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HYDROCRACKING PROCESS IN SEVERAL STAGES AND REGULATING THE HYDROCRACKING BY VARYING THE AMOUNT OF HYDROGEN SULFIDE IN THE REACTION ZONES

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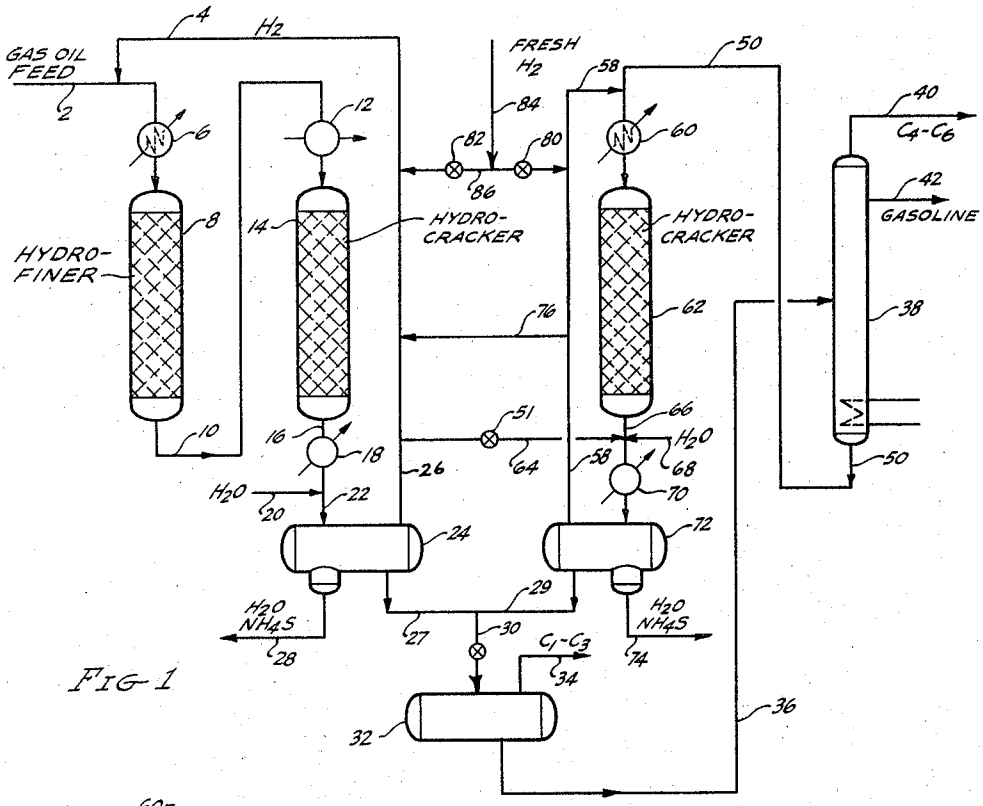


FIG-1

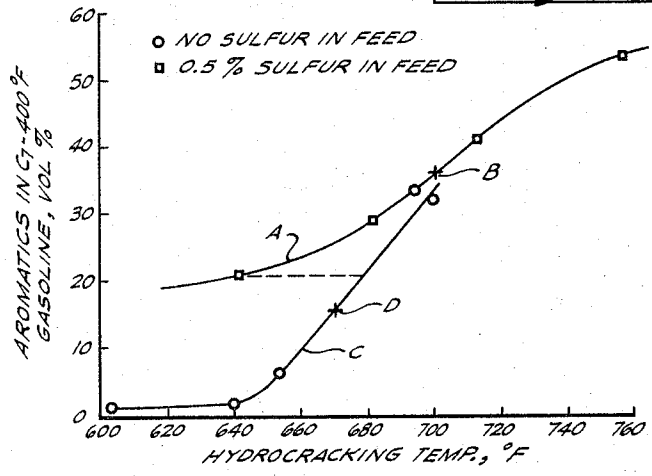


FIG-2

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HYDROCRACKING PROCESS IN SEVERAL STAGES AND REGULATING THE HYDROCRACKING BY VARYING THE AMOUNT OF HYDROGEN SULFIDE IN THE REACTION ZONES

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This invention relates to catalytic hydrocracking, and more particularly is concerned with the manufacture of high-quality, aromatic gasoline by the hydrocracking of gas oil feed-stocks, while at the same time providing for maximum run lengths between catalyst regenerations. The invention is concerned specifically with hydrocracking processes wherein gas oil feed-stocks are hydrocracked over a fixed-bed of Group VIII noble metal hydrocracking catalyst at relatively low pressures and temperatures, and wherein an extended run length of, e.g., 6–24 months is obtained by incrementally raising the hydrocracking temperature in order to compensate for progressive catalyst deactivation. Briefly, the principal novel feature of the process comprises shifting the hydrogen sulfide concentration in the reaction mixture downwardly at some one or more intermediate points during the run, and correlating the hydrocracking temperature with the hydrogen sulfide concentration so as to maintain throughout the run a substantially constant overall conversion to gasoline, and a relatively high concentration of aromatic hydrocarbons in the gasoline product. It has been found that hydrogen sulfide is desirable during the initial, low-temperature part of the run in order to produce a more aromatic gasoline, but is undesirable during the latter, high-temperature portion of the run, because its presence tends to reduce the permissible run length without increasing product aromaticity.

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 substantially in the absence of nitrogen compounds, to produce high-octane aromatic gasoline over the entire run length comprising the initial low-temperature, high-sulfur portion, and the terminal low-sulfur, high-temperature portion. By operating in this manner, high octane aromatic gasoline can be produced as the principal product from both stages over the entire run length, while at the same time affording maximum run lengths in the second stage.

A principal object of the invention is to provide a hydrocracking process capable of operating at relatively low temperatures and low pressures over long operating periods without catalyst regeneration, while producing throughout the run a gasoline product of relatively high octane value and aromatic content. A specific objective is to correlate sulfur content of the hydrocracking reaction mixture with hydrocracking temperature so as to realize the maximum in benefits obtainable from the use of a sulfided hydrocracking catalyst, while avoiding its detrimental effects on run length (by shifting during the latter portion of the run to a non-sulfided form of the catalyst which is overall more active than the sulfided form). Other objects will be apparent from the more detailed description which follows.

It has recently been discovered 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 1.0 millimole per mole of hydrogen, are substantially immediately reflected in a significant change in product aromaticity, even without a change in hydrocracking temperature. But, at temperatures above about 750° F. hydrogen sulfide concentration appears to have little effect on product aromaticity, while at pressures above about 2,500 p.s.i.g., the magnitude of the effect is substantially decreased. Moreover, 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 1.0 millimole, or in the range below about 0.01 millimole 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 1.0 millimole, and especially between about 0.01 and 0.5 millimole. While the explanation for this observed sensitivity to hydrogen sulfide concentration is not certain, 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. Other operative factors may however be involved.

In commercial hydrocracking processes, the normal procedure is to initiate a run at relatively low temperatures with a fresh catalyst, and then as the catalyst activity declines, to increase the temperature periodically in order to maintain the desired conversion per pass. This is continued until a terminal temperature is reached at which there is an economically undesirable product distribution, with relatively large portions of feed being converted to light gases and coke rather than gasoline. At this point, the run is terminated and the catalyst is regenerated. The terminal temperature is mainly a function of the specific catalyst employed, and for the catalysts of this invention, will generally fall within the range of about 675–750° F. The terminal temperature being relatively fixed, it then becomes apparent that the length of a hydrocracking run depends upon two factors, viz., (1) the permissible initial temperature at which the desired conversion can be obtained, and (2) the rate at which the temperature must be raised to maintain that conversion. The rate of temperature increase is herein designated as "Temperature Increase Requirement" (TIR), and is expressed as the daily temperature increase in degrees F. required to maintain a given constant conversion. In any given run, it is found that this figure remains substantially constant for long periods of time, and tends to vary therefrom only at the beginning and end of the run.

When hydrocracking essentially nitrogen-free feedstocks with the catalysts of this invention, longest run lengths are generally obtainable by operating in a sulfur-free system, as compared to a run where sulfur is present throughout. This is mainly because of the higher intrinsic activity of the non-sulfided catalysts, which permits the initiation of a run at temperatures about 20–60° F. lower than are required for the same conversion using the corresponding sulfided catalyst. However, to take advantage of this superior activity, the hydrocracking run must be commenced at very low temperatures, in the neighborhood of about 500–600° F. At these low temperatures, and at successively higher temperatures up to about 650° F., the gasoline product is almost completely saturated, the aromatic content being less than about 5% by volume. In order to convert such gasolines to high-octane motor fuels, it is necessary to subject them to extensive and severe reforming, which greatly adds to the overall cost of the final product. The severity and cost of the reforming operation could be considerably reduced if the aro-

matic content of the hydrocracked gasoline could be kept above about 15–20% by volume at all times.

It has now been found that it is possible to attain substantially the long run lengths characteristic of sulfur-free hydrocracking runs, while at the same time producing during the early part of the run (below about 650° F.) a gasoline product containing at least about 5–10 times the aromatic content obtainable at the same temperature in the absence of sulfur. Specifically, at all hydrocracking temperatures above about 600° F., the C_7—400° F. gasoline product will contain at least 10%, and usually more than 15% by volume, of aromatic hydrocarbons. This is accomplished by initiating the hydrocracking run at a temperature between about 525° and 650° F. in the presence of hydrogen sulfide in or above the critical ratios previously specified, continuing with gradually rising temperatures until the product distribution becomes undesirable (usually at about 675–750° F.), then eliminating hydrogen sulfide from the system and cutting back the hydrocracking temperature to the level required to maintain the same conversion with the partially deactivated catalyst in a sulfide-free state. The cut-back in temperature may range anywhere from about 20° to 60° F. or more. Assuming an average TIR of about 0.25° F. per day, this then will add about 80–240 days to the normal run length obtainable with a sulfided catalyst.

According to an alternative mode of operation, the hydrocracking run may be initiated as before in the presence of sulfur, and then as the run progresses and temperatures are raised, the hydrogen sulfide concentration of the system may be gradually or periodically reduced so as to maintain a substantially constant aromatics content in the product of, e.g., about 15–25% by volume until the temperature reaches about 670–685° F., at which point the hydrogen sulfide concentration will be substantially zero. The run may then be continued with rising temperatures and increasingly aromatic products until the desired terminal temperature is reached.

The foregoing may be aptly illustrated with reference to the attached FIGURE 2, which is a graph depicting data obtained in several 1,500 p.s.i.g., 1.5 LHSV hydrocracking runs utilizing a prehydrofined catalytic cycle oil feed (30.4° API; 350–750° F. boiling range; 46.5 weight-percent aromatics; 0.3 p.p.m. nitrogen), and hydrocracking temperatures adjusted to give 50 volume percent conversion per pass to 400° F. end-point gasoline. The catalyst was composed of 0.5% palladium combined by ion exchange with a magnesium zeolite of the Y molecular sieve crystal type. Curve A of FIGURE 2 represents hydrocracking carried out with 0.5% sulfur added to the feed as thiophene. Curve C represents sulfur-free hydrocracking, and it will be noted that in the absence of sulfur, a desirable aromatics content in the product was not obtained until temperatures of about 670° F. were reached. Curve A shows however that in the presence of sulfur, the aromatic content varied from a minimum of about 20% up to 54% by volume. To obtain the benefits of the present invention, hydrocracking as represented by Curve A would be initiated at about 640° F. or lower, and continued with gradually increasing temperatures until a point B is reached. At this point, hydrogen sulfide is eliminated from the system, and the temperature is cut back to about 670° F. to produce a gasoline containing about 15% aromatics. The hydrocracking run is then continued on curve C until a temperature of about 700° F. is reached, at which point the product contains about 32% by volume aromatics. Thus, the portion of run length lost by initiating the run at 640° F. instead of 600°, is substantially made up in the terminal portion of the run when the temperature is shifted from 700° back to about 670°.

In the alternative mode of operation, after initiation of hydrocracking as represented by curve A, the hydrogen sulfide concentration is gradually reduced, with more slowly rising temperatures, so that a substantially constant aromatics content of about 20% is maintained for a long period of time. This is continued as represented by the horizontal dotted line until curve C is intercepted, at which point the system will be substantially free of hydrogen sulfide. Hydrocracking then proceeds in the absence of sulfur to the terminal temperature.

A critical feature of the process resides in the use of hydrocarbon feedstocks which are substantially aromatic in character. Typical feedstocks include coker distillate gas oils, cycle oils derived from catalytic or thermal cracking operations, aromatic straight-run gas oils, etc., any of which may be derived from petroleum crude oils, shale oils, tar sand oils, or the like. Specifically, it is preferred to employ gas oils 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. Aromatic feedstocks of this character are required because the low temperatures and relatively high pressures required do not thermodynamically favor the synthesis of aromatics from non-aromatics; hence the aromatics appearing in the product are primarily unhydrogenated fragments of high-boiling aromatics initially present in the feed.

If suitable pretreatment facilities are available, the initial feedstock may also contain from about 0.4% to 5% by weight of sulfur, and from about 0.1% to 2% by weight of nitrogen. It is important to note however that in the particular contacting stage in which the hydrogen sulfide concentration is to be shifted, basic nitrogen compounds should be substantially absent, i.e., below about 25 parts per million of feedstock. Where nitrogen compounds are present in excess of about 25 parts per million, higher hydrocracking temperatures are required in order to overcome the poisoning effect. And as noted above, at high temperatures, variations in hydrogen sulfide concentration are relatively insignificant with respect to product aromaticity.

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 preferably, 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.

In two-stage hydrocracking, the feed to the second stage is primarily the unconverted oil from the first stage, and is essentially 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 FIGURE 1, 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.

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 VI–B and/or Group VIII metals, preferably supported on adsorbent oxide carriers such as alumina, silica, titania, and the like. The hydrofining operation may be conducted either adiabatically or isothermally, and under the following general conditions:

HYDROFINING CONDITIONS

	Operative	Preferred
Temperature, ° F	600–850	650–750
Pressure, p.s.i.g	500–3,000	800–2,000
LHSV, v./v./hr	0.3–10	0.6–5
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 organic nitrogen content of the feed to below about 25 parts per million, and preferably below about 10 parts per million.

The total hydrofined produce 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.

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 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 10. 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 between about 4–6, are preferred, either in their hydrogen form, a divalent metal form, or a mixture divalent metal-hydrogen form. Normally, such molecular sieves are prepared first in the sodium or potassium form, and the monovalent metal is ion-exchanged out with a divalent metal, or where the hydrogen form is desired, with an ammonium salt followed by heating to decompose the zeolitic ammonium ion and leave a hydrogen ion. 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 0.05% to 25% (based on free metal) of a Group VI–B or Group VIII metal promotor, e.g., an oxide or sulfide of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. Preferably, the Group VIII noble metals are employed, in amounts between about 0.05% and 2% by weight, e.g., platinum, palladium, rhodium or iridium. 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 suitable 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.

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, e.g., from about 4 to 18 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-end-points. 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 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 removed via line **27**, blended with the second-stage product condensate from line **29**, and the mixture 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 transferred via line **36** to fractionating column **38**.

Fractionating column **38** is operated primarily for the purpose of recovering 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 overheard 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 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 considererably 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, the desired mid-run shift in sulfur concentration in hydrocracker **62** is 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 with added hydrogen sufide, valve 51 is opened sufficiently to permit the desired portion of sour recycle gas in line 26 to flow through line 64 into reactor effluent line 66, where it mingles with the total effluent from hydrocracker 62. By adding the cool recycle hydrogen at this point, a partial quench of the hot effluent in line 66 is effected.

An additional water wash may also be utilized in line 66 in order to remove traces of ammonia remaining in the sour recycle gas, the water being added via line 68. The resulting mixture is then passed through condenser 70 and into high-pressure separator 72, from which the total recycle gas for reactor 62 is removed via line 58. Spent wash water containing ammonium sulfide is removed via line 74. The washing at this stage will remove some of the hydrogen sulfide, but most of it remains in the recycle gas in line 58. In order to prevent the buildup of light hydrocarbons and/or excess hydrogen in the recycle system for hydrocracker 62, a bleed line 76 is provided to permit withdrawal of a bleed stream of total recycle gas from line 58 back to line 26. In cases where excess hydrogen is supplied via line 64, requiring a bleed via line 76, fresh makeup hydrogen is ordinarily not required in hydrocracker 62. In that case, makeup hydrogen supply valve 80 may be closed and valve 82 opened, thereby permitting the total fresh hydrogen supply for the system to flow via lines 84 and 86 to the first-stage recycle line 26. In cases where the sour bleed stream in line 64 is insufficient to supply all the makeup hydrogen for hydrocracker 62, valve 80 will be partially opened in order to permit some of the fresh hydrogen from line 84 to flow into recycle line 58.

To operate hydrocracker 62 in the absence of sulfur (separate recycle systems) valve 51 is closed, and valve 80 opened sufficiently to supply the necessary makeup hydrogen. In one mode of operation, during the sweet cycle of operation valve 82 may be closed completely, thus diverting all of the fresh hydrogen through valve 80 and line 58. In this case, the makeup hydrogen for hydrocracker 14 is bled off through line 76 from line 58. This mode of operation presents the advantage of providing a continuous purge of small amounts of hydrogen sulfide formed in hydrocracker 62 to the recycle system of hydrocracker 14.

Operating conditions for second-stage hydrocracker 62 fall in general within the following ranges:

SECOND-STAGE OPERATING CONDITIONS

	Operative	Preferred
Temperature, ° F	500–800	525–750
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

Normally, the conditions of pressure, space velocity, and hydrogen-to-oil ratios are set at a constant value for the entire hydrocracking run. Temperature is then adjusted periodically throughout the run in order to maintain the desired conversion, normally about 40–70% by volume, to C_4+ gasoline. Starting temperatures in the sour operating cycle commonly fall within the range of about 525–650° F. Assuming an average TIR of about 0.25° F., this operation may be continued for about 6–18 months, until a terminal temperature of about 675–750° F. is reached. At this point the sweet cycle is initiated by closing valve 51, and lowering the reactor temperature until a point is reached at which the predetermined conversion level is again obtained. This normally entails lowering the temperature by about 20–60° F. The run is then continued for at least another one or two months, and up to 6–8 months, until the terminal temperature is again reached at which product distribution becomes undesirable. At this point, the run is terminated and the catalyst regenerated.

One disadvantage of the foregoing operation is that the aromaticity of the gasoline product is constantly changing during the run. Where maximum uniformity of product composition is desired, both temperature and hydrogen sulfide concentration are periodically or continuously adjusted. To accomplish this objective, valve 51 may be motor-controlled in response to the aromaticity of the gasoline product in line 42, thereby continuously cutting back on the volume of sour bleed stream in line 64 in response to rising aromaticity of the product, so as to maintain a continuously decreasing hydrogen sulfide concentration in recycle line 58, downwardly through the range of about 1.0 to 0.01 millimole per mole of hydrogen.

For successful operation of hydrocracker 62 as described, it is necessary to use a catalyst comprising a highly active cracking base and a hydrogenating metal whose activity is reversibly sensitive to hydrogen sulfide concentration. Specifically, it is necessary to use a cracking base having an activity greater than that indicated by a Cat.-A Activity Index of about 40. The operative hydrogenating metals are the Group VIII noble metals, e.g., platinum, palladium, rhodium or iridium, used in amounts of 0.05% to 2% by weight of finished catalyst. The preferred catalysts comprise platinum or palladium in combination with the high-silica molecular sieves previously described, particularly the molecular sieve zeolites of the Y crystal type, either in their hydrogen ("decationized") form, a divalent metal form such as magnesium, or the mixed hydrogen-divalent metal forms. Here again, the hydrogenating metal is preferably combined with the zeolitic cracking base by ion-exchange methods.

The following examples are cited to illustrate certain critical aspects of the process, and to illustrate the operation and results of the process as above described in connection with FIGURE 1. These examples should not however be construed as limiting in scope:

EXAMPLE I

This example demonstrates the reversible sensitivity of the catalysts of this invention to hydrogen sulfide concentration, with respect to product aromaticity.

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, hydrogen ("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 C_7—400° F. gasoline product characteristics were as follows:

Total aromatics, vol. percent	0.4–0.6
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 gasoline product characteristics were as follows:

Total aromatics, vol. percent	19.9
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 gasoline product characteristics then being:

Total aromatics, vol. percent	0.9
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 reached 725° F., the C_7—400° F. gasoline product contained 31.5% aromatics, which is only slightly 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

This example illustrates preferred techniques and results obtainable in practicing the invention in a two-stage modification, substantially as illustrated in FIGURE 1. The catalyst used in the hydrofining pretreatment is 3% CoO and 15% MoO_3 on a carrier composed of 5% SiO_2 coprecipitated with 95% Al_2O_3, the catalyst being sulfided before use. The catalyst used in both stages of hydrocracking is a magnesium-hydrogen zeolite of the "Y" molecular sieve crystal type, containing about 3.5% by weight of zeolitic magnesium (about 50% of ion exchange sites protonated), and loaded by ion-exchange with 0.5% 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, together with the second-stage product condensate, 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 for about 10 months with a sour recycle hydrogen stream (about 0.5% by volume H_2S), and then for about 5 months with a sweet recycle hydrogen stream (less than 10 parts per million H_2S).

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

Initial feedstock

Boiling range, ° F.	400–850
Gravity, ° API	22.2
Aromatics, wt. percent	37
Nitrogen, wt. percent	0.345
Sulfur, wt. percent	2.1

Hydrofining conditions

Temperature av. bed, ° F. (start of run)	700
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. (start of run)	710
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 hydrocracking conditions

	Sour Recycle Gas	Sweet Recycle Gas
Temperature, Av. Bed, ° F.:		
Start of run	560	670
End of run	700	700
Pressure, p.s.i.g.	1,500	1,500
LHSV	1.5	1.5
H_2/oil ratio, s.c.f./b	8,000	8,000
Conversion per pass to 400° F. E.P. gasoline and lighter, vol. percent	60	60

The quality of the C_7—400° F. gasoline produced at various temperatures during the run (second-stage gasoline only) is indicated in the following table:

	Sour Recycle Gas				Sweet Recycle Gas			
Run Temp., ° F.	600	640	680	700	670	680	690	700
Vol. percent aromatics	16	21	29	36	15	19	25	34
Octane Numbers:								
F–1+3 ml. TEL	85	86	90	95	85	90	93	95
F–1 clear	67	68	71	82	65	71	78	82

Approximate material balances over the entire run, in terms of barrels of combined first and second stage products per 100 barrels of fresh feed are as follows:

Butanes	22
C_5–C_6 gasoline	27
C_7—400° F. gasoline	75

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.

I claim:

1. In a hydrocracking process wherein a substantially nitrogen-free hydrocarbon feedstock boiling above the gasoline range and containing at least about 20% by volume of aromatic hydrocarbons is subjected to hydrocracking over a fixed bed of hydrocracking catalyst for an extended perior of time at temperatures below about 750° F. to effect a substantial conversion to gasoline-boiling-range hydrocarbons, and wherein the hydrocracking temperature is periodically raised during said run in order to maintain a substantially constant conversion to gasoline, said hydrocracking catalyst comprising a solid refractory cracking base having an activity greater than that corresponding to a cat.-A activity index of 40, and combined therewith a minor proportion of a Group VIII noble metal hydrogenating component, the improved method of operating said process in order to maintain throughout the run a relatively high aromatic content in the gasoline product, which comprises: (1) initiating said hydrocracking process at a temperature between about 525° and 650° F.; (2) maintaining a relatively high concentration of hydrogen sulfide in the hydrocracking zone during the initial portion of said run; (3) maintaining a relatively lower concentration of hydrogen sulfide in the hydrocracking zone during a later, relatively high-temperature portion of said run, and (4) controlling and correlating the hydrocracking temperature with the hydrogen sulfide concentration so as to obtain throughout said run at least about 40% by volume conversion to an aromatic gasoline

product, said gasoline containing at least about 10% by volume of aromatic hydrocarbons in the C_7—400° F. fraction at all hydrocracking temperatures above about 600° F.

2. A process as defined in claim 1 wherein said hydrocracking process is terminated at a temperature between about 675° and 750° F., and wherein said run is continued for a period of time in excess of about 4 months, and wherein said hydrocarbon feedstock contains less than about 25 parts per million of nitrogen during said run.

3. A process as defined in claim 1 wherein said hydrocracking catalyst comprises a minor proportion of a Group VIII noble metal hydrogenating component combined by ion-exchange with a crystalline, zeolitic molecular sieve cracking base of the Y crystal type having a SiO_2/Al_2O_3 mole-ratio between about 4 and 6, the zeolitic cations of said cracking base being selected from the class consisting of hydrogen and divalent metals.

4. In a hydrocracking process wherein a substantially nitrogen-free hydrocarbon feedstock boiling above the gasoline range and containing at least about 20% by volume of aromatic hydrocarbons is subjected to hydrocracking over a fixed bed of hydrocracking catalyst for an extended period of time at temperatures below about 750° F. to effect a substantial conversion to gasoline-boiling-range hydrocarbons, and wherein the hydrocracking temperature is periodically raised during said run in order to maintain a substantially constant conversion to gasoline, said hydrocracking catalyst comprising a solid refractory cracking base having an activity greater than that corresponding to a cat.-A activity index of 40, and combined therewith a minor proportion of a Group VIII noble metal hydrogenating component, the improved method of operating said process in order to maintain throughout the run a relatively high aromatic content in the gasoline product, which comprises (1) initiating said hydrocracking process at a temperature between about 525° and 650° F.; (2) carrying out the initial portion of said hydrocracking run while maintaining a relatively high concentration of hydrogen sulfide, above about 0.01 millimole thereof per mole of hydrogen in the hydrocracking zone, until a terminal temperature between about 675° and 750° F. is reached; (3) then reducing the hydrogen sulfide concentration in said hydrocracking zone to a relatively low level, below about 1 millimole thereof per mole of hydrogen, (4) substantially concurrently with said lowering of hydrogen sulfide concentration, reducing the hydrocracking temperature to a lower level in order to maintain the desired conversion to gasoline; (5) thereafter continuing said hydrocracking run with incrementally rising temperatures until a terminal temperature between about 675° and 750° F. is reached; and (6) controlling and correlating the hydrocracking temperature with the hydrogen sulfide concentration so as to obtain throughout said run at least about 40% by volume conversion to an aromatic gasoline product, said gasoline product containing at least about 10% by volume of aromatic hydrocarbons in the C_7—400° F. fraction at all hydrocracking temperatures above about 600° F.

5. A process as defined in claim 4 wherein said run is continued for a period of time in excess of about 4 months, and wherein said hydrocarbon feedstock contains less than about 25 parts per million of nitrogen during said run.

6. A process as defined in claim 4 wherein said hydrocracking catalyst comprises a minor proportion of a Group VIII noble metal hydrogenating component combined by ion-exchange with a crystalline, zeolitic molecular sieve cracking base of the Y crystal type having a SiO_2/Al_2O_3 mole-ratio between about 4 and 6, the zeolitic cations of said cracking base being selected from the class consisting of hydrogen and divalent metals.

7. In a hydrocarbon conversion process wherein a hydrocarbon feedstock containing at least about 20% by volume of 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 subsequent hydrocracking in an extended run period over a fixed bed of hydrocracking catalyst, and wherein the hydrocracking temperature therein is incrementally raised during said run in order to maintain a substantially constant conversion to gasoline, said hydrocracking catalyst comprising a solid refractory cracking base having an activity greater than that corresponding to a cat.-A activity index of 40, and combined therewith a minor proportion of a Group VIII noble metal hydrogenating component, the improved method for obtaining an aromatic gasoline product throughout said run, which comprises: (1) initiating said hydrocracking run at a temperature between about 525° and 650° F. and carrying out the initial portion of said hydrocracking run while maintaining a relatively high concentration of hydrogen sulfide, above about 0.01 millimole thereof per mole of hydrogen in the hydrocracking zone, until a terminal temperature between about 675° and 750° F. is reached; (2) then reducing the hydrogen sulfide concentration in said hydrocracking zone to a relatively low level, below about 1 millimole thereof per mole of hydrogen; (3) substantially concurrently with said lowering of hydrogen sulfide concentration, reducing the hydrocracking temperature to a lower level in order to maintain the desired conversion to gasoline; (4) thereafter continuing said hydrocracking run with incrementally rising temperatures until a terminal temperature between about 675° and 750° F. is reached; and (5) controlling and correlating the hydrocracking temperature with the hydrogen sulfide concentration so as to obtain throughout said run at least about 40% by volume conversion to an aromatic gasoline product, said gasoline product containing at least about 10% by volume of aromatic hydrocarbons in the C_7—400° F. fraction at all hydrocracking temperatures above about 600° F.

8. A process as defined in claim 7 wherein said run is continued for a period of time in excess of about 4 months, and wherein the feed thereto contains less than about 25 parts per million of nitrogen.

9. A process as defined in claim 7 wherein said hydrocracking catalyst comprises a minor proportion of a Group VIII noble metal hydrogenating component combined by ion-exchange with a crystalline, zeolitic molecular sieve cracking base of the Y crystal type having a SiO_2/Al_2O_3 mole-ratio between about 4 and 6, the zeolitic cations of said cracking base being selected from the class consisting of hydrogen and divalent metals.

10. A multi-stage hydrocracking process for converting a hydrocarbon feedstock containing sulfur compounds and at least about 20% by volume of aromatic hydrocarbons and boiling above the gasoline range to relatively high-octane aromatic gasoline, which comprises:

(1) subjecting said feedstock plus added hydrogen to catalytic hydrofining without substantial cracking of hydrocarbons;

(2) subjecting total hydrogen sulfide-containing effluent from said hydrofining to a first stage of catalytic hydrocracking;

(3) separating the effluent from said first-stage hydrocracking into a gasoline product, a substantially sulfur-free unconverted gas oil, and a sour recycle gas which is at least in part recycled to said hydrofining step;

(4) subjecting said unconverted gas oil plus added hydrogen to a second stage of catalytic hydrocracking over a fixed bed of catalyst, initially at a temperature between about 525° and 650° F., and continuing for an extended run period and at incrementally rising hydrocracking temperature within the range of about 525–750° F., said hydrocracking catalyst comprising

a solid refractory cracking base having an activity greater than that corresponding to a cat.-A activity index of 40, and combined therewith a minor proportion of a Group VIII noble metal hydrogenating component;

(5) separating the effluent from said second-stage hydrocracking into a gasoline product, a second-stage recycle oil, and a second-stage recycle gas having a relatively low concentration of hydrogen sulfide which is recycled to said second hydrocracking stage;

(6) during a first part of said second-stage hydrocracking run, blending a portion of said sour recycle gas with said second-stage recycle gas so as to maintain a relatively high concentration of hydrogen sulfide in said second-stage recycle gas;

(7) reducing said sour recycle gas portion during a later portion of said second-stage hydrocracking run so as to maintain a relatively low concentration of hydrogen sulfide therein, and thereafter continuing said run until a terminal temperature between about 675° and 750° F. is reached; and

(8) controlling and correlating the hydrocracking temperature with the hydrogen sulfide concentration so as to obtain throughout said second-stage run at least about 40% by volume conversion to an aromatic gasoline product, said gasoline product containing at least about 10% by volume of aromatic hydrocarbons in the C_7—400° F. fraction at all hydrocracking temperatures above about 600° F.

11. A process as defined in claim **10** wherein said second-stage hydrocracking run is continued for a period of time in excess of about 4 months, and wherein the feed thereto contains less than about 25 parts per million of nitrogen.

12. A process as defined in claim **10** wherein said relatively low concentration of hydrogen sulfide in said second-stage recycle gas is below about 1 millimole thereof per mole of hydrogen.

13. A process as defined in claim **10** wherein the catalyst used in said second-stage hydrocracking comprises a minor proportion of a Group VIII noble metal hydrogenating component combined by ion-exchange with a crystalline, zeolitic molecular sieve cracking base of the Y crystal type having a SiO_2/Al_2O_3 mole-ratio between about 4 and 6, the zeolitic cations of said cracking base being selected from the class consisting of hydrogen and divalent metals.

14. A process as defined in claim **1** wherein the transition from said relatively high concentration of hydrogen sulfide in step (1) to the relatively low concentration thereof specified in step (2) is carried out gradually over an extended period of time during which the hydrocracking temperature is gradually increased at a rate correlated with said reduction in hydrogen sulfide concentration so as to maintain a substantially constant aromaticity in the gasoline product produced during the transitional period.

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