

[54] **CONVERSION OF BLACK OIL TO LOW-SULFUR FUEL OIL**

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[56]

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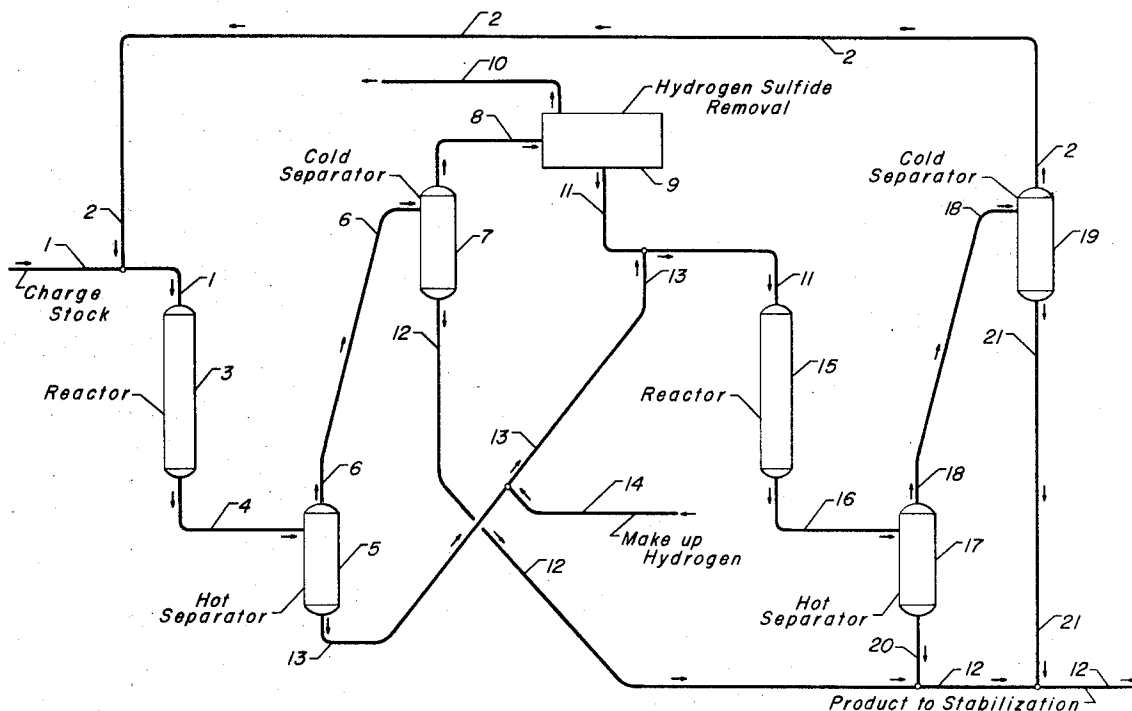
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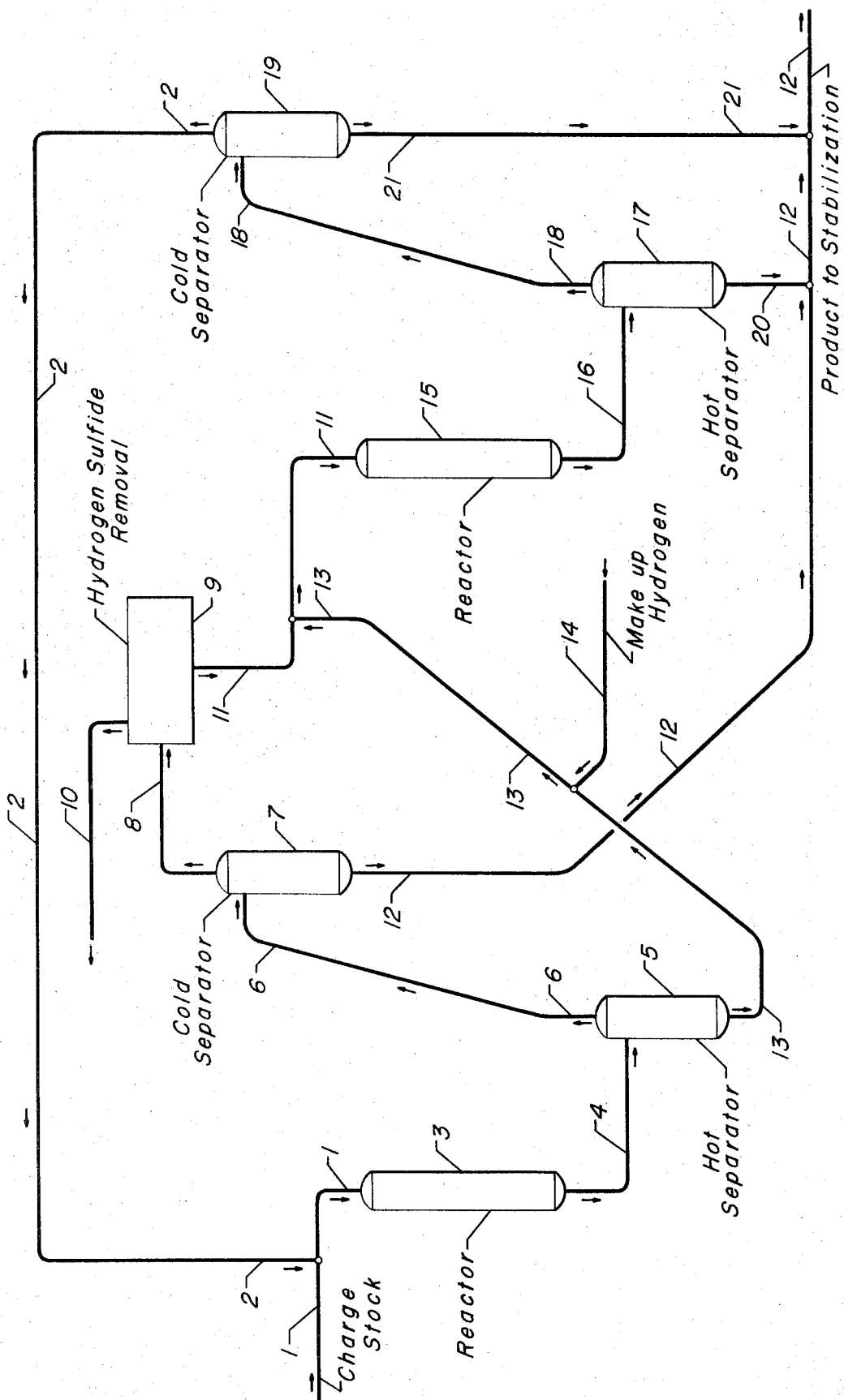
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ABSTRACT

An asphaltic, hydrocarbonaceous black oil, containing more than about 2.0 percent by weight of sulfur, is converted to a low-sulfur fuel oil in a plurality of catalytic conversion zones. The process is designed to afford series-flow of hydrogen through the system, and permits the relatively easier desulfurization of lower-boiling sulfurous compounds to be effected in a relatively less pure hydrogen atmosphere, while the more difficult desulfurization of higher-boiling sulfurous compounds is effected in a relatively concentrated hydrogen atmosphere. The fuel oil product has a sulfur concentration less than about 1.0 percent by weight, and concentrations of 0.5 percent by weight and less are made possible. There exists a significant decrease in the daily utility cost accompanied by a reduction in on-stream time which is lost due to unit shut-down necessitated by mechanical equipment failure.

6 Claims, 1 Drawing Figure





CONVERSION OF BLACK OIL TO LOW-SULFUR FUEL OIL

APPLICABILITY OF INVENTION

Catalytic desulfurization is a well known process which is thoroughly described in petroleum technology; literature relating thereto is replete with a wide spectrum of references directed toward suitable desulfurization catalysts, methods of catalyst manufacture and various process operating techniques. The term "desulfurization" connotes the destructive removal of sulfurous compounds through the conversion thereof into hydrogen sulfide and hydrocarbons, and is often included in the broad term "hydrotreating." Hydrotreating is effected at operating conditions and severity levels which serve to promote denitrification and desulfurization primarily, and asphaltene conversion, non-distillable hydrocarbon conversion, hydrogenation and hydrocracking to a somewhat lesser extent. Thus, the terms "hydrotreating" and "desulfurization" are generally employed synonymously to allude to a process wherein a hydrocarbon feedstock is cleaned-up in order to prepare a charge stock for subsequent utilization in a hydrocarbon conversion system, or for the purpose of recovering a product having an immediate utility. The combination process of my invention is beneficially utilized to produce a fuel oil containing less than about 1.0 percent by weight of sulfur, and often less than about 0.5 percent by weight, while simultaneously effecting at least partial conversion into lower-boiling hydrocarbon products.

Relatively recent recognition of the necessity to inhibit the discharge of the various pollutants into the atmosphere has resulted in governmental controls being imposed in a number of locales. Notable among these is directed toward the burning of high-sulfur content fuels, principally coal and fuel oil, the combustion of which results in the atmospheric discharge of exceedingly large quantities of sulfur dioxide. With respect to fuel oils derived from petroleum crude oil, the demand therefor has increased significantly as a direct result of an increase in world-wide energy requirements: of greater import, however, is the fact that legislation has already been imposed which limits the concentration of fuel oil sulfur, calculated as the element, to a maximum of 1.0 percent by weight. Knowledgeable experts in this area are currently predicting that the next several years will see the sulfur content of fuel oil being restricted to a maximum level of 0.5 percent by weight. It is to this end that the present invention, and the combination process encompassed thereby, is specifically directed; that is, the production of fuel oils containing less than about 1.0 percent by weight of sulfur, and, where required, less than about 0.5 percent by weight. The increasing demand for low-sulfur content fuel oil has also brought about the necessity for effecting the conversion of the "bottom of the barrel." Stated differently, the increasing demand for fuel oil has in turn necessitated the utilization of virtually 100.0 percent of a petroleum crude oil.

In accordance with the present combination process, fuel oils, meeting the limitations with respect to sulfur content, are derived by way of the desulfurization of atmospheric tower bottoms products, vacuum tower bottoms, heavy cycle stocks, crude oil residuum, topped crude oils, coal oils, oils extracted from tar

sands, etc. Crude oils, and the heavier hydrocarbon fractions and/or distillates obtained therefrom, contain nitrogenous and sulfurous compounds in exceedingly large quantities, the latter generally being in the range of about 2.5 percent to about 5.0 percent by weight, calculated as elemental sulfur. In addition, heavy hydrocarbon fractions, sometimes referred to in the petroleum refining art as "black oils," contain organometallic contaminants principally comprising nickel and vanadium, as well as high molecular weight asphaltic material. Illustrative of those charge stocks, to which the present invention is applicable, are a vacuum tower bottoms product, having a gravity of 7.1 °API and containing 4.05 percent by weight of sulfur; a "topped" Middle-East crude oil, having a gravity of 11.0 °API, and containing 5.20 percent by weight of sulfur; and, a vacuum residuum having a gravity of about 8.8 °API, and containing 3.0 percent by weight of sulfur. The utilization of the process of the present invention affords the maximum recovery of low-sulfur fuel oil from these heavier hydrocarbonaceous charge stocks in a manner which affords significant economic advantages.

OBJECTS AND EMBODIMENTS

A principal object of the present invention is to provide a process for effecting the desulfurization of hydrocarbonaceous material. A corollary objective resides in a multiple-stage process for producing a fuel oil containing less than about 1.0 percent by weight of sulfur.

Another object of my invention is to afford a simplified desulfurization process which permits the maximum recovery of a fuel oil product from black oil charge stocks, and at a lower operating severity level.

Therefore, in one embodiment, the present invention encompasses a process for producing a fuel oil, containing less than about 1.0 percent by weight of sulfur, from a sulfurous black oil charge stock, which process comprises the steps: (a) reacting said charge stock with hydrogen in a first catalytic reaction zone, at desulfurization conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons; (b) separating at least a portion of the resulting first reaction zone effluent, in a first separation zone, at substantially the same temperature and pressure, to provide a first principally vaporous phase and a first principally liquid phase; (c) separating at least a portion of said first vaporous phase, in a second separation zone, at substantially the same pressure and a temperature in the range of about 60°F. to about 140°F., to provide a second principally vaporous phase and a second principally liquid phase; (d) removing hydrogen sulfide from said second vaporous phase, and reacting at least a portion of the remainder with at least a portion of said first liquid phase, in a second catalytic reaction zone, at desulfurization conditions selected to convert additional sulfurous compounds into hydrogen sulfide and hydrocarbons; (e) separating the resulting second reaction zone effluent, in a third separation zone, at substantially the same temperature and pressure, to provide a third principally vaporous phase and a third principally liquid phase; (f) separating at least a portion of said third vaporous phase, in a fourth separation zone, at substantially the same pressure and a temperature in the range of about 60°F. to about 140°F., to provide a fourth principally vaporous phase and fourth princi-

pally liquid phase; (g) recycling at least a portion of said fourth vaporous phase to said first reaction zone; and, (h) recovering said fuel oil from said second, third and fourth liquid phases.

Other embodiments of my invention, as hereinafter set forth, reside primarily in preferred ranges of process variables, various processing techniques and preferred catalytic composites for utilization in the fixed-bed catalytic reaction zones. For example, in one such other embodiment, at least a portion of the first principally liquid phase is recycled to the first catalytic reaction zone.

Other contemplated objects and embodiments of my invention will become evident from the following, more detailed description of the combination process encompassed thereby.

SUMMARY OF INVENTION

The present invention utilizes at least two fixed-bed catalytic reaction systems in combination with a particular series of separation facilities which afford more efficient utilization of series-flow hydrogen throughout the entire process. It is understood that each reaction system may consist of one or more reaction vessels having suitable heat-exchange facilities therebetween. Briefly, the combination process is effected by initially reacting the charge stock with a relatively impure (from the standpoint of hydrogen sulfide concentration) hydrogen stream in a first reaction zone. In effect, this first reaction zone accomplishes the relatively easy desulfurization of the lower-boiling sulfurous compounds within the black oil charge stock. The product effluent is separated, at substantially the same temperature and pressure, to provide a higher-boiling normally liquid phase which is reacted in the second reaction system with a relatively pure hydrogen phase. Although the operating conditions, imposed upon both reaction systems, will generally be within identical ranges, the second reaction system will function under an imposed pressure less than that imposed upon the first reaction system. This enables the process to be effected without the necessity for providing the hot pump normally required to introduce the first principally liquid phase into the second reaction system.

In general, the operating conditions within both reaction systems will include a pressure from about 200 to about 3,000 psig., a hydrogen concentration in the range of about 500 to about 30,000 scf./Bbl., a liquid hourly space velocity of about 0.25 to about 2.50 and a maximum catalyst bed temperature in the range of about 600°F. to about 900°F. Preferred operating techniques dictate that the increasing temperature gradient, resulting from the exothermic reactions being effected, be limited to a maximum of about 100°F. In order to control the temperature gradient at the selected desired level, it is within the scope of the present invention to employ quench streams, either normally liquid, or normally gaseous, introduced at one or more intermediate loci of the catalyst bed.

The advantages of the described process are numerous; however, principal among these is a significant reduction in the maximum catalyst bed temperature to achieve the desired degree of desulfurization. Thus, while the maximum catalyst bed temperature may be within the range of about 600°F. to about 900°F., it is not uncommon to conduct the present combination process at maximum catalyst bed temperatures below

about 800°F. Furthermore, the present combination process permits the utilization of a relatively impure hydrogen stream to effect the desulfurization of lower-boiling sulfurous compounds in the first catalytic reaction system. Still another advantage concerns an extension of the effective acceptable life of the catalytic composites employed in both reaction zones.

Although the catalytic composites will possess different physical and chemical characteristics in many situations, they may be identical. Regardless, the catalytic composites employed in the present combination process comprise metallic components selected from the metals of Groups VI-B and VIII of the Periodic Table, as well as compounds thereof. Thus, in accordance with the *Periodic Table of The Elements*, E. H. Sargent and Co., 1964, suitable metallic components are those selected from the group consisting of chromium, molybdenum, tungsten, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum. Additionally, recent investigations in the area of black oil desulfurization have indicated that catalytic composites are improved through the incorporation of a zinc and/or bismuth component. In the present specification and appended claims, the utilization of the term "component," when referring the catalytically active metal, or metals, is intended to encompass the existence of the metal as a compound, such an oxide, sulfide, etc., or in the elemental state. Regardless, the concentrations of metallic components are computed as if the metal existed within the composite in the elemental state. While neither the precise composition, nor the method of manufacturing the various catalytic composites, is considered essential to my invention, certain aspects are preferred. For example, since the charge stock to the present combination process is generally of a high-boiling nature, it is preferred that the catalytically active components possess the propensity to effect hydrocracking while simultaneously promoting the conversion of sulfurous compounds into hydrogen sulfide and hydrocarbons. The concentrations of the catalytically active metallic component, or components, is principally dependent upon the particular metal as well as the physical and/or chemical characteristics of the charge stock. For example, the metallic components of Groups VI-B are generally present in an amount within the range of about 4.0 to about 30.0 percent by weight, the iron-group metals in an amount within the range of about 0.2 to about 10.0 percent by weight, whereas the noble metals of Group VIII are preferably present in an amount within the range of about 0.1 to about 5.0 percent by weight. Where a zinc and/or bismuth component is employed, the same will generally be present in an amount within the range of about 0.01 to about 2.0 percent by weight. All concentrations of the metallic components are calculated as if they existed in the composite in the elemental state.

The porous carrier material, with which the catalytically active metallic component, or components are combined, comprises a refractory inorganic oxide of the character thoroughly described in the literature. When the amorphous type, alumina, or alumina in combination with 10.0 to about 90.0 percent by weight silica, is preferred. It may be appropriate to utilize a carrier material containing a crystalline aluminosilicate, or zeolitic molecular sieve. In many instances, such a carrier material will be utilized in processing the partially desulfurized feed stock to the second reaction

zone. Suitable zeolitic material includes mordenite, faujasite, Type A or Type U molecular sieves, etc., and these may be employed in a substantially pure state; however, it is understood that the zeolitic material may be included within an amorphous matrix such as silica, alumina, or mixtures of alumina and silica. It is further contemplated that the catalytic composites may have incorporated therein a halogen component, such component being selected from the group consisting of fluorine, chlorine, iodine, bromine, and mixtures thereof. The halogen component will be composited with the carrier material in such a manner as results in a final catalytic composite containing from about 0.1 to about 2.0 percent by weight.

The metallic components may be incorporated within the catalytic composite in any suitable manner including coprecipitation or cogellation with the carrier material, ion-exchange or impregnation of the carrier material, or during a co-extrusion procedure. Following the incorporation of the metallic components, the composite is dried and subjected to a high temperature calcination or oxidation technique at a temperature of about 750°F. to about 1,300°F. When a crystalline aluminosilicate is utilized within the carrier material, the upper limit for the calcination technique is preferably about 1,000°F.

With respect to the operating conditions imposed upon the catalytic reaction zones, they are selected primarily to effect the conversion of sulfurous compounds to hydrogen sulfide and hydrocarbons. As hereinabove set forth, the operating conditions imposed upon the second reaction zone will often result in a greater operating severity, although such technique is not essential. In general, the variance in operating severity levels between the two operating reaction zones is obtained by maintaining the first reaction zone at a lower maximum catalyst bed temperature, greater liquid hourly space velocity and at a higher pressure. Thus, the first reaction zone's maximum catalyst bed temperature will be at least about 25°F. less than that of the second catalytic reaction zone, while the pressure is preferably about 50 psig. greater.

Before describing my invention further, and particularly with respect to the embodiment illustrated in the accompanying drawing, several definitions are believed to be necessary in order that a clear understanding be obtained. In the present specification and appended claims, a "pressure substantially the same as," or a "temperature substantially the same as," is intended to connote the pressure or temperature on a downstream vessel, allowing only for the normal pressure drop due to fluid flow through the system, and the normal temperature loss due to transfer of material from one zone to another. For example, where the pressure at the inlet to the first reaction zone is about 2,200 psig. and the exit temperature about 700°F., the first separation zone will function at substantially the same pressure and temperature, about 2,125 psig. and 700°F., respectively. Similarly, the utilization of this phrase "at least a portion of," when referring to either a principally vapor phase, or a principally liquid phase, is intended to encompass both an aliquot portion as well as a select fraction. Thus, at least a portion of the second principally vapor phase is introduced into the second reaction zone following the removal of hydrogen sulfide therefrom, while at least a portion (in this case an ali-

quot portion) of the first principally liquid phase may be recycled to the first catalytic reaction zone.

Other conditions and preferred operating techniques will be given in conjunction with the following description of the present process. In further describing the present combination desulfurization process, reference will be made to the accompanying drawing which illustrates one specific embodiment. The embodiment is presented by way of a simplified flow diagram in which such details as compressors, pumps, heaters and coolers, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as non-essential to an understanding of the techniques involved. The utilization of these miscellaneous appurtenances, to modify the illustrated process, is well within the purview of one skilled in the art, and the use thereof will not remove the resulting process from the scope and spirit of the appended claims. It is understood that the charge stock, stream compositions, operating conditions, design of fractionators, separators and the like are exemplary only, and may be varied widely without departure from the present invention.

DESCRIPTION OF DRAWING

With reference now to the drawing, the illustrated embodiment will be described in conjunction with a commercially-scaled unit designed to produce the maximum quantity of a fuel oil containing less than about 0.5 percent by weight of sulfur from a 53.0 percent true boiling point cut obtained from Kuwait reduced crude oil. The charge stock has a gravity of about 16.0 °API.; other pertinent properties include a sulfur concentration of 3.94 percent by weight, 60.0 ppm. by weight of vanadium and nickel, total nitrogen in the amount of 2,300 ppm. by weight and a Conradson carbon factor of 9.3. The charge stock, in an amount of about 40,000 Bbl./day, is introduced into the process by way of line 1, admixed with a hydrogen-rich recycled gaseous phase in line 2 (the source of which is hereinafter set forth), the mixture continuing through line 1 into catalytic reaction zone 3. Reaction zone 3 is maintained under an imposed pressure of about 2,000 psig., and the reactants contact the catalyst bed at a temperature of about 750°F. The catalyst is a composite of about 2.0 percent nickel and 16.0 percent molybdenum combined with a carrier of 63.0 percent alumina and 37.0 percent silica. The reactants traverse the catalyst bed at a liquid hourly space velocity of about 0.80, and the maximum catalyst bed temperature is controlled at a level of about 800°F.

The product effluent is withdrawn by way of line 4 and introduced, at substantially the same temperature and pressure into hot separator 5 from which a principally vapor phase is withdrawn by way of line 6. The principally vapor phase is introduced into cold separator 7 at a temperature of about 100°F., but at substantially the same pressure, and a hydrogen-rich vapor phase is withdrawn therefrom by way of line 8 and introduced into hydrogen sulfide removal system 9. Hydrogen sulfide, resulting from the conversion of sulfurous compounds, is withdrawn from the process by way of line 10, while the hydrogen-enriched vapor phase is removed by way of line 11.

The first principally liquid phase, withdrawn from hot separator 5 by way of line 13, constitutes the normally liquid charge to reactor 15. Make-up hydrogen, to sup-

plant that consumed in the first catalytic reaction zone, is introduced by way of line 14, and combined with the normally liquid phase in line 13 and the hydrogen-enriched stream in line 11; the mixture continues through line 11 into reactor 15.

Reactor 15 contains a catalytic composite comprising about 1.8 percent by weight of nickel and 16.0 percent by weight of molybdenum combined with a carrier material of 88.0 percent by weight of alumina and 12.0 percent by weight of silica, the liquid hourly space velocity therethrough being about 0.66. The maximum catalyst bed temperature is maintained at a level of about 775°F., the imposed pressure being about 1,850 psig. The product effluent from reactor 15 is withdrawn by way of line 16 and introduced thereby into hot separator 17 at substantially the same temperature and pressure. A hydrogen-rich stream, containing hydrogen sulfide, is withdrawn by way of line 18 and introduced into cold separator 19 at a temperature of about 90°F. A principally vaporous phase is withdrawn through line 2 and recycled to first catalytic reaction zone 3. The average molecular weight of the fourth vaporous phase, being recycled through line 2 via compressive means, is about 4.0 to 5.0. In those prior art processes wherein the third vaporous phase in line 18 is recycled, there is incurred a significantly increased operating utility cost. This third vaporous phase has an average molecular weight of about 7.0 to 12.0 which increases the pressure drop, and, consequently, the load on the compressor required to recycle the same.

The second normally liquid phase withdrawn from cold separator 7, via line 12, constitutes a portion of the product of the present combination process, and is transmitted therethrough to suitable stabilization facilities. The third principally liquid stream from line 20 is admixed with the product in line 12, as is the fourth principally liquid phase from line 21.

Although not illustrated in the drawing, a portion of the principally liquid phase in line 13 may be diverted to combine with the charge stock in line 1, serving as a diluent therefor; similarly, a portion may be combined with the product effluent from reactor 3 for introduction into hot separator 5. Likewise, a portion of the normally liquid phase in line 20 may be diverted to combine with the normally liquid phase in line 13, and/or diverted to combine with the product effluent from reactor 15.

Component yields and product distribution are presented in the following table. Inclusive is a hydrogen consumption of about 1.26 percent by weight of the fresh feed charge stock (approximately 800 scf./Bbl.).

TABLE

Product Distribution and Component Yields		
Component	Wt. %	Vol. %
Ammonia	0.10	—
Hydrogen Sulfide	3.88	—
Methane	0.19	—
Ethane	0.20	—
Propane	0.24	—
Butanes	0.26	0.43
Pentanes	0.19	0.29
Hexanes	0.22	0.30
Heptane-400°F.	2.20	2.74
400°F.-650°F.	8.84	9.86
650°F.-plus	84.94	88.96

The desired fuel oil product, 650°F.-plus, is recovered in an amount of 88.96 percent by volume of the fresh feed charge stock (about 35,600 Bbl./day). The fuel oil has a gravity of about 23.0 °API, and contains only 0.32 percent by weight of sulfur. The 400°-650°F. middle-distillate contains about 0.05 percent by weight of sulfur, while the heptane-400°F. naphtha fraction contains less than about 0.01 percent by weight of sulfur.

The foregoing specification and illustrative embodiment indicate the method by which the present invention is effected and the benefits to be afforded through the utilization thereof in producing maximum quantities of a fuel oil product containing less than about 1.0 percent by weight of sulfur.

I claim as my invention:

1. A process for producing a fuel oil, containing less than about 1.0 percent by weight of sulfur, from a sulfurous black oil charge stock, which process comprises the steps of:

- reacting said charge stock with an impure hydrogen gas containing hydrogen sulfide, in a first catalytic reaction zone, at desulfurization conditions selected to convert lower boiling sulfurous compounds into hydrogen sulfide and hydrocarbons;
- separating at least a portion of the resulting first reaction zone effluent, in a first separation zone, at substantially the same temperature and pressure, to provide a first principally vaporous phase and a first principally liquid phase;
- separating at least a portion of said first vaporous phase, in a second separation zone, at substantially the same pressure and a temperature in the range of about 60°F. to about 140°F., to provide a second principally vaporous phase and a second principally liquid phase;
- removing hydrogen sulfide from said second vaporous phase, and reacting at least a portion of the remaining relatively pure hydrogen with at least a portion of said first liquid phase, in a second catalytic reaction zone, at desulfurization conditions selected to convert additional sulfurous compounds into hydrogen sulfide and hydrocarbons;
- separating the resulting second reaction zone effluent, in a third separation zone, at substantially the same pressure and temperature, to provide a third principally vaporous phase and a third principally liquid phase;
- separating at least a portion of said third vaporous phase, in a fourth separation zone, at substantially the same pressure and a temperature in the range of about 60°F. to about 140°F., to provide a fourth principally vaporous phase containing hydrogen and hydrogen sulfide and a fourth principally liquid phase;
- recycling at least a portion of said fourth vaporous phase to said first reaction zone as said impure hydrogen gas; and,
- recovering said fuel oil from said second, third and fourth liquid phases.

2. The process of claim 1 further characterized in that the desulfurization conditions in said first reaction zone include a pressure greater than that imposed upon said second reaction zone.

3. The process of claim 1 further characterized in that the desulfurization conditions, in said first and sec-

ond reaction zones include a pressure from about 1,000 to about 3,000 psig., a hydrogen concentration in the range of about 1,000 to about 50,000 scf./Bbl., a maximum catalyst bed temperature of from 600°F. to about 900°F. and a liquid hourly space velocity of 0.25 to 2.50.

4. The process of claim 1 further characterized in that at least a portion of said first liquid phase is recycled to said first reaction zone.

5. The process of claim 1 further characterized in that at least a portion of said third liquid phase is recycled to said second reaction zone.

6. The process of claim 1 further characterized in that said first and second reaction zones have therein a catalytic composite of a porous carrier material and at least one metallic component from the metals of Groups VI-B and VIII.

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