basic nitrogen compounds chemisorbed are poisoned for cracking (36), so most of the nitrogen in the charge stock must be removed prior to a catalytic cracking type of refining process.

Morris and Cameron (37) reported that thermal cracking followed by sulfuric acid treatment of the naphtha is a feasible means of producing gasoline and residual fuel oil from Colorado shale oil.

Because catalytic hydrotreating, a process which would not only remove much of the nitrogen and sulfur in the shale oil but also reduce considerably the number of unsaturated compounds, appeared worthy of additional study, investigations employing this process were begun at Montana State College in 1954. Although several of the major oil companies have been interested in shale oil research, the initial investigations here were conducted under the sponsorship of the Esso Research and Engineering Company. They were interested in developing an economical process which would result in a low nitrogen and low sulfur effluent oil which could be used as a charge stock by a conventional petroleum refining process. This research included studies of the effects of the operating variables such as temperature, pressure, space velocity, hydrotreating gas composition, and hydrotreating gas rate on the desulfurization and denitrogenation of shale oil coker distillates; studies of caustic and tetrahydronaphthalene batch treatments of a shale oil coker distillate in order to decrease the nitrogen content of the charge stock; studies of the efficiency of denitrogenation of twelve different catalysts in an effort to find one which would show significantly better denitrogenation of shale oil coker distillates than any of those presently being used; and a kinetic study in order to determine approximately the order of the controlling reaction for the catalytic denitrogenation of shale oil charge stocks.

II EQUIPMENT

A. Flow Diagram.

A schematic flow diagram of the catalytic hydrotreating unit is shown in Fig. 1. All seven of the reactors which are described in the specifications section of this paper were designed for a continuous-flow process and for the use of a fixed-bed catalyst. The arrangement of nichrome-wire heating coils connected to Powerstats made possible operation of the reactor over a wide temperature range, and the Mason-Neilan pressure regulator valve enabled operation at constant pressures ranging from 200 psig to 1200 psig. In conjunction with the reactor and condenser section, a gas recycle section was designed and constructed. Included in this gas recycle section was a storage tank into which the effluent gas from the reactor passed during a recycling process. From here the gas passed into a compression cylinder where oil from the compression oil reservoir displaced the gas and forced it into the feed cylinder for the reactor. The hydrotreating gas from the feed cylinder, pure hydrogen from a hydrogen bottle, or mixed gas from a bottle passed through a rotameter and into a cross at the top of the reactor where it mixed with the charge oil pumped from the oil feed reservoir. Together, the hydrotreating gas and the charge oil entered the stainless steel reactor. Treated oil was condensed in a water condenser and collected in a sample bottle. The effluent gas either passed through caustic scrubbers and was vented to the atmosphere or was fed to the storage cylinder to be recycled. When the charge stock used was the crude shale oil, a heated oil feed reservoir, a heated storage system, and a heated filter were used because the pour point of the crude is above normal room temperature. The filter was used to trap any undesirable solids present in the crude oil.

B. Specifications for Unit for Continuous Flow.

Reactor H-K: This reactor, the first reactor to be used in the shale oil project at Montana State College, was made from an 18-in. length of 2-1/2-in., schedule 80, austenitic stainless steel pipe. The end blocks for the reactor were machined from 18-8 stainless steel. Maximum operating pressure was 3000 psig. The reactor was wound with three nichrome heating coils. The top and bottom coils were 33 feet long and the middle coil was 28 feet long. The nichrome wire for the coils was first strung with ceramic beads and wrapped over a layer of asbestos tape on the reactor wall; then, the coils were covered with a layer of asbestos tape and about one inch of 85 percent magnesia insulation. A 1/2-inch, schedule 80, 18-8 stainless steel pipe was used as a thermowell in the reactor. The bottom of the reactor was fitted with a screw-type union to allow removal and insertion of catalyst and catalyst supports. The catalyst supports were 1/4-in. Alundum balls. Two iron-constantan thermocouples were used to check reactor temperatures. One thermocouple was located in the middle of the preheat section and the other was located in the middle of the catalyst bed.

Reactor B-M: This reactor was made from a 30-in. length of nominal 1-in. OD, seamless, Type 18-8 stainless steel pipe. For easy access it was equipped with a Vogt 6000 lb. flanged union at each end. The reactor was covered with a layer of asbestos tape and then wrapped with three 33-ft. nichrome heating coils. Over these coils was placed a pre-formed section of 85 percent magnesia insulation. A length of 5/32-in. OD stainless steel tubing was utilized as a pyod by brazing shut the end extending into the reactor and by placing an Ermeto tubing union at the top of the reactor. Three iron-constantan thermocouples were used to check the reactor temperature. One thermocouple was located at the top of the catalyst bed, one was located in the middle of the catalyst bed, and one was brazed to the outside of the reactor wall at a position which would correspond to the bottom of the catalyst bed. The catalyst was packed in the reactor so that the end of the pyod would extend only half-way through the catalyst bed. The catalyst supports used were 1/4-in. Alundum balls or 1/8-in. Alundum pellets, depending upon the size of the catalyst employed.

Reactor B-D-1: This reactor was similar to reactor B-M except for the positioning of the pyod and the thermocouples. The pyod was allowed to extend completely through the catalyst bed and an additional thermocouple was added. One thermocouple was placed at the top of the catalyst bed, one was placed one-third of the way down from the top of the catalyst bed, one was brazed to the outside of the reactor wall about two-thirds of the way down from the top of the catalyst bed, and one was located at the bottom of the catalyst bed.

Reactor B-D-2: This reactor is also similar to reactor B-M except for the heating coils and the location of the thermocouples. The top, middle, and bottom coils consisted of 27.0, 30.9, and 29.3 feet of 0.402 ohm electrically-insulated nichrome wire, respectively. Then, 14.0 feet of 0.402 ohm nichrome wire was wrapped over the upper half of the top or preheat coil. A 700-watt bulb was placed in series with the over-laid coil to enable more sensitive temperature control with the variac. The preheat coils were covered with a heavy layer of magnesia insulation, but the coils over the catalyst bed were covered with only a light layer of insulation. A removable insulation jacket was constructed for use over the catalyst-bed section if needed. Again, catalyst was packed in the reactor so that the pyod would extend only to the bottom of the catalyst bed but the thermocouples were positioned in the pyod so that there would be one in the middle of the preheat section, one at the top of the catalyst bed, and one at the bottom of the catalyst bed. A fourth thermocouple was brazed to the skin of the reactor at about the middle of the catalyst bed.

Reactor B-D-3: This reactor was identical to reactor B-D-2 except that within the preheat section was twisted a 3-ft. coil of 1/8-in. stainless steel tubing. A perforated stainless steel disc was used above the catalyst bed and the preheat section was packed with stainless steel Fenske rings.

Reactor B-D-4: This reactor was like reactor B-D-2, except a 6-ft. length of 1/8-in. stainless steel tubing was coiled and twisted into the preheat section. A perforated stainless steel disc was set at the top of the catalyst bed and the preheat section was packed with 1/4-in. Alundum balls.

Reactor B-D-5: This reactor was identical to reactor B-D-2 except the 5/32-in. OD pyod was replaced with a 3/16-in. OD pyod to allow the use of four thermocouples within the reactor. Thermocouples were positioned in the pyod so that there would be one in the middle of the preheat section and one at the top, one at the middle, and one at the bottom of the catalyst bed.

The other equipment used on the unit is described in detail in the appendix, see Table XI. In brief, some of the items of which it consisted are an oil-feed reservoir and a 5-gallon oil-storage reservoir, a Hills-McCanna high-pressure proportioning pump, a water condenser, Jerguson sight glasses, a Mason-Neilan pressure control valve and a Fisher-Wizard pressure controller, Brooks rotameters, Powerstats, a Pesco gear pump, pressure gauges, a Leeds and Northrup temperature indicator, a wet test meter, tubing, and valves.

III MATERIALS, METHODS, AND ANALYSES

A. Materials

Charge stocks: The charge stocks were supplied by the United States Bureau of Mines demonstration plant at Rifle, Colorado, and consisted of nominal 650°F. E.P. coker distillate, 750°F. E.P. coker distillate, 850°F. E.P. coker distillate, and full-range gas-combustion crude shale oil. The coker distillates were prepared from a gas-combustion crude by a recycle delayed coking operation. Table I is a tabulation of some of the laboratory data for these charge stocks.

Hydrotreating gas: The 100 percent hydrogen was supplied by the Whitmore Oxygen Company of Salt Lake City, Utah. The mixed gas and the commercial grade methane were supplied by the Matheson Company of Joliet, Illinois.

Catalysts: The catalysts were obtained from the Harshaw Chemical Company, Peter Spence and Sons, Ltd., and the Esso Research and Engineering Company, or were prepared in the laboratory at Montana State College. Table VII is a tabulation of the various catalysts used for the studies described in this paper.

Catalyst supports: The catalyst supports were 1/4-in. Alundum spheres or 1/8-in. Alundum pellets obtained from the Norton Abrasive Company.

B. Methods

Start-up: The reactor was charged by inverting the reactor tube and placing it in a wall support. Alundum balls or pellets for catalyst support were poured slowly into the tube and the reactor was tapped gently every little while with a hammer so that the catalyst support would pack evenly. After sufficient catalyst support had been added to allow room for the catalyst bed at its proper position in the reactor, the correct weight of catalyst was poured in slowly. The remaining space was filled with catalyst support, and a stainless steel screen was pressed in the union to hold the reactor contents in position. The reactor was then connected at its proper location in the unit. Powerstat cords, gas and oil feed lines, thermocouple leads, and the product receiver were connected. Finally, the unit was readied for a run by evacuation, pressurizing, and heating of the reactor to the desired operating temperature. Hydrotreating gas was allowed to flow through the reactor while it was warming up.

Operation: After the catalyst-bed temperature had remained at operating temperature for approximately an hour, the feed pump was started. By adjusting the stroke of the piston in the feed pump, the space velocity was set at the desired value as measured by the volumetric oil feed rate. Temperatures were lined out as quickly as possible and the product was continuously being drained into the sample receiver. Temperature readings, pressure readings, and rotameter readings were checked every fifteen minutes during the initial portion of the run, and were recorded every half hour for the remainder of the run. When the pressure in the gas-feed cylinder had dropped to within about 100 pounds of the operating pressure, storage-cylinder gas was recompressed in the feed cylinder or a new, full tank of feed gas was connected to the system. Holecek (20) reported the exact procedure used for gas make-up when the hydrotreating gas was recycled and sufficient hydrogen was introduced into the system to keep the composition of the in-going gas constant.

During a run, the weight of charge oil added and the weight of sample recovered were recorded so that approximate yields could be determined. Samples were taken at fifteen-minute intervals, half-hour intervals, hour intervals, or over longer intervals, depending upon the objective of the run. At all times, sufficient effluent oil was allowed to remain in the Jerguson to form a liquid seal and thus prevent loss of pressure in the reactor. All of the samples were stored in glass sample bottles for further analysis. The effluent gases passed through a caustic scrubbing train to remove the hydrogen sulfide. During some of the runs, a wet test meter was connected to the end of the scrubbing train to meter the effluent gases. When it was desirous to know the composition of the hydrotreating gas, a sample line was purged and gas was collected in an eight-liter glass bottle by the displacement of water.

Shut-down: To shut down the unit either because of some mechanical failure, because of coking and consequent plugging of the reactor, or because sufficient data had been collected at a given set of conditions, it was necessary to switch off the oil-feed pump and the Powerstats. Then the sampling valve and the oil-feed line valve were closed. However, the hydrotreating gas was allowed to flow through the reactor until the reactor temperature dropped to at least 200°F. Before the reactor was torn down and dumped, it was necessary to vent the gas in the reactor. This was accomplished by shutting off the air supply to the pressure regulator valve and bleeding the lines leading to the back-pressure valve.

C. Analyses.

The gas samples in the eight-liter bottles were analysed in a low-temperature micro-still cooled with liquid nitrogen and connected to a Micromax automatic temperature recorder. By this method the composition, the volume of hydrogen, methane, ethane, and propane in the gas sample, could be accurately determined.

The API gravities were determined by using a Westphal balance to obtain the specific gravity of the oil sample and then by using the conversion equation, °API = (141.5/sp.gr.)-131.5.

The weight percent nitrogen in a sample was determined by the Boyd Guthrie modification (29) of the Kjeldahl method. This method, designed specifically for shale oil and its fractions, utilizes a mercury catalyst, a catalyst which has been found to be exceptionally effective (28). All samples were water-washed first to remove free nitrogen and then dried with calcium chloride.

The weight percent sulfur in a sample was determined by the lamp-gravimetric method, D90-50T, outlined in the ASTM manual (1). All samples were caustic washed to remove free hydrogen sulfide and then water-washed and dried.

The few distillations run were carried out according to the ASTM distillation procedure, D86-54, (1).

IV THERMODYNAMIC STUDY

Some consideration was also given to the thermodynamics of possible reactions involved in the hydrotreating of shale oil. The following points were studied:

(1) The determination of the equilibrium constants and activity coefficients for several reactions, assuming various nitrogen-containing compounds were present.

(2) The comparison of the conversion of a sulfur-containing compound like thiophene with a nitrogen-containing compound like pyrrole at different pressures. (Two sets of conditions, one, atmosphere pressure and 25°C., and 70 atmospheres pressure and 440°C., were used.)

(3) The thermodynamic calculations for the reaction of a cobalt molybdate catalyst with thiophene at the start of a run.

Since the thermodynamic data available for most of the compounds studied was very limited, several estimations had to be made. Table II gives the values of $H_{f_{298}}'$ and S°_{298} for the various compounds used in the calculations and Table III lists the critical constants. Several methods of estimation were used when possible in order to obtain checks on the values obtained; then, the value which was arrived at by the seemingly most reliable method was used in the calculations. Because of the difficulty of estimation, only a limited number of nitrogen-containing cyclic compounds were considered.

Below are listed the methods of estimation used, and in Table V are given examples of each of these methods:

(1) Entropies and heats of formation calculated by assuming the addition of a methyl group will have the same effect on these thermodynamic properties of compounds of similar structure (4).

(2) Entropy values calculated by using a given entropy value for the change of a single bond to a double bond (40).

(3) Entropy values calculated by considering the changes in molal entropy accompanying the substitution of an NH_2 group for an N_3(39).

(4) Liquid entropies converted to vapor entropies by a general equation relating the two entropies (15).

(5) Heats of formation calculated with the aid of heats of combustion values (30).

The values of the critical constants which were not found in the literature were estimated by the Meissner and Redding method of parachors (35).

The following list of reactions are those reactions which were considered thermodynamically. The equilibrium constants calculated for these reactions are tabulated in Table IV.

(1) $C_4H_5N(g) + 4H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + NH_3(g)$

(2) $C_4H_9N(g) + 2H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + NH_3(g)$

(3) $C_3H_4N\ (g) + 5H_2(g) \rightarrow C_3H_8(g) + 2NH_3(g)$

(4) $C_3H_6N_2(g) + 4H_2(g) \rightarrow C_3H_8(g) + 2NH_3(g)$

(5) $C_5H_5N(g) + 5H_2(g) \rightarrow C_5H_{12}(g) + NH_3(g)$

(6) $C_5H_{10}N(g) + 2\text{-}1/2H_2(g) \rightarrow C_5H_{12}(g) + NH_3(g)$

(7) $CH_3C_5H_4N(g) + 5H_2(g) \rightarrow C_6H_{14}(g) + NH_3(g)$

(8) $C_6H_5NH_2(g) + 5H_2(g) \rightarrow C_6H_{14}(g) + NH_3(g)$

(9) $C_4H_4S(g) + 4H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + H_2S(g)$

To summarize the results of this portion of the study, it may be said that all of the reactions for the hydrogenation of heterocyclics which were checked were favorable except for the reaction involving pyrrolidine. Although the equilibrium constant for the reaction of pyrrolidine with hydrogen to form ammonia as the nitrogen-containing product improves considerably with increased temperature, it is still 10^{-13} at 440°C.

From the calculations of the K_N's, see Table IV, it was shown that pressure favors the two reactions considered. For these reactions, when the K_N's were greater than 10^8, the conversion was greater than 99 percent.

even at 70 atmospheres pressure.

To check the possibility of the catalyst forming sulfides and then going back and forth between these sulfides as hydrogen sulfide is released, a series of reactions were tested thermodynamically. The catalyst studied was cobalt molybdate because this catalyst had been found to be the most efficient for both sulfur and nitrogen removal from shale oils and because considerable data are available on the oxides and sulfides of cobalt molybdate. The composition of the catalyst was assumed to be similar to that of a Peter Spence catalyst given in Table VII. Below is given a list of the reactions postulated and the values of the equilibrium constants for each reaction at two temperatures.

(1) $C_4H_4S(g) + 3H_2(g) + Co(s) \rightarrow n\text{-}C_4H_{10}(g) + CoS(s)$

$$K_{eq298} = 7.94 \times 10^{39}; \quad K_{eq713} = 2.95 \times 10^{6}$$

(2) $2CoS(s) + C_4H_4S(g) + 3H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + Co_2S_3(s)$

$$K_{eq_{298}} = 3.16 \times 10^{24}; \quad K_{eq_{713}} = 1.38 \times 10^{-5}$$

(3) $Co_2S_3(s) + H_2(g) \rightarrow 2CoS(s) + H_2S(g)$

$$K_{eq_{298}} = 0.724; \quad K_{eq_{713}} = 135$$

(4) $2C_4H_4S(g) + 6H_2(g) + Mo(s) \rightarrow 2n\text{-}C_4H_{10}(g) + MoS_2(s)$

$$K_{eq_{298}} = 6.31 \times 10^{88}; \quad K_{eq_{713}} = 3.98 \times 10^{15}$$

(5) $MoS_2(s) + C_4H_4S(g) + 3H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + MoS_3(s)$

$$K_{eq_{298}} = 1.78 \times 10^{27}; \quad K_{eq_{713}} = 1.77$$

(6) $MoS_3(s) + H_2(g) \rightarrow MoS_2(s) + H_2S(g)$

$$K_{eq_{298}} = 2.82 \times 10^{3}; \quad K_{eq_{713}} = 4.17 \times 10^{3}$$

(7) $MoS_3(s) + C_4H_4S(g) + 3H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + MoS_4(s)$

$$K_{eq_{298}} = 4.47 \times 10^{31}; \quad K_{eq_{713}} = 1.12 \times 10^{2}$$

(8) $MoS_4(s) + H_2(g) \rightarrow MoS_3(s) + H_2S(g)$

$$K_{eq_{298}} = 0.106; \quad K_{eq_{713}} = 63.1$$

These calculations indicate that it is possible for the higher sulfides to form for both cobalt and molybdenum. It also appears very possible for the higher sulfides to go to the lower sulfides accompanied by the release of hydrogen sulfide gas.

V DISCUSSION AND EXPERIMENTAL RESULTS

A. General Considerations

Following the completion of the construction of the shale oil hydrotreating unit, a few shake-down runs were made to check the system for gas and oil leaks, for faulty electrical connections, for pressure control, for control of feed rates, and for general smoothness of operation. Then a few runs of about 100 hours each were made to determine what approximately would be the optimum operating conditions.

The operating conditions used in this study varied over the following ranges: catalyst-bed temperature -- 385°C. to 496°C. (725°F. to 925°F.); reactor pressure -- 200 psig to 1200 psig; hydrotreating gas flow rate -- 2000 SCF/bbl to 7500 SCF/bbl; hydrotreating gas composition -- 30 percent hydrogen and 70 percent methane to 100 percent hydrogen; space velocity -- 0.1 g/g hr to 3.0 g/g hr; and grams of catalyst -- 50 grams to 300 grams. In Table IX are tabulated the specific operating conditions for most of the runs made with the unit. Also included in this table are the product data: yields based on weight of oil charged, results of gravimetric sulfur analyses, and results of Kjeldahl nitrogen analyses.

The four charge stocks used and the weight percent sulfur and nitrogen which they contained are as follows: 650°F. E.P. coker distillate (0.63 percent sulfur, 1.65 percent nitrogen), 750°F. E.P. coker distillate (0.61 percent sulfur, 1.90 percent nitrogen), 850°F. E.P. coker distillate (0.63 percent sulfur, 1.95 percent nitrogen), and gas-combustion crude shale oil (0.77 percent sulfur, 2.07 percent nitrogen).

The first two run series were made using an 850°F. E.P. coker distillate, 100 grams of Union oil cobalt molybdate catalyst (see Table VII), a shallow catalyst bed (1-1/2 inches in depth), catalyst-bed temperatures ranging from 725°F. to 925°F., reactor pressures of 500 and 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 65 percent hydrogen, 35 percent methane. This series demonstrated that 1000 psig reactor pressure was more conducive to both nitrogen and sulfur removal than 500 psig. Runs 3 and 8 show that by increasing the reactor pressure to 1000 psig, sulfur conversion at 825°F. was increased from 34.2 percent to 71.5 percent and nitrogen conversion was increased from 13.8 percent to 33.4 percent. These runs also indicated that the denitrogenation and desulfurization properties of the catalyst decrease as the deactivation increases. The activity level of the catalyst varied the most at 925°F. when a rapid deactivation did occur, perhaps due to increased carbon lay-down on the catalyst. Runs 9 and 10 show that at 925°F., nitrogen conversion was 15.8 percent after 16 hours on stream at that temperature, and was dropping, whereas at 875°F., nitrogen conversion was 48.7 percent after 16 hours on stream and was remaining fairly constant. Other runs also show this steady increase in nitrogen conversion at 925°F. but to a lesser degree. At this time in the study, 875°F. seemed to be the optimum operating temperature.

During the course of the runs to determine the effects of the operating variables like temperature, pressure, space velocity, gas feed rate, and recycle gas composition, several problems arose. One of these problems was the operation with a gas-combustion crude shale oil. Run 72 of 48 hours duration, and Run 74 of 300 hours duration were both made at 825°F. with a Harshaw cobalt molybdate catalyst, with 1000 psig reactor pressure, with a feed gas composition of 100 percent hydrogen, and with a space velocity varying from about 0.1 to 0.5 g/g hr. Run 72 was made with a recycle gas rate of 7500 SCF/bbl, whereas Run 74 was made with a recycle gas rate of 2500 SCF/bbl. Both runs indicated that after about 15,000 grams of charge oil had passed into the reactor, the preheat section of the reactor became plugged solid with coke. One might conclude from this that a coker distillate of indefinite characteristics was being formed in the preheat section. One method of preventing this coking in the preheat section might be to devise a preheater with a very low residence time for the crude oil. However, all the runs both prior to Run 72 and following Run 78 were made using coker distillate as the charge stock.

Several ASTM distillations were carried out on the effluent oils. Table VI gives the results of these distillations. Those ASTM distillations performed on product oil from a series of runs made with the only variable being the mol percent hydrogen in the recycle gas showed that there seems to be no correlation between the hydrogen content of the recycle gas and the boiling range of the product. Although the mol percent hydrogen in the recycle gas varied from 40 to 100 percent, 45 to 50 volume percent of each of the products obtained was in the gasoline boiling range (below 400°F.). Furthermore, the distillation end points, around 630°F., were nearly the same for every product. The ASTM distillations performed on product oil from runs made with four different catalysts, palladium promoted molybdenum oxide, indium promoted molybdenum oxide, Peter Spence 5/32" cobalt molybdate pellets, and Harshaw 1/8" cobalt molybdate pellets, at 875°F. using 650°F. E.P. coker distillate, showed that the palladium catalyst and the Peter Spence catalyst gave higher percentages of material, 60 to 62 percent, in the gasoline range than the other two catalysts used. These two catalysts, the indium catalyst and the Harshaw catalyst, gave only 48 to 53 percent in the gasoline range.

One run, Run 107, was performed with regenerated 1/8" Peter Spence cobalt molybdate catalyst at 825°F., 1000 psig, and 7500 SCF/bbl, with a feed gas composition of 100 percent hydrogen and a space velocity of 1.0 g/g hr.. The value for the nitrogen content of the product oil after equilibrium had been reached was about the same as the value for a similar product from a run, Run 104, using fresh catalyst, namely, 0.57 weight percent nitrogen.

An attempt was made to determine the required line-out time, the time required for equilibrium to be reached. Equilibrium was considered to have been obtained when nitrogen conversion values for samples of effluent oil fluctuated about some constant value and showed no definite upward or downward trend. The nitrogen analyses tablulated in Table IX for the effluent oil from Run 41 indicate that about 12 hours of operation are required to reach equilibrium. This time was about 12 hours either when starting up with fresh catalyst or when changing gas composition within a run. All variations following this time and up to at least 200 hours on stream were attributed to fluctuations in operating conditions and slight catalyst deactivation. In later runs, Runs 100 to 142, however, the nitrogen value used to compare the results of various operating conditions and catalysts was an average value for the period between 6 and 8 hours of operation. By this time, excessive cycling of the values for the nitrogen content of the effluent oil had ceased in nearly all instances.

As far as duplication of results is concerned, Figure 2 shows that with reactor B-M, reproducibility was good. Three successive runs were made, Runs 100, 101, and 102, all three of which gave a series of values for the percent nitrogen conversion which fell on the same line. These three runs were each carried out with a 750°F. E.P. coker distillate charge stock and with 100 grams of Peter Spence 5/32" cobalt molybdate catalyst pellets in the 1-in. OD reactor (reactor B-M) so the catalyst-bed depth was about 10 inches. The operating conditions were 825°F., 1000 psig, 1.0 g/g hr. space velocity, 7500 SCF/bbl gas feed rate, and 100 percent hydrogen feed gas composition. The nitrogen conversion value after 6 hours on stream was about 0.42 percent.

Excessive channeling was believed to be the major cause of failure to get good reproducibility when a shallow catalyst bed, one less than 1-1/2 inches in depth, was used. The channeling was thought to be due partially to catalyst orientation (position acquired by the catalyst pellets in the catalyst bed as a result of pouring the catalyst into the reactor), partially to the catalyst pellet size, and partially to the extension of the thermowell all the way through the catalyst bed.

A fractionation was run on an effluent oil obtained from the hydrotreating of a 650°F. E.P. coker distillate in order to obtain cuts of 30, 30, 20, and 20 volume percent. Then nitrogen analyses were run on these cuts and a nitrogen profile was drawn, see Figure 3. The purpose of this fractionation was to determine wherein the majority of the nitrogen-bearing compounds lie, for it might be feasible to produce a low-nitrogen gasoline from a shale oil coker distillate by hydrotreating only a fraction of the coker distillate. Figure 3 shows that the 30, 30, 20, and 20 volume percent cuts contained respectively, 0.020, 0.105, 0.267, and 0.356 weight percent nitrogen. Therefore it is evident that the bulk of the nitrogen is in the high molecular weight portion of the oils.

B. Effects of Process Variables

Temperature: Optimum catalyst-bed operating temperature for the desulfurization and denitrogenation of shale oil coker distillates was the first variable studied. Sulfur analyses show that with two of the catalysts tested, Union Oil's cobalt molybdate and the indium promoted molybdenum oxide, the point of maximum sulfur conversion (77.8 percent) was at about 875°F., see Figure 5. Two other catalysts, palladium promoted molybdenum oxide and 5/16" Peter Spence cobalt molybdate pellets, showed a continued excellent sulfur conversion (93.6 percent) up to at least 925°F.; however, the product yield at this high temperature was low, 69 to 76 percent, see Table IX. The charge stock for these runs was either 650 or 850°F. E.P. coker distillate and the other operating conditions were 500 or 1000 psig, 1.0 g/g hr. space velocity, 7500 SCF/bbl gas feed rate, and 65 percent hydrogen-35 percent methane feed gas composition.

In general, product yields vary inversely with the operating temperature and directly with the space velocity. For example, Runs 12-16 (made with 100 grams of indium promoted molybdenum oxide catalyst and 650°F. E.P. coker distillate charge stock at 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composed of 65 percent hydrogen and 35 percent methane) show that as the reactor temperature increases from 725 to 925°F., product yields drop from 99 to 71 weight percent. Runs 50 and 51 (made with 100 grams of Harshaw 1/16" cobalt molybdate pellets and 650°F. E.P. coker distillate charge stock at 825°F., 1000 psig, a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 100 percent hydrogen) show that when the space velocity is increased from 0.25 to 1.0 g/g hr., product yield increases from 82 to 91 weight percent. The nitrogen analyses for Runs 1-16 indicate that the efficiency of nitrogen removal increases with temperature up to at least 825°F. Run 12 at 725°F. gave a nitrogen conversion of 30.8

percent, whereas Run 14 at 825°F. gave a nitrogen conversion of 48.7 percent. These results are shown graphically in Figures 4A and 4B. Runs 57, 60, and 63 (made with 100 grams of Harshaw 1/16" cobalt molybdate pellets and 750°F. E.P. coker distillate charge stock at 1000 psig, a space velocity varying from 0.25 to 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 100 percent hydrogen) show that the minimum weight percent nitrogen in the effluent oil is 0.32 percent and occurs at an operating temperature of about 835°F. Runs 22-31 (made with Peter Spence 5/32" cobalt molybdate catalyst pellets of Harshaw 1/8" cobalt molybdate pellets and 650°F. E.P. coker distillate at 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 65 percent hydrogen and 35 percent methane) indicate that at these conditions denitrogenation is best at 875°F., but that product yields are only about 82 percent at 875°F compared to about 92 percent at 825°F. A value for the nitrogen content of the effluent oil of about 0.5 weight percent nitrogen was obtained at 875°F., whereas at 825°F. a value of 0.57 weight percent nitrogen was obtained. Therefore, it appears that, although the optimum reactor temperature will vary to some extent with other operating conditions, the charge stock, and the catalyst used, this optimum temperature is between 825°F. and 875°F., see Figures 4A and 4B.

Pressure: Within the range of pressures studied, between 200 and 1000 psig, both nitrogen and sulfur analyses show that the higher pressures affect denitrogenation and desulfurization of shale oil coker distillate advantageously. Figure 7 shows that for Runs 112, 133, and 146 (made using 50 grams of Peter Spence 1/8" cobalt molybdate catalyst pellets, a 750°F. E.P. coker distillate charge stock, 825°F., a space velocity of 0.5 g/g hr., a gas feed rate of 7500 SCF/bbl, and 100 percent hydrogen feed gas) increasing the reactor pressure from 200 to 1000 psig increased the nitrogen conversion from 36.5 percent to 85.5 percent; and Figure 6 shows that for Runs 3 and 8 (made using 100 grams of Union Oil 3/16" cobalt molybdate catalyst pellets, in 850°F. E.P. coker distillate charge stock, 825°F., a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a 65 percent hydrogen-35 percent methane feed gas) increasing the reactor pressure from 500 to 1000 psig increased the sulfur conversion from 34.2 percent to 71.5 percent. Figure 7 also shows the effect of pressure on the weight percent nitrogen in the effluent oil as indicated by runs at space velocities of 1.0 and 2.0 g/g hr. using a reactor containing a 5-1/2 in. deep cobalt molybdate catalyst bed, reactor B-D-2. Pressure shows the same effects on these runs as on Runs 112, 133 and 146 just indicated, but because of the higher space velocities used, at 1000 psig the values for the weight percent nitrogen in the effluent oil were 0.79 and 1.07 for space velocities of 1.0 and 2.0, respectively. At 200 psig, these values were only 1.47 and 1.62 for space velocities of 1.0 and 2.0, respectively.

Space Velocity: Space velocity was another variable affecting the denitrogenation of shale oil coker distillates and crude shale oil which was studied. Figure 8 shows graphically the ease with which two coker distillates and a crude shale oil can be denitrogenated in a narrow space velocity range. It indicates that for space velocities between 0.1 and 0.3 g/g hr., space velocity does exercise a stronger effect on a heavy charge stock like the crude shale oil than it does on a light stock like the 650°F. E.P. coker distillate. When the charge stock was crude shale oil, increasing the space velocity from 0.1 to 0.3 lowered the nitrogen conversion 24 percent; when the charge stock was 650°F. E.P. coker distillate, increasing the space velocity from 0.1 to 0.3 lowered the nitrogen conversion only 2 percent. Early coking in the preheat section of the reactor and the high extent to which the reaction was exothermic, prevented the obtaining of reliable data at space velocities above 0.5 g/g hr. with the crude shale oil charge stock. Figure 9 shows the relationship between space velocity and weight percent nitrogen in the effluent oil for a 750°F. E.P. coker distillate. Included in this Figure 9 are the values for the weight percent nitrogen in the effluent oil from Runs 130, 131, and 142 made with Peter Spence 1/8" cobalt molybdate catalyst pellets and with 750°F. E.P. coker distillate at 825°F., 1000 psig, a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 100 percent hydrogen. These values result in a curve which shows that as the space velocity increases from 0.5 to 2.0, the nitrogen content of the effluent oil increases from 0.42 to 1.14 weight percent. Accompanying this increase in nitrogen is an increase in product yield of from 76 to 84 percent at 875°F., as seen in Table IX.

Gas Feed Rate: In Figure 10 is shown graphically the effect of the hydrotreating-gas feed rate on the denitrogenation of a shale oil coker distillate. Since previous work (32) showed that a hydrogen feed rate of at least 2000 SCF/bbl was necessary for effective removal of nitrogen, only hydrogen feed rates between 2000 SCF/bbl and 7500 SCF/bbl were used during this study. The operating conditions were 825°F., 1000 psig, a space velocity of 0.5 to 2.0 g/g hr., and a feed gas composition of 100 percent hydrogen with a 750°F. E.P. coker distillate charge stock and Peter Spence 1/8" cobalt molybdate catalyst pellets. The results of this study showed that hydrogen feed rates within this range do not affect denitrogenation noticeably.

Mol Percent Hydrogen in Hydrotreating Gas: The mol percent hydrogen in the hydrotreating gas is another variable affecting both the desulfurization and denitrogenation of shale oil coker distillate. An analysis of the data from Runs 35-45 made with a shallow bed (1-1/2 inches deep) of Harshaw 1/8" cobalt molybdate catalyst pellets with 650°F. E.P. coker distillate charge stocks, and at 825°F., 1000 psig, a space velocity of 1.0 g/g hr., and a gas feed rate of 7500 SCF/bbl, showed that in the 50 to 100 mol percent hydrogen range, the amount of sulfur in the effluent oil varied linearly with the mol percent hydrogen in the hydrotreating gas. A regression equation for this portion of the line was reported by Holecek (16) as $S = 0.305\ H + k$,

where S = the percent sulfur removed from the charge stock
H = the mol percent hydrogen in the hydrotreating gas, and
k = the intercept dependent upon the physical characteristic of the reaction system.

By increasing the mol percent hydrogen in the recycle gas from 50 percent to 100 percent, the sulfur conversion was increased from 74 percent to 88 percent.

In a similar manner, a regression equation was found for the 50 to 100 mol percent hydrogen range for denitrogenation and this equation was $N = 0.523\ H + k'$,

where N = the percent nitrogen removed from the charge stock,
H = the mol percent hydrogen in the hydrotreating gas, and
k' = the intercept dependent upon the physical characteristics of the reaction system.

By increasing the mol percent hydrogen in the recycle gas from 40 percent to 100 percent, the nitrogen conversion was increased from 16 percent to 48 percent. These data are plotted in Figure 11 together with data from Runs 110-143. The data from Runs 110-143 (made with a deep bed (5-1/2 inches deep) of Peter Spence 1/8" cobalt molybdate catalyst pellets, with 750°F. E.P. coker distillate, and at 825°F., 1000 psig, a space velocity of 0.5 to 2.0 g/g hr., and a gas feed rate of 7500 SCF/bbl) show the same trend as the data from Runs 35-45. The two sets of lines are probably as close as can be expected, considering the wide variation in operating conditions between the two run series and considering that two different reactor designs were used.

C. Batch Treatments

Two types of batch treatments using the Parr bomb reaction apparatus were investigated as a possible means of denitrogenating coker distillate. For both treatments, a 750°F. E.P. coker distillate was used and the temperature in the bomb was kept at 842°F. In one case, 100 grams of coker distillate plus 100 grams of anhydrous caustic were heated and rocked for nine hours. This treatment removed only 12.6 percent of the nitrogen present in the charge stock.

In the second case, 100 cc of the coker distillate plus 100 cc of tetrahydronaphthalene were pressurized with hydrogen gas to 500 psig and heated for four hours. This treatment removed 5.3 percent of the nitrogen present in the charge stock. Therefore, neither of these processes appeared promising as a method for the denitrogenation of shale oil coker distillates.

D. Catalyst Study

Twelve different catalysts were used during the series of hydrotreating studies. These catalysts were, namely, Peter Spence cobalt molybdate 5/32-in. pellets, large-pore cobalt molybdate, HF-activated cobalt molybdate, molybdenum sulfide, platinum (Type 1000), MoO_3 deposited on DA-1 cracking catalyst, Oronite hydroforming catalyst, Harshaw cobalt molybdate 1/16-in. pellets, Harshaw molybdate 1/8-in. pellets, Harshaw molybdenum oxide 1/8-in. pellets promoted with indium, Harshaw molybdenum oxide 1/8-in. pellets promoted with palladium, and Union Oil cobalt molybdate 3/16-in. pellets. The specifications of these catalysts are given in Table VII. As a method of comparing the denitrogenation efficiency of these catalysts on shale oil coker distillates, the weight percent nitrogen in the effluent oil from the Peter Spence catalyst considered as the "standard" was divided by the weight percent nitrogen in the effluent oil from the catalyst being considered. In all instances, the catalyst being tested and the standard catalyst were checked under the same operating conditions, as nearly as possible. The tabulation of the efficiency values given in Table VIII shows that at both sets of operating conditions (Set No. 1: 825°F., 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 2500 SCF/bbl, a feed gas composition of 100 percent hydrogen, and 750°F. E.P. coker distillate; Set No. 2: 950°F., 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 4000 SCF/bbl, a feed gas composition of 100 percent hydrogen, and 750°F. E.P. coker distillate), the HF-activated cobalt molybdate was superior to all other catalysts investigated. At one set of conditions, Set No. 2 above, used in Runs 89 and 92, nitrogen conversion with the HF-activated cobalt molybdate catalyst was about 18 percent better than with the Peter Spence 1/8" cobalt molybdate catalyst pellets, the next best catalyst.

E. Kinetic Study

Before commencing on a study to determine if film diffusion was a variable or rate-controlling factor, three consecutive runs were made at identical operating conditions to check the degree of reproducibility possible at this stage in the studies. Figure 2 is a plot of the fraction of nitrogen in the charge stock converted versus the hours on stream. This figure shows that the reproducibility is excellent in spite of slight variations in the operating conditions, such as space velocity and temperature, and in spite of experimental error in nitrogen analysis determination. Early in the investigation it was found that the accuracy of nitrogen analyses was ± 0.005 weight percent and that the accuracy of sulfur analyses was ± 0.01 weight percent.

An examination of the data for most of the runs from Run 103 on will show a characteristic decrease in nitrogen conversion for the first two hours on stream. This is most likely due to absorption of oil by the catalyst. However, the only probable explanation for the cycling of the conversion curve for the remainder of the hours on stream is that non-isothermal conditions existed throughout the reactor during the course of the runs. It will be noted, though, that after approximately four hours of on-stream time, the cycling tends to occur at a fairly definite conversion value for any particular run. This mean conversion value was then used as the value characteristic of the operating conditions employed. In Table X are listed these mean conversion values for a majority of the runs from 108 to 147.

Next, a study was performed to determine if film diffusion of a gas flowing at a moderately high velocity through a catalyst bed with 1/8-in. catalyst pellets in an integral-type reactor was a controlling factor in the reaction rate. Figure 12 is a plot of the nitrogen conversion versus the grams of catalyst in the catalyst bed and shows that at a constant space velocity, a horizontal line is obtained. Figure 13 is a plot of the nitrogen conversion versus the reciprocal space velocity for two different weights of catalyst. Both of these plots show that film diffusion is a non-rate-controlling step (10), and that the mean cycling values for the various runs can be used with a sufficient degree of confidence.

With the data obtained from the kinetics study, four plots were prepared. Three of these plots, Figures 14, 15, and 16, drawn to determine the rates of the denitrogenation reaction being studied, show the effects of catalyst bed temperature, reactor pressure, and hydrotreating gas hydrogen content. The fourth, Figure 17, is an Arrhenius plot. The rate of chemical reaction may be expressed as the mass or moles of a product, or reactant consumed in any given time. This rate is a function of the concentrations of the components existing in the reaction mixture, temperature, pressure, and any variables which may be associated with the catalyst. For experimental investigations, it is highly desirable to keep the number of factors changing simultaneously to a minimum. If, when the logarithm of the concentration is plotted against the time a straight line is produced, the reaction is said to be first order. The slope of this straight line times 2.303 gives the specific reaction-rate constant. The plots, Figures 14, 15, and 16, indicated that the slowest reaction, the rate determining reaction, is about first order.

A first-order reaction is a reaction in which the rate is directly proportional to the concentration of the reacting substance. Mathematically it may be described as follows:

$$\frac{-dC_A}{dt} = kC_A$$

where C_A is the concentration of the reacting material A,
k is the proportionality constant,
t is the time, and

$\frac{-dC_A}{dt}$ is the rate at which the concentration decreases.

Integrating this equation gives the following equation:

$$-\ln C_A = kt + \text{constant, or}$$

$$-\log C_A = (k/2.303)t + \text{constant.}$$

If definite limits are used, the following equations are arrived at:

$$-\int_{C_1}^{C_2} \frac{dC}{C} = k\int_{t_1}^{t_2} dt$$

$$-\ln C_2 + \ln C_1 = k(t_2 - t_1)$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}$$

where C_1 is the concentration at time t_1, and
C_2 is the concentration at time t_2.

If "t" is defined as the elapsed time, if "C" is defined as the concentration after any elapsed time, and if "C_o" is defined as the initial concentration, the preceding equation may be written as follows:

$$k = \frac{2.303}{t} \quad \log \frac{C_o}{C}$$

This equation may also be written as shown below:

$$k = \frac{2.303}{t} \ \log \frac{a}{a-x}$$

where a = the initial quantity of reacting material A,
x = the amount reacting in time t, and
a-x = the amount remaining after time t.

As stated above, the specific reaction rate constant "k" was obtained by multiplying the slope of the straight line by 2.303. Using these constants for different temperatures, an Arrhenius plot was drawn, see Figure 17.

The basic Arrhenius equation, $k = se^{-E/RT}$, is obtained from the van't Hoff equation, $d(\ln K)/dT = \Delta H/RT^2$, which shows the variation of the equilibrium constant K with temperature, at constant pressure. Since the following relationships are true,

$$K = k/k'$$

where k = the forward reaction rate constant, and
k' = the reverse reaction rate constant,

and

$$\Delta H = \Delta H - \Delta H' = E - E'$$

where ΔH = the over-all heat of reaction, and
E = the activation energy,

the equation $d(\ln K)/dT = \Delta H/RT^2$ may be written as

$$d(\ln k)/dT - d(\ln k')/dT = E/RT^2 - E'/RT^2.$$

For the forward reaction alone, $d(\ln k)/dT = E/RT^2$. This equation upon integration gives $k = se^{-E/RT}$ where "s" is equal to the proportionality factor characteristic of the system and is termed the frequency factor, E is equal to the energy of activation in cal per mole, and $e^{-E/RT}$ is equal to the fraction of molecules with energy greater than E. This equation set in logarithmic form is

$$\ln k = \ln s - E/RT .$$

Therefore, a straight line is obtained when the logarithm of the specific reaction rate constant is plotted against the reciprocal of the absolute temperature.

Integrating the equation $d(\ln k)/dT = E/RT^2$ between definite limits gives

$$\log(k_2/k_1) = \frac{E}{2.303\ R} \ \frac{(T_2 - T_1)}{(T_2 . T_1)} ,$$

and, when the values for k_1 at one temperature and k_2 at another temperature are picked from the Arrhenius plot, Figure 17, and substituted in this equation, the activation energy was found to be 14,750 cal/mol. Substituting this value for the activation energy in the Arrhenius equation set in logarithmic form gave a value of 2.54×10^4 for the constant "s". Therefore, the Arrhenius equation showing the influence of temperature on shale oil denitrogenation became $k = 2.54 \times 10^4 e^{-14,750/RT}$

VI SUMMARY

The graphical method of analysis of the operating variables for the denitrogenation of shale oil coker distillates showed the following:

1. Depending upon the catalyst used, the minimum weight percent nitrogen in the effluent oil was obtained at a temperature between 440°C. and 468°C. (825°F. and 875°F.). For example, the nitrogen conversion was 69 percent at 850°F. using a 650°F. E.P. coker distillate, 5/32" Peter Spence cobalt molybdate catalyst pellets, 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 7500 SCF/bbl, and a feed gas composition of 65 percent hydrogen-35 percent methane. When 750°F. E.P. coker distillate, 1/16" Harshaw cobalt molybdate catalyst pellets, 100 percent hydrogen feed gas, and a space velocity of 0.25 g/g hr. were used, the nitrogen conversion was 85 percent at 825°F.

2. Decreasing the space velocity or increasing the reactor pressure, at least to 1000 psig, definitely improved denitrogenation. For example, be decreasing the space velocity from 1.50 g/g hr. to 0.50 g/g hr., the nitrogen conversion for one set of operating conditions (825°F., 1000 psig, a gas feed rate of 7500 SCF/bbl, a feed gas composition of 100 percent hydrogen, 1/8" Peter Spence cobalt molybdate catalyst pellets, and 750°F. E.P. coker distillate charge stock) was increased from 43.5 percent to 77.4 percent. Increasing the reactor pressure from 200 psig to 1000 psig increased the nitrogen conversion from 36.5 percent to 85.5 percent.

Product yield varied inversely with the catalyst-bed temperature but directly with the space velocity. When the reactor temperature was increased from 725°F. to 925°F., the product yield dropped from 99 to 71 weight percent; and, when the space velocity was increased from 0.25 to 1.0 g/g hr., the product yield increased from 82 to 91 weight percent.

3. The gas rate, provided it was above consumption level or about 2000 SCF/bbl, did not seem to affect nitrogen removal until it was above at least 5000 SCF/bbl. Even at 7500 SCF/bbl, the nitrogen conversion was only about 5 percent better than it was at 5000 SCF/bbl.

4. A lower level of desulfurization and denitrogenation accompanied a decreased hydrogen content of the recycle gas. As the mol percent hydrogen in the recycle gas increased from 50 to 100 percent, the sulfur conversion increased from 74 percent to 88 percent and the nitrogen conversion increased from 21 percent to 48 percent. The relationship is linear and both the nitrogen and sulfur content of the effluent oil vary in direct proportion to the hydrogen content of the recycle gas.

A nitrogen profile made of cuts obtained by the fractionation of a hydrogenated 650°F. E.P. coker distillate showed that the low-boiling materials contain almost no nitrogen, 0.02 weight percent. Reproducibility of results proved to be excellent when a deep catalyst bed, one about 5-1/2 inches deep and 1 inch across, was used and when the operating variables, particularly temperature and space velocity, were carefully controlled. Thermocouple location within the pyod and start-up procedure were found to be critical factors, also. Analyses of samples taken every 15 minutes near the beginning of several runs showed an apparent absorption of oil by the catalyst and then a cycling of the nitrogen conversion values when these values were plotted against the hours on stream. The nitrogen conversion values for a run in which regenerated catalyst was used were essentially the same as those for a run at the same conditions in which fresh catalyst was used. The life of the cobalt molybdate catalyst was shown to be in excess of 200 hours, for samples which were collected after 200 hours on stream and were analysed contained about the same amount of nitrogen as samples collected after 20 hours on stream.

Batch chemical treatments using either hot caustic or tetrahydronaphthalene in a rocking bomb at the processing conditions investigated did not result in effective removal of nitrogen from a 750°F. E.P. coker distillate. The nitrogen content of the charge stock was decreased by only 12.6 percent by hot caustic treatment and by only 5.3 percent by tetrahydronaphthalene treatment.

Of the twelve different catalysts studied in an effort to find one which would be significantly better than any of the ones presently being used for the denitrogenation of shale oil coker distillates, only a laboratory preparation of an HF-activated cobalt molybdate was found to be definitely superior. At the operating conditions 950°F., 1000 psig, a space velocity of 1.0 g/g hr., a gas feed rate of 4000 SCF/bbl, and a feed gas composition of 100 percent hydrogen, and with a 750°F. E.P. coker distillate charge stock, nitrogen conversion with the HF-activated cobalt molybdate catalyst was 89.5 percent, whereas for the next best catalyst, the Peter Spence cobalt molybdate catalyst, the conversion was 71.1 percent.

A short diffusion study performed prior to the kinetic study showed that film diffusion was not a rate controlling step in the reaction mechanism and was, therefore, a possible variable which could be neglected. Several plots were made of the log A/(A-x) versus time, as the reciprocal space velocity, and all of these plots indicated that the denitrogenation reaction is primarily one of first order. A plot of the specific reaction constant versus the reciprocal of the absolute temperature was drawn and the following Arrhenius equation was obtained:

$$k = 2.54 \times 10^4 e^{\frac{-14,750}{RT}}.$$

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IX APPENDIX

IX APPENDIX (continued)

IX APPENDIX (continued)

TABLE I

PROPERTIES OF THE CHARGE STOCKS

Charge Stock	Coker Distillates			
	650°F. E.P.*	750°F. E.P.*	850°F. E.P.*	Crude Shale Oil
Gravity, °API at 60°F.	35.4	25.6	25.4	21.0
Viscosity, S.U. at 130°F., sec.	31.0	46.0	43.0	90.0+
Carbon Residue, Ramsbottom, wt. percent	0.62	0.98	0.86	1.30
Sulfur, wt. percent	0.63	0.61	0.63	0.77
Nitrogen, wt. percent	1.65	1.90	1.95	2.07
ASTM Distillation, °F. (Corrected to 760 mm. Hg.)				
IBP	161	257	113	370
5%	253	362	295	----
10%	297	425	385	517
20%	354	484	475	577
30%	396	529	525	----
40%	432	571	570	----
50%	464	612	620	699 (cut point)
60%	492	647	665	
70%	522	682	710	
80%	554	716	760	
90%	591	742	805 (cut point)	
95%	616	754		
EP	672	754		
Recovery vol. %	98	97	89	50

*Charge stock: Gas-combustion crude shale oil

TABLE II

THERMODYNAMIC DATA

Compound	$H_{f\ 298}$ (g) kcal/mol	S°_{298} (g) E.U./mol
Thiophene	27.8**	69.3**
Hydrogen	0.0	31.21 (18)
n-Butane	-29.81 (18)	74.5 (18)
Hydrogen sulfide	-5.3 (5)	49.15 (18)
Pyrrole	29.67**	65.03**
Ammonia	-11.00 (5)	46.03 (25)
Co(c)	0.0	6.8 (24)
CoS(c)	-20.2 (19)	16.1 (24)
Co_2S_3(c)	-51.0 (19)	32.0*
Mo(c)	0.0	6.83 (25)
MoS_2(c)	-55.5	15.1 (19)
MoS_3(c)	-61.2 (19)	15.9 (26)
Pyrrolidine	-72.75***	70.43*
Pyrazole	165.06***	63.96*
Pyrazoline	104.86***	66.36*
Pyridine	33.63**	64.02*
Piperidine	-15.62***	71.22*
o-Picoline	27.16**	76.10*
Aniline	23.83*	62.6*
Nitrogen	0.0	45.79 (25)
Methane	-17.89 (30)	44.50 (25)
Ethane	-20.24 (30)	54.85 (47)
Propane	-24.82 (30)	64.70 (18)
n-Pentane	-35.00 (47)	83.40 (47)
n-Hexane	-39.96 (47)	92.83 (47)

*Estimated values.

**Values obtained from Chemical Abstracts.

***Values calculated from heats of combustion, the values for which were obtained from Lange (30) or Hodgman (19).

TABLE III

CRITICAL CONSTANTS

Compound	T_c (°K)	P_c (atm)
Thiophene	590	48
Hydrogen	33.1	12.8
n-Butane	426	36
Hydrogen sulfide	373.4	88.9
Pyrrole	636*	61.5*
Ammonia	405.4	111.5
Pyrrolidine	575*	48.4*
Pyrazole	716*	73.8*
Pyrazoline	654*	69.0*
Pyridine	617	60.0
Piperidine	600*	32.8*
O-Picoline	641	43.0*
Aniline	699	52.4
Nitrogen	125.9	33.5
Methane	190.5	45.8
Ethane	305.1	48.8
Propane	368.6	43
n-Pentane	470.2	33.0
n-Hexane	507.8	29.5

*Values calculated by Meissmer and Redding method of parachors (35).

The remainder of the values were obtained from Perry (42).

TABLE IV

THERMODYNAMIC DATA

Compound Considered	ΔH_{298} kcal/mol	ΔS_{298} E.U./mol	ΔF_{298} cal/mol	F_{713} cal/mol	K_{eq} 290°K.	K_{eq} 713°K.	Reaction Number
Thiophene	−62.90	−70.49	−41,910	−12,610	7.94×10^{30}	7.59×10^{3}	(9)
Pyrrole	−60.51	−32.13	−50,950	−37,560	2×10^{37}	3.02×10^{11}	(1)
Pyrrolidine	31.91	−12.32	35,580	40,700	6.31×10^{-27}	3.16×10^{-10}	(2)
Pyrazole	−211.84	−63.25	−193,110	−166,840	3.16×10^{141}	10^{51}	(3)
Pyrazoline	−151.74	−34.40	−141,470	−127,240	3.16×10^{103}	7.94×10^{38}	(4)
Pyridine	−79.66	−90.64	−52,660	−15,060	3.98×10^{38}	4.07×10^{4}	(5)
Piperidine	−35.37	−10.39	−32,270	−25,710	4.27×10^{23}	7.25×10^{7}	(6)
α-Picoline	−78.15	−93.29	−50,350	−11,850	7.94×10^{36}	4.27×10^{3}	(7)
Aniline	−74.82	−79.79	−51,020	−17,820	5.01×10^{37}	3.02×10^{5}	(8)

TABLE IV (continued)

ACTIVITY COEFFICIENTS AND K_N

$C_4H_4S(g) + 4H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + H_2S(g)$

Pressure atm	Temp. °C.	K_{eq}	$\gamma n\text{-}C_4H_{10}$	γH_2S	γC_4H_4S	γH_2	K_γ	K_N
1	25	7.94×10^{30}	0.9691	0.9917	0.9391	1.0006	1.022	7.77×10^{30}
70	440	7.59×10^{3}	0.9114	0.7686	1.0180	0.916	0.916	2.84×10^{9}
100	440	"	0.8756	0.7660	0.6866	1.026	0.883	8.6×10^{9}
200	440	"	0.7670	0.5864	0.4710	1.052	0.778	7.8×10^{10}
400	440	"	0.5153	0.3440	0.2223	1.107	0.531	9.15×10^{10}
600	440	"	0.4509	0.2019	0.1048	1.165	0.470	3.49×10^{11}

$C_4H_5N(g) + 4H_2(g) \rightarrow n\text{-}C_4H_{10}(g) + NH_3(g)$

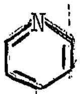
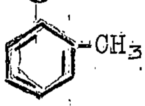
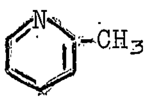
Pressure atm	Temp. °C.	K_{eq}	$\gamma n\text{-}C_4H_{10}$	γNH_3	γC_4H_5N	γH_2	K_γ	K_N
1	25	2×10^{37}	0.9691	0.9914	0.9958	1.0006	0.965	2.07×10^{37}
70	440	3.02×10^{11}	0.9114	0.9768	0.7642	0.916	1.082	9.57×10^{16}
100	"	"	0.8756	0.7148	0.6810	1.026	0.831	3.64×10^{17}
200	"	"	0.7670	0.5115	0.4640	1.052	0.690	3.51×10^{18}
400	"	"	0.5153	0.2612	0.2153	1.107	0.487	4.63×10^{19}
600	"	"	0.4509	0.1337	0.1000	1.165	0.327	1.995×10^{20}

TABLE V

EXAMPLES OF METHODS OF ESTIMATION USED
TO DETERMINE ENTROPIES AND HEATS OF FORMATION.

Method 1.

Example (a) Heat of Formation for o-Picoline

		$H_{f_{298}}$ (g) kcal/mol	
	Benzene	19.820	13.81 Difference
	Pyridine	33.63**	
	Toluene	11.95	13.81 Difference
	o-Picoline	25.76* 27.16**	

Example (b) Entropy of o-Picoline

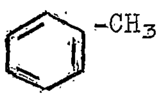
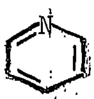
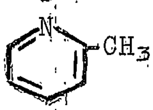
		S_{298} (g) EU/mol	
	Benzene	64.34	12.08 Difference
	Toluene	76.42	
	Pyridine	64.02*	12.08 Difference
	o-Picoline	76.10*	

TABLE V (continued)

EXAMPLES OF METHODS OF ESTIMATION USED
TO DETERMINE ENTROPIES AND HEATS OF FORMATION.

Method 2.

Example (a) Entropy of Pyrrolidine

Pyrrole

Pyrrolidine

S°_{298} = 65.03 EU/mol S°_{298} = 70.43* EU/mol

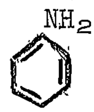
(The conversion of a single bond into a double bond equals +2.7e, where e equals the number of bonds in the molecule.

65.03 + 2(2.7) = 70.43*)

Method 3.

Example (a) Entropy of Aniline

Benzene



Aniline

S_{298} (l) = 41.9 EU/mol S_{298} (l) = 45.8 EU/mol
(g) = 64.34 EU/mol (g) = 65.* EU/mol

(The change in molal entropy for the substitution of an NH_2 group for an H is 0.0 for liquids, but the change for gases is not known exactly.)

TABLE V (continued)

EXAMPLES OF METHODS OF ESTIMATION USED
TO DETERMINE ENTROPIES AND HEATS OF FORMATION.

Method 4.

Example (a) Entropy of Aniline

$$S_{298}(g) = S_{298}(l) + \frac{\Delta H_{298}}{298} + R\ln p_{298}$$

$$= 45.8 + 9650/298 + 1.99(2.3)\ \log 0.3/760$$

$$= 62.6^{*}\ \text{EU/mol}$$

Method 5.

Example (a) Heat of formation for methylamine

$$CO_2(g) + 2\text{-}1/2H_2O(g) + 1/2N_2(g) \rightarrow CH_3NH_2(g) + 2\text{-}1/4O_2(g) \qquad \Delta H = 256.1\ \text{k.cal}$$

$$C(dia) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -94.05\ \text{k.cal}$$

$$\underline{2\text{-}1/2H_2(g) + 1\text{-}1/4O_2(g) \rightarrow 2\text{-}1/2\ H_2O(g)} \qquad \Delta H = 5(-34.19)\ \text{k.cal}$$

$$C(dia) + 2\text{-}1/2H_2(g) + 1/2N_2(g) \rightarrow CH_3NH_2(g)$$

$$\Delta H = -8.90\ \text{k.cal/mol}$$

The value for the heat of formation of an organic compound is equal to the sum of the heats of formation of the products of combustion less the heat of combustion of the organic compound.

*Estimated values
**Value from Chemical Abstracts

TABLE VI

ASTM DISTILLATION RESULTS

Operating Conditions:

Temperature	875°F.
Pressure	1000 psig.
Space Velocity	1.0 g/g hr.
Gas Rate	7500 SCF/bbl.
Gas Composition	65% H_2
Charge Stock	650°F. E.P. coker distillate
Catalyst	

	Indium MoO_3 °F.	Palladium MoO_3 °F.	Peter Spence Cobalt MoO_3 °F.	Harshaw Cobalt MoO_3 °F.
IBP	158	130	134	153
10%	270	189	199	228
50%	417	346	364	391
90%	563	538	548	566
EP	625	623	614	640
Recovery (volume)	98%	98%	97%	98%

(Temperatures corrected to 760 mm Hg)

Operating Conditions:

Temperature	825°F.
Pressure	1000 psig
Space Velocity	1.0 g/g hr.
Gas Rate	7500 SCF/bbl.
Catalyst	Harshaw cobalt molybdate 1/8" pellets
Charge Stock	650°F. E.P. coker distillate
Gas Composition	

	100% H_2 °F.	60% H_2 °F.	47% H_2 °F.	66% H_2 °F.	83% H_2 °F.	40% H_2 °F.
IBP	150	144	138	138	132	148
10%	228	224	220	218	228	236
50%	400	391	416	414	416	412
90%	564	562	582	580	580	584
EP	630	634	646	624	606	618
Recovery (volume)	97%	98%	97%	97%	96%	97%

TABLE VII

COMPOSITION AND IDENTIFICATION OF CATALYSTS

Catalyst Name and Composition	Identification Code	Catalyst Manufacturer
Cobalt molybdate 9.5% MoO_3 3.0% CoO 5.0% SiO_2 2.0% Graphite 80.5% Al_2O_3	Co-Mo-0201-T-1/8" Co-Mo-0201-T-1/16" Co-Mo-0201-T-3/16"	Harshaw Chemical Co.
Cobalt molybdate 2.5% CoO 14.0% MoO_3 Graphite base	Graphite-type pellets 5/32" diameter	Peter Spence & Sons, Ltd.
Molybdenum oxide* 16% MoO_3 79% Al_2O_3 5% SiO_3	Mo-0203-T-1/8"	Harshaw Chemical Co.
Cobalt molybdate $CoMoO_4$-Al_2O_3 Large pore	#2127-2	Humble Oil and Refining Co.
Cobalt molybdate 2.5% CoO 14.0% MoO_3	Calcined stearate-type pellets 1/8" diameter R.D. 2846A R.D. 2919	Peter Spence and Sons, Ltd.
Cobalt molybdate	3/16" diameter pellets	Union Oil Co.
Oronite hydroforming catalyst		Esso Research
HF-activated cobalt molybdate		Esso Research
Platinum (Type 1000)		Esso Research

TABLE VII (continued)

COMPOSITION AND IDENTIFICATION OF CATALYSTS

Catalyst Name and Composition	Identification Code	Catalyst Manufacturer
MoO_3 deposited on DA-1 cracking catalyst 86.5% DA-1 13.5% MoO_3	#9816	Esso Research
Molybdenum sulfide		Esso Research
Zinc oxide-MgO-MoO_3 Equimolar dry mix	#9817	Esso Research

*Used for the preparation of indium and palladium promoted catalysts.

TABLE VIII

CATALYST ACTIVITY

Catalyst	Activity at Operating Condition #1	#2
Peter Spence cobalt molybdate, 5/32-in. pellets	1.00 (Standard)	1.00 (Standard)
Large-pore cobalt molybdate	0.71	0.82
HF-activated cobalt molybdate	1.30	2.70
Molybdenum sulfide	0.59	-
Platinum (Type 1000)	0.59	0.51
MoO_3 deposited on DA-1 cracking catalyst	0.50	0.37
Oronite hydroforming catalyst	0.66	0.75
Harshaw cobalt molybdate 1/16-in. pellets	0.78*	-
Harshaw cobalt molybdate 1/8-in. pellets	0.70*	0.59*
Harshaw molybdenum oxide 1/8-in. pellets promoted with indium	0.36*	0.49*
Harshaw molybdenum oxide 1/8-in. pellets promoted with palladium	0.70*	1.00*
Union Oil cobalt molybdate 3/16-in. pellets	0.43*	0.33*

TABLE VIII (continued)

CATALYST ACTIVITY

Operating Variable	Condition #1	Condition #2
Catalyst-bed temperature, °C.	440	510
Reactor pressure, psig	1000	1000
Space velocity, g/g hr.	1.0	1.0
Gas rate, SCF/bbl.	2500	4000
Gas composition, % H_2	100	100
Charge stock, 750°F. E.P. coker distillate		

*Slight variation from standard operating conditions existed, so values were corrected.

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
1	A	0- 8	385	386	500			1.788
	B	8-16	385	386	"	98	0.497	1.810
	C	16-24	381	385	"			1.820
2	A	26-34	417	413	"			1.820
	B	34-42	416	413	"	99	0.435	1.735
	C	42-50	413	413	"			
3	A	50-58	439	441	"			
	B	58-66	441	441	"	95	0.417	1.683
	C	66-74	440	441	"			
4	A	74-82	468	467	"		0.390	1.772
	B	82-90	466	468	"	92	0.402	1.800
	C	90-98	460	467	"		0.505	1.897
5	A	98-106	496	496			0.604	2.185
	B	106-114	494	495	"	87	0.852	2.225
	C	114-116	496	498	"		0.796	2.245

Catalyst - Union Oil Co. CoMo, 3/16"
Catalyst Wt. - 100 g.
Charge Stock - 850°F. E.P. Coker Distillate
Reactor Number - H-K
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl) - 7500
Mol Percent H_2 in Feed Gas - 65

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
6	A	2-10	386	386	1000	---	0.202	1.662
	B	10-18	384	385	"	95	0.253	1.590
	C	18-26	386	387	"	99	0.308	1.630
7	A	26-34	417	413	"	100	0.129	1.720
	B	34-42	416	409	"	97	0.176	1.525
	C	42-50	412	414	"	98	0.209	1.510
8	A	50-58	436	438	"	96	0.188	1.372
	B	58-66	440	440	"	96	0.107	1.242
	C	66-74	437	440	"	89	0.214	1.340
9	A	74-82	465	469	"	91	0.152	0.964
	B	82-90	470	465	"	---	0.123	0.850
	C	90-98	467	466	"	89	0.087	1.030
10	A	98-106	493	495	"	77	0.112	1.165
	B	106-114	498	496	"	73	0.189	1.651
	C	114-122	497	501	"	76	0.276	1.663

Catalyst - Union Oil Co. CoMo, 3/16"
Catalyst Wt. - 100 g.
Charge Stock - 850°F. E.P. Coker Distillate
Reactor Number - H-K
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl) - 7500
Mol Percent H_2 in Feed Gas - 65

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht.(°C)	Temperature Cat.(°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
12	A	2-10	384	386	1000	99	0.440	1.340
	B	10-18	385	387	"	99	0.478	1.345
	C	18-26	388	388	"	100	0.425	1.375
13	A	26-34	413	415	"	99	0.308	1.256
	B	34-42	413	416	"	98	0.318	1.210
	C	42-50	413	417	"	97	0.304	1.252
14	A	50-58	439	441	"	97	0.283	1.070
	B	58-66	435	442	"	96	0.294	1.004
	C	66-74	441	441	"	96	0.227	1.023
15	A	74-82	465	476	"	---	0.218	0.870
	B	82-90	466	469	"	---	0.195	0.940
	C	90-98	467	473	"	93	0.172	0.927
16	A	98-106	486	499	"	68	0.308	0.870
	B	106-114	494	497	"	71	0.342	1.020
	C	114-122	488	497	"	71	0.186	1.162

Catalyst - Harshaw's Molybdenum Oxide
promoted with Indium; 1/8".
Catalyst Wt. - 100 g.
Charge Stock - 650°F. E.P. Coker Distillate.
Reactor Number - H-K.
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl - 7500.
Mol Percent H_2 in Feed Gas - 65.

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
17	A	2-10	385	387	1000	98	0.535	1.203
	B	10-18	386	386	"	96	0.283	1.194
	C	18-26	385	386	"	100	0.251	1.194
18	A	26-34	415	415	"	87	0.132	1.000
	B	34-42	413	412	"	---	---	0.961
	C	42-50	411	415	"	97	0.134	0.960
19	A	50-58	438	440	"	98	0.072	0.795
	B	58-66	445	441	"	95	0.086	0.802
	C	66-74	439	437	"	97	0.084	0.807
20	A	74-82	465	468	"	88	0.061	0.527
	B	82-90	469	463	"	80	---	0.588
	C	90-98	464	464	"	92	0.041	0.651
21	A	98-106	494	492	"	83	---	0.409
	B	106-114	494	494	"	74	0.022	0.527
	C	114-122	498	497	"	70	---	0.601

Catalyst - Harshaw's Molybdenum Oxide
promoted with Palladium; 1/8"
Catalyst Wt. - 100 g.
Charge Stock - 650°F. E.P. Coker Distillate
Reactor Number - H-K
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl) - 7500
Mol Percent H_2 in Feed Gas - 65

TABLE IX — OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
22	A	2-10	390	386	1000	97		1.092
	B	10-18	387	388	"	92	0.076	1.031
	C	18-26	384	386	"	98		1.026
23	A	26-34	410	414	"	97		0.755
	B	34-42	415	408	"	100	0.032	0.775
	C	42-50	414	417	"	99		0.682
24	A	50-58	437	443	"	94		0.523
	B	58-66	441	441	"	94	0.054	0.569
	C	66-74	441	439	"	96		0.566
25	A	74-82	466	469	"	87		0.371
	B	82-90	468	470	"	81	0.018	0.413
	C	90-98	464	464	"	83		0.517
26	A	98-106	505	496	"	65		0.427
	B	106-114	497	493	"	69	0.022	0.561
	C	114-122	491	497	"	72		0.511

Catalyst - Peter Spence & Sons, Ltd. CoMo; 5/32"
Catalyst Wt. - 100 g.
Charge Stock - 650°F. E.P. Coker Distillate
Reactor Number - H-K
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl) - 7500
Mol Percent H_2 in Feed Gas - 65

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
27	A	0-8	382	387	1000	98		1.300
	B	8-16	390	386	"	98	0.327	1.488
	C	16-24	387	386	"	----		1.325
28	A	24-32	406	416	"	99		1.070
	B	32-40	415	411	"	----	0.153	1.048
	C	40-48	413	413	"	97		1.080
29	A	48-56	439	440	"	98		0.772
	B	56-64	440	445	"	85	0.079	0.776
	C	64-72	443	440	"	91		0.863
30	A	72-80	460	465	"	83		0.659
	B	80-88	465	473	"	78	0.057	0.642
	C	88-96	465	470	"	78		0.756
31	A	96-104	490	516	"	49		0.700
	B	104-112	501	495	"	62	0.076	0.913

Catalyst - Harshaw's CoMo; 1/8"
Catalyst Wt. - 100 g.
Charge Stock - 650°F. E.P. Coker Distillate
Reactor Number - H-K
Space Velocity - 1.0 g/g hr.
Gas Flow Rate (SCF/bbl) - 7500
Mol Percent H_2 in Feed Gas - 65

TABLE IX --OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Mol % H_2 in Feed Gas	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
32	A	24-32	442	445	0.972	100.0	92	0.089	0.635
	B	32-40	445	438	1.000	100.0	92	0.084	0.670
	C	40-48	437	439	0.990	100.0	94	0.084	0.684
33	A	24-32	439	443	0.998	76.8	94	0.086	0.807
	B	32-40	438	441	1.006	81.8	96	0.090	0.771
	C	40-48	445	442	0.992	82.2	94	0.095	0.792
34	T	24-28	438	439	1.112	100.0	86	0.049	0.410
	A	32-40	436	443	0.989	60.2	88	0.075	0.727
	B	40-48	440	435	0.961	55.0	91	0.064	0.739
	C	48-56	443	441	0.987	60.2	88	0.053	0.687
35	T	24-28	441	439	1.055	100.0	88	0.163	1.072
	A	32-40	437	443	0.994	41.2	88	0.296	1.386
	B	40-48	441	442	1.000	46.3	87	0.266	1.472
	C	48-56	440	440	1.008	47.2	88	0.277	1.489
36	TR	88-92	434	434	1.020	100.0	93	0.096	0.914
	AR	100-104	435	437	1.031	66.4	94	0.207	1.305
	BR	104-108	441	444	1.000	67.2	91	0.136	1.257
	CR	108-112	444	440	0.980	64.9	90	0.151	1.306
37	T	120-124	446	443	1.028	100.0	93	0.147	1.104
	A	132-136	436	435	0.987	83.4	94	0.146	1.285
	B	136-140	436	440	1.040	82.1	90	0.153	1.142
	C	140-144	437	440	1.025	84.6	93	0.105	1.117

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate

Reactor No.: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl: 7500

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Mol % H_2 in Feed Gas	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
38	A	152-156	437	442	0.965	100.0	96	0.112	1.015
	B	156-160	442	441	0.973	100.0	94	0.074	1.009
	C	160-164	441	437	1.012	100.0	90	0.124	1.032
39	A	172-176	435	439	0.987	38.5	91	0.184	1.357
	B	176-180	438	444	0.942	39.5	92	0.155	1.762
	C	180-184	440	441	0.950	40.8	89	0.170	1.430
40	T	24-28	444	441	0.950	100.0	94	0.087	0.902
	A	38-46	442	440	0.978	81.0	96	0.075	0.944
	B	46-54	443	441	0.959	81.1	96	0.076	0.971
	C	54-62	439	437	0.973	81.8	95	0.062	0.977
41	TA	12-16	440	440	1.025	100.0	97	---	0.727
	TB	16-20	438	438	1.054	"	96	---	0.796
	TC	20-24	441	444	1.030	"	96	---	0.741
	TD	24-28	441	440	1.015	"	97	---	0.803
	TE	28-32	449	434	1.038	"	97	---	0.839
	TF	32-36	443	437	1.079	"	93	---	0.718
	TG	36-40	441	441	1.051	"	97	0.0272	0.686

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate

Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl: 7500

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Mol % H_2 in Feed Gas	Yield (Percent of Charge)	Product Data Wt. % S	Product Data Wt. % N
41	A	40-44	438	446	---	---	--	---	0.769
	B	44-48	441	446	---	---	--	---	0.907
	C	48-52	442	440	0.980	---	94	---	1.060
	D	52-56	444	446	0.985	---	93	---	1.034
	E	56-60	441	439	1.018	---	97	---	1.083
	F	60-64	445	442	0.996	---	95	---	1.030
	G	64-68	444	438	0.996	---	96	---	1.065
	H	68-72	436	435	1.015	---	96	---	1.028
	I	72-76	442	438	1.030	70.2	93	0.0518	0.997
42	T	84-88	441	440	1.013	100.0	98	0.0318	0.722
	A	104-112	432	436	0.992	62.5	96	0.0973	1.100
43	T	124-132	442	442	0.983	100.0	97	0.0230	0.71
	A	144-152	438	439	1.018	57.6	96	0.0801	1.14
44	T	164-172	440	437	0.960	100.0	100	0.0467	0.80
	A	184-192	435	441	0.961	50.2	95	0.0944	1.15
45	T	192-204	440	440	0.961	100.0	94	---	0.76

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate

Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl: 7500

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
46	A	5-9	447	438	0.260	82	0.180
	B	9-13	441	440	0.270	91	0.154
	C	13-17	439	437	0.232	82	0.152
	D	17-21	439	440	0.217	86	0.110
	E	21-25	444	439	0.175	94	0.112
	F	25-29	442	438	0.245	84	0.102
	G	29-33	443	441	0.242	81	0.094
	H	33-37	441	438	0.245	86	0.100
	I	37-41	436	443	0.237	87	0.111
	J	41-45	438	441	0.227	86	0.090
	K	45-49	439	440	0.217	80	0.100
	L	49-53	435	439	---	--	0.096

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker-Distillate
Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl: 7500
Mol Percent H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
47	A	0-4	431	460	---	--	0.338
	B	4-6	443	454	1.072	97	0.210
	C	6-8	444	441	1.362	81	0.280
	D	8-10	437	426	1.424	71	0.363

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 300 g.
Charge Stock: 650°F. E.P. Coker Distillate
Reactor Number: H-K

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
48	A	2-6	430	476	0.995	90	0.538
	B	6-10	420	446	1.000	89	0.757
	C	10-14	417	440	0.968	93	0.811
	D	14-18	410	438	0.986	93	0.859
	E	18-22	410	443	1.002	94	0.842
	F	22-26	420	441	0.974	90	0.828
	G	26-30	413	444	0.986	94	0.811
	H	30-34	415	435	0.985	94	0.818
	I	34-38	414	439	1.005	93	0.882
	J	38-42	424	448	1.028	92	0.785
	K	42-46	422	442	0.918	97	0.869
	L	46-50	421	441	---	--	0.895

Catalyst: Harshaw Co., CoMo; 1/8"
Catalyst Wt.: 200 g.
Charge Stock: 650°F. E.P. Coker Distillate
Reactor Number: H-K

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
49	A	4-8	442	441	0.990	--	0.187
	B	8-12	441	439	0.980	78	0.206
	C	12-16	439	440	0.986	77	0.206
	D	16-20	441	441	---	78	0.194
	E	20-24	438	440	0.991	78	0.215
	F	24-28	439	438	0.920	85	0.224
	G	28-32	445	443	0.887	83	0.234
	H	32-36	442	439	0.899	86	0.238
	I	36-40	440	439	0.849	84	0.257
	J	40-44	437	439	1.000	86	0.227
50	A	2-6	446	442	0.960	93	0.257
	B	6-10	444	440	0.980	92	0.233
	C	10-14	443	441	0.960	93	0.249
	D	14-18	441	437	0.948	94	0.240
	E	18-22	437	442	1.028	89	0.234
	F	22-26	440	440	0.995	94	0.279
	G	26-30	442	440	1.041	88	0.269
	H	30-34	447	439	0.976	92	0.292
	I	34-38	443	441	0.970	95	0.299
	J	38-42	440	441	---	94	0.330
	K	42-46	436	440	1.029	94	0.313
	L	46-50	437	439	1.006	87	0.326

Catalyst: Harshaw Co., CoMo; 1/16"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate
Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol Percent H_2 in Feed Gas: 100

TABLE IX --OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
51	A	3-11	452	442	0.292	66	0.516
	B	11-19	453	439	0.263	82	0.151
	C	19-27	438	441	0.275	70	0.136
	D	27-35	448	441	0.251	81	0.182
	E	35-43	441	440	0.232	83	0.097
	F	43-51	437	441	0.161	82	0.069
	G	51-59	440	440	0.236	88	0.120
	H	59-67	440	441	0.310	74	0.219
	I	67-75	440	441	0.314	90	0.221
	J	75-83	440	440	0.277	85	0.165
	K	83-91	441	441	0.312	83	0.153
	L	91-99	438	440	0.319	82	0.148
	M	99-108	440	441	0.300	85	0.163
	N	108-115	440	440	0.359	85.3	0.154
	O	115-123	438	442	0.298	89.1	0.188
	P	123-131	442	442	0.319	77.6	0.173
	Q	131-139	441	440	0.321	--	---
	R	139-147	438	441	0.322	79.0	0.151

Catalyst: Harshaw Co., CoMo; 1/16"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate
Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol Percent H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
55	31	409	412	1000	1.148	--	1.129
56	31-46	408	413	"	0.496	--	0.786
57	46-63	413	413	"	0.271	--	0.535
58	63-83	441	438	"	0.956	--	0.674
59	83-96	432	440	"	0.700	91	0.690
60	96-115	441	440	"	0.241	84	0.279
61	115-130	465	466	"	1.060	79	0.960
62	130-143	460	467	"	0.509	76	0.657
63	143-164	467	470	"	0.244	64	0.446
64	164-174	470	470	1200	0.281	65	0.252
65	174-190	440	440	1200	0.284	89	0.412

Catalyst: Harshaw Co. CoMo; 1/16"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate

Reactor Number H-K
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Reactor Pressure (psig)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
66	190-222	442	442	1000	0.982	90	0.222
67	222-254	444	440	1000	0.438	89	0.0414
68	254-278	444	439	1000	0.316	93	0.0413

Catalyst: Harshaw Co. CoMo; 1/16"
Catalyst Wt.: 100 g.
Charge Stock: 650°F. E.P. Coker Distillate
Hydrogenated

Reactor Number: H-K
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
72	A	31-36	440	442	0.513	79	0.874
	B	36-44	443	441	0.616	73	0.816
	C	61-70	439	439	0.129	90	0.663
	D	70-79	440	442	0.237	90	0.563
	E	79-92	441	439	0.084	79	0.510
	F	92-100	439	442	0.591	--	0.868
	G	100-108	443	440	0.195	--	0.727
	H	108-116	440	440	0.198	70	0.680
	I	116-124	438	442	0.349	83	0.850
	J	124-132	---	---	0.240	79	1.031
	K	132-140	435	436	0.120	70	0.689
	L	140-148	440	439	0.090	--	0.465
72	M	148-156	439	440	0.105	67	---
	N	156-164	441	441	0.096	66	0.465
	O	164-172	440	441	0.105	64	0.455
	P	172-180	441	440	0.126	63	0.470
	Q	180-188	440	439	0.091	--	0.470
	R	188-196	441	441	0.087	--	0.470
	S	196-204	441	441	0.108	66	0.477
	T	204-212	440	439	0.119	64	0.467
	U	212-228	441	441	0.096	69	0.467
	V	228-244	440	440	0.170	68	0.534
	W	244-260	441	441	0.086	--	0.519
	X	260-276	440	441	---	68	---
	Y	276-292	441	440	0.091	--	0.401
	Z	292-308	439	441	---	69	0.713

Catalyst: Harshaw Co. CoMo;
3/16" ground to 10/14 mesh
Catalyst Wt.: 100 g.
Charge Stock: Crude Shale Oil

Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
72	AA	324-340	441	441	0.231	--	0.830
	BB	340-348	439	441	0.103	--	0.859
	CC	348-364	441	440	0.067	--	0.425
	DD	364-380	440	440	0.079	--	0.425
	EE	380-396	440	440	0.130	--	0.737
	FF	396-412	440	440	0.114	--	0.191
	GG	412-428	440	441	0.337	--	0.437

Catalyst: Harshaw Co. CoMo;
3/16" ground to 10/14 mesh
Catalyst Wt.: 100 g.
Charge Stock: Crude Shale Oil

Reactor Number: H-K
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
74	A	238-246	439	440	0.211	80	---
	B	246-254	441	443	0.173	80	---
	C	254-260	439	440	0.186	80	---
	D	260-267	440	441	0.203	80	0.650
	E	267-273	439	441	0.206	80	0.698
	F	273-279	441	440	0.232	80	---
	G	279-282	439	441	0.189	80	---
	H	282-288	440	440	0.242	85	0.800
	I	288-294	440	443	0.249	85	0.958
	J	294-300	438	440	0.314	84	---

Catalyst: Harshaw Co. CoMo; 1/16"
Catalyst Wt.: 200 g.
Charge Stock: Crude Shale Oil
Reactor Number: H-K

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
85	A	15-17	442	438	1.017	88	0.802
	B	23-25	439	439	"	"	0.945
	C	32-34	440	440	"	"	0.960
	D	40-42	442	440	"	"	0.980
	E	47-49	441	439	"	"	---
86	A	0- 2	435	434	1.045	95	0.749
	B	2- 4	436	437	"	"	0.807
	C	4- 6	444	447	"	"	0.678
	D	6- 8	439	439	"	"	0.807
	E	8-12	439	442	"	"	0.707
	F	12-20	438	439	"	"	0.826
	G	20-28	441	441	"	"	0.870
	H	28-36	440	439	"	"	0.922
	I	36-44	440	442	"	"	0.928
87	A	0- 2	430	444	0.987	97	0.598
	B	2- 4	439	448	"	"	0.617
	C	4- 6	440	443	"	"	0.618
	D	6- 8	443	439	"	"	0.689
	E	8-12	439	438	"	"	0.702
	F	12-19	440	440	"	"	0.713
	G	19-24	443	443	"	"	0.819

Catalyst: Peter Spence CoMo; 5/32"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX — OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
88 A	0- 2	435	437	1.010	--	0.798
B	2- 4	442	442	"	--	0.843
C	4- 6	443	444	"	--	0.785
D	6- 8	442	444	"	--	0.809
E	8-12	441	442	"	--	0.863
F	12-20	440	440	"	--	0.871
G	20-28	441	440	"	--	0.885
89-I-A	0- 2	438	443	1.030	98.4	1.008
B	2- 4	441	441	"	"	0.856
C	4- 6	438	443	"	"	0.762
D	6- 8	441	448	"	"	0.742
E	8-12	441	444	"	"	0.748
F	12-20	440	442	"	"	0.791
G	20-24	439	440	"	"	0.825

Catalyst: Peter Spence CoMo; 5/32"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
89-II-A	27-29	503	520	1.017	81.3	0.325
B	29-31	506	514	"	"	0.501
C	31-33	520	526	"	"	0.656
D	33-35	507	502	"	"	0.523
E	35-39	511	511	"	"	0.536
F	39-47	509	509	"	"	---

Catalyst: Peter Spence CoMo; 5/32"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
91-I-A	0- 2	477	491	1.040	96.7	1.100
B	2- 4	443	442	"	"	1.019
C	4- 6	443	443	"	"	1.020
D	6- 8	441	436	"	"	1.118
E	8-12	441	439	"	"	1.080
F	12-20	442	441	"	"	1.170
G	20-26	441	440	"	"	---

Catalyst: Humble Large-pore CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
91-II-A	30-32	495	481	1.050	90.0	1.074
B	32-34	508	502	"	"	0.864
C	34-36	479	461	"	"	1.123
D	36-38	514	506	"	"	0.698
E	38-42	508	511	"	"	0.673
F	42-50	508	507	"	"	0.670

Catalyst: Humble Large-pore CoMo; 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
92-I-A	0- 2	435	439	0.960	96.1	0.551
B	2- 4	435	434	"	"	0.578
C	4- 6	436	403	"	"	0.500
D	6- 8	440	441	"	"	0.536
E	8-12	440	441	"	"	0.578
F	12-20	441	442	"	"	0.583
G	20-28	440	440	"	"	0.670

Catalyst: Esso HF-activated CoMo
Catalyst Wt.: 90 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
92-II-A	31-33	511	530	0.975	80.0	0.104
B	33-35	506	509	"	"	0.147
C	35-37	509	510	"	"	0.203
D	37-39	513	514	"	"	0.181
E	39-43	510	507	"	"	0.206
F	43-51	511	508	"	"	0.210
G	51-59	512	514	"	"	0.198

Catalyst: Esso HF-activated CoMo
Catalyst Wt.: 90 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
93-I-A	0- 2	439	436	1.000	95.0	0.576
B	2- 4	442	441	"	"	0.863
C	4- 6	441	440	"	"	0.994
D	6- 8	443	444	"	"	1.038
E	8-12	437	440	"	"	1.238
F	12-20	436	431	"	"	1.413
G	20-25	453	444	"	"	1.528

Catalyst: Esso MoS_2
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
93-II-A	31-33	509	511	1.020	85.0	1.538
B	33-35	510	511	1.020	85.0	1.747

Catalyst: Esso MoS_2
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
94-I-A	0-2	459	442	1.010	92.0	1.629
B	2-4	439	439	"	"	---
C	4-6	440	439	"	"	1.723
D	6-8	439	440	"	"	---
E	8-12	440	440	"	"	---
F	12-20	440	441	"	"	1.645

Catalyst: $ZnO-MgO-MoO_3$ No. 9817
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
94-II-A	22-24	508	517	0.980	87.0	1.128
B	24-26	508	510	"	"	---
C	26-28	508	507	"	"	1.297
D	28-30	510	511	"	"	---
E	30-34	510	512	"	"	1.441

Catalyst: $ZnO-MgO-MoO_3$ No. 9817
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
95-I-A	0- 2	441	441	0.990	99.0	1.136
B	2- 4	441	441	"	"	---
C	4- 6	443	441	"	"	1.212
D	6- 8	440	440	"	"	---
E	8-12	441	440	"	"	1.350
F	12-20	446	446	"	"	1.380
G	20-28	442	439	"	"	1.474

Catalyst: Esso Pt Type (1000)
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
95-II-A	37-39	509	511	1.010	85.0	1.058
B	39-41	507	507	"	"	1.039
C	41-43	508	510	"	"	1.419
D	43-45	511	506	"	"	---
E	45-49	511	508	"	"	1.011
F	49-57	507	505	"	"	1.071

Catalyst: Esso Pt (Type 1000)
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
96-I-A	0- 2	438	433	1.000	96.0	1.155
B	2- 4	444	444	"	"	---
C	4- 6	440	438	"	"	1.376
D	6- 8	441	441	"	"	---
E	8-12	443	442	"	"	1.510
F	12-20	442	441	"	"	---

Catalyst: Esso MoO_3 on DA-1
Cracking Cat. #9816
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate

Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
96-II-A	25-27	507	514	1.000	85.0	1.090
B	27-29	507	510	"	"	---
C	29-31	507	509	"	"	1.322
D	31-33	510	512	"	"	---
E	33-37	509	509	"	"	1.420
F	37-45	511	511	"	"	1.483

Catalyst: Esso MoO_3 on DA-1
Cracking Cat. # 9816
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate

Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
97-I-A	0- 2	432	429	0.990	95.0	1.120
B	2- 4	440	451	"	"	---
C	4- 6	433	439	"	"	1.108
D	6- 8	440	445	"	"	---
E	8-12	440	442	"	"	1.196
F	12-20	441	442	"	"	1.230

Catalyst: Esso Oronite Hydro-
forming catalyst.
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate

Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Yield (Percent of Charge)	Wt. % N
97-II-A	21-23	510	519	1.000	86.0	0.547
B	23-25	508	509	"	"	---
C	25-27	512	514	"	"	0.579
D	27-29	508	507	"	"	---
E	29-33	510	510	"	"	0.652
F	33-41	512	509	"	"	0.752

Catalyst: Esso Oronite Hydro-forming catalyst
Catalyst Wt.: 100 g.
Charge Stock: 750°F. E.P. Coker Distillate

Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 4000
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversions (percent)
99	A	20	439	441	1.0	0.914	0.514
	B	22	443	441	"	0.932	0.504
100	A	3-3 1/2	440	441	1.07	1.041	0.446
	B	3 1/2-4	439	441	"	1.069	0.432
	C	4-4 1/2	440	439	"	1.088	0.422
	D	8 1/2-9	442	440	"	1.098	0.416
	E	14 1/2-15	441	440	"	1.166	0.380
101	A	2-2 1/2	442	441	1.03	1.000	0.468
	B	2 1/2-3	438	439	"	1.022	0.456
	C	3-3 1/2	441	441	"	1.043	0.444
	D	7 1/2-8	440	441	"	1.093	0.418
	E	13 1/2-14	440	440	"	1.123	0.403
102	A	1-1 1/2	441	440	0.99	0.955	0.492
	B	1 1/2-2	441	441	"	0.985	0.476
	C	2-2 1/2	440	440	"	1.007	0.464
	D	6 1/2-7	440	440	"	1.093	0.418

Catalyst: Peter Spence Co., CoMo; 5/32"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversions (percent)
103	A'	0-1/4	440	441	1.08	0.593	0.685
	A"	1/4-1/2	437	443	"	0.324	0.828
	A	1-1 1/2	439	439	"	0.793	0.579
	B	2 1/2-3	440	441	"	0.827	0.560
	C	4-4 1/2	441	443	"	0.814	0.567
	D	5 1/2-6	442	441	"	0.829	0.559
	E	7-7 1/2	440	440	"	0.798	0.576
	F	8 1/2-9	442	443	"	0.729	0.618
	G	10-10 1/2	442	446	"	0.716	0.619
	H	11 1/2-12	441	444	"	0.746	0.603
	I	13-13 1/2	440	440	"	0.773	0.589
	J	14 1/2-15	440	440	"	0.867	0.534
	K	16-16 1/2	440	439	"	0.925	0.508

Catalyst: Peter Spence Co., CoMo; 5/32"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-M

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversions (percent)
104	B	1/2-3/4	439	447	0.96	0.280	0.851
	C	3/4-1	436	440	"	0.409	0.752
	D	1-1 1/4	432	432	"	0.607	0.677
	E	1 1/4-1 1/2	438	441	"	0.780	0.585
	F	1 1/2-1 3/4	444	445	"	0.762	0.595
	G	1 3/4-2	444	447	"	0.685	0.636
	H	2-2 1/2	439	443	"	0.690	0.633
	I	2 1/2-3	437	439	"	0.822	0.563
	J	4-4 1/2	443	443	"	0.803	0.573
	K	5 1/2-6	442	439	"	0.933	0.504
	L	7-7 1/2	443	441	"	0.764	0.594

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversions (percent)
107 A	1/2-3/4	449	445	1.0	0.445	0.763
B	3/4-1	441	441	"	0.560	0.702
C	1-1 1/2	422	424	"	0.659	0.650
D	1 1/2-2	438	442	"	0.841	0.553
E	2-2 1/2	455	465	"	0.552	0.707
F	2 1/2-3	453	470	"	0.269	0.857
G	4-4 1/2	446	448	"	0.577	0.697
H	5 1/2-6	437	433	"	0.987	0.476
I	7-7 1/2	442	444	"	0.740	0.606
J	8 1/2-9	439	441	"	0.783	0.584
K	10-10 1/2	437	433	"	0.858	0.543
L	11 1/2-12	442	441	"	0.756	0.598
M	13-13 1/2	431	434	"	0.875	0.535
N	14 1/2-15	443	439	"	0.843	0.552
O	15 1/2-16	441	445	"	0.745	0.614

Catalyst: Regenerated Peter Spence Co. CoMo, 1/8"
Catalyst Wt. 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-M
Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
108	A	1 3/4-2 1/4	437	437	1.0	0.624	0.668
	B	2 3/4-3 1/4	441	443	"	0.741	0.606
	C	3 3/4-4 1/4	442	441	"	0.778	0.586
	D	4 3/4-5 1/4	443	440	"	0.779	0.586
	E	5 3/4-6 1/4	440	439	"	0.770	0.591
	F	6 3/4-7 1/4	440	440	"	0.798	0.576
	G	7 3/4-8 1/4	439	440	"	0.798	0.576

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-1

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
109	A	2	468	415	1.0	1.008	0.464
	B	---	438	427	"	---	---
	C	3	443	439	"	1.048	0.444
	D	3 1/2	442	441	"	0.986	0.476
	E	4	440	445	"	0.821	0.563
	F	4 1/2	443	447	"	0.798	0.576
	G	5	445	447	"	0.857	0.544
	H	5 1/2	443	445	"	1.001	0.467
	I	6	433	443	"	0.853	0.546
	J	6 1/2	435	445	"	0.810	0.569
	K	7	441	447	"	0.878	0.533
	L	7 1/2	443	449	"	0.879	0.533

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 150 g.
Charge Stock: 750°F. EPCD
Reactor Number B-D-2

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g g hr)	Wt. % N	Conversion (percent)
110	A	2	444	444	3.0	0.989	0.475
	C	3	446	445	"	0.893	0.525
	E	4	443	442	"	0.856	0.545
	G	5	433	440	"	0.058	0.438
	I	6	443	440	"	0.030	0.466
	K	7	435	438	"	1.198	0.363
	L	7 1/2	440	438	"	1.254	0.333
	M	8	441	440	"	1.211	0.355

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-2

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g g hr)	Wt. % N	Conversion (percent)
111	A	2	422	433	3.0	1.391	0.260
	C	3	444	436	"	1.443	0.232
	E	4	435	438	"	1.468	0.219
	G	5	440	431	"	1.541	0.180
	I	6	442	445	"	1.324	0.295
	K	7	460	441	"	1.421	0.244
	L	7 1/2	443	442	"	1.502	0.301
	M	8	442	438	"	1.441	0.234

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-2

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
112	A	2	451	455	0.5	0.412	0.781
	C	3	445	442	"	0.414	0.780
	E	4	437	440	"	0.300	0.840
	G	5	440	440	"	0.339	0.820
	I	6	442	441	"	0.329	0.825
	K	7	440	441	"	0.284	0.849
	L	7 1/2	440	440	"	0.300	0.840
	M	8	440	438	"	0.277	0.853

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-2

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
113	A	2	442	441	0.5	0.140	0.925
	C	3	442	441	"	0.169	0.910
	E	4	443	441	"	0.198	0.894
	G	5	440	440	"	0.256	0.864
	I	6	440	441	"	0.267	0.858
	K	7	441	441	"	0.267	0.858
	L	7 1/2	442	440	"	0.278	0.853
	M	8	441	440	"	0.275	0.854

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 100 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-2

Reactor Pressure (psig): 1000
Gas Flow Rate(SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
117	4	4	437	440	1.0	1.005	0.466
	4 1/2	4 1/2	442	438	"	1.140	0.394
	6	6	432	439	"	1.208	0.357
	8	8	435	437	"	1.798	0.043

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-4

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
118	2	2	438	441	1.0	0.572	0.696
	4	4	438	441	"	0.626	0.667
	6	6	439	441	"	0.667	0.645
	8	8	439	442	"	0.667	0.645

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
119 2	2	432	443	1.0	0.882	0.531
3	3	439	439	"	0.890	0.527
4	4	438	440	"	0.962	0.489
5	5	444	441	"	0.969	0.485
6	6	438	440	"	0.938	0.501
7	7	446	440	"	1.010	0.463
7 1/2	7 1/2	440	441	"	1.005	0.465
8	8	438	441	"	1.001	0.467

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 60

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
120 2	2	415	442	1.0	1.311	0.302
3	3	320	434	"	1.376	0.268
4	4	390	450	"	1.535	0.183
5	5	410	431	"	1.501	0.200
6	6	425	444	"	1.513	0.195
7	7	420	439	"	1.656	0.120
7 1/2	7 1/2	425	441	"	1.755	0.067
8	8	429	441	"	1.713	0.089

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 30

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
121 2	2	430	432	0.5	1.056	0.438
3	3	440	454	"	---	---
4	4	429	440	"	1.267	0.327
5	5	431	442	"	1.373	0.270
6	6	435	440	"	1.188	0.368
7	7	451	439	"	1.302	0.307
7 1/2	7 1/2	436	439	"	1.320	0.298
8	8	436	440	"	1.342	0.286

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 30

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
122 2	2	442	443	0.5	0.763	0.595
3	3	430	445	"	0.776	0.597
4	4	420	429	"	0.703	0.626
5	5	440	445	"	0.782	0.585
6	6	440	440	"	0.722	0.616
7	7	442	441	"	0.783	0.584
7 1/2	7 1/2	443	441	"	0.782	0.585
8	8	440	439	"	0.786	0.582

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 60

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
123 2	2	378	447	2.0	1.280	0.320
3	3	376	439	"	1.290	0.315
4	4	393	439	"	1.362	0.276
5	5	403	443	"	1.748	0.072
6	6	398	440	"	1.545	0.177
7	7	405	442	"	1.370	0.272
7 1/2	7 1/2	401	440	"	1.391	0.260
8	8	403	440	"	1.424	0.243
124 2	2	377	420	1.0	0.843	0.552
3	3	393	415	"	0.882	0.531
4	4	396	413	"	1.040	0.447
5	5	400	414	"	1.099	0.415
6	6	402	413	"	1.111	0.408
7	7	403	413	"	1.130	0.398
7 1/2	7 1/2	400	413	"	1.155	0.385
8	8	394	412	"	1.211	0.355

Sample 123:

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 60

Sample 124:

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
125 2	2	414	463	1.0	0.199	0.894
3	3	411	463	"	0.265	0.859
4	4	408	463	"	0.143	0.924
5	5	412	463	"	0.186	0.901
6	6	414	463	"	0.195	0.896
7	7	414	463	"	0.154	0.918
7 1/2	7 1/2	414	462	"	0.198	0.895
8	8	415	461	"	0.278	0.852

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
126 2 1/2	2 1/2	395	440	1.0	0.538	0.714
3	3	398	441	"	0.551	0.707
4	4	400	440	"	0.568	0.698
5	5	407	439	"	0.652	0.653
6	6	407	439	"	0.640	0.660
7	7	411	441	"	0.645	0.657
7 1/2	7 1/2	411	441	"	0.611	0.675
8	8	409	440	"	0.617	0.672

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 5000
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
127	2	2	437	465	0.5	0.137	0.927
	3	3	433	461	"	0.126	0.933
	4	4	435	465	"	0.196	0.896
	5	5	434	463	"	0.213	0.887
	6	6	438	464	"	0.240	0.872
	7	7	439	463	"	0.225	0.880
	7 1/2	7 1/2	439	463	"	0.228	0.879
	8	8	439	463	"	0.232	0.877
128	2	2	402	412	"	0.496	0.736
	3	3	403	412	"	0.678	0.639
	4	4	403	413	"	0.717	0.619
	5	5	408	414	"	0.703	0.626
	6	6	405	413	"	0.633	0.663
	7	7	407	413	"	0.682	0.637
	7 1/2	7 1/2	410	413	"	0.693	0.632
	8	8	408	413	"	0.705	0.625

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g-hr)	Wt. % N	Conversion (percent)
129	2	2	418	430	0.5	0.267	0.858
	3	3	440	443	"	0.489	0.740
	4	4	420	438	"	0.475	0.747
	5	5	424	443	"	0.427	0.773
	6	6	421	440	"	0.395	0.790
	7	7	419	439	"	0.412	0.781
	7 1/2	7 1/2	422	439	"	0.412	0.781
	8	8	421	439	"	0.420	0.777

Catalyst: Peter Spence Co., CoMo, 1/8" — Reactor Pressure (psig): 1000
Catalyst Wt.: 50 g. — Gas Flow Rate (SCF/bbl): 5000
Charge Stock: 750°F. EPCD — Mol % H_2 in Feed Gas: 100
Reactor Number: B-D-5

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g-hr)	Wt. % N	Conversion (percent)
130	2	2	417	442	0.5	0.304	0.838
	3	3	417	440	"	0.365	0.806
	4	4	415	439	"	0.429	0.772
	5	5	414	441	"	0.413	0.780
	6	6	415	440	"	0.397	0.789
	7	7	414	440	"	0.412	0.781
	7 1/2	7 1/2	414	440	"	0.415	0.780
	8	8	414	440	"	0.404	0.785

Catalyst: Peter Spence Co., CoMo, 1/8" — Reactor Pressure (psig): 1000
Catalyst Wt.: 50 g. — Gas Flow Rate (SCF/bbl): 2000
Charge Stock: 750°F. EPCD — Mol % H_2 in Feed Gas: 100
Reactor Number: B-D-5

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
131 2	2	420	441	1.0	0.802	0.573
3	3	420	439	"	0.862	0.542
4	4	411	441	"	0.816	0.566
5	5	412	440	"	0.875	0.535
6	6	419	439	"	0.817	0.565
7	7	420	441	"	0.845	0.550
8	8	420	440	"	0.806	0.572

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2000
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
133 3	3	410	445	0.5	0.673	0.642
4	4	392	437	"	0.698	0.629
5	5	405	441	"	0.762	0.595
6	6	402	441	"	0.845	0.550
6 1/2	6 1/2	403	441	"	0.825	0.561
7	7	410	440	"	0.828	0.559
7 1/2	7 1/2	411	441	"	0.823	0.562
8	8	408	443	"	0.842	0.552

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 600
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
134 2	2	394	440	1.0	0.956	0.492
3	3	397	442	"	0.910	0.516
4	4	393	440	"	0.928	0.506
5	5	410	439	"	0.910	0.517
6	6	402	440	"	0.948	0.497
7	7	391	440	"	0.982	0.477
7 1/2	7 1/2	389	440	"	1.012	0.462
8	8	379	440	"	0.995	0.471

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 600
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
135 2	2	406	439	0.5	0.750	0.601
3	3	403	443	"	1.026	0.455
4	4	395	439	"	1.138	0.395
5	5	397	440	"	1.208	0.357
6	6	397	441	"	1.310	0.304
7	7	393	440	"	1.300	0.308
7 1/2	7 1/2	393	440	"	1.298	0.310
8	8	392	441	"	1.310	0.304

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 200
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX –– OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
136	2	2	405	441	1.0	——	——
	3	3	402	439	"	1.215	0.344
	4	4	407	440	"	1.458	0.412
	5	5	405	443	"	1.470	0.415
	6	6	402	440	"	1.305	0.369
	7	7	404	441	"	1.455	0.411
	7 1/2	7 1/2	406	442	"	1.459	0.412
	8	8	405	441	"	1.468	0.414

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 200
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Rate: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
137	2	2	369	445	2.0	1.985	——
	3	3	365	440	"	1.580	0.158
	4	4	365	441	"	1.608	0.146
	5	5	357	440	"	1.623	0.137
	6	6	358	440	"	1.566	0.168
	7	7	358	440	"	1.608	0.146
	7 1/2	7 1/2	356	440	"	1.654	0.120
	8	8	355	440	"	1.660	0.117

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 200
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
138 2	2	365	445	2.0	1.222	0.350
3	3	357	435	"	1.358	0.278
4	4	367	442	"	1.360	0.277
5	5	369	440	"	1.410	0.250
6	6	367	441	"	1.403	0.253
7	7	366	440	"	1.415	0.247
7 1/2	7 1/2	372	440	"	1.431	0.238
8	8	374	441	"	1.570	0.166

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 600
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
139 2	2	366	416	2.0	1.305	0.307
3	3	368	419	"	1.330	0.293
4	4	378	409	"	1.426	0.242
5	5	380	413	"	1.455	0.227
6	6	378	412	"	1.204	0.359
7	7	388	415	"	1.380	0.266
7 1/2	7 1/2	384	413	"	1.409	0.252
8	8	385	409	"	1.425	0.243

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
140 2	2	435	463	2.0	0.757	0.597
3	3	445	463	"	0.938	0.502
4	4	439	462	"	0.866	0.539
5	5	427	462	"	0.834	0.557
6	6	422	463	"	0.724	0.615
7	7	419	463	"	0.830	0.559
7 1/2	7 1/2	426	465	"	0.825	0.561
8	8	425	462	"	0.845	0.551

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
141 2	2	417	440	2.0	1.200	0.363
3	3	410	440	"	1.145	0.391
4	4	417	440	"	1.141	0.393
5	5	420	440	"	1.162	0.382
6	6	421	440	"	1.125	0.402
7	7	415	440	"	1.202	0.361
7 1/2	7 1/2	410	439	"	1.200	0.363
8	8	409	439	"	1.196	0.364

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 5000
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
142	2	2	425	439	2.0	0.974	0.482
	3	3	432	453	"	1.000	0.468
	4	4	419	439	"	1.071	0.420
	5	5	414	440	"	1.092	0.418
	6	6	407	440	"	1.111	0.409
	7	7	415	440	"	1.152	0.387
	7 1/2	7 1/2	410	440	"	1.140	0.393
	8	8	408	441	"	1.152	0.387

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 2000
Mol % H_2 in Feed Gas: 100

Sample Number		Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
143	6	6	340	437	2.0	0.827	0.173
	7	7	342	441	"	0.911	0.089
	7 1/2	7 1/2	345	440	"	0.894	0.106
	8	8	346	440	"	0.925	0.075

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 30

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g-hr)	Wt. % N	Conversion (percent)
144 6	6	433	462	1.0	0.674	0.326
7	7	435	463	"	0.656	0.344
7 1/2	7 1/2	435	462	"	0.661	0.339
8	8	441	462	"	0.646	0.354

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g-hr)	Wt. % N	Conversion (percent)
145 6	6	408	440	1.0	0.630	0.370
7	7	404	440	"	0.592	0.408
7 1/2	7 1/2	403	440	"	0.590	0.410
8	8	403	440	"	0.593	0.407

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 1000
Gas Flow Rate (SCF/bbl): 5000
Mol % H_2 in Feed Gas: 100

TABLE IX -- OPERATING CONDITIONS AND PRODUCT DATA (continued)

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
146 6	6	433	440	0.5	0.623	0.377
7	7	435	440	"	0.613	0.387
7 1/2	7 1/2	433	440	"	0.630	0.370
8	8	433	440	"	0.652	0.348

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 200
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

Sample Number	Time on Stream (hr)	Temperature Prht. (°C)	Temperature Cat. (°C)	Space Velocity (g/g hr)	Wt. % N	Conversion (percent)
147 6	6	439	440	1.0	0.758	0.242
7	7	438	440	"	0.786	0.214
7 1/2	7 1/2	437	439	"	0.793	0.207
8	8	440	440	"	0.782	0.218

Catalyst: Peter Spence Co., CoMo, 1/8"
Catalyst Wt.: 50 g.
Charge Stock: 750°F. EPCD
Reactor Number: B-D-5

Reactor Pressure (psig): 200
Gas Flow Rate (SCF/bbl): 7500
Mol % H_2 in Feed Gas: 100

TABLE X

SUMMARY OF DATA FOR RUNS 108 TO 147
(Values Used For Graphs)

Run No.	S.V.	1/S.V.	Weight Percent Nitrogen and Nitrogen Conversion	Operating Variable
108, 118	1	1	0.793; 0.580	S.O.C.
110	3	0.33	1.204; 0.360	S.O.C.(S.V. 3)
110*	2	0.50	1.071*; 0.420*	S.O.C.
112	1/2	2	0.278; 0.850	S.O.C.
120	1	1	1.670; 0.100	30% H_2
121	1/2	2	1.326; 0.300	30% H_2
122	1/2	2	0.793; 0.580	60% H_2
123	2	0.50	1.391; 0.260	60% H_2
124	1	1	1.145; 0.390	775°F.
125, 144	1	1	1.244**; 0.622**	865°F.
126, 145	1	1	1.069**; 0.534**	5000 SCF/bbl
127	1/2	2	0.225; 0.880	865°F.
128	1/2	2	0.693; 0.630	775°F.
129	1/2	2	0.415; 0.780	5000 SCF/bbl
130	1/2	2	0.415; 0.780	2000 SCF/bbl
131	1	1	0.825; 0.560	2000 SCF/bbl
133	1/2	2	0.825; 0.560	600 psig.
137	2	0.5	1.623; 0.137	200 psig.
138	2	0.5	1.426; 0.240	600 psig.

TABLE X (continued)

SUMMARY OF DATA FOR RUNS 108 TO 147
(Values Used For Graphs)

Run No.	S.V.	1/S.V.	Weight Percent Nitrogen and Nitrogen Conversion		Operating Variable
139	2	0.5	1.409;	0.250	775°F.
140	2	0.5	0.825;	0.560	865°F.
141	2	0.5	1.190;	0.365	5000 SCF/bbl
142	2	0.5	1.145;	0.390	2000 SCF/bbl
143	2	0.5	1.712;	0.089	30% H_2
146	1/2	2	1.182;	0.370	200 psig.
147	1	1	1.470;	0.218	200 psig.

S.O.C. (Standard Operating Conditions)

Catalyst-bed temperature, 825°F. (440°C.)
Reactor pressure, 1000 psig.
Feed-gas composition, 100% H_2
Gas rate, 7500 SCF/bbl
Catalyst, Peter Spence CoMo, 1/8" pellets
Catalyst weight, 50 grams
Charge Stock, 750°F. E.P. coker distillate

These standard operating conditions were used for each run except where indicated otherwise in column headed "Operating Variable".

* Values obtained by interpolation.
** Values obtained by averaging the values from the two runs.

TABLE XI

DETAILED SPECIFICATIONS OF ACCESSORY EQUIPMENT

Oil feed reservoir: The oil feed reservoir made from a 2-in., schedule 40, black-iron pipe 21 in. long was wound with 10 ft. of nichrome wire. It was then insulated with 85 percent magnesia. A 50-cc. burette was attached through a side arm so that the level of the oil in the reservoir could be determined readily. A light bulb was mounted behind the burette.

Oil storage reservoir: The storage reservoir, made from a 5-gallon can, was wound with a 33-ft. nichrome heating coil and then insulated with 85 percent magnesia. A small gear pump driven by a 1/4-HP Emerson electric motor was installed between the oil storage reservoir and a filter to force the charge oil through the filter cartridge and into the oil feed reservoir.

Sediment bowl: A standard automobile-type sediment bowl was used. (This was not used with reactor H-K.)

Crude filter: A Chrysler full-flow automobile filter unit was used. (This was not used with reactor H-K.)

Oil feed pump: A Hills-McCanna high-pressure proportioning pump with a 1/4-in. piston was used. It has a maximum capacity of 1.02 gph and a maximum pressure of 2900 psi. It was powered by a 1/4-HP General Electric motor.

Condenser: A water condenser made from a 16-in. length of 1/2-in., schedule 80, black-iron pipe and closed at both ends by caps welded in place was used with reactor H-K. With all the other reactors a 9-in. length of schedule 80, black-iron pipe surrounded by a 1-1/2-in., schedule 40, black-iron pipe to serve as a water jacket was used.

Sight glasses: Eight-inch Jerguson sight glasses with 1/2-in. standard pipe taps.

Capacity tank: A 9-1/2-in. length of 2-in., schedule 160, black-iron pipe. This was used with reactors H-K and B-M only.

Pressure control valve: An air-to-close, Type No. 107-1, 1/2-in., Mason-Neilan diaphragm valve rated at 6000 psi at 100°F.

Pressure controller: A reverse-acting, Type 4100 UR, Fisher-Wizard pressure controller with a 5000 psi Bourdon tube.

Rotameters: Brooks armored rotameters with 3/32-in. balls. An aluminum ball was used throughout the study.

Autotransformers: Two-hundred-twenty volt Powerstats and 110 volt Powerstats.

Recompression pump: A Pesco #05 1012-020 gear pump rated at 4.5 gal/min at 2800 rpm and 1200 psi. The pressure limit for continuous operation is 1200 psi. It was directly coupled at a 3.2:1 pulley ratio to a 1-HP, 115/230 volt, Power-Kraft repulsion-induction type electric motor.

Gas cylinders: Harrisburg Steel Corporation cylinders; two of 1320-cu.ft. capacity, and one of 2640-cu.ft. capacity.

Compression oil reservoir: Two 5-gal. oil cans.

High pressure piping: Schedule 80 black-iron.

High pressure pipe fittings: Henry Vogt 3000 psi forged steel.

Low pressure piping: Schedule 40 black-iron.

High Pressure tubing: Type 304 SS, 1/8-in. OD, 0.020-in. wall.

Low pressure tubing: Copper, 1/4-in. OD.

High pressure valves: Hoke #321 SS blunt-spindle needle valves.

Metering valves: Hoke brass-body, 20-turn-to-open needle valves.

Gas meter: Precision Scientific 20-cu.ft. Wet Test Meter.

Gages: Marshall 2000 psi.

Thermocouples: Iron-constantan. The thermocouples were positioned in all the reactors so that the following temperatures could be ascertained: the temperature of the feed as it entered the catalyst bed, the temperature at that point in the catalyst bed where it would be at its maximum, and the temperature near the end of the catalyst bed.

Temperature indicator: A Leeds and Northrup, 18-point indicating potentiometer.

Rupture disc: A Black, Sivalls, and Bryson 2250 psi disc.

Scrubbers: Erlenmeyer flasks, 750 ml. capacity, with 15 percent caustic solution.

Pressure reaction apparatus for batch treatments consisted of the following piece of equipment: A Parr Instrument Company rocking bomb, 1500 watt, maximum rating 6000 psig at 400°C.

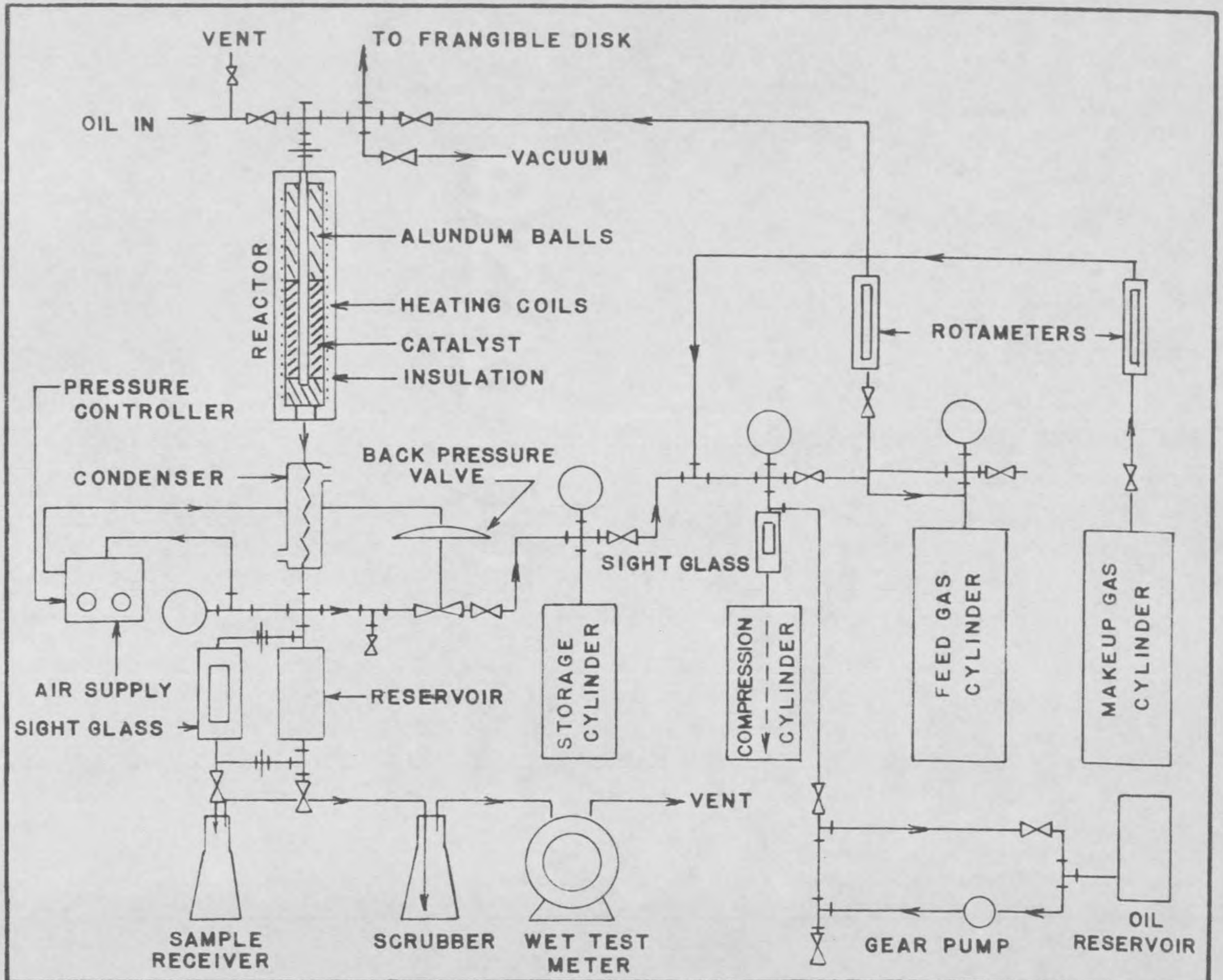


Figure 1. Schematic Flow Diagram of the Hydrotreating Unit.

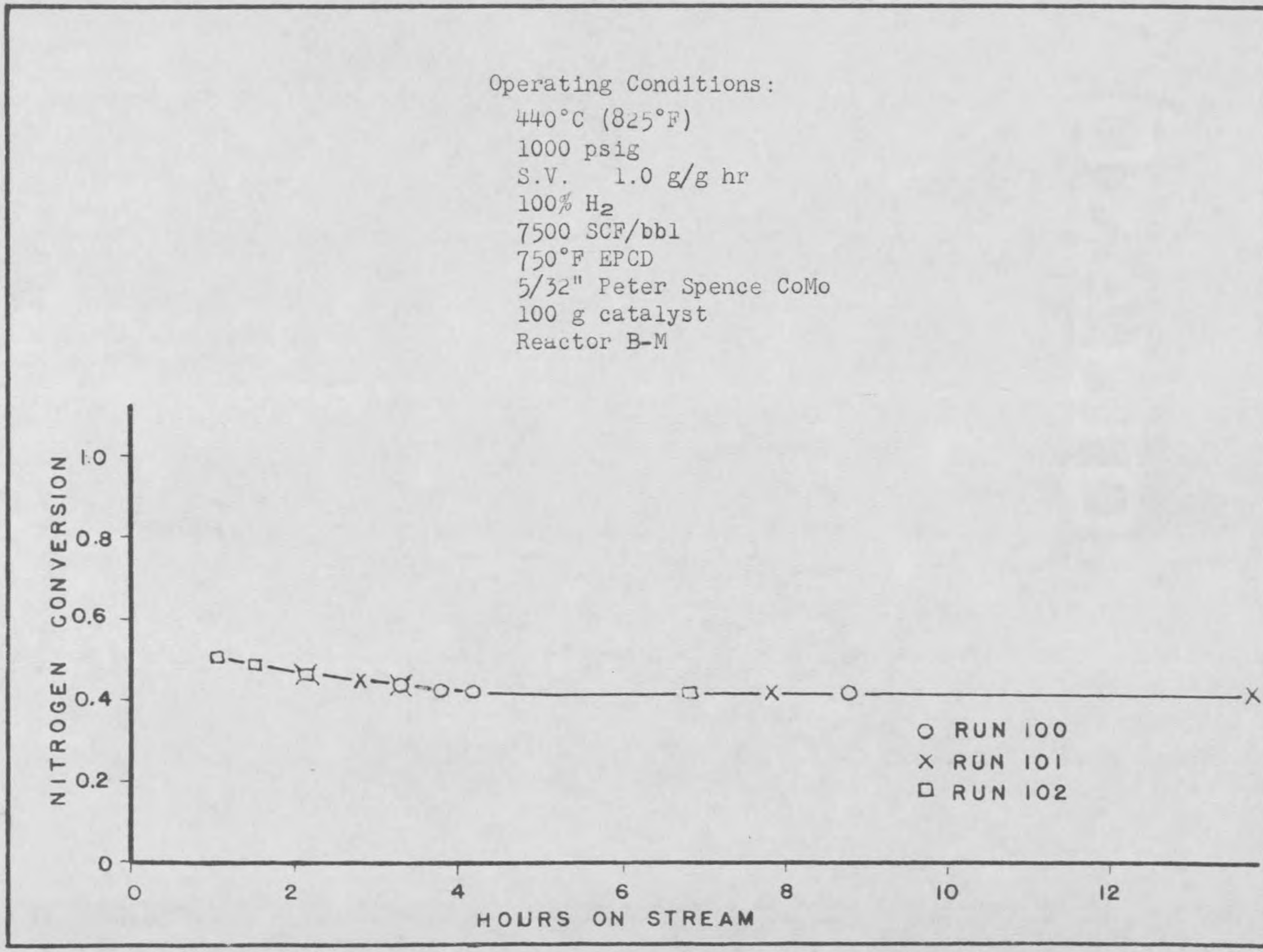


Figure 2. Plot of Nitrogen Conversion versus Hours on Stream for Three Consecutive Runs to Show the Degree of Reproducibility Possible.

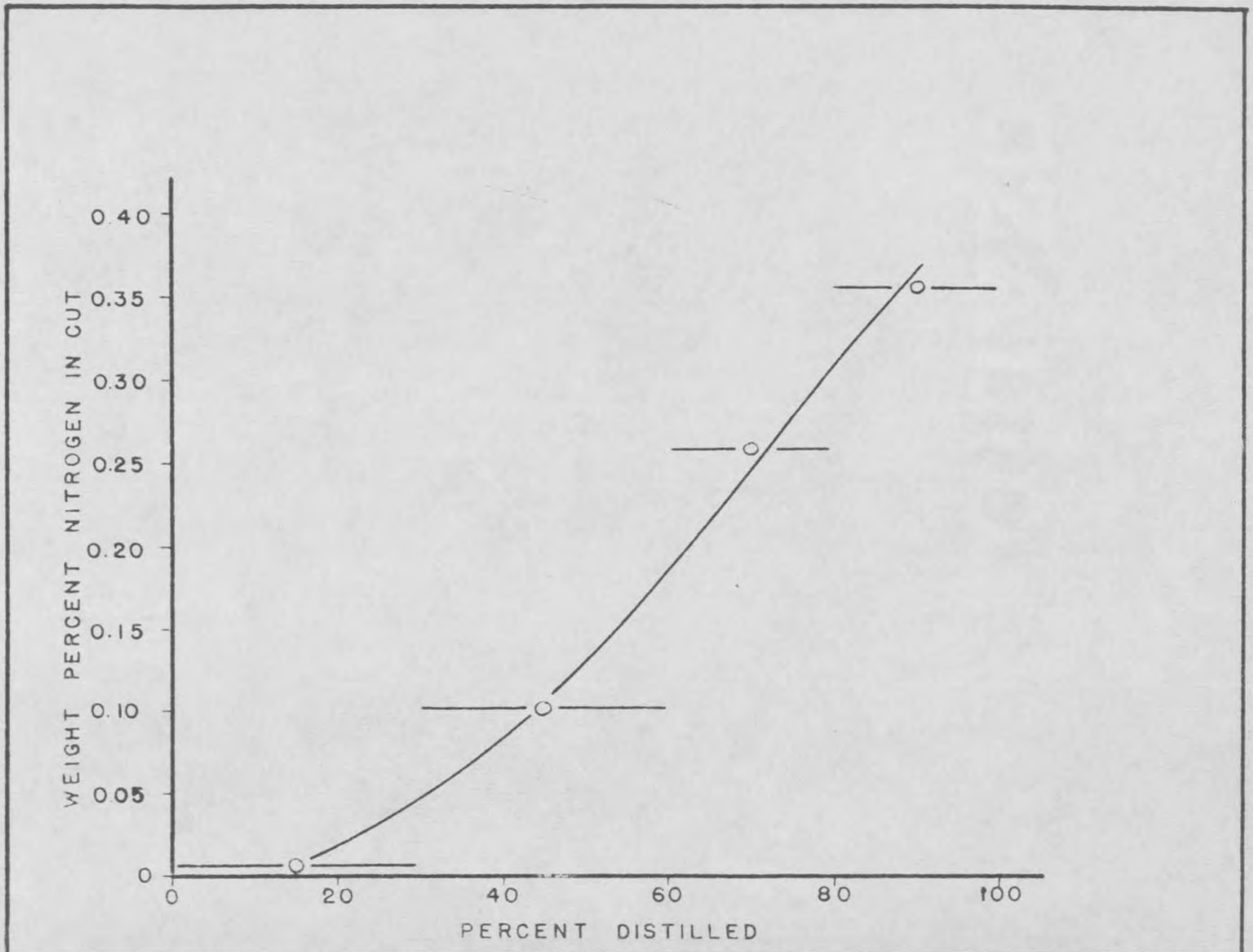


Figure 3. Weight Percent Nitrogen in Cuts Produced by Fractionating a Hydrogenated 650°F. E.P. Coker Distillate Sample versus the Percent Distilled.

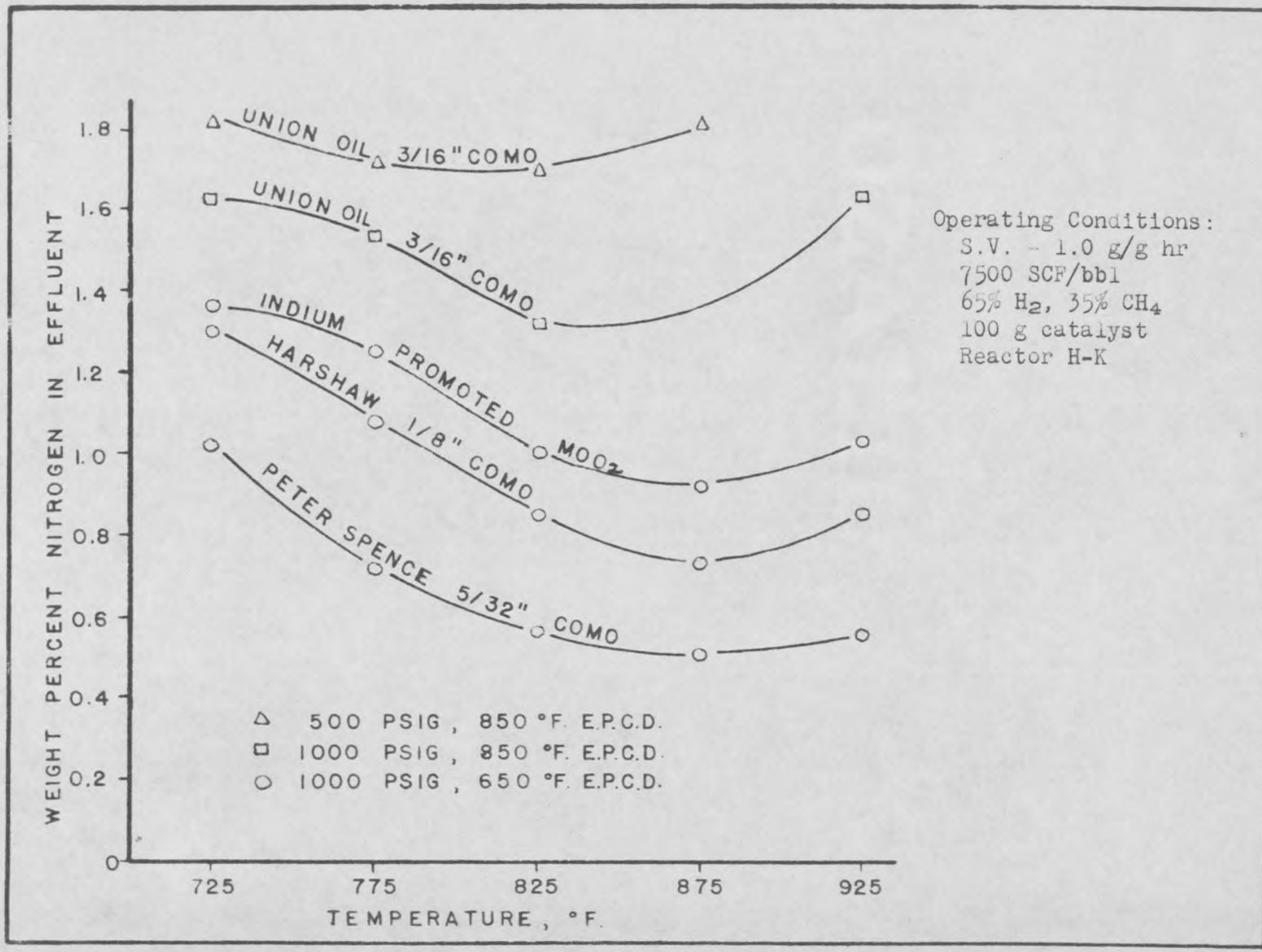


Figure 4A. The Effect of the Catalyst-Bed Temperature on the Denitrogenation of Three Shale Oil Coker Distillates, Runs 1-31.

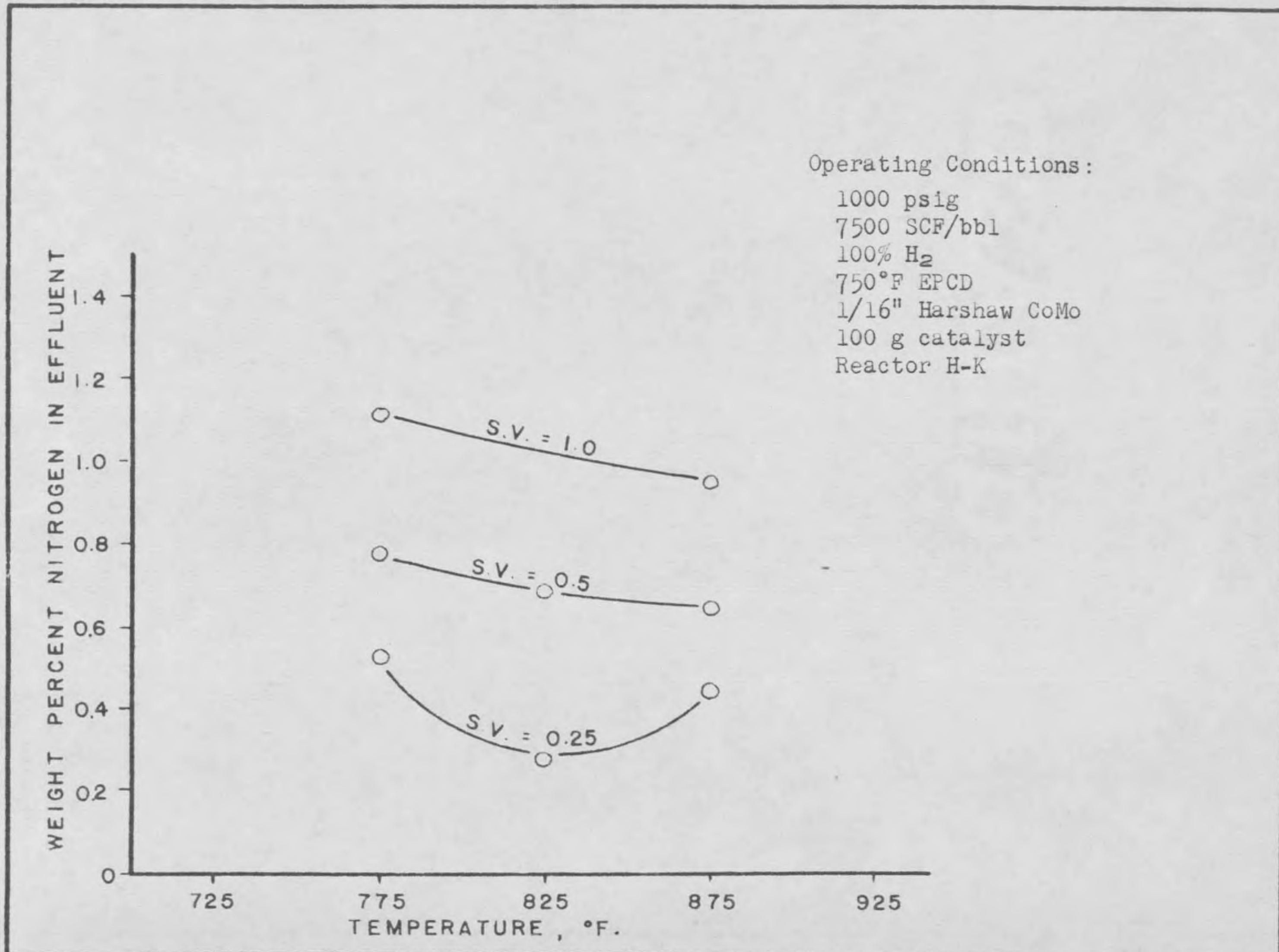


Figure 4B. The Effect of the Catalyst-Bed Temperature on the Denitrogenation of Three Shale Oil Coker Distillates, Runs 55-63.

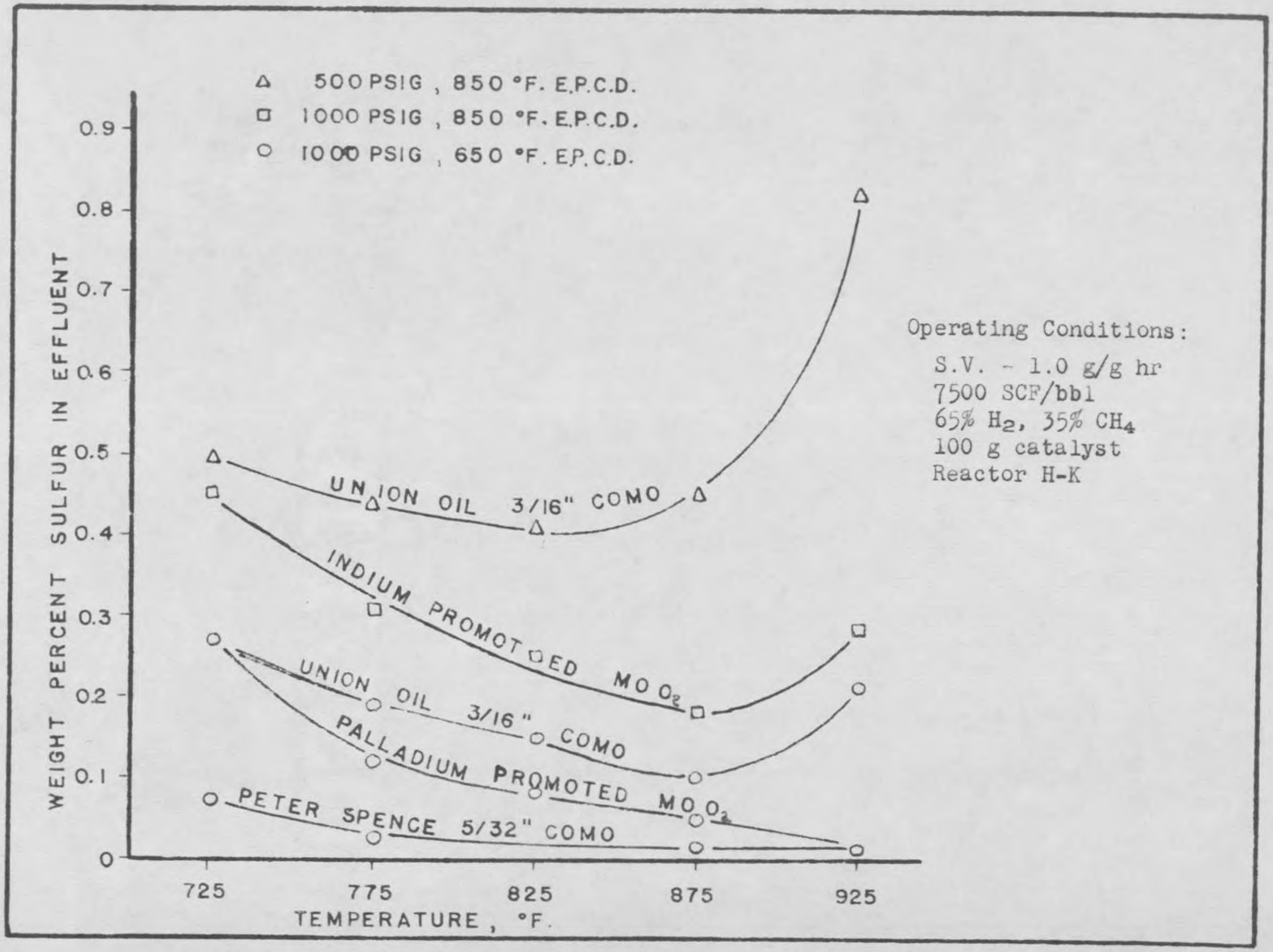


Figure 5. The Effect of the Catalyst-Bed Temperature on the Desulfurization of Two Shale Oil Coker Distillates.

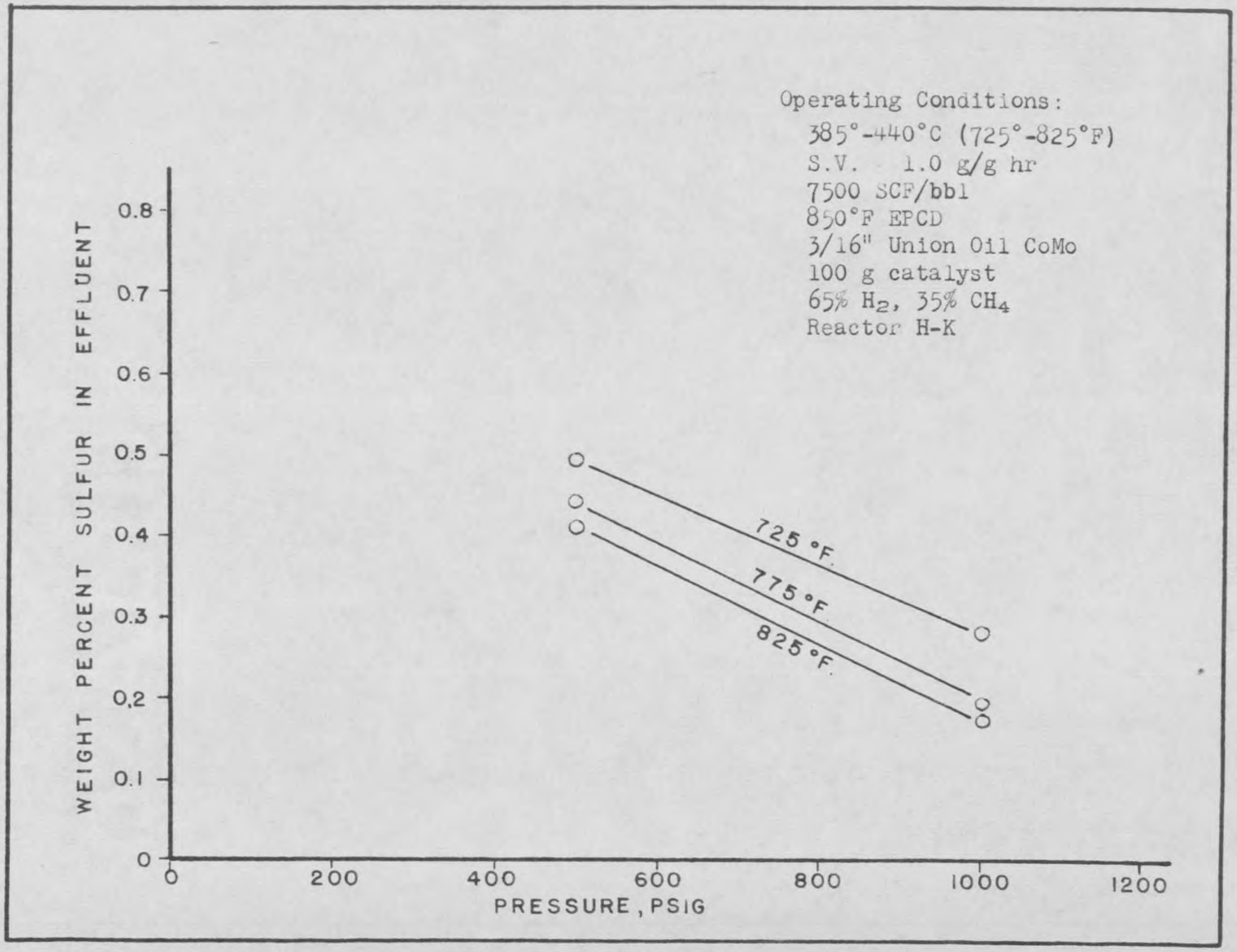


Figure 6. The Effect of Reactor Pressure on the Desulfurization of a Shale Oil Coker Distillate.

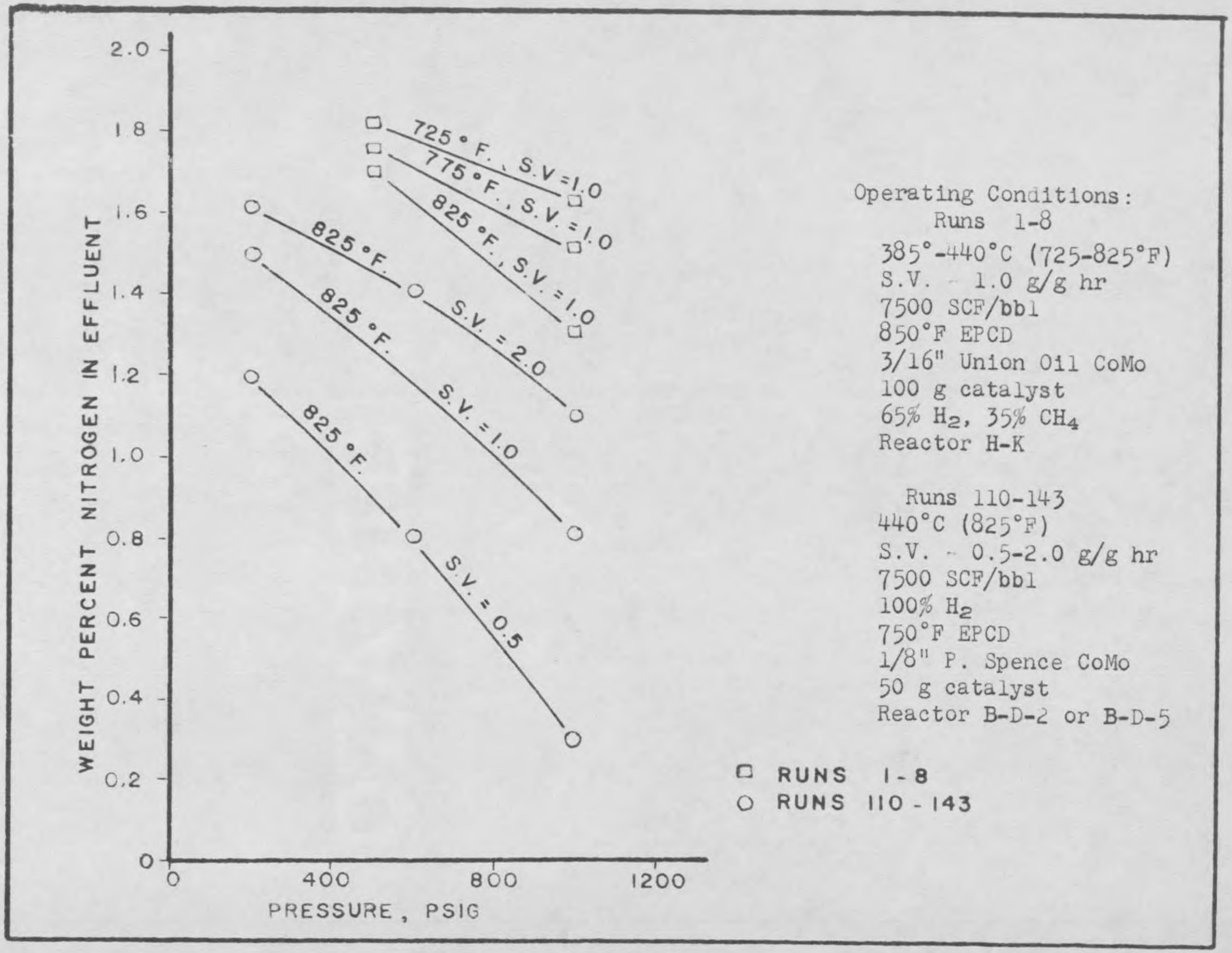


Figure 7. The Effect of Reactor Pressure on the Denitrogenation of Two Shale Oil Coker Distillates.

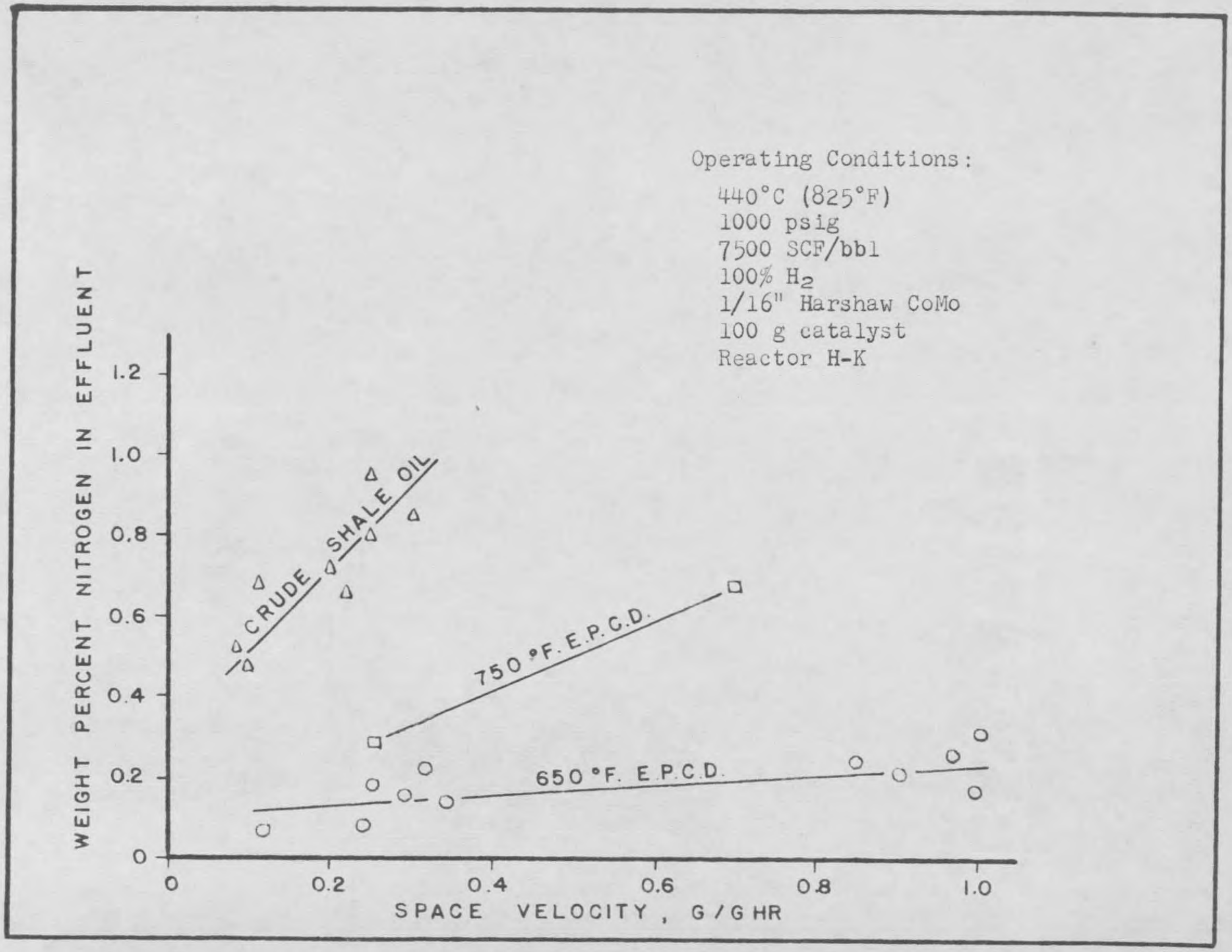


Figure 8. The Effect of Space Velocity on the Denitrogenation of Two Shale Oil Coker Distillates and a Gas-Combustion Crude.

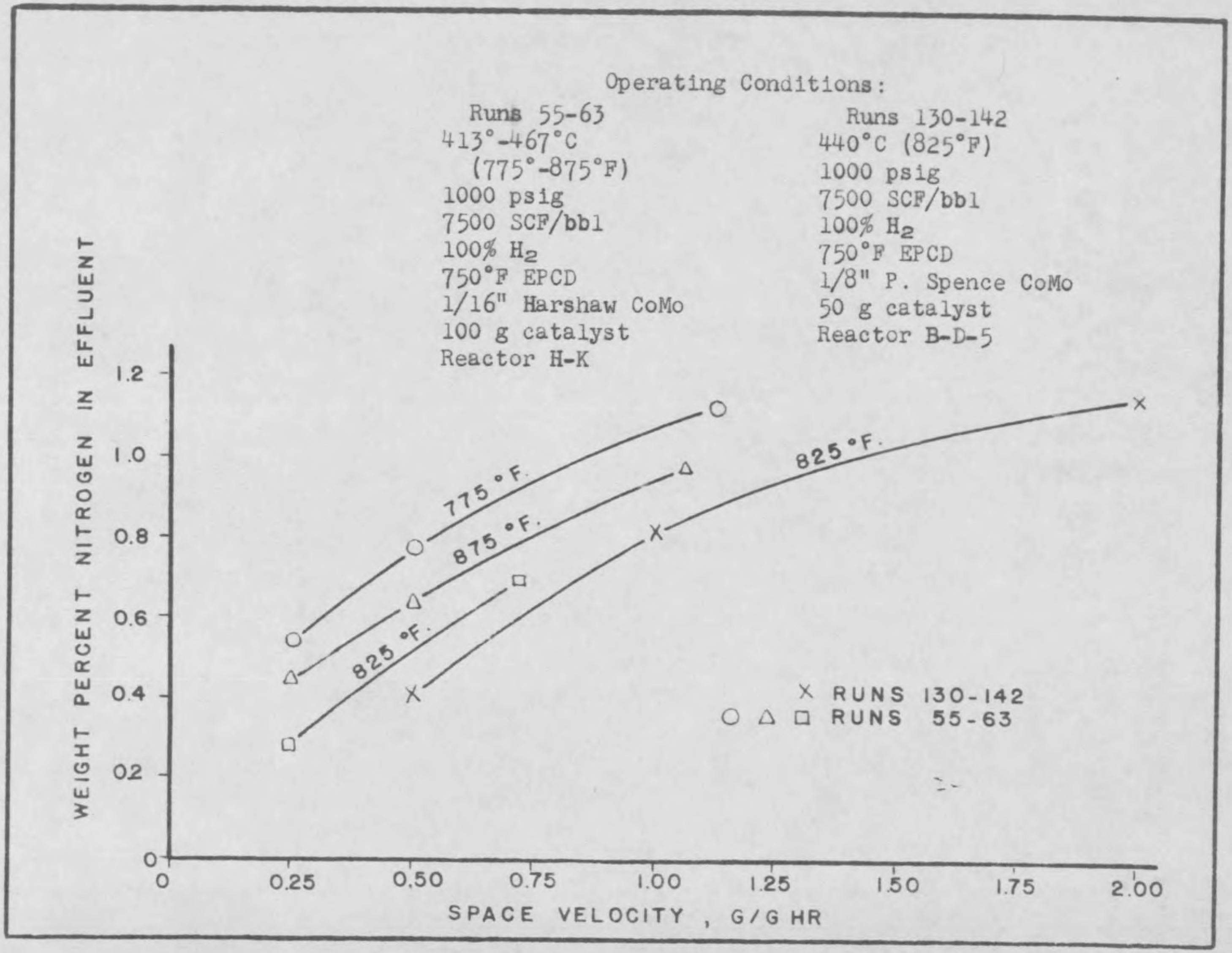


Figure 9. The Effect of Space Velocity on the Denitrogenation of a Shale Oil Coker Distillate.

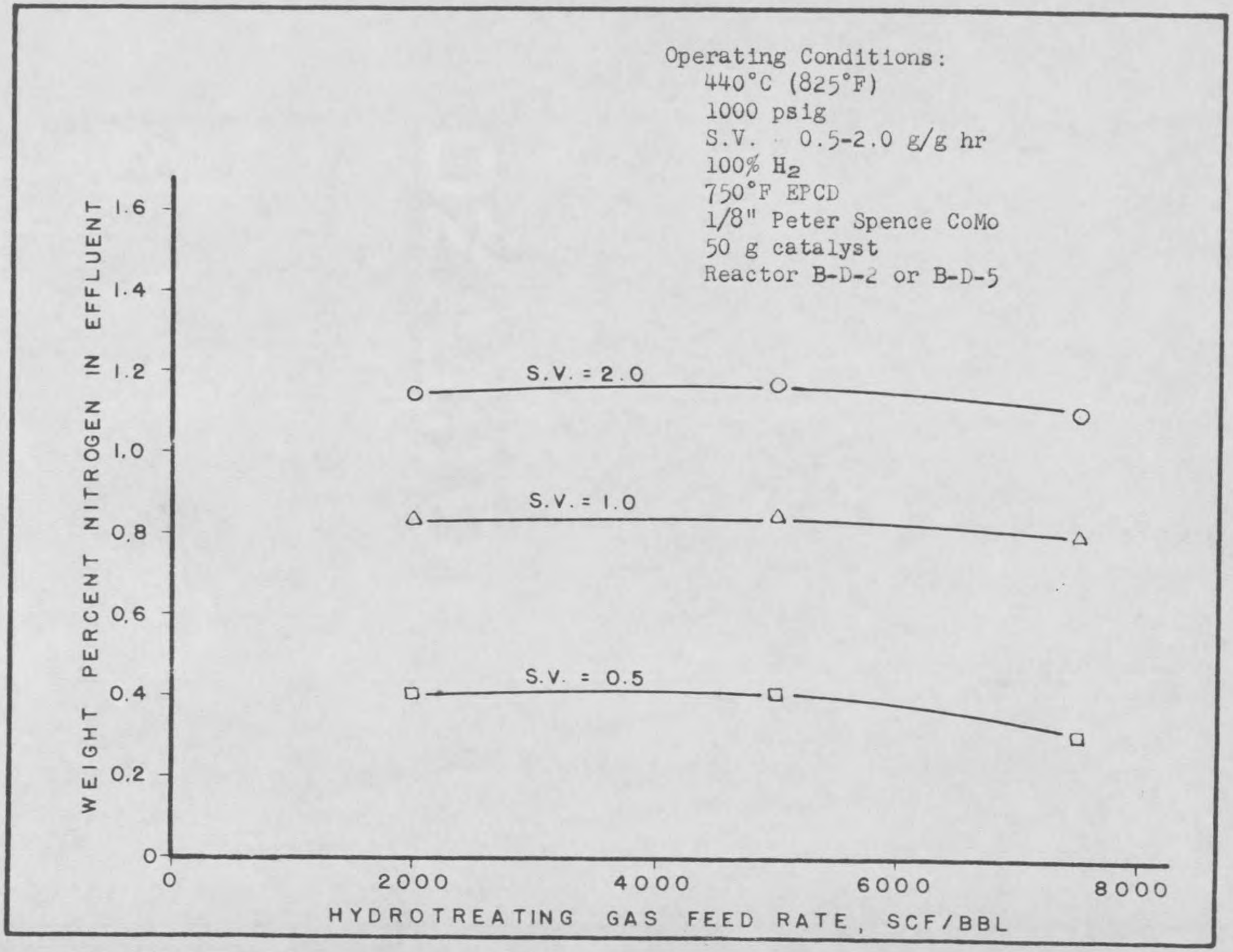


Figure 10. The Effect of the Hydrotreating Gas Feed Rate on the Denitrogenation of a Shale Oil Coker Distillate.

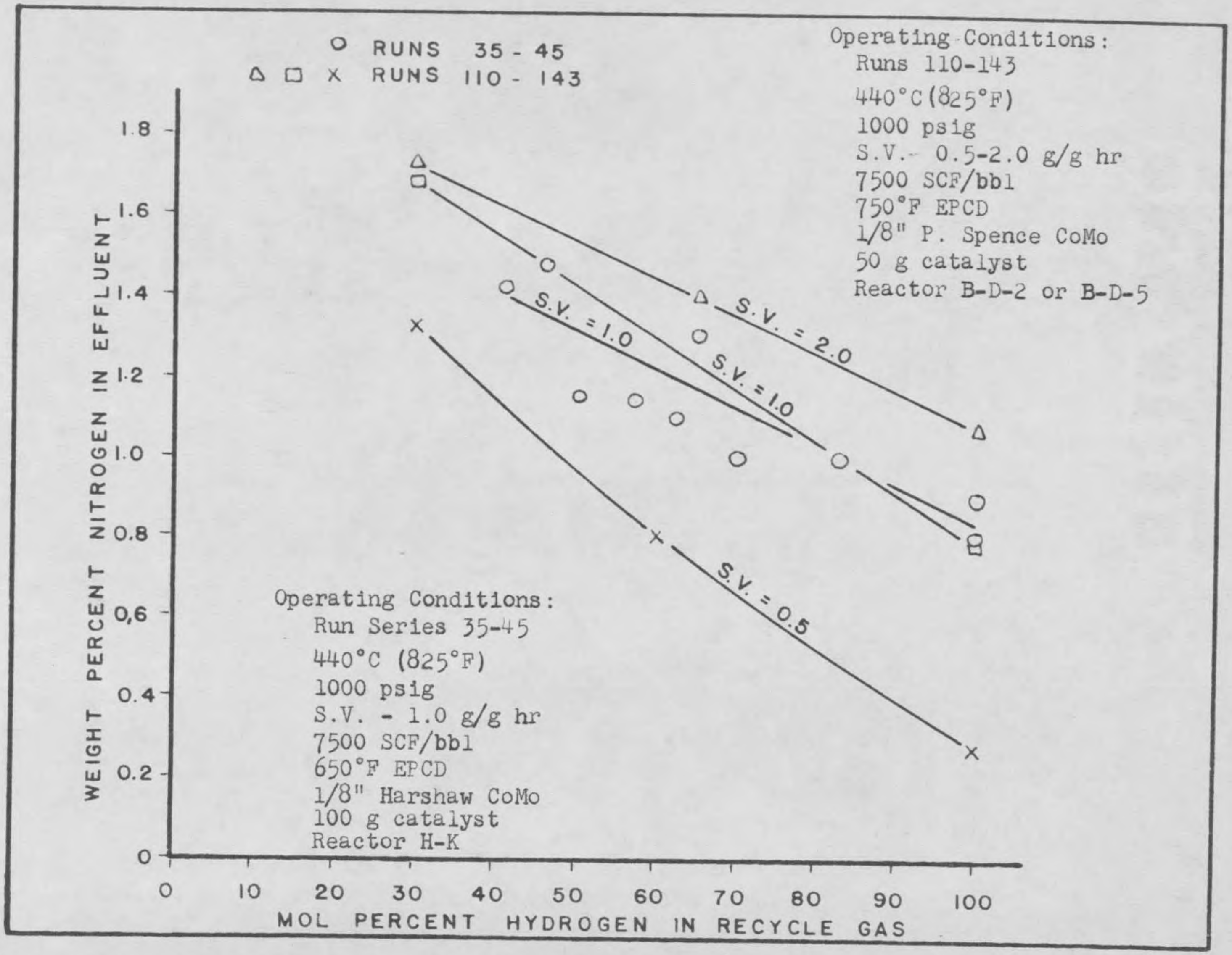


Figure 11. The Effect of the Hydrogen Content of the Recycle Gas on the Denitrogenation of Two Shale Oil Coker Distillates.

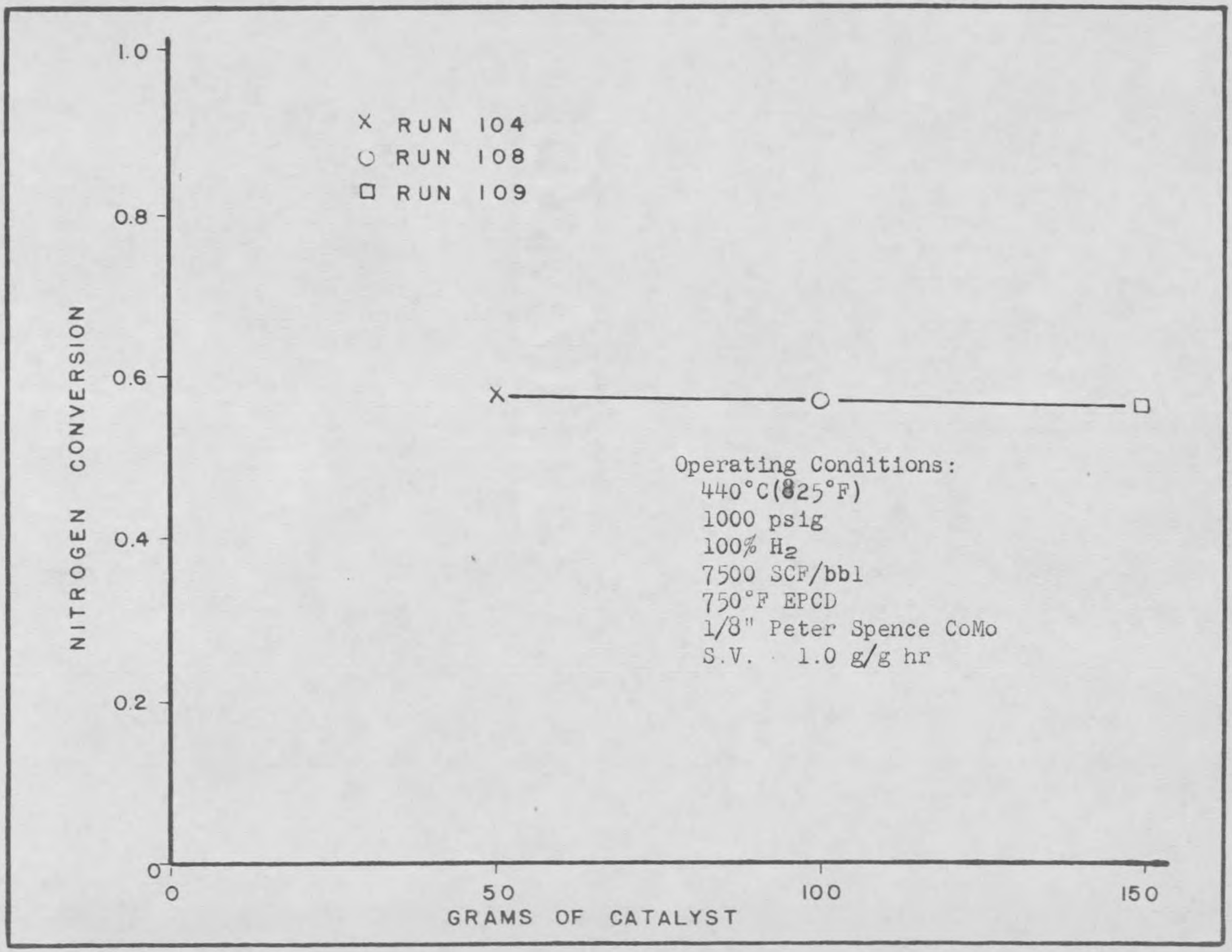


Figure 12. A Plot of the Nitrogen Conversion versus the Grams of Catalyst Charged to the Reactor When the Space Velocity Was Held at 1.0 g/g hr.

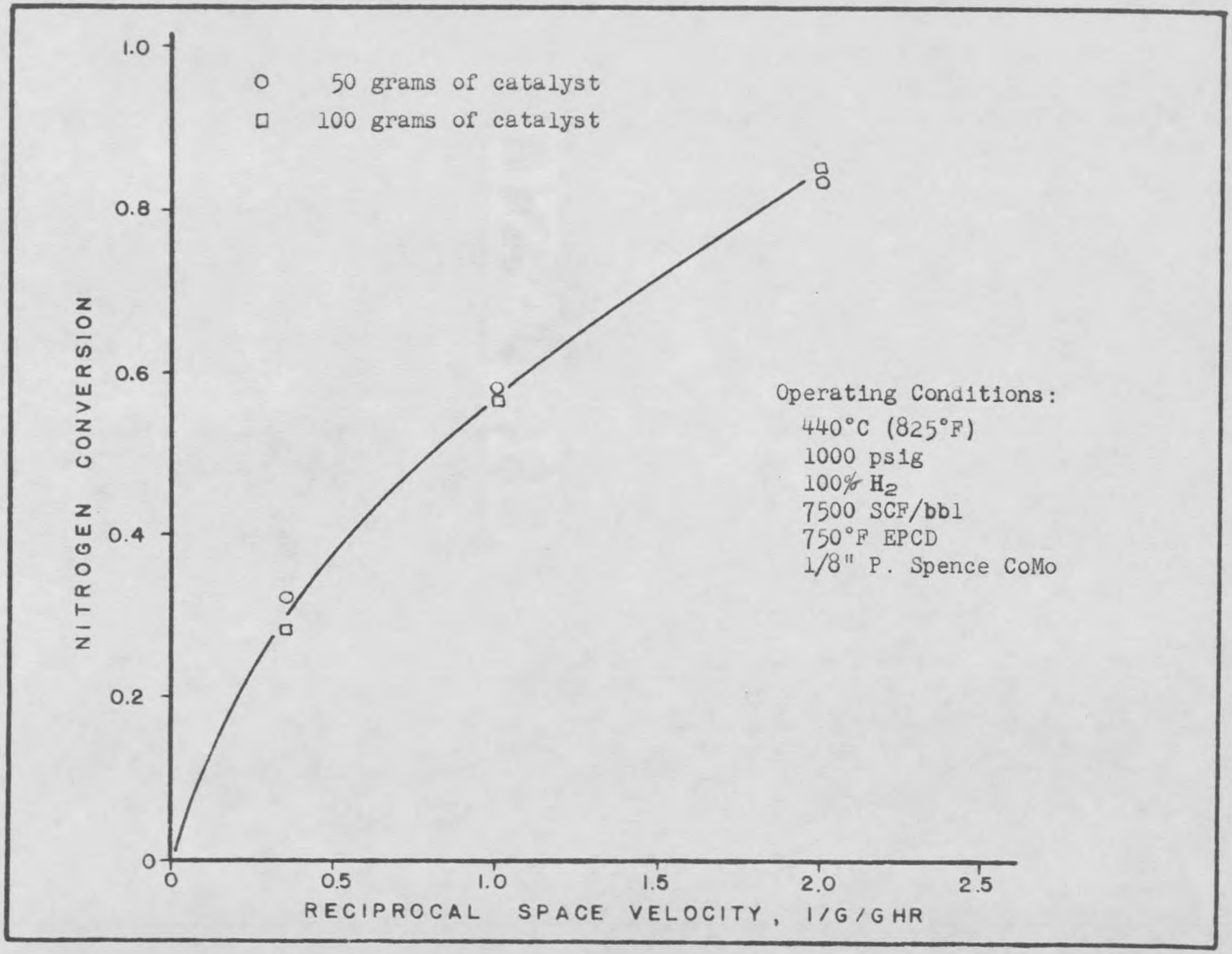


Figure 13. A Plot of the Nitrogen Conversion versus the Reciprocal Space Velocity for Two Different Weights of Peter Spence Cobalt Molybdate Catalyst.

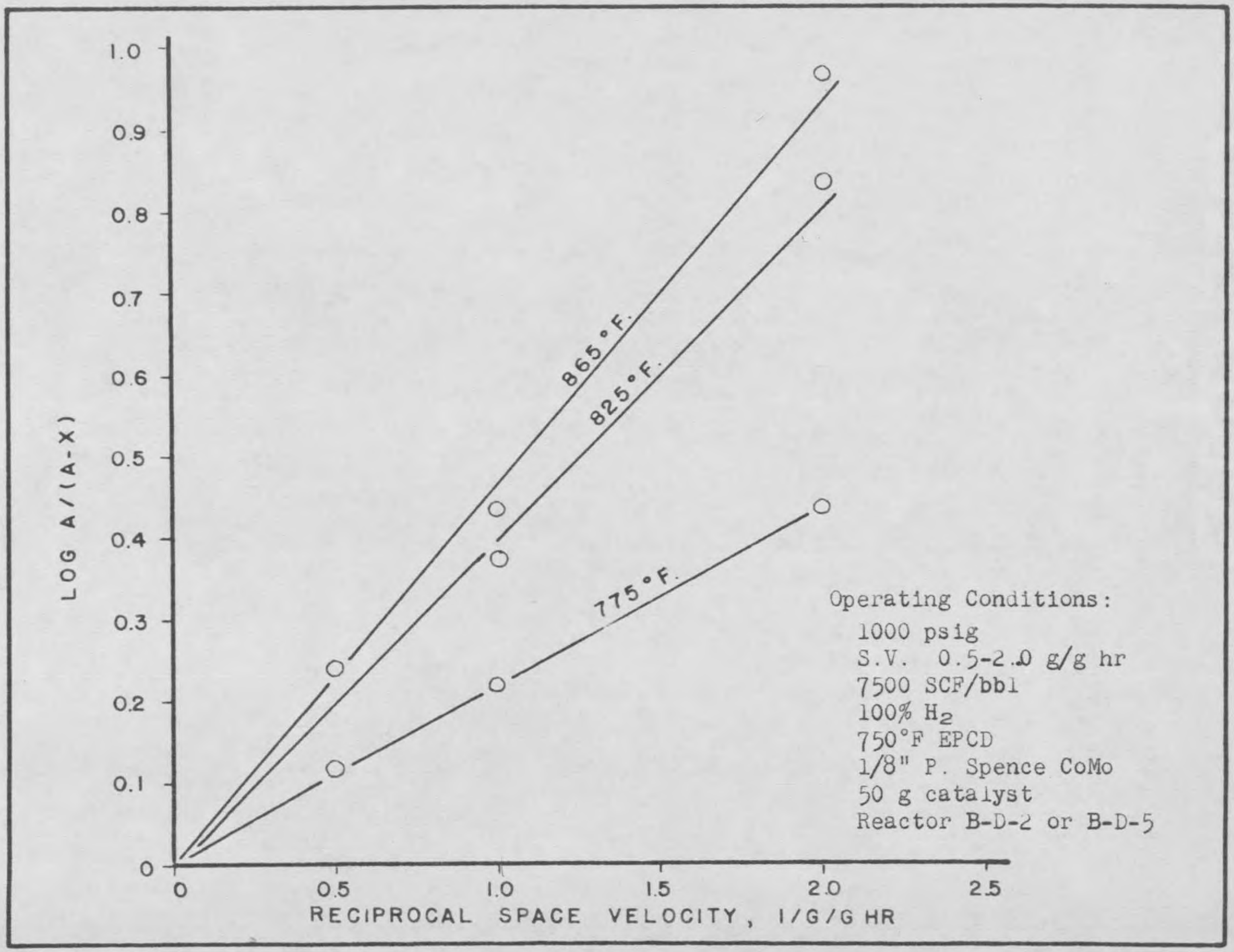


Figure 14. Plot of Log A/(A-x) versus Reciprocal Space Velocity Showing the Effect of Temperature.

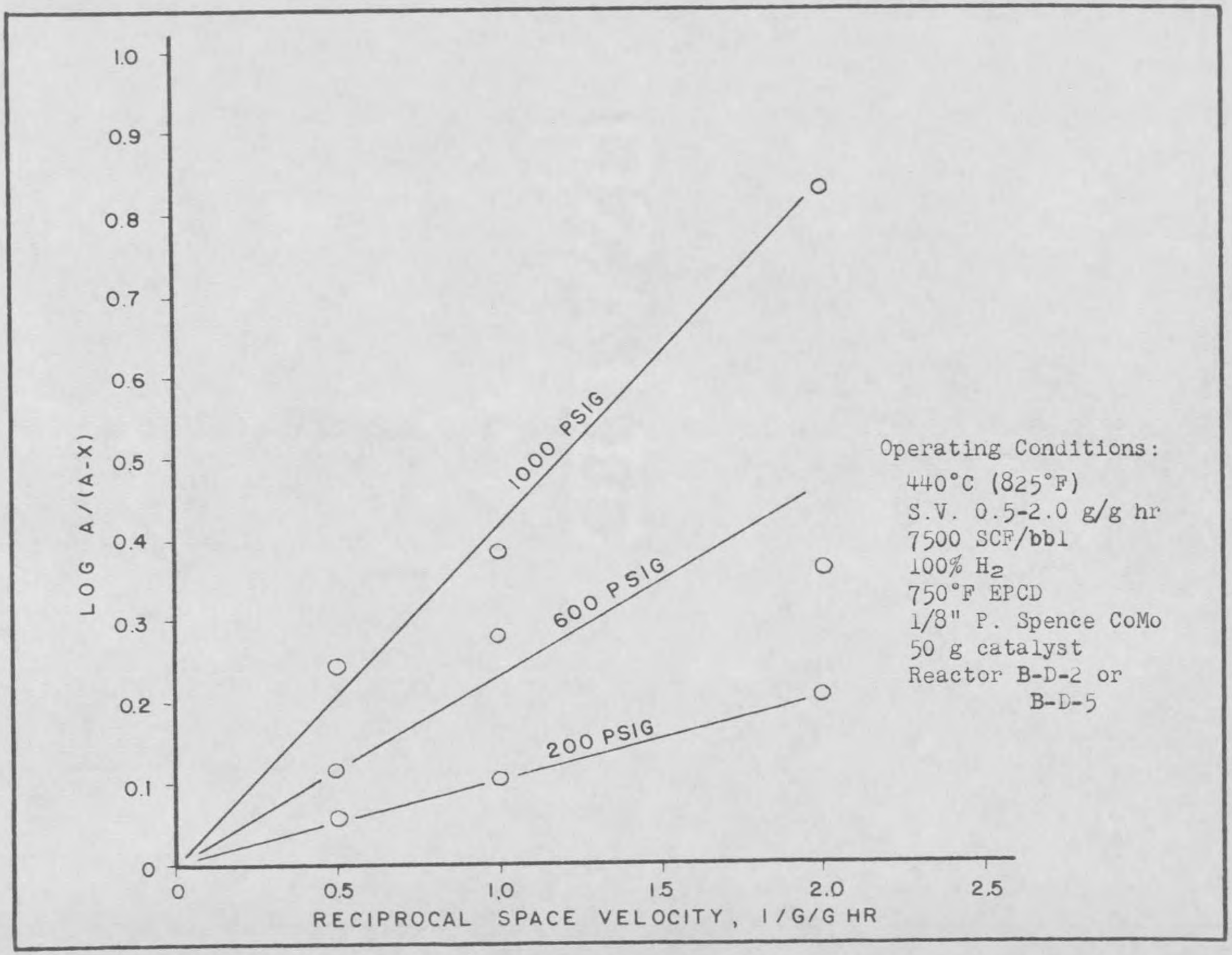


Figure 15. Plot of Log A/(A-x) versus Reciprocal Space Velocity Showing the Effect of Pressure.

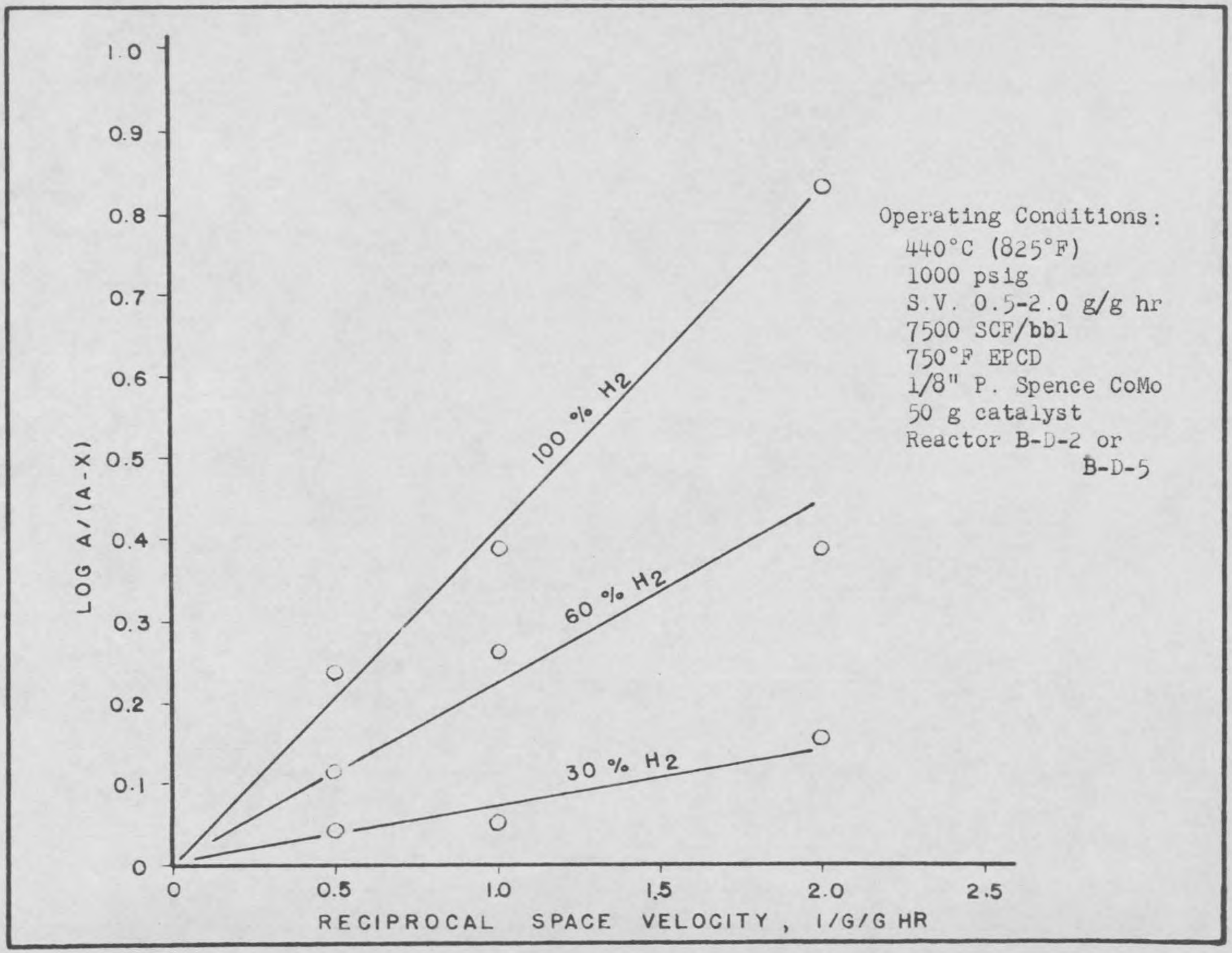


Figure 16. Plot of Log A/(A-x) versus Reciprocal Space Velocity Showing the Effect of the Hydrogen Content of the Hydrotreating.

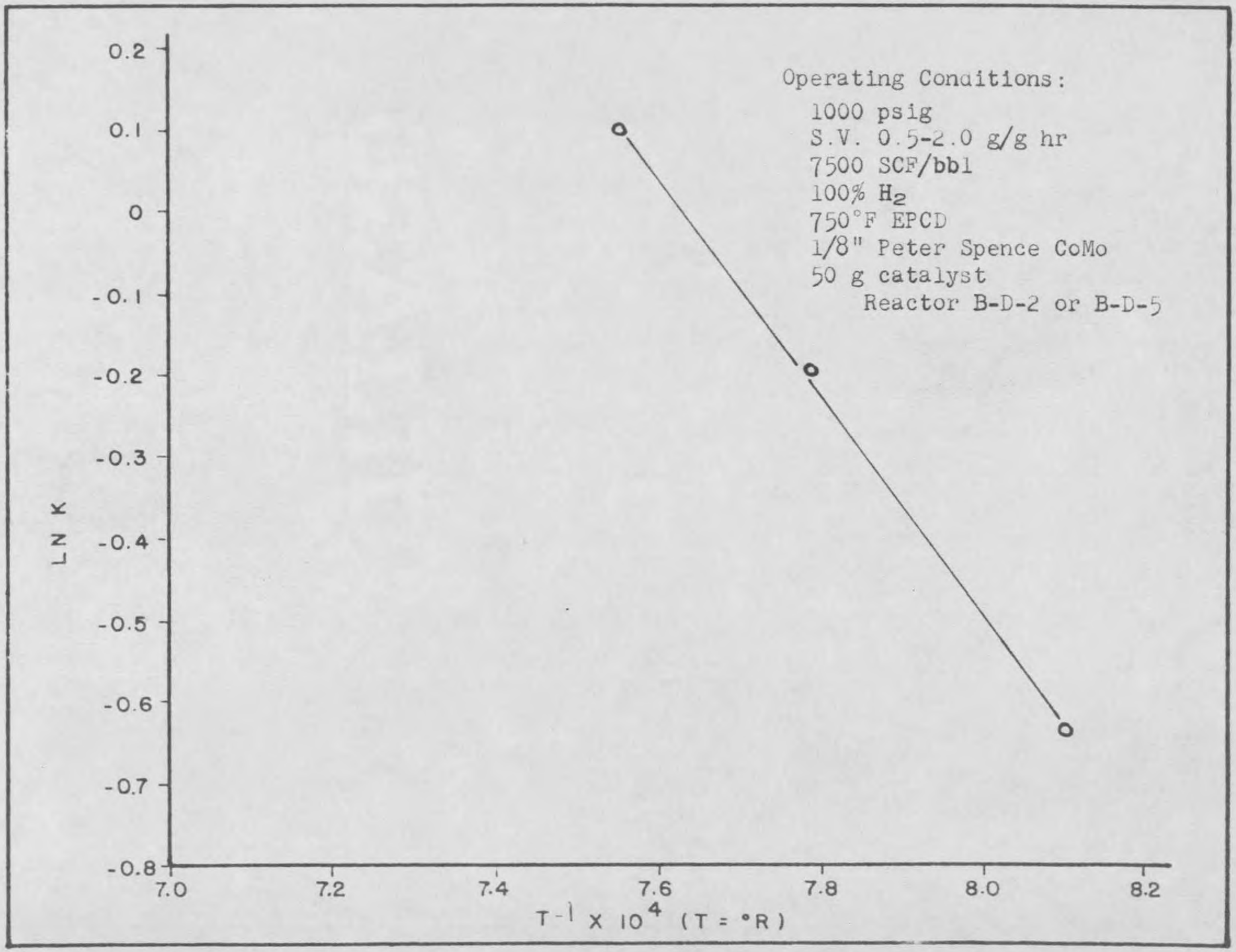


Figure 17. Arrhenius Plot.