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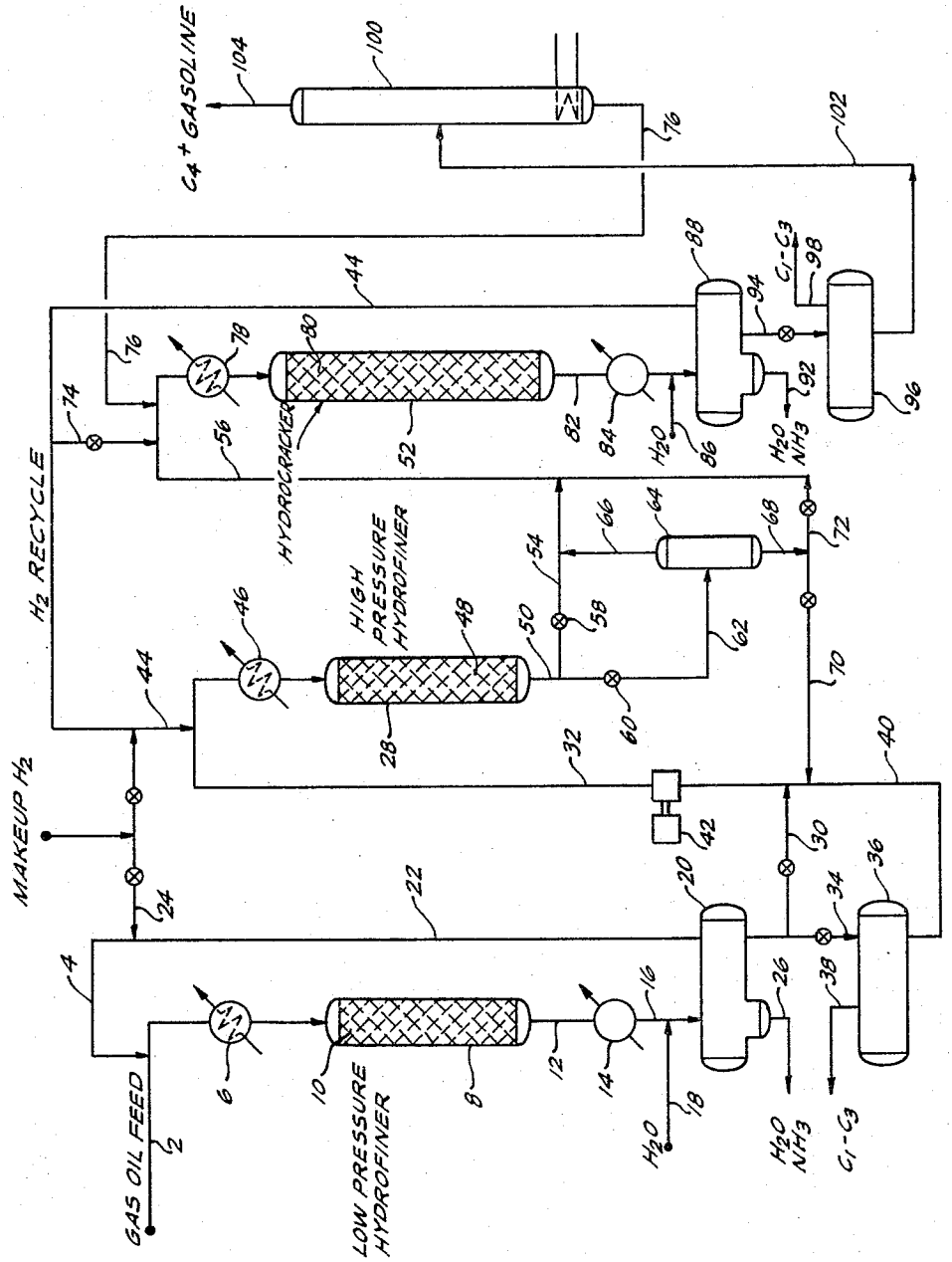

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HYDROCRACKING PROCESS WITH PRE-HYDROFINING

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This invention relates to the catalytic hydrocracking of high-boiling hydrocarbons to produce relatively lower boiling hydrocarbons, boiling for example in the gasoline and/or jet fuel range. More specifically, the invention is directed to a novel two-stage prehydrofining treatment, wherein the second hydrofining stage is operated integrally with a succeeding hydrocracking stage. An "integral" hydrofining-hydrocracking sequence, as the term is employed herein means that effluent from the hydrofining zone is sent directly to the hydrocracking zone without significant interstage treatment or purification, so that the hydrocracking is carried out in the presence of ammonia formed in the preceding hydrofining stage.

Briefly stated, the invention comprises the following steps:

(1) Subjecting a nitrogen-containing hydrocarbon feedstock to catalytic hydrofining in a separate hydrofining unit, preferably operated at relatively low pressures and high space velocities, to effect a limited hydrofining involving the conversion to ammonia of only about 30–90% of the initial feed nitrogen content;

(2) Subjecting effluent from the first hydrofining treatment to a purification procedure for removing at least the major portion of ammonia contained therein;

(3) Subjecting the deammoniated effluent from step (2) to a second hydrofining operation, preferably at relatively high pressures, and under conditions adjusted to effect a further substantial reduction in organic nitrogen content, preferably to less than about 50 parts per million; and

(4) Subjecting effluent from second hydrofining step, together with the ammonia formed therein, to catalytic hydrocracking at high pressures, preferably the same as in the second-stage hydrofiner, under conditions adjusted to provide a substantial conversion per pass to desired low-boiling hydrocarbons.

The overall object of the invention is to provide a hydrofining-hydrocracking combination process wherein the size of the high-pressure reactors is reduced to a minimum, while at the same time obtaining the economic advantages of an "integral" hydrofining-hydrocracking combination. A specific object is to provide economical means for hydrocracking feedstocks containing relatively large amounts of organic nitrogen, i.e., above about 0.30 weight percent. Another object is to increase the octane number of the gasoline product resulting from an integral hydrofining-hydrocracking combination. Still another object is to provide convenient means for controlling the ammonia and nitrogen content of feed to the hydrocracking zone in an integral hydrofining-hydrocracking combination. Other objects will be apparent from the more detailed description which follows.

It is known in catalytic hydrocracking that the nitrogen compounds contained in hydrocarbon feedstocks exert a marked poisoning effect upon hydrocracking catalysts. To avoid this problem, it has become standard practice

to subject nitrogen-containing feedstocks to a preliminary catalytic hydrofining treatment so as to reduce the nitrogen content to below about 10 parts per million. Typically, this is accomplished in a non-integral hydrofiner, wherein the hydrofiner effluent is cooled, condensed, depressured and water-washed to remove ammonia, then re-pressured and re-heated for the hydrocracking stage. These interstage treatments, particularly the cooling and re-heating involved, add greatly to the expense of the overall operation.

In copending application, Ser. No. 142,182, now U.S. Patent No. 3,159,568, filed Oct. 2, 1961, it is proposed to avoid this expense by eliminating interstage treatment, and passing the entire hydrofiner effluent through the succeeding hydrocracker. This proposal was based upon the discovery that the ammonia formed during hydrofining is much less deleterious than organic nitrogen compounds in their effects upon hydrocracking catalyst activity. Specifically, it was found that the effects of ammonia are reversible, and moreover can be much more readily overcome by increasing hydrocracking temperatures than can the effects of organic nitrogen compounds. Organic nitrogen compounds tend to bring about progressive catalyst deactivation until temperatures in the range of about 850 to 900° F. are reached. Temperatures in this range are undesirable because of the increased catalyst coking rates and production of light hydrocarbons in the C_1–C_4 range. When the organic nitrogen compounds were converted to ammonia, hydrocracking could successfully be carried out at temperatures in the range of about 650° to 780° F. without encountering progressive deactivation resulting from nitrogen poisoning.

It has now been found, however, that in cases where the ammonia partial pressure in the hydrocracking zone exceeds about 4–5 p.s.i., it is difficult to maintain desired conversion levels at temperatures below about 780° F. Optimum hydrocracking temperatures are considered to lie in the range between about 680° and 780° F., for in this range product quality (octane value) is optimum when correlated with yield structure. At hydrocracking temperatures below about 680° F., there is a marked lowering in octane values; at temperatures above about 780° F. the increased rate of production of coke and light hydrocarbon gases offsets the further slight increase in octane value obtained. It would therefore be desirable to maintain only sufficient ammonia in the hydrocracking zone to permit the desired conversion per pass to gasoline at temperatures in the range of about 680 to 780° F. This invention provides economical means for achieving this objective.

The organic nitrogen compounds contained in mineral oil feedstocks are varied in nature. The less refractory compounds are easily decomposed during hydrofining at relatively low pressures. Other more refractory nitrogen compounds, particularly those found in the heavier portions of the feedstock, are very resistant to decomposition at low pressures, but can be effectively decomposed at higher hydrofining pressures. The cost of high-pressure hydrofining, however, increases markedly as the size of the reactor increases. According to the present invention, high-pressure hydrofining is utilized only for completing the decomposition of refractory nitrogen compounds after most of the less refractory nitrogen compounds have been decomposed in a more economical low-pressure reactor. This permits a substantial increase in space velocities, and

thus minimizes catalyst and reactor volume required in the high-pressure hydrofiner.

At the same time, the degree of denitrogenation which takes place in the low-pressure hydrofiner can be independently controlled, so as to leave in the effluent therefrom a controlled amount of organic nitrogen calculated to provide, through its decomposition in the high-pressure hydrofiner, the ammonia partial pressure in the hydrocracking zone (normally about 0.5–5 p.s.i.) which is desired for maintaining an optimum hydrocracking temperature therein. Thus, by gradually increasing the severity of hydrofining in the low-pressure reactor during a run, it is possible to gradually decrease the resultant partial pressure of ammonia in the hydrocracker during the run so as to compensate for catalyst deactivation while maintaining a substantially constant desired temperature in the hydrocracker throughout the run. The end result is a more uniform product quality from the hydrocracker at an optimum yield-octane structure.

For a more detailed description of the invention reference is made to the accompanying drawing which is a flow sheet illustrating a preferred modification thereof. The initial feedstock is brought in through line **2**, mixed with recycle and fresh hydrogen from line **4**, preheated to incipient hydrofining temperatures in preheater **6**, and passed into the low-pressure hydrofiner **8** containing a bed of granular hydrofining catalyst **10**. Suitable hydrofining conditions in hydrofiner **8** are as follows:

LOW-PRESSURE HYDROFINING CONDITIONS

	Operative	Preferred
Average Bed Temp., ° F	600–850	650–800
Pressure, p.s.i.g	200–2,000	500–1,000
Liquid Hourly Space Velocity	0.5–20	1.0–8
H_2/Oil Ratio, M s.c.f./b	0.5–20	0.8–10

The above conditions should be suitably correlated so as to effect conversion of at least about 30% and up to about 90% of the organic nitrogen to ammonia, and in any case to reduce the organic nitrogen content to below about 0.30 weight percent. Suitable hydrofining catalysts are described hereinafter.

The effluent from hydrofiner **8** is withdrawn through line **12** and condensed in cooler **14**. The condensed effluent in line **16** is then subjected to water-washing by means of water injected via line **18**, and the mixture is then transferred to high-pressure separator **20** from which hydrogen-rich recycle gas is withdrawn via line **22**, and mixed with fresh make-up hydrogen from line **24** for recycle via line **4** as previously described. Spent wash water containing dissolved ammonia, and some of the hydrogen sulfide formed in hydrofiner **8** is withdrawn via line **26**. The high-pressure liquid hydrocarbon condensate in separator **20** may either be passed directly to the high-pressure hydrofiner **28** via lines **30** and **32**, or it may be depressured via line **34** into low-pressure separator **36** from which light hydrocarbon flash gases are exhausted via line **38**. Ordinarily it is not necessary to utilize the low-pressure separator **36**, but it may be desirable in some cases, as where hydrofining conditions in hydrofiner **8** are relatively severe resulting in the formation in large amounts of C_1–C_3 hydrocarbons. These light hydrocarbons, if present in excessive amounts, tend to reduce the efficiency of hydrofining in high-pressure hydrofiner **28** due to lowering of the hydrogen partial pressure therein. If low-pressure separator **36** is employed, the low-pressure condensate therein is withdrawn via line **40** and passed to high-pressure hydrofiner **28** via line **32** as previously described. In either case, a feed transfer pump **42** is provided in order to maintain the desired high pressure in hydrofiner **28**.

The ammonia-free condensate in line **32** is blended with fresh and recycle hydrogen from line **44**, and the mixture is then passed into high-pressure hydrofiner **28** via preheater **46**. Hydrofiner **28** also contains a granular bed of

hydrofiner catalyst **48**, which may be the same as or different than the catalyst employed in hydrofiner **8**. Operating conditions in hydrofiner **48** fall within the following ranges:

HIGH-PRESSURE HYDROFINING CONDITIONS

	Operative	Preferred
Average Bed Temp., ° F	600–850	650–800
Pressure, p.s.i.g	800–3,500	1,000–2,500
LHSV	0.3–12	1–5
H_2/Oil Ratio, M s.c.f./b	0.5–20	1–10

The above conditions are suitably correlated so as to reduce the organic nitrogen content of the feed to below about 50, and preferably below about 30 parts per million. In cases where the hydrofining severity in low-pressure hydrofiner **8** is gradually increased during the run, so as to provide a gradually decreasing ammonia concentration in the hydrocracker to compensate for catalyst deactivation therein, there will be a concomitant decrease in organic nitrogen content of the effluent from hydrofiner **28** during the run, down to below about 10 parts per million or less at end-of-run conditions.

Effluent from hydrofiner **48** is withdrawn via line **50**, and may be transferred in toto to hydrocracker **52** via lines **54** and **56** (valve **58** open, valve **60** closed). In some cases the hydrofiner effluent in line **50** may comprise a liquid phase, especially where the original feedstock is relatively high boiling. Where such a liquid phase is present, it will include most of the heavy ends of the feed material, and it is this heavier portion which is most difficult to denitrogenate. In such cases, instead of transferring the entire effluent to hydrocracker **52** via line **54**, it may be more desirable to adopt an alternate procedure by closing valve **58** and opening valve **60**, thus diverting the effluent via line **62** to a high-pressure hot separator **64**, from which the hot vapor-phase effluent is withdrawn via line **66** and sent to hydrocracker **52** as previously described. The liquid phase product in separator **64** may be withdrawn via line **68**, and all or a portion thereof recycled via line **70** to high-pressure hydrofiner **28**. By this procedure the heavy portion of the feedstock is hydrofined at a lower effective space velocity than the vapor phase portion, and by this means the light and heavy portions of feeds may be denitrogenated to more nearly equal degrees. Any portion of the liquid phase effluent which is not recycled via line **70** may be transferred directly via lines **72** and **56** to hydrocracker **52**.

The total hydrofiner effluent in line **56** is blended with recycle hydrogen from line **74** (if desired for temperature control and/or make-up purposes), and with recycled unconverted oil from line **76**, and the resulting mixture is then passed via preheater **78** into hydrocracker **52**, containing a bed of granular hydrocracking catalyst **80**. Operating conditions in hydrocracker **52** fall within the following general ranges:

HYDROCRACKING CONDITIONS

	Operative	Preferred
Average Bed Temp., ° F	600–850	680–780
Pressure, p.s.i.g	800–3,500	1,000–2,500
LHSV	0.5–5	1–4
H_2/Oil Ratio, M s.c.f./b	1–20	1–12

The above conditions are suitably correlated so as to provide about 30 to 70% conversion per pass (by volume) to gasoline or other desired low-boiling products. The desired conversion level can be maintained over long run lengths of e.g. 3 months up to about 2 years by gradually increasing the temperature within the above ranges, or by providing a gradually decreasing ammonia concentration in the feed to hydrocracker **52**, by gradually raising the hydrofining severity in hydrofiner **8** as previously described.

Effluent from hydrocracker **52** is withdrawn via line **82** and condensed in cooler **84**. The resulting two-phase mixture may then be washed with water injected via line **86**, and transferred to high-pressure separator **88**, from which substantially ammonia-free recycle gas is withdrawn via line **44** for recycle to hydrofiner **28** as previously described. Spent wash-water containing ammonia and small amounts of hydrogen sulfide is withdrawn via line **92**.

High-pressure condensate in separator **88** is depressured via line **94** into low-pressure separator **96**, from which light hydrocarbon gases may be exhausted via line **98**. Low-pressure condensate in separator **96** is then transferred to distillation column **100** via line **102**. The final gasoline product, or other desired low-boiling hydrocarbon product, is withdrawn as overhead from column **100** via line **104**, and un-converted oil is withdrawn via line **76** for recycle to hydrocracker **52** as previously described. As an alternate, the bottoms product from column **100** may be withdrawn and utilized as diesel or jet fuel if desired, or transferred to a second hydrocracker for further conversion to low-boiling hydrocarbons in the absence of ammonia and at relatively lower temperatures than were employed in hydrocracker **52**.

The hydrofining catalyst to be used in the above hydrofining units may comprise any of the oxides and/or sulfides of the transitional metals, and especially an oxide or sulfide of a Group VIII metal (particularly iron, cobalt or nickel) mixed with an oxide or sulfide of a Group VI–B metal (preferably molybdenum or tungsten). Such catalysts preferably are supported on an adsorbent carrier in proportions ranging between about 2% and 25% by weight. Suitable carriers include in general the difficultly reducible inorganic oxides, e.g., alumina, silica, zirconia, titania, clays such as bauxite, bentonite, etc. Preferably the carrrier should display little or no cracking activity, and hence highly acidic carriers having a Cat-A cracking activity index above about 20 are to be avoided. The preferred carrier is activated alumina, and especially activated alumina containing about 3–15% by weight of coprecipitated silica gel.

The preferred hydrofining catalyst consists of cobalt sulfide or oxide plus molybdenum sulfide or oxide supported on silica-stabilized alumina. Compositions containing between about 1% and 5% of Co, 3% and 20% of Mo, 3% and 15% of SiO_2, and the balance Al_2O_3, and wherein the atomic ratio of Co/Mo is between about 0.2 and 4, are specifically contemplated.

The hydrocracking catalyst to be employed herein may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking bases are those having a Cat-A activity index above about 20, and preferably above 30, including for example mixtures of two or more difficultly reducible oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid-treated clays and the like. Acidic metal phosphates such as aluminum phosphate may also be used. The preferred cracking bases comprise partially dehydrated, zeolitic, crystalline molecular sieves having relatively uniform pore diameters of about 6–14 A., and comprising silica, alumina and one or more exchangeable zeolitic cations. These crystalline zeolites may be used as the sole cracking base, or they may be mixed with one or more of the amorphous cracking bases such as silica-alumina cogel.

A particularly active and useful class of molecular sieve cracking bases are those having a relatively high

$$SiO_2/Al_2O_3$$

mole ratio, e.g., between about 3 and 10. Suitable zeolites found in nature include for example mordenite, stilbite, heulandite, ferrierite, dachiardite, chabazite, erionite, and faujasite. Suitable synthetic molecular sieve zeolites include for example those of the B, X, Y, and L crystal types, or syntheic forms of the natural zeolites noted above, especially synthetic mordenite. The preferred zeolites are those having crystal pore diameters between about 8–12 A., wherein the SiO_2/Al_2O_3 mole ratio is about 3–6. A prime example of a zeolite falling in this preferred group is the synthetic Y molecular sieve.

The naturally occurring molecular sieve zeolites are normally found in a sodium form, an alkaline earth metal form, or mixed forms. The synthetic molecular sieves normally are prepared in the sodium form. In any case, for use as a cracking base it is preferred that most or all of the original zeolitic monovalent metals be ion-exchanged out with a divalent metal, or with an ammonium salt followed by heating to decompose the zeolitic ammonium ions, leaving in their place hydrogen ions and/or exchange sites which have actually been decationized by further removal of water:

$$(NH_4+)_xZ \xrightarrow{\Delta} (H+)_xZ + xNH_3 \quad (1)$$

$$(H+)_xZ \xrightarrow{\Delta} Z + \frac{x}{2}H_2O \quad (2)$$

Mixed divalent metal-hydrogen zeolites may be prepared by ion exchanging first with an ammonium salt, then partially back exchanging with a divalent metal salt, and then calcining. In some cases, as in the case of synthetic mordenite, the hydrogen forms can be prepared by direct acid treatment of the alkali metal sieves. Hydrogen or "decationized" Y sieve zeolites of this nature are more particularly described in Belgian Patents Nos. 598,582, 598,682, 598,683 and 598,686, and U.S. Patent No. 3,130,-006.

There is some uncertainty as to whether the heating of the ammonium zeolites produces a hydrogen zeolite or a truly decationized zeolite, but it is clear that, (a) hydrogen zeolites are formed upon initial thermal decomposition of the ammonium zeolite, and (b) if true decationization does occur upon further heating of the hydrogen zeolites, the decationized zeolites also possess desirable catalytic activity. Both of these forms, and the mixed forms, are designated herein as being "metal-cation-deficient."

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a Group VI–B and/or Group VIII hydrogenating metal promoter, e.g., an oxide or sulfide of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the metals platinum, palladium, rhodium or iridium may be employed. The oxides and sulfides of other transitional metals may also be used, but to less advantage than the foregoing.

In the case of zeolitic type cracking bases, it is desirable to deposit the hydrogenating metal thereon by ion exchange. This can be accomplished by digesting the zeolite with an aqueous solution of a suitable compound of the desired metal, wherein the metal is present in a cationic form, and then reducing to form the free metal, as described for example in Belgian Patent No. 598,686.

Although as indicated above, substantially any hydrocracking catalyst may be used herein, it is not to be assumed that all such catalysts are equivalent, or that they will all give a commercially feasible process. For hydrocracking at below about 850° F. as required herein, and in the presence of ammonia, it is highly desirable to use catalysts which have both a high cracking activity and high hydrogenating activity; otherwise it will be necessary to employ uneconomical low space velocities. For economical processes operated at above about 0.5 LHSV, the preferred catalysts are composed of a Group VIII noble metal, e.g., platinum, palladium, rhodium, iridium or ruthenium, combined by ion exchange with one of the zeolitic molecular sieve cracking bases of the Y crystal type , wherein the zeolitic cations are predominantly hy-

drogen and/or a divalent metal such as calcium, magnesium, or zinc. The more conventional catalysts such as platinum on silica-alumina gel, or nickel on silica-alumina gel, will require low space velocities, in general below about 0.5 in order to achieve the desired conversion at the specified hydrocracking temperatures.

The feedstocks which may be treated herein include in general any mineral oil fraction having an initial-boiling-point above the end-boiling-point of the desired product, and having an end-boiling-point up to about 1,000° F. This includes straight run gas oils, coker distillate gas oils, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically, it is preferred to employ feedstocks boiling between about 400° and 900° F., having an API gravity of 20° to 35°, and containing at least about 20% by volume of acid-soluble components (aromatics+olefins). Such oils may also contain from about 0.1% to 5% of sulfur and from about 0.01% to 2% by weight of nitrogen.

The following example is cited to illustrate the invention and the results obtainable, but is not to be construed as limiting in scope.

Example

This example illustrates process conditions and results obtainable in an extended hydrocracking run carried out as described in connection with the drawing, with low-pressure hydrofiner effluent being transferred directly from separator **20** to the high-pressure hydrofining unit, and with total effluent from the high-pressure hydrofiner being transferred directly to the hydrocracker. The initial feedstock is a blend of straight-run gas oil and catalytic cracking cycle oil, having an API gravity of about 23.2°, a boiling range of about 420 to 850° F., and containing about 1.06 weight-percent sulfur and 0.9 weight-percent nitrogen. The hydrofining catalyst employed in each of the hydrofiners is the sulfided equivalent of 3% cobalt oxide and 15% molybdenum oxide supported on an alumina carrier stabilized by the addition of about 5% SiO_2, in the form of ⅛" pellets. The hydrocracking catalyst is a co-pelleted mixture of about 80 weight-percent of a Y molecular sieve zeolite containing 0.5 weight-percent palladium, and 20 weight-percent of an activated alumina binder containing 0.3 weight-percent palladium. The Y molecular sieve cracking base has a SiO_2/Al_2O_3 mole ratio of about 4.7, about 35% of the zeolitic ion exchange capacity thereof being satisfied by magnesium ions (3 weight-percent MgO), about 10% by sodium ions, and the remainder by hydrogen ions. Process conditions are adjusted so as to reduce the organic nitrogen content of the feed to about 0.3 weight-percent in the low-pressure hydrofiner, and to about 20 parts per million in the high-pressure hydrofiner. Hydrocracking conditions are adjusted to provide about 60 volume-percent conversion per pass. To achieve these objectives, the major process conditions in the various units are as follows:

PROCESS CONDITIONS

	Low-Pressure Hydrofiner	High-Pressure Hydrofiner	Hydrocracker
Temp., Av. Bed, ° F.:			
Start of Run	730	730	680
End of Run	780	780	770
Pressure, p.s.i.g.	750	1,500	1,500
Pressure, LHSV	3.0	2.0	2.0
H_2/Oil Ratio, M s.c.f./b	6.0	6.5	8.0

At end-of-run conditions, product distribution and quality is approximately as follows:

Dry gas make (C_1–C_3), s.c.f./b. fresh feed	120
Liquid yields, vol. percent fresh feed:	
Butanes	19
Pentanes	15
C_6	16
C_7—400° F. gasoline	72
C_4—400° F. gasoline	122
C_5+gasoline octane No., F–1+3 ml. TEL	91

The relatively high octane value of the gasoline product is attributable in part to the use of low pressures during the first hydrofining zone. If all of the hydrofining were performed at the high pressure of 1,500 p.s.i.g., a gasoline product about two octane numbers lower would be obtained.

It is not intended that the invention should be limited to the details described herein, since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

We claim:

1. A process for hydrocracking a mineral oil feedstock in the optimum hydrocracking temperature range of about 680–780° F. to obtain a relatively high-octane gasoline with a minimum production of light hydrocarbon gases, said feedstock boiling above the gasoline range and containing at least about 0.3% by weight of organic nitrogen, which comprises:

(1) contacting said feedstock plus added hydrogen with a hydrofining catalyst at elevated temperatures and pressures in a first hydrofining zone and controlling the severity of hydrofining so as to (a) effect about 30–90% denitrogenation of said feedstock, and (b) leave in said feedstock a remaining amount of organic nitrogen calculated to yield in step (3) an amount of ammonia sufficient to control the hydrocracking temperature in step (4) within the limits of about 680–780° F., said remaining amount of organic nitrogen being between about 0.03 and 0.3 weight percent;

(2) treating the effluent from said first hydrofining zone to separate ammonia therefrom and to recover a partially refined oil;

(3) contacting said partially refined oil plus added hydrogen with a hydrofining catalyst comprising a Group VI–B metal oxide and/or sulfide plus a Group VIII metal oxide and/or sulfide at elevated temperatures in a second hydrofining zone maintained at a pressure substantially higher than the pressure in said first hydrofining zone, to reduce the organic nitrogen content thereof to below about 50 p.p.m. with resultant formation of ammonia;

(4) passing effluent from said second hydrofining zone, including ammonia formed therein and hydrogen through a bed of hydrocracking catalyst at an elevated pressure, temperatures between about 680° and 780° F. and a space velocity between about 0.5 and 5, said conditions being correlated to give about 30–70 volume-percent conversion per pass to gasoline; and

(5) recovering high-octane gasoline from said hydrocracking step.

2. A process as defined in claim **1** wherein the hydrofining catalyst employed in each of said hydrofining zones is a composite of a Group VI–B metal oxide and/or sulfide with a Group VIII metal oxide and/or sulfide supported on an adsorbent carrier having a Cat-A cracking activity index below about 20, and wherein said hydrocracking catalyst comprises a Group VIII metal hydrogenating component supported on a cracking base having a Cat-A cracking activity index above about 20.

3. A process as defined in claim **2** wherein said hydrocracking catalyst comprises a Group VIII noble metal

hydrogenating component supported on a zeolitic aluminosilicate molecular sieve cracking base having a SiO_2/Al_2O_3 mole-ratio between about 3 and 10, and comprising zeolitic cations selected from the class consisting of hydrogen ions and divalent metal ions.

4. A process as defined in claim 1 wherein said hydrocracking step (4) is continued for a period of at least about 3 months while maintaining substantially constant conversion per pass therein by incrementally raising the hydrocracking temperature within the stated range of 680–780° F. to compensate for catalyst deactivation.

5. A process as defined in claim 1 wherein said hydrocracking step (4) is continued for a period of at least about 3 months while maintaining a substantially constant hydrocracking temperature within the stated range of 680–780° F., and wherein hydrocracking catalyst deactivation during said 3-month period is compensated by incrementally increasing the severity of hydrofining in step (1) whereby progressively lesser amounts of ammonia are formed in said hydrofining step (3) and passed to the hydrocracking step.

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