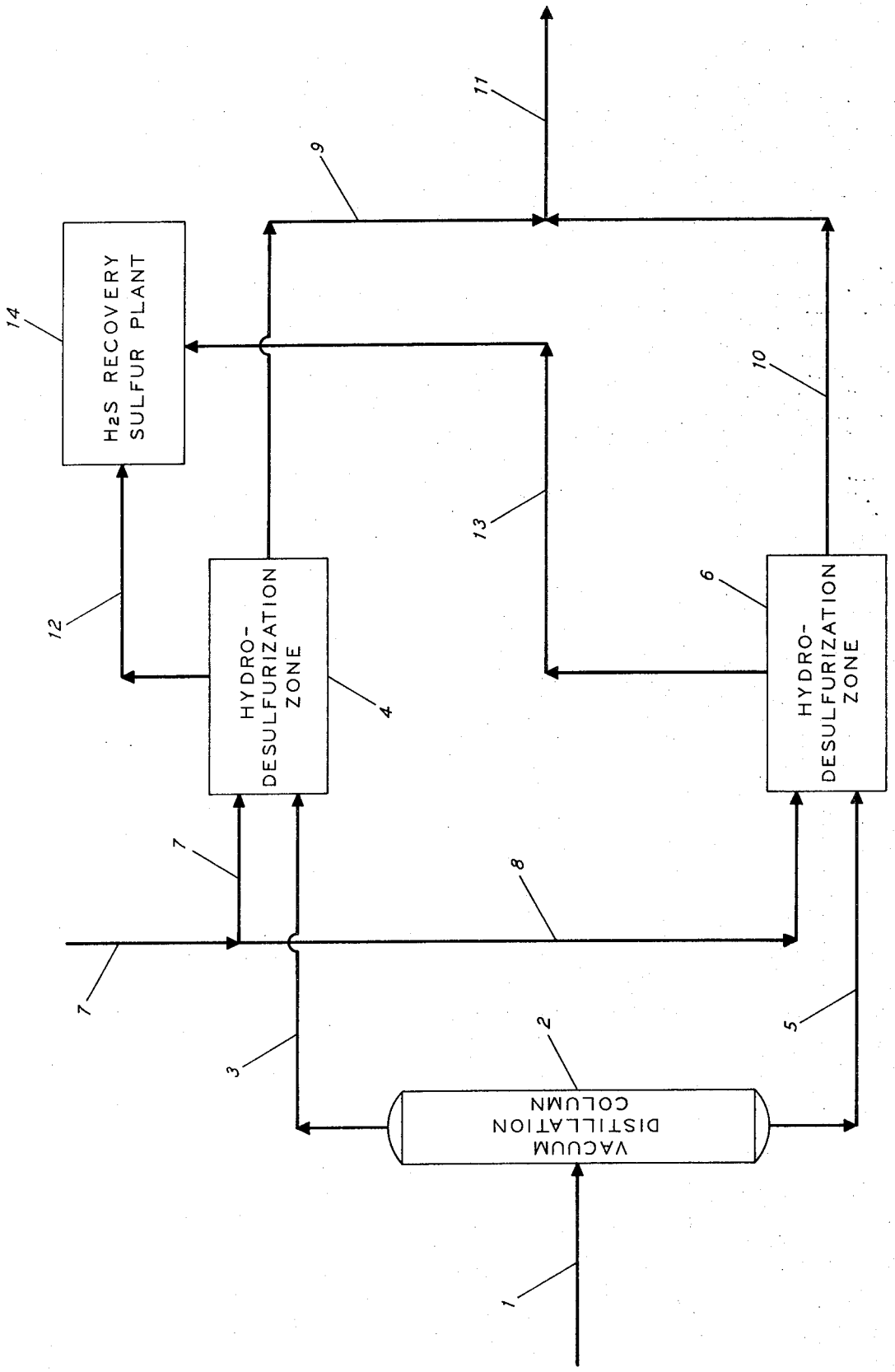
VACUUM RESIDUUM AND VACUUM GAS OIL DESULFURIZATION

Filed March 20, 1972



United States Patent Office 3,830,731
Patented Aug. 20, 1974

3,830,731

VACUUM RESIDUUM AND VACUUM GAS OIL DESULFURIZATION

Echol M. Reed, Jr., Berkeley, and Donald A. Bea, Lafayette, Calif., assignors to Chevron Research Company, San Francisco, Calif.

Filed Mar. 20, 1972, Ser. No. 236,295
Int. Cl. C10g 23/02
U.S. Cl. 208—211 11 Claims

ABSTRACT OF THE DISCLOSURE

A process for treating heavy hydrocarbon feedstocks is disclosed comprising separating the feedstock into a vacuum gas oil fraction having an end boiling point of from about 1000° F. to about 1200° F. and a vacuum residuum (VR) fraction. The vacuum gas oil (VGO) fraction is contacted at a temperature in the range of from 650° F. to 850° F. and a pressure of from 300 to 1200 p.s.i.g. at a liquid hourly space velocity of from 1.0 to 4.0, with a hydrodesulfurization catalyst comprised of at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals, in intimate association with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed.

The vacuum residuum fraction is contacted with a hydrodesulfurization catalyst at a temperature of from 650° to 850° F., a pressure of from 800 to 3000 p.s.i.g., and a liquid hourly space velocity of from 0.1 to 1.5, with said hydrodesulfurization catalyst having the same composition as the catalyst used to desulfurize the VGO.

BACKGROUND OF THE INVENTION

Field of the Invention

With the growing demand for improved air quality, the need for the desulfurization of fuel oil to lower and lower levels of sulfur content is a foregone conclusion. Many major cities in the United States presently have sulfur content level requirements for fuel oil of 0.5% by weight. Additionally, it is contemplated that even lower levels, on the order of 0.3% or even less, are in the not-too-distant future.

In view of the continuing and increasing demand for low-sulfur fuel oils, the development of efficient methods for reducing the sulfur content of heavy fuels is of continuing and increasing concern to fuel-oil suppliers.

This invention is directed to a process for the removal of sulfur from liquid hydrocarbon streams, particularly hydrocarbon residuums, and for the production of low-sulfur-level fuel oils.

Description of the Prior Art

Numerous patents have issued directed to removal of sulfur from heavy hydrocarbon feedstocks. See, for example, U.S. Pats. 2,892,774, 2,983,676, 3,440,164, 3,423,-307, 3,341,448, 3,617,526, and Netherlands Patent Application 7004814.

The general procedure followed is to split a heavy hydrocarbon feedstock into two or more fractions (generally at atmospheric conditions) to form a gas oil fraction and a bottoms or residuum fraction and to desulfurize these fractions separately.

For instance, U.S. Pat. 3,440,164 teaches splitting an atmospheric residuum by vacuum distillation to provide a gas oil fraction and a bottoms fraction. The gas oil fraction is desulfurized by catalytic hydrodesulfurization and the bottoms fraction is desulfurized by contact with molten KOH.

U.S. Pat. 2,983,676 teaches hydrofining of heavy oil bottoms by separating a gas fraction boiling below about 500° F. and a liquid fraction boiling above about 500° F., adn separately hydrofining the two portions. The separation is carried out at a pressure of from 0 to 2000 p.s.i.g.

U.S. Pat. 3,617,526 teaches hydrodesulfurization of an atmospheric residuum by separating it into vacuum gas oil and a vacuum residuum and desulfurizing the gas oil fraction with the previously desulfurized heavy residuum.

Additionally, a wide variety of catalysts have been suggested for hydrotreating hydrocarbon feedstocks. See, for example, U.S. Pats. 3,493,517 and 3,546,105.

It has been found that by the process of the subject invention hereinafter described certain advantages not disclosed or suggested by the prior art can be obtained. Among these are: (1) sulfur level reduction to the area of 0.5% or even less in the heavy hydrocarbon feedstock; (2) reduced hydrogen consumption; (3) better product structures; (4) a minimal reduction in viscosity of the residual fuel oil product (desirable because existing burner equipment is designed to operate on viscous fuel oils); (5) less coking; and (6) lower hydrogen pressure requirements with the concomitant improved economy in process design.

SUMMARY OF THE INVENTION

A process for treating heavy hydrocarbon feedstocks is disclosed comprising separating the feedstock into a vacuum gas oil (VGO) fraction having an end boiling point of from about 1000° F. to about 1200° F. and a vacuum residuum fraction. The vacuum gas oil fraction is contacted at a temperature in the range of from 650° to 850° F. and a pressure of from 300 to 1200 p.s.i.g. at a liquid hourly space velocity of from 1.0 to 4.0, with a hydrodesulfurization catalyst comprised of at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals, in intimate association with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed.

The vacuum residuum (VR) fraction is contacted with a hydrodesulfurization catalyst at a temperature of from 650° to 850° F., a pressure of from 800 to 3000 p.s.i.g., and a liquid hourly space velocity of from 0.1 to 1.5, with said hydrodesulfurization catalyst having the same composition as the catalyst used to desulfurize the VGO.

DETAILED DESCRIPTION OF THE INVENTION

Drawing

The drawing is a diagrammatic illustration of apparatus and flow paths suitable for carrying out one embodiment of the process of the present invention.

Statement of the Invention

In accordance with the present invention, there is provided a hydrodesulfurization process for removing sulfur from a heavy hydrocarbon feedstock which comprises separating the feedstock into a vacuum gas oil fraction and a vacuum residuum fraction and desulfurizing the fractions in separate hydrodesulfurization zones.

The vacuum gas oil fraction will encompass substantially all of the material boiling below about 1000°–1200° F., with the vacuum residuum fraction encompassing the remainder of the feedstock. The vacuum gas oil fraction will be desulfurized at a temperature of 650° to 850° F., at a pressure of from 300 to 1200 p.s.i.g., and at a liquid hourly space velocity based on the VGO feed of from 1.0 to 4.0. The catalyst used in desulfurizing the vacuum gas oil fraction will be comprised of at least one hydrogenat-

ing component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals, in intimate association with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed. A particularly preferred catalyst is nickel sulfide and molybdenum sulfide in intimate contact with an alumina carrier in which titanium phosphate particles are uniformly dispersed.

The vacuum residuum fraction will be hydrodesulfurized at a temperature of from 650° to 850° F., at a pressure of from 800 to 3000 p.s.i.g., and at a liquid hourly space velocity of from 0.1 to 1.5. The catalyst utilized in the hydrodesulfurization of the vacuum residuum fraction will have the same composition as the catalyst used to desulfurize the VGO. The particularly preferred catalyst for VGO hydrodesulfurization is also particularly preferred for the VR hydrodesulfurization. After the desulfurization steps, the desulfurized vacuum gas oil and desulfurized vacuum residuum fractions can be recombined to form a blended fuel oil having a sulfur content of 0.5%, or more preferably 0.3%, or even less.

Heavy Hydrocarbon Feedstocks

The heavy hydrocarbon feedstocks supplied to the vacuum distillation column can encompass a wide variety of materials. For example, the process of the present invention can utilize crude oils, reduced or topped crude oils, atmospheric residua, crude shale oils, coal tar distillates, and the like. Mixtures of crude oils and distillate fractions as well as mixtures of petroleum crudes and crude shale oils, etc., are also satisfactory feedstocks. All of the feedstocks contemplated contain substantial amounts of materials boiling above 1000° F.

A particularly preferred feedstock is a residuum from an atmospheric distillation of crude oil, i.e., a 650° F.+ residuum from which substantially all of the lighter-boiling materials have been removed.

Sulfur Content of the Feedstock

The sulfur content of the feedstock fed to the vacuum distillation column will generally vary from about 1% to as much as 5% by weight of sulfur. The hydrofining process of the subject invention reduces the sulfur content on a blended fuel oil to a maximum of about 0.5 wt. percent sulfur, and preferably as little as 0.3 wt. percent sulfur, or even less. Additionally, a certain amount of hydrogenation and hydrocracking also occurs.

More hydrocracking of the 1000° F.+ feed takes place when a vacuum residuum is desulfurized than is observed when an atmospheric residuum is processed. Despite this, an over-all reduced hydrogen consumption is achieved and the low-sulfur-content fuel oil obtained does not have an undesirably reduced viscosity. This surprising reduction in hydrogen consumption results in an improved efficiency in the over-all process, albeit more complex desulfurization facilities are required.

Vacuum Gas Oil Hydrofining Catalyst

The hydrofining catalyst comprises at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals. Preferred combinations of hydrogenating components include nickel sulfide and molybdenum sulfide, and cobalt sulfide and molybdenum sulfide.

The hydrofining catalyst comprises a carrier of alumina in which discrete, substantially insoluble metal phosphate particles are dispersed in said carrier and consisting essentially of at least one metal phosphate selected from phosphates of zirconium, titanium, tin, thorium, cerium and hafnium, and containing substantially the entire phosphorus content of said catalyst. Preferred insoluble metal phosphate components are phosphates of zirconium and titanium.

The general type of catalyst and procedure for making said catalyst are disclosed in U.S. Pats. 3,546,105 and 3,493,517, both of which patents are incorporated herein by reference. As in U.S. Pat. 3,546,105, substantially no silica or potentially deleterious fluorine are present in the catalysts used in the present invention.

Vacuum Residuum Hydrofining Catalyst

The hydrofining catalyst used in treating the VR has the same composition as that used in the VGO hydrofining step. That is, a catalyst comprising a Group VI metal or metal compound, a Group VIII metal or metal compound, on a carrier of alumina, together with metal phosphate particles, is utilized. While the "same composition" falling within this description is used in hydrofining both the VGO and VR, the same catalyst need not be used in treating a given feed. That is, the VGO may, for instance, be treated with an Ni-MO catalyst, while the VR may be treated with a Co-Mo catalyst.

Operating Conditions

The hydrodesulfurization of the vacuum gas oil fraction is carried out at a temperature in the range of about 650° to about 850° F., preferably in the range of from about 700 to about 800° F.; at a liquid hourly space velocity of from about 1.0 to about 4.0., preferably about 1.5 to about 3.0; and at a pressure of from about 300 to 1200 p.s.i.g., preferably about 600 to about 1000 p.s.i.g.

The desulfurization of the vacuum residuum fraction is carried out at a temperature of from about 650° to about 850° F., preferably from about 700 to about 800° F.; at a liquid hourly space velocity from about 0.1 to about 1.5, preferably about 0.3 to about 1.0; and at a pressure from about 800 to about 3000 p.s.i.g., preferably from about 1000 to about 2000 p.s.i.g.

The hydrogen supply rate (makeup and recycle hydrogen) to the hydrodesulfurization zone is, for the vacuum gas oil fraction, in the range of from about 1000 to about 10,000 s.c.f./bbl., preferably about 2000 to about 4000 s.c.f./bbl., and for the vacuum residuum fraction in the range of from about 1000 to about 10,000 s.c.f./bbl., preferably about 3000 to about 6000 s.c.f./bbl.

The vacuum distillation column is operated at a reduced pressure of from about 5 to about 150 mm./Hg, preferably from about 100 to about 140 mm./Hg, and at a temperature of from about 700° to about 80° F., preferably from about 760° to about 800° F. Operation of the vacuum distillation column is carried out to take substantially all of the feedstock having an end boiling point of from about 1000° to about 1200° F. (depending on the particular feedstock) overhead. While low pressures of 5 mm./Hg can be used, in actual operation higher reduced pressures of 90 to 150 mm./Hg are preferred for improved operating efficiency.

Process Operation With Reference to Drawing

Referring now to the drawing, which represents a preferred embodiment of the present invention, a hydrocarbon feedstock comprised of a 650° F.+ residuum from an atmospheric distillation column is fed via line **1** to vacuum distillation column **2**. An overhead vacuum gas oil fraction having a boiling range end point of 1100° F. is taken overhead via line **3** and fed to hydrodesulfurization zone **4**, which contains a hydrodesulfurization catalyst comprising at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals in intimate association with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed.

The vacuum residuum fraction from vacuum distillation column **2** is fed via line **5** to hydrodesulfurization

zone 6, which contains a hydrodesulfurization catalyst having the same composition as the catalyst used to desulfurize the VGO. Hydrogen is fed to hydrodesulfurization zones 4 and 6 via lines 7 and 8. Desulfurized vacuum gas oil is removed from hydrodesulfurization zone 4 via line 9. Desulfurized vacuum residuum is removed from hydrodesulfurization zone 6 via line 10. The desulfurized products are then combined to form a blended fuel oil which is passed to storage via line 11. Hydrogen sulfide is removed from hydrodesulfurization zones 4 and 6 via lines 12 and 13, respectively, and sent to hydrogen sulfide recovery sulfur plant 14.

While the drawing constitutes one preferred embodiment of the present invention, it is clear that various modifications can be made in the present invention without departing from the spirit of the invention. For instance, all of the desulfurized vacuum residuum fraction need not be blended with the desulfurized vacuum gas oil fraction. If desired, a portion of the desulfurized vacuum residuum fraction can be drawn off as a vacuum tar and utilized for hydrogen manufacture or for refinery fuel.

Additionally, the cutoff point for forming vacuum gas oil need not be 1100° F.; it can be as low as about 1000° F. or as high as 1200° F. Similarly, the feedstock fed to the vacuum distillation column can be a straight crude, in which case the vacuum gas oil fraction will encompass considerable quantities of material having a boiling point below 650° F. This material may be processed with the portion of the vacuum gas oil boiling in the range of from 650° to 1100° F., or can be separated and processed independently.

EXAMPLES

In order that the invention may be better understood, the following examples will serve to further illustrate the invention.

Example 1

An Arabian light reduced crude was separated into two fractions by subatmospheric distillation at a pressure of 5–6 mm./Hg and a temperature of 700° F. The lighter vacuum gas oil (VGO) fraction, with a boiling range of 650°–1050° F. and 22.9° API gravity, contained 2.4 weight percent sulfur. The heavier vacuum residuum (VR) fraction, with 1050° F. initial boiling point and 6.5° API gravity, contained 4.3 weight percent sulfur.

The lighter of the aforesaid feed portions was hydrodesulfurized on a once-through basis in a first conversion zone in the presence of a catalyst comprising nickel sulfide, molybdenum sulfide and alumina in which metal phosphate particles are uniformly dispersed. The catalyst had the compositions, based on the oxides, set forth in Table I below. The catalyst particles were ⅛"—crushed to pass through an 8-mesh screen but remain on a 16-mesh screen. At a temperature of 775° F., 900 p.s.i.g., and an LHSV of 2.4, the total sulfur content of the effluent was 0.2 weight percent. The net quantity of hydrogen consumed in the desulfurization of said lighter fraction at said conditions was 360 s.c.f. per barrel of lighter feed.

TABLE I

Component:	Weight percent
NiO	10.9
MoO_3	26.1
TiO_2	11.4
P_2O_5	6.7
Al_2O_3	44.9
	100.0

The VR fraction was hydrodesulfurized in a second conversion zone in the presence of a catalyst having the same chemical makeup as that of the catalyst used to desulfurize the VGO. The catalyst particles were 1/16". At a temperature of 740° F., 2280 p.s.i.g. and 0.45 LHSV, the effluent contained 1.09 weight percent sulfur. The net quantity of hydrogen consumed was 735 s.c.f. per barrel of heavier feed.

The effluent from the second conversion zone was blended with the effluent from the first conversion zone. The resulting blended product had a sulfur content of 0.45 weight percent. Total quantity of hydrogen consumed in the two aforesaid conversion zones was 475 s.c.f. per barrel of reduced crude feed.

For comparison purposes, the same feedstock used in Example 1, instead of being separated into two portions as in Example 1, was passed wthiout separation into contact in a conversion zone with the same catalyst used in Example 1 to hydrodesulfurize the VR on a once-through basis at a temperature of 740° F. and a pressure of 1950 p.s.i.g., at 0.74 LHSV. The effluent from said conversion zone had a sulfur content of 0.42 weight percent. The net quantity of hydrogen consumed was 640 s.c.f. per barrel of reduced crude, or 35% more hydrogen than was consumed using the process of the present invention, as demonstrated in Example 1.

It is apparent that many widely different embodiments of the invention may be made without departing from the scope and spirit thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. In a process for desulfurizing a heavy hydrocarbon feed by separating the feed into a vacuum gas oil fraction and a vacuum residuum fraction and contacting said fractions and hydrogen with a hydrodesulfurizing catalyst at a temperature in the range from about 650° to 850° F., the improvement comprising:
   (a) vacuum distilling said heavy hydrocarbon feedstock at a temperature in the range of from 700 to 800° F., and at a pressure of from 5 to 150 mm./Hg, to produce a vacuum gas oil fraction having an end boiling point of from about 1000° to about 1200° F. and a vacuum residuum fraction boiling above a temperature of from about 1000° to about 1200° F.;
   (b) hydrodesulfurizing said vacuum gas oil fraction at a liquid hourly space velocity in the range from about 1.0 to 4.0 and a pressure in the range from about 300 to about 1200 p.s.i.g.;
   (c) hydrodesulfurizing said vacuum residuum fraction at a liquid hourly space velocity in the range from about 0.1 to about 1.5, and a pressure in the range from about 800 to about 3,000 p.s.i.g.;
   (d) wherein said hydrodesulfurizations are carried out in separate pressure vessels employing separate hydrodesulfurizing catalysts, said catalysts comprising at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals, said components being intimately associated with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed, said particles comprising at least one metal phosphate selected from the group consisting of zirconium, titanium, tin, thorium, cerium and hafnium; and
   (e) said two separate hydrodesulfurizations, relative to hydrodesulfurization of the unfractionated feed, being operated with reduced hydrogen consumption per barrel of heavy hydrocarbon feed processed.

2. A process in accordance with Claim 1 wherein said vacuum distilling is carried out at a pressure of from 90 to 150 mm./Hg and a temperature of from 760° to 800° F.

3. A process in accordance with Claim 2, wherein said desulfurized vacuum gas oil fraction and at least a portion of said desulfurized vacuum residuum fraction are blended to produce a fuel oil having a sulfur content of 0.5 weight percent or less.

4. A process in accordance with Claim 3 wherein said fuel oil has a sulfur content of 0.3 weight percent or less.

5. A process in accordance with Claim 2 wherein said first catalyst comprises nickel sulfide, molybdenum sulfide and alumina containing uniformly dispersed titanium phosphate particles, and said second catalyst comprises nickel sulfide, molybdenum sulfide, and alumina containing uniformly dispersed titanium phosphate particles.

6. A process as in Claim 5 wherein the vacuum residuum fraction boils above about 1050° F., step (b) is carried out at a temperature of about 775° F., pressure of about 900 p.s.i.g., and an LHSV of about 2.4, and step (c) is carried out at a temperature of about 740° F., a pressure of about 2280 p.s.i.g., and an LHSV of about 0.45.

7. In a process for desulfurizing a heavy hydrocarbon feed by separating the feed into a vacuum gas oil fraction and a vacuum residuum fraction and contacting said fractions and hydrogen with a hydrodesulfurizing catalyst at a temperature in the range from about 650° to 850° F., the improvement comprising:

(a) vacuum distilling said heavy hydrocarbon feedstock at a temperature in the range of from 700 to 800° F., and at a pressure of from 5 to 150 mm./Hg, to produce a vacuum gas oil fraction having an end boiling point of from about 1000° to about 1200° F. and a vacuum residuum fraction boiling above a temperature of from about 1000° to about 1200° F.;

(b) hydrodesulfurizing said vacuum gas oil fraction at a liquid hourly space velocity in the range from about 1.5 to about 3.0 and a pressure in the range from about 600 to about 1000 p.s.i.g.;

(c) hydrodesulfurizing said vacuum residuum fraction at a liquid hourly space velocity in the range from about 0.3 to about 1.0, and a pressure in the range from about 1000 to about 2000 p.s.i.g.;

(d) wherein said hydrodesulfurizations are carried out in separate pressure vessels employing separate hydrodesulfurizing catalysts, said catalysts comprising at least one hydrogenating component selected from Group VI metals and compounds of Group VI metals and at least one hydrogenating component selected from Group VIII metals and compounds of Group VIII metals, said components being intimately associated with an alumina carrier in which discrete, substantially insoluble metal phosphate particles are uniformly dispersed, said particles comprising at least one metal phosphate selected from the group consisting of zirconium, titanium, tin, thorium, cerium and hafnium; and

(e) said two separate hydrodesulfurizations, relative to hydrodesulfurization of the unfractionated feed, being operated with reduced hydrogen consumption per barrel of heavy hydrocarbon feed processed.

8. A process in accordance with Claim 1 wherein said vacuum distilling is carried out at a pressure in the range from 90 to 150 mm./Hg and a temperature in the range from 760° to 800° F.

9. A process in accordance with Claim 7, wherein said desulfurized vacuum gas oil fraction and at least a portion of said desulfurized vacuum residuum fraction are blended to produce a fuel oil having a sulfur content of 0.5 weight percent or less.

10. A process in accordance with Claim 9, wherein said fuel oil has a sulfur content of 0.3 weight percent or less.

11. A process in accordance with Claim 7, wherein said catalysts comprise nickel sulfide, molybdenum sulfide and alumina containing uniformly dispersed titanium phosphate particles.

References Cited

UNITED STATES PATENTS

3,658,681	4/1972	Wilson et al.	208—211
3,546,105	12/1970	Jaffe	208—216
3,617,525	11/1971	Moritz et al.	208—211
3,691,152	9/1972	Nelson et al.	208—210
3,531,398	9/1970	Adams et al.	208—211
3,577,353	5/1971	White	208—216
3,620,968	11/1971	Bridge et al.	208—216

DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner

U.S. Cl. X.R.

208—216, 218