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MIXED-PHASE HYDROFINING OF HYDROCARBON OILS

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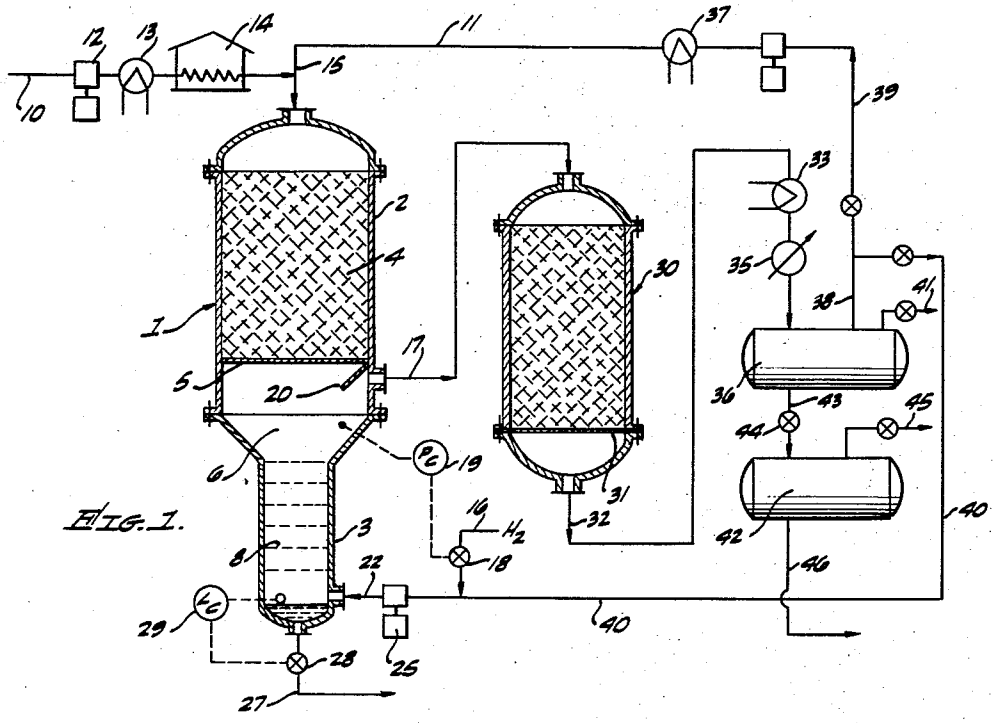


FIG. 1.

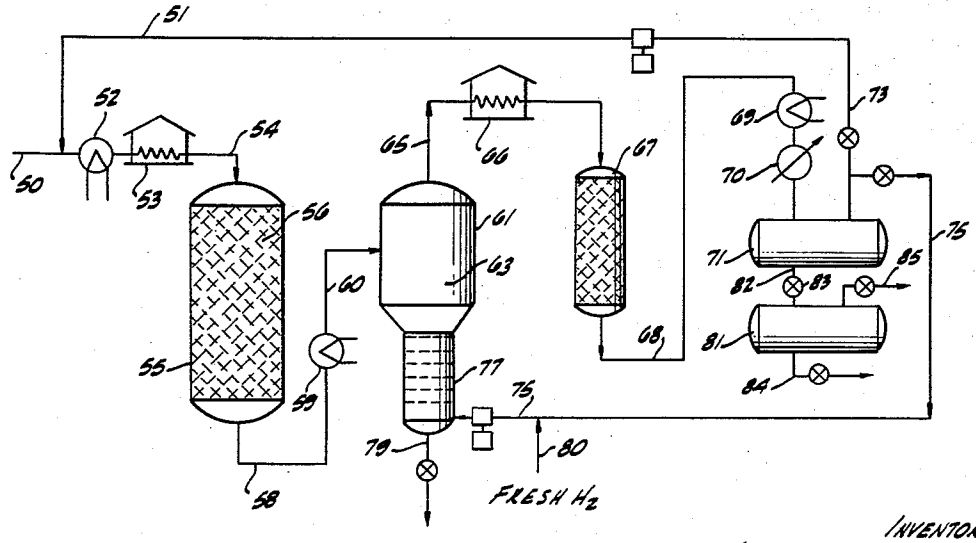


FIG. 2.

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MIXED-PHASE HYDROFINING OF HYDROCARBON OILS

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This invention relates to the catalytic hydrofining of mineral oils wherein the conditions of treatment are such that a portion of the feed normally remains in the liquid phase, and another portion remains in the vapor phase during processing. More specifically, the invention is concerned with means for increasing the degree of hydrofining of the vapor-phase fraction relative to that of the heavy fraction, but without necessarily increasing the severity of the processing with respect to the liquid-phase fraction.

The gist of the invention consists in first subjecting the total feed to mixed-phase hydrofining in a first catalytic hydrofining zone until the liquid phase is sufficiently refined, then effecting a separation of the gas phase from the liquid phase, said separation being performed at essentially the pressure prevailing in the first reactor, and transferring the separated gas phase to a second catalytic hydrofining zone for further treatment to remove more completely the remaining sulfur compounds and nitrogen compounds. In a preferred aspect of the invention, fresh makeup hydrogen for the system is first employed as a stripping gas for the liquid-phase product from the first hydrofining zone, and is then mingled with the vapor-phase products from the first hydrofining zone, and the combined gas phase is then treated in the second hydrofining zone. Recycle hydrogen from the second hydrofining zone is then recycled to the first hydrofining zone. In still another modification, the total effluent from the first hydrofining zone is partially cooled prior to separating the gas phase from the liquid phase. In this manner part of the gaseous products are condensed, and control may be maintained over the boiling range of the vapor-phase product which is to be further treated in the second hydrofining zone.

One of the principal objects of the invention is to provide simple and economical methods for the controlled catalytic hydrofining of wide-boiling-range feedstock. A more specific object is to provide convenient and inexpensive methods for subjecting a selected light fraction of a given feed to a more severe hydrofining treatment than the remaining heavy fraction. Another object is to provide optimum catalysts and conditions for liquid-phase and for vapor-phase hydrofining. Another object is to provide for the most efficient possible utilization of catalyst where it is desired to hydrofine rigorously the light ends of a wide-boiling-range feedstock, and to hydrofine lightly the heavy ends thereof. Another object is to provide novel combinations of apparatus for effecting the herein-described hydrofining treatments. Other objects and advantages will be apparent from the more detailed description which follows:

The term "hydrofining" as used herein means the selective hydrocracking of hydrocarbon feedstocks contaminated with various organic impurities such as sulfur compounds, nitrogen compounds, and oxygen compounds, with resultant net chemical consumption of hydrogen. The catalysts used, and the reaction conditions are chosen

so as to effect a selective hydrogenation and decomposition of the sulfur, nitrogen, and oxygen compounds, without causing any appreciable hydrocracking of the hydrocarbon components. Such hydrofining processes have become widely used for refining selected feedstocks, e.g. gasolines, heavy gas oils, light gas oils, kerosene, solvent naphthas, and the like. In these known processes, the feed is admixed with e.g. 300–5000 s.c.f. of hydrogen per barrel of feed, preheated to a temperature of about 650°–875° F., and then passed through a bed of the desired catalyst. Pressures of about 300 to 5000 p.s.i.g. are normally employed, along with feed rates amounting to about 0.5 to 15 volumes of feed per volume of catalyst per hour.

Under the foregoing processing conditions, the light feeds such as gasoline are normally present wholly, or almost wholly, in the vapor phase. Heavier materials such as gas oils are normally present both in the liquid and the vapor phase. The present invention is concerned specifically with the problems which arise when such heavy, and/or wide-boiling-range feeds, are employed that a considerable proportion of the total feed, e.g. 20% to 90%, would normally be present in the vapor phase, the remainder going through as liquid.

Where a liquid phase is present, it will form a liquid film covering the entire active catalyst surface. Consequently, the feed which remains in the gas phase can react only by diffusion through the liquid film on the catalyst. It is obvious that under such conditions, the liquid-phase portion of the feed will tend to react more rapidly than the vapor phase, at least under conditions where the volume of liquid present, and its state of turbulence, are not such as to too greatly impair mass-transfer rates between liquid and catalyst. In any event, the extent of hyrofining of the liquid phase which occurs in any given pass through the reactor is seldom the same as that of the accompanying vapor-phase hydrocarbons.

However, the process of this invention is useful not only in those cases where the conversion rates of gas and liquid phases are different, but in all cases where the objective is to effect a more complete hydrofining of the light fraction than can be obtained without over-treatment of the heavy fraction in normal mixed-phase hydrofining. This condition may occur for example where it is desired to process a 300°–650° F. boiling-range fraction which would include both heavy naphtha and light gas oil, the light gas oil being subsequently used for diesel fuel or cracking stock, and the heavy naphtha being used as reforming stock. For purposes of reforming over sulfur-sensitive catalysts such as platinum, it is necessary to reduce the sulfur content to below about 0.05% and the nitrogen content to below about 0.0001%. On the other hand, cracking charge stocks or diesel fuels can tolerate substantially larger amounts of sulfur and nitrogen compounds. Another instance of utility involves the treatment of a wide-range gas oil, wherein the light gas oil is to be used as jet fuel, and the heavy gas oil as cracking charge stock.

In still other instances, product specifications for the light and heavy fractions may be substantially the same in terms of sulfur and nitrogen content. However, where only a small part of the charge is in the liquid phase, e.g. 5–20%, it may become sufficiently hydrofined before product specifications are met on the vapor-phase portion, due to the differential conversion rates discussed above. It would be disadvantageous to increase the overall severity of treatment to obtain the desired vapor-phase conversion, because this would involve overtreatment of the liquid-phase portion with resultant losses in product yield and increased rates of catalyst deactivation resulting from gum and coke deposits. Hence, the two-

stage hydrofining of this invention may be useful even where a single ultimate product is desired.

It will hence be apparent that the process of this invention is useful wherever it is desired to hydrofine a charge stock in a single treating unit under conditions where part of the charge is normally liquid and part is gaseous, and wherein it is desired that a light fraction of the charge be subjected to additional hydrofining in the absence of the heavy portion.

Feedstocks which may be treated herein include in general any mineral oil stock having an end-boiling-point in excess of about 450° F. and an initial boiling point at least about 75° F. lower than the end-boiling-point. When using stocks of this type, it is almost inevitable that the heavy ends will constitute a relatively fixed and unchanging liquid phase during hydrofining, while the light ends will undergo treatment predominantly in the vapor phase. Specific examples of such stocks include crude oils, reduced crude oils, deasphalted reduced crude oils, light gas oils, heavy gas oils, kerosene-gas oil fractions, heavy naphtha-gas oil fractions, fuel oil fractions, etc. These stocks may be derived from petroleum, shale, tar sands and similar natural deposits.

Operation of the process may be more readily understood with reference to the accompanying drawings. Figure 1 is a schematic flow diagram illustrating one modification, and Figure 2 is a schematic flow diagram illustrating a slightly different modification. Neither of these illustrations however is intended to be limiting in scope.

In Figure 1, the principal piece of apparatus comprises a reactor-stripper **1**, comprising an enclosed upper cylindrical reactor shell **2**, and a communicating, subjacent cylindrical stripping column **3**. A bed of suitable granular hydrofining catalyst **4** is supported in reactor shell **2** by means of a perforated supporting plate **5**. Immediately below plate **5** is provided a substantial open space **6** wherein phase separation of the initial hydrofining products takes place.

Stripping column **3** is removable attached to reactor shell **2**, and is preferably of smaller diameter. The interior of stripping column **3** preferably contains a series of perforated plates **8**, or bubble cap trays of conventional design. Alternatively, stripping column **3** may be packed with suitable conventional packing such as Raschig rings, glass beads, porcelain chips, etc. The entire reactor-stripper **1** may suitably be constructed of mild steel, stainless steel, or any other pressure-retaining, corrosion-resistant material which will withstand temperatures up to about 1000° F.

In operation, the initial feed is brought in through line **10**, pump **12**, heat exchanger **13**, final preheater **14**, and line **15** into the top of reactor **2**. Recycle hydrogen from line **11** is mingled with the preheated feed in line **15**. The mixture of feed and hydrogen then flows downwardly through catalyst bed **4** and is discharged into separation zone **6**. The liquid portion of product falls by gravity into stripping column **3**, and the vapor phase portion is withdrawn from the reactor through line **17**. A segmental deflector plate **20** welded to the inner surface of reactor shell **2** serves to deflect liquid product away from vapor outlet line **17** and prevents entrainment of liquid in the withdrawn gases.

The liquid phase accumulating in stripping column **3** percolates downwardly countercurrently to a stream of hydrogen admitted via line **22** near the bottom of stripping column **3**. This stripping hydrogen preferably comprises all or a part of the makeup hydrogen required in the process, i.e. the hydrogen required to replace that which is chemically consumed in the process. It may be introduced at a low temperature of e.g. 50°–300° F., and become heated by contact with the oil, or it may be introduced at a higher temperature. The fresh hydrogen is added via line **16** at a rate regulated by valve **18** and pressure controller **19** so as to maintain the desired pressure in the system.

The use of fresh hydrogen as a stripping agent is desirable in that it provides for a more efficient stripping of the light fractions from the liquid in the column. If additional gas is required for effective stripping, a portion of the final recycle gases may be admixed with the fresh hydrogen, the latter being admitted via line **24** to recycle line **40**, and the whole being injected into column **3** by means of pump **25**. The hydrogen introduced via line **22** then accumulates in separator space **6** and is withdrawn via line **17** along with the vapor-phase products from reactor **2**. The liquid product in column **3** is withdrawn via line **27**, the rate of withdrawal being controlled by valve **28** operated by liquid-level controller **29**.

The total vapor-phase product in line **17** is then transferred directly to vapor-phase reactor **30**, which is conventional in design and consists of a cylindrical iron or steel shell containing a bed of suitable hydrofining catalyst supported on perforated plate **31**. Vapors pass downwardly through reactor **30** in contact with the catalyst to carry the hydrofining to the desired degree of completion. The effluent from vapor-phase reactor **30** is withdrawn via line **32**, precooled in exchanger **33** against incoming fresh feed or other cool process stream, and subjected to final cooling in condenser **35**. The condenser product then collects in accumulator **36**, which is maintained at substantially the same pressure as reactor **30**. Recycle gases are removed from separator **36** via line **38**, and passed either in whole or in part via line **39** and preheater **37** to mingle with fresh feed in line **15**. A portion of the recycle gases may be passed via line **40** for use in stripping column **3** as previously described. A small portion of recycle gas may be bled off via line **41** to prevent the buildup of inerts in the recycle stream.

The liquid product in separtor **36** is then transferred to low-pressure separator **42** via line **43**, and liquid-level-controlled valve **44**. In low-pressure separator **42**, off-gases containing mainly methane, ethane, hydrogen sulfide and hydrogen are withdrawn via line **45**. The liquid product is withdrawn via line **46** and transferred to final fractionating units not shown.

Referring now to Figure 2, the general processing scheme is similar to that in Figure 1 but is modified to permit a greater degree of control over the boiling range of the liquid product withdrawn after initial reaction, as well as the boiling range of the light fraction which is subjected to further processing. In this modification the initial feed is brought in via line **50**, mingled with recycle hydrogen from line **51**, and transferred via heat exchanger **52**, final preheater **53**, and line **54**, into the top of mixed-phase reactor **55**. The construction of the processing equipment and the instrumentation in this modification is similar to that in Figure 1 and hence will not be described in detail. The mixed feed passes through catalyst bed **56** and is withdrawn via line **58**.

The product in line **58** is then passed through a heat exchanger **59** to effect partial cooling, i.e. to the degree required to condense the desired portion of the vapor-phase product. The partially condensed mixture is then transferred via line **60** to separtor-stripper **61**. The total products are flashed into open space **63** to allow separation of liquid by deceleration and gravity. The vapor phase from separator **63** is then withdrawn via line **65**, reheated in heater **66** to the desired reaction temperature, and then admitted to vapor-phase reactor **67** wherein final processing takes place as previously described for reactor **30**. The vapor-phase product from reactor **67** is then withdrawn via line **68**, precooled in exchanger **69**, condensed in condenser **70**, and then passed into high-pressure separator **71**. Recycle gas is withdrawn from separator **71** and transferred via lines **73** and **51** to feed line **50**, and may in part be diverted through line **75** to

be used as stripping gas for the liquid product in stripping column 77.

Stripping column 77 is operated similarly to column 3 of Figure 1. Here again it is preferable to introduce at this point the entire amount of makeup hydrogen to increase stripping efficiency. This fresh hydrogen is admitted via lines 80 and 75. If additional hydrogen is required, it is supplied via line 75 from separator 71. The stripped liquid-phase product is continuously withdrawn from stripper 77 via line 79, and transferred to storage or final fractionation.

The liquid product in separator 71 is then transferred to low-pressure separator 81 via line 82 and valve 83. Final product is withdrawn via line 84 and off-gases via line 85.

It will be understood that the temperatures, pressures, and feed rates in reactors 2, 30, 56 and 67 are substantially within the ranges above described as being generally applicable for hydrofining operations.

The catalysts employed herein may consist of any conventional hydrofining catalyst. In general, the oxides and sulfides of transitional metals are useful, and especially the group VI–B and group VIII metal oxides and sulfides. In particular, the combination of one or more group VI–B metal oxide or sulfide with one or more of group VIII metal oxide or sulfide is preferred. For example, combinations of nickel-tungsten oxides and/or sulfides, cobalt-molybdenum oxides and/or sulfides, are specifically contemplated. However, iron oxide, iron sulfide, cobalt oxide, cobalt sulfide, nickel oxide, nickel sulfide, chromium oxide, chromium sulfide, molybdenum oxide, molybdenum sulfide, tungsten oxide or tungsten sulfide may be used alone to less advantage.

In all the foregoing cases, it is preferable to support the active catalyst on a relatively inert carrier. Generally, minor proportions of the active metal compounds are used, ranging between about 1% and 25% by weight. Suitable carriers include for example activated alumina, activated alumina-silica, zirconia, titania, activated clays such as bauxite, bentonite and montmorillonite, and the like. Preferably the active components are added to the carrier by impregnation from aqueous solutions followed by drying and calcining to activate the composition. Suitable calcining temperatures range between about 500° and 1200° C.

The preferred catalyst for use herein comprises the composition usually known as cobalt-molybdate, which actually may be a mixture of cobalt and molybdenum oxides. This mixture is preferably distended upon activated alumina, or still more preferably activated alumina containing 1% to 15% of coprecipitated silica gel. The ratio of cobalt to molybdenum may be between 0.4 and 5.0, and the total proportion of active ingredients is preferably between about 7% and 22% by weight, comprising about 1–7% of CoO, and 6–15% of MoO_3. Catalysts of this type may be prepared by coprecipitation of both components on the carrier as described in U.S. Patent No. 2,369,432, and No. 2,325,033, or by co-impregnation of both components on the carrier as described in U.S. Patent No. 2,486,361. Preferably however the catalyst is prepared by separate alternate impregnations as described in U.S. Patent No. 2,687,381.

The catalyst employed in the mixed-phase hydrofiner may be identical to that employed in the vapor-phase hydrofiner, or the two may be different. It has been found that in using mixtures of group VIB-group VIII type catalysts, it is preferable to use compositions containing a higher total proportion of group VIII metal, and higher group VIII/group VIB metal ratios, when processing liquid-phase hydrocarbons than when only vapor-phase material is being processed. In vapor-phase processing using cobalt molybdate for example, the degree of conversion obtainable under a given set of conditions appears to level off when the total cobalt content reaches about 3%, the molybdenum content remaining constant at about 10%. However, when a liquid phase is present it is found that substantially increased conversions are obtainable at cobalt oxide contents ranging up to about 7%. It is therefore preferred to use catalysts containing about 6%–15% of molybdenum oxide in either case, but to use those containing about 1%–3.5% of cobalt oxide in the vapor-phase hydrofining, and those containing about 3.0–7.0% of cobalt oxide when a liquid phase is present. The same preferred ratios hold where other group VIII metals are substituted for cobalt, and other group VIB metals for molybdenum.

Typical results obtainable in practice of the present invention are illustrated by the following examples. These examples however should not be construed as limiting in scope.

Example I

It is desired to hydrofine a gas oil feed which is high in both sulfur and nitrogen. The light fraction from this feed is to be used as jet fuel and requires a high degree of nitrogen removal. The heavy fraction of the feed is to be used as feedstock to a fluid catalytic cracking unit, and as much as 0.15% nitrogen can be tolerated therein. In order to achieve the desired hydrofining of both fractions, a processing scheme similar to that shown in Figure 1 is used. The catalyst employed in both reactors 2 and 30 is 3% cobalt oxide-9% molybdenum oxide composite supported on a 95% alumina-5% silica carrier. The fresh stripping hydrogen used in stripping column 3 comprises 900 s.c.f. per barrel of total feed of 95% hydrogen. The details of operating conditions, feed and product characteristics are as follows:

	Reactor 2	Reactor 30
Feed:		
Gravity, ° API	25.0	38.0
Boiling range, ° F	400–800	100–700
Sulfur, wt. percent	2.5	0.03
Nitrogen, wt. percent	0.3	0.05
Product:		
Gravity, ° API	24.0	40.0
Boiling range, ° F	600–750	100–650
Sulfur, wt. percent	0.07	0.001
Nitrogen, wt. percent	0.08	0.004
Volume percent of original feed	42	61
Reactor Operating Conditions:		
Temp.:		
In, ° F	700	780
Out, ° F	780	800
Pressure:		
In, p.s.i.g	1100	1080
Out, p.s.i.g	1090	1070
Hydrogen to oil ratio, s.c.f./bbl	2000	3600
Hydrogen Consumption, s.c.f./bbl	700	200
Liquid hourly space velocity	1.5	1.5

It will thus be apparent that the product from reactor 2 is suitable in quality for catalytic cracking charge stocks, while the product from reactor 30 is suitable for use as a jet fuel. The procedure of this example is especially useful for treating oils having an initial boiling point between about 350–450° F., and an end boiling point between about 750–850° F.

Example II

The procedure of Example I is repeated, except that the catalyst in reactor 2 is modified to contain 5.0% by weight of cobalt oxide. The catalyst in reactor 30 is the same 3% cobalt oxide-9% molybdenum oxide catalyst used in Example I. The respective products obtained from reactors 2 and 30 are found to contain about 10% less sulfur and 15% less nitrogen. When this operating sequence is repeated using a 9% molybdenum oxide-5% cobalt oxide catalyst in reactor 30, and the 9% molybdenum oxide-3% cobalt oxide catalyst in reactor 2, substantially no improvement in desulfurization or denitrogenation is obtained over that shown in Example I.

Example III

It is desired to hydrofine a wide-range petroleum fraction having a boiling range of 300–650° F., and to

use the naphtha fraction thereof as feed to a platinum catalyst reforming unit, and to use the heavy fraction for diesel fuel. For use as a catalytic reformer feed, the naphatha fraction must contain less than 0.05% sulfur and less than 0.0001% nitrogen. To process this feed, it is introduced into a reactor similar to that shown at **56** in Figure 2, and processed under the conditions described in Example I for reactor **2**. The effluent is then partially cooled to a temperature of about 500° F., and introduced into a liquid-gas separator. The liquid phase is stripped countercurrently with about 750 s.c.f. of fresh hydrogen per barrel of initial feed, the stripping hydrogen being introduced at about 200° F. The vapor phase resulting from the stripping operation is allowed to mingle with the vapor-phase naphtha from the first hydrofining operation, and the mixture is then reheated to about 780° F. and passed through a second hydrofiner at about 1000 p.s.i.g. and a liquid hourly space velocity of 2.0. The naphtha product recovered is found to have a boiling range of about 250–450° F. and contains about 0.05% sulfur and 0.0001% nitrogen and is thus suitable reforming stock.

The liquid product has a boiling range of about 400° to 600° F., and contains about 0.05% sulfur and 0.06% nitrogen. The initial feedstock contained 2.1% sulfur and 0.25% nitrogen.

The procedure of this example is especially useful for treating oils having an initial boiling point between about 250–350° F., and an end boiling point between about 600–750° F.

Results similar to those described in the examples are obtained when other catalysts within the scope of this invention are substituted for the cobalt-molybdate. Similarly, other processing conditions may be employed to obtain commensurate benefits. The scope of the invention should not be construed as limited to the exemplary details. The true scope of the invention is intended to be embraced by the following claims.

We claim:

1. In a process wherein a mineral oil feedstock having an end-boiling-point above about 500° F. and an initial-boiling-point at least 75° F. lower than said end-boiling-point is subjected to mixed-phase hydrofining at an elevated pressure in the presence of hydrogen and a catalyst, and wherein the conditions of hydrofining are such that a portion of said feedstock is in the vapor-phase and another portion is in the liquid-phase, the improvement which comprises (1) terminating said mixed-phase contacting after said liquid-phase has been sufficiently treated to decompose a substantial desired proportion of organic impurities therein but before said vapor-phase has been sufficiently treated to effect removal therefrom of the desired proportion of organic impurities, (2) separating the total vapor-phase product from the liquid-phase product at substantially the pressure prevailing in said mixed-phase hydrofining, (3) subjecting said liquid-phase product to countercurrent stripping with a hydrogen-rich gas stream at substantially the pressure prevailing in said mixed-phase hydrofining to strip dissolved low boiling hydrocarbons therefrom, (4) mixing said separated vapor-phase product with the vapor-phase stripping effluent from said stripping step, and (5) subjecting the resulting combined vapor-phase mixture to further hydrofining at an elevated pressure in the presence of a hydrofining catalyst but substantially in the absence of a liquid phase to effect further removal of organic impurities therefrom.

2. A process as defined in claim 1 wherein the products from said vapor phase hydrofining are cooled and condensed without substantial reduction in pressure, and the resulting hydrogen-rich gas phase is recycled to said mixed-phase hydrofining.

3. A process as defined in claim 1 wherein the catalysts employed for said mixed-phase hydrofining and said vapor-phase hydrofining comprise two active components in intimate admixture, one of said components being selected from the class consisting of the oxides and sulfides of group VIB metals, and the other of said components being selected from the class consisting of the oxides and sulfides of group VIII metals.

4. A process as defined in claim 1 wherein the catalysts employed in said mixed-phase hydrofining and said vapor-phase hydrofining consist essentially of cobalt molybdate distended on a major proportion of an adsorbent oxide carrier.

5. A process as defined in claim 1 wherein the catalyst employed in said vapor-phase hydrofining is essentially cobalt molybdate on alumina wherein the cobalt oxide content is between about 1% and 3.5% by weight, and the catalyst employed in said mixed-phase hydrofining is essentially cobalt molybdate on alumina wherein the cobalt oxide content is (1) higher than that of said vapor-phase hydrofining catalyst, and (2) between about 3% and 7% by weight, the molybdenum oxide content of each of said catalysts being between about 6% and 15% by weight.

6. A process as defined in claim 1 wherein the total effluent from said mixed-phase hydrofining is partially cooled to effect a partial condensation of the vapor phase prior to said separation of vapor phase from liquid phase.

7. A method for hydrofining a gas oil feedstock having an initial boiling point between about 350–450° F., and an end boiling point between about 750–850° F., to obtain therefrom a light fraction suitable for use as jet fuel, and a heavy fraction suitable for use as catalytic cracking charge stock, which comprises first subjecting said feedstock to mixed-phase hydrofining at an elevated pressure in the presence of hydrogen and a catalyst, wherein the conditions of hydrofining are such that the heavy ends are predominantly in the liquid phase and the light ends are predominantly in the vapor phase, both of said phases being in concurrent downflow while in contact with said catalyst, terminating said mixed-phase contacting after said liquid phase has been sufficiently refined for use as cracking charge stock but before said vapor phase has been sufficiently refined for use as jet fuel, separating the total vapor-phase product from the liquid-phase product at substantially the pressure prevailing in said mixed-phase hydrofining, stripping said liquid phase with fresh hydrogen at substantially the pressure prevailing in said mixed-phase hydrofining to strip dissolved low-boiling hydrocarbons therefrom, mixing the vapor phase resulting from said stripping with the vapor-phase product from said mixed-phase hydrofining, and subjecting the resulting combined vapor-phase mixture to further hydrofining at an elevated pressure in the presence of a hydrofining catalyst and in the absence of liquid phase, recovering from said stripping operation a heavy fraction suitable for use as cracking charge stock, and recovering from said vapor-phase hydrofining a light fraction suitable for use as jet fuel.

8. A process as defined in claim 7 wherein the total effluent from said mixed-phase hydrofining is partially cooled to effect a partial condensation of the vapor phase prior to said separation of vapor phase from liquid phase.

9. A process as defined in claim 7 wherein the catalysts employed in said mixed-phase hydrofining and said vapor-phase hydrofining consist essentially of cobalt molybdate distended on a major proportion of an adsorbent oxide carrier.

10. A method for hydrofining a gas oil feedstock having an initial boiling point between about 250–350° F. and an end boiling point between about 600–750° F. to obtain therefrom a naphtha fraction suitable for reforming charge stock, and a heavy fraction suitable for use as diesel fuel, which comprises first subjecting said feedstock to mixed-phase hydrofining at an elevated pressure in the presence of hydrogen and a catalyst, wherein the conditions of hydrofining are such that the heavy ends are predominantly in the liquid phase, and the light ends

are predominantly in the vapor phase, both of said phases being in concurrent downflow while in contact with said catalyst, terminating said mixed-phase contacting after said liquid phase has been sufficiently refined for use as diesel fuel but before said vapor phase has been sufficiently refined for use as reforming charge stock, separating the total vapor-phase product from the liquid-phase product at substantially the pressure prevailing in said mixed-phase hydrofining, stripping said liquid phase with fresh hydrogen at substantially the pressure prevailing in said mixed-phase hydrofining to strip dissolved low-boiling hydrocarbons therefrom, mixing the vapor phase resulting from said stripping with the vapor-phase product from said mixed-phase hydrofining, and subjecting the resulting combined vapor-phase mixture to further hydrofining at an elevated pressure in the presence of a hydrofining catalyst and in the absence of liquid phase, recovering from said stripping operation a heavy fraction suitable for use as diesel fuel and

recovering from said vapor-phase hydrofining a naphtha fraction suitable for use as reforming charge stock.

11. A process as defined in claim 10 wherein the total effluent from said mixed-phase hydrofining is partially cooled to effect a partial condensation of the vapor phase prior to said separation of vapor phase from liquid phase.

12. A process as defined in claim 10 wherein the catalysts employed in said mixed-phase hydrofining and said vapor-phase hydrofining consist essentially of cobalt molybdate distended on a major proportion of an adsorbent oxide carrier.

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