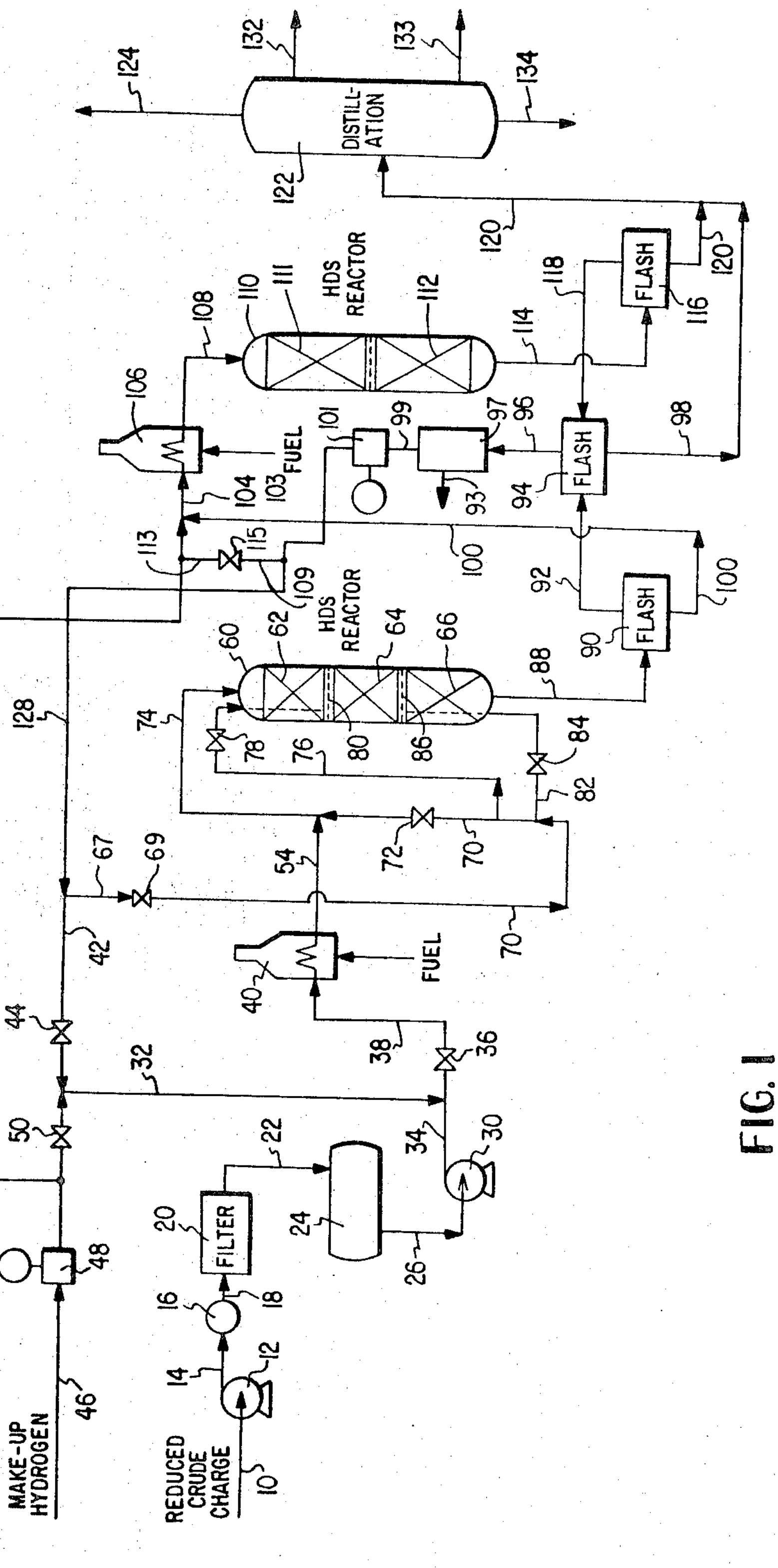

MAKE-UP HYDROGEN
46
COMPRESSOR
48
102
105
107
50
44
32
42
128
67
69
REDUCED CRUDE CHARGE
10
12
14
16
18
20
FILTER
22
24
26
30
34
36
38
40
FUEL
54
70
72
74
76
78
80
82
84
86
60
62
64
66
HDS REACTOR
88
90
FLASH
92
100
94
96
97
98
99
101
93
109
113
115
103
FUEL
104
106
108
110
111
112
HDS REACTOR
114
118
116
FLASH
120
122
DISTILL-ATION
124
132
133
134

FIG. I

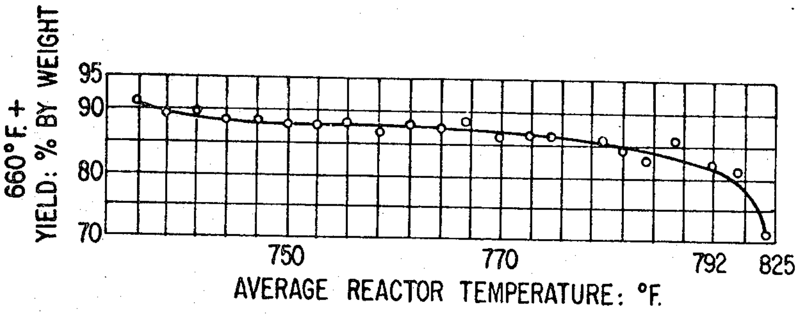

660° F.+
YIELD: % BY WEIGHT
95
90
80
70
750
770
792
825
AVERAGE REACTOR TEMPERATURE: °F.

FIG. 2

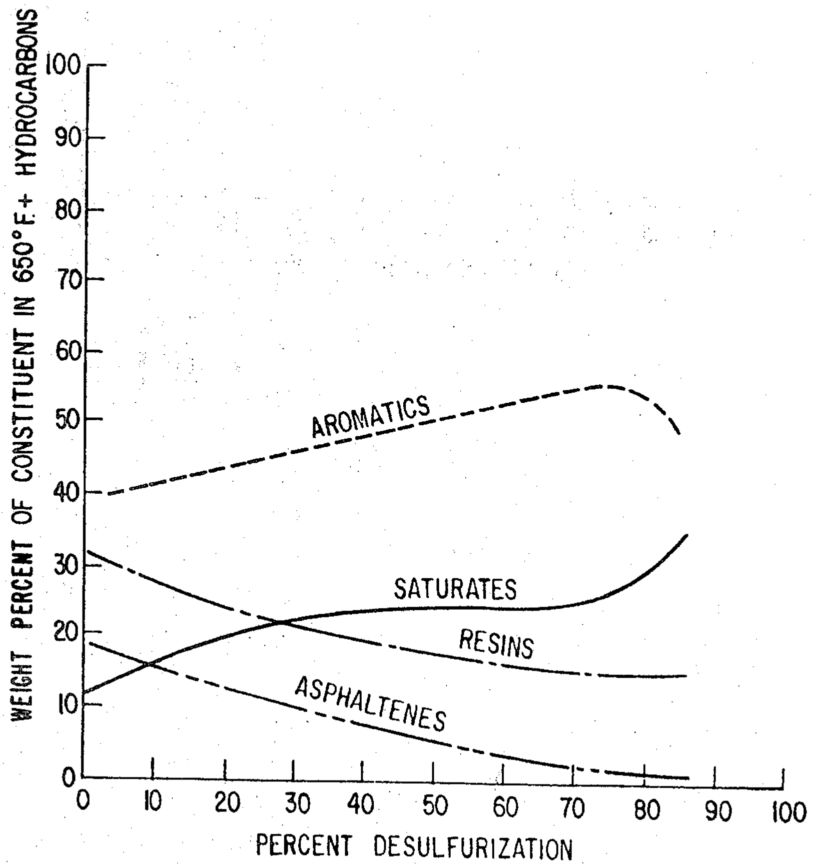
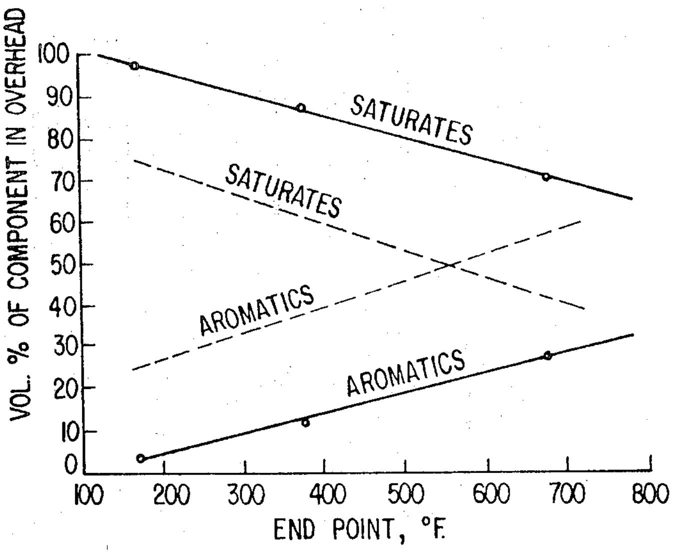

WEIGHT PERCENT OF CONSTITUENT IN 650° F.+ HYDROCARBONS
100
90
80
70
60
50
40
30
20
10
0
AROMATICS
SATURATES
RESINS
ASPHALTENES
0
10
20
30
40
50
60
70
80
90
100
PERCENT DESULFURIZATION

FIG. 3

FIG. 4



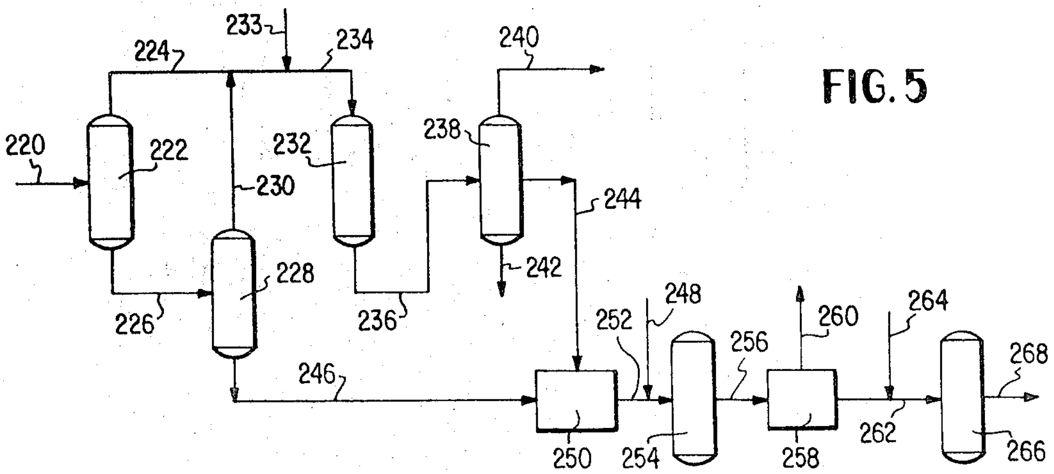


FIG. 5

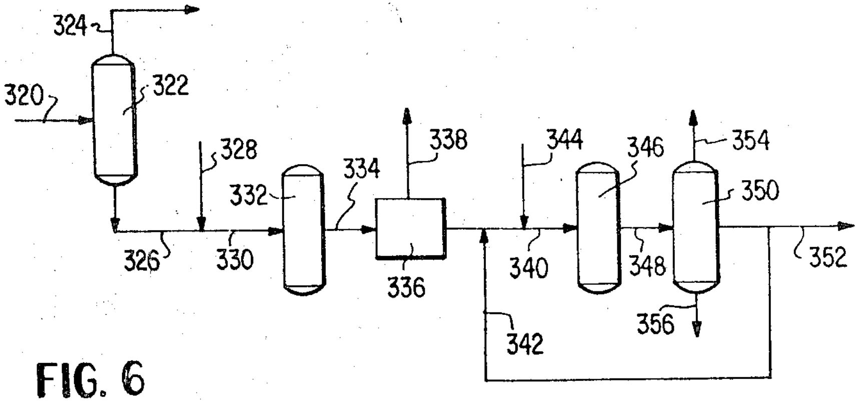


FIG. 6

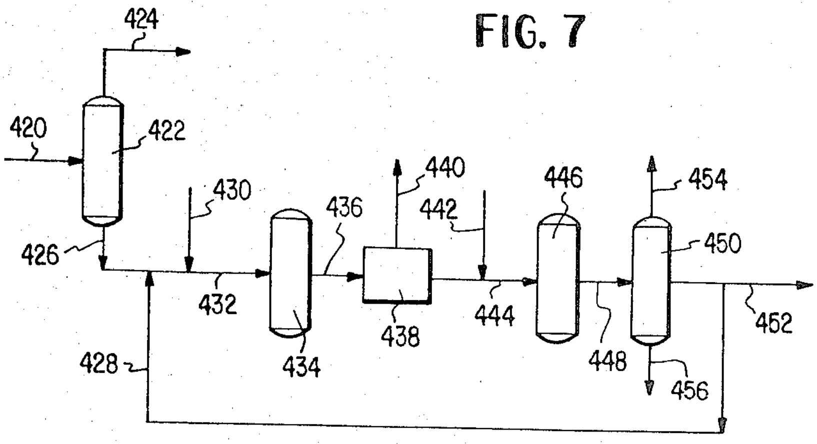


FIG. 7

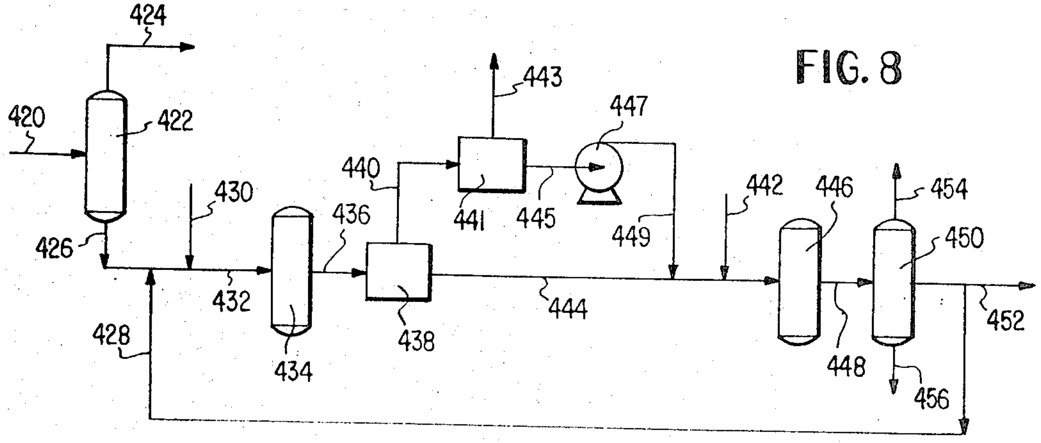


FIG. 8

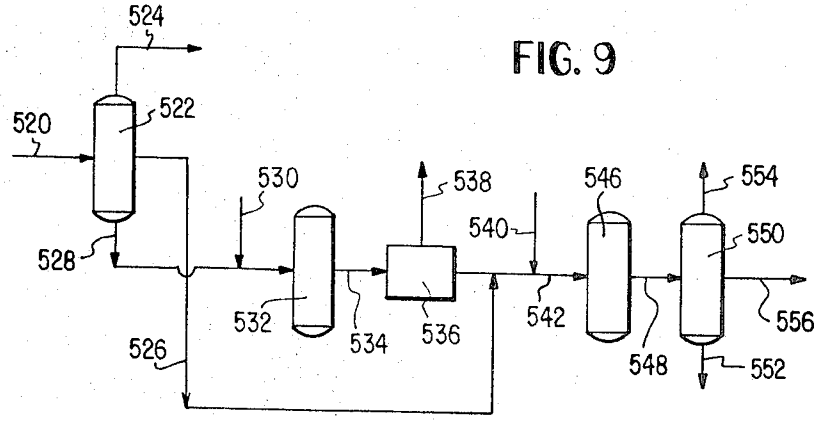


FIG. 9

United States Patent Office

3,775,304

Patented Nov. 27, 1973

3,775,304

INCREASING THE RATIO OF AROMATICS TO SATURATES IN HYDRODESULFURIZATION OF HEAVY ASPHALTIC FEED OIL

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Int. Cl. C10g *23/02*
U.S. Cl. 208—210 7 Claims

ABSTRACT OF THE DISCLOSURE

Asphalt-containing oils are desulfurized to remove refractory, asphaltic sulfur without excessively converting the asphaltenes and resins present in a hydrodesulfurization process, wherein the ratio of aromatics to saturates is increased to provide the proper solvation for the asphaltenes and resins and thereby increase their desulfurization rate.

This invention relates to a process for the production of crude or residual oils having an especially low sulfur content. More particularly, this invention relates to a hydrodesulfurization process for producing an asphaltic fuel oil having a low sulfur content.

Various processes have been proposed for the desulfurization of petroleum hydrocarbons, and such processes have been highly effective in the removal of sulfur from the relatively lighter distillate fractions that are obtained from the distillation of crude oil. However, crude oil and reduced crude oil fractions contain a heavy, residue fraction boiling above 1040° F. commonly referred to as "asphalt," which renders the oil much more difficult to desulfurize. Asphalt is a generally low-grade material that has been isolated from the crude oil and utilized in road construction. In addition, it has been proposed to treat the asphaltic fraction of crude oil in some manner so as to upgrade this material into a more valuable product such as a fuel oil. However, asphalt, when isolated, is highly viscous and is difficult to process over a catalyst. Moreover, it consists of large molecules of fused, aromatic rings and contains the greatest amount of the total sulfur content of the full range crude on a relative basis. A further problem is that some of the sulfur content of the asphalt is tied up in the interior of the large molecules thereof, rendering the asphalt especially difficult to desulfurize. In addition, asphalt contains metals, principally nickel and vanadium, which readily deposit on desulfurization catalysts tending to deactivate the catalyst. The cumulative effect of such factors is that much more severe conditions in the form of higher temperatures and pressures are required as well as a different type of catalyst in order to remove the sulfur from heavy, asphaltic oils as compared with desulfurization of a distillate oil.

Sulfur is a major contributor to air pollution. Accordingly, certain municipalities, both local and foreign, have placed an upper limit on the sulfur content of fuel oils. In the past, such locales have placed a one percent by weight sulfur limit on heavy fuel oils, but the trend has been to a lower maximum sulfur content, such as 0.5 percent. Such limitations have provided a major impediment to the use of heavy asphaltic hydrocarbon oil fractions as fuel oil, since an asphaltic fuel oil having an 0.5 percent sulfur content is not easily obtained from some high sulfur crudes merely by passing the crude oil over a desulfurization catalyst.

For reasons previously unappreciated, the sulfur content of a particular asphaltic crude or reduced oil could be reduced to one percent sulfur in a hydrodesulfurization zone, but if the sulfur level was to be reduced below one percent, the desulfurization temperature had to be increased to a point at which excessive hydrocracking to lower boiling materials resulted. Thus, while it had been relatively easy to reduce the sulfur level of such residual oils from 4 to 1 percent by weight of sulfur without incurring excessive cracking of the feed, it is substantially more difficult for a majority of typical feeds to remove more than about 75 percent of the sulfur without excessive hydrocracking. Excessive hydrocracking is undesirable since it unnecessarily consumes hydrogen and produces undesired light products and coke on the desulfurization catalyst. Furthermore, the nature of the resulting product can be altered to the extent that it is not a heavy fuel oil whereas heavy oils generally have a higher heating value than lighter oils.

Alternatives to attempted in-depth desulfurization of such asphaltic fractions have included blending of the asphaltic hydrocarbon oil with essentially sulfur-free middle distillate oils in order to provide a low sulfur-containing fuel oil. Other proposals have involved hydrofining asphaltenic oils, under conditions wherein the asphaltic material is hydrocracked to extinction to produce lower boiling hydrocarbon products.

It would be highly desirable to provide a process for desulfurizing asphalt-containing hydrocarbon oils so as to render them suitable for use as heavy fuel oils without the need for either blending such materials with lighter oils or converting the asphalt content of such oils to lower-boiling products of a completely different nature which would prematurely deactivate the catalyst.

It has now been found that a particular heavy fuel oil containing an asphalt fraction may be produced having a sulfur content below one percent by weight by means of the present invention which comprises a process for the desulfurization of a sulfur-containing, asphaltic, hydrocarbon oil feedstock comprising an asphaltic fraction and an oil fraction containing saturates and aromatics. The oil fraction will be referred to as a "light oil" to contrast with the higher boiling asphaltic fraction, which comprises asphaltenes and resins. The present process comprises passing said asphaltic fraction and at least a portion of the light oil fraction to a hydrodesulfurization zone in the presence of hydrogen, said light oil fraction comprising aromatics and saturates and having a boiling range below that of the asphaltic fraction, and controlling the amount of the aromatics-containing light oil fraction in the hydrodesulfurization zone so as to increase the desulfurization rate of the asphaltic fraction and thereby provide a low sulfur asphaltic fuel oil.

Surprisingly, it has been discovered that by controlling the amount of light oil and thus the amount of aromatics, since the light oil comprises both aromatics and saturates having a boiling point below that of the asphalt fraction contained in the original crude or reduced crude, that is passed along with the asphaltic fraction through the hydrodesulfurization zone, the sulfur content of the resulting heavy crude oil can be reduced more easily and with less catalyst to below one percent, for example, to below 0.5 and 0.3 percent by weight sulfur.

Thus, the present invention can provide an asphalt-containing heavy fuel oil, which is practically sulfur free, without the need for blending the asphaltic fuel oil with a sulfur-free middle distillate oil in order to obtain an oil having a low sulfur content, although such blending is not precluded in accordance with the present invention.

The aromatics-containing light oil control system of the present invention may be employed in a single stage or in each hydrodesulfurization stage of a two-stage hydrodesulfurization system, so long as refractory sulfur-containing asphaltic fractions are being desulfurized. Thus, for example, an asphaltic fraction containing more than about one percent sulfur may be passed through a first hydrodesulfurization zone in the presence of hydrogen and an aromatics-containing, light oil fraction wherein sufficient aromatics are present to provide a weight ratio of aromatics to resins plus asphaltenes in the asphaltic fraction of at least 1 to 1, for example, 2.5 to 1 up to 5 to 1. A first effluent is withdrawn from the first hydrodesulfurization zone comprising hydrogen sulfide, a light gas fraction, an oil fraction containing aromatics and saturates, and a higher boiling asphaltic fraction. The hydrogen sulfide, the light gas fraction, and a low boiling portion of the light oil fraction are separated from the first effluent, and the remaining portion of the first effluent comprising the asphaltic fraction and a higher boiling portion of the light oil fraction is passed through a second hydrodesulfurization zone in the presence of hydrogen. Likewise, the second hydrodesulfurization zone is controlled so that the weight ratio of aromatics to resins plus asphaltenes will provide proper solvation of the resins and asphaltenes and permit desulfurization thereof. Suitable ratios of aromatics to resins plus asphaltenes include, for example, between about 1 to 1 and about 5 to 1, preferably between about 2.5 to 1 and about 5 to 1, is the situation with the first hydrodesulfurization zone.

The interstate removal of the lower boiling portion of the light oil fraction will usually serve to increase the aforesaid ratio and provide sufficient aromatics in the second stage of desulfurization. However, as will be hereinafter demonstrated, additional aromatics may be added to either desulfurization stage. Each hydrodesulfurization zone is provided with a hydrodesulfurization catalyst that is disposed on a non-cracking support. An asphaltic hydrocarbon oil is withdrawn from the second hydrodesulfurization zone which oil provides a heavy, asphaltic fuel oil containing less than one percent by weight sulfur.

A modification of the present invention relates to a process for controlling the hydrodesulfurization of an asphaltic, heavy oil, which process comprises passing a crude oil or residual oil, for example, which oil contains an asphaltic fraction, through a hydrodesulfurization zone in the presence of hydrogen. The oil increases in aromatic hydrocarbon content as it passes through the hydrodesulfurization zone due to in situ aromatics production. The asphaltic oil having a substantially reduced sulfur content is from said hydrodesulfurization zone at substantially the point at which the aromatic content of the oil no longer increases.

The term "asphalt" or "asphaltic" as employed in the present specification is intended to include the resins and asphaltenes present in crude oil. Asphalt can constitute approximately 5 to 30 percent by volume or more of crude oil and has an initial boiling point of about 1040° F. It is obtained in refineries by a propane deasphalting process (solvent extraction), or from the residues obtained from distillation. Asphaltenes are highly aromatic and consist of large molecules of fused aromatic rings and normally contain the greatest sulfur concentration of any constituent of the full range crude. Unlike other crude fractions, asphalt also contains metals, principally nickel and vanadium. Thus, the asphaltenes and resins may be distinguished from the remainder of the crude oil, which material comprises "saturates" and "aromatics," by virtue of the solubility of these aromatics and saturates in propane and the insolubility of the asphaltenes and resins in propane.

The propane-soluble "aromatics" include benzenes, naphthalenes, thiophenes, benzothiophenes, and dibenzothiophenes as the predominant molecular species, while the "saturates" include the non-aromatic, propane-soluble species, such as the naphthenes, e.g., cyclohexanes, and the paraffins, e.g., dodecane, and sulfur-containing compounds, such as s-butyl mercaptan. Thus, the material commonly referred to as "asphalt" comprises the residue of a propane extraction. On the other hand, resins and asphaltenes are themselves separable by a pentane extraction, by virtue of the fact that asphaltenes are insoluble in pentane, while both resins and oils are soluble in pentane.

It has been proposed to subject crude oil or a reduced crude containing the asphaltene fraction to a hydrodesulfurization reaction in order to reduce the sulfur content of the crude. The crude oil or reduced crude is passed over Group VI and Group VIII metals on a non-cracking support, such as alumina, in the presence of hydrogen and the sulfur level is relatively easily reduced from about 4 to about 1 percent by weight, i.e., a 75 percent sulfur removal. However, after about 75 percent sulfur removal is effected with a particular feed, such as a Kuwait crude for example, the sulfur content of the feed suddenly becomes quite refractory and a great deal of hydrocracking is experienced in order to accomplish additional sulfur removal thereby consuming a great deal of hydrogen and changing the nature of the product. Thus, the point at which the sulfur remaining in the crude oil becomes refractory may vary with the nature of the particular type of crude oil. This point may be easily determined experimentally. As previously mentioned, the asphaltenes consist of large molecules of fused aromatic rings and contain sulfur in the interior of the large molecules, thereby rendering the sulfur extremely difficult to remove. In addition, the asphalt contains all of the metals, such as nickel and vanadium that are present in the crude, and these metals readily deposit on the catalyst tending to deactivate the catalyst and reduce its effectiveness. For these reasons, more severe conditions in the form of higher temperatures and pressures are required to remove more than 75 percent of the sulfur from the asphaltic oil and such severe conditions result in hydrocracking, i.e., a severing of the carbon-carbon bonds of the asphaltene molecule resulting in lower molecular weight materials, rather than desulfurization by splitting carbon-sulfur bonds.

In order to more fully understand the process of the present invention, reference is made to the drawings wherein:

FIG. 1 is a flow diagram illustrating the desulfurization of an asphaltic, reduced crude in two stages;

FIG. 2 illustrates graphically the percent yield of materials boiling above the initial boiling point of the feed to a desulfurization reactor as the average reactor temperature increases;

FIG. 3 graphically illustrates the change in concentration of the aromatic, saturate, asphaltene and resin fractions of an asphalt-containing reduced crude as the degree of desulfurization increases;

FIG. 4 graphically illustrates volume percentages of aromatics and saturates that are removed at various interstage flash points; and

FIGS. 5 to 9 are diagrammatic schemes for obtaining a low sulfur, light aromatic-rich fraction from one portion of the feedstock to solubilize and reduce the viscosity of the solution of asphaltenes and resins present in the residual portion of the feed prior to desulfurization of the asphaltenes and resins.

Referring to FIG. 1, a reduced crude such as a 50 percent reduced Kuwait crude which contains the entire asphalt content of the full crude and therefore also contains all of the nickel and vanadium and most refractory sulfur content of the full crude is charged to the process through line **10** and is pumped through line **14**, preheater **16**, line **18**, solids filter **20** and line **22** to drum **24**. From drum **24** the liquid oil charge is passed through line **26** to feed pump **30**.

Liquid from pump **30** is admixed with hydrogen from line **32** and passed through line **34**, valve **36**, line **38** and furnace **40**. Liquid flow valve **36** is disposed in a non-fully preheated liquid hydrocarbon line. Recycled hydrogen along with make-up hydrogen (if desired) are introduced into the liquid charge to the reactor prior to the preheating thereof. Recycled hydrogen is passed through line **42** and valve **44**, while make-up hydrogen may be charged through line **46**, compressor **48** and valve **50**. The recycled hydrogen and any makeup hydrogen are introduced to the relatively cool liquid charge through line **32**.

A preheated mixture of liquid charge and hydrogen in line **54** may be passed through a guard reactor (not shown), if desired. An effluent stream from the guard reactor is charged to the main reactor **60** containing catalyst beds **62**, **64** and **66**. This stream may have a 650° F.+ boiling range, for example.

The hydrodesulfurization catalyst employed in the process of the present invention is conventional and comprises, for example, Group VI and Group VIII metals on a non-cracking support. Thus, the catalyst may comprise nickel-cobalt-molybdenum or cobalt-molybdenum on an alumina support. The alumina may be stabilized with 1 to 5 percent by weight of silica. The preferred catalyst is a nickel-cobalt-molybdenum on alumina containing less than 1 percent silica which catalyst may or may not be sulfided. Magnesia is also a non-cracking support. An especially preferred catalyst comprises a particulate catalyst comprising particles between about $\frac{1}{20}$ and $\frac{1}{40}$ inch in diameter, such as described in U.S. Pat. 3,562,800 to Carlson et al., which patent is hereby incorporated by reference. The same or a different hydrodesulfurization catalyst can be employed in each stage.

An essential feature of the present invention is that the catalyst is provided on a non-cracking support, since the process of the present invention is essentially a non-cracking process in that very little material is produced having a boiling point below the initial boiling point of the feed. However, high boiling material in the feed may be cracked to produce lower boiling products still in the boiling range of the feed. Thus, whereas prior processes have employed techniques involving, for example, high silica-containing catalysts, e.g. 10 percent or more silica, to hydrocrack the asphaltenes in the feedstock, the process of the present invention involves mainly the severance of carbon-sulfur bonds of the asphaltenes and resins in order to desulfurize the difficultly desulfurizable asphalt, rather than cracking carbon-carbon bonds, which results in lower molecular weight materials. Of course, sulfur is removed from oils during the present process, but this type of sulfur removal is relatively easy to accomplish. In other words, the cracking of carbon-carbon bonds as in prior processes employing cracking produces a material other than a heavy fuel oil and is outside the scope of the present invention. Thus, a relatively minor amount of material is produced having a boiling point below the initial boiling point of the feed to the hydrodesulfurization unit.

As previously mentioned, hydrogen is introduced along with the feedstock by means of line **32**. Conventional reaction conditions in the hydrodesulfurization reactor are employed, for example, a hydrogen partial pressure of 1000 to 5000 pounds per square inch, preferably 1000 to 3000 pounds per square inch, is employed. A hydrogen partial pressure of 1500 to 2500 pounds per square inch is especially preferred. The gas circulation rate may be between about 200 and 20,000 standard cubic feet per barrel, generally, or preferably about 3000 to 10,000 standard cubic feet per barrel of feed, and preferably containing 85 percent or more of hydrogen. The mol ratio of hydrogen to oil may be between about 8:1 and 80:1.

It is an essential feature of the present invention that a hydrogen partial pressure of at least 1000 pounds per square inch is provided. This is necessary in order to desulfurize the asphaltic oil of the present invention to the necessary extent and in order to get the hydrogen to the reactive surface of the asphaltene molecule. It is the chemical activity as expressed by the partial pressure of hydrogen rather than total reactor pressure which determines hydrodesulfurization activity.

Hydrodesulfurization reactor temperatures may range between about 650° and about 900° F., and preferably between about 680° and 800° F.

Referring again to FIG. 1, each succeeding catalyst bed **62**, **64** and **66**, may have a larger volume than the bed just prior to it. If desired, there may be 4 to 6 catalyst beds in the reactor and, if desired, each reactor bed may have 25 percent, 50 percent, 100 percent or more catalyst than the bed just prior to it.

As previously mentioned, because there is no guard chamber line **54** will lead directly to the reactor. The effluent in line **54** is joined by a hydrogen stream from line **67**, valve **69**, line **70** and valve **72** so that a hyrocarbon and hydrogen stream is charged to the top of the reactor through line **74**. As previously mentioned, the reactor stream is passed through catalyst bed **62** and due to the exothermic nature of the hydrodesulfurization reaction, it becomes heated in passage therethrough. Temperatures between the various catalyst beds may be controlled by employing a hydrogen quench which may be introduced by means of line **76**, valve **78**, sparger **80**, and line **82**, valve **84** and sparger **86**. Finally, the reaction mixture passes through catalyst bed **66** and then leaves the reactor with, for example, about a one percent by weight sulfur content.

Referring now to FIG. 2, it is seen that as an asphaltic hydrocarbon crude oil residue containing 4 percent sulfur is passed through a hydrodesulfurization zone, such as reactor **60** in FIG. 1, to produce a 1 percent sulfur-containing 660° F.+product, well over 80 percent of the product boils at 660° F. or above (the initial boiling point of the feed) as the average reactor temperature is increased to compensate for catalyst aging. However, when the reaction temperature is raised to 800° F., excessive hydrocracking to lower boiling materials results. This causes a drop in the curve as to the materials boiling below the initial boiling point of the feed. At this point excessive hydrocracking occurs in order to produce a 1 percent sulfur-containing 660° F.+product.

As will be hereinafter demonstrated, the process of the present invention permits the efficient removal of greater than 75 percent sulfur from an asphaltic oil and overcomes the refractory nature of such oils.

Reference is now made, once again to FIG. 1. Next, the effluent in line **88** is passed to a high pressure flash chamber **90** wherein light hydrocarbon gases, hydrogen sulfide, hydrogen and a controlled portion of the relatively highly desulfurized saturates and aromatics are removed by means of line **92**. The operation of this interstage flash chamber **90** constitutes a critical feature of the present invention. By carefully selecting the flash temperature at the process pressure, the proper amount of light oil, which is to be removed from the feedstock to the second hydrodesulfurization feed streams, is determined. The reason for the removal of an amount of light oil will be demonstrated by reference to FIG. 3.

Referring now to FIG. 3, the composition of a 650° F.+hydrocarbon oil containing various proportions of aromatics, saturates, resins and asphaltenes is presented, as the oil is passed through a hydrodesulfurization reactor, such as reactor **60** of FIG. 1. As shown in FIG. 3, the resins and asphaltenes content of the feed steadily decreases with increasing sulfur removal due to the severing of carbon-sulfur bonds thereby breaking off molecular fragments. The accumulation of these molecular fragments is reflected in the build-up of lower molecular saturates and aromatics and particularly aromatics. This increase in aromatics content in the liquid is beneficial because the aromatics constitute a solvent for the highly viscous resins and asphaltenes, whereas the resins and asphaltenes are not solvated by saturates. The desulfurization of each fraction continues until about 75 percent sulfur removal, and at that point the resins and aromatics curves reach a plateau which indicates no further cracking of fragments therefrom. At the same time, the total aromatics and saturates content does not increase further, but an increase in saturates level is accompanied by a decrease in aromatics level. This indicates that at 75 percent sulfur removal the aromatics tend to become saturated, which represents not only a fruitless consumption of hydrogen, but deprives the remaining resins and asphaltenes of aromatic solvent, while merely increasing the amount of saturates, which is a mere dispersant.

At the 75 percent sulfur-removal level, the sulfur becomes refractory to further desulfurization so that further desulfurization is accompanied by a loss in aromatics and a sharp increase in saturates. Both of these factors are detrimental in regard to removing further sulfur and overcoming the refractory nature of the oil at this point, since at the 75 percent sulfur-removal level most of the unremoved sulfur is concentrated in the resins and asphaltenes. Thus, a loss of aromatics deprives the viscous resins and asphaltenes of some solvation, while the formation of saturates imparts an excessive dispersion to the system tending to excessively dilute the remaining sulfur and thereby lower the reaction rate.

Thus, while operating the first hydrodesulfurization reactor, the aromatic content of the oil can be measured as it passes through the reactor, and the oil should be withdrawn from the reactor when the aromatic content of the oil is no longer increased. This was the situation at 75 percent desulfurization in FIG. 3. The aromatic content can increase 25 to 40 percent by weight or more as it passes through the reactor. Even a small increase in aromatics concentration is beneficial, e.g. 2 to 5 or 10 percent by weight. Of course, the aromatics concentration should not increase to such a great extent that it unduly dilutes the sulfur which is to be removed.

Without attempting to limit the present invention to any particular theory or mechanism, it is believed that up to the 75 percent sulfur removal there is a removal of fringe sulfur from the complex heterocyclic ring structure of the asphaltene molecule accompanied by an in situ production of aromatic hydrocarbons mainly due to a severing of the carbon-sulfur bonds on the fringe aromatic rings. This production of aromatics is important, since asphaltene molecules have a tendency to form colloidal crystallites or aggregates, if the molecules are poorly solubilized. Thus, up to the 75 percent sulfur removal level, there is sufficient in situ production of aromatics to solubilize the asphaltene particle and permit contact of the internal, heterocyclic sulfur with the hydrogen and catalyst necessary to desulfurize the asphaltene. However, at the 75 percent desulfurization level, the ratio of aromatics to saturates is sufficiently small that there is insufficient solvent and too much diluent to effect the removal of the refractory sulfur.

For this reason, it is necessary to control the aromatic content of the asphaltic feed to the second hydrodesulfurization zone. This may be accomplished by flashing or otherwise separating, e.g. by distillation or flashing followed by partial condensation of flashed hydrocarbon and recycle, a controlled portion of the normally liquid effluent oil from the first desulfurization zone to provide the proper aromatics content to the stream.

Thus, it is essential to include sufficient aromatics in the feed to the second desulfurization reactor to solubilize the resins and asphaltenes in the soil and to deagglomerate any asphaltene aggregate which may be formed. At any given flash temperature, the removal of a particular quantity of aromatic hydrocarbons normally removes an even greater quantity of saturated hydrocarbons. With certain crudes the flash may remove more aromatics than saturates, in which case the benefit of the flash will be derived from removal of excess dispersant. A compromise must be reached wherein sufficient aromatics are charged along with the feed to the second hydrodesulfurization stage so that the resins and asphaltenes are adequately solvated in order to permit proper desulfurization of the resins and asphaltenes, without the quantity of aromatics being so high that the total aromatics and saturates fed to the second stage will excessively dilute and disperse the sulfur to be removed and thereby reduce the reaction rate. The volume of aromatics and saturates, respectively, which may be removed at a given flash point is shown in FIG. 4.

Referring now to the solid lines of FIG. 4, an analysis of the saturate and aromatic content of the first sulfur removal stage effluent is shown for various flash points when measured at atmospheric pressure. Thus, if the interstage flash point is 500° F., all of the aromatics boiling above 500° F. will enter the second stage and will be available for solvating the resins and asphaltenes. However, at 500° F., the stream comprises about 81 percent by volume saturates and about 19 percent by volume aromatics. This amount of aromatics together with the even greater amount of saturates which necessarily accompany it, might excessively dilute the asphaltic compounds and thereby lower the reaction rate. On the other hand, if the interstage flash point is as high as 800° F., the oil fed to the second stage will have a higher ratio of aromatics to saturates which is desirable in order to accomplish high solvation with minimum diluent. However, at the 800° F. flashpoint, the total amount of aromatics which enter the second stage may not be great enough to dissolve the resins and asphaltenes and to sufficiently lower their viscosity to permit desulfurization. Accordingly, a proper balance of aromatics to saturates must be employed in order to obtain optimum desulfurization. This point may be easily experimentally determined for a particular stream undergoing desulfurization. For example, employing as a feed the residue represented by the overhead designated by the solid lines of FIG. 4, the best results are obtained by flashing at the temperature which gives about a 650° F. separation regardless of the elevated pressure of the flash. This provides not only sufficient total amount of aromatics in the stream, but a ratio of about 72 percent saturates by volume to about 26 percent aromatics in the overhead. As will be hereinafter demonstrated, the employment of an excessive amount of aromatics in the desulfurization reaction can be as detrimental to sulfur removal as employing too little aromatics.

The dashed lines of FIG. 4 designate another possible overhead saturates and aromatics distribution in which aromatics begin to predominate in a 550° F. overhead fraction. However, since a 550° F. flash includes all the lighter material, the total overhead will still predominate in saturates over aromatics.

Referring again to FIG. 1, a predetermined amount of liquid is flashed and removed by means of line **92**. Depending upon the nature of the feedstock employed and the conditions utilized in the desulfurization reaction, the flashed material in line **92** may contain, for example, between about 5 and about 60 percent by weight of the liquid effluent from the desulfurization reactor **60**, preferably between about 10 and about 35 percent by weight. Suitable flash temperatures include, for example, between about 500° and about 800° F., preferably between about 600° and about 700° F. (These temperatures refer to atmospheric pressure and of course will be different at the process pressure.) An especially preferred flash point for the interstage flash is 650° F. The most desirable amount of liquid to be flashed or otherwise separated from the desulfurization effluent stream may be easily determined experimentally. The flashed material in line **92** is passed to a high pressure flash chamber unit **94** wherein hydrogen, hydrogen sulfide and light hydrocarbon gases are separated from a liquid hydrocarbon fraction. The gases are withdrawn by means of line **96** and are subjected to purification and separation, including various scrubbing operations and the like, in recycle gas recovery unit **97**. Substantially all of the hydrogen sulfide that is produced in reactor **60** is recovered by means of line **93**. Hydrogen now free from hydrogen sulfide and light hydrocarbon gases is recovered from unit **97** and is passed by means of line **99** to recycle gas compressor **101** and recycled for utilization in the process by means of line **103**. The non-flashed liquid fraction is discharged from flash unit **4** by means of line **98**.

The bottoms fraction from the flash unit **90** is discharged by means of line **100** and is admixed with make-up hydrogen, which is provided by means of line **102**, valve **105** and line **107**. In addition, recycle hydrogen may be added to the make-up hydrogen in line **107** from line **103** by means of line **109**, valve **115** and line **113**. If desired, make-up hydrogen may be passed from line **103** directly to line **108** by appropriate valving (not shown). The combined stream may be charged to a furnace **106** in order to raise the temperature of this stream if desired. However, furnace **106** is optional, as the stream **104** may be already at the desired desulfurization temperature for introduction by means of line **108** to the second hydrodesulfurization reactor **110**.

The temperatures and pressures employed in reactor **110** may be the same as those described for the hydrodesulfurization reactor **60**. Likewise, the desulfurization catalyst which is employed in reactor **110** may be identical to that described previously for reactor **60**. It is noted at this point that the hydrodesulfurization catalyst is even more active for removal of nickel and vanadium than it is for removal of sulfur. Most of these metals will be removed in the first hydrodesulfurization reactor **60**. The heaviest laydown of such metals is at the inlet to reactor **60**. The second desulfurization reactor **110** will act as a metals clean-up stage, and the catalyst therein will not collect as much metals as does the catalyst in reactor **60**. Hence, the first stage catalyst will remove most of the metals and will become deactivated by metals much faster than the second stage catalyst.

The desulfurized effluent from reactor **110** is discharged by means of line **114** and is passed to a flash unit **116** for removal of light gases including hydrogen, hydrogen sulfide and light hydrocarbons. This gaseous stream is sent by means of line **118** to high pressure flash unit **94**. Meanwhile, a bottoms fraction including the asphaltic product stream of the present invention is passed by means of line **120** to a distillation column **122**. A sulfur-containing stream comprising sour gas and sour water is removed from column **122** by means of line **124**. This stream is passed to a gas treatment plant (by a means not shown) to recover sulfur therefrom. A naphtha fraction is withdrawn from the column **122** by means of line **132**. This naphtha stream may be employed as a wash liquid for the separation of the light hydrocarbons from the hydrogen in line **96** (by a means not shown). A furnace oil or heavier fraction may be withdrawn through line **133** and be employed in a manner hereinafter described to provide additional aromatics to the second stage desulfurization reactor **110**. A product stream **134** is discharged from the distillation column **122**. This desulfurized oil stream contains asphaltenes and resins, and is especially useful, without further blending, as a fuel oil, particularly since less than one percent by weight sulfur is contained therein. Thus, this heavy, asphaltic fuel oil contains, for example, between about 0.3 and about 0.5 percent by weight sulfur or less, which is well within the requirements of even the strictest ordinances for sulfur content of heavy fuel oils.

The process of the present invention provides a percent yield of not less than 40 or 50 and up to 80 or 90 percent by weight of material having a boiling point greater than the initial boiling point (I.B.P.) of the feed to the first desulfurization reactor. Therefore, very little hydrocracking occurs in accordance with the present invention and the hydrogen consumption will be generally in the range of only 150 to 1500 and preferably in the range of 300 to 1000 standard cubic feet per barrel of feed. The feed to the hydrodesulfurization reactor can have an I.B.P. of not less than 375° F., and will preferably have an I.B.P. of at least 620° or 650° F.

Thus, the amount of material obtained from the second hydrodesulfurization zone whose boiling point is lower than 375° F., or 650° F. will not exceed 50 or 60 percent, generally, or preferably 10 or 20 weight percent. A feed having an I.B.P. greater than 650° F., e.g. vacuum tower bottoms having an I.B.P. in the range of 750° F. to 900° F. or more may be employed in the process of the present invention. In that event, the amount of material obtained from the second hydrodesulfurization zone whose boiling point is below 650° F. will not exceed 10 or 20 weight percent. Accordingly, the process of this invention may be characterized as an "essentially non-cracking process."

Likewise, the fuel oil product from each hydrodesulfurization unit has a total asphaltenes plus resins content of at least 10 or 20 and can have 30 or 40 up to 80 percent by weight of that present in the feed to the first hydrodesulfurization unit. The fuel oil product from the second hydrodesulfurization unit has a preferred total content of resins plus asphaltenes of at least 40, 50 or 70 up to 90 percent by weight of that present in the feed to the second hydrodesulfurization zone. This is a further indication that the resins, and particularly the asphaltenes may be desulfurized without their complete destruction, as was previously proposed.

A modification of the process shown in FIG. 1 is illustrated in FIG. 5, which is a simplified schematic diagram.

Referring now to FIG. 5, a reduced crude oil is introduced by means of line **220** to an atmospheric distillation unit **222** wherein a light asphalt-free distillate fraction having a 630°–650° F. end point (E.P.) is withdrawn by means of line **224**, while a heavy asphalt-containing 630°–650° F.+ fraction containing 4 percent sulfur is discharged by means of line **226** from the distillation column **222**. The asphalt-containing bottoms fraction **226** is passed to a vacuum distillation unit **228** wherein additional light oil is discharged by means of line **230** and is admixed with the lighter fraction in line **224** and introduced along with hydrogen from line **233** into a hydrodesulfurization zone **232** by means of the line **234**. Zone **232** may be operated with a conventional gas oil desulfurization catalyst but at a lower temperature and hydrogen pressure (e.g., below 1000 p.s.i.) than are employed for the desulfurization of an asphaltic oil. The asphalt-free distillate is easily completely desulfurized in the zone **232** and is discharged by means of line **236** and passed to distillation unit **238** from which an overhead containing hydrogen, hydrogen sulfide and light gases is removed by line **240** and processed as previously described to recover hydrogen and light hydrocarbons.

An aromatic-rich, furnace oil and higher fraction is discharged from the distillation unit **238** by means of line **244**. Meanwhile, an asphalt-containing oil is withdrawn from the vacuum distillation unit **228** by means of a line **246**. This stream may have, for example, an initial boiling point of about 1000° F. and contain about 5.5 percent by weight sulfur. The stream **246** is passed through a blending zone **250** wherein the asphalt-containing stream is admixed with a controlled portion of the aromatic-rich fraction from the line **244** in order to obtain the desired viscosity and solvency for the asphaltenes and resins contained in the stream. Then hydrogen is added through line **248**. The heaviest product from distillation unit **242** can be blended with the product **268**, if desired.

Next, the asphaltic fraction containing solubilized resins and asphaltenes is passed by means of line **252** to a first hydrodesulfurization zone **254** and subjected to desulfurization under the conditions previously described in regard to the reactor **60** of FIG. 1. The effluent from zone **254** has a reduced sulfur content and is passed by means of line **256** to an interstage flash unit **258** wherein hydrogen, hydrogen sulfide, light hydrocarbon gases, and a controlled portion of aromatics and saturates is discharged by means of line **260**. As previously discussed, a flash point is selected so as to optimize the amount of aromatic solvent available for solubilizing the asphaltenes and resins in the feed to the second hydrodesulfurization zone. An effluent stream **262** is discharged from the flash unit **258** and is admixed with hydrogen which is introduced by means of line **264**. The combined hydrogen-oil stream is passed to a second hydrodesulfurization unit **266** wherein the sulfur content of the asphaltic oil is reduced to below one percent by weight. The heavy oil product stream is discharged from the second hydrodesulfurization unit **266**, which unit is operated in the manner described for unit **110** in FIG. 1, and is withdrawn by means of the line **268** and treated as previously described for separation of hydrogen sulfide, light gases and the like.

Thus, the system of FIG. 5 provides a parallel mode of operation wherein an initially-separated lighter portion of the crude is desulfurized and is utilized to provide the desired viscosity and solvency for desulfurization of the heavy, asphaltic portion of the crude oil.

Another modification of the FIG. 1 process is illustrated in FIG. 6. Referring now to FIG. 6, an asphaltic oil is introduced by means of line **320** to a distillation unit **322** for separation into an aromatic-poor fraction on which is withdrawn from unit **322** by means of line **324** and an aromatic-rich fraction containing 4 percent sulfur. An aromatic-rich asphaltic oil is discharged from unit **322** by means of a line **326**. For example, distillation unit **322** may be operated to provide an asphaltic fraction having an initial boiling point of about 650° F.

The asphaltic stream in line **326** is admixed with hydrogen which is introduced by means of line **328** and the combined stream is passed by means of line **330** into a hydrodesulfurization unit **332** which is operated in the manner previously described. The effluent from zone **332** is withdrawn by means of line **334** and is introduced into a high pressure flash unit **336** where, for example, material boiling below 800° F. is discharged by means of line **338**. Accordingly, an asphaltic oil having a boiling point of 800° F.+ is discharged from the flash unit **336** by means of the line **340**.

Referring momentarily to FIG. 4, it is seen that at an 800° F. flash point there is a relatively high aromatic to saturate ratio. However, the total aromatic content of the oil at this point may be less than desired. Accordingly, a controlled amount of an aromatic-rich fraction is introduced into the stream in line **340** by means of line **342** in order to provide the resins and asphaltenes with a proper degree of solvency. The combined stream is then admixed with hydrogen, which is introduced by means of line **344** and introduced into hydrodesulfurization reactor **346** where the sulfur level of the asphaltic fuel oil is reduced to below one percent by weight.

The effluent from zone **346** is removed by means of line **348** and is introduced into distillation unit **350** where an aromatic-rich fraction is separated and recovered by means of line **352**. A controlled portion of the material in stream **352** is recycled by means of line **342** for admixture with the asphaltic stream in line **340** as previously described. The light gases are discharged from distillation unit **350** by means of line **354**, while a substantially sulfur-free, asphaltic, heavy fuel oil is recovered from line **356**. Substantially all of the asphaltenes and resins fed to distillation unit **350** are recovered in line **356** with the asphaltic fuel oil. The recycle stream **342** is devoid of asphaltenes. The asphaltenes are not recycled to the first hydrodesulfurization zone, since they would deactivate the catalyst prematurely. They are not recycled to the second hydrodesulfurization zone, since they have already been desulfurized, and such recycle would serve no useful purpose.

In the foregoing manner depicted in FIG. 6, a light, desulfurized, aromatics-rich solvent for the asphaltic material is obtained from the product stream.

Still another modification of the present invention is shown in FIG. 7, wherein an asphaltic feed stream is introduced by means of a line **420** to a distillation unit **422** to reduce the feed and prepare a hydrodesulfurization feed for passage through line **426**. The asphaltic fraction is discharged by means of the line **426** from unit **422** and is admixed with a controlled portion of an aromatic-rich stream which is introduced by means of line **428**. The stream in line **428** can be an aromatic-rich fraction boiling within the range of between about 400 and about 1050° F., preferably between about 650° F. and about 900° F. The combined stream is admixed with hydrogen, which is introduced by means of line **430**, and a stream having a boiling point of about 650° F.+ and containing about 4 percent by weight sulfur is introduced by means of line **432** into hydrodesulfurization zone **434**. This unit may be operated at a temperature of 690°–790° or 800° F. An effluent stream having a sulfur content of about one percent by weight sulfur is introduced by means of line **436** into flash unit **438**. A light oil and gas fraction containing substantially all of the hydrogen sulfide produced is flashed from the unit **438** and discharged by means of the line **440**, which stream may have, for example, a 650° F. E.P.

An asphaltic stream having a boiling point of, for example, 650° F.+ is admixed with hydrogen which is introduced by means of line **442** and introduced by means of line **444** into second hydrodesulfurization zone **446**, which may be also operated at about 690 to 790 or 800° F. The effluent from the second desulfurization zone **446** has a sulfur content of less than one percent and is passed by means of line **448** to distillation unit **450**. An aromatics-rich, asphaltene-free fraction is withdrawn from unit **450** by means of line **452** and is recycled by means of line **428** for admixture to the asphaltic oil feedstock to the first desulfurization zone **434**. Hydrogen sulfide and light gases are withdrawn from the distillation unit **450** by means of line **454**, while a low sulfur asphaltic fuel oil is recovered by means of line **456**. Excess from stream **452** not recycled can be blended with product in line **456** to reduce the sulfur content of the product.

Thus, the arrangement of FIG. 7 utilized a low sulfur aromatic-rich product stream for solubilizing the asphaltenes and resins in a heavy desulfurization feedstock having a relatively high I.B.P.

A modification of the system of FIG. 7 is shown in FIG. 8.

The process of FIG. 8 is similar to FIG. 7, however, as shown in FIG. 8, the effluent from flash unit **438** that is withdrawn by means of line **440** is passed to a flash unit which is provided with cooling coils. Hydrogen sulfide and light gases are withdrawn by means of line **443**. The remaining heavier effluent is withdrawn from the flash unit **441** by means of the line **445** and is passed by means of pump **447** for admixture with stream **444** for introduction into the second stage desulfurization unit **446**.

The mode of operation of FIG. 8 permits the employment of a flash temperature for unit **438**, which temperature may be the same as that employed in the hydrodesulfurization units **434** and **446**. At the same time the lower temperature flash unit **441** which is provided with cooling coils permits the separation of hydrogen sulfide and light gases and the reintroduction of a material having the optimum aromatics content and initial boiling point.

Thus, for example, if it were determined that the optimum interstage flash temperature corresponded to 650° F. at atmospheric pressure and the desulfurization units **434** and **446** are being operated at about 700° F., the flash unit **438** may also be operated at 700° F. However, the lower temperature flash unit **441** is operated at 650° F. and thus permits the return by means of the 650° F.+ material by means of line **449**.

Thus, the modification of FIG. 8 avoids the need for reducing the temperature of the stream in line **436** and the reheating of stream **444**.

Referring now to FIG. 9, an asphaltic, sulfur-containing, hydrocarbon oil is introduced by means of line **520** to distillation unit **522** for separation of the feed into light gases, which are withdrawn by means of line **524**, and an aromatic-rich fraction, which is discharged by line **526**, which is to be employed in a manner hereinafter described. This aromatic-rich fraction may have a 650° F. E.P.

An asphaltic bottoms fraction having an initial boiling point of, for example, about 650° F. is discharged by means of line **528** and is admixed with hydrogen from line **530** prior to introduction into first desulfurization zone **532**. The desulfurized effluent from zone **532** is introduced by means of line **534** into flash unit **536**. As before, the optimum flash point has been previously determined and a light oil fraction containing saturates and aromatics is flashed off along with light gases and hydrogen sulfide by means of line **538**.

The asphaltic oil is passed from the flash unit **536** and mixed with hydrogen from line **540** and introduced by means of line **542** to the second stage desulfurization zone **546**. In addition, the asphaltic feed to the zone **546** is admixed with the aromatic-rich stream **526**. Thus, the distillation operation unit **522** is conducted under conditions so that the stream **526** has a selected boiling range and aromatics content which provides maximum solvation for the asphaltenes present in the feed to the second desulfurization zone **546**. The effluent from zone **546** is discharged by means of the line **548** and is passed to distillation unit **550** for separation of the asphaltic fuel oil produced therefrom by means of line **552**. Light gas stream **554** and naphtha stream **556** are recovered and treated as usual.

The following examples are presented to further illustrate the invention.

EXAMPLE 1

An asphalt-containing, reduced crude oil containing about 4.09 weight percent sulfur and hydrogen are introduced into a hydrodesulfurization zone containing a nickel-cobalt-molybdenum catalyst disposed on a non-cracking, alumina support. The hydrodesulfurization operation is conducted at temperatures of about 650–820° F. and a hydrogen partial pressure of 2000 p.s.i.g., and the resulting asphaltic material is flashed at a temperature corresponding to 650° F. at one atmosphere so as to optimize the amount of aromatics and saturates present in the effluent. The 650° F.+ asphaltic fraction that is withdrawn from the flashing unit has a sulfur content of about 1.09 weight percent sulfur and is introduced into a second hydrodesulfurization zone where the desulfurization is also conducted at about 650° F. to 820° F. while employing the same catalyst that is employed in the first stage.

A heavy fuel oil is obtained having a sulfur content of 0.58 weight percent sulfur. The distribution of sulfur in each of the various fractions of the oil undergoing desulfurization is set forth in Table I, below:

TABLE I

	Feed to first HDS zone		Feed to second HDS zone		Fuel oil product	
	Fraction (percent by wt.)	Sulfur in fraction (percent by wt.)	Fraction (percent by wt.)	Sulfur in fraction (percent by wt.)	Fraction (percent by wt.)	Sulfur in fraction (percent by wt.)
Saturates	17.98	3.42	22.24	0.80	22.34	0.49
Aromatics	55.45	5.04	60.45	1.12	61.91	0.56
Resins	16.73	5.59	13.76	2.37	12.72	1.56
Asphaltenes	9.84	6.99	3.55	4.95	3.03	3.13

As seen from Table I, it is apparent that in an asphaltic feed containing a total of about 4.09 weight percent sulfur, the sulfur content of such feed is relatively evenly distributed between the saturates, aromatics, resins and asphaltenes. However, after the feed is passed through the first desulfurization zone and the 650° F. E.P. fraction is removed, i.e., at 1.09 weight percent total sulfur, the saturates and aromatics have lost sulfur to the greatest extent, viz, they are down to 0.80 and 1.12 weight percent sulfur respectively, while the resins and asphaltenes have lost sulfur to the least extent, viz, 2.37 and 4.95 percent by weight sulfur, respectively. Finally, even after the second stage desulfurization, the only significant sulfur remaining is present in the resins and asphaltenes.

In addition, it is seen from Table I, that the aromatic content of the feed has gone from 55.45 weight percent to 60.45 weight percent after the first stage flashing, and finally up to 61.91 weight percent aromatics in the product. At the same time the weight ratio of aromatics to resins plus asphaltenes increases from about 2 to 1 to about 4 to 1. Thus, Table I clearly illustrates the criticality of providing sufficient aromatics in the asphaltic stream in order to solubilize the resins and asphaltenes and to deagglomerate any asphaltene aggregates so as to permit desulfurization thereof. Likewise, this table shows the criticality of avoiding an excess of liquid including aromatics, especially saturates, beyond what is required to contribute a solubilizing effect, since such an excess of low-sulfur liquid will only tend to disperse and dilute the sulfur-containing resins, resins and asphaltenes and diminish their chance of contact with the catalyst. It should be further noted that the aromatic content of the feed to the second stage is richer in aromatics, i.e., 60.45 weight percent than is the feed to the first stage, i.e., 55.45 weight percent. This is due, in part to the 650° F. interstage flashing which removes saturates in much greater proportion relative to the aromatics present in the flashed, light oil stream. In each stage, the weight ratio of aromatics to resins plus asphaltenes to accomplish solvation should be at least 1 to 1 and is preferably 1.5 or 2 to 1, and can be 4 or 5 to 1. The aromatics can be present in the feed, can be introduced by recycle or can be produced in situ.

It is further interesting to note that Table I reveals that the saturates, which are flashed off, are the most highly desulfurized fraction and therefore have the least need for passage through the second stage of desulfurization.

The following example illustrates the refractory nature of an asphaltic feedstock when it is attempted to remove more than one percent sulfur without employing the process of the present invention.

EXAMPLE 2

A 22 percent reduced Kuwait crude containing an asphalt fraction and 5.43 percent by weight sulfur is subjected to desulfurization. The initial boiling point of the crude is 556° and the boiling range extends to 1400° F.+. After the sulfur content is reduced to 4.77, the I.B.P. is 514° and the boiling range extends to 1400° F.+. As desulfurization continues, and the sulfur content is reduced to 1.41, the I.B.P. is 509° with the boiling range extending to 1400° F.+. However, when the sulfur content is reduced to 0.83, the I.B.P. drops 90° F. to 466° F. with the boiling range extending to 1400° F.+.

The results of this run are shown in Table II, below:

TABLE II

	Feedstock	Reduction in sulfur content during desulfurization		
Sulfur, percent by wt	5.43	4.77	1.41	0.83
Boiling range, ° F	566-1,400+	514-1,400+	509-1,400+	466-1,400+
Desulfurization, percent		12.2	74.0	85.0
°API	6.5	8.7	17.7	20.3

The foregoing data shows that the sulfur content of the feed becomes very refractory at about 74 percent desulfurization. At 12 percent sulfur removal the I.B.P. is reduced to 415° F., while at 74 percent sulfur removal the I.B.P. is only reduced to 509° F. However, in order to obtain 85 percent sulfur removal, the I.B.P. is reduced all the way to 466° F. Thus, in single stage operation, hydrocracking begins to predominate over hydrodesulfurization, i.e., carbon-carbon bonds are becoming severed, rather than carbon-sulfur bonds, beyond 74 percent sulfur removal.

The following Table III, below, shows the composition of the feed during the course of the desulfurization reaction:

TABLE III

	Feedstock (percent by wt.)	Composition change during desulfurization (percent by wt.)		
Desulfurization		12.2	74	85
Saturates	11	16.7	26.1	33.2
Aromatics	39	41.2	56.6	49.9
Resins	32	25.7	15.1	15.3
Asphalteness	18	16.4	2.2	1.6

The foregoing data show that as the depth of sulfur removal increases, resins and asphaltenes diminish and are converted to saturates and aromatics.

The following Table IV gives a molecular weight comparison of the aromatics, saturates and residuals during the course of desulfurization.

TABLE IV

	Feedstock	Molecular weight change during desulfurization		
Desulfurization, percent		12.2	74	85
Saturates, M.W		430.0	400	410
Aromatics, M.W		490.0	530	400
Total residuals, M.W	1,080	590.0	490	420

The data in Table IV show that as the depth of desulfurization increases, the molecular weight of the total residuals decrease, but not significantly below the molecular weight of the initially formed saturates and aromatics. This molecular weight pattern further illustrates that during the breaking of carbon-sulfur bonds in the resins and asphaltenes, hydrocarbon fragments are produced which are about in the same molecular weight range as are the feed saturates and aromatics.

EXAMPLE 3

In order to illustrate the effect of both dilution and concentration of the resins and asphaltenes in the second stage feed upon the second stage desulfurization rate, a 650° F. flash temperature is employed on a feedstock that had been subjected to a single stage of hydrodesulfurization. The asphaltic, flash residue is subjected to a second stage hydrodesulfurization, and it exhibits a desulfurization reaction rate constant of about 85. The desulfurization reaction rate constant is calculated in a conventional manner, i.e.

$$\left(\frac{\text{lb. oil}}{\text{lb. sulfur}}\right)\times\left(\frac{\text{lb. oil}}{\text{hr.-lb. catalyst}}\right)$$

This reaction rate constant can also be expressed as

$$R=\left(\frac{1}{S_P}-\frac{1}{S_F}\right)\text{LHSV}$$

where S_p is pounds of sulfur per pound of oil in the product; S_F is pounds of sulfur per pound of oil in the feed; and LHSV is volume of oil per hour per volume by catalyst.

For comparative purposes, a desulfurized furnace oil having a boiling point in the range of 400° to 650° F. and containing 0.07 weight percent sulfur is added to the residue of the 650° F. flash operation. The furnace oil is comprised of about one-half saturates and one-half aromatics. Upon passing this asphaltic feed through a second stage desulfurization, the desulfurization reaction rate drops to 75. Thus, excessive dilution of the feed to the second stage actually reduces the desulfurization reaction rate, even though aromatics are being added.

For further comparison, 30 percent by weight of a light portion of the second desulfurization stage feed is removed making the feed equivalent to about the residue of an 800° F. flash. In this instance, the reaction rate for desulfurization in the second stage falls to 40 thereby illustrating the effect of inadequate solvation for the resins and asphaltenes. It is clearly evident that the amount of saturates plus aromatics which accompanies the resins and asphaltenes into the second stage has a distinct effect upon the second stage reaction rate, and that too much diluent can have a detrimental effect upon desulfurization reaction rate, just as does too little aromatic solvent.

EXAMPLE 4

In order to determine the effect of adequate, as contrasted to excessive solubilization of an asphalt-containing feed, a residual, high-boiling feed having an initial boiling point of about 800° F. is charged to a hydrodesulfurization process, and 76.2 percent by weight desulfurization is accomplished. Next, a second sample of the feed is diluted with 30 volume percent of a lower boiling gas oil which had been previously desulfurized to the extent of 90 to 95 percent by weight. The addition of the gas oil, which comprises a high proportion of aromatics, increases the desulfurization to 80.3 percent by weight.

For comparative purposes, a further sample of the feed is diluted with 40 percent by volume of a gas oil and is subjected to desulfurization as before. In this instance, there is a loss in desulfurization activity and the desulfurization drops to 76.3 percent by weight. The employment of 64 percent by volume of gas oil reduces the degree of desulfurization even lower to 69.4 percent by weight. The results of these tests are illustrated in Table V below:

TABLE V

	Effect of gas oil dilution			
Gas oil, percent by vol	0	30.0	40.0	64.0
Desulfurization, percent by wt	76.2	80.3	76.3	69.4
Vanadium removal, percent by wt	83.5	78.6	74.6	77.8

The foregoing data illustrate the initial advantage that is realized in the hydrodesulfurization of an asphaltic oil due to the solvating power of the aromatics in the gas oil diluent upon the resins and asphaltenes. However, these data further show that this advantage can be more than offset by an excessive amount of diluent, which may disperse the sulfur molecules excessively and thereby reduce the desulfurization reaction rate. Furthermore, an excessive amount of diluent may also reduce the sulfur removal by imparting an excessive increase in space velocity in the desulfurization reactor.

EXAMPLE 5

A test is performed utilizing in the first and second stages a one-thirty-second inch nickel-cobalt-molybdenum on alumina catalyst. In the first stage the catalyst exhibits a six month life with a start-of-run temperature of 690° F. and an end-of-run temperature of about 790° F. in hydrodesulfurizing a Kuwait reduced crude from 4 to 1 weight percent sulfur at a LHSV of about 0.8. The catalyst life in the second stage is even longer. The one weight percent sulfur effluent from the first stage is flashed to remove 650° F. end point material based on atmospheric pressure and is charged to the second stage with hydrogen to reduce the sulfur level to 0.5 weight percent. The second stage start-of-run temperature is 690° F. and the temperature at 170 days is only 763° F. The test can continue until the temperature is 790° F. Therefore, the first and second stages of this invention can operate for 3, 4, 5, 6 or even 7, 8 or 12 months at a LHSV generally ranging between 0.1 and 10 or preferably between 0.3 and 1.25. The life of the second stage catalyst is longer than the life of the first stage catalyst.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore, and as defined in the appended claims.

We claim:

1. A process for the hydrodesulfurization at a hydrogen partial pressure between 1,000 and 5,000 p.s.i. in a two-zone reaction of a heavy asphaltic feed oil to produce a heavy asphaltic fuel oil product of reduced sulfur content containing propane and pentane insoluble asphaltenes and propane insoluble but pentane soluble resins, said feed oil being partially desulfurized in a first hydrodesulfurization zone with a catalyst comprising a Group VI and a Group VIII metal on alumina containing less than one percent silica at a severity at which the resins and asphaltenes content of said oil cannot be further hydrodesulfurized without diminishing by hydrogenation aromatics present in said oil to saturates, said aromatics being capable of solvating the asphaltenes in said oil while saturates tend to disperse the high-sulfur asphaltics in said oil, separating the effluent from said first zone into a lower-boiling fraction and a higher-boiling fraction and passing said higher-boiling fraction to the second zone, the separated lower-boiling fraction being relatively richer in saturates than aromatics, said higher-boiling fraction having an increased weight ratio of aromatics to saturates than the weight ratio of aromatics to saturates present in the first zone effluent, said increased ratio of aromatics to saturates remaining in said higher-boiling fraction being effective to solvate resins and asphaltenes therein and to increase the hydrodesulfurization reaction rate in said second zone, passing the second zone feed with said increased ratio of aromatics to saturates downflow in the presence of hydrogen through said second zone containing at least one bed of hydrodesulfurization catalyst particles 1/20 to 1/40 inch in diameter at a temperature between about 680 to 790° F., the temperature being increased gradually to about 790° F. to compensate for loss of hydrodesulfurization reaction rate due to catalyst aging, said second zone catalyst comprising a Group VI and a Group VIII metal on alumina containing less than one percent silica, operating said second zone for at least three months at a liquid hourly space velocity between 0.1 and 10, and withdrawing a second effluent stream from said second hydrodesulfurization zone comprising a low sulfur heavy asphaltic hydrocarbon fuel oil, and recovering said product having less than 1 weight percent sulfur, of said product not less than 50 percent by weight having a boiling point greater than the initial boiling point of said feed oil to the first zone and not more than 20 percent by weight having a boiling point lower than 375° F., said fuel oil product containing saturates, aromatics, resins and asphaltenes.

2. The process of claim 1 wherein the weight ratio of aromatics to resins plus asphaltenes in said second hydrodesulfurization zone is at least 1 to 1.

3. The process of claim 1 wherein the weight ratio of aromatics to resins plus asphaltenes in said second hydrodesulfurization zone is between about 1.5 to 1 and about 5 to 1.

4. The process of claim 1 wherein said higher boiling fraction of the effluent from said first zone which is charged to said second zone comprises an increased percentage of aromatics as compared to the total effluent from the first zone.

5. The process of claim 1 wherein the higher-boiling fraction of the effluent from said first zone contains oil which boils below 800° F.

6. The process of claim 1 wherein the higher-boiling fraction of the effluent from said first zone contains oil which boils below 650° F.

7. The process of claim 1 wherein said product boiling below 375° F. does not exceed about 10 weight percent.

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