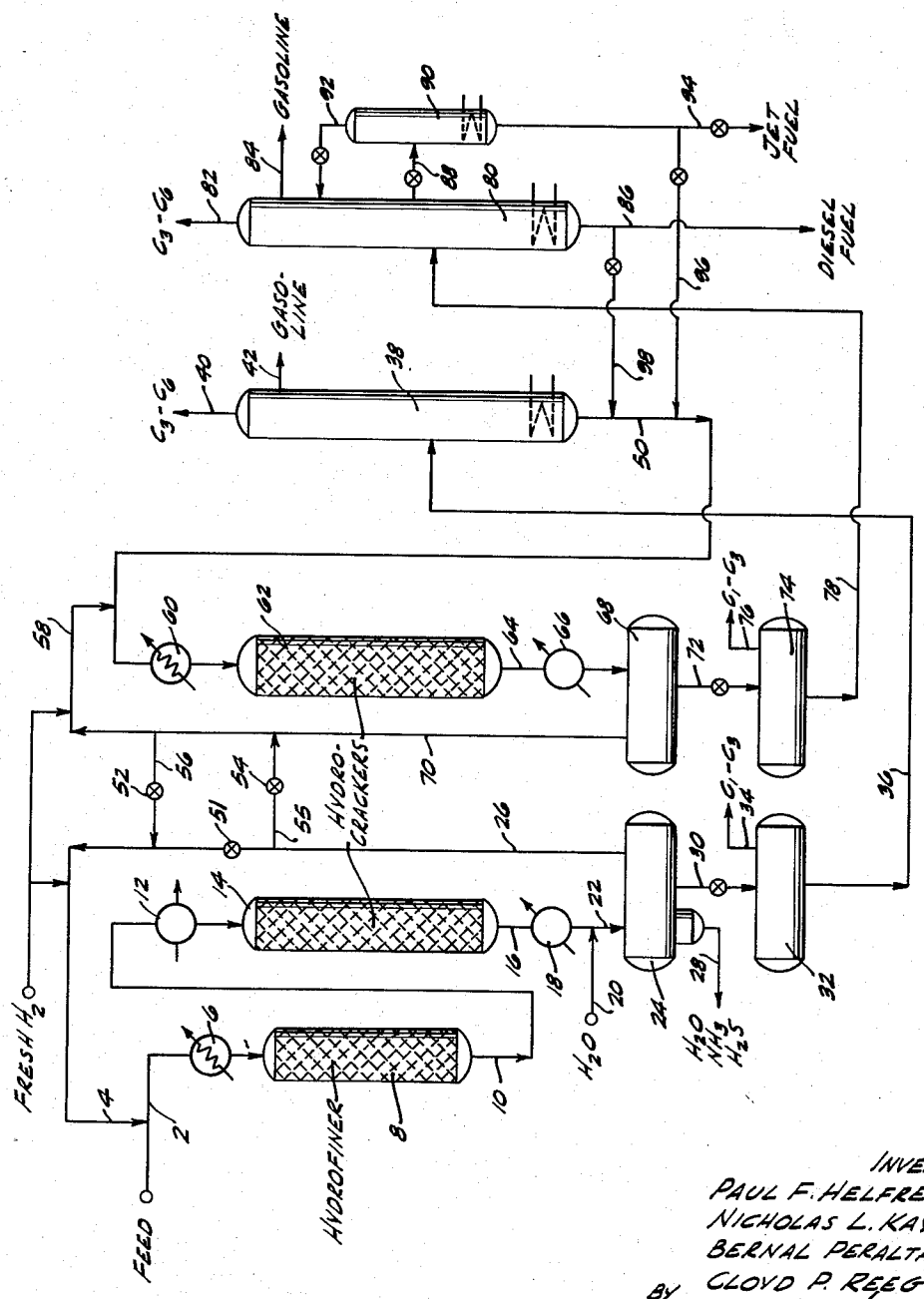
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HYDROCRACKING PROCESS WITH REGULATION OF THE AROMATIC CONTENT OF THE PRODUCT

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HYDROCRACKING PROCESS WITH REGULATION OF THE AROMATIC CONTENT OF THE PRODUCT

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This invention relates to a catalytic hydrocracking process affording a maximum degree of flexibility in reference to variety and quality of products obtainable therefrom. More specifically, the process is designed to produce from hydrocarbon feedstocks a relatively aromatic product boiling in the gasoline range, and/or relatively non-aromatic products boiling in the jet fuel-diesel fuel range. In broad aspects, the principal operative features of the process comprise contacting the hydrocarbon feedstock with a group VIII noble metal hydrocracking catalyst at pressures below about 2,500 p.s.i.g. and temperatures between about 400° and 750° F., and adjusting the hydrogen sulfide concentration in the reaction mixture upwardly when the major desired product is high octane gasoline, and downwardly when the major desired product is a highly paraffinic jet fuel and/or diesel fuel. In a preferred aspect of the invention, two separate hydrocracking stages are employed, the first operating in the presence of hydrogen sulfide and nitrogen compounds and at relatively high temperatures to produce high octane gasoline, and the second operating with a group VIII noble metal hydrocracking catalyst, and substantially in the absence of nitrogen compounds, to produce either high octane gasoline when the hydrogen sulfide concentration is relatively high, or highly saturated jet fuels and/or diesel fuels at lower hydrogen sulfide concentrations. The process thus affords maximum flexibility, permitting the refiner to meet changing market demands for the various products, while minimizing the quantity of low octane gasoline produced which must be subjected to a subsequent severe reforming step to obtain the desired octane balance in the refinery.

A principal object of this invention is to provide an integrated hydrocracking process designed mainly for the production of gasoline, but which can be easily regulated to produce a high quality jet fuel boiling for example in the 350–550° F. range, and/or a high quality diesel fuel boiling for example in the 400–800° F. range. A further objective is to minimize the total reforming capacity required in any given refinery to produce the desired quantity of high octane gasoline. Another object is to provide a flexible hydrocracking process which will permit the refiner to shift rapidly and easily from jet fuel to gasoline products as his market may require. Other objects will be apparent from the more detailed description which follows.

The invention rests basically upon our discovery that, within the temperature range of about 400–750° F., group VIII noble metal hydrocracking catalysts are remarkably sensitive to hydrogen sulfide concentration in the reaction mixture, in respect to product aromaticity. Moreover, this sensitivity is reversible, and is such that variations in hydrogen sulfide concentration, within the range of about 0 to 0.5 millimole per mole of hydrogen, are substantially

immediately reflected in a significant change in produuct aromaticity even without change in hydrocracking temperature. This sensitivity does not appear to be displayed at temperatures above about 750° F., while at pressures above about 2,500 p.s.i.g., the magnitude of the effect is substantially decreased. It is found also that this reversible sensitivity to hydrogen sulfide concentration is not displayed in the same order of magnitude by other hydrocracking catalysts such as those wherein the hydrogenating component is nickel. It is found also that variations in hydrogen sulfide concentration within the range above about 0.5 millimole, or in the range below about 0.01 millilmole per mole of hydrogen, bring about relatively insignificant changes in product aromaticity. The critical concentration range for practical purposes hence appears to lie between about 0.01 and 0.5 millimole. While we do not wish to be found by any theoretical explanation for this observed sensitivity to hydrogen sulfide concentration, it would appear to involve in some degree a change in the group VIII noble metal hydrogenating component from the free metal to a sulfide state, and vice versa. But we do not exclude the possibility that other operative factors may be involved.

Another critical feature of the process resides in the use of an initial hydrocarbon feedstock which is substantially aromatic in character. This includes coker distillate gas oils, cycle oils derived 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° and 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 from about 0.1% to 5% by weight of sulfur and from about 0.01% to 2% by weight of nitrogen. Aromatic feedstocks of this character are required inasmuch as the low temperatures and relatively high pressures required do not thermodynamically favor the synthesis of aromatics from non-aromatics, and hence the aromatics appearing in the product are primarily unhydrogenated fragments of high boiling aromatics initially present in the feed. If non-aromatic feedstocks were employed, the products obtained under the conditions of pressure and temperature employed herein would be almost entirely paraffinic and/or naphthenic, regardless of the hydrogen sulfide concentration in the reaction mixture.

While as noted above, the initial feedstock may contain nitrogen compounds, it is important to note that in the particular contacting stage of the process in which the hydrogen sulfide concentration is to be varied periodically in order to change the aromaticity of the product, nitrogen should be substantially absent, i.e., below about 25 parts per million by weight, based on hydrocarbon feedstock. The presence of nitrogen compounds militates against a flexible operation (embracing in one cycle the production of highly saturated products), because of the relatively high temperatures, usually above about 700° F., which are required in order to overcome the poisoning effect of the nitrogen compounds. And, as noted above, at these high temperatures, variations in hydrogen sulfide concentration are relatively insignificant with respect to

product aromaticity, the product always being substantially aromatic in character.

It is further to be noted that the hydrocracking catalyst employed in the zone where flexibility of product aromaticity is desired, should preferably be one comprising a very active cracking base. This is required in order to obtain the desired cracking activity at temperatures below 750° F. In general, the cat-A cracking activity of the cracking component should be at least about 25 and preferably greater than about 35. Catalysts of this nature will be described more in detail hereinafter.

The process of this invention may be operated either in a single stage or in plural stages of hydrocracking. Raw feedstocks may be employed in many instances, but in most cases it is preferable to employ a hydrofining pretreatment to effect at least partial desulfurization, denitrogenation, stabilization, etc. Where the feedstock contains substantial quantities of nitrogen compounds, it is normally preferable to employ two stages of hydrocracking, and still more preferable a preliminary hydrofining treatment ahead of the first hydrocracking stage. The hydrofining treatment in this instance may desirably be of the "integral" type, i.e., wherein the entire hydrofiner effluent is passed directly through the first hydrocracking stage without intervening condensation or purification.

Since in these multi-stage operations, the first stage feed will normally contain substantial quantities of sulfur and/or nitrogen compounds in the form of hydrogen sulfide and ammonia, the first stage will usually be operated exclusively for gasoline production, since the hydrocarbon product is inherently substantially aromatic. The feed to the second hydrocracking stage is primarily the unconverted oil from the first stage, and is substantially free of nitrogen compounds and sulfur compounds. The second stage may hence be operated with any desired concentration of hydrogen sulfide present. The desired hydrogen sulfide concentration can be maintained for example by blending the feed with a sulfur-containing feed, varying the proportion of hydrogen sulfide-containing recycle gas employed therein, simply adding hydrogen sulfide, or any equivalent method. Any product oil from the second hydrocracking stage which is not converted to the desired boiling range, is normally recycled back to that stage.

Reference is now made to the attached drawing, which is a flow sheet illustrating the invention in one of its multi-stage adaptations. In the succeeding description, it will be understood that the drawing has been simplified by the omission of certain conventional elements such as valves, pumps, compressors, and the like. Where heaters or coolers are indicated, it will be understood that these are merely symbolic, and in actual practice many of these will be combined into banks of heat exchangers and fired heaters, according to standard engineering practice. The product fractionating equipment is merely illustrative of a system providing for maximum flexibility in handling different feedstocks and products; in actual practice, specific desired product distributions would require modifications in the fractionating equipment for maximum economy.

In the drawing, the initial feedstock is brought in via line **2**, mixed with recycle and makeup hydrogen from line **4**, preheated to incipient hydrofining temperature 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, 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, preferbaly 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	600–850	650–750
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.	500–20,000	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 total hydrofined product from hydrofiner **8** is withdrawn via line **10** and transferred via heat exchanger **12** to first-stage hydrocracker **14**, without intervening condensation or separation of products. Heat exchanger **12** is for the purpose of suitably adjusting the temperature of feed to hydrocracker **14**; this may require either cooling or heating, depending upon the respective hydrofining and hydrocracking temperatures employed. 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.

The catalyst employed in reactor **14** may consist of any desired combination of a refractory cracking base with a suitable hydrogenating component. Suitable cracking bases include for example mixtures of two or more difficultly reducible oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphates such as aluminum phosphate may also be used. The preferred cracking bases comprise composites of silica and alumina containing about 50–90% silica; coprecipitated composites of silica, titania, and zirconia containing between 5% and 75% of each component; partially dehydrated, zeolitic, crystalline molecular sieves, e.g., of the "X" or "Y" crystal types, having relatively uniform pore diameters of about 8 to 14 angstroms, and comprising silica, alumina and one or more exchangeable zeolitic cations.

A particularly active and useful class of molecular sieve cracking bases are those having a relatively high SiO_2/Al_2O_3 ratio, e.g., between about 2.5 and 6.0. The most active forms are those wherein the exchangeable zeolitic cations are hydrogen and/or a divalent metal such as magnesium, calcium or zinc. In particular, the "Y" molecular sieves, wherein the SiO_2/Al_2O_3 ratio is about 5, are preferred, either in their hydrogen form, or a divalent metal form. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolite ammonium ion and leave a hydrogen ion. It is not necessary to exchange out all of the monovalent metal; the final compositions may contain up to about 6% by weight of Na_2O, or equivalent amounts of other monovalent metals. Molecular sieves of this nature are described more particularly in Belgian Patents Nos. 577,642, 598,582, 598,683 and 598,682.

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

The foregoing cracking bases are compounded, as by impregnation, with from about 0.5% to 25% (based on free metal) of a group VIB or group VIII metal promoter, e.g., an oxide or sulfide of chromium, tungsten,

cobalt, nickel, or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the metals platinum, palladium, rhodium or iridium may be employed. The oxides and sulfides of other transitional metals may also be used, but to less advantage than the foregoing.

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

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

The process conditions in hydrocracker **14** are suitably adjusted so as to provide about 20–60% conversion to gasoline per pass, while at the same time permitting relatively long runs between regenerations, i.e., from about 2 to 8 months. 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 endpoints. The range of operative conditions contemplated for reactor **14** are as follows, assuming the feed thereto contains more than about 25 parts per million of nitrogen:

FIRST-STAGE HYDROCRACKING CONDITIONS

	Operative	Preferred
Temperature, ° F	625–850	650–800
Pressure, p.s.i.g	400–2,500	800–2,000
LHSV, v./v./hr	0.5–10	1–5
H_2/oil ratio, s.c.f./b	500–20,000	1,000–10,000

The effluent from hydrocracker **14** is withdrawn via line **16**, condensed in condenser **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 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 methane, ethane, propane and the like are withdrawn via line **34**. The liquid hydrocarbons in separator **32** are then transferred via line **36** to fractionating column **38**.

Fractionating column **38** is operated primarily for the purpose of recovering C_7+ gasoline and an unconverted gas oil feed for the second-stage hydrocracker. Light gasoline, boiling up to the C_6 range is normally taken off as overhead via line **40**. The C_7+ gasoline is withdrawn as a side-cut via line **42**. The bottoms from column **38** constitutes the primary feedstock for the second-stage hydrocracking, and is withdrawn via line **50** for that purpose.

The second-stage feedstock in line **50** is then mixed with recycle and makeup hydrogen from line **58**, preheated to incipient hydrocracking temperatures in heater **60**, and passed into second-stage hydrocracker **62**. This feedstock differs considerably from the feed to the first-stage hydrocracker, in that it is substantially free of nitrogen compounds and sulfur compounds. The choice is thus presented of operating the second stage with or without significant amounts of sulfur being present. In the modification illustrated, variations in sulfur concentration in hydrocracker **62** are obtained by the alternate use of separate and mixed hydrogen recycle gas systems from hydrocrackers **14** and **62**. The recycle gas from separator **24** normally contains a substantial proportion of hydrogen sulfide which was not removed by the previous water-washing operation. To operate hydrocracker **62** 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 hydrocracker **62** via lines **70** and **58**. To operate 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 hydrocracker **62** via line **58**.

In the sweet cycle of operation in hydrocracker **62**, it is normally desirable to adjust the process variables, principally temperature, so as to maximize jet fuel and/or diesel fuel production, and minimize the conversion to gasoline. Specifically, it is preferred to limit the conversion to gasoline to below about 20% per pass by volume. To achieve this objective, while obtaining maximum quality of the jet fuel-diesel fuel products, the hydrogen sulfide concentration should be maintained at a value below about 0.2, and preferably below about 0.01 millimole per mole of hydrogen, and the other process conditions are adjusted within the following ranges:

SWEET SECOND-STAGE OPERATING CONDITIONS

	Operative	Preferred
Temperature, ° F	400–750	450–650
Pressure, p.s.i.g	400–2,500	800–2,000
LHSV, v./v./hr	0.5–15	1–10
H_2/oil ratio, s.c.f./b	500–20,000	2,000–12,000

As will be understood by those skilled in the art, the specific selection of operating conditions within these ranges will depend on several factors, mainly the relative activity of the catalyst and general refractoriness of the feed.

In the sour cycle of operation in hydrocracker **62**, the process variables are normally adjusted so as to obtain a maximum conversion to gasoline per pass which is consistent with the desired run length (which in turn depends on the rate of catalyst deactivation), and desired efficiency of conversion to gasoline. If the crack per pass is too high, the catalyst deactivation rate is accelerated, and a relatively large proportion of feed is converted to C_1–C_3 dry gases and butanes. Satisfactory run lengths (3–12 months) and conversion efficiencies are normally obtained at conversions to 400° F. end-point gasoline of between about 40 and 80% by volume per pass. To achieve these objectives, while obtaining maximum gasoline quality, the hydrogen sulfide concentration should be maintained at a value above about 0.01, and preferably above about 0.2 millimole per mole of hydrogen, and the other process conditions are adjusted within the following ranges:

SOUR SECOND-STAGE OPERATING CONDITIONS

	Operative	Preferred
Temperature, ° F	450–850	500–750
Pressure, p.s.i.g	400–2,500	800–2,000
LHSV, v./v./hr	0.5–10	1–5
H_2/oil ratio, s.c.f./b	500–20,000	2,000–12,000

The catalyst used in hydrocracker **62** comprises about 0.05–3% by weight of a group VIII noble metal supported on substantially any of the cracking bases previously described for use in hydrocracker **14**. Specifically

included are the metals, ruthenium, rhodium, palladium, osmium, iridium and platinum, with palladium being preferred. Specifically preferred cracking bases are the high-silica zeolitic molecular sieves, and especially the decationized or divalent metal forms of the Y molecular sieves previously described.

At the conversion levels and conditions prescribed for the second-stage hydrocracker, the run length between regenerations can be adjusted to coincide substantially with the run length in reactor **14**, e.g., between about 3 and 12 months. In extended runs such as these, it is normally preferably to maintain substantially constant conversion in each stage by incrementally raising the temperature as the activity of the catalyst declines. The rate of catalyst activity decline in reactors **14** and **62** under the prescribed conditions is such that constant conversion in both reactors can be obtained by raising the respective temperatures between about 0.1° and 3° F. per day, on the average. The average temperature in hydrocracker **62** will normally be about 25°–125° F. lower than the average temperature in hydrocracker **14**.

The total effluent from hydrocracker **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 condensed hydrocarbons in separator **68** are then flashed via line **72** into low pressure separator **74**, from which C_1–C_3 flash gases are withdrawn via line **76**. The 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. Light gasoline blending stock is withdrawn as overhead via line **82**, C_7+ gasoline via line **84**, a diesel bottoms fraction via line **86**, and a jet fuel side-cut via line **88**. The jet fuel side-cut is transferred to a small stripping column **90**, from which overhead gasoline hydrocarbons are returned to column **80** via line **92**. During the sweet operating cycle, the entire bottoms from stripper **90** may be withdrawn from the system via line **94** and sent to jet fuel blending and storage facilities. During the sour operating cycle, the jet fuel fraction from line **94** is normally diverted via line **96** and recycled to second-stage hydrocracker **62** via line **50**. Also, during the sour operation, the diesel fraction withdrawn as bottoms via line **86** is recycled via lines **98** and **50** to hydrocracker **62**. Where both the jet fuel and diesel fuel fractions are to be recycled, there is of course no need to recover them separately, and hence both fractions can be recovered as bottoms from column **80** and recycled via lines **86**, **98** and **50**, thus eliminating the need for stripping column **90**. Where maximum jet fuel production is desired during the sweet operation, all or a portion of the diesel fraction in line **86** may be recycled to hydrocracker **62** for conversion to jet fuel. It will be understood that the choice of the various recycle alternatives depends largely upon the desired refinery balance and market demands.

The following examples are presented to illustrate certain critical variables in the process, as well to illustrate the operation and results of the process as above described in connection with the drawing. These examples should not however be construed as limiting in scope:

Example I

This example demonstrates the remarkable flexibility of the process of this invention in shifting rapidly from highly paraffinic to moderately aromatic products.

The feedstock was an unconverted gas oil (400–740° F. boiling range) derived from a previous hydrofining-hydrocracking operation, containing about 37% by weight of total aromatics and about 7 parts per million of sulfur by weight. This amount of sulfur corresponds to 0.0036 millimole of hydrogen sulfide per mole of hydrogen in the reaction mixture. The catalyst was a copelleted mixture of (1) 50% by weight of 100–325 mesh activated alumina, the alumina being impregnated with 25% by weight of nickel oxide, and (2) 50% by weight of a powdered, decationized Y molecular sieve loaded by ion-exchange with 0.5% by weight of palladium. Process conditions constant throughout the run were:

Pressure, p.s.i.g.	1,500
LHSV	1.5
H_2/oil ratio, s.c.f./b	8,000

During the initial 450 hours of processing at about 50% conversion to C_7—400° F. end-point gasoline (temperature, 560–575° F.), and with no sulfur added to the feed, the product characteristics were as follows:

	C_7—400° F. gasoline	400° F.+gas oil
Total aromatics, vol. percent	0.4–0.6	0.1–0.5
Octane No.:		
F-1 +3 ml. TEL	73.8–75.0	----------
F-1 clear	51.5–54.0	----------

The foregoing operation was then modified for 8 hours by incorporating 0.5% by weight of sulfur (as thiophene) in the feed, corresponding to about 2.44 millimoles of H_2S per mole of hydrogen. At 620° F. (to maintain 50% conversion to gasoline), the product characteristics were as follows:

	C_7—400° F. gasoline	400° F.+gas oil
Total aromatics, vol. percent	19.9	22
Octane No.:		
F-1 +3 ml. TEL	83.4	----------
F-1 clear	65.5	----------

After the 8-hour run with 0.5% sulfur in the feed, the original low-sulfur feed was used for 8 hours at 624° F., the product characteristics then being:

	C_7—400° F. gasoline	400° F.+gas oil
Total aromatics, vol. percent	0.9	1.23
Octane No.:		
F-1 +3 ml. TEL	78.9	----------
F-1 clear	57.5	----------

It will thus be apparent that product aromaticity is almost immediately responsive to changes in sulfur concentration. This responsiveness however, is only apparent at temperatures below about 750° F., for when the above run was continued without sulfur until the temperature level reached 725° F. (to maintain the 50% conversion to gasoline with the relatively more deactivated catalyst), the C_7—400° F. gasoline product contained 31.5% aromatics which is only slighly lower than the aromaticity obtainable at this temperature in the presence of added sulfur. However, the efficiency of conversion to C_7—400° F. gasoline was only 42% at 725° F., compared to 75–80% at 570–625° F. "Efficiency" is a measure of the proportion of feed converted which went to the desired product, and in this case is expressed as:

(volumes of C_7—400° F. gasoline, percent of fresh feed) ÷(total volume percent conversion of fresh feed)×100

Example II

A run similar to that of Example I was carried out, using as the catalyst a magnesium "Y" molecular sieve containing about 3% by weight of zeolitic magnesium, and loaded by ion-exchange with 0.5% by weight of palladium (Linde hydrocracking catalyst MB 5382). During a pre-run period this catalyst was heavily sulfided for 8 hours with a feed containing 2.5% sulfur. Sulfur-free feed (7 p.p.m. sulfur) was then fed to the unit for 44 hours at

600° F., and then 0.5% sulfur was added for 8 hours at 641° F. The results were as follows:

	Total Aromatics, vol. percent	Octane No.	
		F-1 +3 ml. TEL	F-1 clear
Sulfur-free feed, 600° F.:			
C_7—400° F. gasoline	0.4	73.4	52.5
400° F.+gas oil	0.22		
0.5% sulfur feed, 641° F.:			
C_7—400° F. gasoline	20.9	85.2	68.0
400° F.+gas oil	23.3		

The gas oil products produced from the sulfur-free operation of this example, and Example I, constitute excellent diesel fuels, and by fractionating said products to 550° F. endpoint, excellent jet fuels are obtained. The gas oils produced from the high-sulfur feeds are preferably recycled to the hydrocracker for further conversion to aromatic gasoline.

The low-octane gasolines produced from the sulfur-free runs are preferably subjected to catalytic reforming, while the high-octane gasolines produced from the high-sulfur feeds can be used directly as gasoline blending stocks.

Example III

This example illustrates preferred techniques and results obtainable in practicing the invention in a two-stage modification, substantially as illustrated in the drawing. The catalyst used in the hydrofining pretreatment is 3% CoO and 15% MoO_3 on a carrier composed of 5% SiO_2 co-precipitated with 95% Al_2O_3, the catalyst being sulfided before use. The catalyst used in both stages of hydrocracking is similar to that of Example I, being a copelleted mixture of (1) 50% by weight of 100–325 mesh activated alumina, the alumina being impregnated with 25% by weight NiO, and (2) 50% by weight of a powdered, decationized Y molecular sieve loaded by ion exchange with 1% by weight of palladium. The initial feed is a blend of coker distillate and thermally cracked gas oils derived from California crude oils. After an initial hydrofining treatment, the total hydrofining effluent is passed to the first stage of hydrocracking where hydrocracking proceeds in the presence of the ammonia and hydrogen sulfide formed during hydrofining. The first-stage hydrocracking effluent is water-washed and fractionated to recover gasoline product fractions, and a substantially sulfur-free gas oil which constitutes feed to the second stage of hydrocracking.

The second hydrocracking stage is operated alternately with a sour recycle hydrogen stream (about 0.5% by volume H_2S), and with a sweet recycle hydrogen stream (less than 10 parts per million H_2S). During the sour recycle sequence, the reactor effluent is condensed and fractionated to recover gasoline product fractions, and the remaining oil boiling above the gasoline range is recycled to the second hydrocracking stage.

During the sweet recycle sequence the reactor effluent is fractionated to recover a light gasoline (C_5–C_6) and heavier products such as a C_7+ gasoline for reforming, a jet fuel fraction, and a diesel fuel fraction. Any remaining oil boiling above the end-point of the heaviest product desired is recycled to the second hydrocracking stage.

In one of the sweet second-stage operations shown below, the heaviest desired product is a 330–483° F. jet fuel; in another, a C_7-plus reformer charge stock and a 370–630° F. diesel fuel are produced. In the latter case, it will be clear that a jet fuel fraction could also be produced simply by changes in the fractionation employed, without altering the reactor operating conditions or the volume and composition of the recycle oil.

The significant conditions and results of the process are as follows.

Initial feedstock:	
Boiling range, ° F	400–857
Gravity, ° API	22.2
Aromatics, wt. percent	37
Nitrogen, wt. percent	0.345
Sulfur, wt. percent	2.1
Hydrofining conditions:	
Temperature, av. bed, ° F	725
Pressure, p.s.i.g	1,500
LHSV	0.75
H_2/oil ratio, s.c.f/b	8,000
First-stage hydrocracking conditions:	
Temperature, av. bed, ° F	765
Pressure, p.s.i.g	1,500
LHSV	1.5
H_2/oil ratio, s.c.f./b	8,000
Conversion per pass to 400° F. E.P. gasoline and lighter, vol. percent	40
Second-stage hydrocarcking conditions:	
Temperature, av. bed, ° F.—	
During sour operation	650
During sweet operation for jet fuel	565
During sweet operation for diesel fuel	545
Pressure, p.s.i.g	1,500
LHSV—	
During sour operation	1.5
During sweet operation	1.3
H_2/oil ratio, s.c.f./b	8,000
Conversion per pass, vol. percent—	
To 400° F. E.P. gasoline during sour operation	60
To 483° F. E.P. jet fuel during sweet operation for jet fuel	70
To 630° F. E.P. diesel fuel during sweet operation for diesel fuel	70

	First Stage	Second Stage		
		Sour—Gasoline Case	Sweet	
			Jet Fuel Case	Diesel Fuel Case
Gasoline Products, Octane Numbers:				
Light Gasoline (C_5—C_6) F-1 +3 ml. TEL	99.5	99.5	98.7	97.7
C_7=plus Gasoline:				
F-1 +3 ml. TEL	87.2	80.0	[a] 84.2	[a] 82.9
End Point, ° F	400	400	280	332
Second Stage Jet Fuel Product:				
Boiling Range, ° F			330–483	
Aniline-Gravity Product			6866	
Freezing Point, ° F			−73	
Volume Percent Aromatics			0	
CFR Luminometer Number			75	
Second Stage Diesel Fuel Product:				
Boiling Range, ° F				370–630
Aniline Point, ° F				169.5
Sulfur, wt. Percent				0.0004
Volume Percent Aromatics				3
Cetane Number				52.6
Approximate Material Balances, Barrels of combined First and Second Stage Products per 100 Barrels Fresh Feed:				
Butanes		22	13	9
C_5–C_6 Gasoline		27	24	16
C_7—400° F. Gasoline		75	51	39
Jet Fuel			33	
Diesel Fuel				52

[a] Higher octane numbers here reflect low end-points of the respective gasolines, as compared to the 400° F. end-point gasoline produced during the sour operation. If 400° F. end-point gasolines were produced during these sweet operations, their octane numbers would be lower than that of the gasoline from the sour operation.

Results analogous to those indicated in the foregoing examples are obtained when other hydrocracking catalysts and conditions, other feedstocks and other hydrofining

conditions within the broad purview of the above disclosure are employed. It is hence not intended to limit the invention to the details of the examples or the drawing, but only broadly as defined in the following claims.

We claim:

1. In a catalytic hydrocracking process wherein a hydrocarbon feedstock boiling above the gasoline range and containing aromatic hydrocarbons is contacted with a group VIII noble metal-containing hydrocracking catalyst in the presence of added hydrogen at a pressure between about 400 and 2,500 p.s.i.g. and at a temperature between about 400–750° F. selected to give a substantial conversion to at least one desired product selected from the class consisting of gasoline, jet fuel and diesel fuel, the improved method for controlling and alternately varying the aromaticity of said desired product which comprises: maintaining alternately (A) a relatively high, continuous concentration of hydrogen sulfide, above about 0.01 millimole thereof per mole of hydrogen in the hydrocracking zone, to produce a relatively aromatic product, and (B) a relatively low continuous partial pressure of hydrogen sulfide, below about 0.2 millimole thereof per mole of hydrogen in the hydrocracking zone, to produce a relatively non-aromatic product.

2. A process as defined in claim 1 wherein said group VIII noble metal is palladium.

3. A process as defined in claim 1 wherein said hydrocracking catalyst comprises a zeolitic, alumino-silicate molecular sieve of the Y crystal type containing zeolitic cations from the class consisting of hydrogen and divalent metals.

4. A process as defined in claim 1 wherein the sulfur concentration during said alternate (A) is maintained at above about 0.2 millimole per mole of hydrogen, and during said alternate (B) at below about 0.01 millimole per mole of hydrogen.

5. In a hydrocarbon conversion process wherein a hydrocarbon feedstock containing aromatic hydrocarbons and boiling above the gasoline range is first subjected to a hydrogenating treatment wherein organic sulfur compounds are decomposed and removed, and wherein essentially sulfur- and nitrogen-free hydrocarbon effluent boiling above the gasoline range from said first hydrogenating treatment is subjected to a subsequent hydrocracking step in contact with a group VIII noble metal-containing hydrocracking catalyst and at a temperature between about 400–750° F. to produce at least one product selected from the class consisting of an aromatic gasoline, a non-aromatic jet fuel and a non-aromatic diesel fuel; the improvement which comprises maintaining in said subsequent hydrocracking step a concentration of hydrogen sulfide which is (A) relatively low, less than about 0.2 millimole per mole of hydrogen when the desired product to be recovered therefrom is selected mainly from the jet fuel-diesel fuel class, and (B) relatively high, greater than about 0.01 millimole per mole of hydrogen when the desired product to be recovered is mainly gasoline.

6. A process as defined in claim 5 wherein said group VIII nobel metal is palladium.

7. A process as defined in claim 5 wherein said hydrocracking catalyst comprises a zeolitic, alumino-silicate molecular sieve of the Y crystal type containing zeolitic cations from the class consisting of hydrogen and divalent metals.

8. A process as defined in claim 5 wherein the sulfur concentration during said alternate (A) is maintained at above about 0.2 millimole per mole of hydrogen and during said alternate (B) at below about 0.01 millimole per mole of hydrogen.

9. A process as defined in claim 5 wherein said hydrogenating treatment is catalytic hydrofining.

10. A process as defined in claim 5 wherein said hydrogenating treatment is catalytic hydrocracking.

11. A multi-stage hydrocracking process for converting a hydrocarbon feedstock containing aromatic hydrocarbons and boiling above the gasoline range to high-octane gasoline and a desired proportion, from 0% to about 80% by volume, of a non-aromatic product fraction boiling in the jet fuel-diesel fuel range, which comprises:

(A) subjecting said feedstock plus added hydrogen to hydrocracking in a first hydrocracking zone in contact with a hydrocracking catalyst comprising a hydrogenating metal sulfide distributed on a solid cracking base;

(B) maintaining in said first hydrocracking zone a pressure between about 400 and 2,500 p.s.i.g. and a temperature adjusted to give a converison per pass to 400° F. end-point gasoline of about 20–60% by volume;

(C) fractionating effluent from said first hydrocracking zone to recover high-octane gasoline and unconverted oil;

(D) subjecting said unconverted oil plus added hydrogen to hydrocracking in a second hydrocracking zone in contact with a hydrocracking catalyst comprising a group VIII noble metal-containing hydrogenating component distributed on a solid cracking case;

(E) maintaining in said second hydrocracking zone a pressure between about 400 and 2,500 p.s.i.g., and a temperature between about 400–750° F. and adjusted to give a substantial conversion per pass to lower-boiling hydrocarbons;

(F) treating the effluent from said second hydrocracking zone to recover at least one product selected from the class consisting of (*a*) an aromatic gasoline, (*b*) a non-aromatic jet fuel and (*c*) a non-aromatic diesel fuel; and

(G) maintaining in said second hydrocracking zone a concentration of hydrogen sulfide which is (*a*) relatively low, less than about 0.2 millimole per mole of hydrogen when the product recovered in step (F) is selected mainly from the jet fuel-diesel fuel class, and (*b*) relatively high, greater than about 0.01 millimole per mole of hydrogen when the product recovered in step (F) is mainly gasoline.

12. A process as defined in claim 11 wherein said feedstock is first subjected to catalytic hydrofining, and the total effluent from said catalytic hydrofining is then subjected to said first hydrocracking step (A).

13. A process as defined in claim 11 wherein the catalyst in step (D) comprises palladium distributed on a zeolitic alumino silicate molecular sieve of the Y crystal type containing zeolitic cations from the class consisting of hydrogen and divalent metals.

14. A hydrocracking process for converting a substantially nitrogen-free hydrocarbon feedstock containing aromatic hydrocarbons and boiling above the gasoline range to high-octane gasoline, which comprises subjecting said feedstock plus added hydrogen to catalytic hydrocracking at a pressure between about 400 and 2,500 p.s.i.g., and a temperature between about 500° F. and 750° F. in contact with a group VIII noble metal-containing hydrocracking catalyst, and maintaining during said contacting a concentration of hydrogen sulfide greater than about 0.01 millimole per mole of hydrogen.

15. A process as defined in claim 14 wherein said group VIII noble metal is palladium.

16. A process as defined in claim 14 wherein said hydrocracking catalyst comprises a zeolitic, alumino-silicate molecular sieve of the Y crystal type containing zeolitic cations from the class consisting of hydrogen and divalent metals.

17. A hydrocracking process for converting a substantially nitrogen-free hydrocarbon feedstock containing aromatic hydrocarbons and boiling above the gasoline range to a non-aromatic product selected from the class consisting of jet fuel and diesel fuel, which comprises subjecting said feedstock plus added hydrogen to

catalytic hydrocracking at a pressure between about 400 and 2,500 p.s.i.g., and a temperature between about 400° and 750° F., in contact with a group VIII noble metal-containing hydrocracking catalyst, and maintaining during said contacting a concentration of hydrogen sulfide less than about 0.2 millimole per mole of hydrogen.

18. A process as defined in claim 17 wherein said group VIII noble metal is palladium.

19. A process as defined in claim 17 wherein said hydrocracking catalyst comprises a zeolitic, alumino-silicate molecular sieve of the Y crystal type containing zeolitic

cations from the class consisting of hydrogen and divalent metals.

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Disclaimer

3,132,090.—*Paul F. Helfrey*, Montebello, *Nicholas L. Kay*, Fullerton, *Bernal Peralta*, Anaheim, and *Cloyd P. Reeg*, Orange, Calif. HYDROCRACKING PROCESS WITH REGULATION OF THE AROMATIC CONTENT OF THE PRODUCT. Patent dated May 5, 1964. Disclaimer filed Aug. 13, 1969, by the assignee, *Union Oil Company of California.*

Hereby enters this disclaimer to claims 14 and 15 of said patent.

[*Official Gazette September 23, 1969.*]