



Hydrogenolysis of quinoline-constituted synthetic shale-oil
by Robert A Damon

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

A reaction system that consisted of a quinoline-constituted synthetic shale-oil which was undergoing hydrogenolysis in the presence of a cobalt-molybdate catalyst was studied. This study was undertaken to gain fundamental information concerning the behavior of a reaction system in which one of the typical heterocyclic nitrogen-compounds that are found in the distillates of shale oil is subjected to hydrogenolysis.

A bench scale, fixed bed, flow type, catalytic reactor was used.

The synthetic shale-oil, which contained 2 wt% nitrogen, was made up from quinoline and Penetek, a commercial mineral-oil which approximates the physical properties of cetane. Integral conversion data was gathered at 830°F for reaction pressures of 250, 500, and 1,000 psig. A hydrogen flow-rate of 7500 SCF/bbl was used. The catalyst was Peter Spence cobalt-molybdate which contained 2.5% CoO and 14.0% MoO₃.

Information that pertained to the chemisorptive behavior of heterocyclic nitrogen-compounds and that concerned the reaction products of the hydrogenolysis of quinoline was presented. A framework or outline for the reaction mechanism was developed from this information. The surface-rate-equation theory was used in conjunction with the framework of the reaction mechanism to postulate several mechanisms or models which would represent the behavior of the reaction system. Overall rate-equations were derived for the possible rate-controlling steps of these mechanisms. Conversion data and initial-rate data for the reaction system at 830°F were analyzed via these rate equations. Other data from Ryffel's thesis (31) which was gathered for this reaction at the temperature range of 725-775°F, was also analyzed. These analyses indicated that a complex-series reaction mechanism involving the series reactions of quinoline to dihydro-quinoline to tetrahydro-quinoline to alkyl-aniline to alkyl-benzene and ammonia, and involving dual-site reactions of quinoline and the intermediates with molecular hydrogen could be used to represent the behavior of the reaction system. They also indicated that a transition temperature existed between 775°F and 830°F where the rate-controlling step of the reaction mechanism changed. At 725-775°F, the rate-controlling step was the dual-site reaction of o-propyl aniline with molecular hydrogen. At 830°F, the rate-controlling step was the adsorption of quinoline. The rate expression for the reaction at 830°F was utilized to obtain an empirical equation which would represent the reaction system. The constants in this equation were determined from the data at 830°F and 500 psig. The close conformity of the resulting equation to the experimental data at 830°F and 500 psig supported the above mentioned mechanism indications for the 830°F reaction.

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SYNTHETIC SHALE-OIL

by

ROBERT A. DAMON

A THESIS

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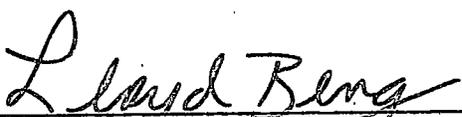
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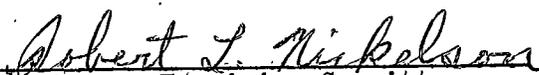
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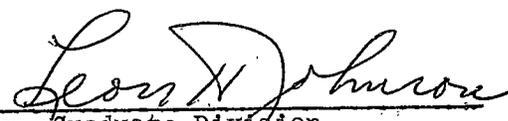
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ABSTRACT

A reaction system that consisted of a quinoline-constituted synthetic shale-oil which was undergoing hydrogenolysis in the presence of a cobalt-molybdate catalyst was studied. This study was undertaken to gain fundamental information concerning the behavior of a reaction system in which one of the typical heterocyclic nitrogen-compounds that are found in the distillates of shale oil is subjected to hydrogenolysis.

A bench scale, fixed bed, flow type, catalytic reactor was used. The synthetic shale-oil, which contained 2 wt% nitrogen, was made up from quinoline and Penetek, a commercial mineral-oil which approximates the physical properties of cetane. Integral conversion data was gathered at 830°F for reaction pressures of 250, 500, and 1,000 psig. A hydrogen flow-rate of 7500 SCF/bbl was used. The catalyst was Peter Spence cobalt-molybdate which contained 2.5% CoO and 14.0% MoO₃.

Information that pertained to the chemisorptive behavior of heterocyclic nitrogen-compounds and that concerned the reaction products of the hydrogenolysis of quinoline was presented. A framework or outline for the reaction mechanism was developed from this information. The surface-rate-equation theory was used in conjunction with the framework of the reaction mechanism to postulate several mechanisms or models which would represent the behavior of the reaction system. Overall rate-equations were derived for the possible rate-controlling steps of these mechanisms. Conversion data and initial-rate data for the reaction system at 830°F were analyzed via these rate equations. Other data from Ryffel's thesis (31) which was gathered for this reaction at the temperature range of 725-775°F, was also analyzed. These analyses indicated that a complex-series reaction mechanism involving the series reactions of quinoline to dihydro-quinoline to tetrahydro-quinoline to alkyl-aniline to alkyl-benzene and ammonia, and involving dual-site reactions of quinoline and the intermediates with molecular hydrogen could be used to represent the behavior of the reaction system. They also indicated that a transition temperature existed between 775°F and 830°F where the rate-controlling step of the reaction mechanism changed. At 725-775°F, the rate-controlling step was the dual-site reaction of *o*-propyl aniline with molecular hydrogen. At 830°F, the rate-controlling step was the adsorption of quinoline. The rate expression for the reaction at 830°F was utilized to obtain an empirical equation which would represent the reaction system. The constants in this equation were determined from the data at 830°F and 500 psig. The close conformity of the resulting equation to the experimental data at 830°F and 500 psig supported the above mentioned mechanism indications for the 830°F reaction.

I. INTRODUCTION

Natural-resource conservationists have voiced alarm over the rising annual consumption of petroleum-based fuels. However, world petroleum reserves appear to be maintained despite increasing annual consumption, but it is important to note that the producing cost for crude-oil is continually increasing. In due time, when petroleum supplies become inadequate or when the costs of crude-oil production warrant it, synthetic fuels based on coal and probably to a lesser extent on shale oil will become sources of liquid fuels (15).

Prior to and during the second world war, the lack of petroleum sources in European countries led to the development of full-scale processes for the production of synthetic fuels by coal hydrogenation and by the Fischer-Tropsch synthesis. Work was also directed toward the development of a process for producing liquid fuels from oil shale (15).

Here in the United States, a great deal of interest was shown in the possibilities of producing liquid fuels from oil shale because of the extensive deposits of oil shale in the Pichance Creek Basin of Northwestern Colorado. The United States Bureau of Mines has expended considerable research effort in the investigation of this problem (4, 5, 36, 37).

The distillates obtained from these oil shales by various retorting processes are rich in heterocyclic nitrogen-compounds similar to

those found in the distillates of coal tars (28, 39). Consequently, interest has also been shown in the Colorado oil-shale deposits as a source of these chemicals.

The Pichance Creek Basin extends over an area of approximately 1,000 square miles. In this area, the oil-shale deposits contain a potential 350 billion barrels of shale oil. This is approximately 4/5 of the total shale-oil reserves known to exist in the United States at the present time. This quantity of shale oil is significant in that it is three times as large as the world's known reserve of petroleum (4).

The exploitation of these oil-shale deposits can be classified according to the following three considerations:

1. Mining of the oil shale.
2. Retorting of the mined oil-shale.
3. Refining and upgrading of the crude shale-oil obtained from the retorting process.

At the present time, satisfactory methods for mining and retorting have been developed, and considerable progress has been made in the refining and upgrading of the crude shale-oil obtained from the retorts (4, 5).

The mining methods that are now used for mining the oil shale enable a recovery of only 75 per cent of the oil-shale deposit. Twenty-five per cent of the deposit must be left in the mine as supporting pillars.

The mined oil-shale is crushed and then subjected to a retorting operation. Ninety-two per cent of the crude shale-oil which is present in the oil shale can be recovered by this retorting operation.

The crude shale-oil from the retorting process is usually subjected to a coking operation to adjust the boiling range to a value which is consistent with fuels which are currently in volume demand. Approximately 79.6 per cent of the crude shale-oil that is fed to the coking operation can be recovered as a 700°F end-point distillate.

The mining-retort-coking sequence that is now in use will permit a recovery of about 55 per cent of the shale oil that is present in the mine as oil-shale deposits. Efforts to boost this recovery-figure have not been successful. It is therefore imperative that any process for upgrading the coker distillate should be of such a nature that nearly all of the coker distillate can be converted to usable products. (28).

The coker distillate contains heterocyclic nitrogen, sulfur, and oxygen, and a large percentage of olefinic compounds. The sulfur and nitrogen contents of the distillate are approximately one and two per cent by weight, respectively.

Any upgrading process for the distillate would require removal of the organically-combined sulfur, nitrogen, and oxygen. It should also accomplish saturation of the olefinic compounds.

Upgrading could be achieved by conventional petroleum-processing, but the nitrogen compounds which are present in the coker distillate cause rapid deactivation of cracking catalysts (27). Gum removal and desulfurization processes, exclusive of hydrofining processes, lead to a significant volume loss from the feed to the product (5). This would be objectionable since a loss in the recovery of usable products from the shale-oil should be avoided.

The most promising method of upgrading the coker distillate appears to be catalytic hydrogenation in the presence of a cobalt-molybdate catalyst. This method enables the breaking of carbon-nitrogen, carbon-sulfur, and carbon-oxygen bonds, yielding H_2S , NH_3 , and H_2O , respectively. Also, olefins are saturated in this process. The advantage of this hydrofining process is that nitrogen, sulfur, and oxygen removal and saturation of the olefinic bonds are all accomplished in one step (4). The cobalt-molybdate catalyst is selective in that it does not promote hydrogenation of aromatic compounds. This renders the hydrogen consumption less than it would be for other hydrofining catalysts (15). Eighty-five per cent of the coker distillate can be recovered as premium fuels by this process (5).

The cobalt-molybdate hydrofining method for upgrading coker distillates has been investigated by the Chemical Engineering Department at Montana State College (6, 19, 21, 24). In these studies, four catalysts were found to be effective: HF-activated cobalt-molybdate,

Peter Spence cobalt-molybdate, palladium-promoted Harshaw molybdenum-oxide, and Harshaw cobalt-molybdate.

The optimum operating conditions were found to be:

catalyst-bed temperature: 825-875°F

treat-gas flow rate: 2000-7500 SCF/bbl

operating pressure: 1000 psig

space velocity: 1.0 gm oil/(gm catalyst)(hr)

In the hydrofining of coker distillates with cobalt-molybdate catalysts, sulfur and oxygen are easily removed. The removal of nitrogen is not achieved as easily as the removal of sulfur and oxygen is achieved. For this reason, a kinetic study which was based on the conversion of the nitrogen content of coker distillates to ammonia was undertaken by Benson at Montana State College (6).

The nitrogen compounds which are present in the shale-oil coker-distillates appear chiefly as pyridine, quinoline, acridine, and similar type compounds (23). Investigations by Clyde Berg of the Union Oil Company have indicated that a typical reaction for the removal of nitrogen from a nitrogen-containing compound in the coker distillate is as follows (4):



Pyridine

Pentane Isomers

In Benson's kinetic study of shale-oil hydrogenation at Montana State College, the hydrogen feed-rate was held in excess at 50 mols of hydrogen per mol of nitrogen, so that the reaction would be dependent only upon the concentration of nitrogen in the coker-distillate charge stock. By using this method, the effects of the various process variables on the reaction were obtained. Benson's study determined that the transfer of the reactants to the catalyst's surface by external diffusion did not control the rate of nitrogen removal.

Professor L. G. Mayfield of the Chemical Engineering Department at Montana State College suggested that more insight into the process of nitrogen removal from shale oil might be obtained if a synthetic shale-oil which contained only one nitrogen compound were to be studied (23). On the basis of this suggestion, a decision was made to undertake such an investigation. This thesis is a report of that study by the author.

The synthetic shale-oil used in this study was a mixture of "Penetek", and the nitrogen-containing compound, quinoline. "Penetek" is a commercial mineral oil which closely approximates the properties of cetane.

The synthetic shale-oil contained two weight-per-cent of nitrogen. This approximates the nitrogen content of shale-oil coker-distillate.

II. OBJECTIVES AND MODE OF INVESTIGATIONS

As mentioned in the introduction of this report, a kinetic study was undertaken by Benson at Montana State College to obtain fundamental kinetic information concerning the reaction which led to the conversion of the nitrogen compounds contained in shale-oil coker-distillate to ammonia and aromatic hydrocarbons when these nitrogen compounds were destructively hydrogenated with the aid of a cobalt-molybdate catalyst. By holding the hydrogen feed-rate at approximately 50 mols of hydrogen per mol of nitrogen compounds in the initial charge stock, Benson was able to fit an empirical, pseudo-first-order rate-equation to the conversion data which he obtained. He was also able to determine whether diffusion of the reactants to the catalyst surface or diffusion of the products from the catalyst surface were controlling the rate of the conversion of the shale-oil's nitrogen compounds to ammonia.

Use of the order-of-reaction concept for fitting empirical equations to rate data or to integral data has proven very useful in many situations where a rate equation was needed for designing a reactor. However, this concept often does not provide an empirical rate-equation which fits the kinetic data well for some types of vapor-phase reactions which are catalyzed by solid catalysts. Another disadvantage of applying this concept to the analysis of kinetic data obtained from solid-catalyzed, vapor-phase reactions is that this concept does not give much insight into the reaction mechanism.

The surface-rate-equation theory does, however, enable an investigator to obtain a fair amount of information about the reaction mechanisms of solid-catalyzed vapor-phase reactions. This theory has been successfully applied in recent years and numerous examples of its application appear in the literature. In this theory it is postulated that the reaction mechanism consists of a series of integrated steps in which the reactants diffuse to the catalyst and into the pores of the catalyst, become adsorbed on the surface of the catalyst, react on the catalyst surface, desorb from the surface of the catalyst, and finally diffuse from the pores of the catalyst and from the catalyst to the main gas stream.

Application of this theory to the study of a given reaction involves the postulation of various feasible mechanisms which follow the above pattern, the derivation of overall rate-equations based on the assumption that one of the steps of the mechanism is the rate controlling step, and the correlation of kinetic data to these equations. A detailed explanation of this theory and its applications is given in the discussion section of this report.

It was decided that it would be desirable to apply the surface-rate-equation theory to the reaction for removing nitrogen from shale oil by destructive hydrogenation with a cobalt-molybdate catalyst. However, this study would be extremely complex and difficult because of the variety of heterocyclic nitrogen-compounds contained in shale-oil coker-

distillate. Many mechanisms would be possible for each of the heterocyclic nitrogen-compounds, and to distinguish what is happening with each one when all of them are reacting together from the same feed stock would be a defeating task. It was for this reason that Benson was unable to apply the surface-rate-equation theory to his study with shale-oil-coker-distillate.

If, however, a synthetic shale-oil were to be studied which contained only a single heterocyclic nitrogen-compound, insight into the mechanism for this single compound could be gained without the complications which would be involved with the coker distillate. Studies of a number of synthetic shale-oils each based on a different heterocyclic nitrogen-compound found in shale oil could be made. These could then be correlated to give an understanding of the shale-oil coker-distillate reaction.

The objective of this particular investigation was to gain information about the mechanism of the catalytic destructive hydrogenation (hydrogenolysis) of a quinoline-constituted synthetic shale-oil. It was hoped that any information gained in this study would be useful in helping to understand the removal of nitrogen from shale-oil coker-distillate by catalytic destructive hydrogenation.

The overall plan of this investigation was to apply the surface-rate-equation theory to postulated feasible mechanisms. This was to be done by gathering experimental initial-rate data and using these in

conjunction with the above theory to determine which of the postulated mechanisms would be the most probable.

The reactor to be used in this study was a tubular, fixed bed, flow type, catalytic reactor. It was designed to produce integral reaction data. The initial-rate data was to be obtained from conversion vs. reciprocal-space-velocity curves. These curves were to be obtained at operating pressures of 250, 500, and 1000 psig, each curve yielding an initial rate value at this pressure. Each curve was to be determined by measuring the conversion of the nitrogen in quinoline to ammonia for the series of space velocities: 10.0, 7.5, 5.0, 1.0, and 0.5 (gm oil)/(gm catalyst)/(hr).

The other variables, as far as possible, were chosen as those values of these variables which gave optimum conversion of the nitrogen compounds in shale-oil coker-distillate to ammonia. These variables were held fixed for determining the conversion vs. reciprocal-space-velocity curves at the three above-mentioned pressures. These fixed variables were:

charge stock: Penetek and quinoline, 2 wt% nitrogen

hydrogen flow rate: 7500 SCF/bbl oil

temperature: 830°F (443°C)

catalyst: Peter Spence graphite-base cobalt-molybdate,
1/8" pellets, R.D. 3718, 2.5% CoO, 14.0% MoO₃

treat gas: 100% hydrogen

Prior to the actual gathering of the main body of experimental data, it was necessary to do some work toward redesigning the bench-scale reactor that was to be used in this study. It was planned to use the same reactor for this study that was used in Benson's shale-oil study. During the shale-oil studies, however, difficulty with maintaining isothermal conditions in the reaction zone was experienced. This was due to the necessity for both adding and removing heat energy in different zones of the same reactor. It was necessary, especially for high space-velocity runs, to provide a large preheat-load for the reaction stream. The exothermic nature of the hydrogenation reactions which were involved meant that the reactor must be capable of dissipating a large amount of the heat-of-reaction from the reaction zone of the reactor.

To alleviate this difficulty, a number of runs were made prior to the main body of experimental runs in which various locations of the heating coils were tried, various distributions for the insulation were examined, and various preheater arrangements were tested. A satisfactory system for all but the extremely high space-velocities was found. This system is described in the section of this report on equipment. A method for dissipating the heat-of-reaction at high space-velocities, in which the catalyst was distributed evenly among the catalyst supports in the reaction zone, was suggested by Dr. R. L. Nickelson. This method was successfully used and it solved the problem of runaway reaction-temperatures at high space-velocity runs at high pressures.

III. EQUIPMENT

A. The Hydrotreating Unit

The experimental runs were carried out in an integral type reactor which was designed for continuous flow over a fixed-bed catalyst. The feed oil was pumped into a radiant preheater and from there to the top of the reactor. Hydrogen flow was adjusted by a needle valve. The hydrogen was passed through a deoxygenating unit, a drying unit, a rotameter, and then it entered the reactor top.

A pressure regulator valve controlled the operating pressure and enabled operating at constant pressures ranging from 200 psig to 1200 psig.

The reactor was heated by means of nichrome-wire heating coils. These heating coils were connected to Powerstats which made possible a wide range of temperature control.

After the oil had passed through the reactor and had been condensed, it was collected in a receiving flask. Gaseous material which left the reactor was given a caustic scrub and then vented into the atmosphere.

A schematic flow diagram of the catalytic hydrotreating unit is shown in Figure 1.

B. The Reactor

The reactor was made from a 30-inch length of nominal 1-inch O.D., seamless, Type 18-8 stainless steel pipe. It was equipped with a flanged union at each end. The reactor was covered with a layer of asbestos tape, and the nichrome heating coils were wrapped on the reactor over this tape. A three-inch layer of 85 per cent magnesia insulation was placed over the heating coils and the insulation was covered with sheet aluminum-foil.

The lower 20-inch length of the reactor was covered with a single heating coil and another heating coil was overlaid on the bottom four inches of the first coil. The catalyst zone started at the top of the first heating coil and extended down the reactor for a length of ten inches when 100 grams of catalyst were used and five inches when fifty grams of catalyst were used.

A third coil was wrapped around the top eight inches of the reactor. Thus, a length of two inches in which there were no heating coils was allowed above the top of the catalyst zone.

A length of 3/16-inch O.D., stainless steel tubing, brazed shut at the lower end, was inserted down the center of the reactor and contained the thermocouples which were used to measure the temperature in the reactor. Thermocouples were located at the top, center, and bottom of the catalyst zone and one was located in the preheat zone.

C. The Preheater

The preheater consisted of a 3" x 11" cylinder formed from sheet stainless-steel and closed at either end. The cylinder was wrapped with asbestos tape and a heating coil and was covered with a two-inch layer of magnesia insulation. Six feet of 1/8-inch O.D. stainless steel tubing was coiled to a length of 10 inches and a diameter of one inch. This coil was placed in the center of the preheater and the oil was pumped through the coil before it entered the reactor.

IV. MATERIALS, METHODS, AND ANALYSES

A. Materials

1. The Charge Stock

The quinoline used for preparing the charge stock was purified by fractionation from a commercial type quinoline containing 90 per cent quinoline and 10 per cent quinaldine and isoquinoline. The purity of the distillate was determined by its refractive index. To keep the quinoline isolated from oxygen, the distillate was collected under an atmosphere of natural gas.

The charge stock was prepared by mixing quinoline with a pure mineral oil such that the resulting mixture was two weight per cent nitrogen.

The mineral oil used was purchased from the Penn-Drake Company and is commercially known as "Penetek". This oil very closely approximates the physical properties of cetane. It has a specific gravity of 0.797 and has a boiling range of 250-270°C.

The mixture of quinoline and Penetek was stored in a 50-liter container and kept under an atmosphere of natural gas. It was then siphoned from the container to the holding vessel of the charge-stock pump whenever it was needed for a run.

2. The Catalyst, Catalyst Supports, and Treat Gas

The catalyst used for the study was a cobalt molybdate catalyst. It was in the form of 1/8-inch pellets and it was manufactured by Peter Spence and Sons, Ltd. The catalyst was a graphite-base catalyst and was 2.5% CoO and 14.0% MoO₃.

Catalyst supports used in the reactor were 1/8-inch aluminum pellets which were obtained from the Norton Abrasive Company.

The hydrotreating gas was 100 per cent hydrogen and was supplied by Whitmore Oxygen Company. There was sufficient cause to believe that this hydrogen contained small amounts of oxygen and for this reason, the hydrogen was treated in a "deoxo" unit to remove the oxygen before being sent to the reactor. The "deoxo" unit contained a palladium catalyst and removed the oxygen by catalytically promoting the reaction of oxygen with enough hydrogen to form water. The water was then removed by passing the hydrogen through a tube packed with "Drierite".

B. Methods

1. Control and Measurement of Process Operating Variables

The reactor temperature was controlled by adjusting the voltage to the heating coils by means of Powerstats. Constant voltage was supplied to the Powerstats by a constant voltage transformer. Temperatures were measured at 15-minute intervals with iron-

constantan thermocouples used in conjunction with a Leeds and Northrup indicating potentiometer.

The reactor pressure was measured with a pressure gage which was tapped into the system at the lower end of the reactor. A Fisher-Wizard controller and a Mason-Neilan air-to-close regulator valve were used to maintain the reactor at a given pressure.

The flow rate of hydrogen to the reactor was controlled manually with a gas flow-meter and a needle valve. The type used was the Brooks calibrated rotameter. A constant pressure drop across the meter was maintained by the pressure regulator valve and the needle valve on the flow meter. During the course of a run, the flow reading was checked and corrected, if necessary, every fifteen minutes.

2. Preparation of the Reactor

The reactor was designed so that it could be removed from the hydrotreating system by disconnecting the charge-stock and hydrogen feed-lines, the thermocouple connections, the blow-out line, and by separating the union at the lower end of the reactor. When the reactor was removed from the system it was inverted and charged with catalyst supports. The reaction zone was then charged with catalyst, and the remainder of the reactor was filled with catalyst supports. At 3- to 4-inch reactor-length intervals during the charging of the reactor, the reactor was tapped sharply with a

hammer until the material present in the reactor indicated no further tendency to settle. This was done to insure that there would be no shifting of the catalyst when the reactor was re-inverted and placed back in the hydrotreating system. After the reactor had been charged, the catalyst and supports were kept in place with a piece of stainless-steel screen.

3. The Time-Length of Individual Runs

During the investigations with shale oil, it was found that during the first four hours of a run the conversion of the nitrogen content of the charge stock to ammonia rose sharply to a maximum conversion and then decreased. Shortly after this first four-hour period, the conversion leveled to a reasonably constant value. Furthermore, this constant conversion was found to be maintained in runs with a duration of up to 16 hours. The time at which the maximum conversion occurred was found to vary with the space velocity (6).

This characteristic type of behavior was also found to exist in the runs made with quinoline. Figure 2 shows this behavior for runs at various space velocities.

Thus, it was decided to run for a minimum of five hours until the first sample was collected, provided that isothermal conditions were maintained in the reactor during this period. If isothermal conditions were not maintained, the time for collecting the first

sample was extended until isothermal conditions had been maintained for at least one hour. Samples of the processed oil were then collected during the last four hours of a run.

4. Operating Procedure

The same operating procedure was used for each run.

After being charged with catalyst, the reactor was heated to the operating temperature of 830°F. During the heating period, hydrogen was allowed to flow through the reactor at a low flow rate. Approximately three hours were required to heat the reactor to the operating temperature.

When the reactor had reached the operating temperature and indicated a tendency to remain at this temperature, the charge stock was pumped into the reactor at a rate determined by the space velocity. The time at which this took place was considered to be the start of the run. Periodically, during the course of the run, the flow rate of charge stock was checked and the pump was adjusted, if necessary.

The processed oil was collected in a Jerguson sight glass and allowed to drain off at a steady rate in order to avoid any sudden pressure drops in the system which would be caused by draining large amounts of product in a short time interval.

The length of the run was determined in the manner mentioned in the above section.

At 15-minute intervals the temperatures in the reactor were recorded and the hydrogen-flow rate was checked. Also, periodic checks were made to see whether or not the correct space velocity was being maintained and if isothermal conditions were being maintained in the reactor. The latter check was made by moving the thermocouples to various positions in the reactor such that a temperature profile of the catalyst zone was obtained.

C. Analyses

The conversion of the nitrogen in the charge stock to ammonia was determined by analyzing the product for nitrogen content. The samples were collected and placed in a flask where nitrogen gas was bubbled through the sample for a period of 15 minutes in order to remove any ammonia which might have been absorbed by the product oil. They were then dried with calcium chloride and filtered.

The nitrogen content of each sample was determined by the Kjeldahl method.

The product was also subjected to infrared analysis and analysis by fractionation. This was done in order to obtain a qualitative picture of the product.

V. DISCUSSION

A. Introductory Remarks

As stated in Section II of this report, the objective of this particular investigation was to gain information about the catalytic, destructive hydrogenation of a quinoline-constituted, synthetic shale-oil. This reaction was studied at a temperature of 830°F; at pressures of 250, 500, and 1000 psig; with a hydrogen flow-rate of 7500 SCF/bbl oil; and with a cobalt-molybdate catalyst of 2.5% CoO, 14.0% MoO₃.

In this discussion, known information which is pertinent to the above reaction will be presented first. This information will then be used to develop a framework for the reaction mechanism. This will be followed by a presentation of kinetic techniques which are used for tubular flow-reactors and heterogeneous reactions, and then by a presentation of rate-equation theory for fluid-phase reactions catalyzed by solids.

An example derivation of a rate equation by the surface-rate-equation method will be given. Possible mechanisms for the catalytic hydrogenolysis of quinoline will be discussed and a series of rate equations will be derived based on the surface-rate-equation theory. These rate equations will be analyzed through the application of experimental data to obtain information about the mechanism of the reaction.

B. Nitrogen Compounds and Chemisorption

Nitrogen compounds found in various crude oils have long been troublesome to the petroleum industry because of their effect of deactivating cracking catalysts (39, 2). This deactivating effect is especially pronounced when shale oils are subjected to catalytic cracking. Evidence indicated that the degree of deactivation was directly proportional to the amount of nitrogen-containing compounds present in the feed to the cracking unit. Up until the early 1950's, there was some difference of opinion as to what exactly caused this deactivation. The general concensus of opinion was that the deactivation was caused by a laydown of carbonaceous residue on the catalyst. While this was to some extent true, as evidenced by the cracking of feedstocks which were devoid of nitrogen content, there was no experimentally-backed explanation of the specific role of nitrogen compounds in the deactivation.

To resolve this question, the Houdry Process Laboratory undertook an investigation of the poisoning of cracking catalysts by nitrogen compounds (26, 27). Since catalytic action is highly specific, it has been concluded that specific chemical properties of catalysts are involved in catalytic action (8). The Houdry study attempted to establish the essential chemical properties or active principles of a number of catalysts. The nitrogen compounds pyridine and quinoline were investigated with both inactive silica gels and active metal-oxide catalysts at various pressures and temperatures from 250-500°C.

Both inactive silica gels and active catalysts were saturated with gaseous quinoline. It was found that the quinoline could be completely desorbed from the catalytically inactive silica gels by a stream of nitrogen gas, whereas under the same conditions only a very small part of the quinoline was desorbed from the active catalyst. On boiling a quinoline-treated catalyst with aqueous HCl solution an extract was obtained which was shown to contain quinoline. These observations indicated that quinoline is held as such by the catalyst rather than as its decomposed or polymerized product.

When the adsorption of quinoline and pyridine were compared, differences were found in the amount of quinoline and in the amount of pyridine chemisorbed under identical operating conditions. These differences were directly attributable to the differences in the strength of the two substances as bases. The two chief conclusions of this study were:

1. Nitrogen containing compounds are chemically held to active metal-oxide catalysts, and the amount chemisorbed is decreased with an increase in temperature.
2. The chemical properties exhibited by the active sites on the catalyst surface identify the active principle as an "acid".

Thus, it appears feasible that the basic nature of quinoline would allow it to react with the acidic function of the catalyst. This is probably the next step in the reaction mechanism of the hydrogenolysis

of quinoline after the quinoline has diffused through the surface film and into the pores of the catalyst (25). The work of Mills, et. al., indicates that while there is some physically adsorbed quinoline on the surface of the catalyst after the diffusional steps, the adsorbed quinoline is predominately present as chemisorbed and non-decomposed quinoline on the surface of the catalyst. At increased temperatures and pressures, the ratio of physically-held quinoline to chemically-held quinoline increases, but the amount of physically-held quinoline is still small compared to the amount of chemically-held quinoline.

The heterocyclic ring of quinoline is more amenable to reduction than the carbocyclic ring (16). It may be supposed that some vapor-phase hydrogenation of quinoline could occur, and that the resulting dihydro- and tetrahydro-quinolines would compete with quinoline for active chemisorption sites on the catalyst surface. Work by several investigators has shown that significant conversion of quinoline to tetrahydroquinoline can only be obtained through the use of various hydrogenation catalysts (16, 29, 33). Thus, the quinoline molecule is probably chemisorbed as such.

C. Reaction Products

Sugino and others have hydrogenated quinoline in the presence of copper catalysts to get up to 95% yields of tetrahydroquinoline (33, 16). Rapoport studied the hydrogenolysis of quinoline with a molybdenum catalyst, a hydrogen pressure of 80 atmospheres, and temperatures of

420-450°C. He obtained yields of 95-98% tetrahydroquinoline (29). The tetrahydroquinoline further decomposed to give o-propyl aniline, o-ethyl aniline, o-methyl aniline, aniline, and methane. These same investigators indicate that the further hydrogenation of tetrahydroquinoline to decahydroquinoline is difficult and that as a reaction proceeds very slowly.

Ryffel also identified the above nitrogen compounds in the product oil. Through the use of gas-chromatography techniques, the following compounds were identified (31):

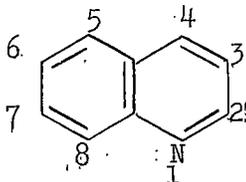
- tetrahydro quinoline
- o-propyl aniline
- o-ethyl aniline
- o-methyl aniline
- aniline
- ammonia
- quinoline

In addition, the following pertinent compounds were also identified in the product oil:

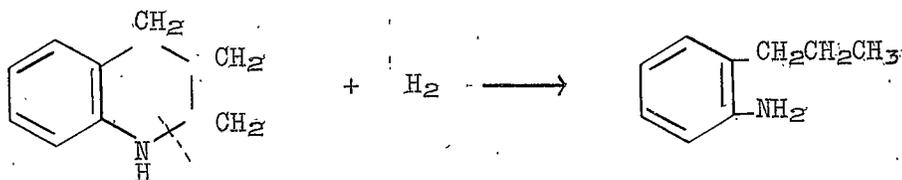
- n-propyl benzene
- iso-propyl benzene
- ethyl benzene
- toluene
- benzene
- o-ethyl toluene
- propyl cyclohexane
- ethyl cyclohexane
- methyl cyclohexane
- cyclohexane

D. Ring Cleavage

Atomic positions in the fused, six-membered, ring system of quinoline are, by agreement, numbered in the following manner:



The presence of aniline and some of its homologs in the product oil probably indicates that the heterocyclic ring of tetrahydroquinoline was cleaved between the 1 and 2 positions. The absence of alkylamine substituted benzenes indicates that cleavage probably did not occur between the 1 position and the adjacent carbon in the benzene ring:



E. Order of Nitrogen Removal

The alkyl cyclohexanes present in the product oil are probably hydrogenation products of alkyl benzenes. It is also significant that no amine-substituted alkyl cyclohexanes were found in the product oil. This would indicate that the amine group must have been removed from the aniline homologs prior to the subsequent hydrogenation which yielded the alkyl cyclohexanes:

