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HYDROGENATION OF HIGH BOILING OILS

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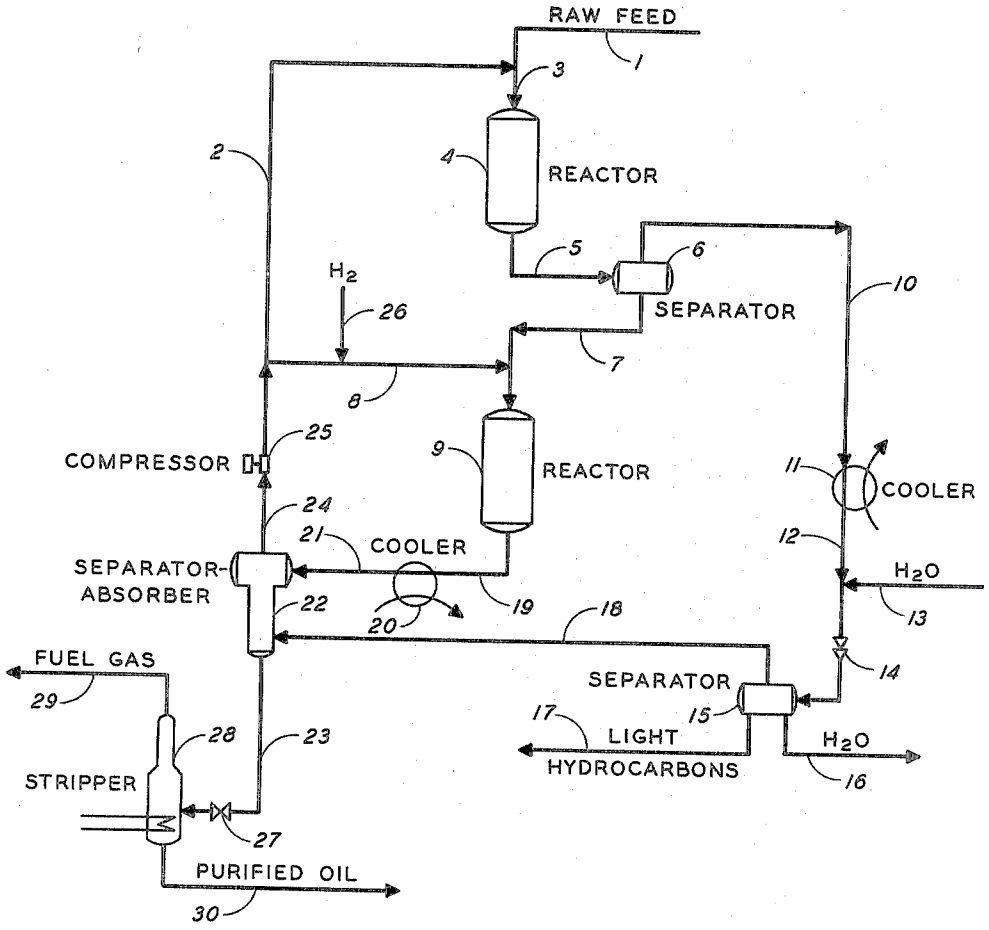


FIG. 1

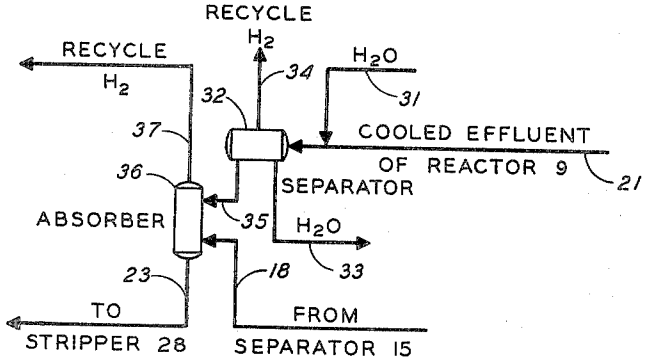


FIG. 2

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HYDROGENATION OF HIGH BOILING OILS

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This invention relates to processes for hydrogen-treating hydrocarbon oils, and more particularly it relates to a catalytic hydrogenation process for the removal of nitrogen compounds from high boiling oils in at least two stages of contacting with sulfactive hydrogenation catalyst, including a last or second stage and a prior or first stage, with treatment of the effluents of the last stage and at least one prior stage.

By "high boiling" is meant those hydrocarbon fractions which remain substantially entirely in the liquid phase at reaction conditions. Specifically, the high boiling oils boil at least 90% above 600° F. and at least 10% above 750° F. It is particularly desired to provide a process for the removal of nitrogen compounds from oils boiling more than 50% above 750° F. As examples of such oils may be mentioned reduced crude, deasphalted residuum, heavy straight run gas oils, lube oils, waxes, heavy cracked cycle oils, coker gas oils, shale oil distillates, etc., and raffinates or other components of such oils.

Several factors have a multiplying effect to make the removal of nitrogen compounds from hydrocarbon oils by catalytic hydrogenation progressively more difficult as feeds of increasingly higher boiling point are considered. Thus, the rate of hydrogenation of nitrogen compounds is slower with feeds of higher boiling point and with feeds of higher nitrogen content; and higher boiling feeds ordinarily contain higher concentrations of nitrogen compounds. Hence, if a given low nitrogen content is desired in the product, more nitrogen compounds must be hydrogenated. Yet another factor is that the reaction by which nitrogen compounds are converted to ammonia follows pseudo first order reaction kinetics. Consequently, to convert for example 75% of the nitrogen content of an oil requires twice the catalyst volume or contacting time as to convert 50% of the nitrogen.

The above factors all dictate the use of relatively more severe conditions when treating higher boiling oils for the removal of nitrogen compounds. Because there are practical limitations on the extent to which the contacting time can be raised, the reaction rate must be increased, for example by using a higher temperature. Because higher temperatures tend to increase the rate of coking and catalyst deactivation, a higher hydrogen partial pressure must be used to counteract this effect. Unfortunately, the use of higher temperatures also tends to increase the production of light hydrocarbons by hydrocracking, thereby diluting the hydrogen and reducing the hydrogen partial pressure.

The following comparative examples are presented to illustrate the effects of feed boiling point and feed nitrogen content on the reaction rate.

Example I

This example shows that low boiling oils are comparatively easily purified. A light cracked cycle oil boiling from 400 to 600° F. and containing 775 p.p.m. nitrogen was contacted with a sulfided Ni-Mo-alumina catalyst containing 5.6% Ni and 20.3% Mo at 590° F., 818 p.s.i.g., and 1.0 LHSV, together with 4000 s.c.f. H_2 per barrel of oil. After removal of NH_3, the product was found to contain 25 p.p.m. N. Thus, 96.8% of the nitrogen compounds was converted at these relatively mild conditions.

Example II

This example shows that high boiling oils are quite difficult to purify. A heavy straight run gas oil having the following inspections was selected:

Gravity, ° API		21.9
Aniline point, ° F		149
Viscosity, SSU, at 100° F		152
Sulfur, wt. percent		0.74
Nitrogen, total p.p.m		2,455
Distillation:		
Start	° F	550
10%	° F	645
50%	° F	720
90%	° F	792
End	° F	850

This high boiling oil was contacted with a catalyst identical to that used in Example I at 665° F., 1460 p.s.i.g., 0.76 LHSV, and 4000 s.c.f. H_2/bbl. The product contained 500 p.p.m. N after removal of NH_3. Thus, only 80% of the nitrogen was converted even though conditions were more severe than in Example I.

Example III

This example shows that the nitrogen content of the feed is an independent factor affecting the ease of purification. Another portion of the heavy gas oil feed of Example II was hydrogenated in a first stage at a lower space velocity to reduce the nitrogen content to 165 p.p.m. This NH_3-free material was then contacted in a second stage with the 5.6% Ni-20.3% Mo sulfided catalyst at 650° F., 1500 p.s.i.g., 0.75 LHSV, and 4000 s.c.f. H_2/bbl. The product contained 5 p.p.m. N after removal of NH_3. Thus, 97% of the nitrogen was converted in the second stage at a lower temperature than was used in Example II. Over-all, 99.8% of the nitrogen was removed.

Based on pseudo first order reaction kinetics, the above data show that by removing 93% of the initial nitrogen content of the high boiling feed, and the NH_3 formed therefrom, the reaction rate of the remaining nitrogen compounds was increased more than two and one-half times, in Example III. Nevertheless, more severe operating conditions were still required as compared to those used with the lower boiling feed of Example I.

The present invention is based upon the concept of counteracting the inhibiting effect of the high nitrogen content of high boiling oils by removing NH_3 from the system, while at the same time increasing the hydrogen partial pressure by eliminating light hydrocarbons from the system. The invention comprises a process wherein a high boiling hydrocarbon oil is contacted in the liquid phase with a sulfactive hydrogenation catalyst in at least two stages, including a last stage and a prior stage. The process may be described as comprising eight steps, as follows:

(1) Pass the oil and hydrogen-rich gas through a prior stage at elevated temperature and pressure,
(2) Separate the effluent of the prior stage into a liquid phase and a vapor phase at substantially said elevated temperature and pressure,
(3) Pass the liquid phase through a last stage at elevated temperature and pressure, with additional hydrogen-rich gas,
(4) Cool the vapor phase separated in step 2, to condense light hydrocarbons therein, and remove NH_3 and the condensed light hydrocarbons to obtain a clean vapor,
(5) Cool the entire effluent of the last stage (step 3), at substantially the elevated pressure used in said last stage, to obtain a cooled liquid hydrocarbon effluent,
(6) Contact the clean vapor obtained in step 4 with the

cooled liquid hydrocarbon effluent obtained in step 5, at substantially the elevated pressure of the last stage, to obtain a purified hydrogen-rich gas and a liquid hydrocarbon effluent containing dissolved hydrocarbons,

(7) Recycle the purified hydrogen-rich gas obtained in step 6 to at least one stage, and

(8) Recover purified high boiling hydrocarbon oil from the liquid hydrocarbon effluent obtained in step 6.

Any number of stages in series may be used. Where a large volume of oil is to be purified, it will be convenient to use multiple parallel trains of series stages. The detailed description herein is in terms of a two-stage process, i.e., a last stage and a prior stage. Where there are multiple prior stages, the effluent of at least one is treated in the manner described. The effluents of other prior stages may be treated in the same manner or in a conventional manner before passing to the next stage. It is especially preferred to use the invention in conjunction with the final two stages, i.e., the last stage and the stage just prior to the last, because the greatest benefits are obtained from the invention in removing the last traces of nitrogen compounds to produce purified oil having a very low nitrogen content.

In accordance with the invention, a high boiling hydrocarbon oil in the liquid phase and hydrogen-rich gas are passed at elevated temperature and pressure through a prior stage containing a sulfactive hydrogenation catalyst. For example, the raw feed may comprise a heavy gas oil boiling from about 650° F. to about 1100° F. and containing contaminating nitrogen compounds. In general, the temperature will be within the range 550–850° F., and the total pressure will be above 800 p.s.i.g. Preferred operating conditions for such high boiling feeds are a temperature of 650–750° F. at the inlet and a hydrogen partial pressure of 650–2500 p.s.i.a. Hydrogen should be employed in a ratio of from about 1000 to 10,000 standard cubic feet per barrel of oil, preferably about 3000 to 5000 s.c.f./bbl. Under these conditions the high boiling oil is maintained substantially in the liquid phase.

The catalyst generally comprises an alumina or silica-alumina support carrying one or more iron group metals and one or more metals of Group VI–B of the Periodic Table in the form of their oxides or sulfides. Typical catalyst metal combinations are cobalt-molybdenum, nickel-tungsten, nickel-molybdenum-tungsten, cobalt-nickel-molybdenum, nickel-molybdenum, etc. Preferably, the catalyst comprises a high metal-content, sulfided, nickel-molybdenum-alumina catalyst containing 3–10% nickel and 12–30% molybdenum, especially 4–10% Ni and 15.5–30% Mo. Such high metal-content sulfied catalysts are several times as active as the conventional hydrofining catalysts for the hydrogenation of nitrogen compounds. The volume of catalyst employed is such that the liquid hourly space velocity is about 0.4–4 volumes of oil per hour per volume of catalyst, preferably about 1 LHSV.

The effluent of this prior stage consists of a liquid phase, comprising partially purified high boiling hydrocarbon oil containing a small amount of dissolved gases, in equilibrium with a vapor phase, comprising hydrogen, ammonia and other by-products, and vaporized light hydrocarbons. The phases are separated at the elevated temperature and pressure of the prior stage. The liquid phase and added hydrogen-rich gas are passed at elevated temperature and pressure through a last stage, also containing a sulfactive hydrogenation catalyst. The operating conditions in the last stage are in the same ranges as recited above for the prior stage, and the catalyst is of the same general type.

The effluent of the last stage consists of a liquid phase, comprising purified high boiling hydrocarbon oil containing a small amount of dissolved gases, in equilibrium with a vapor phase, comprising hydrogen, ammonia and other by-products, and vaporized light hydrocarbons. This entire effluent is cooled, to near atmospheric temperature while still at substantially the elevated pressure, to obtain a cooled liquid hydrocarbon effluent, which dissolves nearly all of the ammonia and other by-products and light hydrocarbons in the system, and a cooled hydrogen-rich gas containing only a small amount of diluent gases. The ammonia may be removed separately, if desired, for example by water washing the effluent.

The vapor phase separated from the effluent of the prior stage is also cooled, to near atmospheric temperature while still at substantially the elevated pressure, whereby a major portion of the light hydrocarbons therein condense to form a liquid hydrocarbon phase, containing substantial amounts of ammonia and other by-products, in equilibrium with a vapor phase, comprising hydrogen, undissolved ammonia and other by-products, and uncondensed light hydrocarbons. The ammonia, and preferably the other by-products, are removed from this vapor phase. The resulting clean vapor, comprising hydrogen and uncondensed light hydrocarbons, is contacted with the cooled liquid hydrocarbon effluent of the last stage, whereby the uncondensed light hydrocarbons are absorbed in said cooled liquid hydrocarbon effluent, yielding a purified hydrogen-rich gas. This purified hydrogen-rich gas is recycled to at least one of the prior and last stages. Make-up hydrogen is continuously introduced into the system to compensate for that consumed in the reactions. Ammonia and other by-products are removed from the contacted liquid hydrocarbon effluent to recover purified high boiling hydrocarbon oil product.

By proceeding in the above manner it is found that the total catalyst volume required for accomplishing a given degree of purification of a high boiling oil is much less than would otherwise be required, because the reaction rate of nitrogen compounds in the last stage is severalfold more rapid than in the prior stage. Surprisingly, it is also found that rates of hydrogenation of aromatics, particularly polynuclear aromatics, and of other color, gum, and coke precursors are also increased in the last stage. Consequently, the invention provides improved processes for the treatment of lube oils and for the production of high grade heating oils. Lower temperatures may be employed in both stages than would otherwise be possible, thereby reducing the rate of catalyst deactivation as well as improving product quality.

A particular advantage of the process, however, is that it makes feasible the complete removal of nitrogen compounds from much higher boiling oils than it was heretofore considered possible to purify, in a process having a long on-stream time. By "complete removal" is meant the conversion to ammonia of more than 90% of the nitrogen initially contained in the oil. Preferably, more than 99% of the nitrogen is so removed. It is especially desired to reduce the nitrogen content of the oils to below 10 p.p.m. (0.001 weight percent expressed as elemental nitrogen). By a long on-stream time is meant that the time between catalyst regenerations is sufficiently long such that it is more economical to shut down the process and regenerate the catalyst than it would be to provide stand-by or "swing" reactors for use while the deactivated catalyst in other reactors is being regenerated. More particularly, it is desired to provide a process wherein catalyst deactivation is so slow that the process can be kept on-stream for at least 1000 hours without catalyst regeneration. Using the preferred high metal content, sulfided, nickel-molybdenum-alumina catalysts in the process of this invention, that objective is attainable with all but the highest boiling and highly contaminated oils. By eliminating light hydrocarbons from the system, this invention maintains a high hydrogen partial pressure without the necessity of using an inordinately high total pressure to prevent rapid catalyst deactivation. The high hydrogen partial pressure also increases the reaction rate of nitrogen compounds in high boiling oils.

Preferred modes of carrying out the invention are illustrated by the flow diagrams of the attached FIGURES 1 and 2. In these figures, only the most important equipment items are shown, the usual additional heat exchangers, furnaces, auxiliary piping, pressure control valves, etc., not being shown, for simplicity.

In FIGURE 1, a high boiling hydrocarbon oil feed is introduced to the process through line 1. Hydrogen-rich gas is added to the oil feed through line 2, and the combined streams pass through line 3 to reactor 4. The oil and hydrogen are supplied at an elevated temperature near the temperature employed in the reactor and at elevated pressure. Reactor 4 contains a sulfactive hydrogenation catalyst in the form of one or more fixed beds of small pellets or particles. In reactor 4, the major portion of the nitrogen compounds in the oil feed are hydrogenated to ammonia. Thus, for example, if the oil initially contained about 2500 p.p.m. nitrogen and it were desired to reduce this ultimately to about 10 p.p.m. nitrogen (99.6% removal), conditions in reactor 4 should be such as to reduce the nitrogen content to about 500 p.p.m. It will be noted that although this represents a major portion of the nitrogen compounds being removed (80%), actually it is only a minor portion of the over-all task because of the nature of the denitrification reaction. To reduce the nitrogen content to 10 p.p.m. in a single stage would require the use of a reactor from 3 to 4 times the size of reactor 4.

In addition to nitrogen compounds being hydrogenated to ammonia, sulfur, oxygen, and halogen compounds are hydrogenated to by-product gases, and virtually all of the olefins and a portion of the aromatics in the feed are hydrogenated. Also, some of the feed is hydrocracked to light hydrocarbons, which are substantially in the vapor phase at the reaction conditions. When using the preferred high metal-content, sulfided, nickel-molybdenum-alumina catalysts, the production of non-condensable hydrocarbons such as methane and ethane by hydrocracking is quite small. Most of the light hydrocarbons produced have 4 or more carbon atoms to the molecule. The light hydrocarbons accumulate in the recycle gas stream in conventional processes until a high equilibrium concentration is reached at which the net production will dissolve in the product oil. By the process of this invention the concentration of light hydrocarbons in the system is greatly reduced because a large portion of such materials is separately removed.

The effluent of reactor 4 passes through line 5 to separator 6, wherein it is separated at the reactor temperature and pressure into two phases. The liquid phase comprises partially purified high boiling hydrocarbon oil containing only a small amount of dissolved light hydrocarbons and impurities. The vapor phase comprises hydrogen, ammonia and other by-products, such as H_2S, H_2O, etc., and vaporized light hydrocarbons, including low boiling components in the feed as well as those produced by hydrocracking reactions in reactor 4. The hydrocarbon oil phase separated in separator 6 flows by gravity or pressure differential, still at substantially reactor temperature, through line 7 to reactor 9. Hydrogen-rich gas is also introduced through line 8. Instead of providing separate reactor vessels and an external phase separator, reactor 4 may represent an upper bed and reactor 9 a lower bed within a single vessel, and separator 6 may be a vapor-sealed distributor tray between the beds.

Reactor 9 is preferably similar in all respects to reactor 4 although the pressure will be somewhat lower due to pressure drop through the system. It is found that the total quantity of catalyst required in reactors 4 and 9 is slightly less if reactor 9 is made somewhat smaller than reactor 4. Nevertheless, the savings is so small (usually under 10%) that, for convenience in fabrication, it is usually preferable to make the reactors the same size. Also, the optimum manner of distributing the catalyst between reactors 4 and 9 depends on the degree of nitrogen removal desired, and the greater the degree of purification desired, the more nearly equal the reactors should be.

Since most of the olefins and other hydrocarbons having a tendency to deactivate catalysts by forming coke have been hydrogenated in reactor 4, it will be found that a somewhat higher temperature may be used in reactor 9 without causing increased catalyst fouling. For example, the temperature may be increased 5–50° F., depending on the nature of the feed and the conditions in reactor 4. In all cases it is found that, by virtue of excluding from reactor 9 the ammonia, other by-products, and light hydrocarbons contained in the vapor phase effluent of reactor 4, a much higher rate of conversion of nitrogen compounds to ammonia is realized in reactor 9 even at the same temperature. For example, when 80% of the initial nitrogen is converted in reactor 4 (nitrogen content reduced from 2500 to 500 p.p.m.), 98% of the remaining nitrogen is converted in reactor 9 at the same temperature and space velocity (to 10 p.p.m. residual). Moreover, as previously mentioned, the rate of hydrogenation of other contaminants and of aromatics is higher in the last stage, reactor 9.

The vapor phase from separator 6, still at substantially the temperature and pressure of reactor 4, is withdrawn through line 10 and then cooled, as in heat exchanger 11, to condense a major portion of the light hydrocarbons therein. Preferably, the temperature is reduced to near atmospheric conditions, in any case below 150° F. The condensed light hydrocarbons and non-condensable vapors then continue through line 12 to separator 15 wherein the condensed light hydrocarbons separate as a liquid oil phase from the uncondensed vapors while still at substantially reactor pressure. The condensed light hydrocarbons dissolve much of the ammonia and other by-products, but the vapor phase in equilibrium therewith also contains ammonia as well as uncondensed light hydrocarbons. The ammonia is to be removed from this vapor phase in accordance with the invention. Preferably, this is accomplished by injecting liquid water through line 13 with provisions for intimate contacting, such as mixing valve 14. In that case, a three-phase system is formed in separator 15 comprising a liquid water phase, containing in solution nearly all of the ammonia in the system, a liquid light hydrocarbon oil phase, containing in solution ammonia, other by-products and normally gaseous hydrocarbons, and a vapor phase, comprising hydrogen, uncondensed light hydrocarbons, and only a small amount of ammonia and other by-products. The liquid water phase is withdrawn from the system through line 16; the liquid hydrocarbon phase is withdrawn through line 17; and the vapor phase is withdrawn from separator 15 through line 18. Alternately, or in addition, ammonia and other by-products may be removed from the cooled vapor phase by other means, such as by adsorption on a solid contact agent, such as silica-alumina beads, molecular sieves, etc.

In reactor 9, the desired conversion of nitrogen compounds to ammonia is completed, other impurities are converted to gaseous by-products, some further hydrogenation of aromatics occurs, and some further hydrocracking of the high boiling oil to light hydrocarbons occurs. The effluent of reactor 9 is withdrawn through line 19. At this point the effluent consists of a liquid phase, comprising purified high boiling liquid hydrocarbon oil containing only a small amount of dissolved light hydrocarbons and impurities, and a vapor phase comprising hydrogen, ammonia and other by-products, and vaporized light hydrocarbons. This effluent is cooled, as in heat exchanger 20, to condense the light hydrocarbons at substantially reactor pressure. Preferably, the effluent is cooled to near atmospheric temperature, in any case below 150° F. The effluent continues through line 21 to separator-absorber 22. In line 21 the system consists of a high boiling liquid hydrocarbon oil phase, having dissolved therein most of the ammonia produced in reactor 9 and nearly

all of the light hydrocarbons, in equilibrium with a vapor phase, comprising hydrogen, a minor amount of ammonia and other by-products, and a minor amount of uncondensed light hydrocarbons. These phases separate in the upper portion of separator-absorber 22. The vapor phase passes out through line 24. The oil phase passes downward, countercurrent to the upflowing cooled vapor stream introduced at the bottom through line 18, and continues out of the multiple stage absorber via line 23. In the absorber section of separator-absorber 22 the uncondensed light hydrocarbons in the stream in line 18 are absorbed in the high boiling hydrocarbon oil because the oil is higher boiling than that separated in separator 15 and because there is a much larger quantity of high boiling oil to absorb the light hydrocarbons. Also, since most of the light hydrocarbons produced in reactor 4 are withdrawn through line 17, the high boiling oil has a greater capacity to dissolve the remaining portion than would otherwise be the case. A hydrogen-rich gas stream is thereby produced which passes up through separator-absorber 22 and commingles with the vapor phase separated from the cooled effluent of reactor 9 to provide a hydrogen-rich recycle gas in line 24. The combined hydrogen-rich gases are returned through lines 2 and 8 to reactors 4 and 9 by means of recycle gas compressor 25. Make-up hydrogen is added to the system to compensate for that consumed in the reactions. Preferably, the make-up hydrogen, if of high purity, is added through line 26 to line 8 in order that the hydrogen to reactor 9 will be slightly more pure than that to reactor 4.

It is within the contemplation of this invention to inject stream 18 directly into stream 21, in effect reducing to one the number of trays in separator-absorber 22. Water may also be injected into the separator to assist in removal of NH_3 produced in reactor 9.

The liquid high boiling hydrocarbon oil in line 23 passes to stripper 28, which operates at a materially lower pressure, as signified by valve 27. Ammonia and other by-products are taken overhead through line 29 and disposed of, for example, as fuel gas. The purified high boiling hydrocarbon oil product is withdrawn through line 30. The light hydrocarbons may also be separately recovered using stripper 28, if desired.

FIGURE 2 illustrates another manner of effecting separation of the cooled liquid hydrocarbon oil effluent of the second reactor for contact with the vapor phase separated after cooling and removing light hydrocarbons and ammonia from the vapor phase effluent of the first reactor. Separator-absorber 22 of FIGURE 1 is divided into two separate vessels, whereby the ammonia and light hydrocarbon content of the recyle gas is further reduced. As shown in FIGURE 2, the cooled effluent of reactor 9 in line 21 passes to separator 32. Liquid water is injected through line 31 such that in separator 32 a three-phase system is formed consisting of a liquid water phase, containing the ammonia and other by-products produced in reactor 9 a liquid oil phase comprising high boiling hydrocarbon oil and dissolved light hydrocarbons, and a vapor phase, comprising hydrogen-rich gas containing only minor amounts of ammonia and other by-products. The hydrogen-rich gas is withdrawn through line 34 and recycled to the reactors, as before. The liquid water phase is disposed of through line 33. The liquid hydrocarbon oil phase is withdrawn through line 35 to absorber 36 wherein it passes downward countercurrent to the upflowing vapors from separator 15 introduced through line 18. The hydrocarbon oil thereby absorbs the light hydrocarbons contained in stream 18, and the oil is then passed through line 23, as before, to the stripper. Hydrogen-rich gas thereby produced is withdrawn overhead through line 37 and recycled to the reactors separately or in combination with stream 34.

I claim:

1. A process for the removal of nitrogen compounds initially contained in a high boiling hydrocarbon oil boiling at least 90% above 600° F. and at least 10% above 750° F. in at least two stages of contacting with sulfactive hydrogenation catalyst, including a second stage and a first stage, which process comprises the steps:

(1) passing high boiling hydrocarbon oil in the liquid phase and hydrogen-rich gas through a first stage at elevated temperature and pressure to convert a major portion of the nitrogen compounds initially contained in said oil to ammonia,

(2) separating the effluent from step (1) into a liquid phase and a vapor phase at substantially said elevated temperature and pressure,

(3) passing hydrogen-rich gas and said liquid phase separated in step (2) through a second stage at elevated temperature and pressure, to convert a major portion of the remaining nitrogen compounds to ammonia,

(4) cooling said vapor phase separated in step (2) and removing ammonia and condensed light hydrocarbons therefrom to obtain a clean vapor comprising hydrogen and uncondensed light hydrocarbons,

(5) cooling the entire effluent from step (3) at substantially said elevated pressure to obtain a cooled liquid hydrocarbon effluent,

(6) contacting the clean vapor from step (4) with the cooled liquid hydrocarbon effluent from step (5) at substantially said elevated pressure to absorb light hydrocarbons from said clean vapor in said cooled effluent and thereby obtain a purified hydrogen-rich gas and a liquid hydrocarbon effluent containing dissolved light hydrocarbons,

(7) recycling said purified hydrogen-rich gas from step (6) to at least one stage, and

(8) recovering purified high boiling hydrocarbon oil from the liquid hydrocarbon effluent from step (6).

2. The process of claim 1 wherein said clean vapor from step (4) is contacted with said cooled liquid hydrocarbon effluent in step (6) by admixing said clean vapor with the entire cooled effluent of step (5), and in step (7) said hydrogen-rich gas is recycled to both said last stage and said prior stage.

3. The process of claim 1 wherein ammonia is removed from the vapor phase separated in step (2) by cooling said vapor, adding water thereto, and separating water containing dissolved NH_3 from the clean vapor.

4. The process of claim 1 wherein said sulfactive hydrogenation catalyst comprises a high metal-content, sulfided, nickel-molybdenum-alumina catalyst containing 3–10% nickel and 12–30% molybdenum.

5. The process of claim 1 wherein more than 90% of the nitrogen initially contained in said oil is converted to ammonia.

6. The process of claim 4 wherein the process is kept on-stream for at least 1000 hours without catalyst regeneration.

7. The process of claim 1 wherein said high boiling hydrocarbon oil boils at least 50% above 750° F.

8. The process of claim 1 wherein said high boiling hydrocarbon oil is a lube oil.

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