

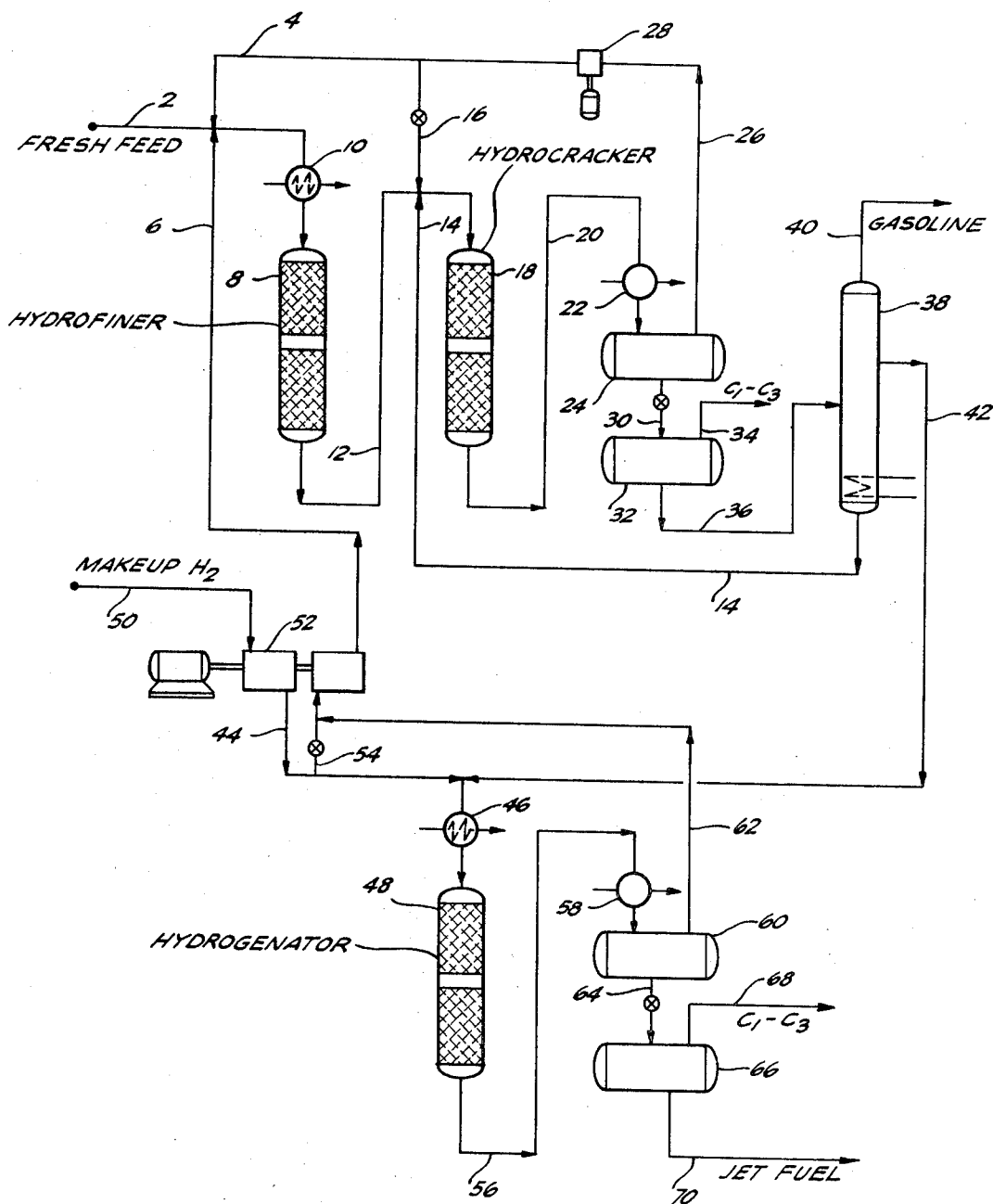
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COMBINATION HYDROCRACKING-HYDROGENATION PROCESS

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COMBINATION HYDROCRACKING- HYDROGENATION PROCESS

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7 Claims

ABSTRACT OF THE DISCLOSURE

An advantageous hydrogen supply system is disclosed for the hydrogenation of certain undesirably aromatic product fractions derived from hydrocracking systems, whereby essentially the same equipment and power required to supply makeup hydrogen to the hydrocracking system is used to circulate hydrogen once-through the post-hydrogenation system, thereby eliminating the need for separate makeup and recycle gas compressors for the latter. Due to the relatively high chemical hydrogen consumption in the hydrocracking system, and the relatively low feed rate and mild conditions in the hydrogenation system, it is found that the multi-stage makeup gas compressor required for the hydrocracking system can be advantageously utilized to move the makeup hydrogen required for the hydrocracker first through the hydrogenation system, and that such makeup hydrogen is fortuitously sufficient to operate the hydrogenation system in once-through fashion, i.e. without recycle.

BACKGROUND AND SUMMARY OF THE INVENTION

Recent years have witnessed a phenomenal growth in the application of catalytic hydrocracking processes. Initially, the primary desired product from such processes was gasoline, and it was found at an early stage that a desirably aromatic gasoline product was obtained by carrying out the hydrocracking in a "sour" hydrogen atmosphere, i.e. one containing at least about 50 volume parts per million of H_2S .

Increasing demands for non-aromatic hydrocracked products such as jet fuels and diesel fuels have created somewhat of a dilemma in the design of hydrocracking units, particularly where both an aromatic gasoline product and a non-aromatic jet fuel type product are desired, either concurrently or alternately. A "sweet," H_2S -free hydrocracking process is desirable for maximum jet fuel quality, whereas the sour systems are desirable for maximum gasoline quality. In cases where the hydrocracking feedstock is free of sulfur, as e.g. by virtue of a separate prehydrofining operation, the problem can sometimes be solved by operating alternately sweet and sour, as disclosed in U.S. Pat. No. 3,132,090. However, in many cases it is desirable to carry out the hydrocracking in a continuously sour atmosphere, as for example when a prehydrofiner is operated integrally with the hydrocracker, with total H_2S -containing effluent from the hydrofiner being passed through the hydrocracker. In such cases, a sweet hydrocracking cycle is not feasible, and when a jet fuel product of satisfactory quality is desired the two principal alternatives are: solvent extraction to remove aromatics from the jet fuel fraction, or catalytic hydro-

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genation of such fraction. Where a completely separate hydrogenation unit is required, with its own internal hydrogen recycle system, the economic choice between these two alternatives is sometimes very close, and may favor the solvent extraction route.

I have now found that in cases where there is a substantial chemical consumption of hydrogen in the hydrocracking unit, e.g. at least about 1000 s.c.f. per barrel of feed, and where the volume of hydrocracked product to be hydrogenated is less than the volume of hydrocracker feed, the economic balance is tipped decisively in favor of the hydrogenation route, for in such cases the makeup hydrogen required for the hydrocracker is sufficient to operate the hydrogenation facility in once-through fashion, without recycle. The first stage or stages of the multi-stage makeup gas compressor required for the hydrocracker can then be utilized to pass such hydrogen through the hydrogenation system, and the off-gas therefrom is then supplied to the hydrocracker via the latter stage or stages of the makeup gas compressor. This eliminates the expense of separate makeup and recycle gas compressors for the hydrogenation system, a small increase in capacity and power requirement for the hydrocracker makeup gas compressor being sufficient to overcome pressure drop through the hydrogenation system.

Although in the context of present technology, the principles of the invention apply most fortuitously to the hydrocracking-hydrogenation systems described, it will be apparent that such principles can be applied to a broader spectrum of hydro-processing combinations. In its broadest aspect, the invention is conceived as being applicable to any combination of hydrogen-consuming catalytic contacting processes comprising (1) a processing unit involving a relatively high chemical consumption of hydrogen, and operated at a relatively high pressure, e.g. above about 1,000 p.s.i.g., and (2) a second contacting unit wherein the feed rate, catalyst and process conditions are such that the makeup hydrogen required for the first unit is sufficient to operate the second in once-through fashion while maintaining adequate catalyst life therein, the second unit being operated at a pressure no higher than the first.

DETAILED PROCESS DESCRIPTION

For a more detailed description of the invention, reference is made to the attached drawing, which is a simplified flow sheet illustrating one advantageous application thereof. Fresh feed, e.g. gas oil, is brought in via line 2, mixed with recycle and makeup hydrogen from lines 4 and 6 respectively, and passed into the top of catalytic hydrofiner 8 via preheater 10. The catalyst in hydrofiner 8 may comprise any of the oxides and/or sulfides of the transitional metals, and especially an oxide or sulfide of a Group VIII metal (particularly cobalt or nickel) mixed with an oxide or sulfide of a Group VI-B metal (preferably molybdenum or tungsten). The metals are preferably supported on an adsorbent carrier in proportions ranging between about 2% and 25% by weight. Suitable carriers include in general the difficulty reducible inorganic oxides, e.g. alumina, silica, zirconia, clays, etc. Preferably the carrier should display little or no cracking activity, and hence highly acidic carriers having a Cat-A cracking activity index above about 20 are to be avoided. The preferred carrier is activated alumina, and

especially activated alumina containing about 3–15% by weight of coprecipitated silica gel.

Suitable process conditions for the hydrofining operation are as follows:

HYDROFINING CONDITIONS

	Broad range	Preferred range
Average bed temp., ° F.....	600–850	650–800
LHSV.....	0.3–20	0.5–5
Hydrogen/oil ratio, M s.c.f./b.....	0.5–20	2–12
Pressure, p.s.i.g.....	500–4,000	1,000–3,000

The above conditions are suitably correlated and adjusted to achieve the desired degree of desulfurization and denitrogenation. Normally it is desirable to reduce the organic sulfur level to below about 50 p.p.m., and the organic nitrogen level to below about 10 p.p.m.

Total effluent from hydrofiner 8 is withdrawn via line 12, mixed with hydrocracker recycle oil from line 14, and quench hydrogen from line 16, and passed into the top of hydrocracker 18. Suitable catalysts to be employed in hydrocracking 18 may comprise any desired combination of a refractory cracking base with a suitable hydrogenating component. Desirable cracking bases are those having a Cat-A activity index above about 30, preferably above 40, including for example mixtures of two or more difficultly reducible oxides such as silica-alumina, silica-magnesia, silica-zirconia, silica-zirconia-titania, acid treated clays and the like. Acidic metal phosphates such as aluminum phosphite may also be used. The preferred cracking bases comprise zeolitic crystalline molecular sieves having relatively uniform pore diameters of about 6–14 Å., and comprising silica, alumina and one or more exchangeable zeolitic cations. These crystalline zeolites may be used as the sole cracking base, or they may be mixed with one or more of the amorphous cracking bases such as silica-alumina cogel.

A particularly active and useful class of molecular sieve cracking bases are those having a relatively high SiO₂/Al₂O₃ mole ratio, e.g. between about 3 and 10. Suitable zeolites found in nature include for example mordenite, chabazite, faujasite and the like. Suitable synthetic molecular sieve zeolites include for example those of the B, Y, X, and L crystal types, or synthetic forms of the natural zeolites noted above, especially synthetic mordenite. Preferred zeolites are those having crystal pore diameters between about 8–12 Å., wherein the SiO₂/Al₂O₃ mole ratio is about 3–6, e.g. Y molecular sieve.

The zeolitic cations of the molecular sieve cracking bases preferably comprise mainly hydrogen ions, polyvalent metal ions, "decationized" exchange sites, or any combination of such moieties. Hydrogen or "decationized" Y zeolites are more particularly described in U.S. Pat. No. 3,130,006. Preferred polyvalent metal cations include magnesium, calcium, zinc, the rare earth metals, chromium, nickel and the like, or in general any of the polyvalent metals of Group I–B through Group VIII. The preferred polyvalent metals are the alkaline earths, zinc, and the rare earth metals.

The foregoing cracking bases are compounded as by impregnation, but preferably by ion exchange, with from about 0.5% to 25% (based on free metal) of a Group VI–B and/or Group VIII hydrogenating metal, e.g. an oxide or sulfide of chromium, molybdenum, tungsten, cobalt, nickel or the corresponding free metals, or any combination thereof. Alternatively, even smaller proportions, between about 0.05% and 2% of the Group VIII noble metals, preferably platinum or palladium, may be employed.

Hydrocracking conditions to be employed in conjunction with the foregoing catalysts fall within the following general ranges:

HYDROCRACKING CONDITIONS

	Broad range	Preferred range
Average bed temp., ° F.....	550–850	650–800
LHSV.....	0.5–20	1–10
Hydrogen/oil ratio, M s.c.f./b.....	0.5–20	4–12
Pressure, p.s.i.g.....	500–4,000	1,000–3,000

The foregoing hydrocracking conditions are suitably adjusted and correlated so as to achieve the desired conversion per pass to products boiling below the initial boiling points of the feed. Preferred conversion levels fall within the range of about 25–70 volume percent of feed. At these conversion levels, the chemical consumption of hydrogen in hydrofiner 8 and hydrocracker 18 normally runs between about 1,000–3,000 s.c.f. per barrel of fresh feed, assuming a feed containing substantially proportion of aromatic hydrocarbon, i.e., at least about 20 volume percent. As indicated above, my process is particularly well adapted for use in connection with feedstocks which consume at least about 500, and preferably at least about 1,000 s.c.f. of hydrogen per barrel of feed in the hydrofining-hydrocracking zones.

Effluent from hydrocracker 18 is withdrawn via line 20, and passed via condenser 22 into high pressure separator 24, from which hydrogen-rich recycle gas is withdrawn via line 26 and returned via recycle gas compressor 28 to reactors 8 and 18 as previously described. Normally, it is preferable to water-wash this recycle gas in separator 24 by conventional means not shown, to remove ammonia and excess hydrogen sulfide.

High-pressure condensate in separator 24 is flashed via line 30 into low-pressure separator 32, from which C₁–C₃ flash gases are exhausted via line 34. Low-pressure condensate in separator 32 is transferred via line 36 to fractionation column 38, from which the aromatic gasoline product is withdrawn overhead via line 40, and a jet fuel side cut, boiling for example between about 300°–500° F. via line 42, while unconverted recycle oil is withdrawn and recycled via line 14 as previously described.

The undesirably aromatic jet fuel fraction in line 42 is blended with all or a portion of the makeup hydrogen required in hydrofiner 8 and hydrocracker 18, plus an increment required for hydrogenation of the jet fuel fraction, and the mixture is then passed via preheater 46 into the top of hydrogenator 48. The raw makeup hydrogen, e.g. catalytic reformer off-gas at 450 p.s.i.g., is brought in via line 50 to the first stage of reciprocating multi-stage compressor 52, and is withdrawn therefrom at e.g. 900 p.s.i.g. via line 44 and mixed with the jet fuel fraction in line 42. Any excess makeup gas not required in hydrogenator 48 may be bled via flow-controlled line 54 into the second stage of compressor 52.

Hydrogenator 48 is filled with any desired catalyst having suitable activity for the hydrogenation of aromatic hydrocarbons. Suitable catalysts include for example finely divided Group VIII metals, e.g., nickel, cobalt, palladium, platinum and the like, preferably supported upon a non-cracking support similar to those described above in connection with the hydrofining catalysts. Preferred hydrogenation catalysts consist of 0.1 to 2 weight-percent of platinum and/or palladium supported on activated alumina, including for example conventional platinum-alumina reforming catalysts. Catalysts comprising Group VI–B metals, e.g. molybdenum or tungsten may be used

to less advantage. Suitable hydrogenation conditions may be summarized as follows:

HYDROGENATION CONDITIONS

	Broad range	Preferred range
Average bed temp., ° F.....	300-850	450-700
LHSV.....	1-20	2-12
Hydrogen/oil ratio, M s.c.f./b.....	2-20	3-8
Pressure, p.s.i.g.....	200-3,000	400-3,000

The foregoing conditions are suitably adjusted and correlated so as to achieve the desired degree of hydrogenation of aromatic hydrocarbons. In the case of jet fuels for example, it may be desirable to reduce the aromatic content from an initial 10 to 50 volume percent to 0-20 percent. It is important to observe that the minimum H₂/oil ratio of about 2,000 s.c.f./b. is normally required in order to maintain suitable hydrogenation catalyst life of e.g. 4-12 months between regenerations. This ratio could not be maintained without a separate recycle gas system if the feed rate to the hydrogenator was substantially greater than the feed rate to hydrofiner 8, or if the chemical hydrogen consumption in hydrofiner 8 and hydrocracker 18 was too small.

Effluent from hydrogenator 48 is withdrawn via line 56 and passed via condenser 58 to high-pressure separator 60, from which hydrogen-rich off-gas is withdrawn via line 62 at e.g. 850 p.s.i.g. and returned to the second stage of makeup gas compressor 52. In the second stage of compressor 52, hydrogenator off-gas from line 62 and any bleed gas from line 54 is compressed to the pressure desired in hydrofiner 8 and hydrocracker 18, e.g. about 1500-2000 p.s.i.g., and passed via line 6 to hydrofiner 8 as previously described.

High-pressure liquid condensate in separator 60 is flashed via line 64 into low-pressure separator 66, from which C₁-C₃ flash gases are exhausted via line 68, while the desired low-aromatic jet fuel product is withdrawn via line 70.

From the foregoing, it will be apparent that makeup hydrogen compressor 52, which is a required adjunct of the hydrocracking system described, is advantageously utilized to operate the entire gas circulation system for hydrogenator 48, thereby eliminating the conventional separate makeup gas compressor and separate recycle gas compressor normally required for such a unit. This saving is normally accomplished with no incremental increase in the cost of compressor 52 except in rare cases where an additional compression stage may be required to compensate for the pressure drop through the hydrogenation system. Moreover, the slight additional power requirement for operating compressor 52 to recompress the hydrogenator off gases back to inlet pressure (i.e. the pressure in line 44) is less than the power which would be required to operate separate recycle and makeup gas compressors for that unit. Moreover, the once-through flow of hydrogen through the hydrogenation system leads to another advantage which is obtained in cases where the makeup hydrogen in line 50 is diluted with light hydrocarbon gases, as e.g. in the case of reformer off gases. Due to the normally low chemical consumption of hydrogen in reactor 48, and the solubility of light hydrocarbons in the high pressure condensate in separator 60, an overall enrichment of the hydrogen stream in line 62 is often obtained. In such cases, the makeup hydrogen supplied to hydrofiner 8 via line 6 may be of greater purity than the hydrogen initially supplied via line 50.

In the foregoing description of the drawing, it will be understood that certain non-essential details have been omitted. In particular it should be noted that in reactors 8, 18 and 48 it will normally be desirable to inject cool quench hydrogen at one or more points therein to control the exothermic heat of reaction.

The feedstocks which may be employed in the above process include in general any mineral oil fraction boil-

ing above about 200° F., including straight run gas oils and heavy naphthas, coker distillate gas oils and heavy naphthas, deasphalted crude oils, cycle oils derived from catalytic or thermal cracking operations and the like.

These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Specifically, for the manufacture of gasoline and jet fuel products, it is preferred to employ feedstocks boiling between about 500° and 1000° F., having a API gravity of 20 to 35°, and containing at least about 20 volume percent of aromatic hydrocarbon.

The following example is cited to illustrate the invention more specifically and the results obtainable, but is not to be construed as limiting in scope:

EXAMPLE

A 5,000 barrel per day hydrocracking-hydrogenation unit similar to that illustrated in the drawing was designed for the conversion of a California straight-run vacuum gas oil alternately to 100% gasoline, and to 50% gasoline-50% jet fuel. Inspection data on feedstock was as follows:

Gravity, ° API.....	20.3
Boiling range D-1160, ° F.:	
IBP.....	520
10%.....	641
50%.....	728
90%.....	820
Max.	890
Sulfur, wt. percent.....	1.33
Nitrogen, wt. percent.....	0.227
Total aromatics, wt. percent.....	35.2
Olefins, wt. percent.....	2.4

The catalyst employed in hydrofiner 8 was a presulfided composite of 3.1 weight-percent NiO and 14.7 weight-percent MoO₃ supported on a coprecipitated alumina-silica cogel containing 3.2 weight-percent SiO₂, in the form of 1/16-inch extrudate. The catalyst in hydrocracker 18 was a copelleted composite of 80 weight-percent of a magnesium-hydrogen Y zeolite (3 weight-percent MgO), and 20 weight-percent of an activated alumina binder, the composite containing 0.5 weight-percent of Pd added by ion exchange. The catalyst in hydrogenation unit 48 was a 1/16-inch extrudate of 0.5 weight-percent Pt deposited by ion-exchange on an 80% alumina-20% silica cogel carrier, the carrier having a pore volume of 1.19 ml./g., of which about 50% was in pores of diameter greater than 100 Å.

Start-of-run operating conditions in the three catalytic units for the 50% gasoline-50% jet fuel cycle of operation are as follows:

	Hydrofiner 8	Hydrocracker 18	Hydrogenator 48
Average bed temp., ° F.....	710	720	560
Inlet pressure, p.s.i.g.....	2050	2020	820
LHSV.....	0.6	1.8	6.0
Gas rates, s.c.f./b.:			
Recycle.....	¹ 3,800	² 10,700	
Makeup.....	2,500		5,400

¹ About 76 volume-percent H₂; includes 800 s.c.f./b. used as quench at mid-point of reactor.

² Includes 3,000 s.c.f./b. used as quench.

Makeup hydrogen is supplied to the system via a conventional two-stage reciprocating compressor, the first stage of which compresses 450 p.s.i.g. reformer off-gas (81% H₂) up to 820 p.s.i.g. for once-through passage through hydrogenator 48, while the second stage compresses the 800 p.s.i.g. off-gas (84% H₂) from the hydrogenator up to 2050 p.s.i.g. for passage through hydrofiner 8 and hydrocracker 18. Chemical consumption of hydrogen in the hydrogenator is about 375 s.c.f. per barrel of jet fuel fed thereto, while the combined hydrogen consumption in hydrofiner 8 and hydrocracker 18 is about 2500 s.c.f. per barrel of fresh feed, most of which is con-

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sumed in the hydrocracker. At these hydrogen consumption levels, product yields and quality are as follows:

YIELDS, VOLUME-PERCENT OF FRESH FEED

	From hydrocracker 18	From hydrogenator 48
Butanes.....	11	
C ₇ -C ₈	21.5	
185-304° F.....	38.9	
300-550° F. turbine fuel.....	49.8	50.6

PRODUCT QUALITY

	From hydrocracker 18	From hydrogenator 48
C ₇ -304° F. gasoline:		
Gravity, ° API.....	54.6	
Res. octane No.:.....		
Clear.....	69.7	
Plus 3 ml. TEL.....	86.4	
Iso-paraffins, vol.-percent.....	27.0	
N-paraffins, vol.-percent.....	3.5	
Naphthenes, vol.-percent.....	60.1	
Aromatics, vol.-percent.....	9.4	
Sulfur, p.p.m.....	10	
Turbine fuel (300-540° F.):		
Gravity, ° API.....	38.9	40.8
Aromatics, vol.-percent.....	30	17
Sulfur, p.p.m.....	10	1
Smoke point, mm., D-1322.....		20.5
Luminometer No. D-1740.....		47
Freezing point, ° F. D-2386.....		-57

Results substantially similar to those described above are obtained when other feedstocks, process conditions and catalysts within the purview of this invention are employed. It is not intended that the invention should be limited to the details described since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A combination hydrocracking-hydrogenation process for the concurrent manufacture of a relatively aromatic hydrocarbon product and a relatively non-aromatic hydrocarbon product, which comprises:

- (1) subjecting a mineral oil feedstock to hydrocracking at a relatively high pressure in the presence of hydrogen and a hydrocracking catalyst to effect a substantial conversion of said feedstock to lower boiling products with resultant chemical consumption of at least about 500 s.c.f./b. of hydrogen;
- (2) separating effluent from said hydrocracking into a recycle gas, a desired aromatic product, and an undesirably aromatic product;
- (3) recycling said recycle gas to step (1);
- (4) subjecting said undesirably aromatic product to hydrogenation in the presence of a hydrogenation

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catalyst at a relatively lower pressure than is maintained in step (1) to effect a substantial hydrogenation of aromatic hydrocarbons;

- (5) supplying low-pressure hydrogen to a multi-stage compressor at a rate sufficient to make up for chemical hydrogen consumption in steps (1) and (4);
- (6) withdrawing sufficient intermediate-pressure hydrogen from an initial stage of said compressor, and supplying the same to step (4), to provide therein, without recycle, a hydrogen/oil ratio of about 2,000-20,000 s.c.f. per barrel;
- (7) separating and withdrawing total unconsumed hydrogen from the effluent from step (4) and supplying such withdrawn hydrogen to a terminal stage of said compressor; and
- (8) passing high-pressure effluent hydrogen from the terminal stage of said compressor to step (1) as makeup for chemical hydrogen consumption therein.

2. A process as defined in claim 1 wherein said desired aromatic product in step (2) is gasoline, and said undesirably aromatic product is a jet fuel fraction.

3. A process as defined in claim 1 wherein step (1) is carried out in the presence of recycle gas containing at least about 50 volume parts per million of H₂S.

4. A process as defined in claim 1 wherein said hydrocracking catalyst is a Group VIII noble metal-promoted zeolite cracking base.

5. A process as defined in claim 1 wherein said hydrogenation catalyst is a Group VIII noble metal supported on activated alumina.

6. A process as defined in claim 1 wherein the chemical consumption of hydrogen in step (1) is at least about 1000 s.c.f. per barrel of feed, and the hydrogen/oil ratio in step (6) is between about 3000 and 8000 s.c.f. per barrel of feed thereto.

7. A process as defined in claim 1 wherein any intermediate-pressure hydrogen from said initial compressor stage in step (6) which is not supplied to step (4) is transferred to said terminal compressor stage in step (7) for use in step (8).

References Cited

UNITED STATES PATENTS

2,909,475	10/1959	Bushnell	208—35
3,172,833	3/1965	Kozłowski et al.	208—143
3,329,605	7/1967	Tokuhsa et al.	208—130

HERBERT LEVINE, Primary Examiner

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