

[54] HYDROFINING-REFORMING PROCESS

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[58] Field of Search **208/89, 210**

[56] References Cited

UNITED STATES PATENTS

2,143,078	1/1939	Lyman et al.	208/210
3,556,986	1/1971	Beck et al.	208/89
3,714,030	1/1973	Winsor et al.	208/210

FOREIGN PATENTS OR APPLICATIONS

1,141,966	2/1969	United Kingdom	208/210
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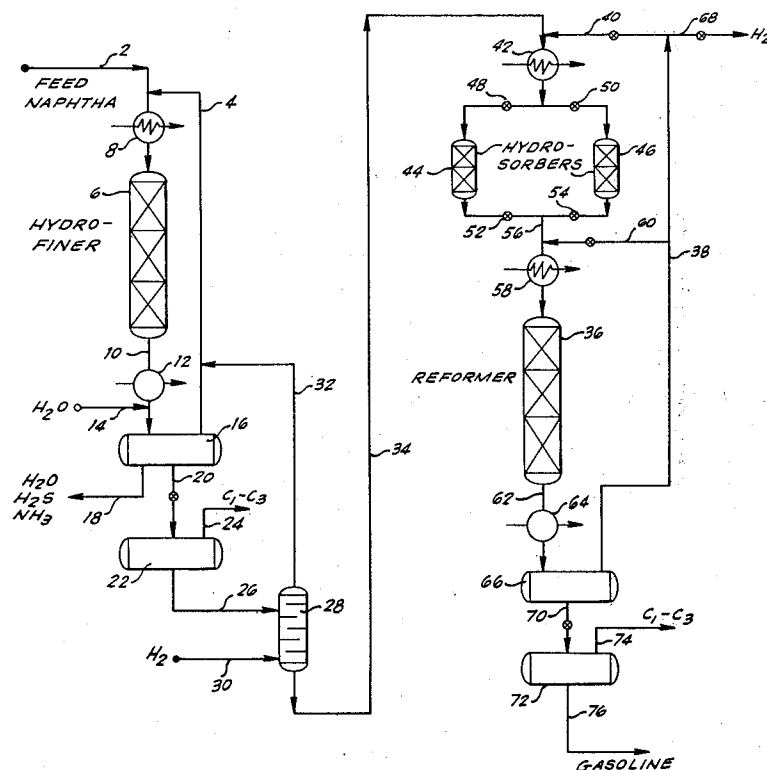
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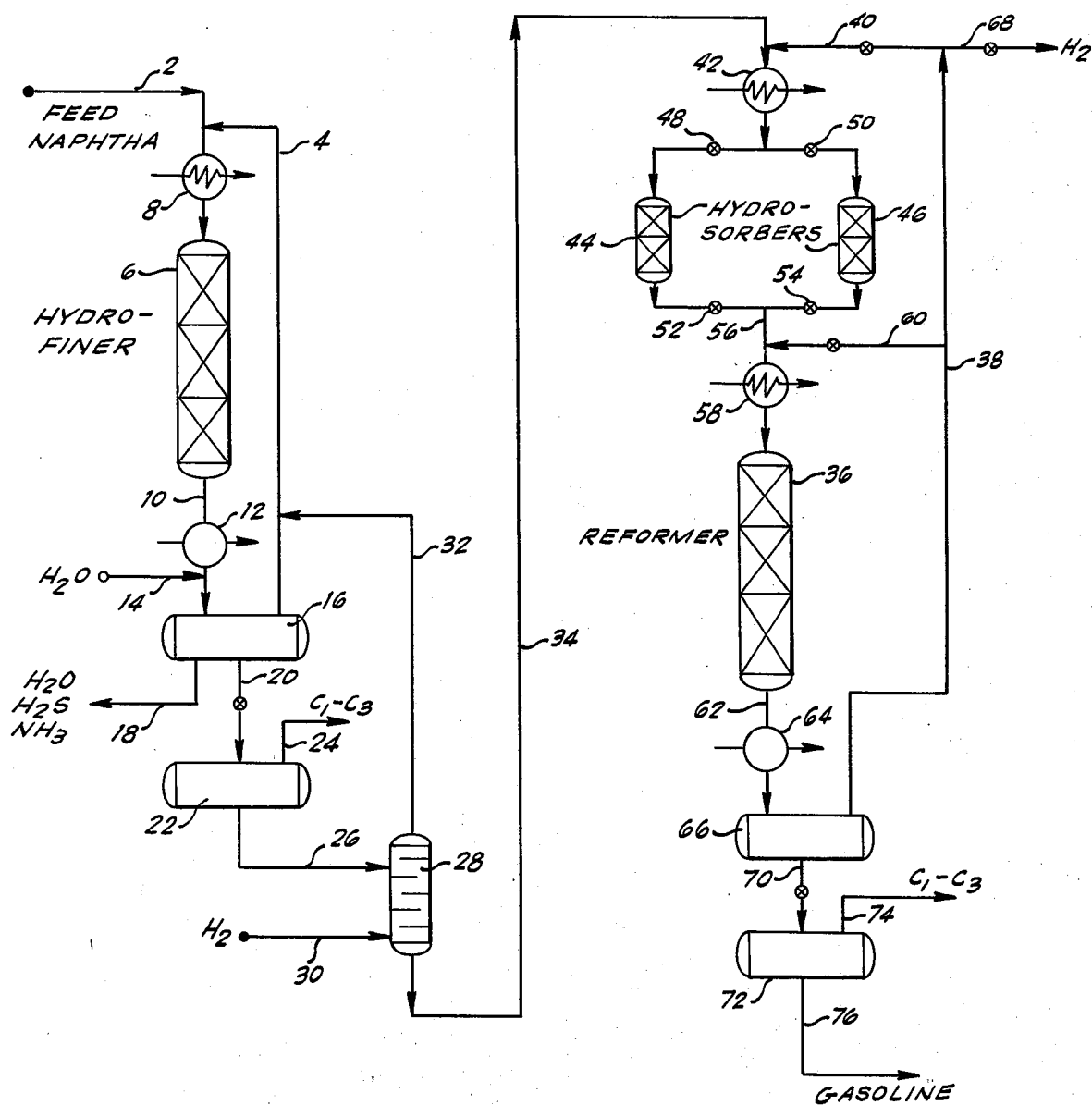
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ABSTRACT

Hydrocarbon feedstocks containing organic sulfur are subjected to a two-stage hydrofining treatment. In the first stage a sulfided hydrofining catalyst is utilized to effect hydrodecomposition of the bulk of the sulfur compounds and produce an effluent containing, e.g., about 0.5–10 ppm of residual sulfur. In the second stage, the first stage product is contacted with a molybdenum-Group VIII metal hydrofining catalyst maintained at least partially in a reduced state, so as to effect a substantial and more efficient hydrodecomposition of the remaining sulfur compounds. The two-stage process is particularly useful for the pretreatment of naphtha feedstocks to a subsequent reforming step employing highly sulfur-sensitive catalysts such as the bimetallic platinum-rhenium-alumina composites.

12 Claims, 1 Drawing Figure





HYDROFINING-REFORMING PROCESS RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 183,793, filed Sept. 27, 1971, and now abandoned.

BACKGROUND AND SUMMARY OF INVENTION

Catalytic hydrofining processes as commonly practiced in commercial applications utilize a presulfided catalyst composite of a Group VIB metal and an iron group metal supported on a refractory oxide carrier such as alumina. The presulfided catalyst is regarded as being more active than catalysts which are initially put on-stream in an oxidized or reduced form, later becoming sulfided by contact with feed sulfur. In most hydrofining operations, the objective is to reduce the feed sulfur content to somewhere in the range of about 2–50 ppm. Perhaps the most well known application of hydrofining in this area involves the pre-treatment of naphtha feedstocks to reduce the sulfur content to about 2–10 ppm for subsequent conversion to high octane gasoline in a platinum-alumina reforming zone. As is well known, these platinum-alumina catalysts are poisoned by sulfur compounds, but nevertheless can be most tolerate small amounts of sulfur in the range of about 2–5 ppm. The small poisoning effect of sulfur in this concentration range is more than offset by the savings achieved by operating the hydrofining zone for incomplete desulfurization.

It will thus be seen that the choice as to hydrofining severity to be used in pretreating reformer feedstocks involves an economic balance between the benefits to be gained in the reforming zone versus the added expense required in the hydrofining zone (in the form of increased catalyst volume required, or decreased catalyst life resulting from using more severe hydrofining conditions). When using conventional presulfided hydrofining catalysts, and conventional platinum-alumina reforming catalysts, this economic balance has generally dictated controlling the hydrofining operation to produce a reformer feed containing from about 2–10 ppm of sulfur.

However, with the advent of the newer bimetallic platinum-rhenium-alumina reforming catalysts, this picture has changed somewhat. The bimetallic reforming catalysts offer the advantages over conventional platinum-alumina catalysts of giving higher yields and longer life. But the evidence now appears to indicate that these advantages largely disappear if the feed to the reformer is not almost completely sulfur-free. It has been found for example that there is a very significant difference in catalyst deactivation rates as between the reforming of feedstocks containing 2.0 ppm versus 0.2 ppm of sulfur. There is thus a stronger incentive when using the bimetallic reforming catalysts to seek ways of improving desulfurization efficiency in the hydrofining step.

In hydrofining, the hydrodesulfurization reaction is generally considered to conform to first order kinetics as expressed by the rate constant equation, $K = LHSV \ln S_f/S_p$, where S_f represents sulfur in the feed, and S_p represents sulfur in the product. From this equation, it will be seen that under a given set of hydrofining conditions conforming to a rate constant of, e.g., 8.0, it would require about a 50 percent increase in catalyst volume to reduce the sulfur content of a feed originally containing 1,000 ppm of sulfur to 1 ppm instead of 10

ppm. Thus, it requires only one volume of catalyst to reduce the sulfur content of such a feed from 1,000 to 10 ppm, and 1.5 volumes to reduce the sulfur content from 1,000 to 1 ppm. If the same objective is pursued by raising the hydrofining temperature so as to increase the rate constant while using the same volume of catalyst, the permissible run length is considerably shortened. Hence, it will be seen that either of these alternatives involve significant added expense.

The foregoing however does not completely delineate the added expense involved in desulfurizing to very low sulfur levels, below 5 ppm. The kinetics discussed above are an optimistic oversimplification. The same rate constant obviously cannot apply to all of the very different types of sulfur compounds found in any given feedstock. Some compounds such as mercaptans and sulfides are very easily decomposed, whereas others such as thiophenes are relatively more difficult. In heavy gasolines, it has been found that still more difficultly decomposable sulfur compounds, presumably of the condensed-ring thiophene types, also are found. When these compounds are present in the feed, they will comprise most of the sulfur remaining in a feed which has been hydrofined to a sulfur level of, e.g., about 1–20 ppm. When operating under conditions corresponding to a rate constant of 8 as discussed above, the actual rate constant pertaining to these refractory sulfur compounds will be substantially lower, perhaps in the order of 1–2. Hence, in the case illustrated above, it would actually require at least doubling the catalyst volume to obtain a product containing 1 ppm of sulfur instead of 10 ppm.

According to our invention, instead of increasing the severity or size of the primary hydrofining zone, we provide a separate post-treatment zone, termed a "hydrosorption" zone, which is operated in the absence of hydrogen sulfide and with a reduced form of hydrofining catalyst. We have discovered that the residual, refractory sulfur compounds which strongly resist hydrodecomposition in a conventional sulfided catalyst system, are much more readily decomposed by hydrogenation and cracking in contact with a hydrofining catalyst in which the active components are in a reduced form, reduced for example with hydrogen at elevated temperatures.

In the preferred adaptation of the process as a pre-treatment for reformer feedstocks, the hydrosorption zone is operated "integrally" with the reforming zone, i.e., with total effluent from the hydrosorption zone going to the reformer without intervening condensation, depressuring or purification. It has been found that the reduced hydrofining catalyst is not only more efficient for converting refractory sulfur compounds, but that it acts as an efficient sorbent for the hydrogen sulfide which is generated. Since the washed effluent from the conventional hydrofiner normally contains only about 1–10 ppm of sulfur, a very large volume of such effluent can be treated in the hydrosorption zone before the catalyst is completely converted to a sulfide form, resulting in breakthrough of H_2S in the effluent therefrom. Thus, it will be seen that the hydrosorption zone acts both as a hydrosorption zone and as a guard chamber for the reformer. If desired, a pair of swing reactors may be provided, operated alternately on feed contacting and regeneration cycles, whereby one of the hydrosorption reactors may be maintained on stream at all times. Preferably the hydrosorption zone is operated

at essentially the same pressure as the reformer whereby both zones may be incorporated in the same recycle gas loop, with a single compressor serving both zones.

In addition to the foregoing, we have discovered that for the above-discussed "hydrosorption" purposes, conventional mixed Group VIB-Group VIII metal hydrofining catalysts are not equivalent in their reduced state for the hydrodecomposition of thiophene-type compounds. Specifically, it has been found that combinations of molybdenum with Group VIII metals are much more active at temperatures above about 575°F than presumably equivalent combinations of tungsten with Group VIII metals. Accordingly, we employ for hydrosorption purposes the molybdenum-Group VIII metal combinations, and utilize temperatures above about 575°F. Strangely enough, at temperatures below 575°F, the molybdenum-and tungsten-containing catalysts appear to be approximately equivalent in activity.

U.S. Pat. No. 3,714,030 discloses a two-step desulfurization process in which a benzene feedstock is first partially desulfurized over a conventional Group VIB-Group VIII catalyst, and then over a metallic nickel catalyst to reduce the sulfur level to below about 1 ppm. We have found however that the combination of nickel with molybdenum is much more effective than nickel alone, while the tungsten-nickel combination appears to be approximately equivalent to nickel alone.

DETAILED DESCRIPTION

A. Description of Drawing

Reference is now made to the attached drawing which is a simplified flow diagram illustrating one preferred modification of the invention. The raw feed naphtha, which may comprise straight run and/or catalytically cracked gasolines, is brought in via line 2, mixed with recycle and makeup hydrogen from line 4, and passed into hydrofiner 6 via preheater 8. In hydrofiner 6, which is filled with a suitable sulfided hydrofining catalyst as described hereinafter, hydrofining takes place under the following general conditions:

Hydrofining Conditions

	Broad Range	Preferred Range
Temperature, °F	500 - 850	650 - 825
Pressure, psig	300 - 3000	800 - 2000
LHSV	0.4 - 10	1 - 5
H ₂ /Oil Ratio, MSCF/B	0.5 - 15	1 - 10

These conditions are suitably adjusted and correlated so as to reduce the feed sulfur content to between about 0.2 and 20, preferably 0.5 and 10, ppm.

Effluent from hydrofiner 6 is withdrawn via line 10, cooled to, e.g., about 100°-200°F in heat exchanger 12, mixed with wash water injected via line 14, and transferred into high pressure separator 16, from which recycle gas is withdrawn via line 4. The aqueous phase in separator 16, containing substantially all of the ammonia generated in hydrofiner 6, and a substantial proportion of the hydrogen sulfide, is withdrawn for disposal via line 18. High-pressure condensate in separator 16 is then flashed via line 20 into low-pressure separator 22, from which light hydrocarbon flash gases are exhausted via line 24. The low-pressure condensate in separator 22 is then transferred via line 26 to stripping column 28 into which fresh makeup hydrogen is in-

jected at the bottom thereof via line 30 to strip out remaining traces of H₂S from the liquid condensate. Hydrogen-rich stripping gases containing some H₂S are taken overhead from stripper 28 via line 32 and blended with the recycle hydrogen in line 4.

Stripped condensate from stripper 28 is withdrawn via line 34, blended with hydrogen-rich recycle gas from reformer 36 via lines 38 and 40, and then passed via preheater 42 into one of the swing hydrosorbers 44 and 46, the flow being suitably controlled by means of valves 48, 50, 52 and 54. Hydrosorbers 44 and 46 are filled with a suitable hydrofining catalyst initially in a reduced or oxidized form. In either case it is believed that the operative form of the catalyst is a reduced form, inasmuch as the oxide forms are rapidly reduced by the feed-hydrogen mixture. The on-stream hydrosorber is slowly, over a period of many days or several months, converted to a sulfide form, as detected by the presence of H₂S in the off-gases therefrom. When this occurs the illustrated valving arrangement is manipulated to shift the flow of feed to the other hydrosorber while the off-stream unit is being regenerated.

Suitable operating conditions to be maintained in the onstream hydrosorber are as follows:

Hydrosorption Conditions

	Broad Range	Preferred Range
Temperature, °F	575 - 800	600 - 750
Pressure, psig	100 - 800	300 - 600
LHSV	5 - 30	10 - 25
H ₂ /Oil Ratio, MSCF/B	0.2 - 15	0.5 - 5

It will be understood that the foregoing conditions are suitably adjusted and correlated so as to maintain the desired minimum value of sulfur in the effluent therefrom. Normally, when using a bimetallic catalyst in reformer 36, it is desirable to maintain sulfur values below 2 ppm, and preferably below 1 ppm.

Regeneration of the exhausted catalyst beds in hydrosorbers 44 and 46 is carried out by conventional procedures, involving first the stripping out of adsorbed hydrocarbons, followed by oxidation with oxygen-containing gases at temperatures between about 700° and 1200°F. Regeneration is complete when the off-gases are substantially free of SO₂. Following oxidation, the catalyst may be again placed on-stream as such, but preferably it is first reduced in a stream of hydrogen at temperatures of about 700°-1200°F, until the off-gases are substantially free of water.

Desulfurized effluent from hydrosorber 44 or 46 is passed directly via line 56 and preheater 58 into reformer 36. If desired a portion of the recycle gas in line 38 may be diverted via line 60 to blend with the hydrosorber effluent in line 56. In reformer 36, which is filled with a suitable reforming catalyst described hereinafter, reforming takes place under the following general conditions:

Reforming Conditions

	Broad Range	Preferred Range
Temperature, °F	750 - 1050	850 - 1000
Pressure, psig	100 - 800	300 - 600
LHSV	0.4 - 8	1 - 5
H ₂ /Oil Ratio, MSCF/B	0.5 - 15	1 - 10

Those skilled in the art will readily understand that the foregoing conditions are suitably adjusted and correlated so as to achieve the desired yield-octane values.

Effluent from reformer 36 is withdrawn via line 62 and passed via condenser-heat exchanger 64 into high-pressure separator 66, from which hydrogen-rich recycle gas is withdrawn via line 38. Excess reformer make gas is withdrawn via line 68, and may if desired be utilized as stripping-makeup hydrogen injected into the hydrofiner recycle gas system via line 30. High-pressure condensate in separator 66 is flashed via line 70 into low-pressure separator 72 from which light hydrocarbon flash gases are exhausted via line 74, and reformate gasoline is withdrawn via line 76.

B. Catalysts

Operative catalysts for use in hydrofiner 6 comprise essentially one or more of the Group VIB metals in combination with any one or more of the Group VIII metals, in sulfided form. Specifically, any of the sulfides of molybdenum, tungsten or chromium may be used in combination with any of the sulfides of iron, cobalt, nickel, palladium or platinum, either alone or supported on a suitable refractory oxide carrier such as alumina, silica, zirconia, titania, clays, etc. Preferably the carrier should have a relatively low cracking activity, corresponding to a Cat-A cracking activity index below about 25. Preferred combinations comprise a sulfide of molybdenum and/or tungsten combined with a sulfide of nickel and/or cobalt. Specifically preferred composites consist of about 1-8 weight-percent of nickel as NiO and about 5-30 weight-percent of molybdenum as MoO₃, supported on an activated alumina carrier. These catalysts are well known in the art and hence need not be described in detail, except to observe they are ordinarily employed in the form of pellets or extrudates ranging in size from about 1/32-inch to 1/4-inch in diameter.

Sulfiding procedures are also well known in the art and hence need not be described in detail. Normally, following impregnation with the active metals, the catalyst is first calcined in air to form an oxide form, and then the sulfided form is produced by passing a stream of gas containing hydrogen sulfide through the catalyst bed at temperatures ranging between about 200° and 1200°F.

Operative catalysts for use in hydrosorbers 44 and 46 are of the molybdenum-Group VIII metal type described above for use in hydrofiner 6, except that they are initially placed on stream in an oxidized or reduced state. Preferably the calcined catalyst is subjected to a prereduction treatment with hydrogen at temperatures between about 500° and 1200°F until the effluent gas becomes substantially free of water vapor. By this treatment, the reducible metal oxides on the catalysts are converted either to free metals or to lower valent oxides. In this form they combine readily with the hydrogen sulfide generated in the hydrosorbers, forming metal sulfides. It is preferred to employ catalysts containing sufficient molybdenum and Group VIII metal to provide a sorption capacity for H₂S of at least about 3 weight-percent, preferably at least 5 weight-percent, expressed as elemental sulfur. Preferred metal contents range between about 4 and 10 weight-percent NiO and/or CoO, combined with about 15-35 weight-percent of MoO₃.

Suitable catalysts for use in reformer 36 may comprise any one or more of the Group VIII noble metals supported on a porous refractory metal oxide carrier such as alumina. The preferred catalysts comprise about 0.2-2 weight-percent of platinum and about 0.2-2 weight-percent of rhenium supported on an activated alumina carrier. Optionally, the catalyst may also contain a combined halogen, preferably chlorine, in amounts ranging between about 0.2 and 3 weight-percent. Suitable such catalysts are disclosed for example in U.S. Pat. No. 3,415,737.

C. Feedstocks

Feedstocks which may be desulfurized by the process of this invention include substantially any sulfur-containing hydrocarbon fraction boiling in the range of about 100° to 1200°F. The two-stage desulfurization technique is however of greatest value for treating feedstocks which contain more than about 200 parts per million of sulfur. Exemplary feedstocks include gasolines and naphthas, kerosene, turbine fuel, petroleum solvents and the like. Naphtha feedstocks for reforming normally boil in the range of about 100°-450°F. The desulfurization technique of this invention is most useful for the treatment of reformer feedstocks having an end-boiling point between about 425° and 450°F.

The following examples illustrate the critical aspects of the invention, but are not to be construed as limiting in scope:

EXAMPLE I

Two parallel reforming runs were carried out under severe conditions selected to accelerate deactivation rates of the respective catalysts, and thus to demonstrate the sensitivity of platinum-rhenium reforming catalysts to very small amounts of sulfur in the feed. The initial feedstock was a blend of hydrofined gasoline with a boiling range of 212°-408°F, and containing 0.9 ppm of sulfur. For Run A sufficient thiophene was added to a portion of this feed to provide a total sulfur content of 2.0 ppm; for Run B another portion of this feed was further hydrofined to reduce the sulfur level to 0.2 ppm. Both runs were carried out at 200 psig, 2.0 LHSV with 5,000 SCF of hydrogen per barrel of feed, and with the temperature adjusted to give a product having an average research clear octane number of 100.5.

At beginning of the runs, both catalysts required a temperature of about 925°F to give the desired octane product. As the runs progressed, a definite spread in temperature requirements began to develop; at 90 hours run A required about 953°F, while run B required only 945°F; at 180 hours run A required 972°F while run B required only 955°F. This spread in temperature at 180 hours, when translated into terms of catalyst activity, means that the catalyst in run A was only about 50 percent as active as the catalyst in run B at 180 hours. In both of these runs, the initial catalyst was a commercial reforming catalyst containing 0.33 weight-percent platinum, 0.34 weight-percent rhenium, and 1.0 weight-percent chloride, supported on a predominantly eta alumina base having a surface area of 474 m²/g. It is evident from the foregoing data that

this catalyst is quite sensitive to very small amounts of sulfur in the feedstock.

EXAMPLE II

A hydrosorption catalyst of this invention was prepared by reducing a calcined composite of 3 weight-percent NiO and 18 weight-percent MoO₃ supported on a 99% Al₂O₃-1% SiO₂ base. The reduction was carried out by heating the catalyst in hydrogen to 700°F in 2.5 hours, holding 2 hours at 700°F, and then reducing the temperature to about 550-600°F for feed introduction. The feedstock was a naphtha having the same boiling range as the feed of Example I, and which had been previously hydrofined over a sulfided nickel-molybdenum-alumina catalyst to a residual sulfur content of 1.7 ppm. Four hydrosorption runs were carried out at 400 psig and 20 LHSV, using 4,000 SCF of hydrogen per barrel of feed. The results of these runs at various temperatures were as follows:

Temperature, °F.	Sulfur in Product, ppm
550	0.54
600	0.13
650	0.12
700	0.12

percent tungsten as WO₃ supported on a base consisting of about 3 weight-percent of a rare earth X zeolite dispersed in a predominantly silica gel matrix. This catalyst was prereduced in hydrogen as described in Example II, and then tested for desulfurization activity, employing the same feed and reaction conditions as described in Example II. At various temperature levels the results were as follows:

Temperature, °F.	Sulfur in Product, ppm
550	0.4
600	0.3
650	0.2
700	0.4

It will be apparent from the foregoing data that at temperatures above about 575°F, the Ni-Mo catalyst of Example II becomes very active, while the Ni-W catalysts of Examples III and IV did not exhibit nearly as great a temperature response. In order to bring out more clearly the relative activities of these catalysts, the first order rate constants, K were calculated for each of the runs, giving the following tabulation:

Desulfurization at 400 psig					
Example	Temp, °F	LHSV	S in Feed, ppm	S in Product, ppm	Rate Constant K
II (Ni-Mo)	550	20	1.7	0.54	23
	600	20	1.7	0.13	97.5
	650	20	1.7	0.12	99.3
	700	20	1.7	0.12	99.3
III (Ni-W)	550	10	1.7	0.7	8.8
	600	10	1.7	0.4	14.5
	650	10	1.7	0.3	17.3
IV (Ni-W)	550	20	1.7	0.4	29
	600	20	1.7	0.3	34.8
	650	20	1.7	0.2	43
	700	20	1.7	0.4	29

To achieve these same sulfur levels by adding incremental sulfided catalyst to the initial hydrofining zone in which the sulfur was previously reduced to 1.7 ppm, would require at least about ten times the volume of the reduced catalyst employed in this example.

EXAMPLE III

Another hydrosorption catalyst was prepared by reducing a calcined catalyst containing 3 weight-percent NiO and 19 weight-percent WO₃ supported on a 99% Al₂O₃-1% SiO₂ base. The reduction conditions were the same as described in Example II. Using the same feed as in Example II, and at 400 psig, 10 LHSV and 4,000 SCF of hydrogen per barrel of feed, product sulfur contents were as follows at various temperatures:

Temperature, °F.	Sulfur in Product, ppm
550	0.7
600	0.4
650	0.3

Another hydrosorption catalyst was prepared containing 5 weight-percent nickel as NiO and 22 weight-

The marked superiority of the Ni-Mo catalyst of Example II is readily apparent.

It is not intended that the invention should be limited to exemplary details described herein; the true scope of the invention is intended to be defined by the following claims and their obvious equivalents.

We claim:

1. A process for the hydrodesulfurization of a sulfur-containing hydrocarbon feedstock, at least a portion of the sulfur in said feedstock appearing in compounds comprising a thiophene ring, which comprises:

1. contacting said feedstock plus added hydrogen with a sulfided Group VIB and Group VIII mixed-metal hydrofining catalyst under hydrofining conditions adjusted to reduce the organic sulfur content of said feedstock to between about 0.2 and 20 ppm;

2. separating hydrogen sulfide from the resulting intermediate product oil; and

3. contacting said intermediate product oil plus added hydrogen with a hydrogen-reduced, initially substantially sulfur-free molybdenum and Group VIII mixed-metal hydrofining catalyst under hydrofining-sorption conditions adjusted to effect a further substantial reduction in the organic sulfur content thereof and sorption of substantially all of the

resulting hydrogen sulfide on said hydrogen-reduced hydrofining catalyst, said hydrofining-sorption conditions including a temperature above 575°F.

2. A process as defined in claim 1 wherein the hydrofining catalysts recited in steps (1) and (3) each comprise nickel and/or cobalt plus molybdenum supported on a refractory, porous oxide carrier.

3. A process as defined in claim 1 wherein the hydrofining catalysts recited in steps (1) and (3) each comprise nickel and molybdenum supported on activated alumina.

4. A process as defined in claim 1 wherein the liquid hourly space velocity in step (3) is between about 10 and 25.

5. A process as defined in claim 1 wherein step (3) is continued until break-through of hydrogen sulfide in the effluent therefrom, and the catalyst employed therein is then regenerated to remove sulfur therefrom and then placed back on-stream.

6. A process for the hydrodesulfurization and reforming of a sulfur-containing naphtha feedstock, at least a portion of the sulfur in said feedstock appearing in compounds comprising a thiophene ring, which comprises:

1. contacting said feedstock plus added hydrogen with a sulfided Group VIB and Group VIII mixed-metal hydrofining catalyst under hydrofining conditions adjusted to reduce the organic sulfur content of said feedstock to between about 0.5 and 10 ppm;
2. separating hydrogen sulfide from the resulting intermediate gasoline product;
3. contacting said intermediate gasoline product plus added hydrogen with a hydrogen-reduced, initially substantially sulfur-free molybdenum and Group

VIII mixed-metal hydrofining catalyst under hydrofining-sorption conditions adjusted to effect a further substantial reduction in the organic sulfur content thereof, to a level below about 2 ppm, and also to sorb substantially all of the hydrogen sulfide thereby generated on said hydrogen-reduced hydrofining catalyst, said hydrofining-sorption conditions including a temperature above about 575°F; and

4. subjecting total effluent from step (3) to catalytic reforming in contact with a sulfur-sensitive Group VIII noble metal reforming catalyst.

7. A process as defined in claim 6 wherein said reforming catalyst recited in step (4) comprises platinum and rhenium.

8. A process as defined in claim 6 wherein steps (3) and (4) are carried out at substantially the same pressure, and wherein hydrogen-rich recycle gas from step (4) is recycled to step (3).

9. A process as defined in claim 6 wherein the hydrofining catalysts recited in steps (1) and (3) each comprise nickel and/or cobalt molybdenum supported on a refractory, porous oxide carrier.

10. A process as defined in claim 6 wherein the hydrofining catalysts recited in steps (1) and (3) each comprise nickel and molybdenum supported on activated alumina.

11. A process as defined in claim 6 wherein the liquid hourly space velocity in step (3) is between about 10 and 25.

12. A process as defined in claim 6 wherein step (3) is continued until break-through of hydrogen sulfide in the effluent therefrom, and the catalyst employed therein is then regenerated to remove sulfur therefrom and then placed back on-stream.

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