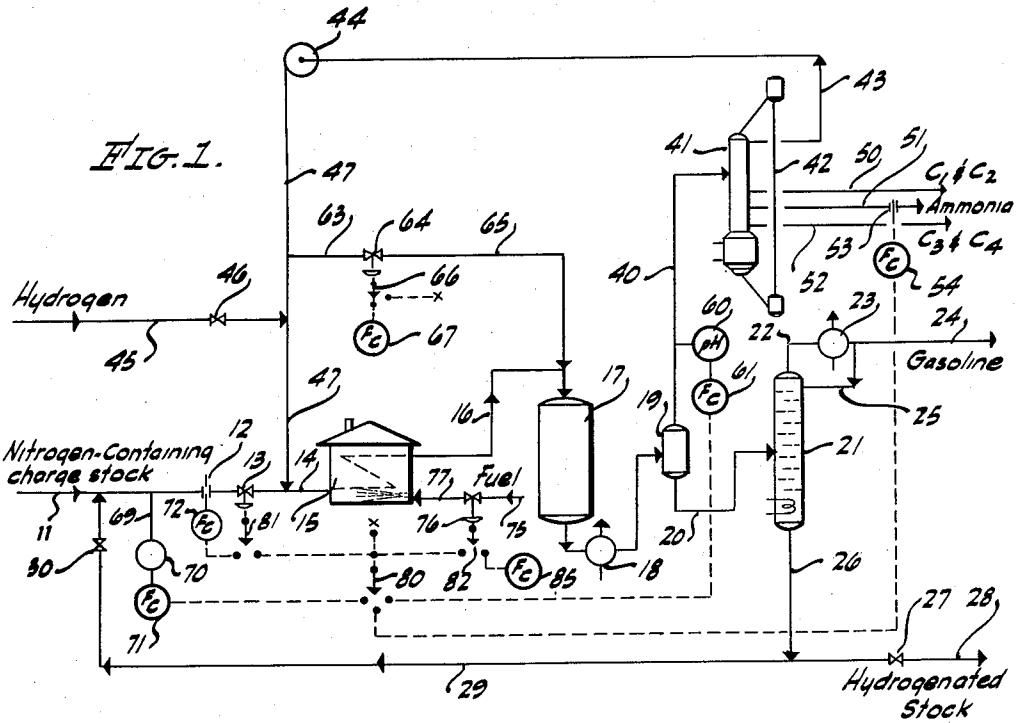
Nov. 3, 1959 R. A. HANSON 2,911,356

HYDROCRACKING OF HYDROCARBONS WITH REACTION CONDITIONS DEPENDENT ON NITROGEN CONTENT OF FEED

Filed Feb. 18, 1957

FIG. 1.



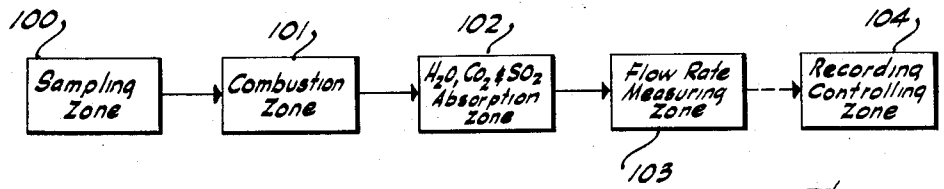
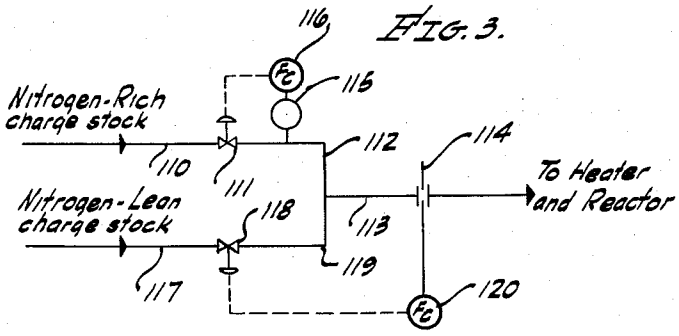


FIG. 2.

FIG. 3.



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2,911,356

HYDROCRACKING OF HYDROCARBONS WITH REACTION CONDITIONS DEPENDENT ON NITROGEN CONTENT OF FEED

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Application February 18, 1957, Serial No. 640,805

6 Claims. (Cl. 208—110)

This invention relates broadly to methods for the catalytic conversion of hydrocarbon oils in the presence of hydrogen. More particularly, this invention relates to methods for controlling the conversion temperature in accordance with the nitrogen content of a hydrocracking feedstock whereby the efficiency of the hydrocracking reaction is improved.

The hydrocracking of petroleum oils, shale oils, hydrogenated coal distillates and the like is well known in the art. In general, the hydrocracking reaction involves the scission of one or more carbon bonds in the hydrocarbon molecule with an attendant absorption of hydrogen to saturate the hydrocarbon fragments and the resultant formation of two or more smaller hydrocarbon molecules. Denitrogenation, desulfurization, hydrogenation, and the like occur simultaneously.

It has now been found that the catalytic hydrocracking reaction is greatly inhibited by the nitrogen content of the feedstock. Furthermore, it has been found that the inhibiting action of the nitrogen compounds is lessened by raising the temperature for a given feedstock. In the absence of nitrogen compounds, a high conversion temperature promotes destructive hydrogenation leading to the formation of less valuable gaseous hydrocarbons and/or extensive carbon deposition on the catalyst for a given combination of reaction conditions and feedstock. It has been found that as the nitrogen content of the charge stock increases, the reaction temperature should correspondingly be increased, while as the nitrogen content of the charge stock decreases the reaction temperature should be decreased in order to maintain an optimum conversion.

It is an object of this invention to vary a hydrocracking reaction temperature in accordance with the nitrogen content of the feedstock.

It is another object of this invention to vary the reaction temperature during a hydrocracking process in accordance with fluctuations of the nitrogen content of the feedstock so as to maintain the reaction conditions which are most favorable for the instantaneous feedstock being processed.

It is another object of this invention to analyze the feedstock flowing to a hydrocracking reactor to determine its nitrogen content and to regulate the reaction temperature in accordance with the nitrogen content of the feedstock.

It is another object of this invention to estimate the nitrogen content of a feedstock by means of pH measurements on either the feedstock flowing to the reactor or the gaseous or liquid products from the reactor and to vary the reaction temperature in accordance therewith.

It is another object of this invention to estimate variations in the nitrogen content of a feedstock by corresponding variations in the synthetic ammonia content of the products of reaction and to regulate the reaction temperature in accordance with fluctuations in the quantity of synthetic ammonia.

It is another object of this invention to provide a

continuous method for the determination of nitrogen in a hydrocarbon feedstock.

It is another object of this invention to vary the proportions of a relatively nitrogen-rich feedstock and a relatively nitrogen-lean feedstock flowing to a hydrocracking reaction zone so as to supply thereto a relatively uniform volumetric flow of feedstock which has approximately a constant nitrogen content.

It is another object of this invention to control the temperature of the charge stock heating zone supplying heated hydrocarbons to a hydrocracking reaction zone by varying either the fuel supply thereto or the charge stock flow rate thereto in accordance with the nitrogen content of the charge stock.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly, this invention relates to methods and apparatus for controlling the reaction temperature in a hydrocracking process in accordance with the nitrogen content of the feedstock whereby the gasoline yield therefrom is increased and the carbon deposition on the catalyst is minimized. In one modification of the invention the reaction temperature is maintained substantially constant and two or more feed stocks are continuously blended to produce a constant flow rate of charge stock having a substantially uniform nitrogen content.

Two general methods may be employed to estimate the nitrogen content of a feedstock, viz. physical or chemical analysis of the feedstock and physical or chemical analysis of the products of the reaction.

In one modification of the first method a small portion of the charge stock is continuously sampled and is passed first through a combustion zone, thence through an absorption zone for the removal of water and carbon dioxide and sulfur dioxide, after which the flow rate of the residual nitrogen gas is determined. In the preferred modification the flow rate of the nitrogen gas is determined by an orifice plate connected to a flow controller which is in turn employed to actuate appropriate motor valves on the charge stock supply line, or on the fuel supply to the heater, or on a motor valve which bypasses cold hydrogen recycle gas around the heater.

In one modification of either the first or the second methods, the nitrogen content of the hydrocarbon feedstock may be estimated from pH measurements of either the feedstock or the products of the reaction. A high pH of either the liquid feed or the reaction products indicates a high nitrogen content in the feedstock. In one modification employing pH measurements the naphthenic acids are removed prior to the pH measurement by suitable contact with an acid-absorbing organic resin.

In one modification of the second method the increased nitrogen content of a feedstock is reflected by corresponding increases in the synthesis of ammonia during the hydrocracking reaction. Under most circumstances the removal of nitrogen and resulting synthesis of ammonia is not quantitative. However, fluctuations of the synthetic ammonia arise in part from fluctuations in the nitrogen content of the feedstock. In a preferred application of this modification the ammonia gas is separated from the residual uncondensed gases and the flow rate thereof is determined and is employed to actuate a flow-recording controller which is in turn employed to actuate an appropriate motor valve. In the preferred form of the invention, the nitrogen content of the feed is determined indirectly from a determination of the synthetic ammonia production.

Figure 1 shows one modification of the invention wherein nitrogen analysis, or pH measurement, or production of synthetic ammonia is employed to control the reaction temperature in a hydrocracking process.

Figure 2 shows one sequence of steps which can be employed for analyzing the nitrogen content of a hydrocarbon stream.

Figure 3 shows a method for blending a nitrogen-rich charge stock with a nitrogen-lean charge stock so as to provide a substantially constant flow rate of charge stock having a substantially uniform nitrogen content to a hydrocracking reactor system.

The hydrocarbon stocks which may be employed in this hydrocracking process may be derived from petroleum, shale oil, hydrogenated coal distillates and the like. These feedstocks are preferably distillates, but in certain cases other hydrocarbon fractions, such as deasphalted crude oil, solvent-treated oil, and the like, may also be employed. Distillates which are particularly suitable for hydrocracking in this process include distillates boiling generally in the range of about 350° F. to 900° F. Preferably such distillates boil in the temperature range of about 400° F. to 800° F.

Feedstocks treated herein may contain nitrogen in amounts ranging between 0% and 2.5% by weight. Temperature adjustments to obtain optimum gasoline yields are most effective over the nitrogen-content interval of about 0.05% to about 0.5%. Where the stock contains less than 0.05% nitrogen, the optimum hydrocracking temperature is not significantly different from the optimum at 0.05% nitrogen. Where the stock contains more than 0.5% nitrogen, the optimum temperature is not significantly different from the optimum at 0.5% nitrogen. The approximate optimum temperatures for various stocks are illustrated in the following table:

N content, wt. percent:	Optimum hydrocracking temperature, ° F.
0–0.05	750–850
0.1	840–880
0.2	870–900
0.3	890–925
0.5–2.5	925–975

Within the specified temperature ranges, the exact optimum will depend upon the specific catalyst used, the specific stock, and the other conditions of hydrocracking.

For purposes of this invention, the feedstocks may hence be divided roughly into three categories: (1) those which contain less than 0.05% nitrogen, (2) those containing from .05% to 0.5% nitrogen, and (3) those containing more than 0.5% nitrogen. Temperature adjustment is indicated whenever the nitrogen content of the feed changes from one category to another, or whenever there is a substantial variation within the second category. Stated differently, whenever there is a change in nitrogen content between a higher and a lower value, between which lies a value within the range of 0.05% to 0.5%, the temperature should be adjusted between the limits 750°–975° F. Some constant temperature within the lower interval of 750°–850° F. is used for any stock containing less than 0.05% nitrogen, and some constant temperature within the higher interval of 925°–975° F. is used for any stock containing more than 0.5% nitrogen.

The catalysts which may be employed for catalytic hydrocracking in this invention include adsorptive oxides such as silica, alumina, zirconia, thoria, magnesia, magnesium hydroxide, and the like or combinations of these oxides either with or without additional metal oxides, sulfides and the like compounds of the relatively heavier metals. When heavier metals are employed as the principal catalytic agent, the foregoing materials may be employed as carriers for distending such catalytic oxides, sulfides and the like.

The preferred adsorptive oxides for use in this invention comprise mixtures of silica and alumina, or of silica, zirconia and titania, in coprecipitated form. Such mixtures may themselves be employed as catalysts, but preferably they are employed as carriers for distending other materials.

In the preparation of the carrier for either the initial or a subsequent impregnation, the carrier is usually activated by heating in order to render it sufficiently adsorbent for the impregnation. This activation may, for example, be effected by heating for 2 to 6 hours at 800° F. to 1200° F. The carrier is then cooled and immersed in the impregnation solution. The impregnation solution is adsorbed by the carrier and the excess solution is thereafter removed. The impregnated carrier is drained and dried in a low temperature oven to remove the bulk of the water. Following the drying at, for example, 180° F. to 230° F., the mixture is activated by heating it to a temperature of, for example, 800° F. to 1200° F. for 2 to 6 hours.

Catalytic agents which may be employed in the catalysts of this invention include the oxides, sulfides, or other compounds of heavier metals such as chromium, molybdenum, cobalt, nickel, zinc, iron, lead, beryllium, cadmium, vanadium, manganese, tantalum, tungsten, platinum, columbium, scandium, thorium, aluminum, uranium, zirconium, tin, copper, etc., or combinations of two or more of such compounds.

Of these catalytic agents those which appear to be most effective and consequently find the greatest usage are the compounds of the heavy metals of atomic Nos. 22 to 42 including titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, columbium and molybdenum. The oxides of molybdenum, and of cobalt in the presence of molybdenum, have been found to be the preferred catalytic agents for the hydrocracking process of this invention.

The pressure employed in the hydrocracking reaction is normally in the range between about 14 and 10,000 p.s.i. and is preferably between about 200 and 2000 p.s.i. The liquid hourly space velocity is normally between 0.1 and 10 and preferably between about 0.2 and 2 wherein the liquid hourly space velocity is the ratio of volumes of liquid feed per volume of catalytic material per hour. A recycle rate between about 500 and 10,000 is normally employed and this is preferably in the range of about 1500 to 5000 cubic feet of recycle gas per barrel of charge stock. The weight ratio of catalyst to oil is generally in the range of 0.1 to 20 and is preferably in the range of 0.5 to 2.

Perhaps the process of this invention can best be understood by reference to the drawings.

Referring now more particularly to Figure 1, a nitrogen-containing charge stock is introduced as feedstock through line **11** and flows through orifice plate **12**, the flow control zone of motor valve **13** and line **14** to heater **15**. Hot oil effluent from the heating zone of heater **15** flows through transfer line **16** to hydrocracking reaction zone in reactor **17**. The reaction zone of reactor **17** is filled with a hydrocracking catalyst of the type described hereinbefore. The reaction product is withdrawn from reactor **17**, cooled in condenser **18**, and it then flows to gas-liquid separator **19**. The liquid accumulating in gas-liquid separator **19** discharges through line **20** into product fractionating tower **21** which serves to fractionate the gasoline from the portion of the product boiling above the gasoline range. Gasoline is withdrawn as the overhead product of fractionating tower **21** through line **22**, condenser **23** and line **24** whence it flows to gasoline product storage not shown. A portion of the gasoline overhead returns from line **24** to fractionating tower **21** through line **25** as reflux. Fractionating tower **21** produces a bottom product through line **26** which in one modification flows through valve **27** and line **28** to hydrogenated stock storage not shown. Alternatively, the bottoms product in line **26** is withdrawn into line **29** and flows by means of pumps, not shown, through block valve **30** and as a recycle stream joins incoming feedstock flowing in line **11**.

The gaseous phase from gas-liquid separator **19** is withdrawn through line **40** and passes to a gas separation

system which in the modification shown in Figure 1 is a hypersorber denoted as **41**.

Hypersorber **41** is of the type shown in U.S. Patent 2,519,873 for example. Hypersorber **41** is adapted for the withdrawal of charcoal from the bottom, for lifting the charcoal through conveyance line **42** to a point above the top whence it is returned to the adsorption zones within the body of the hypersorber. In the adsorption zones gas from line **40** passes upwardly through the descending bed of charcoal whereupon constituents heavier than hydrogen are adsorbed on the charcoal. The nonadsorbed gas, consisting mainly of hydrogen, is withdrawn at the top of the adsorption zone through line **43** whence it passes to blower **44** and thence through line **47** to line **14** wherein it joins the feedstock flowing to the heater **15**. When required, makeup hydrogen from an external source is introduced through line **45** and block valve **46** whence it joins effluent hydrogen from blower **44** in line **47**.

Referring again to hypersorber **41**, charcoal-containing adsorbed constituents follows through successive desorption and readsorption zones which selectively desorb the most readily desorbable compounds stepwise. In the first desorption zone a C_1–C_2 fraction is removed, in the second an ammonia-rich fraction is removed, and in the third a C_3–C_4 and heavier fraction is removed. The desorption is accomplished by heating the charcoal at the bottom of the desorption zone whereupon a portion of the adsorbed constituents is desorbed and passes upwardly through the descending charcoal stream whereupon it serves to displace lighter constituents selectively. In the lowermost desorption zone the desorption is effected by means of steam and the hot desorbed charcoal is withdrawn, conveyed to the top through conveyance line **42**, cooled and resupplied to the adsorption zone at the top. By this process the C_1–C_2 fraction is withdrawn through line **50**, the ammonia-rich fraction is withdrawn through line **51**, and the C_3–C_4 and heavier fraction is withdrawn through line **52**. Ammonia in line **51** passes through orifice plate **53** which is coupled to flow controller **54** which is employed to control a motor valve as described hereinafter.

Line **40** which carries gases from gas-liquid separator **19** is sampled by pH determining mechanism **60** which in turn actuates flow controller **61** which in turn regulates motor valves as described hereinafter.

Referring now more particularly to Figure 2, a nitrogen-containing hydrocarbon stream which is to be analyzed for its nitrogen content is continuously sampled in sampling zone **100**. In the sampling zone a minor portion of the stream is continuously bled from the system. The sample thus taken is atomized in a pure carbon dioxide gas stream and passed to a combustion zone **101** where, in the presence of copper oxide at a temperature between about 600° C. and 800° C., the sample is combusted to form gases, i.e. nitrogen, carbon dioxide, water and sulfur dioxide. The combustion preferably is conducted in a zone containing alternating layers or beds of copper and copper oxide. Any nitrogen oxides are reduced by the metallic copper and are oxidized by the copper oxide to form nitrogen gas. The combustion gases from the combustion zone **101** pass through adsorption zone **102** which absorbs the water, carbon dioxide and sulfur dioxide, leaving only residual nitrogen gas. Absorption zone **102** is generally filled with an aqueous alkali metal solution such as with strong sodium hydroxide, potassium hydroxide or the like. The residual nitrogen gas which is unabsorbed in absorption zone **102** passes through flow rate measuring zone **103** wherein the flow rate of such residual nitrogen gas is measured. The flow rate is electrically or pneumatically transmitted to recording controlling zone **104** which is in turn employed to operate appropriate motor valves as described hereinafter.

Referring again more particularly to Figure 1, feedstock flowing in line **11** is sampled and the sample flows through line **69** to nitrogen analyzer **70**, which according to the method described in Figure 2 determines the electrical or pneumatic equivalent corresponding to the nitrogen content of the feedstock which is transmitted to flow controller **71** which is in turn employed to control motor valves as described hereinafter.

Orifice plate **12**, through which the feedstock flows, is coupled to flow controller **72** which is employed to control motor valves as described hereinafter.

Fuel supply for heater **15** is introduced through line **75** and flows through motor valve **76** and line **77** into heater **15**.

As has been described hereinbefore, the temperature of the reaction zone in reactor **17** may be controlled either by varying the fuel supply or by varying the flow rate of the charge stock to heater **15**. Furthermore, the nitrogen content of the feedstock may be directly or indirectly determined by one of three methods, for example, analysis, pH determinations, or production of synthetic ammonia.

In order to permit such control a series of three switches have been provided, viz., switch **80**, switch **81**, and switch **82**. Switch **80** has three possible contact positions which connect it electrically or pneumatically to flow controller **71**, flow controller **54**, or flow controller **61**. The contacting arm of switch **80** is connectable so as to contact either a contact of switch **81** or a contact of switch **82**. Where it is desired that one of the three possibilities controlled by switch **80** be employed to control the fuel supply, for example, switch **82** is positioned so that the contact arm thereof is connected to the contact arm of switch **80**. Under this arrangement contact arm of switch **81** is usually positioned to connect to flow controller **72** which, operating through orifice plate **12**, will maintain a constant predetermined flow rate through motor valve **12**. Also switch **82** attached to motor valve **76** on the fuel supply will be controlled by one of the three possible variables determined by the nitrogen content.

Alternatively, any of the three possible variables may be employed to control the flow rate of the feedstock while maintaining the fuel supply constant. Under these conditions switch **82** is connected to flow controller **85** which is set to maintain a predetermined constant flow rate through motor valve **76**. Switch **81** is connected to the contact connected with the contact arm of switch **80** so that the one of the three variables then controls the flow through motor valve **13**.

It is thus apparent that analysis, or pH determinations, or synthetic ammonia production, may be employed to control either the fuel supply or the flow rate of feedstock.

In addition to controlling the flow rate of feedstock and the flow rate of the fuel supply to the heating zone, other methods may be employed to vary the temperature of the reaction zone. Thus in the case of moving catalyst beds, e.g. moving granules, fluidized particles and the like, the temperature of the recycle catalyst, the flow rate of either relatively hot or cold catalyst to the reaction zone and other such factors may be employed to control the reaction temperature. In one modification cold hydrogen may be added to the vapors flowing to the reactors in appropriate amounts to control the temperature of the reaction zone.

Referring again to Figure 1, cold hydrogen in line **47** may be withdrawn into line **63** by opening motor valve **64**, whence it flows through line **65** and joins the vapors flowing in line **16** to reactor **17**.

Motor valve **64** is normally positioned by flow controller **67** when the temperature of the reaction zone in reactor **17** is controlled by a method other than the introduction of cold hydrogen. In regulating the conversion temperature by the introduction of cold hydrogen, switch

66 is positioned to connect motor valve 64 to "x" which in turn is connected to "x" attached to switch 80. By this means the analysis, or pH determinations, or synthetic ammonia production may be employed to control motor valve 64 and regulate the introduction of cold hydrogen into reactor 17.

Referring now more particularly to Figure 3, a mixture of relatively nitrogen-rich charge stock and relatively nitrogen-lean charge stock may be passed through a heating zone which is maintained at substantially constant temperature and thence to the reactor system. In this modification of the invention the nitrogen-rich charge stock is introduced through line 110, whence it flows through motor valve 111, line 112, and line 113, whence it flows through orifice plate 114 to the heater and reactor system. A portion of the nitrogen-rich charge stock is withdrawn into nitrogen analyzer 115, which is of the type described hereinbefore in connection with Figure 2. Nitrogen analyzer 115 in turn regulates motor valve 111. Accordingly motor valve 111 opens and closes to vary the flow of nitrogen-rich charge stock in inverse proportion to its nitrogen content, thereby maintaining a substantially constant flow rate of nitrogen compounds therethrough.

Nitrogen-lean charge stock is introduced through line 117, whence it flows through motor valve 118, line 119 and thence joins the flow of nitrogen-rich charge stock in line 113. The flow through orifice plate 114 actuates flow controller 120 which in turn regulates motor valve 118.

Under these conditions the total volumetric flow rate of the combined feedstocks through orifice plate 114 is maintained substantially constant by the opening and closing of motor valve 118 and the nitrogen content of the combined stream is maintained substantially constant by the opening and closing of motor valve 111. In the particular case shown it is assumed that the nitrogen content of the nitrogen-lean charge stock is negligible with respect to the nitrogen content of the nitrogen-rich charge stock. This is generally the case in practice. However, where the nitrogen content of the nitrogen-lean charge stock is not relatively negligible, a nitrogen analyzer on the nitrogen-lean charge stock may be employed to compensate therefor.

In its most practical aspect, the blending of feeds herein is practiced mainly when one stock contains more than 0.05% nitrogen; dilution of such stocks with a lower nitrogen stock then permits the use of lower optimum temperatures. In all cases, sufficient of the low-nitrogen stocks should be used to give a final blend containing between about 0% and 0.5% nitrogen, because only when the nitrogen content is reduced to within this range is a reduction in hydrocracking temperature of practical significance.

Perhaps the process of this invention can best be understood by reference to the following examples.

Example I

A synthetic coprecipitated silica-alumina catalyst, containing substantially 75% by weight of SiO_2 and approximately 20% by weight of Al_2O_3 and about 5% by weight of water and other volatile matter, was prepared by coprecipitation of a sodium silicate-sodium aluminate solution with carbon dioxide. The precipitate was washed until it was substantially free of sodium ions, and dried at 90–110° C. The resulting gel was ground to a powder and pressed into tablet form and then activated by heating for about 2 hours at 1100° F.

For carrying out the process of the invention a low-nitrogen feedstock was obtained as a gas oil distillate from an East Texas crude oil. The distillate boiled substantially in the range of about 380° F. to 700° F. The API gravity of the feed was about 35.9° and it contained about 0.1% by weight of sulfur and 0.009% by weight of nitrogen.

A second high-nitrogen feedstock was prepared from the low-nitrogen feedstock by the addition of about 2% by volume of quinaldine; the resulting high-nitrogen feedstock contained about 0.26% by weight of nitrogen. It has been found that a considerable portion of the nitrogen compounds present in petroleum oils, shale oils, and the like are of the substituted pyridine type, such as quinaldine.

The coprecipitated silica-alumina catalyst was evaluated for hydrocracking each of the two feedstocks and at a series of temperatures in the interval of 850–950° F. In each case, the conditions other than temperature were maintained constant as follows:

Pressure, p.s.i.g.	1000
Liquid hourly space velocity	1.0
Hydrogen addition, cubic feet/barrel	3000
Process period, hours	2

The product from each of the runs was fractionated to remove the gasoline which was then examined as to quality and amount. The following tabulation shows the yield of synthetic gasoline, based on the volume percent of the feedstock, for each of the two feedstocks and at three different reaction temperatures:

	Gasoline Yields, Volume Percent of Feed		
Reaction Temperature, ° F	950	900	850
0.01% N. in Feed	35	40	39
0.26% N. in Feed	34	28	16

The foregoing data show that the optimum hydrocracking temperature for the low-nitrogen feedstock (0.01% N.) lies below 950° F. and in the interval 850° F. to 900° F. Conversely the optimum hydrocracking reaction temperature for the high-nitrogen feedstock (0.26% N.) is 950° F. or above while the gasoline conversion drops off considerably as the temperature decreases. It is apparent therefore that the optimum hydrocracking temperature for a given oil is a marked function of the nitrogen content of such feedstock.

Example II

The silica-alumina catalyst of Example I was impregnated with molybdic oxide as follows: About 85 g. of ammonium para-molybdate (assaying about 82% by weight of MoO_3) was dissolved in a mixture of about 200 ml. of aqueous 28% ammonia and 200 ml. of distilled water. The resulting mixture was diluted to 1000 ml. by the addition of distilled water. About 620 g. of the silica-alumina catalyst of preceding Example I, which had been precalcined at 1100° F. and subsequently cooled, was immersed in the impregnation solution for one hour. The tablets were drained, dried, and calcined for two hours at 1100° F. The catalyst upon analysis was found to contain 3.5% by weight of MoO_3.

This catalyst was then tested in substantially the same manner as described for testing the catalyst in Example I for its ability to hydrocrack each of the two feedstocks in Example I. The following data were obtained which relate the gasoline yield based on the volume percent of the feed for the two feedstocks and at various reaction temperatures:

	Gasoline Yields, Volume Percent of Feed			
Reaction Temperature, ° F	950	900	850	800
0.01% N. in Feed	46	56	58	63
0.26% N. in Feed	48	44	19	-------

The foregoing data again establish that low-nitrogen stocks have relatively lower optimum conversion temperatures while high-nitrogen stocks have relatively higher optimum conversion temperatures.

Example III

A second coprecipitated silica-alumina gel was prepared in substantially the same manner as described in Example II, with the exception of that the silica content was only about 5% by weight and the alumina was substantially 91% by weight, the balance being volatile matter. This gel, after tableting, was calcined and impregnated with molybdic oxide in substantially the same manner as described in Example II to obtain a catalyst which contains approximately 3.5% by weight of MoO_3.

This catalyst was then employed for hydrocracking the two feedstocks of Example I at reaction temperatures of 900° F. and 950° F. with the remaining conditions being maintained substantially as described in Example I. The following data were obtained for the gasoline yield based on the volume percent of the feed.

	Gasoline Yields, Volume Percent of Feed	
Reaction Temperature, ° F	950	900
0.01% N. in Feed	52	59
0.26% N. in Feed	49	45

The foregoing data again establish that low-nitrogen stocks have relatively lower optimum conversion temperaperatures while high-nitrogen stocks have relatively higher optimum conversion temperatures.

Example IV

An alumina-silica gel containing approximately 95% Al_2O_3 and 5% SiO_2 on a volatile-matter-free basis was prepared by the coprecipitation of an aqueous mixture of sodium aluminate and sodium silicate with carbon dioxide. The precipitate was washed until substantially free of sodium ions, dried at 90°–110° C., formed into pills by compressing, and activated by heating for two hours at 600° C. A solution of ammonium molybdate was prepared by dissolving about 1700 parts by weight of ammonium para-molybdate, assaying about 81% by weight of MoO_3, in about 1,940 parts by weight of 28% aqueous ammonia and about 1,550 parts by weight of distilled water. About 4,400 parts by weight of the activated gel were immersed in the ammoniacal solution of ammonium molybdate, drained, dried and heated at 600° C. for about two hours. An aqueous solution of cobalt nitrate was prepared by dissolving about 1,433 parts by weight of cobalt nitrate hexahydrate in about 2,000 parts by weight of water. The carrier supporting the molybdic oxide was then immersed in the cobalt nitrate solution, drained, dried and activated by heating to 600° C. for two hours. The catalyst prepared by this method contained about 9.1% MoO_3 and 3.0% CoO; the atomic ratio of Co/Mo was 0.93.

The cobalt molybdate-type catalyst prepared by this method is then tested for hydrocracking under the following conditions:

Pressure, p.s.i.g.	250
Liquid hourly space velocity	1.0
Hydrogen addition, cubic feet/barrel	3000
Process period, hours	2

Under these conditions when reaction temperatures of 900° F. and 950° F. are examined, it is found that the low-nitrogen feedstock of Example I gives a higher conversion at the lower temperature while the high-nitrogen feedstock of Example I gives a higher conversion at the higher reaction temperatures. The results obtained are similar in magnitude to those reported in Example II. The presence of the cobalt gives a synthetic gasoline which contains less nitrogen and less sulfur than when only molybdic oxide is employed.

Example V

The silica-alumina gel of Example I is impregnated with chromium oxide as follows: About 91 g. of chromiumtrioxide is dissolved in about 250 ml. of distilled water and the resulting mixture is diluted to 1000 ml. by the further addition of distilled water. About 620 g. of the silica-alumina gel (precalcined and precooled) are soaked in the impregnation solution for about one hour, after which they are drained, dried, and calcined at about 110° F. for two hours. The resulting catalyst contained 4.1% by weight of chromium when calculated as Cr_2O_3.

The foregoing chromium catalyst is tested in the same manner as that employed for testing the cobalt molybdate-type catalyst in Example V. The data which are obtained show that the optimum hydrocracking temperature for the low-nitrogen feedstock over the chromium catalyst is about 900° F., while the optimum temperature for the high-nitrogen feedstock is about 950° F.

Example VI

Nickel oxide is deposited on the silica-alumina gel of Example I by impregnating the gel with an impregnation solution prepared by dissolving about 268 g. of nickelous nitrate in sufficient distilled water to make a total volume of 1000 ml. The resulting catalyst contained 6.5% by weight of NiO. The catalyst is tested in substantially the same manner as that described in Example VI and analogous results are obtained showing an optimum conversion for low-nitrogen stocks at low temperatures and an optimum conversion of high-nitrogen stocks at higher temperatures.

Example VII

A gas oil from California crude oil boiling in the range of 400° F. to 800° F. and contains 0.245% by weight of nitrogen. The nitrogen content is reduced to about 0.07% by weight upon a single extraction with 90% sulfuric acid using 10 pounds of acid per barrel of feed. When the original untreated oil and the acid-treated oil are tested for hydrocracking with the catalyst and under the conditions described in Example I, it is found that the optimum cracking temperature for the untreated oil is about 950° F. while that for the acid-treated oil is about 875° F.

It is apparent that in its broad aspect this invention encompasses a method for increasing the yield of gasoline in a hydrocracking process by taking into account the concentration of the nitrogen in the feedstock, whether by direct or indirect method, selecting a more favorable conversion temperature for each charging stock in accordance with the concentration of nitrogen compounds in such charging stock, and then operating such process at such favorable conversion temperature.

This application is a continuation-in-part of my prior application Serial No. 203,506, filed December 29, 1950, and now abandoned.

The foregoing disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. In a catalytic hydrocracking process wherein a mineral oil feedstock boiling above the gasoline range is contacted with a catalyst consisting essentially of an adsorbent oxide carrier plus a minor proportion of an oxide of a metal having an atomic number between 22 and 42 inclusive, in the presence of at least about 1500 s.c.f. of hydrogen per barrel of feedstock and at a pressure between about 15 and 10,000 p.s.i., and wherein said feedstock contains a weight-proportion of nitrogen which varies substantially from time to time between an upper and a lower value, both of which lie within the range 0–2.5%, and between which lies a value within the range of 0.05% to 0.5%, the improvement which comprises concomitantly adjusting the temperature level in the hy-

drocracking zone within the range from about 750°–975° F. in direct response to each of said variations in nitrogen content, said temperature level being adjusted upwardly within said range in response to high feed nitrogen levels, and downwardly within said range in response to lower feed nitrogen levels, the temperature at the 0.05% nitrogen level and below being maintained substantially constant within the range of 750°–850° F., and the temperature at the 0.5% nitrogen level and above being maintained substantially constant within the range of 925°–975° F., thereby obtaining a greater volumetric yield of gasoline than could be obtained by conducting said hydrocracking at any single temperature employed in the process.

2. A process according to claim 1 wherein the variation in nitrogen content of said feedstock is detected by continuously combusting a side-stream of said feedstock thereby generating combustion gases, absorbing water, carbon dioxide and sulfur dioxide from said combustion gases and detecting changes in the flow rate of the residual elemental nitrogen.

3. A process according to claim 1 wherein the variation in nitrogen content of said feedstock is detected by detecting changes in the pH of a basic nitrogen compound containing stream in said process.

4. A process according to claim 1 wherein the variation in nitrogen content of said feedstock is detected by separating ammonia from the reaction products from said hydrocracking zone and determining the rate of ammonia production thereby and relating said rate of ammonia production to the nitrogen content of said feedstock.

5. A process for the simultaneous catalytic hydrocracking of two mineral oil feedstocks boiling above the gasoline range, said stocks differing substantially from one another in nitrogen content, the first containing between about 0.05% and 2.5% by weight of nitrogen and the second containing substantially less nitrogen than the first, which comprises blending said stocks in proportions controlled to produce a combined feed of constant nitrogen content between about 0 and 0.5% by weight, and thereafter subjecting said combined feed in admixture with at least about 1500 s.c.f. of hydrogen per barrel to hydrocracking in the presence of a catalyst consisting essentially of an adsorbent oxide carrier plus a minor proportion of an oxide of a metal of atomic number 22–42 inclusive, said hydrocracking being carried out at a pressure between about 14 and 10,000 p.s.i. and a substantially constant temperature between about 750° and 975° F., said constant temperature being relatively high within said range for combined feeds of high-nitrogen content near the 0.5% level, and relatively low within said range for combined feeds of low-nitrogen content near the 0% level, thereby obtaining a greater volumetric yield of gasoline than could be obtained by subjecting said initial feedstocks serially to hydrocracking at the same constant temperature level.

6. A process according to claim 5 wherein said catalyst consists essentially of a major proportion of a carrier selected from the group consisting of alumina, silica, and combinations thereof, and a minor proportion, between about 1% and 25% by weight of a component selected from the group consisting of molybdenum oxide and molybdenum oxide plus cobalt oxide.

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