

Aug. 23, 1966

J. W. SCOTT, JR., ETAL

3,268,438

HYDRODENITRIFICATION OF OIL WITH COUNTERCURRENT HYDROGEN

Filed April 29, 1965

2 Sheets-Sheet 1

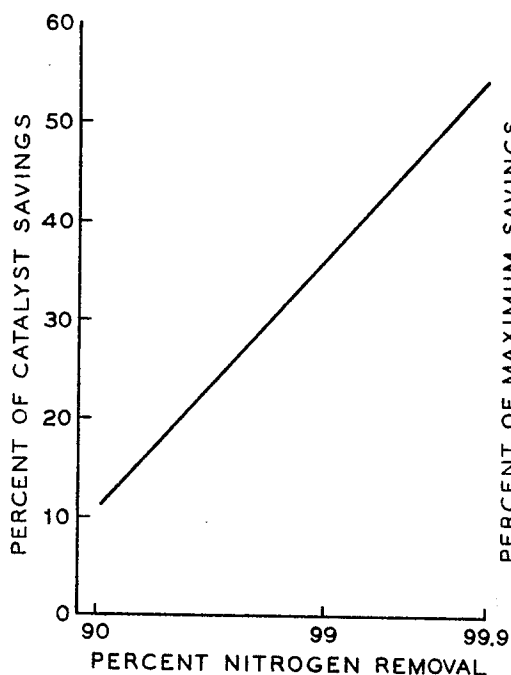


FIG. 2

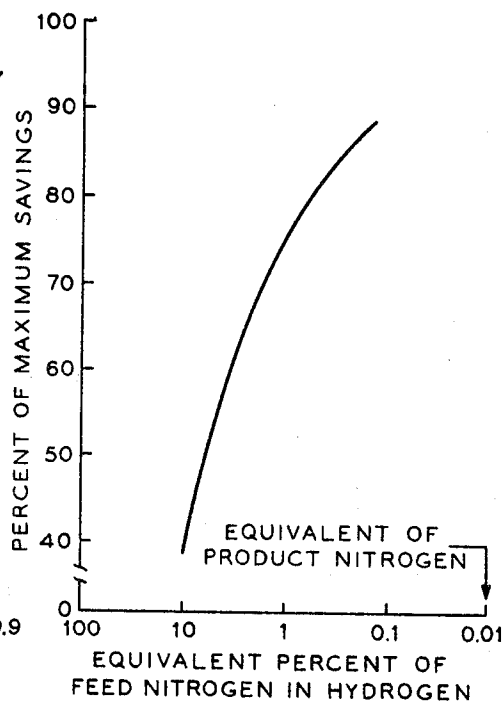


FIG. 3

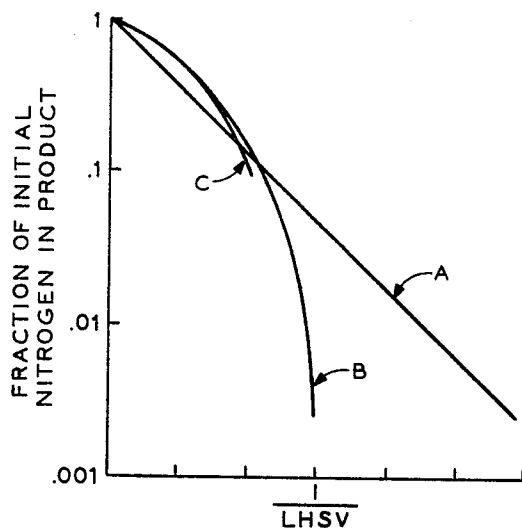


FIG. 1

INVENTORS
JOHN W. SCOTT, JR.
ROBERT L. JACOBSON

BY Frank E. Johnston
Jack M. Whitney
ATTORNEYS

Aug. 23, 1966

J. W. SCOTT, JR., ETAL

3,268,438

HYDRODENITRIFICATION OF OIL WITH COUNTERCURRENT HYDROGEN

Filed April 29, 1965

2 Sheets-Sheet 2

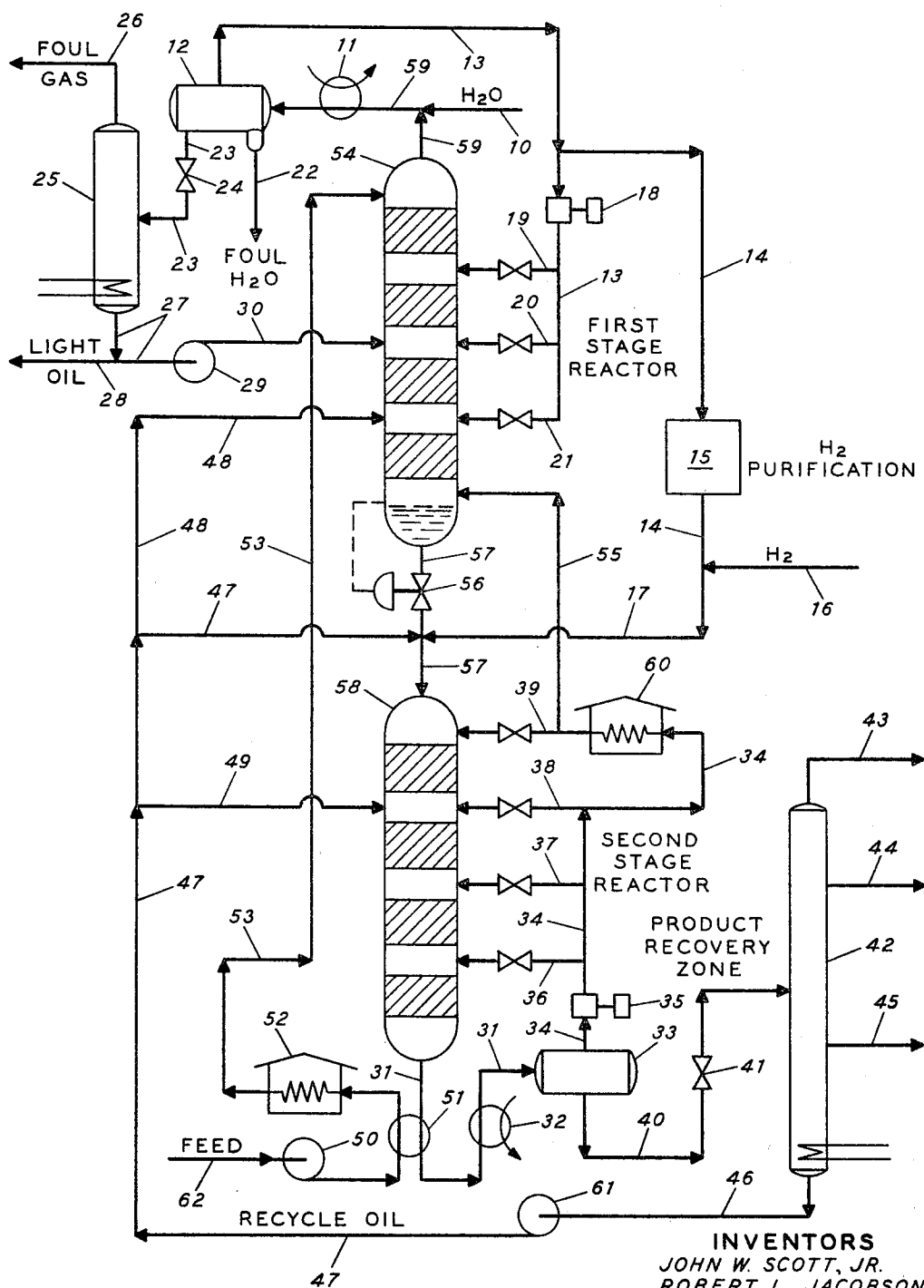


FIG. 4

INVENTORS
JOHN W. SCOTT, JR.
ROBERT L. JACOBSON
BY *Frank C. Johnston*
Jack M. Whitney
ATTORNEYS

1

2

3,268,438

**HYDRODENTRIFICATION OF OIL WITH
COUNTERCURRENT HYDROGEN**

John W. Scott, Jr., Ross, and Robert L. Jacobson, Pinole,
Calif., assignors to Chevron Research Company, a cor-
poration of Delaware

Filed Apr. 29, 1965, Ser. No. 451,845

4 Claims. (Cl. 208—89)

This application is a continuation-in-part of our pending application Serial No. 161,463, filed December 22, 1961, now abandoned.

This invention relates to catalytic hydrocarbon conversion processes for upgrading nitrogen-containing high boiling hydrocarbon oils. In particular, the invention relates to processes for the removal of nitrogen present in organic nitrogen compounds from high boiling hydrocarbon oils by hydrogen treating using countercurrent flow of hydrogen and oil.

The removal of naturally occurring nitrogen compounds from hydrocarbon oils is known to improve the properties of the oils in several respects. Thus, usually the color and stability of the oil are improved; the removal of nitrogen from a catalytic cracker feed greatly improves the cracking conversion; and the removal of nitrogen greatly enhances conversions during subsequent processing with catalysts which are poisoned by such nitrogen compounds. Recently, hydrocracking processes have been developed for the conversion of middle distillates to gasoline and for the conversion of high boiling oils to middle distillate and gasoline. The hydrocracking catalysts employed in these processes are sensitive to contaminants, especially nitrogen compounds. Accordingly, nitrogen compounds are removed from the hydrocarbon oil feed, usually by hydrogen treating in a first stage, before hydrocracking in a second stage. In general, use of the hydrocracking process is limited by the ability of the hydrogen treating process to remove contaminating nitrogen compounds from the feed. Such becomes increasingly more difficult as feed nitrogen content and/or feed boiling point increases. Although known processes and catalysts are theoretically capable of purifying any feed stock, with high boiling oils these processes require the use of low space velocities, high pressures, and high temperatures. Low space velocities and high pressures increase the equipment cost. The use of high temperatures leads to short on-stream times due to rapid catalyst fouling. High heating and cooling costs are also associated with the use of elevated temperatures and pressures. Another expensive item is the cost of pumping the oil to elevated pressure and of compressing and recycling high pressure hydrogen.

Various techniques have been proposed for carrying out hydrogen treating processes for removing nitrogen compounds from high boiling oils, including the use of reactors containing fluidized catalyst particles, catalyst particles suspended in oil slurries, or fixed beds of catalyst particles, with flow of oil and hydrogen concurrently upwards or downwards or in opposite directions. In practice it has heretofore been found preferable to pass the oil and hydrogen together downwards through fixed beds of catalyst particles supported in a reactor comprising an upright cylindrical pressure vessel. Certain advantages would appear to be obtainable by passing the oil downward and the hydrogen upwards. For example, a light by-products and vaporizable oil would be carried upward in the vapor stream so that the down-flowing heavy liquid components in the oil feed would achieve better contact with the catalyst and for a longer time as compared to the volatile components. This is advantageous because the heavier oils generally require more severe or longer treatment for purification than the lighter oils. Also, further distillation of the heavy oil product might be avoidable as it would contain less low boiling components. It

is found, however, that the expected advantages are usually outweighed by certain disadvantages of the countercurrent design. For example, the factors entering into the design of packed stripping columns must be considered to avoid channeling of liquid or vapor, slug flow, flooding, entrainment of liquid in the vapor, and excessive disruption of the catalyst particles causing rapid attrition and plugging. The result is that a reactor with countercurrent flow is less flexible in operation with respect to use with varying feed and hydrogen flow rates and for the treatment of feeds of different boiling range other characteristics. Consequently, except in special cases, the reactors are usually designed for flow of oil and vapor in the same direction.

It has now been found that by operating in accordance with the present invention additional and unexpected advantages can be obtained in countercurrent processing, and these new advantages far outweigh the abovementioned disadvantages.

In accordance with this invention, nitrogen is removed from a high boiling hydrocarbon oil by a process which comprises introducing the high boiling oil at the top of a reaction zone containing sulfactive hydrogenation catalyst as at least one fixed bed. Downflowing purified hydrocarbon oil effluent is withdrawn from the bottom of the reaction zone. Hydrogen-rich gas essentially free of ammonia is introduced at the bottom of the reaction zone, and upflowing hydrogen-rich vapor effluent is withdrawn from the top of the reaction zone. Conditions of temperature, hydrogen partial pressure, flow of hydrogen relative to oil, and flow of oil relative to catalyst are maintained in the reaction zone whereby to convert at least 90% of the nitrogen initially contained in the oil to ammonia which is carried out in the upflowing hydrogen-rich vapor effluent of the reaction zone. The hydrogen-rich gas introduced into the reaction zone below the catalyst for passage upwards therethrough comprises a recycled portion of the hydrogen-rich vapor effluent which has been purified to remove NH_3 contained therein. The ammonia content of the hydrogen-rich gas introduced at the bottom of the reaction zone is maintained at a concentration below about 0.02 percent by volume and less than the equivalent of 10% of the initial nitrogen content of the high boiling hydrocarbon oil. Preferably, the ammonia content of the hydrogen-rich gas is less than 0.01% and less than the equivalent of 2.5% of the initial nitrogen content of the oil, and still more preferably the hydrogen-rich gas contains no more ammonia than the equivalent of the residual organic nitrogen content of the purified downflowing hydrocarbon oil effluent. In any event, the concentration of NH_3 in the gas is to be below 0.02% by volume. Control of the operating conditions in the reaction zone to obtain a high percent conversion of the nitrogen to ammonia, coupled with control of the ammonia content of the hydrogen-rich gas to a low concentration, are novel and critical features whereby the unusual advantages of this invention are obtained.

In the process of this invention, as in previously known or suggested processes, a high boiling hydrocarbon oil containing organic nitrogen compounds is passed downflow through at least one bed of sulfactive hydrogenation catalyst particles comprising a reaction zone. Hydrogen-rich gas, at least 1000 s.c.f./bbl of oil, is passed upflow through at least the same reaction zone. Reaction conditions of temperature and pressure for converting organic nitrogen compounds to NH_3 are maintained in the reaction zone. Upflowing vapors containing essentially all the NH_3 produced are withdrawn from the reaction zone and cooled to condense and separate normally-liquid hydrocarbon oil contained therein from hydrogen-rich gas, at least portion of which gas is recycled to the reaction zone. The net amount of NH_3

produced is removed from the system. A portion of the NH_3 is usually removed in solution in the condensed normally-liquid hydrocarbons. Another portion may be removed by purging or bleeding out of the system a minor portion of the gas available for recycling. This is a usual practice to prevent methane and other normally gaseous hydrocarbons or by-products, either produced in the process or introduced as impurities in the fresh hydrogen added to make up for that consumed in the hydrogenation reactions, from building up to concentrations in the hydrogen-rich gas which would adversely suppress the hydrogen partial pressure. "Hydrogen-rich" gas refers to gas which is more than 50% H_2 by volume, and it is usually found uneconomical to use hydrogen-rich gas which is less than about 60% H_2 . Thus, in removing light gases NH_3 is also removed, such that the concentration of NH_3 in the recycled hydrogen-rich gas builds up to an equilibrium concentration which is rarely more than about one percent by volume representing a minor contaminant having negligible effect on the hydrogen partial pressure.

Also, the heavy oil feeds usually contain sulfur compounds in addition to nitrogen compounds, and at least a portion of the sulfur is converted to H_2S . The NH_3 and H_2S can react under anhydrous conditions to form solid ammonium sulfide or bisulfide which can deposit on the internal surfaces of the equipment, especially in heat exchangers causing restrictions, plugging, and less efficient heat transfer. Consequently, it is not unusual in known processes to inject water into the effluent streams leaving the reaction zone in an amount sufficient to dissolve these and other salts when they form. The water containing the dissolved salts is later separated and withdrawn from the system, thereby removing another portion of the net NH_3 produced. Ammonia exhibits a substantial vapor pressure over aqueous solutions of NH_4HS , however, so that the hydrogen-rich gas available for recycling to the reaction zone in previously known processes still contained a small equilibrium concentration of NH_3 of above at least about 0.02 percent by volume, usually about 0.1–0.2%. This obviously represents an insignificant diluent insofar as having any effect on the hydrogen partial pressure is concerned. Also, NH_4HS is very soluble in water at the separation conditions used, about 100–200° F., so that heat exchanger fouling can be effectively prevented with a minimal amount of water injection. The operation of the process cannot be improved in this respect by using larger amounts of water. In fact, periodic water injection is usually found to be adequate.

We have found that the rate of hydrogenation of the last traces of nitrogen compounds in high boiling oils to ammonia is greatly increased, as compared to hydrogen treating processes heretofore used, if the hydrogen-rich gas introduced at the bottom of the reaction zone is essentially free of ammonia. That is, NH_3 must be removed to a concentration far below the equilibrium concentration ordinarily obtained. Because of the increased reaction rate, less catalyst is required in the hydrogen treating process of this invention and/or more moderate temperatures may be used whereby coke formation on the catalyst is decreased and a longer on-stream time attained. The increased reaction rate is observed, however, only when operating at conditions for nearly completely removing all organic nitrogen in the oil by hydrogenation to NH_3 , and then only when the NH_3 concentration in the hydrogen-rich gas supplied is far lower than ordinarily is obtained. In particular, therefore, the invention provides an economical process for the removal of virtually all of the nitrogen contained in a high boiling hydrocarbon oil; i.e., to remove more than 99% of the nitrogen initially contained in the oil.

The attached figures, discussed in more detail hereinafter, illustrate graphically the importance of the aforementioned novel features of this invention, and

show one process flow scheme for practicing the invention. Briefly:

FIG. 1 is a first-order plot of percent nitrogen removal versus contact time, comparing concurrent flow of oil and hydrogen with countercurrent flow;

FIG. 2, based on FIG. 1, is a plot of catalyst savings attainable by the invention versus percent nitrogen removal;

FIG. 3 is a plot of percent of maximum catalyst savings attained versus the ammonia content of the hydrogen used in the invention; and

FIG. 4 illustrates one particular method of using the invention in a two-stage process.

The feed to the process of this invention is any nitrogen-containing high boiling oil which remains substantially in the liquid phase at the conditions of treatment used in the hydrogen treating. Examples of such oils are reduced crude, deasphalted residuum, heavy straight-run gas oils, lube oils, waxes, heavy cracked cycle oils, heavy coker gas oils, and like heavy oils derived from petroleum, shale oil, or other hydrocarbon sources. The oil should boil at least 90° above 400° F. Preferred hydrocarbon oils boil at least 90° above 600° F. and at least 10° above 750° F. The process is also especially advantageous when applied to oils having high nitrogen contents of 1000 p.p.m. or greater.

The catalyst employed is any hydrogenation catalyst which is not permanently poisoned by sulfur, i.e., a sulfactive catalyst, since the feeds treated usually contain sulfur, and which is active for the hydrogenation of nitrogen compounds. Typical catalysts comprise the oxides and/or sulfides or other compounds of Group VI-B metals and of Group VIII metals, and combinations thereof, unsupported or supported on a carrier; for example, hydrofining catalysts such as cobalt-molybdate on alumina. Hydrocracking may be achieved along with hydrogenation by using an acidic carrier such as silica-alumina, or by using higher temperatures with a non-acidic carrier. A catalyst particularly preferred because of its unusually high activity for the hydrogenation of nitrogen compounds is a high metal content, sulfided, nickel-molybdenum-alumina catalyst containing 3–10% nickel and 12–30% molybdenum, especially 4–10% nickel and 15.5–30% molybdenum.

The temperature will generally be in the range 500–850° F., more usually in the range 550–800° F. Using the aforementioned preferred nickel-molybdenum-alumina catalysts, temperatures at the lower end of this range may be used, preferably temperatures below 750° F. if hydrocracking is to be avoided.

The pressure in the hydrogen treating process of this invention is in excess of 200 p.s.i.g. usually 500–4000 p.s.i.g. The important factor is to maintain a relatively high hydrogen partial pressure, whereby the feed is maintained substantially liquid, catalyst fouling by coke deposition is inhibited, and the hydrogenation rate is advantageously increased, in the case of the high boiling feeds. With the aforementioned preferred nickel-molybdenum-alumina catalysts, the hydrogen partial pressure is preferably maintained in the range 400–2000 p.s.i.a. Excess hydrogen is provided over and over that required for reaction with the nitrogen, sulfur, oxygen, halogen, and other contaminants, as well as that consumed in hydrogenation of olefins and aromatics in the hydrocarbon oil. Hydrogen consumption depends greatly on the properties of the hydrocarbon oil feed, but is, of course, influenced by the temperature and pressure employed. In general, 1000–15,000 standard cubic feet of hydrogen-rich gas are passed upflow per barrel of downflowing oil, preferably 2000–6000 s.c.f./bbl.

The catalyst is contained in the reaction zone as one or more fixed beds of small catalyst particles. The dimensions of the beds are fixed both by the hydraulics of a system and by the reaction kinetics. Thus, the diameter of the beds is sufficiently narrow to permit even

5

distribution of the downflowing liquid oil across the bed cross section for efficient contacting of oil and catalyst with the upflowing hydrogen while sufficiently broad to prevent excessive entrainment of liquid or disruption of the bed. The total height of catalyst is then determined by the properties of the hydrocarbon oil, its initial nitrogen content, and the degree of purification specified, i.e., to provide the requisite contact time in terms of the reciprocal of volumes of oil per hour per volume of catalyst

$$\left(\frac{1}{\text{LHSV}} \right)$$

Generally, the space velocity will be in the range of 0.2–10 LHSV, preferably 0.3–3.

Vapors formed in the reaction zone, including NH_3 , H_2S , H_2O , normally gaseous hydrocarbons, and light hydrocarbons vaporizable at the reaction conditions, are swept upward by the hydrogen introduced at the bottom, and pass out with the upflowing hydrogen effluent. The stripping action of the upflowing hydrogen provides a purified, dry, hot downflowing hydrocarbon oil effluent. Hydrogen-rich gas introduced at the bottom of the reaction zone should be essentially free of ammonia. By this is meant that any ammonia contained in the hydrogen-rich gas is present in a low concentration, less than 0.02% and less than the equivalent of 2.5% of the nitrogen content of the high boiling oil. It is especially advantageous to have as low a concentration of ammonia as is commercially practical in the gas in contact with the oil at the bottom of the reaction zone, where the last traces of nitrogen compounds are being converted; i.e., this is particularly important where a very low residual nitrogen content is desired. The hydrogen may, however, contain H_2S , and in some cases, as where over 99% nitrogen removal is specified, it is desirable to add H_2S to keep the catalyst at the bottom of the reaction zone sulfided.

The upflowing hydrogen-rich vapor effluent of the reaction zone is recycled. No special purification of the recycle hydrogen is necessary if it is used only in the uppermost portions of the reaction zone, except to remove the net production of ammonia and other by-products and the net input of light hydrocarbons vaporized in the reaction zone. On the other hand, it is important that the hydrogen introduced at the bottom of the reaction zone be relatively free of ammonia. Accordingly, the hydrogen which is recycled and introduced at the bottom is first purified, for example, by water washing and/or contacting with an adsorbent such as alumina or molecular sieves. A preferred method of purifying the upflowing hydrogen effluent is to cool that effluent and to add water thereto sufficient to scrub out the ammonia. A three-phase system is thereby formed, consisting of a partially purified hydrogen-rich gas phase, a liquid light hydrocarbon phase containing dissolved impurities, and a liquid water phase containing dissolved impurities. The phases are separated in a high pressure separator, at substantially the pressure of the reaction zone. The hydrogen-rich gas may be sufficiently pure to be recycled to the reaction zone if acidified water or a large excess of water is used, but it may need to be further purified to remove the last traces of ammonia prior to being introduced at the bottom of the reaction zone. The water may be discarded. The oil is stripped, preferably removing ammonia from the upflowing hydrocarbons, and it may then usually be blended with the final products or recovered as a separate product.

If no special provisions are made for scrubbing or otherwise removing ammonia from the upflowing hydrogen effluent, the hydrogen cannot be recycled to the bottom of the reaction zone with the expectation of obtaining the improved results of the invention. This is because ammonia is not sufficiently soluble in the con-

6

densed oil, and would build up to too high a concentration in the recycle. Also, the small amount of water sometimes used to remove ammonium bisulfide salts will not provide a low enough NH_3 concentration in the gas.

To illustrate the above remarks, hydrogen-rich vapors obtained as the vapor effluent of essentially complete denitrification of a heavy oil at 2800 p.s.i.g. with 10,000 s.c.f. hydrogen-rich gas per barrel contains, after preliminary separation of oil condensed at 450° F., 78% H_2 , about 2% C_4 –500° F. hydrocarbons, about 1% H_2S , and 0.2% C_4 –500° F. hydrocarbons, about 1% H_2S , and 0.2% NH_3 , on a volume basis. When cooled to 150° F. and contacted with water to form an aqueous phase containing 10 wt. percent NH_4HS , the NH_3 -depleted gas in equilibrium with the water contains 0.045 vol. percent NH_3 . This is at 2800 p.s.i.g. At lower pressure the hydrogen-rich gas would contain more NH_3 . The aqueous solution of NH_4HS is more dilute than needed, i.e., represents the addition of more water than needed to prevent or remove precipitation of the salt in the equipment.

In accordance with the invention, the operating conditions in the reaction zone must also be so selected and controlled that at least 90% of the nitrogen in the high boiling hydrocarbon oil feed is converted to ammonia. Higher temperatures and pressures and lower space velocities give more complete conversion. The importance of controlling to a high percent conversion is shown graphically by FIGS. 1 and 2.

Referring to FIG. 1, there is shown as curve A a first order reaction rate plot of the fraction of the initial nitrogen content remaining in a hydrocarbon oil after contacting in a conventional reactor with a sulfactive hydrogenation catalyst, using concurrent flow of oil and hydrogen, for varying lengths of time in terms of reciprocal space velocities

$$\left(\frac{1}{\text{LHSV}} \right)$$

Runs with over twenty different oils at a variety of conditions have demonstrated that the denitrification reaction follows a first order rate curve when concurrent flow of oil and hydrogen is used. In contrast thereto, we have found that the reaction approaches a one-half order rate curve when countercurrent flow of oil and hydrogen is used, provided the hydrogen supplied contains no ammonia. Curve B is a one-half order reaction rate plot, based on converting 99.75% of the nitrogen in an oil to ammonia at the same conditions of temperature, pressure, and hydrogen flow as for curve A. Curve C is a one-half order reaction rate plot based on converting 90% of the nitrogen to ammonia at the same conditions of temperature, pressure, and hydrogen flow.

It can be seen that little or no advantage is obtained by countercurrent contacting even if the hydrogen contains no NH_3 , insofar as nitrogen removal is concerned, unless the conditions used are such as to give at least about 90% conversion. On the other hand, if greater than 90% removal of nitrogen is specified, countercurrent contacting is extremely beneficial provided the hydrogen has a very low NH_3 content.

This is further demonstrated by FIG. 2, which shows the percent savings in catalyst and reactor volume as a function of percent nitrogen removal, comparing the countercurrent contacting of curve B with the concurrent contacting of curve A in FIG. 1. As shown, greater benefits are obtained the greater the percent nitrogen removal above 90%.

FIG. 2 and curves B and C of FIG. 1 are based on using hydrogen introduced at the bottom of the reaction zone which contains no ammonia, whereby maximum benefits are obtained. Results intermediate to curves A and B of FIG. 1 are obtained if the hydrogen contains a small concentration of ammonia. If the hydrogen contains ammonia in an amount equivalent to only about 2.5% of the nitrogen content of the oil feed, the

results differ only slightly from curve B down to about 99% nitrogen removal (fraction remaining=0.01). But, if the ammonia content of the hydrogen is equivalent to 10% of the feed nitrogen, only about half or less of the possible savings in catalyst and reactor volume can be realized. Thus, it is especially desirable to limit the ammonia content of the hydrogen to much less than that amount equivalent to about 10% of the feed nitrogen content. Preferably the ammonia content of the hydrogen does not exceed the equivalent of 2.5% of the feed nitrogen. Even lower ammonia contents are preferred if over 99.5% of the feed nitrogen is to be removed. At least 90% of the maximum possible benefit is obtained if the ammonia content of the hydrogen does not exceed the equivalent of the specified nitrogen content of the purified oil, and accordingly this represents the most preferred operation.

The foregoing remarks are further illustrated by FIG. 3. In FIG. 3, 100% of the maximum possible benefit, in terms of reduced catalyst and reactor volume, is obtained by using hydrogen which contains no ammonia, when removing 99.99% of the nitrogen from a high boiling oil. If the hydrogen contained ammonia equivalent to 10% of the feed nitrogen, only about 40% of the benefit would be obtained; at ammonia equivalent to 2.5% of the feed nitrogen, about 70-75% of the benefit would be obtained. If less than 99.99%, but more than 90%, of the nitrogen is to be removed, the catalyst savings obtainable by the invention is not as great, but a greater portion of the possible savings is obtained at a given equivalent ammonia concentration. That is to say, the ammonia content also becomes less critical as a lesser degree of denitrification is accomplished. In a countercurrent process where less than 90% of the nitrogen is converted to ammonia the benefits of the invention do not accrue and there is no advantage obtainable by eliminating NH_3 from the recycled gas.

The ammonia concentration in the hydrogen equivalent to the nitrogen content of the oil may be calculated in the following manner:

Equivalent p.p.m. NH_3 (volume) in H_2 =

$$\text{p.p.m. N (weight) in oil} \times \frac{\text{oil density, lbs./bbl.}}{\text{s.c.f. } \text{H}_2/\text{bbl. of oil}} \times \frac{379}{14}$$

Thus, for example, when the ratio of hydrogen-rich gas to oil is 4000 s.c.f./bbl., and the desired nitrogen content of the oil (300 lbs./bbl.) is 1 p.p.m., over 90% of the maximum benefit is obtained if the hydrogen contains not over 2 p.p.m. ammonia (0.002%) (equivalent to the 1 p.p.m. in the product oil). If the oil feed contained 1000 p.p.m. nitrogen, the ammonia content of the hydrogen equivalent to 10% of the feed nitrogen would be 200 p.p.m. (0.02%). As can be seen from FIGS. 2 and 3, with this amount of NH_3 in the gas only a small savings in catalyst volume would be attainable, and the operation of the process would be improved very little. To obtain sufficient improvement to outweigh the inherent problems in countercurrent operation the NH_3 concentration in the gas would have to be below 100 p.p.m., and preferably the ammonia content would not exceed 50 p.p.m., equivalent to 2.5% of the feed nitrogen.

How closely the actual process operation will approach the one-half order rate reaction depends on a number of factors besides ammonia content of the hydrogen. Inefficient contacting, due to gas bypassing or liquid channeling in the reactor bed, will tend to raise the apparent reaction order. Feed source, boiling range, initial nitrogen content, and prior treatment influence the apparent kinetics. A one-half order reaction is explainable on the basis that NH_3 is competing with organic nitrogen for active catalyst sites. If the initial hydrocarbon nitrogen compounds in the oil compete equally with ammonia for

active catalyst sites, a one-half order reaction is possible. The evidence is, however, that ammonia is adsorbed by the catalysts less strongly than the nitrogen compounds in refractory high boiling oils of moderately low nitrogen content, for example, below 300 p.p.m. Nevertheless, even if the nitrogen compounds adsorb several times more readily than ammonia, distinct advantages are obtained by the invention if conditions are controlled to convert substantially all of the nitrogen compounds to ammonia and the hydrogen supplied is essentially free of ammonia. The greatest advantage is thus obtained in substantially completely purifying high boiling oils of high initial nitrogen content using hydrogen-rich gas supplied with a very low NH_3 concentration of not over about 100 p.p.m.

Successful operation of the process of this invention is predicated on careful control of the operating variables. As can be seen from curve B of FIG. 1, a small change in feed rate can result in a several-fold change in the nitrogen content of the purified oil effluent of the reaction zone. In actual practice, the space velocity, hydrogen circulation, and pressure for a particular installation are decided in advance, by design, and held relatively constant. The primary operating control variable is the contacting temperature. At high conversion rates, especially above 95% nitrogen removal, the nitrogen content of the effluent oil is extremely sensitive to temperature changes, much more so than in concurrent contacting. Accordingly, it is especially desirable to provide various means for making small temperature adjustments. The temperature of the hydrogen introduced at the bottom of the reaction zone should be controlled within narrow limits. In particular, it is more important to maintain a steady hydrogen temperature than to maintain a particular hydrogen flow rate.

The following examples present comparative data showing the advantages gained by means of this invention and the importance of certain features thereof. In these examples the same catalyst (sulfided 6% nickel-20% molybdenum on alumina) was used in order that direct comparisons could be made.

Examples I-IV

In the first example (I), in accordance with the invention, a heavy gas oil boiling from 570 to 980° F. and containing 660 p.p.m. nitrogen was introduced at the top of a reactor containing the catalyst, and 3000 s.c.f. of hydrogen per barrel was introduced at the bottom. Upflowing hydrogen effluent withdrawn from the top carried with it 2% (based on oil feed) of a light distillate boiling up to 400° F. and containing about 2 p.p.m. nitrogen. Operating conditions were 700° F., 1500 p.s.i.g., and 0.5 LHSV. The light distillate and ammonia were removed from the upflowing hydrogen effluent, by cooling and water washing, to provide a hydrogen recycle gas which, together with added make-up hydrogen, was returned to the bottom of the reactor. The total hydrogen-rich gas stream contained less than 1 p.p.m. ammonia and about 5% H_2S . The downflowing liquid hydrocarbon effluent contained 17 p.p.m. nitrogen.

In the second example (II), the same feed, catalyst, and operating conditions were employed, except that both the oil and the hydrogen were introduced at the top of the reactor and flowed downward concurrently in accordance with the prior art. After cooling the effluent, separating hydrogen-rich recycle gas, and stripping and water washing the liquid hydrocarbon effluent, the product contained 27 p.p.m. nitrogen.

In the third (III) and fourth (IV) examples, the first and second examples, respectively, were repeated in substance, but at more severe conditions of 725° F. to obtain more complete nitrogen removal. The product from the countercurrent process of this invention contained 4 p.p.m. nitrogen while the product from the prior art concurrent process contained 16 p.p.m. nitrogen.

The following tabulation summarizes the foregoing examples:

Example.....	I	II	III	IV
Process.....	Inven- tion	Prior Art	Inven- tion	Prior Art
Temperature, ° F.....	700	700	725	725
Pressure, p.s.i.g.....	1,500	1,500	1,500	1,500
Space velocity, LHSV.....	0.5	0.5	0.5	0.5
Nitrogen in product, p.p.m.....	17	27	4	16
Nitrogen removal, percent.....	97.4	95.9	99.4	97.6

To obtain the 97.4% nitrogen removal of Example I at 700° F. by the concurrent process of the prior art would require the use of a space velocity of 0.44 LHSV, or 14% more catalyst volume. To obtain the 99.4% nitrogen removal of Example III at 725° F. by the concurrent process of the prior art would require the use of a space velocity of 0.37, or 35% more catalyst volume. Thus, a much greater advantage is obtained by the process of this invention the greater the percent nitrogen removal.

As previously mentioned, the removal of nitrogen from hydrocarbon oils is of particular value as the first step in a two-stage process comprising hydrogen treating a hydrocarbon oil for the removal of nitrogen compounds in a first stage and then hydrocracking the hydrogen-treated oil in a second stage for conversion to lower boiling products. In the two-stage processes heretofore used in the prior art, hydrocarbon oil inadmixture with hydrogen is preheated and then passed at elevated pressure through a first stage reactor containing sulfactive hydrogenation catalyst. Mixed phase flow of oil results as the oil is at least partially vaporized at the conditions of temperature and pressure employed. Gaseous and vaporized by-products are formed, including ammonia. The mixed phase effluent is cooled, usually by heat exchange with the raw feed. If the heat exchanger leaks, the feed to the second stage is contaminated by the raw feed, which contains nitrogen compounds poisonous to the second stage catalyst. The first stage effluent is further cooled to condense normally liquid hydrocarbons, including light by-products. Water is injected to wash out ammonia. With very heavy feeds, emulsion problems then may arise. After separating recycle hydrogen and uncondensed gases, the liquid oil is passed to a low pressure stripper to remove dissolved gases and by-products including NH₃ not dissolved in the water. The oil must then be pumped to the second stage pressure, admixed with additional hydrogen, and reheated. It is then passed downflow through the second stage reactor containing nitrogen-sensitive hydrocracking catalyst. The second stage effluent is cooled and recycle hydrogen is separated, and the liquid oil is then further processed to eliminate gaseous by-products and to recover desired products. The hydrogen recycle systems and the general operation of the two stages are essentially independent of each other.

In the novel two-stage process of this invention, high boiling hydrocarbon oil is passed downflow through a first stage contacting with sulfactive hydrogenation catalyst countercurrent to upflowing hydrogen, at elevated temperature and pressure whereby at least 90% of the nitrogen contained in the oil is hydrogenated to ammonia and carried out in upflowing hydrogen effluent of the first stage. The downflowing hydrocarbon oil effluent of the first stage is passed directly, and preferably without intervening treatment, through a second stage contacting with nitrogen-sensitive hydrocracking catalyst in the presence of excess hydrogen essentially free of ammonia, at elevated temperature and pressure whereby high boiling hydrocarbons are converted to lower boiling hydrocarbon products. Hydrogen-rich gas essentially free of ammonia is recovered from the effluent of the second stage, and at least a portion of this hy-

drogen-rich gas is passed upflow through the first stage.

As previously mentioned, it is especially preferred that the ammonia content of the hydrogen which is introduced at the bottom of the first stage does not exceed the equivalent of the desired nitrogen content of the purified oil effluent of the first stage. By operating in accordance with this embodiment of the invention, that unique situation is readily attained. Nitrogen compounds contained in the oil effluent of the first stage may pass through the second stage unconverted, or adsorb on the second stage catalyst, or convert to ammonia, which is either adsorbed on the catalyst or else recovered in the effluent hydrogen. Only in the latter case will ammonia appear in the hydrogen-rich gas recovered from the second stage effluent, and then always in an amount less than the equivalent of the residual nitrogen content of the purified downflowing hydrocarbon oil effluent of the first stage.

Cooling down the effluent of the first stage to separate gaseous by-products and then reheating the liquid hydrocarbons fed to the second stage is no longer necessary because the downflowing effluent of the first stage is freed of such by-products by upflowing NH₃-free hydrogen derived from the second stage. The feed to the first stage may be preheated by heat exchange with the effluent of the second stage. If this heat exchanger leaks, slight contamination of the final product is readily detected, and the second stage catalyst is not exposed to these contaminants. Depressuring of the first stage effluent to flash off deleterious by-products, followed by repumping of the liquid to the second stage pressure, as heretofore practiced, is no longer necessary. Hydrocarbons vaporizable at the conditions used in the first stage are prevented from entering the second stage. The operation of the second stage is thereby improved because such components are relatively more resistant to hydrocracking than the heavier hydrocarbons.

The ability to use lower temperatures in the countercurrent first stage of this invention, whereby coke formation is decreased and a longer on-stream time attained, is especially important because a principal advantage of the second stage is that high boiling feeds are hydrocracked with very little coke formation, whereby long on-stream times are employed. Thus, it is advantageous to have a long on-stream time in the first stage also, to avoid repeated interruption of the feed to the second stage for regeneration of the first stage catalyst. It may be mentioned that in both stages the temperatures are gradually raised to compensate for catalyst fouling over a period of time.

The catalyst in the second stage is an acidic hydrocracking catalyst comprising a hydrogenating-dehydrogenating component and a cracking component. Typically, the catalyst comprises a Group VI and/or VIII metal, oxide, sulfide, or other compound in conjunction with an acidic cracking catalyst support. A preferred catalyst comprises nickel sulfide on an active silica-alumina cracking catalyst support, which catalyst has an unusually high specific activity for the conversion of high molecular weight paraffins, naphthenes, and aromatics at low temperatures of 350-750° F. to lower molecular weight isoparaffins, naphthenes, and aromatics with only a very small production of gaseous hydrocarbons. The catalysts are sensitive to nitrogen compounds. Accordingly, it is desired that the hydrocarbon oil passed to the second stage have only a relatively low residual nitrogen content, of less than 100 p.p.m. nitrogen, preferably less than 10 p.p.m. nitrogen, and especially less than 1 p.p.m. nitrogen. Also, the hydrogen employed in the second stage should have no more than a correspondingly low ammonia content.

In general, the ranges of temperature, pressure, and space velocity which may be used in the second stage are similar to those in the first stage, but in a particular case both the temperature and pressure will usually be lower in the second stage than in the first stage, especially

with very high boiling hydrocarbon feeds. Preferred conditions are 500–700° F., 1000–2000 p.s.i.g., 0.4–4 LHSV, and 3000–10,000 s.c.f. H₂/bbl., with a feed containing less than 1 p.p.m. nitrogen. Higher temperatures and pressure are used with the higher nitrogen content feeds.

In the second stage, countercurrent flow of oil and hydrogen may be used, similarly to the first stage. In this way, ammonia produced by hydrogenation of the residual nitrogen compounds in the feed to the second stage is swept upward by the hydrogen whereby poisoning of the catalyst is minimized. Vaporized hydrocarbon products of the second stage hydrocracking are also carried upward by the hydrogen whereby the residence time of such hydrocarbons in the second stage is reduced and over-cracking is minimized. This is especially advantageous where it is desired to maximize the production of middle distillate products from the second stage. Also, a major portion of the required product distillation may be accomplished within the reactor.

Where countercurrent flow of hydrogen and oil is employed in the second stage, the upflowing hydrogen effluent of the second stage may be cooled to condense the hydrocarbons carried overhead and thereby to separate hydrogen-rich gas, at least a portion of which is passed upflow through the first stage. Another portion of this hydrogen-rich gas may be recycled through the second stage. Alternately, the entire upflowing hydrogen effluent of the second stage may be passed directly upflow through the first stage. Both stages may be contained within a single reactor.

The usual objective is to maximize high octane gasoline production in the second stage. For this and other reasons, it is preferred to use concurrent flow of hydrogen and oil in the second stage. The downflowing hydrocarbon oil effluent of the first stage is passed directly, and preferably without intervening treatment, downflow through the second stage contacting with nitrogen-sensitive hydrocracking catalyst concurrent with downflowing hydrogen essentially free of ammonia. The entire effluent of the second stage is cooled to condense hydrocarbons having 4 or more carbon atoms to the molecule. Hydrogen-rich gas, essentially free of ammonia, is separated from the condensed hydrocarbons at substantially the pressure of the second stage, and at least a portion of this hydrogen-rich gas is passed upflow through the first stage.

Another portion of the hydrogen-rich gas may be recycled. Ordinarily, this hydrogen-rich gas is inherently essentially free of ammonia because of the preferred low nitrogen content of the first stage effluent feed to the second stage. Nevertheless, it is sometimes advisable to provide for purification of the recycle hydrogen.

In one embodiment of the invention, substantially all of the hydrogen-rich gas separated from the effluent of the second stage is passed upflow through the first stage. The entire upflowing hydrogen effluent of the first stage is then passed downflow through the second stage, after purification to remove substantially all ammonia, and preferably other by-products and condensable hydrocarbons. A higher pressure is used in the first stage than in the second stage whereby the downflowing liquid hydrocarbon effluent of the first stage is pressured directly to the second stage. Only the recycle hydrogen separated from the second stage effluent requires compression, to the first stage pressure, in effect a single recycle gas system serving both stages.

Make-up hydrogen must, of course, be added to the system in order to supply that consumed in the hydrogenation reactions. Such may conveniently be introduced into both of the recycling hydrogen streams, where there are two hydrogen recycles, but preferably it is introduced into the second stage. At least a portion of the hydrogen-rich gas effluent of the second stage is passed upflow through the first stage. Make-up hydrogen is thereby

provided to both stages in a specific manner, which, along with the manner of effecting gas recycle and contacting of hydrocarbon and gas in the first stage, achieves the desirable and unexpected results as described herein.

Reference is now made by way of example to the drawing, FIG. 4, which illustrates a preferred embodiment of the invention as a two-stage process used to produce gasoline from a heavy straight-run gas oil.

Referring to FIG. 4, feed in line 62 comprising, for example, a heavy straight-run vacuum distillate of crude petroleum, boiling from 570 to 980° F. (corrected to atmospheric pressure), having a gravity of 24.8° API, and containing 660 p.p.m. nitrogen, is introduced into the process by pump 50, preheated in heat exchanger 51, and further preheated in furnace 52 prior to passing through line 53 to first stage reactor 54. The temperature of the oil at the inlet to reactor 54 is about 680° F. and the pressure is about 1500 p.s.i.g. As shown, reactor 54 contains several beds of small particles of sulfative hydrogenation catalyst, in this case a high metal content sulfided catalyst containing about 6 weight percent nickel and about 20 weight percent molybdenum supported on alumina. About 3000 s.c.f. per barrel of preheated hydrogen-rich gas derived from the second stage is introduced through line 55 into the bottom of reactor 54 at a temperature of about 680° F. This hydrogen contains less than 10 p.p.m. ammonia. The oil flows downward through the catalyst beds counter-current to the upflowing hydrogen and collects as a pool in the bottom of reactor 54, the liquid level being controlled by valve 56. At a space velocity of 0.5 volume of oil feed per volume of catalyst per hour and an average catalyst temperature of 725° F., the first stage product is found to contain only 4 p.p.m. residual nitrogen and is free of moisture. The oil collected at the bottom of first stage reactor 54 comprises 100 volume percent of the feed, boils from 460–980° F., and has an API gravity of about 33. The oil is then passed through valve 56 and line 57 to the second stage reactor 58.

In a concurrent flow system of the prior art to accomplish this same degree of nitrogen removal in the first stage requires the use of a much lower space velocity of 0.37 LHSV at the indicated average temperature and pressure. By raising the temperature to 745° F. in the concurrent flow system, the same purification can be accomplished at 0.5 LHSV, but the catalyst then fouls appreciably more rapidly.

In the system shown, upflowing hydrogen in the first stage strips ammonia, H₂S, and vaporizable hydrocarbons from the downflowing oil and carries them out overhead through line 59. Water is injected through line 10 and the combined stream is then cooled in heat exchanger 11 and passed to high pressure separator 12. Water containing in solution most of the ammonia formed in reactor 54 is withdrawn from the system through line 22. Condensed hydrocarbons are withdrawn as a separate phase through line 23, and a recycle hydrogen is separated and withdrawn through line 13. A portion of this recycle hydrogen is taken off through line 14 and given a final cleanup for ammonia removal in zone 15. This may be accomplished by means of an adsorbent, acid, or acidic solution. Make-up hydrogen is then added through line 16 and the combined hydrogen streams pass through line 17 to combine with the liquid hydrocarbon oil feed to second stage reactor 58.

The hydrogenation reactions in reactor 54 are exothermic. The hydrogen tends to carry the heat upwards while the oil tends to carry the heat downward. Thus, a maximum temperature zone tends to be created, usually above the reactor mid-point. To compensate for this, a portion of the recycle hydrogen in line 13 is passed through compressor 18 and utilized as quench between catalyst beds in reactor 54 by means of quench lines 19, 20, and 21. Quench hydrogen flows are adjusted to control the average catalyst temperature in reactor 54 at about 725° F. and

to maintain preferably a fairly uniform temperature from top to bottom.

The light hydrocarbons withdrawn from separator 12 through line 23 are passed through pressure reduction valve 24 to stripper 25 where, under the influence of heat and reduced pressure, normally gaseous hydrocarbons and foul gas products including H_2S are taken overhead through line 26. The stripped oil is recovered through line 27 and passed through line 28 to product storage. With the feed exemplified, a yield of about 3.5 volume percent of a light distillate boiling from about 180–460° F. is recovered through line 28. In some cases, it is advantageous to recycle a portion of these light hydrocarbons by means of pump 29 and line 30 to an intermediate point in reactor 54 for additional temperature control and hydrogenation or nitrogen removal.

The effluent of the first stage enters the second stage hydrocracking reactor 58 at a temperature of about 540° F. and a pressure of about 1500 p.s.i.g. The inlet temperature may be controlled at the desired value by adjusting the temperature of hydrogen in line 17 and/or by adjusting the temperature of recycle oil in line 47. In addition to the hydrogen admixed with the feed through line 17, additional downflowing hydrogen may be introduced at the top of reactor 58 through line 39, after preheating in furnace 60. As shown, reactor 58 preferably contains several fixed beds of nitrogen-sensitive hydrocracking catalyst particles, in this case a catalyst comprising about 8% nickel sulfide on an active silica-alumina cracking catalyst support. The reactions in reactor 58 are also highly exothermic, usually even more so than in the first stage. Quench hydrogen is introduced through quench lines 36, 37, and 38 to control the average catalyst temperature in reactor 58 at about 540° F. Heavy recycle oil quench may also be introduced interbeds by means of line 49, but usually any recycle oil is admixed with the feed through line 47. At a space velocity of 0.6 LHSV based on the flow of purified oil from the first stage, and at the indicated temperature and pressure, about 60% conversion per pass to product boiling below the initial boiling point of the feed is obtained. Recycle oil flow rate is thus about two-thirds volume per volume of fresh purified oil.

The combined liquid and vapor effluent of reactor 58 is withdrawn through line 31, passed through heat exchanger 51, further cooled in exchanger 32, and collected in high pressure separator 33. The temperature in separator 33 is usually between 70° F. and 150° F. Hydrogen-rich recycle gas is withdrawn through line 34 and returned to the process by means of compressor 35. As indicated, portions of the cool hydrogen are utilized as quench through lines 36, 37 and 38, while a major portion is passed through furnace 60 and then split into an internal recycle portion in line 39 and a portion in line 55 which is passed upflow through the first stage reactor.

The condensed liquid hydrocarbons recovered in separator 33 are withdrawn through line 40 and passed through pressure reduction valve 41 to product recovery still 42. Several stills are usually employed, and any number of product cuts may be obtained, but in general there will be a portion comprising butane and lighter hydrocarbons recovered in line 43, a light normally liquid product recovered in line 44, and a heavier product boiling below the feed initial boiling point recovered in line 45. The bottoms comprising heavy recycle oil may be withdrawn through line 46 and returned to the process at one or more of the indicated points (lines 47, 48, and 49) by pump 61. Since the effluent of the first stage is usually hotter than the temperature desired at the inlet to the second stage, it is advantageous to use the recycle oil as quench for temperature adjustment by means of line 47. In some cases, it is advantageous to further hydrogenate the recycle oil before it enters the second stage. In the process of this invention, such may be accomplished by adding recycle oil to the downflowing liquid oil in the first stage at a point

intermediate the top and bottom of the first stage by means of line 48. This would not be practical in a conventional two-stage process because all of the processing equipment between stages would have to be enlarged. Also, the catalyst near the bottom of the countercurrent first stage zone of the invention is surprisingly more active for hydrogenation. Apparently this is associated with the stripping action of the clean upflowing hydrogen introduced at the bottom. It is found that hydrogenation reactions are favored if the hydrogen is kept free of H_2S , whereby the catalyst at the bottom of the first stage is at least partially reduced and desulfided.

With the exemplified feed and operating conditions in the first and second stages, there is recovered from the recovery section 42 a yield of 21 volume percent of iso- and normal butanes, 36 volume percent light hydrocrackate boiling from about 95 to about 180° F., and 64 volume percent heavy hydrocrackate boiling from about 180° F. to about 400° F. Together with the light distillate recovered from the first stage through line 28, there is thus an over-all yield of 124.5 volume percent. The relative amounts and boiling ranges of the respective products are readily adjusted to meet varying demand situations, for example, by controlling the recycle cut point, i.e., initial boiling point of the heavy recycle oil, and/or by recycling more or less of the light product through line 30 to the first stage.

The foregoing illustrative embodiment is intended to be nonlimiting. Many further modifications as to equipment arrangement, catalysts, and conditions employed could be made. Thus, for example, both stages could be contained within a single reactor and the hydrogen introduced between stages, with a portion split off to flow upward through the first stage while another portion flows downward through the second stage. Recovery of products from the overhead of the first stage could be combined with the final product recovery section.

The present invention is directed to the purification and conversion of high boiling oils which are liquid at the conditions used. If a portion of the feed oil vaporizes at the top of the countercurrent reaction zone, any unconverted nitrogen compounds in the vaporized portion are not considered included in the initial nitrogen content of the high boiling oil. Percent conversion of nitrogen compounds to ammonia is with reference to the liquid portion of the feed oil. In the treatment of a broad boiling range oil containing a significant amount of vaporizable constituents, the vaporized portion may be separately purified with the upflowing hydrogen effluent of the countercurrent reaction zone in a known manner.

We claim:

1. In a process comprising passing a high boiling hydrocarbon oil containing organic nitrogen compounds downflow through at least one bed of sulfactive hydrogenation catalyst particles comprising a reaction zone and passing at least 1,000 standard cubic feet of hydrogen-rich gas per barrel of oil upflow through at least the same reaction zone, at reaction conditions of temperature and pressure for converting organic nitrogen compounds to ammonia, wherein downflowing purified hydrocarbon oil effluent is withdrawn from the bottom of said reaction zone, wherein upflowing vapors containing essentially all the ammonia produced are withdrawn from the reaction zone and cooled to condense and separate normally liquid hydrocarbon oil contained therein from hydrogen-rich gas which is recycled to the reaction zone, and wherein the net amount of ammonia produced is removed from the system but the hydrogen-rich gas available for recycling contains a small equilibrium concentration of ammonia of from above 0.02% to about 1% by volume having a negligible effect on the hydrogen partial pressure, the improved method of operation which comprises controlling the reaction conditions in said reaction zone to convert more than 90% of the organic nitrogen originally contained in the oil to ammonia, and

removing ammonia from the hydrogen-rich gas to maintain the concentration of ammonia in the gas introduced into the reaction zone below the catalyst for passage upwards therethrough below 0.02% by volume and less than the equivalent of 2.5% of the initial nitrogen content of the oil.

2. A method in accordance with claim 1 wherein at least 99% of the organic nitrogen originally contained in the oil is converted to ammonia.

3. A method in accordance with claim 1 wherein at least 99% of the organic nitrogen originally contained in the oil is converted to ammonia, and the concentration of ammonia in hydrogen-rich gas introduced into the reaction zone below the catalyst for passage upwards therethrough is maintained no more than the equivalent of the residual organic nitrogen content of the downflowing purified hydrocarbon oil effluent.

4. A two-stage hydrocarbon denitrification and hydrocracking process employing a higher pressure in the denitrification stage than in the hydrocracking stage which comprises passing high boiling hydrocarbon oil substantially in liquid phase downflow through a high pressure denitrification stage in contact with sulfactive hydrogenation catalyst countercurrent to upflowing hydrogen having an ammonia content less than 0.02% by volume and less than the equivalent of 2.5% of the initial nitrogen content of the oil, at elevated temperature and pressure whereby at least 99% of the nitrogen contained in said oil is hydrogenated to ammonia and carried out in upflowing hydrogen effluent of said denitrification stage, depressing the entire downflowing hydrocarbon oil effluent of said denitrification stage and passing it directly and without intervening treatment downflow through a lower pressure hydrocracking stage in contact with nitrogen-sensitive hydrocracking catalyst concurrent with downflowing hydrogen containing less than 0.02% by volume of ammonia, at elevated temperature and pressure where-

by high boiling hydrocarbons are converted to lower boiling hydrocarbon products, cooling the effluent of said hydrocracking stage to condense hydrocarbons having 4 or more carbon atoms to the molecule, separating hydrogen-rich gas containing less than 0.02% by volume of ammonia from the condensed hydrocarbons at substantially the pressure of said hydrocracking stage, compressing at least a portion of the hydrogen-rich gas so separated to the higher pressure of said denitrification stage, passing the compressed hydrogen-rich gas upflow through said denitrification stage as the aforesaid upflowing hydrogen, separating hydrogen-rich gas containing a small equilibrium concentration of ammonia from the hydrogen effluent of said denitrification stage and removing ammonia therefrom substantially at the pressure of said denitrification stage to provide purified hydrogen-rich gas containing less than 0.02% by volume of ammonia, and passing at least a portion of said purified hydrogen-rich gas to said hydrocracking stage.

References Cited by the Examiner

UNITED STATES PATENTS

2,671,754	3/1954	De Rosset et al.	208—89
2,952,625	9/1960	Kelley et al.	208—254
2,952,626	9/1960	Kelley et al.	208—254
3,026,260	3/1962	Watkins	208—254
3,114,701	12/1963	Jacobson et al.	208—254

References Cited by the Applicant

UNITED STATES PATENTS

3,145,160	8/1964	Jacobson.
3,159,564	12/1964	Kelley et al.

DELBERT E. GANTZ, *Primary Examiner*.

S. P. JONES, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,268,438

August 23, 1966

John W. Scott, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 67, for "otherwise removing ammonia from the upflowing hy-" read -- erably at a lower pressure, to remove the dissolved by- --; column 6, lines 10 and 11, strike out "about 1% H₂S, and 0.2% C₄-500° F. hydrocarbons,".

Signed and sealed this 1st day of August 1967.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents