United States Patent [19]

van der Toorn et al.

[11] **3,714,031**

[45] **Jan. 30, 1973**

[54] RESIDUAL OIL

[75] Inventors: **Lambertus J. van der Toorn,** both of Amsterdam; **Jacobus S. M. Ouwerkerk,** both of 3 Badhuisweg, Amsterdam, Netherlands; **Jakob van Klinken,** Houston, Tex.

[73] Assignee: **Shell Oil Company,** New York, N.Y.

[22] Filed: **Nov. 18, 1970**

[21] Appl. No.: **90,502**

[30] **Foreign Application Priority Data**

Nov. 18, 1969 Great Britain....................56,357/69

[52] **U.S. Cl.**..................................**208/213,** 208/216

[51] **Int. Cl.** **C10g 23/02**

[58] **Field of Search**...............................208/213, 216

[56] **References Cited**

UNITED STATES PATENTS

3,441,500 4/1969 Wunderlich........................208/216

Primary Examiner—Daniel F. Wyman

Assistant Examiner—Werten F. W. Bellamy

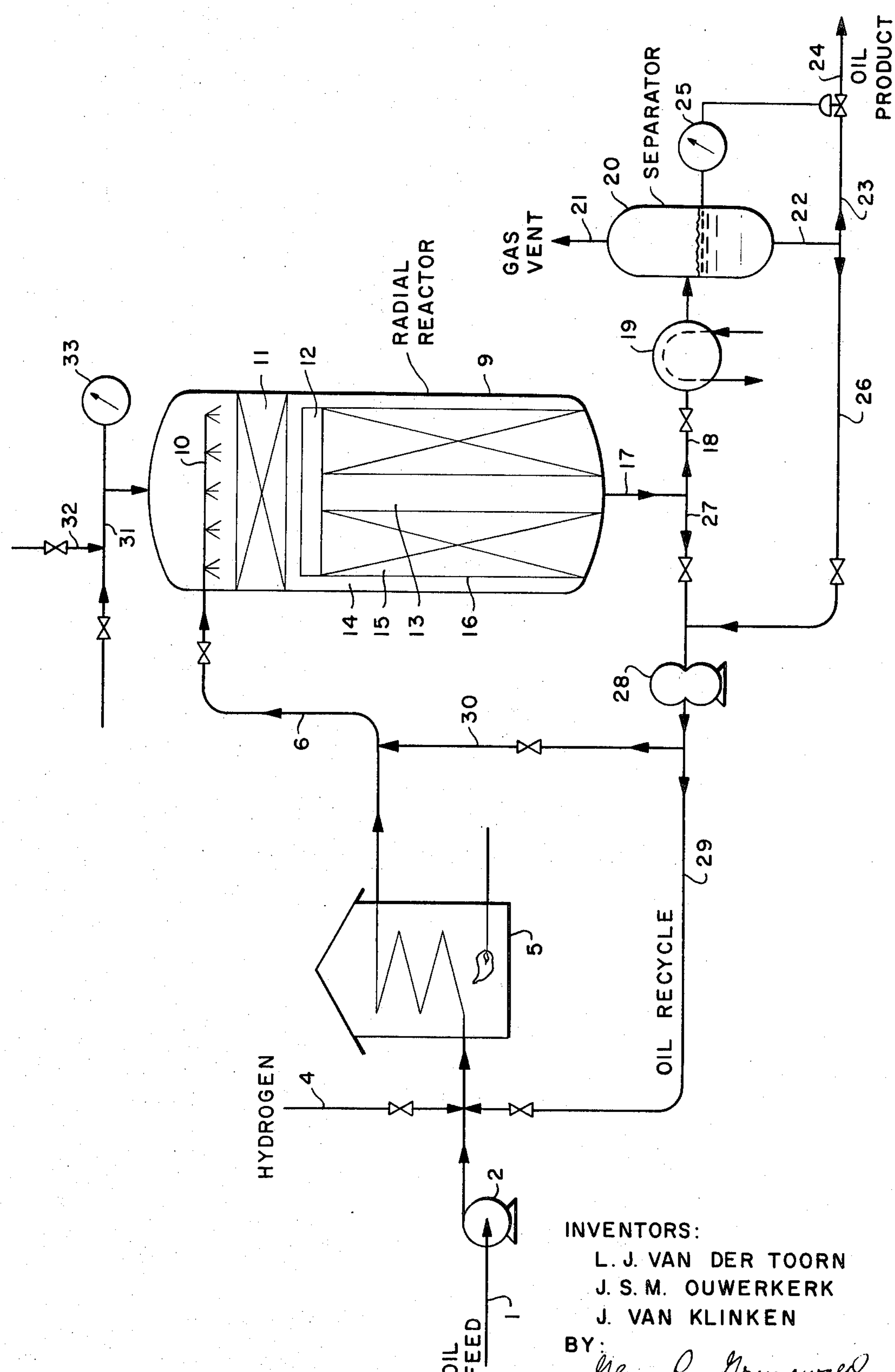
Attorney—Glen R. Grunewald and John H. Colvin

[57] **ABSTRACT**

A desulfurized product of constant sulfur content is obtained by hydrodesulfurizing a sulfur-containing residual oil in the liquid phase over a fixed catalyst bed and applying an external product recycle of at least 3 volumes of desulfurized product per volume of residual oil, the recycle stream having a hydrogen sulfide content of at least 0.05 percent w.

10 Claims, 1 Drawing Figure

PATENTED JAN 30 1973 3,714,031



INVENTORS:
L. J. VAN DER TOORN
J. S. M. OUWERKERK
J. VAN KLINKEN
BY: Glen R. Grunewald
THEIR ATTORNEY

RESIDUAL OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the catalytic hydrodesulfurization of a sulfur-containing hydrocarbon oil or oil fraction. It particularly relates to a process in which a residual oil feedstock is hydrodesulfurized substantially in the liquid phase over a fixed catalyst.

2. Description of the Prior Art

In view of growing concern on air pollution by sulfur dioxide resulting from the combustion of relatively highly sulfur-containing fuels, government regulations are increasing with respect to the sulfur content of fuels. Consequently, residual petroleum oils or oil fractions containing relatively high proportions of sulfur compounds and highly sulfur-containing crude oils are becoming relatively less saleable unless first desulfurized. However, catalytic hydrodesulfurization of the heavy oils and crudes via the direct route constitutes a problem both from a catalytic and technological point of view.

Light petroleum oil fractions and other hydrocarbon distillates containing sulfur-compounds can be easily desulfurized in a fixed-bed process in which the oil fractions and distillates are passed over suitable hydrodesulfurization catalysts in the presence of hydrogen. The technology for this type of process is well-established and amply described in the literature. Fixed-bed hydrodesulfurization of residual oils and crude oils is, however, deemed to be economically unattractive as the hydrodesulfurization reactor has to be shut down very frequently to replace the catalyst. As is known, petroleum crude oils including topped or vacuum-reduced crude oils as well as other heavy hydrocarbon oil fractions such as black oils, visbreaker effluent, tarsand oils and the like contain various metal-containing and metal-free high molecular weight components. These components detrimentally affect the catalytic hydrodesulfurization process to which such crude oils or heavy hydrocarbon oil fractions are subjected as well as the particular catalyst employed in the process as will be explained hereinafter.

Included in the metal-free components are large quantities of resins, polyaromatics and asphaltenes. The asphaltenes are particularly objectionable in the process as they are high-molecular weight, non-distillable oil compounds comprising sulfur, nitrogen and/or oxygen and form oil-insoluble coke precursors. Asphaltenes are generally colloidally dispersed within the petroleum crude oil or oil fraction and when subjected to high temperatures have the tendency to flocculate and to deposit on the catalyst particles. Flocculation is favored at the high conversion temperatures applied during hydrodesulfurization conditions since the aromaticity of the liquid phase in which the said asphaltenes are colloidally dispersed is reduced by hydrogenation and hydrocracking of the (poly)aromatic compounds.

Of the metal-containing contaminants those containing nickel and vanadium are found to be most common. According to the literature a vacuum-reduced crude oil may contain over 500 ppmw vanadium and over 100 ppmw nickel, calculated as metal. Generally, these metals occur in the form of thermally stable, organometallic complexes such as metallo-porphyrins. A considerable quantity of the organometallic complexes are associated with the asphaltenes and thus become concentrated in the residual fraction.

The primary difficulty in hydrodesulfurizing crude oils and/or heavy oil fractions is the deposition of asphaltenes on the catalyst particles as it results in heavy coke formation due to the degradation of the asphaltenic compounds. The simultaneous deposition of the heavy metals onto the catalyst particles together with coke formation from these asphaltenes interferes with the capability of the catalyst to effect a conversion of, in particular, sulfur-containing compounds. Secondly, the carbonaceous deposit formed during asphaltene flocculation causes the catalyst particles to become bound together resulting in plugging of the fixed catalyst bed accompanied by a rapidly increasing pressure drop. Coke formation will in the long run also contribute to this pressure drop. The increasing pressure drop requires extra compression power which in practice is often no longer available and finally the pressure drop may become so high that it cannot be overcome. The process then has to be interrupted and the catalyst inventory to be replaced or regenerated, if possible.

As discussed above, coke formation and metal deposition interfere with the catalyst activity and hence with the stability of the operation. As the catalyst activity declines a higher temperature is required in order to obtain a suitable degree of desulfurization of the residual oil or heavy oil fraction treated. In practice this procedure is generally used and the process is started at the lowest possible temperature at which the desired conversion reaction will occur. Although this procedure yields a product of substantially constant sulfur content in the case of hydrodesulfurization, other properties of the desulfurized product, e.g., viscosity, are constantly varying as a result of the increasing temperature. As the temperature raises, hydrocracking reactions increase so that to an increasing extent the oil to be desulfurized is converted to gases and lower-boiling oil fractions such as light gasoline, naphtha, kerosene and the like. Consequently, a fuel oil with varying product properties or quality is produced. Moreover, the catalyst life in this procedure will be relatively very short as at the lower temperatures applied in the beginning the deposition of asphaltenes and of a carbonaceous deposit will be highest.

Alternatively, hydrodesulfurization could be started close to the maximally allowable temperature. In this case, however, as a result of too high catalyst activity, hydrodesulfurization will be too deep and no fuel oil will be produced as a result of severe hydrocracking. Such a process will moreover be very difficult to control since the hydrogen consumption will not be constant as a result of changing desulfurization level as the catalyst deactivates.

It is known to use hydrogen sulfide in hydrocarbon conversion processes. In these prior art processes hydrogen sulfide or its precursor compound are present either to presulfide the sulfur resistant catalyst or to keep the catalyst in the sulfided state because the hydrocarbon oil to be converted is poor in sulfur. So the general purpose of these sulfur containing compounds is to activate the catalyst used. In the present invention hydrogen sulfide improves the catalyst stability by reducing the activity of the sulfur-resistant catalyst. Moreover, the prior art processes mentioned are conducted in the gaseous phase or mixed phase.

SUMMARY OF THE INVENTION

A direct hydrodesulfurization process has now been found in which a residual oil remains substantially in the liquid phase and wherein the liquid phase comprises dissolved hydrogen sulfide and/or a sulfur compound which is easily converted to hydrogen sulfide.

Accordingly, the present invention concerns a direct hydrodesulfurization process which is carried out substantially in the liquid phase, in the presence of a solid sulfur-resistant catalyst, and in which hydrogen sulfide and/or a hydrogen sulfide precursor is added to the oil in a quantity of at least 0.05 percent w, basis feed, at the beginning of the process, but which quantity is decreased continuously or stepwise in the course of the process to less than 80 percent of the quantity added in the beginning of the process. Although the most important application of the process of the invention is in the catalytic hydrodesulfurization of residual hydrocarbon oils, the process may also be used for other catalytic hydroconversions of residual hydrocarbon oils such as hydrocracking, for instance, for the production of HVI lubricating base oils from long or short residues.

Hydrogen sulfide and/or the dissolved sulfur compound which easily yields hydrogen sulfide are preferably present in the liquid phase in an amount of and/or corresponding to at least 0.1 percent w and more preferably at least 0.5 percent w of hydrogen sulfide. During the run the quantity of hydrogen sulfide and/or hydrogen sulfide precursor added to the feed is lowered so as to keep the level of hydrodesulfurization essentially constant. The quantity of hydrogen sulfide and/or hydrogen sulfide precursor added to the oil is preferably decreased in the course of the process to a quantity of less than 65 percent and more preferably less than 50 percent of the quantity added at the beginning of the process. The sulfur-compound which is a hydrogen sulfide precursor should be present in the liquid phase in a quantity which is equivalent to the amount of hydrogen sulfide required. Hydrogen sulfide precursors include, e.g., sulfur dioxide, carbon disulfide, and the lower alkyl mercaptans with up to eight carbon atoms in the molecule.

Surprisingly, as a result of the presence of hydrogen sulfide or of the sulfur compound mentioned, the hydrodesulfurization process is more stable and a more constant desulfurization level is obtained. More important, however, is that the catalyst life is considerably prolonged and that the catalyst can tolerate a higher metal lay-down before it loses its hydrodesulfurization activity. Owing to the greatly improved catalyst stability, the sulfur-containing hydrocarbon oil or oil fraction will be hydrodesulfurized at substantially constant reaction conditions and the desulfurized product will consequently show substantially constant quality.

The marked effect of hydrogen sulfide or of the hydrogen sulfide precursor compound in the liquid phase on catalyst stability and catalyst life is the more surprising since the feed to be hydrodesulfurized generally has a large sulfur content, at least 1.0 percent w or more, of its own and in desulfurizing the feed hydrogen sulfide is generated. In order to obtain the advantages of the invention hydrogen sulfide or its precursor compound should apparently be present in the liquid phase at the very moment of the hydrodesulfurization reaction proper.

The process of the invention is carried out substantially in the liquid phase. This means that during the hydrodesulfurization at least 80 percent v of the residual hydrocarbon oil is present in the liquid phase.

If the hydrogen sulfide is introduced into the process via a product recycle stream, decreasing the quantity of hydrogen sulfide added to the residual oil feed as the run progresses can very suitably be achieved by removing part of the hydrogen sulfide from the recycle stream, for instance, by partly depressurizing and/or partly stripping said recycle stream and/or by increasing the temperature in the high pressure separator used. If the hydrogen sulfide is introduced into the process via a gas recycle stream, decreasing the quantity of hydrogen sulfide added to the residual oil feed can also very suitably be achieved by decreasing the gas rate used.

If the hydrodesulfurization is to be performed substantially in the liquid phase no more hydrogen should be used for hydrodesulfurizing than can be dissolved in the liquid hydrocarbon phase at the prevailing reaction conditions, thus preventing the creation of a gas phase. In order to provide sufficient dissolved hydrogen for desulfurization at least part of the desulfurized oil product obtained is recycled for admixture with the residual oil or oil fraction to be desulfurized. In this particular case the liquid phase is thus composed of the residual oil and part of desulfurized oil product recovered from the hydrodesulfurization and recycled thereto. It is preferred that the oil product is recycled in an amount of at least three volumes of oil product, and more preferably, of from five to 30 volumes of oil product, for each volume of residual oil or oil fraction. For most hydrodesulfurization purposes a recycle ratio of from 5 to 15 will be sufficient.

Preferably, the process is carried out in a fixed-bed operation. Fixed beds with axial or radial flow may be used. If a fixed bed with axial flow is applied, the process may be carried out either in upflow or downflow. If the process is operated completely in the liquid phase, a radial flow reactor is preferred. Relative long on-stream periods or catalysts lives will be obtained according to the present invention by applying a radial flow fixed catalyst bed and using a catalyst particle size which is smaller than is usually employed in trickle flow operation. The actual catalyst lives obtained will depend on the heavy metal and asphaltenes content of the oil processed.

In order to prevent maldistribution of liquid flow through the catalyst bed when applying radial flow, measures should be taken that at least 40 percent by volume and more preferably 45 to 50 percent volume of the liquid phase passes through the top half of the catalyst bed. This desired flow may be obtained by using a perforated center pipe in the catalyst bed with a relatively large diameter in comparison to the reactor diameter and/or by applying a special center pipe shape, i.e., narrow at the top and wide at the bottom, and/or by providing more apertures at the top of the said center pipe than at its bottom. The liquid phase may flow radially through the fixed catalyst bed either turned away from or towards the center pipe provided in the bed.

The hydrogen required for the hydrodesulfurization may be provided as a hydrogen-containing gas stream, such as a reformer off-gas stream, or as substantially pure hydrogen. Preferably, the hydrogen-containing gases contain at least 60 percent volume of hydrogen. The rate of introduction of such gases or of hydrogen is adjusted to provide the process of the invention with hydrogen in an amount of from 5 to 30 Nl and more preferably of from 15 to 20 Nl per kilogram of total feed. By total feed is understood the fresh residual oil feed admixed with the recycled desulfurized oil product.

The hydrogen supplied may be introduced via the fresh feed or via the oil product recycle. It is preferred, however, to pass both fresh oil feed and recycle product with hydrogen through a hydrogen saturation zone prior to contacting the admixed feed with the hydrodesulfurization catalyst. This saturation zone is preferably near the entrance of the hydrodesulfurization reactor and may be either inside or outside the reactor. In this zone the hydrogen supplied will completely dissolve in the total feed as defined at the operation conditions. It is preferred to supply enough hydrogen that the total feed is substantially completely saturated at the conditions applied.

It is observed that in common parlance the oil product recovered in a hydrodesulfurization process is called the (hydro)desulfurized product. This need not necessarily mean that the produce is substantially sulfur-free, but as is well known the product has a reduced sulfur content in comparison to the fresh feed. Depending on the initial sulfur level the desulfurized product may occasionally show a sulfur content close to zero.

The hydrogen sulfide or its precursor compound as defined may be introduced together with the hydrogen required for desulfurization or it may be introduced separately either with the fresh feed or via the oil product-recycle. In a particularly preferred embodiment of the invention the hydrogen sulfide is introduced through the recycled desulfurized oil product proper. It has been found that if prior to depressurizing the desulfurized oil product recovered, part of it is recycled for admixture with the oil or oil fraction to be desulfurized, said recycle oil contains sufficient hydrogen sulfide to provide the residual oil feed with the required quantity of hydrogen sulfide.

Any of the well-known hydrodesulfurization catalysts may be used in the process of the invention. Particularly preferred are the sulfur-resistant catalysts comprising one or more metals of Group VIB, VIIB and/or VIII metals, their sulfides and/or oxides deposited on an amorphous refractory inorganic oxide of Group II, III or IV elements or compositions of said inorganic oxides. Suitable examples of catalysts of the preferred type comprise nickel-tungsten, nickel-molybdenum, cobalt-molybdenum, nickel-cobalt-molybdenum on silica, alumina, magnesia, zirconia, thoria, boria or hafnia or compositions of the said inorganic oxides, such as silica-alumina, silica-magnesia, alumina-magnesia and the like.

The catalyst mentioned may comprise further additives such as boron phosphate or phosphorus, and/or halogens such as fluorine and chlorine. Boron phosphate may be present in an amount from 10 to 40 percent w basis the total catalyst and more preferably from 15 to 30 percent w, whereas the halogens and phosphorus are used in an amount of less than 10 percent w.

Although the metal components may be present in any amount, the catalyst used preferably contains from 2 to 35 percent w and more preferably from 5 to 25 percent w of total metal. The metals of Group VIII are generally applied in a minor quantity of about 0.1 to 10 percent w and the metals of Group VIB are generally applied in a major quantity, of about 2.5 to 30 percent w, the total amount of metal components preferably being less than 35 percent. The atomic ratio of Group VII and Group VIB metals may vary within wide ranges, a range of from 0.1 to 5 being preferred, however.

Particularly suitable catalysts for the purpose of the present invention are a commercially available hydrodesulfurization catalyst comprising 4.1 pbw Co/10.3 pbw Mo/100 pbw Al_2O_3 and another one comprising 3.1 pbw Ni/11.7 pbw Mo/2.6 pbw P/100 pbw Al_2O_3.

Instead of the inorganic oxide carriers, carriers of the zeolitic type may be used. Particularly suitable alumino-silicate zeolites are the zeolite having a SiO_2/Al_2O_3 molar ratio of at least 3, such as zeolite Y. Alumino-silicate zeolites may be used as such or embedded in an inorganic oxide matrix, such as alumina. Usually the matrix is applied in an amount of from 20–80 percent w of the carrier.

The catalyst particle size is preferably below 2.0 mm and more preferably in the range of from 0.4 to 1.5 mm. Particularly favorable results have been obtained with a catalyst sieve fraction of 0.5 to 1.0 mm (35–18 mesh).

The reaction conditions used for hydrodesulfurization are conventional for this type of operation and may vary within wide limits depending on the type of feedstock used. The temperature is in the range of from 300° to 475°C and more preferably from 385° to 445°C and total pressures are of from 30 to 350 kg/cm² and more preferably from 75 to 225 kg/cm². The weight hourly space velocity may vary between wide ranges and is generally between 0.1 and 10 parts by weight of fresh oil feed per part by volume of catalyst per hour, 0.3 to 5 pbw of fresh oil feed being preferred. The severity of the hydrodesulfurization operation is preferably such that at least 40 percent of desulfurization is obtained and more preferably 50 to 85 percent.

The recycled desulfurized product may be combined with the fresh oil feed before or after the oil feed has been heated. The recycled product may also be separately introduced in the hydrogen saturation zone. Whatever operation modification is being used, it is preferred that the product to be recycled is taken from the hydrodesulfurization effluent stream prior to depressurizing that stream as discussed.

The residual oil to be hydrodesulfurized can be any sulfur-containing petroleum oil comprising residual material. Partial denitrification will occur simultaneously if nitrogen-containing compounds are present in fixed catalyst bed, a long residue of a Caribbean crude oil was treated with hydrogen in the presence of a commercially available hydrodesulfurization catalyst. Hydrodesulfurization was performed on a pilot plant scale, using a reactor with a catalyst inventory of 1,000 ml. The length of the fixed catalyst bed was about 90 cm. The pilot plant was inter alia provided with means to recirculate liquid desulfurized product to the reactor. The recycled product was combined with fresh feed and the total stream was heated prior to introduction into the top of the reactor. A separate hydrogen saturation zone was provided for outside the reactor. Make-up hydrogen was introduced with the fresh feed.

The hydrodesulfurization catalyst used was a $Co/Mo/Al_2O_3$ catalyst and had the following composition: 4.9 pbw CoO and 15.7 pbw MoO_3 per 100 pbw Al_2O_3 (dry basis). The catalyst particle size ranged from 0.5 to 1.0 mm. It was presulfided by means of a hydrogen sulfide-containing gas mixture (10 percent volume of H_2S) at a pressure of 10 kg/cm^2 and a gas hourly space velocity of 400 $l.l^{-1}.h^{-1}$ and a stepwise increase of the temperature from ambient temperature to 350°C. Thereafter the reactor was flushed with hydrogen at a pressure of 50 kg/cm^2. The pressure was finally increased to 150 kg/cm^2 and the feed to be hydrodesulfurized cut in:

The Caribbean crude-derived long residue was processed at the following conditions:

Pressure	150 kg/cm^2
Temperature	420°C
WHSV (fresh feed)	2.0 $kg.l^{-1}.h^{-1}$
Recycle ratio of product fresh feed	10:1
Inlet H_2-gas rate 250 Nl H_2/kf fresh feed	
Desulfurization level	above 55%

Hydrodesulfurization under the above conditions was effected in substantially liquid phase. The recycle product was taken from the low-pressure separator and stripped free of hydrogen sulfide with nitrogen before it was combined with the fresh feed.

The hydrodesulfurized product obtained had an average sulfur content of about 0.8 percent w sulfur. After desulfurization of 2.1 tons of feed/kg catalyst rapid catalyst deactivation was observed and the life test was terminated. After depressurizing and cooling the spent catalyst was removed for analysis. Based on fresh catalyst about 22 percent w of vanadium and 2.6 percent w of nickel had been laid down on the catalyst. The sulfur content of the catalyst amounted to 15.6 percent w.

In the following table the properties of the feedstock and of the hydrodesulfurized product recovered at the beginning of the run and near the end thereof are given in Table 1:

TABLE 1

Product Analysis	Feedstock	Product Beginning of the Run	Product End of the Run
Carbon, %w		86.97	86.64
Hydrogen, %w		12.10	11.99
Sulfur, %w	2.1	0.66	1.04
Nitrogen, ppmw	3200	2300	2600
Vanadium, ppmw	212	96	142
Nickel, ppmw	30	16	22
Ramsbottom Carbon residue, %w	2.9	5.8	6.6
Viscosity at 210°F, cS	37.1	16.23	16.89
Specific gravity, d 70/4°	0.9204	0.8935	0.8964
Pour point, °C	+23	+ 17	+20
Flash point, °C	175	132	103

EXAMPLE II

The influence of dissolved hydrogen sulfide in the recycle product on the stability of the desulfurization operation is demonstrated in this example.

The total liquid effluent of the reactor of the pilot plant described in Example I was cooled down to 70°C by heat exchanging it with hot water. Part of the cooled desulfurized product was recycled before the product was conducted to the high-pressure separator and subsequently depressurized in the low-pressure separator. The recycle product, still being under pressure, was admixed with the pressurized fresh feed comprising fresh hydrogen and after heating the total feed was introduced in the reactor.

The feed used was the Caribbean crude-derived long residue of Example I and the hydrodesulfurization conditions were as follows:

Pressure	150 kg/cm^2
Temperature	410°–420°C
WHSV (fresh feed)	2.0 $kg.l^{-1}.h^{-1}$
Recycle ratio of product to fresh feed	10:1
Inlet H_2-gas rate	125 Nl H_2/kg fresh feed
Desulfurization level	about 50%

Fresh $Co/Mo/Al_2O_3$ catalyst of the same particle size was used, the catalyst having been presulfided as previously described.

At the beginning of the run the quantity of hydrogen sulfide in the liquid recycle stream was 1.1 percent w and decreased during the run to 0.8 percent w at the end of the run. Under these conditions the operation was almost stable and the catalyst decline was much slower than without hydrogen sulfide in the recycle stream. The amount of fresh hydrogen supplied (purity about 99.8 percent volume) is rather low, but the recycled product also contains dissolved hydrogen not consumed in the desulfurization reaction.

The hydrodesulfurized product obtained had a constant sulfur content of 1.05 percent w in total liquid product. The catalyst life reached was 3.2 tons of oil feed per kg of catalyst (about 1,050 hours). Based on fresh catalyst about 29 percent w of vanadium, 3 percent w of nickel and 16 percent w of carbon had been laid down on the spent catalyst.

The properties of the desulfurized product obtained at the beginning, the middle and near the end of the life test are given in Table 2:

TABLE 2

Product Analysis	Beginning of the Run	Product Middle of the Run[a]	End of the Run[a]
Carbon, %w	86.74	86.65	86.51
Hydrogen, %w	11.91	11.98	11.97
Sulfur, %w	1.06	1.06	1.14
Nitrogen, ppmw	2,770	2,460	2,570
Vanadium, ppmw	103	102	125
Nickel, ppmw	15.6	15.0	17.4
Ramsbottom carbon residue, %w	5.95	5.11	6.12
Viscosity at 210°F, cS	15.32	14.54	13.02

the oil. The present process is especially advantageous in connection with residual oils comprising at least 20 ppmw vanadium and having a sulfur content of at least 1.0 percent w. It will be evident that the feedstock may be a whole crude. However, since the high sulfur components of a crude oil and also of the metallo-organic compounds tend to concentrate in the higher boiling fraction the present process will more commonly be applied to a bottoms fraction of a petroleum crude, i.e., one obtained by topping of the crude or by atmospheric of vacuum distillation of the crude. Typical residues will normally be substantially composed of hydrocarbons and/or one or more hetero-atoms-containing a substantial amount of asphaltic material. Thus, the oil feed can be one having an initial boiling point or a 5 percent boiling point somewhat below 360°C provided that a substantial proportion, for example, 40 to 50 volume percent or more, of its hydrocarbons boil above 360°C. In essence the residual oil or oil fraction may be a topped crude, a long residue or a short residue. Although the oil fractions may be subjected to a feed pretreatment such as deep-flashing, deasphalting, hydrorefining with hydrogen or hydrogen-containing gas mixtures in the absence of any catalyst or the like this is not required for the present direct desulfurization process.

Other heavy oil fractions which may be processed according to the invention are black oils, visbreaker effluents, tar sand oils and the like or mixtures of such oil fractions. These oil fractions may also be processed admixed with the residual oils or oil fractions mentioned.

It is preferred that the residual oil or oil fraction have an alkali metal and/or alkaline earth metal content of less than 50 ppmw. Preferably, this alkali metal and/or alkaline earth metal content is in the range of from 1 to 25 ppmw. If the metals content in the oil or oil fraction to be hydrodesulfurized is above the range indicated, it should preferably be reduced by appropriate treatment, such as washing or the like.

BRIEF DESCRIPTION OF DRAWING

The invention will be further explained with reference to the accompanying drawing which is a schematic flow diagram using a radial flow fixed catalyst bed.

In the drawing the residual petroleum feedstock to be hydrodesulfurized is introduced into the system by means of line **1** and pump **2**. The pressurized oil flows to furnace **5** via line **3** in which it is mixed with hydrogen introduced via line **4** and with recycled desulfurized product introduced via line **29**. As will be discussed hereinafter the product still contains hydrogen sulfide as it has not been depressurized after hydrodesulfurization. The heated mixture of fresh feed, recycled product and dissolved hydrogen and hydrogen sulfide is conducted to radial flow reactor **9** via line **6**. The feed mixture is introduced at the top of the reactor by means of conduit **10** provided with nozzles. The oil flows via saturation zone **11** consisting of ceramic balls or other inert material such as Raschig rings or the like to feed distribution zone **12**. Saturation zone **11** is provided to ensure that the hydrogen fed to the system is completely dissolved in the feed mixture before the latter comes into contact with the catalyst. The feed which under the prevailing reaction conditions is still in the liquid phase flows into the annular space **14** between the reactor inner wall and the perforated cylindrical catalyst bed support **16**. The catalyst zone **15** is filled with a suitable, shaped hydrodesulfurization catalyst of a convenient size. The oil feed enters the catalyst bed through the apertures provided in catalyst bed support **16** and flows through the bed to the center pipe **13** and into the inner space thereof via the apertures provided in pipe **13**. The desulfurized oil leaves the reactor **9** by means of line **17**. The desulfurized product which is still at the working pressure is partly taken from the system and partly recycled to the reactor via line **27**, hot recycle pump **28** and line **29**. As the product recycled is not depressurized it still contains hydrogen sulfide formed during desulfurization and hydrogen not consumed during desulfurization. If desired, the recycled product may be diverted via line **30** to line **6**, thus bypassing furnace **5**. This may be desirable for temperature control and for cooling down the catalyst bed before catalyst replacement.

The desulfurized product diverted via line **18** is first cooled in heat-exchanger **19** and then conducted to high-pressure separator **20**. A gaseous phase formed and mainly comprising hydrogen, hydrogen sulfide, ammonia and light gaseous hydrocarbons is vented via line **21** and used and/or treated in a manner known in the art (recycle gas). The liquid phase formed and consisting of desulfurized product is withdrawn from the system by means of lines **22** and **23**. Line **23** is provided with a valve **24** which is automatically controlled by means of level controller **25**.

When the catalyst inventory has to be replaced by fresh catalyst the desulfurized product may be used for cooling said inventory. To this end valve **24** in line **23** is shut and the cooled product recycled via line **26**, pump **28** and line **30** to the reactor. The valve provided in line **27** may also be kept closed so that the total liquid product is routed via heat-exchanger **19** and separator **20**.

Reactor **9** is provided with means to introduce an inert gas like nitrogen or additional hydrogen into the reactor (lines **32** and **31** provided with meter **33**). The nitrogen is required for displacing any hydrogen before finally opening the reactor for catalyst replacement.

As hydrogen sulfide has a beneficial effect on the hydrodesulfurization process the gaseous phase vented via line **21** may bypass the usual gas scrubber for removing hydrogen sulfide and be directly recycled to reactor **9** for providing the required hydrogen gas make-up together with hydrogen sulfide. Ammonia may be removed in the usual way by washing with water of either the liquid reactor effluent prior to flashing it in the high pressure separator or of the gaseous phase formed after flashing.

An advantage of the process is that the desulfurized products are very stable as such or in blends with other fuels as demonstrated by a peptization value (P-value) above 1 and a value for the hot filtration test below 0.10 percent w, as further explained in the following examples, which are not considered limiting, but which illustrate the invention and its advantages.

EXAMPLE I

In order to demonstrate the feasibility of residue hydrodesulfurization in the liquid phase applying a

Specific gravity, d 70/4°	0.8977	0.8939	0.8938
Stability tests			
P-value[b]	1.3	1.5	1.3
Hot filtration test[c], 1)	>0.01	>0.01	
2)	>0.01	>0.01	

[a] Half way through the run it was decided to switch to a Caribbean crude derived long residue of different origin which had about the same properties as the first feed but differed mainly in viscosity (28.96 cS at 210° F.) and nitrogen content (2,940 ppmw N); this accounts for the deviations.

[b] P- (peptization) value is determined from P_o/FR_{max} in which P_o stands for the peptizing power of the oil medium and FR_{max} is flocculation ratio of the asphaltenes at infinite dilution. A stable fuel has a P-value above 1.0; for the asphaltenes of the crude used FR_{max} is 35.

[c] In the hot filtration test the fuel is heated to 100° C. and filtered; the residue on the filter is given in % by weight and called existent residue (1). After 24 hrs. at 100° C. the fuel is again filtered and the residue obtained is called potential residue (2). A stable fuel should have existent and potential values as low as possible (< 0.10%w).

EXAMPLE III

The influence of the hydrogen sulfide content of the recycle desulfurized product on catalyst life and on the metal-lay down on the catalyst is further shown in this example.

The pilot plant experiments with the Caribbean crude-derived long residue of Example I having a sulfur content of 2.1 percent w and comprising 212 ppmw of vanadium were continued with a run in which the liquid recycle stream was cooled and depressurized to atmospheric pressure. At the beginning of the run the quantity of hydrogen sulfide in the liquid recycle stream was 0.1 percent w and decreased during the run to 0.06 percent w. For this run a fresh batch of the $Co/Mo/Al_2O_3$ catalyst crushed to 0.5–1.0 mm particles was used. The operating conditions applied were similar to those used in Example II but the hydrogen gas rate which was 200 Nl per kg of fresh oil feed.

In Table 3A the product properties of the desulfurized product recovered at the beginning of the run and near the end thereof are given.

TABLE 3A

Product Analysis	Product: Beginning of the Run	Product: End of the Run
Carbon, %w	86.81	86.94
Hydrogen, %w	11.98	11.90
Sulfur, %w	0.8	0.9
Nitrogen, ppmw	2,530	2,630
Vanadium, ppmw	104	119
Nickel, ppmw	16.2	18
Ramsbottom carbon residue, %w		5.1
Specific Gravity, d 70/4°	0.8931	
Pour point, °C.	+14	+14
Flash point, °C.	80	
Stability tests		
P-value	1.3	1.3
Hot filtration test, %w 1)	0.02	
2)	0.01	

In Table 3B the desulfurization results of Examples I to III with respect to catalyst life and metal lay-down have been summarized.

TABLE 3B

H_2S in Recycled Product, %w	Average Sulfur Content of Desulfurized Product, %w	Catalyst Life: Tons Feed/kg Cat.	Catalyst Life: Hours	V+Ni Metal Lay-Down on Catalyst, %w
Nil	0.8	2.1	700	25
About 0.07	0.9	2.4	800	28
0.85	1.05	3.2	1,050	32

From the above it can be concluded that increasing the H_2S-content of the recycle stream results in an increased metal lay-down on the catalyst and in an extended catalyst life. Moreover, application of a H_2S-containing recycle stream results in an almost constant desulfurization level without the need to raise the temperature.

EXAMPLE IV

In order to show the influence of increasing temperature on the product properties, in particular on the viscosity of the desulfurized product obtained, the Caribbean crude-derived long residue of Example I was desulfurized at constant sulfur level by raising the temperature stepwise during operation. A life test was run in a bench scale apparatus with a catalyst inventory of 100 ml. The catalyst was the same as used in the previous examples. Its particle size was 0.5–1.0 mm and it was presulfided before use. The operating conditions were: temperature: from 380° to 420° C; pressure: 150 kg/cm²; WHSV (fresh feed): 2.0 kg.l⁻¹h.⁻¹; recycle ratio of H_2S-free, desulfurized product to fresh feed: 10 to 1; inlet H_2 gas rate: 250 Nl H_2/kg fresh feed; sulfur level of total liquid product: 0.9–1.0 percent w.

The life test was terminated at about 1,000 hours as the deactivation of the catalyst was such that in order to maintain the desired sulfur level the temperature had to be raised unduly high. The results obtained at several stages during the run are given in Table 4.

TABLE 4

Product Analysis	After 130 hrs(temp. 380° C.)	After 446 hrs(temp. 405° C.)	After 694 hrs(temp. 410° C.)	After 1,029 hrs(temp. 430° C.)
Carbon, %w	86.50	86.64	86.74	86.54
Hydrogen, %w	11.82	11.92	11.96	11.91
Sulfur, %w	1.14	0.92	0.97	1.25
Nitrogen, ppmw	1,500	2,680	2,670	2,710
Vanadium, ppmw	132	115	123	146

Nickel, ppmw			18.1	21.1
Ramsbottom carbon residue, %w	3.98	5.13	5.95	6.8
Viscosity at 210°F, cS	27.65	21.30	20.49	14.83
Specific gravity, d 70/4°	0.9055	0.8994	0.8998	0.8970
Pour point, °C.	+23	+20	+20	+2
Flash point, °C.	138	114	120	79
Stability tests				
P-value	2.6	2.0	1.9	1.3
Hot filtration test,				
%w, 1)	0.03	0.01	>0.01	0.02
%w, 2)	0.03	0.01	0.01	0.02

The above results were obtained by applying a recycle of desulfurized product which prior to recycling had been degassed by stripping with hydrogen. It was thus free of hydrogen sulfide. From the product analysis given it appears that, for instance, the viscosity at 210°F is not constant as it continuously decreases with rising hydrodesulfurization temperature. Also, the sulfur content of the product obtained is less constant than that of the product prepared according to the invention (see Example II).

EXAMPLE V

The influence of alkali metal present in residual oils on the desulfurization activity of the catalyst is shown in the following example.

A Middle-East crude-derived long residue was hydrodesulfurized over a fixed bed prepared from a fresh batch of the $Co/Mo/Al_2O_3$ catalyst of Example I. The average particle size of the catalyst was 0.7 mm. The liquid recycle stream was stripped free of hydrogen sulfide at atmospheric pressure in order to demonstrate only the alkali metal effect.

Both a long residue with a high sodium content and one with a low sodium content were processed. The properties of said residue are the following:

	Sodium Content	
Feedstock Analysis	High	Low
Carbon, %w	84.21	83.99
Hydrogen, %w	11.25	11.42
Sulfur, %w	4.05	3.91
Nitrogen, ppmw	2,100	2,100
Vanadium, ppmw	50	49
Nickel, ppmw	15	13
Sodium, ppmw	65	3.5
Ramsbottom carbon residue, %w	7.7	8.6
Specific gravity, d 70/4°	0.9280	0.9184
Viscosity at 210° F., cS	37.41	26.1
Pour point, °C.	+11	+14
Flash point, °C.	172	154

The above feedstocks were hydrodesulfurized substantially in the liquid phase applying a large product recycle. The catalyst used was presulfided. The results obtained together with the conditions applied are given in Table 5.

TABLE 5

Sodium Content of Feed, ppmw	65	3.5
Process conditions		
Temperature, °C.	420	420–455
Pressure, kg/cm²	150	150
WHSV (fresh feed), kg.l⁻¹.h⁻¹	1.0	0.75
Inlet H_2 gas rate, Nl/kg fresh feed	300	300
Recycle ratio of H_2S-free product to fresh feed	20:1	about 20
Catalyst life, hours	1,400	4,400
Tons feed/kg catalyst	2.1	5.0
Average sulfur content (TLP), %w	0.9	0.9
Metals deposited on catalyst %w on fresh catalyst		
V+Ni	13	27
Na	4.6	1.2

From the above it can be concluded that a low sodium content of the oil feed to be desulfurized greatly improves catalyst life. It is thus preferred to reduce the sodium content of the feed to below 50 ppmw if it is not already below this value.

EXAMPLE VI

A topped Caribbean crude (96.9 percent yield on crude) having sulfur content of 2.84 percent w, a vanadium content of 393 ppmw and a nickel content of 54 ppmw was hydrodesulfurized in an upflow recycle operation carried out substantially in the liquid phase over a fixed catalyst bed prepared from a fresh batch of the $Co/Mo/Al_2O_3$ catalyst of Example I (particle size used between 0.4 and 1.5 mm). The catalyst was presulfided. In one life test the recycle stream of desulfurized product was stripped free from hydrogen sulfide at atmospheric pressure, in another life test the recycle stream was not depressurized nor stripped free of H_2S. In that case the quantity of hydrogen sulfide in the liquid recycle stream amounted to 2.0 percent w at the beginning of the run and was gradually decreased during the run to 0.8 percent w at the end of the run. The decrease in hydrogen sulfide content of the liquid recycle stream was achieved by gradually increasing the temperature of the high-pressure separator from 60°C at the beginning of the run to 80°C at the end of the run.

The results obtained together with the conditions applied are given in Table 6.

TABLE 6

H_2S Content of Recycle Stream, %w	Nil	1.2
Process conditions		
Temperature, °C.	415–420	415–420
Pressure, kg/cm²	150	150
WHSV (fresh feed) kg.l⁻¹.h⁻¹	1.0	1.0
Inlet H_2-gas rate, Nl/kg	250	250
Recycle ratio of product to fresh feed	20:1	10:1
Catalyst life, tons feed/kg catalyst	0.7	1.8
Average desulfurization level, %	70	50–55
Metal lay-down (V+Ni), %w on fresh catalyst	13	33

The inhibiting effect of H_2S on the desulfurization activity of the catalyst is unambiguously shown by the results tabulated. It is, however, also evident that the presence of H_2S in the recycle stream has a favorable effect on catalyst stability resulting in a prolonged catalyst life at almost constant desulfurization level. Under these conditions the catalyst apparently can tolerate a higher metal lay-down before it finally becomes deactivated.

EXAMPLE VII

A Caribbean long residue having a sulfur content of 2.1 percent w was hydrodesulfurized substantially in the liquid phase over a fixed catalyst bed of 0.5–1.0 mm crushed particles of the $Co/Mo/Al_2O_3$ catalyst described in Example I. The catalyst was presulfided. The hydrodesulfurization was carried out in upflow operation with product recycle. In one life test the recycle stream of desulfurized product was stripped free from hydrogen sulfide at atmospheric pressure. In another life test the liquid recycle stream was not depressurized and not stripped free from hydrogen sulfide. In that case the quantity of hydrogen sulfide in the liquid recycle stream amounted to 1.0 percent w at the beginning of the run and was gradually decreased in the course of the run to 0.4 percent w at the end of the run. The decrease in hydrogen sulfide content of the liquid recycle stream was achieved by gradually increasing the exit gas rate from 80 Nl/kg at the beginning of the run to 225 Nl/kg at the end of the run.

The results obtained together with the conditions applied are given in Table 7.

TABLE 7

H_2S Content of Recycle Stream, %w	Nil	1.0–0.4
Process conditions		
Temperature, °C.	420	420
Pressure, kg/cm^2	150	150
WHSV (fresh feed), $kg.l^{-1}.h^{-1}$	2.0	2.0
Exit gas rate, Nl/kg	250	80–225
Recycle ratio of product to fresh feed	3:1	3:1
Catalyst life, hours	700	1,000
Catalyst life, tons feed/kg cat	2.1	3.0
Average sulfur content of desulfurized product, %	0.7	1.06

The figures in Table 7 show that addition of a certain quantity of hydrogen sulfide to the feed and decreasing this quantity during the course of the run results in a longer catalyst life and a more stable operation.

We claim as our invention:

1. A process for the catalytic hydrodesulfurization of a sulfur-containing residual hydrocarbon oil carried out substantially in a liquid phase in the presence of dissolved hydrogen and a solid sulfur-resistant catalyst which comprises adding to the feedstock a sulfur compound selected from the group consisting of hydrogen sulfide and a hydrogen sulfide precursor in an amount to provide at least 0.05 percent w of hydrogen sulfide in the liquid phase at the beginning of the process, and decreasing the quantity of sulfur compound added during the course of the process to less than 80 percent of the initial quantity as required to maintain an essentially constant hydrodesulfurization level, and withdrawing a desulfurized product.

2. The process of claim 1 wherein the sulfur compound added to the feed comprises an amount to provide at least 0.5 percent w of hydrogen sulfide and the sulfur content of the residual oil feedstock is reduced by at least 40 percent w.

3. The process of claim 1 wherein the liquid phase is a combined feedstock comprising residual oil and recycled desulfurized oil product in an amount of at least 3 volumes of product for each volume of residual oil, and wherein the quantity of added sulfur compound is decreased in the course of the process to less than 65 percent of that added initially.

4. The process of claim 3 wherein part of the desulfurized oil product is cooled and recycled for admixture with the residual oil without depressuring said product.

5. The process of claim 3 wherein the added sulfur compound is decreased by removing part of the hydrogen sulfide from the desulfurized product and recycling said product for combination with the residual oil feedstock.

6. The process of claim 3 wherein the hydrodesulfurization is carried out in the presence of from 5 to 30 Nl of hydrogen per liter of combined liquid feed and the sulfur content of the residual oil feedstock is reduced by at least 40 percent w.

7. The process of claim 3 wherein the combined feed is passed with hydrogen through a hydrogen saturation zone prior to contacting the solid sulfur-resistant catalyst.

8. The process of claim 1 wherein the liquid phase flows radially through a fixed catalyst bed in which at least 40 percent volume of the liquid phase flows through the top half of the catalyst bed, the solid sulfur-resistant catalyst has a particle size less than 2.0 mm, and the residual oil has a sulfur content of at least 1.0 percent w.

9. The process of claim 8 wherein the residual oil is substantially composed of hydrocarbons and one or more hetero atoms-containing organic carbon compounds boiling above 360°C, a substantial amount of asphaltic material, and has a sodium content of less than 50 ppmw; and the hydrodesulfurization is carried out at a temperature in the range of from 300°C to 475°C, a total pressure of from 30 to 350 kg/cm^2, and a weight hourly space velocity of 0.3 to 5 parts by weight of residual oil per part by volume of catalyst per hour.

10. The process of claim 1 wherein the residual oil feedstock has a sulfur content of at least 1.0 percent w, which is reduced to from 50 to 85 percent w of its initial value in the presence of a fixed-bed catalyst having a particle size from 0.4 to 1.5 mm; from 5 to 15 volumes of desulfurized oil product are recycled for each volume of residual oil feedstock; and wherein the process is carried out at a temperature from 385° to 445°C, a total pressure from 75 to 225 kg/cm^2, a weight hourly space velocity of 0.3 to 5 parts by weight of fresh oil feed per part by volume of catalyst per hour and a hydrogen gas rate of 15 to 20 Nl hydrogen per kilogram of total feed.

* * * * *