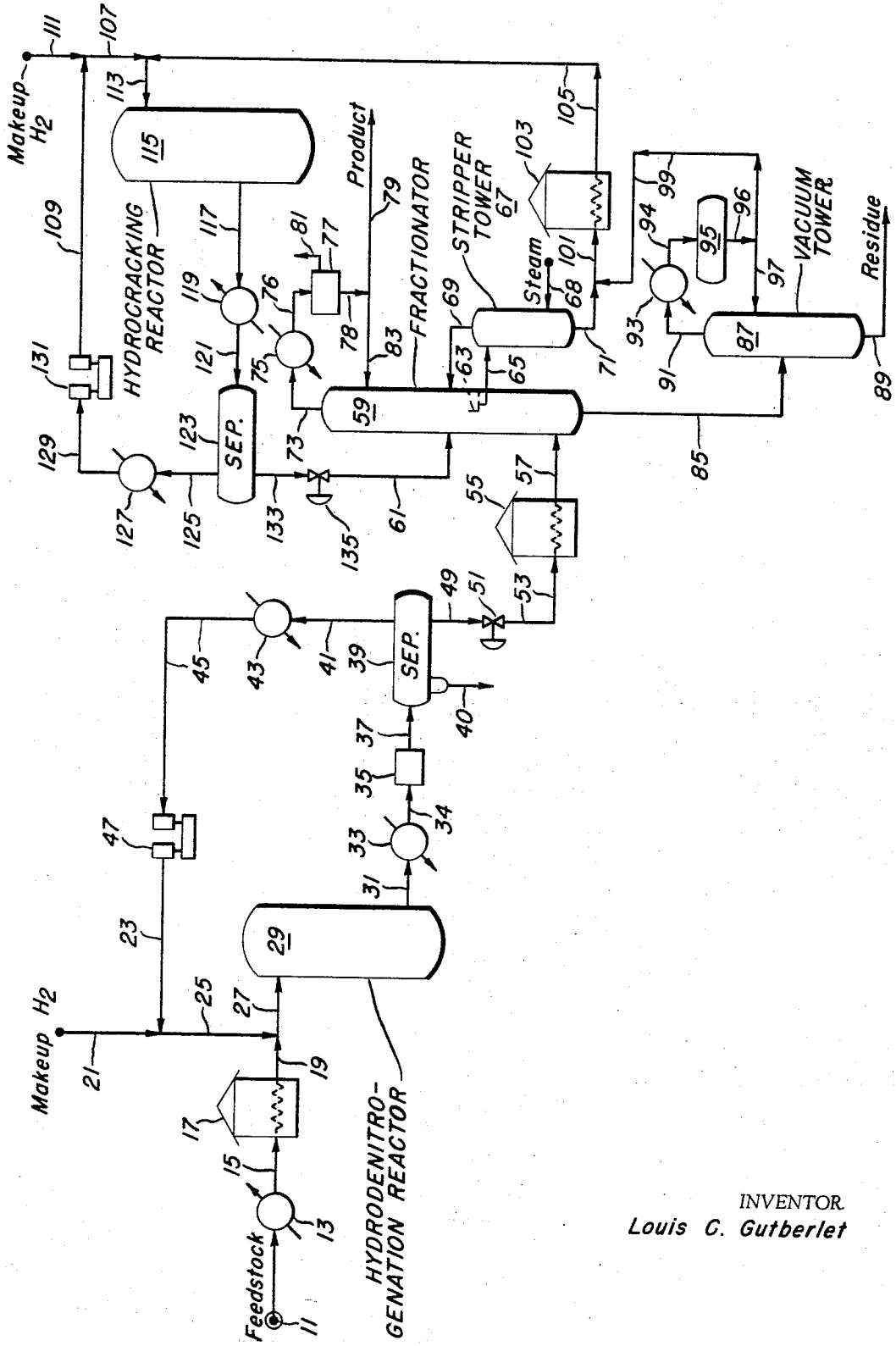
Sept. 5, 1967 L. C. GUTBERLET 3,340,179

PROCESS FOR HYDROCRACKING FEEDSTOCKS CONTAINING AT LEAST 50 PARTS PER MILLION NITROGEN

Filed March 31, 1966



INVENTOR.
Louis C. Gutberlet

United States Patent Office 3,340,179 Patented Sept. 5, 1967

3,340,179

PROCESS FOR HYDROCRACKING FEEDSTOCKS CONTAINING AT LEAST 50 PARTS PER MILLION NITROGEN

Louis C. Gutberlet, Crown Point, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Filed Mar. 31, 1966, Ser. No. 547,681
10 Claims. (Cl. 208—89)

This is a continuation-in-part of co-pending application, Ser. No. 213,700, filed July 31, 1962, now abandoned, in the name of Louis C. Gutberlet, and assigned to the Standard Oil Company (Indiana).

This invention relates to a hydrocarbon conversion process and more particularly, it relates to an improved method of hydrocracking a relatively high boiling hydrocarbon feedstock to produce lower boiling hydrocarbons boiling predominantly within the gasoline boiling range.

Hydrocracking is a general term applied to refining processes wherein hydrocarbon feedstocks of relatively high molecular weight are converted to mixtures of hydrocarbons of lower molecular weights, and wherein the conversion is carried out at elevated temperature and pressure in the presence of a hydrogen-affording gas. In hydrocracking, typically, hydrocarbon feeds such as catalytic cycle oils and gas oils boiling in the range of about 350° F. to 1,000° F. are hydrocracked to obtain gasoline boiling range products and light distillates. Usually, the hydrocarbon feeds are first subjected to hydrodenitrogenation conditions to substantially remove the nitrogen containing components in the feed.

An important consideration in a hydrocracking process is the rate at which the higher boiling hydrocarbons are converted into the desired lower boiling hydrocarbons. A maximum conversion rate is naturally desirable together with a product having the desired characteristics. One of the objects of this invention is an improvement in the conversion rate for a hydrocracking process and the production of a product having the desired characteristics. Other objects will become apparent from the detailed description in the specification.

It has been discovered that an improved conversion rate is achieved in a hydrocracking process when a hydrocarbon feed which contains at least 50 parts per million nitrogen is first denitrogenated over an acidic-base catalyst to a low nitrogen content and then distilled to remove a small amount as bottoms prior to being fed as a bottoms-free fraction to the hydrocracking process. It has also been discovered that the rejected bottoms and particularly a fraction of the rejected bottoms contains a material which acts as a violent poison in the hydrocracking process. This material, when in a semi-isolated form, appears in some instances as a black viscous tar although its form may differ depending on the method of isolation and the particular feedstock employed in the process.

In the present invention, a feed containing higher boiling hydrocarbons and at least 50 parts per million nitrogen is processed under hydrodenitrogenation conditions in the presence of an acidic-base hydrodenitrogenation catalyst to produce a stream which contains a low amount of nitrogen, about 2 parts per million or less. The stream is then distilled or fractionated to remove a small amount as bottoms, after which the bottoms-free stream is fed to the hydrocracking process. Removal of this small amount, in the order of from about 1 weight percent or less up to about 10% by weight also accomplishes the removal of a material which acts as a poison in the hydrocracking process. The result is an improved conversion rate for the hydrocracking process and a product which contains appreciable amounts of gasoline and lighter products.

The invention will be better understood by reference to the following description and accompanying drawing which is illustrative of a preferred process employing distillation of the feed prior to subjecting it to hydrocracking conditions.

A hydrocarbon feed which contains at least 50 parts per million nitrogen is first processed under conventional hydrodenitrogenation conditions in the presence of an acidic-base catalyst to product a denitrogenated stream which contains only a low amount of nitrogen. The feed may be high boiling fractions of crude oil. Normally, the feed will boil above about 300° F. and may boil up to about 1200° F., although usually up to about 1000° F. Feeds containing a substantial amount of hydrocarbons boiling about 400° F. and higher are advantageously processed by this invention, since these higher boiling hydrocarbons after being denitrogenated usually contain the above described poisonous material in more objectionable amounts. Examples of desirable feedstocks are light catalytic cycle oil having a boiling range of from about 350° F. to 650° F., heavy catalytic cycle oil boiling in the range of about 500° F. to 850° F., virgin gas oil boiling from about 400° F. to 1,000° F. and coker gas oil boiling in the range of about 350° F. to 800° F. When heavy catalytic light oil is the feed, the process of this invention results in very beneficial improvements in the conversion rate for the hydrocracking process.

The feedstock is first subjected to hydrodenitrogenation conditions in the presence of an acidic-base hydrodenitrogenation catalyst. The feedstock to the hydrodenitrogenation process usually contains substantial amounts of nitrogen, e.g., greater than 50 parts per million, typically 100–200 parts per million, and may contain amounts in the order of a thousand parts per million (0.1%) and higher. The nitrogen is normally a component of compounds in the feedstock.

My improved process is particularly adapted to upgrade hydrocarbon feedstocks which contain at least 50 parts per million nitrogen.

The feedstock is denitrogenated to produce a stream which contains nitrogen (in compound form), in the order of about 2 parts per million or less and preferably, about 1 part per million or less. Conventional hydrodenitrogenation processes often reduce the nitrogen content to from about 0.1 to about 0.4 part per million. Streams containing the very low nitrogen content are generally preferred for hydrocracking because of the detrimental effect of nitrogen on the hydrocracking catalyst. The process of this invention provides particularly beneficial results when these streams containing the very low nitrogen content are employed for hydrocracking, since these streams contain in general, significant amounts of the poisonous material which adversely affects the conversion rate in the hydrocracking process. The removal of this material from the denitrogenated stream results in a significant improvement in this conversion rate.

The usual conditions are employed in the hydrodenitrogenation process. Particularly, the temperature is in the order of 600 to 800° F. and the pressure in the order of 1000 to 3000 p.s.i.g. Hydrogen is present in an amount ranging from 1500 to 20,000 standard cubic feet per barrel of feedstock and more usually in the order of 5000 standard cubic feet per barrel. The catalyst is a supported hydrogenation catalyst comprising a Group VIII metal in the Periodic Table, such as one of the iron group metals, including nickel, cobalt or iron or one of the platinum group metals such as palladium, platinum, iridium, or ruthenium on a suitable support. Generally, it is preferred that an oxide or sulfide of the Group VIII metal (particularly iron, cobalt or nickel) be present in mixture with an oxide or sulfide of a Group VI–B metal (preferably molybdenum or tungsten). Suitable carriers or supports

include acidic supports such as: silica-alumina, silica-magnesia, and other well-known cracking catalyst bases; the acidic clays; fluorided alumina; and mixtures of inorganic oxides, such as alumina, silica, zirconia, and titania, having sufficient acidic properties providing high cracking activity. Since it is generally contemplated to reduce the nitrogen content to 2 parts per million or less and especially 1 part per million or less, a strongly acidic-type carrier or support, such as silica-alumina cracking catalyst containing from about 10 to 40 percent alumina is used. These carriers have been favorably employed by industry, particularly, where feedstocks containing the lower amounts of nitrogen (2 parts per million or less) are being prepared for hydrocracking. An especially suitable catalyst is cobalt molybdenum on silica-alumina cracking catalyst.

The denitrogenated stream is then distilled or fractionated to remove a small amount as bottoms from the stream. This small amount contains material which acts as a violent poison in the hydrocracking process and removal of it from the stream greatly improves the conversion rate of the process.

The poisonous material in the bottoms portion of the feed is thought to contain appreciable amounts of polycyclic compounds such as the naphthalenes and their derivatives. For example, the bottoms portion from a heavy catalytic cycle oil reveals upon further separation that the poisonous material is contained in significant amounts in a black viscous tar. Analysis of the tar indicates the presence of naphthalene nuclei. The actual form of the poison in the feedstock may be other than as a tar, since the method of isolation of this fraction may produce the tar. In some feeds, such as heavy cycle oil, appreciable amounts of wax are also found in the bottoms portion from the denitrogenated stream.

Fractionation of the denitrogenated stream removes a small amount containing this poisonous material as bottoms from the stream. This small amount is generally 10 weight percent or less and preferably from about 1 weight percent to about 10 weight percent and especially about 3 weight percent. Since the poisonous material is normally present in a very small amount (in the order of about 0.1 weight percent and below), special distillation or fractionation techniques, such as the use of an especially long column having a large number of trays, the use of multiple towers, etc., may also be employed to reduce the bottoms fraction to a value even below 1 weight percent.

The distillation or fractionation of the denitrogenated stream is usually carried out under conventional conditions and in conventional distillation equipment. A single tower or multiple towers may be utilized. Normally, the conditions are dependent somewhat on the feedstock and process. In general, temperatures in the range of from about 400° F. to about 700° F. and pressures in the range of from subatmospheric to about 1500 p.s.i.g. are suitable. Vacuum distillation is particularly suitable for the usual denitrogenated streams (or feeds for the hydrocracking process), since lower temperatures may be employed in the distillation step. When heavy catalytic cycle oil is the feedstock being processed, the distillation may be advantageously carried out under vacuum, at a temperature in the order of 400 to 500° F. and at a pressure in the order of 0.05 to 5.0 p.s.i.a.

The bottoms-free stream is next subjected to hydrocracking conditions in the presence of a hydrocracking catalyst. The process conditions which are employed in the hydrocracking process can be selected over a relatively wide range and are correlated, according to the nature of the feed or denitrogenated stream and of the particular catalyst employed, so as to produce either a desired conversion; i.e., as the percentage of feed converted to product, or a product of a desired octane number. The formation of alkylbenzenes from polynuclear aromatics is favored by higher temperatures and moderate pressures, and an increase in both of these variables has the effect of increasing the degree of conversion. Satisfactory conversions are obtained with the above described feedstocks at pressures in the range of about 200 and 2,000 p.s.i.g., and temperatures in the range of about 400- F. to 1,000° F., although pressures and temperatures outside of these ranges may be employed when utilizing certain feeds, particularly highly refractory feeds. Advantageously, pressures in the range of about 750 to 1,500 p.s.i.g., and temperatures between about 500° F. to 700° F. are employed. It may be desirable during the course of a run to increase the temperature within the reaction zone as the catalyst deactivates in order to compensate for a drop in catalyst activity. Thus, with a fresh or newly regenerated catalyst it may be desirable to come on stream at a temperature of about 500° F. and to gradually increase the operating temperature towards about 700° F. during the course of a run. In most instances it is desirable to maintain a low operating temperature, since higher temperatures have been found to result in increased coking and increased amounts of gas formation.

The space velocity, expressed herein as liquid hourly space velocity (LHSV), in terms of volumes of oil charged to the reaction zone per hour per volume of catalyst, may range from about .1 to 10, normally from about 0.2 to 5, and preferably from about 0.25 and 2 LHSV. Lower space velocities tend to increase the degree of conversion.

Hydrogen is consumed in the process and it is necessary to maintain an excess of hydrogen in the reaction zone. However, the process is relatively unaffected by changes in the hydrogen to oil ratio within the general range of operations. The hydrogen to oil ratio employed, desirably is in the range of about 1,000 to 20,000 standard cubic feet of hydrogen gas per barrel of feed (s.c.f.b.) and advantageously about 5,000 to 15,000 s.c.f.b. is employed.

With a light catalytically cracked cycle oil as feed, it has been found that over wide ranges of operating conditions the products of the hydocracking process predominantly boil within the gasoline boiling range. The dry gas make-up; i.e., methane through propane, generally is less than about 5 weight percent and typically is in the order of 2 to 3 weight percent. Typically, the butane-pentane fraction of the product also is about 15 to 30 weight percent, with the amount produced being more dependent upon operating conditions and the nature of the feed. When employing a feed such as heavy catalytic cycle oil the pentane-plus to 400° F. fraction of the product generally will range upwardly from about 70 weight percent of the total converted product.

Typically, when it is desired to maximize the production of light distillates, i.e., materials boiling above the gasoline range and having an end point of about 550–600° F., a heavy catalytic cycle oil boiling above about 600° F. can be utilized as feed. The hydrocrackate is fractionated to provide a heavy bottoms fraction boiling above about 600° F. which is recycled to the hydrocracking zone. The amounto f heavy hydrocarbons converted to distillates can be further increased by decreasing the conversion per pass.

The catalyst employed in the hydrocracking process may be selected from the various well known hydrocracking catalysts, which typically comprise a hydrogenation component and a solid acidic cracking component. Preferably, the hydrocracking catalyst further comprises an activity control-affording material which effectively balances the catalyst activities to provide a low rate of hydrogenation relation to the isomerization occurring during the overall conversion. Such catalysts having balanced activities have been found to be capable of providing a product of suitable characteristics, such as more highly branched paraffins and better product distribution. These activity control-affording elements are normally

employed in relatively small amounts, depending upon the activity of the hydrogenation component relative to that of the acidic component, and are further described herein below.

The acidic cracking component of the catalyst may comprise one or more solid acidic components such as silica-alumina (naturally occurring and/or synthetic) silica-magnesia, silica-alumina-zirconia, and the like. Also, acid-treated-aluminas, with or without halogens, such as fluorided alumina, boria-alumina, and the heteropoly-acid-treated aluminas, i.e., treated with phosphotungstic acid, phosphovanadic acid, silicotungstic acid, silicomolybdovanadic acid and the like, may be employed. However, it is critical that such materials possess substantial cracking activity in the finished catalyst composite. A preferred acidic component of the catalyst composition is one of the commercially available synthetic silica-alumina cracking catalysts which may contain about 5 to 40 weight percent alumina and which has been treated with a fluorided affording compound, such as hydrogen fluoride or ammonium fluoride. Preferably, the acidic component of the catalyst is employed as a support and it is highly porous, having a surface area of between about 100 and 500 square meters per gram. The preparation and properties of the acidic cracking components are well known in the art and they need not be described further herein for the purpose of the present invention. For example, see the series entitled, "Catalysts," by Emmett (Reinhold Publishing Corporation), particularly volume VII, pp. 1–91.

Many of the well-known metallic hydrogenation catalysts may be incorporated in the present catalyst, but preferably, the metallic constituent of this component is selected from the metals of Group VIII of the Periodic Table which are shown to possess satisfactory hydrogenation activities, especially nickel, platinum, cobalt, palladium, rhodium and ruthenium. The hydrogenation component of the catalyst advantageously can be incorporated into the catalyst by impregnating a porous acidic cracking component with a heat-decomposable compound of the hydrogenation metal, followed by calcining to provide a composite. Typically, a silica-alumina cracking catalyst or an acid-treated alumina base is impregnated with a solution of nickel acetate, chloroplatinic acid or the like, and then dried followed by pelleting and calcining at an elevated temperature (about 1,000° F.).

However, it is contemplated that the finished catalyst may also be produced by various methods such as by cogelling the various components and by other well-known variations in catalyst preparation techniques to produce a finished catalyst having the desired properties.

The amount of the hydrogenation component incorporated in the catalyst can vary over a wide range, with the amount being selected to provide the desired catalyst activity. For example, large amounts of nickel, e.g., up to about 30 weight percent can be employed, and relatively small amounts of nickel, e.g., as little as about 0.1 weight percent is also effective with about 1 to 10 weight percent nickel being preferred. Typically, about 0.1 to 2 weight percent platinum is effective in the catalyst and preferably about 0.1 to 1 weight percent platinum is employed. The amount of the hydrogenation component employed in the catalyst thus will depend upon the catalytic ability and economic factors.

Elements which have been found to be capable of providing an advantageous balance in activities between the metallic hydrogenation component and the solid acidic component include the normally solid elements of Group VI–A of the Periodic Table, especially sulfur; the normally solid elements of Group V–A of the Periodic Table, especially arsenic and antimony; and metals such as lead, mercury, copper, silver, zinc, cadmium and the like, especially silver, mercury and copper. These catalyst modifying elements typically are incorporated into the catalyst during the catalyst manufacture by impregnating a composite such as nickel on silica-alumina with a solution of an organic or inorganic compound, such as triphenyl arsine, arsenic trioxide, triphenyl stibine, silver nitrate, or mercuric nitrate, and/or by treating with sulfur compounds, such as carbon disulfide and hydrogen sulfide, which may be present in the feed or in the hydrogen. Where the composite is impregnated with a liquid solution such as an organo-metallic compound of the desired element, the liquid is evaporated to leave a deposit on the base and the impregnated deposit is then treated with hydrogen at an elevated temperature, typically about 850° F., to reduce the catalyst. However, it is also contemplated that the above elements may be introduced into the reaction zone during the on-oil period or during the other processing periods such as during the regeneration to contact the catalyst base in situ and thereby incorporate the element into the catalyst. As mentioned above, only small amounts of activity control-affording elements are generally required in the catalyst. Typically about 0.01 to 2 moles of arsenic or antimony, preferably 0.01 to 1 mole and optimally 0.1 to 0.5 mole of these elements per mole of the hydrogenation metal is employed. Likewise, about 0.03 to 5, optimally about 0.05 to 2 and preferably about 0.1 to 1 mole of the metals such as copper, silver or mercury per mole of the hydrogenation metal is incorporated into the catalyst.

A particularly desirable hydrocracking catalyst is a nickel arsenide on fluorided silica alumina.

Among the benefits obtained from employing the balanced catalysts discussed in the preceding paragraphs in the present hydrocracking process are the increased production of branched chain paraffins, more favorable control of catalyst activity and the simplification of catalyst reactivation techniques whereby a readily regenerable catalyst can be employed in the process.

Turning now to the drawing, a hydrocracking feedstock such as a heavy catalytic cycle oil boiling in the range from about 500° F. to about 850° F. and containing nitrogen in an amount of about 500 parts per million is passed by way of line **11** into heat exchanger **13** and removed by way of line **15** at a higher temperature (about 500–600° F.). The feedstock is further heated in furnace **17** to about 600–800° F. and removed by way of line **19**. Make-up hydrogen and recycle hydrogen (1,000–20,000 s.c.f.b.) are passed by way of lines **21** and **23**, respectively, and in line **25**, collectively, and mixed with the heated feedstock in line **19**. The hydrogen containing feedstock is then passed by way of line **27** into hydrodenitrogenation reactor **29** containing a bed of cobalt-molybdenum (2.8% Co and 8.5% Mo) on silica-alumina (25% Al_2O_3). Conditions within the hydrodenitrogenation reactor **29** include a temperature within the range of 600–800° F., a pressure within the range of 1,000–2,000 p.s.i.g. and an overall liquid hourly space velocity between about 0.25 and 2.0 volumes of hydrocarbon per hour per volume of catalyst. A denitrogenated stream is withdrawn from reactor **29** by way of line **31** and cooled in heat exchanger **33** and water spray drum **35** to about 100° F. after which it is passed by way of line **37** into separator **39**. Water is withdrawn by way of line **40**. A hydrogen-rich gas is separated from the liquid denitrogenated stream in separator **39** and passed by way of line **41** to heat exchanger **43** where the gas is cooled and then passed by way of line **45** to compressor **47**. Compressed gas (mainly hydrogen) is then recycled to hydrodenitrogenation reactor **29** by way of lines **23**, **25** and **27**.

The liquid stream from separator **39** is removed by way of line **49** and depressurized by valve **51** to atmospheric pressure. The stream is then passed by way of line **53** to furnace **55** where the stream is heated to about 500–700° F. and passed by way of line **57** to fractionating tower **59**. Tower **59** is also fed with a hydrocrackate by way of line **61**. A fraction boiling about 400–800° F. is withdrawn from tray **63** (representing a section of tower **59**) by way of line **65** to stripper tower **67** where steam

is injected by way of line **68** to produce a gas which is returned by way of line **69** to tower **59** and a liquid portion which is removed by way of line **71**. The overhead from tower **59** is removed by way of line **73** and passed through condenser **75**, through line **76** to reflux drum **77**, and then removed by way of lines **78** and **79**. The noncondensables are removed by way of line **81**. The overhead contains substantial amounts of hydrocarbons boiling in the gasoline range and above with some heavier products. A portion of the overhead is recycled to tower **59** by way of lines **78** and **83**. The bottoms from tower **59** are withdrawn by way of line **85**. This bottoms stream is about 20–30 weight percent of the feed being introduced to tower **59** by way of line **57**.

The bottoms stream is fed to vacuum tower **87** operating at 200–400 mm. Hg and 550–650° F. A bottoms fraction, amounting to 5–10 weight percent of the denitrogenated stream in line **57**, is withdrawn from vacuum tower **87** by way of line **89**. The overhead is fed by way of line **91** to condenser **93** and then to reflux drum **95**. A reflux stream is fed from drum **95** by way of line **97** to tower **87**. The remaining overhead is added by way of line **99** to the liquid stream in line **71** from stripper tower **67**. The combination is then fed to furnace **103** by way of line **101** where it is heated to about 550–700° F., withdrawn by way of line **105** and mixed with hydrogen from line **107**. The hydrogen is derived from recycle hydrogen from line **109** and made-up hydrogen from line **111**. The hydrogen-rich feed is then passed by way of line **113** to hydrocracking reactor **115** where it is processed.

Reactor **115** contains a bed of arsenided nickel on fluorided silica-alumina catalyst. The catalyst contains 5% nickel, 2.5% arsenic, 3% fluorine, and the silica-alumina support contains about 25% Al_2O_3. The conditions in reactor **115** are a temperature in the range of 500–700° F. a pressure in the range of 750 to 1500 p.s.i.g., a hydrogen to hydrocarbon ratio between about 1,000 and 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon, an overall liquid hourly space velocity between about 0.5 and 5 volumes of hydrocarbon per hour per volume of catalyst. The effluent is withdrawn from reactor **115** by way of line **117**, cooled by passing through heat exchanger **119** and passed by way of line **121** into separator **123** wherein a hydrogen-rich gas is separated from the liquid hydrocrackate and passed by way of line **125** to heat exchanger **127** wherein the gas is cooled. The cooled gas is passed by way of line **129** to compressor **131** where it is compressed and returned to the hydrocracking reactor **115** by way of lines **109**, **107**, and **113**.

The remaining liquid hydrocrackate in separator **123** is then passed by way of line **133** to valve **135** where it is depressurized to atmospheric pressure and passed by way of line **61** to fractionating tower **59**.

The present invention will be better understood by reference to the following examples which illustrate the beneficial effects on the operation of a hydrocracking process obtained by the removal of the poisonous material from the denitrogenated stream. It is to be understood that the following examples are given for the purpose of illustration only and do not serve in any way to limit the scope of the present invention.

Example I

A heavy catalytic cycle oil containing about 1.7 weight percent sulfur, about 500 p.p.m. nitrogen, and having an API gravity of 20° was contacted with a hydrodenitrogenation catalyst, cobalt-molybdenum on silica-alumina, at a temperature of 700° F. and a pressure of 1,500 p.s.i.g. The treated oil containing about 54 p.p.m. sulfur and about 0.8–1.2 p.p.m. nitrogen, was distilled under vacuum (about 1–2 mm. Hg and 420° F.) in a Claisen-Vigreux distillation column fitted with a condenser until the residue equalled about 3 weight percent of the treated oil. The overhead (about 97 weight percent) was hydrocracked over a catalyst prepared by treating 2,500 g. silica-alumina with an ammoniacal solution containing nickel (from 252.5 g. nickel carbonate), arsenic (from 84.0 g. arsenic trioxide) and fluorine (from 157.5 g. ammonium fluoride) followed by drying at 300° F., pelleting and then calcining the treated combination at 1,000° F. The final catalyst contained, by analysis, 4.9 weight percent N, 2.7 weight percent As and 2.2 weight percent F. The results of hydrocracking the distilled fraction of the treated oil are listed below in Table I together with the results from hydrocracking the undistilled treated oil. The conversion was determined by gas chromatography in which the 421° F. pt. indicates the split between the fraction boiling in the gasoline range and above. The chromatographic analysis used is a temperature programmed technique which elutes from the chromatographic column the various components of a hydrocarbon mixture strictly according to boiling point so that the cumulative chromatogram gives results similar to a TBP distillation of the mixture. The weight percent below 421° F. in the chromatogram is taken to correspond to a 400° F., EP gasoline on an ASTM basis.

TABLE I

Feed	P.p.m. N	Hours on Stream	Conversion, Wt. Percent (Gasoline and Lighter)
Undistilled Oil	0.8–1.2	1,136–1,280	35
Distilled Oil	0.7	1,928–2,240	54

The above results demonstrate that the conversion rate for the distilled oil was 54 weight percent while that for the undistilled oil was 35 weight percent, an increase of approximately 54 percent over the conversion rate for the undistilled oil. This large improvement was not caused by the difference in the nitrogen content but largely due to the distillation of the oil.

Example II

The 3 weight percent bottoms (from Example I) in hexane was percolated through activated alumina and analyzed with the following results:

TABLE II

Material	Weight percent	Percent C	Percent H	Percent S	Percent N
White Wax	99.4	84.67	14.15	0.049	0.0005
Yellow Waxy Solid	4.35				
Black Viscous Tar	0.9	92.38	6.15	0.091	0.0122
Brown Amorphous Powder (insol. in hexane solution)	0.35				

The white wax and black tar were individually added back to a denitrogenated and distilled heavy catalytic cycle oil prepared as described in Example I to determine which fraction of the rejected bottoms poisoned the catalyst. The three samples—distilled oil, distilled oil with white wax, and distilled oil with black tar—were subjected to hydrocracking under the conditions described in Example I and gave the results listed in Table III.

TABLE III

	P.p.m. N	Hours on Stream	Conversion Wt. percent (Gasoline and Lighter)
Distilled Oil	0.8	220–272	47
D.O. plus 5.7 wt. percent wax		272–362	47
D.O. plus 0.3 wt. percent tar		362–411	28

The above results demonstrate that addition of the black tar to the distilled oil reduced the conversion rate from 47 weight percent to 28 weight percent, a reduction of approximately 40 percent. This is unusual since the increased nitrogen content (from 0.8 to about 1.1 p.p.m. N) of the distilled oil plus tar accounts for only a small decrease (about 4%) in the conversion rate. Thus, distillation of the oil removed material which, although a minor constituent of the rejected bottoms, is a violent poison in the hydrocracking process—a poison not entirely associated with the nitrogen content of the oil.

Example III

To feedstocks were prepared for charging to a hydrocracking reactor. The first was a heavy catalytic cycle oil which was hydrodenitrogenated over a commercial NALCOMO–471 catalyst manufactured by the National Aluminate Company. This catalyst was in the form of 0.1-inch diameter extrudates which contained 2.8 weight percent cobalt oxide and 13.2 weight percent molybdenum trioxide on alumina. The second feed was a mixture of the heavy catalytic cycle oil, half of which had been hydrodenitrogenated over a cobalt-molybdenum-on-silica-alumina catalyst, and half of which had been hydrodenitrogenated over a cobalt-molybdenum-on-silica-magnesia catalyst. The cobalt-molybdenum-on-silica-alumina catalyst contained 3.4 weight percent cobalt oxide and 12.8 weight percent molybdenum trioxide on a support of National Aluminate "High-Alumina" silica-alumina cracking catalyst. The cobalt-molybdenum-on-silica-magnesia catalyst comprised 3.6 weight percent cobalt oxide and 12.8 weight percent molybdenum trioxide on Davison silica-magnesia SM–30 cracking catalyst. Thus, the first feed was pretreated with a non-acidic base catalyst while portions of the second feed were each pretreated with an acidic-base catalyst. Nominal operating conditions for the hydrodenitrogenation were: a temperature of 660°–730° F.; a pressure of 1500 p.s.i.g.; and a liquid hourly space velocity of 0.25–1.0 volume of hydrocarbon per hour per volume of catalyst.

The hydrocarbon feed which was hydrodenitrogenated over the non-acidic-base catalyst contained 1.8 parts per million nitrogen subsequent to the hydrodenitrogenation while the hydrocarbon feed which was hydrodenitrogenated over the acidic-base catalyst contained 0.8 parts per million nitrogen after the hydrodenitrogenation.

The above two feedstocks were alternately charged to a bench-scale isothermal hydrocracking flow-reactor. This hydrocracking reactor had an internal diameter of ⅝-inch and a cross-sectional area, excluding the axial thermowell, of 3.45 square centimeters. The catalyst bed in this reactor was approximately 9 centimeters in length. The hydrocracking catalyst used therein comprised arsenided-nickel-on-fluoride-silica-alumina. The support of this catalyst was a commercial high-alumina cracking catalyst manufactured by the National Aluminate Company. The catalyst contained 4.5 weight percent nickel, 2.3 weight percent arsenic, and 2.9 weight percent fluorine. Nominal hydrocracking test conditions were: a temperature of about 644° F.; a pressure of 1400 p.s.i.g.; a liquid hourly space velocity of 1 volume of hydrocarbon per hour per volume of catalyst; and a hydrogen addition rate of about 12,000 standard cubic feet of hydrogen per barrel of hydrocarbon.

After the hydrocracking test run had been on stream for 244 hours, the feed pretreated with the non-acidic-base catalyst was employed. After 1132 hours on stream, the feed pretreated with the acidic-base catalyst was used. Periodic samples of hydrocrackate were obtained to and subsequent to this latter feed change. These samples were submitted for various analyses. The results of which were used in the calculation of the amount of convesion to liquid material boiling below 386° F. and the zero-order rate constants representing the hydrocracking reaction. The results of these calculations are shown in Table IV.

TABLE IV

Sample No.	Time On Stream, Hrs.	Conversion, Wt. percent	Rate Constant At 640° F.	Base Of Pre-Treat Catalyst
1	988	30.0	0.28	Non-acidic.
2	1,012	30.8	0.28	Do.
3	1,036	33.8	0.30	Do.
4	1,060	33.4	0.30	Do.
5	1,084	31.0	0.28	Do.
6	1,108	32.2	0.29	Do.
7	1,132	31.5	0.29	Do.
8	1,156	23.0	0.21	Acidic.
9	1,180	25.9	0.24	Do.
10	1,204	26.7	0.22	Do.
11	1,228	25.1	0.23	Do.
12	1,252	23.0	0.21	Do.
13	1,276	24.8	0.22	Do.

The above results demonstrate that a hydrocarbon feedstock which has been hydrodenitrogenated previously over an acidic-base catalyst will more deleteriously affect subsequent hydrocracking than a hydrocarbon feedstock which has been hydrodenitrogenated previously over a non-acidic-base catalyst.

Hydrodenitrogenation can be more effectively accomplished by using an acidic-base catalyst. However, when such a catalyst is used, the effluent obtained from the hydrodenitrogenation section will more deleteriously affect subsequent hydrocracking than if the hydrodenitrogenation had been carried out over a non-acidic-base catalyst. My process can be used to effectively hydrocrack a hydrocarbon feedstock which contains substantial amounts of nitrogen by using an acidic-base catalyst in the hydrodenitrogenation section without resulting in reduced performance of the subsequent hydrocracking. Hence, my improved hydrocracking process combines the benefit of more efficient hydrodenitrogenation produced by an acidic-base catalyst with improved hydrocracking conversion.

Thus having described the invention, what is claimed is:

1. A combination process for converting a hydrocarbon feedstock which boils between about 400° F. and about 1000° F. and which contains at least 50 parts per million nitrogen to lower boiling hydrocarbons, which process consists essentially of contacting said feedstock in a hydrodenitrogenation reaction zone with a hydrodenitrogenation catalyst, said hydrodenitrogenation catalyst comprising a metallic hydrogenation component supported on an acidic cracking catalyst, under hydrodenitrogenation conditions in the presence of hydrogen gas to provide a denitrogenated liquid hydrocarbon stream containing less than about 2 parts per million nitrogen and also containing a minor proportion of a tarry material which acts to poison the hereinafter-named hydrocracking catalyst; fractionating said denitrogenated stream to separate a heavy bottoms fraction and a lighter bottoms-free fraction, said bottoms fraction containing said tarry catalyst-poisoning material; and contacting said lighter bottoms-free fraction in a hydrocracking reaction zone with a hydrocracking catalyst under hydrocracking conditions in the presence of hydrogen to convert said feedstock to said lower boiling hydrocarbons at an improved conversion rate.

2. The process of claim **1** wherein said bottoms fraction constitutes less than about 10% by weight of said denitrogenated stream.

3. The process of claim **1** wherein said feedstock comprises a catalytic cycle oil.

4. The process of claim 1 wherein said bottoms fraction constitutes from about 1% to about 3% by weight of said denitrogenated stream.

5. The process of claim 1 wherein said hydrocracking catalyst comprises a Group VIII metallic hydrogenation component supported on silica-alumina cracking catalyst.

6. A process for converting a hydrocarbon feedstock which contains at least 50 parts per million nitrogen and which boils between about 350° and 850° F. to a product predominantly within the gasoline boiling range, which process consists essentially of contacting said feedstock in a hydrodenitrogenation reaction zone with a hydrodenitrogenation catalyst comprising a Group VIII metal hydrogenation catalyst supported on an acidic cracking catalyst, at a temperature between about 600° F. and 800° F. and a pressure between about 1000 p.s.i.g. and 3000 p.s.i.g., and in the presence of hydrogen gas to provide a denitrogenated liquid hydrocarbon stream containing less than about 2 parts per million nitrogen and also containing a minor proportion of a tarry material which acts to poison the hereinafter-named hydrocracking catalyst; fractionating said denitrogenated stream to separate a heavy bottoms fraction and a lighter bottoms-free fraction, said bottoms fraction constituting less than about 10% by weight of said denitrogenated stream and containing said tarry catalyst-poisoning material; and contacting said lighter bottoms-free fraction, without further treatment, in

a hydrocracking reaction zone with a hydrocracking catalyst comprising a Group VIII metal hydrogenation catalyst on an acidic cracking catalyst.

7. The process of claim 6 wherein said acidic cracking catalyst in said hydrodenitrogenation catalyst is silica-alumina and said acidic cracking catalyst in said hydrocracking catalyst is silica-alumina.

8. The process of claim 6 wherein said hydrodenitrogenation catalyst comprises cobalt and molybdenum supported on silica-alumina cracking catalyst and said hydrocracking catalyst comprises arsenided nickel supported on silica-alumina cracking catalyst.

9. The process of claim 6 wherein said bottoms fraction constitutes about 1% to about 3% by weight of said denitrogenated stream.

10. The process of claim 6 wherein said feedstock is a catalytic cycle oil.

References Cited

UNITED STATES PATENTS

2,911,352	11/1959	Goretta et al.	208—89
3,132,086	5/1964	Kelley et al.	208—211
3,132,089	5/1964	Hass et al.	208—254

DELBERT E. GANTZ, *Primary Examiner.*

S. P. JONES, *Assistant Examiner.*