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MULTISTAGE HYDROFINING PROCESS

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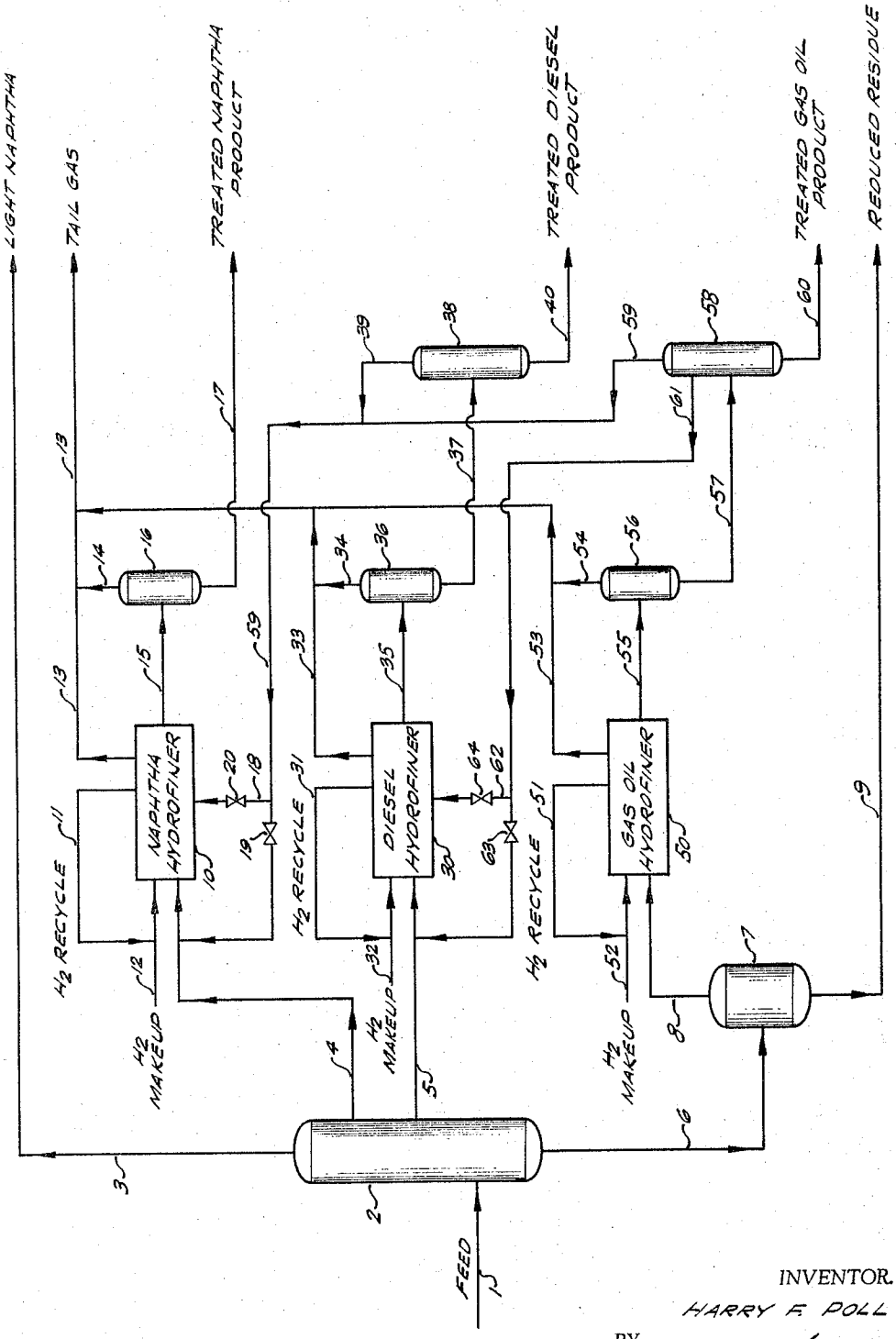

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MULTISTAGE HYDROFINING PROCESS

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This invention relates to a multistage catalytic hydrofining process for treating high-sulfur, high-nitrogen mineral oil fractions, and more particularly to a process for producing a substantially nitrogen-free naphtha, a moderately severely treated diesel and a less severely treated gas oil. Briefly, the process comprises the following steps:

(1) Subjecting a nitrogen-containing raw gas oil feedstock to catalytic hydrofining under relatively mild conditions;

(2) Fractionating the effluent from Step 1 to recover a partially refined gas oil product, a lower boiling partially refined synthetic diesel fraction, and a still lower boiling partially refined synthetic naphtha fraction;

(3) Subjecting a nitrogen-containing raw diesel feedstock to catalytic hydrofining in a separate hydrofining zone along with said synthetic diesel fraction, under relatively more sever conditions than were employed in Step 1;

(4) Fractionating the effluent from Step 3 to recover a diesel product fraction of lower nitrogen content than said gas oil product, and a lower-boiling, partially refined synthetic naphtha fraction;

(5) Subjecting a nitrogen-containing raw naphtha feedstock to catalytic hydrofining in a separate hydrofining zone along with said synthetic naphtha feed fractions from Steps 2 and 4 under relatively more severe conditions than were employed in Step 3; and

(6) Recovering a substantially nitrogen-free naphtha product fraction from the effluent from Step 5.

Many mineral oil fractions, such as petroleum and shale oil distillates, must be treated to remove sulfur, nitrogen, oxygen and other undesirable contaminants, and to hydrogenate unsaturated components in order that resultant products meet commercial quality standards, or are otherwise suitable for subsequent catalytic processing. Although, under suitable processing conditions, essentially all such contaminants can be removed, it is frequently uneconomical and unnecessary to fully refine all fractions of a crude oil. Ideally, each fraction should be treated in such manner as to effect the minimum quality improvement necessary, depending on the requirements of subsequent refining processes or ultimate commercial product specifications. Single-stage hydrofining of a full-range feed is not practical where each of the treated product fractions, resulting from fractionation of the full-range effluent, require different degrees of refining. In single-stage treating, not only must some of the fractions be over-treated to assure that those fractions having more stringent quality requirements receive adequate treatment, but optimum processing conditions for each fraction cannot be attained.

Prefractionation of a wide-boiling-range hydrocarbon feedstock, followed by separate hydrofining of individual distillate fractions, does not fully overcome these disadvantages. Although prefractionation may permit processing of each distillate fraction under optimum conditions, overtreating or undertreating of some of the resulting product fractions may still be a problem due to the formation of lower boiling components in the hydrofining process. Catalytic hydrofining of a contaminated feedstock results in a treated effluent of higher gravity and substantially wider boiling range, primarily due to the production of light hydrocarbons resulting from the decomposition of organic sulfur, nitrogen, and oxygen compounds. These "synthetic" light hydrocarbons must frequently be removed from the treated product to meet flash point, initial boiling point or other specifications, yet they are often not sufficiently refined in the first treating stage to meet product specifications for that particular boiling range fraction, therefore requiring additional hydrofining treatment.

I have found that multistage hydrofining wherein the lighter, partially refined product fractions are further treated in admixture with untreated feed stocks, or other partially treated hydrocarbons, of similar boiling range, can be adapted to effectively overcome these inherent difficulties and achieve desired treatment of the various product fractions under optimum processing conditions. In one comprehensive aspect, my process comprises prefractionation of a crude oil, crude shale oil, or other wide-boiling-range hydrocarbon feed into raw naphtha, diesel and gas oil feed fractions; separate hydrofining of the distillate feed fractions under optimum conditions; removal of low-boiling fractions formed as a by-product of the hydrofining reactions; and secondary treatment of these low-boiling synthetic fractions in combination with a raw feed fraction of comparable boiling range. The wide-boiling feed is thus converted to a substantially nitrogen-free naphtha, a commercial diesel oil, and a gas oil of improved quality, each like-boiling fraction of the net treated product, thereby being refined to comparable sulfur and nitrogen levels. Although my process is adapted to the treatment of any nitrogen-containing hydrocarbon feedstock, it is particularly advantageous in the treament of high nitrogen feedstocks, such as those having nitrogen contents above about 0.3 weight percent.

The overall object is to upgrade high-nitrogen naphtha, diesel and gas oil fractions to treated products comparable in boiling range to the feed fractions by processing in a hydrofining complex providing maximum economy in hydrogen consumption, catalyst utilization and product yields. A more specific object is to remove sulfur, nitrogen, and other undesirable constituents from crude petroleum or shale oil fractions so as to yield a naphtha reformer feed stock essentially free of sulfur and nitrogen, and yield less completely refined diesel and gas oil products. Another object is to provide a multistage hydrofining process wherein several component feed fractions receive optimum hydrofining treatment, thereby minimizing overtreatment of the product fractions. Other objects will be apparent from the more detailed description which follows.

The extent to which sulfur, nitrogen and oxygen compounds must be removed from a given feed depends on the subsequent catalytic processing steps to be employed, and the end use of the fraction. For example, the gasoline fractions of both petroleum and shale oils are typically low in octane value and must be reformed to improve engine performance. Most catalytic reforming processes are susceptible to sulfur, nitrogen and oxygen contained in the feed, in that these contaminants effect a reduction in catalyst activity, and can even render such process completely inoperable. On the other extreme, little or no hydrogen treatment of high boiling residuum fractions is required, as these materials are generally blended directly to fuel oil, visbroken for fuel oil blending, converted to asphalt, or coked to increase the yield of light distillates. The treatment required of middle distillate fractions is generallyy intermediate between the severe treatment required of gasoline, jet fuel and solvents on the one extreme, and the slight treatment required of high boiling residuum on the other. Stove oil and diesel distillate fractions generally require intermediate treatment to remove substantial amounts of sulfur, nitrogen and oxygen, and may require hydrogenation of unstable olefin, diolefin and acetylene-type hydrocarbons to improve burning characteristics, performance, color, pour point and storage stability. However, middle distillate fractions may require more severe treatment if they are to be

subjected to subsequent catalytic processing such as catalytic hydrocracking.

The term "hydrofining," as employed herein, means the contacting of hydrocarbon feed stock with a suitable solid catalyst at elevated temperature and pressure in the presence of hydrogen, under conditions whereby there is no net production of hydrogen and little or no hydrocracking of hydrocarbon molecules. The net effect of hydrofining is to bring about a selective decomposition of organic sulfur, nitrogen and oxygen compounds and like contaminants, and to saturate olefin, diolefin, and acetylene bonds with hydrogen. The organically bound sulfur, nitrogen and oxygen atoms (herein termed "heteroatoms") are replaced in the contaminant molecules with hydrogen, the hereteroatoms being converted to hydrogen sulfide, ammonia and water, respectively.

Usually the heteroatoms in a contaminant molecule will form a connecting linkage in a ring, chain or side-chain structure. Replacement of the heteroatom with hydrogen causes a cleavage of the molecule, resulting in an opening of the ring, or severing of the chain or side chain. Frequently, several heteroatoms will be contained in a single molecule, and when they are removed the original molecule will be broken into several fragments. The effect of removing the heteroatoms from the molecule is usually a reduction in molecular size, and accordingly, the formation of lower boiling fractions. Thus, the hydrofining of a contaminated feedstock almost always results in a treated product of wider boiling range and higher API gravity (lower density) than the corresponding feedstock. Although some higher boiling fractions may be formed by polymerization, or other mechanism, the boiling range increase is largely attributable to the formation of lower boiling fractions.

In the usual case, processing conditions will be controlled to accomplish only moderate treatment of higher boiling fractions. Under such conditions, a number of the molecules containing a heteroatom may have only one carbon-hereteroatom bond severed, thereby resulting in the formation of mercaptans, primary amines, alcohols and the like. Other contaminant molecules, containing a plurality of hereteroatoms may have only one heteroatom removed, thereby forming lighter molecules still containing one or more heteroatoms. Thus, the result of partial treatment of heavy stocks is that at least a portion of the lighter synthetic fractions formed do not meet the quality standards for the lower boiling fractions and must be subjected to subsequent hydrofining treatment. My hydrofining process accomplishes secondary treatment of these lower boiling synthetic fractions by combining them with untreated or partially treated raw feed fractions of similar boiling range for subsequent hydrofining.

The catalyst employed in my process 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 iron, cobalt or nickel) mixed with an oxide or sulfide of a group VI–B metal (preferably molybdenum or tungsten). Such catalysts may be employed in undiluted form, but preferably are distended and supported on an adsorbent carrier in proportions ranging betwen about 2% and about 25% by weight. Suitable carriers include in general the difficultly reducible inorganic oxides, e.g., alumina, silica, zirconia, titania, clays such as bauxite, bentonite, etc. The carrier should display little or no cracking activity, and hence highly acidic carriers are to be avoided. Preferably, the catalyst base should have a Cat–A activity index below about 20. The preferred carrier is activated alumina, and especially activated alumina containing about 3–15% by weight of coprecipitated silica gel.

The preferred hydrofining catalyst consists of sulfided composites of cobalt oxide plus molybdenum oxide supported on silica-stabilized alumina. Compositions originally containing between about 2% and 8% of CoO 4% and 20% of MoO_3, 3% and 15% of SiO_2, and the balance Al_2O_3, and wherein the mole-ratio of CoO/MoO_3 is between about 0.2 and 4 are especially preferred.

The naphtha, diesel and gas oil hydrofining zones may each consist of a single hydrofining reactor arranged as described herein, or a large number of reactors may be employed in a single zone. The catalyst may be disosed in a fixed stationary bed, or any of the various moving or fluidized bed techniques may be utilized. The individual reactors can be operated under either vapor phase or liquid-vapor mixed phase conditions. In any case, hydrogen and liquid hydrocarbon feedstocks are preheated to an appropriate inlet temperature of between about 450° F. and about 800° F., either separately or in combination. The preheated hydrogen, usually a mixture of recycle and make-up hydrogen, and hydrocarbon feedstock are then contacted with the bed of hydrofining catalyst. The reactions occurring in the hydrofining zone are largely exothermic, giving rise to an increase in temperature, the increase depending on the degree of contamination of the feed, the completeness of treatment and the recycle gas ratio. Conditions are generally controlled to maintain maximum temperatures below about 875° F., and preferably below about 800° F. Where the increase is greater than about 200° F., it may be desirable to provide intercooling, either by means of exchange of the reactant with a coolant, or by addition of a cold hydrogen quench gas to the system.

The feed rate, temperature, pressure, hydrogen gas purity, hydrogen gas rate and space velocity can all be controlled to yield the desired degree of refining. The reactor effluent, consisting of unreacted hydrogen, hydrocarbon gases, normally liquid hydrocarbons, hydrogen sulfide, ammonia and water, is partially condensed by cooling, usually at least a portion of the heat being interchanged with the feed. The resulting gas phase may be recycled to the reactor, a portion being withdrawn as a purge gas to prevent accumulation of non-condensible gases which dilute the hydrogen. Water may be added to the condensing effluent for removal of hydrogen sulfide and ammonia, and subsequently withdrawn as a separate aqueous phase. The condensed hydrocarbon effluent is then stripped to remove light gases and residual hydrogen sulfide and ammonia.

The details of my multistage hydrofining process can be more readily comprehended by reference to the accompanying drawing which is a flow-sheet illustrating one specific embodiment thereof. Auxiliary equipment, such as pumps, heat exchangers, vessels, heaters, instrumentation, etc. is of conventional design and deleted for clarity. Similarly, the individual hydrofining steps are illustrated in block fashion, since any appropriate hydrofining process may be employed. The flow sheet and description thereof is illustrative of only one operable embodiment, and is not meant to exclude other modifications.

Referring to the drawing, a crude petroleum oil, crude shale oil, or other wide-boiling liquid hydrocarbon feedstock, is fractionated in atmospheric fractionator **2** to prepare distillate feedstocks of narrower boiling range. The wide-boiling range feed enters fractionator **2** through line **1**, and in this embodiment, a light naphtha is produced via line **3** as an overhead product. Although the light naphtha usually consists of C_5 and lighter hydrocarbons boiling below about 100° F., heavier hydrocarbons boiling up to about 230° F., or higher, can be included. A raw heavy naphtha distillate and a raw diesel distillate are produced as side cuts through lines **4** and **5**, respectively. The heavy naphtha will usually have an initial boiling point between about 120° F. and about 160° F., and a final boiling point between about 350° F. and about 450° F. The heavy naphtha and diesel distillates may be contiguous fractions, or an intermediate boiling fraction may be produced. Where the diesel and heavy naphtha are contiguous, the diesel will have an initial boiling point between about 350° F. and about

450° F., and normally will have a final boiling point between about 600° F. and about 675° F. An atmospheric fractionator bottoms is withdrawn from fractionator **2**, and fed, via line **6**, to vacuum fractionator **7**.

Vacuum fractionator **7** is a conventional vacuum flash separator operated at reduced pressure to separate a raw gas oil distillate from a reduced residuum bottoms product. The gas oil distillate is produced overhead through line **8**, and the reduced residuum is withdrawn from the bottom of the fractionator through line **9**. The gas oil distillate usually has an initial boiling point between about 600° F. and about 675° F. and a final boiling point between about 950° F. and about 1,050° F. Vacuum fractionator **7** is usually operated between about 25 and about 5 mm., and preferably between about 20 and about 10 mm. of Hg absolute pressure. If the distillate feed stocks are of suitable boiling range, both the atmospheric and vacuum fractionation steps may be eliminated and the feed stocks fed directly to the appropriate hydrofiner.

Raw gas oil distillate is fed through line **8** to gas oil hydrofiner **50** for mild catalytic hydrofining to reduce the sulfur and nitrogen content and partially saturate the unsaturated hydrocarbon bonds. A high-nitrogen gas oil may contain between about 10,000 p.p.m. and about 30,000 p.p.m. nitrogen. Full refining of the gas oil fraction is unnecessary and undesired. The gas oil nitrogen content is typically reduced to between about 1/5 and about 1/40 of the feed value in this hydrofining step, thereby typically yielding a product containing between about 200 and 6,000 p.p.m. nitrogen, although processing conditions can be varied to effect more or less nitrogen removal. Gas, primarily hydrogen, separated from the treated effluent, is recycled to the reactor inlet via line **51**, and make-up hydrogen is supplied via line **52**. Purge gas is withdrawn via line **53**. The treated liquid effluent is produced through line **55** to stripper **56**, the C_3 and lighter constituents being removed overhead through line **54**. A C_4+ treated gas oil effluent is withdrawn from treated gas oil stripper **56** and fed to treated gas oil fractionator **58** through line **57**. Treated gas oil fractionator **58** is operated to produce a partially treated synthetic naphtha overhead, a partially treated synthetic diesel fraction as a side cut, and a gas oil product fraction is withdrawn as bottoms through line **60**. The treated gas oil product normally will have a boiling range similar to that of the feed to hydrofiner **50**. Relatively sharp fractionation of each of the synthetic fractions is nceessary to prevent heavy ends entering the higher severity hydrofiners.

The partially refined synthetic hydrocarbons boiling in the diesel boiling range, formed on hydrofining the gas oil feed fraction, are withdrawn from fractionator **58** through line **61** and combined with the raw diesel distillate in line **5**. The combined diesel fraction is fed to the inlet of diesel hydrofiner **30**. Aternatively, where the synthetic diesel fraction requires less hydrofining than the raw diesel distillate, the synthetic fraction can be fed to an intermediate hydrofining reaction stage by closing valve **63** and opening valve **64**, the synthetic diesel then flowing through line **62** to a downstream section of the hydrofiner. Recycle hydrogen flow is maintained via line **31** and make-up hydrogen is supplied via line **32**. Purge gas is withdrawn through line **33** and a treated liquid effluent is withdrawn through line **35** for subsequent stripping in treated diesel stripper **36**. The propane and lighter constituents of the treated diesel effluent are produced overhead via line **34** and a C_4+ diesel effluent is withdrawn from the bottom of the stripper through line **37**. The lower boiling naphtha fraction of the C_4+ diesel effluent is removed in diesel fractionator **38**, thereby yielding a treated diesel bottoms product produced through line **40**, the diesel product normally having a boiling range similar to that of the combined diesel feed to hydrofiner **30**. The diesel fraction of a high-nitrogen crude oil will normally contain between about 1,000 and about 20,000 p.p.m. nitrogen. Product nitrogen is normally reduced to between about 1/50 and 1/200 of the feed value.

The partially treated, synthetic naphtha boiling range materials produced in the gas oil and diesel hydrofiners are conveyed, via lines **59** and **39**, respectively, to line **4**, where they are admixed with the raw naphtha feed fraction. Combined naphtha is fed to naphtha hydrofiner **10** for severe hydrofining to remove substantially all of the organic sulfur, nitrogen and oxygen, and to saturate substantially all of the olefin, diolefin and acetylene bonds. Raw naphtha distillate nitrogen contents can be as high as 10,000 p.p.m. Typically, the treated naphtha product will have less than 100 p.p.m. nitrogen, and if hydrofined for subsequent reforming, less than 5 p.p.m. nitrogen, and preferably less than 1.0 p.p.m. Under proper conditions it is possible to completely remove any last traces of nitrogen contamination. Where the synthetic naphtha requires less hydrofining than the raw feed naphtha, the combined synthetic naphthas in line **59** can be fed to an intermediate hydrofining stage by closing valve **19** and opening valve **20**, the synthetic naphtha then flowing through line **18** to a downstream section of the hydrofiner. Hydrogen is recycled through line **11** and make-up hydrogen supplied through line **12**. Purge gas is withdrawn through line **13**. The treated naphtha effluent is withdrawn through line **15** and fed to naphtha stripper **16** for removal of propane and lighter constituents as an overhead product, the gases being produced through line **14**. A C_4+ treated naphtha product is withdrawn from the bottom of naphtha stripper **16** via line **17**. The C_4+ treated naphtha may be fractionated to yield a light treated naphtha and a heavy treated naphtha, if desired, by the inclusion of an additional fractionation step, not shown.

The various purge gases and stripper overhead gases may be directed to tail gas for subsequent treatment and disposal as fuel, as illustrated, or subjected to any number of other process steps without affecting the critical features of my process. The various treated liquid products may also be further processed, blended or fractionated into additional distillate fractions without affecting the scope of the invention.

The following example is cited to illustrate the quality improvement obtainable on catalytically hydrofining shale oil distillates according to the method of this invention. Since this example is illustrative of only one embodiment of my invention, it is not to be construed as limiting the scope thereof.

Example

In this example, a crude Colorado shale oil, recovered by combustive retorting and subsequently stabilized, is fractionated and hydrofined substantially as illustrated in the drawing. Characteristic properties of the stabilized crude shale oil are set forth in Table I.

TABLE I.—CRUDE SHALE OIL PROPERTIES

Gravity, °API	20
Basic nitrogen, wt. percent	0.95
Total nitrogen, wt. percent	1.90
Total sulfur, wt. percent	0.75
ASTM Distillation (D-1160)	
i	180
50%	690
ep	1,050
Percent Rec.	92.5
Percent Res.	7.5

Approximately 30,000 b.p.s.d. of stabilized crude shale oil is fed to the atmospheric fractionator, operating at about 30 p.s.i.g. A virgin C_4–C_5 light distillate is produced overhead from the atmospheric fractionator at a rate of about 1,150 b.p.s.d. This distillate fraction is not hydrofined as it is not a desirable reformer feedstock,

and may be more effectively desulfurized by other processing techniques. A C_6–380° F. naphtha distillate and a 380° F.–625° F. diesel fraction are withdrawn as side cuts from the atmospheric fractionator. The atmospheric fractionator bottoms are subjected to vacuum flash separation to yield a gas oil fraction boiling between about 625° F. and about 1,000° F., and a heavy residuum boiling above about 1,000° F. The heavy residuum is produced at a rate of 5,750 b.p.s.d. without further treatment.

The raw naphtha, diesel and gas oil distillate fractions are hydrofined in separate reaction systems, with the light hydrocarbons formed on hydrofining the heavier stocks being further treated with the raw distillate of comparable boiling range. The catalyst employed in each reaction system is a presulfided cobalt molybdate, pelleted catalyst comprising (before sulfiding) about 4% by weight of cobalt oxide and about 15% by weight molybdenum oxide supported on a 5% silicon dioxide, 95% alumina coprecipitated carrier. Target nitrogen contents are about 1 p.p.m. for the naphtha, about 300 p.p.m. for the diesel, and about 2,000 p.p.m. for the gas oil. Illustrative processing conditions to achieve these product nitrogen contents are summarized in Table II.

TABLE II.—SUMMARY OF HYDROFINING CONDITIONS

	Naphtha Hydrofiner	Diesel Hydrofiner	Gas Oil Hydrofiner
Reactor Inlet Press., p.s.i.g.	800	1,200	1,800
Recycle Gas Rate [1] (85 mole percent H_2), c.s.f./BFF [2]	3,000	3,000	3,000
Reactor Average Temperature, ° F.	680	650	625
Liquid Hourly Space Velocity	1.00	0.51	1.5
Chemical Hydrogen Consumption, [1] s.c.f./BFF_2	1,050	1,330	1,620

[1] Gas rates based on raw distillate feeds only.
[2] Barrels of Fresh (Raw) Feed.

Feed characteristics and flow rates to the various hydrofining zones are as follows:

TABLE III.—SUMMARY OF HYDROFINER FEED RATES AND PROPERTIES

	Boiling Range, ° F.	Feed Rate, b.p.s.d.	Total Nitrogen, p.p.m.
Naphtha Hydrofiner:			
Fresh Feed	C_6–380	4,500	6,300
Synthetic Feed:			
From Diesel Hydrofiner	C_4–380	3,560	40
From Gas Oil Hydrofiner	C_4–380	2,325	123
Combined Naphtha Feed	C_4–380	10,385	2,870
Diesel Hydrofiner:			
Fresh Feed	380–625	7,200	14,000
Synthetic Feed, From Gas Oil Hydrofiner	380–625	4,780	1,290
Combined Diesel Feed	380–625	11,980	9,000
Gas Oil Hydrofiner: Fresh Feed	625–1,000	11,400	20,100

The final product characteristics and yields are summarized in Table IV.

TABLE IV.—SUMMARY OF PRODUCT YIELDS AND PROPERTIES

	Boiling Range, ° F.	Yield, b.p.s.d.	Total Nitrogen, p.p.m.
Naphtha	C_4–380	10,550	0.8
Diesel	380–625	8,720	137
Gas Oil	625–1,000	4,640	1,990

The foregoing example may be modified by employing different catalysts, by adjusting the reaction conditions to achieve different degrees of refining treatment, by fractionating the feed and products into distillate fractions of different boiling ranges, by producing a portion of the semi-refined products without secondary hydrogen treatment, or otherwise as may be obvious to those skilled in the art, without departing from the scope and spirit of my invention as defined by the following claims.

I claim:

1. A method of refining nitrogen-containing naphtha, diesel and gas oil feed fractions which require different degrees of refining comprising:
- catalytically hydrofining a raw gas oil feed in a gas oil hydrofiner operated under relatively mild hydrofining conditions to yield a gas oil effluent;
- fractionating said gas oil effluent to recover a partially refined first synthetic naphtha fraction, a partially refined synthetic diesel fraction and a gas oil fraction, and withdrawing said gas oil fraction as a treated gas oil product of reduced nitrogen content;
- catalytically hydrofining a raw diesel feed in admixture with said partially refined synthetic diesel fraction in a separate diesel hydrofiner operated under hydrofining conditions relatively more severe than employed in said gas oil hydrofining to yield a diesel effluent;
- fractionating said diesel effluent to recover a second partially refined synthetic naphtha fraction and a diesel effluent fraction, and withdrawing said diesel effluent fraction as a treated diesel product of reduced nitrogen content;
- catalytically hydrofining a raw naphtha feed in admixture with said first and said second synthetic naphtha fractions in a separate naphtha hydrofiner operated under relatively more severe hydrofining conditions than employed in said diesel hydrofining to yield a naphtha effluent; and
- recovering a treated naphtha product of reduced nitrogen content from said naphtha effluent.

2. The method of claim 1 wherein said naphtha, diesel and gas oil feed fractions are obtained from a crude shale oil.

3. The method of claim 1 wherein said hydrofining zones contain cobalt molybdate catalyst and wherein said feed fractions are contacted with said catalyst in the presence of hydrogen at temperatures between about 450° F. and about 875° F.

4. The method of claim 1 wherein at least one of said feed fractions is partially hydrofined prior to admixture with said synthetic fraction, the admixed fractions then being subjected to secondary hydrofining.

5. The method of claim 1 wherein said gas oil hydrofining conditions are controlled to reduce the nitrogen content of said treated gas oil product to between about $\frac{1}{5}$ and about $\frac{1}{40}$ of the nitrogen content of said raw gas oil feed.

6. The method of claim 1 wherein said diesel hydrofining conditions are controlled to reduce the nitrogen content of said treated diesel product to between about $\frac{1}{50}$ and about $\frac{1}{200}$ of the nitrogen content of said raw diesel feed.

7. The method of claim 1 wherein said naphtha hydrofining conditions are controlled to reduce the nitrogen content of said treated naphtha product to less than about 5 p.p.m.

8. A process for refining a nitrogen-containing crude oil comprising:
- fractionating said crude oil to recover a raw naphtha feed fraction, a raw diesel feed fraction and a raw gas oil feed fraction;
- catalytically hydrofining said raw gas oil feed fraction in a gas oil hydrofiner operated under relatively mild hydrofining conditions to yield a gas oil effluent of increased boiling range;
- fractionating said gas oil effluent to recover a partially refined first synthetic naphtha fraction, a partially refined synthetic diesel fraction and a gas oil effluent fraction substantially comparable in boiling range to said raw gas oil feed fraction, and withdrawing said gas oil effluent fraction as a treated gas oil product of reduced nitrogen content;

catalytically hydrofining said raw diesel feed fraction in admixture with said partially refined synthetic diesel fraction in a separate diesel hydrofiner operated under hydrofining conditions relatively more severe than employed in said gas oil hydrofining to yield a diesel effluent of increased boiling range;

fractionating said diesel effluent to recover a partially treated second synthetic naphtha fraction and a diesel effluent fraction substantially comparable in boiling range to said raw diesel feed fraction, and withdrawing said diesel effluent fraction as a treated diesel product of reduced nitrogen content;

catalytically hydrofining said raw naphtha feed fraction in admixture with said first and said second synthetic naphtha fractions in a separate naphtha hydrofiner operated under relatively more severe hydrofining conditions than employed in said diesel hydrofining to yield a naphtha effluent; and

recovering a treated naphtha product of reduced nitrogen content from said naphtha effluent.

9. The process of claim **8** wherein said raw naphtha feed fraction is primarily in the C_6–380° F. boiling range, said raw diesel feed fraction boils between about 380° F. and about 625° F. and said raw gas oil feed fraction boils between about 625° F. and about 1,000° F.

10. The process of claim **8** wherein said crude oil feed stock is a crude shale oil.

11. The process of claim **8** wherein said gas oil hydrofiner contains a cobalt molybdate catalyst maintained at a temperature of between about 450° F. and about 875° F.

12. The process of claim **8** wherein said diesel hydrofiner contains a cobalt molybdate catalyst maintained at between about 450° F. and about 875° F.

13. The process of claim **8** wherein said naphtha hydrofiner contains a cobalt molybdate catalyst maintained at between about 450° F. and about 875° F.

14. The process of claim **8** wherein at least one of said hydrofiner feed fractions is partially hydrofined prior to admixture with said synthetic fraction, the admixed fractions then being subjected to secondary hydrofining.

15. The process of claim **8** wherein said gas oil hydrofining conditions are controlled to reduce the nitrogen content of said treated gas oil product to between about 1/5 and about 1/40 of the nitrogen content of said raw gas oil feed fraction.

16. The process of claim **8** wherein said diesel hydrofining conditions are controlled to reduce the nitrogen content of said treated diesel product to between about 1/50 and about 1/200 of the nitrogen content of said raw diesel feed fraction.

17. The process of claim **8** wherein said naphtha hydrofining conditions are controlled to reduce the nitrogen content of said treated naphtha product to less than about 5 p.p.m.

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