May 5, 1964   R. H. HASS ETAL   3,132,089
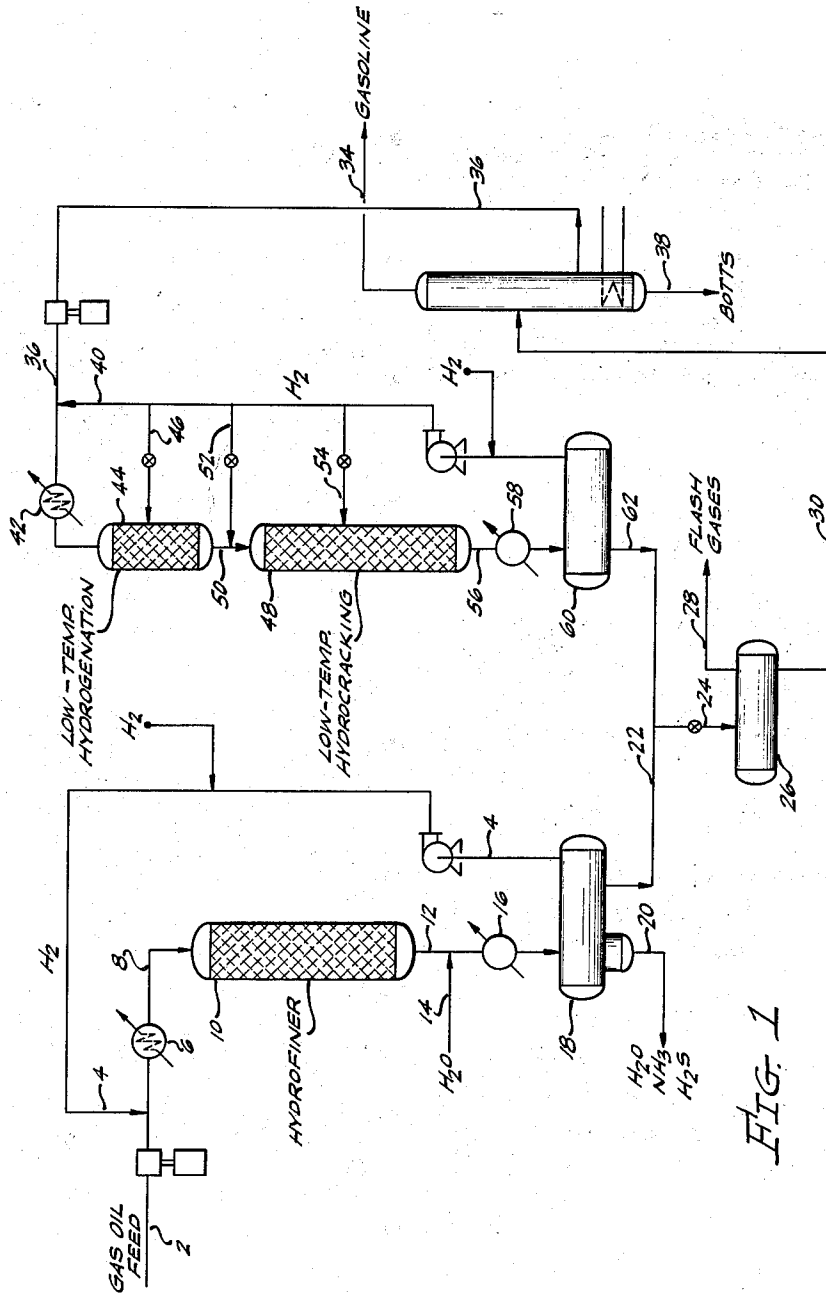   HYDROCRACKING PROCESS WITH PRE-HYDROGENATION
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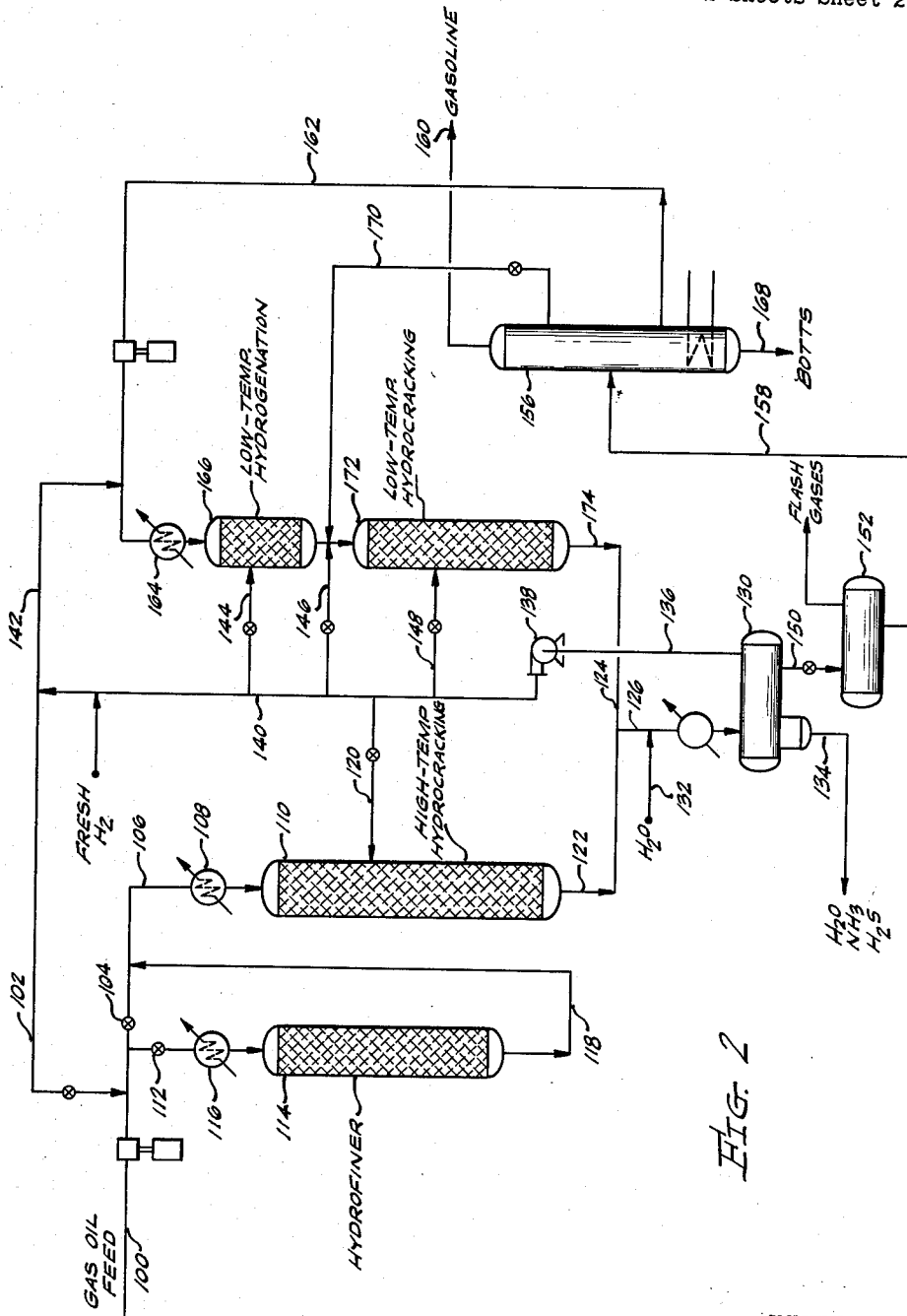   2 Sheets-Sheet 1

FIG. 1

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FIG. 2

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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 particu-
larly with certain optimum pre-hydrogenation techniques
for conditioning the feedstock so that maximum effi-
ciency 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 feed-
stocks, 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 combina-
tion of (1) a substantially non-cracking pre-hydrogena-
tion step conducted at temperatures below about 725° F.,
and utilizing an active group VIII, free-metal hydro-
genation catalyst, followed by (2) a hydrocracking step
carried out at temperatures below about 725° F. The
feed to step (1) must ordinarily be substantially free from
organic nitrogen compounds; where the feed is so con-
taminated, it is normally subjected first to a hydrofining
and/or hydrocracking treatment, using a transitional
metal sulfide-type hydrogenation catalyst at a tempera-
ture which is normally, though not necessarily, higher
than the temperature used in the free-metal hydrogena-
tion step. Thus, in a more comprehensive aspect, the
invention embraces two distinct pre-hydrogenation 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 hydrogen-
ate under conventional hydrofining conditions.

It is well known in the art that hydrocracking catalysts
become temporarily poisoned by basic nitrogen com-
pounds in the feedstock. This poisoning effect is evi-
denced 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 over-
come 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 gen-
erally feasible solution to the problem. The solution
most generally adopted involves pretreating the feed-
stock, as by catalytic hydrofining, to decompose the or-
ganic nitrogen compounds to ammonia, and then send-
ing the nitrogen-free feedstock to the hydrocracking re-
actor.

It has now been found that the foregoing pre-hydro-
fining 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 hydro-
fining, there is still a substantial, progressive deactivation
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

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hypothesized that, at the low pressures and temperatures
employed, the heavy polycyclic aromatic hydrocarbons
become rather permanently adsorbed on the active crack-
ing centers of the catalyst and are not effectively hydro-
genated, 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 cen-
ters on the catalyst is such that they cannot act upon
molecules which become first adsorbed on active crack-
ing 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, con-
taining less than 25 and preferably less than 10 parts per
million of basic nitrogen, is subjected to a further hydro-
genation, using catalysts and conditions selected so as to
effect a partial hydrogenation of polycyclic hydrocar-
bons. Ordinarily, this second hydrogenation is con-
ducted at a lower temperature than the hydrofining step,
but since the catalyst used in the second hydrogenation
is intrinsically more active for hydrogenating aromatics
than was the hydrofining catalyst, substantial beneficial
effects are obtainable even at temperatures similar to
those used in the hydrofining step.

With respect to feedstocks containing organic sulfur
and/or nitrogen compounds, the invention is based upon
the precept that hydrogenating conditions and catalysts
which are optimum for decomposing the organic nitro-
gen and sulfur compounds are not optimum for the
partial hydrogenation of polycyclic hydrocarbons. In
hydrofining operations, the catalyst must not be sensitive
to poisoning by nitrogen and sulfur compounds, and this
in itself precludes the use of catalyst which are most
effective for hydrogenating aromatic hydrocarbons.
Catalysts of the cobalt-molybdate type, or sulfided forms
thereof, are most effective for desulfurization and de-
nitrogenation, while metallic catalysts such as platinum
or nickel are most effective for hydrogenating aromatics,
as compared to the corresponding oxides or sulfides.
Moreover, denitrogenation is most efficient when con-
ducted at relatively high temperatures, i.e., above about
700° F., and preferably above about 725° F. In the
temperature range of about 700° to 800° F., the hydro-
genation-dehydrogenation equilibrium for partially hy-
drogenated polycyclic aromatic hydrocarbons is unfavor-
able for hydrogenation. Hence, it will be seen that the
catalysts and temperatures which are best for hydrofining
are not optimum for partial hydrogenation of polycyclic
aromatics. According to the present invention, the two
operations are hence conducted separately under opti-
mum conditions for each.

It is perhaps possible that a single hydrofining opera-
tion 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.

From the foregoing, it will be apparent that the prin-
cipal 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 opera-
tion combined with a partial saturation of polycyclic
aromatics. Still another object is to provide methods of
pretreatment which will permit the efficient hydrocrack-
ing 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 sulphur 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 this 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.	650–850	700–825
Pressure, p.s.i.g.	500–3,000	800–2,000
LHSV, v./v./hr.	0.5–10	1–5
H₂/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 or 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 product of

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 as overhead via line 34, and at least the bulk of the remaining hydrofined gas oil and unconverted cycle oil from the hydrocracker is withdrawn as a side-cut via line 36 for treatment in the hydrocracker. Due to the second hydrogenation step to be subsequently employed, the entire bottoms product from column 32 can be utilized, but sometimes a small bottoms fraction is withdrawn via line 38 to prevent the buildup of non-hydrogenatable materials, if such be present. Ordinarily this bottoms product will amount to only about 1 to 10% by volume of the total feed to the column. In most cases however it is possible to recycle via line 36 the entire bottoms product from column 32, i.e., the entire fraction boiling above the gasoline range.

The gas oil 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 second hydrogenation reactor 44. The preferred catalysts for use in unit 44 comprise the group VIII metals in finely-divided free form, deposited upon a substantially neutral adsorbent carrier such as alumina, activated charcoal, zirconia, titania and the like. As active hydrogenating components, the metals platinum, palladium, rhodium, iridium, ruthenium, nickel, cobalt and iron are specifically contemplated. The noble metals are ordinarily used in amounts of about 0.1 to 2% by weight, while the iron group metals are used in amounts of about 2% to 20% by weight. Suitable hydrogenation conditions for use in reactor 44 are as follows:

HYDROGENATION CONDITIONS

	Operative	Preferred
Temperature, ° F.	400–725	500–700
Pressure, p.s.i.g.	500–3,000	800–2,000
LHSV, v./v./hr.	0.5–20	1–15
H₂/oil ratio, s.c.f./b.	500–15,000	1,000–10,000

It may be noted that the above conditions overlap somewhat upon those specified for the hydrofining operation. The use of the preferred metallic catalysts on reactor 44 makes it feasible to use the same or higher temperatures therein than the temperatures used in hydrofiner 10. However, it is preferred in most cases to use lower temperatures. 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. If desired, additional cool hydrogen may be injected into line 50 via line 52 in order to bring the mixture to the desired initial hydrocracking temperature.

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 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" crys-

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tal 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 normally 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 temperatures 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, s.c.f./b	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 the 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 first hydrogenation-hydrocracking stage involves two possible modes of operation. 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

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to be employed in the subsequent low-temperature hydrocracking step. 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 C_1–C_3 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, or the total bottoms fraction, is withdrawn via line 162, blended with recycle hydrogen from line 142, passed through preheater 164, and into low temperature hydrogenation unit 166. In rare cases where it is necessary to withdraw a bottoms product from column 156, this is done via line 168. According to one modification of the process, a light sidecut may be withdrawn

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from column 156 via line 170, and sent directly into low temperature hydrocracking reactor 172, thus bypassing the hydrogenation unit 166. This particular modification is advantageous where the lighter portion of the gas-oil to be hydrocracked (e.g., the fraction boiling below about 500° F.) is relatively lean in polycyclic aromatic hydrocarbons, i.e., contains less than about 5% by weight thereof. In most cases however, it is preferred to send substantially the entire gas oil fraction boiling above gasoline from column 156 through low-temperature hydrogenation unit 166.

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 expense. 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 the critical conditions required to achieve adequate pre-hydrogenation of polycyclic aromatic hydrocarbons.

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%

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by weight of naphthalenic compounds, and substantial amounts of higher polycyclic hydrocarbons, as indicated in Table 1, 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.

To demonstrate the feasibility of further improving this product for use as a hydrocracking feedstock, several hydrogenation runs were carried out over an activated charcoal catalyst containing about 1 weight-percent of platinum. All runs were carried out at 2 space velocity, and at temperatures indicated in Table 1. Analyses of the respective products for aromatic types gave the following results:

TABLE 1

Product Analyses, wt. percent	Feed	Hydrogenation Temperature, ° F.			
		503	550	600	657
Naphthalenes	3.7	0.96	0.42	0.29	0.34
Biphenyls	2.0	0.64	0.28	0.16	0.19
Triaromatics	0.94	0.135	0.016	0.01	0.02
Benzofluorenes	0.12	0.037	0.017	0.012	0.014
Pyrenes	0.114	0.009	0.002	0.002	0.007

This is thus evident that hydrogenation under any of the foregoing conditions substantially reduced the amount of polycyclic aromatic hydrocarbons present in the feedstock. It would further seem that optimum results are obtained at temperatures between about 600° and 657° F. However, substantial beneficial results are obtained at temperatures up to about 725° F.

Example II

The hydrofined feedstock of Example I (having an API gravity of 30.8°, and an Engler boiling range of about 400–790° F.) 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 A, 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%.

The foregoing run was repeated except that the feed was first passed over a bed of 0.5% platinum-on-alumina hydrogenation catalyst, and thence directly into the hydrocracking zone. The hydrogenation conditions were substantially the same as the hydrocracking conditions. Over a period of 12 hours, the average conversion to gasoline and lighter materials was above 95%, and the API gravity of the 2-hour product cuts dropped only from 63.6 to 60.5, demonstrating a much lower rate of activity decline, and better cracking efficiency.

This run was then continued for another 40 hours at a reduced temperature of 525° F., during which time the conversion dropped from about 60% to about 35.5%. However, most significantly, during the last 14 hours of the run, the API gravity of the progressive 2-hour product cuts was substantially constant (43.9, 43.7, 44.1, 42.7,

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42.8, 42.9 and 42.8), proving that the rate of catalyst deactivation had levelled out. At this point the hydrocracking temperature was again raised to 550° F., for 12 hours, and the conversion rose to 49.5% and remained substantially constant at that level, as indicated by 2-hour progressive product cut gravities of 46.6, 47.1, 46.7, 47.5, 47.1 and 46.9. Hence, even at 550° F., the catalyst activity was remaining substantially constant, indicating a steady state condition.

Example III

This example demonstrates that even with optimum prehydrogenation 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 reblended 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 reblended with its aliquot of 80% overhead, giving hydrocracking feed "B."

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

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

TABLE 2

Aromatics	Feed A (Al₂O₃-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 hy-

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

TABLE 3

Run No.	1	2	3
Feed	A (Al₂O₃-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 boiling above the gasoline range, and containing polycyclic aromatic hydrocarbons boiling above about 600° F. and organic nitrogen compounds, to produce therefrom hydrocarbons boiling in the gasoline range, which comprises:

(A) subjecting said feedstock plus added hydrogen to an initial catalytic hydrofining treatment at a temperature between about 650° and 850° F. in the presence of a hydrofining catalyst selected from the class consisting of the group VIB and group VIII metal sulfides supported on a substantially neutral adsorbent carrier;

(B) subjecting the effluent from said hydrofining without intervening separation of ammonia, to a first catalytic hydrocracking at a temperature between about 600° and 850° F., in contact with a hydrocracking catalyst comprising a group VIII metal sulfide hydrogenation component supported upon a refractory oxide cracking base selected from the class consisting of silica-alumina cogels, zeolitic alumino-silicate molecular sieves, and halide-promoted cracking bases;

(C) treating the product from said first hydrocracking step to separate out ammonia, gasoline, and unconverted gas oil;

(D) subjecting said unconverted gas oil to a second hydrogenation under non-cracking conditions at a temperature which is (a) between about 400° and 700° F. and (b) lower than the hydrofining temperature employed in step (A), and in the presence of a metallic group VIII noble metal hydrogenation catalyst supported on a substantially neutral adsorbent carrier;

(E) subjecting the hydrocarbon effluent from said second hydrogenation to a second catalytic hydro-

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cracking at a temperature which is (*a*) between about 400° and 725° F. and (*b*) lower than the temperature employed in said first hydrocracking step (B), and in the presence of a hydrocracking catalyst comprising a group VIII noble metal supported on a refractory cracking base selected from the class consisting of silica-alumina cogels, zeolitic aluminosilicate molecular sieves, and halide-promoted cracking bases;

(F) recovering gasoline-boiling-range hydrocarbons from the hydrocracked product from step (E), and wherein

(G) all of said hydrofining, hydrogenation and hydrocracking steps are conducted at pressures between about 500 and 3,000 p.s.i.g.

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

3. A process as defined in claim 1 wherein unconverted gas oil recovered from the effluent from said second hydrocracking step is recycled to said second hydrogenation step.

4. A process as defined in claim 1 wherein said substantially neutral adsorbent carrier used in steps (A) and (D) is activated alumina.

5. A process as defined in claim 1 wherein said refractory cracking base used in steps (B) and (E) is a de-

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cationized crystalline molecular sieve of the Y crystal type wherein the mole-ratio of silica/alumina is between about 4/1 and 6/1.

6. A process as defined in claim 1 wherein the group VIII noble metal on said hydrocracking catalyst used in step (E) is palladium.

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