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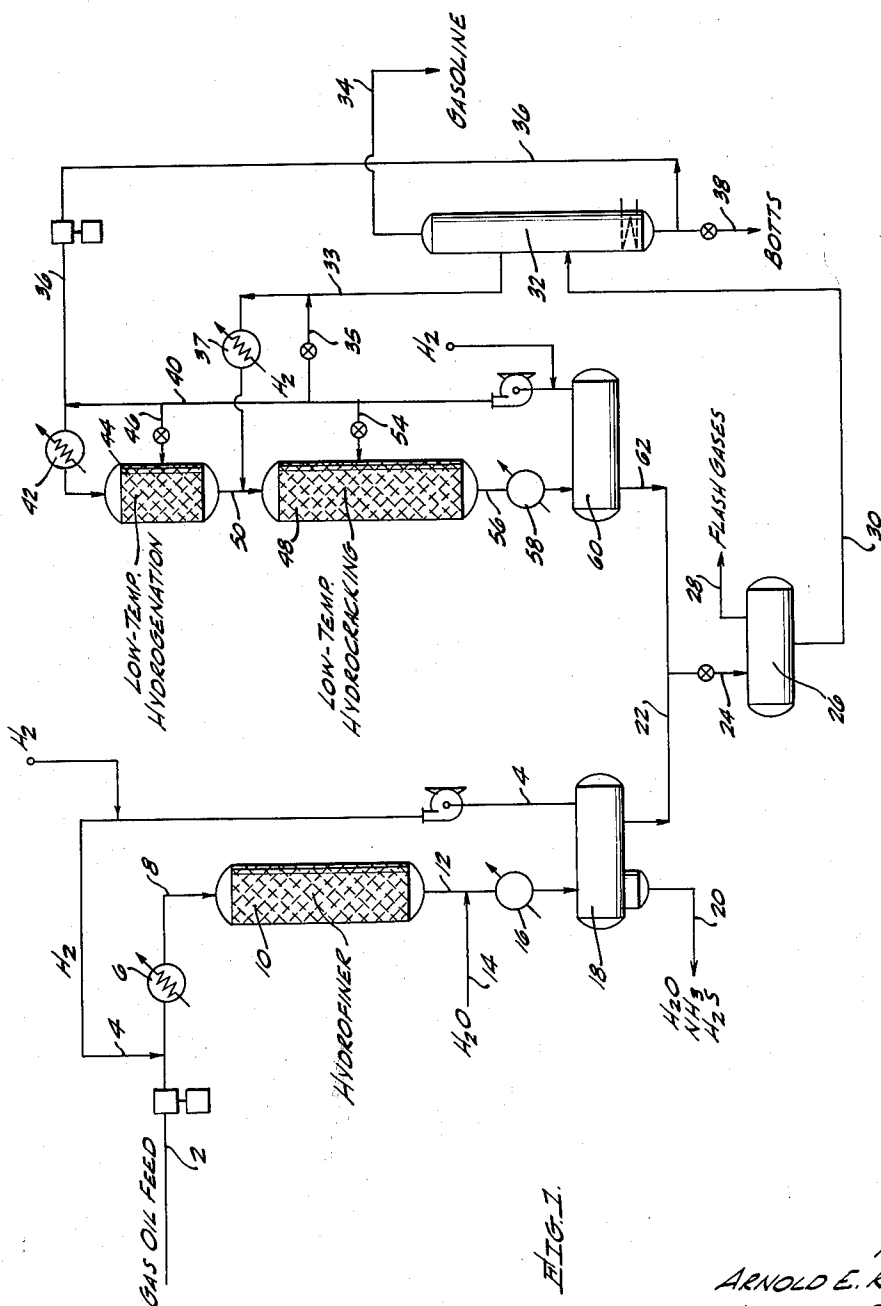
A. E. KELLEY ETAL

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HYDROCRACKING PROCESS WITH PRE-HYDROGENATION

Filed Jan. 23, 1961

2 Sheets-Sheet 1



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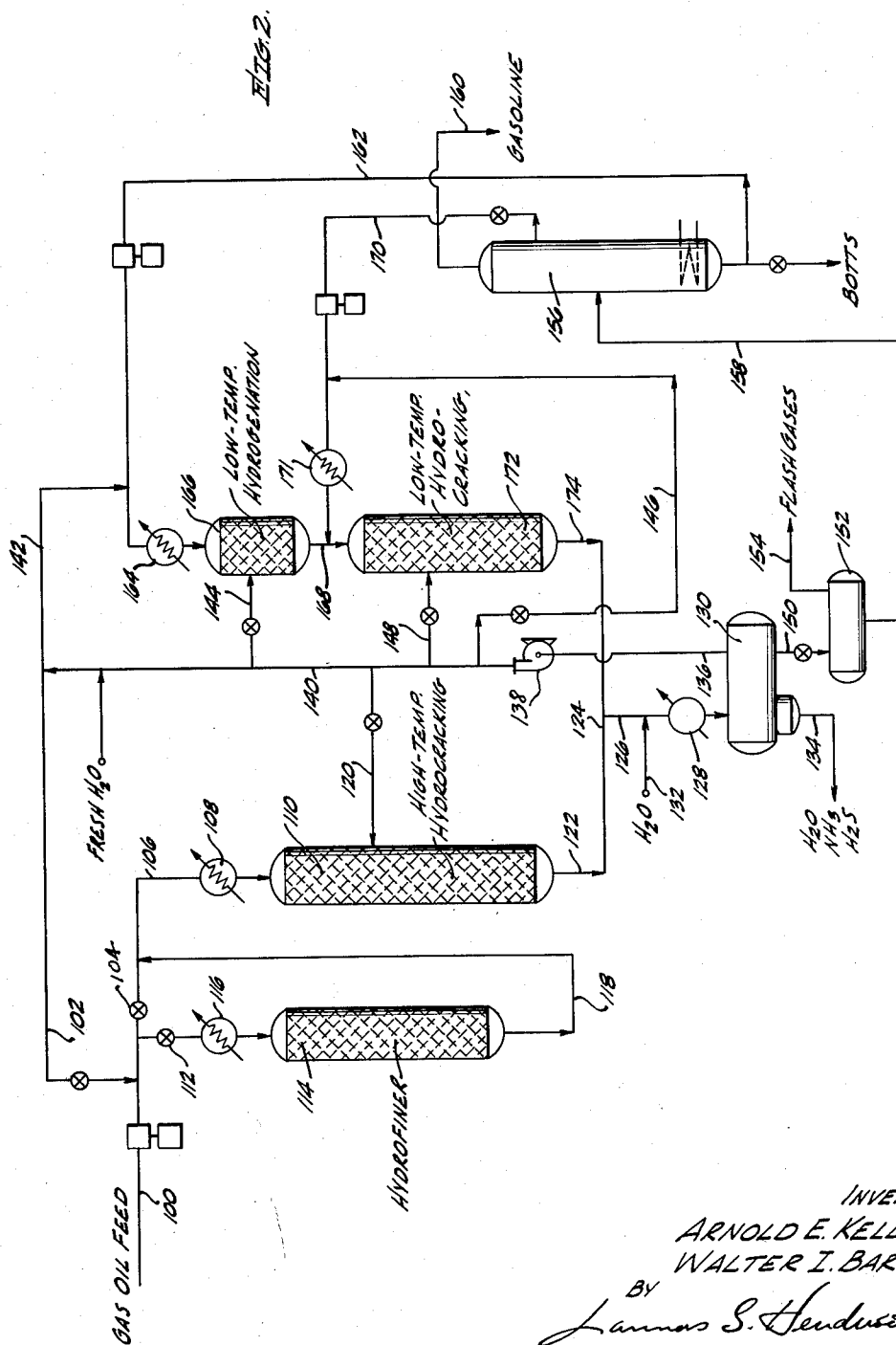
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HYDROCRACKING PROCESS WITH
PRE-HYDROGENATION

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This invention relates to the hydrocracking of high-boiling hydrocarbons to produce therefrom lower boiling hydrocarbons, boiling for example in the gasoline or jet fuel range. The invention is concerned more particularly with certain optimum pre-hydrogenation techniques for conditioning the feedstock so that maximum efficiency and catalyst life are obtainable in hydrocracking operations conducted at relatively low pressures of below about 3,000 p.s.i.g., and relatively low temperatures, below about 725° F. The invention is especially adapted for the hydrocracking of refractory, high-end point feedstocks, containing aromatic components boiling above 600° F., and which may also be contaminated with organic nitrogen compounds and sulfur compounds.

In broad aspect, the invention comprises a combination of (1) a substantially non-cracking, low-temperature pre-hydrogenation step conducted at temperatures below about 725° F., in the presence of a catalyst selected from the class consisting of the oxides and/or sulfides of the group VIB metals and/or of the iron group metals, i.e., iron, cobalt or nickel, followed by (2) a low-temperature hydrocracking step carried out at temperatures below about 725° F. The feed to step (1) must be substantially free from organic nitrogen compounds; where the feed is so contaminated, it is subjected first to a hydrofining and/or hydrocracking treatment, using a transitional metal sulfide-type hydrogenation catalyst at a temperature higher than that used in the low-temperature pre-hydrogenation step. Thus, in a more comprehensive aspect, the invention embraces two distinct prehydrogenation steps, the first serving the purpose of purifying the feed by decomposing non-hydrocarbon impurities, and the second serving the purpose of partially hydrogenating certain hydrocarbon components which are difficult to hydrogenate under conventional hydrofining conditions.

It is well known in the art that hydrocracking catalysts become temporarily poisoned by basic nitrogen compounds in the feedstock. This poisoning effect is evidenced by decreased conversion of the feedstock under a given set of conditions, a tendency which is reversed when the nitrogen compounds are removed from the feedstock. Further, it is known that the poisoning effect of nitrogen compounds can, to some extent, be overcome by operating at higher temperatures. However, the use of higher temperatures leads to increased coking rates and decreased catalyst life, and is hence not a generally feasible solution to the problem. The solution most generally adopted involves pretreating the feedstock, as by catalytic hydrofining, to decompose the organic nitrogen compounds to ammonia, and then sending the nitrogen-free feedstock to the hydrocracking reactor.

It has now been found that the foregoing pre-hydrofining technique does not offer a complete solution to the hydrocracking catalyst deactivation problem, at least in hydrocracking processes conducted at low pressures of below about 3,000 p.s.i.g., and preferably below 2,000 p.s.i.g. It has been found that, even when all of the nitrogen compounds are removed from the feed by hydrofining, there may still be a substantial, progressive deacti-

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vation of the catalyst as the run proceeds. This deactivation problem is particularly acute when using high-boiling feedstocks which contain aromatic components boiling above about 600° F., and up to about 950° F. It is hypothesized that, at the low pressures and temperatures employed, the heavy polycyclic aromatic hydrocarbons become rather permanently adsorbed on the active cracking centers of the catalyst and are not effectively hydrogenated or cracked, thus blocking the active sites. Eventually, the adsorbed polycyclics may be converted to coke-like bodies through reactions of condensation and the like. It would appear that the distribution of active hydrogenation centers on the catalyst is such that they cannot act upon molecules which become first adsorbed on active cracking centers, at least in a substantial number of cases.

It has now been found that this deactivation effect can be substantially avoided if the hydrofined feedstock, containing less than 25, and preferably less than 10 parts per million, of basic nitrogen, is subjected to a further hydrogenation over a catalyst which may be the same as that employed for hydrofining, but using lower temperatures to effect an optimum partial hydrogenation of polycyclic hydrocarbons. With respect to feedstocks containing organic sulfur and/or nitrogen compounds, the invention is based upon the precept that hydrogenating conditions which are optimum for decomposing the organic nitrogen and sulfur compounds are not optimum for the partial hydrogenation of polycyclic hydrocarbons. Catalytic hydro-denitrogenation is most efficient when conducted at relatively high temperatures, i.e., above about 700° F., and preferably above about 725° F. But, in the temperature range of about 725° to 800° F. (and at pressures below about 3,000 p.s.i.g.), the hydrogenation-dehydrogenation equilibrium for partially hydrogenated polycyclic aromatic hydrocarbons is unfavorable for hydrogenation. Hence, it will be seen that temperatures which are best for hydrofining are not optimum for partial hydrogenation of polycyclic aromatics. According to the present invention, provision is made for separate pretreatments under optimum conditions for each.

It is perhaps possible that a single hydrofining operation could be designed to effect both purposes, using for example a cobalt molybdate catalyst. However, this would require either an enormous capital investment in catalyst and reactors to permit operating at low space velocities, or expensive high-pressure equipment and facilities to permit operating at pressures above about 3,000 p.s.i.g.

The dual prehydrogenation treatment of this invention is of little or no benefit (as compared to a single hydrofining treatment) in hydrocracking operations conducted at above about 725° F., assuming pressures below about 3,000 p.s.i.g. Apparently, at hydrocracking temperatures above 725° F., a substantial portion of the partially hydrogenated aromatics tends to dehydrogenate back to the more refractory poly-aromatics before they are hydrocracked, and thus again become available as catalyst deactivators.

From the foregoing, it will be apparent that the principal object of this invention is to provide optimum pre-hydrogenation treatments for feedstocks which are to be subjected to hydrocracking at relatively low temperatures and pressures. A more specific objective is to provide maximum efficiency in a catalytic denitrogenation operation combined with a partial saturation of polycyclic aromatics. Still another object is to provide methods of pretreatment which will permit the efficient hydrocracking of feedstocks containing fractions boiling above about 650° F. Still another object is to improve the efficiency

and extend the catalyst life in hydrocracking operations conducted at below 3,000 p.s.i.g. and below about 725° F. Other objects will be apparent from the more detailed description which follows.

The feedstocks which may be treated herein include in general any mineral oil fraction boiling above the conventional gasoline range, i.e., above about 300° F. and usually above about 400° F., and having an end-boiling point of up to about 900° F. This includes straight-run gas-oils and heavy naphthas, coker distillate gas oils and heavy naphthas, 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 30% 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. Products derived therefrom include gasolines, naphthas, jet fuels, diesel fuels and the like.

Reference is now made to the attached FIGURE 1, which is a flowsheet illustrating the invention in one of its simpler aspects. This modification involves two stages of prehydrogenation, in both of which hydrocracking is minimized. The initial feedstock is brought in via line 2, mixed with recycle and makeup hydrogen from line 4, preheated to hydrofining temperatures in heater 6, and transferred via line 8 to hydrofiner 10, where hydrofining proceeds under substantially conventional conditions. Suitable hydrofining catalysts include for example mixtures of the oxides and/or sulfides of cobalt and molybdenum, or of nickel and tungsten, preferably supported on a carrier such as alumina, or alumina containing a small amount of coprecipitated silica gel. Other suitable catalysts include in general the oxides and/or sulfides of the group VIB and/or group VIII metals, preferably supported on adsorbent oxide carriers such as alumina, silica, titania, and the like. The hydrofining operation may be conducted either adiabatically or isothermally, and under the following general conditions:

HYDROFINING CONDITIONS

	Operative	Preferred
Temperature, ° F.....	675-850	725-825
Pressure, p.s.i.g.....	500-3,000	800-2,000
LHSV, v./v./hr.....	0.5-10	1-5
H ₂ /oil ratio, s.c.f./b.....	500-15,000	1,000-10,000

The above conditions are suitably adjusted so as to reduce the nitrogen content of the feed to below about 25 parts per million, and preferably below about 10 parts per million. The resulting product is then withdrawn via line 12 and mixed therein with wash water introduced via line 14. The mixture is then cooled and condensed in condenser 16 and transferred to high pressure separator 18. Aqueous wash liquor containing dissolved ammonia, hydrogen sulfide, etc., is removed via line 20. Recycle hydrogen is withdrawn and recycled via line 4 as previously described.

Although little or no hydrocracking of hydrocarbons occurs in hydrofiner 10, the liquid product in separator 18 will still contain some hydrocarbons in the gasoline range (e.g., 2 to 15% by volume), which constitute mainly the hydrocarbon fragments from the decomposed nitrogen and sulfur compounds of the feed. This hydrofined product may be sent directly to second hydrogenation reactor 44 and hydrocracker 48, but normally it is preferable to first separate the gasoline fraction. For this purpose, the hydrofined product is advantageously blended with the effluent from the subsequent hydrocracking reactor to

permit simultaneous recovery of the gasoline produced in both operations. The condensate from separator 18 is hence passed via lines 22 and 24 to low pressure separator 26 (along with the liquid product from the hydrocracker). From separator 26, low pressure flash gases are withdrawn via line 28, while the combined liquid product is taken off via line 30 and transferred to fractionating column 32.

The combined gasoline product is withdrawn from column 32 as overhead via line 34. A side-cut fraction boiling above the gasoline range, and normally having an end-boiling-point in the 450°-600° F. range, is withdrawn via line 33, mixed with recycle hydrogen from line 35, preheated to hydrocracking temperatures in preheater 37, and transferred directly to hydrocracker 48, via line 50, in admixture with the total hydrogenated product from low-temperature hydrogenation unit 44. This side-cut fraction is ordinarily sufficiently non-deactivating to be used directly in the low-temperature hydrocracking operation. At least the bulk of the remaining hydrofined gas oil and unconverted cycle oil from the hydrocracker is withdrawn from column 32 as bottoms via line 36 for treatment in low-temperature hydrogenation unit 44. Due to the low-temperature hydrogenation step, the entire bottoms product can be utilized, but sometimes a slipstream is withdrawn via line 38 to prevent the buildup of nonhydrogenatable materials, if such be present. Ordinarily, the recycled bottoms product will amount to about 10-40% by volume of the total feed to the column.

The bottoms fraction in line 36 is then blended with recycle and makeup hydrogen from line 40, and the mixture is passed through preheater 42 and thence into low-temperature hydrogenation reactor 44. Catalysts for use in reactor 44 are selected from the same class of hydrofining catalysts previously described for use in hydrofiner 10. Here again, it is preferred to use the sulfide forms of hydrofining catalyst, since they are found to be more active for hydrogenating aromatic hydrocarbons than the oxide forms. To maintain the catalyst in a sulfided state, small amounts of hydrogen sulfide, or other sulfur compounds, may be added periodically or continuously to the feed, or to the recycle hydrogen. Suitable hydrogenation conditions for use in reactor 44 are as follows:

HYDROGENATION CONDITIONS

	Operative	Preferred
Temperature, ° F.....	500-725	575-700
Pressure, p.s.i.g.....	500-3,000	800-2,000
LHSV, v./v./hr.....	0.5-20	1-15
H ₂ /oil ratio, s.c.f./b.....	500-15,000	1,000-10,000

In addition to the absolute temperature limits specified, it is also required that the average bed temperature in unit 44 be maintained at a lower level than the average bed temperature in hydrofiner 10, preferably about 25°-100° F. lower. Only by maintaining a significant temperature differential between the two reactors is a substantial benefit obtained by the dual prehydrogenation technique. To maintain the desired temperature in reactor 44 (the reaction being exothermic) a portion of the cooled recycle hydrogen in line 40 may be diverted via line 46 to one or more mid-points in the reactor. However, any other desired temperature control means may be utilized.

The effluent from reactor 44 is transferred directly to low-temperature hydrocracking reactor 48 via line 50. Inasmuch as reactors 44 and 48 are preferably operated at the same pressure, it is entirely feasible to enclose both contacting zones within a single reactor, using appropriate temperature control means.

The catalyst employed in reactor 48 may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking

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bases include for example mixtures of two or more refractory oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphate gels such as aluminum phosphate may also be used. The preferred cracking bases comprise composites of silica and alumina containing about 50%-90% silica; composites of silica, titania and zirconia containing between 5% and 75% of each component; decationized, zeolitic, crystalline molecular sieves of the "Y" crystal type, having relatively uniform pore diameters of about 9 to 10 angstroms, and consisting substantially exclusively of silica and alumina in mole-ratios between about 4:1 and 6:1. Any of these cracking bases may be further promoted by the addition of small amounts, e.g., 1 to 10% by weight, of halides such as fluorine or boron trifluoride.

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 20% (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 1.5% 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.

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

A key feature of the process resides in utilizing economically feasible pressures in reactor 48 (below about 3,000 p.s.i.g., and preferably below 2,000 p.s.i.g.), while at the same time utilizing temperatures sufficiently low to avoid the dehydrogenation of the partially hydrogenated polycyclic hydrocarbons which were hydrogenated in reactor 44. At temperatures above about 725° F., the dehydrogenation of these materials become significant and is reflected in a relatively rapid rate of deactivation of the catalyst. However, at temperatures below about 725° F., and preferably below 700° F., it is found that highly efficient hydrocracking, with 30% to 75% conversion per pass, may be maintained for very long periods of time, i.e., for periods of at least about 4 months, and usually more than 8 months. Here again, suitable means may be employed to control the exothermic temperature rise, as for example by injecting cool hydrogen at one or more points in the reactor, as illustrated via line 54. Reaction conditions contemplated for reactor 48 are as follows:

HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F.....	400-725	500-700
Pressure, p.s.i.g.....	500-3,000	800-2,000
LHSV, v./v./hr.....	0.5-15	1-10
H ₂ /oil ratio.....	500-15,000	2,000-12,000

The products from reactor 48 are withdrawn via line 56, condensed in condenser 58 and transferred to high-pressure separator 60. Recycle hydrogen is withdrawn via line 40 and recycled as previously described, while the liquid product is transferred (in admixture with the hydrofiner effluent) via lines 62, 22 and 24, to low pressure separator 26 and column 32, as previously described.

Reference is now made to attached FIGURE 2, which is a flowsheet illustrating a modification of the invention wherein the first stage of hydrogenation also involves a hydrocracking operation. This hydrogenation-hydrocracking combination involves two possible modes of op-

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eration. The first mode presumes that the initial feedstock contains about 2-50 parts per million of nitrogen as organic nitrogen compounds, in which case it may be brought in via line 100, mingled therein with recycle hydrogen from line 102, passed through open valve 104, line 106, preheater 108, and thence directly into high-temperature hydrocracking reactor 110. Valve 112 is closed, thereby bypassing hydrofining reactor 114. In hydrocracker 110, the feed is subjected to hydrocracking conditions at temperatures relatively higher than those to be employed in the subsequent low-temperature hydrogenation and hydrocracking steps. Denitrogenation and desulfurization take place concurrently with hydrocracking. Catalysts suitable for use in hydrocracker 110 may be of the same general type as previously described for use in hydrocracker 48 of FIGURE 1. However, it is preferred to use here a catalyst wherein the hydrogenating component is in the form of a sulfide, e.g., nickel sulfide. Hydrocracking conditions contemplated for reactor 110 are as follows:

HIGH-TEMPERATURE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F.....	600-850	650-800
Pressure, p.s.i.g.....	500-3,000	800-2,000
LHSV, v./v./hr.....	0.5-10	1-5
H ₂ /oil ratio, s.c.f./b.....	500-15,000	1,000-10,000

In cases where the initial feedstock in line 100 contains substantial quantities of organic nitrogen compounds (e.g., more than about 50 parts per million of nitrogen), an alternative operation is preferred, utilizing hydrofiner 114. This alternative may also be utilized for feeds containing less than 50 parts per million of nitrogen, if desired. In either case, valve 104 is closed and valve 112 opened, whereby the feed-hydrogen mixture flows through preheater 116 into hydrofiner 114, where it is subjected to hydrofining, utilizing catalysts and conditions as previously described in connection with hydrofiner 10 of FIGURE 1. The total effluent from hydrofiner 114 is then withdrawn via line 118 and sent via line 106 and preheater 108, to hydrocracking reactor 110, where it is subjected to hydrocracking under the conditions previously described. Preferably, the hydrofining effluent in line 118 is sent directly to hydrocracking, without intervening condensation and separation of ammonia and hydrogen sulfide, but the alternative operation is also contemplated. Removing the ammonia and hydrogen sulfide improves the efficiency of hydrocracking in reactor 110, but entails the added expense of the additional facilities and utilities required. The temperature in reactor 110 may be controlled by the injection of cool recycle hydrogen at one or more midpoints, as illustrated via line 120.

In either of the above alternatives, the effluent from hydrocracker 110 is withdrawn via line 122, blended in line 124 with effluent from the succeeding low temperature hydrocracker, and the resulting blend is then passed via line 126 and condenser 128 to high pressure separator 130. Where the effluent in line 122 contains ammonia and/or hydrogen sulfide, it is preferred to inject wash water into line 126 via line 132, which is later withdrawn from separator 130 via line 134. It will be noted that this modification of the process embraces a single hydrogen recycle system for the entire process. All of the recycle hydrogen is withdrawn from separator 130 via line 136, repressured in blower 138, and distributed via lines 140, 120, 102, 142, 144, 146 and 148 to the various process units.

The liquid condensate in separator 130 is withdrawn via line 150 and flashed into low pressure separator 152, from which C₁-C₃ flash gases are withdrawn via line 154. The liquid product in separator 152 is then transferred to fractionating column 156 via line 158, wherein

it is subjected to fractionation in a manner similar to that described in connection with column 32 of FIGURE 1. Here again, the gasoline product is taken overhead via line 160, and a gas-oil sidecut having an end-boiling-point between about 450° and 600° F. is withdrawn via line 170, blended with recycle hydrogen from line 146, passed through preheater 171, and thence directly into low-temperature hydrocracking unit 172. The bottoms product from column 156, or at least the major portion thereof, is transferred via line 162 and preheater 164 to low-temperature hydrogenation unit 166, in admixture with recycle hydrogen from line 142. The total effluent from hydrogenation unit 166 is then transferred via line 168 to low-temperature hydrocracking unit 172, in admixture with the sidecut fraction from line 170.

The catalysts and conditions of reaction to be utilized in hydrogenation unit 166 and hydrocracking unit 172 are substantially the same as those previously described in connection with hydrogenation unit 44 and hydrocracking reactor 48, respectively, of FIGURE 1, and hence will not be again described. The effluent from hydrocracking reactor 172 is withdrawn via line 174, blended with the product from line 122, and the blend is then treated as previously described for recovery of gasoline and unconverted gas oil feed for units 166 and 172.

The particular advantage of the combined process of FIGURE 2 resides primarily in the obtaining of an appreciable conversion of the initial feedstock to gasoline by an operation which is substantially integral with the pre-hydrofining treatment. It has been found that where the initial feedstock is low in nitrogen, or if high in nitrogen has been treated by hydrofining to convert the organic nitrogen to ammonia, a substantial degree of hydrocracking may be carried out economically in reactor 110 before the product is condensed to remove ammonia and hydrogen sulfide. This hydrocracking operation is not as efficient in absolute terms as the hydrocracking in reactor 172, but is advantageous because the added conversion can be obtained at a total cost which does not greatly exceed the cost of hydrofining alone. Thus, by converting about 15 to 35% of the feed to gasoline in hydrofiner 114 and hydrocracker 110, the size of units 166 and 172 may be appreciably reduced thereby reducing the overall capital investment. The key to the success of this operation resides in maintaining higher temperatures in hydrocracker 110 (e.g., 50–100° F. higher than in hydrocracker 172), thereby permitting a 10 to 25% conversion to gasoline without encountering rapid deactivation of the catalyst as a result of the nitrogen and sulfur present.

The following examples are cited to illustrate the critical novel features of the invention, but are not to be construed as limiting in scope.

Example I

This example illustrates the difficulty encountered in obtaining adequate pretreatment of hydrocracking feedstocks by hydrofining alone, and also illustrates conditions required to achieve adequate pre-hydrogenation of polycyclic aromatic hydrocarbons with hydrofining catalysts.

The initial feedstock was a heavy coker distillate gas-oil obtained by the delayed coking of a California crude oil, and boiling between about 417° and 860° F. (5 to 95% boiling points, Engler). This feedstock contained about 0.363 weight-percent nitrogen, and 2.1% sulfur. It had an API gravity of 21.9°, an aniline point of 120° F., and contained 65 weight-percent acid-soluble components.

Hydrofining.—The foregoing feedstock was subjected to hydrofining at 1,800 p.s.i.g., 0.5 LHSV, average bed temperatures 755° to 760° F., employing 5,000 s.c.f. of hydrogen per barrel. The catalyst was a presulfided cobalt oxide-molybdenum oxide-alumina catalyst containing the equivalent of about 3% CoO and 15% MoO₃. Analysis of the hydrofined product showed that the sulfur content had been reduced to 19 parts per million, and the basic nitrogen content to 1 part per million. However,

it still contained a substantial proportion of aromatic components, as indicated by an acid-solubility of 25%. By ultraviolet spectranalysis it was found to contain 3.7% by weight of naphthalenic compounds, and substantial amounts of higher polycyclic hydrocarbons, as indicated in Table I below. It will be shown in Example II that this hydrofined product rapidly deactivates a hydrocracking catalyst when the hydrocracking is conducted at low temperatures and pressures.

TABLE I

Product analysis, wt. percent:

Naphthalenes	3.7
Biphenyls	2.0
Triaromatics	0.94
Benzofluorenes	0.12
Pyrenes	0.114

It has been found that, by subjecting this product to further hydrogenation over the same type of hydrofining catalyst, but at 700° F. and 1.0 space velocity, at least about 90% of the remaining naphthalenes and biphenyls are hydrogenated to tetralin and decalin, and an even higher proportion of the polycyclics are hydrogenated to non-deactivating materials. It should be noted that the tricyclic and higher aromatic hydrocarbons will deactivate the hydrocracking catalyst at a substantially faster rate than the bicyclic aromatics. Hence, the feasibility of fractionating the hydrofined product and subjecting only the heavy ends to the low temperature hydrogenation, while sending the light fraction containing most of the bicyclics, but substantially no tricyclic and higher materials, directly to hydrocracking.

Example II

The hydrofined product of Example I (having an API gravity of 30.8°, and an Engler boiling range of about 400°–790° F.), without further hydrogenation, was subjected to low-temperature hydrocracking, using a highly active catalyst consisting of a copelleted mixture of 50% powdered activated alumina, and 50% of a powdered commercial isomerization catalyst comprising 0.5% of palladium impregnated upon a decationized, zeolitic "Y" type molecular sieve having a uniform pore diameter of about 9–10 Å., and composed of 75±1% SiO₂, 25±1% Al₂O₃ and about 1.5% NaO. This palladium-impregnated molecular sieve is a commercial isomerization catalyst manufactured by Linde Co., Tonawanda, N.Y., under the trade name "MB 5390." Upon subjecting the feedstock to hydrocracking over the composite catalyst at 550° F., 1,500 p.s.i.g., 1.0 LHSV, with 10,000 s.c.f. of hydrogen per barrel of feed, a 68.3% average conversion to gasoline and lighter materials was obtained over a 12-hour run. However, the API gravity of progressive product cuts taken at 2-hour intervals dropped from 58.9 to 48.4 over the run, showing that the conversion was dropping rapidly. It is hence apparent that the catalyst was being rapidly deactivated, as was confirmed by continuing the run another 4 hours, at which point the product gravity had dropped to 44.1, which corresponds to a conversion of about 39%.

In contrast to the foregoing, when the hydrofined feed is subjected to further hydrogenation over the same hydrofining catalyst, but at a temperature of 675° F. and a space velocity of 1.0, and is then hydrocracked at 550° F., substantially higher conversions and lower deactivation rates are observed. After 16 hours on stream, the conversion to gasoline and lighter materials is greater than 50%, as contrasted to the 39% conversion obtained at this point when hydrocracking the hydrofined feed without intermediate low-temperature hydrogenation. Moreover, this is substantially the equilibrium conversion level, indicating that the catalyst is not being further deactivated by the small remaining proportion of polycyclic aromatics present.

This example demonstrates that even with the best possible pre-hydrogenation of the feed, unsatisfactory results are obtained in subsequent hydrocracking operations conducted at temperatures above 725° F., at least in terms of catalyst deactivation rates. It also demonstrates the actual deleterious effects of polycyclic aromatics in low-pressure hydrocracking.

The primary feedstock was a light coker gas oil boiling between 400° and 600° F., having an API gravity of 30.3, and containing 2% by weight of sulfur, 0.15% nitrogen, and 51 volume percent acid solubles. The initial pre-hydrogenation treatment was an integral hydrofining-hydrocracking combination as illustrated in FIGURE 2. The hydrofining conditions were: temperature 725°–750° F., pressure 1,575 p.s.i.g., space velocity 2.0, H₂/oil ratio 5,000 s.c.f./b. The hydrofining catalyst was the same as in Example I. Hydrocracking of the hydrofiner effluent in reactor 110 was carried out at 1,500 p.s.i.g. and about 750° F., over a hydrocracking catalyst consisting of a coprecipitated composite of the oxides of nickel, silica, zirconia and titania (NiO—25%, SiO₂—15%, ZrO₂—37.5%, TiO₂—22.5%), the entire composition having been completely presulfided. Notwithstanding the presence of ammonia in the hydrocracking zone, about 21% by volume of the feed was converted to gasoline in the hydrofining-hydrocracking combination, and recovered by distillation. The unconverted gas oil was essentially free of nitrogen and sulfur, but still contained a substantial proportion of monocyclic and polycyclic aromatics, as indicated in Table 2 below. This unconverted oil (blended with a smaller proportion of a hydrocracking cycle oil of similar characteristics) was then used as the experimental feedstock in the following comparisons:

A. A portion of the experimental feedstock was fractionated to recover a 20% bottoms fraction boiling above about 550° F., and the bottoms fraction was treated with activated alumina to adsorb heavy aromatics, then rebled with the 80% overhead fraction, giving hydrocracking feed "A."

B. Another portion of the 550° F.+ bottoms fraction prepared as in "A" above, was hydrogenated at 550° F. and 1,500 p.s.i.g. over a 0.5% platinum on alumina catalyst, using 10,000 s.c.f. of hydrogen per barrel of feed. The hydrogenated product was then rebled with its aliquot of 80% overhead, giving hydrocracking feed "B."

C. Hydrocracking feed "C" was a portion of the untreated experimental feedstock.

Ultraviolet spectranalysis of the above feeds showed the following aromatics contents:

TABLE 2

Aromatics	Feed A (Al ₂ O ₃ - treated)	Feed B (Hydro- genated)	Feed C (Un- treated)
Monocyclic, wt. percent.....	25.4	23.7	24.6
Naphthalenes, wt. percent.....	2.2	1.8	2.56
Biphenyls, wt. percent.....	1.06	0.9	1.29
Tri-aromatics, wt. percent.....	0.008	0.009	0.138

It will be seen that the tri-aromatics were markedly reduced, both by the hydrogenation and alumina treatments. But in the case of hydrogenation, the partially hydrogenated tricyclics and bicyclics still remain in the product, while they were physically removed by the alumina treatment.

Each of the foregoing stocks was then subjected to hydrocracking at 1,500 p.s.i.g. over the sulfided nickel-silica-zirconia-titania catalyst used in the initial hydrocracking treatment, while gradually raising the temperature so as to maintain a substantially constant conversion of about 60%, the rate of catalyst deactivation then being measurable in terms of the average daily temperature in-

crease requirement (TIR) to maintain constant conversion. The results were as follows:

TABLE 3

Run No.-----	1	2	3
Feed-----	A (Al ₂ O ₃ - treated)	B (Hydro- genated)	C (Un- treated)
Length of run, hrs.-----	56	56	72
Temperature range over run, ° F.-----	725-731	734-750	748-777
Temperature increase per day, ° F. (TIR)-----	2.9	6.9	9.4
Average vol. percent conversion---	63.8	60.2	57.7

It will thus be seen that, at hydrocracking temperatures above about 725° F., the hydrogenated feed B was only slightly better than the untreated feed, in respect to catalyst deactivation rates. However, feed A, from which the tri-aromatics and higher had been physically removed gave markedly improved results. As indicated in Example II, however, feed B would have given satisfactory results at lower hydrocracking temperatures.

Results analogous to those indicated in the foregoing examples are obtained when other hydrogenation catalysts, hydrocracking catalysts and conditions described herein are employed. It is hence not intended to limit the invention to the details of the examples, but only broadly as defined in the following claims.

We claim:

1. A process for hydrocracking a mineral oil feedstock containing polycyclic aromatic hydrocarbons boiling above about 600° F. and organic nitrogen compounds, and boiling above the gasoline range to produce therefrom hydrocarbons boiling in the gasoline range, which comprises subjecting said feedstock to an initial hydrogenation at a temperature between about 600° and 850° F. and in the presence of a hydrogenation catalyst selected from the class consisting of the group VIB and group VIII metal sulfides separating ammonia and hydrogen sulfide from the denitrogenated product and fractionating the liquid product to recover a light gas oil fraction boiling between about 400° and 600° F. and a heavier fraction, subjecting at least a portion of said heavier fraction to a second hydrogenation under non-cracking conditions in the presence of a hydrofining catalyst selected from the class consisting of the oxides and sulfides of iron, cobalt, nickel and the group VIB metals and at an average bed temperature which is (a) lower than the average bed temperature employed in said initial hydrogenation, and (b) between about 500° and 750° F.; then subjecting the hydrocarbon product from said second hydrogenation plus said light gas oil fraction to catalytic hydrocracking at a temperature between about 400° and 725° F. in the presence of a hydrocracking catalyst comprising a group VIII metal hydrogenating component, and under conditions adjusted to give at least about 30% conversion per pass to 400° F. end-point gasoline, recovering gasoline-boiling-range hydrocarbons from the hydrocracked product, and continuing said catalytic hydrocracking for a total operating period of at least about 4 months without regeneration of said hydrocracking catalyst, said initial hydrogenation, said second hydrogenation and said hydrocracking step all being conducted at pressures between about 500 and 3,000 p.s.i.g.

2. A process as defined in claim 1 wherein said initial hydrogenation is carried out under substantially non-cracking conditions at an average bed temperature between about 675° and 850° F., using a metal sulfide hydrogenation catalyst which is substantially devoid of cracking activity.

3. A process as defined in claim 1 wherein said feedstock contains between about 2 and 50 parts per million of basic nitrogen, and wherein said initial hydrogenation is carried out under mildly hydrocracking conditions at

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temperatures between about 600° and 850° F. in the presence of a hydrocracking catalyst comprising a group VIII metal sulfide hydrogenation component deposited upon a refractory oxide cracking base.

4. A process as defined in claim 1 wherein said second hydrogenation is carried out at an average bed temperature at least 25° F. lower than the average bed temperature of said initial hydrogenation.

5. A process as defined in claim 1 wherein each of said hydrogenation and hydrocracking steps are carried out at pressures below about 2,000 p.s.i.g.

6. A process for hydrocracking a mineral oil feedstock containing polycyclic aromatic hydrocarbons boiling above about 600° F. and organic nitrogen compounds, and boiling above the gasoline range, to produce therefrom hydrocarbons boiling in the gasoline range, which comprises subjecting said feedstock to an initial catalytic hydrofining treatment at a temperature between about 675° and 850° F., subjecting the hydrofining effluent, without intervening separation of ammonia, to a first catalytic hydrocracking at a temperature between about 600° and 850° F., and in contact with a hydrocracking catalyst comprising a group VIII metal sulfide hydrogenation component deposited upon a refractory oxide cracking base, treating the product from said first hydrocracking step to separate ammonia, gasoline, a light gas oil boiling between about 400° and 600° F., and a remaining bottoms fraction, subjecting at least a portion of said bottoms fraction to a second hydrogenation under non-cracking conditions in the presence of a hydrofining catalyst selected from the class consisting of the oxides and sulfides of iron, cobalt, nickel and the group VIB metals, and at an average bed temperature which is (a) lower than the average bed temperature employed in said initial hydrofining, and (b) between about 500° and 750° F.; then subjecting the hydrocarbon product from said second hydrogenation plus said light gas oil fraction to a second catalytic hydrocracking at a temperature between about 400° and 725°

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F. and in the presence of a hydrocracking catalyst comprising a group VIII metal hydrogenating component, and under conditions adjusted to give at least about 30% conversion per pass to 400° F. end-point gasoline, recovering gasoline-boiling-range hydrocarbons from the hydrocracked product, and continuing said catalytic hydrocracking for a total operating period of at least about 4 months without regeneration of said hydrocracking catalyst, all of said hydrofining hydrogenation and hydrocracking steps being conducted at pressures between about 500 and 3,000 p.s.i.g.

7. A process as defined in claim 6 wherein said second hydrogenation is carried out at an average bed temperature at least 25° F. lower than the average bed temperature of said initial hydrofining treatment.

8. A process as defined in claim 6 wherein each of said hydrofining hydrogenation and hydrocracking steps are carried out at pressures below about 2,000 p.s.i.g.

9. A process as defined in claim 6 wherein said first hydrocracking step is carried out at a substantially higher temperature than said second hydrocracking step.

10. A process as defined in claim 6 wherein unconverted gas oil recovered from the effluent from said second hydrocracking step is fractionated to recover a light recycle gas oil boiling between about 400° and 600° F., and a remaining recycle bottoms fraction, and wherein said light recycle gas oil is recycled directly to said second hydrocracking step, and said recycle bottoms fraction is recycled to said second hydrogenation step.

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