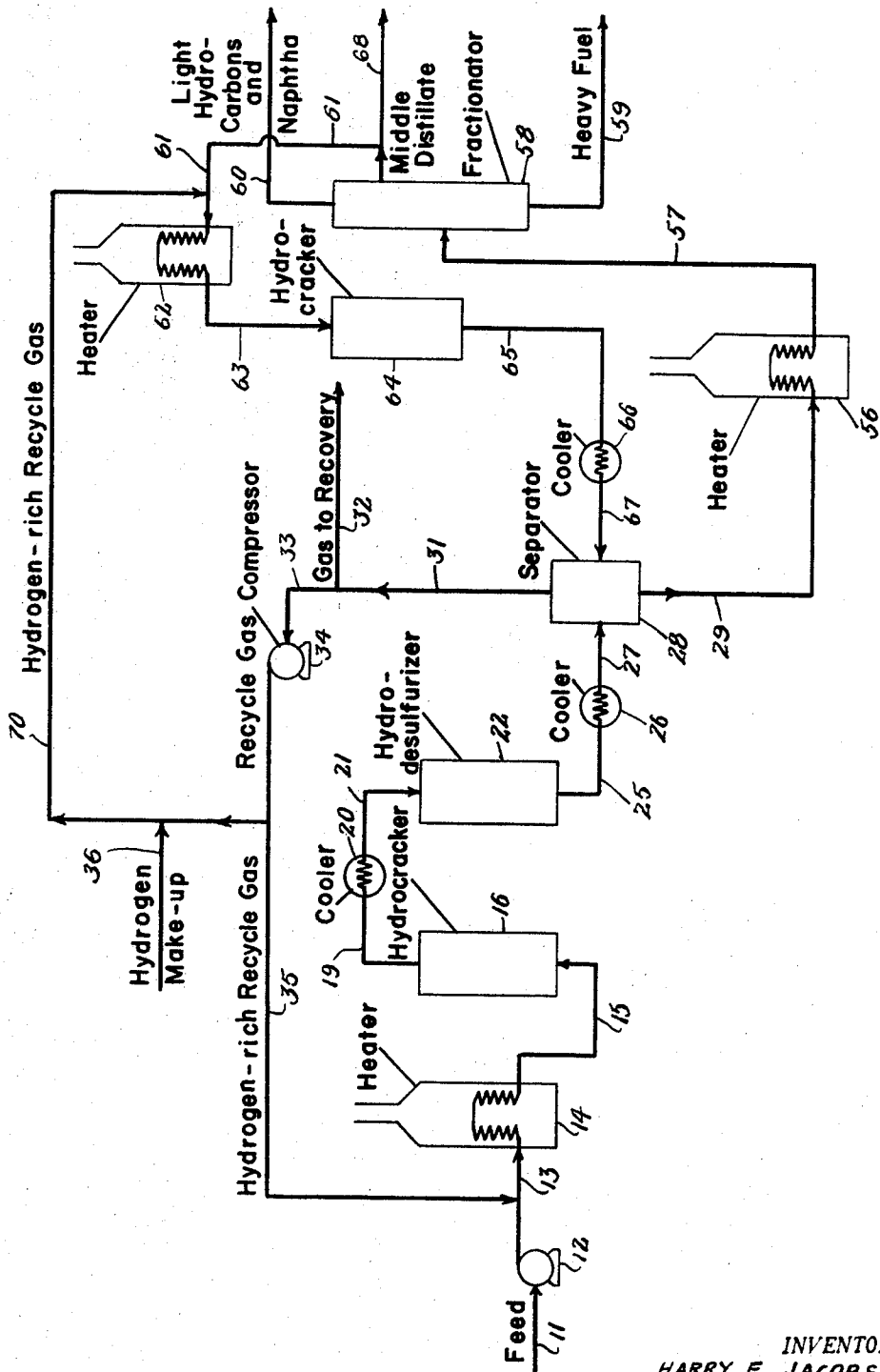


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PROCESS FOR REMOVAL OF SULFUR AND METALS
FROM PETROLEUM MATERIALS
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PROCESS FOR REMOVAL OF SULFUR AND METALS FROM PETROLEUM MATERIALS

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ABSTRACT OF THE DISCLOSURE

A process for treating a petroleum material containing a residuum fraction in order to remove sulfur and metal compounds contained therein and to produce a naphtha fraction suitable for use as an ethylene charge stock and a low sulfur content fuel oil comprising subjecting said petroleum material at a high temperature and high pressure to hydrocracking in the presence of hydrogen and a catalyst, to produce a hydrocracked product, subjecting said hydrocracked product to hydrodesulfurization at a high temperature and high pressure in the presence of hydrogen and a highly active catalyst to produce a hydrodesulfurized product and then fractionating said hydrodesulfurized product to obtain a naphtha product, a furnace oil and a heavy fuel oil. The furnace oil is then recycled and subjected to further treatment in order to increase the yield of the naphtha product.

BACKGROUND OF INVENTION

This invention relates to the treatment of petroleum materials containing residuum fractions. Particularly, this invention relates to a process for the treatment of said petroleum materials containing appreciable quantities of sulfur, nitrogen and metal containing compounds. More particularly, this invention relates to a process for the treatment of said petroleum materials in order to produce more valuable products, such as naphtha suitable for use as an ethylene charge stock, and low sulfur content heavy fuel oil. The naphtha produced in the method of our invention has the desirable features of an ethylene charge stock in that it will approximate a virgin naphtha from the standpoint of cyclic content and low iso to normal ratio of paraffins. Further, the heavy fuel oil produced has a sulfur content of less than 0.5 weight percent.

It has been known for some time that petroleum materials containing residuum fractions contain significant quantities of metallic impurities, e.g., vanadium, nickel, sodium, iron, copper and zinc. These impurities may be in the form of insoluble compounds suspended in the oil or oil-soluble metallo-organic compounds. When petroleum materials containing residuum fractions are subjected to desulfurization, metallo-organic compounds present in such fractions tend to form a layer of ash on the surfaces of the catalyst, thus blocking or otherwise adversely affecting the activity of the catalyst and often permanently poisoning it in terms of both activity and selectivity. This is quite different from the ordinary inactivation of the catalyst by coke formation which is alleviated by regeneration, e.g., burning off of the carbonaceous deposits formed during the reaction. While metallic impurities present in such fractions in the form of suspended solid particles may be removed by relatively simple physical means like filtration, oil-soluble metallo-organic compounds present a more difficult problem of elimination. Accordingly, the art has necessarily relied upon various systems involving extensive replacement of the catalyst. Replacement of the catalyst, however, necessitates interruption of the catalytic conversion operations or, as is

more frequently the case, the provision of duplicate reactors. In any event, costs associated with replacement of the catalyst have made it virtually impractical to refine petroleum materials containing residuum fractions of high metal content. Further, these metals, and in particular vanadium, are undesirable in residual petroleum fractions because of the corrosion and pitting of metals resulting from combustion of such residual fuels.

With the increasing use of crude oils obtained from foreign sources such as the Middle East and South America, the presence of the metallic impurities in the crudes has become a considerable problem. The amounts of such metals in domestic sources of crude oil such as Mid-Continent and East Texas crudes, are so small as to present no problem in the refining of the crudes and in the use of the petroleum fractions obtained from such crudes. For example, with two Texas crudes containing only 0.1 part per million of vanadium and 2 and 4 p.p.m. of nickel, the crudes can be processed satisfactorily in hydrogenation systems and their fractions employed in the usual way. On the other hand with a Kuwait crude containing 78 p.p.m. of vanadium and 28 p.p.m. of nickel in the long residuum, the problem does exist; while with Venezuelan crudes which contain 200 to 1000 p.p.m. or more of vanadium and up to 100 p.p.m. of nickel in the long residuum, the problem is serious. Briefly stated, the oils with which this invention is concerned are those which contain sufficient amounts of heavy metals so as to cause catalyst contamination problems in desulfurization processes and/or corrosion problems in the use as fuel. It is desirable to reduce the metals content to less than 100 p.p.m. and preferably below 20 p.p.m.

It is also known in the petroleum refining art that the presence of sulfur is objectionable in heavy fuel oils. High sulfur content in such oils contributes significantly to air pollution problems.

SUMMARY OF INVENTION

This invention is concerned with petroleum materials containing residuum fractions such as total crude as well as topped or reduced crude. These terms may be defined as follows:

"Total crude" is defined as a naturally occurring petroleum oil containing residuum fractions which has not been processed in any manner, but preferably separated from water and sediment and desalted.

"Topped or reduced crude" is defined as the residuum petroleum fraction resulting from removal of all or some of those straight run fractions such as gas, gasoline, kerosene, naphtha, furnace oil, gas oil, etc., which are normally removed from the above defined total crude by the process of atmospheric and/or vacuum topping or distillation. Our invention is, however, particularly suitable for the treatment of reduced crudes.

It will be understood, however, to those skilled in the art that the method of our invention will also be suitable for treating petroleum like materials obtained from shale oil, tar sands and coal, said petroleum like materials having properties which are comparable to petroleum materials containing residuum fractions as hereinabove defined.

In accordance with our invention, a petroleum material containing residuum fractions, hereinafter referred to as charge stream, is subjected to a hydrocracking and hydrodesulfurization treatment. In the first stage the charge stream is subjected to hydrocracking in a first hydrocracker. The total effluent from the hydrocracking stage is then subjected to hydrodesulfurization. In these stages the material treated is maintained largely in the liquid phase. The hydrodesulfurized material is subjected to fractionation in order to separate a naphtha fraction, a furnace oil

fraction and a heavy fuel oil fraction. The furnace oil fraction is then recycled and subjected substantially in vapor phase to hydrocracking in a second hydrocracker in order to increase the yield of the naphtha fraction.

The use of the first hydrocracker or the use of the desulfurizer alone cannot adequately treat a petroleum material containing a residuum fraction in order to economically and simultaneously remove sulfur and metal compounds therein and to produce in high yield naphtha fraction suitable for use as an ethylene charge stream. We have discovered, however, that in the combination of our process the first stage does an effective job of demetallizing, and provides for adequate hydrocracking, while the second stage with its superior catalyst system, not only provides for improved desulfurization but also hydrogenates the unstable components of the effluent from the first stage. Improved yields of naphtha are obtained through use of the novel recycle step of our invention.

It is therefore an object of our invention to provide an improved method for the treatment of petroleum materials containing residuum fractions, i.e., fractions which cannot be practically distilled.

Another object of our invention is to provide an improved method for the treatment of petroleum materials containing residuum fractions to maximize the production of a naphtha fraction suitable for use as an ethylene charge stock.

Still another object of our invention is to provide an improved treatment process for the removal of sulfur and metal compounds contained in petroleum materials containing residuum fractions.

Yet another object of our invention is to provide an improved method for obtaining a naphtha fraction suitable for use as an ethylene charge stock and a heavy fuel oil having a low sulfur content while simultaneously limiting the production of furnace oil.

Other objects, advantages and features of our invention will be apparent to those skilled in the art without departing from the spirit and scope of our invention, and it should be understood that the latter is not necessarily limited to the accompanying discussion and drawing.

In a broad aspect, our invention relates to a process for removing sulfur and metallic compounds from a petroleum material containing a residuum fraction in order to produce a naphtha fraction and a low sulfur content fuel oil comprising cracking said petroleum material while substantially in the liquid phase in the presence of hydrogen and a catalyst, desulfurizing the thus cracked oil while substantially in the liquid phase with hydrogen in the presence of a catalyst comprising essentially a minor amount of a member of the group consisting of oxides and sulfides of metals of Group VI lefthand column of the Periodic System and of iron group metals composited with a major amount of an activated alumina prepared by drying and calcining a substance which is predominantly composed of an aluminum hydroxide containing from 1.2 to 2.6 mols of water of hydration to produce a desulfurized fraction, and then fractionating said desulfurized fraction to obtain a naphtha fraction, a furnace oil fraction and a heavy fuel oil fraction, and subjecting said furnace oil fraction to hydrocracking while substantially in the vapor phase in the presence of hydrogen and a catalyst in order to increase the yield of naphtha fraction.

DESCRIPTION OF DRAWING

In order to more fully understand the method of this invention, reference is made to the accompanying drawing which diagrammatically represents a typical flow sheet embodying the process. Apparatus not considered necessary to an understanding of the invention has been omitted.

Referring to the drawing, a charge stream enters line 11 and is pumped by means of pump 12 through line 13 to heater 14 where it is heated either before or after mixing with hydrogen-rich gas. In the drawing the hydro-

gen-rich recycle gas passing through line 35 is combined with the feed passing through line 13. The mixture of the charge and the hydrogen-rich gas passes through line 15 into the hydrocracker 16. The effluent from the hydrocracker passes by means of line 19, cooler 20 and line 21 into the hydrodesulfurizer 22. The desulfurized product leaves the desulfurizer 22 by means of line 25, cooler 26 and line 27 and passes into the high pressure separator 28. The desulfurized liquid bottoms material is withdrawn from the separator by means of line 29.

Gases from the high pressure separator 28 are withdrawn through line 31. A first portion of the gas flows from line 31 through line 32 to conventional gas recovery facilities. A second portion of the gas flows through line 33 and is compressed by compressor 34. The gas then passes through line 35. This hydrogen-rich gas is preheated separately or in admixture with the charge stream in heater 14. The admixture then flows through line 15 as previously described.

Bottoms material in line 29 is heated by heater 56 before passing through line 57 to fractionating unit 58. Three fractions, viz., a naphtha fraction, a middle distillate or furnace oil fraction and a heavy fuel oil fraction are withdrawn from the fractionator through lines 60, 61 and 59, respectively. A portion of the furnace oil fraction is withdrawn through line 68. The remaining portion passes through line 61 to heater 62 and then through line 63 to second hydrocracker 64. The effluent from this hydrocracking operation passes through line 65, cooler 66 and line 67 to separator 28.

Hydrogen-rich recycle gas is passed from line 35 through line 70 to line 61. Hydrogen-rich makeup gas is added to line 70 by means of line 36.

PREFERRED EMBODIMENT

In the first stage hydrocracker in the method of our invention, the charge stream is subjected to liquid phase hydrocracking in the presence of a catalyst and a hydrogen-containing gas at elevated temperatures and pressures. Suitable hydrocracking temperatures fall in the range from about 700° F. to about 1000° F., preferably in the range of from about 750° F. to about 900° F. This pressure is maintained in the range of from about 500 p.s.i.g. to about 5000 p.s.i.g., although a pressure in the range of from about 1500 p.s.i.g. to about 3500 p.s.i.g. is preferred. Any conventional means for contacting the charge stream with the hydrogen-containing gas and catalyst can be used. For example, the process can be operated by using various manipulative steps, e.g., upflow, downflow and horizontal flow of the liquid, concurrent and counter-current flow of the gasiform material relative to the flow of liquid and the use of solid contact materials in the form of fixed, moving and fluidized beds. A particularly suitable means for accomplishing the purposes of our invention resides in the use of an ebullated bed. In an ebullated bed reactor, the liquid and gasiform material is concurrently passed upwardly through a vessel containing particulate catalyst, the mass of the catalyst being maintained in random motion in the vessel by the upflowing streams. The mass of catalyst in this state of random motion in the liquid medium is described as "ebullated." The motion of the catalyst makes the reactor free from pressure drop limitations prevalently obtained in fixed beds due to carbon formation, and results in a narrow temperature gradient from the top to the bottom of the reactor. Ebullated bed reactors are now well known to those skilled in the art.

The total effluent stream from the hydrocracker is then passed to a hydrodesulfurizer where it is contacted in the presence of a catalyst with hydrogen-containing gas at elevated temperatures and pressures. The temperature is maintained in the range from about 600° F. to about 850° F., preferably from about 700° F. to about 825° F., and the pressure is maintained in the range from about 500 p.s.i.g. to about 5000 p.s.i.g., preferably from about

1500 p.s.i.g. to about 3500 p.s.i.g. Any convenient means for effecting hydrosulfurization can be used. A fixed bed reactor, however, is particularly suitable and is preferred.

In the second hydrocracker in the method of our invention, furnace oil is subjected to substantially vapor phase hydrocracking in the presence of a catalyst and a hydrogen-containing gas at elevated temperatures and pressures. Suitable hydrocracking temperatures fall in the range of from about 700° F. to 1000° F., preferably in the range of from about 750° F. to about 900° F. The pressure is maintained in the range of from about 500 p.s.i.g. to about 5000 p.s.i.g., although a pressure in the range of from about 1500 p.s.i.g. to about 3500 p.s.i.g. is preferred. Any conventional means for contacting the furnace oil with the hydrogen-containing gas and catalyst can be used. A fixed bed reactor, however, is particularly suitable and is preferred.

The hydrogen supplied to the system need not be 100 percent pure hydrogen but may contain such other constituents as nitrogen, methane, ethane, etc. Preferably, the hydrogen-rich gas stream should contain not less than 50 volume percent hydrogen. The hydrogen-containing gas is recycled to line 13 at a rate to provide at least 2500 s.c.f. of hydrogen per barrel of charge to the hydrocracker. Preferably, hydrogen is recycled to line 13 at a rate to provide about 5000 s.c.f. to about 10,000 s.c.f. of hydrogen per barrel of the charge to the hydrocracker. Hydrogen is recycled to line 61 at the same rate (s.c.f. hydrogen per barrel of material passing through line 61) as indicated for recycle to line 13. Hydrogen makeup is added to the system in an amount equivalent to that consumed in reactions plus losses to the recovery system.

The liquid hourly space velocity in each of the reactors is maintained in the range from about 0.25 to about 5.0. Preferably, in the range from about 0.5 to 3.0.

Applicable catalysts for the first and second hydrocrackers comprise low-acidity catalysts in the form of beads, pellets, powder, extrudates or like particles. The size and shape of the catalyst employed depends on the particular conditions of the process, e.g., the density, viscosity and velocity of the liquid involved in the process.

In general, suitable catalyst include the metals of Groups VI and VIII of the Periodic Table of Elements, and their oxides or sulfides, either alone or in admixture with each other, deposited on amorphous metal oxide support wherein the metal oxide is selected from the group consisting of silica, oxides of metals in Groups II-A, III-A and IV-B of the Periodic Table, and mixtures thereof. Examples of Group VI metals are tungsten and chromium, with the preferred Group VI metal being molybdenum in the form of a molybdate; examples of Group VIII metal components are cobalt and nickel; and examples of the metal oxides in the amorphous support are alumina, silica, zirconia, magnesia, titania, ceria, thoria, etc. In particular, such catalysts are typified by nickel sulfide-tungsten sulfide, molybdenum sulfide or oxide, combinations of metal sulfides or oxides such as ferric oxide, molybdenum oxide or sulfide and cobalt oxide, all of which are supported on the above amorphous metal oxide supports. Other suitable catalysts include catalysts having from about 1 to 10, preferably 2-4 weight percent of a Group VIII metal oxide, preferably cobalt oxide; and from about 5-30, preferably 10-15 weight percent of a Group VI metal oxide, preferably molybdenum; supported on the amorphous metal oxide support, preferably alumina.

The initial hydrocracking operation effectively accomplishes molecular weight reduction of the charge stream, partial removal of sulfur, and effective removal of metal containing compounds—thereby protecting the catalyst bed in the subsequent hydrogenation stage.

The charge streams used in this process can vary widely in metals content and also in the type of the metals. The metals are contained primarily in the as-

phaltene and resin components in the charge stream and under hydrocracking conditions in the first stage will react readily with and be deposited on the catalyst. As the metals from the feed stream accumulate on the catalyst, they change its properties substantially and will, together with the coke deposition that takes place, reduce its activity. The principal metals to contend with are vanadium and nickel. However, the effect of the deposition of these metals is different since nickel is known to be an effective hydrogenation metal, whereas vanadium is not. Since these metals are contained in molecules that are high in molecular weight, their deposition is primarily on the surface of the catalyst particle.

Nevertheless, in accordance with another embodiment of our invention, we have discovered that advantage can be made of this mode of deposition by manufacturing extremely low cost catalyst in situ. This is accomplished by employing a base which does not have strict purity requirements but has a reasonable pore volume and surface area as the catalyst support material. Concentrations of less than 5 percent of molybdenum, cobalt, nickel, iron or mixtures thereof in such concentrations composited on such base materials provide sufficient hydrogenation activity to catalyze the in situ manufacture of the catalyst by metal deposition from the charge stream when the charge stream has a metal content greater than about 100 p.p.m.

A relatively inexpensive and preferred catalyst, containing 1 to 5 percent by weight of an active metal such as nickel deposited on a modified fluid bed coke base is particularly effective in the selective removal of metals such as vanadium. Fluid coke not only contains a desirable particle size range but is very durable. However, in order to be a suitable base or carrier for the active metal component, the fluid coke must first be subjected to careful oxidation in a fluidized bed at a temperature level of about 700° F. until the material obtains a pore volume of at least 0.2 cc./gm. and a surface area of at least 50 square meters/gram. The active metal component is then added to the modified coke material by impregnation in known manner. When this catalyst becomes contaminated with deposits of metallic impurities, catalyst rejuvenation is readily effected by the method set forth in Connor et al. Patent No. 3,123,548 (1964) and Leum et al. Patent No. 3,041,270 (1962) which methods are incorporated by reference herein.

Well-known hydrosulfurization catalysts are not effective in the method of our invention. A highly active catalyst must be employed. We have discovered that a particularly effective catalyst for hydrosulfurization in the present method is a catalyst which comprises a member of the group consisting of oxides and sulfides of metals such as vanadium, chromium or molybdenum metals of the left-hand column of Group VI of the Periodic Table of Elements or iron, cobalt, nickel, platinum, etc. composited with a major amount of an activated alumina prepared by drying and calcining a substance which is predominantly composed of an aluminum hydroxide containing from 1.2-2.6 moles of water of hydration. The preparation of this catalyst is disclosed in Flinn et al. Patent No. 3,222,273 (1965), which patent is hereby incorporated by reference.

It should be understood that the flow sheet shown to illustrate the embodiment of the present invention is highly simplified for the purpose of clarity. Conventional means for heating and cooling, including but not limited to the use of heat exchange with feed or products streams, can be employed in place of various heating and cooling units. It will also be understood that, if desired, additional hydrogen can be added at various points within the system. Also, it may be preferable in some instances to utilize multiple reactors in series or in parallel.

In order to more fully understand the method of our invention reference is made to the following example.

EXAMPLE

An integrated process similar to the complete process illustrated in the drawing is described in this example. As an aid to the understanding of this example, reference will be made to the drawing whenever applicable. A charge stream having the following composition is fed into conduit 11 at the rate of 10,000 bbls./day.

Charge stream: Lagomedio long resid. (47.2 vol. percent of crude).	
Gravity, ° API	17.4
Sulfur content, wt. percent	2.06
Vanadium content, p.p.m.	271
Nickel content, p.p.m.	24

At least 95 percent of this resid. material has a boiling point above 675° F. The charge stream is combined with 10,000 s.c.f. of hydrogen/bbl. of feed. The combined stream is passed through heater 14 into the hydrocracker 16. Hydrocracking in unit 16 is carried out in the presence of a cobalt molybdate catalyst containing 3 percent cobalt oxide and 12 percent molybdenum oxide by weight on an alumina support at a pressure of approximately 2500 p.s.i.g. and at a temperature of approximately 850° F.

The effluent from the hydrocracker 16 is cooled and then subjected to hydrodesulfurization in unit 22. Hydrodesulfurization in unit 22 is carried out at a pressure of approximately 2500 p.s.i.g. and at a temperature of approximately 725° F.

The catalyst is nickel, cobalt and molybdenum (respectively, 0.5, 1.0 and 8.0 percent by weight) deposited on calcined (1000° F. for 10 hours) aluminum hydroxide containing 1.7 moles of water of hydration. The catalyst is prepared in the manner as set forth in Example I in Patent No. 3,222,273 to Flinn et al. (1965).

The effluent from the hydrodesulfurizer 22 is cooled in cooler 26 and then flashed at 100° F. in separator 28. The liquid bottoms portion emerging from separator 28 is passed through line 29 and heater 56 in order to raise the temperature for fractionation in unit 58. Heavy fuel oil is removed from the fractionator 58 by means of line 59, and naphtha is removed as an overhead stream through line 60. A furnace oil fraction is removed through line 61 at the rate of 3800 bbls./day. The furnace oil fraction is combined with 10,000 s.c.f. of hydrogen/bbl. of furnace oil fraction. The combined stream is then recycled to hydrocracker 64. Hydrocracking in unit 64 is carried out in the presence of a cobalt molybdate catalyst containing 3 percent cobalt oxide and 12 percent molybdenum oxide by weight on an alumina support at a pressure of approximately 2500 p.s.i.g. and at a temperature of approximately 850° F. The effluent from the hydrocracker 64 is then passed through a cooler 66 into the separator 28.

The combined gas stream (line 32), naphtha stream (line 60), heavy oil stream (line 59) and the furnace oil stream (line 68) is removed at the rates as follows:

C ₁ -C ₃	lbs./day	230,000
C ₄ -400° F. (naphtha fraction)	bbls./day	5,500
Furnace oil (0.1 wt. percent sulfur) (400° F.-675° F. B.P. range)	bbls./day	700
Heavy fuel oil (B.P. 675° F.+) (0.3% sulfur)	bbls./day	4,600

The liquid hourly space velocity in hydrocracker 16 (ebullated bed) measured at the expanded bed condition is 1.0. The liquid hourly space velocity in hydrodesulfurizer 22, and the second hydrocracker 64 is 1.0.

The hydrogen makeup gas passing through line 36

is added at the rate of 2900 s.c.f./bbl. of feed entering line 11. Gases, including hydrogen sulfide, ammonia and hydrogen are removed from the system by means of line 32.

The material leaving the hydrocracker 16 through line 19 has a nickel plus vanadium content of less than 100 p.p.m.

Thus, a novel process is provided by the present invention for treating high metal content petroleum materials containing residuum fractions to produce a product from which high yields of naphtha suitable for use as an ethylene charge stock and heavy fuel oil of low sulfur content can be obtained. Obviously, many modifications and variations of the present invention as hereinbefore set forth may be made without departing from the spirit and scope thereof.

What is claimed is:

1. A process for removing sulfur and metallic compounds from a petroleum material containing a residuum fraction and having therein metallic contaminants in excess of 100 p.p.m., comprising the steps of:

- (1) cracking said petroleum material while substantially in the liquid phase in the presence of hydrogen and a catalyst in a first hydrocracker at a temperature in the range from about 700° F. to about 1000° F., at a pressure in the range from about 500 p.s.i.g. to about 5000 p.s.i.g.,
- (2) reacting the thus cracked oil at a temperature in the range of from about 600° F. to about 850° F. and at a pressure in the range from about 500 p.s.i.g. to about 5000 p.s.i.g. while substantially in the liquid phase with hydrogen in the presence of a catalyst comprising essentially a minor amount of a member of the group consisting of oxides and sulfides of metals of Group VI left-hand column of the Periodic System and of iron group metals composited with a major amount of an activated alumina prepared by drying and calcining a substance which is predominantly composed of an aluminum hydroxide containing from 1.2 to 2.6 moles of water of hydration, in order to produce a hydrodesulfurized product,
- (3) fractionating said desulfurized product to obtain a naphtha fraction, a furnace oil fraction and a heavy fuel oil fraction, and
- (4) subjecting at least a portion of said furnace oil fraction to substantially vapor phase hydrocracking in a second catalytic hydrocracker at a temperature between about 700 and 1000° F. and at a pressure in the range of about 500 p.s.i.g. to about 5000 p.s.i.g. to maximize production of a naphtha fraction.

2. The process according to claim 1 wherein the cracking of said petroleum material in the first hydrocracker is performed at a temperature in the range from about 750° F. to about 900° F. and at a pressure in the range of from about 1500 p.s.i.g. to about 3500 p.s.i.g.

3. The process according to claim 2 wherein the metals content of the petroleum material is reduced to less than 100 p.p.m. by cracking in the first hydrocracker.

4. The process according to claim 2 wherein the hydrocracking in said second hydrocracker is performed at a temperature in the range from about 750° F. to about 900° F. and at a pressure in the range of from about 1500 p.s.i.g. to about 3500 p.s.i.g.

5. The process according to claim 2 wherein the reacting of the thus cracked oil is performed at a temperature in the range of from about 700° F. to about 825° F. and at a pressure in the range of from about 1500 p.s.i.g. to about 3500 p.s.i.g.

6. The process according to claim 2 wherein said cracking in said first hydrocracker and said second hydrocracker takes place in the presence of a catalyst comprising 3 weight percent cobalt oxide and 12 weight percent molybdenum oxide on alumina support.

7. The process according to claim 1 wherein said first hydrocracker is an ebullated bed hydrocracker.

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8. The process according to claim 1 wherein said cracking takes place in the presence of a catalyst comprising less than about 5 weight percent of an active metal of the group consisting of molybdenum, cobalt, nickel, iron, or mixtures thereof supported on a carrier material. 5

9. The process according to claim 8 wherein said carrier material is fluid bed coke having a surface area of at least 50 square meters/gram and a pore volume of at least 0.2 cc./gm.

10. The process according to claim 9 wherein the active metal is nickel. 10

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