

[54] HYDROCRACKING-HYDROGENATION PROCESS

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[58] Field of Search 208/59, 143, 144

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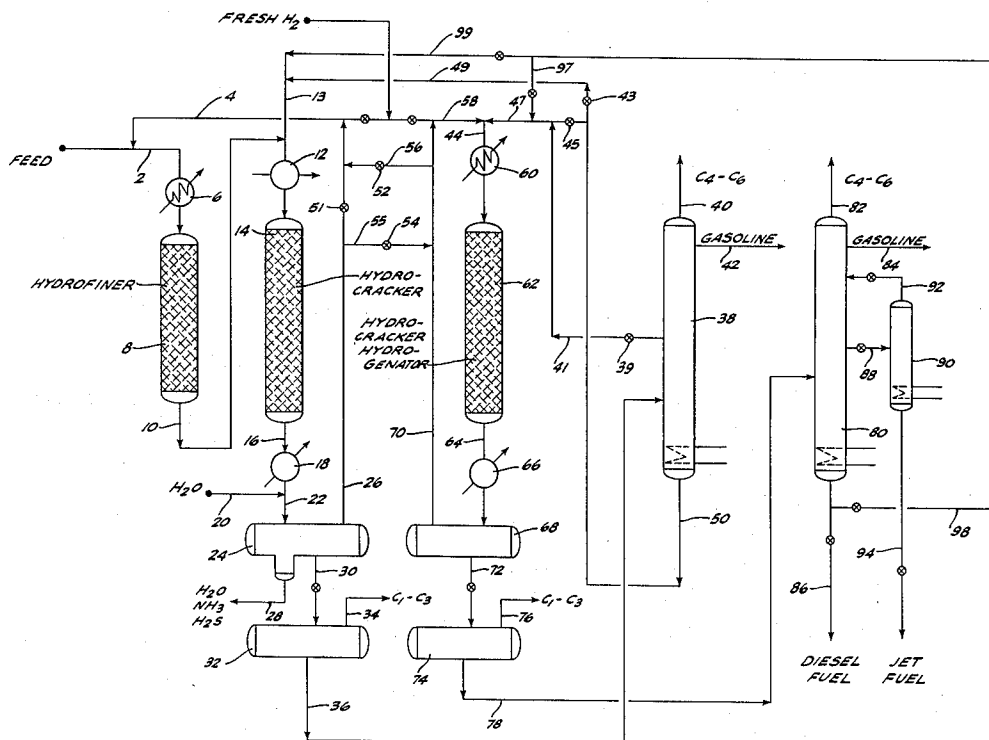
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[57]

ABSTRACT

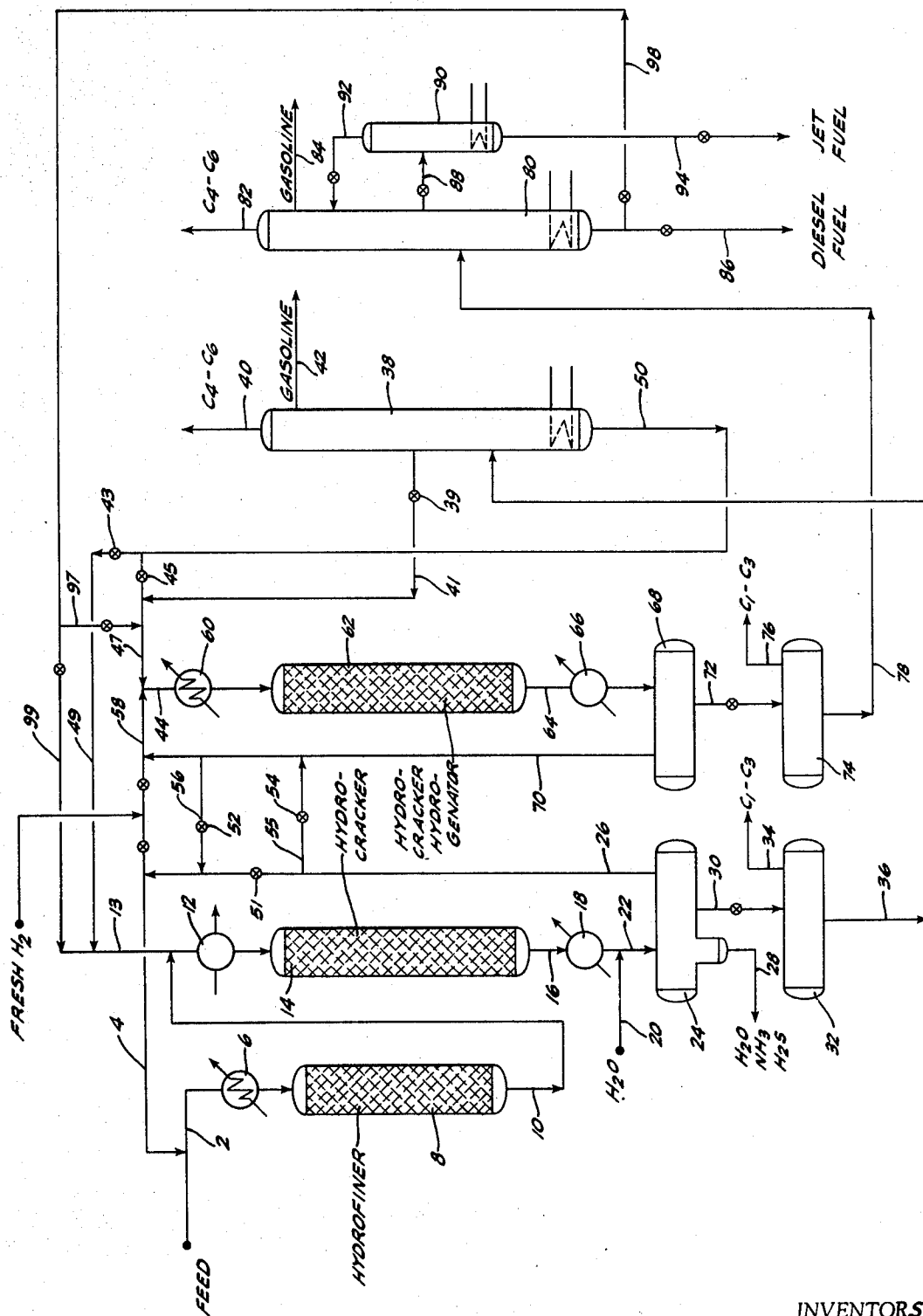
A cyclic hydrocracking-hydrogenating process comprising a gasoline-producing cycle, passing a mineral oil feedstock through a first and second catalyst contact zone to effect a substantial synthesis of gasoline; and in a middle distillate producing cycle, passing the feedstock through the first zone to effect a substantial synthesis to middle distillate and passing unconverted oil and middle distillate from the first contacting zone in the substantial absence of hydrogen sulfide through the second contacting zone to substantially hydrogenate without substantially hydrocracking and unconverted oil and middle distillate; the catalyst in the second contacting zone comprising a Group VIII noble metal hydrogenation component support on an active zeolitic cracking base.

25 Claims, 1 Drawing Figure



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HYDROCRACKING-HYDROGENATION PROCESS RELATED APPLICATIONS

This application is a continuation-in-part of copending application, Ser. No. 792,619, filed Jan. 21, 1969, now abandoned which in turn is a continuation-in-part of Ser. No. 592,482, filed Nov. 7, 1966, now abandoned.

BACKGROUND AND SUMMARY OF INVENTION

This invention relates to catalytic hydrocracking, and more particularly is concerned with a two-stage process wherein the first stage converts fresh feed at relatively high temperatures to high-octane gasoline, and unconverted oil from the first stage is treated in the second stage which is operated alternately as either (1) a hydrocracker for producing additional gasoline, or (2) a non-cracking hydrogenator for producing a relatively saturated middle distillate product such as jet fuel and/or diesel fuel. Basic novel features of the process consist in operating the second stage during the non-cracking hydrogenation cycle substantially in the absence of hydrogen sulfide, and at very low temperatures such that the average molecular weight of the feed thereto is not substantially reduced, and in recycling any hydrocarbon effluent therefrom boiling above the desired middle distillate product range to the first stage for additional hydrocracking. During this cycle of operation, there is substantially no production of gasoline by hydrocracking in the second stage, which is advantageous in that the gasoline produced under low-temperature hydrocracking conditions is of very poor quality.

To convert the process to maximum gasoline production, process conditions, principally temperature, are adjusted in the second stage whereby the cracking activity of the catalyst becomes operative and there is a resultant substantial synthesis of gasoline therein, with unconverted oil therefrom being recycled either to the first stage or the second stage. Further, when the second stage is operated under these cracking conditions, it is preferred to reduce the hydrogenation activity of the catalyst as e.g., by adding a reversible poison to the feed such as hydrogen sulfide, and/or to operate at even higher hydrocracking temperatures while avoiding over-cracking by adjusting space velocity upwardly and/or reducing the cracking activity of the catalyst by adding reversible poison such as ammonia to the feed. Reducing hydrogenation activity and/or raising hydrocracking temperatures is required in order to obtain a high-octane, aromatic gasoline from the second stage. It will be understood that the first stage of the process operates throughout under these optimum gasoline-producing conditions.

A principal object of the invention is to provide an integrated hydrocracking process designed mainly for the production of gasoline, but which can be easily regulated to produce substantial yields, as the seasonal demands of the market may require, of high quality jet fuel boiling for example in the 350°-530° F. range, and/or a high quality diesel fuel boiling for example in the 400°-650° F. range. A further objective is to minimize the total reforming capacity required to produce the desired quantity of high-octane gasoline. A specific object of the invention is to provide an integrated hydrocracking-hydrogenation process of the nature described wherein maximum gasoline quality is achieved by substantially eliminating gasoline production under jet fuel hydrogenation conditions, and wherein the aromaticity of the jet fuel product is also readily controllable. Other objects will be apparent from the more detailed description which follows.

The process of this invention, in its basic objectives and in some of its physical features, bears a substantial similarity to the process described in U.S. Pat. No. 3,132,090. The process of the patent also embraces a two-stage hydrocracking system wherein the first stage is operated at relatively high temperatures for the production of gasoline, and wherein the second stage is operated alternately (A) with added sulfur at relatively high temperatures for gasoline production, or (B) at relatively low temperatures in the absence of sulfur for jet fuel

production. However, the patented process always envisages substantial hydrocracking in the second stage, both in the (A) and (B) cycles of operation, as is clearly evident from the fact that any unconverted oil from the second stage which is not desired as product is always recycled back to the second stage. Such an operation obviously could not be maintained unless substantial hydrocracking, i.e., molecular weight reduction, is taking place in the second stage.

In the process of the above patent, it is not possible to maintain a significant conversion of high boiling hydrocarbons to lower molecular weight jet fuel hydrocarbons in the (B) cycle of operation without also synthesizing substantial amounts of gasoline, which, under the disclosed conditions, is highly saturated and has a very poor octane value. Moreover, under the (B) cycle hydrocracking conditions it is difficult or impossible to control the degree of aromaticity of the jet fuel product, such product always being substantially completely saturated. Complete saturation of aromatic hydrocarbons in the jet fuel product is seldom required in order to meet commercial specifications, and represents an unnecessary and wasteful consumption of hydrogen. In the process of this invention the first stage is operated at relatively high temperatures in the presence of hydrogen sulfide whereby high-octane aromatic gasoline is produced with a minimum of hydrogen consumption. And in the non-cracking, hydrogenation cycle designed for jet and/or diesel fuel production, the second stage functions merely as a saturator for like-boiling-range material derived from the first stage. Hydrogenation without cracking is achieved by the conjoint effect of a sulfur-free environment and the use of low temperatures, correlated with the space velocity to avoid any substantial cracking. At the same time, these conditions can be further adjusted to control kinetically the degree of hydrogenation of the product. As noted, such kinetic control over the extent of hydrogenation is substantially impossible under the hydrocracking conditions of the patent.

Furthermore, in the process of the invention herein, the unconverted oil from the second stage is saturated without being substantially hydrocracked to gasoline and/or middle distillate during the hydrogenation cycle and this oil may be recycled to the first stage for conversion to jet fuel and/or diesel fuel. It has been found that middle distillate yields and quality are improved when the feed is largely saturated and therefore the process of the invention allows the improvement in middle distillate yield and/or quality of the recycling of the saturated unconverted oil to the first stage. Prior art processes have always recycled unconverted oil from the second stage back to the second stage with substantial conversion occurring therein. In the process herein, unconverted oil from the second stage is recycled to the first stage wherein conversion to gasoline and/or middle distillate occurs. Hence, substantial conversion to products need not occur in the second stage and the second stage is utilized principally for saturating the middle distillate and/or unconverted oil. The process of the invention thereby attains the above-described advantages of higher gasoline octane and improved middle distillate quality.

A critical feature of the invention resides in the nature of the catalyst employed in the second hydrocracking zone. For maximum efficiency in the hydrocracking cycle, it is desirable to employ a catalyst comprising a highly active cracking base which will effectively crack hydrocarbons at temperatures below about 700° F. Such cracking bases include primarily the crystalline zeolites, e.g., of the X, Y or L crystal types, wherein the zeolitic cations are predominately hydrogen ions and/or polyvalent metal ions. Yet it is precisely this type of cracking base which would appear to be of most doubtful operability in the hydrogenation cycle of the process where hydrogenation activity must be maintained at temperatures below effective cracking temperatures.

It has now been discovered that the Group VIII noble metals, particularly palladium and platinum, when supported upon such zeolite cracking bases, exhibit extraordinarily high hydrogenation activity such that, if a substantially sulfur-free

atmosphere is maintained, effective hydrogenation of aromatic hydrocarbons can occur at temperatures of 200°–500° F., pressures of 500–3,000 pgs, and at space velocities of 0.5–20 and that those conditions may be correlated such that little or no cracking of hydrocarbons occurs. Further, it has been discovered that in the hydrocracking cycle of the second stage, any one or more of several process variables can be altered so as to effect substantial hydrocracking with minimal hydrogen consumption and the production of a high quality aromatic gasoline. It would be a simple matter to initiate hydrocracking simply by raising the temperature, but this alone has been found to result in substantially complete saturation of aromatics and consumes much hydrogen. To avoid the latter consequences, any one or more of the following procedures are adopted:

1. Sufficient sulfur, as for example in the form of hydrogen sulfide, is mixed with the second-stage feed to provide at least about 0.01, and preferably at least 0.5, millimoles of hydrogen sulfide per mole of hydrogen. Concomitantly, temperatures are raised by about 50°–150° F. to achieve the desired crack per pass. The added hydrogen sulfide appears to repress the hydrogenation activity of the catalyst, and the temperature elevation activates the cracking centers of the catalyst.
2. A basic nitrogen compound such as ammonia is added to the feed in amounts between about 50 and 2,000 parts per million of nitrogen based on feed, and temperatures are concomitantly raised about 100°–350° F. The ammonia appears to repress cracking activity to such an extent that temperatures can be elevated to a level at which hydrogenation is not thermodynamically favored.
3. Space velocity can be elevated to a level of e.g., 5 to 20, and temperatures concomitantly raised about 50°–200° F. Under these conditions, cracking rates tend to outstrip hydrogenation rates with the result that an aromatic gasoline can be produced with minimal hydrogen consumption.

Obviously, any combination of two or more of the foregoing alternates may be adopted, with the resultant hydrocracking temperature being in all cases adjusted to maintain a predetermined conversion per pass to gasoline, normally about 30–70 volume percent based on feed. Alternates (1) and (3), or a combination of both are normally preferred.

Another critical feature of the process resides in the use of an initial feedstock which is substantially aromatic in character. Suitable feeds include coker distillate gas oils, cycle oils from catalytic or thermal cracking operations, as well as aromatic straight-run gas oils. These feedstocks 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°–1,000° F. having an API gravity of about 20°–35°, and containing at least about 20% by volume of aromatic hydrocarbons. Such oils may also contain up to about 5% by weight of sulfur and up to about 2% by weight of nitrogen. Aromatic feedstocks of this character are required inasmuch as the relatively low hydrocracking temperatures and relatively high pressures employed do not thermodynamically favor the synthesis of aromatics from non-aromatics, and hence the aromatics appearing in the gasoline product are primarily unhydrogenated fragments of high boiling aromatics initially present in the feed. If non-aromatic feedstocks were employed, the products obtained herein would all be substantially paraffinic and/or naphthenic, and the non-cracking hydrogenation cycle in the second stage would have little or no utilitarian value.

The process may be operated either with raw feedstock or with preliminary hydrofining thereof. Normally, for feedstocks containing substantial quantities of sulfur and/or nitrogen compounds, it is preferred to employ a prehydrofining step to effect at least partial desulfurization, denitrogenation, stabilization, etc. The hydrofining treatment may desirably be of the "integral" type, i.e., wherein total hydrofiner effluent is passed directly to the first hydrocracking

stage without intervening condensation or purification to remove ammonia and/or hydrogen sulfide.

Reference is now made to the attached drawing, which is a flow sheet illustrating a preferred mode of practicing the invention. It will be understood that the drawing has been simplified by the omission of certain conventional elements such as valves, pumps, compressors, instrumentation and the like. The initial feedstock is brought in via line 2, mixed with recycle and makeup hydrogen from line 4, preheated to incipient hydrofining temperatures in heater 6 and then passed directly into hydrofiner 8, where catalytic hydrofining proceeds under substantially conventional conditions. Suitable hydrofining catalysts include for example mixtures of the oxides and/or sulfides of cobalt and molybdenum, of nickel and molybdenum, or of nickel and tungsten, preferably supported on a substantially non-cracking 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 carriers such as alumina, silica, titania and the like. Suitable hydrofining conditions are in general as follows:

HYDROFINING CONDITIONS

	Broad Range	Preferred Range
Temperature, °F.	550–850	650–750
Pressure, psig	500–5,000	800–2,500
LHSV, v./v./Hr.	0.5–10	1–5
H ₂ /oil ratio, MSCF/B	0.5–20	2–10

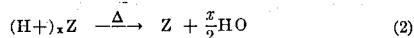
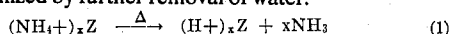
The above conditions are suitable adjusted so as to reduce the organic nitrogen content of the feed to below about 100 parts per million, preferably below about 25 parts per million.

The total hydrofined product from hydrofiner 8 is withdrawn via line 10, blended with any of the hereinafter described recycle oils in line 13, and transferred via heat exchanger 12 to first-stage hydrocracker 14, preferably without intervening condensation or separation of products. Heat exchanger 12 is for the purpose of suitably adjusting the temperature of the total feed to hydrocracker 14; this may require either cooling or heating, depending upon the respective hydrofining and hydrocracking temperatures employed and the relative volume of cool recycle oils in line 13. Inasmuch as first-stage hydrocracker 14 and hydrofiner 8 are preferably operated at essentially the same pressure, it is entirely feasible to enclose both contacting zones within a single reactor, using appropriate temperature control means.

FIRST-STAGE HYDROCRACKING CATALYST

Suitable catalysts for use in hydrocracker 14 comprises in general any refractory, solid cracking base having a cracking activity in excess of that corresponding to a Cat-A Activity Index of about 40, upon which is distributed a minor proportion of Group VIII metal or metal sulfide hydrogenating components. Operative cracking bases include for example mixtures or 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 crystalline, siliceous zeolites, sometimes referred to in the art as molecular sieves, composed usually of silica, alumina and one or more exchangeable cations such as hydrogen, magnesium, rare earth metals; or other polyvalent metal ions. These zeolites are further characterized by crystal pores of relatively uniform diameter between about 4 and 14 Angstroms. Suitable zeolites include for example the synthetic molecular sieves, A, L, S, T, X and Y, and natural zeolites such as chabazite, mordenite, etc. It is preferred to employ zeolites having a relatively high SiO₂/Al₂O₃ mole-ratio, between about 3.0 and 12, and even more preferably between about 4 and 8. Specifically preferred zeolites are those of the Y and L crystal types.

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



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

Both the hydrogen zeolites and the decationized zeolites described above possess desirable catalytic activity. Both of these forms, and the mixed forms are designated herein as being "metal-cation-deficient." The preferred cracking bases are those which are at least about 10%, and preferably at least 20%, metal-cation-deficient, based on the initial ion-exchange capacity. A specifically desirable and stable class of zeolites are those wherein at least about 20% of the ion-exchange capacity is satisfied by hydrogen ions, and at least about 10% by polyvalent metal ions such as magnesium, calcium, zinc, rare earth metals, etc.

The essential active metals employed herein as hydrogenation components are those of Group VIII, i.e., iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, or mixtures thereof. The noble metals are preferred, and particularly palladium and platinum. In addition to these metals, other promoters may also be employed in conjunction therewith, including the metals of Groups VIB and VIIB.

The amount of hydrogenating metal in the catalyst can vary within wide ranges. Broadly speaking, any amount between about 0.05 and 20% by weight may be used. In the case of the noble metals, it is normally preferred to use about 0.1-3% by weight. The preferred method of adding the hydrogenating metal is by ion exchange. This is accomplished by digesting the zeolite, preferably in its ammonium form, with an aqueous solution of a suitable compound of the desired metal wherein the metal is present in a cationic form, as described for example in U.S. Pat. No. 3,200,083.

Following addition of the hydrogenating metal, the resulting catalyst powder is then filtered off, dried, pelleted with added lubricants, binders, or the like if desired, and calcined at temperatures of e.g., 700-1,200° F. in order to activate the catalyst and decompose zeolitic ammonium ions. The foregoing catalysts may be employed in undiluted form, or the powdered catalyst may be mixed and copelleted with other relatively less active adjuvants, diluents or binders such as activated alumina, silica gel, coprecipitated silica-alumina cogel, magnesia, activated clays and the like in proportions ranging between about 5 and 50% by weight. These adjuvants may be employed as such, or they may contain a minor proportion of an added hydrogenating metal, e.g., a Group VIB and/or Group VIII metal.

The process conditions in hydrocracker 14 are suitably adjusted so as to provide about 20-70% conversion to gasoline per pass, while at the same time permitting relatively long runs between regenerations, i.e., from about 4 to 12 months or more. The specific selection of operating conditions depends largely on the nature of the feedstock, pressures in the high range normally being used for highly aromatic feeds, or feeds with high end points. The range of operative conditions contemplated for reactor 14 are as follows, assuming the feed thereto is hydrofiner effluent containing ammonia and hydrogen sulfide:

FIRST STAGE HYDROCRACKING CONDITIONS

	Broad Range	Preferred Range
Temperature, °F.	625-850	650-800
Pressure, psig	400-5,000	800-2,500
LHSV, v./v./Hr.	0.5-10	1-5
H ₂ /oil ratio, MSCF/B	0.5-20	2-10

The effluent from hydrocracker 14 is withdrawn via line 16, condensed in heat exchanger 18, then mixed with wash water injected via line 20 into line 22, and the entire mixture is then transferred to high-pressure separator 24. Sour recycle hydrogen, now substantially free of ammonia but still containing substantial proportions of hydrogen sulfide, is withdrawn via line 26, and aqueous wash water containing dissolved ammonia and some of the hydrogen sulfide is withdrawn via line 28. The liquid hydrocarbon phase in separator 24 is then flashed via line 30 into low-pressure separator 32, from which flash gases comprising hydrogen, methane, ethane, propane and the like are exhausted via line 34. The liquid hydrocarbon phase in separator 32 is then transferred via line 36 to fractionating column 38.

Fractionating column 38 performs the dual function of separating gasoline products synthesized in first-stage hydrocracker 14, and of recovering unconverted higher boiling oils for treatment in second-stage hydrocracker-hydrogenator 62 and/or for recycle to the first-stage hydrocracker 14. Light C₄-C₆ gasoline is normally taken off as overhead via line 40, while C₇+ gasoline is withdrawn as a light-side-cut via line 42. The remaining unconverted oil may be treated according to two principal alternates, as follows:

ALTERNATE A

In this alternate, which generally is preferred where maximum jet and/or diesel fuel yields are desired, the entire bottoms fraction from column 38 boiling above the gasoline range is sent to second-stage hydrocracker-hydrogenator 62. To operate in this manner side-cut line 41 is closed via valve 39, valve 43 is closed and valve 45 opened, whereby the entire bottoms from column 38 is transferred via lines 50, 47, 44, and preheater 60 to hydrocracker-hydrogenator 62.

ALTERNATE B

In this alternate, which has the advantage of maximizing gasoline quality, only the fraction from column 38 which boils substantially within the range of the desired jet and/or diesel fuel product is treated in hydrocracker-hydrogenator 62 during the non-cracking hydrogenation cycle. Any higher boiling material is recycled to the first stage for further cracking. To operate in this manner, valves 39 and 43 are opened and valve 45 closed, whereby the intermediate side-cut fraction taken from column 38 via line 41 becomes the sole feed to hydrocracker-hydrogenator 62, the remaining bottoms fraction being transferred via lines 50, 49 and 13 to hydrocracker 14.

During the total gasoline production cycle, when hydrocracker-hydrogenator 62 is being operated under cracking conditions, side-cut line 41 is normally not utilized, all products from column 38 boiling above the gasoline range being recycled to hydrocracker-hydrogenator 62 via lines 50 and 47, or to hydrocracker 14 via lines 50 and 49, or a portion may be recycled to each zone. Normally it is preferred to recycle all or a substantial portion of the bottoms fraction to the second-stage reactor 62 in order to keep the cracking loads more evenly balanced in the two reactors.

In any of the foregoing alternates, the second-stage feedstock in line 47 is mixed with the recycle and makeup hydrogen from line 58, preheated to incipient hydrocracking or hydrogenation temperatures in heater 60 and passed into second-stage hydrocracker-hydrogenator 62. This second-stage feedstock differs considerably from the feed of nitrogen and sulfur compounds. The choice is thus presented of operating the second stage with or without significant amounts of added sulfur.

In the modification illustrated, variations in sulfur concentrations in hydrocracker-hydrogenator 62 are obtained by the alternate use of separate and mixed recycle gas systems from high-pressure separators 24 and 68. As previously noted, the recycle gas from separator 24 normally contains a substantial proportion of hydrogen sulfide which was not removed by the water-washing operation. To operate hydrocracker-hydrogenator 62 in the non-cracking cycle and substantially in the absence of sulfur (separate recycle systems), valve 51 is opened and valves 52 and 54 closed, thus sending the sour recycle gas from line 26 through line 4 back to hydrocracker 14, and the sweet recycle gas from separator 68 back to hydrogenator 62 via lines 70 and 58. To operate reactor 62 as a hydrocracker with added sulfur, valve 51 is closed and valves 52 and 54 opened, thereby diverting sour recycle gas from line 26 into lines 55 and 70, where it mingles with sweet recycle gas from separator 68. The mixed gases are then split, one portion flowing to hydrofiner 8 via lines 56 and 4, and the other portion flowing to reactor 62 via line 58.

While operating under Alternate A, the process variables are suitably adjusted in hydrocracker 14 for maximum jet fuel and/or diesel fuel synthesis (e.g., 30–70% conversion per pass). The temperature and space velocity in hydrocracker-hydrogenator 62 are correlated so as to effectively hydrogenate the unconverted oil and middle distillate without substantial conversion of unconverted oil to middle distillate and gasoline (e.g., less than about 15%, preferably less than 10%, to 530° F. minus and less than about 20%, preferably less than 15%, to 650° F. minus). For purposes herein, conversion is defined as the volume percent of unconverted oil in the hydrogenator feedstock minus the volume percent of unconverted oil in the hydrogenator effluent divided by the volume percent of unconverted oil in the feedstock, with unconverted oil being defined as the oil boiling above the end point of the particular middle distillate. For example, if the feed to the hydrocracker-hydrogenator contains 70% oil boiling higher than 530° F. and the effluent contains 60% boiling above 530° F., the conversion to 530° F. jet fuel and below is $70 - 60 / 70 \times 100\%$ or 14.3%. A substantial portion, if not the total, of the conversion in the process herein is due to boiling-point reduction from hydrogenation alone and not from hydrocracking. As an illustration, the boiling point of naphthalene is 424° F. which when saturated yields decalin having a boiling point of 382° F., a 42° F. boiling-point reduction from hydrogenation alone. Hence, the fact that some of the hydrocracker-hydrogenator feedstock is converted to middle distillate and gasoline does not necessarily mean that the feed is hydrocracked.

The same variables are correlated for hydrogenation of the middle distillate in Alternate B. For purposes of the operation wherein the feed to the hydrocracker-hydrogenator comprises only middle distillate, conversion is defined as that portion of the middle distillate boiling above the temperature corresponding to the 50% point of the feed which is converted to hydrocarbons boiling below that temperature. The 50% point for jet fuel, for example, is about 400° F. and the 50% point for diesel oil is about 530° F. The conversion in middle distillate hydrogenation is generally less than 10% and is preferably less than 5%.

In order to operate hydrocracker-hydrogenator 62 under substantially non-cracking conditions, the reactor inlet temperature is reduced to a level such that the cracking activity of the catalyst becomes substantially inoperative, and the average molecular weight of the C_4+ effluent therefrom does not differ by more than plus-or-minus 15%, preferably not more than about plus-or-minus 10%, from the average molecular weight of the feed thereto. Under these conditions there is substantially no synthesis of gasoline or middle distillate by hydrocracking; the effluent may, however, contain slightly larger proportions (e.g., 1–10% preferably 1–5%) of these materials than the feed to hydrogenator 62 by virtue of a slight reduction in boiling range brought about principally by hydrogenation. Ordinarily, however, the total gasoline synthesis is less than 10 volume-percent, preferably less than 5%, based on feed.

To achieve the desired objective of effecting substantial hydrogenation without cracking, the hydrogen sulfide concentration in the hydrogenation zone should be maintained at a value below about 0.2, and preferably below about 0.01 millimols hydrogen sulfide per mole of hydrogen. This assures maximum hydrogenation activity at temperatures sufficiently low to avoid cracking. Hydrogen sulfide concentrations between about 0.01 and 0.2 millimols per mole of hydrogen may be preferred in order to control the degree of hydrogenation and therefore avoid wasteful hydrogen consumption while still producing a middle distillate meeting product specification. Operative hydrogenation conditions fall within the following general ranges:

15 NON-CRACKING SECOND-STAGE HYDROGENATION CONDITIONS

	Broad Range	Preferred Range
20 Temperature, °F.	200–500	250–450
Pressure, psig	400–5,000	800–2,500
LHSV, v.v./Hr.	0.2–20	1–8
H ₂ /Oil Ratio, MSCF/B	0.5–20	2–12
H ₂ S/H ₂ Ratio, millimoles/mole	<0.2	<0.01

As will be understood by those skilled in the art, the specific selection of operating conditions within these ranges to substantially saturate the feed (e.g. effect sufficient hydrogenation to meet product quality specifications) without substantial conversion will depend on several factors, mainly the relative activity of the catalyst and the aromaticity of the feed. The aromatic content of the feed to the hydrocracker-hydrogenator is generally between about 20 to 70% and normally above 30%. For satisfactory jet fuel quality, it is usually desirable to reduce the aromatic content of the feed to below a maximum of 20% and preferably to below 15%; and for satisfactory diesel fuel quality, the aromatic content should be reduced to below 20%, and preferably below 15%. When feedstocks containing at least 30% aromatics are hydrogenated to products containing less than 20% aromatics, it will be apparent that at least one-third of the aromatic hydrocarbons are being hydrogenated. The degree of hydrogenation desired can readily be controlled by simply varying temperature and/or space velocity. For example, while operating under Alternate A, space velocities between about 1.2 and 3.0 and temperatures between about 325° and 450° F. generally give satisfactory hydrogenation with little if any attendant hydrocracking. At higher space velocities, higher temperatures are maintained to achieve the necessary saturation yet not substantially hydrocrack the unconverted oil. The operation at the lower space velocities and temperatures is, however, preferred to the operation at higher space velocities and temperatures.

While operating under Alternate B, lower temperatures (e.g., 250°–425° F.) are utilized to hydrogenate the jet fuel and/or diesel oil and generally lower space velocities are prevalent due to the decrease volume of hydrocarbons available for hydrogenation in the hydrocracker-hydrogenator.

It is contemplated also that ammonia in amounts between about 1 and 2,000 parts per million by weight may be included with the feed being hydrogenated in order to further repress cracking activity of the catalyst. If sufficient ammonia is added, e.g., 200–2,000 ppm, hydrogenation temperatures in excess of 500° F., and up to about 700° F. may be attained without encountering cracking and without significant reduction in hydrogenation activity of the catalyst.

In order to convert hydrocracker-hydrogenator 62 to the hydrocracking cycle, the principal operative requirement is to raise the inlet temperature to a level which gives the desired crack per pass. However, as previously noted, raising the temperature is not alone sufficient to give a gasoline product of desired aromaticity. Any one or more of the previously mentioned expedients of (1) adding sulfur to the feed, (2) adding ammonia to the feed, and (3) raising the space velocity may be employed to reduce effective hydrogenation of the product. Suitable hydrocracking conditions for the production

of an aromatic gasoline product fall within the following ranges:

SECOND-STAGE HYDROCRACKING CONDITIONS

	Broad Range	Preferred Range
Temperature, °F.	500-850	550-800
Pressure, psig	400-5,000	800-2,500
LHSV v.v./Hr.	0.5-30	1-10
H ₂ /Oil Ratio, MSCF/B	0.5-20	2-12
Sulfur, Millimoles/Mole H ₂	>0.01	>0.2
Ammoniacal Nitrogen, ppm of feed	0-2000	2-200

SECOND-STAGE CATALYSTS

A critical feature of the invention resides in the nature of the catalyst employed in hydrocracker-hydrogenator 62. To achieve the desired flexibility of operating under either cracking or non-cracking conditions, an active hydrogenating component comprising one or more Group VIII noble metals in amounts of about 0.05-4% by weight is required. Specifically included are the metals, ruthenium, rhodium, palladium, osmium, iridium, and platinum, with palladium being preferred. These hydrogenating metals may be supported on substantially any of the previously described cracking bases used in the first stage of the process, but is is distinctly preferred to employ a zeolite base in its hydrogen or deca-tionized form, i.e., one which is at least about 20%, and preferably at least about 35%, metal-cation-deficient, which bases display maximum cracking activity. While cracking activity is generally regarded as being substantially independent of hydrogenation activity, it has now been found that the hydrogenation activity of Group VIII noble metals is greatly enhanced when supported upon one of the metal-cation-deficient zeolites. This is dramatically illustrated by a series of low-temperature hydrogenations carried out with several different palladium-zeolite catalysts, wherein naphthalene and tetralin feedstocks were subjected to hydrogenation in a stirred autoclave:

TABLE 1

Feed	Catalyst	Temp., ° F.	Hydrogen pressure, p.s.i.g.	Moles H ₂ consumed per hr. per gm. of Pd	
				N→T ¹	T→D ²
Tetralin.....	0.53% Pd on hydrogen Y zeolite.....	200	167	-----	1.9
Do.....	1% Pd on magnesium Y zeolite.....	200	167	-----	0.49
Do.....	1% Pd on sodium Y zeolite.....	200	167	-----	0.28
Naphthalene.....	1% Pd on mixed hydrogen-magnesium Y zeolite.....	250	172	9.1	1.5
Do.....	1% Pd on magnesium Y zeolite.....	250	172	3.6	0.63
Do.....	1% Pd on sodium Y zeolite.....	250	172	3.6	0.56

¹ Naphthalene to Tetralin. ² Tetralin to Decalin.

Thus, palladium deposited on hydrogen zeolites appears to exhibit a hydrogenation activity about 3 to 7 times that of palladium deposited upon sodium zeolites or magnesium zeolites. Hence, a preferred catalyst is one where a substantial amount (e.g., 50-90%) of the total of the exchangeable cations in the zeolite are satisfied by hydrogen ions and a most preferred catalyst is palladium on a hydrogen Y zeolite.

To complete the process description, effluent from hydrocracker-hydrogenator 62 is withdrawn via line 64, condensed in cooler 66 and transferred to high-pressure separator 68, from which recycle hydrogen is withdrawn via line 70 and utilized as previously described. The liquid hydrocarbons in separator 68 are then flashed via line 72 into low-pressure separator 74 from which C₁-C₃ flash gases are withdrawn via line 76. The remaining liquid hydrocarbon product in separator 74 is withdrawn via line 78 and transferred to second-stage product fractionation column 80, wherein it is fractionated into various gasoline, jet fuel and diesel fuel fractions as may be desired.

During the gasoline-producing hydrocracking cycle in second-stage reactor 62, light gasoline blending stock is withdrawn overhead from column 80 via line 82, C₇-plus gasoline via line 84, and the remaining unconverted oil is

withdrawn as bottoms via line 98 and recycled to the second stage via lines 97, 47 and 44, or to first-stage reactor 14 via lines 99 and 13, or a portion may be recycled to each reactor. During this operation, side-cut stripping column 90 is ordinarily not used.

During the non-cracking hydrogenation cycle in reactor 62, very small amounts of gasoline fractions may be recovered via lines 82 and 84, and the major jet fuel product is withdrawn as a side-cut via line 88 and transferred to stripping column 90, from which overhead gasoline hydrocarbons are returned to column 80 via line 92, while the desired jet fuel product is withdrawn as bottoms via line 94. Remaining bottoms fraction from column 80 may be withdrawn via line 86 as diesel fuel, or recycled via lines 98, 99 and 13 to first-stage hydrocracker 14. It will be understood however that column 80 is normally operated in this manner only when second-stage reactor 62 is operated according to Alternate (A) described above, i.e., when the feed to reactor 62 comprises the entire non-gasoline bottoms fraction from column 38. When reactor 62 is operated according to Alternate (B), i.e., when the feed thereto comprises only the light side-cut withdrawn via line 41 from column 38, fractionator 80 can be by-passed with the entire effluent stream in line 78 being sent directly to side-cut stripping column 90 for separation of any minor gasoline fraction from the jet fuel product. In some cases, the gasoline content of the effluent from reactor 62 is so insignificant that the entire product in line 78 may be sent to storage and blending facilities without fractionation.

The following examples are presented to illustrate the operation and results of the process as above described, but these examples should not be construed as limiting in scope:

EXAMPLE 1.

A series of three two-stage operations as described in connection with the drawing were carried out, with the second-stage being used under non-cracking hydrogenation conditions according to Alternate (A) described above, and with

second-stage product boiling above the jet fuel range being recycled to the first stage. The initial feedstock was a blend of catalytic cracking cycle oils and straight-run gas oils having a gravity of 23.9° API, a boiling range of 400°-870° F., containing 69 volume-percent aromatics, 0.184 weight-percent nitrogen, and 1.2 weight-percent sulfur. The feed to the hydrocracker-hydrogenator contained about 38 volume-percent aromatics. The hydrofining catalyst was composed of about 3% NiO and 15% MoO₃ supported on a carrier composed of 5% SiO₂ coprecipitated with 95% Al₂O₃, the catalyst being sulfided before use. The catalyst used in the first-stage hydrocracker, and in the second-stage hydrogenator was a copelletted mixture of (a) 20% by weight of activated alumina and (b) 80% by weight of a Y molecular sieve zeolite containing 0.5 weight-percent palladium, and wherein about 30% of the ion-exchange capacity was satisfied by magnesium ions, 10% by sodium ions, and 60% by hydrogen ions. During runs 1 and 2, the second-stage hydrogenation was operated substantially in the absence of sulfur, while in run number 3 the indicated proportion of sulfur was added to the feed. Each contacting zone was operated at a pressure of about 1,500 psig, with hydrogen/oil ratios of 8,000-10,000 SCF/B of oil. The significant conditions and results of the runs were as follows:

TABLE 2

Run number	1	2	3
Hydrofining conditions:			
Avg. bed temp., ° F.	700	700	700
LHSV	0.75	0.75	0.75
First-stage hydrocracking:			
Avg. bed temp., ° F.	726	730	731
LHSV	2.5	2.7	2.7
Conv./pass to 400° F. minus	40	40	40
Yields, vol. percent fresh feed:			
C ₅ -C ₈ gaso.	23.2	23.3	23.8
C ₇ + gaso.	55.4	58.5	56.0
Octane Nos., F-1 plus 3 ml. TEL:			
C ₅ -C ₈ gaso.	98.9	99.1	99.4
C ₇ -400° F. gaso.	84.0	85.3	83.6
Second-stage hydrogenation:			
Avg. bed temp., ° F.	431	390	450
LHSV	1.5	1.6	1.6
H ₂ /H ₂ ratio, millimoles/mole	0.005	0.005	0.46
Feed properties, vol. percent:			
C ₅ -400° F. gaso.	2	2	2
400° F.-530° F. jet fuel.	23	18	18
400° F.-650° F. diesel fuel.	69	66	66
530° F. plus	76	80	80
650° F. plus	30	32	32
Effluent properties, vol. percent:			
C ₅ -400° F. gaso.	6	4	3
400° F.-530° F. jet fuel.	26	21	25
400° F.-650° F. diesel fuel.	68	68	68
530° F. plus	68	75	72
650° F. plus	26	28	28
Conversion to 530° F. minus, percent.	9.3	6.3	-----
Conversion to 650° F. minus, percent.	13.3	12.5	10.0
Avg. mol. wt. ratios: 2nd stage feed C ₄ plus product.	1.123	1.097	1.097
Jet fuel products:			
Gravity, °API	40.3	39.0	36.5
Aromatics, vol. percent	4	10	34
Saturates, vol. percent	96	89	65
H ₂ consumption, s.c.f./b.	2,030	2,010	1,870

The effect of sulfur in run 3 on product aromaticity is readily apparent, and runs 1 and 2 illustrate the ease with which product aromaticity can be controlled by varying temperature in a sulfur-free environment.

If runs 1 and 2 are modified by raising the second-stage temperature to around 510° F. and recycling effluent boiling above the jet fuel range back to the second-stage (as in U.S. Pat. No. 3,132,090), a jet fuel product of substantially zero aromatic content is obtained, with concomitant synthesis of about 20 volume-percent of C₇-400° F. gasoline, which gasoline has a leaded octane rating of about 72. Hydrogen consumption also increases markedly.

Run 3 above can easily be modified for 100% gasoline production by raising the second-stage temperature to about 600°-625° F., and recycling thereto all material boiling above gasoline. The second-stage gasoline produced under these conditions is slightly inferior to the first-stage gasoline, having a leaded octane number in the range of about 78-80, which is nevertheless much superior to the second-stage gasoline produced at lower temperatures in the absence of hydrogen sulfide.

EXAMPLE 2.

Another run was carried out under conditions described in Example 1, but operating according to Alternate (B), i.e., with the 525° F.± fraction of effluent from the first-stage hydrocracker being recycled directly to that stage, the sole feed to the second-stage hydrogenation unit being the 400°-525° F. fraction of first-stage effluent. The significant conditions and results of this run were as follows:

TABLE 3

Run No.	6
First-Stage Hydrocracking	
Avg. Bed Temp., °F.	744
LHSV	2.94
Conv./Pass to 400°F. minus	40
Yields, Vol. % of Fresh Feed	
C ₅ -C ₈ Gaso.	27.9
C ₇ -400°F. Gaso.	57.6
Octane No's., F-1 + 3 ml TEL	
C ₅ -C ₈ Gaso.	99.5
C ₇ -400°F. Gaso.	89.8

Second-stage Hydrogenation

Avg. Bed Temp., °F.	414
LHSV	0.29
H ₂ /H ₂ Ratio, millimoles/mole	0.005

Property	Feed	Product
ASTM Boiling Range, °F.	406-554	400-537
Gravity	36.0	40.6
Aromatics	38	3
Saturates	60	97
Avg. Mol. Wt. Ratios, 2nd Stage Feed/C ₄ + Product		1.016
H ₂ Consumption, SCF/B		2,100

Although lower jet fuel yields are obtained in the above run as compared to Examples 1 and 2, the yield-octane value of the total gasoline product is improved without sacrificing jet fuel quality.

The following claims are believed to define the true scope of the invention, which is not limited to the exemplary details described above:

We claim:

1. In a catalytic hydrocracking-hydrogenation system, a process for converting a mineral oil feedstock containing aromatic hydrocarbons and boiling above the gasoline range alternately to a relatively aromatic gasoline product, and to a plurality of products including an aromatic gasoline and a substantial proportion of a relatively non-aromatic middle-distillate product boiling at least partially above the gasoline range, said feedstock also comprising a heavy fraction boiling above the end-boiling-point of said middle distillate product, which comprises:

1. in a periodic gasoline-producing cycle, passing said feedstock in admixture with hydrogen through a first catalyst contacting zone in contact with an active hydrocracking catalyst at an elevated pressure and a temperature above about 625° F. to effect a substantial synthesis of gasoline, separating the resulting effluent into an aromatic gasoline product and an unconverted higher boiling fraction, passing said higher boiling fraction through a second catalyst contacting zone at an elevated pressure and a temperature above about 500° F. in the presence of hydrogen, hydrogen sulfide and a hydrocracking catalyst comprising a Group VIII noble metal hydrogenation component supported on an active zeolite cracking base wherein at least half of the original zeolitic sodium ions have been replaced by hydrogen ions, polyvalent metal ions, decationized sites, or a combination thereof, to thereby effect a substantial synthesis of gasoline, separating the resulting second-stage effluent into an aromatic gasoline fraction and an unconverted recycle oil, and recycling at least a portion of said recycle oil to said first and/or second contacting zones;
2. in an alternating periodic middle distillate-producing cycle, passing said feedstock in admixture with hydrogen through said first catalyst contacting zone as defined in step (1), separating the resulting effluent into an aromatic gasoline product and a relatively aromatic bottoms fraction comprising middle distillate and a heavier fraction, passing at least the middle distillate portion of said bottoms fraction plus added hydrogen through said second catalyst contacting zone at an elevated pressure substantially in the absence of hydrogen sulfide, and at a temperature correlated with space velocity so as to saturate at least about one-third of the aromatic hydrocarbons in said middle distillate portion but to substantially avoid cracking reactions, recovering a relatively non-aromatic middle distillate product from the resulting effluent, and recycling to said first catalytic zone a heavier fraction recovered from the effluent from said first and/or second catalytic contacting zones.

2. A process as defined in claim 1 wherein the catalyst employed in said second contacting zone is a molecular sieve zeolite having a SiO₂/Al₂O₃ mole-ratio above about 3, at least

about 20% of the ion-exchange capacity thereof being satisfied by hydrogen ions, and deposited thereon between about 0.1% and 3% by weight of palladium or platinum.

3. A process as defined in claim 1 wherein the entire bottoms fraction recovered from the effluent from said first contacting zone in step (2) is passed through said second contacting zone, and wherein the effluent from said second contacting zone in step (2) is fractionated to recover said non-aromatic middle distillate product and said heavier fraction, and wherein said heavier fraction is recycled to said first contacting zone.

4. A process as defined in claim 1 wherein said bottoms fraction recovered from the effluent from said first contacting zone in step (2) is further fractionated to separate said middle distillate from said heavier fraction, and wherein the separated heavier fraction is recycled to said first contacting zone.

5. A process as defined in claim 1 wherein said relatively non-aromatic middle distillate product is a jet fuel boiling in a range of about 350°–530° F.

6. A process as defined in claim 1 wherein a temperature between about 200° and 500° F. is maintained during step (2) in said second contacting zone.

7. In a catalytic hydrofining-hydrocracking-hydrogenation system, a process for converting a mineral oil feedstock boiling above the gasoline range alternately to a relatively aromatic gasoline product, and to a plurality of products including an aromatic gasoline and a relatively non-aromatic middle distillate product boiling at least partially above the gasoline range, said feedstock also comprising a heavy fraction boiling above the end-boiling-point of said middle distillate product, which comprises:

1. passing said feedstock plus added hydrogen through a catalytic hydrofining zone at an elevated temperature and pressure to effect decomposition of organic sulfur and/or nitrogen compounds contained therein without substantial cracking of hydrocarbons;

2. in a periodic gasoline-producing cycle:

a. passing effluent from said hydrofining zone, without intervening purification to remove ammonia and hydrogen sulfide, through a second catalytic contacting zone at an elevated pressure and a temperature between about 625° and 850° F., in contact with a hydrocracking catalyst comprising a minor proportion of a Group VIII metal and/or an oxide or sulfide thereof supported on a crystalline zeolitic cracking base wherein the zeolitic cations are predominately hydrogen ions and/or polyvalent metal ions, to effect about 30–80 volume-percent conversion per pass to gasoline-boiling range material,

b. separating the effluent therefrom into an aromatic gasoline product, and a bottoms fraction comprising middle distillate and a heavier fraction,

c. passing said bottoms fraction through a third catalytic contacting zone in admixture with hydrogen and hydrogen sulfide at an elevated pressure and a temperature between about 500° and 850° F. in the presence of a hydrocracking catalyst as defined in step 2(a), wherein the Group VIII metal is a noble metal,

d. separating effluent from said third contacting zone into an aromatic gasoline product and an unconverted recycle oil, and

e. recycling said unconverted recycle oil to said second and/or third contacting zone; and

3. in an alternating periodic middle distillate producing cycle:

a. continuing the operation of said hydrofining step (1) and said second contacting zone as defined in steps (2)(a) and (2)(b),

b. passing at least the middle distillate portion of said bottoms fraction through said third catalytic contacting zone in admixture with hydrogen, but substantially in the absence of hydrogen sulfide, and at a temperature correlated with space velocity so as to saturate at least

about one-third of the aromatic hydrocarbons in said middle distillate portion, but to substantially avoid cracking reactions,

c. recovering said relatively non-aromatic middle distillate product from the effluent of said third contacting zone; and

d. recycling to said second contacting zone the heavier fraction boiling above said middle-distillate product, said heavier fraction being recovered from the effluent from said second and/or third contacting zones.

8. A process as defined in claim 7 wherein the catalyst employed in said third contacting zone is a molecular sieve zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole-ratio above about 3, at least about 20% of the ion-exchange capacity thereof being satisfied by hydrogen ions, and deposited thereon between about 0.1 and 3% by weight of palladium or platinum.

9. A process as defined in claim 7 wherein the entire bottoms fraction recovered from the effluent from said second contacting zone in step (3)(a) is passed through said third contacting zone, and wherein the effluent from said third contacting zone in step (3) is fractionated to recover said non-aromatic middle distillate product and said heavier fraction, and wherein said heavier fraction is recycled to said second contacting zone.

10. A process as defined in claim 7 wherein said relatively non-aromatic middle distillate product is a jet fuel boiling in the range of about 350°–530° F.

11. A process as defined in claim 7 wherein the bottoms fraction recovered from the effluent from said second contacting zone in step (3)(a) is further fractionated to separate said middle distillate from said heavier fraction, and wherein the separated heavier fraction is recycled to said second contacting zone.

12. A process as defined in claim 7 wherein a temperature between about 200° and 500° F. is maintained during step (3)(b) in said third contacting zone.

13. In a catalytic hydrocracking-hydrogenation system, a process for converting a mineral oil feedstock containing aromatic hydrocarbons and boiling above the gasoline range alternately to a relatively aromatic gasoline product, and to a plurality of products including an aromatic gasoline and a substantial proportion of a relatively non-aromatic middle-distillate product boiling at least partially above the gasoline range, which comprises:

1. In a periodic gasoline-producing cycle, passing said feedstock in admixture with hydrogen through a first catalyst contacting zone in contact with an active hydrocracking catalyst at an elevated pressure and a temperature above about 625° F. to effect a substantial synthesis of gasoline, separating the resulting effluent into an aromatic gasoline product and an unconverted higher boiling fraction, passing said higher boiling fraction through a second catalyst contacting zone at an elevated pressure and a temperature above about 500° F. in the presence of hydrogen, hydrogen sulfide and a hydrocracking catalyst comprising a Group VIII noble metal hydrogenation component supported on an active zeolite cracking base wherein at least half of the original zeolitic sodium ions have been replaced by hydrogen ions, polyvalent metal ions, decationized sites, or a combination thereof, to thereby effect a substantial synthesis of gasoline, separating the resulting second-stage effluent into an aromatic gasoline fraction and an unconverted recycle oil, and recycling at least a portion of said recycle oil to said first and/or second contacting zones;

2. In an alternating periodic middle distillate-producing cycle, passing said feedstock in admixture with hydrogen through said first catalyst contacting zone as defined in step (1), separating the resulting effluent into an aromatic gasoline product and a relatively aromatic unconverted higher-boiling fraction, passing said higher-boiling fraction plus added hydrogen through said second catalyst contacting zone at an elevated pressure and substantially

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in the absence of hydrogen sulfide and at a substantially non-cracking temperature below about 450° F., correlated with space velocity so as to saturate at least about one-third of the aromatic hydrocarbons in said unconverted oil which synthesizing less than about 5 volume-percent of C₄-400° F. gasoline by hydrocracking, and recovering a relatively non-aromatic middle distillate product from the resulting effluent.

14. A process as defined in claim 13 wherein the catalyst employed in said second contacting zone is a molecular sieve zeolite having a SiO₂/Al₂O₃ mole-ratio above about 3, at least about 20% of the ion-exchange capacity thereof being satisfied by hydrogen ions, and deposited thereon between about 0.1 and 3 percent by weight of palladium or platinum.

15. A process as defined in claim 13 wherein the effluent from said second contacting zone in step (2) is fractionated to recover said non-aromatic middle distillate product and a higher boiling recycle fraction, and wherein said higher boiling recycle fraction is recycled to said first contacting zone.

16. A process as defined in claim 13 wherein said relatively non-aromatic middle distillate product is a jet fuel boiling in a range of about 350°-530° F.

17. A process as defined in claim 13 wherein a temperature between about 250° and 450° F. is maintained during step (2) in said second contacting zone.

18. In a catalytic hydrofining-hydrocracking-hydrogenation system, a process for converting a mineral oil feedstock boiling above the gasoline range alternately to a relatively aromatic gasoline product, and to a plurality of products including an aromatic gasoline and a relatively non-aromatic middle distillate product boiling at least partially above the gasoline range, which comprises:

1. passing said feedstock plus added hydrogen through a catalytic hydrofining zone at an elevated temperature and pressure to effect decomposition of organic sulfur and/or nitrogen compounds contained therein without substantial cracking of hydrocarbons;
2. in a periodic gasoline-producing cycle:
 - a. passing effluent from said hydrofining zone, without intervening purification to remove ammonia and hydrogen sulfide, through a second catalytic contacting zone at an elevated pressure and a temperature between about 625° and 850° F., in contact with a hydrocracking catalyst comprising a minor proportion of a Group VIII metal and/or an oxide or sulfide thereof supported on a crystalline zeolitic cracking base wherein at least half of the original zeolitic sodium ions have been replaced by hydrogen ions, polyvalent metal ions, decationized sites, or a combination thereof, to thereby effect about 30-80 volume-percent conversion per pass to gasoline-boiling range material,
 - b. separating the effluent therefrom into an aromatic gasoline product, and an unconverted higher boiling fraction,
 - c. passing said unconverted higher boiling fraction through a third catalytic contacting zone in admixture with hydrogen and hydrogen sulfide at an elevated pressure and a temperature between about 500° and 850° F. in the presence of a hydrocracking catalyst as defined in step 2-(a), wherein the Group VIII metal is a noble metal,

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d. separating effluent from said third contacting zone into an aromatic gasoline product and an unconverted recycle oil, and

e. recycling said unconverted recycle oil to said second and/or third contacting zone; and

3. in an alternating periodic middle distillate producing cycle:

a. continuing the operating of said hydrofining step (1) and said second contacting zone as defined in steps (2)-(a) and (2)-(b),

b. passing said unconverted higher boiling fraction through said third catalytic contacting zone in admixture with hydrogen, but substantially in the absence of hydrogen sulfide, and at a substantially non-cracking temperature between about 250° and 450° F., correlated with space velocities above about 1.0 so as to saturate at least about one-third of the aromatic hydrocarbons in said unconverted oil while synthesizing less than about 5 volume-percent of C₄-400° F. gasoline by hydrocracking, the conversion to hydrocarbons boiling below 530° F. being less than about 15 volume-percent; and

c. recovering said relatively non-aromatic middle distillate product from the effluent of said third contacting zone.

19. A process as defined in claim 18 wherein the catalyst employed in said third contacting zone is a molecular sieve zeolite having a SiO₂/Al₂O₃ mole-ratio above about 3, at least about 20% of the ion-exchange capacity thereof being satisfied by hydrogen ions, and deposited thereon between about 0.1 and 3% by weight of palladium or platinum.

20. A process as defined in claim 18 wherein the effluent from said third contacting zone in step (3) is fractionated to recover said non-aromatic middle distillate product, and a higher boiling recycle fraction, and wherein said higher boiling fraction is recycled to said second contacting zone.

21. A process as defined in claim 18 wherein said relatively non-aromatic middle distillate product is a jet fuel boiling in a range of about 350°-530° F.

22. A process as defined in claim 18 wherein the aromatic content of the unconverted oil fed to said third contacting zone is above 30 volume-percent and the aromatic content of the middle distillate product is below 20 volume percent.

23. A method for the hydrogenation of aromatic hydrocarbons in a mineral oil feedstock, which comprises contacting said feedstock plus added hydrogen, but substantially in the absence of hydrogen sulfide, with a hydrocracking catalyst at an elevated pressure and at a substantially non-cracking temperature between about 250° and 425° F., said temperature being correlated with space velocity so as to saturate at least about one-third of the aromatic hydrocarbons in said feedstock while synthesizing less than about 5 volume-percent of C₄-400° F. gasoline by hydrocracking, said hydrocracking catalyst comprising a minor proportion of a Group VIII noble metal supported on a crystalline zeolite cracking base wherein at least half of the original zeolitic sodium ions have been replaced by hydrogen ions, polyvalent metal ions, decationized sites, or a combination thereof.

24. A process as defined in claim 23 wherein said Group VIII noble metal is palladium.

25. A process as defined in claim 23 wherein the conversion of middle distillate is less than 10 volume percent.

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