Dec. 1, 1964 F. C. PRICE ETAL 3,159,568

LOW PRESSURE HYDROCRACKING PROCESS WITH HYDROFINING OF FEED

Filed Oct. 2, 1961 2 Sheets-Sheet 1

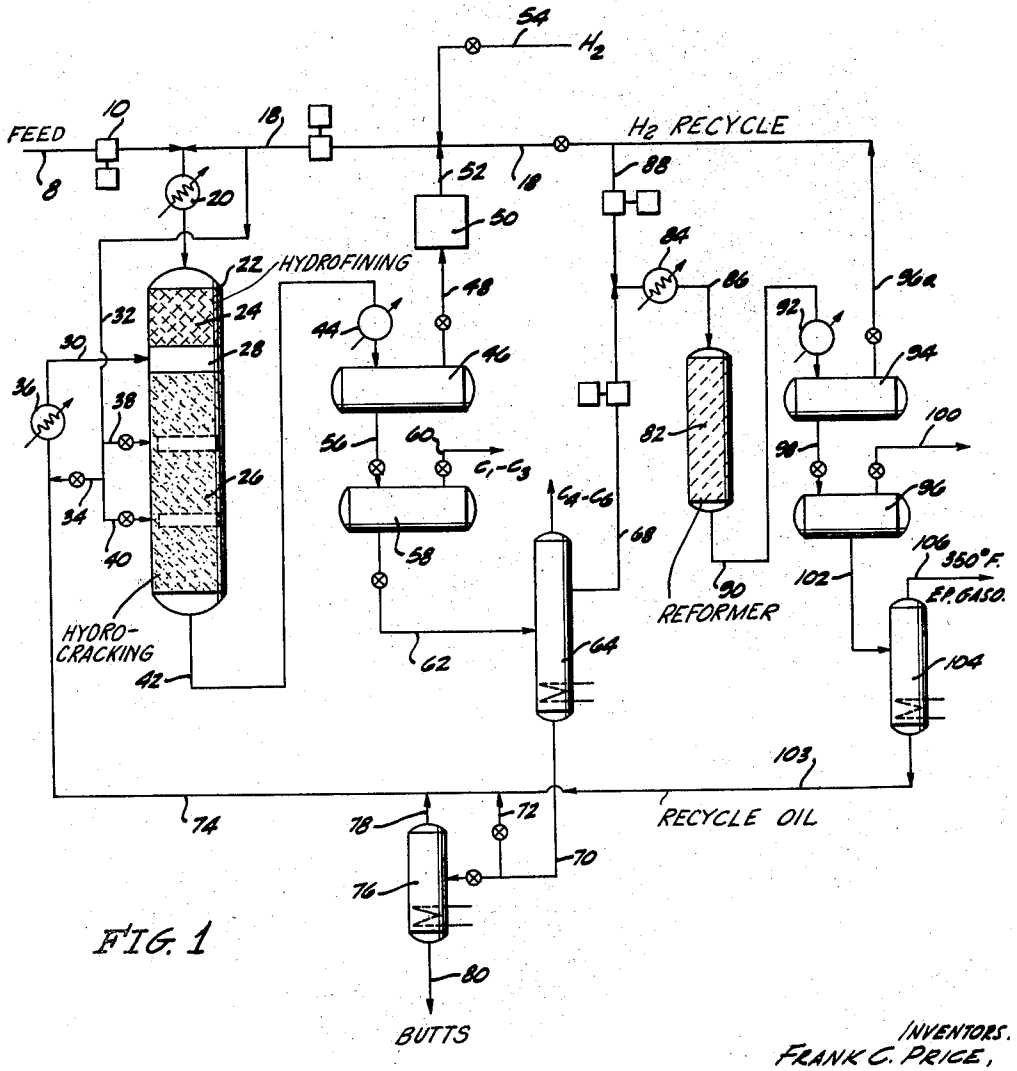


FIG. 1

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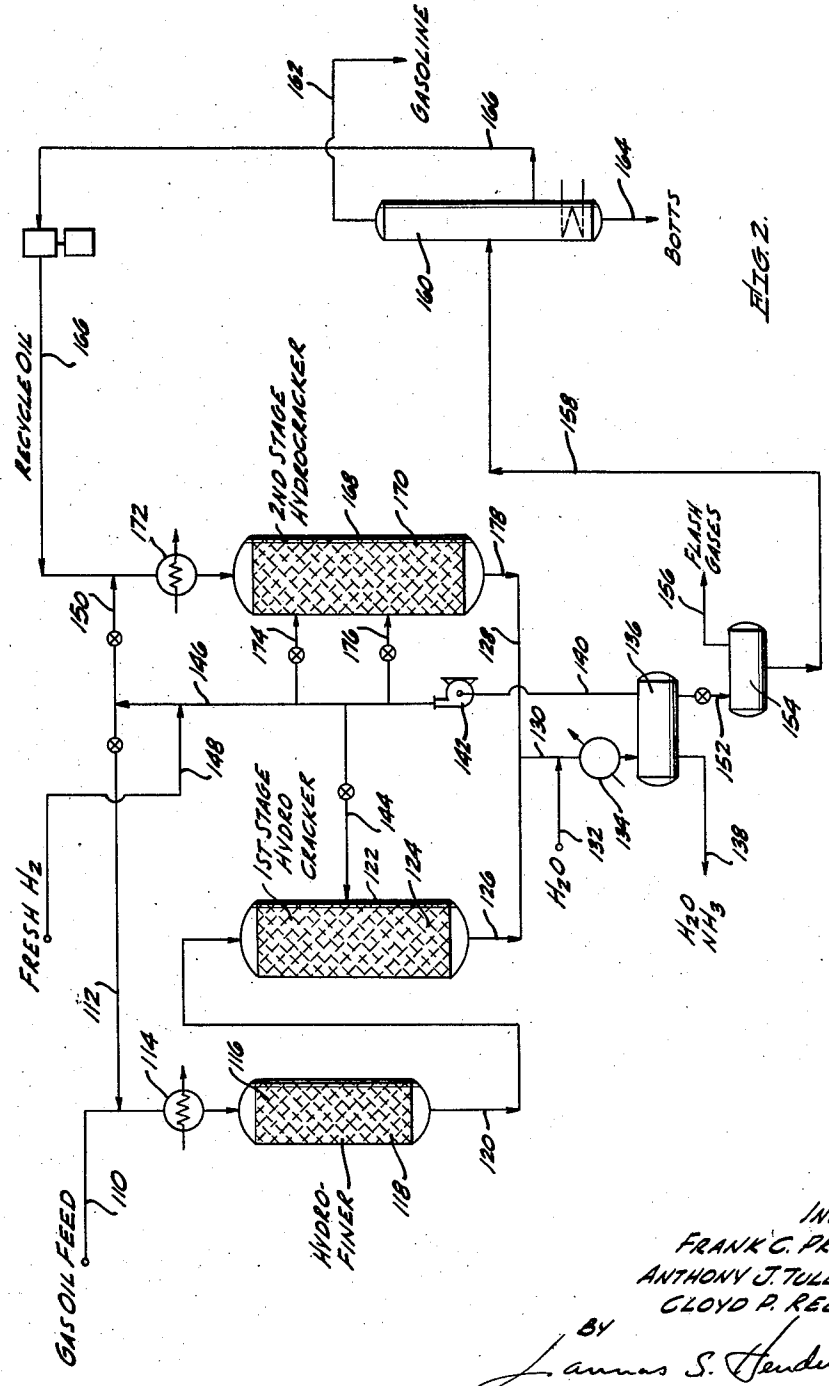


FIG 2.

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LOW PRESSURE HYDROCRACKING PROCESS WITH HYDROFINING OF FEED

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This invention relates to novel methods for carrying out the catalytic hydrocracking of high boiling hydrocarbons to produce therefrom lower boiling hydrocarbons, boiling for example in the gasoline or jet fuel range. More specifically, the process is designed to effect hydrocracking at relatively low pressures, e.g., below about 2,000 p.s.i.g., while maintaining the catalyst at high activity levels for relatively long periods of time between regenerations.

Briefly, as applied to gasoline production, the process comprises first subjecting the feed to a catalytic prehydrogenation or "hydrofining" treatment at below 2,000 p.s.i.g., then subjecting the entire hydrofining effluent, without intervening condensation or purification, to at least one stage of catalytic hydrocracking at below 2,000 p.s.i.g. The catalyst used in the first hydrocracking stage following the hydrofiner preferably comprises a Group VIII hydrogenating metal component. The effluent from the first (or only) hydrocracking stage is then condensed and partially purified, as by washing with water to remove ammonia, and fractionated to recover the gasoline. The unconverted residue may then be reheated and recycled to the same hydrocracker, or preferably passed through a second bed of hydrocracking catalyst under conditions adjusted to give about 30–80% conversion to gasoline per pass, the conversion normally, though not necessarily, being higher than in the first hydrocracking stage.

The effluent from the second stage of hydrocracking may, if desired, be mingled with the effluent from the first stage, and the mixture condensed to recover a common recycle gas for the hydrofining step and both hydrocracking stages. A combined liquid condensate comprising the net gasoline production from both stages, plus the unconverted oil from both stages, is also recovered and fractionated, in a single fractionating unit if desired, to recover the gasoline. The unconverted oil is then preferably recycled to the second hydrocracking stage. Thus, where two stages of hydrocracking are utilized, the feed to the second consists of the unconverted residue from both the first and second stages.

As a result of the increasing demand for light motor fuels, and the decreasing demand for heavier petroleum products such as fuel oil and the like, there is much current interest in more efficient methods for converting the heavier products of refining into gasoline. The conventional methods of accomplishing this such as catalytic cracking, coking, thermal cracking and the like always result in the production of a more highly refractory unconverted oil, or cycle oil, which cannot be economically converted to gasoline. It is known that such refractory materials can be converted to gasoline by catalytic hydrocracking. However, the application of the hydrocracking technique has in the past been extremely limited due to the expense involved.

The principal problem in hydrocracking centers around the three-horned dilemma of how to make the catalyst work efficiently, i.e., give high conversions per unit of catalyst, without undergoing rapid deactivation by coking, and without resorting to expensive, high-pressure processing. Previous attempts to apply hydrocracking have foundered economically upon at least one of the horns of this dilemma.

Most of the previously proposed hydrocracking processes are designed to operate at high pressures, i.e., above 3,000 p.s.i.g. By operating at high pressures, satisfactory catalyst life and efficiency can often be attained. However, there is a critical economic disparity between operating at 3,000 p.s.i.g. and, for example, at 1,500 p.s.i.g. The costs in plant equipment and utilities for operating at the 3,000 p.s.i.g. level are generally prohibitive under present economic conditions, while an operation conducted at 1,500 p.s.i.g. would be distinctively attractive, provided that commensurate catalyst life and efficiency could be maintained.

Operations conducted at below 2,000 p.s.i.g. immediately encounter the problem of rapid deactivation rates resulting from the deposition of coke and other deposits upon the catalyst. The classical solutions to this problem involve either frequent regenerations of the catalyst, or using low temperatures and low space velocities whereby the work load per unit of catalyst is decreased. The latter of these solutions entails a large and generally prohibitive catalyst inventory. The former leads to two other unfeasible alternatives, i.e., the use of moving-bed or fluidized bed techniques, or frequent shut-downs of fixed bed reactors for regeneration. The moving-bed or fluidized bed techniques are difficult to apply and require expensive equipment when operating at above about 500 p.s.i.g., and it is distinctly preferable in hydrocracking to operate at above 500 p.s.i.g. Frequent shutdowns of fixed bed reactors for regeneration necessitate either duplicate stand-by reactors, or interrupted production, and in any case, each regeneration is an expensive operation.

It has been known for some time that the efficiency of catalytic hydrocracking can be improved if the feed is first subjected to hydrogenation under non-cracking conditions. However, in the past, where low pressure hydrocracking is the objective, it has always been the practice to condense the products of hydrogenation, separate gaseous impurities such as ammonia and hydrogen sulfide, and reheat and repressure the liquid product prior to the hydrocracking thereof in order, presumably, to avoid deactivation of the hydrocracking catalyst. These intermediate steps require much additional equipment and facilities, including separate reactors for the hydrogenation step and the hydrocracking step, separate heat exchangers, pumps, tankage, etc. This added expense has generally been considered prohibitive.

It has now been found that, for purposes of this invention, the intermediate condensation, separation and reheating steps following hydrofining are unnecessary; a substantial improvement in hydrocracking efficiency at low pressures is obtained even when the total effluent from the hydrofining step is transferred directly to the hydrocracking step without intervening condensation or purification. This improvement is reflected in higher conversions to gasoline, the production of a less refractory cycle oil, improved liquid yields and a marked reduction in nitrogen content of the hydrocracker gasoline. This latter feature is highly important where the hydrocracker gasoline is to be subjected to reforming in the presence of a platinum catalyst, since very minor amounts (1–5 parts per million) of basic nitrogen will cause rapid deactivation of platinum reforming catalysts.

For all the above reasons, it has in the past been considered necessary in hydrocracking either (1) to use high pressures, (2) to regenerate or replace the catalyst at frequent intervals, or (3) to use low pressures (below 2,000 p.s.i.g.) only after a separate hydrofining treatment with intervening cooling, washing, reheating and repressuring. It is the principal object of this invention to provide a hydrocracking process which may be carried out entirely at pressures below about 2,000 p.s.i.g., while

maintaining a relatively constant and economical conversion level for periods in excess of about 3 months without catalyst regeneration, and without separate or non-integral pre-hydrofining. Another object is to provide specific hydrocracking catalysts which are regenerable, and are particularly adapted to low pressure, fixed-bed operation, and which are relatively tolerant of nitrogen and sulfur compounds in the feed. Another objective is to provide a two-stage hydrocracking process utilizing a single recycle gas system, and a single product recovery system for both stages. Other objectives will be apparent from the more detailed description which follows.

The process will now be described with reference to FIGURE 1 of the attached drawings, which is a flowsheet illustrating the invention in one of its broader aspects. The initial feedstock is pumped in via line **8** and pump **10**, admixed with recycle hydrogen from line **18**, and the mixture is then passed through preheater **20** into the top of combined hydrofining-hydrocracking reactor **22**. Reactor **22** is divided into an upper hydrofining catalyst zone **24**, and a lower hydrocracking catalyst zone **26**.

In hydrofining zone **24** the feed plus hydrogen is contacted with a suitable sulfactive hydrofining catalyst under conditions of hydrofining. The catalyst is preferably disposed in a fixed stationary bed, and 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 VIB metal (preferably molybdenum or tungsten). Such catalysts may be employed in undiluted form, but 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 carrier should display little or no cracking activity, and hence highly acidic carriers 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.

Suitable hydrofining conditions are as follows:

	Operative	Preferred
Average bed temp., ° F.	600–850	650–750
Pressure, p.s.i.g.	400–3,000	500–2,000
Liquid hourly space velocity	0.5–20	1–5
Hydrogen ratio, s.c.f./b.	500–12,000	800–8,000

In hydrofining zone **24**, an exothermic rise in temperature occurs, so that the products emerging therefrom are at a higher temperature than at the top. In interspace **28**, the total hydrofining products may be mingled with hydrocracking recycle oil injected via line **30**. Additional hydrogen may also be added via lines **32** and **34** if desired. The recycle oil, with or without added hydrogen, is preferably raised to a suitable temperature in heater **36**, so that upon admixing with the hydrofining products in space **28**, the final mixture will be at the desired initial hydrocracking temperature. Thus, the injection of recycle oil in interspace **28** serves the additional purpose of aiding in temperature control of the overall exothermic reactions taking place in reactor **22**.

In hydrocracking zone **26**, the mixture of hydrofiner products plus recycle oil is contacted with a bed of suitable hydrocracking catalyst under conditions of hydrocracking. The average bed temperature in the hydrocracking zone should range between about 600° and 850° F., preferably between about 650° and 800° F., the pressure may range between about 400 and 2,000 p.s.i.g., and preferably between about 500 and 1,800 p.s.i.g. The liquid hourly space velocity may range between about 0.5 and 8.0 volumes of liquid feed per volume of catalyst per hour. Suitable hydrogen ratios are from 800 to 15,000 s.c.f./b. of feed. It will be understood that these conditions should be adjusted to meet the peculiarity of the specific feedstock which is being treated, and the catalyst employed. For highly aromatic stocks, the conditions should be relatively severe; for feeds which, after hydrofining, contain substantial proportions of naphthenes, the conditions should be relatively mild.

An important feature of economy in the process of this invention resides in the fact that the hydrocracking in zone **26** may be conducted at the same pressure as the hydrofining in zone **24**. This means that both reactions may be conducted in the same reactor, although it is not meant to exclude the possible use of two separate reactors.

Since the hydrocracking in zone **26** is exothermic in character, provision is made for interstage cooling by injection of one or more streams of cool hydrogen via lines **32** and **38** and/or lines **32** and **40**. In some cases, as, e.g., where relatively mild hydrocracking conditions are employed, there will be relatively little heat generated, and hence the use of interstage cooling is not always necessary.

The total product from hydrocracking zone **26** is withdrawn via line **42**, cooled in condenser **44** to e.g., about 100°–250° F., and transferred to high pressure separator **46**. Hydrogen-rich recycle gas is withdrawn via line **48**, and may be subjected to an optional purification step in zone **50**, e.g., oil scrubbing, in order to prevent the build-up of light hydrocarbon gases in the recycle stream. The purified recycle gas is then transferred via line **52** to line **18**, wherein it mingles with net make-gas from the reforming operation hereinafter described, and with fresh make-up hydrogen from line **54** if necessary. The combined hydrogen stream is then blended with feed in line **8** as previously described.

The liquid product in high pressure separator **46** is then flashed via line **56** into low pressure separator **58**, from which light hydrocarbon gases are withdrawn via line **60**. Low pressure separator **58** may be maintained at any desired pressure, from about atmospheric up to the pressure prevailing in the reforming zone hereinafter described.

Liquid product from separator **58** is then transferred via line **62** to a fractionating column **64**, or the equivalent thereof. A light overhead fraction boiling up to about the C_6 range is taken overhead via line **66**, and a naphtha fraction boiling up to about 400° F. is withdrawn as a side-cut via line **68**, and makes up the preferred feedstock to the reformer.

The bottoms from column **64**, boiling above about 400° F. makes up the cycle oil for the hydrocracking zone. In cases where relatively non-refractory, low boiling feedstocks to the hydrofining zone are employed, it is preferable to transfer this cycle oil via lines **70**, **72**, **74** and **30**, back to hydrocracking zone **26**. It will be understood that sufficient hydrogen is added via line **34** and/or line **18** to provide the overall hydrogen ratios herein specified for the total feedstock-plus-recycle oil which is passed through hydrocracking zone **26**.

In some cases, as for example where the feed to the hydrofining step is a refractory oil of high end-point, e.g., above about 750° F., it may be desirable to transfer the cycle oil in line **70** to distillation column **76** for recovery overhead of a light fraction boiling below about 750° F., which is transferred via lines **78**, **74** and **30** to hydrocracking zone **26**. The minor bottoms fraction (e.g., about 5% to 20% by volume) from column **76** is then withdrawn from the process via line **80**.

The hydrocracked naphtha in line **68** may now be transferred in its entirety to reforming zone **82** via pre-

heater 84 and line 86, in admixture with recycle hydrogen from line 88. Alternatively, the naphtha in line 68 may be subjected to a solvent extraction step, not shown, in order to separate the aromatic hydrocarbons from the remaining naphthene-rich hydrocarbons. In this case only the non-aromatic fraction is passed to the reformer. Suitable solvents for this purpose include, for example, ethylene glycol, diethylene glycol, propionitrile, or the like. The solvent separation step is particularly attractive where the hydrocracker gasoline is relatively rich in aromatic hydrocarbons. These solvent extraction procedures are conventional and hence need not be described in detail.

In reforming zone 82 the hydrocracked gasoline is subjected to mild reforming conditions adapted to convert the major portion of the naphthenes to aromatics. Such conditions include average bed temperatures between about 825°–950° F., space velocities between about 1.0 and 5.0, pressures between about 200 and 800 p.s.i.g., and hydrogen rates between about 4,000 and 12,000 s.c.f. per barrel of feed. The preferred temperatures are between about 850° and 925° F., at preferred space velocities of 1.5–4. The usual hydroforming conditions include space velocities of about 2 at temperatures of 925°–975° F. These conditions are unnecessary herein and may cause a reduction in liquid yield uncompensated by any sufficient increase in gasoline quality.

While the above conditions of reforming are preferred, the more conventional temperatures (925°–975° F.) may also be employed. The character of the feed is such that severe reforming conditions, such as would cause substantial reduction in yield when using conventional feeds, do not unduly impair liquid yields herein. This reflects the low paraffin content of the feed, which is the major contributor of light cracked products.

The catalyst employed in the reforming zone may be conventional. For example, composites of activated alumina with minor proportions of platinum, palladium, rhodium, molybdenum oxide, vanadium oxide, or chromium oxide may be employed. The preferred catalysts comprise activated alumina containing minor proportions of fluorine, and minor proportions, from about 0.05% to 1.0%, of platinum. Platinum supported on steam-deactivated silica, or silica-alumina may also be employed. These catalysts are conventional in the art and hence need not be described in detail.

Another type of reforming catalyst which may be used to advantage consists of cobalt molybdate supported on activated alumina, bauxite, or other clays. Such catalysts generally contain between about 2% and 8% by weight of CoO, and between about 4% and 20% of MoO_3. Preferably they are prepared by alternate impregnation as described in U.S. Patent No. 2,687,381.

The total products from reforming zone 82 are withdrawn via line 90, cooled in condenser 92 to e.g., 50°–200° F., and then transferred to high pressure separator 94, from which hydrogen-rich recycle gas is withdrawn via line 96. The major portion of this recycle gas is returned to the reformer via line 88, and the net make gas is sent to hydrofining zone 24 via line 18 as previously described.

The liquid product in separator 94 is then flashed into low pressure separator 96 via line 98, from which light hydrocarbon gases are withdrawn via line 100. The naphtha in separator 96 ordinarily contains from about 0.5 to 5% by volume of undesirable heavy ends or "polymer," boiling above about 400° F. This material is largely synthesized during reforming, and is detrimental in final gasoline blends in that it contributes to gum and lacquer formation. It is therefore preferable to fractionate out these heavy ends. In the past, this has resulted in decreasing the liquid yield of 400° F. end-point gasoline by as much as 4–5%.

Present trends in automotive design also require increasingly large proportions of high-octane components in the lighter gasoline fractions boiling below about 300° F. There is hence a corresponding decrease in the demand for high octane heavy fractions boiling above about 300° F. The overall value of a reforming operation would hence be greatly increased if means could be provided for converting heavy reformate to light reformate without unduly restricting the end-point (and thus the available volume) of feed to the reformer.

In the combined process of this invention, provision is made for converting any of the foregoing unwanted heavy fractions back to high-octane gasoline of the desired end-point. This is accomplished for example by transferring the naphtha from separator 96 to distillation column 104 via line 102, and recovering 350° F. end-point gasoline overhead via line 106. The 350° F.+bottoms fraction is taken off via line 108 and recycled via lines 74 and 30 to hydrocracking zone 26. In this manner, provision is made for continuously converting the heavy polymer material, and/or any other undesired heavy fractions back to naphtha of the desired end-point with little or no reduction in liquid yield.

The final gasoline product recovered via line 106 is sent to storage facilities, not shown, and is found to be of exceptionally high quality. Its aromatic content typically ranges between about 70% and 90% by volume, and its octane rating (F—1+3 ml. TEL) typically ranges between about 103 and 108.

Reference is now made to the attached FIGURE 2, which is a flowsheet illustrating the preferred modification utilizing two stages of hydrocracking. The initial gas oil feedstock is brought in through line 110 and blended with fresh and recycle hydrogen from line 112. The mixture is then preheated to suitable hydrofining temperatures in preheater 114, and passed into catalytic hydrofiner 116, in which is disposed a suitable bed of hydrofining catalyst 118. The hydrofining catalyst and conditions in hydrofiner 116 are the same as those previously described in connection with hydrofining zone 24 of FIGURE 1.

The effluent from hydrofiner 116 is withdrawn via line 120 and transferred directly to first-stage hydrocarcker 122, in which is disposed a bed of suitable hydrocracking catalyst 124. It will be apparent that the feed to first-stage hydrocracker 122 will contain all of the nitrogen and sulfur which was present in the initial feed, most of which will have been converted to ammonia and hydrogen sulfide in hydrofiner 116. It has been found generally advisable under these conditions, and at the desired low pressures, to limit the conversion per pass to gasoline in the first stage hydrocracker, so as to avoid rapid deactivation of the catalyst. Specifically, it is preferred to adjust the temperature so as to limit the conversion to about 20%–60% per pass.

The rate of coking or catalyst deactivation in this hydrocracking process may be conveniently expressed from an operating standpoint in terms of the "Temperature Increase Requirement" (TIR), which is the average daily temperature increase required to maintain a given conversion level at a constant feed rate. This factor determines the run length between regenerations. For example, starting with a fresh catalyst, a 40% conversion may be initially obtained at about 700° F. It is found that, to maintain the 40% conversion, it is necessary to increase the temperature in the hydrocracking zone by about 1° F. per day until the temperature reaches 825° F. This provides an operating period of 125 days, after which regeneration of the catalyst is required. It is a notable fact that over this temperature range of at least about 100° F., the TIR appears to be substantially a linear function, and only when high temperatures are reached, above about 850° F., does the TIR curve become exponential. It is preferred to discontinue the hydrocracking substantially as soon as the TIR curve begins to indicate that excessive temperature rises, e.g., of more than about 2° to 3° F. per day are being required in order to maintain conversion, for this indicates the transition to thermal

cracking, accompanied by a rapid coking rate and a substantially increased rate of dry gas production. It should be noted, however, that it is unnecessary actually to carry out a daily temperature rise in this mode of operation; TIR refers to the average increase per day, and from an operational standpoint, it may be more desirable to adjust the temperature periodically, e.g., every 2 to 7 days to provide the average daily increase. For practical purposes of this invention, temperatures in the respective hydrocracking stages are controlled so as to provide a TIR amounting to not more than about 3° F. per day in each stage.

The actual hydrocracking conditions of temperature and space velocity to be employed in the first stage will thus depend upon the refractoriness of the feed, its nitrogen content, the pressure, the predetermined desired run length between regenerations, as well as the relative activity of the catalyst. In general, suitable hydrocracking conditions may be selected within the following ranges:

FIRST STAGE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, °F.:		
Start of run	600–800	650–750
End of run	650–875	750–850
Pressure, p.s.i.g	400–3,000	500–2,000
LHSV, v./v./hr	0.5–10	1–5
H_2/oil, s.c.f./b	500–15,000	1,000–10,000

The effluent from the first stage hydrocracker is withdrawn via line **126** and mingled in line **128** with effluent from the second stage hydrocracker to be subsequently described. The resulting mixture then flows through line **130**, into which water is injected via line **132**. The mixture is then condensed in cooler **134** and transferred to high pressure separating vessel **136**. The amount of water added via line **132** is preferably adjusted so as to remove substantially all ammonia. The aqueous wash liquor from separator vessel **136**, containing dissolved ammonia and ammonium sulfide, is withdrawn via line **138** and sent to waste or recovery disposal.

Hydrogen-rich recycle gas for both hydrocracking stages and the hydrofining stage is withdrawn from separator **136** via line **140** and repressured via compressor **142** for recycle. A portion of this cool recycle hydrogen is preferably diverted through line **144** to one or more intermediate points in first stage hydrocracker **122** to act as a quench for control of the exothermic reaction. The major portion of the recycle gas is blended in line **146** with fresh make-up hydrogen for the entire process from line **148**. The mixture of fresh and recycle hydrogen is then distributed from line **146** via lines **112** and **150** to the hydrofiner-first stage hydrocracker, and to the second stage hydrocracker respectively.

The condensed liquid hydrocarbons in separator **136** are then flashed via line **152** into low pressure separator **154**, from which flash gases including light hydrocarbons and hydrogen sulfide are taken off via line **156**. The liquid hydrocarbons, now at substantially atmospheric pressure, are transferred via line **158** to a fractionating column **160**, from which desired end-point gasoline product is taken overhead via line **162** and sent to finishing and storage facilities not shown. If desired, a heavy bottoms product may be removed from the process via line **164**, thereby preventing build-up in the process of coke-forming compounds. This is ordinarily desirable only when very high end-point feedstocks are being treated; in most cases the entire fraction boiling above gasoline can be treated in the second hydrocracking stage.

A side-cut recycle oil from column **160** is withdrawn via line **166**, comprising unconverted oil from both the first and second hydrocracking stages. This side-cut, with or without the bottoms fraction from line **164**, makes up the feed to the second stage hydrocracker **168**, which likewise contains a bed of suitable hydrocracking catalyst **170**. This recycle oil, after blending with hydrogen from line **150**, is preheated to the desired hydrocracking temperature in preheater **172**, and passed through second-stage hydrocracker **168** in much the same manner as in the first-stage hydrocracker. To control the temperature at the desired level, one or more quench streams of cool recycle hydrogen may be admitted at intermediate points in the reactor via lines **174** and **176**. Product effluent is withdrawn via line **178** and transferred to line **128** for treatment as previously described in connection with the first-stage hydrocracker effluent.

The recycle oil which is treated in the second stage hydrocracker is considerably less refractory than the feed which was treated in the first-stage hydrocracker. Hence, it is found that a considerably higher conversion can normally be maintained in the second-stage hydrocracker than in the first-stage, without encountering rapid catalyst deactivation. Here again, the hydrocracking is initiated with fresh catalyst at a suitably low temperature, and the temperature is gradually raised over a period of several months to maintain relatively constant conversion, preferably about 40% to 70% per pass to 400° F. end-point gasoline.

The process may be operated with equal or different run-lengths in each hydrocracking reactor. If the run-lengths are unequal, as is normally the case where each stage is operated at maximum efficiency levels, a stand-by reactor may be provided, into which the feed to whichever stage becomes next deactivated can be diverted. With this "switch" type of operation, maximum catalyst treating efficiency is generally obtainable, at the expense of providing a third reactor.

The hydrocracking conditions to be employed in the second stage will depend mainly upon the activity of the catalyst, the desired conversion per pass, and upon the boiling range of the recycle oil feed. In general suitable operating conditions may be selected within the following ranges:

SECOND STAGE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F.:		
Start of run	450–800	550–700
End or run	600–875	750–850
Pressure, p.s.i.g	400–3,000	500–2,000
LHSV, v./v./hr	0.5–10	1–5
H_2/oil, s.c.f./b	500–15,000	1,000–10,000

The hydrofining conditions employed herein are designed to decompose nearly all the organic sulfur, nitrogen and oxygen compounds present in the feed, while avoiding any appreciable hydrocracking of hydrocarbons. Any olefins present are mostly hydrogenated. The polycyclic aromatic compounds are only partially hydrogenated. Under these hydrofining conditions, only small amounts of gasoline are produced, nearly all of which consists of hydrocarbon fragments resulting from the splitting out of sulfur, nitrogen and oxygen from heterocyclic compounds. Hydrogen consumption in this step is usually between about 200 and 2,000 s.c.f. per barrel of feed, and constitutes between about 20% and 50% of the total hydrogen consumption in the hydrofining and hydrocracking steps.

As a result of hydrofining, the succeeding hydrocracking step may be carried out under milder conditions, since the major objective becomes primarily one of effecting scission of naphthenic rings attached to aromatic rings, or aliphatic side-chains attached to aromatic rings. Consequently, high partial pressures of hydrogen, such as would be required to prevent rapid coking of the catalyst in the presence of raw feed, can be avoided. At the same time, an economically attractive degree of conversion

per pass can be maintained, even in the presence of the basic nitrogenous products from the hydrofining step.

The catalysts to be employed in the respective hydrocracking stages may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking bases include 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 composites of silica and alumina containing about 50%–90% silica; coprecipitated composites of silica, titania, and zirconia containing between 5% and 75% of each component; partially dehydrated, zeolitic, crystalline molecular sieves, e.g., of the "X" or "Y" crystal types, having relatively uniform pore diameters of about 8 to 14 angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations.

The foregoing molecular sieve type cracking bases, when compounded with a hydrogenating metal, are particularly useful for hydrocracking at relatively low temperatures of 450°–700° F., and relatively low pressures of 500–1,500 p.s.i.g. It is preferred to employ molecular sieves having a relatively high SiO_2/Al_2O_3 ratio, e.g., between about 2.5 and 6.0. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen and/or a divalent metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the SiO_2/Al_2O_3 ratio is about 5, are preferred, either in their hydrogen form, or a divalent metal form. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolitic ammonium ion and leave a hydrogen ion. It is not necessary to exchange out all of the monovalent metal; the final compositions may contain up to about 4% by weight of NaO, or equivalent amounts of other monovalent metals.

As in the case of the X molecular sieves, the Y sieves also contain pores of relatively uniform diameter in the individual crystals. In the case of X sieves, the pore diameters may range between about 6 and 14 A., and this is likewise the case in the Y sieves, although the latter usually are found to have crystal pores of about 9 to 10 A. in diameter.

Table 1 below shows the X-ray powder diffraction pattern of the Y sieve. In obtaining the diffraction pattern, standard techniques were employed, utilizing as the radiation source the K_α doublet of cobalt (λ=1.7889 A.), and a Geiger counter spectrometer with a strip chart pen recorder. The peak heights, I, and the value of the respective Bragg angles were read from the spectrometer chart. From these, the relative intensities, I/I_1, were estimated (strongest peak=100), and the interplaner spacings, d(A.), were calculated from the equation, $\lambda=2d \sin \theta$, λ being the wave length of the source, θ the Bragg angle, and d the interplaner spacing in angstroms.

TABLE 1

d(A.)	I/I_1	d(A.)	I/I_1
14.6	100	3.30	20
8.85	15	3.32	<10
7.50	10	3.02	<10
5.69	25	2.91	<10
4.75	15	2.85	14
4.37	17	2.76	<10
3.50	<10	2.70	<10
3.76	30	2.63	<10
3.46	<10	2.59	<10
		2.37	<10

Any of the foregoing cracking bases may be further promoted by the addition of small amounts, e.g., 1% to 10% by weight, of halides such as fluorine, boron trifluoride or silicon tetrafluoride.

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a Group VIB or Group VIII 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 the molecular sieve type catalysts, it is desirable to distribute the hydrogenating metal preferentially in the internal pore areas thereof. This can be accomplished either by forming the sieve crystals in an aqueous medium containing an appropriate, alkali-stable complex of the hydrogenating metal, or by ion-exchanging the hydrogenating metal onto the sieve and reducing to form the free metal and redistribute it into the pores.

A particularly suitable class of hydrocracking catalysts is composed of about 75%–95% by weight of a coprecipitated hydrocracking base containing 5%–75% SiO_2, 5%–75% ZrO_2, and 5%–75% TiO_2, and incorporated therein from about 1%–30%, preferably 10%–25%, based on free metal, of a Group VIII metal or metal sulfide, e.g., nickel or nickel sulfide.

The feedstocks which may be treated herein include in general any mineral oil fraction having an initial boiling point above the conventional gasoline range, i.e., above about 350° F., and having an end-boiling-point of 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 0.1% to 2% by weight of nitrogen.

The following examples are cited to illustrate certain adaptations of the invention and the results obtainable, but are not to be construed as limiting in scope.

Example I

An extended hydrocracking run was carried out using the two-stage contacting technique illustrated in FIGURE 2. The feedstock was a gas oil blend mainly composed of coker distillate gas oils. Its principal characterictics were:

End-boiling-point ° F.	600
Gravity, ° API	30.3
Sulfur content, wt. percent	2
Nitrogen content, wt. percent	0.15
Acid-solubles, vol. percent	51

This feed oil was passed first over a hydrofining catalyst consisting of the sulfided equivalent of 3% cobalt oxide and 15% molybdenum oxide, supported on an alumina carrier which was stabilized by the addition of about 5% SiO_2. The hydrofining conditions throughout the run were:

Temperature (av. bed) ° F.	700–710
Pressure p.s.i.g.	1,575
Space velocity	2.0
Hydrogen/oil, s.c.f./b.	5,000

The total hydrofining effluent was then passed continuously into a first-stage hydrocracking reactor filled with a nickel-promoted silica-zirconia-titania catalyst, containing about 16% silica, 40% zirconia, 24% titania and 20% nickel by weight. This catalyst was prepared by coprecipitating the silica-zirconia-titania base, impregnating with nickel nitrate, drying, calcining and pre-sulfiding with H_2S.

The effluent from the first stage of hydrocracking was then blended with the effluent from the second stage of hydrocracking, described hereinafter, and the blend was condensed while simultaneously washing with water to remove ammonia. Hydrogen-rich recycle gas was recovered and recycled in part to the hydrofining step and in part to the second hydrocracking stage. The liquid condensate was fractionated to recover the gasoline product boiling up to about 400° F. The residue of oil boiling above 400° F. was then fractionated to recover a bottoms fraction boiling above about 560° F., which was removed from the process. Remaining recycle oil (400°–560° F. boiling range) was passed continuously through the second hydrocracking reactor, which was filled with an equal quantity of the same hydrocracking catalyst. Conditions in the respective hydrocracking zones at the start of the operation were as follows:

	First Hydrocracking Zone	Second Hydrocracking Zone
Temperature, ° F. (av. bed)	750	680
Pressure, p.s.i.g.	1,570	1,550
Space Velocity	2	1.5
H_2/oil ratio, s.c.f./b.	9,000	10,000
Conversion per pass [1]	36	60

[1] Average conversion to below 400° F. material.

Under the above conditions, the average efficiency of conversion to C_5—400° F. end-point gasoline was about 104%, i.e., the volume of C_5—400° F. gasoline recovered was 104% of the volume of fresh feed which was converted to all products boiling below 400° F. It was found that, by periodically increasing the temperature by an average of about 0.7° F. per day in the first hydrocracking zone, and 0.8° F. in the second zone, the same conversion levels were maintained for over 64 days of continuous operation. This operation can be continued until the temperatures reach about 850° F. in the first zone and 800° F. in the second, resulting in a catalyst life of 4–5 months between regenerations.

In contrast to this operation, if an equivalent degree of conversion is attempted in a single hydrocracking stage at the same conditions of pressure, and with the same pre-hydrogenation treatment, it is necessary to utilize lower space velocities and/or higher temperatures. If lower space velocities are used, then a much larger quantity of catalyst is required per volume of feed. If higher temperatures are employed, then the rate of catalyst deactivation becomes markedly accelerated, so that regeneration is required every few days.

If the pre-hydrogenation treatment is omitted in the above example, the rate of catalyst deactivation in the first hydrocracking stage increases markedly, at the same conversion level. Therefore, to obtain the combined benefits of low pressure operation, long catalyst life, and satisfactory catalyst efficiency, it is necessary to provide both a pre-hydrogenating treatment and a two-stage hydrocracking process with removal of nitrogen compounds from the feed to the second-stage of hydrocracking.

Example II

This example demonstrates the benefits obtained by employing an integral pre-hydrofining step ahead of the first hydrocracking zone, and that such benefits do not accrue when the hydrofining catalyst is replaced by a like amount of hydrocracking catalyst.

Two parallel runs were carried out, using a 600° F. end-point coker gas oil feed, containing 0.14% by weight of nitrogen. In Run A, the feed was passed at 1.0 space velocity through a bed of Linde MB 5382 hydrocracking catalyst (a magnesium Y molecular sieve loaded with 0.5% Pd). In Run B, the feed was passed first through a bed of hydrofining catalyst at 2.0 space velocity, and then directly through the Linde MB 5382 hydrocracking catalyst at 2.0 space velocity, the overall space velocity in Run B thus being 1.0, as in Run A. The hydrofining catalyst was the same type of sulfided Co-Mo-Al_2O_3 catalyst used in Example I. The hydrocracking temperature in each run was adjusted to give a constant 38% conversion to 400° F. end-point gasoline. The results were as follows:

TABLE 2

Run No.	A	B
Catalyst:		
First half of bed	Hydrocracking	Hydrofining.
Second half of bed	Hydrocracking	Hydrocracking.
Hydrocracking temp., ° F. (to give 38% conversion).	780	708.
TIR	1°	Less than 0.1°.

Hence, even though in Run B, the hydrocracking space velocity was 2.0, as compared to 1.0 in Run A, the same conversion was obtainable in Run B at a temperature 72° F. lower than in Run A. Moreover, in Run A there was considerably more dry gas make than in Run B, indicating poorer selectivity of conversion. This clearly demonstrates the efficacy of the integral pre-hydrofining technique for improving the efficiency of a subsequent catalytic hydrocracking operation.

This application is a continuation-in-part of application Serial No. 5,913, filed February 1, 1960, now abandoned, and of application Serial No. 759,661, filed September 8, 1958, now abandoned.

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 converting to lower boiling hydrocarbons a mineral oil feedstock boiling above the gasoline range and containing at least one impurity from the class consisting of organic nitrogen and sulfur compounds, which comprises subjecting said feedstock to hydrofining in the presence of added hydrogen and a sulfactive transitional metal hydrofining catalyst under conditions effective for decomposing said organic nitrogen and sulfur compounds without substantial cracking of hydrocarbons, passing total effluent from said hydrofining step, without intervening purification to remove the decomposition products of said impurity, into a hydrocracking zone and contacting said effluent therein with a hydrocracking catalyst at a space velocity between about 0.5 and 10 and at hydrocracking temperatures effective to give a substantial cracking of hydrocarbons, said hydrocracking catalyst comprising a Group VIII metal sulfide hydrogenation component deposited upon a solid refractory cracking base, the pressure in said hydrofining zone and in said hydrocracking zone being less than about 2,000 p.s.i.g., and treating the effluent from said hydrocracking zone to recover low-boiling hydrocarbons.

2. A process as defined in claim 1 wherein said cracking base is a partially dehydrated, zeolitic alumino-silicate molecular sieve of the Y crystal type having a silica-alumina mole-ratio greater than 2.5 and wherein the zeolitic cations are selected mainly from the class consisting of hydrogen and divalent metals, and wherein said hydrogenation component is a Group VIII noble metal sulfide.

3. A process as defined in claim 1 wherein said cracking base is a coprecipitated composite of silica, zirconia and titania, and said hydrogenation component is nickel sulfide.

4. A process as defined in claim 1 wherein said hydrofining catalyst comprises a minor proportion of cobalt plus molybdenum supported on a major proportion of a carrier which is essentially activated alumina.

5. A process as defined in claim 1 wherein a gasoline fraction is recovered from said hydrocracking zone and

is thereafter subjected to mild reforming in the presence of added hydrogen and a reforming catalyst at a temperature between about 825° and 950° F. and a space velocity between about 1.0 and 5.0, and wherein the gasoline produced from said reforming step is fractionated to recover a light gasoline boiling below about 300° F., and a heavy fraction boiling above about 300° F., and wherein said heavy fraction is recycled back to said hydrocracking step.

6. A process as defined in claim 1 wherein the hydrocracking in said hydrocracking zone is initiated at a temperature between about 600° and 800° F. and is continued for at least about three months while periodically raising the temperature by an average of not more than about 3° F. per day to maintain a substantially constant conversion per pass therein without intervening oxidative regeneration of said hydrocracking catalyst.

7. A process for producing high-octane gasoline from a mineral oil feedstock boiling above the gasoline range and containing at least one impurity from the class consisting of organic nitrogen and sulfur compounds, which comprises subjecting said feedstock to hydrofining in the presence of added hydrogen and a hydrofining catalyst comprising a minor proportion of a sulfactive transitional metal hydrogenating component supported on a difficultly reducible, non-cracking adsorbent oxide carrier, maintaining hydrofining conditions including temperatures between about 600° and 850° F., and pressures between about 400 and 2,000 p.s.i.g., so as to effect substantial decomposition of said organic sulfur and nitrogen compounds, subjecting total effluent from said hydrofining treatment, without intervening purification to remove the decomposition products of said impurity, to hydrocracking in the presence of added hydrogen and a hydrocracking catalyst comprising a solid refractory cracking component and a Group VIII metal sulfide hydrogenating component, maintaining hydrocracking conditions including space velocities between about 0.5 and 10, temperatures between about 600° and 850° F., and pressures between about 400 and 2,000 p.s.i.g., thereby producing a hydrocracker gasoline containing substantial proportions of monocyclic aromatics and naphthenes, then subjecting said hydrocracker gasoline to reforming in the presence of added hydrogen and a reforming catalyst, maintaining reforming conditions including temperatures between about 825° and 950° F., and pressures between about 200 and 800 p.s.i.g., and recovering high-octane gasoline reformate from said reforming step.

8. A process as defined in claim 7 wherein said gasoline reformate is fractionated to recover a light naphtha boiling below about 300° F., and a heavy fraction boiling above about 300° F., and wherein said heavy fraction is recycled back to said hydrocracking step.

9. A process as defined in claim 7 wherein said feedstock comprises unconverted aromatic cycle oil derived from a non-hydrogenative cracking operation.

10. A process for producing high-octane gasoline from a hydrocarbon feedstock rich in polycyclic hydrocarbons and contaminated with at least about 0.01% by weight of nitrogen in the form of organic nitrogen compounds, said feedstock boiling between about 400° and 900° F., having an API gravity of not greater than 35°, and containing at least about 20% by volume of acid-soluble components, which comprises subjecting said feedstock to hydrofining at a pressure below about 2,000 p.s.i.g. in the presence of added hydrogen and a hydrofining catalyst comprising a minor proportion of a sulfactive transitional metal hydrogenating component supported on a difficultly reducible adsorbent oxide carrier, and under hydrofining conditions adjusted to give a substantial decomposition of said organic nitrogen compounds with resultant formation of ammonia, subjecting total effluent from said hydrofining treatment, without intervening condensation or purification to remove ammonia, to hydrocracking at a space velocity between about 0.5 and 10 and a pressure below about 2,000 p.s.i.g. in the presence of added hydrogen and a hydrocracking catalyst comprising a solid refractory cracking component and a Group VIII metal sulfide hydrogenating component, separating from the hydrocracking effluent a hydrocracker gasoline fraction containing substantial proportions of monocyclic naphthenes, and then, without further purification, subjecting said hydrocracker gasoline to mild reforming in the presence of added hydrogen and a reforming catalyst at a temperature between about 825° and 950° F., and a space velocity between about 1.0 and 5.0, and recovering high octane gasoline from said reforming step.

11. A process as defined in claim 10 wherein said hydrocracking step is carried out at substantially the same pressure as said hydrofining step.

12. An improved, low-pressure process for hydrocracking a mineral oil feedstock boiling above the gasoline range and containing organic nitrogen compounds, which comprises first subjecting said feedstock to catalytic hydrofining under substantially non-cracking conditions in the presence of added hydrogen and a hydrofining catalyst comprising a hydrogenting component from the class consisting of the oxides and sulfides of molybdenum, tungsten and the Group VIII metals supported on a substantially non-cracking inorganic oxide carrier, and under hydrofining conditions adjusted to give a substantial decomposition of said organic nitrogen compounds with resultant formation of ammonia, subjecting effluent from said hydrofining step, without intervening purification to remove ammonia, to a first stage of hydrocracking at a space velocity between about 0.5 and 10 in the presence of a hydrocracking catalyst comprising a solid refractory cracking base and a Group VIII metal sulfide hydrogenating component, treating mixed effluent from said first stage of hydrocracking and the effluent from the hereinafter defined second stage of hydrocracking to separate ammonia and low-boiling hydrocarbons therefrom, subjecting remaining oil boiling above the gasoline range to a second stage of hydrocracking in the presence of hydrogen and a fixed bed of hydrocracking catalyst comprising a solid refractory cracking base and a Group VIII metal hydrogenating component, and combining the effluent from said second stage of hydrocracking with said first-stage hydrocracking effluent to form said mixed effluent, each of said hydrofining and hydrocracking steps being carried out at pressures between about 400–2,000 p.s.i.g., and temperatures between about 450° and 875° F.

13. A process as defined in claim 12 wherein said hydrofining catalyst comprises a small proportion of cobalt and molybdenum deposited upon a carrier which is essentially activated alumina.

14. A process as defined in claim 12 wherein the refractory cracking base employed in at least one of said hydrocracking stages is a coprecipitated composite of silica, zirconia and titania.

15. A process as defined in claim 12 wherein the refractory cracking base employed in at least one of said hydrocracking stages is a partially dehydrated, zeolitic alumino-silicate molecular sieve cracking base of the Y crystal type having a silica/alupmina mole-ratio of at least 2.5, and wherein the zeolitic cations are selected mainly from the class consisting of hydrogen and divalent metals.

16. A process as defined in claim 12 wherein the catalyst empoyled in each of said hydrocracking stages is composed of a partially dehydrated zeolitic alumino-silicate molecular sieve cracking base of the Y crystal type having a silica/alumina mole-ratio of at least 2.5 and wherein the zeolitic cations are selected mainly from the class consisting of hydrogen and divalent metals, and incorporated therein a minor proportion of a Group VIII noble metal hydrogenation component.

17. A process as defined in claim 12 wherein said feedstock contains at least about 0.01% by weight of nitrogen, and the conditions of temperature and space velocity in said hydrocracking stages are adjusted so as to provide a

substantially greater conversion per pass to gasoline in the second stage than in the first stage.

18. A process as defined in claim 12 wherein said first-stage hydrocracking is initiated at a temperature between about 600° and 800° F. and is continued for at least about 3 months while periodically raising the temperature by an average of not more than about 3° F. per day to maintain a substantially constant conversion per pass therein, and wherein said second-stage hydrocracking is initiated at a temperature between about 450° and 800° F. and is continued for at least about 3 months while periodically raising the temperature by an average of not more than about 3° F. per day to maintain a substantially constant conversion per pass therein.

19. A process as defined in claim 18 wherein the catalyst employed in each of said hydrocracking stages is composed of a partially dehydrated zeolitic alumino-silicate molecular sieve cracking base of the Y crystal type having a silica/alumina mole-ratio of at least 2.5 and wherein the zeolitic cations are selected mainly from the class consisting of hydrogen and divalent metals, and incorporated therein a minor proportion of a Group VIII noble metal hydrogenation component.

20. An improved, low-pressure process for hydrocracking gas oils boiling up to about 1,000° F. and containing at least about 0.01% by weight of nitrogen in the form of organic nitrogen compounds, to convert the same to gasoline-boiling-range hydrocarbons at low catalyst coking rates, which comprises first subjecting said gas oil to catalytic hydrofining under substantially non-cracking conditions in the presence of added hydrogen and a hydrofining catalyst comprising a hydrogenating component from the class consisting of the oxides and sulfides of the Group VIB and Group VIII metals supported on a substantially non-cracking inorganic oxide carrier, and under hydrofining conditions adjusted to give a substantial decomposition of said organic nitrogen compounds with resultant formation of ammonia subjecting effluent from said hydrofining step without intervening purification to remove ammonia, to a first stage of hydrocracking at a space velocity between about 0.5 and 10 in the presence of a fixed bed of hydrocracking catalyst comprising a solid refractory cracking base upon which is deposited a Group VIII metal sulfide hydrogenating promoter, cooling and condensing the effluent from said first-stage hydrocracking while water-washing the same to remove substantially all ammonia therefrom, transferring the washed effluent into a gas-liquid separator in admixture with condensed effluent from the second-stage hydrocracking hereinafter defined, recovering hydrogen-rich recycle gas from said separator, recovering liquid condensate from said separator and fractionating the same to recover a gasoline product and a recycle oil boiling above the gasoline range, subjecting said recycle oil in admixture with a portion of said hydrogen-rich recycle gas to a second stage of hydrocracking in the presence of a fixed bed of hydrocracking catalyst comprising a refractory solid cracking base upon which is deposited a Group VIII metal hydrogenating promoter, cooling and condensing the effluent from said second-stage hydrocracking and admitting the same to said gas-liquid separator as previously described, each of said hydrofining and hydrocracking steps being carried out at pressures between about 400 and 2,000 p.s.i.g., and temperatures between about 450° and 875° F.

21. A process as defined in claim 20 wherein the conditions of temperature and space velocity in said hydrocracking stages are adjusted so as to provide a substantially greater conversion per pass to gasoline in the second stage than in the first stage.

22. A process as defined in claim 20 wherein the refractory cracking base employed in each of said hydrocracking stages is a coprecipitated composite of silica, zirconia, and titania.

23. A process as defined in claim 20 wherein the catalyst employed in each of said hydrocracking stages is composed of a partially dehydrated, zeolitic alumino-silicate molecular sieve cracking base of the Y crystal type having a silica/alumina mole-ratio of at least 2.5, and wherein the zeolitic cations are selected mainly from the class consisting of hydrogen and divalent metals, and incorporated therein a minor proportion of a Group VIII noble metal hydrogenating component.

24. A process for converting to lower boiling hydrocarbons a mineral oil feedstock boiling above the gasoline range and containing at least one impurity from the class consisting of organic nitrogen and sulfur compounds, which comprises subjecting said feedstock to hydrofining in the presence of added hydrogen and a sulfactive transitional metal hydrofining catalyst under hydrofining conditions including temperatures between about 600° and 850° F., and pressures between about 400 and about 2,000 p.s.i.g. so as to effect substantial decomposition of said organic nitrogen and sulfur compounds, passing total effluent from said hydrofining step, without intervening purification to remove the decomposition products of said impurity, into a hydrocracking zone and contacting said effluent therein with a hydrocracking catalyst at a space velocity between about 0.5 and 10 and at hydrocracking temperatures effective to give a substantial cracking of hydrocarbons, said hydrocracking catalyst comprising a Group VIII metal sulfide hydrogenation component deposited upon a solid refractory cracking base, the pressure in said hydrocracking zone being less than about 2,000 p.s.i.g., and treating the effluent from said hydrocracking zone to recover low-boiling hydrocarbons.

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