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[72] Inventors Karsten H. Moritz;
Robert C. W. Welch, both of Baton Rouge, La.

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[73] Assignee Esso Research and Engineering Company

[54] RESIDUUM HYDRODESULFURIZATION

5 Claims, 1 Drawing Fig.

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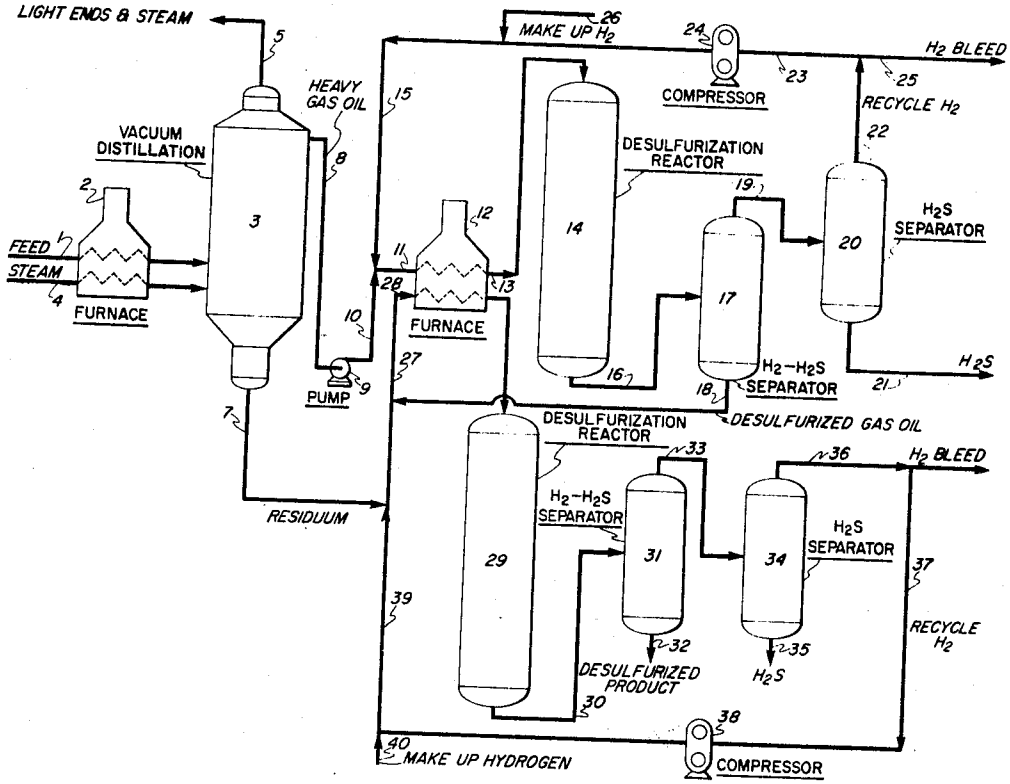
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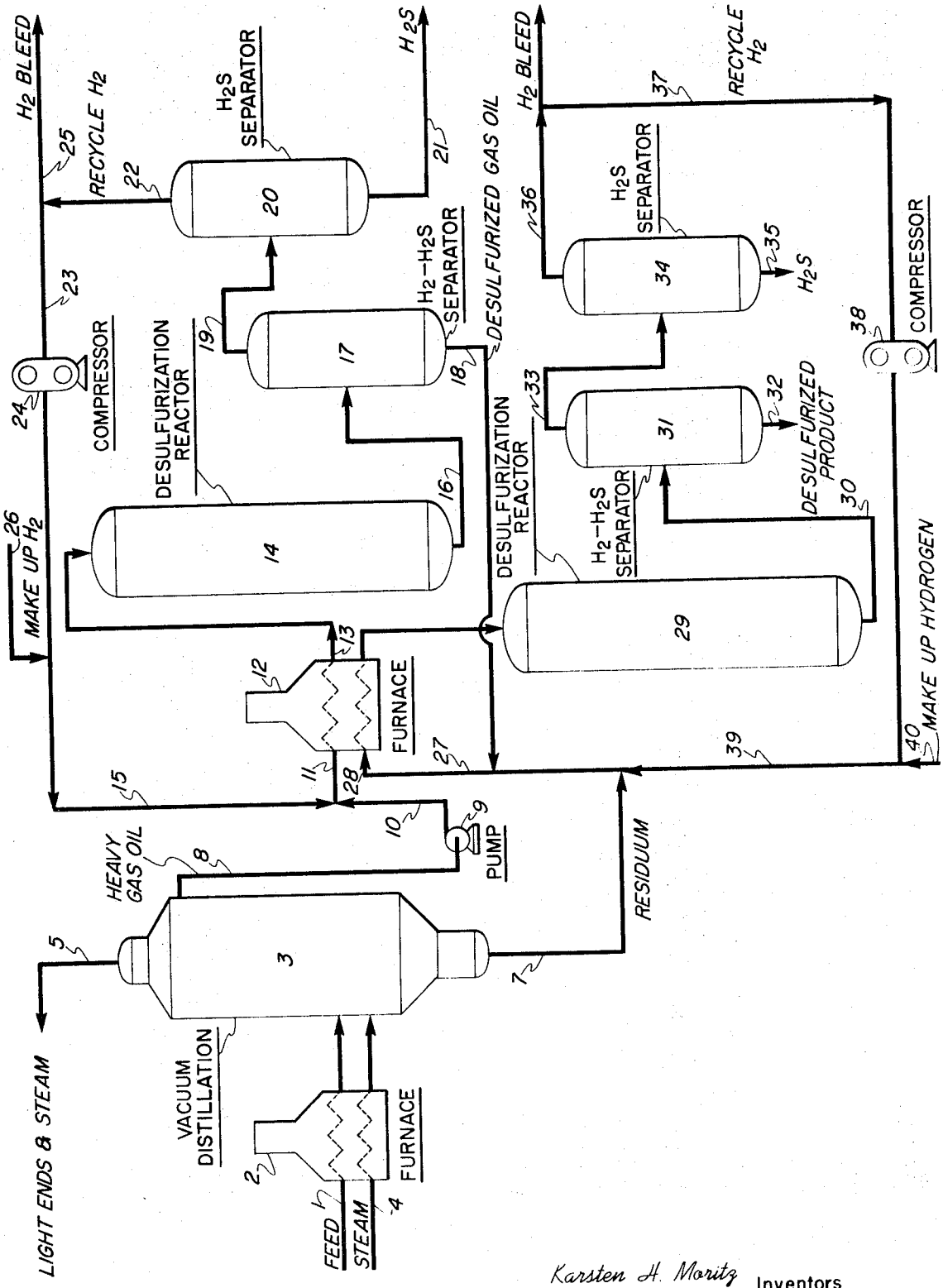
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Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. J. Crasaniakis
Attorneys—Pearlman and Stahl and C. D. Stores

ABSTRACT: An atmospheric residuum is desulfurized by first separating it into a gas oil fraction and a heavy residual fraction, desulfurizing the gas oil in the presence of hydrogen, combining the desulfurized gas oil with the heavy residual fraction and hydrodesulfurizing the mixture.





Karsten H. Moritz
Robert C.W. Welch
Inventors

By

Attorney

RESIDUUM HYDRODESULFURIZATION

BACKGROUND OF THE INVENTION

This invention relates to the hydrodesulfurization (HDS) of hydrocarbon residua and relates more specifically to a method of maintaining catalyst activity in such a process.

The maintenance of catalyst activity is of prime importance for the hydrodesulfurization of hydrocarbon residua. The process is commercially unattractive and its cost prohibitive if catalyst life is too short. Residuum obtained by atmospheric distillation can be desulfurized as such or it can be distilled under vacuum to give a vacuum gas oil overhead and a vacuum residuum, either or both of which can be desulfurized. Generally in any refinery setup the first hydrodesulfurization unit set up is for vacuum gas oil since catalyst activity maintenance is not a problem. However as the sulfur specification is lowered, the desulfurization of vacuum gas oil becomes inadequate and the vacuum residuum or the total atmospheric residuum must be desulfurized. In such a case the difficulty of catalyst activity maintenance becomes a problem, since the residuum contains materials, such as metals and resins which contaminate the catalyst.

SUMMARY OF THE INVENTION

In accordance with this invention the above disadvantages are overcome by diluting the vacuum residuum with the desulfurized gas oil and then subjecting the mixture to hydrodesulfurization.

As a result of this procedure it has been found that catalyst life is greater and the reactor volume is smaller than that for conventional desulfurization of atmospheric residuum. The dilution thus renders the hydrodesulfurization of vacuum residuum commercially feasible. Furthermore the dilution lowers the temperature rise across the reactor since the same heat of reaction is used to heat a larger quantity of feed, with the result that a desirable decrease in outlet temperature occurs.

BRIEF DESCRIPTION OF THE DRAWING

The sole drawing is a diagrammatic representation of the flow plan of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawing an atmospheric residuum boiling above 650° F. 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. Typical vacuum distillation conditions include a temperature in the range of 550° 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 normally in the range of 3 to 10 feet per second and 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, multiring aromatic hydrocarbons and other coke-formers which rapidly deactivate a conventional hydrodesulfurization catalyst. A stream comprising light ends and steam is recovered by line 5. Steam can be recovered and recycled by means not shown. A residuum fraction having an initial boiling point of 1,050° F. is recovered by line 7. A vacuum gas oil boiling 650°–1,050° F. is passed via line 8, pump 9, lines 10 and 11, furnace 12 and line 13 to desulfurization reactor 14.

In furnace 12 the feed is preheated to a temperature in the range of 600° to 850° 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 is arranged in a series of stacked fixed beds. If desired, expanded-bed and ebbulating-bed or slurry-type operation can be employed. The oil and hydrogen are passed downwardly through the reactor but upflow techniques and countercurrent techniques can also be used.

Catalysts used may be any sulfactive hydrogenation catalyst such as a Group VIB compound, specifically a molybdenum compound or a tungsten compound, such as the oxide or sulfide and mixtures of these alone or together with a Group VIII compound, specifically a nickel or cobalt compound, such as the oxide or sulfide. The preferred metal compounds are nickel oxide with tungsten oxide or cobalt oxide with molybdenum oxide, used in the following proportions: 1 to 15 weight percent, preferably 2 to 10 weight percent, of nickel or cobalt oxide, 5 to 25 , preferably 10 to 20 weight percent of tungsten or molybdenum oxide on a suitable support, such as alumina or alumina containing small amounts of silica. A particular suitable support is alumina containing 1 to 6 weight percent silica wherein the surface area of the catalyst support in pores having a diameter of 30 to 70 A. is at least 100 square meters per gram, preferably 100 –300 square meters per gram. All of these catalysts are preferably used in the sulfided form.

Typical reaction conditions in desulfurization zone 14 are as follows:

	Broad	Narrow
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 to 10/1	0.5/1 to 5/1
Hydrogen Rate s.c.f./bbl. of Fresh Feed	500–10,000	1,000–5,000

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 percent sulfur, i.e. 0.1 to 1.0 weight 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 H_2S separator 20. H_2S and light ends are separated by conventional means such as cooling and amine treating. H_2S 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.

The desulfurized oil from H_2.H_2S separator 17 flowing in line 18 is passed to line 27 where it meets vacuum residuum from line 7 and recycle hydrogen from line 39. The mixture is passed by line 28 through furnace 12 where it is heated to a temperature in the range of 500 °–825° F. and then passed by line 28 to desulfurization reactor 29. Typical reaction conditions in reactor 29 are as follows:

	Broad	Preferred
Temperature, °F.	500–825	650–800
Pressure, p.s.i.g.	500–2,500	1,000–1,800
Space Velocity, V/V/Hr.	0.2–5.0	0.5–2.0
Hydrogen Rate s.c.f./bbl.	500–7,500	1,000–5,000

The catalyst may be any sulfactive hydrogenation catalyst but is preferably the same catalyst as that used in desulfurization zone 14.

Desulfurized product is withdrawn through line 30 and passed to separator 31 from which liquid product containing no more than 1percent sulfur is removed by line 32. A gas stream is removed overhead by line 33 and passed to hydrogen sulfide separator 34 wherein H_2S and light ends are separated as in separator 20 and removed by line 35. Hydrogen is removed and recycled by lines 36 and 37, compressor 38 and line 39. Make up hydrogen is added as required by line 40.

The following example shows the advantage obtained in accordance with this invention in comparison with desulfurization of the atmospheric residuum without separating the gas oil.

EXAMPLE 1

When a Tia Juana Medium atmospheric residuum boiling 650° F. +(AR) is vacuum distilled and the 650 °–1050° F. gas oil fraction (VGO) is desulfurized at a pressure of 800 p.s.i.g. and a temperature of 725° F. in the presence of a fixed bed catalyst consisting of 3.5 weight percent CoO and 12.5 weight percent MoO_3 on an alumina support containing 1 to 6 weight percent SiO_2 and having a surface area of 266 square meters per gram, a pore volume of 0.50 cc. per gram and a surface area in 30 –70A. pores of 174 grams per square meter, the resulting product contains less than 1 percent sulfur and can be mixed with the vacuum residuum boiling 1050° F.+ (VR) and the mixture can be desulfurized over the same fixed bed catalyst used to desulfurize the gas oil, under a pressure of 1,500 p.s.i.g. and at a temperature of about 650° F. This procedure shows advantages over the desulfurization of the original atmospheric residuum of the same crude boiling 650° F. + under similar conditions without removing the gas oil. A comparison of the two procedures is shown in table I.

TABLE I

Tia Juana Medium 650° F.+ HDS

Processing Scheme	AR HDS	Diluted VR HDS*
Pressure, p.s.i.g.	1,500	1500 (VR) 800 (VGO)
LHSV, V/Hr./V	0.58	1.24 (VGO + VR) 0.65 (VGO)
S.O.R. Temperature, °F.	649	653 (VGO + VR)
Gas Rate, SCF/B	1,500	
Hydrogen Purity, Mol.%	96	
Sulfur in Feed, Wt.%	2.17	
Vanadium in Feed, w.p.p.m.	290	
Catalyst Life, Days to Reach 800° F.	154	248 (VGO + VR) 650 (VGO)
Total Reactor Volume Relative to VGO-Diluted VR Case Here	1.06	1.00

*All of VGO blended with all of VR for final desulfurization step.

The above data show that a 60 percent increase in minimum catalyst life occurs when the gas oil is separated from the atmospheric residuum, desulfurized separately and then used as a diluent in the desulfurization of the vacuum residuum. Furthermore, the total reactor volume (VGO and VGO+VR) required for the desulfurization of the diluted residuum is smaller. It should be noted that the overall improvement in catalyst life is even greater than 60 percent since the catalyst in the VGO-alone HDS reactor has a life of about 2 years.

EXAMPLE 2

A similar run using Kuwait 650° F.+ atmospheric (VGO gives results comparable to those obtained with Tia Juana Medium as the following data show.

TABLE II

Kuwait 600° F.+Kuwait.

Processing Scheme	AR HDS	Diluted VR HDS*
Pressure, p.s.i.g.	1500	1500 (VR) 800 (VGO)
LHSV, V/Hr./V	0.50	1.41 (VGO + VR) 0.60 (VGO)
S.O.R. Temperature, °F.	662	685 (VGO + VR)
Gas Rate, SCF/B	3,000	
Hydrogen Purity, Mol.%	96	
Sulfur in Feed, Wt.%	3.80	
Vanadium in Feed, w.p.p.m.	43	
Catalyst Life, Days to Reach 800° F.	258	335 (VGO + VR) 650 (VGO)
Total Reactor volume Relative to VGO-Diluted VR Case Here	1.18	1.00

* All of VGO blended with all of VR for final HDS step.

From the above data it is clear that when operating in accordance with this invention minimum catalyst life is extended from about 60 percent with Tia Juana Medium to about 30 percent with Kuwait. Overall catalyst life in both cases is extended even more. Also reactor volume is decreased from about 6 percent with Tia Juana Medium to about 18 percent with Kuwait.

The nature of the present invention having thus been fully set forth and illustrated and specific examples of the same given, what is claimed as new, useful and unobvious and desired to be secured by Letters Patent is:

1. A process for removing sulfur from a hydrocarbon fraction having a boiling point above about 650° F. which comprises:
   - separating said hydrocarbon fraction into a gas oil fraction having a boiling point between about 650° F. and about 1,050° F. and a heavy residuum fraction boiling above about 1,050° F.,
   - catalytically hydrodesulfurizing said gas oil fraction until said gas oil fraction contains less than 1 percent sulfur based on weight of said gas oil fraction in a first reaction zone;
   - diluting said heavy residuum fraction with said desulfurized gas oil fraction in a second reaction zone; and
   - catalytically hydrodesulfurizing said blended fractions in said second reaction zone.

2. A process for removing sulfur from a heavy residuum having a boiling point above about 1,050° F. which comprises:
   - diluting said heavy residuum with a gas oil having a boiling point between about 650° and about 1,050° F. and having a sulfur content of less than 1 weight percent, in a reaction zone containing a sulfactive hydrogenation catalyst;
   - introducing hydrogen into said reaction zone at a rate of about 500 to about 7,500 SCF/bbl.; and
   - reacting said gas oil and heavy residuum with said hydrogen in the presence of said sulfactive hydrogenation catalyst in said reaction zone operating at a temperature between about 500° and 825° F., and at a pressure between 500 and 2,500 p.s.i.g.

3. A process of claim 2 wherein said catalyst consists of about 1 to about 15 weight percent of nickel or cobalt sulfide, and about 5 to about 25 weight percent tungsten or molybdenum sulfide on an alumina support having a surface area in pores of 30 to 70A. of at least 100 square meters per gram and containing about 1 to about 6 weight percent silica.

4. A process for removing sulfur from a residual oil having a boiling point above about 650° F. which comprises:
   - separating said residual oil into a gas oil having a boiling point between about 650° and about 1,050° F. and a heavy residuum having a boiling point above about 1,050° F.;
   - introducing hydrogen at a rate of about 500 to about 10,000 SCF/bbl. along with said gas oil into a first reaction zone containing a sulfactive hydrogenation catalyst;

reacting said hydrogen and said gas oil in the presence of said catalyst in said first reaction zone at temperatures between about 600° and 850° F. and at pressures between about 300 and 1,000 p.s.i.g. so as to remove substantially all sulfur from said gas oil;

diluting said heavy residuum with said substantially desulfurized gas oil in a second reaction zone containing said sulfactive hydrogenation catalyst;

introducing hydrogen at a rate of about 500 to about 750 SCF/bbl. into said second reaction zone; and

reacting said hydrogen and said gas oil and heavy residuum in the presence of said sulfactive hydrogenation catalyst

in said second reaction zone at temperatures between about 500° and 825° F. and at pressures between about 500 and about 2,500 p.s.i.g.

5. A process according to claim 4 wherein said sulfactive hydrogen catalyst consists of about 1 to about 15 weight percent of nickel or cobalt sulfide, and about 5 to about 25 weight percent tungsten or molybdenum sulfide on an alumina support having a surface area in pores of 30 to 70 A. of at least 100 square meters per gram and containing about 1 to about 6 weight percent silica.

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