

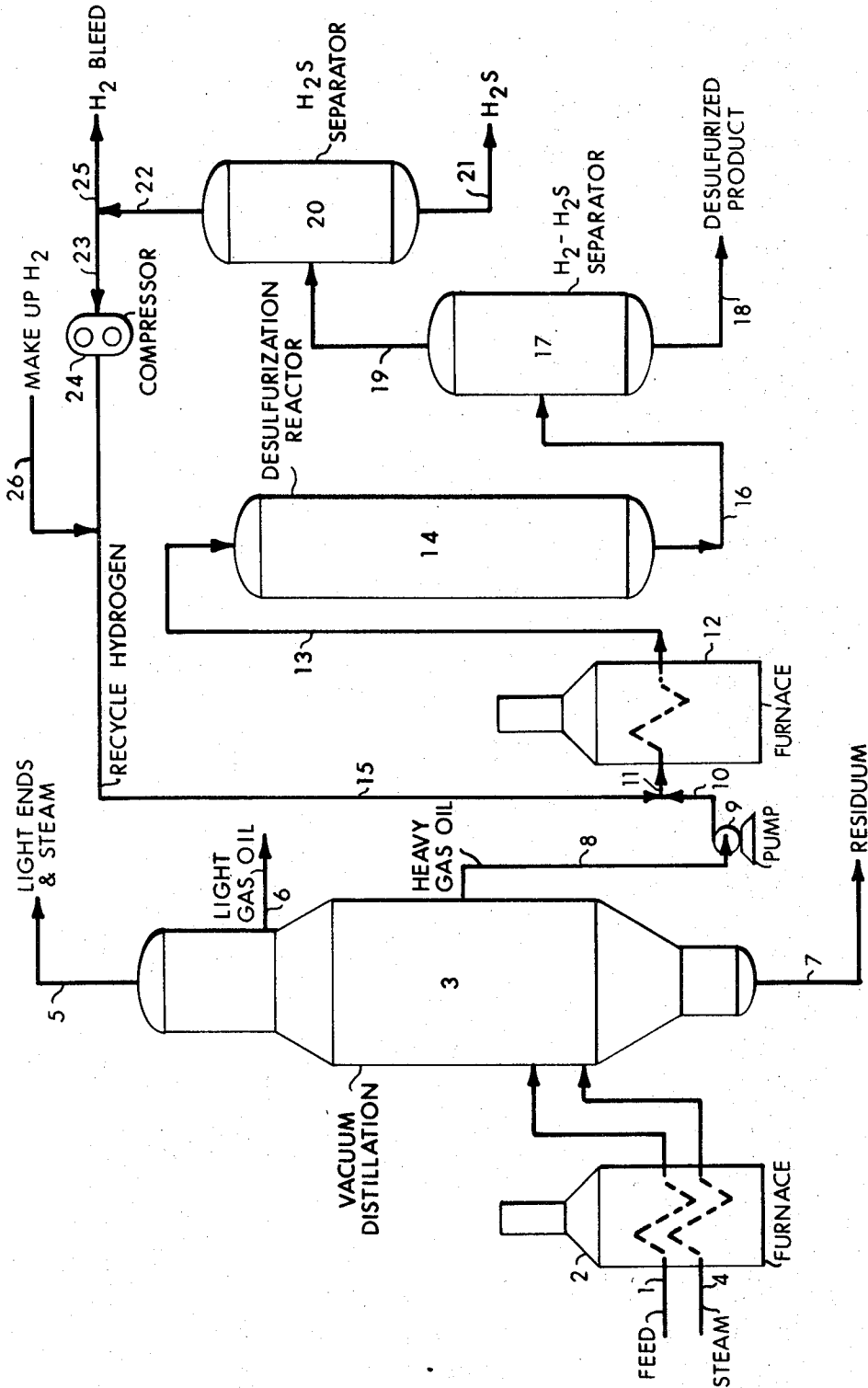
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HYDRODESULFURIZATION OF HEAVY PETROLEUM DISTILLATES

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CLARK ADAMS
WILLIAM HOUSE

Inventors

By *C. W. Crady Jr.*

Patent Attorney

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**HYDRODESULFURIZATION OF HEAVY
PETROLEUM DISTILLATES**

Clark E. Adams and William T. House, Baton Rouge,
La., assignors to Esso Research and Engineering Com-
pany, a corporation of Delaware

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8 Claims

ABSTRACT OF THE DISCLOSURE

A process for the production of low-sulfur fuel oil by means of a continuous liquid phase hydrodesulfurization process for petroleum gas oil feed having an end point in the range of 750° to 1300° F. The process is applied to atmospheric gas oils, vacuum gas oils and the like, containing about 0.1 up to 5.0 weight percent sulfur. The catalyst used is a mixture of a Group VIII metal salt with a Group VI-B metal salt deposited on a silica-stabilized alumina, characterized by having a high surface area, a maximum of the total surface area in pores having a diameter of 30 to 70 A., there also being a minimum of the pore volume in pores having a diameter greater than 100 A.

This invention relates to an improved hydrodesulfurization process for the production of a low sulfur industrial fuel oil or fuel oil component as the major product. More specifically, heavy petroleum distillates such as gas oils are hydrodesulfurized with a high activity maintenance catalyst consisting essentially of a cobalt salt or a nickel salt and a molybdenum salt or a tungsten salt deposited on a support material consisting essentially of 1 to 6 wt. percent silica and 94 to 99 wt. percent alumina, said support being characterized by a maximum pore volume and surface area in pores 30 to 70 A. in diameter. In a preferred embodiment, the support is prepared with specific quantities of particular ingredients and with precise control of conditions.

The process of the invention is applied to heavy petroleum distillates. More particularly, the process is applied to atmospheric gas oils and vacuum gas oils. The principal object of the present invention is to reduce the sulfur content of petroleum distillates without significantly changing the viscosity, pour point and gravity of the oil. The process is centered on non-destructive hydrodesulfurization as distinguished from destructive hydrogenation or hydrocracking. Thus, in the preferred embodiment conversion to gas and light ends is minimized. If desired, a minor amount of the oil can be cracked to lighter materials such as gasoline and middle distillates. Another object of this invention is to provide a process specifically designed to treat a feed consisting entirely of a heavy petroleum distillate as distinguished from the lighter petroleum distillates such as naphthas and kerosenes or specialty fractions such as lubricating oils. In most cases satisfactory processes and catalysts have been developed for the lighter materials and for heavy feedstocks diluted with lighter materials.

Another object of this invention is to provide a hydrodesulfurization process for heavy petroleum distillates which is economically feasible in view of the low return available from the marketing of the treated distillate as industrial fuel oil. Cost studies have shown that the key factors are hydrogen consumption, catalyst activity and catalyst activity maintenance. Another specific object of the invention is to provide a process which is carried out at moderate temperature, pressure, and other conditions with a catalyst which features low cost and high activity maintenance. By low pressure we mean pressures less

than 1000 p.s.i.g. and by low temperature we mean temperatures less than about 850° F.

In petroleum processes of this type one of the chief objects is to maintain the process on stream for the longest period of time possible without regeneration of the catalyst. A limitation on continuous operation is the gradual reduction in the activity of the catalyst. Any operating period of less than about six months is considered uneconomical because regeneration or changeover to new catalyst and cleaning of the unit may require about three weeks. Thus service factor is reduced.

Another characteristic of these processes is that the temperature of the reaction must be slowly increased over the operating period in order to sustain the desired percentage of sulfur removal. For example, with conventional catalysts when it is desired to remove from 80 to 90% of the sulfur from a typical gas oil containing about 2% sulfur, it would be necessary to raise the temperature of operation from about 725° F. at the start of the run to about 800° F. at the end of the run. The temperature increase requirement (TIR) is due to the gradual accumulation of coke and metals upon the surface of the catalyst, slowly decreasing its activity. The increase in temperature is conducive to increased cracking of the lighter hydrocarbons in the feed and this reduces the quantity of desired fuel oil product. Furthermore, the temperature increase aggravates the tendency of the catalyst to crack the feedstock accelerating coke lay down on the catalyst.

Summarizing briefly, the objects of the invention are attained by hydrodesulfurizing heavy petroleum distillates at moderate conditions in the presence of a catalyst comprising an oxide or sulfide of nickel or cobalt and an oxide or sulfide of molybdenum or tungsten deposited on a suitable support material consisting essentially of 1 to 6 wt. percent silica and 94 to 99 wt. percent alumina. The catalyst has a maximum pore volume and surface area in pores 30 to 70 A. in diameter.

The drawing is a flow sheet disclosing a preferred embodiment.

The process feedstock is a heavy petroleum distillate. The most suitable feeds are gas oils such as atmospheric gas oil, vacuum gas oil, coker gas oil, and visbreaker gas oil. The feed can also be a blend of any of these materials and may include small quantities of other fractions such as cat cracked fractions and small quantities of residual fractions. The process can also be applied to deasphalted oils. The initial boiling point of the fraction will be in the range of from about 350° to about 700° F. The end point of the fraction will be in the range of from about 750° to about 1300° F. The process is uniquely applicable to heavy vacuum gas oils having an initial boiling point in the range of from about 650° to about 750° F. and an end point over 1000° F., i.e. 1050° to 1150° F. Ordinarily the metals content of the gas oil will be relatively low, i.e. from 1 to 50 p.p.m., preferably 0.05 to 10 p.p.m., metals. The gas oil will contain from about 0.1 to 5.0 wt. percent sulfur, some of the sulfur being in the form of thiophene-type ring compounds. The Conradson carbon of the feed will be at least 0.2 and more often at least 0.5.

The process of the invention is uniquely applicable to a "dirty gas oil." This type of material is encountered when a vacuum distillation unit is being pushed to obtain the maximum quantity of vacuum gas oil from the crude oil or atmospheric fraction fed to the still. Because of variations in operating conditions, a large slug of residual material is occasionally carried overhead from the vacuum still and this type of material can rapidly deactivate a conventional hydrodesulfurization catalyst. The process is designed to treat a feedstock without any preproc-

essing other than vacuum distillation or solvent de-asphalting. Typical feedstocks treated have the following properties and inspections:

TABLE I.—FEEDSTOCK INSPECTIONS

	Feed			
	A	B	C	D
	Crude Source and Description			
	Arabian vacuum gas oil	Venezuelan 700/1,050° F. vacuum gas oil	Venezuelan 850/1,100° F. vacuum gas oil	Venezuelan deasphalted oil
Gravity, ° API	20.2	23.2	15.9	15.2
Sulfur, wt. percent	2.95	1.56	2.45	2.17
Conradson carbon, wt. percent	0.37	0.28		6.89
Modified naphtha insolubles, wt. percent	0.4			1.0
C-H analysis:				
Wt. percent C	85.20			85.67
Wt. percent H	11.79			11.66
Metals, p.p.m.:				
Ni	0.3	0.7	1.4	4
Fe		3.3	24	2
V	0.4	0.7	3.4	27
Viscosity:				
At 122° F., SSF	30.0	24	140	1,801
At 140° F., SSF	21.5	19	73	743
Flash, COC, ° F	414			605
Pour point, ° F	87	90		70
ASTM D-1160 at 1 mm. Hg				
I.B.P., ° F. (Atmos. eqn.)	555	693	787	828
5%	710	724	835	956
10%	772	737	847	991
20%	815	761	871	1,034
30%	847	780	889	
40%	857	808	907	
50%	895	835	925	
60%	896	874	949	
70%	913	889	966	
80%	931	925	995	
90%	949	969	1,036	
95%	963	1,007	1,047	
F.B.P., ° F	971	1,007	1,047	1,047
Recovery, percent	97	95	95	24

The high activity maintenance catalyst used in the process of the invention comprises a mixture of a salt of a Group VIII-B metal, e.g. cobalt or nickel, and a salt of a Group VI-B metal, e.g. molybdenum or tungsten, deposited on a support material consisting essentially of 1 to 6 wt. percent silica and 94 to 99 wt. percent alumina. The finished catalyst has a total pore volume of at least 0.25 cc./g. and a total surface area of at least 150 m.²/g. Preferably the total pore volume is at least 0.4 cc./g. and a total surface area of at least 250 m.²/g. In addition, a maximum of the total surface area, i.e. at least about 100 m.²/g., of the surface area is in pores having a diameter of 30 to 70 Å.

Furthermore, since pores of the larger diameter seem to accelerate deactivation of the catalyst in the hydrodesulfurization of petroleum oils, it is preferred that the catalysts have a minimum of pores having a diameter of more than 100 Å., i.e. less than 0.25 cc./g.

The procedure followed in the preparation of the support is an important aspect of the invention.

In general, the support can be prepared by precipitating the oxides or hydrated oxides of aluminum and silicon from aqueous solutions of water-soluble salts of these metals. For example, suitable proportions of the water-soluble salts of aluminum as the sulfate, chloride or nitrate, and suitable proportions of water-soluble silicon salts such as sodium silicate are precipitated from solution by adjusting the pH of the solution with acidic or basic material. The precipitate is washed and otherwise treated to remove impurities as necessary. The support can be impregnated with the metals while it is wet or after drying and calcining.

A preferred method of preparing the catalyst is to treat alkaline aqueous aluminate solutions which contain predetermined amounts of silica with acidic reagents to precipitate an aluminosilicate in the hydrous form. A slurry produced by this technique is then dried and treated by known methods to furnish a preferred catalyst support of this invention. The supports of the types prepared above are then impregnated with metals which promote the hydrodesulfurization reaction. The pre-

ferred alkaline aqueous aluminate solution is a solution of sodium aluminate. It should be understood that other alkali metal aluminates can be used except that

they are not preferred from an economic standpoint. The acidic reagents which can be used are the mineral acid salts of aluminum, e.g. aluminum halides, nitrates and sulfates. Also useful are the well-known mineral acids themselves, e.g. hydrochloric, nitric, sulfuric acids and the like.

Preferably, the conditions for preparing the support are so controlled that the finished support has an apparent bulk density of less than 0.70 g./cc. It is further characterized as being opaque as distinguished from glassy in appearance (indicating that a large quantity of the alumina is in a crystalline form). The catalyst is extrudable.

The first variable which must be controlled in preparing the support is the alumina concentration. The alumina concentration, expressed as wt. percent Al₂O₃, of the aqueous alkali aluminate solution must be between 1.2 and 5.0, preferably between 1.2 and 3.0, and the most preferred concentration is between 1.2 and 1.7. It is felt that close control of the alumina concentration within the stated ranges is a material factor in producing a support which can be extruded in commercial equipment.

Other important variables include pH and temperature. The precipitation must be effected at a pH between 5 and 9.5, preferably between 6 and 9. Temperatures ranging between 105° and 120° F., preferably 110° to 120° F., must be employed.

In the most preferred embodiment the silica-alumina support is prepared in the presence of a material selected from the group consisting of an aldonic acid or an aldinate, preferably a gluconate or gluconic acid. Galatonic acid, arabonic acid, xylic acid, mannonic acid, and salts thereof can be used as well. Suitable aldonates include the sodium, potassium, zinc, magnesium, calcium and lithium salts of gluconic acid or other aldonic acids. This material is used in the initial solution in amounts ranging from 0.5 to 6.0 wt. percent based on the Al₂O₃ content of the solution. It appears that the addition of aldonates and aldonic acids in the preparation of the silica alumina base has a beneficial effect on the physical characteristics of the final catalyst and its effectiveness in hydrodesulfurization.

In preparing these preferred catalytic materials Table II illustrates preferred conditions and concentrations.

The finished silica-alumina support has a pore volume

TABLE II

Conditions	Broad range	Preferred range
I. Concentration of starting aluminate solution, expressed as Al ₂ O ₃ .	1.2-5 wt. percent	1.2-1.7 wt. percent.
II. Precipitation temperature	105-120° F.	110-120° F.
III. pH	5-9.5	6-9.
IV. Reaction time	¼-6 hrs.	¼-2 hrs.
V. Aldonate or alconic acid	0.5-6 wt percent.	2-3 wt. percent.

Using the above general reaction conditions, the support resulting from the reaction is in the form of a dilute slurry. This slurry may then be concentrated and subjected to spray-drying operations at temperatures ranging between 200° to 2000° F., preferably 200° to 500° F. Spray-drying, particularly at the stated conditions, preserves the catalyst base in the desired spheroidal form.

Using conventional techniques known to the catalyst art, the spray-dried material may be subjected to water washing to remove excess alkali metal ions and sulfate ions. The support can then be impregnated with the catalytic metals and extruded or pilled or otherwise formed into any desired physical form.

The aforementioned silica-alumina hydrogels can be composited with other synthetic and/or semi-synthetic aluminas, silica gels, and/or other silica-alumina-clay hydrogel compositions for the purpose of adjusting the alumina and/or silica present during impregnation. The resulting catalyst when calcined should have a total surface area greater than 150 m.²/g. and the pore volume is preferably greater than 0.25 cc./g. as measured by the BET procedure with nitrogen.

The active metallic components in the finished catalyst are a Group VI-B salt, specifically a molybdenum salt or tungsten salt selected from the group consisting of molybdenum oxide, molybdenum sulfide, tungsten oxide, tungsten sulfide, and mixtures of these and a Group VIII-B salt, specifically a nickel or cobalt salt selected from the group consisting of nickel oxide, cobalt oxide, nickel sulfide and cobalt sulfide and mixtures of these. The preferred active metal salt combinations are nickel oxide with molybdenum oxide and cobalt oxide with molybdenum oxide. Oxide catalysts are preferably sulfided prior to use.

The final catalyst contains the following amounts of each component.

TABLE III.—CATALYST COMPOSITION

	Broad range, wt. percent	Preferred range, wt. percent
Nickel or cobalt (as oxide)	1 to 15	2 to 10.
Tungsten or molybdenum (as oxide)	5 to 25	10 to 20.
Silica	1 to 6	1.5 to 5.
Alumina	93 to 94	86 to 85.

EXAMPLE 1

The following illustrates a typical catalyst preparation. Three solutions are prepared, e.g. A, B and C.

	Ingredient	Amount
Solution A ¹	Water	36 gallons.
	Sodium silicate solution, 28% SiO ₂	113 cc.
	Sodium alumina, 23.5% Al ₂ O ₃ solution	5,323 cc.
	48% gluconic acid solution	76 cc.
Solution B	98% H ₂ SO ₄	850 cc. into 4.5 gallons.
Solution C	9.5% alum. solution	3.3 gallons.

¹ Total Al₂O₃ in solution, 1.3%.

Solution B is added to Solution A over a period of 23 minutes. At this point the temperature of the reaction mixture is 118° F.

Solution C is then added to the mineral acid solution over a 19-minute period. The temperature during addition remains at 118° F. The final pH, after the above additions, is 8.8. The slurry was filtered, reslurried, spray-dried, washed to remove soluble salts, and redried.

of 2.36 cc./g., a surface area of 310 m.²/g., and an apparent bulk density of 0.18 g./cc.

EXAMPLE 2

A silica-alumina support is prepared in the manner set forth in Example 1 and is composited with suitable quantities of molybdenum oxide and cobalt carbonate by impregnation. The slurry is filtered and dried to provide a catalyst (dry weight basis containing 3.5% cobalt oxide, 12.5% molybdenum oxide, 1.7% SiO₂, and the balance alumina). The support can be impregnated with the other hydrogenation metals of the invention, i.e. nickel and tungsten, in the same manner. As stated previously, the catalyst is sulfided prior to use.

The structure of the catalyst is also an important aspect of the invention. In the hydrodesulfurization of petroleum a criticality of pore size has been found with respect to activity maintenance. It has been found that pores having a pore diameter in the 30 to 70 A. range are of critical importance with heavy feeds. Thus, a maximum of surface area, i.e., 40 to 100%, should be present in the pores having a pore diameter in the 30 to 70 A. range and a minimum of pores should be present in pores having a pore diameter of over 100 A., i.e., less than about 20%.

Catalysts having good activity and activity maintenance for hydrodesulfurization are characterized by the following relationship between pore diameter in A., pore volume in cc./g. and surface area in m.²/g. for pores over the range of 30 to 70 A. in diameter.

$$\frac{4 \times 10^4 \times \text{pore volume (cc./g.)}}{\text{pore diameter, A.}} > 100 \text{ m.}^2/\text{g. surface area}$$

The pore volume distribution of a catalyst as defined by this invention is measured by nitrogen adsorption isotherm where the volume of nitrogen absorbed is measured at various pressures. This technique is described in Ballou et al., Analytical Chemistry, vol. 32, April 1960, pp. 532-536. The pore diameter distributions for the examples of the invention were obtained using a Model No. 4-4680 Adsorptomat manufactured by the American Instrument Company, Silver Spring, Md. One skilled in the art can select catalyst manufacturing process steps and process conditions within the specific ranges disclosed herein to prepare catalysts having the required pore diameter, pore size distribution, pore volume, and surface area.

Referring to the drawing, a reduced crude oil feed is fed by line 1 through furnace 2 into vacuum distillation tower 3. Steam is fed by line 4 through the furnace into

the vacuum unit. The feed is preheated in the furnace to a temperature in the range of 725° to 875° F. The vacuum unit is operated to maximize the recovery of a fraction amenable to continuous hydrodesulfurization. A stream comprising light ends and steam is recovered by line 5. Steam can be recovered and recycled by means not shown. A light gas oil fraction having a relatively low sulfur content can be recovered by line 6. A residuum fraction

having an initial boiling point in the range of 1000° to 1150° F. is recovered by line 7. All or part of this material can be used as a fuel oil blending stock. The prime desulfurization feed, a heavy vacuum gas oil, is passed via line 8, pump 9, lines 10 and 11, furnace 12 and line 13 to desulfurization reactor 14. The desulfurization feed may contain small quantities of residual material. Typical vacuum distillation conditions include a temperature in the range of 700° to 850° F. and a pressure in the range of 20 to 100 mm. Hg. Steam is added with the feed and to the bottom of the tower to enhance separation of distillable oil from the bottoms. This steam may amount to 1 to 20 pounds per barrel of oil feed. Velocity of the flow of vapors through the trays or other entrainment barriers above the flash zone is a serious limitation in operation of the vacuum tower. This velocity is normally in the range of 3 to 10 ft. per second. The velocity depends upon oil feed rate, temperature and pressure.

At maximum temperature and minimum pressure with high feed rates, it can be said that the vacuum unit is being pushed and it is under these conditions that an occasional slug of residual petroleum oil is included in the deep cut desulfurization feed. The residual material contains a relatively high proportion of organo-metallic compounds, multi-ring aromatic hydrocarbons and other coke formers which rapidly deactivate a conventional hydrodesulfurization catalyst.

In furnace 12 the feed is preheated to a temperature in the range of 600° to 800° F. A hydrogen containing gas containing 70 to 100 volume percent hydrogen is fed by line 15 into line 11 for mixing with the feed. A conventional liquid or mixed phase reactor is employed. The catalyst, previously described, is arranged in a series of stacked fixed beds in this embodiment. If desired, expanded beds, an ebullating bed or slurry type operation can be employed. In this embodiment the oil and hydrogen are passed downwardly through the reactor but upflow techniques and countercurrent techniques can also be used. With typical gas oil feeds like feeds A and B of Table I the preferred reaction conditions include a temperature in the range of 650° to 800° F., a pressure in the range of 400 to 850 p.s.i.g., and a hydrogen rate of 1000 to 5000 cu. ft./bbl.

A novel feature of the operating conditions is the pressure range. In the past it was felt that pressures above 1000 p.s.i.g., i.e., 1200 to 1500 p.s.i.g., were essential for continuous 50 to 90% hydrodesulfurization of gas oils containing 2 to 3 wt. percent sulfur. We have found that pressures below 1000 p.s.i.g. are entirely suitable when the high activity maintenance catalyst disclosed herein is employed. As shown in Example 3 below, pressures as low as 400 p.s.i.g. are feasible and a temperature of about 700° to 750° F. is suitable throughout the run. These mild operating conditions coupled with the long run length provide numerous cost advantages in initial investment and in operating costs.

Desulfurization effluent is passed by line 16 to gas separator 17. Liquid product is removed by line 18. The treated product will usually contain less than 1% sulfur, i.e. 0.1 to 1.0 wt. percent sulfur, depending principally on the sulfur content of the feed and the severity of the reaction conditions. The gas stream is passed overhead by line 19 to H₂S separator 20. H₂S and light ends are separated by conventional means such as cooling and amine treating. H₂S is removed by line 21. Hydrogen is recycled via lines 22 and 23, compressor 24 and line 15. A hydrogen bleed stream is removed by line 25. Makeup hydrogen is added as required by line 26.

When a deasphalted oil is to be desulfurized, the vacuum unit is replaced by a conventional deasphalting unit including an extraction tower and solvent handling facilities.

The severity of the reaction is preferably controlled to limit conversion of the feed to lower boiling materials to less than 20 volume percent of the feed, and usually to

less than 10 volume percent of the feed. A minor proportion of the feed can be cracked to gasoline and middle distillates if such products are desired.

Typical reaction conditions are as follows:

5 TABLE IV.—REACTION CONDITIONS, NON-DESTRUCTIVE HYDRODESULFURIZATION

	Broad range	Preferred range
10 Temperature, ° F.	600-850	650-800
Pressure, p.s.i.g.	300-1,000	400-850
Fresh feed rate, w./hr./w. on cat.	0.1/1-10/1	0.5/1-5/1
Hydrogen rate, s.c.f./bbl. of fresh feed.	500-10,000	1,000-5,000

EXAMPLE 3

This example discloses the long term effectiveness of the process of the invention at an operating pressure of 400 p.s.i.g. An Arabian vacuum gas oil containing 2.95 wt. percent sulfur was continuously contacted in an isothermal reactor with hydrogen to provide a constant sulfur removal of 85%. The gas oil had properties substantially the same as those shown for oil A in Table I. The start of run temperature was about 695° F. and a comparison was made of the allowable operating days to reach an end of run temperature of 765° F. At the latter temperature, regeneration would be necessary. A cobalt molybdate on silica alumina catalyst prepared according to the method disclosed herein, containing about 2% SiO₂ and having about 170 m.²/g. of its surface area in pores in the 30 to 70 A. diameter range was used in one run. A conventional hydrofining catalyst containing 3.5 wt. percent CoO and 12.5 MoO₃ on a support containing 0.2 wt. percent SiO₂ and the balance alumina and not having the critical pore size distribution required was used in the same test reactor at 400 p.s.i.g. for comparison. The reactor was a pilot plant unit containing 200 cc. of catalyst. The oil was passed down through the catalyst bed. At a space velocity of 0.75 the process will operate continuously for about 180 days with the conventional catalyst compared to a run length of about 260 days when the catalyst of the invention is used. This direct comparison shows the clear advantage of processing vacuum gas oil with the catalyst of the invention. It is believed that an overall catalyst life of 30 months with two interim regenerations can be achieved in an optimized commercial unit.

EXAMPLE 4

A run was made at 800 p.s.i.g. reactor pressure with gas oil B of Table I employing a start of run temperature of 725° F. At this pressure, the temperature increase requirement (TIR) to maintain 85% desulfurization was 0.06° F. per day. With a comparable but slightly different vacuum gas oil feed and using the conventional catalyst, the TIR was 0.20° F. per day. Thus, at any operating pressure in the range of 400 to 850 p.s.i.g., utilization of the high activity maintenance catalyst disclosed herein is indicated for commercial hydrodesulfurization operations with gas oil feeds.

At the conditions disclosed herein, hydrogen consumption is in the range of 150 to 250 cu. ft./bbl. of feed. Because the cost of hydrogen is a major factor in commercial hydrodesulfurization, the relatively low consumption achieved is a major benefit.

Another important aspect of the catalyst used in this type hydrodesulfurization process is stability to regeneration. The catalyst of this invention is quite stable to regeneration and fully recovers its activity upon regeneration, as long as an excessive quantity of metals has not been deposited and relatively mild regeneration conditions are used. It is preferable to keep the regeneration temperature below about 950° F.

EXAMPLE 5

Two samples of the catalyst of this invention were "artificially" deactivated by operation on gas oil A for 18 hours at 775° F., 200 p.s.i.g., 250 s.c.f. H₂/bbl. and 1

v./v./hr. These catalysts were then regenerated under the following conditions:

	1	2
Temperature, ° F.....	600	600
Pressure, p.s.i.g.....	350	350
Regeneration gas:		
Rate, s.c.f./hr./bbl. of cat.....	1,500	3,000
Oxygen, wt. percent.....	1.2	0.6

After regeneration the catalysts were resulfided according to normal procedures and tested for activity. Activity equivalent to fresh catalyst activity was completely recovered in both cases.

The examples show that a gas oil containing about 2% sulfur can be converted into 80 to 95% of 650° F. plus fuel oil in a hydrodesulfurization operation at mild conditions and relatively low hydrogen consumption. The high activity maintenance catalyst will permit continuous operations up to 6 to 8 months before the first regeneration.

Similar results will be obtained with petroleum fractions obtained by solvent deasphalting with solvents such as propane, butane, pentane, etc.

The process of the invention provides a low sulfur fuel oil product or fuel oil blending component that can be blended with higher and lower boiling petroleum fractions to provide low sulfur fuel oils which meet the viscosity, pour point and gravity requirements required in metropolitan markets.

What is claimed is:

1. A continuous liquid phase process for the hydrodesulfurization of a petroleum gas oil feed having an end point in the range of 750° to 1300° F. and containing coke formers which tend to decrease catalyst activity and to increase the TIR, comprising the steps of contacting said gas oil with hydrogen at a temperature in the range of 600° to 850° F. and a pressure in the range of 350 to 1060 p.s.i.g. with a high activity maintenance sulfided catalyst comprising cobalt molybdate on a support comprising 1 to 6 wt. percent silica and 92 to 99 wt. percent alumina, said catalyst being characterized by a maximum of the total surface area having pores in the range of 30 to 70 A. diameters and a minimum of the pore volume in pores having diameters greater than 100 A., whereby the temperature increase requirement (TIR) is less than about 0.36° F./day for continuous hydrodesulfurization process operations of at least 180 days with at least 70% sulfur removal from the feed.

2. A process according to claim 1 in which said catalyst has less than 0.25 cc./g. of its total pore volume in pores having a diameter of more than 100 A. and at least 100 M²/g. of surface area in 30 to 70 A. diameter pores.

3. A continuous process for the hydrodesulfurization of a petroleum gas oil comprising the steps of:

(a) vacuum distilling a residual petroleum oil at a temperature in the range of 725° to 875° F. and a pressure in the range of 20 to 100 mm. Hg to obtain a deep cut vacuum gas oil having an end point in the range of 750° to 1300° F.;

(b) contacting said deep cut vacuum gas oil with hydrogen at a pressure in the range of 350 to 1050 p.s.i.g. and at a temperature in the range of 600° to 850° F. in the presence of a catalyst comprising co-

balt molybdate on an alumina support stabilized with 1 to 6 wt. percent silica, said catalyst having a total surface area greater than 150 m.²/g., a maximum of the total surface area being in 30 to 70 A. diameter pores, and also having a minimum of the pore volume in pores having diameters greater than 100 A.; and

(c) recovering a gas oil product of reduced sulfur content.

4. A process according to claim 3 in which the vacuum distillation is carried out in the presence of added steam.

5. A process according to claim 3 in which the gas oil product recovered from step (c) contains less than 1% sulfur and the hydrogen consumption in step (b) is in the range of 150 to 250 cu. ft./bbl. of gas oil.

6. A process for the hydrodesulfurization of a gas oil feed having an end point between 750° to 1050° F., an °API gravity between 15 to 25 and a sulfur content ranging from 0.25 to 4.5 weight percent which comprises,

(a) heating said gas oil feed to a temperature in the range of 600° to 800° F.;

(b) introducing hydrogen gas to said heated gas oil feed prior to contacting the oil with a catalyst;

(c) contacting the gas oil feed and hydrogen mixture with a hydrodesulfurization catalyst comprising cobalt molybdate on an alumina support stabilized with 1 to 6 wt. percent silica, said catalyst characterized by having a total surface area greater than 150 m.²/g., a maximum of the total surface area being in pores having diameters ranging from 30 to 70 A. and wherein a minimum of the pore volume is in the pores having diameters greater than 100 A.;

(d) the hydrodesulfurization being conducted at a temperature in the range of 650° to 800° F., a pressure in the range of 400 to 850 p.s.i.g. and a hydrogen rate of 1000 to 5000 cu. ft./bbl.

7. A process according to claim 6 in which the heavy petroleum gas oil has an end point in excess of 1000° F. and a Conradson carbon of at least 0.5.

8. A process according to claim 6 in which the catalyst comprises a sulfided mixture of a Group VIII-B metal oxide selected from the group consisting of cobalt oxide and nickel oxide and a Group VI-B metal oxide selected from the group consisting of molybdenum oxide and tungsten oxide deposited on said support.

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DELBERT E. GANTZ, Primary Examiner

G. J. CRASANAKIS, Assistant Examiner

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